Supporting Information

Bifunctional photocatalysts display proximity-enhanced catalytic activity in metallaphotoredox C–O coupling

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Summary

General remarks

The catalytic tests were performed in septum-sealed 10 mL microwave vials (borosilicate glass 3.3 acc. to ISO 3585) or Schlenk tubes (borosilicate glass 3.3). All reactions were performed with the Schlenk technique,[1] under nitrogen or argon atmosphere, unless otherwise specified. Irradiation was performed using Kessil PR160L lamps of the specified wavelength while cooling down with a fan (unless otherwise specified). Analytical thin layer chromatography (TLC) was carried out using commercial silica gel plates, spots were detected with UV light and revealed either with alkaline potassium permanganate, cerium-ammonium molybdate, ninhydrin or 2,4-dinitrophenylhydrazine solution. Flash column chromatography was performed using silica gel (60 Å, particle size 40-64 μm) as stationary phase, following the procedure by Still and co-workers.[2] ^{1}H NMR spectra were recorded on a 400 MHz spectrometer. Proton chemical shifts are reported in ppm (δ) with the solvent reference relative to tetramethylsilane (TMS) employed as the internal standard ($CDCl_3$, δ = 7.26 ppm, CD_2Cl_2, δ = 5.32 ppm, DMSO-d_6, δ = 2.50 ppm, CD_3CN, δ = 1.94 ppm).[3] The following abbreviations are used: s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublets, broad signals are indexed br. (broad). All coupling constants are expressed in Hertz (Hz). $^{13}C\{^{1}H\}$ NMR spectra were recorded on a 400 MHz spectrometer operating at 100.56 MHz, with complete proton decoupling. Carbon chemical shifts are reported in ppm (δ) relative to TMS with the respective solvent resonance as the internal standard ($CDCl_3$ δ = 77.16 ppm, CD_2Cl_2, δ = 53.84 ppm, DMSO-d_6, δ = 39.52 ppm).[3] Yield by NMR were determined by adding the internal standard (1,3,5-trimethoxybenzene) after the reaction time as a solid. IR spectra were recorded using a Jasco FT/IR-4600 ATR spectrometer. The absorption spectra were recorded with a Shimadzu UV-3600 plus spectrophotometer in 1 cm path length quartz cell. Steady state emission and excitation spectra and photoluminescence lifetimes were obtained with a FLS 980 spectrofluorimeter (Edinburgh Instrument Ltd.). Continuous excitation for the steady state measurements was provided by a 450 W Xenon arc lamp. Emission spectra were corrected for the wavelength-dependent sensitivity of the detector. Photoluminescence time-resolved measurements were carried out by TCSPC (time-correlated single-photon counting) method with an Edinburgh Picosecond Pulsed Diode Laser EPL-375 (Edinburgh Instrument Ltd.) and fitted with a sum of exponential decay to obtain the lifetimes of prompt and delayed fluorescence. Absolute photoluminescence quantum yields were measured with a C11347 Quantaurus-QY spectrometer (Hamamatsu Photonics), equipped with a 150 W xenon lamp, an integration sphere, and a multichannel detector. Mass spectrometry analyses were performed at the Mass Spectrometry facility of the Unitech COSPECT at the University of Milan (Italy).

Materials

Dry solvents were either purchased from Acros Organics and Sigma-Aldrich (1,2-dimethoxyethane, *N*,*N*-dimethylpropylene urea), or distilled under nitrogen from calcium hydride (acetonitrile) or sodium/benzophenone (THF). Chemicals were purchased from Sigma Aldrich, Fluorochem and TCI, or synthesized with reported and adaprted literature procedures. Deuterated solvents were purchased from Deutero GmbH, EurisoTop, Sigma-Aldrich or VWR. Photocatalysts 4CzIPN[4] and 3CzFIPN[5] were synthesized according to literature procedures.

Reaction setup

The magnetically stirred reactions were run at room temperature in 10 mL microwave vials sealed with a septum under irradiation from one 40 W Kessil PR160L lamp (λ = 427 nm; distance between lamp and vial(s): 5 cm). A fan was used to dissipate the heat generated by the lamp.

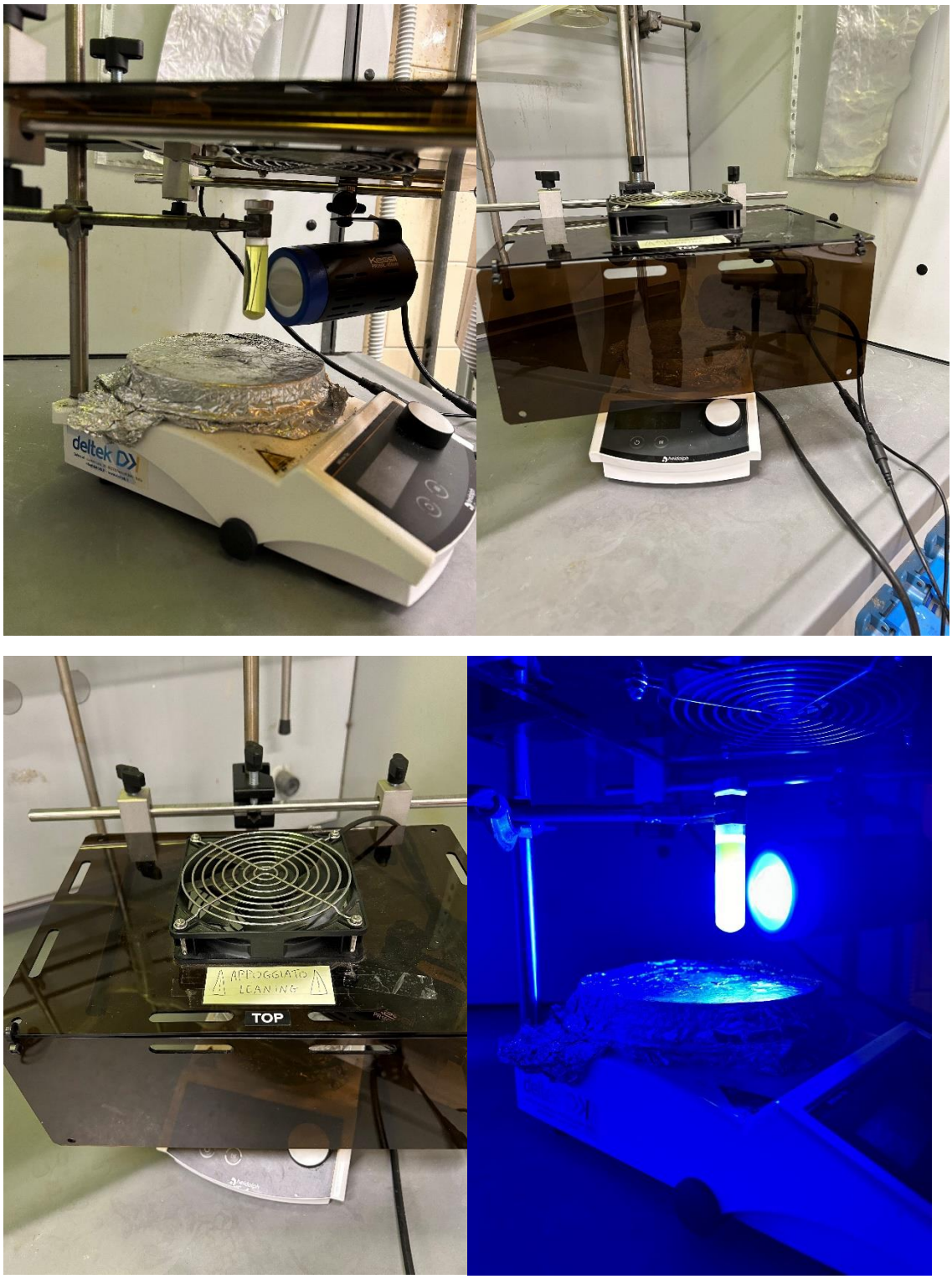
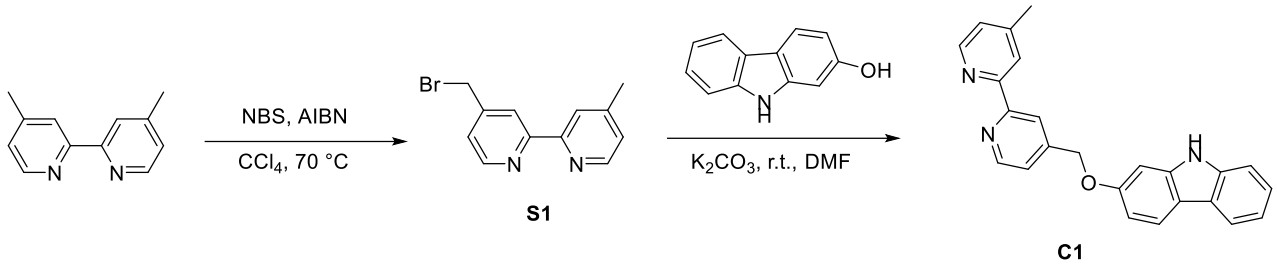


Figure S1. Reaction setup.

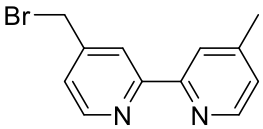
Experimental section

Synthesis of carbazole C1



Scheme S1. Synthesis of **C1.**

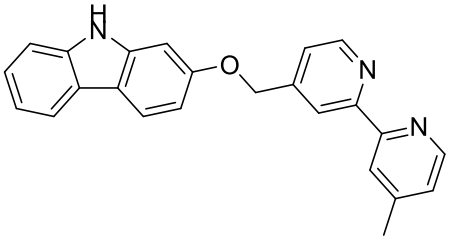
4-(Bromomethyl)-4'-methyl-2,2'-bipyridine (**S1**)



To a solution of 4,4'-dimethyl-2,2'-bipyridine (5.51 g, 29.9 mmol, 1 eq) and NBS (2.18 g, 12.3 mmol, 0.41 eq) in dry CCl_4 (100 mL, 0.3 M), catalytic amount of AIBN (98.0 mg, 0.6 mmol, 0.02 eq) was added and refluxed at 77 °C for 24 h under dry conditions. The solution was filtered while hot and kept for four days to precipitate out any dibromo derivative formed. The solution was filtered, and the filtrate was concentrated under reduced pressure. The residue obtained was purified by silica gel column chromatography (DCM:ethyl acetate = 8:2) to give the pure product **S1** (reddish powder, 1.71 g, 53%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 5.0 Hz, 1H), 8.55 (d, *J* = 5.0 Hz, 1H), 8.45-8.41 (m, 1H), 8.28-8.23 (m, 1H), 7.34 (dd, *J* = 5.0, 1.8 Hz, 1H), 7.19-7.12 (m, 1H), 4.48 (s, 2H), 2.45 (s, 3H). These data are in accordance with those previously reported in the literature.[6]

2-((4'-Methyl-[2,2'-bipyridin]-4-yl)methoxy)-9H-carbazole (**C1**)

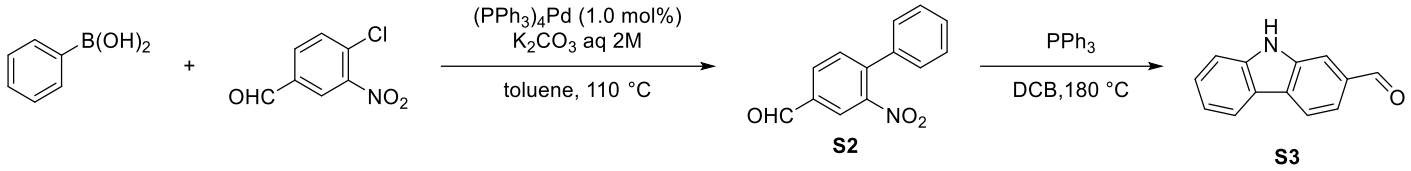


A mixture of 9*H*-carbazol-2-ol (217.6 mg, 1.2 mmol, 1.35 equiv.), **S1** (232.6 mg, 0.9 mmol, 1 equiv.), K_2CO_3 (170.2 mg, 1.2 mmol, 1.4 equiv.) in DMF (1 mL, 0.88 M) was stirred for 24 h. The reaction mixture was then filtered on a celite pad and the solvent evaporated. The residue obtained was purified by silica gel column chromatography (DCM:ethyl acetate = 7:3) to give the pure product **C1** (white powder, 205 mg, 64%). Mp = 220-232 °C.

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.13 (s, 1H), 8.69 (d, *J* = 5.0 Hz, 1H), 8.55 (d, *J* = 4.9 Hz, 1H), 8.51 (s, 1H), 8.26 (s, 1H), 8.03-7.97 (m, 2H), 7.55 (dd, *J* = 4.9, 1.6 Hz, 1H), 7.40 (d, *J* = 8.0 Hz, 1H), 7.31-7.25 (m, 2H), 7.14-7.08 (m, 1H), 7.05 (d, *J* = 2.2 Hz, 1H), 6.91 (dd, *J* = 8.5, 2.2 Hz, 1H), 5.39 (s, 2H), 2.42 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 157.06, 155.53, 154.89, 149.35, 149.04, 147.98, 147.83, 140.90, 139.79, 125.05, 124.27, 122.53, 121.93, 121.29, 121.03, 119.32, 118.57, 118.32, 116.67, 110.62, 108.20, 95.82, 68.05, 20.70; IR (ATR): ν

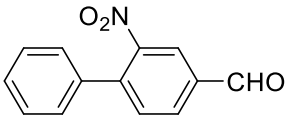
= 3398, 1727, 1686, 1596, 1451, 1358, 1156, 825, 749 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{24}H_{20}N_3O]^+$: 366.1606 $[M+H]^+$; found: 366.1602; *m/z* calcd. for $[C_{24}H_{19}N_3NaO]^+$: 388.1426 $[M+Na]^+$; found: 388.1422.

Synthesis of carbazole C2



Scheme S2. Synthesis of **S3**.

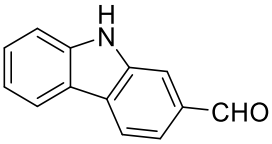
2-Nitro-[1,1'-biphenyl]-4-carbaldehyde (**S2**)



4-Chloro-3-nitrobenzaldehyde (1.00 g, 5.4 mmol, 1 equiv.) and phenyl boronic acid (0.72 g, 5.9 mmol, 1.1 equiv.) were dissolved in dry toluene (7.7 mL, 0.7 M). A solution of K_2CO_3 (1.50 g, 10.8 mmol, 2 equiv.) in water (5.4 mL, 0.2 M) was then added, and the reaction mixture was degassed by bubbling Ar. Finally, $Pd(PPh_3)_4$ (0.17 g, 0.15 mmol, 0.025 equiv.) was added and the reaction mixture was left stirring at 110 °C for 16 hours. The mixture was concentrated under vacuum and purified by silica gel column chromatography (hexane:diethyl ether = 7:3) to give the pure product **S2** (yellowish solid, 864.0 mg, 70%).

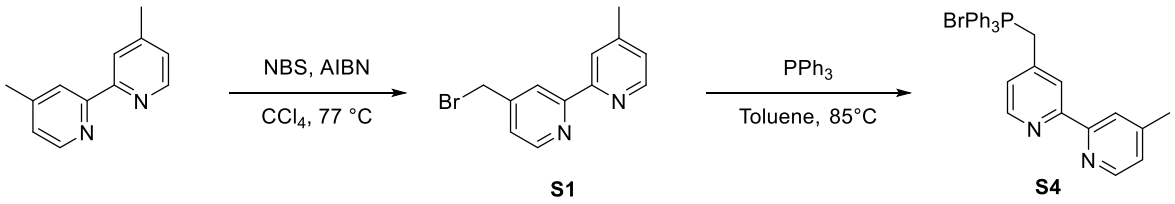
^{1}H NMR (400 MHz, $CDCl_3$): δ 10.11 (s, 1H), 8.34 (d, *J* = 1.6 Hz, 1H), 8.13 (dd, *J* = 7.9, 1.7 Hz, 1H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.51-7.43 (m, 3H), 7.39-7.31 (m, 2H). These data are in accordance with those previously reported in the literature.[7]

9H-Carbazole-2-carbaldehyde (**S3**)



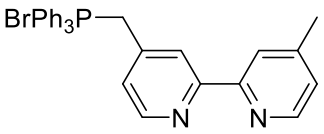
A solution of **S2** (1.80 g, 8.1 mmol, 1 equiv.) and PPh_3 (10.60 g, 40.4 mmol, 5 equiv.) in 1,2-dichlorobenzene (16 mL, 0.5 M) was heated to reflux at 180 °C. After 20 h, the reaction mixture was cooled down to room temperature, transferred into a round bottomed flask and concentrated in vacuo. The mixture was then purified by silica gel column chromatography (DCM) to remove all the solvent and the unreacted PPh_3. This mixture was purified again by silica gel column chromatography (hexane:diethyl ether = 7:3) to give the pure product **S3** (gold powder, 1.39 g, 88%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.14 (s, 1H), 8.32 (br. s, 1H), 8.21 (d, *J* = 8.0 Hz, 1H), 8.18-8.11 (m, 1H), 8.01-7.95 (m, 1H), 7.78 (dd, *J* = 8.0 Hz, 1.4, 1H), 7.57-7.46 (m, 2H), 7.35-7.27 (m, 1H). These data are in accordance with those previously reported in the literature.[8]



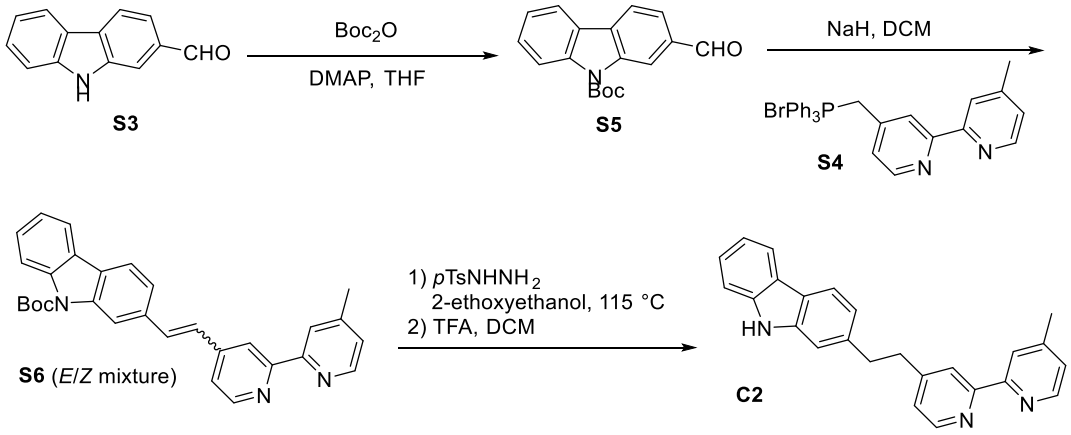
Scheme S3. Synthesis of **S4**.

((4'-Methyl-[2,2'-bipyridin]-4-yl)methyl)triphenylphosphonium (**S4**)



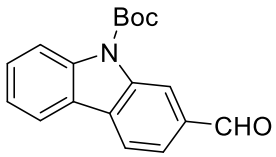
Bromide **S1** (300.0 mg, 1.2 mmol, 1 equiv.) was dissolved in dry acetonitrile (2.3 mL, 0.5 M), and solid triphenylphosphine (337.0 mg, 1.3 mmol, 1.1 equiv.) was added. The reaction mixture was stirred at 85 °C. After 15 min a white precipitate appears. After 16 h, the mixture was filtered, washed with diethyl ether and the precipitate collected and dried to afford the pure phosphonium salt **S4** (beige powder, 520.0 mg, 85%). Mp = 258-263 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.46 (d, *J* = 5.0 Hz, 1H), 8.38 (d, *J* = 5.0 Hz, 1H), 8.15-8.12 (m, 1H), 7.95-7.91 (m, 1H), 7.87-7.80 (m, 6H), 7.79-7.73 (m, 3H), 7.68-7.60 (m, 6H), 7.59-7.54 (m, 1H), 7.12-7.07 (m, 1H), 5.66 (d, *J* = 15.5 Hz, 2H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 155.78, 154.44, 149.94, 148.89, 148.60, 138.22 (d, *J* = 8.1 Hz), 135.33, 134.51 (d, *J* = 10.1 Hz), 130.47 (d, *J* = 12.7 Hz), 127.09 (d, *J* = 5.4 Hz), 125.14, 123.46 (d, *J* = 5.1 Hz), 122.16, 117.49 (d, *J* = 86.2 Hz), 30.34 (d, *J* = 47.2 Hz), 21.37; ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ 23.57; IR (ATR): ν = 1589, 1437, 1109, 829, 741, 714, 683 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{30}H_{26}N_2P]^+$: 445.1828 $[M]^+$; found: 445.1834.



Scheme S4. Synthesis of **C2**.

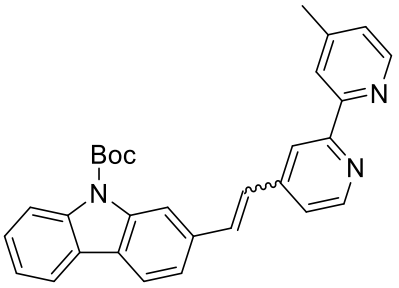
tert-Butyl 2-formyl-9H-carbazole-9-carboxylate (**S5**)



To a solution of **S3** (0.51 g, 3.0 mmol, 1 equiv.) in THF (20 mL, 0.15 M) were added $(Boc)_2O$ (0.73 g, 3.33 mmol, 1.10 equiv.) and DMAP (0.41 g, 3.33 mmol, 1.10 equiv.). The reaction mixture was stirred at room temperature for 3 h. The crude mixture was concentrated under reduced pressured, water was added, and then the resulting solution was extracted with ethyl acetate. The combined organic extracts were dried over Na_2SO_4, filtered and concentrated in vacuo. The mixture was purified by silica gel column chromatography (hexane:ethyl acetate 97:3) to give the pure **S5** (white powder, 0.76 g, 86%). Mp = 125-126 °C.

^{1}H NMR (400 MHz, $CDCl_3$): δ 10.14 (s, 1H), 8.89-8.82 (m, 1H), 8.34 (d, *J* = 8.5 Hz, 1H), 8.11 (d, *J* = 8.0 Hz, 1H), 8.06 (d, *J* = 7.5 Hz, 1H), 7.92 (dd, *J* = 8.0 Hz, 1.4, 1H), 7.60-7.53 (m, 1H), 7.45-7.37 (m, 1H), 1.80 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 192.24, 150.85, 140.06, 138.50, 135.36, 130.94, 128.94, 124.77, 123.94, 123.60, 120.73, 120.06, 119.18, 116.58, 84.91, 28.49; IR (ATR): ν = 2971, 1725, 1686, 1615, 1471, 1423, 1359, 1332, 1221, 1149, 821, 763, 749, 723 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{18}H_{17}NNaO_3]^+$: 318.1106 [*M*+Na]$^+$; found: 318.1098.

tert-Butyl 2-(2-(4'-methyl-[2,2'-bipyridin]-4-yl)vinyl)-9H-carbazole-9-carboxylate (**S6**)



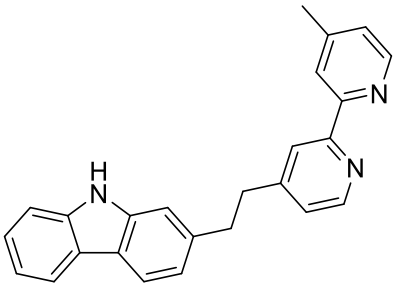
To a suspension of **S4** (0.88 g, 1.7 mmol, 1 equiv.) in DCM (13 mL, 0.13 M) was added NaH (60% suspension in paraffin oil) (0.14 g, 3.4 mmol, 2 equiv.). The resulting mixture was stirred at room temperature for 4 h. Then, a solution of **S5** (0.49 g, 1.7 mmol, 1 equiv.) in DCM (4.5 mL, 0.37 M) was prepared and added to the reaction mixture, and the solution was stirred overnight for 22 h. The crude mixture was quenched with water and extracted three times with DCM. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The mixture was purified by silica gel column chromatography (DCM:ethyl acetate 9:1 + 0.1% triethyl amine) to give the pure **S6** (~ 3:1 = *E*:*Z* ratio of diastereoisomers, orange oil, 682.6 mg, 87%). Mp = 96.5-104 °C.

Analytical data for *Z* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.48 (d, *J* = 5.0 Hz, 1H), 8.43 (d, *J* = 5.1 Hz, 1H), 8.33-8.26 (m, 3H), 8.15 (s, 1H), 7.94 (d, *J* = 7.7 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.49-7.42 (m, 1H), 7.34 (d, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 7.7 Hz, 1H), 7.18-7.14 (m, 1H), 7.11 (d, *J* = 5.0 Hz, 1H), 6.99 (d, *J* = 12.2 Hz, 1H), 6.66 (d, *J* = 12.2 Hz, 1H), 2.41 (s, 3H), 1.60 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 156.91, 156.02, 151.03, 149.10, 149.01, 148.11, 146.14, 139.15, 138.65, 135.31, 134.87, 127.88, 127.35, 125.54, 125.50, 124.75, 123.99, 123.26, 123.20, 121.98, 121.75, 119.69, 119.62, 116.92, 116.40, 84.09, 28.26, 21.24; IR (ATR): ν = 1721, 1590, 1457, 1426, 1361, 1335, 1221, 1151, 823 cm^{-1}.

Analytical data for *E* isomer: ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 5.1 Hz, 1H), 8.62 (s, 1H), 8.59 (d, *J* = 5.0 Hz, 1H), 8.56 (s, 1H), 8.30-8.24 (m, 2H), 7.98 (d, *J* = 7.6 Hz, 2H), 7.66-7.55 (m, 2H), 7.51-7.45 (m, 1H), 7.43-7.39 (m, 1H), 7.36 (t, *J* = 7.5 Hz, 1H), 7.25 (d, *J* = 16.0 Hz, 1H), 7.16 (d, *J* = 4.9 Hz, 1H), 2.46 (s, 3H), 1.81 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 156.89, 156.12, 151.22, 149.68, 149.15, 148.30, 145.97, 139.30, 139.20, 135.59, 134.22, 127.51, 126.42, 126.26, 125.65, 124.91, 123.35, 122.54, 122.19, 121.04, 119.96, 119.90, 118.48, 116.49, 115.11, 84.35, 28.59, 21.35; IR (ATR): ν = 1719, 1588, 1334, 1221, 1150, 957, 822 cm^{-1}.

HRMS (ESI): *m/z* calcd. for $[C_{25}H_{20}N_3]^+$: 362.1657 [*M*+H]$^+$; found: 362.1653.

2-(2-(4'-Methyl-[2,2'-bipyridin]-4-yl)ethyl)-9H-carbazole (**C2**)

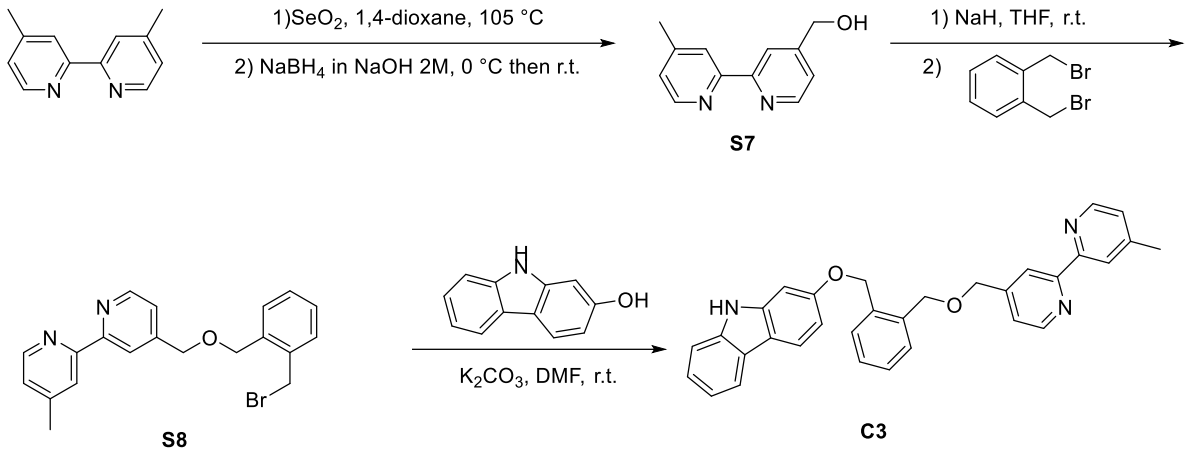


A solution of **S6** (0.75 g, 1.6 mmol, 1 equiv.) and *p*-toluenesulfonylhydrazide (0.80 g, 4.3 mmol, 2.6 equiv.) were heated under reflux in 2-ethoxyethanol (4 mL, 0.4 M) for 3 h. The reaction mixture was poured into water to quench it and extracted with diethyl ether; the combined organic layers were washed with a dilute Na_2CO_3 solution, dried over Na_2SO_4 and concentrated in vacuo. The mixture was then purified by silica gel column chromatography (hexane:ethyl acetate = 8:2 + 0.1% TEA) to give the a mixture of Boc-protected **C4** and **C4** as a colorless oil, which were collected together. This mixture was dissolved in DCM (7 mL, 0.2 M), then TFA (3.5 mL, 45.7 mmol, 29 equiv.) was added. The resulting mixture was stirred at room temperature for 1 h. The solvent was then removed, and the reaction mixture was dissolved in DCM and washed with a solution of NaOH 2M. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The mixture was purified by silica gel column chromatography (hexane:ethyl acetate = 1:1 + 0.1% TEA) to give the pure **C2** (white foam, 348.9 mg, 60%). Mp = 177-185 °C.

Analytical data for Boc-protected **C2:** ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.57-8.52 (m, 2H), 8.33-8.29 (m, 1H), 8.25 (d, *J* = 8.3 Hz, 1H), 8.23-8.20 (m, 2H), 7.96-7.93 (m, 1H), 7.88 (dd, *J* = 7.9 Hz, 0.6, 1H), 7.47-7.40 (m, 1H), 7.37-7.31 (m, 1H), 7.19 (dd, *J* = 7.9 Hz, 1.5, 1H), 7.15-7.12 (m, 1H), 7.10 (dd, *J* = 5.0, 1.7, 1H), 3.21-3.07 (m, 4H), 2.44 (s, 3H) , 1.74 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 156.35, 156.09, 151.67, 151.20, 149.13, 149.00, 148.17, 140.33, 139.01, 138.61, 126.77, 125.83, 124.72, 124.19, 124.09, 123.68, 123.05, 122.13, 121.42, 119.53, 119.45, 116.33, 116.28, 83.92, 37.87, 37.60, 28.44, 21.23; IR (ATR): ν = 1721, 1594, 1456, 1426, 1359, 1331, 1221, 1151, 823, 766, 746, 724 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{30}H_{30}N_3O_2]^+$: 464.2338 [*M*+H]$^+$; found: 464.2336; *m/z* calcd. for $[C_{30}H_{29}N_3NaO_2]^+$: 486.2157 [*M*+Na]$^+$; found: 486.2153.

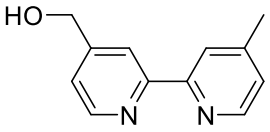
Analytical data for **C2**: ^{1}H NMR (400 MHz, DMSO-d_6): δ 11.12 (s, 1H), 8.53 (t, *J* = 5.3 Hz, 2H), 8.32 (s, 1H), 8.22 (s, 1H), 8.04 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.43 (d, *J* = 8.1 Hz, 1H), 7.36-7.30 (m, 3H), 7.29-7.25 (m, 1H), 7.16-7.06 (m, 2H), 3.14-3.06 (m, 4H), 2.41 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 155.25, 155.18, 151.57, 148.94, 148.89, 147.79, 139.98, 139.76, 138.59, 124.99, 124.80, 124.24, 122.36, 121.21, 120.59, 119.88, 119.79, 119.38, 118.33, 110.75, 110.44, 36.85, 36.38, 20.66; IR (ATR): ν = 3399, 1595, 1458, 1371, 1325, 1242, 820 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{25}H_{22}N_3]^+$: 364.1814 [*M*+H]$^+$; found: 364.1805; *m/z* calcd. for $[C_{25}H_{21}N_3Na]^+$: 386.1633 [*M*+Na]$^+$; found: 386.1626.

Synthesis of carbazole C3



Scheme S5. Synthesis of **C3**.

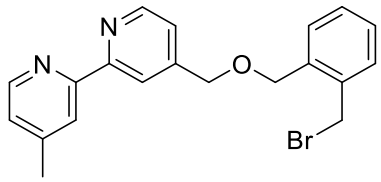
(4'-Methyl-[2,2'-bipyridin]-4-yl)methanol (**S7**)



4,4'-dimethyl-2,2'-bipyridine (501.4 mg, 2.7 mmol, 1 equiv.) was suspended in 1,4-dioxane (25 mL, 0.028 M) and SeO_2 (499.5 mg, 4.5 mmol, 1.65 equiv.) was added. The mixture was stirred at 105 °C for 22 h, then cooled to room temperature and filtered on a celite pad, washing with dioxane. After removal of solvent under reduced pressure, the resulting solid was suspended in methanol (5 mL, 0.54 M), and sodium borohydride (61.8 mg, 1.6 mmol, 0.6 equiv.) in NaOH (0.5 mL of a 2 M solution, 1.0 mmol, 0.37 equiv.) was added dropwise at 0 °C. The mixture was stirred at room temperature for 16 h, then the solvent was concentrated, and the aqueous phase (pH ≈ 9) extracted with DCM three times. The combined organic layers were washed twice with water and once with brine, then the solvent was evaporated under reduced pressure and the residue purified by silica gel column chromatography (DCM:methanol = 98:2 + 1% NH_3 2 M) to give the pure product **S7** (white powder, 303.7 mg, 56%).

^{1}H NMR (400 MHz, Acetonitrile-d_3): δ 8.58 (d, *J* = 5.0 Hz, 1H), 8.51 (d, *J* = 5.0 Hz, 1H), 8.39-8.35 (m, 1H), 8.28-8.24 (m, 1H), 7.36-7.31 (m, 1H), 7.24-7.19 (m, 1H), 4.70 (d, *J* = 4.8 Hz, 2H), 3.47 (t, *J* = 5.9 Hz, 1H), 2.43 (s, 3H). These data are in accordance with those previously reported in the literature.[9]

4-(((2-(Bromomethyl)benzyl)oxy)methyl)-4'-methyl-2,2'-bipyridine (**S8**)

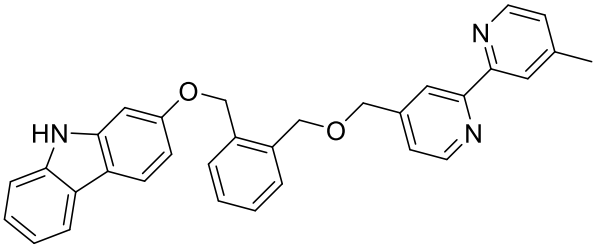


S7 (149.5 mg, 0.75 mmol, 1.0 equiv.) was dissolved in tetrahydrofuran (3 mL, 0.25 M) and NaH (60% dispersion in mineral oil, 46.6 mg, 1.2 mmol, 1.6 equiv.) was added slowly under stirring. After 20 min., the reaction mixture was added dropwise into a solution of 1,2-bis(bromomethyl) benzene (990.2 mg, 3.8 mmol, 5 equiv.) in THF (1.5 mL, 2.5 M), stirring for 18 h at 70 °C. The reaction mixture was concentrated under vacuum, the residue redissolved in DCM and washed twice with water (pH ≈ 9) and once with brine. The organic phase was dried over Na_2SO_4,

concentrated and the brown solid purified by silica gel column chromatography (DCM:methanol = 97:3) to give the pure product **S8** (brownish oil, 156.1 mg, 54%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.66 (d, *J* = 5.0 Hz, 1H), 8.53 (d, *J* = 5.0 Hz, 1H), 8.37-8.33 (m, 1H), 8.25-8.21 (m, 1H), 7.44-7.29 (m, 5H), 7.17-7.11 (m, 1H), 4.78 (s, 2H), 4.69 (s, 2H), 4.64 (s, 2H), 2.44 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 156.31, 155.67, 149.25, 148.91, 148.22, 148.11, 136.24, 130.68, 129.65, 128.86, 128.59, 124.73, 121.92, 121.81, 119.31, 70.97, 70.29, 30.90, 21.09; IR (ATR): ν = 1597, 1456, 1374, 1213, 1079, 823, 756, 604 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{20}H_{20}BrN_2O]^+$: 383.0759 [*M*+H]$^+$; found: 383.0757; *m/z* calcd. for $[C_{20}H_{19}BrN_2NaO]^+$: 405.0578 [*M*+Na]$^+$; found: 405.0573.

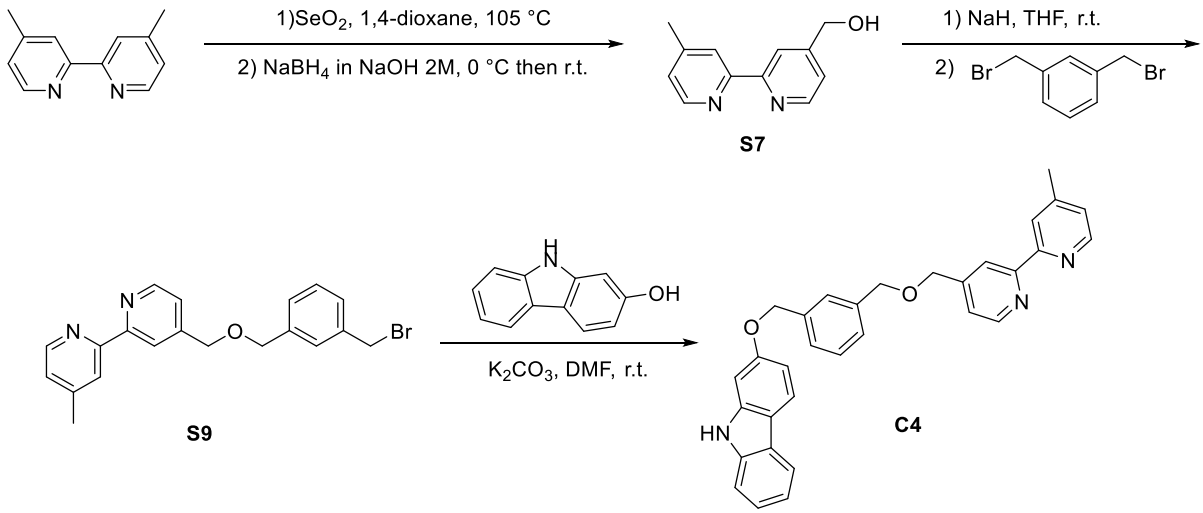
2-((2-(((4'-Methyl-[2,2'-bipyridin]-4-yl)methoxy)methyl)benzyl)oxy)-9H-carbazole (**C3**)



A mixture of 9*H*-carbazol-2-ol (82.4 mg, 0.45 mmol, 1.1 equiv.), **S8** (156.1 mg, 0.41 mmol, 1 equiv.), K_2CO_3 (78.8 mg, 0.57 mmol, 1.4 equiv.) in DMF (0.6 mL, 0.7 M) was stirred for 22 h at 50 °C. The reaction mixture was then filtered on a celite pad and the solvent evaporated. The crude product was purified by silica gel column chromatography (DCM:ethyl acetate = 8:2) to give the pure product **C3** (yellow oil, 67.8 mg, 34%).

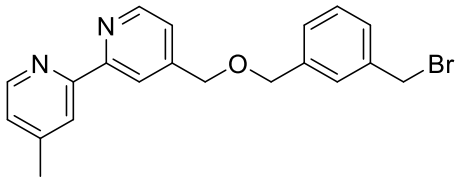
^{1}H NMR (400 MHz, DMSO-d_6): δ 11.06 (s, 1H), 8.59 (d, *J* = 4.9 Hz, 1H), 8.49 (d, *J* = 5.0 Hz, 1H), 8.38 (s, 1H), 8.22 (s, 1H), 7.94 (dd, *J* = 19.2, 8.1 Hz, 2H), 7.61-7.50 (m, 2H), 7.45-7.35 (m, 4H), 7.32-7.22 (m, 2H), 7.10 (t, *J* = 7.4 Hz, 1H), 7.05 (s, 1H), 6.87-6.79 (m, 1H), 4.80 (s, 2H), 4.72 (s, 2H), 2.39 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 157.41, 154.93, 149.13, 148.94, 148.48, 147.83, 140.90, 139.74, 136.18, 135.40, 128.59, 128.49, 127.89, 127.81, 124.87, 124.12, 122.52, 121.99, 121.19, 120.78, 119.18, 118.45, 116.46, 110.54, 108.05, 95.75, 70.22, 69.69, 67.37, 20.63; IR (ATR): ν = 2921, 2851, 1740, 1597, 1461, 1164, 821, 743, 726 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{32}H_{28}N_3O_2]^+$: 486.2182 [*M*+H]$^+$; found: 486.2175; *m/z* calcd. for $[C_{32}H_{27}N_3NaO_2]^+$: 508.2001 [*M*+Na]$^+$; found: 508.1998.

Synthesis of carbazole C4



Scheme S6. Synthesis of **C4**.

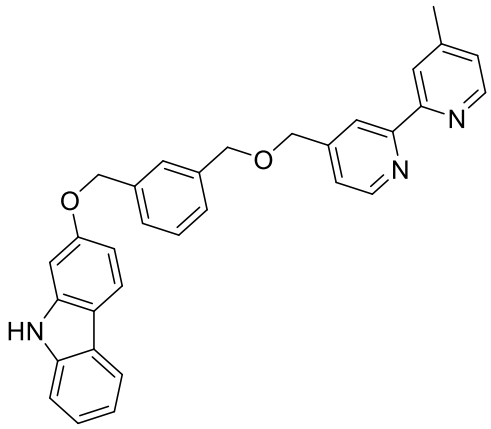
4-(((3-(Bromomethyl)benzyl)oxy)methyl)-4'-methyl-2,2'-bipyridine (**S9**)



S7 (112.7 mg, 0.56 mmol, 1.0 equiv.) was dissolved in tetrahydrofuran (2.2 mL, 0.25 M) and NaH (60% dispersion in mineral oil, 33.6 mg, 0.84 mmol, 1.5 equiv.) was added slowly under stirring. After 20 min., the reaction mixture was added dropwise into a solution of 1,3-bis(bromomethyl) benzene (739.1 mg, 2.8 mmol, 5 equiv.) in THF (1.1 mL, 2.5 M), stirring for 18 h, until completion was revealed by TLC. The reaction mixture was concentrated under vacuum, the residue redissolved in DCM and washed twice with water (pH ≈ 9) and once with brine. The organic phase was dried over Na_2SO_4, concentrated and the brown solid purified by silica gel column chromatography (DCM:methanol = 99:1) to give the pure product **S9** (brownish oil, 145.1 mg, 68%).

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.62 (d, *J* = 5.0 Hz, 1H), 8.50 (d, *J* = 4.9 Hz, 1H), 8.42-8.38 (m, 1H), 8.30-8.26 (m, 1H), 7.45 (s, 1H), 7.39-7.31 (m, 4H), 7.18-7.12 (m, 1H), 4.67 (s, 2H), 4.63 (s, 2H), 4.54 (s, 2H), 2.44 (s, 3H); ^{13}C {^{1}H} NMR (101 MHz, CD_2Cl_2): δ 156.68, 156.08, 149.56, 149.27, 148.78, 148.51, 139.19, 138.60, 129.26, 128.79, 128.68, 128.12, 125.11, 122.19, 122.11, 119.48, 72.74, 71.28, 33.95, 21.35; IR (ATR): ν = 1596, 1556, 1458, 1373, 1212, 1159, 1084, 823, 698 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{20}H_{20}BrN_2O]^+$: 383.0759 [*M*+H]$^+$; found: 383.0760; *m/z* calcd. for $[C_{20}H_{19}BrN_2NaO]^+$: 405.0578 [*M*+Na]$^+$; found: 405.0597.

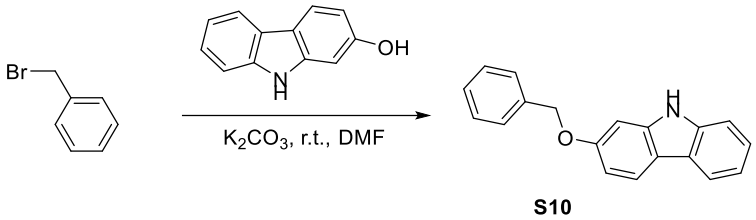
2-((3-(((4'-Methyl-[2,2'-bipyridin]-4-yl)methoxy)methyl)benzyl)oxy)-9H-carbazole (**C4**)



A mixture of 9*H*-carbazol-2-ol (58.8 mg, 0.32 mmol, 1.1 equiv.), **S9** (113.2 mg, 0.29 mmol, 1 equiv.), K_2CO_3 (57.4 mg, 0.41 mmol, 1.4 equiv.) in DMF (0.5 mL, 0.7 M) was stirred for 22 h, until completion was revealed by TLC. The reaction mixture was then filtered on a celite pad and the solvent evaporated. The crude product was purified by silica gel column chromatography (DCM:ethyl acetate = 8:2) to give the pure product **C4** (white solid, 62.2 mg, 44%). Mp = 140-146 °C.

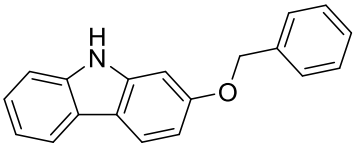
^{1}H NMR (400 MHz, DMSO-d_6): δ 11.10 (s, 1H), 8.61 (d, *J* = 4.7 Hz, 1H), 8.52 (d, *J* = 4.9 Hz, 1H), 8.41-8.37 (m, 1H), 8.27-8.22 (m, 1H), 8.01-7.94 (m, 2H), 7.54 (s, 1H), 7.48-7.35 (m, 5H), 7.31-7.25 (m, 2H), 7.14-7.07 (m, 1H), 7.05 (d, *J* = 2.2 Hz, 1H), 6.85 (dd, *J* = 8.5, 2.3 Hz, 1H), 5.22 (s, 2H), 4.69 (s, 2H), 4.65 (s, 2H), 2.41 (s, 3H); ^{13}C {^{1}H} NMR (101 MHz, DMSO-d_6): δ 157.46, 155.40, 154.96, 149.13, 148.97, 148.58, 147.87, 140.93, 139.74, 138.21, 137.50, 128.45, 127.02, 126.85, 126.76, 124.91, 124.12, 122.57, 121.96, 121.20, 120.82, 119.20, 118.48, 118.40, 116.40, 110.54, 108.24, 95.73, 71.87, 70.00, 69.41, 20.65; IR (ATR): ν = 2957, 2921, 2852, 1733, 1597, 1460, 1371, 1173, 1117, 1018, 814, 726 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{32}H_{28}N_3O_2]^+$: 486.2182 [*M*+H]$^+$; found: 486.2183; *m/z* calcd. for $[C_{32}H_{27}N_3NaO_2]^+$: 508.2001 [*M*+Na]$^+$; found: 508.1997.

Synthesis of carbazole S10



Scheme S7. Synthesis of **S10**.

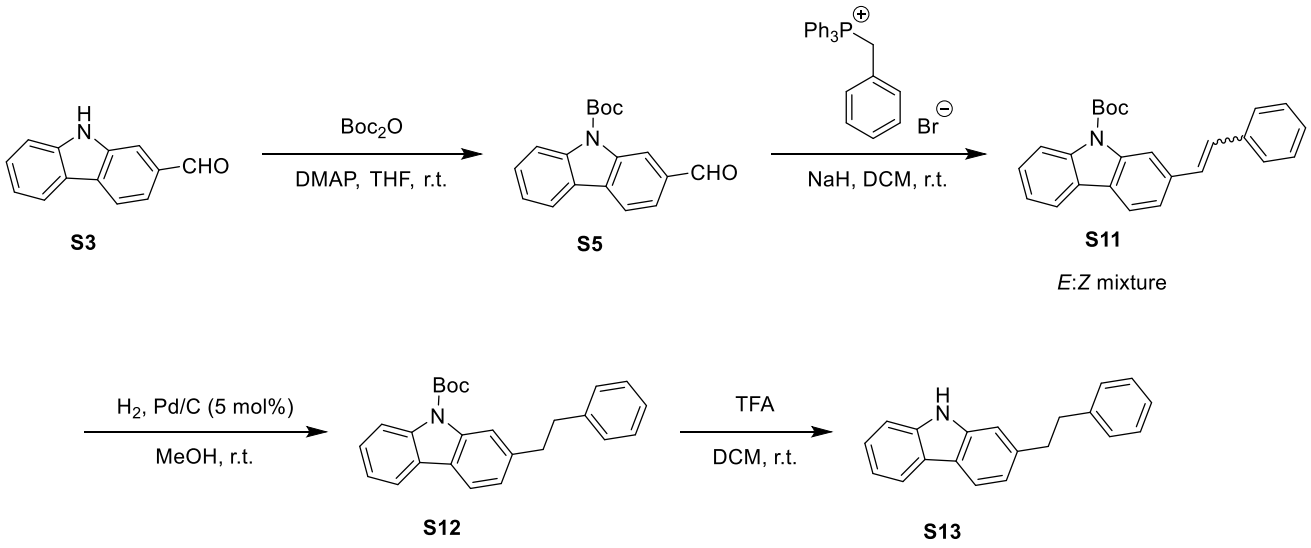
2-(Benzyloxy)-9H-carbazole (**S10**)



A mixture of 9*H*-carbazol-2-ol (526.3 mg, 2.8 mmol, 1.1 equiv.), benzyl bromide (310 µl, 2.5 mmol, 1 equiv.), K_2CO_3 (490.2 mg, 3.5 mmol, 1.4 equiv.) in DMF (4 mL, 0.7 M) was stirred for 24 h. The reaction mixture was then filtered on a celite pad and the solvent evaporated. The residue obtained was purified by silica gel column chromatography (DCM:ethyl acetate = 7:3) to give the pure product **S10** (white powder, 298.4 mg, 43%).

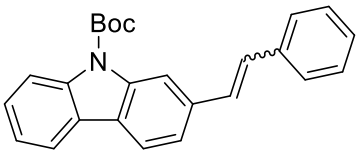
^{1}H NMR (400 MHz, DMSO-d_6): δ 11.09 (s, 1H), 7.97 (dd, *J* = 8.2, 5.6 Hz, 2H), 7.54-7.47 (m, 2H), 7.46-7.38 (m, 3H), 7.37-7.32 (m, 1H), 7.31-7.25 (m, 1H), 7.13-7.07 (m, 1H), 7.04 (d, *J* = 2.2 Hz, 1H), 6.85 (dd, *J* = 8.5, 2.3 Hz, 1H), 5.20 (s, 2H). These data are in accordance with those previously reported in the literature.[10]

Synthesis of carbazole S13



Scheme S8. Synthesis of **S13**.

tert-Butyl 2-styryl-9H-carbazole-9-carboxylate (**S11**)



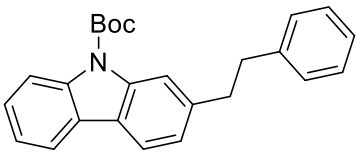
To a suspension of benzyltriphenylphosphonium bromide (320.7 mg, 0.74 mmol, 1 equiv.) in DCM (6 mL, 0.13 M) was added NaH (60% suspension in paraffin oil) (59.6 mg, 1.5 mmol, 2 equiv.). The resulting mixture was stirred at room temperature for 4 h. Then, a solution of **S5** (218.6 mg, 0.74 mmol, 1 equiv.) in DCM (2 mL, 0.37 M) was prepared and added to the reaction mixture, and the solution was stirred overnight for 22 h. The crude mixture was quenched with water and extracted three times with DCM. The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The mixture was purified by silica gel column chromatography (hexane:DCM = 8:2) to give the pure **S11** (~ 1:1 = *E*:*Z* ratio of diastereoisomers, 197.0 mg, 72%).

Analytical data for *Z* isomer (colorless oil): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.33 (d, *J* = 8.4 Hz, 1H), 8.25 (s, 1H), 7.96-7.90 (m, 1H), 7.82 (d, *J* = 8.0 Hz, 1H), 7.48-7.42 (m, 1H), 7.36-7.33 (m, 1H), 7.32-7.24 (m, 3H), 7.23-7.17 (m, 3H), 6.77 (d, *J* = 12.2 Hz, 1H), 6.63 (d, *J* = 12.2 Hz, 1H), 1.60 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 151.15, 139.13, 138.56, 137.27, 136.43, 131.00, 130.27, 129.20, 128.34, 127.27, 127.15, 125.71, 124.93, 124.08, 123.16, 119.57, 119.42, 116.91, 116.39, 83.96, 28.26; IR (ATR): ν = 1721, 1495, 1469, 1456, 1422, 1355, 1330, 1221, 1152, 1049, 1031, 765, 744, 693 cm^{-1}.

Analytical data for *E* isomer (white solid, Mp = 139-142 °C): ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.55 (s, 1H), 8.28 (d, *J* = 8.3 Hz, 1H), 8.00-7.91 (m, 2H), 7.59-7.52 (m, 3H), 7.49-7.27 (m, 6H), 7.22-7.17 (m, 1H), 1.81 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 151.24, 139.23, 139.02, 137.54, 136.63, 129.53, 128.82, 128.71, 127.69, 127.12, 126.64, 125.78, 125.48, 123.22, 122.01, 119.76, 119.67, 116.41, 114.43, 84.09, 28.52; IR (ATR): ν = 1732, 1356, 1329, 1056, 1033, 770, 747, 693 cm^{-1}.

HRMS (ESI): *m/z* calcd. for $[C_{25}H_{23}NNaO_2]^+$: 392.1626 [*M*+Na]$^+$; found: 392.1625.

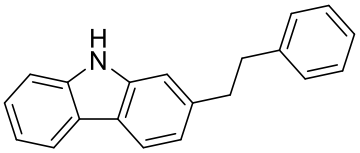
tert-Butyl 2-phenethyl-9H-carbazole-9-carboxylate (**S12**)



To a stirred solution of **S11** (197.0 mg, 0.53 mmol, 1 equiv.) in MeOH (5.5 mL, 0.1 M) was added Pd/C (29.3 mg, 0.0275 mmol, 0.05 equiv.). The flask was connected to the hydrogen line, filled with H_2 (3 cycles vacuum-hydrogen) and left stirring at room temperature for 18 h under H_2 at atmospheric pressure. The mixture was then filtered on a Celite pad, washing with ethyl acetate, the solvent was removed under reduced pressure to obtain the pure **S12** (colorless oil, 196.0 mg, 99%), which was used in the following step without further purification.

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.28 (d, *J* = 8.3 Hz, 1H), 8.21 (s, 1H), 7.95 (d, *J* = 7.7 Hz, 1H), 7.88 (d, *J* = 8.0 Hz, 1H), 7.49-7.41 (m, 1H), 7.38-7.27 (m, 3H), 7.25-7.15 (m, 4H), 3.16-2.98 (m, 4H), 1.77 (s, 9H); ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ 151.14, 141.73, 141.12, 138.89, 138.56, 128.52, 128.36, 126.60, 125.94, 125.87, 123.90, 123.69, 122.96, 119.33, 119.30, 116.28, 116.21, 83.66, 38.79, 38.35, 28.34; IR (ATR): ν = 1721, 1602, 1496, 1456, 1425, 1359, 1331, 1303, 1255, 1221, 1150, 1117, 767, 741, 723, 697 cm^{-1}, HRMS (ESI): *m/z* calcd. for $[C_{25}H_{25}NNaO_2]^+$: 394.1783 [*M*+Na]$^+$; found: 394.1779.

2-Phenethyl-9H-carbazole (**S13**)



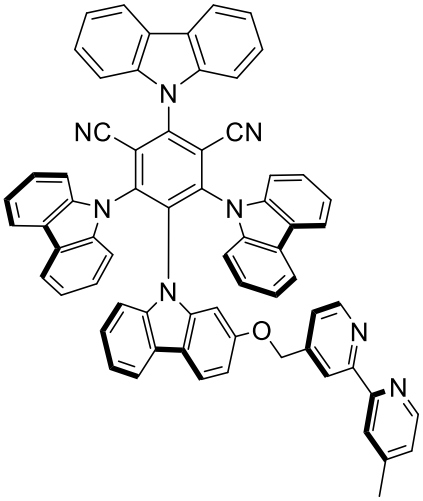
S13 (196.0 mg, 0.53 mmol, 1.0 equiv.) was dissolved in DCM (5.3 mL, 0.1 M), then TFA (2.6 mL, 34.0 mmol, 64 equiv.) was added. The resulting mixture was stirred at room temperature for 1 h. The solvent was then removed, and the reaction mixture was dissolved in DCM and washed with a solution of NaOH 2M. The organic phase was dried over Na_2SO_4 and concentrated in vacuo. The mixture was purified by silica gel column chromatography (hexane:ethyl acetate = 9:1) to give the pure **S13** (yellowish powder, 133.0 mg, 92%). Mp = 205-212 °C

^{1}H NMR (400 MHz, DMSO-d_6): δ 11.12 (s, 1H), 8.05 (d, *J* = 7.7 Hz, 1H), 7.99 (d, *J* = 8.0 Hz, 1H), 7.45 (d, *J* = 8.1 Hz, 1H), 7.37-7.24 (m, 6H), 7.20-7.09 (m, 2H), 7.07-7.02 (m, 1H), 3.08-3.00 (m, 2H), 3.00-2.92 (m, 2H); ^{13}C NMR (101 MHz, DMSO) δ 141.65, 140.02, 139.76, 139.20, 128.40, 128.17, 125.75, 124.98, 122.43, 120.50, 119.84, 119.80, 119.43, 118.34, 110.77, 110.40, 37.73, 37.59; IR (ATR): ν = 3400, 1720, 1590, 1335, 1222, 1152, 961, 823 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{20}H_{17}NNa]^+$: 294.1259 $[M+Na]^+$; found: 294.1248.

General procedure for the nucleophilic aromatic substitution on 3CzFIPN

The functionalized carbazole (1.1 equiv.) was added into a flame-dried flask equipped with a stirring bar. Freshly distilled THF (0.09 M) was then added, and the mixture was cooled down to –78 °C while stirring, then NaH (60% suspension in mineral oil) (2 equiv.) was added and the reaction was left stirring for 45 min. 3CzFIPN (1 equiv.) was dissolved freshly distilled THF (0.08 M) and then added slowly into the flask containing deprotonated carbazole at –78 °C. The mixture was stirred in the warming bath for 16 h. The reaction was stopped by adding distilled water dropwise. THF was then removed and the resulting solid was redissolved in DCM and washed three times with water. The collected organic phases were washed with brine, dried on Na_2SO_2 and the solvent was evaporated. The crude product was then purified by silica gel column chromatography.

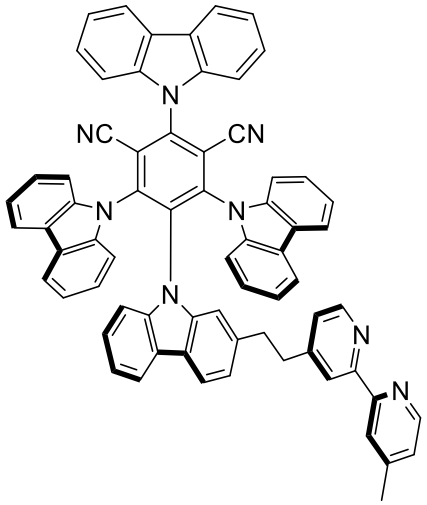
Bifunctional catalyst **B1**



The general procedure was followed using 3CzFIPN (427.6 mg, 0.66 mmol, 1 equiv.), **C1** (268.0 mg, 0.73 mmol, 1.1 equiv,) and NaH (60% suspension in mineral oil) (56.0 mg, 1.4 mmol, 2 equiv.) in THF (12 mL) for 16 h. Purification by silica gel column chromatography (DCM:ethyl acetate = 96:4) afforded the pure **B1** (yellow solid, 353.1 mg, 74%). Mp = 290-300 °C

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.78 (d, *J* = 5.0 Hz, 1H), 8.67 (d, *J* = 4.9 Hz, 1H), 8.52 (s, 1H), 8.40-8.30 (m, 3H), 8.28-8.16 (m, 2H), 7.95-7.82 (m, 6H), 7.82-7.70 (m, 4H), 7.58-7.46 (m, 3H), 7.42-7.32 (m, 4H), 7.28-7.19 (m, 3H), 7.19-7.04 (m, 6H), 6.79 (d, *J* = 7.8 Hz, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 6.58 (d, *J* = 7.6 Hz, 1H), 4.75 (s, 2H), 2.47 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 156.65, 155.65, 155.00, 149.39, 149.18, 148.11, 147.12, 145.61, 144.89, 139.83, 139.77, 139.08, 138.55, 137.87, 136.09, 126.83, 125.65, 125.46, 125.20, 123.68, 123.39, 123.31, 123.11, 122.97, 121.98, 121.39, 121.12, 121.05, 120.66, 120.31, 118.72, 118.49, 117.29, 116.46, 112.37, 111.26, 111.11, 111.00, 110.92, 110.84, 109.28, 97.29, 68.28, 20.78; IR (ATR): ν = 2234, 1598, 1442, 1333, 1293, 1219, 1174, 819, 742, 721 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{68}H_{43}N_8O]^+$: 987.3560 [*M*+H]$^+$; found: 987.3536; *m/z* calcd. for $[C_{68}H_{42}N_8NaO]^+$: 1009.3379 [*M*+Na]$^+$; found: 1009.3365.

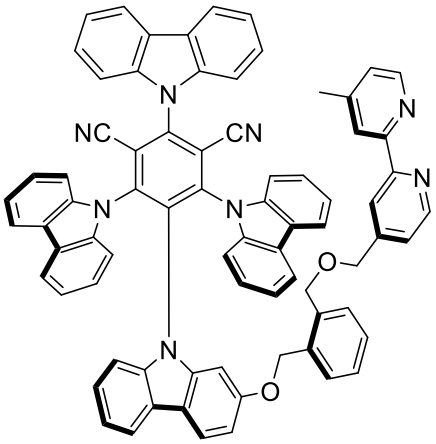
Bifunctional catalyst **B2**



The general procedure was followed using 3CzFIPN (443.8 mg, 0.69 mmol, 1 equiv.), **C2** (275.5 mg, 0.76 mmol, 1.1 equiv,) and NaH (60% suspension in mineral oil) (55.8 mg, 1.4 mmol, 2 equiv.) in THF (12 mL) for 16 h. Purification by silica gel column chromatography (DCM:ethyl acetate = 96:4 + 0.1% TEA) afforded the pure **B2** (yellow solid, 462.4 mg, 68%). Mp = 337-340 °C

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.68 (d, *J* = 4.9 Hz, 1H), 8.64 (d, *J* = 4.9 Hz, 1H), 8.43-8.29 (m, 4H), 8.24 (dd, *J* = 8.3, 2.7 Hz, 2H), 7.94-7.70 (m, 10H), 7.59-7.41 (m, 5H), 7.37-7.33 (m, 2H), 7.31-7.26 (m, 1H), 7.22-7.05 (m, 8H), 6.83-6.65 (m, 3H), 2.65-2.57 (m, 2H), 2.55-2.51 (m, 2H), 2.46 (s, 3H); ^{13}C NMR (101 MHz, DMSO-d_6): δ 155.41, 155.25, 151.49, 149.20, 149.13, 147.99, 145.53, 144.74, 139.82, 139.69, 138.56, 138.48, 137.96, 137.72, 136.09, 126.82, 126.77, 125.53, 125.45, 125.01, 124.08, 123.85, 123.70, 123.66, 123.37, 123.28, 122.90, 122.00, 121.32, 121.10, 121.04, 120.63, 120.50, 120.26, 119.21, 116.40, 112.38, 111.16, 111.00, 110.93, 110.35, 36.78, 36.16, 20.77; IR (ATR): ν = 2237, 1596, 1541, 1443, 1334, 1308, 1218, 1062, 744, 724 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{69}H_{45}N_8]^+$: 985.3767 [*M*+H]$^+$; found: 685.3759; *m/z* calcd. for $[C_{69}H_{44}N_8Na]^+$: 1007.3587 [*M*+Na]$^+$; found: 1007.3581.

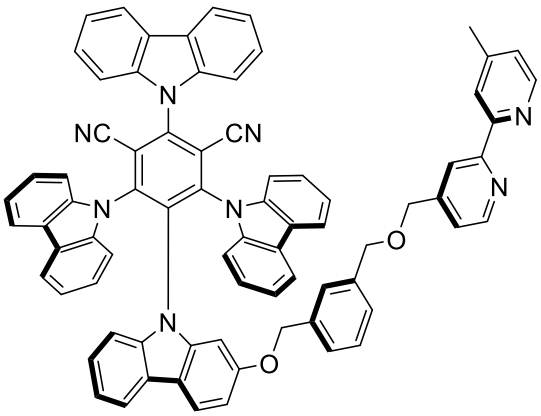
Bifunctional catalyst **B3**



The general procedure was followed using 3CzFIPN (84.9 mg, 0.13 mmol, 1.1 equiv.), **C3** (60.6 mg, 0.12 mmol, 1 equiv,) and NaH (60% suspension in mineral oil) (10.6 mg, 0.27 mmol, 2 equiv.) in THF (3 mL) for 16 h. Purification by silica gel column chromatography (DCM:ethyl acetate = 96:4) afforded the pure **B3** (yellow solid, 69.7 mg, 52%). Mp = 154-157 °C.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.55 (d, *J* = 5.3 Hz, 1H), 8.46 (d, *J* = 4.9 Hz, 1H), 8.42 (s, 1H), 8.30-8.23 (m, 3H), 7.84-7.69 (m, 8H), 7.58-7.48 (m, 3H), 7.46-7.42 (m, 2H), 7.34-7.26 (m, 7H), 7.22 (d, *J* = 8.4 Hz, 1H), 7.18-7.07 (m, 9H), 6.89 (d, *J* = 8.2 Hz, 1H), 6.86-6.80 (m, 1H), 6.63-6.56 (m, 1H), 6.56-6.48 (m, 2H), 4.66 (s, 2H), 4.65 (s, 2H), 4.56 (s, 2H), 2.40 (s, 3H); ^{13}C{^{1}H} NMR (101 MHz, CD_2Cl_2): δ 158.22, 156.75, 156.00, 149.59, 149.25, 148.79, 148.59, 145.56, 145.19, 140.33, 139.04, 138.66, 138.62, 137.62, 136.81, 135.39, 135.29, 129.66, 129.44, 128.85, 128.46, 127.44, 126.38, 126.33, 125.17, 124.91, 124.77, 124.31, 124.05, 122.86, 122.51, 122.45, 122.19, 122.14, 121.75, 121.63, 120.92, 120.87, 119.50, 119.21, 118.30, 116.85, 112.21, 110.54, 110.25, 110.04, 96.16, 71.38, 70.84, 68.59, 21.34; IR (ATR): ν = 1716, 1590, 1457, 1426, 1336, 1221, 1153, 962, 818 739 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{76}H_{51}N_8O_2]^+$: 1107.4135 $[M+H]^+$; found: 1107.4130; *m/z* calcd. for $[C_{76}H_{50}N_8NaO_2]^+$: 1129.3954 $[M+Na]^+$; found: 1129.3947.

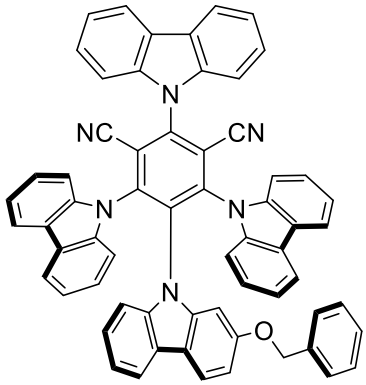
Bifunctional catalyst **B4**



The general procedure was followed using 3CzFIPN (78.0 mg, 0.12 mmol, 1.1 equiv.), **C4** (53.4 mg, 0.11 mmol, 1 equiv,) and NaH (60% suspension in mineral oil) (8.8 mg, 0.22 mmol, 2 equiv.) in THF (3 mL) for 16 h. Purification by silica gel column chromatography (DCM:ethyl acetate = 96:4) afforded the pure **B4** (yellow solid, 89.2 mg, 73%). Mp = 270-273 °C.

^{1}H NMR (400 MHz, CD_2Cl_2): δ 8.64 (d, *J* = 5.0 Hz, 1H), 8.52-8.46 (m, 2H), 8.32-8.25 (m, 3H), 7.85-7.70 (m, 8H), 7.56-7.37 (m, 6H), 7.34-7.25 (m, 7H), 7.19-7.10 (m, 9H), 6.90 (d, *J* = 8.2 Hz, 1H), 6.83 (t, *J* = 7.5 Hz, 1H), 6.63-6.54 (m, 2H), 6.50-6.46 (m, 1H), 4.74 (s, 2H), 4.73 (s, 2H), 4.35 (s, 2H), 2.42 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2): δ 158.36, 156.84, 156.15, 149.64, 149.34, 148.91, 148.59, 145.49, 145.17, 140.37, 139.02, 138.88, 138.61, 137.55, 137.51, 135.15, 129.01, 127.88, 127.56, 127.47, 126.39, 125.17, 124.97, 124.77, 124.38, 124.02, 122.86, 122.55, 122.45, 122.27, 122.19, 121.76, 121.65, 120.99, 120.89, 120.84, 119.58, 119.18, 118.17, 116.80, 112.22, 111.02, 110.59, 110.53, 110.04, 95.56, 73.14, 71.40, 70.41, 21.37; IR (ATR): ν = 1716, 1590, 1457, 1426, 1335, 1221, 1153, 962, 822 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{76}H_{51}N_8O_2]^+$: 1107.4135 [*M*+H]$^+$; found: 1107.4135; *m/z* calcd. for $[C_{76}H_{50}N_8NaO_2]^+$: 1129.3954 [*M*+Na]$^+$; found: 1129.3969.

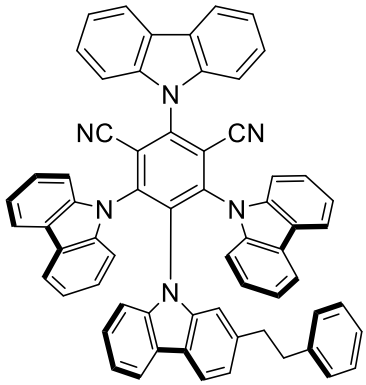
Reference catalyst **R1**



The general procedure was followed using 3CzFIPN (395.3 mg, 0.62 mmol, 1.1 equiv.), **S10** (153.1 mg, 0.56 mmol, 1 equiv,) and NaH (60% suspension in mineral oil) (49.3 mg, 1.2 mmol, 2 equiv.) in THF (14 mL) for 16 h. Purification by silica gel column chromatography (DCM:hexane = 6:4) afforded the pure **R1** (yellow solid, 382.9 mg, 76%). Mp = 318-320 °C

^{1}H NMR (400 MHz, DMSO-d_6): δ 8.36 (d, *J* = 7.7 Hz, 2H), 8.21 (dd, *J* = 16.8, 8.2 Hz, 2H), 7.97-7.82 (m, 6H), 7.81-7.70 (m, 4H), 7.60-7.46 (m, 5H), 7.45-7.32 (m, 5H), 7.25-7.07 (m, 9H), 6.78 (t, *J* = 7.4 Hz, 1H), 6.63 (t, *J* = 7.7 Hz, 1H), 6.50 (d, *J* = 8.2 Hz, 1H), 4.56 (s, 2H); ^{13}C{^{1}H} NMR (101 MHz, DMSO-d_6): δ 157.12, 145.59, 144.81, 139.76, 139.68, 139.11, 138.54, 138.50, 137.77, 136.73, 136.06, 128.42, 127.86, 127.66, 126.76, 125.53, 125.40, 123.66, 123.62, 123.38, 123.28, 123.02, 122.87, 121.93, 121.31, 121.05, 120.98, 120.54, 120.25, 120.20, 120.13, 118.54, 116.82, 116.37, 112.30, 111.22, 111.06, 110.96, 110.88, 110.81, 109.82, 96.46, 69.70, 39.85, 39.66, 39.63, 39.47, 39.41, 39.19; IR (ATR): ν = 2235, 1602, 1539, 1442, 1332, 1308, 1292, 1219, 1175, 1028, 929, 739, 721 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{63}H_{38}N_6NaO]^+$: 917.3005 [*M*+Na]$^+$; found: 917.2980.

Reference catalyst **R2**



The general procedure was followed using 3CzFIPN (224.8 mg, 0.35 mmol, 1 equiv.), **S13** (102.3 mg, 0.38 mmol, 1 equiv,) and NaH (60% suspension in mineral oil) (28.4 mg, 0.71 mmol, 2 equiv.) in THF (6 mL) for 16 h. Purification by silica gel column chromatography (hexane:ethyl acetate = 85:15) afforded the pure **R2** (yellow solid, 274.0 mg, 88%). Mp = 313 -319 °C

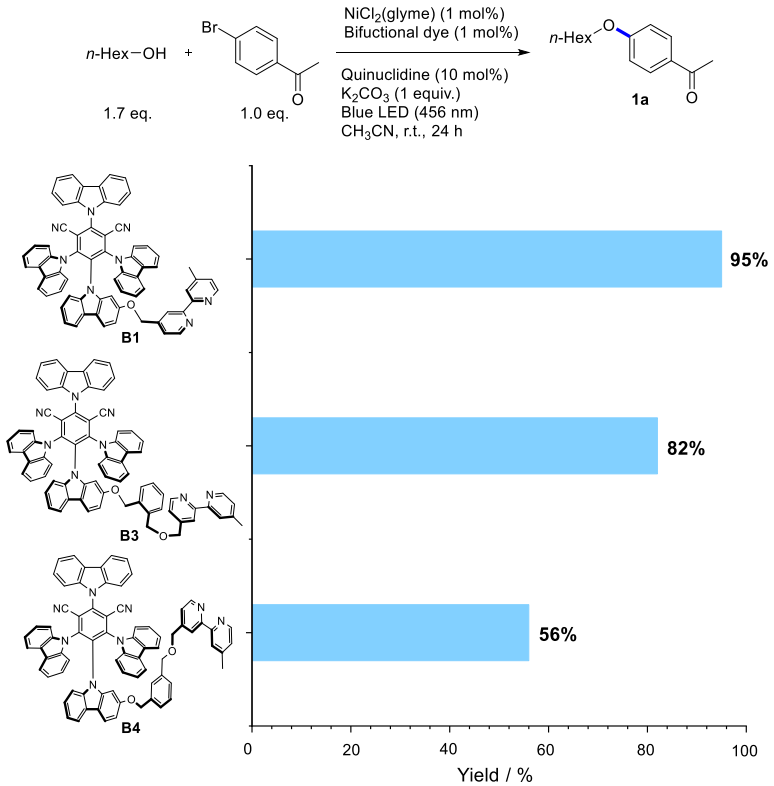
^{1}H NMR (400 MHz, DMSO-d_6): δ 8.36 (d, *J* = 7.8 Hz, 2H), 8.26-8.20 (m, 2H), 7.93-7.86 (m, 4H), 7.84-7.76 (m, 4H), 7.75-7.70 (m, 2H), 7.58-7.48 (m, 3H), 7.44-7.30 (m, 5H), 7.27-7.19 (m, 3H), 7.18-7.06 (m, 8H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.72-6.63 (m, 2H), 2.56-2.51 (m, 2H), 2.47-2.40 (m, 2H); ^{13}C NMR (101 MHz, DMSO) δ 145.55, 144.72, 141.64, 139.82, 139.68, 139.18, 138.56, 138.51, 137.99, 137.71, 136.15, 128.31, 128.28, 126.80, 126.77, 125.83, 125.47, 125.43, 123.77, 123.70, 123.66, 123.37, 123.29, 122.94, 121.99, 121.31, 121.26, 121.07, 121.02, 120.99, 120.45, 120.23, 120.21, 119.13, 119.05, 116.43, 112.37, 111.15, 111.05, 111.01, 110.90, 110.25, 37.31, 37.25; IR (ATR): ν = 2236, 1600, 1441, 1332, 1308, 1220, 1151, 741, 720 cm^{-1}; HRMS (ESI): *m/z* calcd. for $[C_{64}H_{40}N_6Na]^+$: 915.3212 $[M+Na]^+$; found: 915.3217.

General procedure for the C-O coupling catalytic tests

To a vial containing a stirring bar, the aryl bromide (0.5 mmol, 1.0 equiv.), potassium carbonate (69.1 mg, 0.5 mmol, 1 equiv.) and quinuclidine (5.7 mg, 0.05 mmol, 0.1 equiv.) were added. The vial was sealed with a cap with septum and purged with nitrogen for 2 min, then freshly distilled acetonitrile was added (1 mL). A solution of $NiCl_2$·glyme, 4,4'-dimethyl-2,2'-bipyridine (in a 1:1 ratio with Ni) and 4CzIPN or the reference dye (in a 1:1 ratio with Ni) or, alternatively, of $NiCl_2$·glyme and the bifunctional catalyst (in a 1:1 ratio with Ni), in freshly distilled acetonitrile (2 mL) was sonicated and added to the vial. At last, the aliphatic alcohol (1.0 mmol, 2 equiv.) was added, and the reaction mixture was subjected to three freeze-pump-thaw cycles, backfilling with dry nitrogen. The magnetically stirred reaction was run at room temperature for the specified time under irradiation with a blue LED lamp (λ = 456 nm; distance between lamp and vial(s): 5 cm; a fan was used to dissipate the heat generated by the lamp). 1,3,5-Trimethoxybenzene (42.1 mg, 0.25 mmol, 0.5 equiv.)-the internal standard for ^{1}H NMR analysis-was added, and the reaction mixture was stirred for 5 min. Water (10 mL) was added and then the mixture was extracted three times with ethyl acetate. The combined organic extracts were washed with brine, dried (Na_2SO_4) and then concentrated. The crude mixture was analyzed by ^{1}H NMR and then purified by flash column chromatography on silica gel to afford the desired product.

Note on experiments at low catalyst loadings (0.5 mol% and below): in order to avoid weighting too small amounts of $NiCl_2$(glyme), stock solutions were prepared by dissolving $NiCl_2$(glyme) (*C* = 1.1 mg/mL) with an equimolar amount of bifunctional catalyst or 4,4'-dimethyl-2,2'-bipyridine and 4CzIPN/the reference dual catalyst, in freshly distilled acetonitrile. The solution was sonicated for 5 min., after which it turned yellow-green. The desired amount was withdrawn with a Hamilton syringe, i.e. 0.5 mL for 0.5 mol%, 0.3 mL for 0.3 mol% and so on, and added to the reaction vessel. Finally, the reaction mixture was taken to the final volume by addition of acetonitrile.

Comparison of different linkage for the bifunctional systems



Scheme S9. Screening of the bifunctional dyes **B1, B3** and **B4** in the reaction of *n*-hexanol with 4-bromoacetophenone. Yields were determined by ^{1}H NMR using 1,3,5-trimethoxybenzene as internal standard.

Kinetic experiments

Kinetics were set up according to the general procedure above, using 4-bromoacetophenone (99.5 mg, 0.5 mmol, 1.0 equiv.), potassium carbonate (69.8 mg, 0.5 mmol, 1 equiv.), quinuclidine (5.7 mg, 0.05 mmol, 0.1 equiv.), 1-hexanol (126 µL, 2.0 mmol, 2 equiv.), $NiCl_2$(glyme), 4,4'-dimethyl-2,2'-bipyridine (in a 1:1 ratio with Ni), the reference dye (in a 1:1 ratio with Ni), or, alternatively, $NiCl_2$·glyme and the bifunctional catalyst (in a 1:1 ratio with Ni), in acetonitrile (3 mL), under argon atmosphere. At the desired time, an aliquot of 80 µL of reaction solution was withdrawn, without turning off the lamp, using a Hamilton syringe previously rinsed with argon, and it was transferred in a vial containing ethyl acetate. Water was added, the phases separated, and the organic phase concentrated *in vacuo* and analyzed by NMR, determining the ratio between the product and the starting material for the conversion (if needed, considering the amount of dehalogenation).

Table S1. Kinetics comparison of **B1** and **R1** at 1 mol% catalyst loading.

Time (min)	Conv. **B1** (%)	Conv. **R1** + dmbpy (%)
5	20	4
15	71	16
25	91	27
35	99	34
45	100	43
60	100	52
75	100	60
1440	100	95

Table S2. Kinetics comparison of **B1** and **R1** at 0.5 mol% catalyst loading.

Time (min)	Conv. **B1** (%)	Conv. **R1** + dmbpy (%)
5	22	3
15	72	6
25	93	10
35	99	11
45	100	13
60	100	17
75	100	20
1440	100	30

Table S3. Kinetics comparison of **B2** and **R2** at 0.5 mol% catalyst loading.

Time (min)	Conv. **B1** (%)	Conv. **R1** + dmbpy (%)
5	12	24
15	60	61
25	96	79
35	97	90
45	100	96
60	100	96
75	100	96
1440	100	96

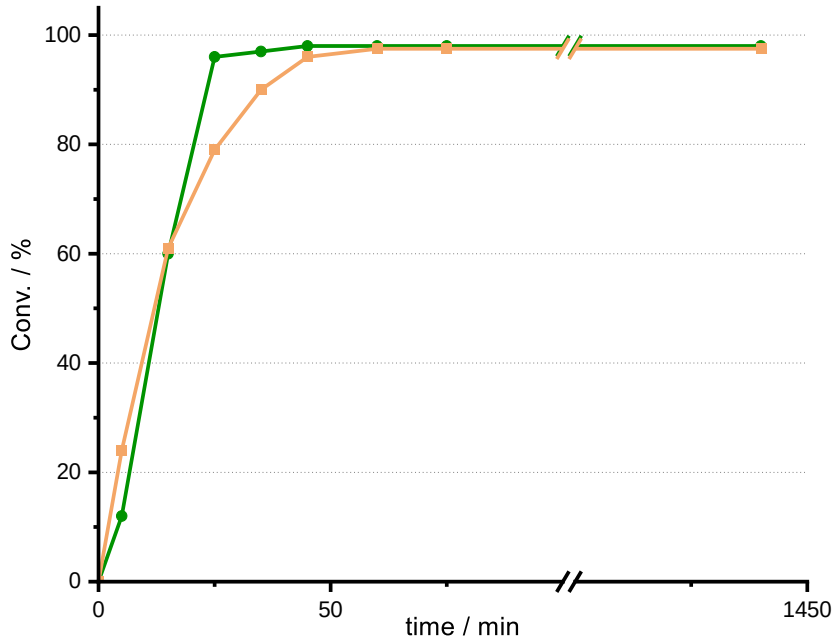
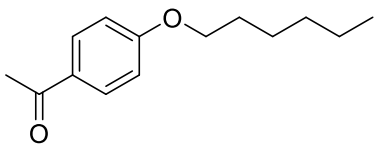


Figure S2. Kinetic profile of the bifunctional system with **B2** (green line) and the dual reference with **R2** (orange line).

Substrate scope

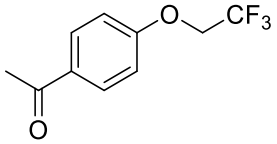
1-(4-(Hexyloxy)phenyl)ethan-1-one (**1a**)



The General Procedure for C-O coupling was followed using 4-bromoacetophenone (99.5 mg, 0.5 mmol, 1 equiv.), potassium carbonate (69.1 mg, 0.5 mmol, 1 equiv.), quinuclidine (5.6 mg, 0.05 mmol, 0.1 equiv.), bifunctional catalyst **B1** or **B2** (2.5 mg, 0.0025 mmol, 0.5 mol%), $NiCl_2$(glyme) (0.55 mg, 0.0025 mmol, 0.5 mol%), 1-hexanol (126 µL, 2.0 mmol, 2 equiv.) in acetonitrile (3 mL) for 16 hours. Purification by silica gel column chromatography (hexane:ethyl acetate = 9:1) afforded the pure **1a** (colorless oil; **B1**: 89.2 mg, 81%; **B2**: 91.4 mg, 83%; Scale up 10x with **B2**: 957.1 mg, 87%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.92 (d, *J* = 8.9 Hz, 2H), 6.91 (d, *J* = 8.9 Hz, 2H), 4.01 (t, *J* = 6.6 Hz, 2H), 2.55 (s, 3H), 1.85-1.76 (m, 2H), 1.52-1.41 (m, 2H), 1.38-1.29 (m, 4H), 0.97-0.87 (m, 3H).

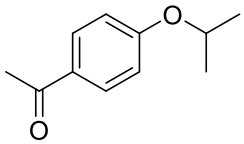
1-(4-(2,2,2-Trifluoroethoxy)phenyl)ethan-1-one (**1b**)



The General Procedure for C-O coupling was followed using 4-bromoacetophenone (99.5 mg, 0.5 mmol, 1 equiv.), potassium carbonate (69.1 mg, 0.5 mmol, 1 equiv.), quinuclidine (5.6 mg, 0.05 mmol, 0.1 equiv.), bifunctional catalyst **B1** or **B2** (9.9 mg, 0.01 mmol, 2 mol%), $NiCl_2$(glyme) (2.2 mg, 0.01 mmol, 2 mol%), 2,2,2-trifluoroethanol (73 µL, 1.0 mmol, 2 equiv.) in acetonitrile (3 mL) for 16 hours. Purification by silica gel column chromatography (hexane:ethyl acetate = 8:2) afforded the pure **1b** (colorless oil; **B1**: 13.9 mg, 14%; **B2**: 38.5 mg, 35%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00-7.93 (m, 2H), 6.99 (d, *J* = 8.9 Hz, 2H), 4.42 (q, *J* = 8.0 Hz, 2H), 2.57 (s, 3H).

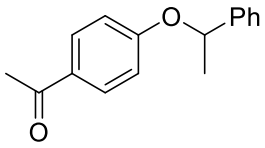
1-(4-Isopropoxyphenyl)ethan-1-one (**1c**)



The General Procedure for C-O coupling was followed using 4-bromoacetophenone (99.5 mg, 0.5 mmol, 1 equiv.), potassium carbonate (69.1 mg, 0.5 mmol, 1 equiv.), quinuclidine (5.6 mg, 0.05 mmol, 0.1 equiv.), bifunctional catalyst **B1** or **B2** (2.5 mg, 0.0025 mmol, 0.5 mol%), $NiCl_2$(glyme) (0.55 mg, 0.0025 mmol, 0.5 mol%), isopropanol (153 µL, 2.0 mmol, 4 equiv.) in acetonitrile (3 mL) for 16 hours. Purification by silica gel column chromatography (hexane:ethyl acetate = 9:1) afforded the pure **1c** (colorless oil; **B1**: 71.9 mg, 81%; **B2**: 65.8 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, *J* = 8.9 Hz, 2H), 6.90 (d, *J* = 8.9 Hz, 2H), 4.64 (p, *J* = 6.1 Hz, 1H), 2.55 (s, 3H), 1.36 (d, *J* = 6.0 Hz, 6H).

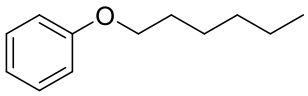
1-(4-(1-Phenylethoxy)phenyl)ethan-1-one (**1d**)



The General Procedure for C-O coupling was followed using 4-bromoacetophenone (99.5 mg, 0.5 mmol, 1 equiv.), potassium carbonate (69.1 mg, 0.5 mmol, 1 equiv.), quinuclidine (5.6 mg, 0.05 mmol, 0.1 equiv.), bifunctional catalyst **B1** or **B2** (2.5 mg, 0.0025 mmol, 0.5 mol%), $NiCl_2$(glyme) (0.55 mg, 0.0025 mmol, 0.5 mol%), 1-phenylethanol (242 µL, 2.0 mmol, 4 equiv.) in acetonitrile (3 mL) for 16 hours. Purification by silica gel column chromatography (hexane:ethyl acetate = 9:1) afforded the pure **1d** (colorless oil; **B1**: 102.5 mg, 85%; **B2**: 88.0 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.80 (m, 2H), 7.38-7.31 (m, 4H), 7.30-7.24 (m, 1H), 6.92-6.86 (m, 2H), 5.39 (q, *J* = 6.4 Hz, 1H), 2.50 (s, 3H), 1.67 (d, *J* = 6.1 Hz, 3H).

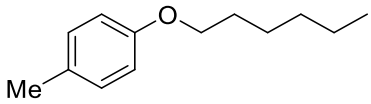
(Hexyloxy)benzene (**1e**)



The General Procedure for C-O coupling was followed using 4-bromobenzene (53 µL, 0.5 mmol, 1 equiv.), potassium carbonate (69.1 mg, 0.5 mmol, 1 equiv.), quinuclidine (5.6 mg, 0.05 mmol, 0.1 equiv.), bifunctional catalyst **B1** or **B2** (9.9 mg, 0.01 mmol, 2 mol%), $NiCl_2$(glyme) (2.2 mg, 0.01 mmol, 2 mol%), 1-hexanol (126 µL, 1.0 mmol, 2 equiv.) in acetonitrile (3 mL) for 16 hours. Purification by silica gel column chromatography (hexane:ethyl acetate = 98:2) afforded the pure **1e** (colorless oil; **B1**: 46.9 mg, 52%; **B2**: 44.1 mg, 49%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.31-7.24 (m, 2H), 6.96-6.87 (m, 3H), 3.96 (t, *J* = 6.6 Hz, 2H), 1.84-1.73 (m, 2H), 1.52-1.41 (m, 2H), 1.40-1.31 (m, 4H), 0.96-0.87 (m, 3H).

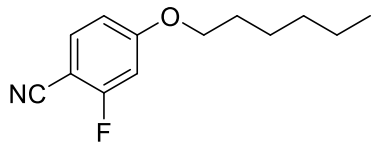
1-(Hexyloxy)-4-methylbenzene (**1f**)



The General Procedure for C-O coupling was followed using 4-bromotoluene (62 µL, 0.5 mmol, 1 equiv.), potassium carbonate (69.1 mg, 0.5 mmol, 1 equiv.), quinuclidine (5.6 mg, 0.05 mmol, 0.1 equiv.), bifunctional catalyst **B1** or **B2** (9.9 mg, 0.01 mmol, 2 mol%), $NiCl_2$(glyme) (2.2 mg, 0.01 mmol, 2 mol%), 1-hexanol (126 µL, 1.0 mmol, 2 equiv.) in acetonitrile (3 mL) for 16 hours. Purification by silica gel column chromatography (hexane:ethyl acetate = 99:1) afforded the pure **2f** (colorless oil; **B1**: 36.8 mg, 39%; **B2**: 37.1 mg, 39%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.10-7.04 (m, 2H), 6.83-6.77 (m, 2H), 3.92 (t, *J* = 6.6 Hz, 2H), 2.28 (s, 3H), 1.81-1.71 (m, 2H), 1.50-1.40 (m, 2H), 1.38-1.29 (m, 4H), 0.95-0.87 (m, 3H).

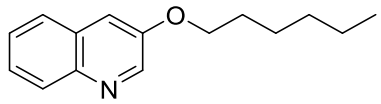
2-fluoro-4-(hexyloxy)benzonitrile (**1g**)



The General Procedure for C-O coupling was followed using 4-bromo-2-fluorobenzonitrile (100.0 mg, 0.5 mmol, 1 equiv.), potassium carbonate (69.1 mg, 0.5 mmol, 1 equiv.), quinuclidine (5.6 mg, 0.05 mmol, 0.1 equiv.), bifunctional catalyst **B1** or **B2** (9.9 mg, 0.01 mmol, 2 mol%), $NiCl_2$(glyme) (2.2 mg, 0.01 mmol, 2 mol%), 1-hexanol (126 µL, 1.0 mmol, 2 equiv.) in acetonitrile (3 mL) for 16 hours. Purification by silica gel column chromatography (hexane:ethyl acetate = 97:3) afforded the pure **1g** (colorless oil; **B1**: 92.1 mg, 83%; **B2**: 81.5 mg, 74%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 7.50 (dd, *J* = 8.7, 7.5 Hz, 1H), 6.77 – 6.72 (m, 1H), 6.71 – 6.65 (m, 1H), 3.99 (t, *J* = 6.5 Hz, 2H), 1.85 – 1.74 (m, 2H), 1.51 – 1.40 (m, 2H), 1.39 – 1.30 (m, 4H), 0.94 – 0.87 (m, 3H).

3-(Hexyloxy)quinoline (**1h**)



The General Procedure for C-O coupling was followed using 3-bromoquinoline (68 µL, 0.5 mmol, 1 equiv.), potassium carbonate (69.1 mg, 0.5 mmol, 1 equiv.), quinuclidine (5.6 mg, 0.05 mmol, 0.1 equiv.), bifunctional catalyst **B1** or **B2** (9.9 mg, 0.01 mmol, 2 mol%), $NiCl_2$(glyme) (2.2 mg, 0.01 mmol, 2 mol%), 1-hexanol (126 µL, 1.0 mmol, 2 equiv.) in acetonitrile (3 mL) for 16 hours. Purification by silica gel column chromatography (hexane:ethyl acetate = 93:7) afforded the pure **1h** (colorless oil; **B1**: 85.8 mg, 75%; **B2**: 73.8 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$): δ 8.67 (d, *J* = 2.9 Hz, 1H), 8.07 – 8.02 (m, 1H), 7.74 – 7.68 (m, 1H), 7.58 – 7.46 (m, 2H), 7.38 – 7.35 (m, 1H), 4.09 (t, *J* = 6.5 Hz, 2H), 1.93 – 1.82 (m, 2H), 1.57 – 1.46 (m, 2H), 1.41 – 1.33 (m, 4H), 0.96 – 0.89 (m, 3H).

Complex formation studies

Bifunctional catalyst **B1** (4.94 mg, 0.005 mmol, 1 equiv.) and $NiCl_2$(glyme) (1.1 mg, 0.005 mmol, 1 equiv.) were dissolved in MeCN (1 mL, 0.005 M). The solution was sonicated for three minutes. Then, the solution was diluted to 1 mM in acetonitrile, and analyzed by HRMS.

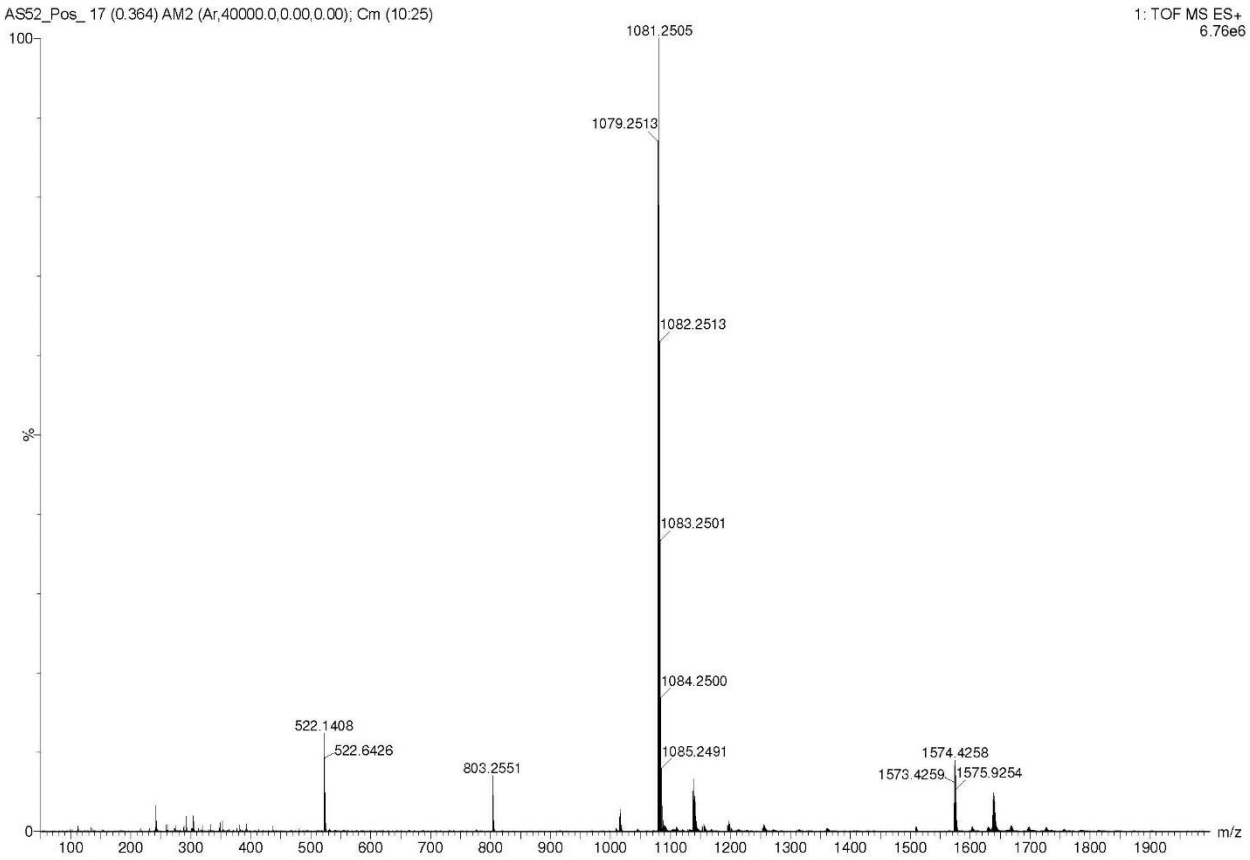


Figure S3. HRMS analysis of the complex formed *in situ*.

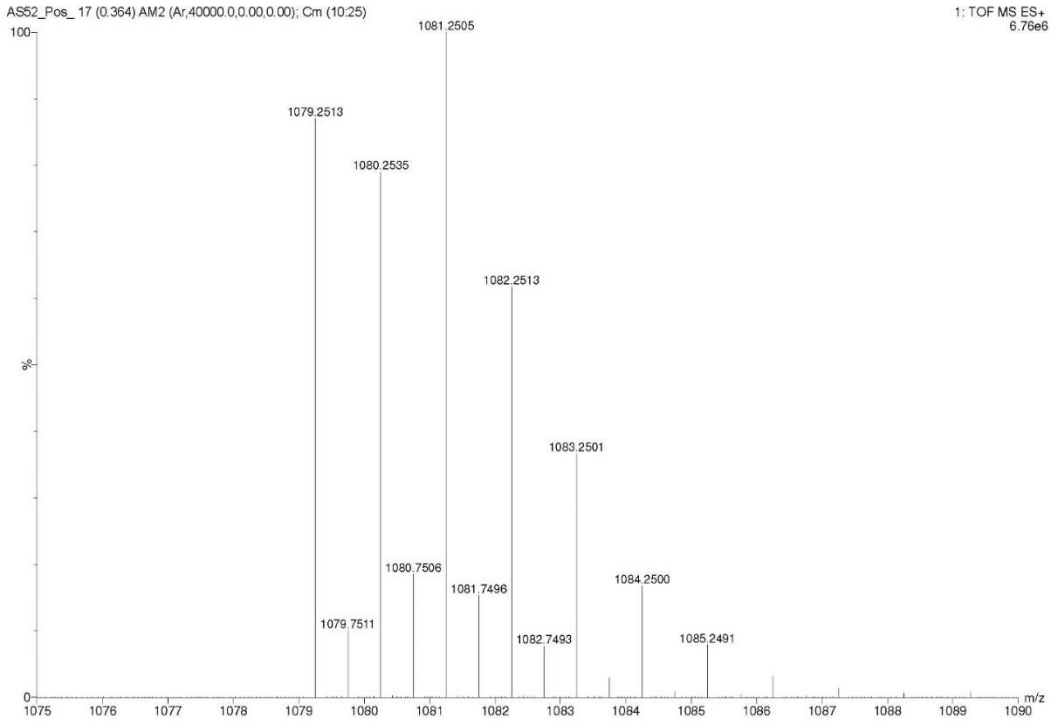
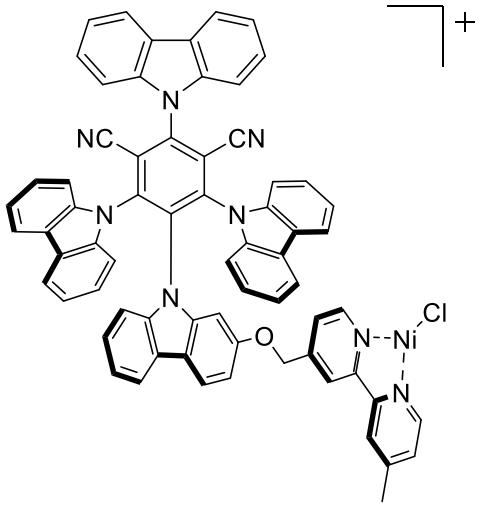


Figure S4. HRMS Analysis of the complex formed *in situ* (ion generated by loss of Cl^-).



Chemical Formula: $C_{68}H_{42}ClN_8NiO$
Exact Mass: 1079.2524

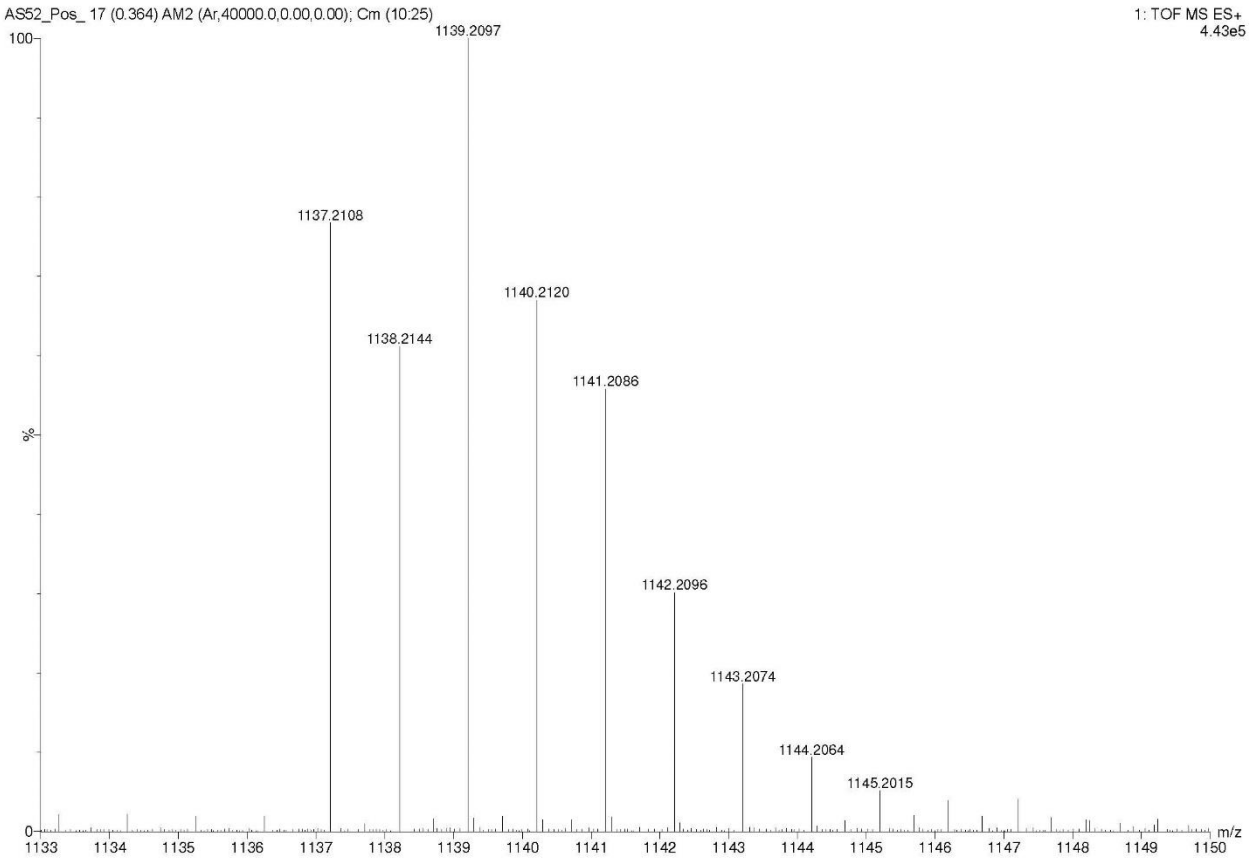
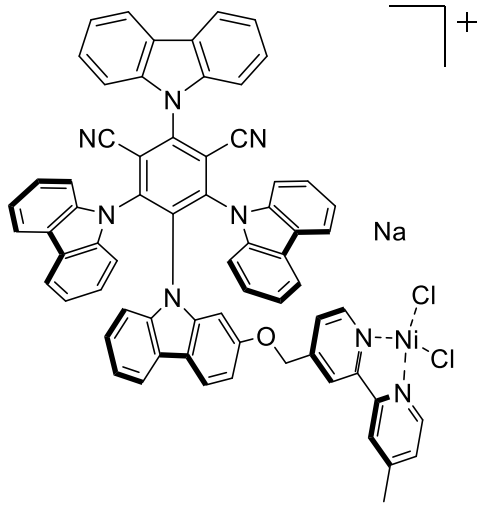


Figure S5. HRMS Analysis of the complex formed *in situ* (ion generated by incorporation of Na^+).



Chemical Formula: $C_{68}H_{42}Cl_2N_8NaNiO$
Exact Mass: 1137.2110

In order to establish the formation of Ni complex between Ni and bifunctional catalyst **B1**, a titration was performed in DMF, changing the ligand:Ni ratios. Since $NiCl_2$(glyme) is not soluble in acetonitrile, the measurements were conducted in DMF.

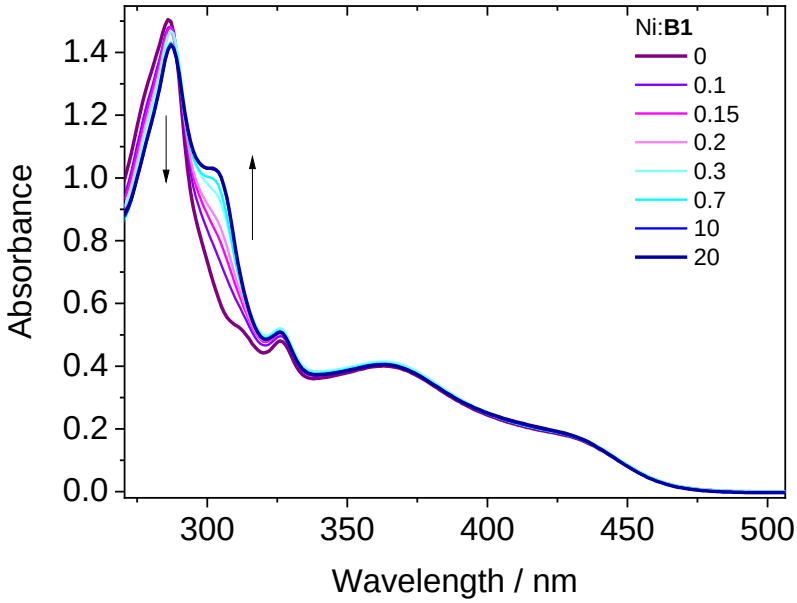


Figure S6. Absorption spectra of DMF solutions with different Ni:**B1** ratios.

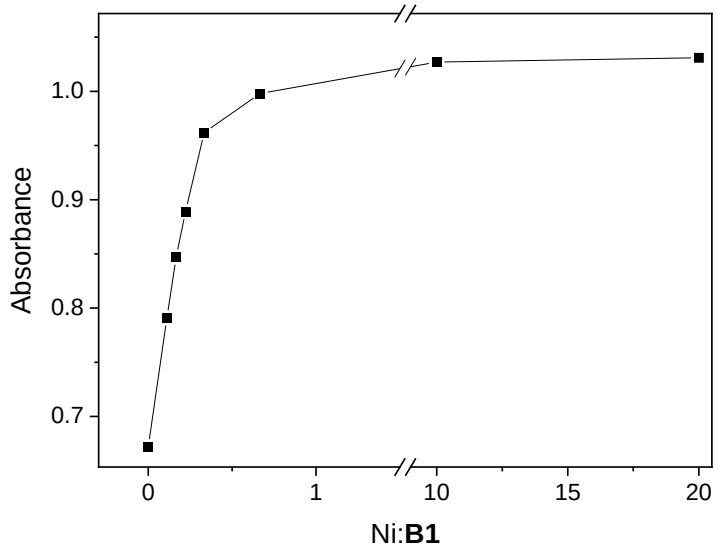


Figure S7. Absorbance measured at 302 nm for DMF solutions at different Ni:**B1** ratios.

Photophysical characterization

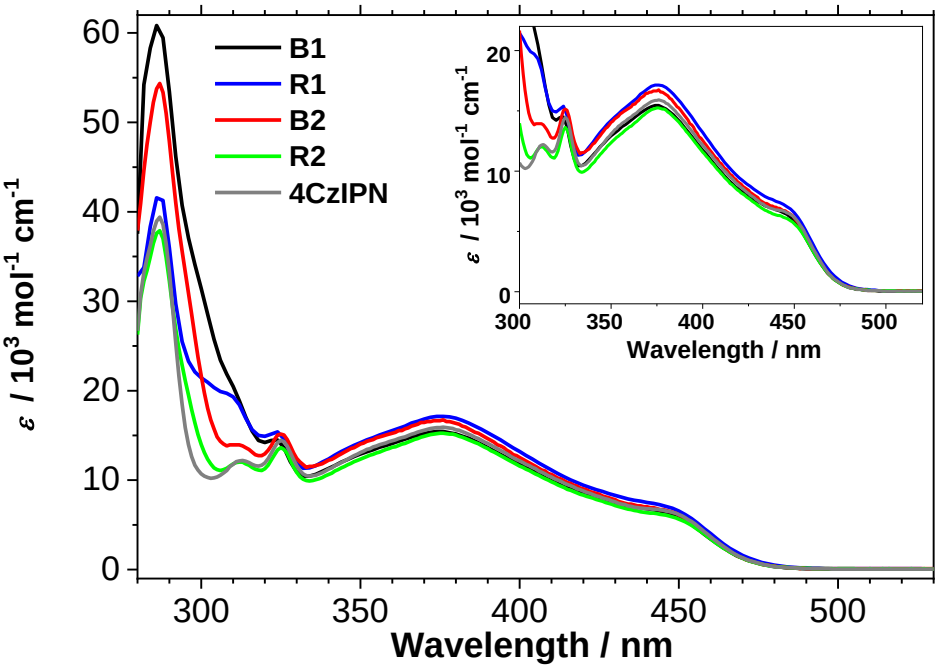


Figure S8. UV-vis absorption spectra of the photocatalysts in toluene.

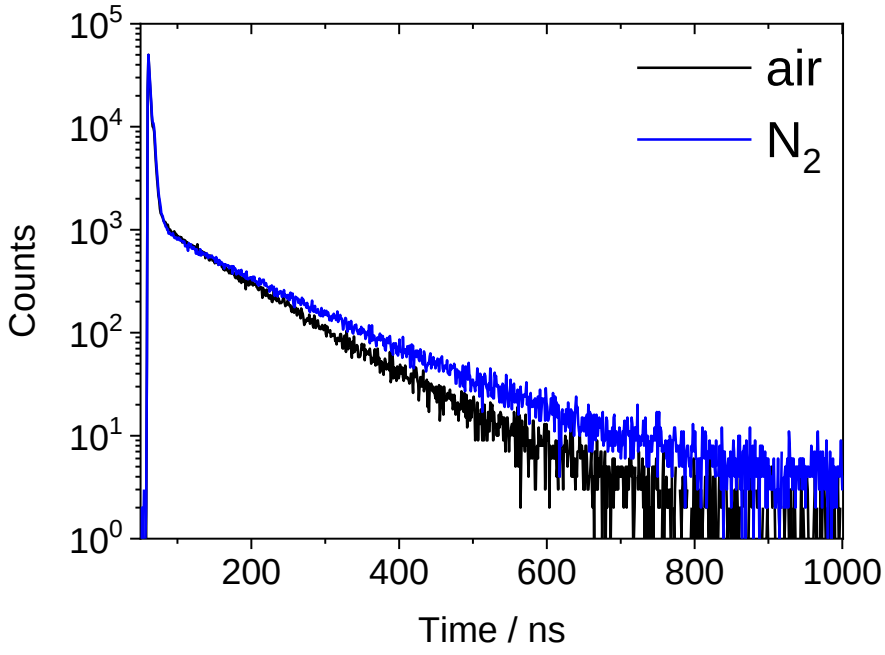


Figure S9. Emission intensity decays of **B1**-Ni in acetonitrile in air (black) and under nitrogen atmosphere (blue) (λ_{ex} = 375 nm, λ_{em} = 550 nm).

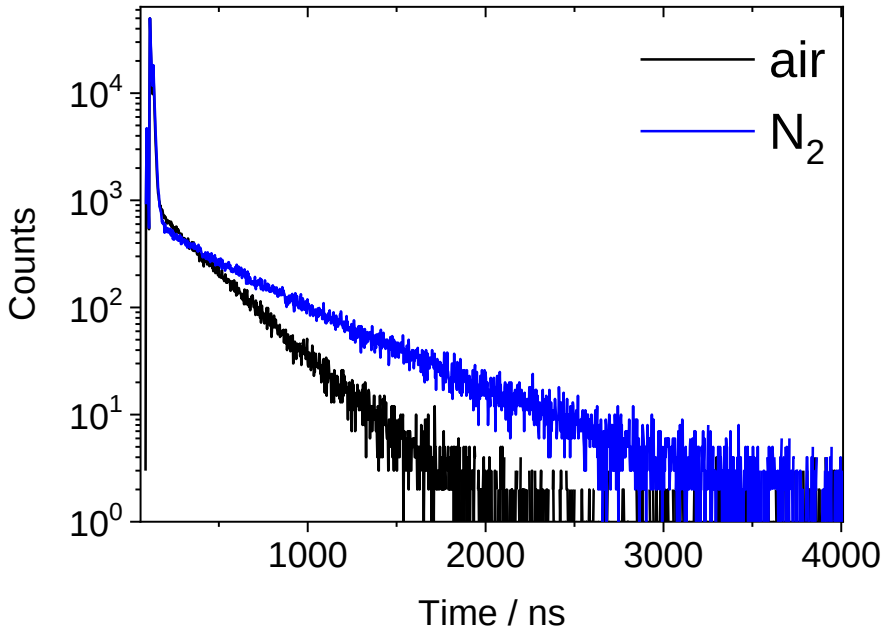


Figure S10. Emission intensity decays of **B2**-Ni in acetonitrile in air (black) and under nitrogen atmosphere (blue) (λ_{ex} = 375 nm, λ_{em} = 550 nm).

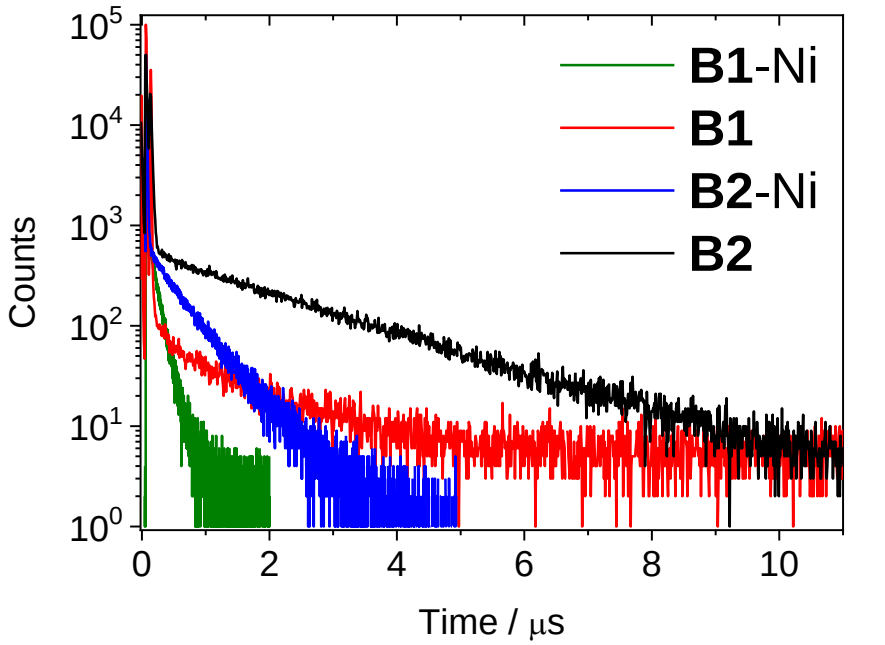


Figure S11. Emission intensity decays of **B1**-Ni, **B1**, **B2**-Ni and **B2** in acetonitrile under nitrogen (λ_{ex}= 375 nm, λ_{em} = 550 nm).

Table S4. Photophysical parameters of the photocatalysts in toluene.

	λ_{abs} (nm) [ε (10^3mol^{-1}cm^{-1})]	$\lambda_{max,em}$ (nm)	PLQY	Φ_{PF}	Φ_{DF}	τ_{PF} (ns)	τ_{DF} (μs)	k_{PF} (10^7 s^{-1})	k_{DF} (10^5 s^{-1})
B1	286 [60.8], 310 [20.5], 324 [14.5], 376 [15.4], 444 [6.4]	516	1.0	0.40	0.60	23.1	3.64	4.3	2.7
R1	286 [41.6], 310 [19.3], 324 [15.4], 376 [17.1], 444 [7.2]	518	0.8	0.25	0.55	29.5	2.94	3.4	3.4
B2	287 [54.3], 312 [13.9], 325 [15.1], 376 [16.7], 444 [6.7]	507	1.0	0.29	0.71	13.3	5.07	7.5	2.0
R2	287 [37.9], 312 [12.0], 325 [13.6], 376 [15.9], 444 [6.2]	509	1.0	0.31	0.69	14.2	4.98	7.0	2.0
4CzIPN	287 [39.4], 313 [12.2], 325 [14.4], 376 [15.9], 444 [6.7]	507	1.0	0.30	0.70	14.9	4.56	6.7	2.2

PLQY refers to the quantum yield measured under N_2 atmosphere, Φ_{PF} under air and Φ_{DF} is the difference between the two. Lifetimes are measured under N_2.

Table S5. Photophysical parameters of the photocatalysts in acetonitrile.

	λ_{abs} (nm) [ε (10^3mol^{-1}cm^{-1})]	$\lambda_{max,em}$ (nm)	PLQY	Φ_{PF}	Φ_{DF}	τ_{PF} (ns)	τ_{DF} (μs)	k_{PF} (10^7 s^{-1})	k_{DF} (10^5 s^{-1})
B1	206 [131], 228 [204], 284 [48.2], 310 [17.0], 324 [15.7], 364 [14.8], 434 [6.1]	571	0.01	0.01	<0.01	30.1	1.16	3.3	8.6
B1-Ni[e]	-	565	0.02	0.02	<0.01	3.7	0.12	27.	80.8
R1	206 [121], 228 [206], 284 [35.6], 310 [17.3], 324 [16.0], 366 [15.2], 434 [6.3]	572	0.01	0.01	<0.01	18.0	1.71	5.5	5.9
B2	206 [136], 228 [202], 284 [49.1], 313 [13.8], 325 [16.4], 364 [15.3], 434 [6.0]	559	0.22	0.14	0.08	20.0	2.09	5.0	4.8
B2-Ni[e]	-	560	0.09	0.09	<0.01	8.6	0.50	11.6	19.8
R2	208 [102], 228 [180], 285 [32.3], 314 [12.0], 325 [14.6], 366 [13.6], 434 [5.4]	560	0.24	0.14	0.10	20.2	2.07	5.0	4.8
4CzIPN	207 [111], 227 [194], 284 [36.5], 314 [13.5], 325 [17.3], 364 [15.7], 434 [6.3]	560	0.23	0.15	0.08	18.2	1.64	5.5	6.1

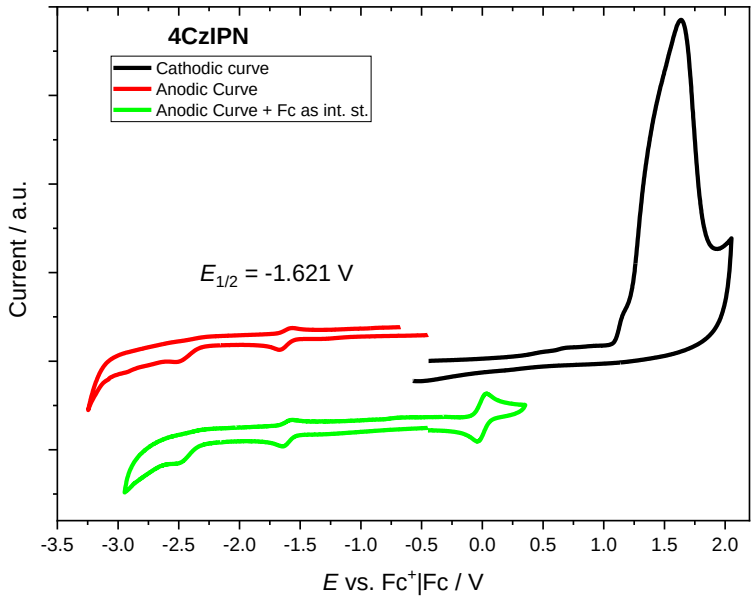
PLQY refers to the quantum yield measured under N_2 atmosphere, Φ_{PF} under air and Φ_{DF} is the difference between the two. Lifetimes are measured under N_2.

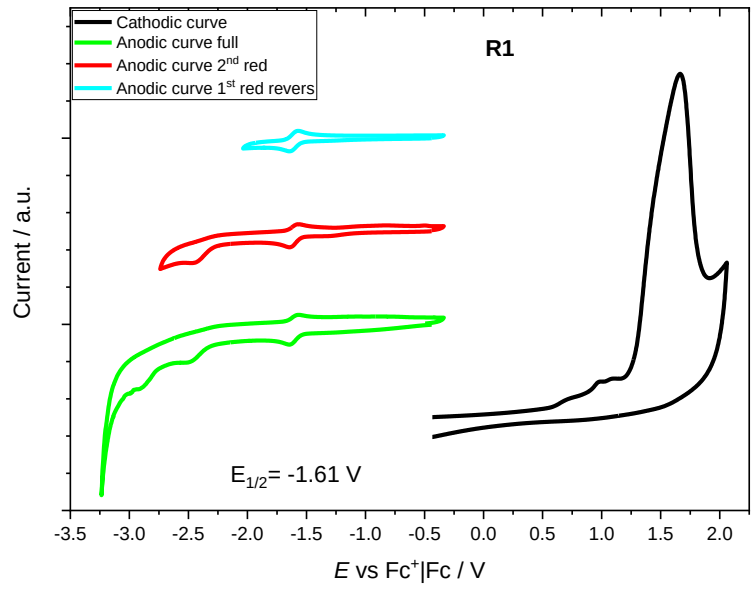
Electrochemical characterization

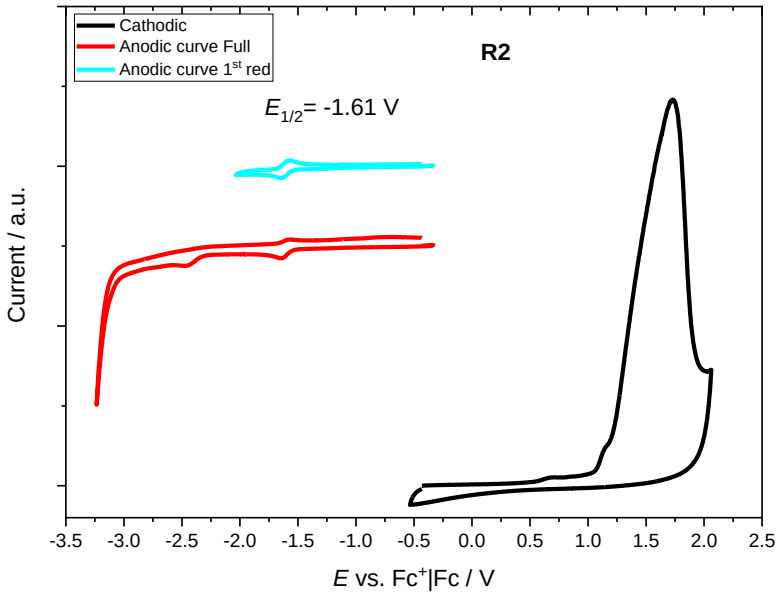
B1, B2, R1, R2, B1-Ni**, B2**-Ni and, for reference, **4CzIPN** together with 4,4'-dimethyl-2,2'-bipyridine have been characterized by cyclic voltammetry (CV) at potential scan rates of 0.2 V/s, at 0.25 mM concentration in CH_3CN and with 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as the supporting electrolyte; solutions were thoroughly deaerated by N_2 purging. The experiments were carried out using an Metrohm AUTOLAB PGSTAT302N potentiostat run by a PC with the Nova 2.0 software of the same manufacturer. The working electrode (WE) was a glassy carbon GC disk embedded in Teflon® (Amel); the counter electrode was a platinum

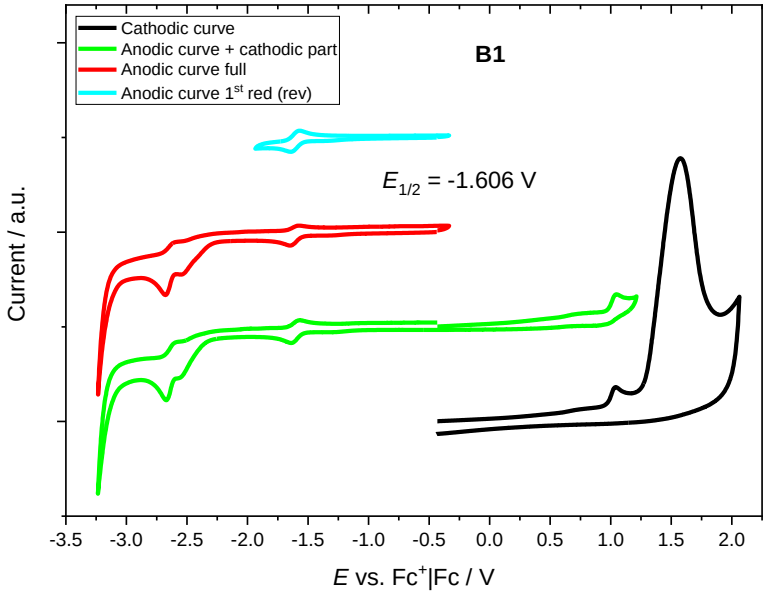
wire. The operating reference electrode was an aqueous saturated SCE. The optimised polishing procedure for the WE consisted in surface treatment with Al_2O_3 powder on a DP-Nap wet cloth of Struers.

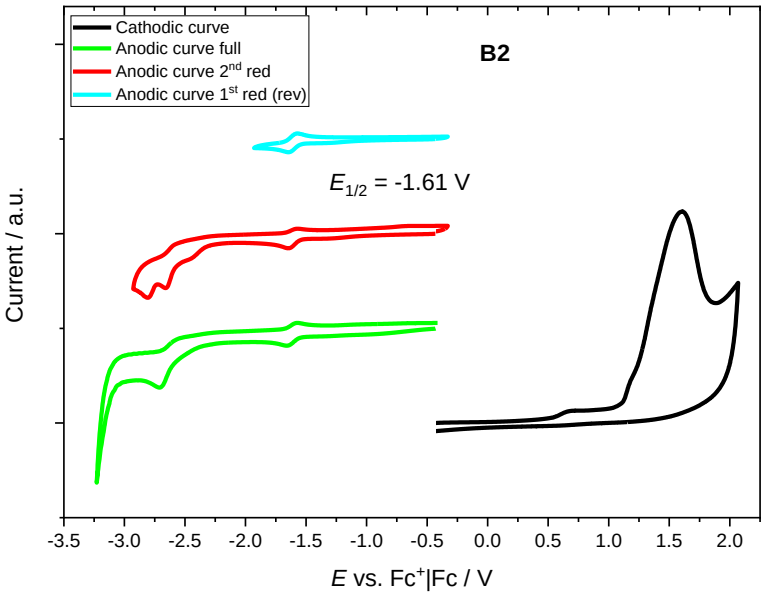
An internal standard of $Fc^+|Fc$ at concentrations 0.25 mM was added after all measurements to compare for the number of electron transfer processes. Peak potential values have been normalized vs the Fc+|Fc redox couple (the intersolvent redox potential couple currently recommended by IUPAC), having a redox potential of 0.39 V (in CH_3CN) vs. the operating SCE reference electrode.[11] **B1-Ni** and **B2-Ni** were characterized upon addition of an equimolar amount of $NiCl_2$(glyme) to the respective **B1**/**B2** solutions and performing CV scans after complete dissolution of the Ni salt, (in analogy to the procedure used in the photophysical characterization of the same Ni complexes). To note that, in order to precisely determine the reduction processes, the WE was cleaned after each scan and the CV measurement were run firstly going to the negative potentials and then towards the positive ones. Otherwise, decomposition products forms on the WE, precluding the measurement of reductions.

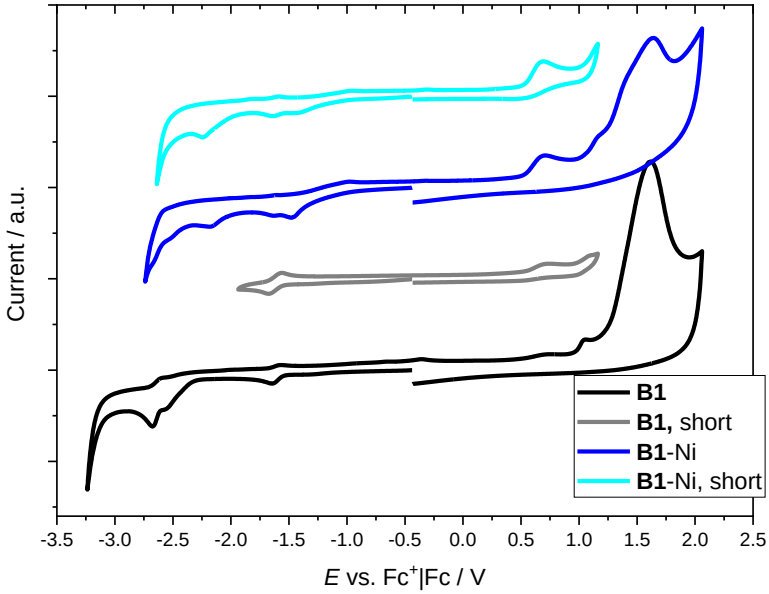


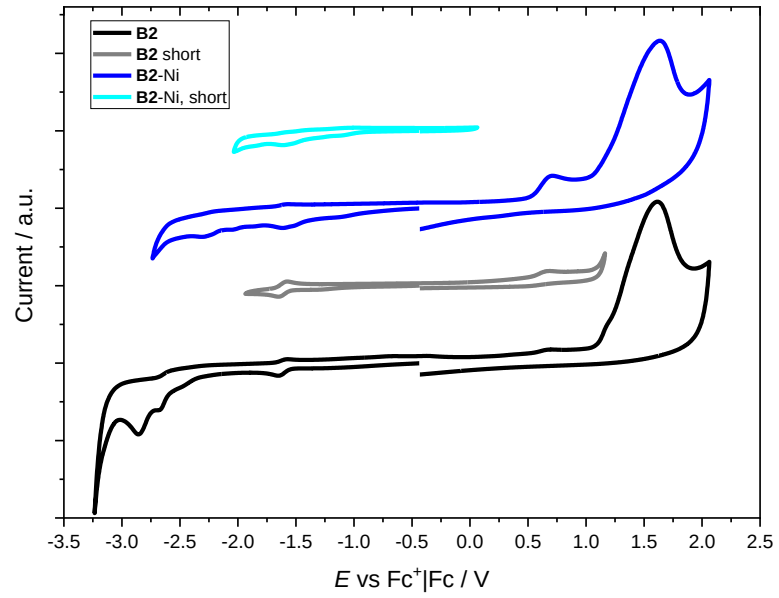


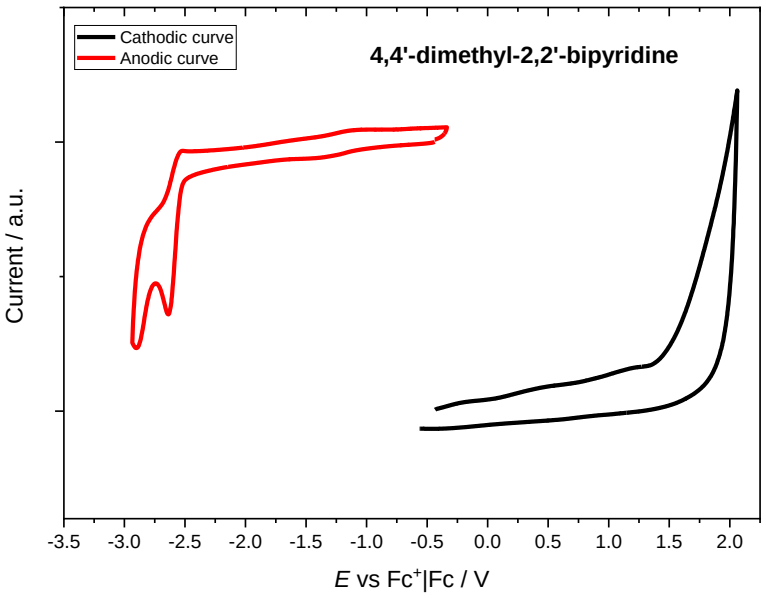

Cathodic
Anodic curve Full
Anodic curve 1st red
R2
E1/2= -1.61 V
Current / a.u.
-3.5 -3.0 -2.5 -2.0 -1.5 -1.0 -0.5 0.0 0.5 1.0 1.5 2.0 2.5
E vs. Fc+|Fc / V


Cathodic curve
Anodic curve + cathodic part
Anodic curve full
Anodic curve 1st red (rev)
B1
E1/2 = -1.606 V
Current / a.u.
-3.5 -3.0 -2.5 -2.0 -1.5 -1.0 -0.5 0.0 0.5 1.0 1.5 2.0
E vs. Fc+|Fc / V


Cathodic curve
Anodic curve full
Anodic curve 2nd red
Anodic curve 1st red (rev)
B2
E1/2 = -1.61 V
Current / a.u.
-3.5 -3.0 -2.5 -2.0 -1.5 -1.0 -0.5 0.0 0.5 1.0 1.5 2.0
E vs. Fc+|Fc / V


B1
B1, short
B1-Ni
B1-Ni, short
Current / a.u.
-3.5 -3.0 -2.5 -2.0 -1.5 -1.0 -0.5 0.0 0.5 1.0 1.5 2.0 2.5
E vs. Fc+|Fc / V


B2
B2 short
B2-Ni
B2-Ni, short
Current / a.u.
-3.5 -3.0 -2.5 -2.0 -1.5 -1.0 -0.5 0.0 0.5 1.0 1.5 2.0 2.5
E vs Fc+|Fc / V


Cathodic curve
Anodic curve
4,4'-dimethyl-2,2'-bipyridine
Current / a.u.
-3.5 -3.0 -2.5 -2.0 -1.5 -1.0 -0.5 0.0 0.5 1.0 1.5 2.0
E vs Fc+|Fc / V

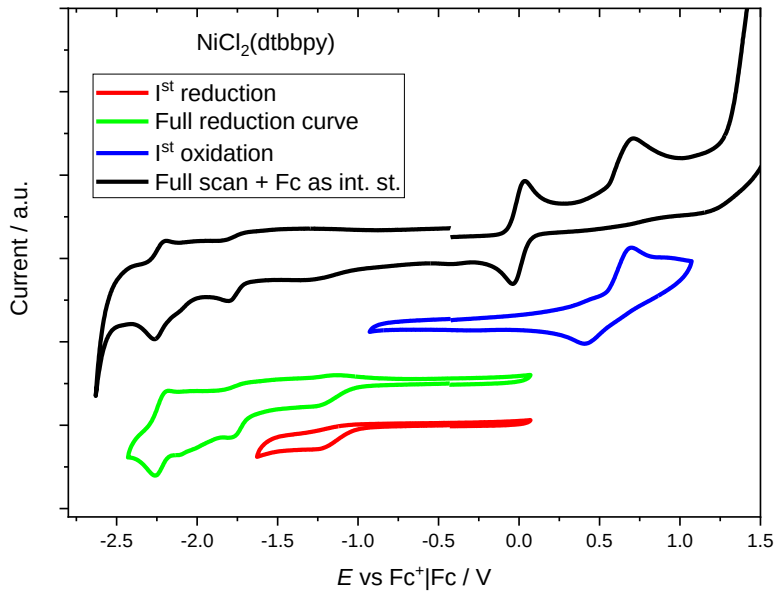


Figure S12. CV traces of several compounds used in this study [**B1**, **B2**, **B1**-Ni, **B2**-Ni, **R1**, **R2**, 4,4'-dimethyl-2,2'-bipyridine, 4CzIPN, $NiCl_2$(dtbbpy)].

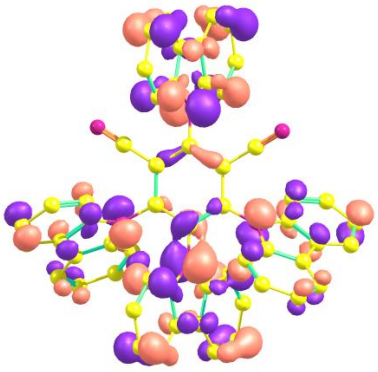
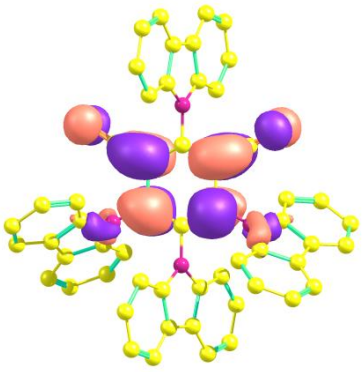
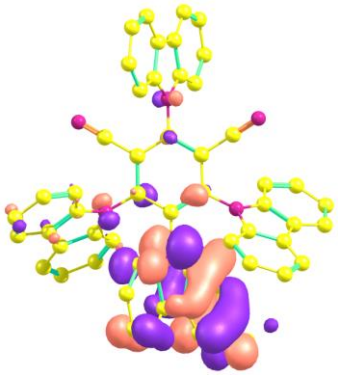
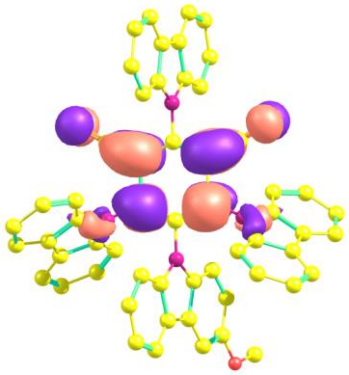
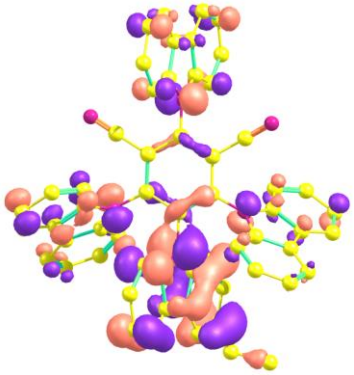
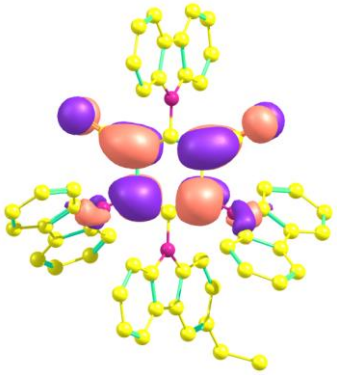
Table S6. Summary of the electrochemical redox potentials of the studied systems (values are referenced to the $Fc^+|Fc$ redox couple)

Compound	I ox	II ox	I red	II red
R1	0,71; 0,97; 1,10; 1.25 onset	1.68	-1.61	-2.43
B1	1.04; 1,30 onset	1.57	-1.61	-2.54; **-2.68**
R2	0,68; 1.15 onset	1.72	-1.61	-2.46
B2	(0.70); 1.14 onset	1.60	-1.61	-2.68; **-2.79**
B1-Ni	0.70; 1.17 onset	1.63	-1.45; -1.606	-2.17; **-2.54**
B2-Ni	0.70; 1,15 onset	1.64	-1.50; -1.605	-2.28; **on the solvent discharge**
4,4'-dmbpy			**-2.62**	

Bold data indicate potential attributed to the monoelectronic reduction of the 4,4'-dmbpy moieties in **B1**/**B2** and the respective Ni complexes. 4,4'-dmbpy = 4,4'-dimethyl-2,2'-bipyridine. Bold data indicate potentials attributed to the monoelectronic reduction of the bipy moieties in **B1**/**B2**, and the respective Ni complexes. The data shown in this table can be referenced to the SCE electrode by applying the following formula: E (vs. SCE) = E (vs. $Fc^+|Fc$) + 0.39 V.

Preliminary DFT calculation on representative photocatalysts

Table S7. Summary of the modeled **4CzIPN** dyes; in order to mimic the functionalization of **R1** and **R2**, the benzyl moieties has been replaced by a methyl group. Calculation performed at the DFT B3LYP/6-31g* level as implemented in the Gaussian 09W package.[12]

Compound	HOMO (energy in eV)	LUMO (energy in eV)
4CzIPN H (eV): -5.84; -5.83; -5.67; L (eV): -2.56; -2.19	 -5.67	 -2.56
4CzIPN-**O**CH_3 H (eV): -5.82; -5.72; -5.42; L (eV): -2.53; -2.16	 -5.42	 -2.53
4CzIPN-**CH_2**CH_3 H (eV): -5.82; -5.79; -5.62; L (eV): -2.55; -2.17	 -5.62	 -2.55

Calculations evidence in all cases that highest occupied molecular orbitals are characterized by a carbazole character and the, the close energetic levels of Homo, Homo-1 and more cored orbital might support the irreversible and multielectronic behaviour of the CV oxidation. The LUMO, being localized on the benzonitrile core instead prove that regardless the functionalization on the carbazole group no variation is observed on the reduction potential in CV.

Stern-Volmer quenching experiments

The quenching of the photoluminescence by quinuclidine was investigated in acetonitrile by Stern-Volmer experiment for bifunctional photocatalysts **B1** and **B2**, in the presence of $NiCl_2$(glyme), and for the reference catalysts 4CzIPN, **R1** and **R2**. A 0.01 mM stock solution of photocatalyst (in the presence of equimolar amount of $NiCl_2$(glyme)) was used to prepare a 0.01 M solution of the quencher. Aliquots of this solution were added to a 5 mL volumetric flask and diluted with the same (0.01 mM) photocatalyst solution. All solutions were degassed with argon for 15 minutes before measuring time-resolved luminescence under 375 nm excitation. The emission wavelength varied from 560 nm to 580 nm, depending on the emission peak of the photocatalyst. The obtained lifetimes of the delayed fluorescence were plotted against the quencher concentration according to the Stern-Volmer equation:

$$\tau_0/\tau = 1 + k_q\tau_0[Q]$$

where τ_0 and τ are the lifetimes of delayed fluorescence in the absence and in the presence of quencher Q, and k_q is the quenching rate constant, which was calculated from the slope of the linear fit against the quencher concentration [Q]. The Stern-Volmer quenching constant K_{SV} is obtained from the following relationship:

$$k_q\tau_0 = K_{SV}$$

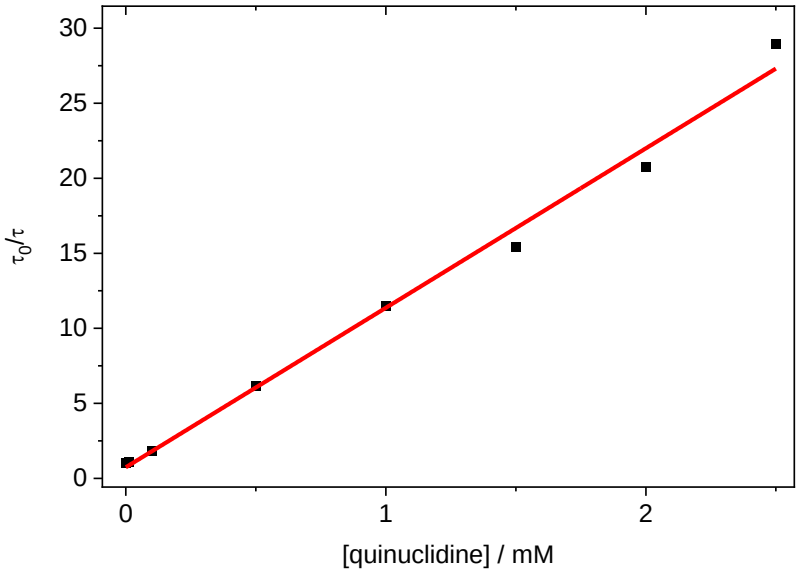


Figure S13. Stern Volmer plot of the quenching of 4CzIPN by quinuclidine.

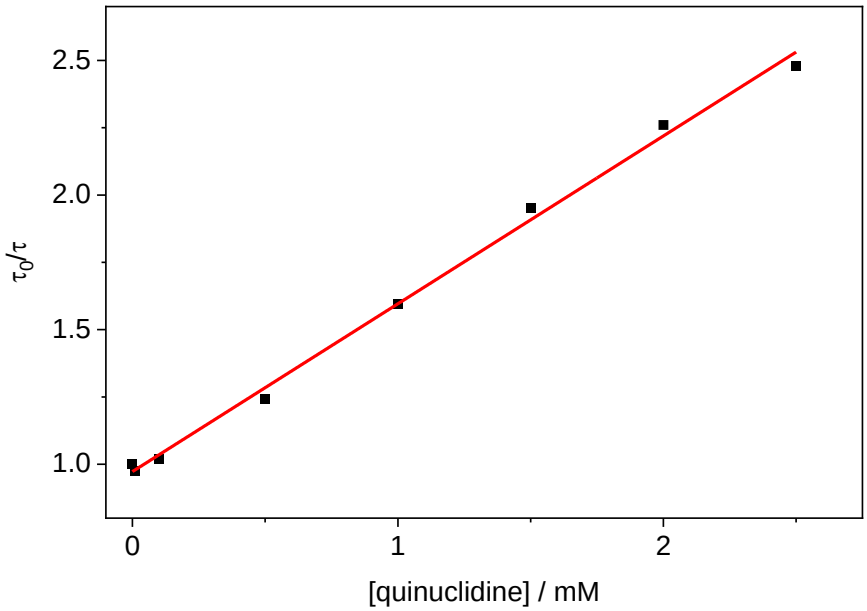


Figure S14. Stern Volmer plot of the quenching of **B1** + $NiCl_2$(glyme) by quinuclidine.

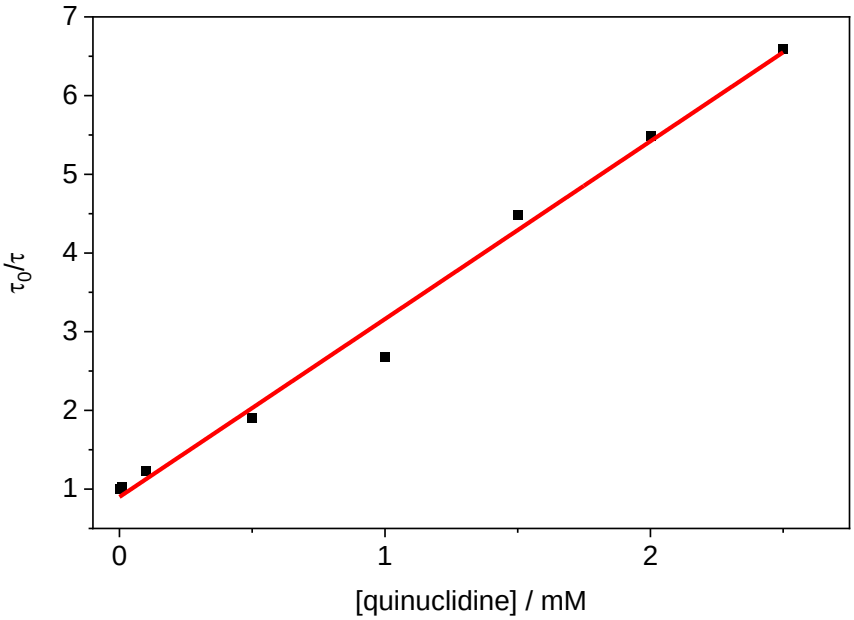


Figure S15. Stern Volmer plot of the quenching of **B2** + $NiCl_2$(glyme) by quinuclidine.

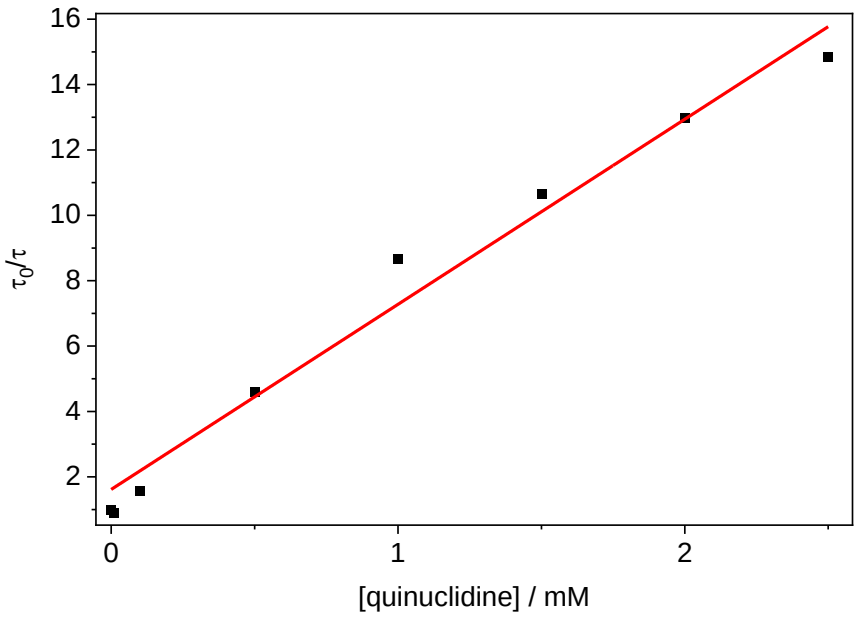


Figure S16. Stern Volmer plot of the quenching of **R1** by quinuclidine.

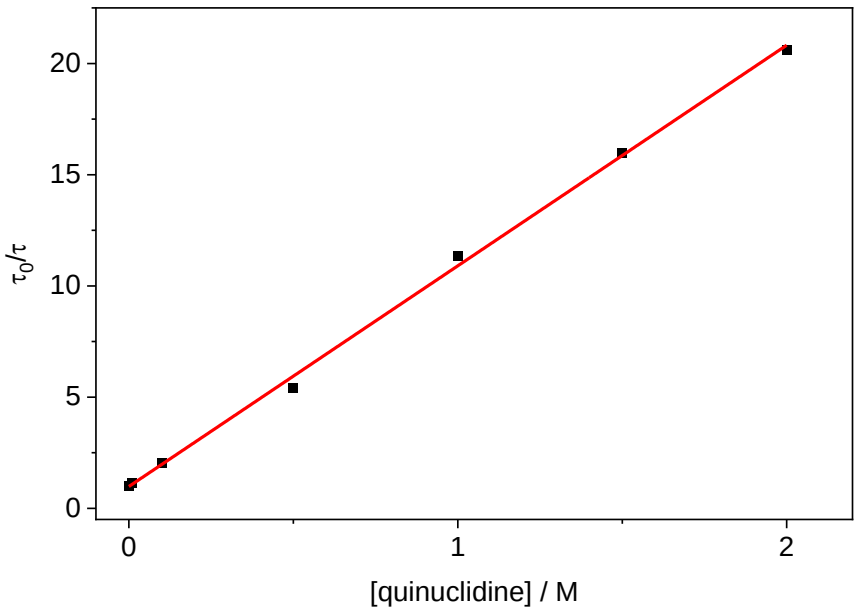
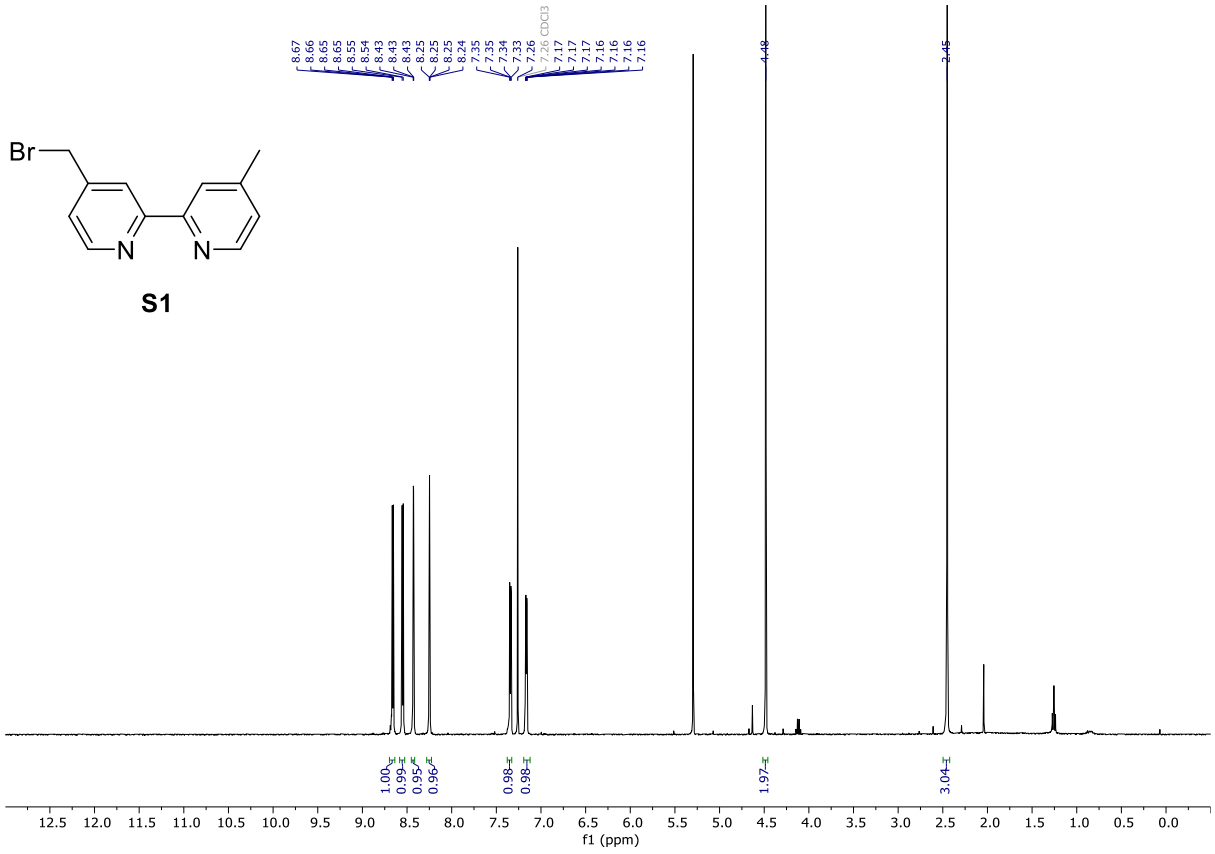
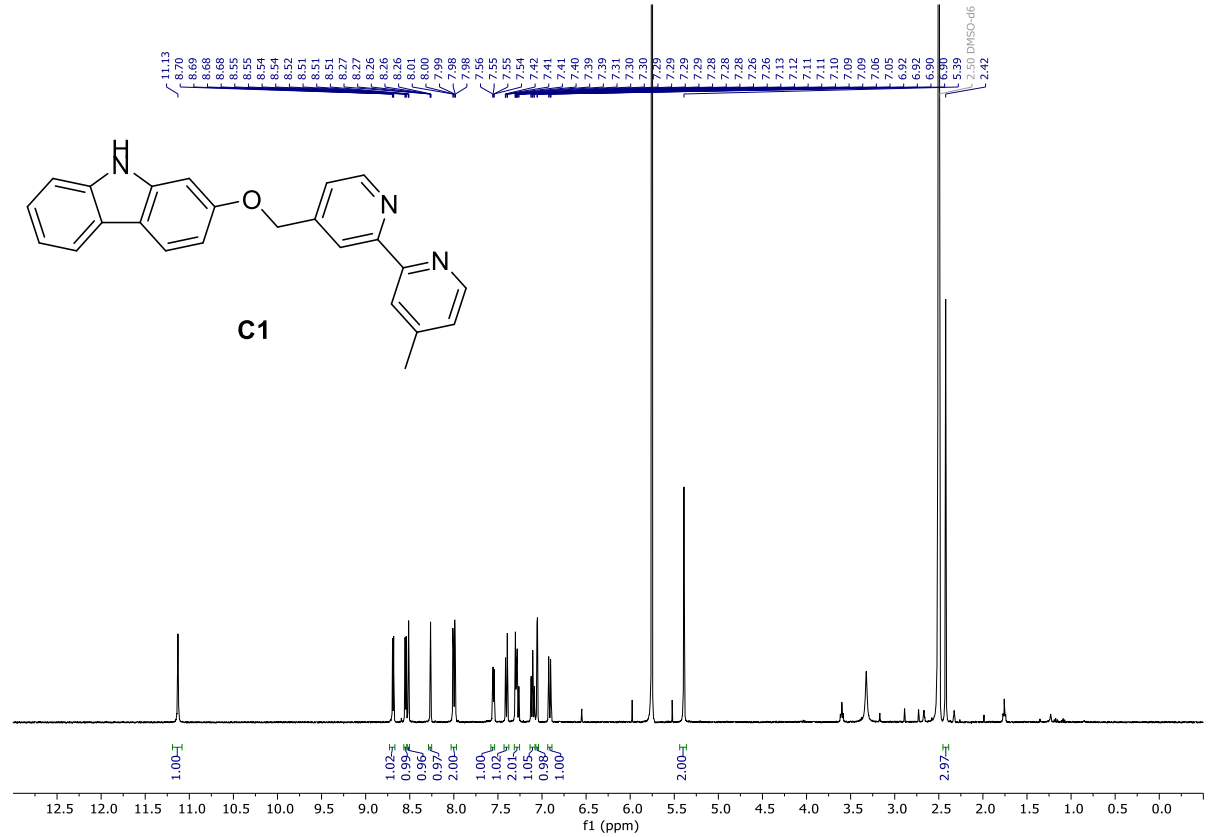
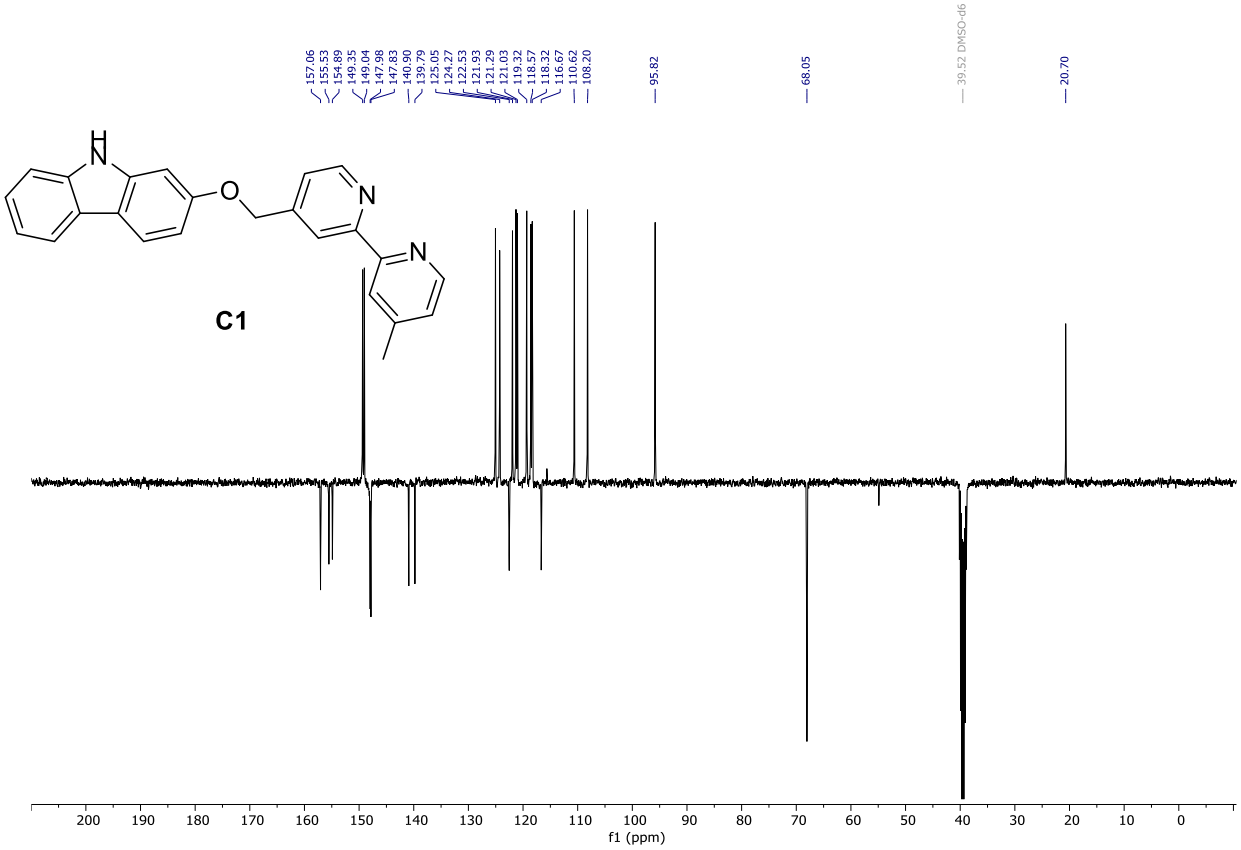


Figure S17. Stern Volmer plot of the quenching of **R2** by quinuclidine.

NMR spectra of the isolated products



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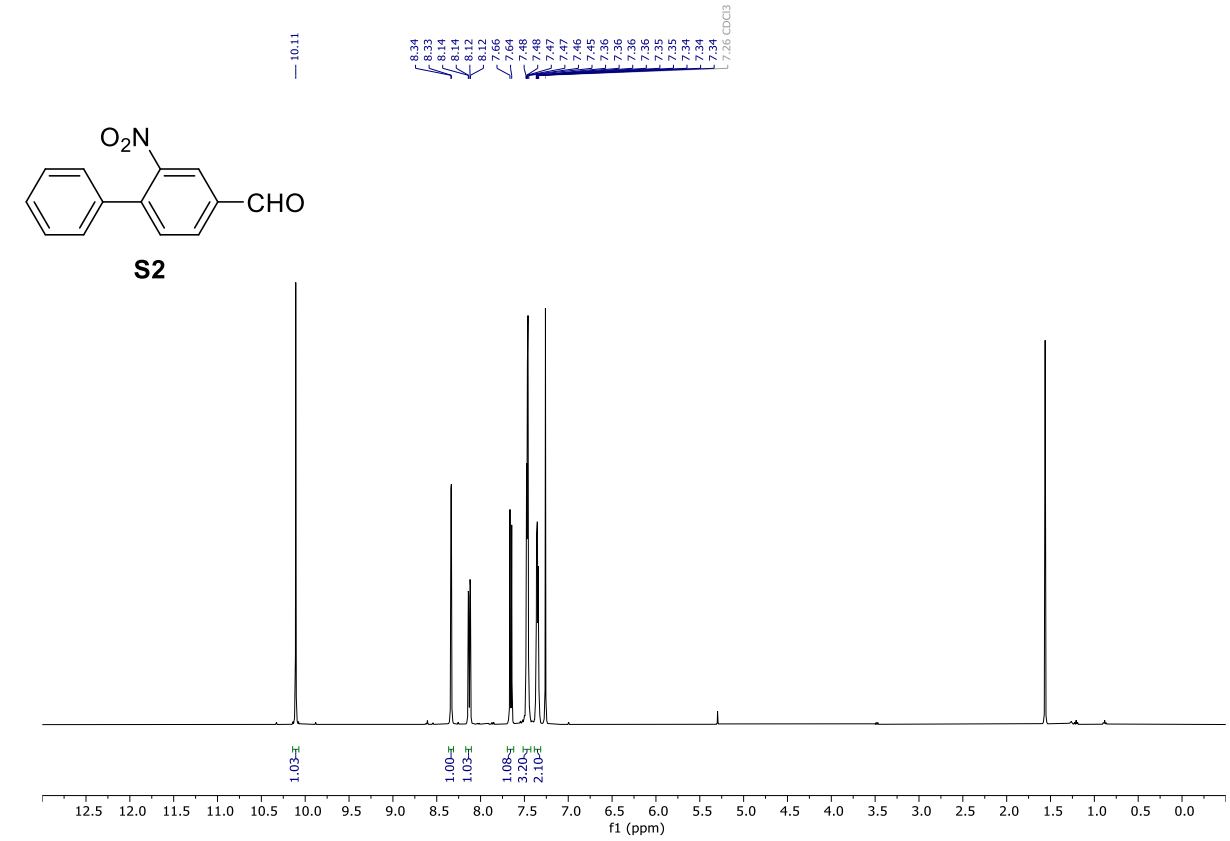
149.35
149.04
147.98
147.83
140.90
139.79
125.05
124.27
122.53
121.93
121.29
121.03
120.32
118.57
118.32
116.67
110.62
108.20
95.82
68.05
39.52 DMSO-d6
20.70
C1
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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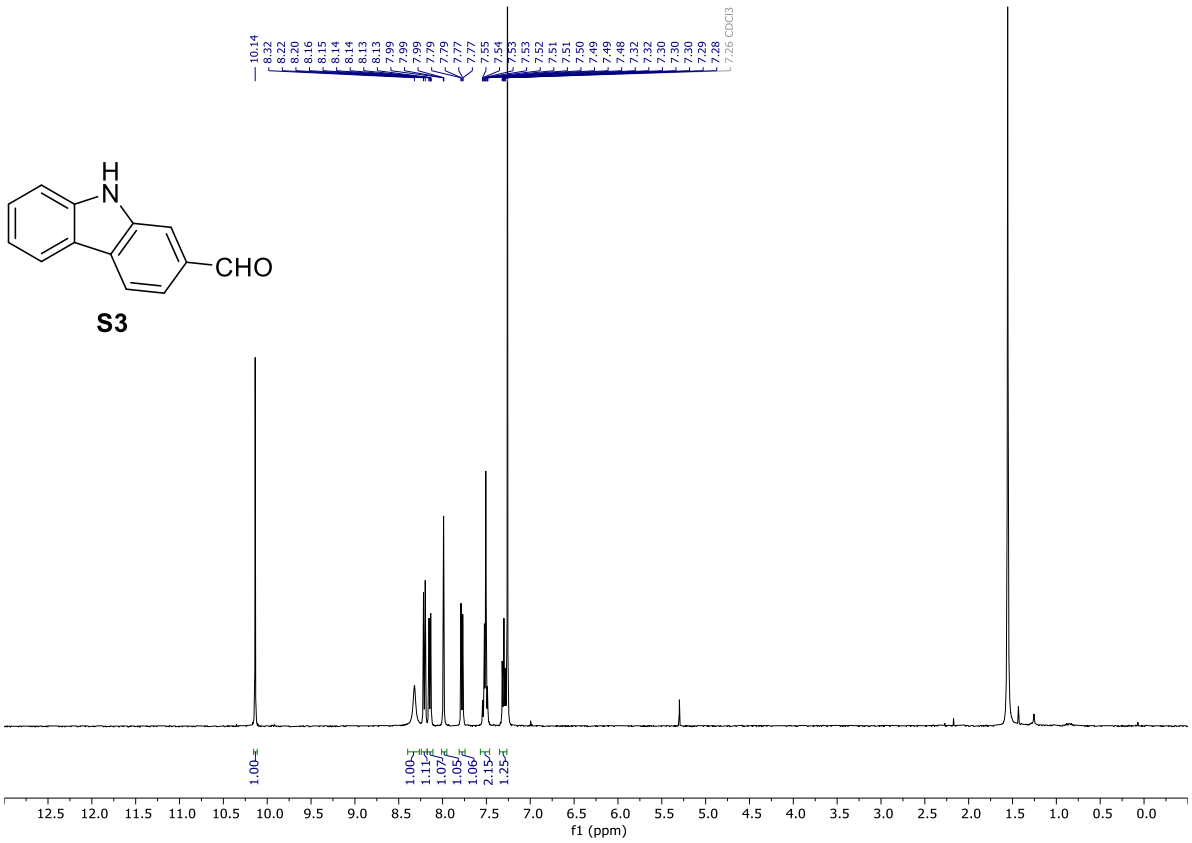
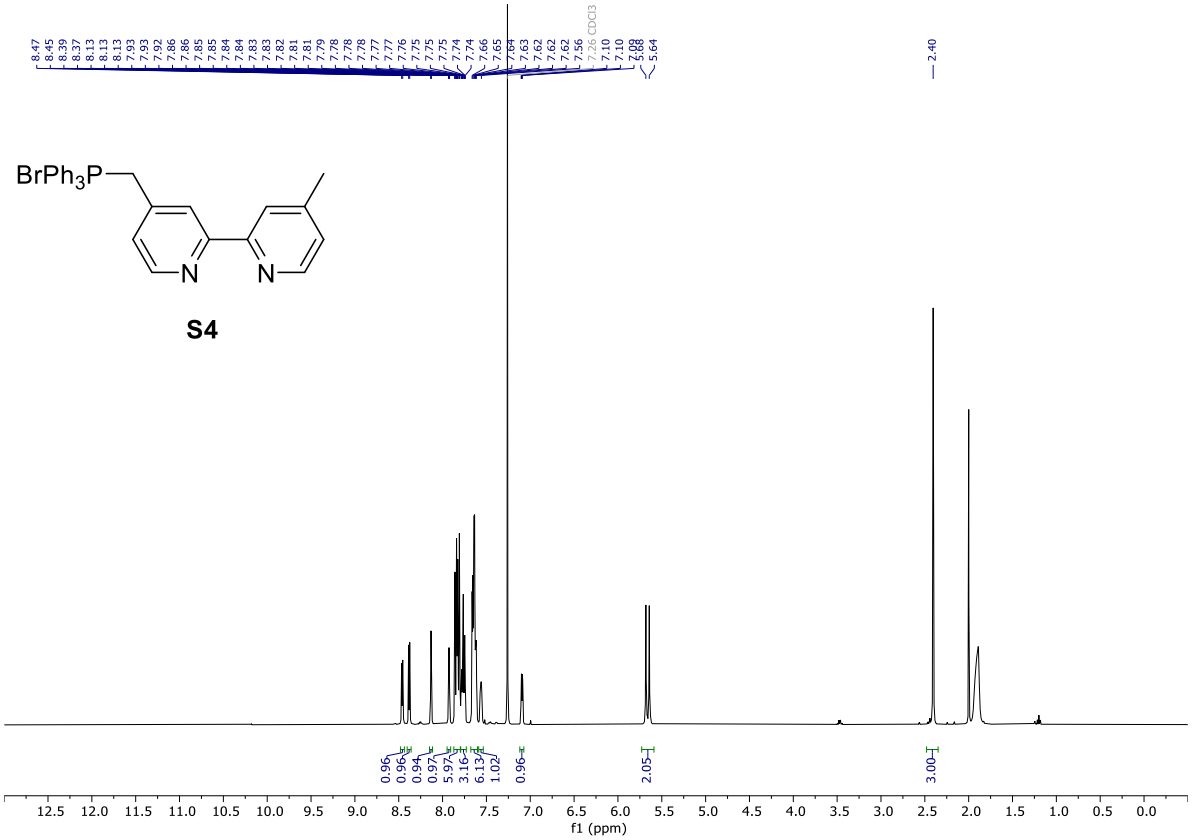
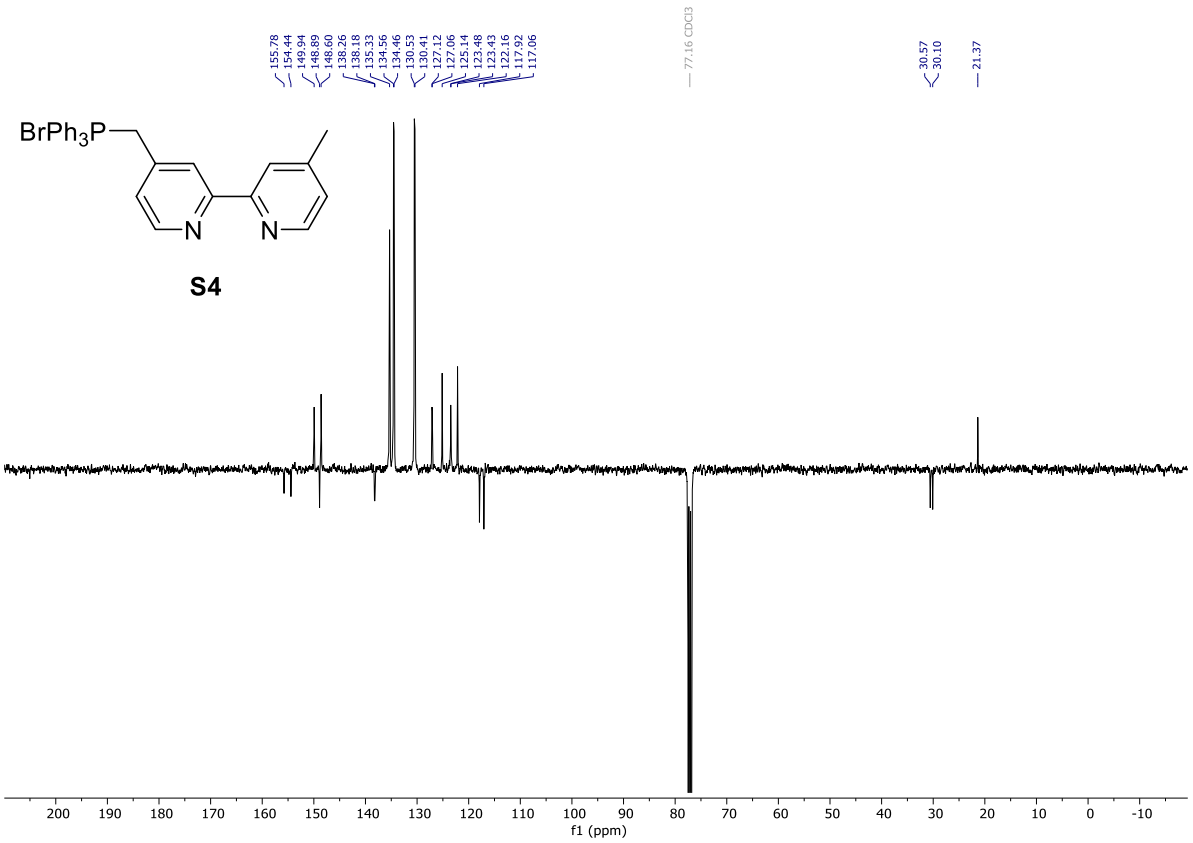
8.34
8.33
8.14
8.14
8.12
8.12
7.66
7.64
7.48
7.48
7.47
7.47
7.46
7.45
7.36
7.36
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.26 CDCl3
O2N
CHO
S2
1.03
1.00
1.03
1.08
3.20
2.10
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


H
N
CHO
S3
f1 (ppm)


BrPh3P
N
N
S4
f1 (ppm)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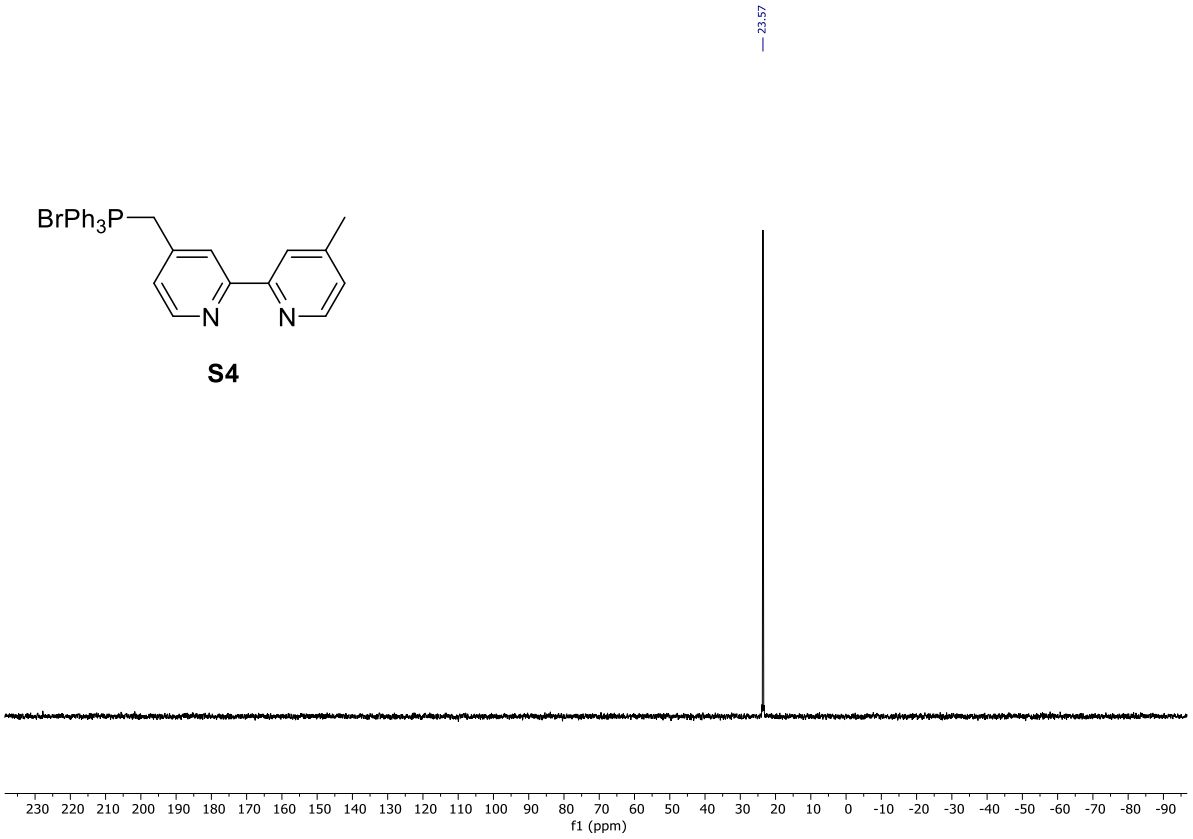
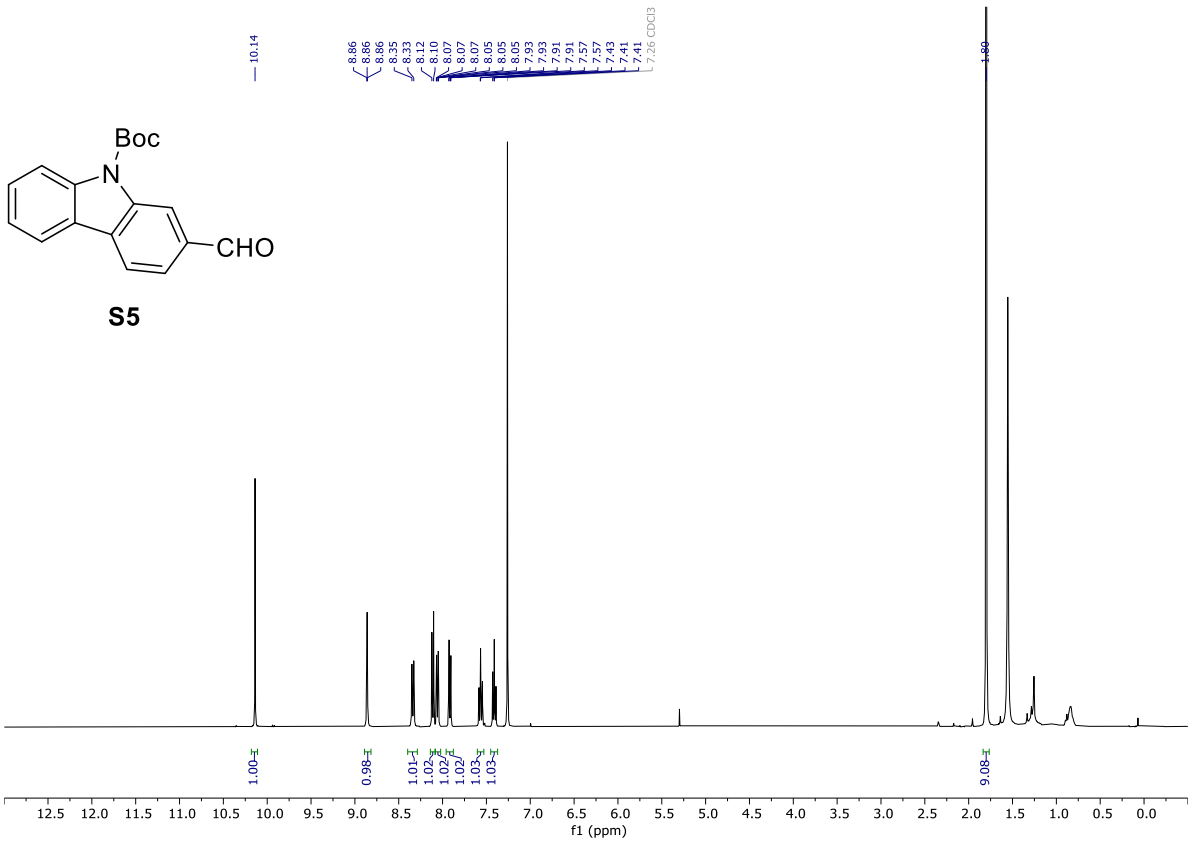
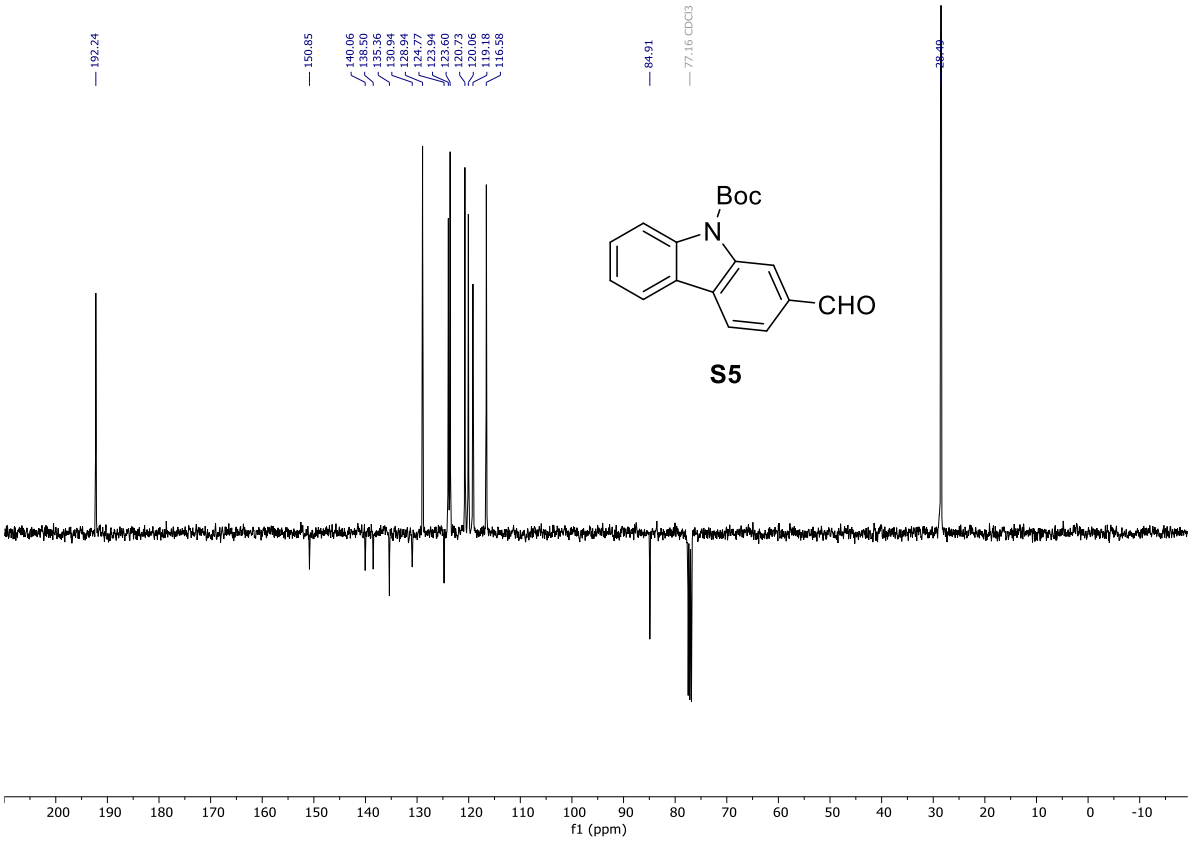
154.44
149.94
148.89
148.60
138.26
138.18
135.33
134.56
134.46
130.53
130.41
127.12
127.06
125.14
123.48
123.43
122.16
117.92
117.06
77.16 CDCl3
30.57
30.10
21.37
BrPh3P
N
N
S4
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


23.57
BrPh3P
N
N
S4
230 220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90
f1 (ppm)


Boc
N
CHO
S5
10.14
8.86
8.86
8.86
8.35
8.33
8.12
8.10
8.07
8.07
8.07
8.07
8.05
8.05
8.05
8.05
7.93
7.93
7.91
7.91
7.57
7.57
7.43
7.41
7.41
7.26 CDCl3
1.89
1.00
0.98
1.01
1.02
1.02
1.02
1.03
1.03
9.08
f1 (ppm)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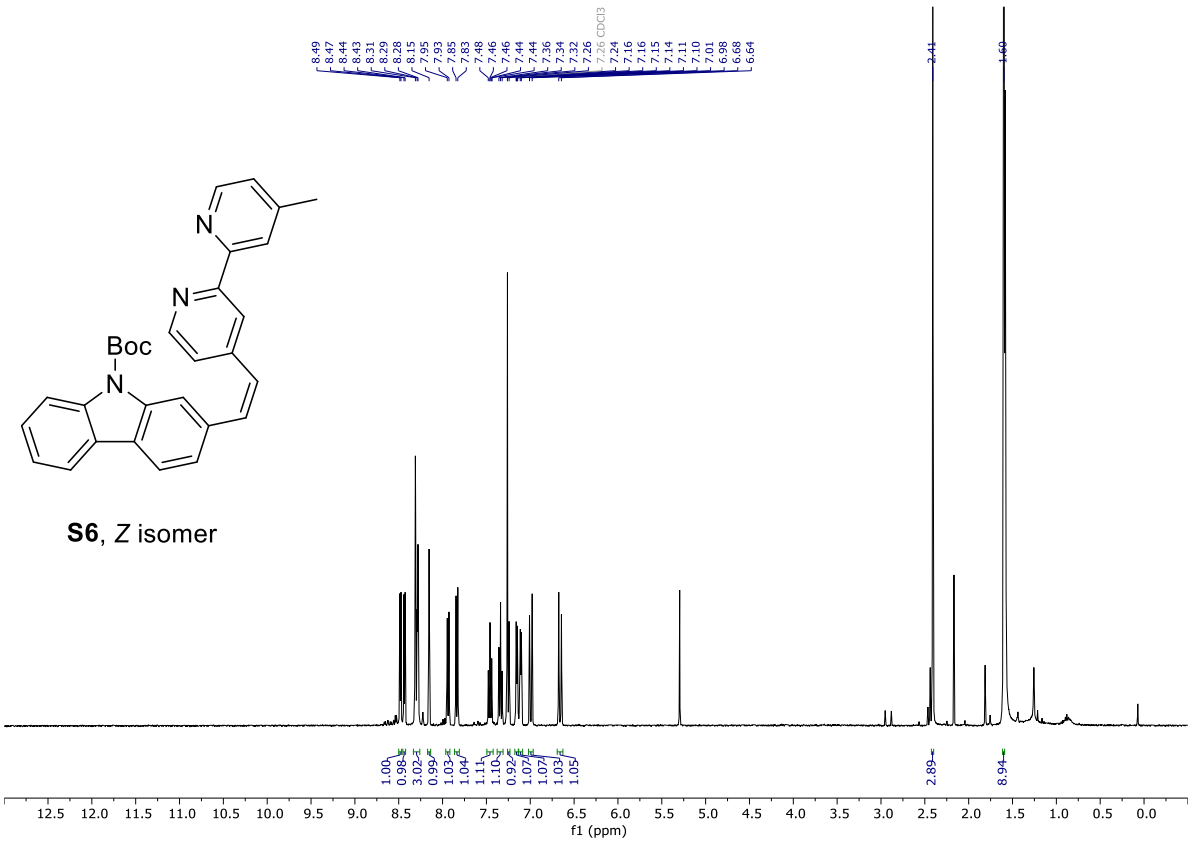
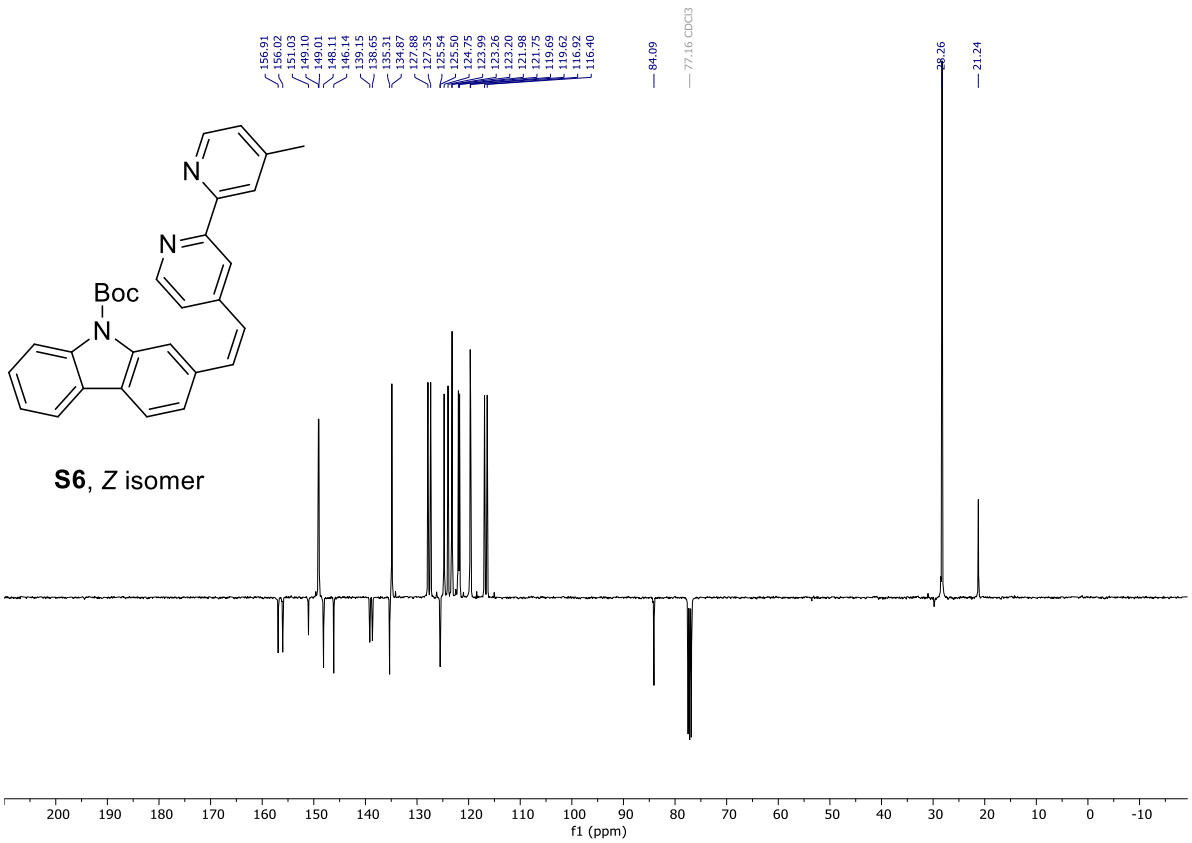
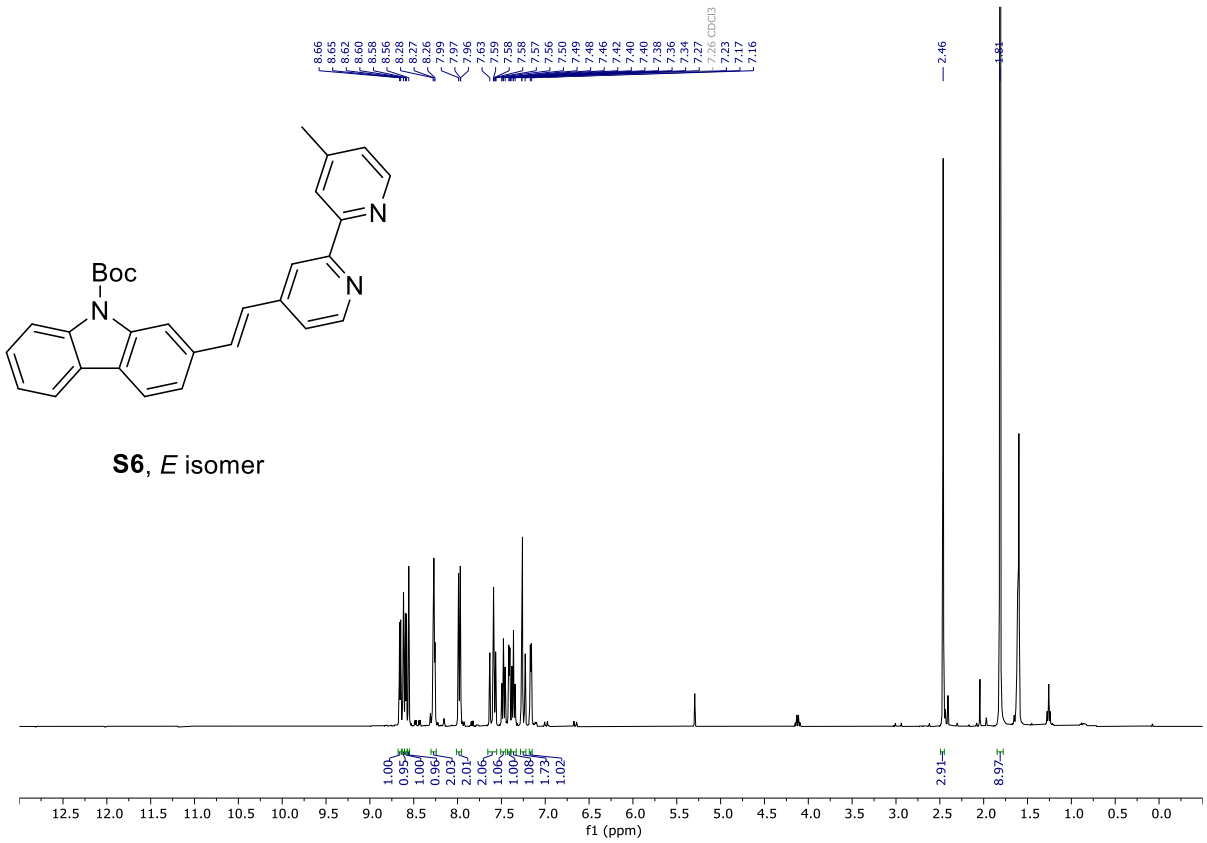
150.85
140.06
138.50
135.36
130.94
128.94
124.77
123.94
123.60
120.73
120.06
119.18
116.58
84.91
77.16 CDCl3
28.49
Boc
N
CHO
S5
f1 (ppm)



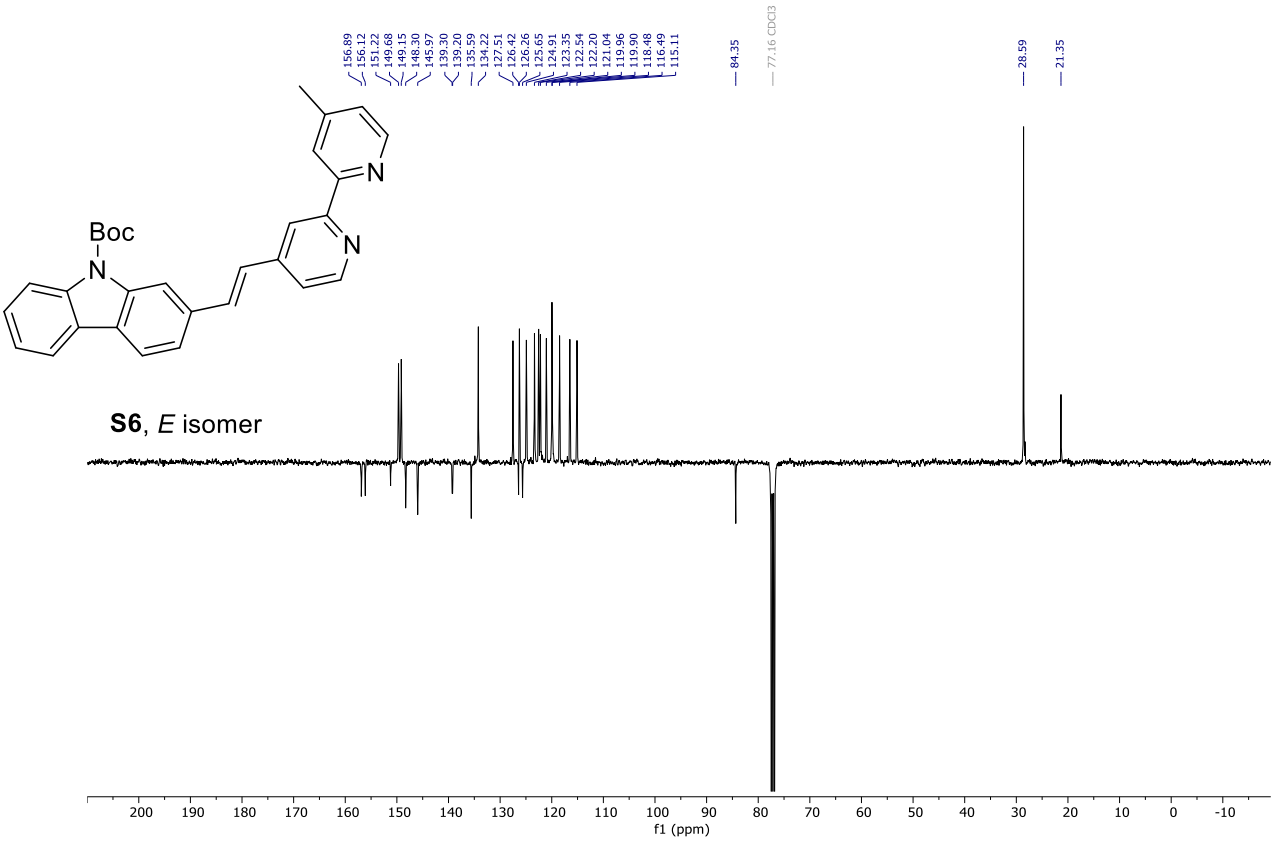
S6, *Z* isomer



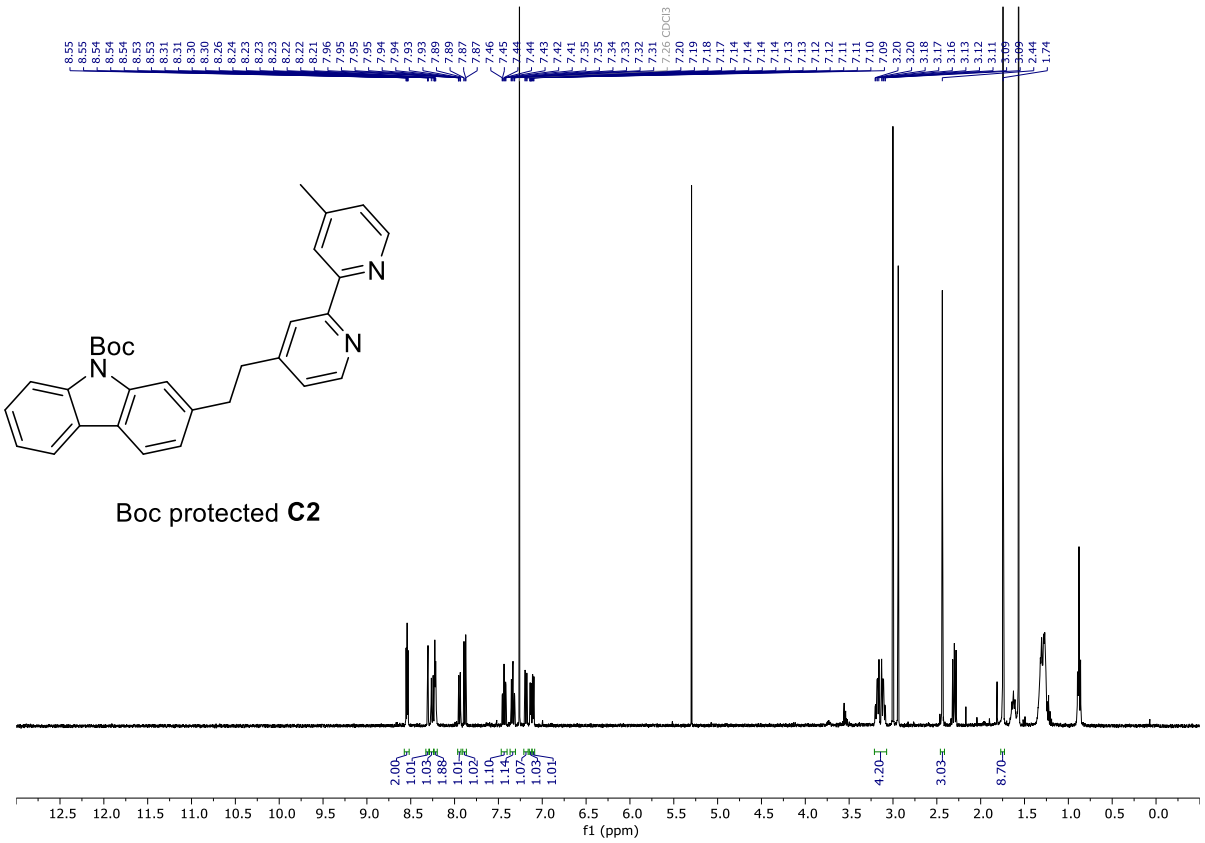
S6, *Z* isomer

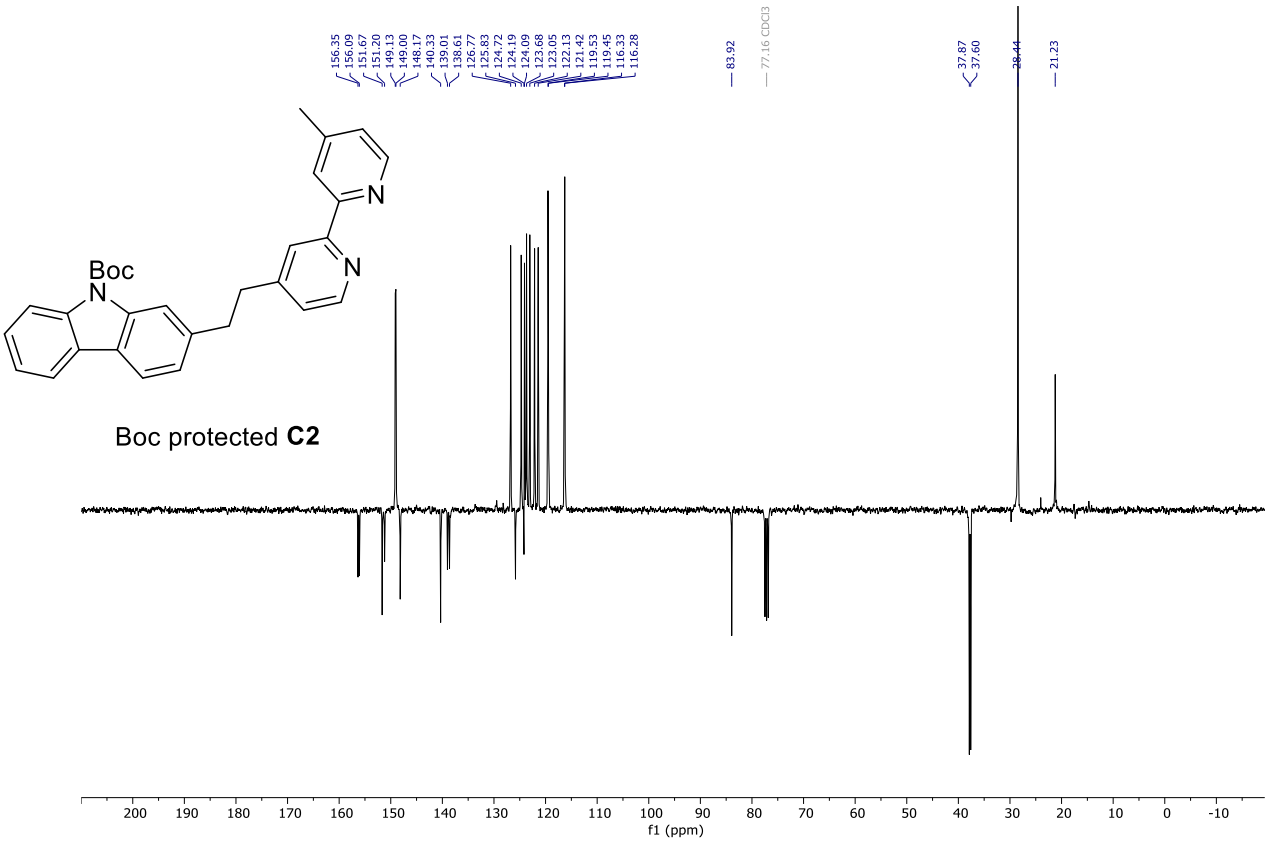


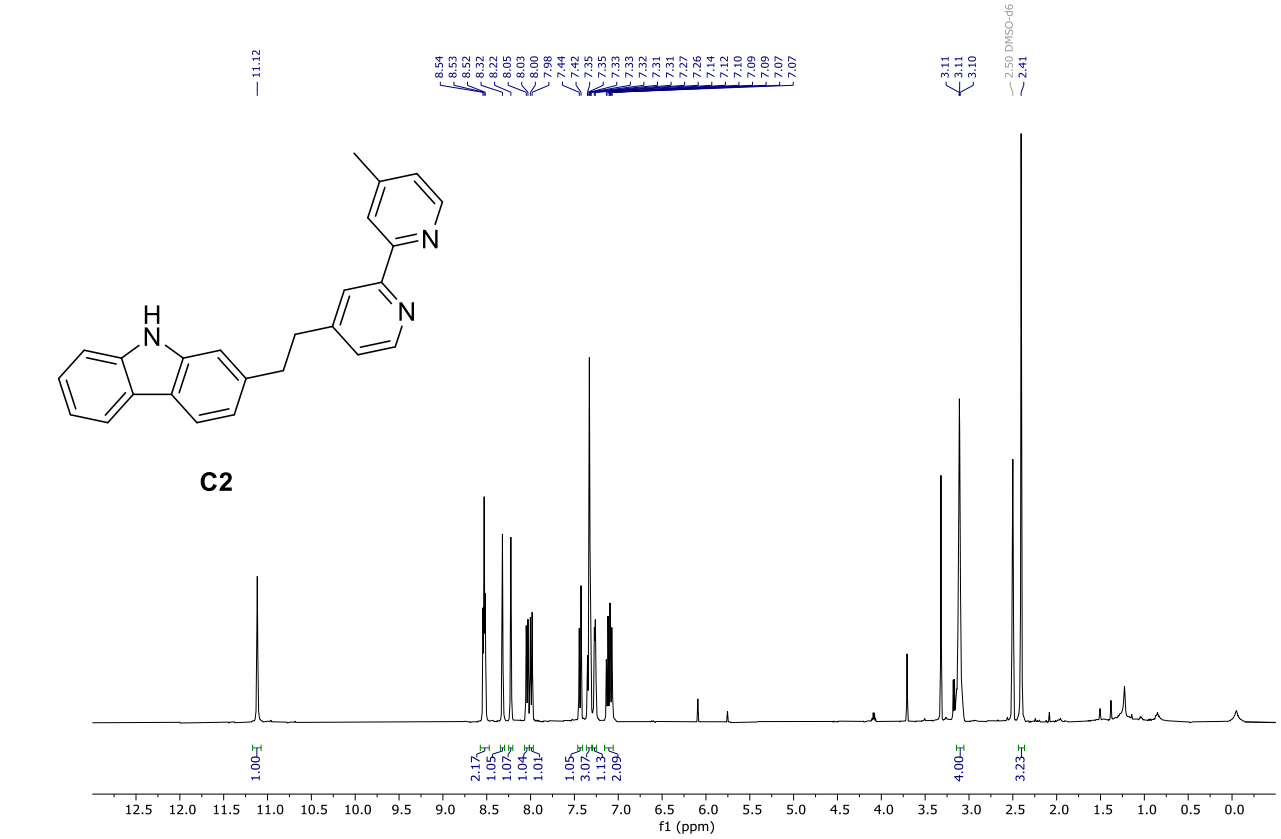
S6, *E* isomer



S6, *E* isomer


Boc
N
N
N
Boc protected **C2**
f1 (ppm)


Boc
N
N
N
Boc protected **C2**
f1 (ppm)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8.52
8.32
8.22
8.05
8.03
8.00
7.98
7.44
7.42
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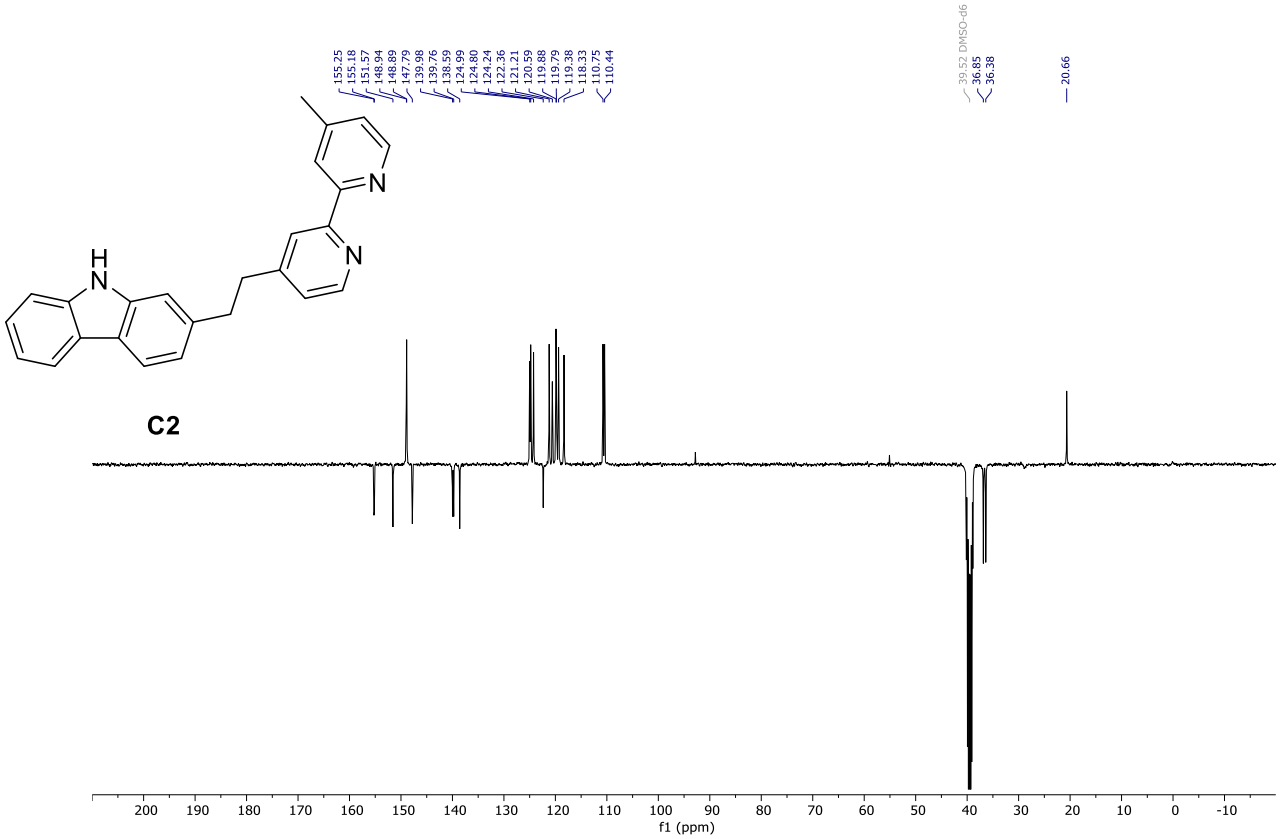
7.35
7.33
7.33
7.32
7.31
7.31
7.27
7.26
7.14
7.12
7.10
7.09
7.09
7.07
7.07
3.11
3.11
3.10
2.50 DMSO-d6
2.41
H
N
N
N
C2
1.00
2.17
1.05
1.07
1.04
1.01
1.05
3.07
1.13
2.09
4.00
3.23
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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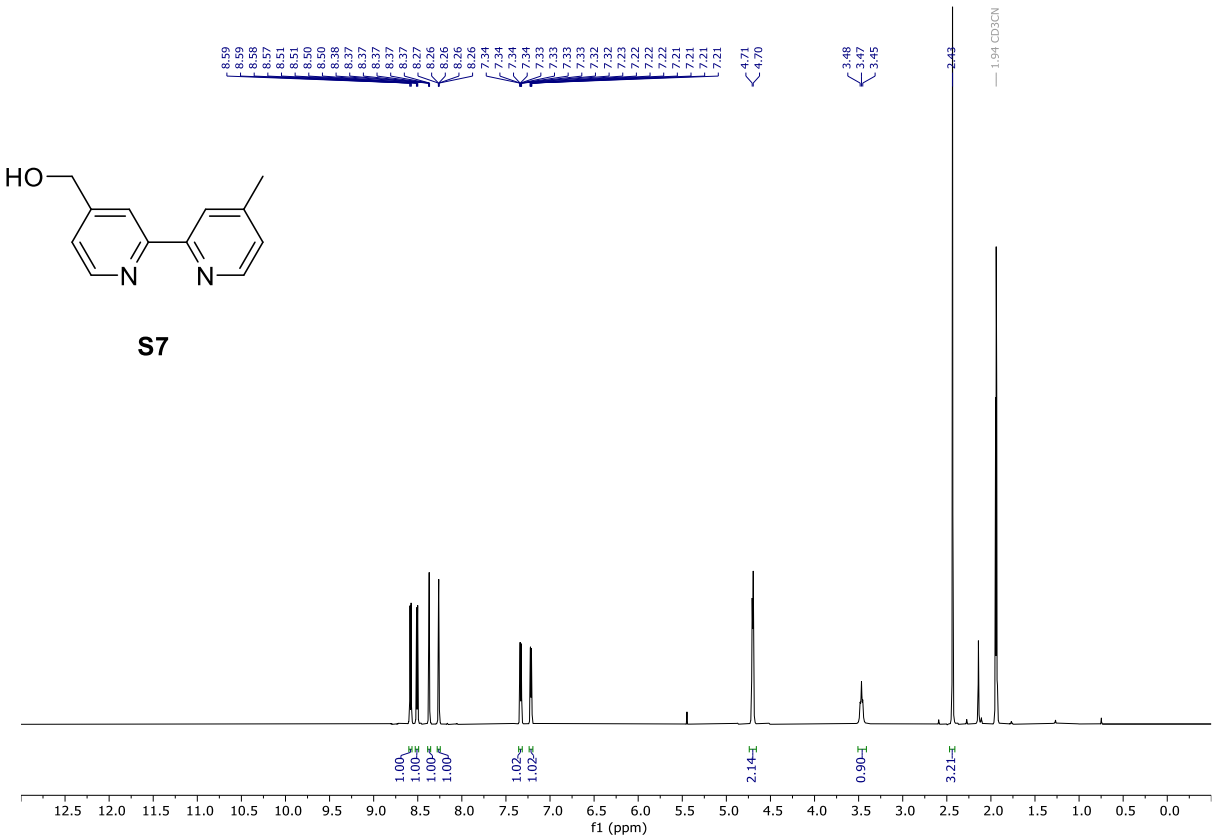
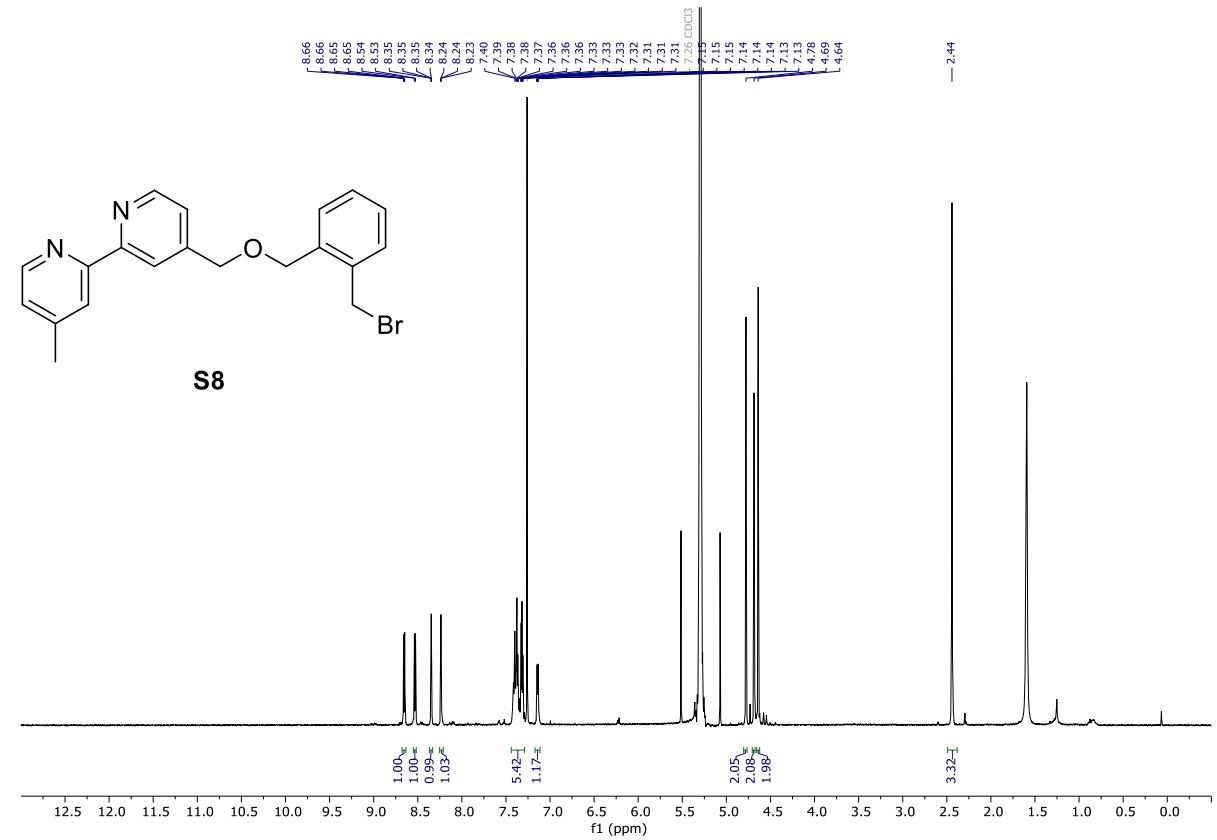
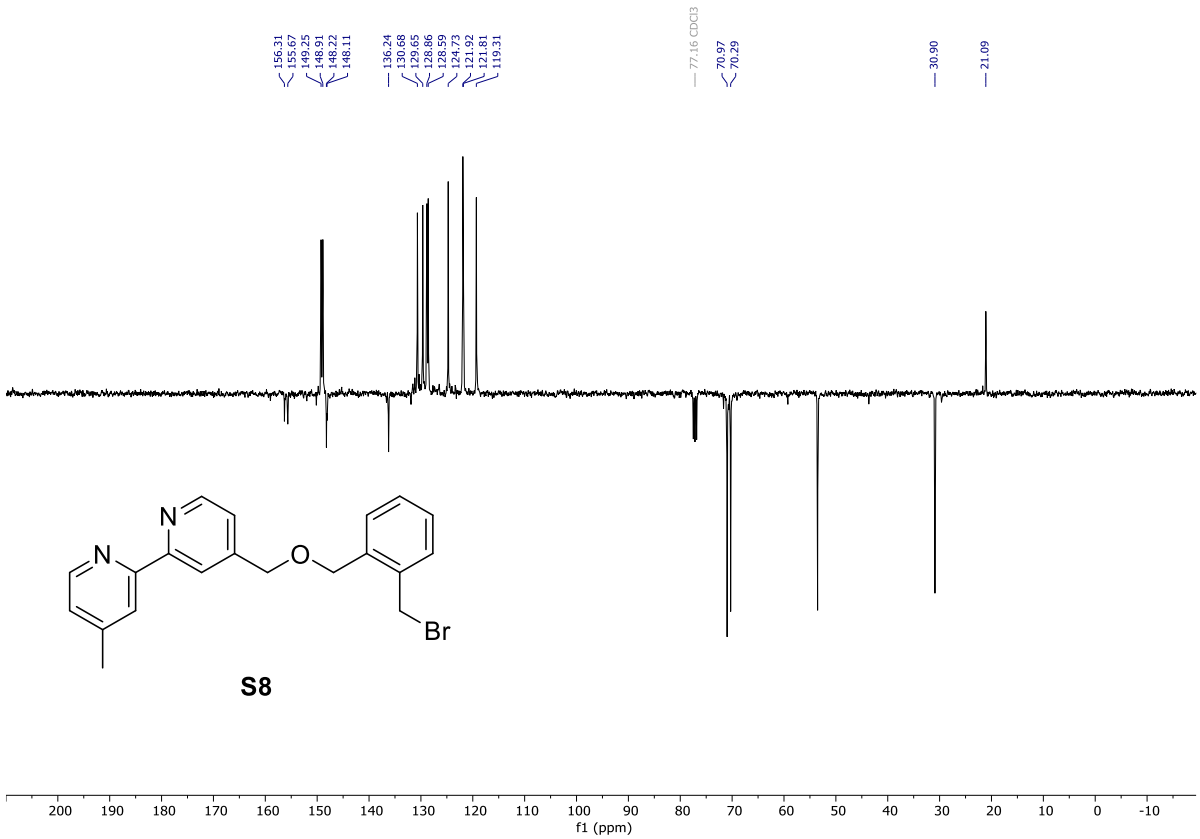
148.89
147.79
139.98
139.76
138.59
124.99
124.80
124.24
122.36
121.21
120.59
119.88
119.79
119.38
118.33
110.75
110.44
39.52 DMSO-d6
36.85
36.38
20.66
H
N
N
N
C2
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


HO
N
N
S7
f1 (ppm)


N
N
O
Br
S8
f1 (ppm)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148.22
148.11
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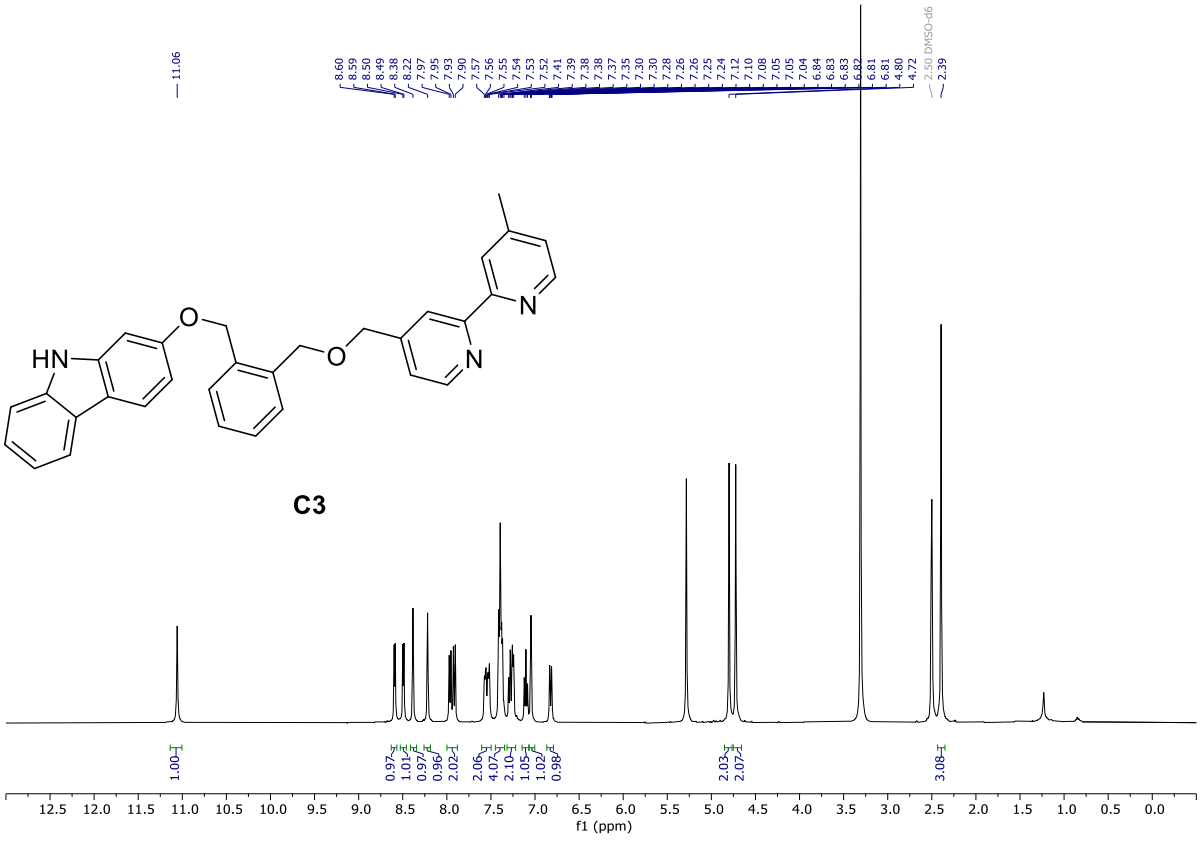
128.86
128.59
124.73
121.92
121.81
119.31
77.16 CDCl3
70.97
70.29
30.90
21.09
N
N
O
Br
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

S8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8.50
8.49
8.38
8.22
7.97
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7.93
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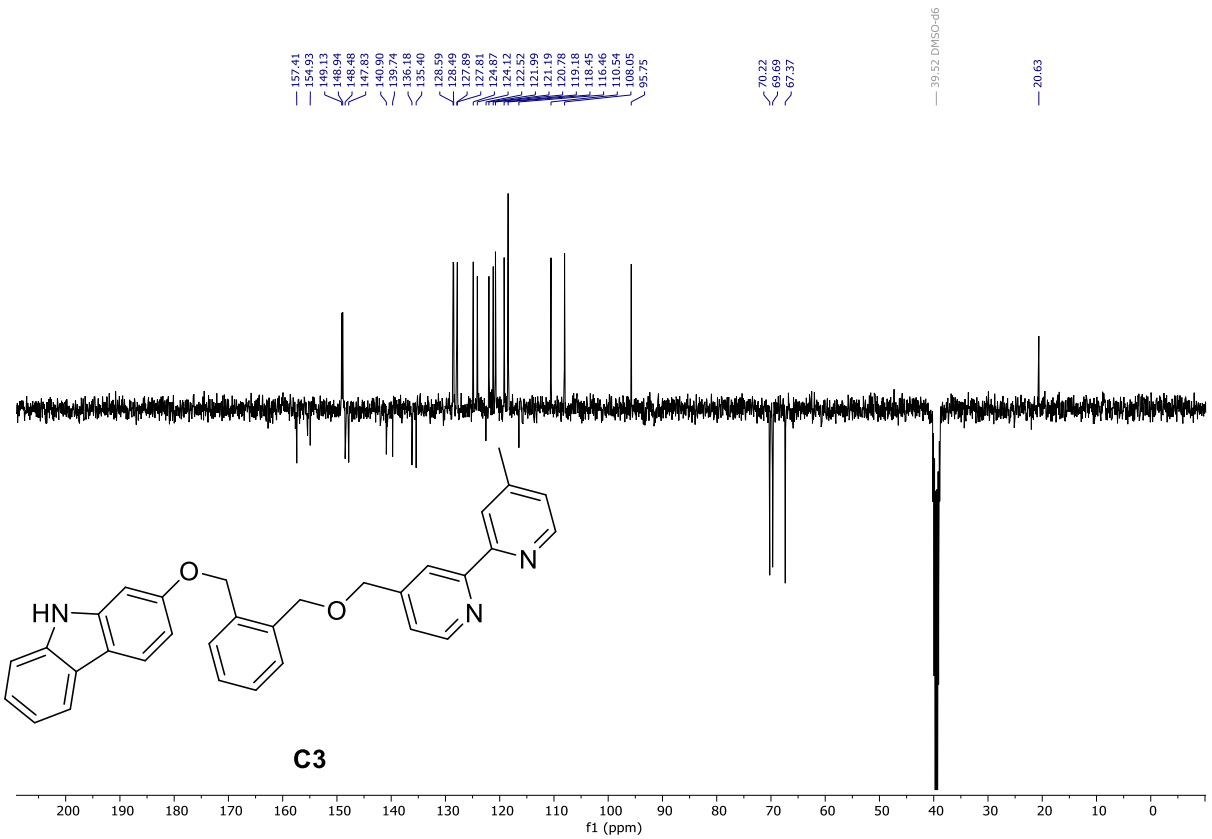
7.54
7.53
7.52
7.41
7.39
7.38
7.38
7.37
7.35
7.30
7.30
7.28
7.26
7.25
7.24
7.12
7.10
7.08
7.05
7.05
7.04
6.84
6.83
6.83
6.82
6.81
6.81
4.80
4.72
2.50 DMSO-d6
2.39
HN
O
O
N
N
1.00
0.97
1.01
0.97
0.96
2.02
2.06
4.07
2.10
1.05
1.02
0.98
2.03
2.07
3.08
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

C3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154.93
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127.89
127.81
124.87
124.12
122.52
121.99
121.19
120.78
119.18
118.45
116.46
110.54
108.05
95.75
70.22
69.69
67.37
39.52 DMSO-d6
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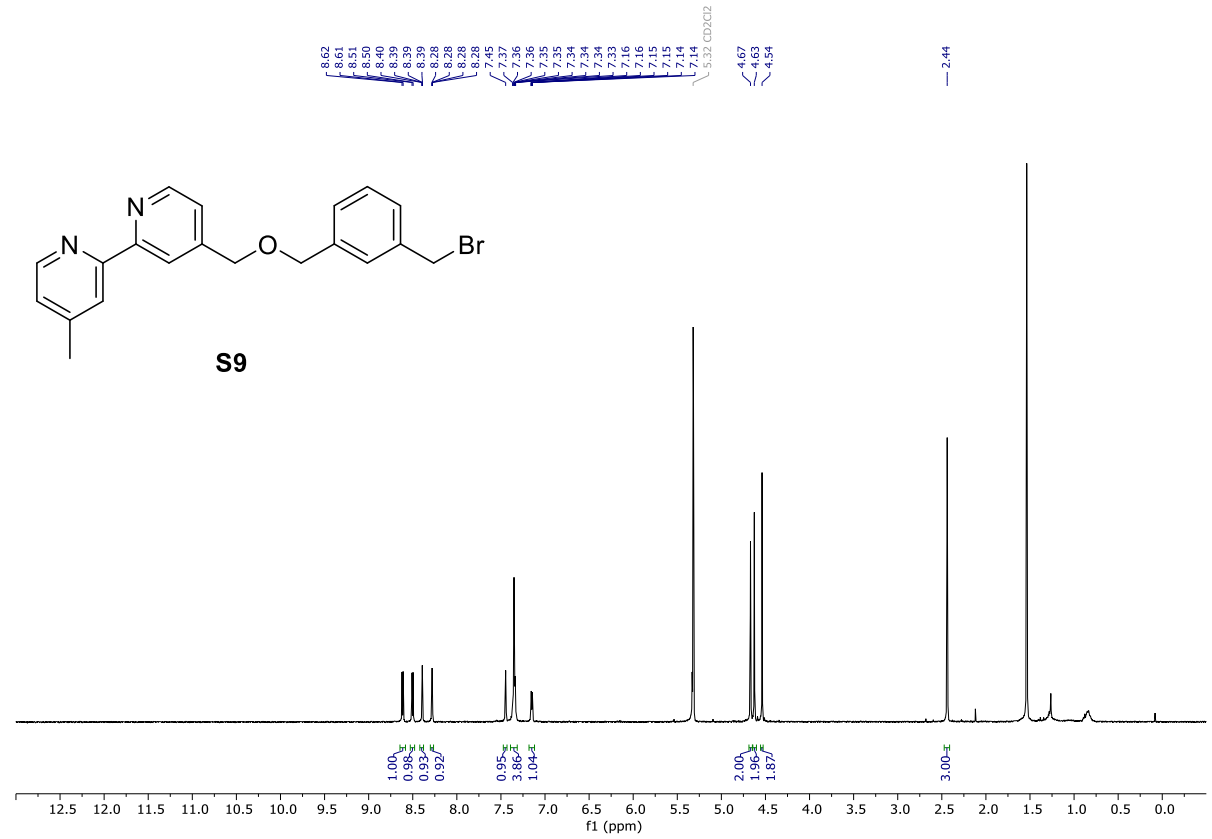
HN
O
O
N
N
C3
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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8.39
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8.28
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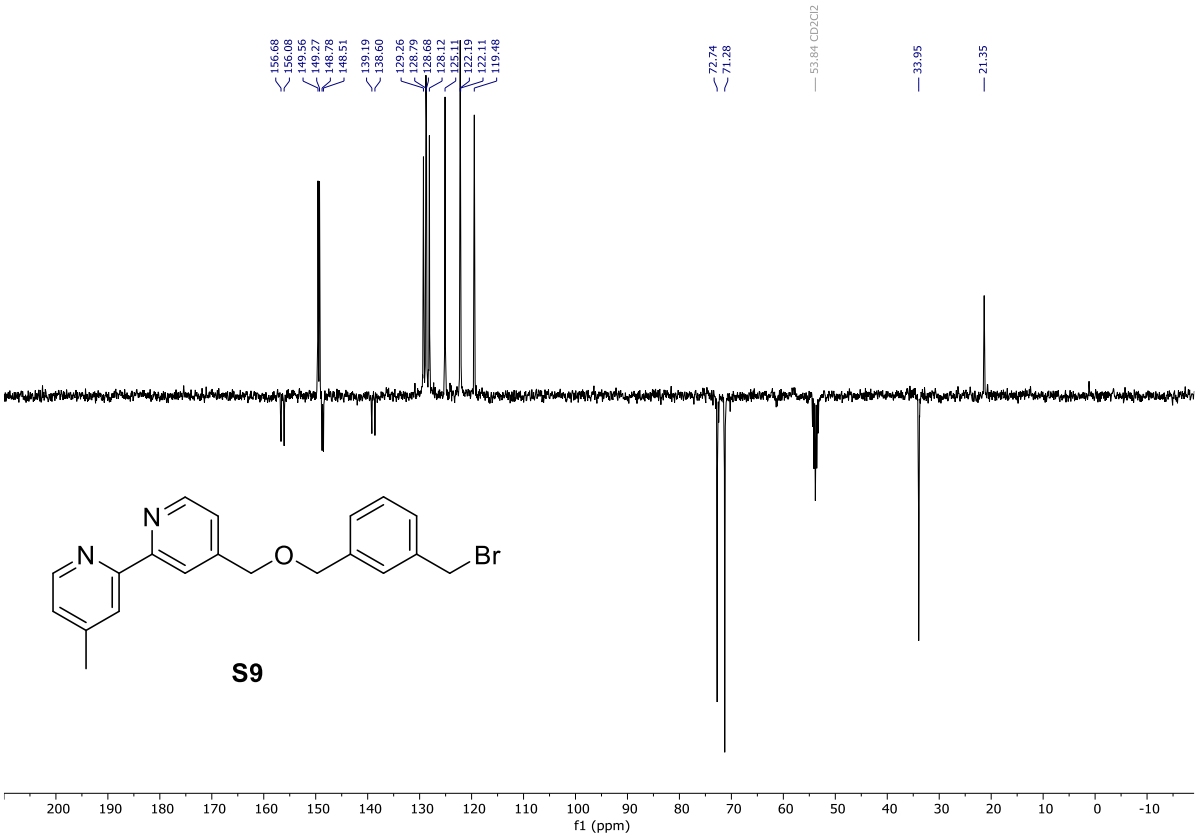
7.37
7.36
7.36
7.35
7.35
7.34
7.34
7.34
7.33
7.16
7.16
7.15
7.15
7.14
7.14
5.32 CD2Cl2
4.67
4.63
4.54
2.44
N
N
O
Br
S9
1.00
0.98
0.93
0.92
0.95
3.86
1.04
2.00
1.96
1.87
3.00
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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148.51
139.19
138.60
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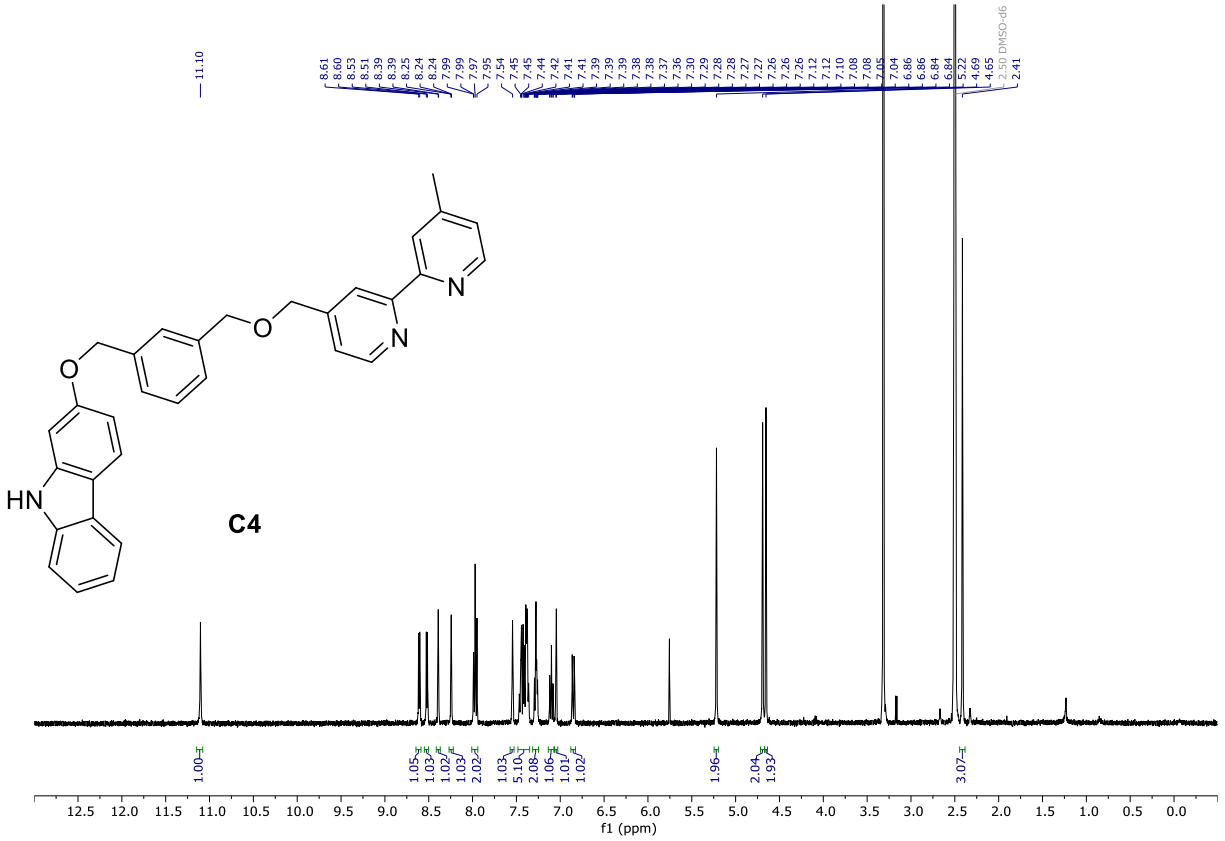
128.79
128.68
128.12
128.11
122.19
122.11
119.48
72.74
71.28
53.84 CD2Cl2
33.95
21.35
N
N
O
Br
S9
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)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8.39
8.39
8.25
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7.99
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7.95
7.54
7.45
7.45
7.44
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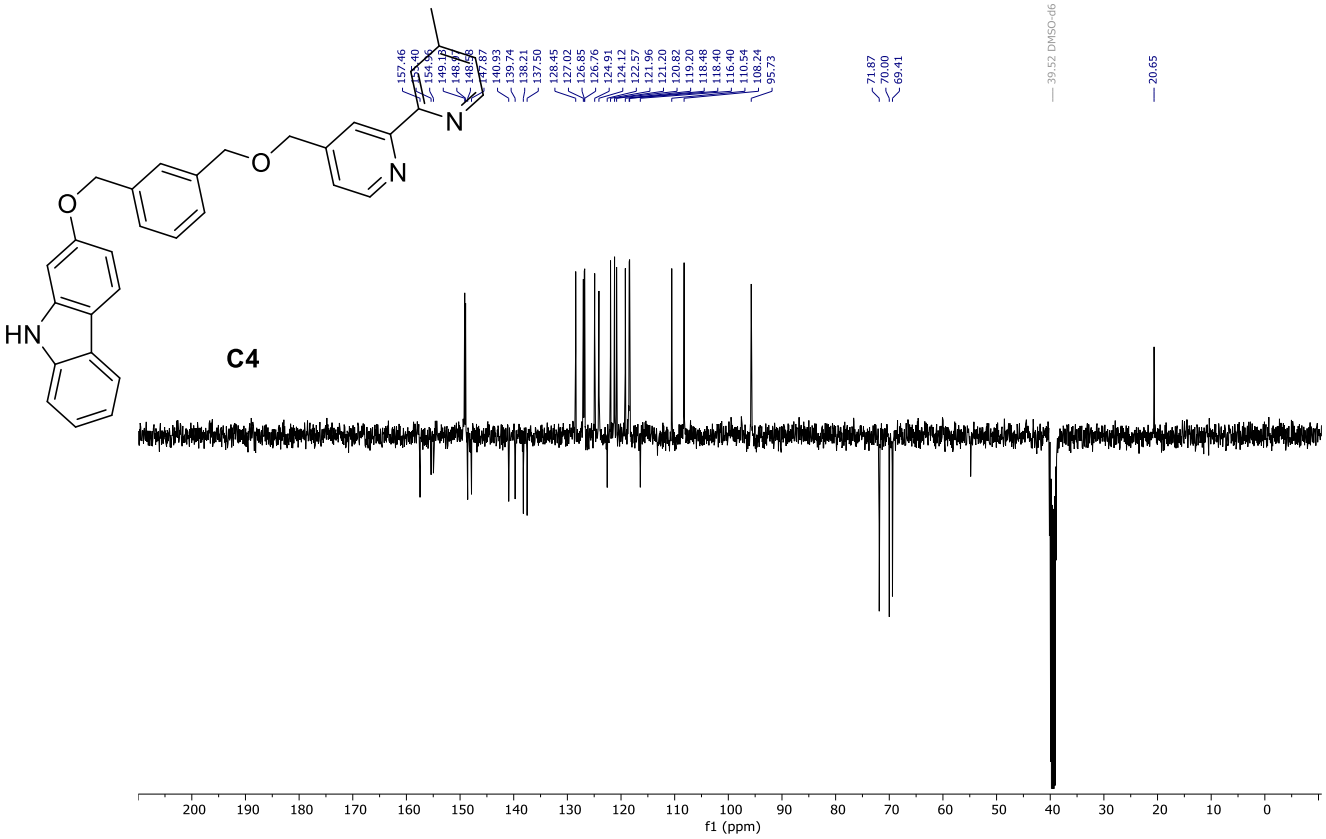
7.41
7.41
7.39
7.39
7.39
7.38
7.38
7.37
7.36
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.26
7.26
7.12
7.12
7.10
7.08
7.08
7.05
7.04
6.86
6.86
6.84
6.84
5.22
4.69
4.65
2.50 DMSO-d6
2.41
N
N
O
O
HN
C4
1.00
1.05
1.03
1.02
1.03
2.02
1.03
5.10
2.08
1.06
1.01
1.02
1.96
2.04
1.93
3.07
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


C4
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154.06
149.18
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148.58
147.87
140.93
139.74
138.21
137.50
128.45
127.02
126.85
126.76
124.91
124.12
122.57
121.96
121.20
120.82
119.20
118.48
118.40
116.40
110.54
108.24
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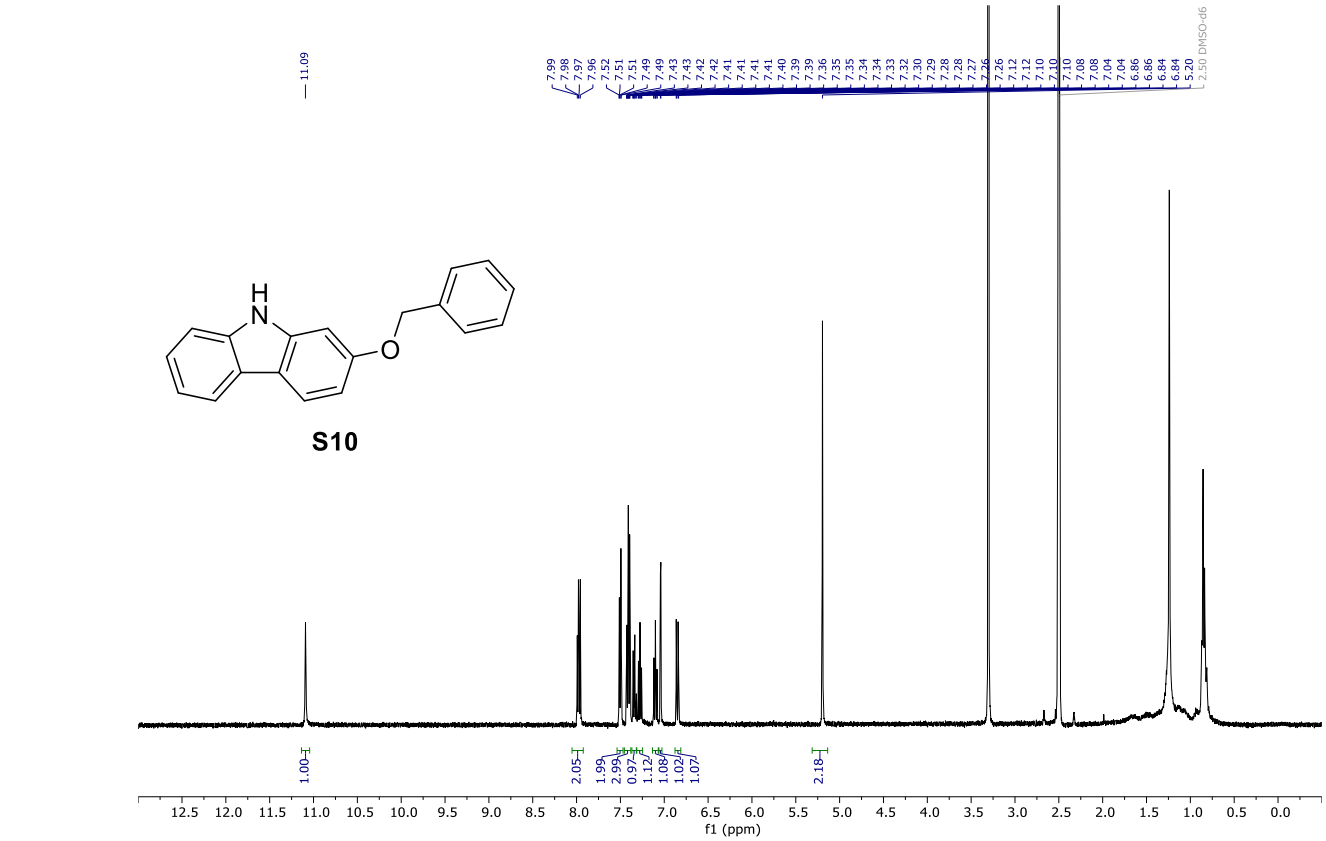
71.87
70.00
69.41
39.52 DMSO-d6
20.65
f1 (ppm)


S10
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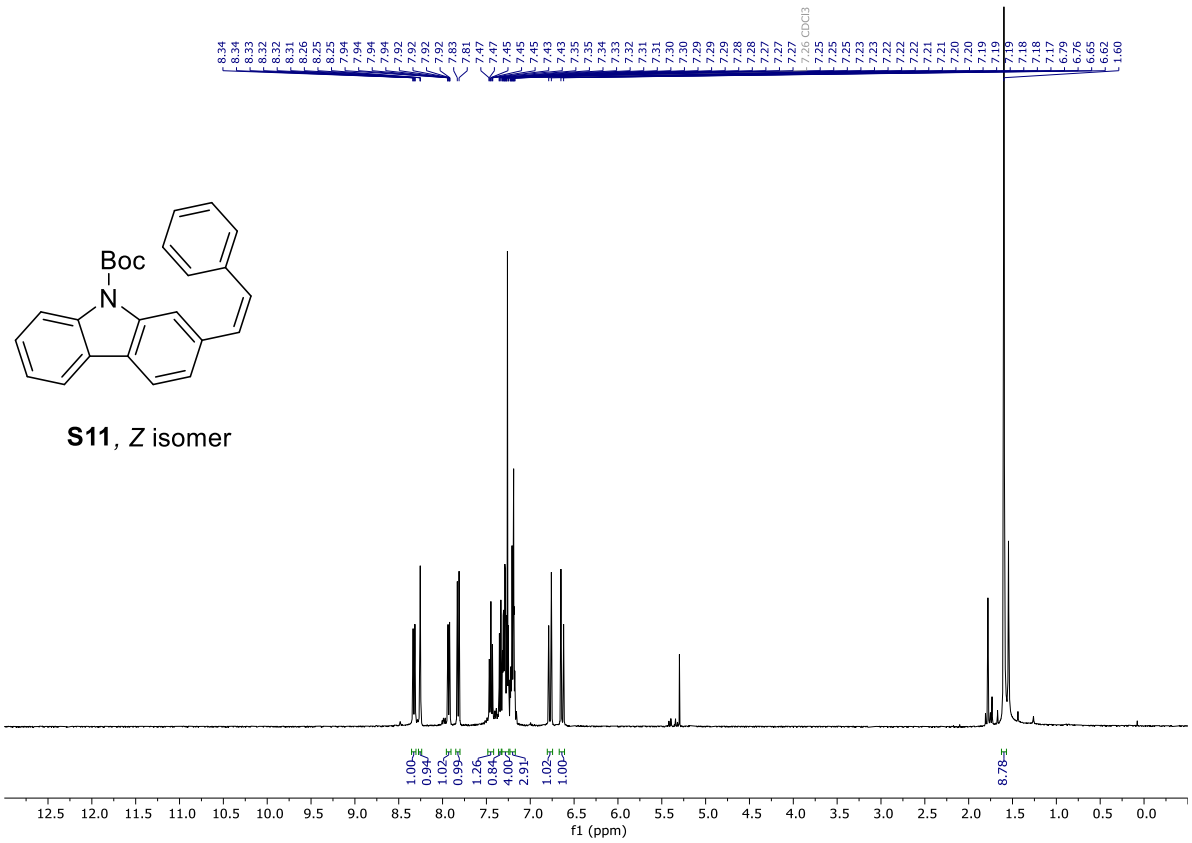
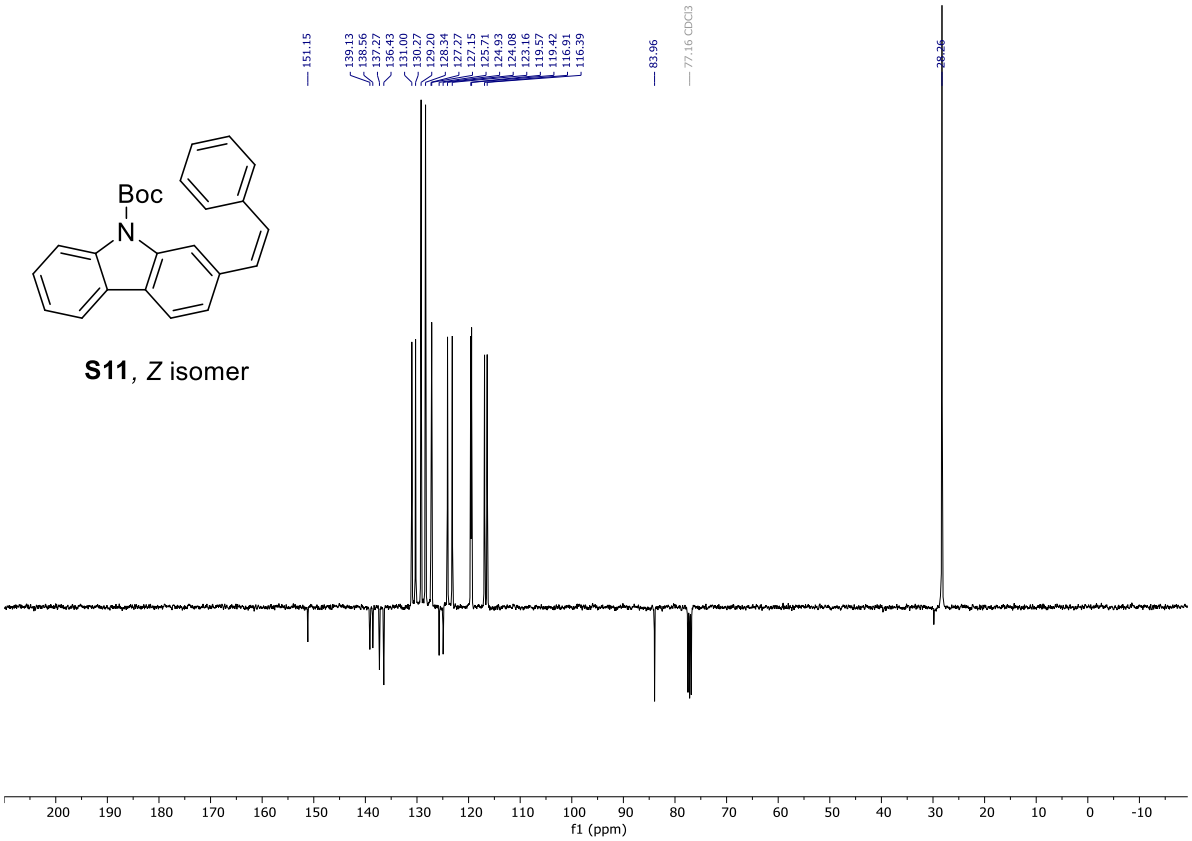
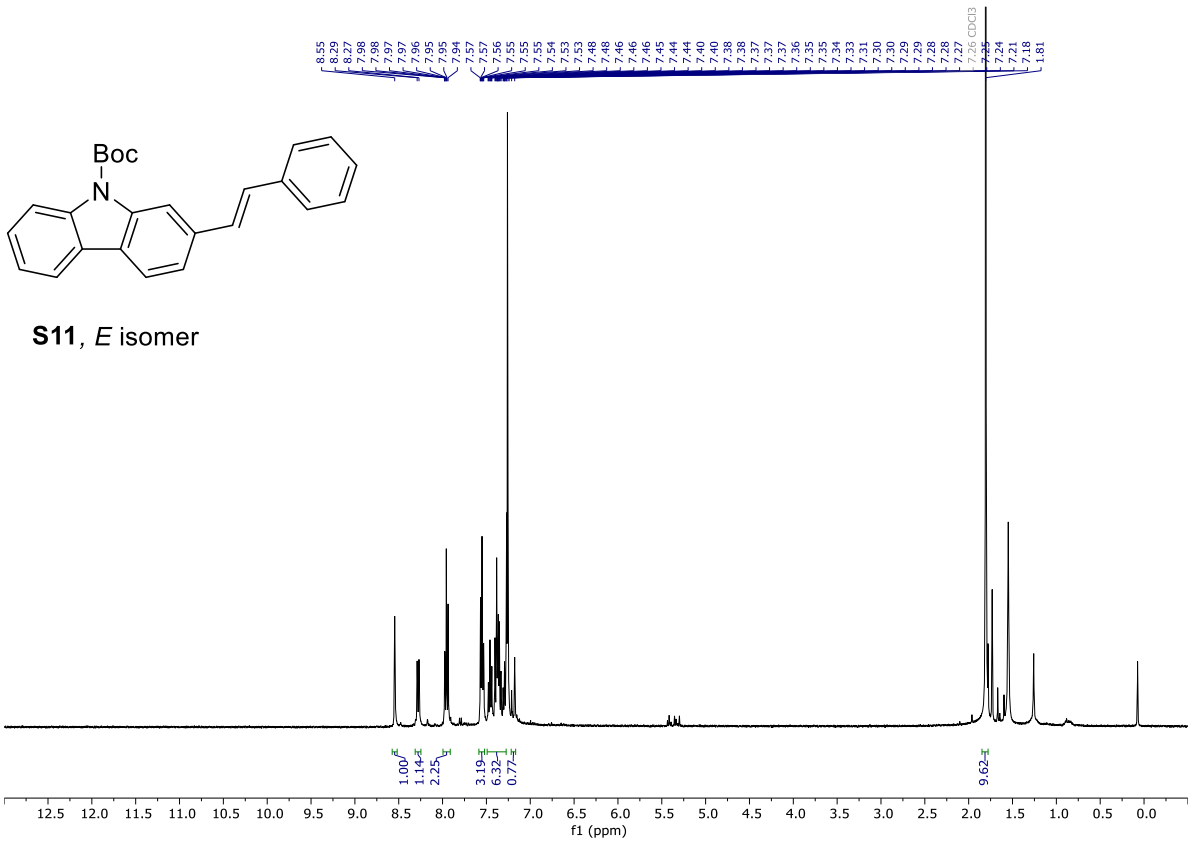
7.96
7.52
7.51
7.51
7.49
7.49
7.43
7.43
7.42
7.42
7.41
7.41
7.41
7.41
7.40
7.39
7.39
7.36
7.35
7.35
7.34
7.34
7.33
7.32
7.30
7.29
7.28
7.28
7.27
7.26
7.26
7.12
7.12
7.10
7.10
7.08
7.08
7.04
7.04
6.86
6.84
6.84
5.20
2.50 DMSO-d6
1.00
2.05
1.99
2.99
0.97
1.12
1.08
1.02
1.07
2.18
f1 (ppm)



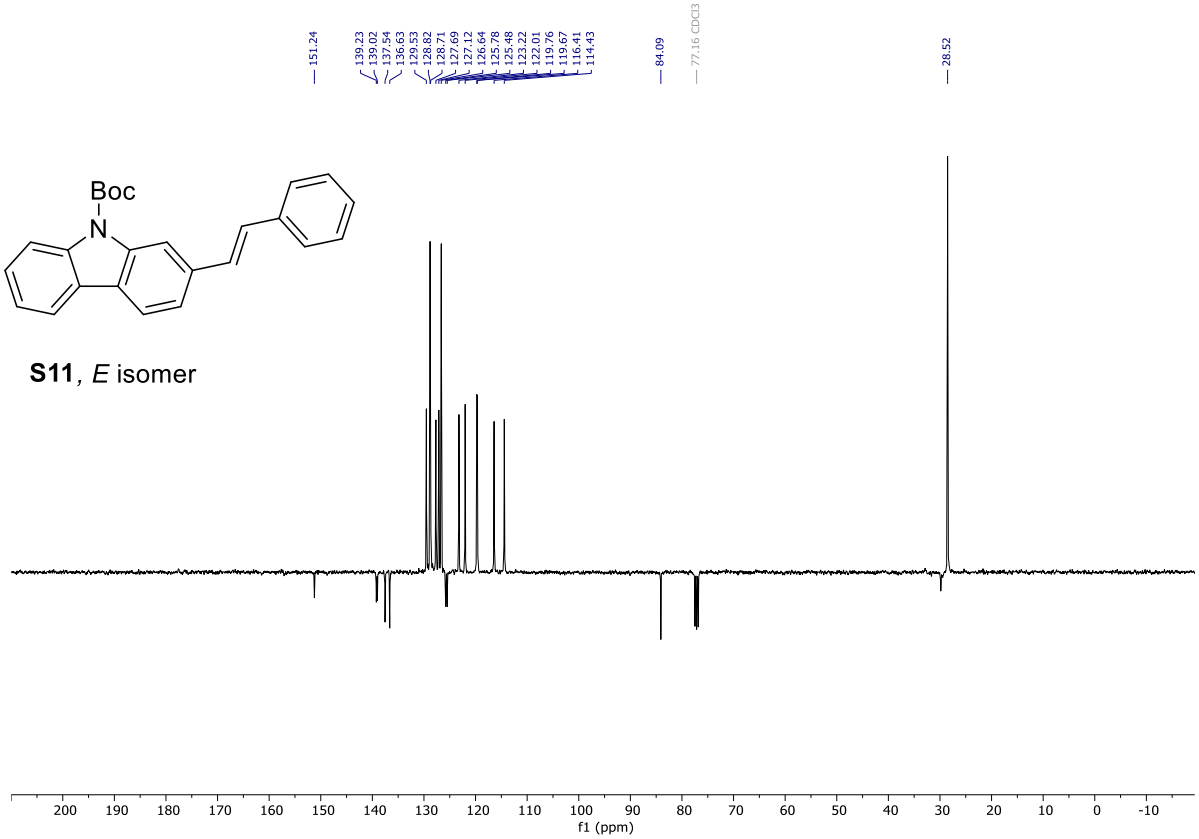
S11, *Z* isomer



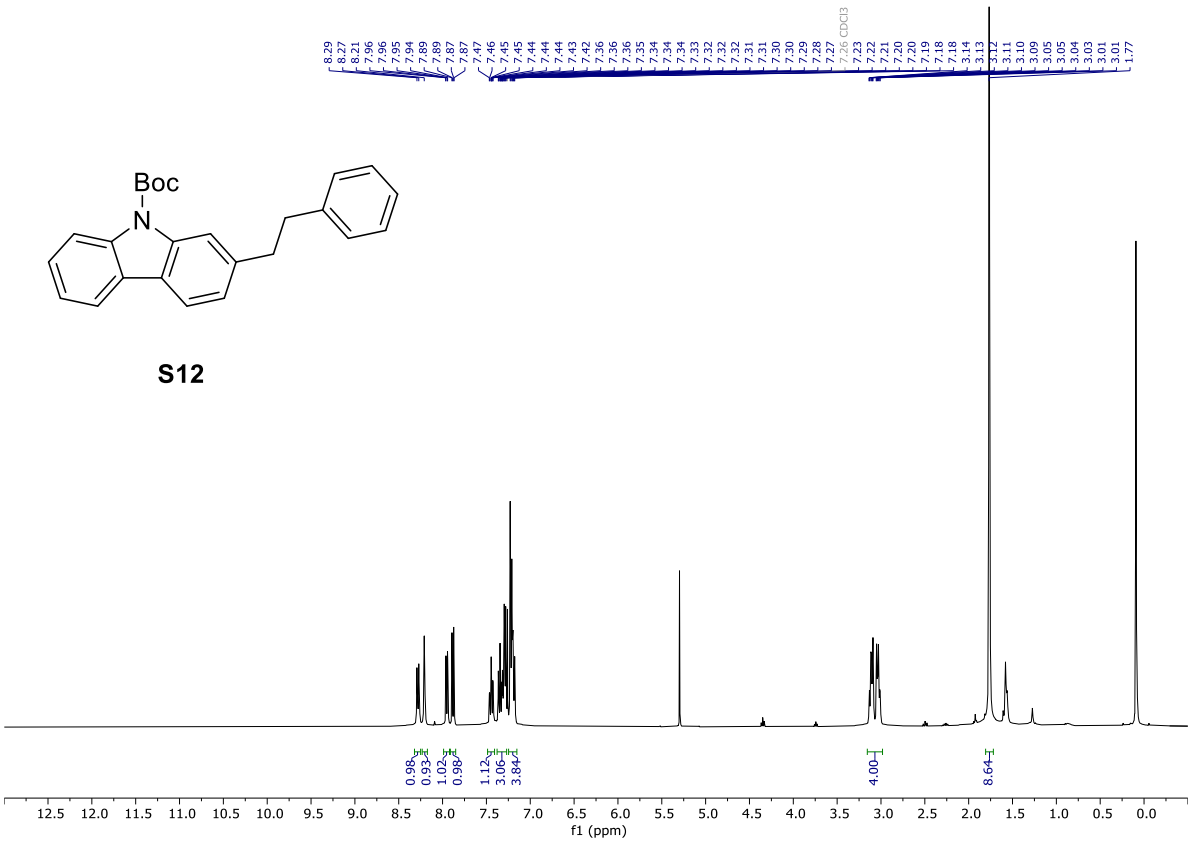
S11, *Z* isomer

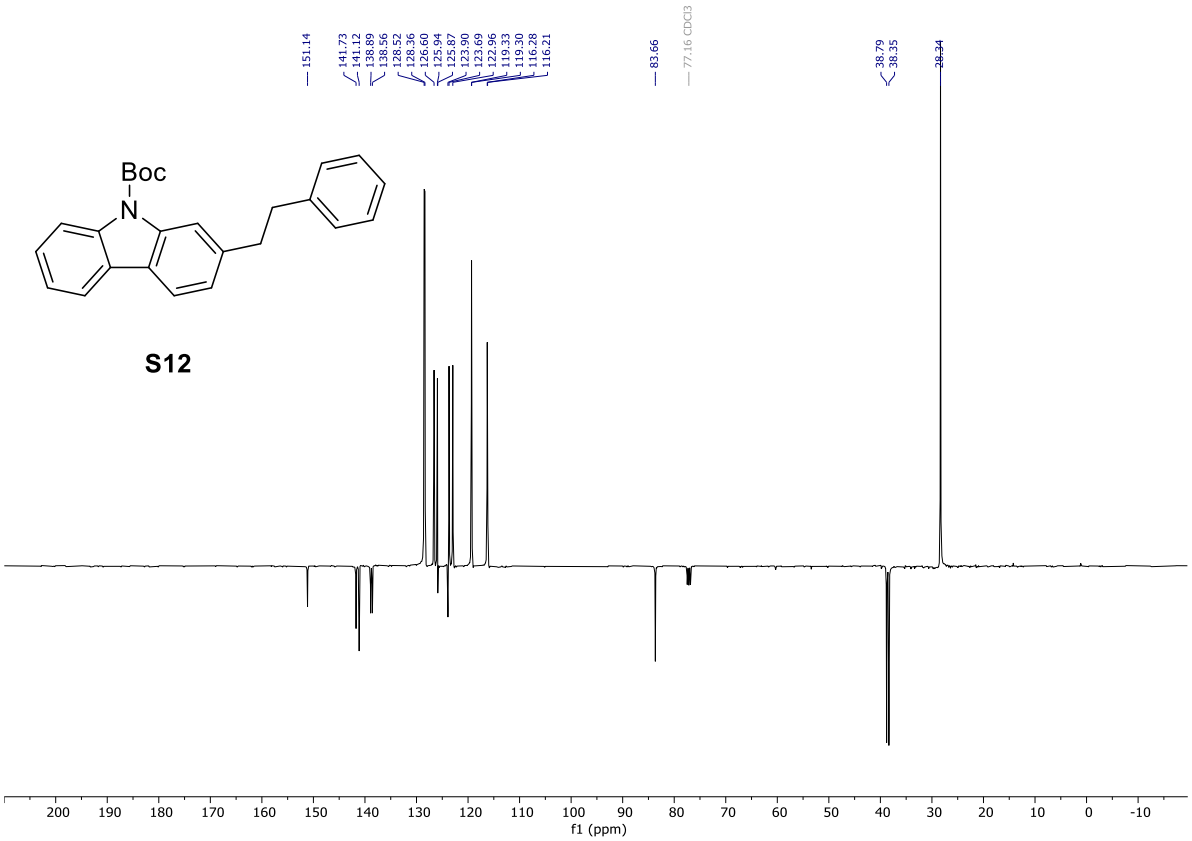


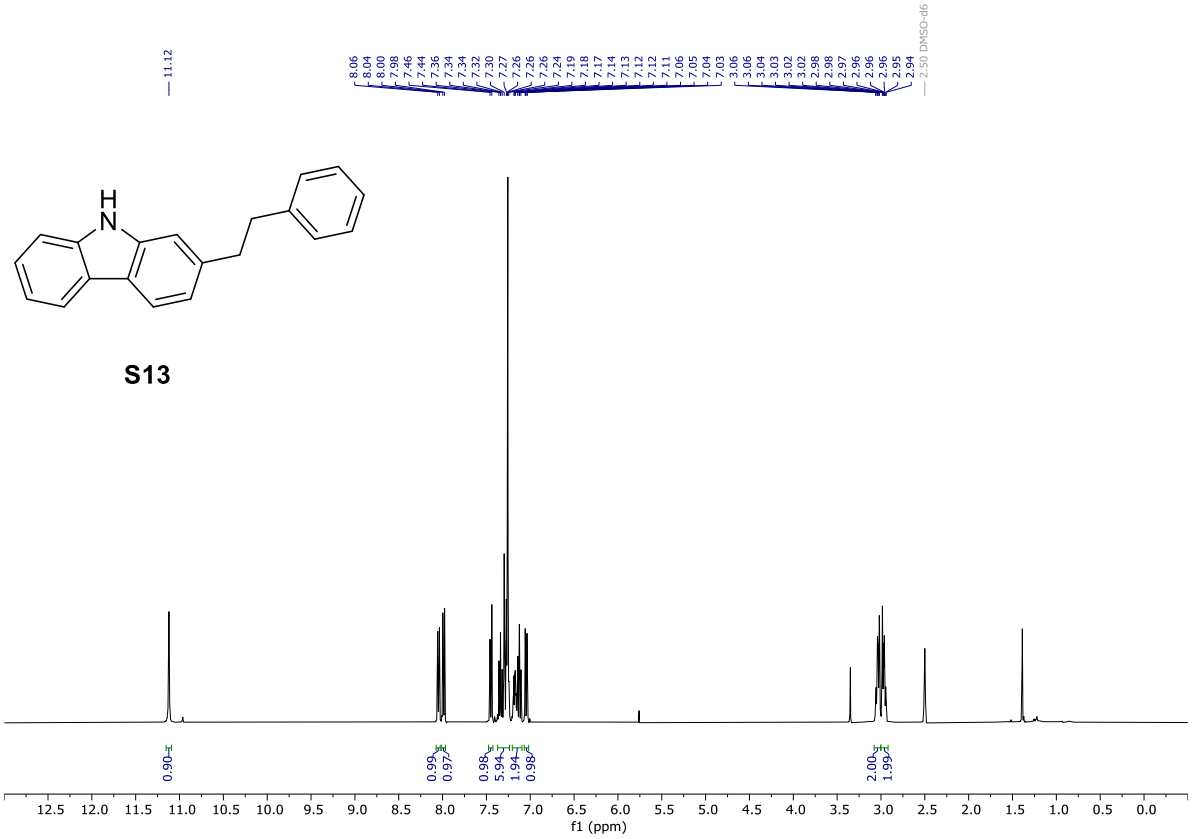
S11, *E* isomer

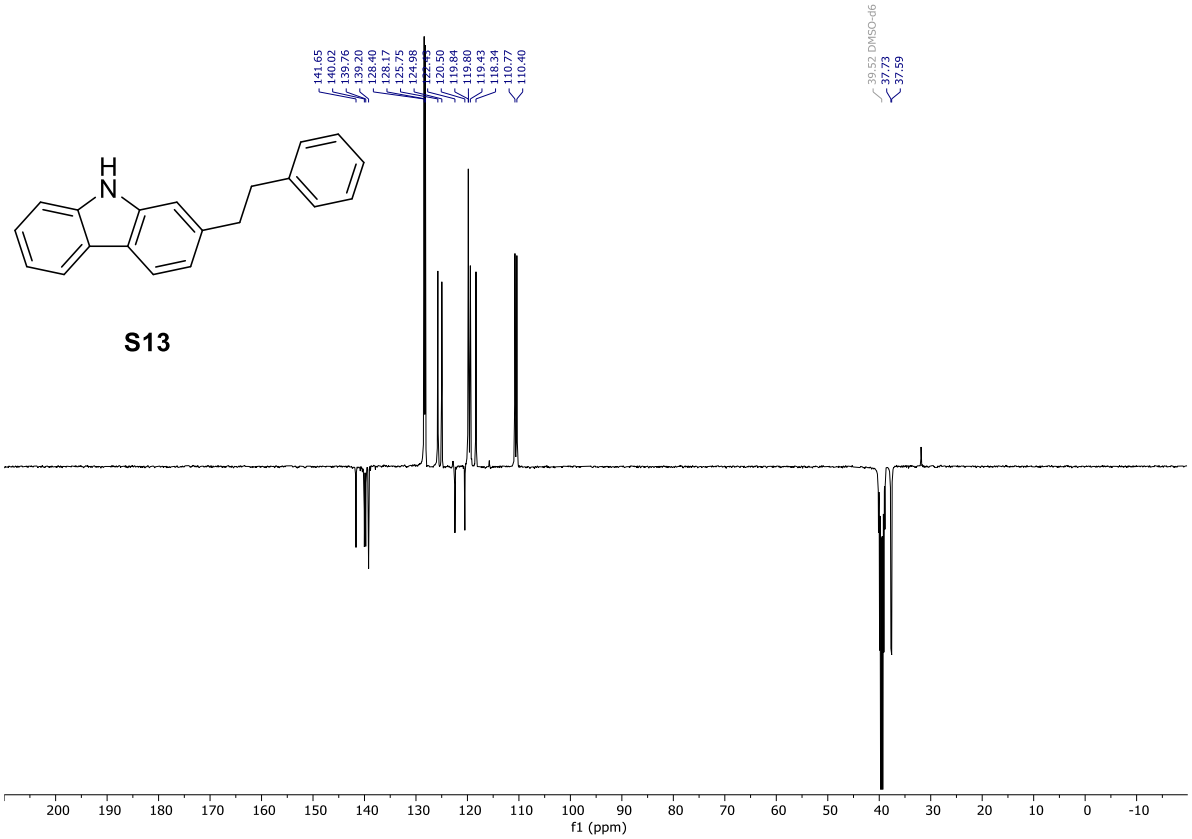


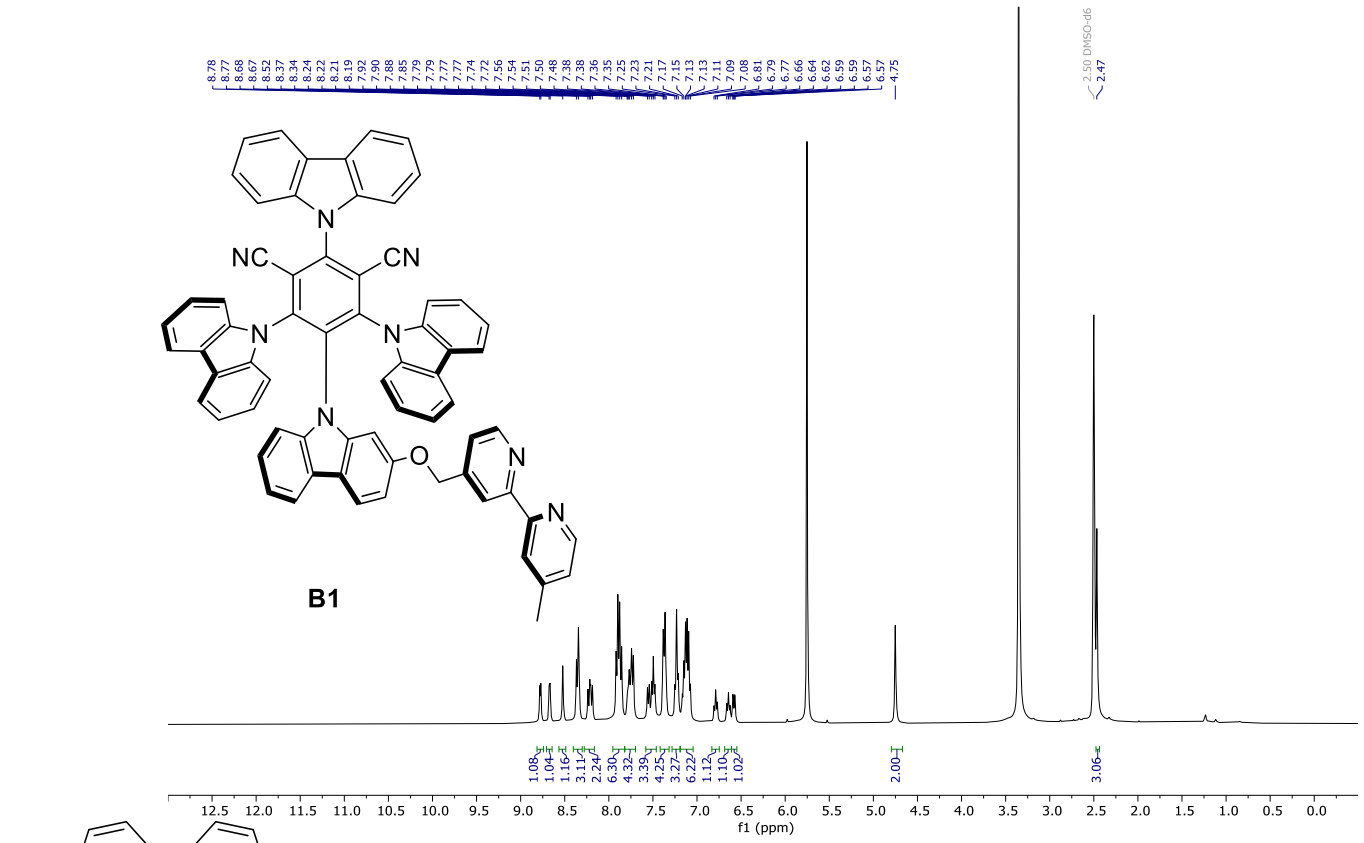
S11, *E* isomer

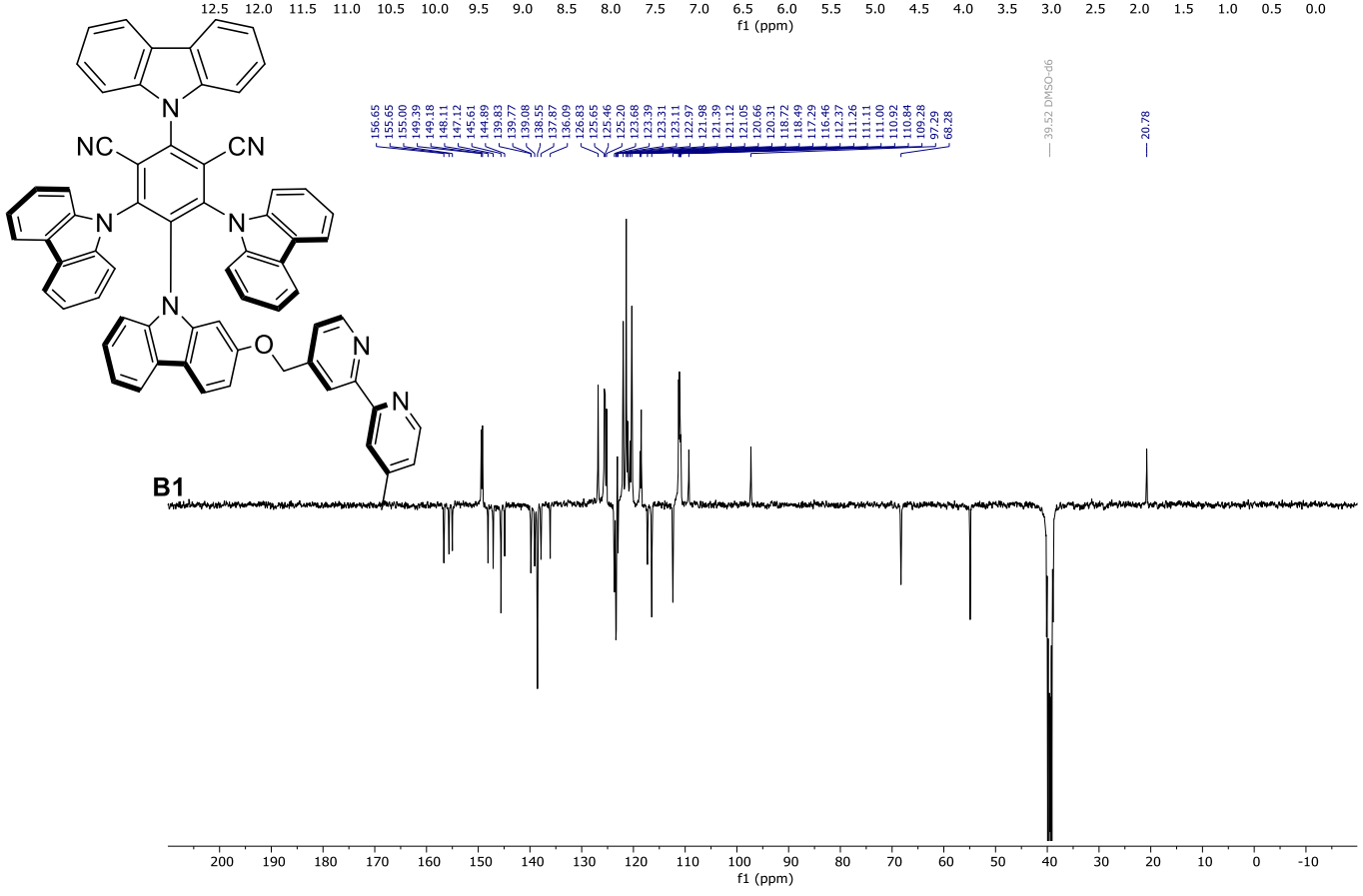

Boc
N
S12
f1 (ppm)

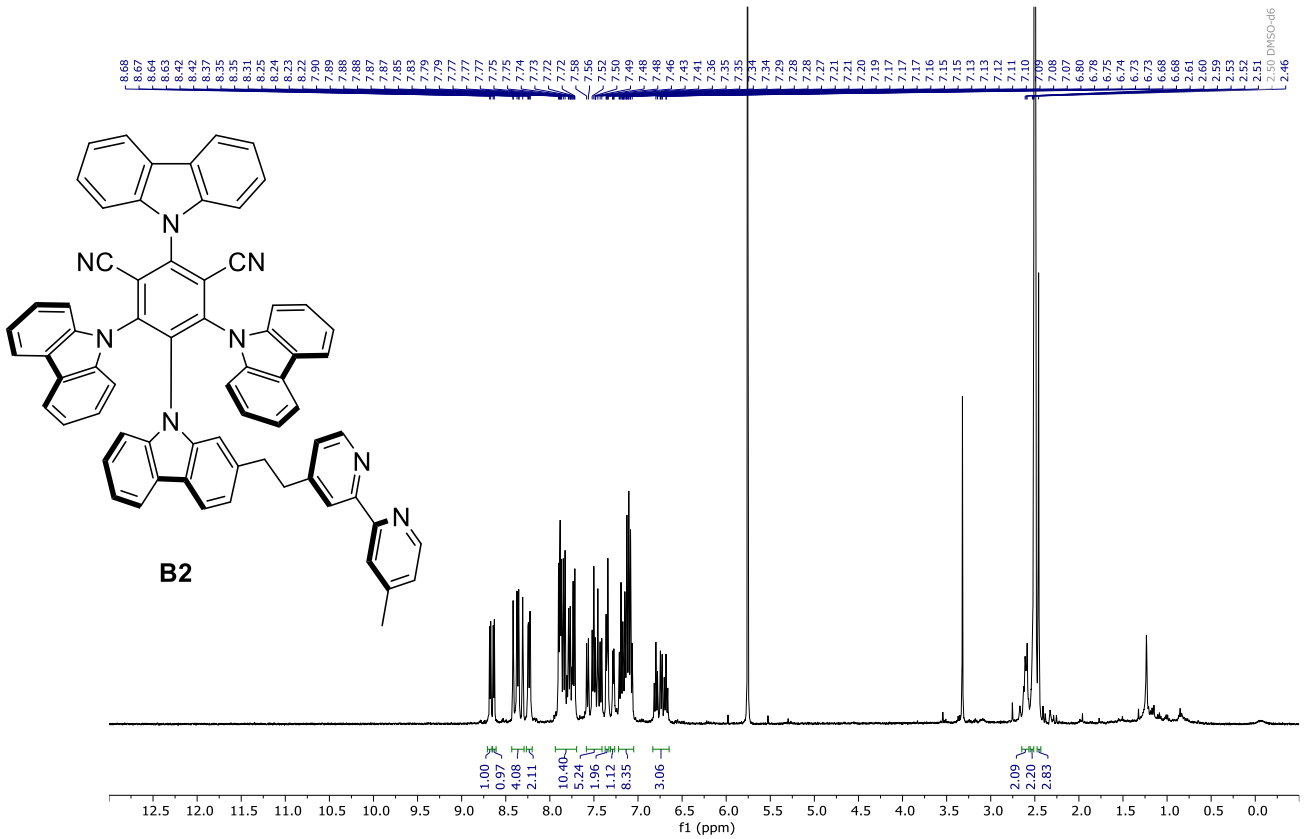

Boc
N
S12
f1 (ppm)

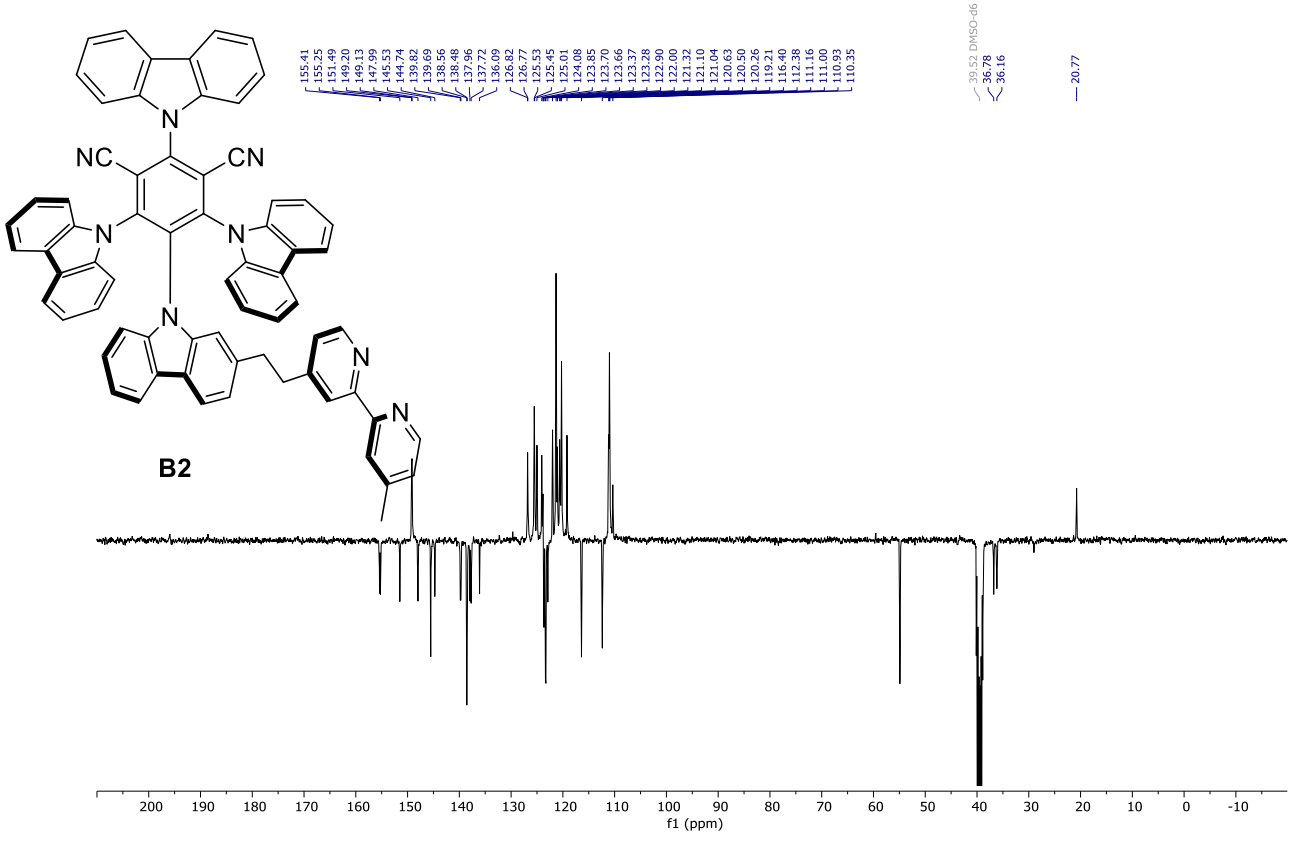

11.12
8.06
8.04
8.00
7.98
7.46
7.44
7.36
7.34
7.34
7.32
7.30
7.27
7.26
7.26
7.26
7.24
7.19
7.18
7.17
7.14
7.13
7.12
7.12
7.11
7.06
7.05
7.04
7.03
3.06
3.06
3.04
3.03
3.02
3.02
2.98
2.97
2.96
2.96
2.95
2.94
2.50 DMSO-d6
H
N
S13
0.90
0.99
0.97
0.98
5.94
1.94
0.98
2.00
1.99
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

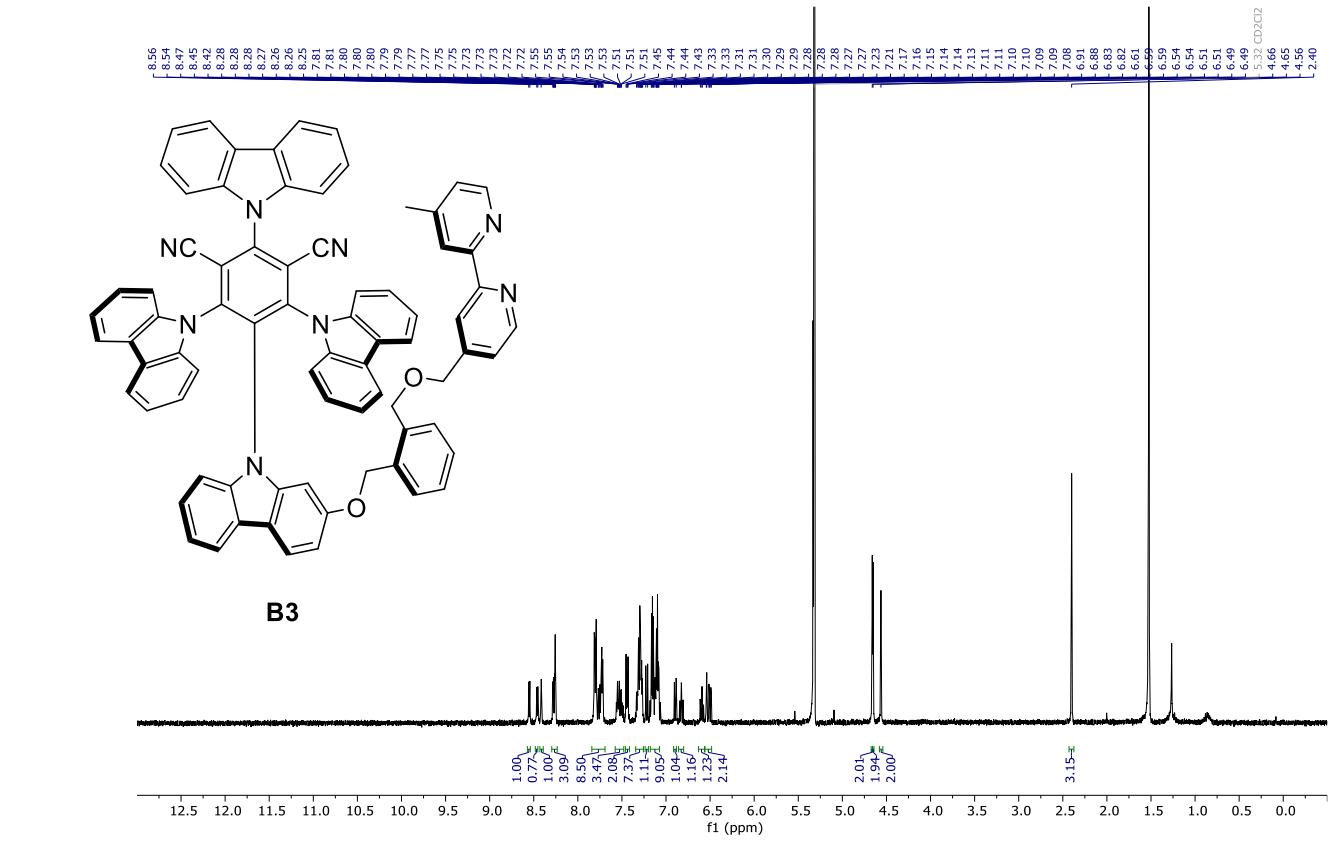

141.65
140.02
139.76
139.20
128.40
128.17
125.75
124.98
122.43
120.50
119.84
119.80
119.43
118.34
110.77
110.40
39.52 DMSO-d6
37.73
37.59
H
N
S13
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

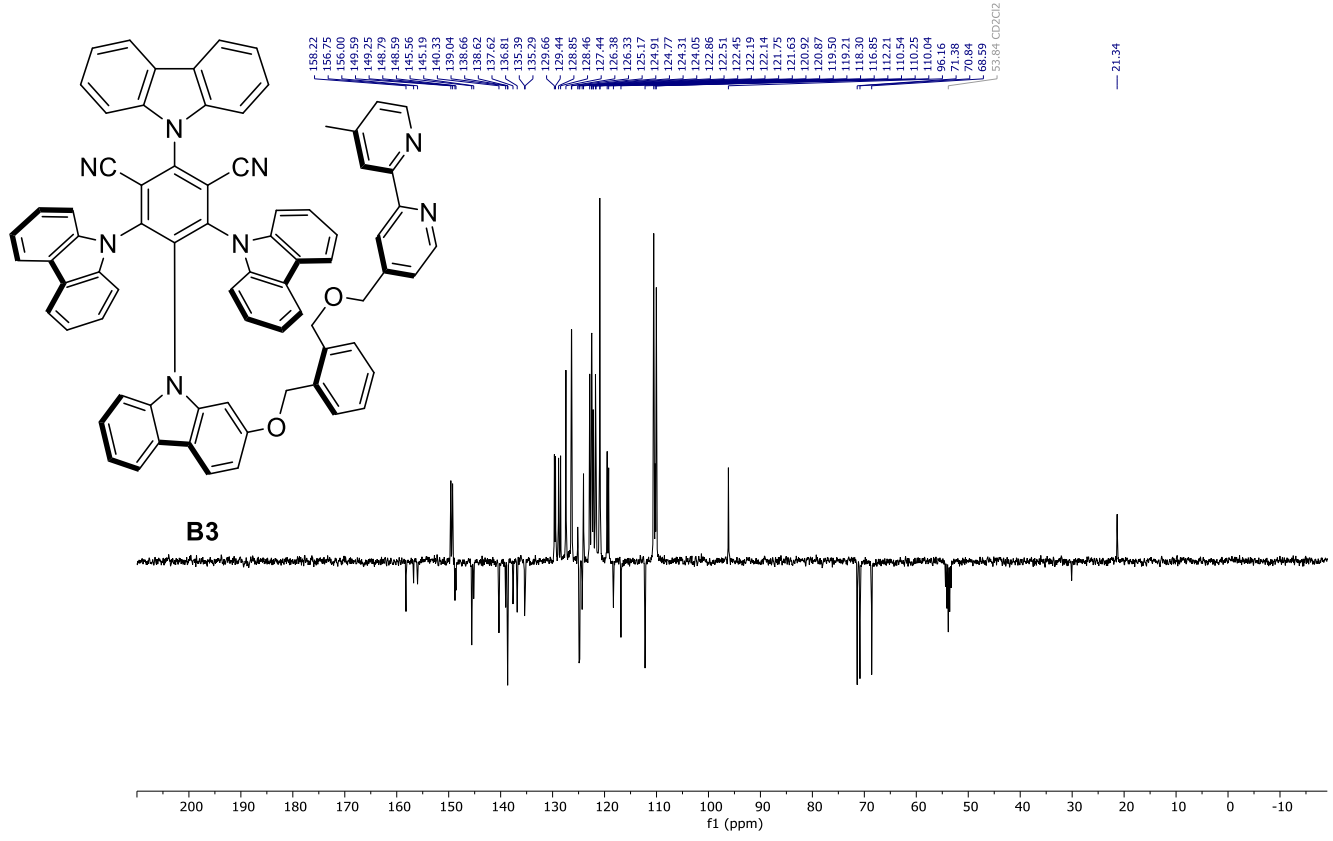

B1
f1 (ppm)

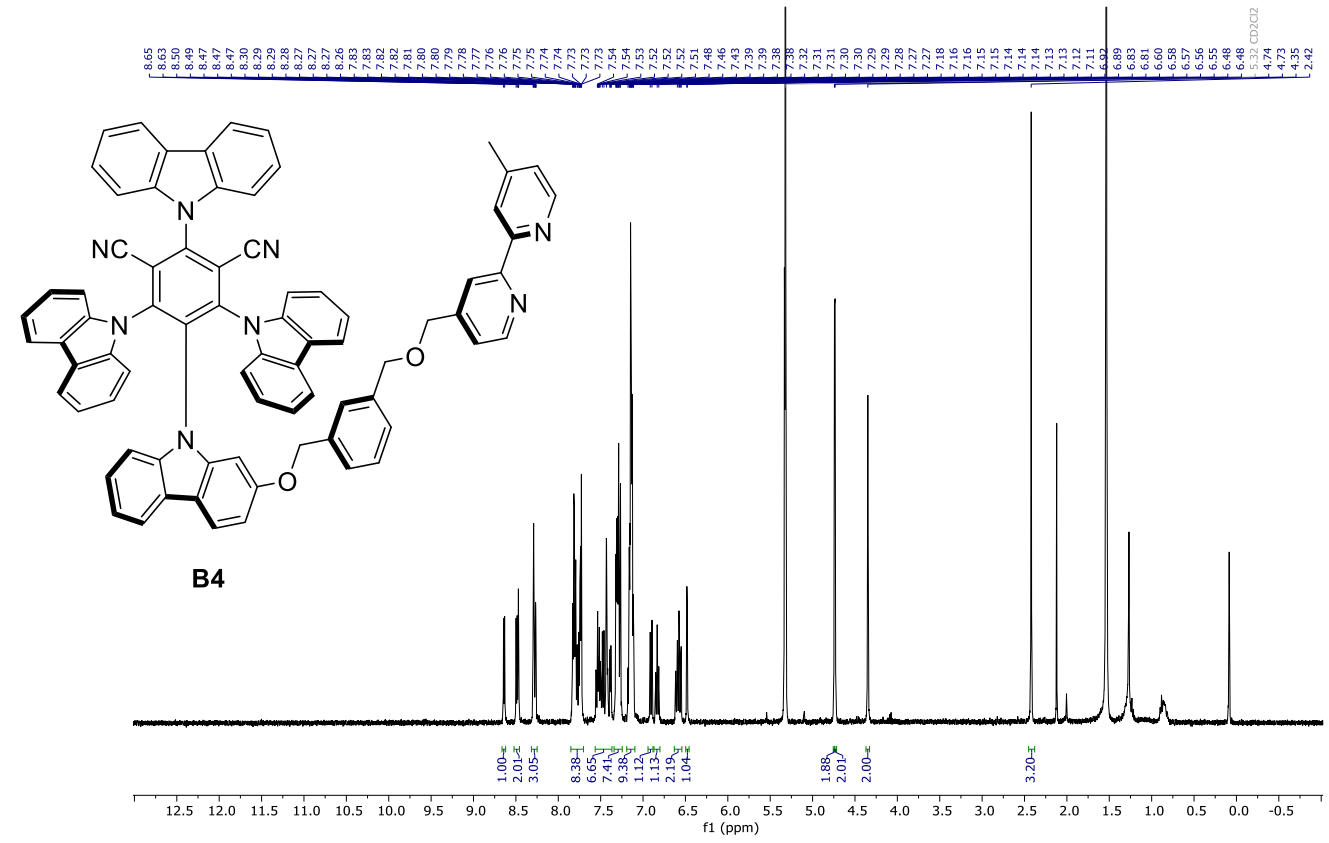

B1
f1 (ppm)

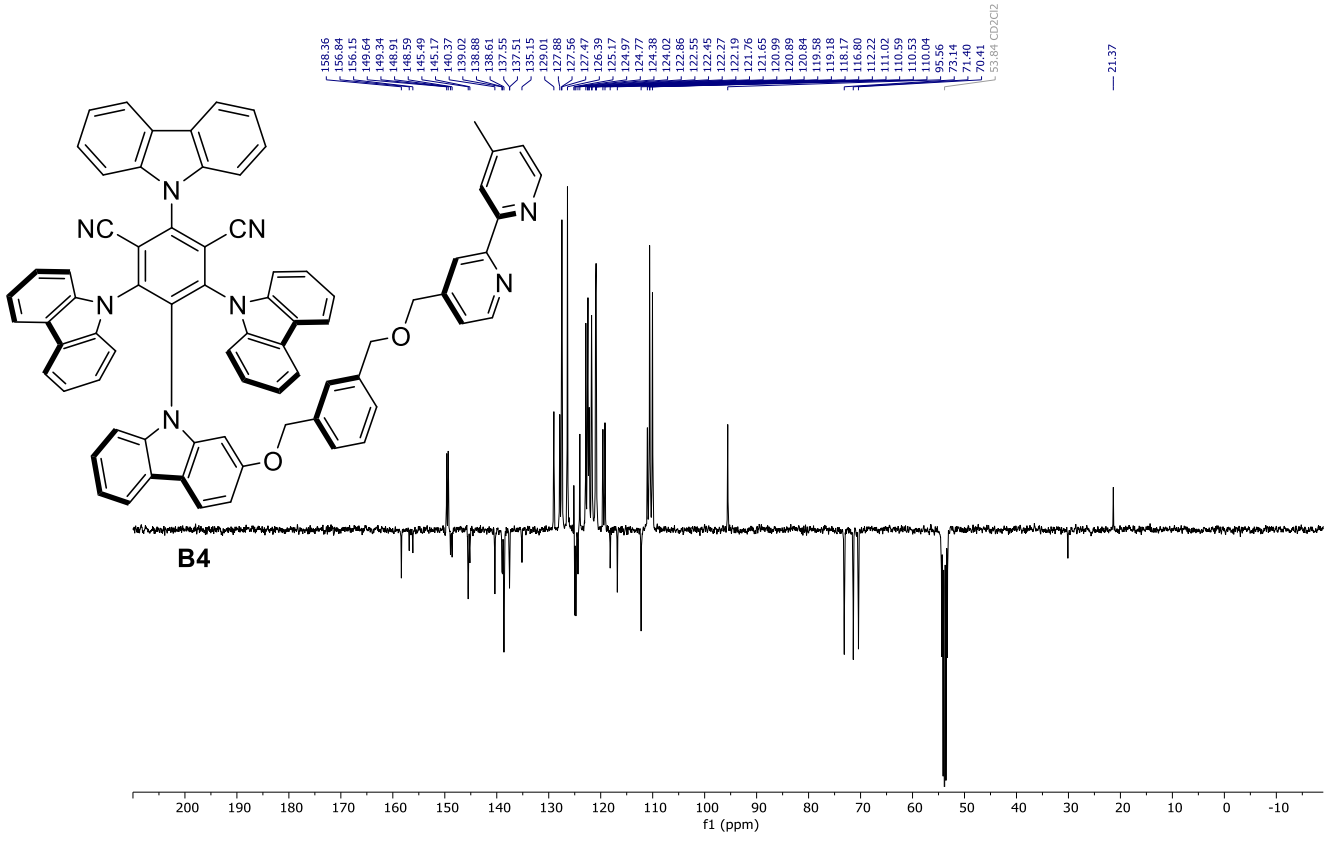

B2
f1 (ppm)

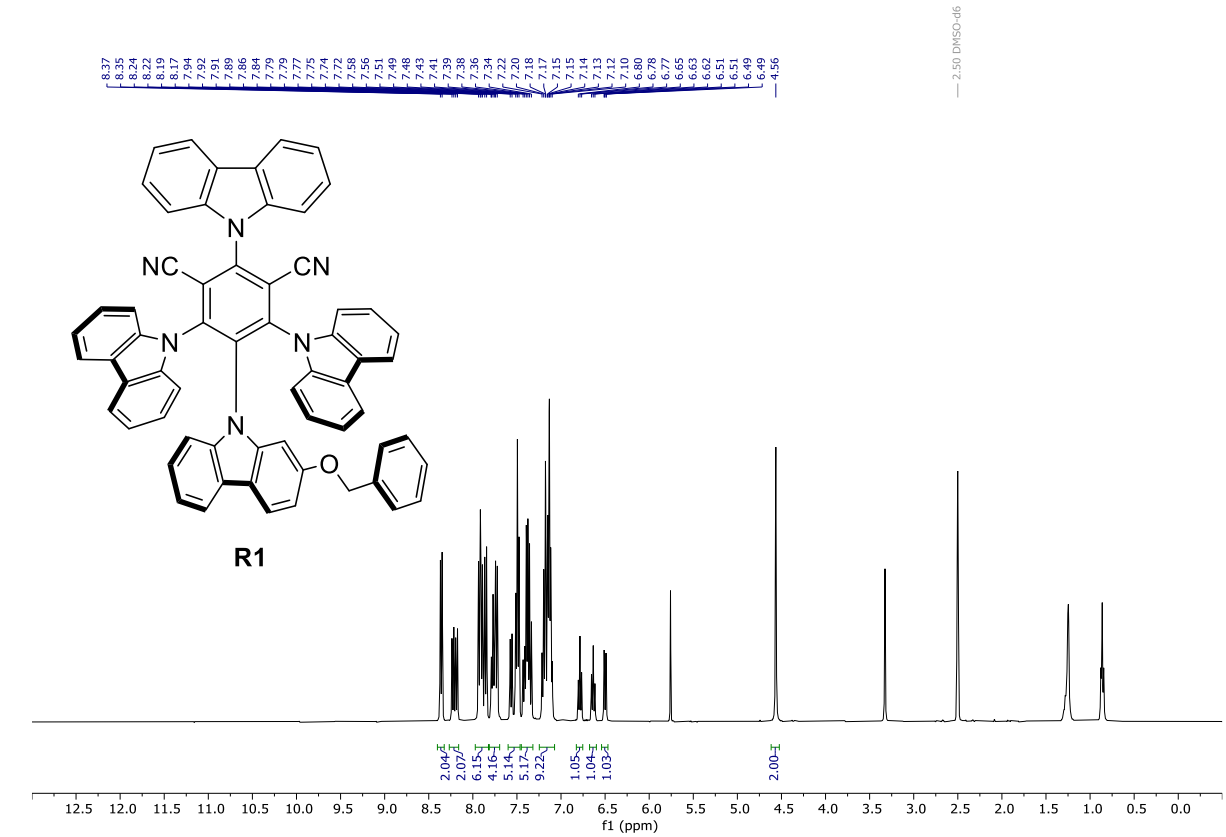

B2
f1 (ppm)

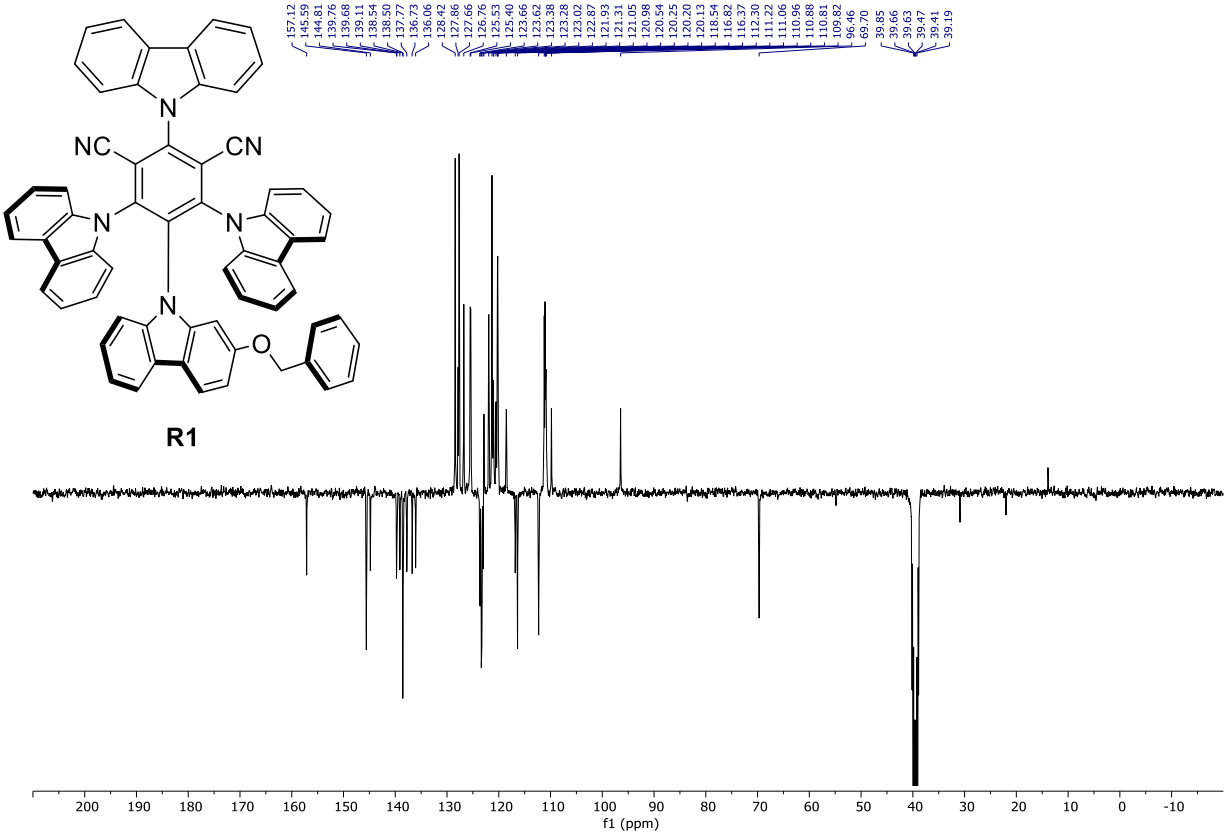

B3
f1 (ppm)

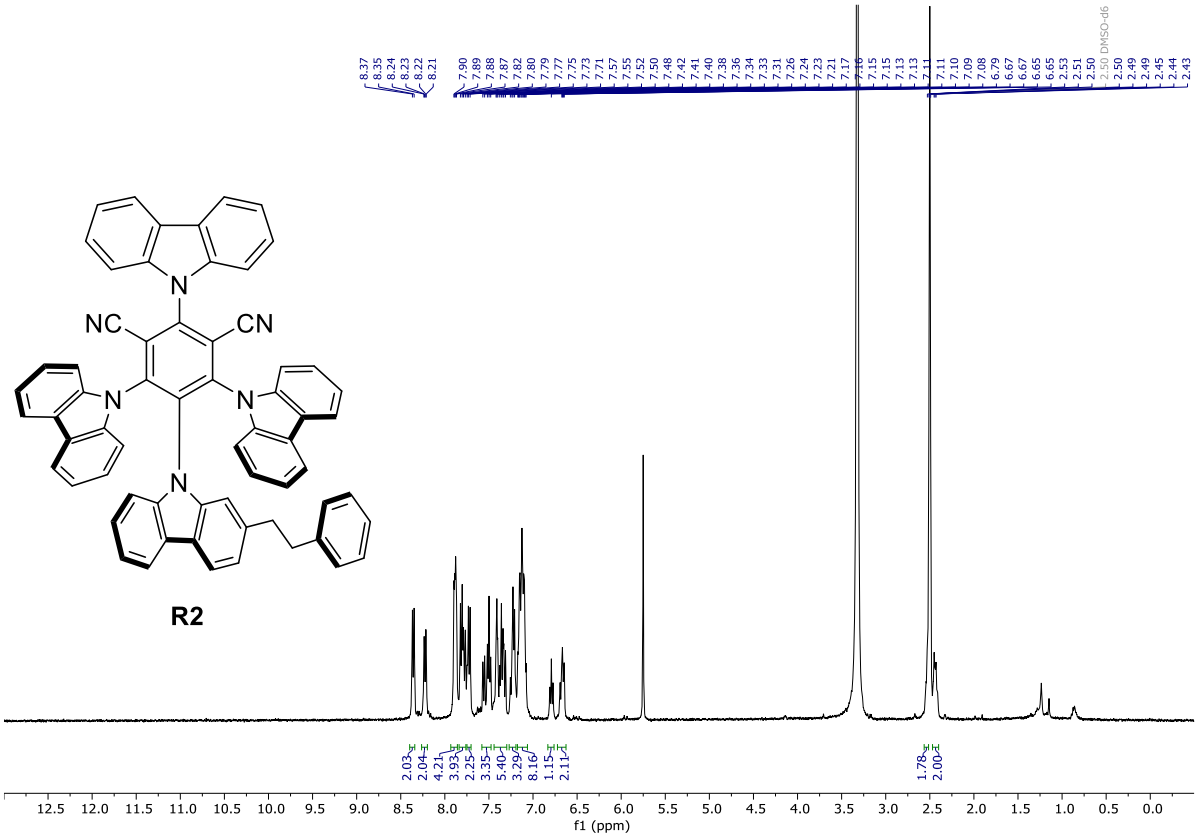

B3
f1 (ppm)

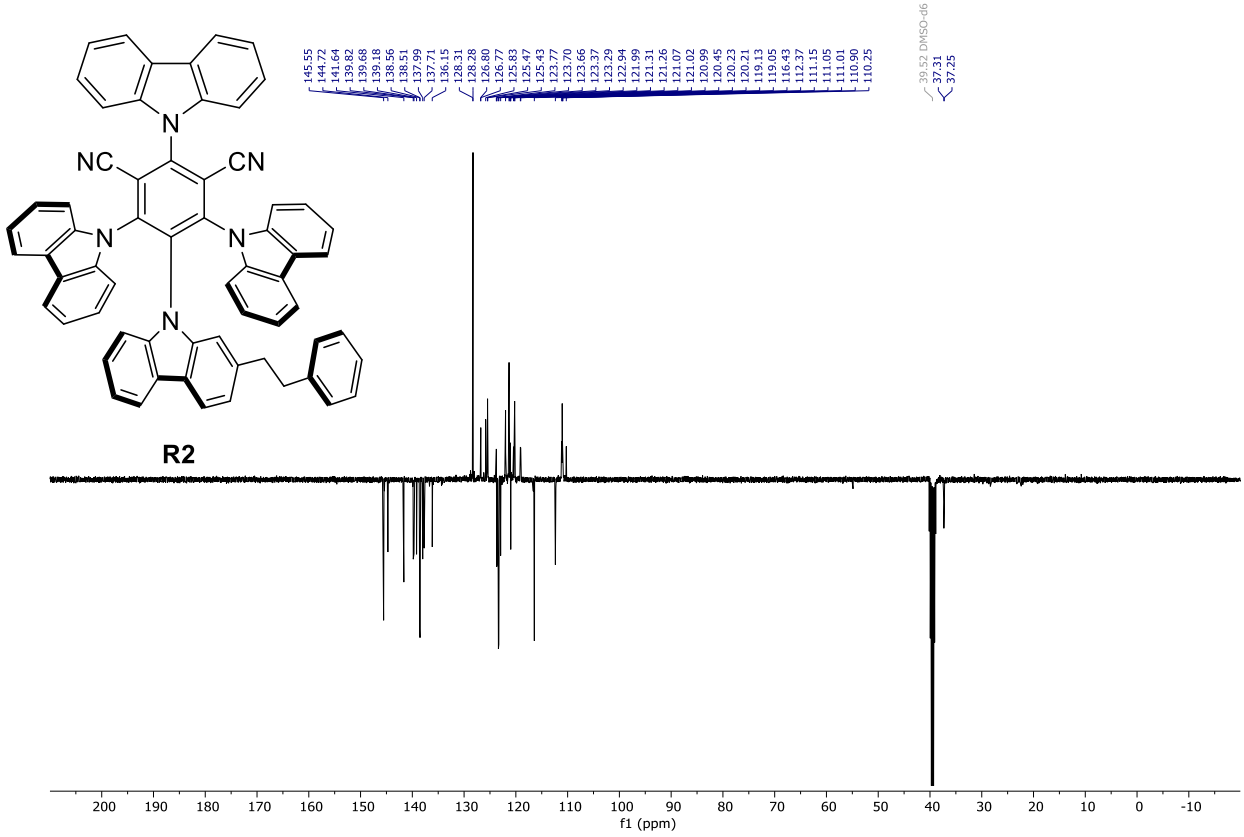

B4
f1 (ppm)

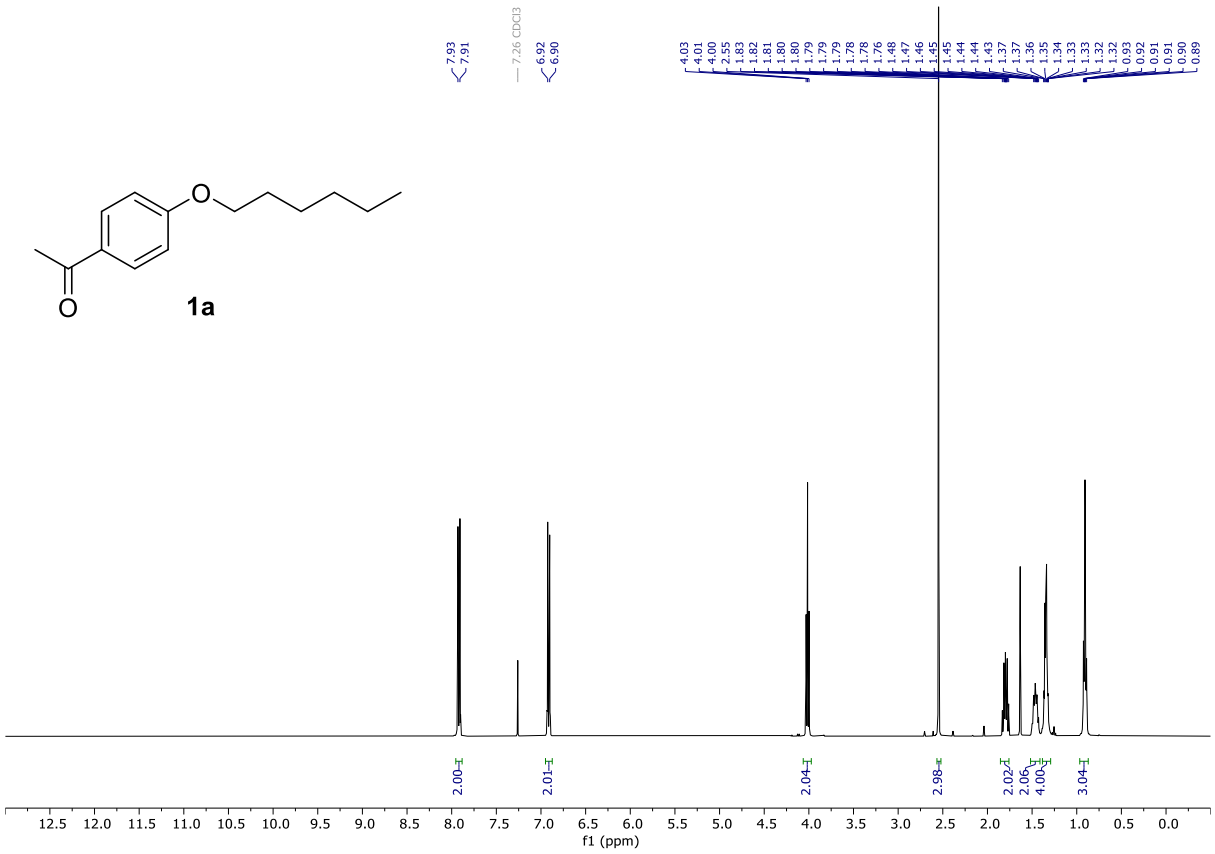

B4
f1 (ppm)


2.50 DMSO-d6
NC
CN
N
O
R1
f1 (ppm)


NC
CN
N
O
R1
f1 (ppm)


NC
CN
N
R2
f1 (ppm)


NC
CN
N
R2
f1 (ppm)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7.91
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6.92
6.90
4.03
4.01
4.00
2.55
1.83
1.82
1.81
1.80
1.80
1.79
1.79
1.79
1.78
1.78
1.76
1.48
1.47
1.46
1.45
1.45
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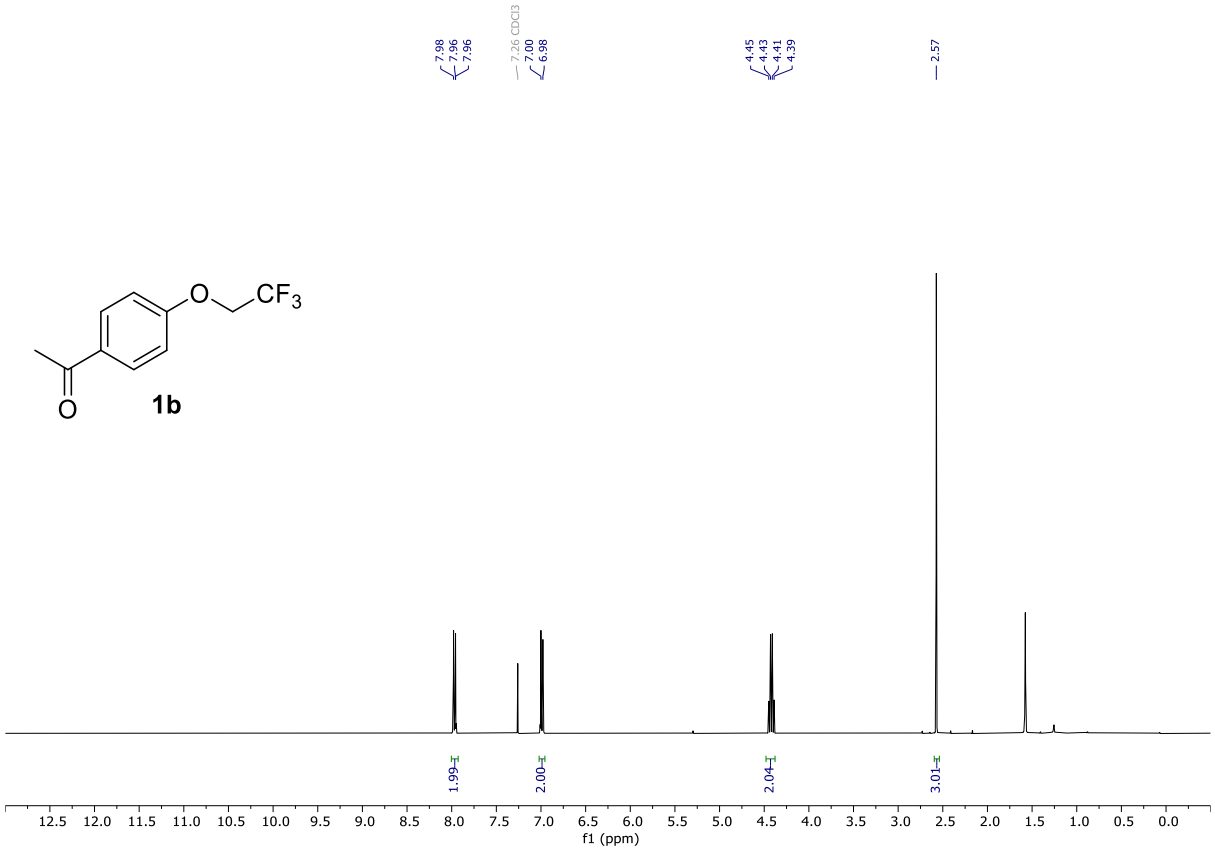
1.43
1.37
1.37
1.36
1.35
1.34
1.33
1.33
1.32
1.32
0.93
0.92
0.91
0.91
0.90
0.89
O
O
1a
2.00
2.01
2.04
2.98
2.02
2.06
4.00
3.04
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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7.96
7.96
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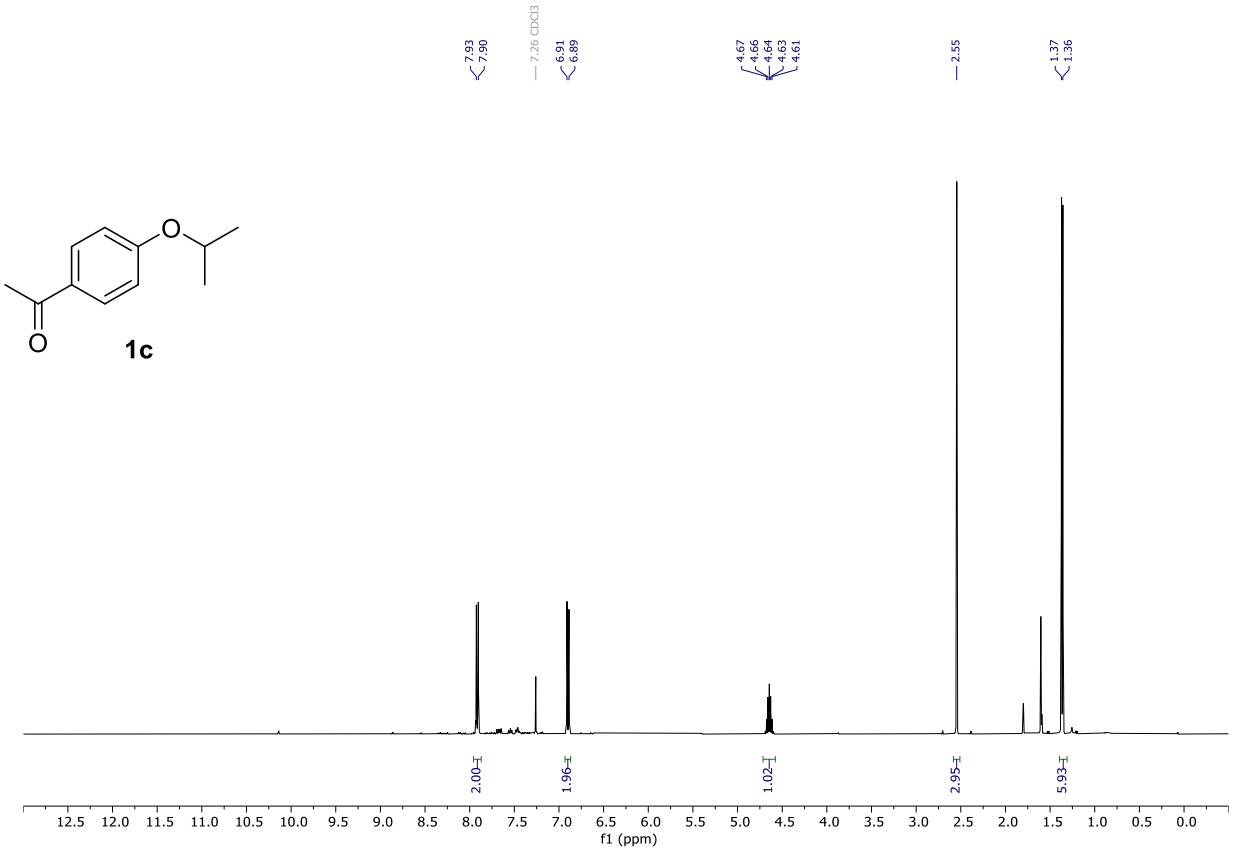
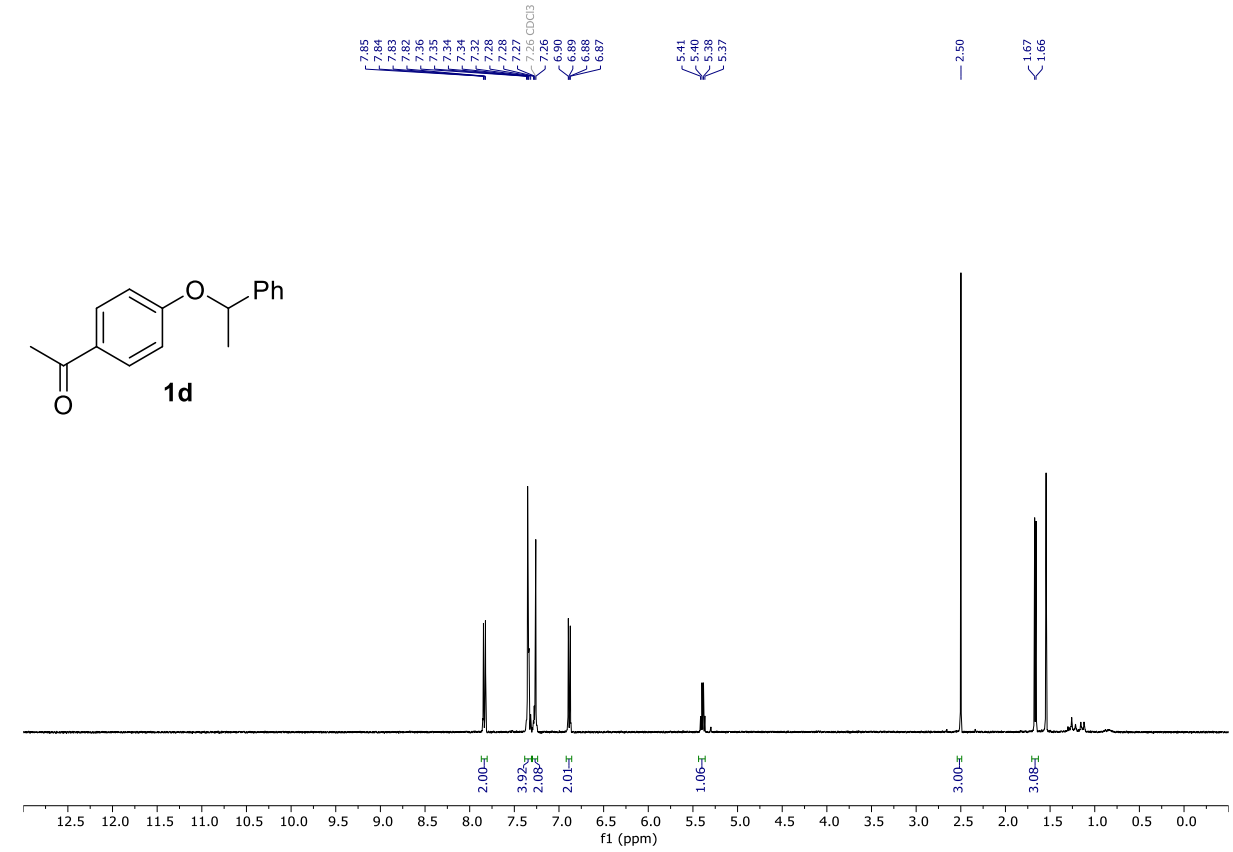
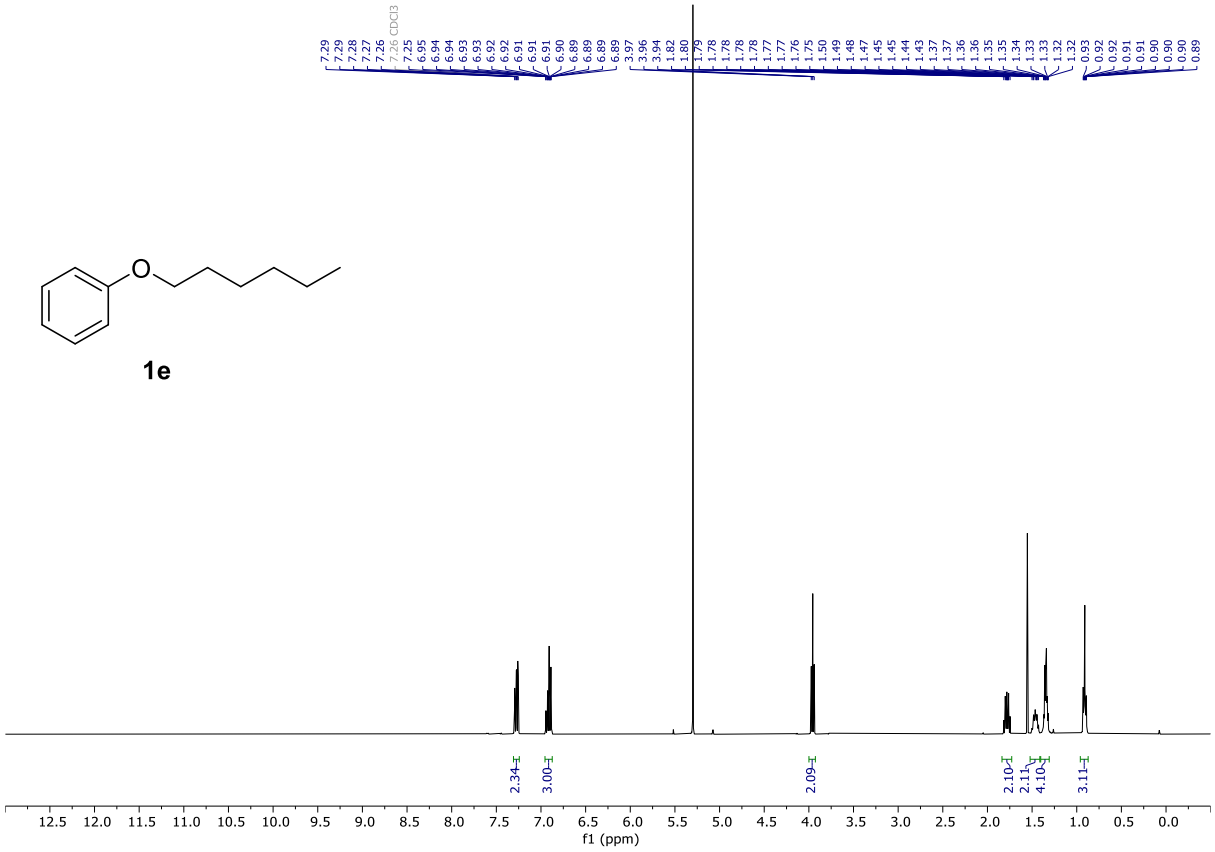
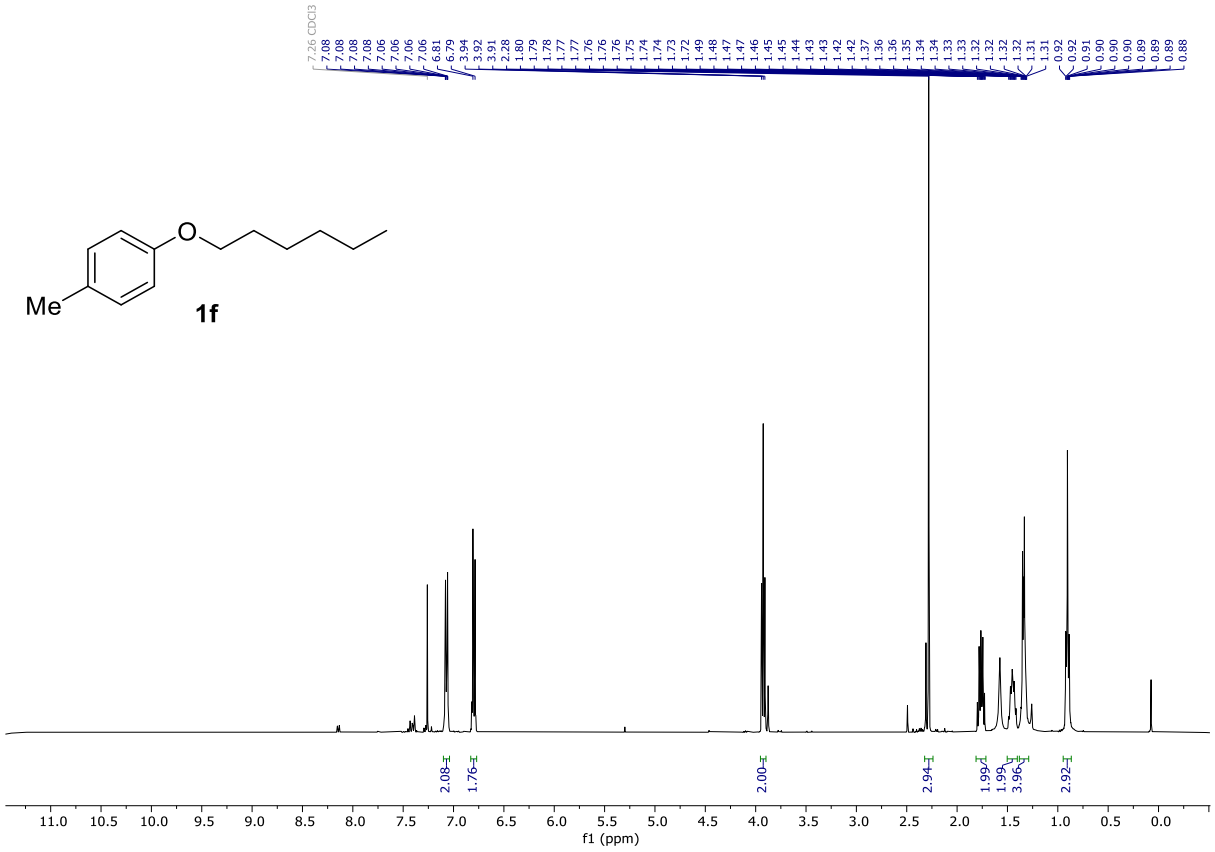
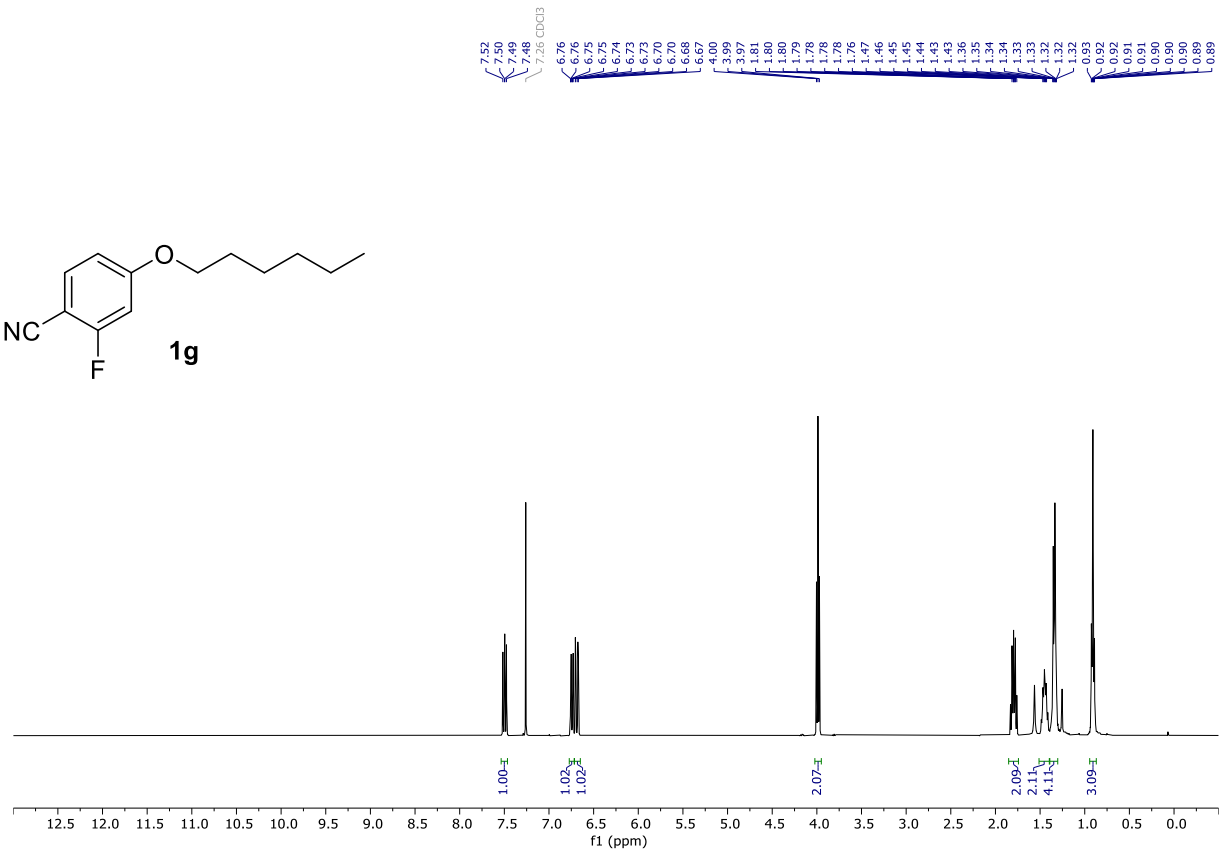
7.00
6.98
4.45
4.43
4.41
4.39
2.57
O
CF3
O
1b
1.99
2.00
2.04
3.01
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

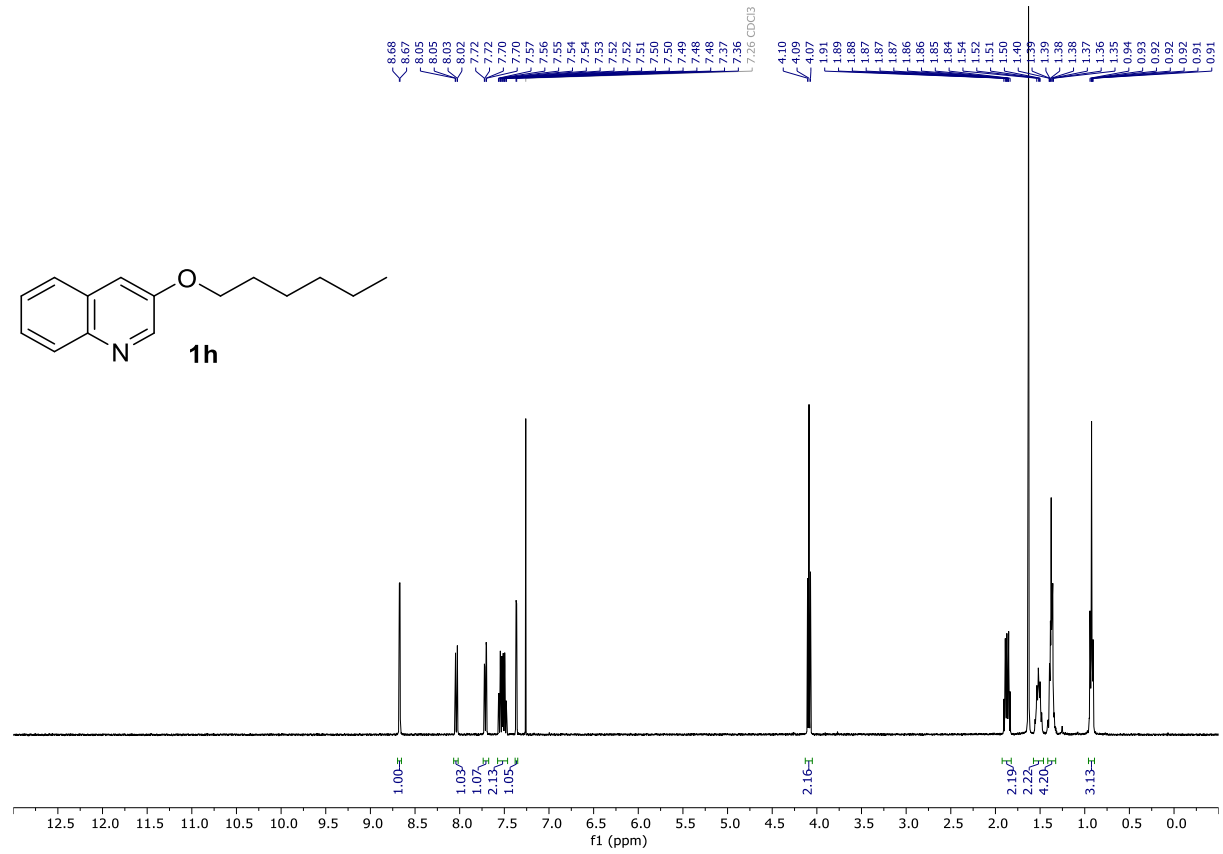

7.93
7.90
7.26 CDCl3
6.91
6.89
4.67
4.66
4.64
4.63
4.61
2.55
1.37
1.36
O
O
1c
2.00
1.96
1.02
2.95
5.93
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


7.85
7.84
7.83
7.82
7.36
7.35
7.34
7.34
7.32
7.28
7.28
7.27
7.26 CDCl3
7.26
6.90
6.89
6.88
6.87
5.41
5.40
5.38
5.37
2.50
1.67
1.66
O
O
Ph
1d
2.00
3.92
2.08
2.01
1.06
3.00
3.08
12.5 12.0 11.5 11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


1e
f1 (ppm)


Me
1f
f1 (ppm)


NC
F
O
1g
f1 (ppm)


N
O
1h
f1 (ppm)

References

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