Supplementary information

Synthesis of New Fluorophore: Wavelength-Tunable Bisbenzo[*f*]isoindolylidenes

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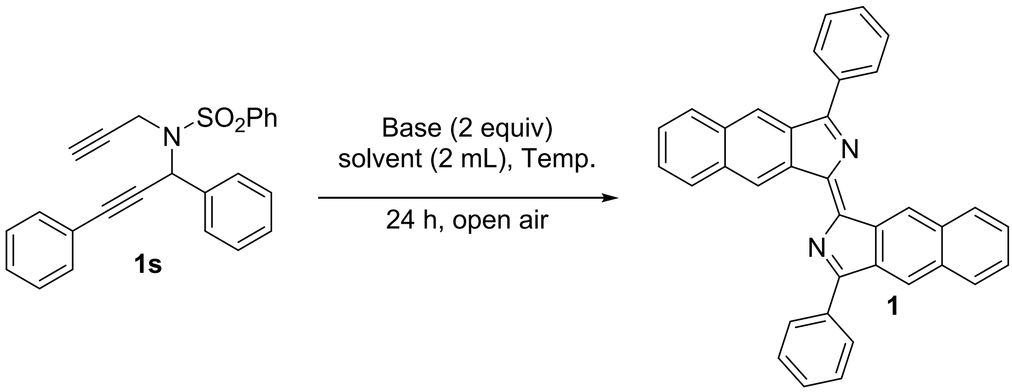
Materials and methods

Commercially obtained reagents were used as received. Solvents were dried by Innovative Technology Solvent Purification System. Liquids and solutions were transferred via syringe. All reactions were monitored by thin-layer chromatography. GC-MS data were recorded on Thermo ISQ QD. ^{1}H and ^{13}C NMR spectra were recorded on Bruker-BioSpin AVANCE III HD and JEOL ECZ600S. Data for ^{1}H NMR spectra are reported relative to TMS as an internal standard (0.00 ppm) and are reported as follows: chemical shift (ppm), multiplicity, coupling constant (Hz), and integration. Data for ^{13}C NMR spectra are reported relative to chloroform as an internal standard (77.16 ppm) and are reported in terms of chemical shift (ppm). HRMS data were recorded on Thermo Fisher Scientific LTQ FTICR-MS and Thermo Scientific Q Exactive HF Orbitrap-FTMS. UV-vis absorption spectra of solution were recorded on Shimadzu UV-2450 UV-Vis spectrophotometer. Photoluminescence spectra of solutions sample were measured on the Edinburgh Instruments FLS5 fluorescence spectrofluorometer. The absolute fluorescence quantum yield was measured on the Edinburgh Instruments FLS1000 three-monochromator spectrophotometer.

Reaction conditions optimizations

General procedure for Table S1: In a flame-dried Schlenk tube, dipropargyl sulfonylamide **1** (0.2 mmol, 1 equiv) and Base (0.4 mmol, 2 equiv) were dissolved in solvent (1 mL) under open air conditions. The reaction mixture was stirred at 80 °C for 24 h. Upon completion of the reaction as monitored by TLC, the reaction was quenched with MeOH (5 mL). The suspension was filtered and the filter residue was washed with 5 mL water and 5 mL MeOH to get the crude product. The crude material was purified by silica gel flash chromatography using petroleum ether and dichloromethane to yield the corresponding product.

Table S1. Optimization of the reaction conditions[a]



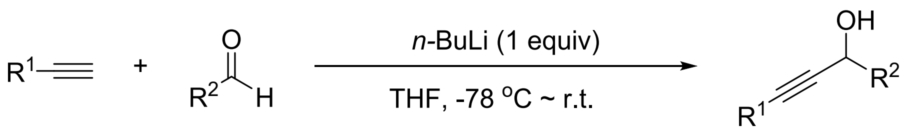
Entry	Solvent	Base	Temperature	Yield
1	*i*-PrOH	Cs_2CO_3	80 °C	30%
2	DMSO	Cs_2CO_3	80 °C	trace
3	Xylene	Cs_2CO_3	80 °C	30%
4	*n*-Heptane	Cs_2CO_3	80 °C	19%
5	1.4-Dioxane	Cs_2CO_3	80 °C	26%
6	DMAc	Cs_2CO_3	80 °C	trace
7	Acetophenone	Cs_2CO_3	80 °C	trace
8	*t*-BuOH	Cs_2CO_3	80 °C	28%
9	*i*-PrOH	K_2CO_3	80 °C	48%
10	*i*-PrOH	KOH	80 °C	trace
11	*i*-PrOH	DMAP	80 °C	28%
12	*i*-PrOH	Na_2CO_3	80 °C	9%
13	*i*-PrOH	Et_3N	80 °C	12%
14	*i*-PrOH	K_2CO_3	rt	trace
15	*i*-PrOH	K_2CO_3	60 °C	35%
16[b]	*i*-PrOH	K_2CO_3	80 °C	40%
17[c]	*i*-PrOH	K_2CO_3	80 °C	trace

[a] Reaction conditions: **1s** (0.2 mmol, 1 equiv), base (0.4 mmol, 2 equiv), solvent (1 mL). [b]Under 1 atm O_2 atmosphere. [c] Under N_2 atmosphere.

Synthesis of dipropargyl benzene sulfonamide

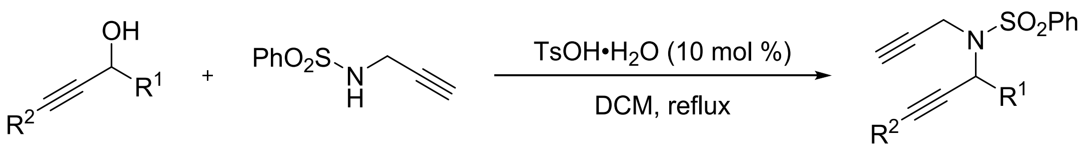
All alkynes and aldehyde were purchased from Adamas-beta, Energy Chemical and Bidepharmatech.

Synthesis of propargyl alcohol.



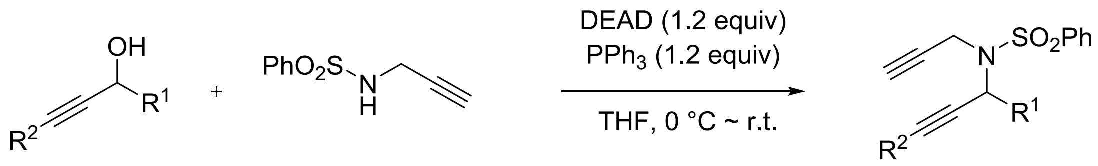
A 50 mL round bottomed flask was charged with terminal alkyne (5 mmol, 1 equiv) and 10 mL of THF. The solution was cooled to -78 °C and *n*-BuLi (2.5 M in THF, 2 mL, 5 mmol, 1 equiv) was added dropwise. The resulting solution was stirred for 20 minutes at room temperature and then cooled to -78 °C again. Aldehyde (5 mmol, 1 equiv) in THF (5 mL) was added dropwise. The reaction mixture was then allowed to warm to room temperature and was monitored by TLC for completion. On completion the reaction was quenched with saturated aqueous NH_4Cl (4 mL). The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine (30 mL), dried over $MgSO_4$ and filtered. Then the solution was concentrated under reduced pressure to afford the crude propargyl alcohol.

Synthesis of **1s**, **2s**, **3s**, **5s**, **8s**, **9s**, **11s**, **12s**, **13s**, **16s**, **18s**.



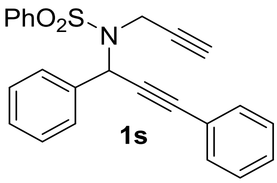
The solution of the resulting crude propargyl alcohol and *N*-propargylbenzenesulfonamide (1.2 equiv) in DCM was added into a round bottom flask under nitrogen atmosphere and then $TsOH{\cdot}H_2O$ (10 mol%) was added at room temperature. The reaction mixture was heated to reflux overnight and was monitored by TLC for completion. On completion of the reaction, saturated aqueous $NaHCO_3$ was added to quench the reaction. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, dried over $MgSO_4$ and filtered. Then the solution was concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate to yield the corresponding dipropargyl benzenesulfonamide.

Synthesis of 4s, 6s, 7s, 10s, 14s, 15s, 17s.



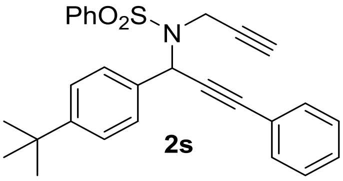
A solution of the resulting crude propargyl alcohol, *N*-propargylbenzenesulfonamide (1.2 equiv), and PPh_3 (1.2 equiv) in THF was taken in a round bottom flask under nitrogen atmosphere and then DEAD (1.2 equiv) was added dropwise at 0 °C. The reaction mixture was stirred at room temperature and was monitored by TLC for completion. On completion the reaction was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with DCM and the combined organic layers were washed with brine, dried over $MgSO_4$ and filtered. Then the solution was concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate to yield the corresponding dipropargyl benzene sulfonamide.

Characterization data for dipropargyl benzene sulfonamide



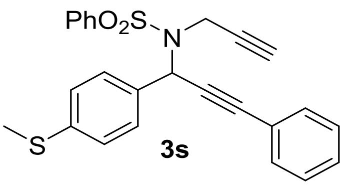
1s

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 2H), 7.70 – 7.68 (m, 2H), 7.58 – 7.54 (m, 1H), 7.51 – 7.48 (m, 2H), 7.41 – 7.37 (m, 2H), 7.37 – 7.33 (m, 1H), 7.33 – 7.29 (m, 1H), 7.28 – 7.25 (m, 2H), 7.20 – 7.17 (m, 2H), 6.32 (s, 1H), 4.13 (dd, *J* = 18.4, 2.6 Hz, 1H), 3.75 (dd, *J* = 18.4, 2.5 Hz, 1H), 1.89 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.33, 135.66, 132.97, 131.59, 128.82, 128.75, 128.69, 128.37, 128.31, 128.29, 122.18, 88.78, 83.26, 78.21, 72.79, 53.80, 33.84. HRMS *m*/*z* (ESI) calcd for [$C_{24}H_{19}NO_2SNa$] ([M+Na]$^+$): 408.1029, found: 408.1030.



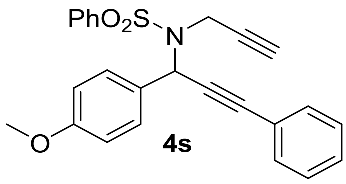
2s

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H), 7.59 (d, *J* = 8.1 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 8.0 Hz, 2H), 7.40 (d, *J* = 8.5 Hz, 2H), 7.32 – 7.28 (m, 1H), 7.27 – 7.25 (m, 2H), 7.20 – 7.16 (m, 2H), 6.28 (s, 1H), 4.15 (dd, *J* = 18.7, 2.8 Hz, 1H), 3.73 (dd, *J* = 18.5, 2.5 Hz, 1H), 1.89 (t, *J* = 2.5 Hz, 1H), 1.32 (s, 9H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 151.91, 139.47, 132.92, 132.61, 131.57, 128.78, 128.67, 128.32, 128.30, 128.08, 125.65, 122.33, 88.46, 83.66, 78.32, 72.73, 53.48, 34.72, 33.76, 31.43. HRMS *m*/*z* (ESI) calcd for [$C_{28}H_{27}NO_2SNa$] ([M+Na]$^+$): 464.1655, found: 464.1656.



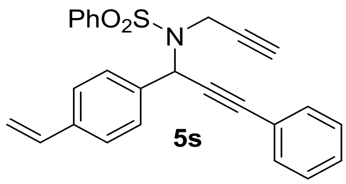
3s

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.4 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 7.31 (t, *J* = 6.8 Hz, 1H), 7.27 – 7.24 (m, 4H), 7.17 (d, *J* = 7.0 Hz, 2H), 6.26 (s, 1H), 4.12 (dd, *J* = 18.4, 2.5 Hz, 1H), 3.74 (dd, *J* = 18.4, 2.5 Hz, 1H), 2.49 (s, 3H), 1.91 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.48, 139.24, 133.01, 132.29, 131.59, 128.84, 128.83, 128.33, 128.28, 126.30, 122.10, 88.80, 83.13, 78.17, 72.92, 53.43, 33.78, 15.66. HRMS *m/z* (ESI) calcd for $[C_{25}H_{21}NO_2S_2Na]$ ($[M+Na]^+$): 454.0906, found: 454.0907.



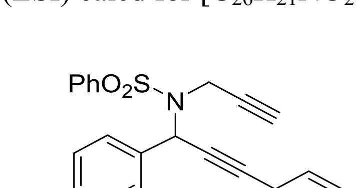
4s

^1H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.02 (m, 2H), 7.63 – 7.59 (m, 2H), 7.58 – 7.54 (m, 1H), 7.52 – 7.48 (m, 2H), 7.33 – 7.30 (m, 1H), 7.29 – 7.25 (m, 2H), 7.21 – 7.17 (m, 2H), 6.95 – 6.89 (m, 2H) 6.28 (s, 1H), 4.14 (dd, *J* = 18.4, 2.6 Hz, 1H), 3.82 (s, 3H), 3.76 (dd, *J* = 18.4, 2.5 Hz, 1H), 1.93 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.98, 139.39, 132.94, 131.59, 129.72, 128.81, 128.73, 128.27, 127.63, 122.24, 114.00, 88.56, 83.62, 78.36, 72.74, 55.45, 53.32, 33.61. HRMS *m/z* (ESI) calcd for $[C_{25}H_{21}NO_3SNa]$ ($[M+Na]^+$): 438.1134, found: 438.1135.



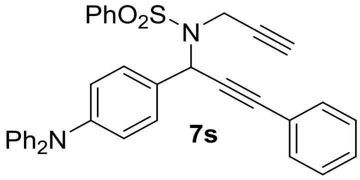
5s

^1H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.03 (m, 2H), 7.66 (d, *J* = 8.1 Hz, 2H), 7.59 – 7.54 (m, 1H), 7.52 – 7.48 (m, 2H), 7.43 (d, *J* = 8.3 Hz, 2H), 7.34 – 7.30 (m, 1H), 7.29 – 7.26 (m, 2H), 7.23 – 7.18 (m, 2H), 6.73 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.31 (s, 1H), 5.79 (dd, *J* = 17.6, 0.8 Hz, 1H), 5.29 (d, *J* = 11.6 Hz, 1H), 4.15 (dd, *J* = 18.4, 2.6 Hz, 1H), 3.78 (dd, *J* = 18.4, 2.6 Hz, 1H), 1.92 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.34, 138.08, 136.31, 135.14, 133.00, 131.61, 128.86, 128.80, 128.59, 128.35, 128.29, 126.51, 122.17, 114.80, 88.84, 83.26, 78.23, 72.96, 53.64, 33.88. HRMS *m/z* (ESI) calcd for $[C_{26}H_{21}NO_2SNa]$ ($[M+Na]^+$): 434.1185, found: 434.1184.



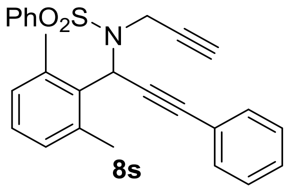
6s

^1H NMR (600 MHz, $CDCl_3$) δ 8.07 (d, *J* = 7.4 Hz, 2H), 7.59 – 7.45 (m, 5H), 7.34 – 7.23 (m, 3H), 7.17 (d, *J* = 7.0 Hz, 2H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.25 (s, 1H), 4.15 (dd, *J* = 18.5, 2.5 Hz, 1H), 3.73 (dd, *J* = 18.5, 2.4 Hz, 1H), 2.96 (s, 6H), 1.94 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 150.77, 139.53, 132.91, 131.58, 129.41, 128.78, 128.61, 128.38, 128.33, 122.64, 122.50, 88.16, 84.20, 78.58, 72.67, 53.37, 40.63, 33.38. HRMS *m/z* (ESI) calcd for $[C_{26}H_{24}N_2O_2SNa]$ ($[M+Na]^+$): 451.1451, found: 451.1450.



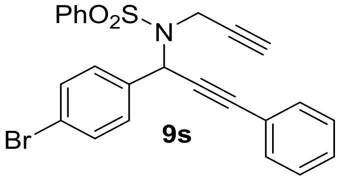
7s

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 – 8.04 (m, 2H), 7.59 – 7.54 (m, 3H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.32 – 7.30 (m, 1H), 7.28 – 7.25 (m, 6H), 7.19 (d, *J* = 7.9 Hz, 2H), 7.12 – 7.08 (m, 6H), 7.05 (t, *J* = 7.7 Hz, 2H), 6.29 (s, 1H), 4.18 (d, *J* = 18.4 Hz, 1H), 3.87 (d, *J* = 18.4 Hz, 1H), 1.97 (s, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 148.38, 147.58, 139.45, 132.97, 131.60, 129.45, 129.36, 129.02, 128.86, 128.76, 128.34, 128.28, 124.70, 123.34, 123.19, 122.22, 88.61, 83.58, 78.52, 72.73, 53.49, 33.77. HRMS *m*/*z* (ESI) calcd for [$C_{36}H_{28}N_2O_2SNa$] ([M+Na]$^+$): 575.1764, found: 575.1760.



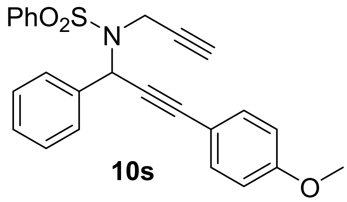
8s

^{1}H NMR (600 MHz, $CDCl_3$) δ 7.78 – 7.73 (m, 2H), 7.45 – 7.41 (m, 1H), 7.30 – 7.27 (m, 3H), 7.26 – 7.22 (m, 4H), 7.07 (t, *J* = 7.6 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 2H), 6.39 (s, 1H), 4.26 – 4.16 (m, 2H), 2.50 (s, 6H), 2.16 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.99, 138.53, 132.52, 132.10, 131.52, 129.68, 128.61, 128.57, 128.32, 128.29, 128.21, 122.65, 87.67, 85.46, 79.20, 73.42, 50.02, 35.89, 21.05. HRMS *m*/*z* (ESI) calcd for [$C_{26}H_{23}NO_2SNa$] ([M+Na]$^+$): 436.1342, found: 436.1342.



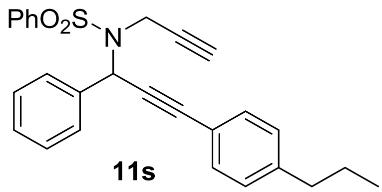
9s

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 – 8.00 (m, 2H), 7.59 – 7.54 (m, 3H), 7.53 – 7.48 (m, 4H), 7.34 – 7.30 (m, 1H), 7.29 – 7.25 (m, 2H), 7.21 – 7.16 (m, 2H), 6.26 (s, 1H), 4.11 (dd, *J* = 18.4, 2.5 Hz, 1H), 3.80 (dd, *J* = 18.4, 2.5 Hz, 1H), 1.93 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.05, 134.99, 133.16, 131.80, 131.65, 130.12, 129.01, 128.97, 128.41, 128.23, 122.95, 121.86, 89.27, 82.53, 78.01, 73.18, 53.44, 34.03. HRMS *m*/*z* (ESI) calcd for [$C_{24}H_{18}NO_2SBrNa$] ([M+Na]$^+$): 486.0134, found: 486.0134.



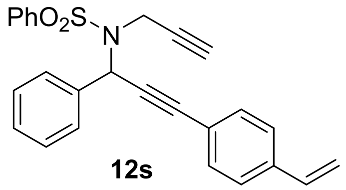
10s

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.06 – 8.03 (m, 2H), 7.70 – 7.66 (m, 2H), 7.58 – 7.54 (m, 1H), 7.51 – 7.47 (m, 2H), 7.40 – 7.36 (m, 2H), 7.36 – 7.32 (m, 1H), 7.12 (d, *J* = 8.9 Hz, 2H), 6.78 (d, *J* = 8.9 Hz, 2H), 6.29 (s, 1H), 4.11 (dd, *J* = 18.4, 2.6 Hz, 1H), 3.80 (s, 3H), 3.75 (dd, *J* = 18.4, 2.5 Hz, 1H), 1.88 (t, *J* = 2.5 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.92, 139.36, 135.88, 133.06, 132.91, 128.79, 128.67, 128.63, 128.38, 128.30, 114.27, 113.91, 88.79, 81.80, 78.30, 72.66, 55.39, 53.94, 33.83. HRMS *m*/*z* (ESI) calcd for [$C_{25}H_{21}NO_3SNa$] ([M+Na]$^+$): 438.1134, found: 438.1134.



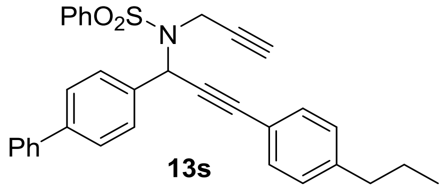
11s

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.02 (m, 2H), 7.72 – 7.68 (m, 2H), 7.58 – 7.54 (m, 1H), 7.52 – 7.48 (m, 2H), 7.41 – 7.37 (m, 2H), 7.36 – 7.33 (m, 1H), 7.11 (d, *J* = 8.3 Hz, 2H), 7.08 (d, *J* = 8.4 Hz, 2H), 6.31 (s, 1H), 4.12 (dd, *J* = 18.4, 2.6 Hz, 1H), 3.76 (dd, *J* = 18.4, 2.6 Hz, 1H), 2.61 – 2.52 (m, 2H), 1.89 (t, *J* = 2.5 Hz, 1H), 1.63 – 1.60 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.73, 139.34, 135.84, 132.95, 131.51, 128.84, 128.70, 128.65, 128.48, 128.39, 128.27, 119.34, 89.05, 82.52, 78.26, 72.75, 53.91, 38.02, 33.85, 24.42, 13.85. HRMS *m*/*z* (ESI) calcd for [$C_{27}H_{25}NO_2SNa$] ([M+Na]$^+$): 450.1498, found: 450.1496.



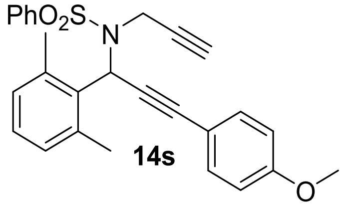
12s

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06 (d, *J* = 7.5 Hz, 2H), 7.69 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.3 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 2H), 7.42 – 7.35 (m, 3H), 7.31 (d, *J* = 8.2 Hz, 2H), 7.15 (d, *J* = 8.2 Hz, 2H), 6.68 (dd, *J* = 17.6, 10.9 Hz, 1H), 6.33 (s, 1H), 5.76 (d, *J* = 17.6 Hz, 1H), 5.30 (d, *J* = 10.9 Hz, 1H), 4.14 (dd, *J* = 18.5, 2.4 Hz, 1H), 3.76 (dd, *J* = 18.5, 2.4 Hz, 1H), 1.90 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.28, 137.88, 136.09, 135.60, 132.93, 131.73, 128.77, 128.71, 128.64, 128.31, 128.24, 126.05, 121.33, 115.16, 88.74, 83.84, 78.17, 72.76, 53.80, 33.79. HRMS *m*/*z* (ESI) calcd for [$C_{26}H_{21}NO_2SNa$] ([M+Na]$^+$): 434.1185, found: 434.1185.



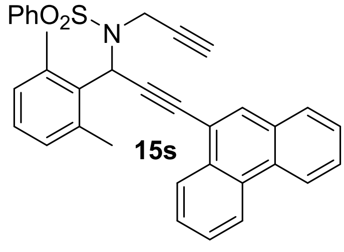
13s

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 – 8.08 (m, 2H), 7.81 (d, *J* = 8.5 Hz, 2H), 7.67 – 7.63 (m, 4H), 7.61 – 7.58 (m, 1H), 7.55 – 7.52 (m, 2H), 7.49 – 7.46 (m, 2H), 7.40 – 7.37 (m, 1H), 7.18 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 6.40 (s, 1H), 4.21 (dd, *J* = 18.4, 2.5 Hz, 1H), 3.86 (dd, *J* = 18.4, 2.5 Hz, 1H), 2.62 – 2.59 (m, 2H), 1.96 (t, *J* = 2.5 Hz, 1H), 1.68 – 1.64 (m, 2H), 0.97 (t, *J* = 7.3 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 143.82, 141.63, 140.58, 139.36, 134.93, 133.05, 131.59, 129.00, 128.91, 128.58, 128.33, 127.71, 127.40, 127.27, 119.37, 89.18, 82.57, 78.33, 73.00, 53.78, 38.07, 33.99, 24.49, 13.93. HRMS *m*/*z* (ESI) calcd for [$C_{33}H_{29}NO_2SNa$] ([M+Na]$^+$): 526.1811, found: 526.1811.



14s

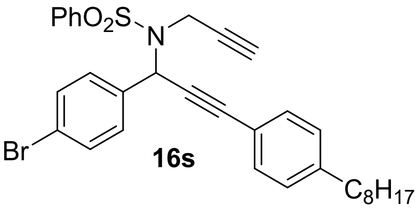
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.74 (dd, *J* = 8.5, 1.2 Hz, 2H), 7.45 – 7.40 (m, 1H), 7.31 – 7.26 (m, 2H), 7.21 – 7.16 (m, 2H), 7.06 (t, *J* = 7.5 Hz, 1H), 6.92 (d, *J* = 7.6 Hz, 2H), 6.81 – 6.77 (m, 2H), 6.37 (s, 1H), 4.22 (d, *J* = 2.4 Hz, 2H), 3.78 (s, 3H), 2.49 (s, 6H), 2.17 (t, *J* = 2.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 159.84, 140.07, 138.47, 133.04, 132.49, 132.37, 129.66, 128.54, 128.31, 128.18, 114.78, 113.93, 87.68, 83.94, 79.33, 73.34, 55.39, 50.15, 35.97, 21.02. HRMS (ESI) *m*/*z* calcd for [$C_{27}H_{25}NO_3SNa$] ([M+Na]$^+$): 466.1447, found: 466.1446.



15s

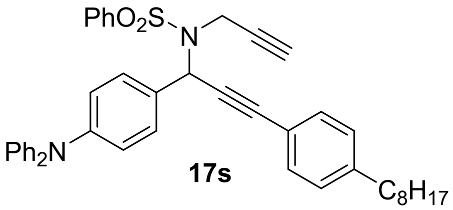
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.66 – 8.62 (m, 2H), 8.23 – 8.19 (m, 1H), 7.83 – 7.80 (m, 2H), 7.78 – 7.76 (m, 1H), 7.73 (s, 1H), 7.68 – 7.64 (m, 2H), 7.60 – 7.57 (m, 1H), 7.57 – 7.54 (m, 1H), 7.36 – 7.33 (m, 1H), 7.24 – 7.20 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 2H), 6.59 (s, 1H), 4.31 (t, *J* = 2.6 Hz, 2H), 2.59 (s, 6H), 2.26 (t, *J* =

2.4 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 139.96, 138.56, 132.57, 132.35, 132.17, 131.11, 131.07, 130.34, 130.05, 129.79, 128.73, 128.53, 128.37, 127.71, 127.18, 127.08, 122.79, 122.73, 119.12, 89.77, 86.28, 79.36, 73.75, 50.23, 35.98, 21.21. HRMS *m/z* (ESI) calcd for [$C_{34}H_{27}NO_2SNa$] ([M+Na]$^+$): 536.1655, found: 536.1656.



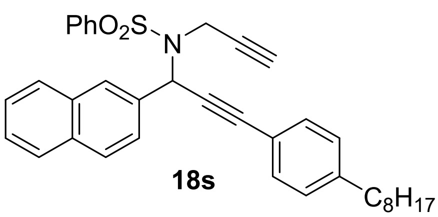
16s

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.01 (dd, *J* = 8.4, 1.2 Hz, 2H), 7.61 – 7.52 (m, 3H), 7.54 – 7.46 (m, 4H), 7.13 – 7.03 (m, 4H), 6.24 (s, 1H), 4.07 (dd, *J* = 18.3, 2.6 Hz, 1H), 3.84 – 3.74 (m, 1H), 2.62 – 2.52 (m, 2H), 1.90 (t, *J* = 2.5 Hz, 1H), 1.64 – 1.54 (s, 2H), 1.31 – 1.22 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.25, 139.06, 135.10, 133.07, 131.72, 131.52, 130.10, 128.92, 128.47, 128.19, 122.86, 118.94, 89.47, 81.77, 78.01, 73.04, 53.50, 35.98, 33.98, 31.95, 31.32, 29.79, 29.51, 29.33, 22.75, 14.20. HRMS *m/z* (ESI) calcd for [$C_{32}H_{34}NO_2SBrNa$] ([M+Na]$^+$): 598.1386, found: 598.1385.



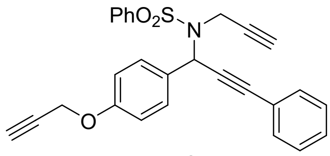
17s

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.08 – 8.04 (m, 2H), 7.59 – 7.54 (m, 3H), 7.52 – 7.49 (m, 2H), 7.28 – 7.25 (m, 4H), 7.12 – 7.07 (m, 10H), 7.05 – 7.03 (m, 2H), 6.28 (s, 1H), 4.16 (dd, *J* = 18.4, 2.4 Hz, 1H), 3.87 (dd, *J* = 18.4, 2.5 Hz, 1H), 2.60 – 2.57 (m, 2H), 1.96 (t, *J* = 2.5 Hz, 1H), 1.61 – 1.57 (m, 2H), 1.31 – 1.26 (m, 10H), 0.89 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.22, 147.52, 143.88, 139.40, 132.81, 131.41, 129.32, 129.27, 129.16, 128.74, 128.33, 128.17, 124.56, 123.18, 123.14, 119.24, 88.75, 82.72, 78.47, 72.52, 53.48, 35.90, 33.66, 31.88, 31.24, 29.44, 29.25, 22.68, 14.12. HRMS *m/z* (ESI) calcd for [$C_{44}H_{44}N_2O_2SNa$] ([M+Na]$^+$): 687.3016, found: 687.3014.



18s

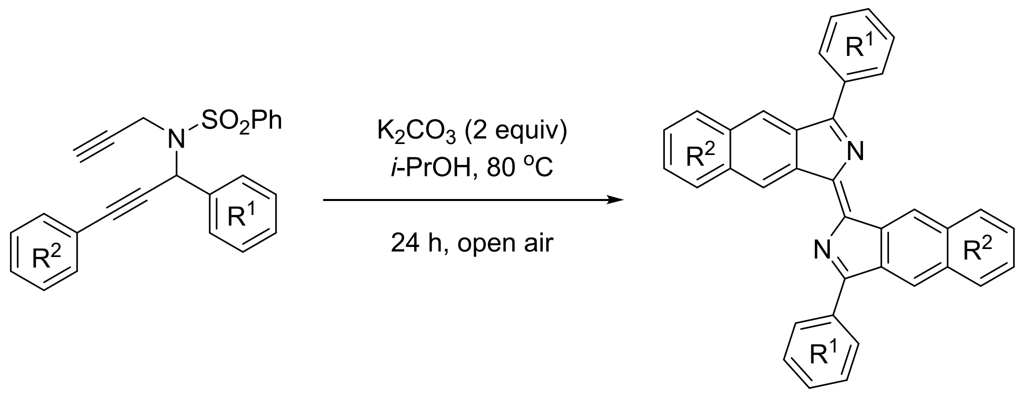
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.10 (d, *J* = 7.6 Hz, 2H), 7.90 – 7.84 (m, 3H), 7.77 (d, *J* = 8.5 Hz, 1H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.54 – 7.49 (m, 4H), 7.17 (d, *J* = 7.9 Hz, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.48 (s, 1H), 4.16 (d, *J* = 20.3 Hz, 1H), 3.78 (d, *J* = 18.5 Hz, 1H), 2.61 (t, *J* = 7.8 Hz, 2H), 1.87 (s, 1H), 1.65 – 1.56 (m, 2H), 1.35 – 1.24 (m, 10H), 0.89 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 144.10, 139.33, 133.41, 133.25, 133.06, 133.01, 131.59, 128.86, 128.67, 128.49, 128.42, 128.36, 127.80, 127.69, 126.69, 126.47, 125.94, 119.33, 89.31, 82.49, 78.26, 72.89, 54.13, 36.02, 33.88, 31.99, 31.38, 29.56, 29.37, 22.79, 14.25. HRMS *m*/*z* (ESI) calcd for [$C_{36}H_{37}NO_2SNa$] ([M+Na]$^+$): 570.2437, found: 570.2439.



24s

^{1}H NMR (600 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.4 Hz, 2H), 7.62 (d, *J* = 8.7 Hz, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.7 Hz, 2H), 7.30 (t, *J* = 7.3 Hz, 1H), 7.26 (t, *J* = 7.3 Hz, 2H), 7.19 (d, *J* = 7.0 Hz, 2H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.27 (s, 1H), 4.69 (d, *J* = 2.3 Hz, 2H), 4.16 – 4.10 (m, 1H), 3.77 (dd, *J* = 18.4, 2.4 Hz, 1H), 2.54 (t, *J* = 2.3 Hz, 1H), 1.93 (t, *J* = 2.1 Hz, 1H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 157.93, 139.32, 133.05, 131.62, 129.76, 128.90, 128.84, 128.66, 128.39, 128.27, 122.15, 115.01, 88.73, 83.46, 78.51, 78.34, 75.98, 72.93, 55.97, 53.33, 33.73. HRMS *m*/*z* (ESI) calcd for [$C_{27}H_{21}NO_3SNa$] ([M+Na]$^+$):462.1134, found:462.1127.

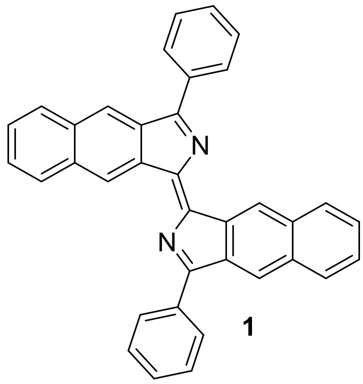
Synthesis of the new fluorophore



General procedure 1: In a flame-dried Schlenk tube, dipropargyl sulfonylamide (0.2 mmol, 1 equiv) and K_2CO_3 (0.4 mmol, 2 equiv) were dissolved in *i*-PrOH (1 mL) under open air conditions. The reaction mixture was stirred at 80 °C for 24 h. Upon completion of the reaction as monitored by TLC, the reaction was quenched with MeOH (5 mL). The suspension was filtered and the filter residue was washed with 5 mL water and 5 mL MeOH to get the crude product. The crude material was purified by silica gel flash chromatography using petroleum ether, dichloromethane and methanol to yield the corresponding product.

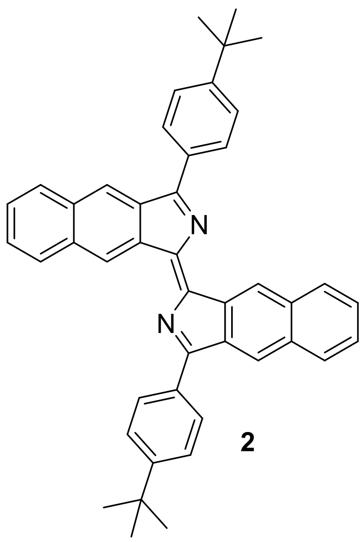
General procedure 2: In a flame-dried Schlenk tube, dipropargyl sulfonylamide (0.2 mmol, 1 equiv) and K_2CO_3 (0.4 mmol, 2 equiv) were dissolved in *n*-BuOH (1 mL) under open air conditions. The reaction mixture was stirred at 110 °C for 24 h. Upon completion of the reaction as monitored by TLC, the reaction was quenched with MeOH (5 mL). The suspension was filtered and the filter residue was washed with 5 mL water and 5 mL MeOH to get the crude product. The crude material was purified by silica gel flash chromatography using petroleum ether, dichloromethane and methanol to yield the corresponding product.

Characterization data for the new fluorophore



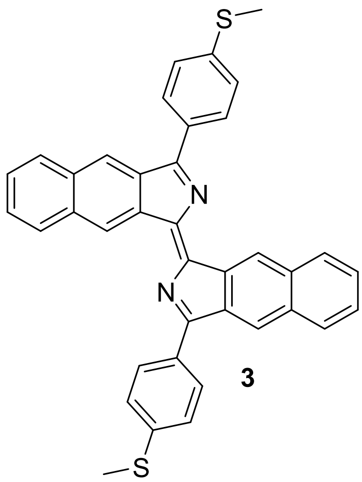
1

Following the general procedure 1, **1** was obtained as a purple solid (23.1 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.49 (s, 2H), 8.45 – 8.40 (m, 4H), 8.36 (s, 2H), 8.12 (d, J = 7.8 Hz, 2H), 7.99 (d, J = 7.8 Hz, 2H), 7.73 – 7.65 (m, 6H), 7.62 – 7.55 (m, 4H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.75, 148.39, 137.13, 135.36, 134.99, 133.73, 133.16, 131.12, 130.06, 129.90, 129.26, 129.06, 127.86, 127.49, 126.96, 122.98. IR (thin film) v 1403, 1411, 1472, 2596, 2851, 2921 cm^{-1}. HRMS m/z (ESI) calcd for [$C_{36}H_{22}N_2H$] ([M+H]$^+$): 483.1856, found: 483.1855.



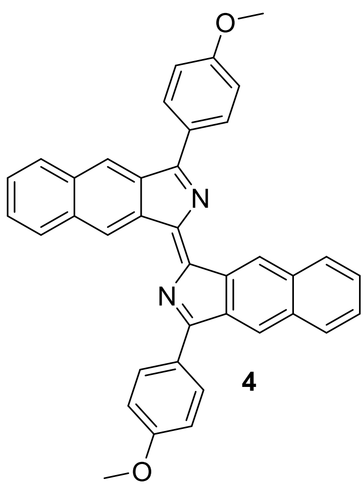
2

Following the general procedure 1, **2** was obtained as a red solid (23.2 mg, 39% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.51 (s, 2H), 8.40 (s, 2H), 8.39 – 8.36 (m, 4H), 8.13 (d, J = 8.0 Hz, 2H), 7.99 (d, J = 7.9 Hz, 2H), 7.72 – 7.70 (m, 4H), 7.60 – 7.57 (m, 2H), 7.57 – 7.54 (m, 2H), 1.46 (s, 18H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.32, 153.53, 147.15, 136.20, 134.44, 132.63, 132.05, 131.19, 128.93, 128.75, 127.92, 126.63, 126.27, 125.75, 124.95, 121.83, 34.12, 30.29. IR (thin film) v 1457, 1473, 1684, 1698, 1716, 2854, 2924, 2960 cm^{-1}. HRMS *m*/*z* (ESI) calcd for [$C_{44}H_{38}N_2H$] ([M+H]$^+$): 595.3108, found: 595.3107.



3

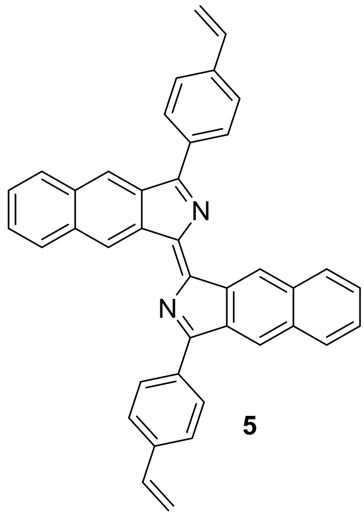
Following the general procedure 1, **3** was obtained as a red solid (32.2 mg, 56% yield). ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 9.54 (s, 2H), 9.07 (s, 2H), 8.31 (d, *J* = 8.3 Hz, 4H), 8.26 (d, *J* = 8.2 Hz, 4H), 8.02 (t, *J* = 7.5 Hz, 2H), 7.95 (t, *J* = 7.5 Hz, 2H), 7.64 (d, *J* = 8.1 Hz, 4H), 2.71 (s, 6H). ^{13}C NMR (150 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 166.84, 156.87, 136.41, 134.55, 134.14, 133.21, 131.97, 131.70, 131.49, 131.12, 130.76, 128.61, 128.23, 128.01, 126.65, 120.88, 14.57. IR (thin film) *v* 1592, 1664, 2932, 3035, 3068, 3082 cm^{-1}. HRMS *m*/*z* (ESI) calcd for [$C_{38}H_{26}N_2S_2Na$] ([M+Na]$^+$): 597.1430, found: 597.1427.



4

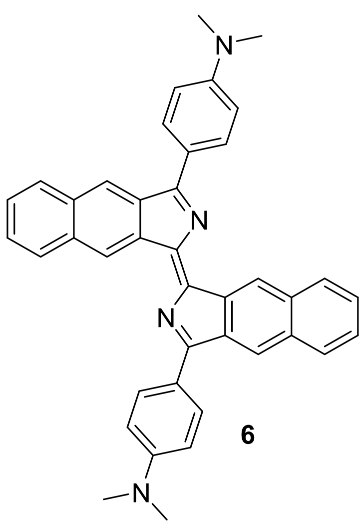
Following the general procedure 2, **4** was obtained as a red solid (31.4 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 9.27 (s, 2H), 8.86 (s, 2H), 8.41 (d, *J* = 8.5 Hz, 4H), 8.28 (d, *J* = 8.1 Hz, 2H), 8.19 (d, *J* = 8.1 Hz, 2H), 7.90 (t, *J* = 7.5 Hz, 2H), 7.83 (t, *J* = 7.5 Hz, 2H), 7.31 (d, *J* = 8.6 Hz, 4H), 4.07 (s, 6H). ^{13}C NMR (150 MHz,

$CDCl_3/CF_3COOD$, 5:1) δ 170.03, 168.16, 136.28, 134.59, 133.76, 133.44, 132.61, 132.33, 131.38, 130.85, 130.74, 129.88, 128.77, 127.97, 118.55, 116.54, 56.48. IR (thin film) *v* 1497, 1555, 1597, 1668, 1743, 2850, 2922 cm^{-1}. HRMS *m*/*z* (ESI) calcd for [$C_{38}H_{26}N_2O_2Na$] ($[M+Na]^+$): 565.1886, found: 565.1881.



5

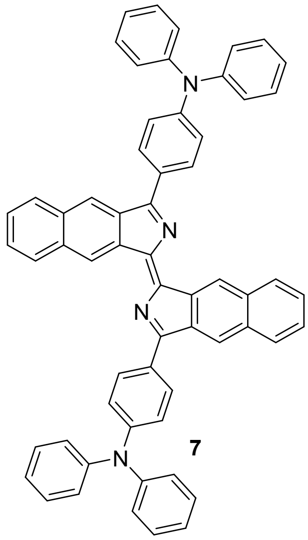
Following the general procedure 1, **5** was obtained as a red solid (12.8 mg, 24% yield). ^1H NMR (600 MHz, $CDCl_3$) δ 9.47 (s, 2H), 8.41 (d, *J* = 8.2 Hz, 4H), 8.37 (s, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 7.98 (d, *J* = 7.9 Hz, 2H), 7.71 (d, *J* = 8.1 Hz, 4H), 7.59 (t, *J* = 7.2 Hz, 2H), 7.55 (t, *J* = 7.9 Hz, 2H), 6.88 (dd, *J* = 17.6, 10.8 Hz, 2H), 5.97 (d, *J* = 17.6 Hz, 2H), 5.43 (d, *J* = 10.9 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.99, 148.39, 140.24, 137.18, 136.51, 135.35, 134.35, 133.69, 133.13, 130.03, 129.89, 129.48, 127.78, 127.49, 126.96, 126.85, 122.95, 115.76. IR (thin film) *v* 1474, 1500, 1603, 1623, 2849, 2918 cm^{-1}. HRMS *m*/*z* (ESI) calcd for [$C_{40}H_{26}N_2H$] ($[M+H]^+$): 535.2169, found: 535.2169.



6

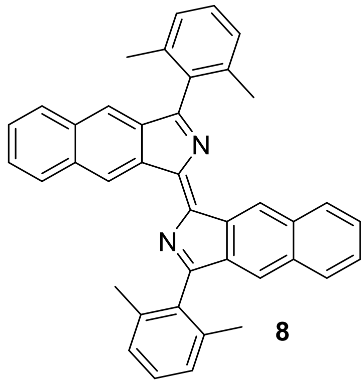
Following the general procedure 2, **6** was obtained as a black solid (25.6 mg, 45 % yield). ^1H NMR (600 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 9.50 (s, 2H), 9.00 (s, 2H), 8.43

(d, J = 8.8 Hz, 4H), 8.26 (d, J = 8.3 Hz, 4H), 7.96 (t, J = 7.6 Hz, 2H), 7.90 (t, J = 7.5 Hz, 2H), 7.59 (d, J = 8.8 Hz, 4H), 3.48 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 159.69, 152.52, 136.01, 134.37, 134.23, 133.89, 132.47, 132.32, 131.42, 131.21, 131.01, 130.24, 128.93, 128.18, 127.01, 119.17, 44.11. IR (thin film) v 1433, 1455, 1598, 2850, 2919 cm^{-1}. HRMS m/z (ESI) calcd for $[C_{40}H_{32}N_4H]$ ($[M+H]^+$): 569.2700, found: 569.2708.



7

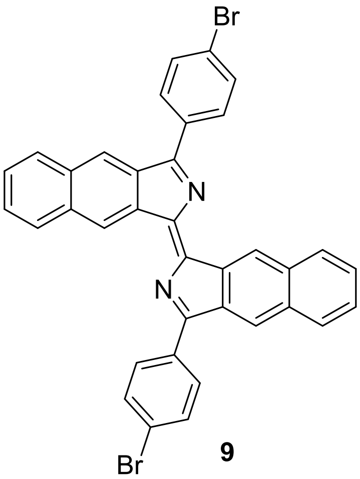
Following the general procedure 1, **7** was obtained as a black solid (28.6 mg, 35% yield). ^{1}H NMR (600 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 8.95 (s, 2H), 8.84 (s, 2H), 8.29 (d, J = 9.1 Hz, 4H), 8.17 (t, J = 8.3 Hz, 4H), 7.86 (t, J = 7.2 Hz, 2H), 7.82 (t, J = 7.5 Hz, 2H), 7.53 (t, J = 7.8 Hz, 8H), 7.43 (t, J = 7.5 Hz, 4H), 7.35 (d, J = 7.5 Hz, 8H), 7.22 (d, J = 9.1 Hz, 4H). ^{13}C NMR (150 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 162.85, 156.94, 143.50, 135.74, 134.16, 133.84, 132.14, 132.02, 130.98, 130.52, 130.42, 129.83, 129.07, 128.94, 128.36, 127.63, 127.30, 127.09, 119.10, 116.27. IR (thin film) v 1448, 1462, 1487, 1583, 2851, 2921, 2958 cm^{-1}. HRMS m/z (ESI) calcd for $[C_{60}H_{40}N_4H]$ ($[M+H]^+$): 817.3326, found: 817.3317.



8

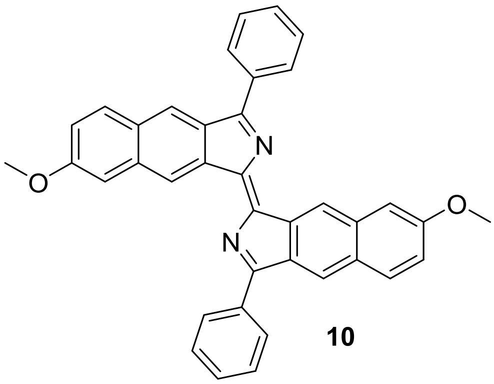
Following the general procedure 1, **8** was obtained as a yellow solid (17.2 mg, 32% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.38 (s, 2H), 8.08 (d, J = 8.1 Hz, 2H), 7.85 (d, J

= 7.9 Hz, 2H), 7.69 (s, 2H), 7.57 – 7.52 (m, 2H), 7.51 – 7.47 (m, 2H), 7.44 – 7.38 (m, 2H), 7.30 (d, *J* = 7.6 Hz, 4H), 2.35 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.84, 148.50, 137.18, 137.05, 135.74, 134.35, 134.17, 133.40, 130.19, 129.63, 129.14, 127.91, 127.81, 127.46, 126.99, 121.81, 20.61. IR (thin film) *ν* 1462, 1647, 1735, 2850, 2955 cm^{-1}. HRMS *m*/*z* (ESI) calcd for [$C_{40}H_{30}N_2H$] ([M+H]$^+$): 539.2482, found: 539.2480.



9

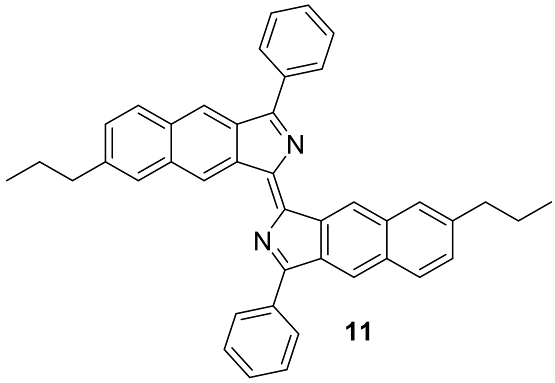
Following the general procedure, **9** was obtained as a red solid (30.6 mg, 48% yield). ^{1}H NMR (600 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 9.19 (s, 2H), 8.87 (s, 2H), 8.25 – 8.19 (m, 8H), 8.02 (d, *J* = 8.6 Hz, 4H), 7.97 (t, *J* = 7.7 Hz, 2H), 7.89 (t, *J* = 7.5 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 172.18, 136.61, 134.91, 134.26, 134.14, 133.93, 133.79, 133.28, 132.30, 132.10, 131.55, 131.05, 130.70, 128.15, 127.66, 124.47. IR (thin film) *ν* 1471, 1507, 1590, 2849, 2919 cm^{-1}. HRMS *m*/*z* (AP-MALDI) calcd for [$C_{36}H_{20}N_2Br_2H$] ([M+H]$^+$): 639.0066, found: 639.0078.



10

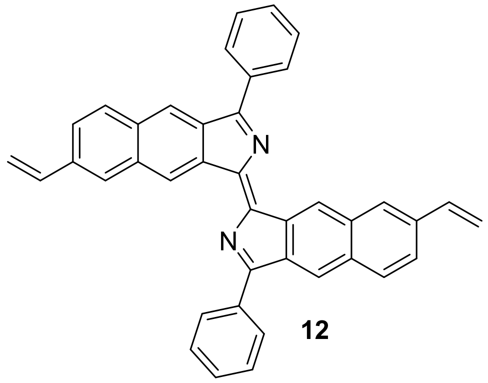
Following the general procedure, **10** was obtained as a red solid (20.1 mg, 37% yield). ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 9.25 (s, 2H), 8.66 (s, 2H), 8.27 (d, *J* = 7.6 Hz, 4H), 8.04 (d, *J* = 9.0 Hz, 2H), 7.94 (t, *J* = 7.4 Hz, 2H), 7.81 (t, *J* = 7.6 Hz, 4H), 7.57 (s, 2H), 7.43 (d, *J* = 8.9 Hz, 2H), 4.06 (s, 6H). ^{13}C NMR (100 MHz,

$CDCl_3/CF_3COOD$, 5:1) δ 172.53, 163.92, 139.41, 136.52, 133.75, 133.57, 133.46, 131.03, 130.17, 129.88, 129.25, 129.16, 126.27, 125.82, 124.11, 109.13, 56.11. IR (thin film) *v* 1511, 1589, 1600, 1780, 2854, 2924 cm^{-1}. HRMS *m/z* (ESI) calcd for $[C_{38}H_{26}N_2O_2H]$ ($[M+H]^+$): 543.2067, found: 543.2070.



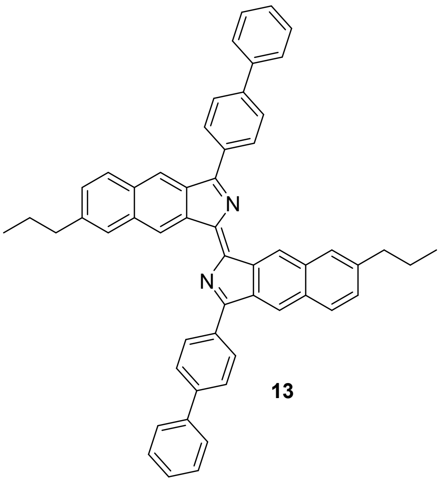
11

Following the general procedure 2, **11** was obtained as a red solid (29.4 mg, 52% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 2H), 8.43 (d, *J* = 7.2 Hz, 4H), 8.31 (s, 2H), 7.95 – 7.86 (m, 4H), 7.73 – 7.62 (m, 6H), 7.41 (d, *J* = 8.2 Hz, 2H), 2.83 (t, *J* = 7.6 Hz, 4H), 1.87 – 1.73 (m, 4H), 1.03 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.79, 148.44, 142.25, 137.30, 135.13, 134.78, 134.00, 131.63, 131.00, 129.71, 129.24, 129.03, 128.69, 128.66, 127.47, 122.77, 38.40, 24.54, 14.00. IR (thin film) *v* 1471, 1501, 1718, 2850, 2923, 2956 cm^{-1}. HRMS *m/z* (ESI) calcd for $[C_{42}H_{34}N_2H]$ ($[M+H]^+$): 567.2795, found: 567.2795.



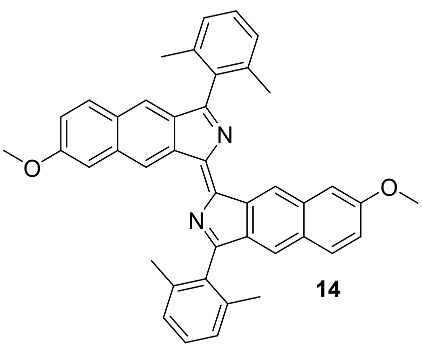
12

Following the general procedure 1, **12** was obtained as a red solid (18.2 mg, 34% yield). ^1H NMR (400 MHz, $CDCl_3$) δ 9.37 (s, 2H), 8.39 (d, *J* = 7.6 Hz, 4H), 8.18 (s, 2H), 7.94 (s, 2H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.71 – 7.66 (m, 8H), 6.94 (dd, *J* = 17.6, 10.9 Hz, 2H), 5.96 (d, *J* = 17.6 Hz, 2H), 5.43 (d, *J* = 10.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.61, 148.42, 137.55, 136.89, 136.59, 135.29, 134.97, 133.83, 132.74, 131.07, 130.07, 129.27, 129.02, 128.49, 127.96, 124.17, 122.64, 115.04. IR (thin film) *v* 1445, 1473, 2980, 3006, 3050 cm^{-1}. HRMS *m/z* (ESI) calcd for $[C_{40}H_{26}N_2H]$ ($[M+H]^+$): 535.2169, found: 535.2169.



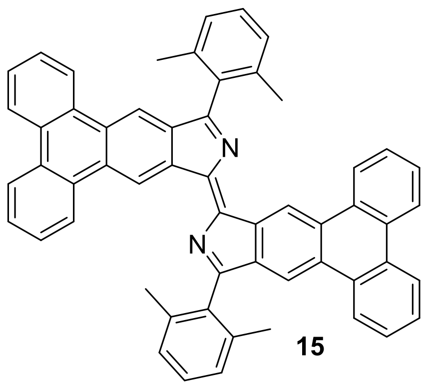
13

Following the general procedure 1, **13** was obtained as a red solid (34.5 mg, 48% yield). ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 9.16 (s, 2H), 8.93 (s, 2H), 8.45 (d, *J* = 8.3 Hz, 4H), 8.17 (d, *J* = 8.4 Hz, 2H), 8.11 – 8.04 (m, 6H), 7.79 (d, *J* = 7.2 Hz, 4H), 7.74 (d, *J* = 8.5 Hz, 2H), 7.63 – 7.53 (m, 6H), 2.90 (t, *J* = 7.6 Hz, 4H), 1.88 – 1.76 (m, 4H), 1.03 (t, *J* = 7.3 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 171.36, 150.80, 150.22, 138.30, 136.97, 134.74, 132.96, 132.44, 132.10, 131.82, 129.96, 129.86, 129.65, 129.47, 128.89, 128.35, 127.55, 126.73, 124.20, 38.50, 23.83, 13.50. IR (thin film) *v* 1556, 1602, 1681, 2873, 2930, 2962 cm^{-1}. HRMS *m/z* (ESI) calcd for $[C_{54}H_{42}N_2H]$ ($[M+H]^+$): 719.3421, found: 719.3420.



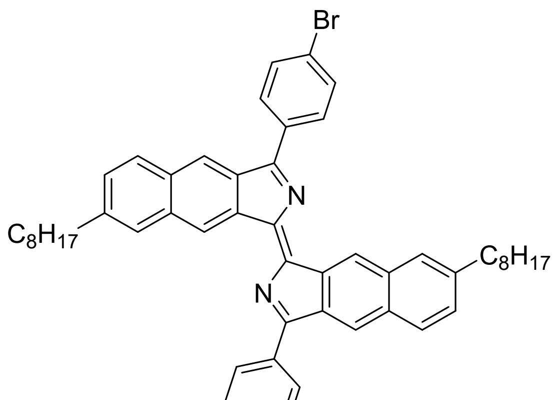
14

Following the general procedure 1, **14** was obtained as a yellow solid (13.2 mg, 22% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 9.29 (s, 2H), 7.72 (d, *J* = 8.9 Hz, 2H), 7.60 (s, 2H), 7.41 – 7.37 (m, 4H), 7.29 (d, *J* = 7.6 Hz, 4H), 7.15 (d, *J* = 8.8 Hz, 2H), 3.94 (s, 6H), 2.35 (s, 12H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 174.73, 158.93, 148.68, 137.19, 136.71, 135.64, 135.48, 134.69, 130.93, 129.02, 128.65, 127.84, 126.67, 121.50, 119.83, 108.03, 55.58, 20.58. IR (thin film) *v* 1417, 1463, 1503, 1620, 2833, 2922, 2960, 3003, 3060 cm^{-1}. HRMS *m/z* (ESI) calcd for $[C_{42}H_{34}N_2O_2Na]$ ($[M+Na]^+$): 621.2512, found: 621.2510.



15

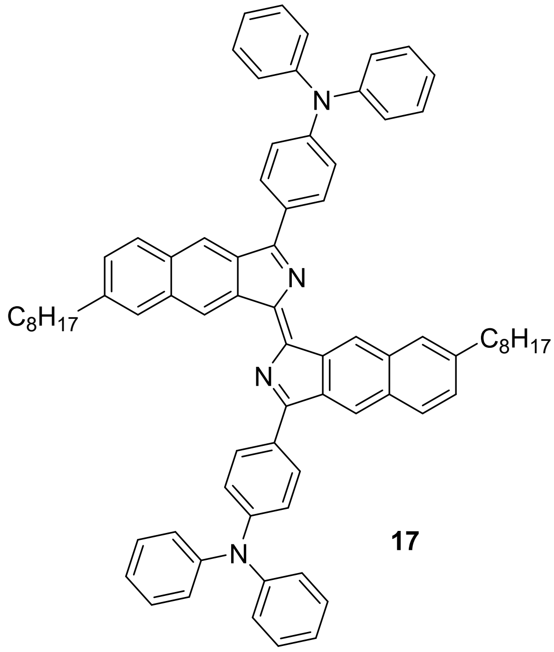
Following the general procedure 1, **15** was obtained as a yellow solid (14.8 mg, 20% yield). ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOD$, 5:0.1) δ 10.30 (s, 2H), 8.86 (d, J = 8.1 Hz, 2H), 8.73 (s, 2H), 8.71 – 8.65 (m, 4H), 8.54 (d, J = 8.1 Hz, 2H), 7.80 – 7.71 (m, 6H), 7.68 (t, J = 7.5 Hz, 2H), 7.58 (t, J = 7.7 Hz, 2H), 7.42 (d, J = 7.7 Hz, 4H), 2.45 (s, 12H). ^{13}C NMR (100 MHz, $CDCl_3/CF_3COOD$, 5:0.1) δ 177.99, 137.03, 134.76, 134.18, 133.70, 132.22, 131.19, 130.97, 129.55, 129.19, 129.10, 129.03, 128.53, 128.34, 127.87, 125.06, 124.86, 123.84, 123.71, 123.47, 121.42, 20.55. IR (thin film) v 1471, 1647, 2850, 2920 cm^{-1}. HRMS m/z (ESI) calcd for [$C_{56}H_{38}N_2H$] ([M+H]$^+$): 739.3108, found: 739.3108.



16

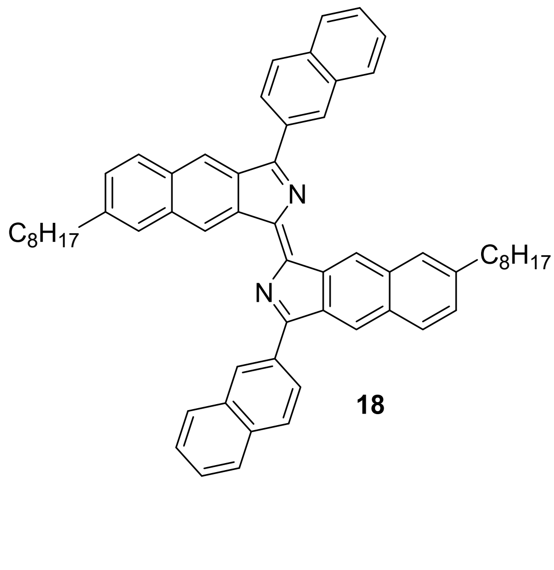
Following the general procedure 1, **16** was obtained as a yellow solid (35.4 mg, 41% yield). ^{1}H NMR (600 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 9.05 (s, 2H), 8.82 (s, 2H), 8.20 (d, J = 8.4 Hz, 4H), 8.13 (d, J = 8.5 Hz, 2H), 8.04 – 7.99 (m, 6H), 7.75 (d, J = 8.3 Hz, 2H), 2.91 (t, J = 7.7 Hz, 4H), 1.79 – 1.74 (m, 4H), 1.45 – 1.28 (m, 20H), 0.87 (t, J = 6.7 Hz, 6H). ^{13}C NMR (150 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 171.59, 151.40, 137.16, 135.15, 134.09, 133.31, 132.48, 132.39, 132.29, 132.16, 130.18, 129.74, 128.14, 126.49, 124.28, 36.73, 31.85, 30.85, 29.77, 29.40, 29.18, 22.64, 13.92. IR (thin film) v

1464, 1584, 2850, 2919 cm^{-1}. HRMS *m*/*z* (AP-MALDI) calcd for [$C_{52}H_{52}N_2Br_2H$] ([M+H]$^+$): 863.2570, found: 863.2582.



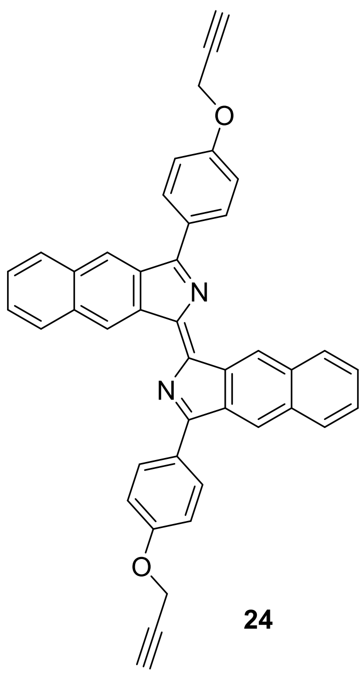
17

Following the general procedure 1, **17** was obtained as a black solid (41.6 mg, 40% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.43 (s, 2H), 8.45 – 8.33 (m, 6H), 7.94 – 7.81 (m, 4H), 7.42 – 7.33 (m, 10H), 7.32 – 7.26 (m, 12H), 7.15 (t, *J* = 7.3 Hz, 4H), 2.81 (t, *J* = 7.7 Hz, 4H), 1.78 – 1.69 (m, 4H), 1.38 – 1.26 (m, 20H), 0.88 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 168.66, 157.01, 150.45, 147.79, 147.10, 142.18, 137.62, 134.76, 133.78, 131.40, 130.25, 129.56, 128.45, 128.30, 128.22, 126.90, 125.61, 124.08, 122.50, 121.86, 36.33, 31.92, 31.51, 29.56, 29.44, 29.31, 22.70, 14.14. IR (thin film) *v* 1408, 1424, 1466, 1489, 1588, 2852, 2924, 2953 cm^{-1}. HRMS *m*/*z* (ESI) calcd for [$C_{76}H_{72}N_4Na$] ([M+Na]$^+$): 1063.5649, found: 1063.5645.



18

Following the general procedure 1, **18** was obtained as a red solid (49.2 mg, 61% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.39 (s, 2H), 8.83 (s, 2H), 8.55 (d, *J* = 8.4 Hz, 2H), 8.27 (s, 2H), 8.10 (d, *J* = 8.1 Hz, 4H), 8.03 – 7.96 (m, 2H), 7.86 (d, *J* = 8.3 Hz, 2H), 7.80 (s, 2H), 7.67 – 7.60 (m, 4H), 7.39 (d, *J* = 8.2 Hz, 2H), 2.79 (t, *J* = 7.7 Hz, 4H), 1.82 – 1.67 (m, 4H), 1.41 – 1.27 (m, 20H), 0.89 (t, *J* = 6.6 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 170.11, 148.45, 142.30, 137.29, 134.71, 134.65, 133.84, 133.28, 132.66, 131.47, 129.63, 129.25, 129.16, 128.61, 128.46, 128.38, 127.97, 127.43, 127.36, 126.58, 126.36, 122.60, 36.30, 31.95, 31.40, 29.59, 29.51, 29.36, 22.72, 14.16. IR (thin film) *v* 1456, 1487, 1597, 1623, 1698, 2851, 2924, 2953 cm^{-1}. HRMS *m*/*z* (ESI) calcd for [$C_{60}H_{58}N_2Na$] ([M+Na]$^+$): 829.4492, found: 829.4497.

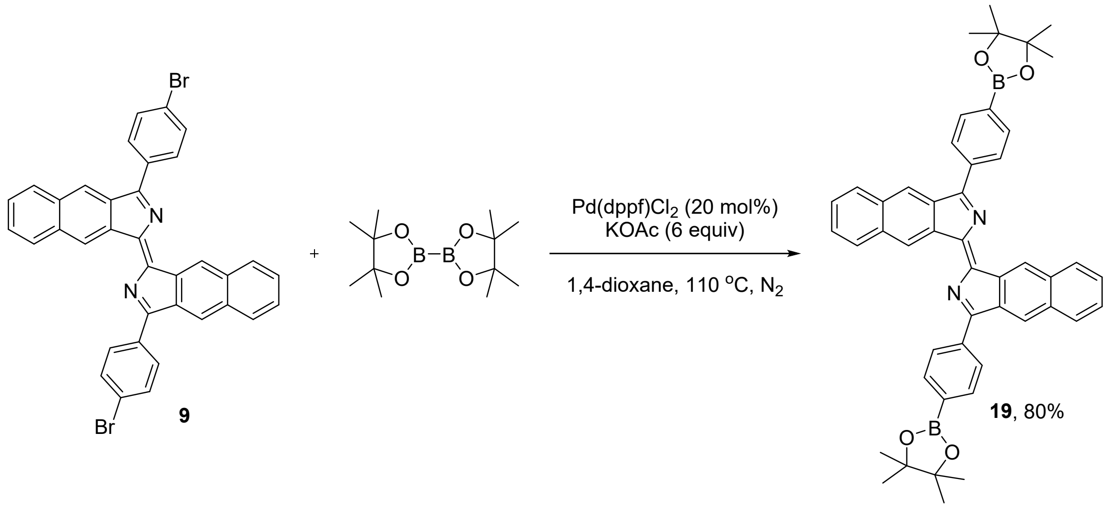


24

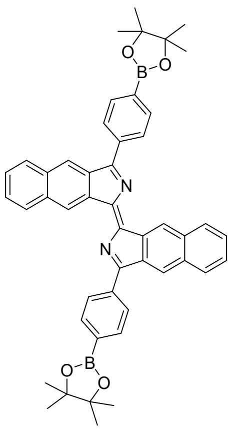
Following the general procedure, **24** was obtained as a purple solid (23 mg, 39% yield). ^{1}H NMR (400 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 9.24 (s, 1H), 8.89 (s, 1H), 8.45 (d, *J* = 8.8 Hz, 2H), 8.28 (d, *J* = 8.2 Hz, 1H), 8.21 (d, *J* = 8.1 Hz, 1H), 7.93 (t, *J* = 7.4 Hz, 1H), 7.86 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 2H), 4.97 (d, *J* = 2.0 Hz, 2H), 2.69 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3/CF_3COOD$, 5:1) δ 170.41, 165.83, 136.30, 134.35, 133.87, 133.72, 132.86, 132.21, 131.46, 130.87, 130.80, 129.93, 128.48, 127.74, 118.99, 117.28, 77.49, 75.90, 56.73. IR (thin film) *v* 1407, 1426, 1452, 1469, 1513, 1601, 2112, 2927, 2956, 3049, 3209, 3279 cm^{-1}. HRMS *m*/*z* (ESI) calcd for [$C_{42}H_{26}N_2O_2H$] ([M+H]$^+$): 591.2067, found: 591.2065.

Synthetic applications

C-B Bond Coupling

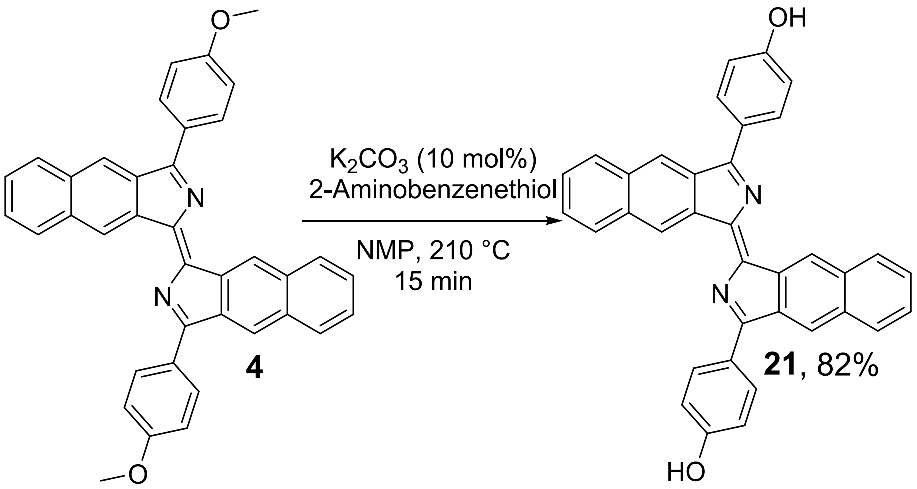


To an oven-dried seal tube were charged with Pd(dppf)Cl_2 (16.2 mg, 0.02 mmol), KOAc (58.9 mg, 0.6 mmol), **8** (0.1 mmol, 63.8 mg), B_2pin_2 (0.22 mmol, 55.9 mg) and 1,4-dioxane (2 mL). The tube was sealed with a Teflon valve, heated at 110 °C and stirred for 24 h. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel using petroleum ether and dichloromethane to give product **19** as a red solid in 80% yield.

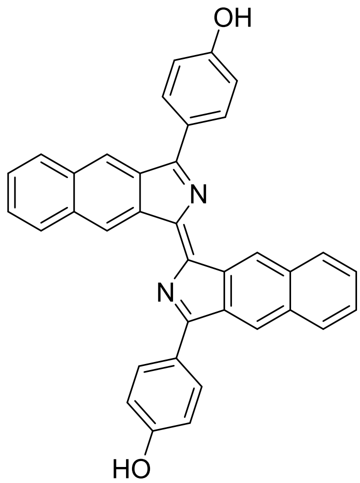


^{1}H NMR (600 MHz, $CDCl_3$) δ 9.46 (s, 2H), 8.39 (d, J = 8.2 Hz, 4H), 8.32 (s, 2H), 8.11 (d, J = 8.2 Hz, 4H), 8.08 (d, J = 8.0 Hz, 2H), 7.97 (d, J = 7.9 Hz, 2H), 7.61 – 7.57 (m, 2H), 7.57 – 7.53 (m, 2H), 1.42 (s, 24H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.89, 148.64, 137.35, 137.05, 135.38, 135.34, 133.74, 133.16, 130.06, 129.94, 128.39, 127.95, 127.57, 127.01, 123.04, 84.22, 25.06. IR (thin film) v 1473, 1519, 1608, 2928, 2977 cm^{-1}. HRMS *m/z* (ESI) calcd for [$C_{48}H_{44}B_2N_2O_4Na$] ([M+Na]$^+$): 757.3395, found: 757.3397.

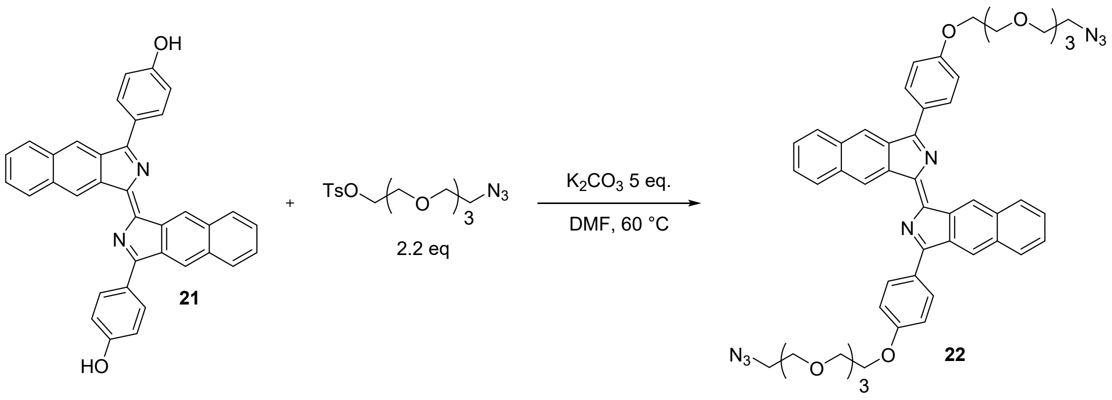
SN$_2$ Substitution Reaction



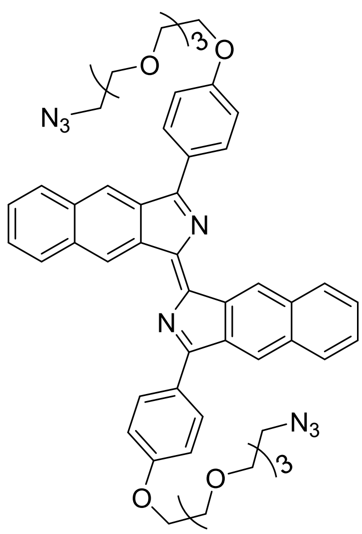
To an oven-dried Schlenk tube were charged with **4** (0.05 mmol, 27.1 mg), 2-Aminobenzenethiol (0.1 mmol, 12.5 mg), K_2CO_3 (0.005 mmol, 0.7 mg) and NMP (1 mL). The tube was heated at 110 ℃ and stirred for 15 min. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel using DCM and CH_3OH to give product **21** as a dark purple solid in 82% yield.



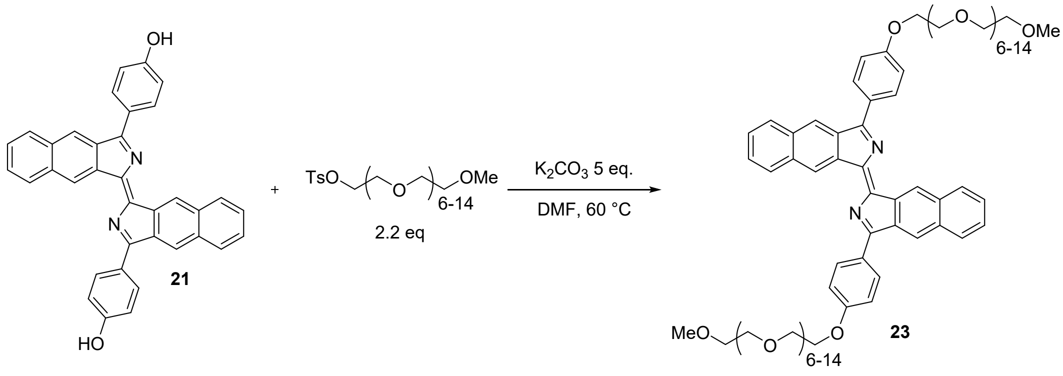
^{1}H NMR (400 MHz, DMSO-*d$_6$*) δ 10.40 (s, 2H), 9.49 (s, 2H), 8.81 (s, 2H), 8.54 (d, *J* = 8.6 Hz, 4H), 8.30 (d, *J* = 7.7 Hz, 2H), 8.26 (d, *J* = 7.7 Hz, 2H), 7.76 – 7.59 (m, 4H), 7.15 (d, *J* = 8.6 Hz, 4H).^{13}C NMR (100 MHz, DMSO-*d$_6$*) δ 168.55, 161.33, 146.95, 137.18, 135.00, 133.25, 131.65, 130.56, 130.05, 128.14, 127.48, 126.97, 125.68, 123.96, 116.61. IR (thin film) *v* 1405, 1450, 1469, 1500, 1587, 1604, 1655, 3130 cm^{-1}. HRMS *m/z* (ESI) calcd for $[C_{36}H_{22}N_2O_2H]$ ($[M+H]^+$): 515.1754, found:515.1749.



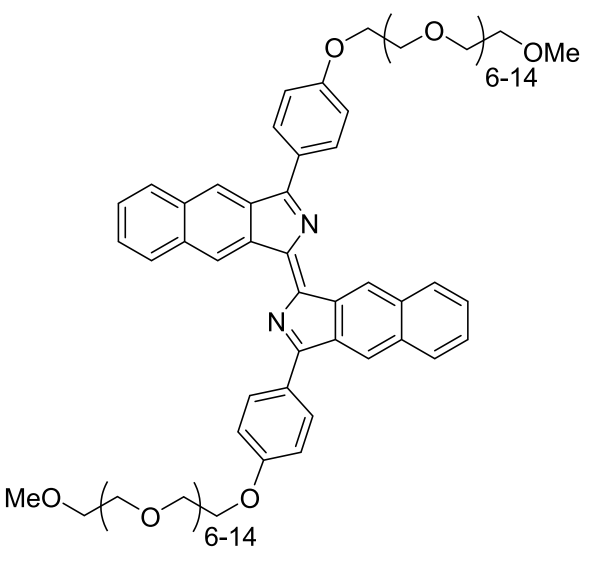
To an oven-dried Schlenk tube were charged with **21** (0.02 mmol, 10.3 mg), 2-(2-(2-(2-azidoethoxy)ethoxy)ethoxy)ethyl 4-methylbenzenesulfonate (0.044 mmol, 16.4 mg), K_2CO_3 (0.1 mmol, 13.8 mg) and DMF (1 mL). The tube was heated at 60 ℃ and stirred for 12 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel using DCM and CH_3OH to give product **22** as a dark purple solid in 85% yield.



^{1}H NMR (400 MHz, $CDCl_3$) δ 9.45 (s, 1H), 8.41 (d, *J* = 8.7 Hz, 2H), 8.35 (s, 1H), 8.11 (d, *J* = 7.9 Hz, 1H), 7.98 (d, *J* = 7.8 Hz, 1H), 7.62 – 7.52 (m, 2H), 7.20 (d, *J* = 8.6 Hz, 2H), 4.31 (t, *J* = 4.8 Hz, 2H), 4.01 – 3.93 (m, 2H), 3.83 – 3.78 (m, 2H), 3.77 – 3.67 (m, 8H), 3.40 (t, *J* = 5.0 Hz, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.16, 161.26, 147.73, 137.31, 135.34, 133.52, 132.97, 130.79, 129.91, 129.76, 127.90, 127.39, 127.22, 126.69, 122.74, 115.02, 70.96, 70.78, 70.75, 70.73, 70.09, 69.71, 67.64, 50.71. IR (thin film) v 1404, 1427, 1448, 1470, 1602, 2090, 2863, 2899 cm^{-1}. HRMS m/z (ESI) calcd for $[C_{52}H_{52}N_8O_8H]$ ($[M+H]^+$): 917.3981, found:917.3969.

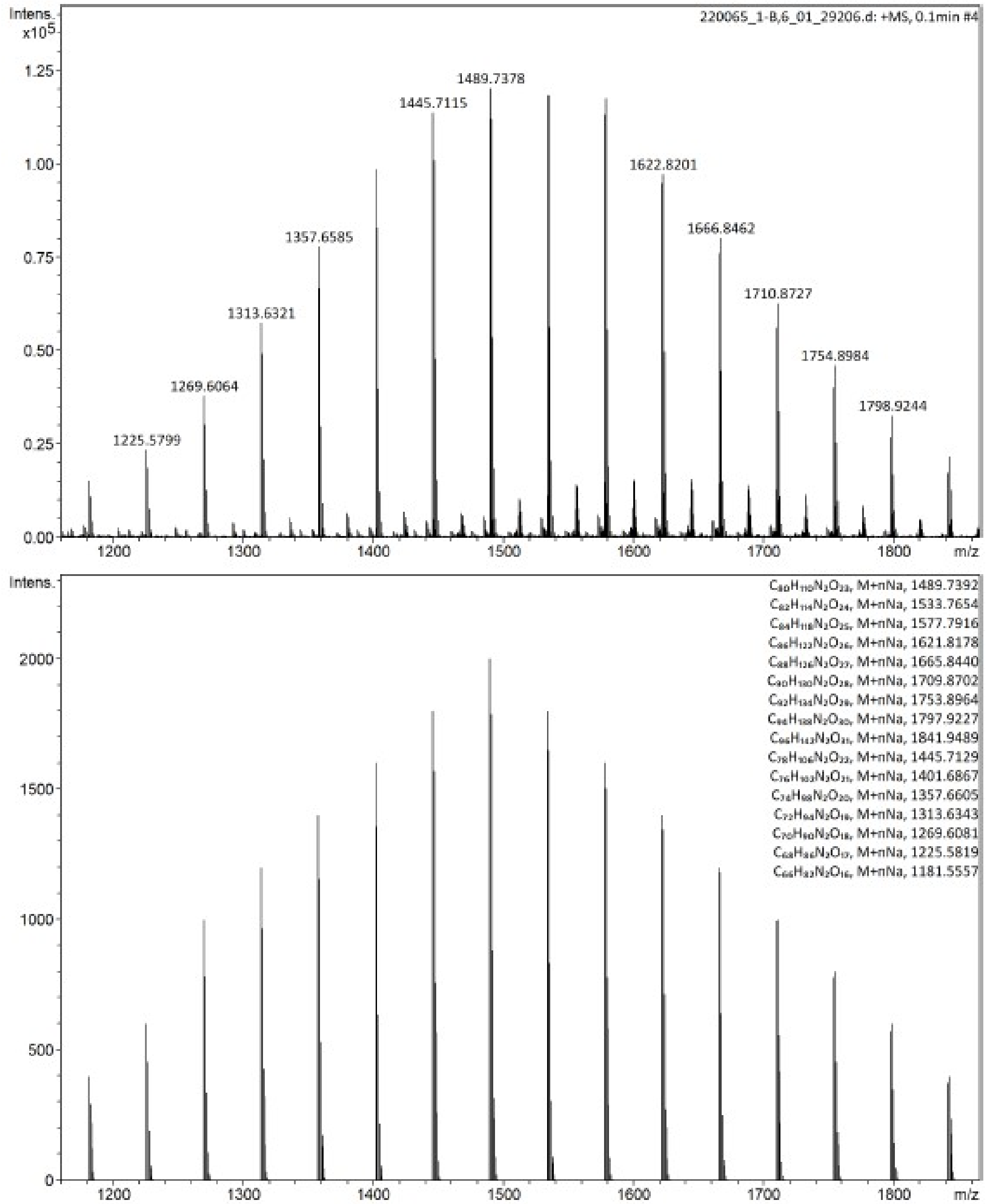


To an oven-dried Schlenk tube were charged with **20** (0.02 mmol, 10.3 mg), Ts-protected PEG monomethyl ether (0.044 mmol, 31.4 mg), K_2CO_3 (0.1 mmol, 13.8 mg) and DMF (1 mL). The tube was heated at 60 °C and stirred for 12 h. The solvent was removed under reduced pressure and the residue was purified by flash column chromatography on silica gel using DCM and CH_3OH to give product **22** as a black solid in 65% yield.

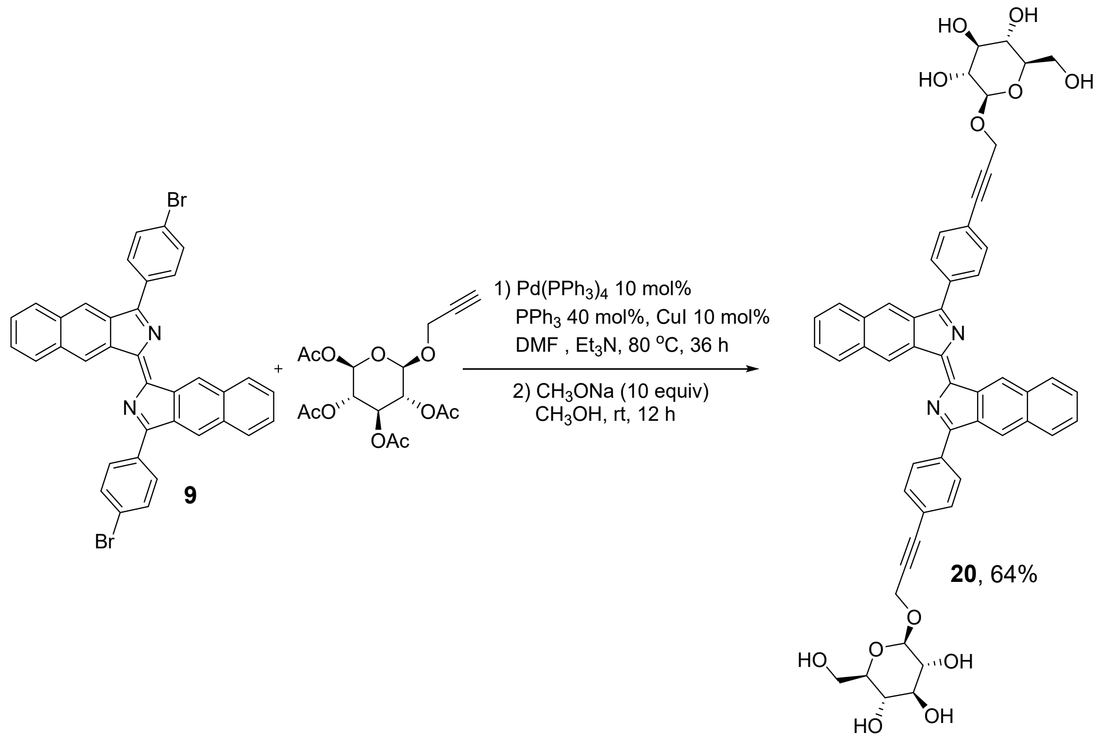


^1H NMR (600 MHz, $CDCl_3$) δ 9.30 (s, 1H), 8.30 (d, J = 7.9 Hz, 2H), 8.19 (s, 1H), 7.99 (d, J = 7.6 Hz, 1H), 7.87 (d, 1H), 7.53 – 7.45 (m, 2H), 7.11 (d, J = 8.1 Hz, 2H), 4.24 – 4.19 (m, 2H), 3.90 (t, J = 4.5 Hz, 2H), 3.76 (t, 2H), 3.70 – 3.68 (m, 2H), 3.62 – 3.56 (m, 42H), 3.50 – 3.48 (m, 2H), 3.31 (s, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 168.94, 161.24, 147.68, 137.31, 135.28, 133.47, 132.96, 130.82, 129.93, 129.80, 127.91, 127.38, 126.65, 122.71, 115.00, 71.94, 71.24, 70.95, 70.69, 70.57, 69.73, 67.65, 59.08. IR (thin film) v 1407, 1451, 1472, 1603, 2870 cm^{-1}.

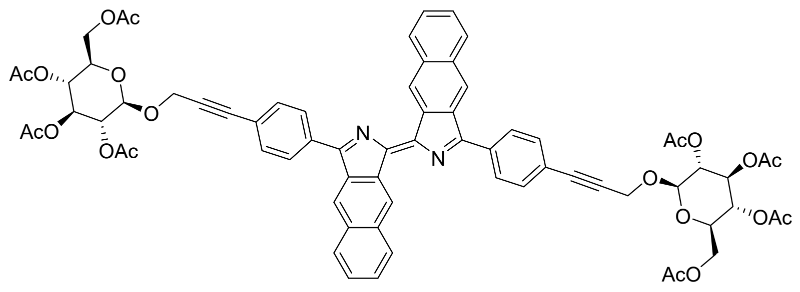
HRMS *m*/*z* (ESI)


Intens.
x10^5
220065_1-B,6_01_29206.d: +MS, 0.1min #4
1489.7378
1445.7115
1622.8201
1666.8462
1357.6585
1710.8727
1313.6321
1754.8984
1269.6064
1798.9244
1225.5799
m/z
Intens.
$C_{80}H_{110}N_2O_{23}$, M+nNa, 1489.7392
$C_{82}H_{114}N_2O_{24}$, M+nNa, 1533.7654
$C_{84}H_{118}N_2O_{25}$, M+nNa, 1577.7916
$C_{86}H_{122}N_2O_{26}$, M+nNa, 1621.8178
$C_{88}H_{126}N_2O_{27}$, M+nNa, 1665.8440
$C_{90}H_{130}N_2O_{28}$, M+nNa, 1709.8702
$C_{92}H_{134}N_2O_{29}$, M+nNa, 1753.8964
$C_{94}H_{138}N_2O_{30}$, M+nNa, 1797.9227
$C_{96}H_{142}N_2O_{31}$, M+nNa, 1841.9489
$C_{78}H_{106}N_2O_{22}$, M+nNa, 1445.7129
$C_{76}H_{102}N_2O_{21}$, M+nNa, 1401.6867
$C_{74}H_{98}N_2O_{20}$, M+nNa, 1357.6605
$C_{72}H_{94}N_2O_{19}$, M+nNa, 1313.6343
$C_{70}H_{90}N_2O_{18}$, M+nNa, 1269.6081
$C_{68}H_{86}N_2O_{17}$, M+nNa, 1225.5819
$C_{66}H_{82}N_2O_{16}$, M+nNa, 1181.5557
m/z

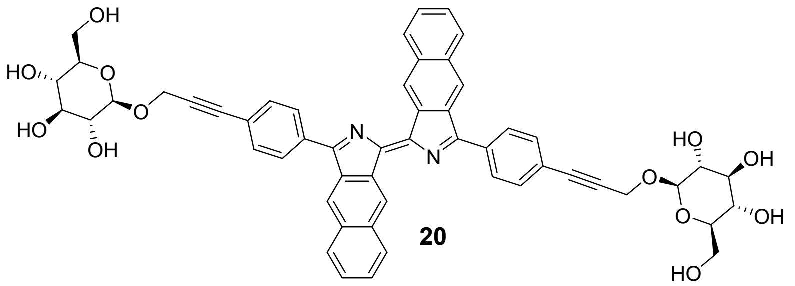
Sonogashira Coupling



In a flame-dried Schlenk tube, **9** (32 mg, 0.05 mmol), 1-O-propargyl 2,3,4,6-tetra-O-acetyl-β-D-glucose (58 mg, 0.15 mmol), PPh_3(5.2 mg, 0.02 mmol), $Pd(PPh_3)_4$ (5.8 mg, 0.02 mmol), CuI (1 mg, 0.005 mmol), triethylamine (0.5 mL, 0.15 mmol) and DMF (0.5 mL). The mixture was heated to 80 °C for 36 h under N_2 and stirring. The reaction mixture was concentrated under reduced pressure and the residue was purified by flash column chromatography on silica gel using methanol and dichloromethane to give desired product. The product was dissolved in anhydrous MeOH (1 mL) and sodium methoxide (0.5 mL, 30 wt% in methanol) was added. The reaction mixture stirred at room temperature for 12 h. Once the reaction was complete, the cationic resin was added to adjust the pH to neutral, the cationic resin was filtered off. Then washed the crude product with 5 mL DCM and 5 mL ethanol to give product **20** as a purple solid in 64% yield.



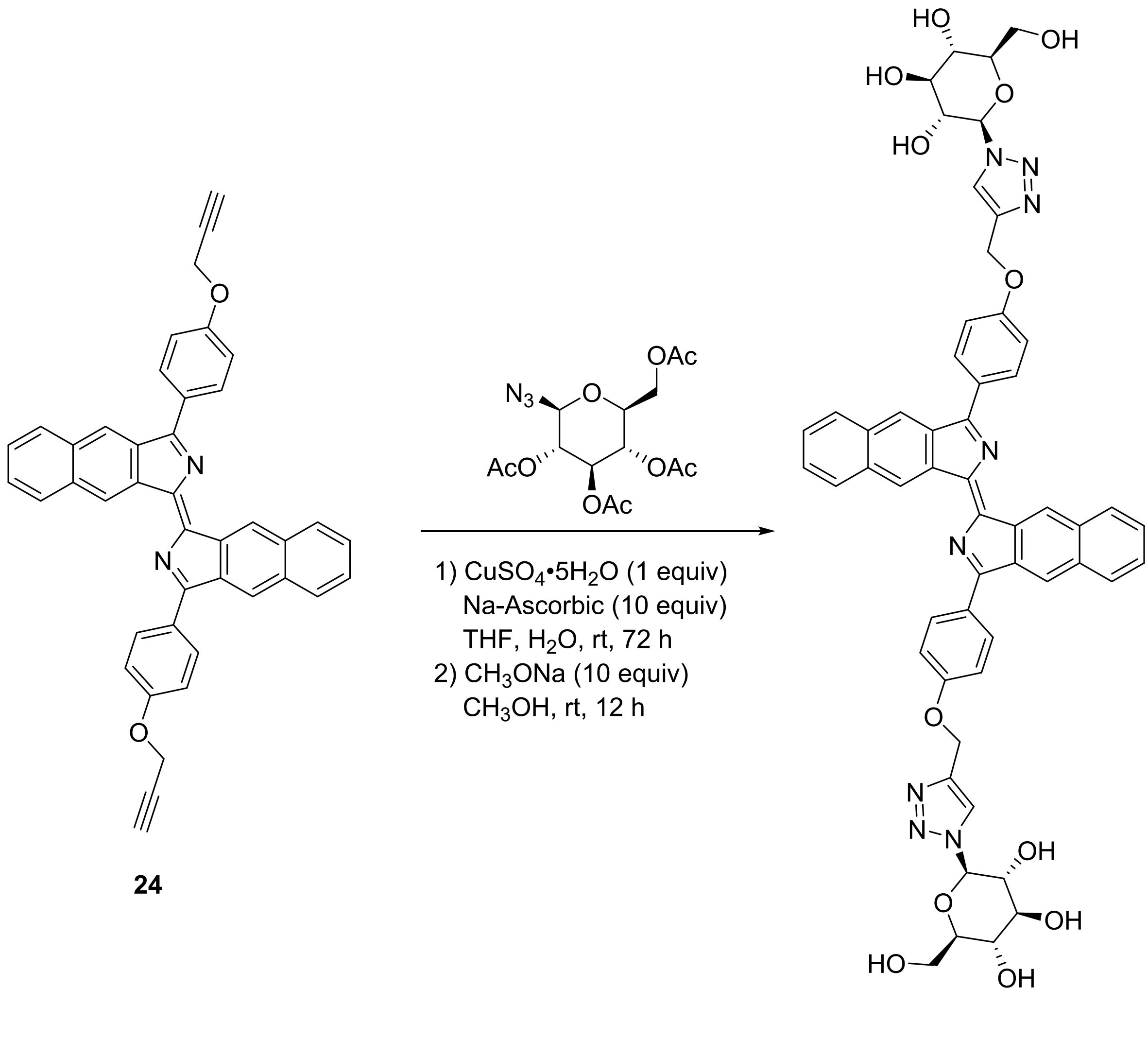
^{1}H NMR (400 MHz, $CDCl_3$) δ 9.47 (s, 1H), 8.42 (d, *J* = 8.0 Hz, 2H), 8.37 (s, 1H), 8.14 (d, *J* = 7.8 Hz, 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.76 (d, *J* = 8.1 Hz, 2H), 7.66 – 7.56 (m, 2H), 5.33 (t, *J* = 9.5 Hz, 1H), 5.18 (t, *J* = 9.7 Hz, 1H), 5.11 (dd, *J* = 9.5, 7.9 Hz, 1H), 4.94 (d, *J* = 7.9 Hz, 1H), 4.71 (s, 2H), 4.35 (dd, *J* = 12.3, 4.5 Hz, 1H), 4.22 (dd, *J* = 12.3, 2.4 Hz, 1H), 3.87 – 3.80 (m, 1H), 2.17 – 2.09 (m, 6H), 2.06 (s, 3H), 2.05 (s, 3H). 13C NMR (100 MHz, $CDCl_3$) δ 166.05, 165.65, 165.00, 164.83, 164.74, 143.81, 132.14, 130.23, 128.90, 128.34, 127.53, 125.27, 125.03, 124.36, 123.19, 122.93, 122.40, 120.05, 118.20, 93.80, 82.27, 81.30, 68.09, 67.26, 66.42, 63.57, 57.09, 52.29, 16.12, 16.07, 15.94, 15.91. IR (thin film) *v* 1471, 1632, 1755, 2857, 2926 3056 cm^{-1}. HRMS *m/z* (ESI) calcd for $[C_{70}H_{62}N_2O_{20}H]$ ($[M+H]^+$): 1251.3969, found: 1251.3965.



20

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.32 (s, 1H), 8.63 (s, 1H), 8.52 (d, J = 8.1 Hz, 2H), 8.23 – 8.11 (m, 2H), 7.79 (d, J = 8.1 Hz, 2H), 7.73 – 7.65 (m, 2H), 5.32 (d, J = 4.9 Hz, 1H), 5.11 (d, J = 4.4 Hz, 1H), 5.06 (d, J = 5.2 Hz, 1H), 4.82 (d, J = 15.8 Hz, 1H), 4.75 – 4.65 (m, 2H), 4.46 (d, J = 7.7 Hz, 1H), 3.84 – 3.74 (m, 1H), 3.59 – 3.53 (m, 1H), 3.30 – 3.22 (m, 2H), 3.17 – 3.10 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.06, 148.00, 136.52, 134.43, 134.27, 133.28, 132.57, 130.66, 130.11, 129.75, 128.45, 127.79, 127.60, 125.22, 124.10, 101.73, 89.19, 85.94, 77.58, 77.18, 73.82, 70.55, 61.68, 56.31. IR (thin film) *v* 1405, 1453, 1470, 1601, 2090, 2858, 2919, 3341 cm^{-1}. HRMS *m/z* (ESI) calcd for $[C_{54}H_{48}N_2O_{12}H]$ ($[M+H]^+$):915.3124, found:915.3119.

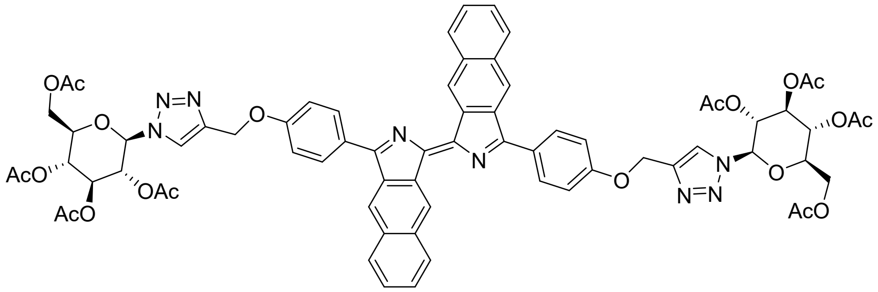
Click Reaction



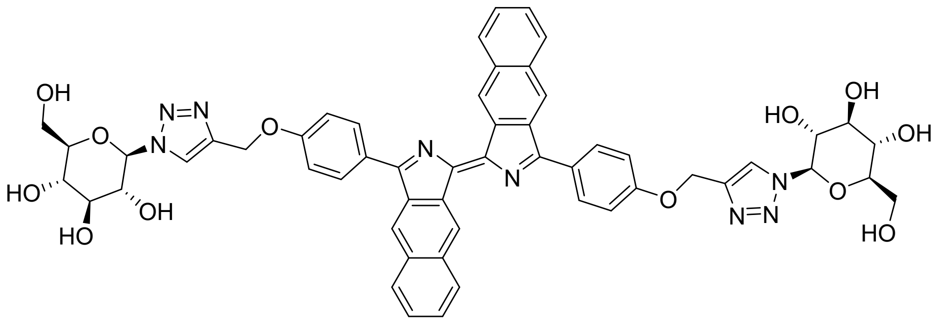
24

25, 57%

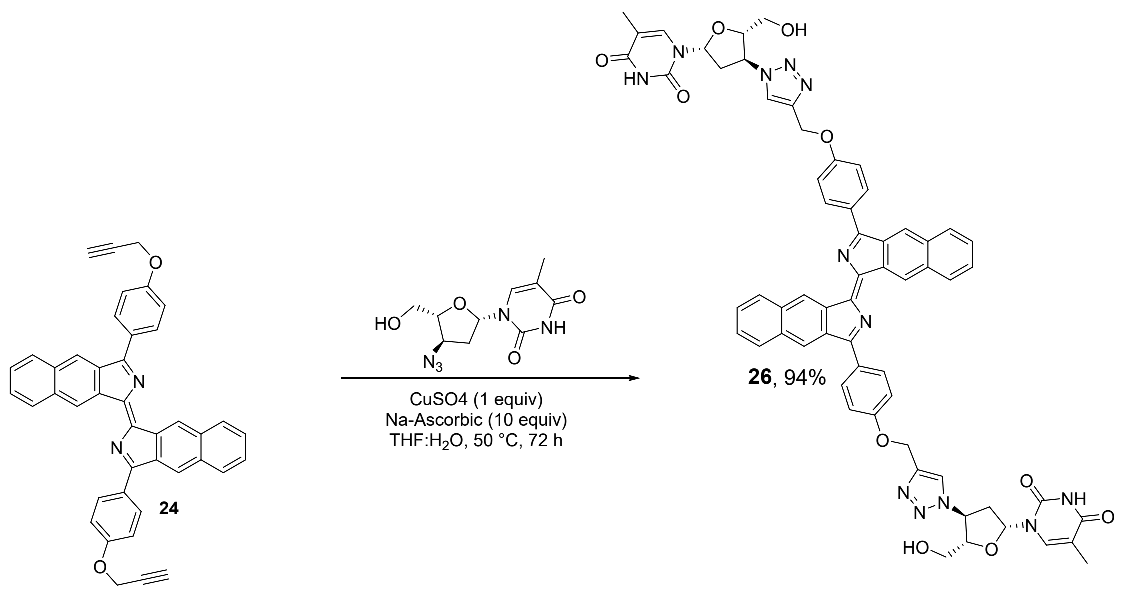
In a flame-dried Schlenk tube, **24** (29.5 mg, 0.05 mmol) and 1-azido-1-deoxy-β-D-glucopyranoside tetraacetate (41.0 mg, 0.11 mmol) were dissolved in a mixture of THF:H_2O (2 mL, 1:1), then copper sulfate pentahydrate (12.5 mg, 0.05mmol) and sodium ascorbate (99.0 mg, 0.50 mmol) were added. The reaction mixture stirred at room temperature for 72 h. Once the reaction was complete, samples were extracted with DCM and dried over $MgSO_4$. The mixture was concentrated under reduced pressure and purified by column chromatography (1:10 methanol: dichloromethane). The product was dissolved in anhydrous MeOH (1 mL) and sodium methoxide (0.5 mL, 30 wt% in methanol) was added. The reaction mixture stirred at room temperature for 12 h. Once the reaction was complete, the cationic resin was added to adjust the pH to neutral, the cationic resin was filtered off. Then washed the crude product with 5 mL DCM and 5 mL ethanol to give product **25** as a purple solid in 57% yield.



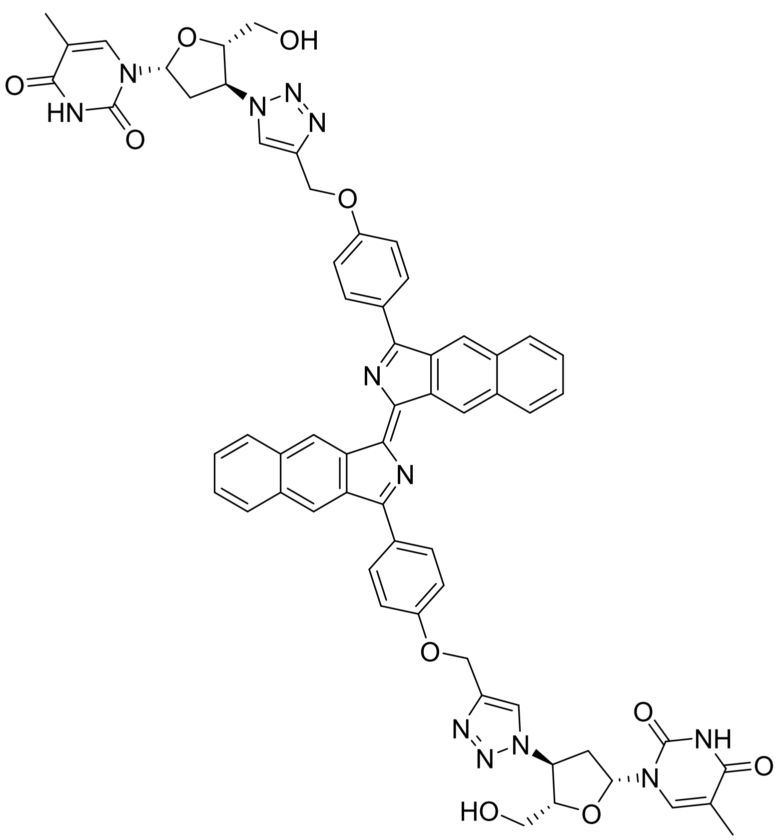
[1]H NMR (400 MHz, $CDCl_3$) δ 9.42 (s, 1H), 8.42 (d, *J* = 8.8 Hz, 2H), 8.33 (s, 1H), 8.09 (d, *J* = 8.1 Hz, 1H), 8.01 (s, 1H), 7.98 – 7.93 (m, 1H), 7.60 – 7.50 (m, 2H), 7.29 – 7.26 (m, 2H), 5.95 (d, *J* = 9.2 Hz, 1H), 5.54 – 5.42 (m, 2H), 5.40 (s, 2H), 5.32 – 5.24 (m, 1H), 4.33 (dd, *J* = 12.7, 5.0 Hz, 1H), 4.17 (dd, *J* = 12.7, 2.0 Hz, 1H), 4.07 – 4.00 (m, 1H), 2.09 (s, 3H), 2.08 (s, 3H), 2.02 (s, 3H), 1.89 (s, 3H). [13]C NMR (100 MHz, $CDCl_3$) δ 170.64, 170.04, 169.49, 169.16, 169.09, 160.48, 147.83, 144.74, 137.30, 135.31, 133.58, 133.03, 130.94, 129.98, 129.81, 128.45, 127.47, 127.33, 126.79, 121.54, 115.31, 85.93, 75.32, 72.72, 70.35, 67.74, 62.02, 61.61, 29.80, 20.82, 20.67, 20.63, 20.29. IR (thin film) *v* 1473,1603, 1755, 2938, 3059 cm^{-1}. HRMS *m/z* (ESI) calcd for [$C_{70}H_{64}N_8O_{20}H$] ([M+H]$^+$):1337.4310, found:1337.4313.



[1]H NMR (400 MHz, DMSO-d_6) δ 9.46 (s, 1H), 8.79 (s, 1H), 8.67 – 8.55 (m, 3H), 8.25 (d, J = 8.1 Hz, 2H), 7.69 (p, J = 7.4, 7.0 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H), 5.62 (d, J = 9.3 Hz, 1H), 5.48 (d, J = 6.0 Hz, 1H), 5.40 (s, 2H), 5.35 (d, J = 4.9 Hz, 1H), 5.21 (d, J = 5.5 Hz, 1H), 4.69 (t, J = 5.5 Hz, 1H), 3.88 – 3.79 (m, 1H), 3.76 – 3.68 (m, 1H), 3.51 – 3.40 (m, 3H), 3.30 – 3.22 (m, 1H). [13]C NMR (150 MHz, DMSO-D6) δ 168.77, 161.39, 147.33, 142.84, 137.08, 134.95, 133.38, 131.55, 130.71, 130.16, 128.38, 127.70, 127.49, 127.25, 124.78, 124.15, 115.94, 88.09, 80.54, 77.50, 72.63, 70.11, 61.86, 61.29. IR (thin film) *v* 1405, 1426, 1435, 1470, 1601, 2850, 2918, 3326 cm^{-1}. HRMS *m/z* (ESI) calcd for [$C_{54}H_{49}N_8O_{12}H$] ([M+H]$^+$):1001.3464, found:1001.3459.



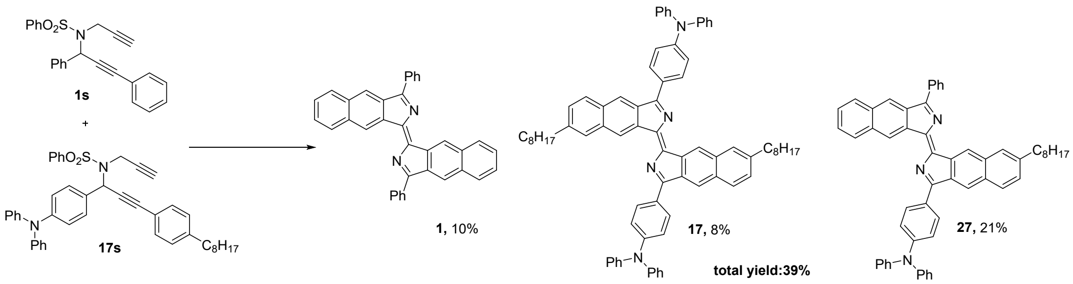
In a flame-dried Schlenk tube, **24** (29.5 mg, 0.05 mmol) and Zidovudine (66.8 mg, 0.25 mmol) were dissolved in a mixture of THF:H_2O (2 mL, 2:1), then copper sulfate pentahydrate (12.5 mg, 0.05mmol) and sodium ascorbate (99.0 mg, 0.50 mmol) were added. The reaction mixture stirred at 50 ^{o}C for 72 h. Once the reaction was complete, the reaction was quenched with DCM (5 mL). The suspension was filtered and the filter residue was washed with 5 mL water and 5 mL ethanol to get the crude product. The crude material was purified by silica gel flash chromatography using dichloromethane and methanol to give product **26** as a dark red solid in 94% yield.



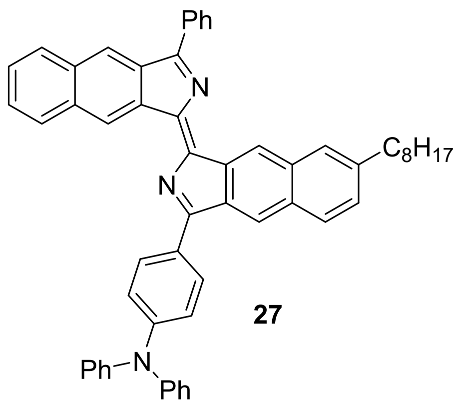
^{1}H NMR (400 MHz, DMSO-d_6) δ 11.40 (s, 1H), 9.49 (s, 1H), 8.82 (s, 1H), 8.72 – 8.49 (m, 3H), 8.27 (s, 2H), 7.85 (s, 1H), 7.77 – 7.62 (m, 2H), 7.43 (d, J = 7.2 Hz, 2H), 6.48 (t, J = 6.4 Hz, 1H), 5.52 – 5.27 (m, 4H), 4.28 (m, 1H), 3.80 – 3.62 (m, 2H), 2.83 – 2.65 (m, 2H). ^{13}C NMR (150 MHz, DMSO-D6) δ 168.72, 164.28, 161.36, 151.00, 147.32, 143.21, 137.08, 136.79, 134.93, 133.36, 131.53, 130.68, 130.12, 128.35, 127.66, 127.51, 127.22, 125.13, 124.10, 115.93, 110.20, 85.01, 84.43, 61.95, 61.32, 59.95, 37.75, 12.83. IR (thin film) *v* 1451, 1470, 1602, 1694, 2929, 3061 cm^{-1}. HRMS *m*/*z* (ESI) calcd for [$C_{62}H_{53}N_{12}O_{10}$] ([M+H]$^{+}$):1125.4002, found:1125.3995.

Mechanism Study

Cross-over Experiment



In a flame-dried Schlenk tube, **1s** (0.1 mmol, 1 equiv), **17s** (0.1 mmol, 1 equiv), K_2CO_3 (0.6 mmol, 3 equiv) were dissolved in i-PrOH (1 mL) under open air conditions. The reaction mixture was stirred at 80 ^oC for 24 h. Upon completion of the reaction as monitored by TLC, the reaction was quenched with MeOH (5 mL). The suspension was filtered and the filter residue was washed with 5 mL of water and 5 mL of MeOH to get the crude product. The crude material was purified by flash chromatography on silica gel using petroleum ether and dichloromethane to yield the corresponding products **1**, **17**, **27** in 10%, 8%, 21% yield, respectively.

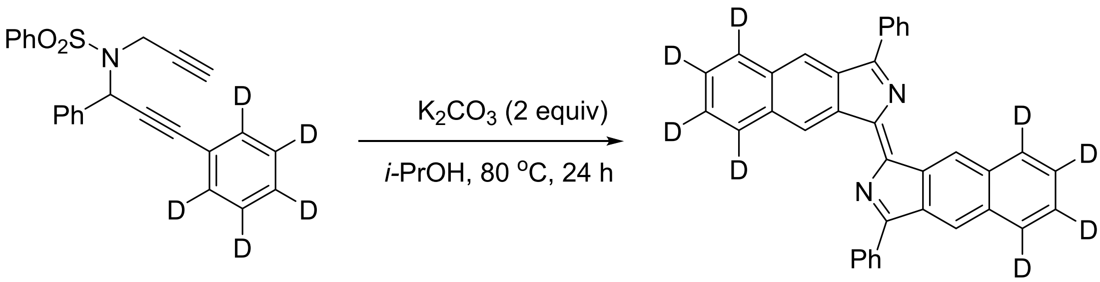


27

^1H NMR (600 MHz, $CDCl_3$) δ 9.46 (s, 1H), 9.42 (s, 1H), 8.43 – 8.41 (m, 2H), 8.37 – 8.33 (m, 4H), 8.09 (d, *J* = 7.3 Hz, 1H), 7.97 (d, *J* = 8.3 Hz, 1H), 7.88 – 7.84 (m, 2H), 7.70 – 7.67 (m, 2H), 7.65 – 7.61 (m, 1H), 7.57 – 7.51 (m, 2H), 7.40 – 7.35 (m, 5H), 7.29 – 7.25 (m, 6H), 7.18 – 7.14 (m, 2H), 2.84 – 2.80 (m, 2H), 1.77 – 1.72 (m, 2H), 1.40 – 1.27 (m, 10H), 0.87 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 169.83, 169.57, 150.80, 149.01, 147.19, 147.05, 142.45, 137.52, 137.30, 135.31, 135.22, 134.86, 133.93, 133.65, 133.01, 131.60, 130.82, 130.46, 130.00, 129.83, 129.68, 129.20, 129.01, 128.59, 128.57, 127.88, 127.44, 127.36, 127.27, 126.71, 125.78, 124.31, 122.87, 122.68, 121.69, 36.38, 32.00, 31.50, 29.65, 29.52, 29.40, 22.78, 14.23.

IR (thin film) *v* 1471, 1489, 1587, 2825, 2923, 2952 cm^{-1}. HRMS *m*/*z* (ESI) calcd for [$C_{56}H_{47}N_3H$] ([M+H]$^+$): 762.3843, found: 762.3846.

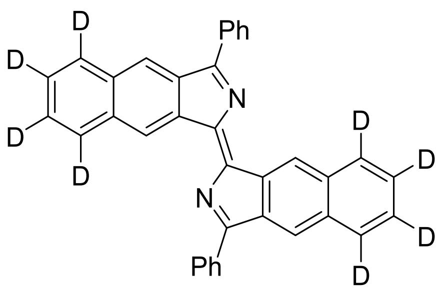
Deuteration Experiments



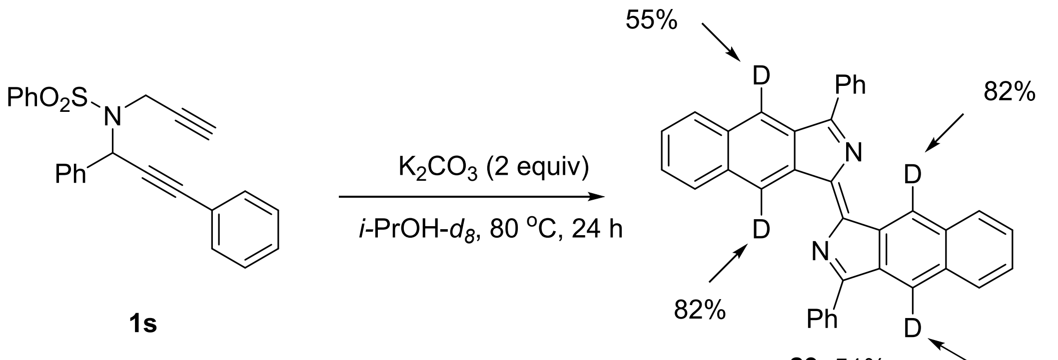
28s

28, 51%

In a flame-dried Schlenk tube, deuterated propargyl sulfonylamide **28s** (0.2 mmol, 1 equiv) and K_2CO_3 (0.6 mmol, 3 equiv) were dissolved in *i*-PrOH (1 mL) under open air conditions. The reaction mixture was stirred at 80 °C for 24 h. Upon completion of the reaction as monitored by TLC, the reaction was quenched with MeOH (5 mL). The suspension was filtered and the filter residue was washed with 5mL of water and 5 mL of MeOH to get the crude product. The crude material was purified by flash chromatography on silica gel using petroleum ether and dichloromethane to yield the deuterated product **28** in 51% yield.



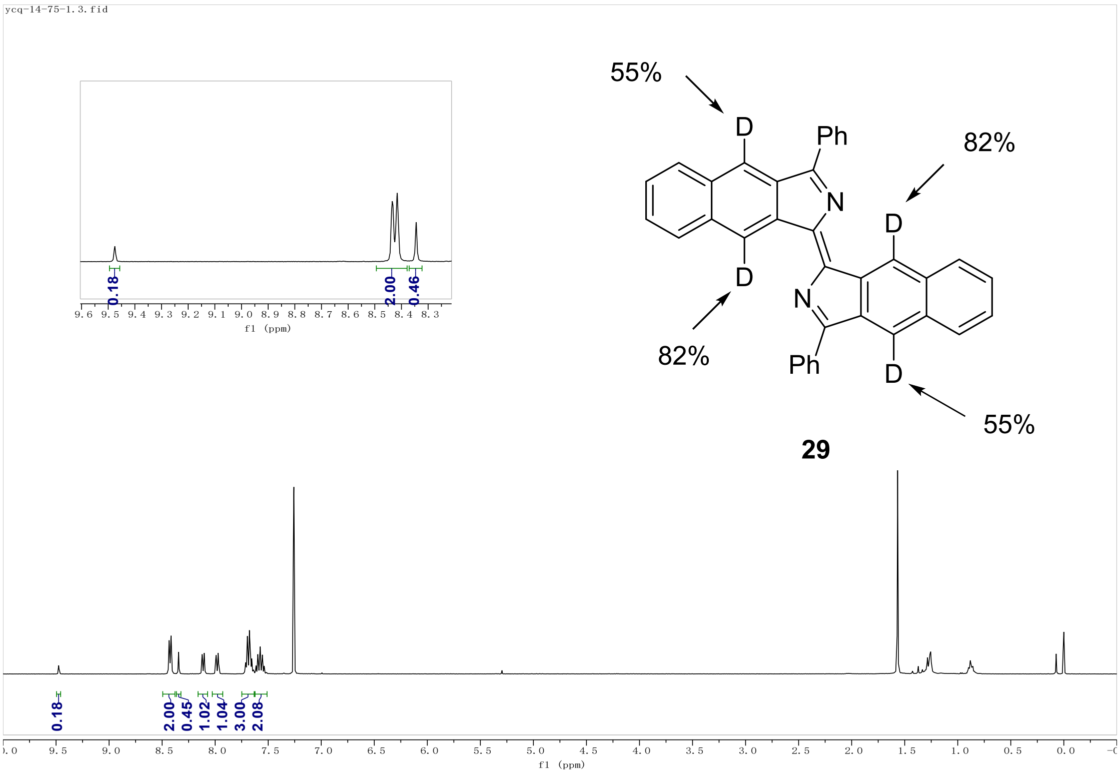
^{1}H NMR (600 MHz, $CDCl_3$) δ 9.49 (s, 2H), 8.42 (d, *J* = 6.9 Hz, 4H), 8.36 (s, 2H), 7.69 (t, *J* = 7.2 Hz, 4H), 7.65 (t, *J* = 7.2 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 170.80, 148.39, 137.12, 135.37, 134.98, 133.66, 133.09, 131.13, 129.25, 129.07, 127.82, 122.96. IR (thin film) *v* 1444, 1645, 1696, 2850, 2921 cm^{-1}. HRMS (ESI) calcd for [$C_{36}H_{14}D_8N_2H$] ([M+H]$^+$): 491.2358, found: 491.2356.



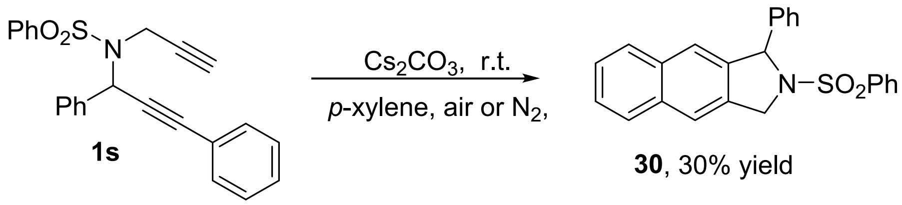
1s

29, 51%

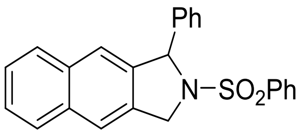
In a flame-dried Schlenk tube, propargyl sulfonylamide **1s** (0.2 mmol, 1 equiv) and K_2CO_3 (0.6 mmol, 3 equiv) were dissolved in *i*-PrOH-d_8 (1 mL) under open air conditions. The reaction mixture was stirred at 80 °C for 24 h. Upon completion of the reaction as monitored by TLC, the reaction was quenched with MeOH (5 mL). The suspension was filtered and the filter residue was washed with 5mL of water and 5 mL of MeOH to get the crude product. The crude material was purified by flash chromatography on silica gel to yield the deuterated product **29** in 51% yield.



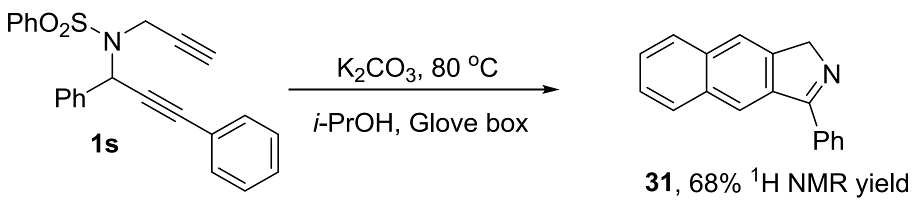
Possible Intermediates



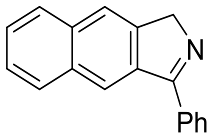
In a flame-dried Schlenk tube, **1s** (0.2 mmol, 1 equiv) and Cs_2CO_3 (0.6 mmol, 3 equiv) were dissolved in *p*-xylene (1 mL) under open air conditions. The reaction mixture was stirred at room temperature for 24 h. On completion the reaction was quenched with saturated aqueous $NaHCO_3$. The aqueous layer was extracted with ethyl acetate and the combined organic layers were washed with brine, dried over $MgSO_4$, and filtered. Then the solution was concentrated under reduced pressure. The crude material was purified by flash chromatography on silica gel using petroleum ether and ethyl acetate to yield the possible intermediate **30** in 30% yield.



^1H NMR (600 MHz, $CDCl_3$) δ 7.78 (d, J = 8.2 Hz, 1H), 7.69 (s, 1H), 7.69 – 7.60 (m, 3H), 7.49 – 7.38 (m, 2H), 7.42 – 7.30 (m, 4H), 7.26 – 7.23 (m, 5H), 6.08 (s, 1H), 5.01 (d, J = 4.8 Hz, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 141.95, 140.03, 138.39, 133.93, 133.30, 133.26, 132.61, 128.95, 128.64, 128.08, 128.02, 127.83, 127.79, 127.37, 126.32, 126.11, 122.71, 121.16, 68.99, 53.52. IR (thin film) v 1446, 1494, 1602, 2858, 2925, 3030, 3060 cm^{-1}. HRMS m/z (ESI) calcd for $[C_{24}H_{19}NO_2SNa]$ ($[M+Na]^+$): 408.1029, found: 408.1027.

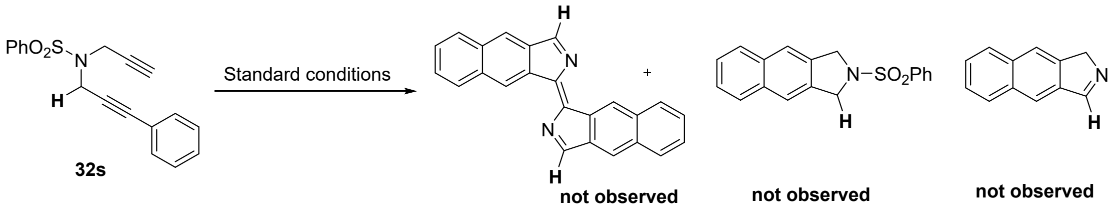


In a flame-dried Schlenk tube, **1s** (0.2 mmol, 1 equiv) and K_2CO_3 (0.2 mmol, 2 equiv) were dissolved in *i*-PrOH (1 mL). The reaction mixture was stirred in glove box under 80 °C for 24 h. Then the solution was concentrated under reduced pressure. The yield of **31** was detected by ^1H NMR in 68 % yield (CH_2Br_2 as an internal standard). The crude material was purified by by thin layer chromatography in glove box. These two reactions suggested that the compound **31** is more likely the intermediate rather than compound **30**.



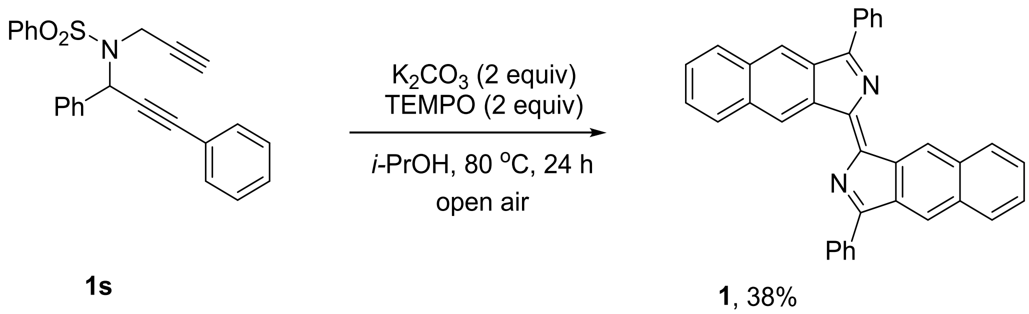
^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (s, 1H), 8.10 – 8.01 (m, 3H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.61 – 7.57 (m, 4H), 7.55 – 7.52 (m, 1H), 5.14 (s, 2H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 172.35, 146.57, 137.23, 134.91, 133.21, 132.73, 130.25, 129.37, 128.88, 128.33, 128.11, 127.26, 125.98, 121.98, 120.83, 63.91. HRMS *m*/*z* (ESI) calcd for [$C_{18}H_{13}NH$] ($[M+H]^+$): 244.1121, found: 244.1121.

Substituent Effect

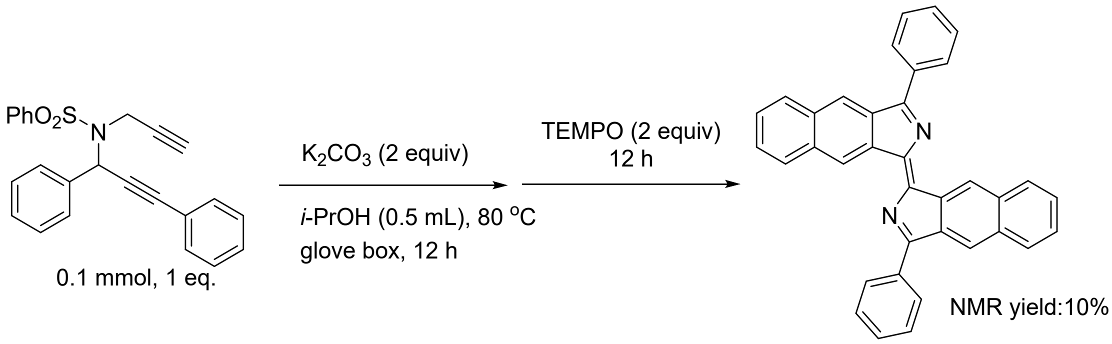


In a flame-dried Schlenk tube, **32s** (0.2 mmol, 1 equiv) and K_2CO_3 (0.4 mmol, 2 equiv) were dissolved in *i*-PrOH (1 mL) under open air conditions. The reaction mixture was stirred at 80 ° C for 24 h. The solution was filtrated with ethyl acetate on silica gel, and then detected by ^{1}H NMR. no reaction occurs, and the starting material was left. This result indicates that the aryl group at R^1 is essential for this reaction.

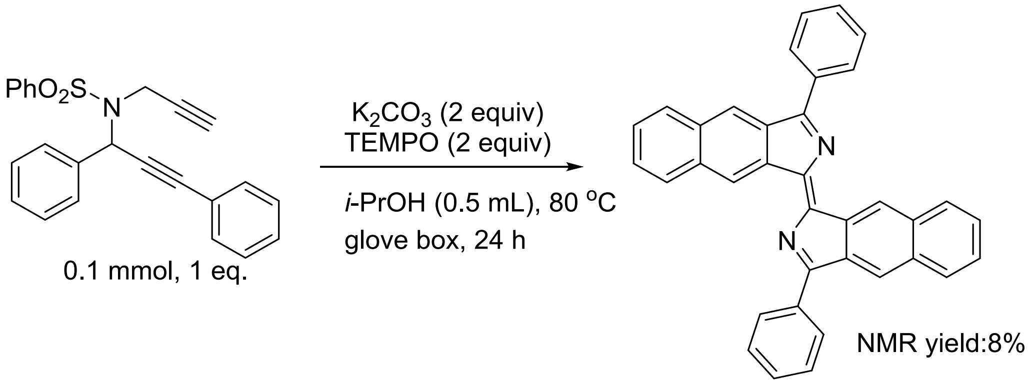
Experiments with TEMPO



In a flame-dried Schlenk tube, **1s** (0.2 mmol, 1 equiv), K_2CO_3 (0.4 mmol, 2 equiv), and TEMPO (0.4 mmol, 2 equiv) were dissolved in *i*-PrOH (1 mL) under open air conditions. The reaction mixture was stirred at 80 °C for 24 h. Upon completion of the reaction as monitored by TLC, the reaction was quenched with MeOH (5 mL). The suspension was filtered and the filter residue was washed with 5 mL of water and 5 mL of MeOH to get the crude product. The crude material was purified by flash chromatography on silica gel using petroleum ether and dichloromethane to give the product **1** in 38% yield.



In a flame-dried Schlenk tube, **1s** (0.2 mmol, 1 equiv) and K_2CO_3 (0.4 mmol, 2 equiv) were dissolved in *i*-PrOH (1 mL) in glove box. The reaction mixture was stirred at 80 °C for 12 h. Then TEMPO (0.4 mmol, 2 equiv) was added and the reaction continued for 12 h. The solution was filtrated, and the filtrate was concentrated under vacuum. 10 % yield of **1** was determined by ^1H NMR analysis with CH_2Br_2 as an internal standard.



In a flame-dried Schlenk tube, **1s** (0.1 mmol, 1 equiv), K_2CO_3 (0.2 mmol, 2 equiv), and TEMPO (0.2 mmol, 2 equiv) were dissolved in *i*-PrOH (0.5 mL) under open air conditions. The reaction mixture was stirred at 80 °C for 24 h. The solution was filtrated and the filtrate was concentrated under vacuum. 8 % yield of **1** was determined by ^1H NMR analysis with CH_2Br_2 as an internal standard.

DFT Caculations

Computation of electronic properties of compound 1, 6 and 8.

The geometrical optimizations and the absorption energy calculations were performed by DFT and TD-DFT methods at the B3LYP-D3/Def2-SVP level of theory with SMD solvation model in solvent THF; in addition, the external iteration for the self-consistent PCM calculations were carried out for the exited states calculations in which the non-equilibrium solvent field was read from the optimized ground states.

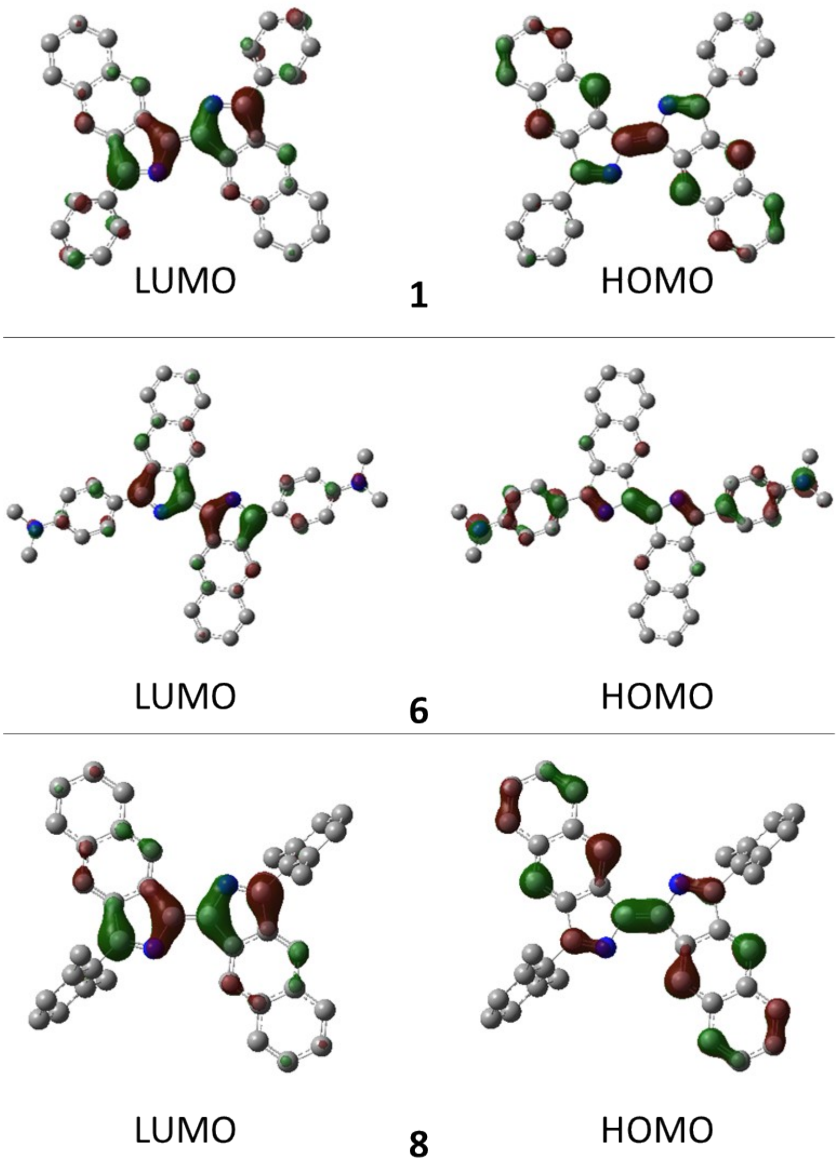


Figure S1. Electronic density contours of the HOMO and LUMO for selected examples at isovalue of 0.04.

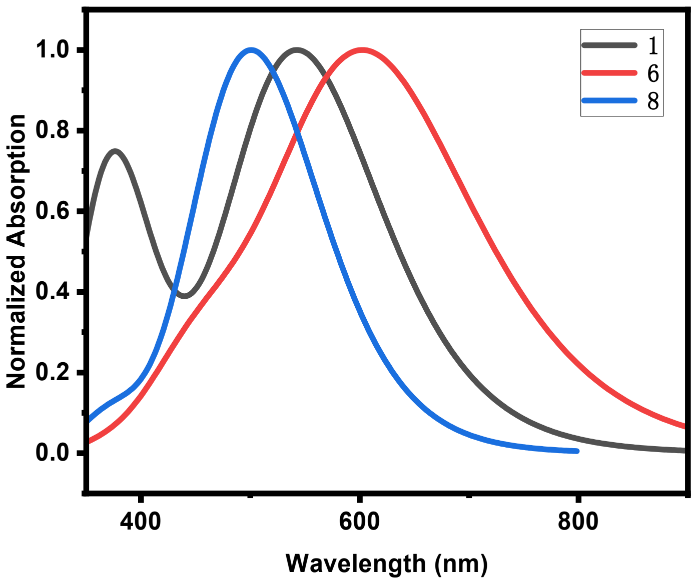


Figure S2. UV-*vis* spectra of **1**, **6** and **8** by TD-DFT method.

Table S2. Calculated data for absorption spectrum.

Compound	$\lambda_{abs,max,exp}$ (nm)	$\lambda_{abs,max,calc}$ (nm)	$E_{gap, opt, calc}$ (eV)	oscillator strength
1	535	543.6	2.28	0.82
6	590	608.7	2.04	1.27
8	499	501.1	2.47	0.84

Table S3. NTO analysis.

Compound	$S_0 \rightarrow S_1$, HOMO→LUMO Transition coefficient
1	1.0
6	1.0
8	1.0

Computation of reaction mechanism

Computational methods: Density functional theory (DFT) computational studies were carried out at B3LYP[1]-D3[2](SMD[3])/Def2-TZVP[4]//B3LYP-D3/Def2-SVP level of theory, in which the D3 dispersion correction is the original D3 damping function. The integration grid option was required at ultrafine for all of calculations. All of structures were optimized in gas-phase with thermal calculations and frequency analyses at 353 K. Transition state structures were searched by simply performing a crude relaxed potential energy surface (RPES) scan connecting reactants and products, and then optimized by the rational function optimization (RFO) method of TS.[5] Imaginary frequencies for all of transition states were verified to be the only one in theirs vibrations and were confirmed the correctness by viewing the normal mode vector or the intrinsic reaction coordinate (IRC)[6] path calculations. The reported Gibbs free energies were the single point electronic energy in 2-Propanol with the gas-phase free energy correction. All calculations were performed by the Gaussian 09 package.[7]

Discussion on the cyclization step through ionic, radical and diradical pathways

Since compound **1s** is activated by addition of a Lewis base, **int1**, a diallenyl benzenesulfonamide intermediate with a relative free energy of -14.1 kcal/mol, was initially thought, based upon the deuteration experiments to cyclize with or without assistance from a potassium ion. The cyclization pathway with potassium assistance is found to be the favorable pathway. **Int2**, combination of **int1** with the potassium ion, turns out to be the most stable species with -22.2 kcal/mol of relative free energy due to the stabilization energy of coordination. The transition state of cyclization, **TS1**, is then located with a barrier of 24.2 kcal/mol leading to the **int3** with a free energy of -55.0 kcal/mol. It is noteworthy that here is a concerted pathway corresponding to the formations of two C-C bonds from **int2** to **int3**. The intrinsic reaction coordinate (IRC) calculation has been conducted to confirm this (Fig. S4). The pathway of neutral species from **int1** without the potassium assistance has also been calculated. However, the free energies of cyclization and benzenesulfonyl migration steps are higher than that through the pathway with the potassium assistance, indicating that the alkaline condition may promote the reaction.

To distinguish the most favorable pathway, radical pathway from **int1** has also been considered. The radical pathway from **int1** homolysis to benzenesulfonyl and diallenylamino radicals (**int6**) has been calculated as well as the cyclization from radical **int6**, but the free energies are much higher, implying that the radical pathway is disfavored. This result is in agreement with the experiment with TEMPO under standard conditions. It is worth to note that the transition state of directly homolytic cleavage of N-S bond in **int1** cannot be located; however, separated benzenesulfonyl radical (•SO_2Ph) and diallenylamino radicals (**int6**) have still been calculated for investigation of the radical cyclization process. The relative free enthalpy of separated SO_2Ph radical with **int6** is 9.1 kcal/mol, much higher than that of **int1,** indicating that homolysis of **int1** to deliver the diallenylamino radical is thermodynamically disfavored. The cyclization TS of C-C coupling, **TS4**, with 17.5 kcal/mol free enthalpy is subsequently located. However, unlike the concerted **TS1**, a stepwise intermediate **int7** can be found which then through the second C-C coupling transition state, **TS5**, with barrier of 27.5 kcal/mol to form **int8**. The relative free energies of radical cyclization process seem thermodynamically disfavored; in addition, the reaction is almost unaffected by TEMPO suggesting that the reaction may not occur through a radical pathway.

On the other hand, biradical intermediates with and without potassium ion attached, **int9** and **int9'**, can be located by using unrestricted self-consistent field (SCF) method with mixed HOMO and LUMO wavefunctions as initial guess functions for the open-shell singlet calculations. These intermediates then cyclize via the TSs of **TS6** and **TS6'** with barriers of 13.0 and 13.9 kcal/mol, respectively, to result in **int3** and **int3'**. Although the biradical intermediates can be calculated on the open-shell singlet state, the spin expectation values of $\langle S^2 \rangle$ are large (1.01 and 0.95 for **int9** and **int9'**, respectively) implying that the open-shell singlet state brings a serious spin contamination problem, and the biradical intermediates may be the artificial errors. Besides, the TEMPO-adduct on the terminal carbons of propargyl groups should be observed if these biradical stationary points are the reasonable existent.

Finally, the elimination of the benzenesulfonyl group from **int3** was investigated. No transition state for the direct benzenesulfonyl elimination was found, but the transition state (**TS2**) of the benzenesulfonyl migration with a barrier of 24.3 kcal/mol, was found to lead to **int4**. The benzenesulfonyl group in **int4** then can abstract the terminal hydrogen of the propargyl group, forming HSO_2Ph with **int5**, from the transition state (**TS3**).

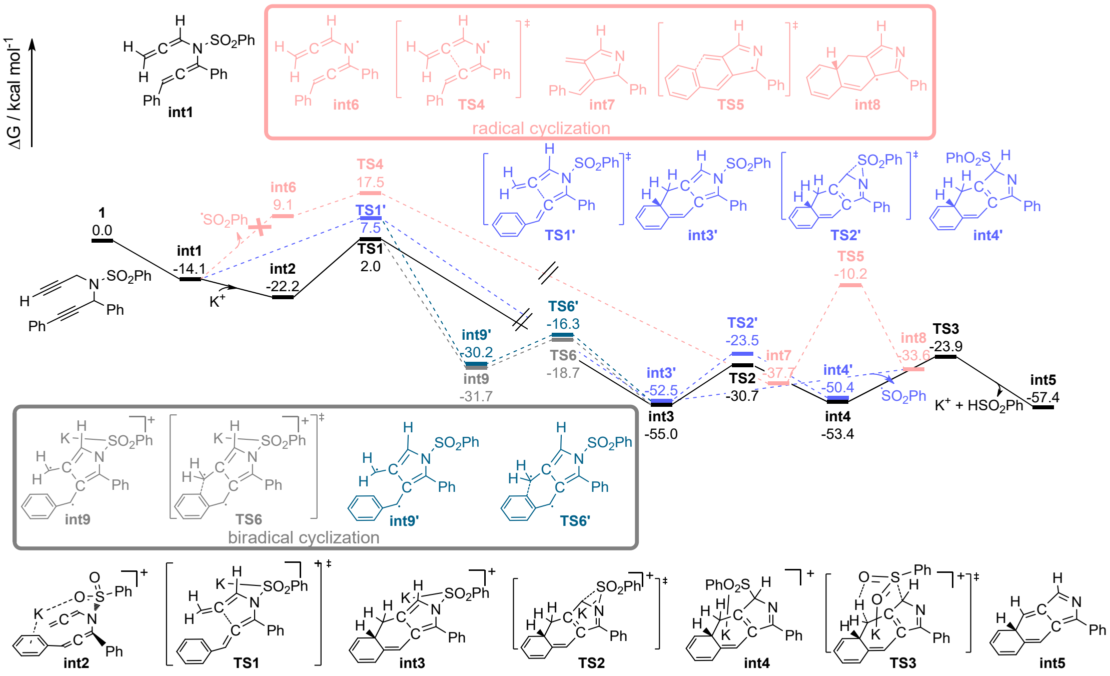


Figure S3. Free energy profile of reaction pathways corresponding to cation, neutral species and radical cyclization process.

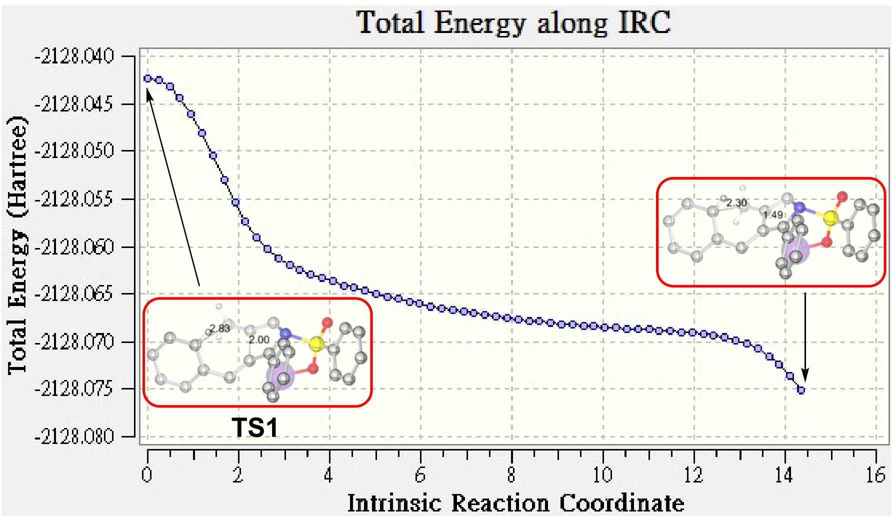


Figure S4. IRC path from **TS1** toward to **int3**. No stationary point (local minimum point) exists in this path.

Table S4. Electronic potential energies and correction to zero point energies, thermal energies, enthalpies, free energies (in Hartree) and imaginary frequencies (cm^{-1}) of optimized structures calculated at the B3LYP-D3/Def2-TZVP/(SMD- 2-Propanol)//B3LYP-D3/Def2-SVP.

Entry	Structure	$E_{el,sol}$	$E_{el,gas}$	$cZPE_{gas}$	$cU_{353,gas}$	$cH_{353,gas}$	$cG_{353,gas}$	Imaginary Frequency
1	**1s**	-1529.751289	-1528.296532	0.365494	0.399215	0.400334	0.290638	
2	**int1**	-1529.772273	-1528.319077	0.364260	0.398018	0.399137	0.289075	
3	K^+	-599.849383	-599.682772	0.000000	0.001678	0.002796	-0.018449	
4	**int2**	-2129.650076	-2128.074121	0.364893	0.401330	0.402448	0.286145	
5	**TS1**	-2129.615783	-2128.042386	0.364460	0.399283	0.400401	0.290531	-441.4025
6	**int3**	-2129.715077	-2128.146136	0.370866	0.404343	0.405461	0.298879	
7	**TS2**	-2129.672318	-2128.106760	0.368095	0.401647	0.402765	0.294804	-171.8287
8	**int4**	-2129.709617	-2128.144442	0.370375	0.404038	0.405156	0.296024	
9	**TS3**	-2129.655670	-2128.105583	0.363262	0.397166	0.398284	0.289150	-652.1045
10	K^++HSO_2Ph	-1380.942036	-1380.188070	0.110481	0.124108	0.125227	0.062718	
11	**int5**	-748.743864	-747.921837	0.255190	0.274388	0.275507	0.203243	
12	**35**	-748.819974	-747.999252	0.257395	0.276231	0.277349	0.205978	
13	**TS1'**	-1529.741232	-1528.290604	0.363336	0.395687	0.396805	0.292574	-511.6211
14	**int3'**	-1529.847576	-1528.404308	0.370556	0.401210	0.402328	0.303248	
15	**TS2'**	-1529.798661	-1528.354976	0.367769	0.398454	0.399572	0.300575	-177.6683
16	**int4'**	-1529.842893	-1528.394473	0.369827	0.400590	0.401709	0.301944	
17	SO_2Ph	-780.436090	-779.809793	0.098653	0.108884	0.110002	0.057057	
18	**int6**	-749.267057	-748.441985	0.259511	0.282124	0.283243	0.199973	
19	**TS4**	-749.255964	-748.431095	0.259320	0.280859	0.281978	0.202170	-505.8355
20	**int7**	-749.350143	-748.528394	0.264135	0.284895	0.286013	0.208494	
21	**TS5**	-749.307529	-748.484113	0.263110	0.282917	0.284036	0.209720	-588.8237
22	**int8**	-749.348026	-748.524941	0.265974	0.285579	0.286697	0.212799	
23	**int9**	-2129.670316	-2128.100700	0.365819	0.400896	0.402015	0.291295	
24	**TS6**	-2129.650950	-2128.080335	0.365286	0.399315	0.400434	0.292684	-544.5143
25	**int9'**	-1529.804202	-1528.360651	0.365478	0.397711	0.398830	0.295498	
26	**TS6'**	-1529.783134	-1528.338256	0.364794	0.396030	0.397148	0.296573	-532.3474

Coordinate of optimized structures

Structure S1.   1s

E(RB3LYP)sol = -1529.75128876   E(RB3LYP)gas = -1528.29653221

6	1.582840	-0.199655	1.033522
6	2.746260	-0.034647	0.728253
6	4.068349	0.189107	0.230363
7	-0.401943	-1.388369	0.265266
6	-0.080667	-2.805143	0.464695
6	-0.885347	-3.392727	1.540473
6	-1.550932	-3.858851	2.438882
1	-2.139149	-4.282775	3.231214
6	5.196490	0.185964	1.074330
6	6.468333	0.409220	0.544964
6	6.632114	0.635355	-0.826120
6	5.515905	0.638995	-1.671186
6	4.240441	0.419187	-1.152127
16	-0.662032	-0.834385	-1.321645
8	0.257000	0.267864	-1.619784
8	-0.706287	-2.033660	-2.165280
6	-2.323417	-0.159661	-1.254350
6	-2.523475	1.189645	-1.539533
6	-3.824133	1.699924	-1.490471
6	-4.895089	0.863589	-1.165776
6	-4.675141	-0.492915	-0.890626
6	-3.383075	-1.015142	-0.936904
1	0.996166	-2.924327	0.688912
1	-0.265006	-3.336951	-0.479536
1	5.064364	0.008071	2.143729
1	7.338423	0.406049	1.206471
1	7.630204	0.808748	-1.236487
1	5.640935	0.815103	-2.742635
1	3.358685	0.419824	-1.797314
1	-1.667625	1.823982	-1.770725
1	-3.996110	2.758515	-1.697933
1	-5.909317	1.268566	-1.124019
1	-5.515046	-1.144946	-0.638947
1	-3.193739	-2.067826	-0.717978
6	0.155667	-0.448707	1.269785
1	0.053130	-0.993118	2.224544
6	-0.705955	0.806667	1.400540
6	-2.006942	0.664288	1.905727
6	-0.257464	2.068697	1.001437
6	-2.849431	1.770318	2.009895
1	-2.362737	-0.328480	2.194089
6	-1.101305	3.179398	1.109282
1	0.746876	2.173831	0.588761
6	-2.396562	3.033742	1.611779
1	-3.864610	1.646829	2.394669
1	-0.743607	4.162333	0.792164
1	-3.056223	3.901784	1.689980

Structure S2.   int1

E(RB3LYP)sol = -1529.77227319   E(RB3LYP)gas = -1528.31907736

6	1.334028	-0.108812	-0.767541
6	2.444214	-0.376399	-1.414591
6	3.810631	-0.202079	-0.883179
7	-0.331383	-0.960313	0.663389
6	-0.060355	-1.128103	2.039425
6	0.709556	-0.331094	2.748831
6	1.485677	0.444048	3.464126
1	1.097527	1.326466	3.989683
6	4.042794	0.309471	0.409241
6	5.343271	0.462478	0.884951
6	6.437224	0.109051	0.083375
6	6.217904	-0.398836	-1.199779
6	4.914453	-0.552567	-1.679615
16	-1.305167	-2.093652	-0.171918
8	-0.701730	-2.304557	-1.484438
8	-1.544846	-3.189096	0.769439
6	-2.840024	-1.203468	-0.415522
6	-2.993189	-0.417171	-1.560172
6	-4.152163	0.349713	-1.696726
6	-5.136536	0.318163	-0.703445
6	-4.974091	-0.489370	0.428767
6	-3.819358	-1.259662	0.580451
1	2.355323	-0.772747	-2.435337
1	-0.541201	-2.003147	2.486133
1	3.191332	0.582875	1.037652
1	5.508347	0.860916	1.889504
1	7.456012	0.230114	0.460011
1	7.065050	-0.677822	-1.831591
1	4.747171	-0.951993	-2.683821
1	-2.210682	-0.408815	-2.319980
1	-4.284058	0.977432	-2.580905
1	-6.039775	0.923233	-0.813945
1	-5.751821	-0.521852	1.195573
1	-3.671949	-1.902200	1.450319
6	0.229683	0.133675	-0.085349

1	2.560704	0.243506	3.566956
6	-0.471866	1.443876	-0.047261
6	-1.575838	1.644433	0.798360
6	-0.050420	2.508069	-0.866267
6	-2.245535	2.869666	0.817185
1	-1.918212	0.833682	1.440490
6	-0.719745	3.730767	-0.845552
1	0.807271	2.366451	-1.528391
6	-1.823680	3.918042	-0.004552
1	-3.106125	3.001061	1.477897
1	-0.379961	4.543472	-1.492784
1	-2.349797	4.875872	0.008526

Structure S3. int2

E(RB3LYP)sol = -2129.65007560 E(RB3LYP)gas = -2128.07412053

6	-0.318995	0.221200	0.883195
6	-1.246785	-0.357654	1.612332
6	-2.694884	-0.085680	1.464493
7	0.843478	0.128544	-1.204993
6	0.295361	0.727805	-2.375250
6	-0.626189	1.672922	-2.351958
6	-1.421761	2.712059	-2.331375
1	-1.017365	3.729233	-2.250725
6	-3.168277	1.040098	0.753598
6	-4.535185	1.209828	0.522794
6	-5.456673	0.263537	0.997105
6	-5.000252	-0.842740	1.722007
6	-3.631331	-1.013458	1.960738
16	0.988199	-1.586059	-1.317149
8	-0.340548	-2.196064	-1.045196
8	1.596985	-1.838426	-2.618266
6	2.093687	-1.968854	0.014678
6	1.630818	-2.698274	1.113014
6	2.533076	-3.000618	2.134970
6	3.862836	-2.573764	2.045633
6	4.307478	-1.851617	0.931111
6	3.423087	-1.547365	-0.103910
1	-0.961893	-1.157178	2.310064
1	0.724995	0.365239	-3.315315
1	-2.452430	1.779824	0.385363
1	-4.888574	2.093266	-0.015332
1	-6.525944	0.401909	0.821120
1	-5.713445	-1.571916	2.114106
1	-3.282470	-1.879034	2.530868
1	0.590155	-3.021430	1.154502
1	2.197783	-3.572978	3.002563
1	4.562661	-2.811263	2.850166
1	5.349074	-1.530577	0.864641
1	3.755335	-1.000811	-0.988227
6	0.575582	0.753652	0.070097
1	-2.512540	2.620430	-2.398762
6	1.342394	1.993185	0.353720
6	2.496791	2.305802	-0.383608
6	0.927422	2.865559	1.376791
6	3.223299	3.464448	-0.098820
1	2.827077	1.636835	-1.179485
6	1.656434	4.019198	1.659596
1	0.025781	2.636222	1.950200
6	2.807552	4.323457	0.922094
1	4.119941	3.696035	-0.678542
1	1.323989	4.688402	2.456632
1	3.376087	5.229904	1.142563
19	-2.722008	-1.335548	-1.541981

Structure S4. TS1

E(RB3LYP)sol = -2129.61578339 E(RB3LYP)gas = -2128.04238551

6	-1.379697	-0.047248	0.167172
6	-2.433767	0.394549	0.917329
6	-3.712836	0.758108	0.376581
7	0.505385	-0.867141	-0.992651
6	-0.488189	-1.770061	-1.444535
6	-1.769149	-1.512981	-1.133147
6	-3.062565	-1.684191	-1.497450
1	-3.388855	-1.499994	-2.525007
6	-3.886331	0.983532	-1.015424
6	-5.154519	1.272781	-1.533482
6	-6.260199	1.333092	-0.687743
6	-6.104249	1.122474	0.696678
6	-4.852755	0.844171	1.222056
16	1.802169	-1.771919	-0.183595
8	1.305413	-2.075525	1.186511
8	2.112222	-2.883897	-1.077700
6	3.170713	-0.659344	-0.070208
6	3.378379	0.064318	1.107675
6	4.449233	0.956678	1.152588
6	5.285751	1.105701	0.040430
6	5.067720	0.358836	-1.123638
6	4.001205	-0.538032	-1.189707

1	-2.364252	0.312119	2.011881
1	-0.148487	-2.653841	-1.986480
1	-3.011358	1.021332	-1.663537
1	-5.271425	1.463321	-2.602833
1	-7.248747	1.559407	-1.094278
1	-6.972875	1.182852	1.356521
1	-4.733540	0.682069	2.297171
1	2.708397	-0.062509	1.957670
1	4.628089	1.540672	2.057416
1	6.120811	1.808829	0.082657
1	5.733453	0.471701	-1.981894
1	3.815999	-1.137221	-2.082774
6	-0.107856	0.174849	-0.209730
1	-3.845168	-1.941782	-0.778140
6	0.641070	1.433479	-0.016258
6	1.525081	1.886721	-1.013250
6	0.479283	2.198306	1.151738
6	2.238582	3.071412	-0.836865
1	1.651498	1.298607	-1.923199
6	1.197430	3.381802	1.326708
1	-0.206888	1.856168	1.929114
6	2.081013	3.820610	0.334365
1	2.921159	3.412802	-1.618370
1	1.068429	3.964732	2.241716
1	2.642645	4.747547	0.472258
19	-1.033287	-3.033059	1.712337

Frequencies -- -441.4025
Red. masses -- 5.7330
Frc consts -- 0.6581
IR Inten -- 6.9104

Structure S5. int3

E(RB3LYP)sol = -2129.71507735 E(RB3LYP)gas = -2128.14613645

6	-1.478385	0.135333	-0.226358
6	-2.488579	1.137710	0.026775
6	-3.797321	0.889155	-0.291764
7	0.391356	-1.063144	-0.638469
6	-0.712516	-1.926407	-0.810467
6	-1.858368	-1.218153	-0.588659
6	-3.308305	-1.600962	-0.654868
1	-3.474831	-2.433501	-1.354608
6	-4.172075	-0.384342	-1.054306
6	-5.645322	-0.698159	-1.041657
6	-6.565382	0.210510	-0.664963
6	-6.159969	1.525413	-0.186631
6	-4.850080	1.840204	-0.004816
16	1.721592	-1.818756	0.229733
8	1.416164	-1.598603	1.665704
8	1.798091	-3.173851	-0.297177
6	3.181169	-0.912886	-0.191273
6	3.758372	-0.059812	0.752723
6	4.923917	0.621580	0.400633
6	5.484371	0.444169	-0.868836
6	4.894097	-0.424977	-1.795817
6	3.734162	-1.122629	-1.460033
1	-2.199601	2.106651	0.441511
1	-0.549470	-2.967715	-1.077555
1	-3.919487	-0.158192	-2.114835
1	-5.948107	-1.683123	-1.409358
1	-7.630903	-0.026871	-0.711723
1	-6.934887	2.255503	0.059826
1	-4.566739	2.813024	0.406793
1	3.295698	0.073290	1.730289
1	5.392129	1.297275	1.119047
1	6.395195	0.983753	-1.138700
1	5.345468	-0.567582	-2.779935
1	3.268908	-1.818137	-2.160927
6	-0.091344	0.209145	-0.250887
1	-3.650925	-1.957461	0.336814
6	0.786755	1.378487	-0.097604
6	1.705701	1.710565	-1.110994
6	0.702811	2.209098	1.034563
6	2.529607	2.827914	-0.983223
1	1.765365	1.084044	-2.002308
6	1.527184	3.329896	1.161346
1	-0.015891	1.980037	1.826956
6	2.446437	3.639199	0.154029
1	3.237915	3.070356	-1.778574
1	1.451583	3.963973	2.047872
1	3.091162	4.515619	0.251901
19	-0.928063	-1.072078	2.666914

Structure S6. TS2

E(RB3LYP)sol = -2129.67231825 E(RB3LYP)gas = -2128.10675952

6	-1.332514	0.375023	-0.681371
6	-2.407850	1.173273	-0.199974
6	-3.710522	0.694940	-0.256482
7	0.638950	-0.379254	-1.518957

6	-0.338603	-1.416285	-1.588379
6	-1.549597	-0.980435	-1.106140
6	-2.883198	-1.642989	-0.926786
1	-3.050262	-2.432980	-1.674029
6	-4.014250	-0.596511	-1.007893
6	-5.373242	-1.172041	-0.732249
6	-6.342108	-0.454306	-0.122556
6	-6.069592	0.888362	0.349396
6	-4.814380	1.430467	0.290301
16	1.395581	-1.832683	0.231444
8	0.731613	-1.097387	1.362538
8	1.337336	-3.307935	0.210202
6	3.107590	-1.310357	0.179958
6	3.446601	-0.025432	0.613514
6	4.783464	0.365264	0.529580
6	5.743898	-0.512987	0.012139
6	5.377694	-1.792568	-0.420714
6	4.045158	-2.204393	-0.345699
1	-2.227439	2.185903	0.168755
1	-0.089022	-2.366949	-2.058983
1	-4.051852	-0.263410	-2.072607
1	-5.572361	-2.181412	-1.103877
1	-7.340559	-0.873440	0.020844
1	-6.886286	1.465178	0.791078
1	-4.625675	2.426111	0.701695
1	2.687328	0.650362	1.006363
1	5.073022	1.362817	0.866676
1	6.787460	-0.196645	-0.054880
1	6.131553	-2.475804	-0.817960
1	3.737395	-3.199548	-0.670627
6	0.061321	0.668024	-0.935781
1	-2.938091	-2.151798	0.059064
6	0.831263	1.880668	-0.615431
6	1.924955	2.243313	-1.424938
6	0.560732	2.651749	0.530436
6	2.715310	3.344803	-1.099580
1	2.148032	1.639951	-2.306397
6	1.354326	3.755068	0.857146
1	-0.265652	2.379560	1.191248
6	2.434288	4.105883	0.041899
1	3.557615	3.614189	-1.741329
1	1.131586	4.340306	1.752729
1	3.053722	4.969825	0.293787
19	-1.364133	-0.551744	2.544934

Frequencies -- -171.8287

Red. masses -- 10.3567

Frc consts -- 0.1802

IR Inten -- 66.3553

Structure S7. int4

E(RB3LYP)sol = -2129.70961713 E(RB3LYP)gas = -2128.14444160

6	-1.048939	0.834852	-0.782988
6	-2.349163	1.214890	-0.276897
6	-3.400823	0.340734	-0.370791
7	1.240873	0.743943	-1.140270
6	0.667987	-0.543602	-1.394587
6	-0.815215	-0.412578	-1.293902
6	-1.859946	-1.467880	-1.416838
1	-1.783015	-2.005175	-2.375595
6	-3.292346	-0.898841	-1.264037
6	-4.264010	-1.990362	-0.895287
6	-5.342838	-1.748666	-0.118416
6	-5.584465	-0.421752	0.427877
6	-4.659654	0.571597	0.302151
16	1.161739	-1.599911	0.111079
8	0.676935	-0.853559	1.309355
8	0.596096	-2.951521	-0.090412
6	2.935706	-1.665464	0.134943
6	3.652818	-0.540747	0.560397
6	5.045866	-0.613975	0.560402
6	5.690764	-1.785810	0.143888
6	4.951882	-2.897342	-0.276352
6	3.556130	-2.846251	-0.287112
1	-2.489754	2.176751	0.217086
1	1.099181	-1.089977	-2.247286
1	-3.598362	-0.521358	-2.265106
1	-4.100466	-2.978236	-1.336465
1	-6.060338	-2.544933	0.095647
1	-6.510989	-0.239520	0.977874
1	-4.825289	1.545374	0.772384
1	3.130380	0.364149	0.870763
1	5.631749	0.247813	0.887120
1	6.782329	-1.832324	0.147504
1	5.462169	-3.808847	-0.594886
1	2.955566	-3.701111	-0.602721
6	0.279659	1.521474	-0.734485
1	-1.663097	-2.264931	-0.668099
6	0.552312	2.908379	-0.318887
6	1.584058	3.619362	-0.963191
6	-0.149566	3.528920	0.731329
6	1.886146	4.925302	-0.581277

1	2.134321	3.132260	-1.770035
6	0.165581	4.832318	1.120627
1	-0.916111	2.980926	1.280461
6	1.176642	5.536229	0.459633
1	2.678523	5.472208	-1.097601
1	-0.377528	5.299409	1.945507
1	1.414716	6.560076	0.757697
19	-1.720720	-1.471877	2.140087

Structure S8.   TS3

E(RB3LYP)sol = -2129.65566976   E(RB3LYP)gas = -2128.10558316

6	-1.596974	-0.545301	-0.746151
6	-1.606181	-1.640262	0.192721
6	-0.836465	-2.751499	-0.017774
7	-1.710239	1.470582	-1.919525
6	-0.738587	0.799967	-2.427489
6	-0.604441	-0.534841	-1.767637
6	0.305612	-1.599927	-1.993651
1	0.706075	-1.678461	-3.015946
6	-0.077042	-2.937599	-1.334783
6	1.094603	-3.884359	-1.216856
6	1.200338	-4.762780	-0.197433
6	0.223657	-4.774147	0.888554
6	-0.731978	-3.805518	0.974100
16	1.387331	0.665415	-0.009793
8	0.885252	0.455708	1.408560
8	2.246611	-0.580205	-0.464763
6	2.664564	1.945158	0.103860
6	2.551795	2.890356	1.126351
6	3.496385	3.919656	1.189675
6	4.519445	3.995113	0.238819
6	4.611130	3.039335	-0.780449
6	3.677216	2.003298	-0.858281
1	-2.180210	-1.559658	1.117211
1	-0.117898	1.171425	-3.247850
1	-0.794255	-3.429564	-2.032603
1	1.823114	-3.885987	-2.032981
1	2.019594	-5.486491	-0.176854
1	0.284923	-5.557055	1.648756
1	-1.423386	-3.783683	1.822314
1	1.747438	2.808752	1.859802
1	3.430218	4.665277	1.985455
1	5.252034	4.803837	0.291764
1	5.416819	3.097510	-1.516013
1	3.744722	1.240042	-1.635568
6	-2.294830	0.668502	-0.881982
1	1.295782	-1.186902	-1.387954
6	-3.444954	1.193154	-0.195830
6	-3.821291	2.546358	-0.415089
6	-4.232573	0.404429	0.684557
6	-4.918068	3.089470	0.244596
1	-3.228083	3.145578	-1.105513
6	-5.331539	0.953760	1.330641
1	-4.001795	-0.649978	0.829531
6	-5.674139	2.299460	1.119951
1	-5.192513	4.132832	0.074532
1	-5.936998	0.335211	1.996762
1	-6.539208	2.726816	1.632855
19	1.989421	-1.890786	1.966988

Frequencies -- -652.1045
Red. masses -- 1.8414
Frc consts -- 0.4614
IR Inten -- 1536.0283

Structure S9. $K^+ + HSO_2Ph$

E(RB3LYP)sol = -1380.94203562   E(RB3LYP)gas = -1380.18806996

16	-0.668125	1.149328	0.805944
8	-1.567857	0.014971	1.230137
8	-1.184014	1.550611	-0.772479
6	0.861083	0.354030	0.280162
6	1.185131	-0.881393	0.853189
6	2.402481	-1.479275	0.513087
6	3.274878	-0.839796	-0.373742
6	2.939545	0.401843	-0.928955
6	1.728766	1.013500	-0.600112
1	0.500682	-1.356625	1.559054
1	2.673255	-2.442644	0.951009
1	4.227359	-1.308751	-0.631114
1	3.624366	0.896136	-1.621526
1	1.455538	1.975844	-1.037353
1	-1.583988	2.438576	-0.738742
19	-2.765450	-1.185784	-0.710498

Structure S10.   int5

E(RB3LYP)sol = -748.743864234   E(RB3LYP)gas = -747.921837389

6	-0.031204	0.472811	0.118365
6	-0.739482	-0.766621	0.057814
6	-2.110525	-0.798129	0.118486
7	1.401683	2.273054	-0.034152
6	0.205618	2.775793	0.028313
6	-0.803157	1.725536	0.138726
6	-2.148032	1.747258	0.232968
1	-2.707795	2.688403	0.251598
6	-2.908150	0.465848	0.416841
6	-4.317912	0.442287	-0.126137
6	-4.924800	-0.726177	-0.415314
6	-4.207310	-1.989247	-0.323206
6	-2.866289	-2.012187	-0.088479
1	-0.198422	-1.700739	-0.106824
1	0.019385	3.853196	0.000199
1	-3.056093	0.447211	1.530341
1	-4.851984	1.393979	-0.201690
1	-5.967078	-0.735708	-0.745661
1	-4.748282	-2.919410	-0.512745
1	-2.316073	-2.957206	-0.122969
6	1.300866	0.862180	0.040805
6	2.528890	0.066451	0.015456
6	3.724370	0.645851	-0.462394
6	2.572380	-1.269069	0.469826
6	4.905431	-0.093449	-0.513887
1	3.700689	1.685667	-0.790969
6	3.756402	-2.004696	0.417419
1	1.680871	-1.724538	0.902383
6	4.928123	-1.424010	-0.080679
1	5.818312	0.372792	-0.894119
1	3.768203	-3.035961	0.780152
1	5.855175	-2.001665	-0.120164

Structure S11. 35

E(RB3LYP)sol = -748.819974353 E(RB3LYP)gas = -747.999251507

6	0.084602	0.531373	-0.062194
6	0.702410	-0.697261	0.059478
6	2.124069	-0.764899	0.080954
7	-1.461887	2.255043	-0.133695
6	-0.140232	2.867368	-0.175364
6	0.851278	1.731756	-0.130475
6	2.223771	1.701466	-0.112849
1	2.814992	2.620528	-0.162676
6	2.896462	0.447562	-0.014822
6	4.316387	0.356101	0.005179
6	4.948954	-0.864696	0.115389
6	4.188938	-2.058684	0.213277
6	2.811291	-2.007138	0.197057
1	0.127366	-1.619843	0.155847
1	-0.023633	3.563446	0.675793
1	-0.048867	3.485751	-1.087204
1	4.902225	1.276614	-0.067901
1	6.040622	-0.916175	0.128839
1	4.700732	-3.020244	0.301808
1	2.222997	-2.925935	0.272397
6	-1.334862	0.969258	-0.086704
6	-2.519142	0.080636	-0.037027
6	-3.690526	0.528371	0.600563
6	-2.518692	-1.188412	-0.641644
6	-4.824536	-0.281658	0.649409
1	-3.689394	1.522085	1.052184
6	-3.659090	-1.995474	-0.598859
1	-1.634743	-1.534071	-1.179987
6	-4.811826	-1.548129	0.052459
1	-5.725606	0.075453	1.154789
1	-3.647745	-2.975813	-1.082087
1	-5.701270	-2.182343	0.091126

Structure S12. TS1'

E(RB3LYP)sol = -1529.74123226 E(RB3LYP)gas = -1528.29060367

6	1.542158	-0.395816	-0.607082
6	2.663195	0.178060	-1.133331
6	3.869717	0.403720	-0.387279
7	-0.449388	-1.356045	0.216212
6	0.448950	-2.431010	0.379353
6	1.758519	-2.179733	0.231853
6	3.012683	-2.520076	0.595230
1	3.267650	-2.728552	1.638919
6	3.908890	0.243317	1.022938
6	5.110203	0.397737	1.723764
6	6.289332	0.703982	1.045232
6	6.268247	0.870555	-0.352121
6	5.082109	0.723317	-1.055915
16	-1.900862	-1.786613	-0.700277
8	-1.706882	-1.422008	-2.104482
8	-2.204767	-3.161071	-0.295766
6	-3.142901	-0.708799	0.000310
6	-3.646041	0.335350	-0.775797

6	-4.617157	1.171391	-0.220382
6	-5.066422	0.953569	1.085566
6	-4.557464	-0.108625	1.844189
6	-3.591448	-0.955984	1.300564
1	2.722906	0.271009	-2.225351
1	0.021795	-3.423404	0.520981
1	2.980478	0.062712	1.563834
1	5.118828	0.282125	2.810769
1	7.226249	0.821548	1.595544
1	7.191039	1.114338	-0.885004
1	5.070560	0.844215	-2.142822
1	-3.260326	0.493514	-1.783351
1	-5.014284	2.002201	-0.807543
1	-5.821387	1.615044	1.517832
1	-4.919088	-0.279281	2.860971
1	-3.186335	-1.795839	1.867735
6	0.264672	-0.205968	-0.251156
1	3.836554	-2.521298	-0.124138
6	-0.405816	1.112719	-0.184198
6	-1.081383	1.496215	0.987576
6	-0.373090	1.995065	-1.274583
6	-1.712162	2.737521	1.065146
1	-1.117246	0.804678	1.831160
6	-1.010266	3.235710	-1.197175
1	0.141641	1.690245	-2.187833
6	-1.681486	3.610231	-0.028291
1	-2.236410	3.022502	1.980528
1	-0.986795	3.911773	-2.055709
1	-2.181346	4.580524	0.029948

Frequencies -- -511.6211
Red. masses -- 5.7820
Frc consts -- 0.8917
IR Inten -- 8.2614

Structure S13. int3'

E(RB3LYP)sol = -1529.84757629 E(RB3LYP)gas = -1528.40430807

6	-1.304981	0.164710	0.535307
6	-2.319258	1.115604	0.147838
6	-3.560249	0.679266	-0.218669
7	0.527804	-0.916510	1.241891
6	-0.521577	-1.844860	1.234300
6	-1.656539	-1.203682	0.824651
6	-3.088296	-1.640602	0.745931
1	-3.175346	-2.718523	0.536061
6	-3.825096	-0.826616	-0.343190
6	-5.289074	-1.175773	-0.428424
6	-6.240133	-0.248953	-0.654749
6	-5.901554	1.164914	-0.766251
6	-4.632065	1.596020	-0.546645
16	2.175520	-1.477099	1.162174
8	2.992525	-0.608641	2.000203
8	2.085740	-2.913554	1.412330
6	2.598494	-1.197621	-0.552338
6	3.310721	-0.047698	-0.902127
6	3.600804	0.170653	-2.251067
6	3.183281	-0.749429	-3.218131
6	2.477378	-1.900446	-2.845802
6	2.180558	-2.135230	-1.502479
1	-2.088525	2.184362	0.158069
1	-0.336376	-2.871703	1.535046
1	-3.369051	-1.133822	-1.311899
1	-5.552259	-2.234806	-0.341472
1	-7.288389	-0.546301	-0.748349
1	-6.695873	1.882000	-0.988521
1	-4.398510	2.664816	-0.570642
1	3.618773	0.659679	-0.131542
1	4.151267	1.067251	-2.544429
1	3.411642	-0.571086	-4.271887
1	2.161058	-2.620008	-3.604538
1	1.642034	-3.030122	-1.185669
6	0.052754	0.328401	0.786700
1	-3.586699	-1.462578	1.717845
6	0.867883	1.538832	0.617372
6	0.758705	2.275602	-0.579406
6	1.737424	2.007410	1.620895
6	1.507650	3.437100	-0.773641
1	0.098660	1.909434	-1.368408
6	2.493454	3.162876	1.417802
1	1.826960	1.452392	2.553632
6	2.384544	3.881246	0.221691
1	1.415792	3.990627	-1.711732
1	3.168540	3.508755	2.204662
1	2.978271	4.786008	0.068086

Structure S14. TS2'

E(RB3LYP)sol = -1529.79866105 E(RB3LYP)gas = -1528.35497555

6	0.418275	0.598600	-0.977541
6	1.299502	1.615417	-0.513679

6	2.636377	1.331896	-0.319656
7	-1.351483	-0.581564	-1.786544
6	-0.156119	-1.297204	-2.021645
6	0.939468	-0.605545	-1.541514
6	2.415788	-0.852611	-1.616776
1	2.650031	-1.927334	-1.558334
6	3.121527	-0.106780	-0.462665
6	4.615868	-0.251275	-0.492567
6	5.445064	0.763851	-0.169245
6	4.916031	2.074892	0.161508
6	3.579397	2.339856	0.079429
16	-1.575900	-2.529084	-0.243765
8	-3.033372	-2.402821	-0.080596
8	-0.955030	-3.848757	-0.488943
6	-0.760294	-1.724358	1.138370
6	-1.412186	-0.669002	1.778603
6	-0.737720	0.012250	2.794417
6	0.560725	-0.366014	3.151801
6	1.196717	-1.429341	2.497494
6	0.543399	-2.108275	1.466419
1	0.932745	2.625702	-0.323416
1	-0.177243	-2.215272	-2.608337
1	2.777840	-0.610487	0.469323
1	5.014180	-1.238298	-0.747056
1	6.528015	0.615536	-0.163194
1	5.612874	2.868990	0.441713
1	3.204245	3.348484	0.275382
1	-2.424282	-0.392844	1.481061
1	-1.230911	0.844680	3.301266
1	1.083543	0.169981	3.947738
1	2.206618	-1.726812	2.789919
1	1.015134	-2.931833	0.928009
6	-1.025831	0.531423	-1.134409
1	2.818839	-0.491784	-2.583044
6	-2.064268	1.463976	-0.663468
6	-1.820941	2.429201	0.332938
6	-3.370488	1.358514	-1.183735
6	-2.840078	3.277591	0.773633
1	-0.838609	2.492841	0.801030
6	-4.386336	2.202466	-0.738316
1	-3.569580	0.591456	-1.933566
6	-4.126630	3.172388	0.237940
1	-2.628472	4.017826	1.550026
1	-5.392013	2.102649	-1.155044
1	-4.924448	3.833956	0.584856

Frequencies -- -177.6683

Red. masses -- 9.8687

Frc consts -- 0.1835

IR Inten -- 12.3014

Structure S15. int4'

E(RB3LYP)sol = -1529.84289283 E(RB3LYP)gas = -1528.39447272

6	-0.359785	-0.785773	-0.826409
6	-1.106874	-1.925619	-0.340023
6	-2.432151	-1.774513	-0.042494
7	1.324444	0.567764	-1.667446
6	0.065790	1.252122	-1.780845
6	-0.992589	0.344980	-1.260584
6	-2.477209	0.494131	-1.226191
1	-2.758874	1.547044	-1.080445
6	-3.045968	-0.371272	-0.085312
6	-4.550890	-0.362510	-0.052229
6	-5.267562	-1.457291	0.271123
6	-4.610970	-2.730686	0.534952
6	-3.268661	-2.877579	0.372853
16	0.177356	2.809313	-0.708596
8	1.273440	3.630323	-1.230071
8	-1.193160	3.345479	-0.617676
6	0.643829	2.140036	0.892120
6	1.982190	1.804427	1.113397
6	2.328812	1.209418	2.328628
6	1.348463	0.973109	3.299560
6	0.016154	1.334092	3.067483
6	-0.346725	1.920700	1.852280
1	-0.627662	-2.902501	-0.248716
1	-0.104655	1.710740	-2.769628
1	-2.703792	0.115825	0.857822
1	-5.045588	0.591450	-0.258672
1	-6.358466	-1.408334	0.324924
1	-5.223799	-3.587726	0.826039
1	-2.797164	-3.854768	0.513127
1	2.721650	1.990928	0.333770
1	3.366965	0.925558	2.515301
1	1.626117	0.505692	4.247747
1	-0.742845	1.156126	3.833023
1	-1.375848	2.215131	1.640131
6	1.087244	-0.572310	-1.085884
1	-2.905917	0.177789	-2.200583
6	2.188297	-1.479345	-0.709391
6	2.094832	-2.311729	0.420438
6	3.383582	-1.467946	-1.452521

6	3.170266	-3.122754	0.792038
1	1.191864	-2.297384	1.032898
6	4.450847	-2.285946	-1.084796
1	3.454231	-0.804769	-2.316549
6	4.346833	-3.117718	0.037252
1	3.089885	-3.757460	1.678162
1	5.371341	-2.275464	-1.673986
1	5.184986	-3.757802	0.324602

Structure S16. SO_2Ph

E(UB3LYP)sol = -780.436089511 E(UB3LYP)gas = -779.809792948

16	1.713459	-0.000017	-0.257069
8	2.203563	-1.304096	0.269194
8	2.203788	1.303992	0.269654
6	-0.097232	-0.000049	-0.085987
6	-0.768554	-1.224555	-0.052963
6	-2.163106	-1.214910	0.032574
6	-2.857054	0.000053	0.072940
6	-2.162939	1.214987	0.032364
6	-0.768398	1.224582	-0.053336
1	-0.202499	-2.157551	-0.075805
1	-2.708877	-2.160674	0.071426
1	-3.947894	0.000063	0.137726
1	-2.708505	2.160879	0.071097
1	-0.202667	2.157744	-0.075678

Structure S17. int6

E(UB3LYP)sol = -749.267057336 E(UB3LYP)gas = -748.441984684

6	0.090214	0.302231	-0.769983
6	-1.013705	-0.186177	-1.289340
6	-2.217160	-0.604462	-0.544775
7	1.509613	2.152131	-0.228985
6	0.513549	3.057592	-0.104455
6	-0.780202	2.844948	0.215528
6	-2.008818	2.691872	0.629447
1	-2.268543	2.726730	1.696054
6	-2.254685	-0.610541	0.863915
6	-3.412116	-0.991060	1.541032
6	-4.556696	-1.370219	0.827899
6	-4.531344	-1.369784	-0.569903
6	-3.371006	-0.991750	-1.249815
1	-1.075443	-0.272146	-2.385656
1	0.828840	4.104331	-0.224970
1	-1.362701	-0.314990	1.420731
1	-3.423701	-0.993590	2.634118
1	-5.463065	-1.667461	1.361320
1	-5.419062	-1.666335	-1.134495
1	-3.356235	-0.992557	-2.343460
6	1.275479	0.812016	-0.365868
1	-2.831222	2.487540	-0.068247
6	2.441295	-0.095229	-0.115263
6	3.706751	0.448356	0.162602
6	2.297396	-1.493546	-0.146079
6	4.800790	-0.387868	0.395982
1	3.814028	1.533270	0.188437
6	3.391512	-2.326810	0.090102
1	1.317244	-1.930273	-0.352564
6	4.649691	-1.777582	0.361142
1	5.779533	0.050769	0.607982
1	3.260717	-3.411794	0.064064
1	5.506639	-2.430322	0.546571

Structure S18. TS4

E(UB3LYP)sol = -749.255964090 E(UB3LYP)gas = -748.431095034

6	0.048609	0.682068	-0.680209
6	-0.938116	-0.053729	-1.214532
6	-2.125029	-0.522331	-0.508315
7	1.696506	2.280172	-0.052515
6	0.681385	3.125313	-0.005346
6	-0.638294	2.699631	-0.028003
6	-1.890200	2.745335	0.392869
1	-2.166221	3.209680	1.349971
6	-2.242991	-0.417139	0.896912
6	-3.393595	-0.860867	1.547322
6	-4.450526	-1.415760	0.815974
6	-4.346344	-1.530592	-0.576356
6	-3.197766	-1.090279	-1.231003
1	-0.907346	-0.248147	-2.297408
1	0.903109	4.200818	-0.044437
1	-1.414153	0.004558	1.468169
1	-3.466594	-0.777237	2.634748
1	-5.351122	-1.762203	1.329066
1	-5.167107	-1.965953	-1.152124
1	-3.120961	-1.178387	-2.318401
6	1.311883	0.970206	-0.283489

1	-2.699811	2.270816	-0.173557
6	2.339119	-0.090057	-0.080871
6	3.665116	0.281567	0.208355
6	2.026542	-1.459148	-0.169895
6	4.650814	-0.690529	0.389936
1	3.903852	1.342943	0.281337
6	3.014026	-2.427491	0.013285
1	0.999323	-1.766888	-0.374806
6	4.331839	-2.048355	0.292602
1	5.676830	-0.383676	0.609850
1	2.751703	-3.486330	-0.057653
1	5.104117	-2.808251	0.437429

Frequencies -- -505.8355
Red. masses -- 3.6151
Frc consts -- 0.5450
IR Inten -- 12.1481

Structure S19. int7

E(UB3LYP)sol = -749.350142970 E(UB3LYP)gas = -748.528394000

6	-0.042972	0.856848	-0.041607
6	-0.729882	-0.319693	-0.227606
6	-2.158942	-0.604743	-0.125106
7	1.788145	2.307079	-0.026832
6	0.707921	3.053811	-0.025150
6	-0.527999	2.274391	-0.034005
6	-1.758597	2.819475	-0.159580
1	-1.859154	3.906961	-0.225080
6	-2.987644	-0.004996	0.848298
6	-4.337180	-0.341613	0.946009
6	-4.894958	-1.287264	0.076857
6	-4.082965	-1.910703	-0.877347
6	-2.730031	-1.584720	-0.967323
1	-0.121256	-1.183024	-0.512644
1	0.756328	4.146449	-0.031158
1	-2.552897	0.710036	1.549240
1	-4.957713	0.128831	1.713200
1	-5.953644	-1.547277	0.153076
1	-4.506461	-2.660346	-1.550687
1	-2.098517	-2.082714	-1.708253
6	1.408484	0.989343	-0.013041
1	-2.671663	2.228851	-0.224280
6	2.433525	-0.048463	0.051596
6	3.731010	0.241291	-0.435224
6	2.209700	-1.324665	0.617922
6	4.741391	-0.715352	-0.393893
1	3.919303	1.234048	-0.846460
6	3.228170	-2.277883	0.660701
1	1.245351	-1.556734	1.070832
6	4.495490	-1.984248	0.147430
1	5.732371	-0.471823	-0.786132
1	3.033405	-3.254067	1.112620
1	5.290405	-2.733642	0.179978

Structure S20. TS5

E(UB3LYP)sol = -749.307528741 E(UB3LYP)gas = -748.484112931

6	-0.055194	0.533923	-0.279794
6	-0.641908	-0.675017	-0.030993
6	-2.073812	-0.802620	0.176133
7	1.445868	2.262732	-0.175523
6	0.154217	2.774776	-0.332695
6	-0.800605	1.795141	-0.437321
6	-2.231878	1.852076	-0.665324
1	-2.765172	2.773729	-0.410766
6	-2.811837	0.306599	0.746081
6	-4.227793	0.191314	0.845684
6	-4.889787	-0.912905	0.328868
6	-4.166512	-1.988036	-0.228908
6	-2.771575	-1.931628	-0.280504
1	-0.034029	-1.583789	0.010980
1	0.006319	3.853785	-0.406397
1	-2.296706	0.934469	1.476616
1	-4.791008	0.986709	1.340356
1	-5.979663	-0.971786	0.393563
1	-4.693915	-2.866120	-0.607984
1	-2.208210	-2.762078	-0.716040
6	1.362447	0.952731	-0.191200
1	-2.639893	1.307563	-1.522372
6	2.547664	0.094304	-0.045599
6	3.671252	0.574944	0.656423
6	2.613582	-1.188097	-0.624261
6	4.812577	-0.213028	0.794943
1	3.622883	1.576898	1.086531
6	3.758810	-1.975304	-0.484549
1	1.777486	-1.555751	-1.222213
6	4.859720	-1.493949	0.230437
1	5.673411	0.171932	1.347944
1	3.796023	-2.965103	-0.946957
1	5.755188	-2.110925	0.340886

Frequencies -- -588.8237
Red. masses -- 5.9534
Frc consts -- 1.2161
IR Inten -- 39.8287

Structure S21. int8

E(UB3LYP)sol = -749.348025640 E(UB3LYP)gas = -748.524940961

6	-0.042773	0.516731	-0.156505
6	-0.673525	-0.714687	-0.051249
6	-2.077340	-0.788813	0.095698
7	1.450939	2.255102	-0.127517
6	0.143226	2.748232	-0.208363
6	-0.794657	1.748066	-0.226545
6	-2.285846	1.719444	-0.369004
1	-2.753978	2.638151	0.018431
6	-2.854427	0.490423	0.378541
6	-4.340646	0.336339	0.238183
6	-4.936290	-0.879921	0.144149
6	-4.148028	-2.083166	0.099517
6	-2.764564	-2.020816	0.061109
1	-0.103188	-1.646265	-0.058660
1	-0.024758	3.826042	-0.256957
1	-2.665164	0.693104	1.460669
1	-4.941576	1.250331	0.266885
1	-6.025401	-0.957552	0.089464
1	-4.651387	-3.051484	0.047992
1	-2.182319	-2.941010	-0.046055
6	1.377856	0.943281	-0.127514
1	-2.567862	1.644481	-1.437390
6	2.576764	0.097517	-0.043884
6	3.745020	0.613581	0.555020
6	2.617190	-1.207315	-0.573884
6	4.902042	-0.158062	0.640375
1	3.715537	1.631123	0.948466
6	3.778534	-1.978503	-0.487494
1	1.747212	-1.608487	-1.096042
6	4.923509	-1.460568	0.125118
1	5.796082	0.256355	1.113879
1	3.792518	-2.985827	-0.912027
1	5.831446	-2.065246	0.194368

Structure S22. int9

E(UB3LYP)sol = -2129.67031604 E(UB3LYP)gas = -2128.10069952

6	1.515929	-0.264590	0.289312
6	2.486507	0.684027	-0.113031
6	3.906705	0.749420	0.157788
7	-0.550196	-1.119100	0.813539
6	0.379485	-2.124992	1.074081
6	1.674044	-1.673122	0.753792
6	2.809617	-2.487646	0.757649
1	2.728056	-3.525637	1.089373
6	4.514410	0.169562	1.300128
6	5.879387	0.312003	1.533209
6	6.681327	1.035005	0.639080
6	6.097039	1.640718	-0.480492
6	4.729772	1.512867	-0.710073
16	-1.989581	-1.746259	-0.029255
8	-1.600598	-1.755817	-1.461459
8	-2.302833	-2.996462	0.647816
6	-3.278057	-0.564638	0.225261
6	-3.668685	0.265661	-0.828663
6	-4.704613	1.172077	-0.602277
6	-5.322894	1.233599	0.651347
6	-4.921012	0.383525	1.689762
6	-3.892558	-0.535253	1.482835
1	2.090771	1.545246	-0.659425
1	0.054230	-3.104458	1.415816
1	3.897821	-0.359943	2.027773
1	6.323504	-0.130902	2.427982
1	7.752526	1.141146	0.825087
1	6.711955	2.223673	-1.170276
1	4.278363	2.003552	-1.577157
1	-3.163063	0.208589	-1.792084
1	-5.025840	1.835847	-1.407244
1	-6.131407	1.948417	0.821259
1	-5.417454	0.429876	2.661305
1	-3.576128	-1.218545	2.272939
6	0.125132	0.003109	0.300634
1	3.791840	-2.118715	0.467559
6	-0.589534	1.256543	0.014750
6	-1.373294	1.858571	1.017580
6	-0.510492	1.876502	-1.245293
6	-2.061937	3.043758	0.762378
1	-1.436095	1.387186	2.000124
6	-1.199043	3.064968	-1.499221
1	0.085378	1.419101	-2.039742
6	-1.977315	3.650495	-0.495793
1	-2.665567	3.499034	1.550656

1	-1.130349	3.534231	-2.483476
1	-2.515037	4.580689	-0.693367
19	0.866268	-2.056805	-2.342269

Structure S23. TS6

E(UB3LYP)sol = -2129.65094959 E(UB3LYP)gas = -2128.08033493

6	-1.486902	0.035270	-0.014389
6	-2.482329	0.971312	0.444614
6	-3.792135	0.957244	-0.074633
7	0.401364	-0.974368	-0.801634
6	-0.680678	-1.865788	-1.000911
6	-1.844183	-1.296115	-0.546380
6	-3.199729	-1.793700	-0.607784
1	-3.451084	-2.584013	-1.318790
6	-4.106771	0.249000	-1.304357
6	-5.454919	0.134574	-1.720965
6	-6.477973	0.675816	-0.960309
6	-6.178951	1.414632	0.216857
6	-4.873814	1.567583	0.637243
16	1.773313	-1.806792	-0.052183
8	1.456686	-1.857184	1.399661
8	1.917689	-3.049135	-0.799555
6	3.181092	-0.766355	-0.299979
6	3.678658	-0.012646	0.766445
6	4.796133	0.791179	0.540529
6	5.389669	0.828395	-0.726005
6	4.880635	0.055184	-1.777253
6	3.767730	-0.759750	-1.570777
1	-2.233804	1.688138	1.231025
1	-0.500154	-2.846184	-1.435677
1	-3.325381	0.133021	-2.055269
1	-5.678220	-0.363775	-2.667366
1	-7.515867	0.577558	-1.286744
1	-6.992264	1.866906	0.789295
1	-4.651318	2.128827	1.549000
1	3.191291	-0.048271	1.740297
1	5.200906	1.394203	1.355594
1	6.262761	1.462747	-0.895902
1	5.357967	0.080412	-2.759125
1	3.364268	-1.382144	-2.371447
6	-0.116500	0.189355	-0.173342
1	-3.852229	-1.696330	0.261457
6	0.723529	1.369238	0.066144
6	1.550178	1.867140	-0.958625
6	0.705343	2.029483	1.307369
6	2.343494	2.992521	-0.741134
1	1.562558	1.363170	-1.926493
6	1.501496	3.156302	1.523516
1	0.075400	1.646978	2.114752
6	2.323395	3.639189	0.499970
1	2.979716	3.369431	-1.544974
1	1.482810	3.658223	2.493776
1	2.945322	4.521408	0.668478
19	-0.909423	-2.029732	2.449925

Frequencies -- -544.5143

Red. masses -- 5.0715

Frc consts -- 0.8859

IR Inten -- 14.8881

Structure S24. int9'

E(UB3LYP)sol = -1529.80420177 E(UB3LYP)gas = -1528.36065108

6	1.305991	-0.459557	-0.783985
6	2.370865	0.462296	-0.626401
6	3.678952	0.286075	-0.045901
7	-0.815703	-1.191727	-1.153187
6	-0.019373	-2.318924	-1.139649
6	1.323963	-1.932509	-0.962063
6	2.408942	-2.797536	-1.093058
1	2.235887	-3.850420	-1.327067
6	4.003716	-0.757814	0.860257
6	5.270042	-0.847017	1.430759
6	6.259646	0.098273	1.125310
6	5.955028	1.151133	0.252623
6	4.687303	1.249946	-0.314096
16	-2.548242	-1.345228	-0.898243
8	-3.220321	-0.433288	-1.813748
8	-2.786301	-2.785037	-0.938788
6	-2.739766	-0.755414	0.775061
6	-3.187118	0.550058	0.993193
6	-3.302278	1.001413	2.309938
6	-2.973560	0.156160	3.374560
6	-2.533195	-1.151870	3.134259
6	-2.415951	-1.621372	1.825608
1	2.143806	1.485370	-0.943100
1	-0.449005	-3.303975	-1.292266
1	3.237916	-1.485982	1.131147
1	5.488903	-1.658005	2.130760
1	7.253820	0.020928	1.572216

1	6.713795	1.901930	0.016216
1	4.457821	2.079191	-0.989202
1	-3.425140	1.195208	0.146901
1	-3.643584	2.021222	2.500331
1	-3.062496	0.517346	4.402131
1	-2.285172	-1.810021	3.970144
1	-2.087220	-2.640236	1.613193
6	-0.038058	-0.047970	-0.928701
1	3.438385	-2.452609	-1.017059
6	-0.581286	1.313956	-0.828353
6	-0.259167	2.112142	0.288977
6	-1.413528	1.857568	-1.826117
6	-0.769558	3.404162	0.414328
1	0.377292	1.695406	1.071886
6	-1.930526	3.147392	-1.692104
1	-1.665285	1.256432	-2.698911
6	-1.614127	3.924795	-0.572731
1	-0.516463	4.003375	1.292727
1	-2.580378	3.550065	-2.473115
1	-2.019848	4.934791	-0.472714

Structure S25. TS6'

E(UB3LYP)sol = -1529.78313387 E(UB3LYP)gas = -1528.33825564

6	1.180931	0.256342	-0.856816
6	2.199998	1.168417	-0.412753
6	3.427235	0.700095	0.093908
7	-0.753052	-0.709750	-1.533540
6	0.280790	-1.636824	-1.745769
6	1.478997	-1.078587	-1.380952
6	2.819451	-1.613764	-1.517250
1	2.965965	-2.697172	-1.516740
6	3.585608	-0.684019	0.505230
6	4.865127	-1.158685	0.880387
6	5.974285	-0.328621	0.834678
6	5.824449	1.037750	0.475558
6	4.585051	1.540239	0.132470
16	-2.340463	-1.331803	-1.139885
8	-3.332700	-0.376464	-1.615720
8	-2.317968	-2.711452	-1.619823
6	-2.328766	-1.320678	0.647370
6	-2.929606	-0.257555	1.326772
6	-2.860263	-0.234496	2.721633
6	-2.199160	-1.257269	3.410006
6	-1.607714	-2.316970	2.710980
6	-1.670854	-2.357941	1.317131
1	2.047053	2.242989	-0.549126
1	0.054788	-2.601414	-2.190652
1	2.707857	-1.227589	0.854189
1	4.967389	-2.191137	1.225482
1	6.959627	-0.711141	1.112735
1	6.698896	1.693616	0.470727
1	4.477134	2.589021	-0.158535
1	-3.430294	0.533153	0.766826
1	-3.320999	0.590195	3.269997
1	-2.145678	-1.231103	4.501225
1	-1.099794	-3.117213	3.254288
1	-1.228965	-3.179236	0.750359
6	-0.191552	0.452430	-0.952496
1	3.573839	-1.023345	-2.041475
6	-0.961277	1.629944	-0.536392
6	-0.660645	2.256924	0.690542
6	-1.980722	2.174266	-1.341503
6	-1.365576	3.387656	1.103875
1	0.113917	1.829393	1.329811
6	-2.687719	3.300803	-0.920015
1	-2.221876	1.700977	-2.292262
6	-2.386016	3.911268	0.302551
1	-1.124967	3.855250	2.062111
1	-3.478632	3.707689	-1.555014
1	-2.943441	4.793147	0.628472

Frequencies -- -532.3474

Red. masses -- 4.8853

Frc consts -- 0.8157

IR Inten -- 2.9282

Measurement and characterization of photophysical properties

Materials and Methods

UV-visible absorption: The UV-visible absorption spectra of samples were dissolved in THF and recorded on Shimadzu UV-2450 UV-Vis spectrophotometer.

Fluorescence: The Fluorescence spectra of sample were dissolved in THF and recorded on the Edinburgh Instruments FLS5 fluorescence spectrofluorometer.

Absolute fluorescence quantum yield: The absolute fluorescence quantum yield of samples was dissolved in THF ($5*10^{-6}$ mol/L) and measured on the Edinburgh Instruments FLS1000 three-monochromator spectrophotometer.

Molar absorption coefficient: The samples were dissolved in THF and mixed into solutions of different concentrations to test their UV-vis absorption spectra. The molar absorption coefficient was obtained by plotting the maximum absorption intensity of different concentrations.

UV-visible absorption spectrum and fluorescence spectra of 1-18

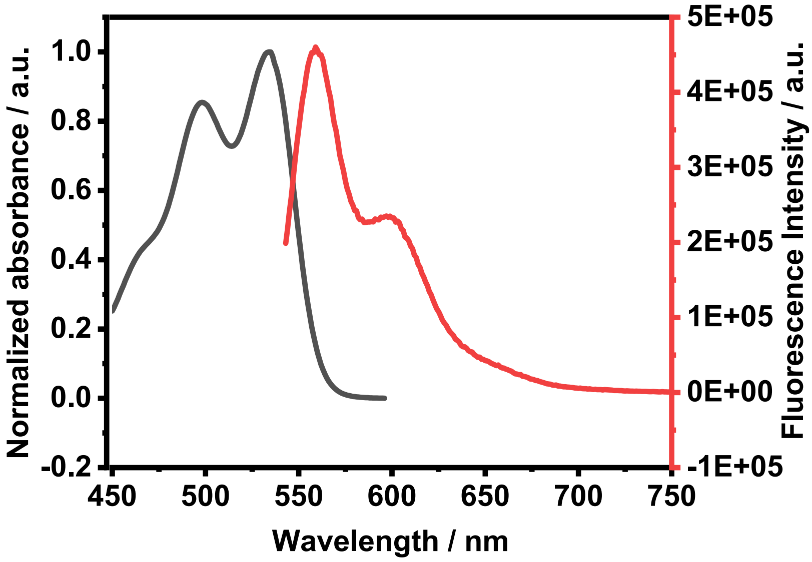


Figure S5. UV-visible absorption spectrum and fluorescence spectrum of **1**

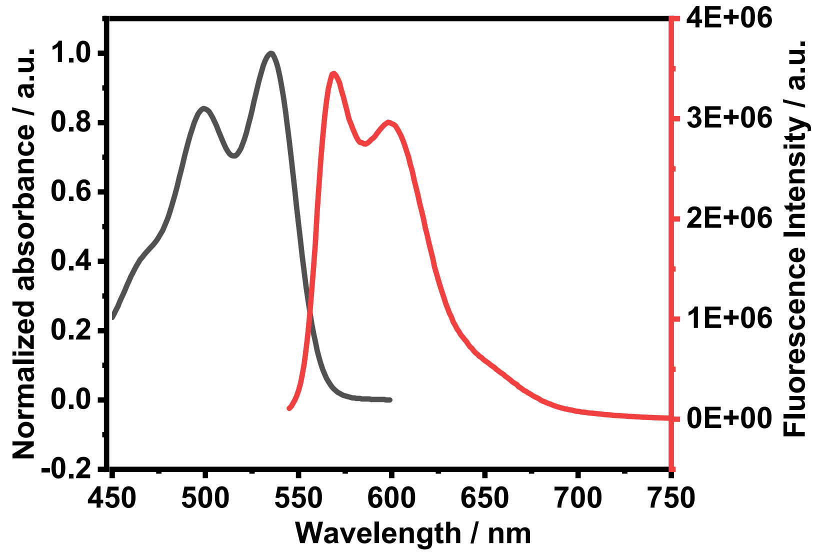


Figure S6. UV-visible absorption spectrum and fluorescence spectrum of **2**

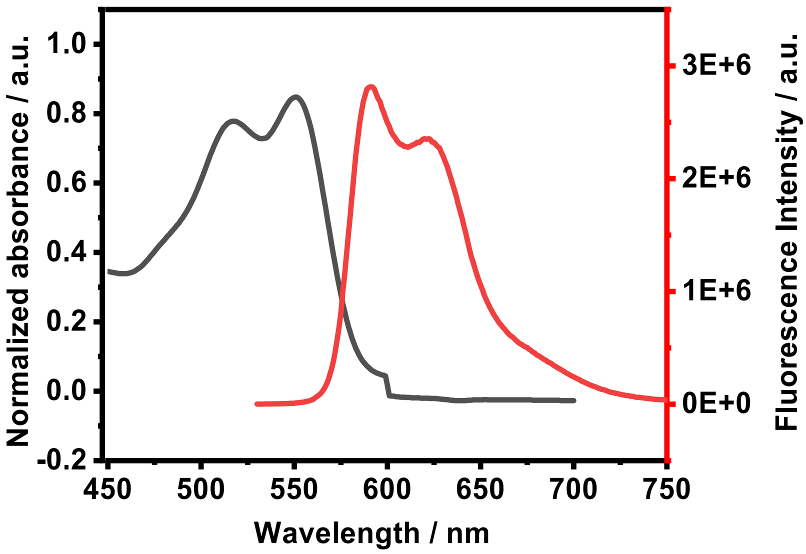


Figure S7. UV-visible absorption spectrum and fluorescence spectrum of **3**

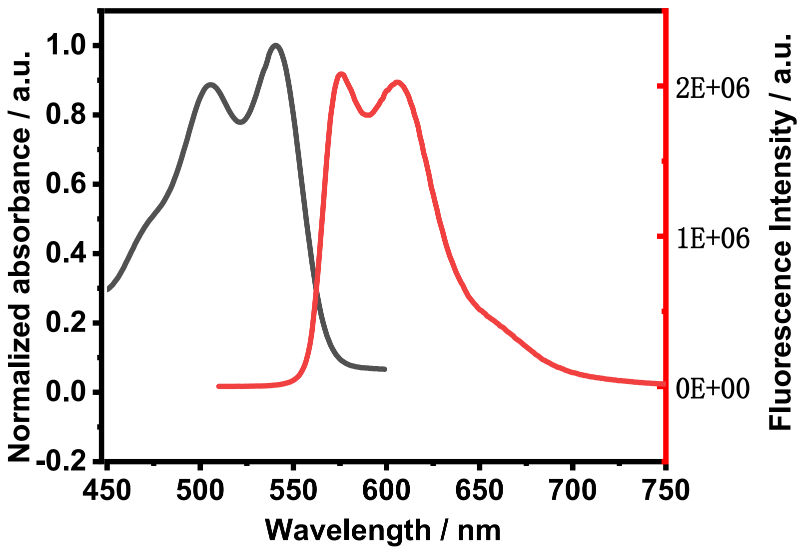


Figure S8. UV-visible absorption spectrum and fluorescence spectrum of **4**

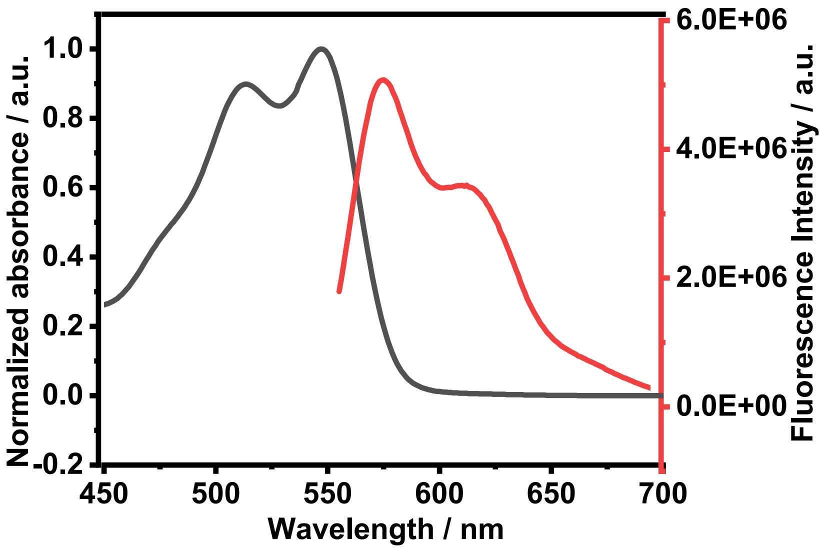


Figure S9. UV-visible absorption spectrum and fluorescence spectrum of **5**

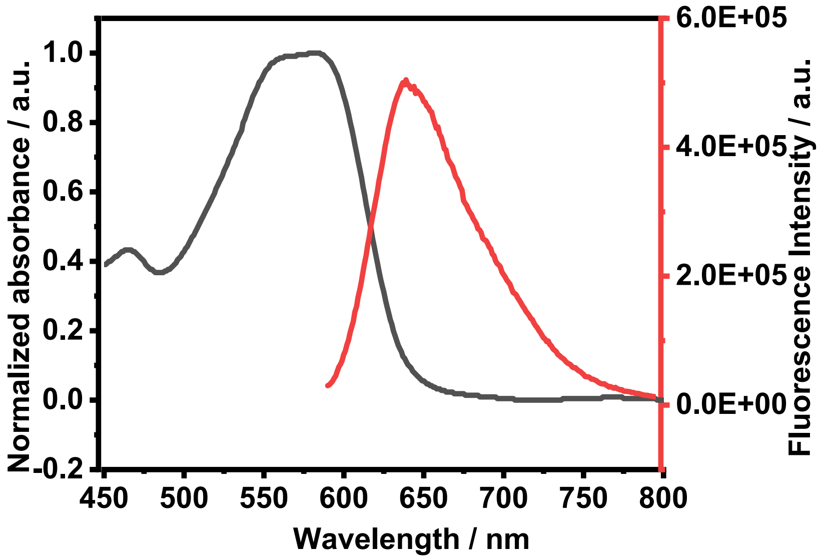


Figure S10. UV-visible absorption spectrum and fluorescence spectrum of **6**

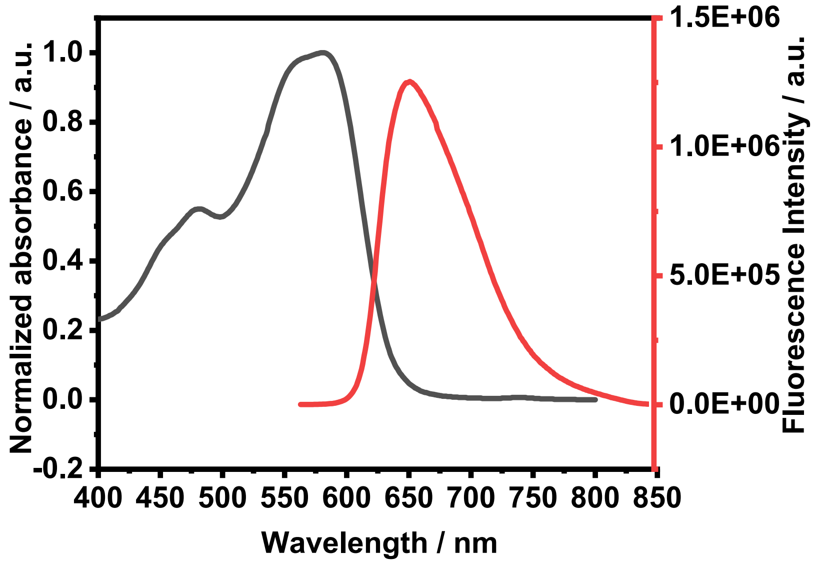


Figure S11. UV-visible absorption spectrum and fluorescence spectrum of **7**

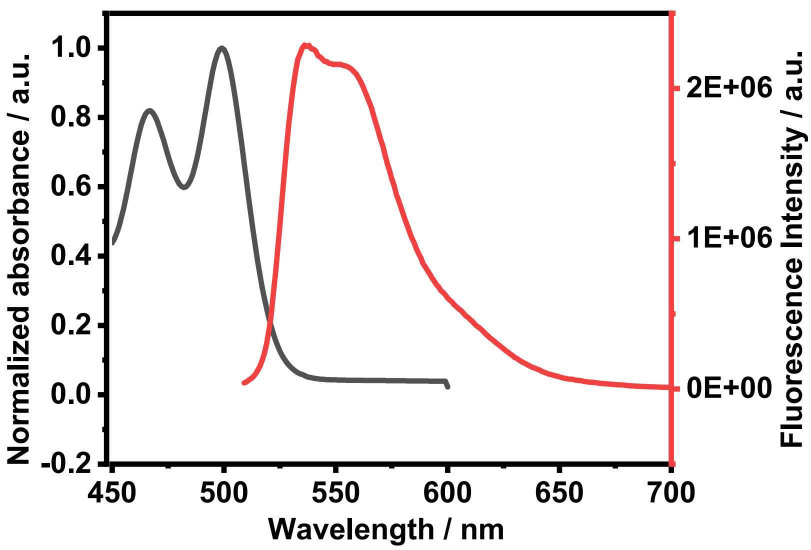


Figure S12. UV-visible absorption spectrum and fluorescence spectrum of **8**

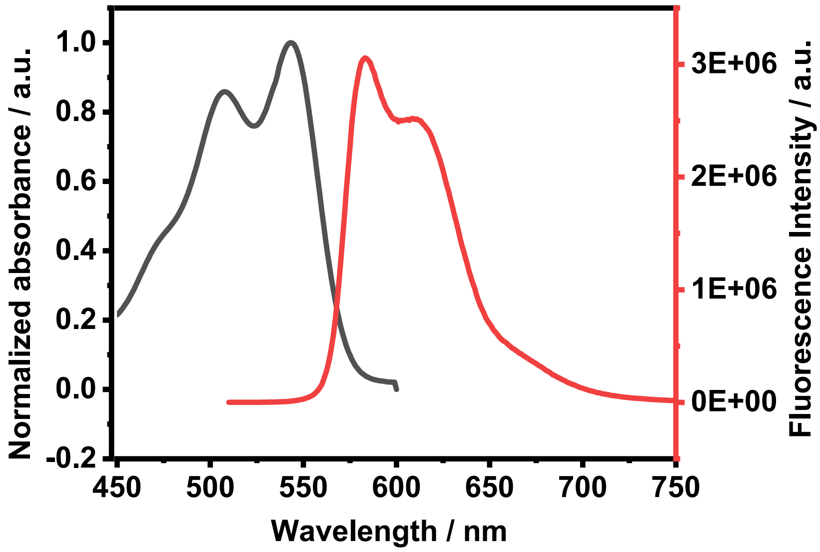


Figure S13. UV-visible absorption spectrum and fluorescence spectrum of **9**

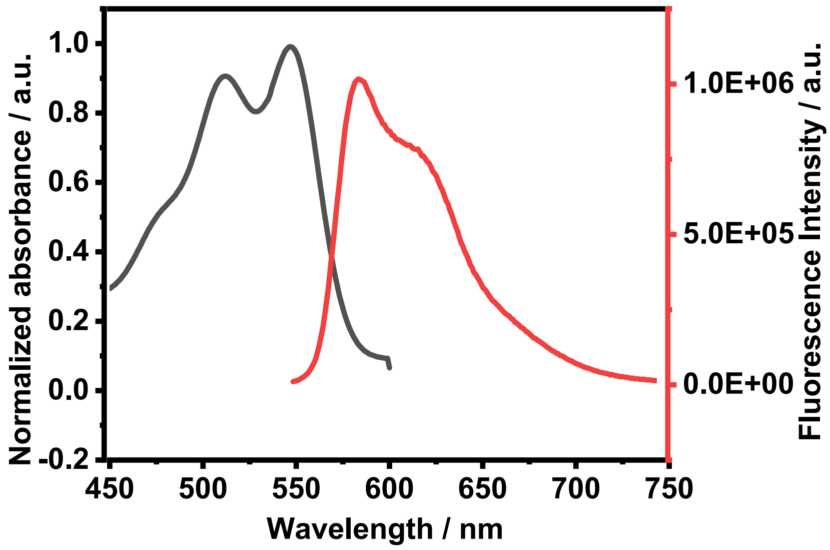


Figure S14. UV-visible absorption spectrum and fluorescence spectrum of **10**

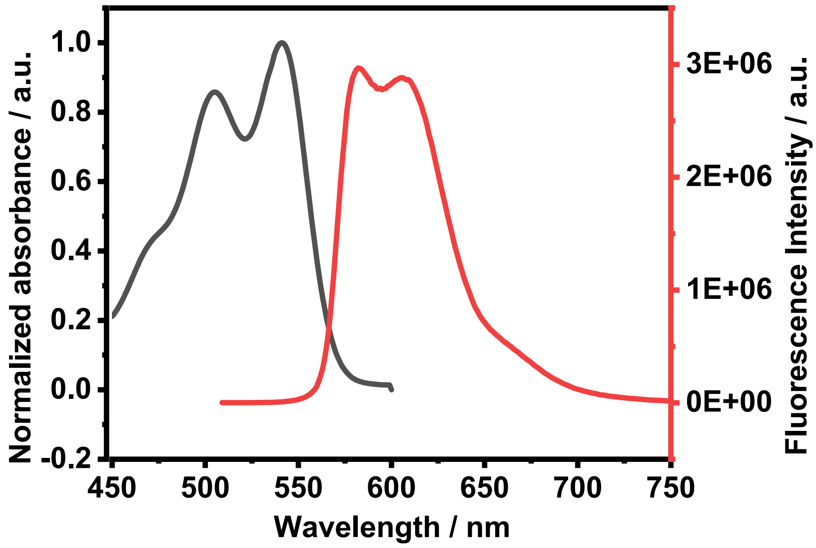


Figure S15. UV-visible absorption spectrum and fluorescence spectrum of **11**

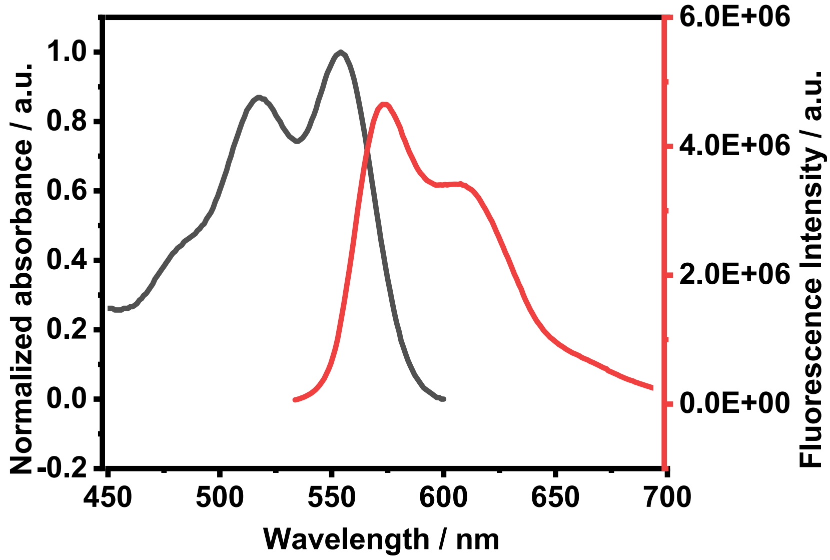


Figure S16. UV-visible absorption spectrum and fluorescence spectrum of **12**

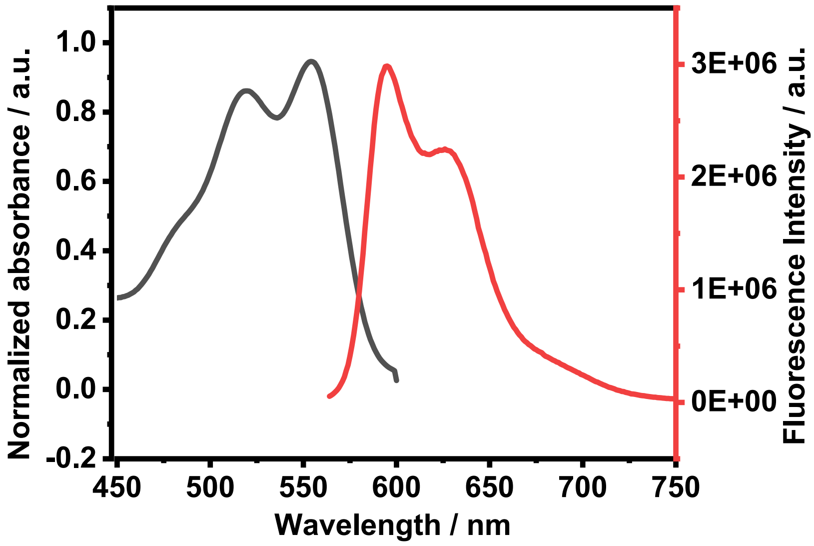


Figure S17. UV-visible absorption spectrum and fluorescence spectrum of **13**

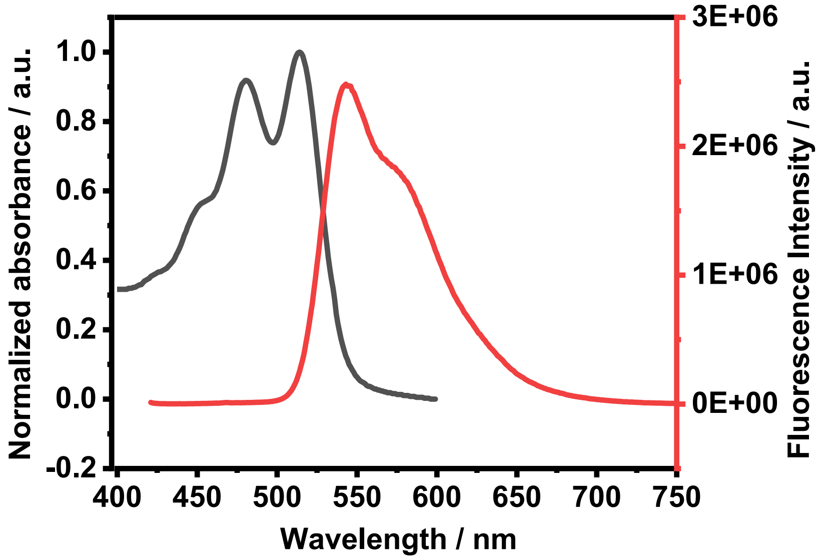


Figure S18. UV-visible absorption spectrum and fluorescence spectrum of **14**

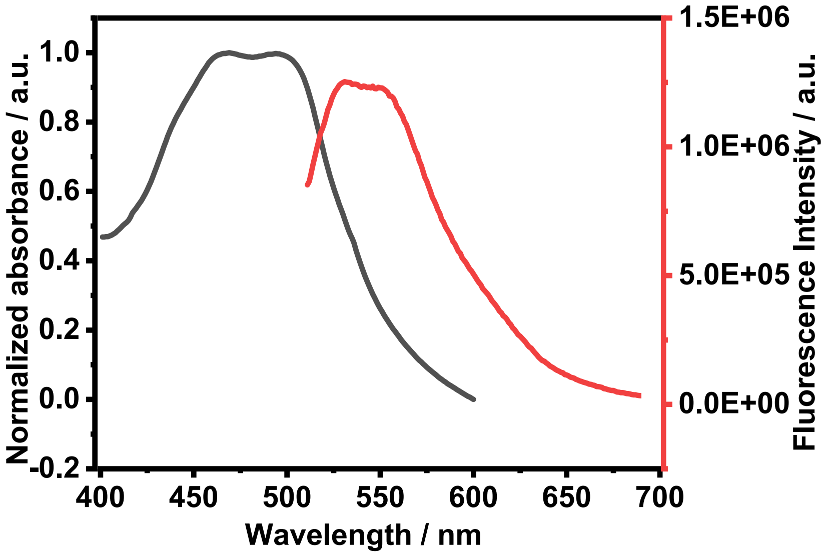


Figure S19. UV-visible absorption spectrum and fluorescence spectrum of **15**

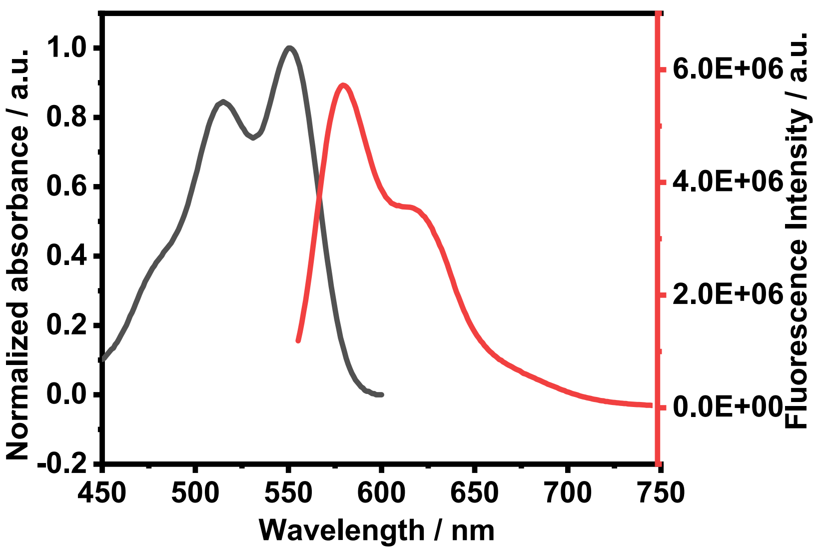


Figure S20. UV-visible absorption spectrum and fluorescence spectrum of **16**

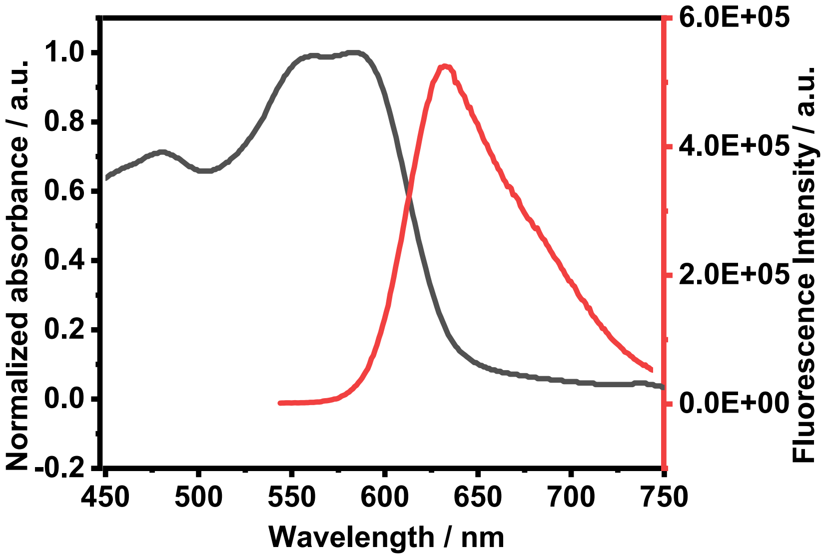


Figure S21. UV-visible absorption spectrum and fluorescence spectrum of **17**

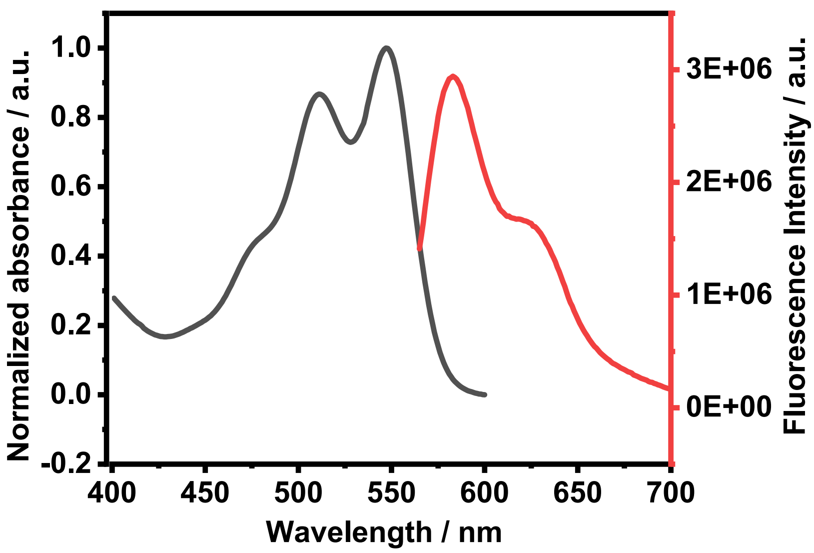


Figure S22. UV-visible absorption spectrum and fluorescence spectrum of **18**

Spectrum of molar absorption coefficient of compound 1, 5, 8.

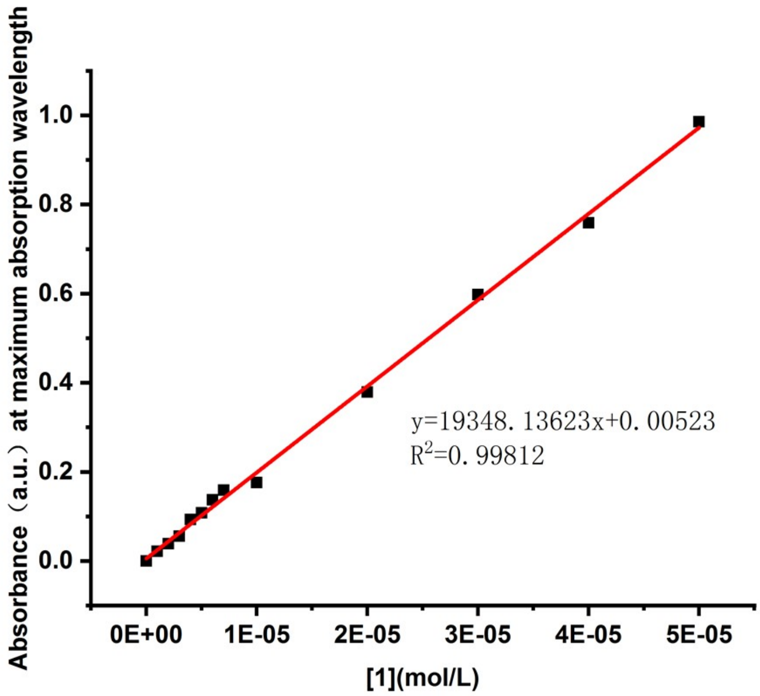


Figure S23. Molar absorption coefficient of **1**.

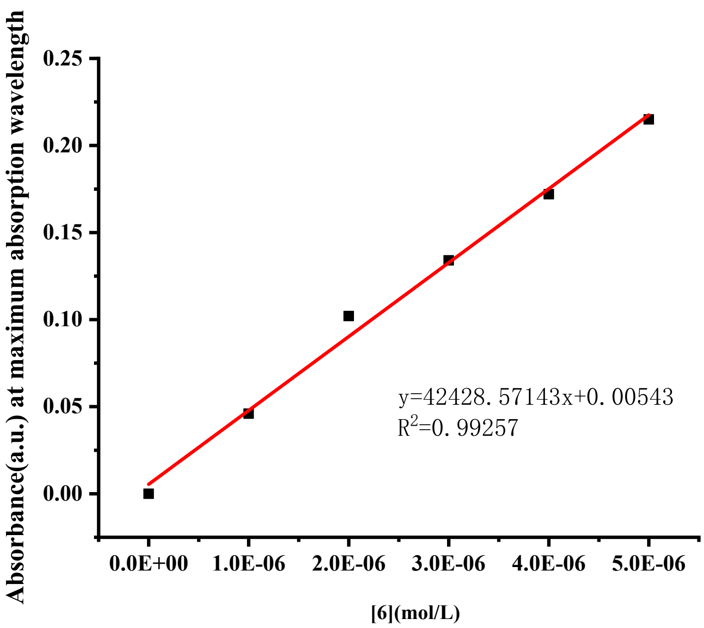


Figure S24. Molar absorption coefficient of **6.**

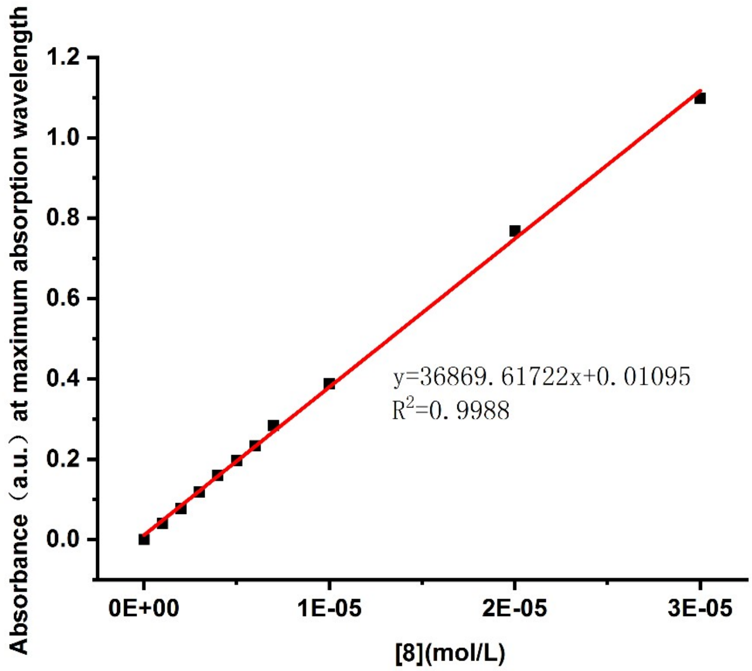


Figure S25. Molar absorption coefficient of **8.**

Photostability experiments

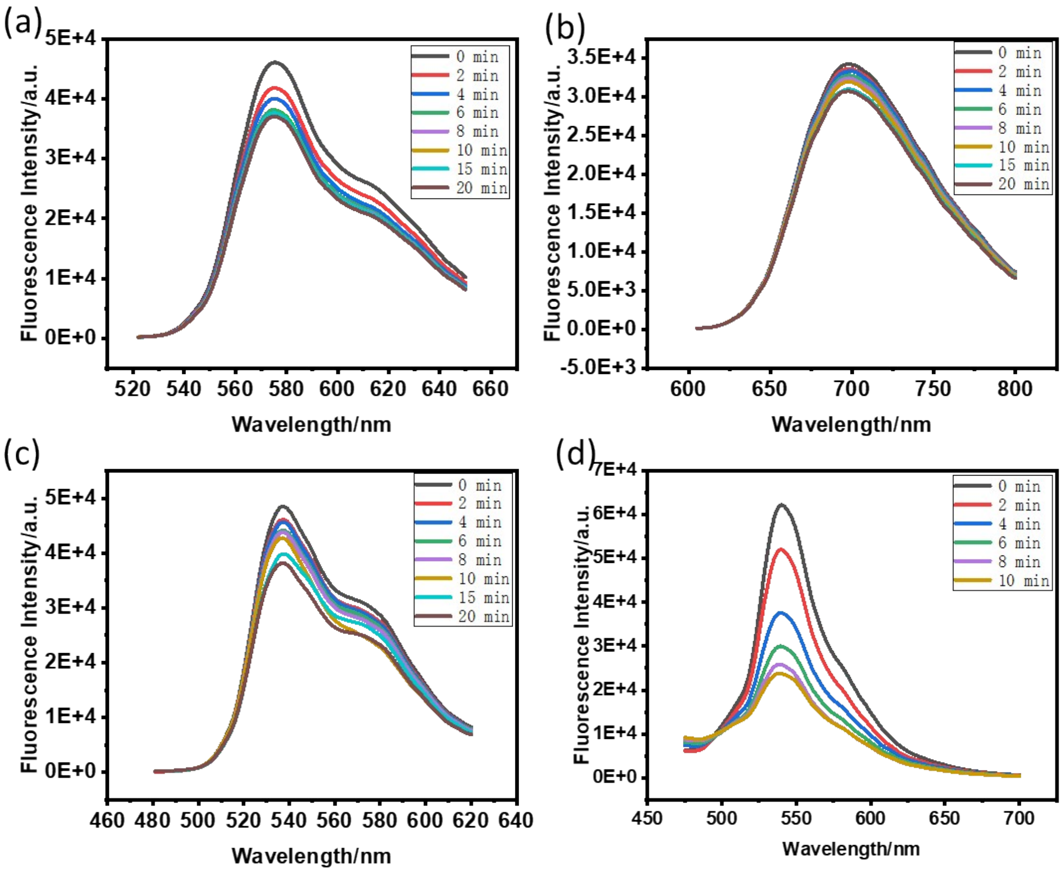


Figure S26. Changes of the fluorescence spectrum of **1** (a) solution in DMSO (10 μM), **6** (b) solution in DMSO (10 μM), **8** (c) solution in DMSO (10 μM) and fluorescein (d) solution in DMSO (10 μM) with K_2CO_3 (20 μM), under the continuous irradiation by a 532 nm laser line (200 mW/cm^2).

Cell experiments

Materials and Methods

Cell lines

L929 cell: Mouse fibroblast cells.

Cell culture

Cells were grown in 5% (vol/vol) CO_2 at 37℃. Cells were cultured in DMEM medium (penicillin (100 U/mL) and streptomycin (100 μg/mL)).

Toxicity experiment

The L929 cells were digested with trypsin to prepare a suspension and then these cells were spread into a 96-well plate. The experiment was divided into three groups, including control group (with cells and CCK-8 solution, without probes), experimental group (with cells, CCK-8 solution and probes), and blank group (with culture medium and CCK-8 solution, without cells and probes). The number of cells in each well was $5*10^3$, and the medium in per well was 200 μL. Cells were cultured for 24 h until cells adhered to the wall firmly. Different concentrations (1, 2, 4, 8, 10 and 15 μM) of compound **1**, **6** and **8** were added to each well. After incubating for 60 minutes, 20 μL of CCK-8 solution was added to each well, cells were incubated in incubator for 3 hours. The solution mixed gently on a shaker, put plate in a microplate reader and measured the absorbance at 450 nm wavelength, the detection wavelength was 450-490 nm, the reference wavelength is 600-625 nm. The experimental repeat 4 times. Cell viability calculate: cell viability (%) = $[A_{experimental\ group} - A_{blank\ group}] / [A_{control\ group} - A_{blank\ group}] * 100\%$

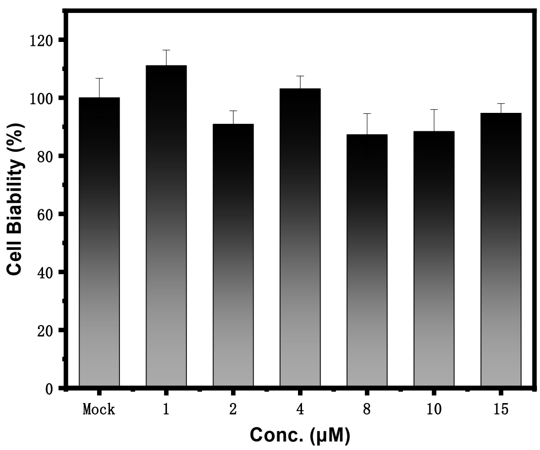


Figure S27. Cell viability of **1** in L929 cell.

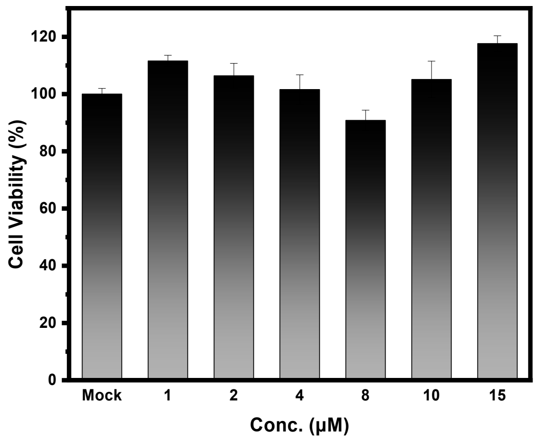


Figure S28. Cell viability of **6** in L929 cell.

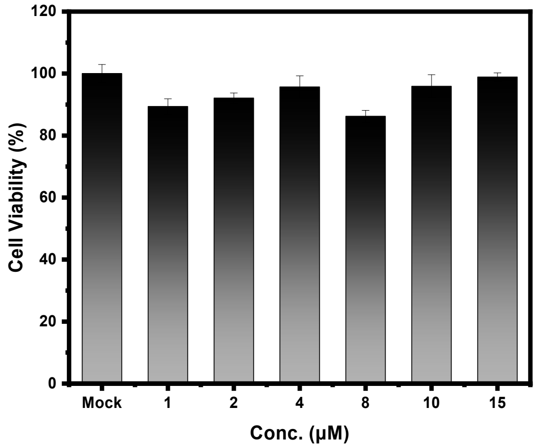


Figure S29. Cell viability of **8** in L929 cell.

Cell Culture and Imaging by Laser Scanning Microscopy

For single-photon living cell imaging, we cultured cells on 15 mm class bottom cell culture dish (Nest). Before labelling cells with probes, we removed the culture medium, and washed the cells twice with Hank's Balanced Salt Solution (HBSS, 1.26 mM $CaCl_2$, 0.49 mM $MgCl_2$, 0.41 mM $MgSO_4$, 5.33 mM KCl, 0.44 mM KH_2PO_4, 4.17 mM $NaHCO_3$, 138 mM NaCl, 0.34 mM Na_2HPO_4, 5.55 mM Glucose, pH = 7.4) to remove away the residual culture medium. 200 µL probes (10 µM) were added to the dish, and incubated with cells for 30 mins in the dark. Cells was washed twice with Hank's Balanced Salt Solution to remove residual probes. 1 mL Hank's solution was added to the dish, cells were observed in an objective with a magnification of 20×, 40× and 100×. The excitation wavelengths are 405 ± 20 nm and 565 ± 20 nm, and the emission wavelengths are 501 ± 20 nm and 580 ± 20 nm. (LSM 780 Zeiss, Germany)

For two-photon living cell imaging, we cultured cells on 6 cm cell culture dish. Before labelling cells with probes, cells were washed twice with Hank's Balanced Salt Solution. 2 mL aqueous solution of probes (10 μM) were added to the dish, and incubated with cells for 30 mins in the dark. Cells was washed twice with Hank's Balanced Salt Solution to remove residual probes. 7 mL Hank's solution was added to the dish, cells were observed in an objective. The two-photon microscopic imaging system contains an inverted commercial laser scanning microscopic imaging system (LSM 880 Zeiss, Germany) and a mode-locked femtosecond Ti: Sapphire laser which emitted linearly polarized 810 nm excitation light. The backscattered signals from tissue samples were simultaneously obtained via two independent channels. One channel detected signal (green color) between 449 nm and 511 nm, and the other detected signal (red color) between 623 nm and 660 nm. A Zeiss 40×/W Plan-Apochromat water immersion objective was employed to acquire images.

Living cell imaging

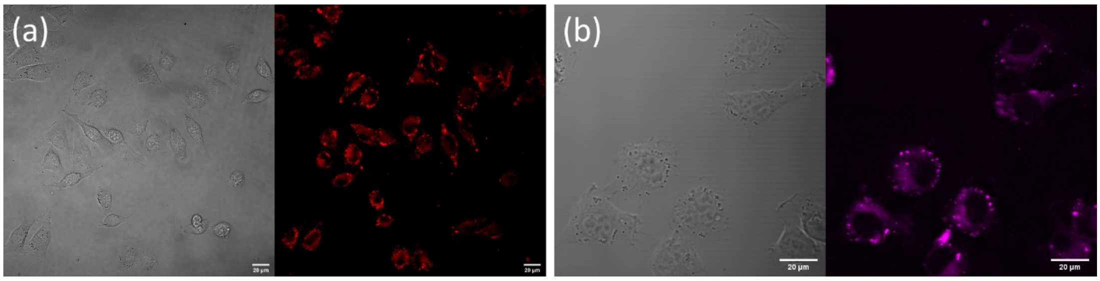


Figure S30. Living cell imaging of **6** in L929 cell: (a) Bright field and red channel (ex. 543 nm, em. 550-600 nm). (b) Bright field and red channel (2P, ex.810 nm, em. 550-600 nm).

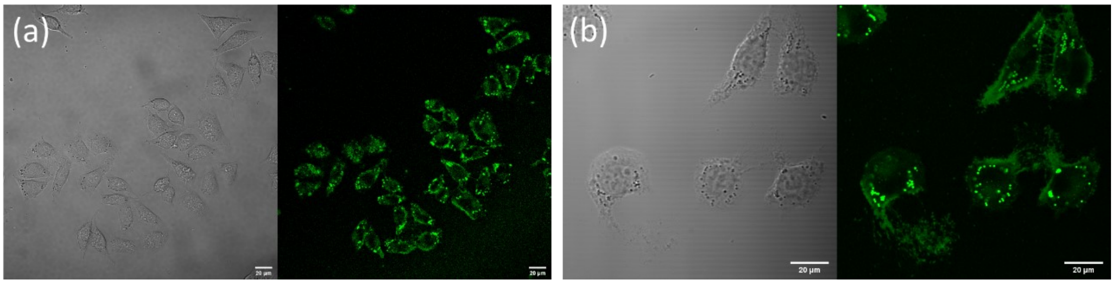


Figure S31. Living cell imaging of **8** in L929 cell: (a) Bright field and green channel (ex. 488 nm, em. 500-540 nm). (b) Bright field and green channel (2P, ex.810 nm, em. 500-540 nm).

Single crystal data

X-ray diffractions for single crystals of **1, 3, 8** and **11** were carried out on Rikagu Synergy Custom (Liquid MetalJet D2 Plus) diffractometer using Ga Kα radiation (λ = 1.3405 Å). Data collection and unit cell refinement were executed by using CrysAlisPro software. Data processing and absorption correction, giving minimum and maximum transmission factors, were accomplished with CrysAlisPro. The structure was solved with the SHELXT and refined with the SHELXL using least-squares minimization. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon bound hydrogen atom positions were determined by geometry and refined by a riding model. CCDC 2128126, 2128125, 2128123, 2128124 contain the supplementary crystallographic data. Crystal data and structure refinements of **1, 3, 8** and **11**are listed in **Table S3**, **Table S4**, **Table S5** and **Table S6**. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/

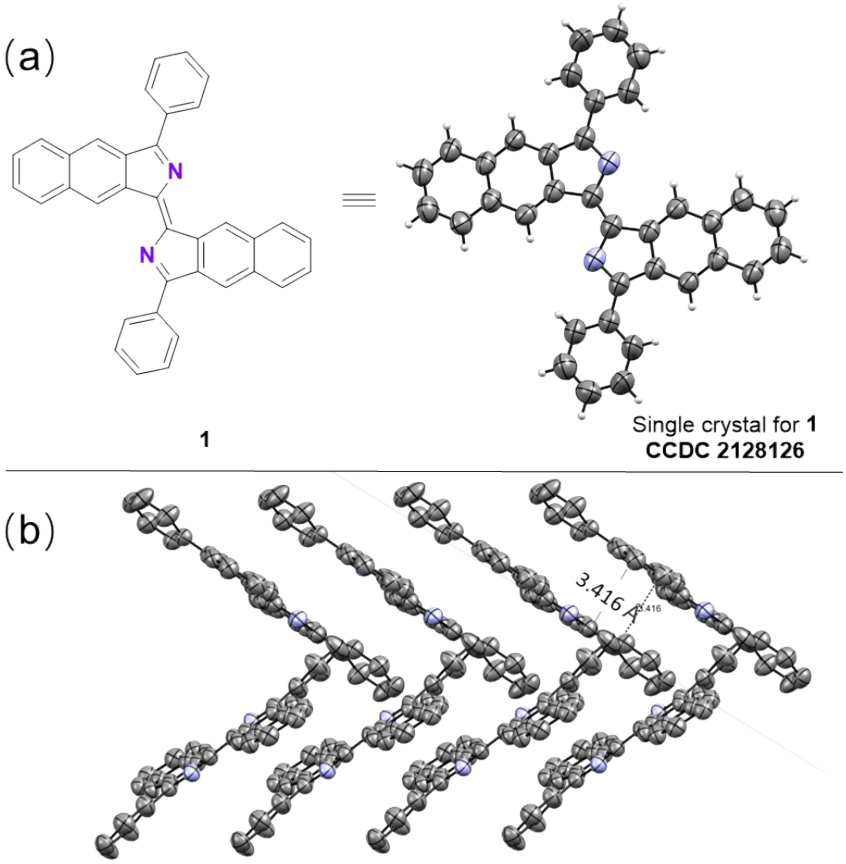
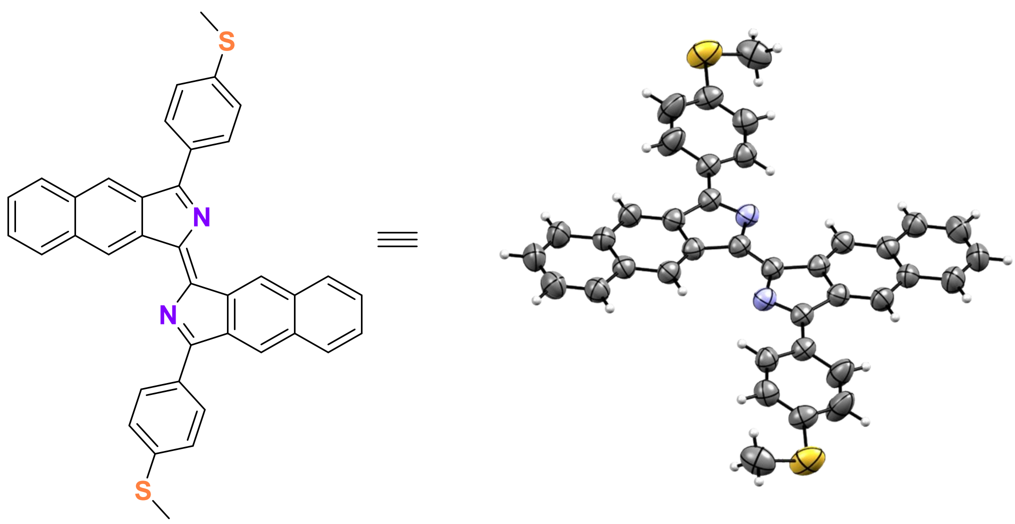


Figure S32. (a) Single-crystal structures of **1**. (b) Molecular packing. Hydrogen atoms are omitted for clarity.

Table S5. Crystal data and structure refinement for **1**

Identification code	**1**
Empirical formula	$C_{36}H_{22}N_2$
Formula weight	482.55

Temperature/K	299.22(19)
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.4695(8)
b/Å	5.8013(3)
c/Å	17.3780(10)
α/°	90
β/°	101.414(6)
γ/°	90
Volume/Å^3	1232.25(13)
Z	2
ρ_{calc}g/cm^3	1.301
μ/mm^{-1}	0.375
F(000)	504.0
Crystal size/mm^3	0.2 × 0.1 × 0.05
Radiation	GaKα (λ = 1.3405)
2Θ range for data collection/°	6.976 to 121.09
Index ranges	$-16 \leq h \leq 16$, $-3 \leq k \leq 7$, $-22 \leq l \leq 22$
Reflections collected	9039
Independent reflections	2730 [R_{int} = 0.0691, R_{sigma} = 0.0603]
Data/restraints/parameters	2730/36/172
Goodness-of-fit on F^2	1.015
Final R indexes [I>=2σ (I)]	R_1 = 0.0617, wR_2 = 0.1756
Final R indexes [all data]	R_1 = 0.0937, wR_2 = 0.2001
Largest diff. peak/hole / e Å^{-3}	0.22/-0.18



3

Single crystal for **3**
CCDC 2128125

Figure S33. Single-crystal structures of **3**.

Table S6. Crystal data and structure refinement for **3**

Identification code	**3**
Empirical formula	$C_{19}H_{13}NS$
Formula weight	287.36
Temperature/K	99.99(10)

Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	11.8893(9)
b/Å	6.3212(5)
c/Å	18.6664(15)
α/°	90
β/°	92.734(7)
γ/°	90
Volume/Å^3	1401.27(19)
Z	4
ρ_{calc}g/cm^3	1.362
μ/mm^{-1}	1.284
F(000)	600.0
Crystal size/mm^3	0.05 × 0.03 × 0.02
Radiation	Ga Kα (λ = 1.3405)
2Θ range for data collection/°	7.506 to 121.564
Index ranges	$-15 \le h \le 13$, $-8 \le k \le 6$, $-24 \le l \le 24$
Reflections collected	17389
Independent reflections	3194 [R_{int} = 0.0362, R_{sigma} = 0.0276]
Data/restraints/parameters	3194/0/191
Goodness-of-fit on F^2	1.086
Final R indexes [I>=2σ (I)]	R_1 = 0.0415, wR_2 = 0.1082
Final R indexes [all data]	R_1 = 0.0547, wR_2 = 0.1151
Largest diff. peak/hole / e Å^{-3}	0.17/-0.38

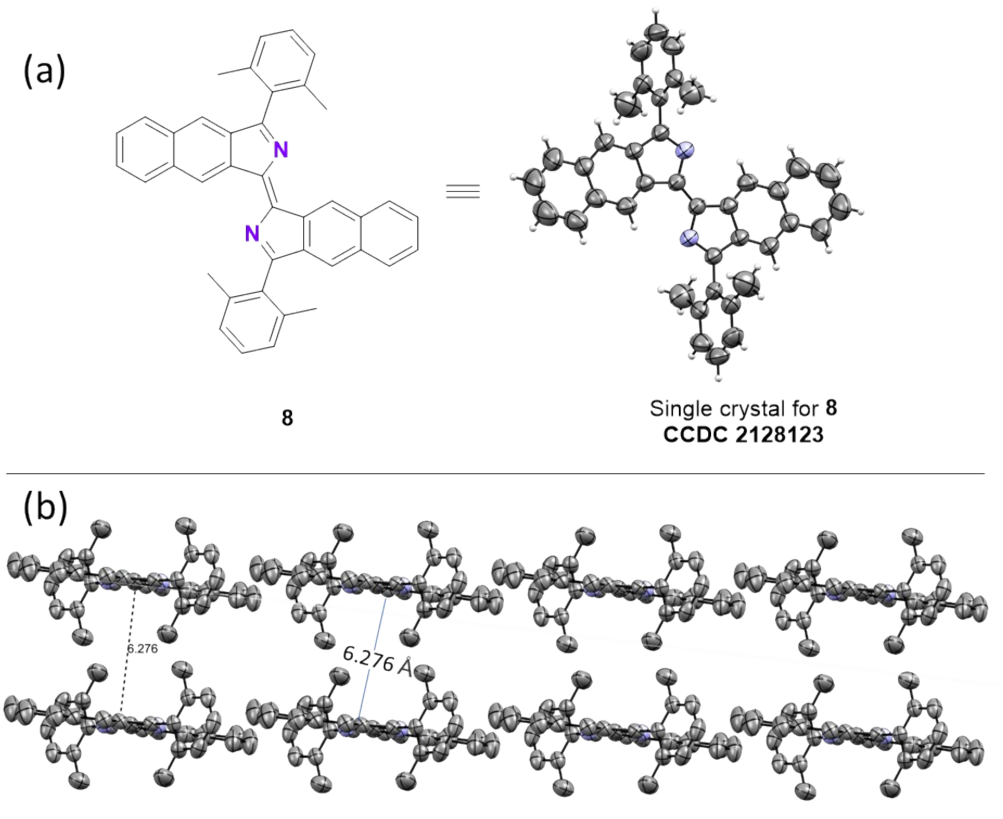


Figure S34. (a) Single-crystal structures of **8**. (b) Molecular packing. Hydrogen atoms are omitted for clarity.

Table S7. Crystal data and structure refinement for **8**

Identification code	**8**
Empirical formula	$C_{40}H_{30}N_2$
Formula weight	269.349
Temperature/K	99.99(10)
Crystal system	triclinic
Space group	P-1
a/Å	8.9783(6)
b/Å	11.2080(6)
c/Å	15.2381(6)
α/°	91.733(4)
β/°	97.302(5)
γ/°	97.178(5)
Volume/Å^3	1507.38(14)
Z	4
ρ_{calc}g/cm^3	1.187
μ/mm^{-1}	0.335
F(000)	569.1
Crystal size/mm^3	0.05 × 0.03 × 0.02
Radiation	Ga Kα (λ = 1.3405)
2Θ range for data collection/°	5.08 to 103.86
Index ranges	$-10 \leq h \leq 10$, $-13 \leq k \leq 13$, $-17 \leq l \leq 17$
Reflections collected	13849
Independent reflections	5021 [R_{int} = 0.0457, R_{sigma} = 0.0441]
Data/restraints/parameters	5021/66/383
Goodness-of-fit on F^2	1.012
Final R indexes [I>=2σ (I)]	R_1 = 0.0562, wR_2 = 0.1562
Final R indexes [all data]	R_1 = 0.0765, wR_2 = 0.1754
Largest diff. peak/hole / e Å^{-3}	0.28/-0.35

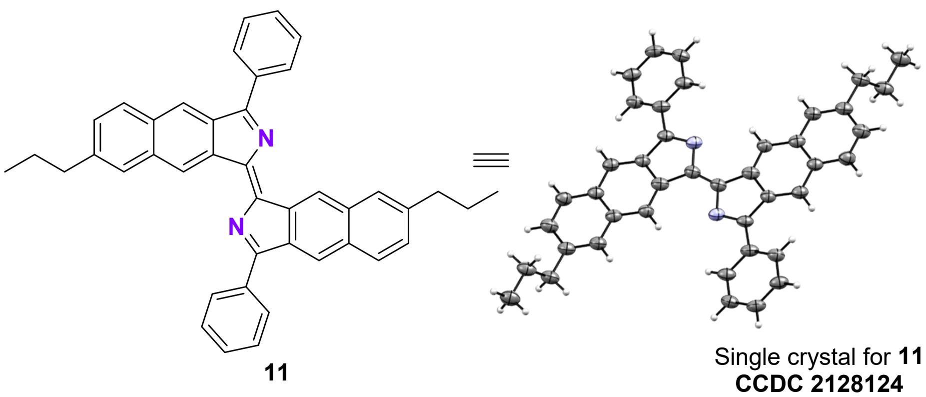


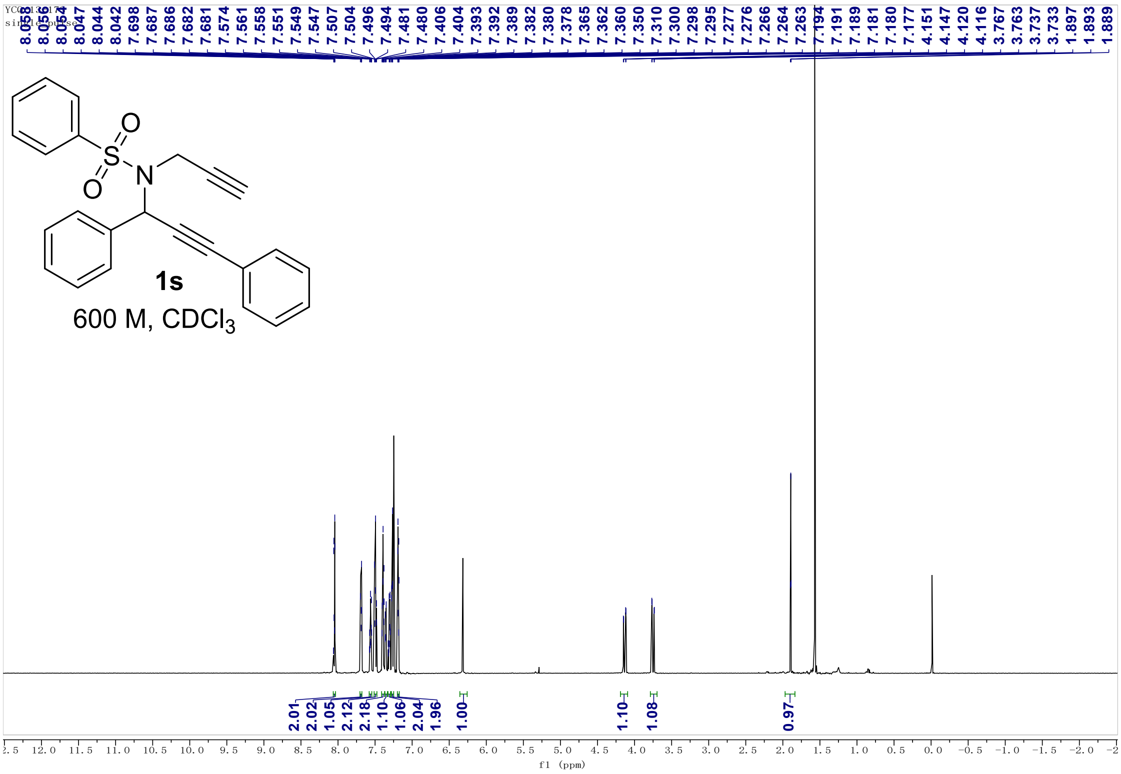
Figure S35. Single-crystal structures of **11**.

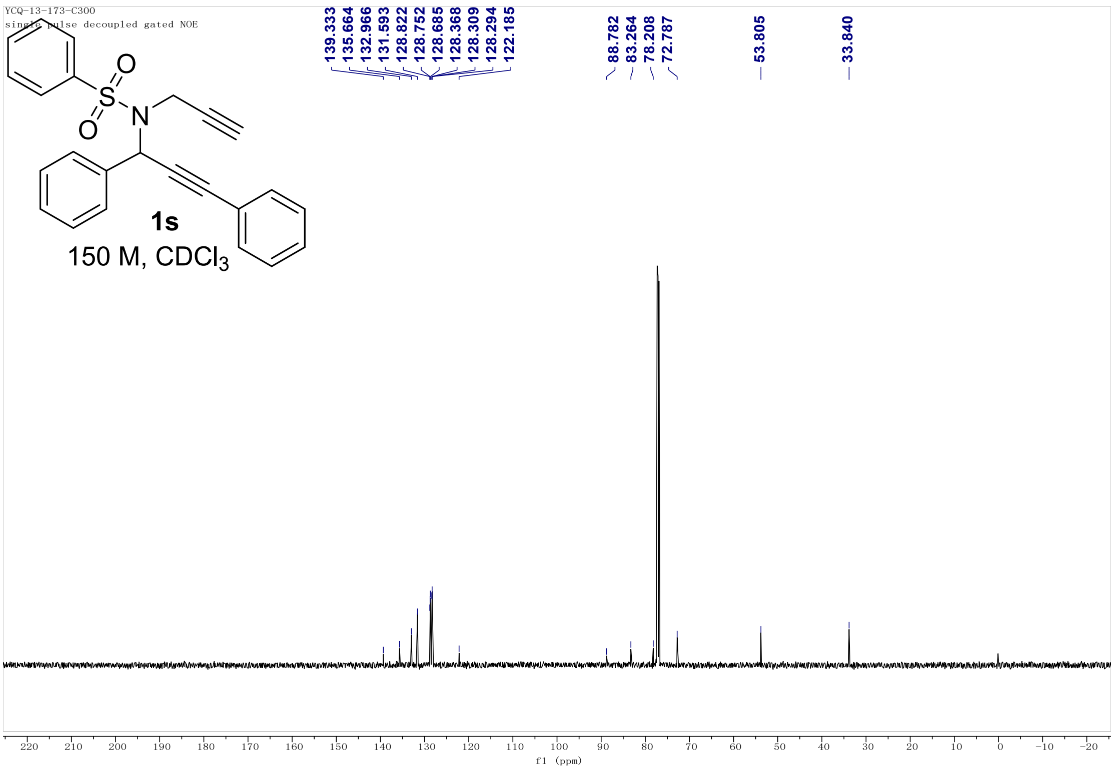
Table S8. Crystal data and structure refinement for **11**.

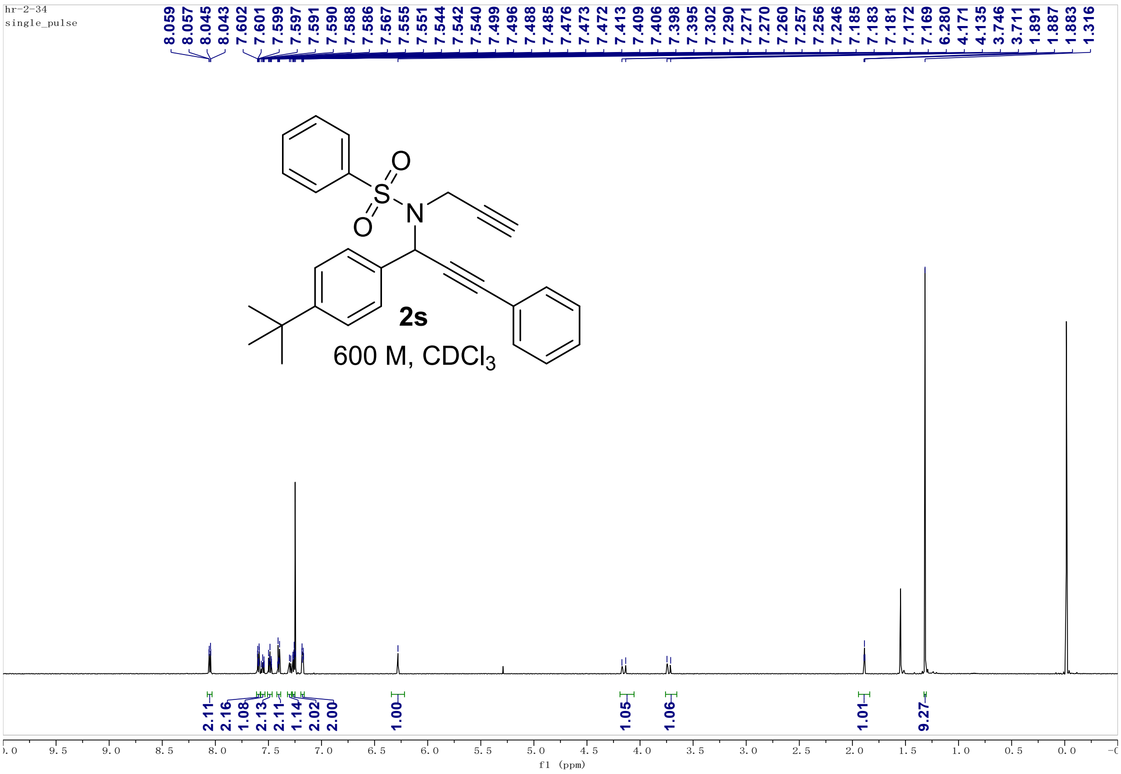
Identification code	**11**
Empirical formula	$C_{42}H_{34}N_2$
Formula weight	566.71
Temperature/K	99.98(10)
Crystal system	monoclinic

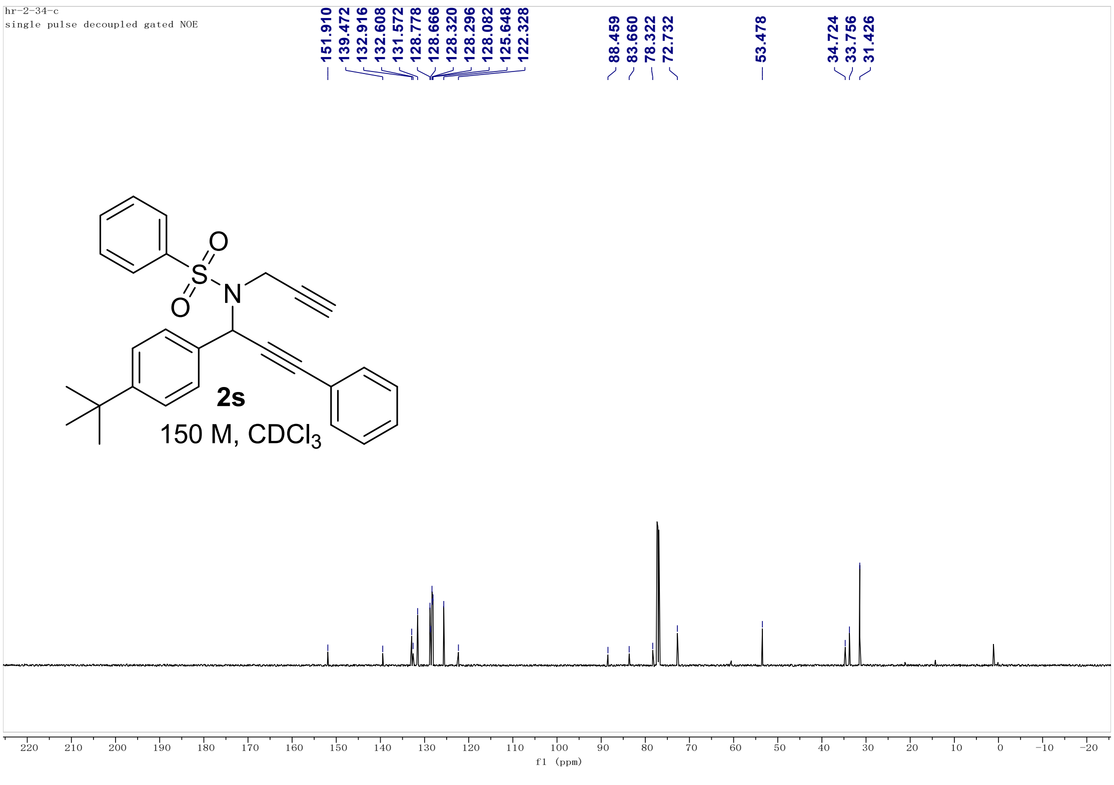
Space group	$P2_1/n$
a/Å	12.7024(8)
b/Å	4.9027(3)
c/Å	23.7070(16)
α/°	90
β/°	93.671(7)
γ/°	90
Volume/Å^3	1473.35(16)
Z	2
ρ_{calc}g/cm^3	1.277
μ/mm^{-1}	0.358
F(000)	600.0
Crystal size/mm^3	0.3 × 0.23 × 0.21
Radiation	Ga Kα (λ = 1.3405)
2Θ range for data collection/°	6.496 to 121.11
Index ranges	$-16 \le h \le 16$, $-6 \le k \le 6$, $-29 \le l \le 30$
Reflections collected	9723
Independent reflections	3254 [R_{int} = 0.0307, R_{sigma} = 0.0350]
Data/restraints/parameters	3254/0/201
Goodness-of-fit on F^2	1.158
Final R indexes [I>=2σ (I)]	R_1 = 0.0756, wR_2 = 0.2215
Final R indexes [all data]	R_1 = 0.0946, wR_2 = 0.2695
Largest diff. peak/hole / e Å^{-3}	0.42/-0.65

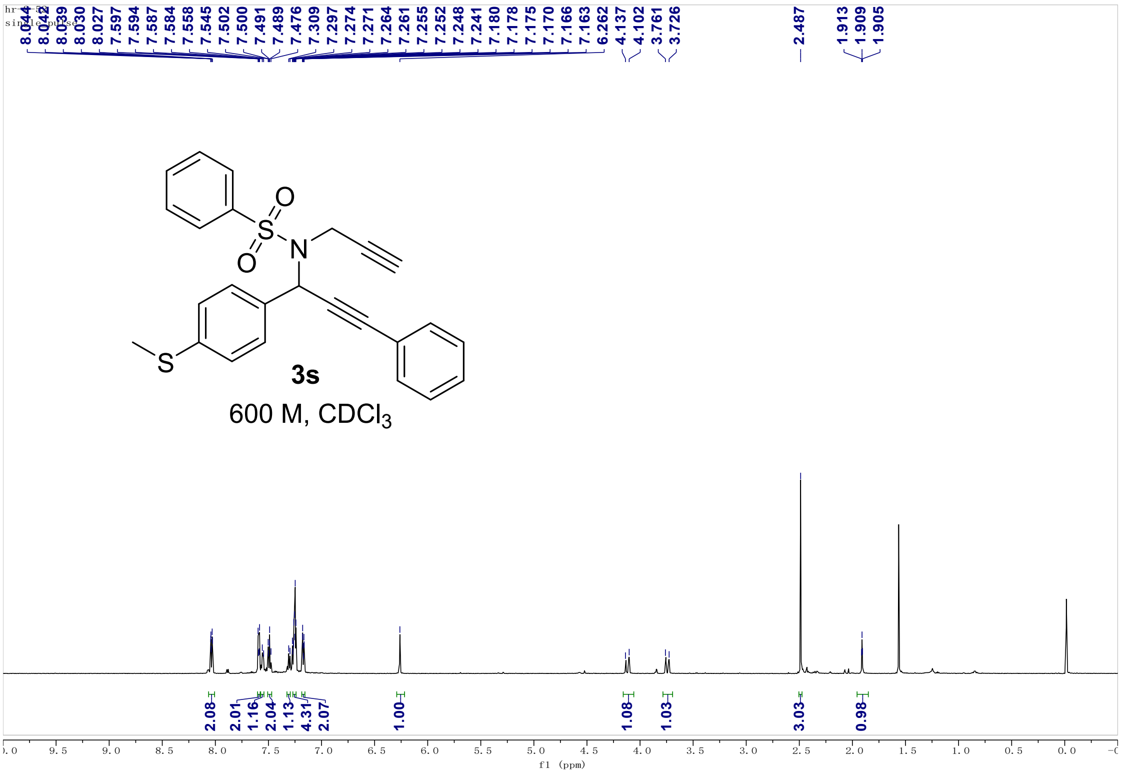
NMR spectra

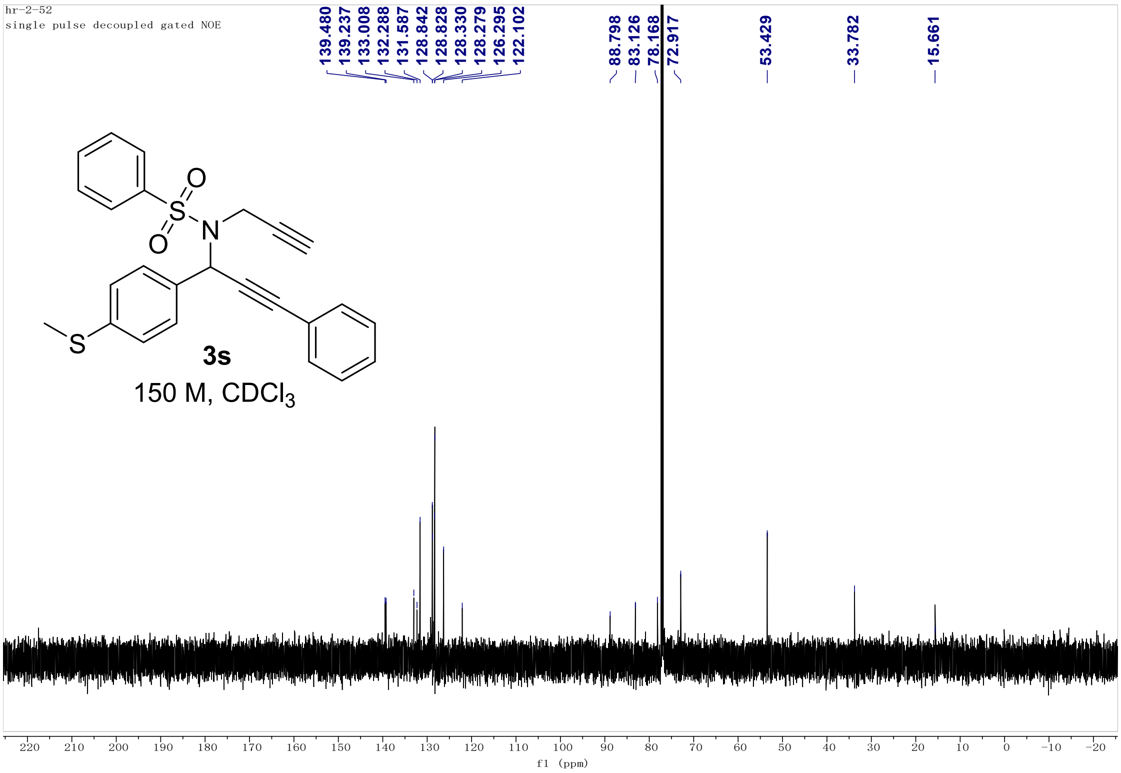

1s
600 M, CDCl3
f1 (ppm)

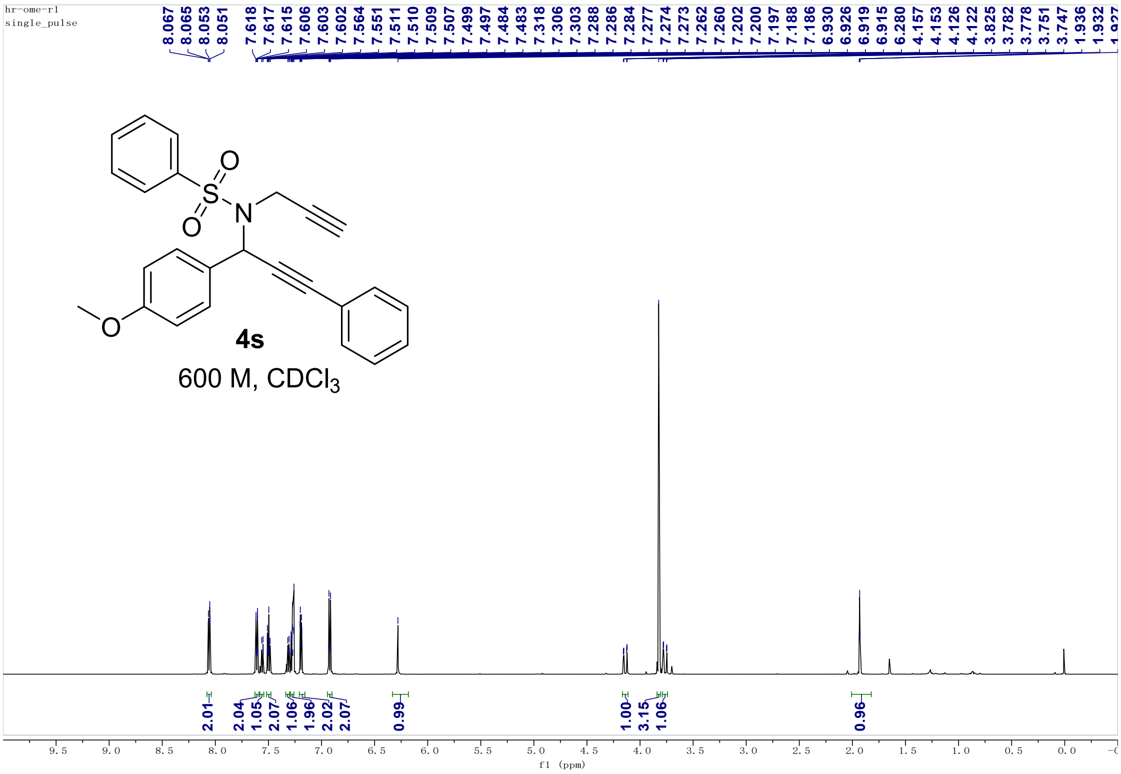

YCQ-13-173-C300
single pulse decoupled gated NOE
1s
150 M, CDCl3
139.333
135.664
132.966
131.593
128.822
128.752
128.685
128.368
128.309
128.294
122.185
88.782
83.264
78.208
72.787
53.805
33.840
f1 (ppm)

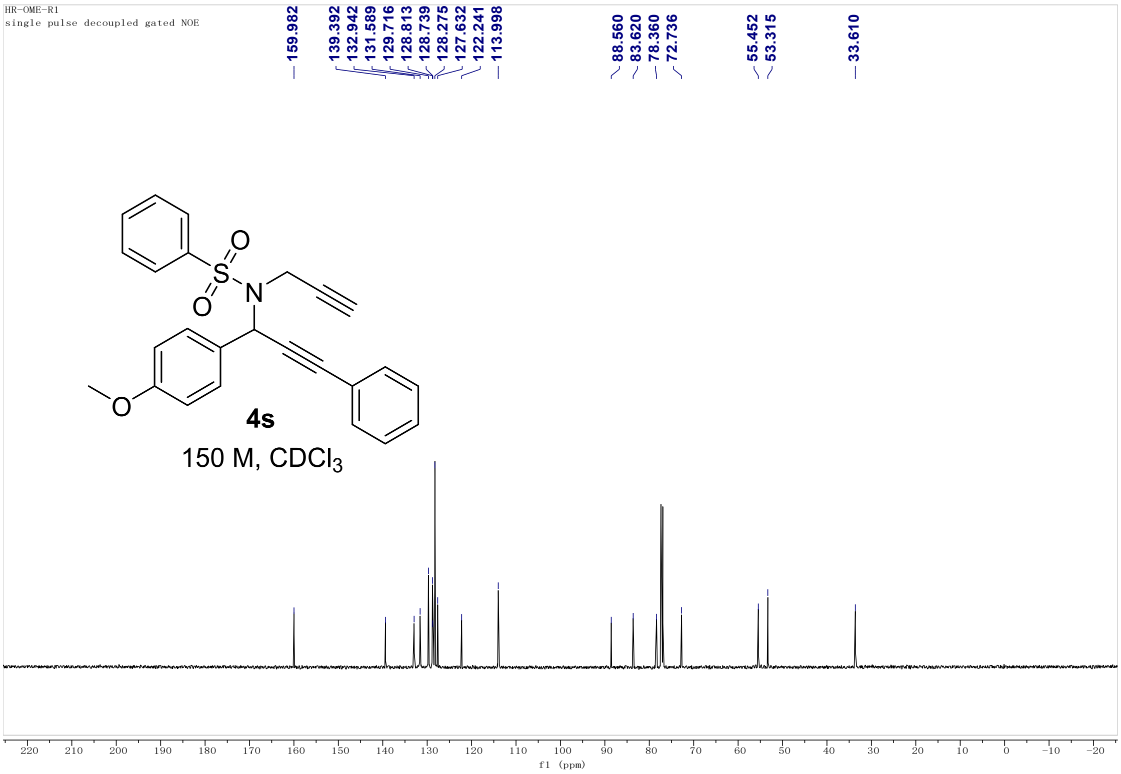


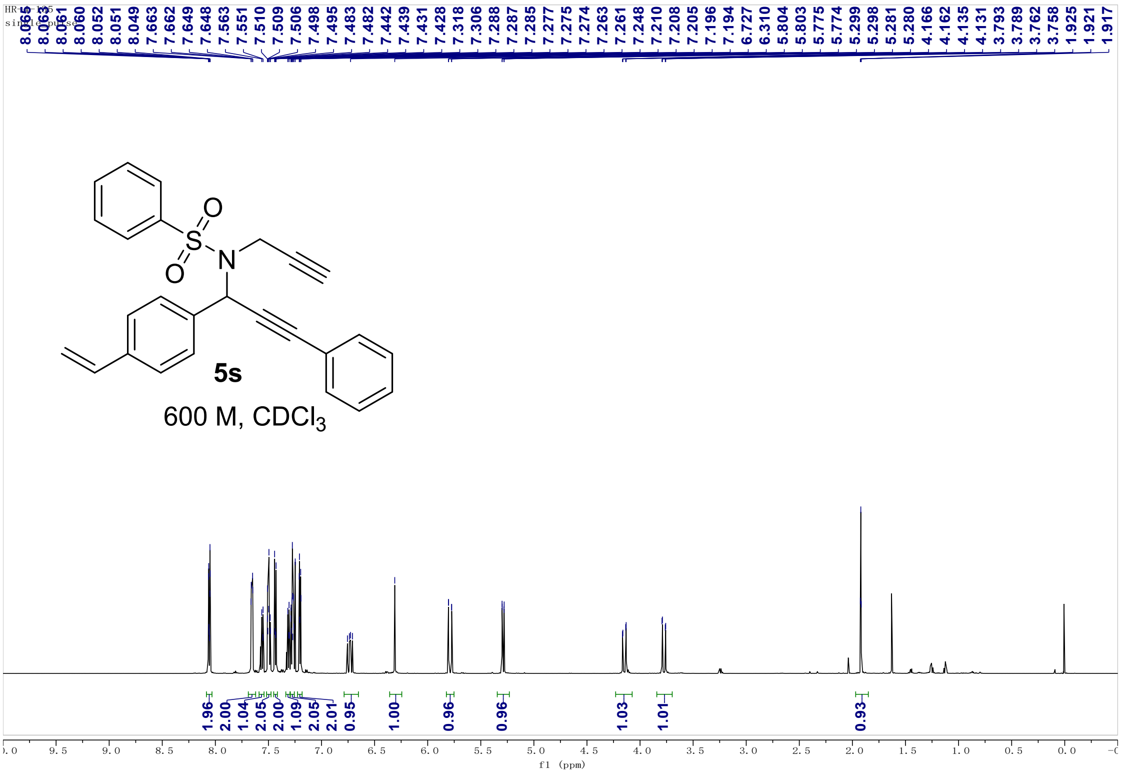


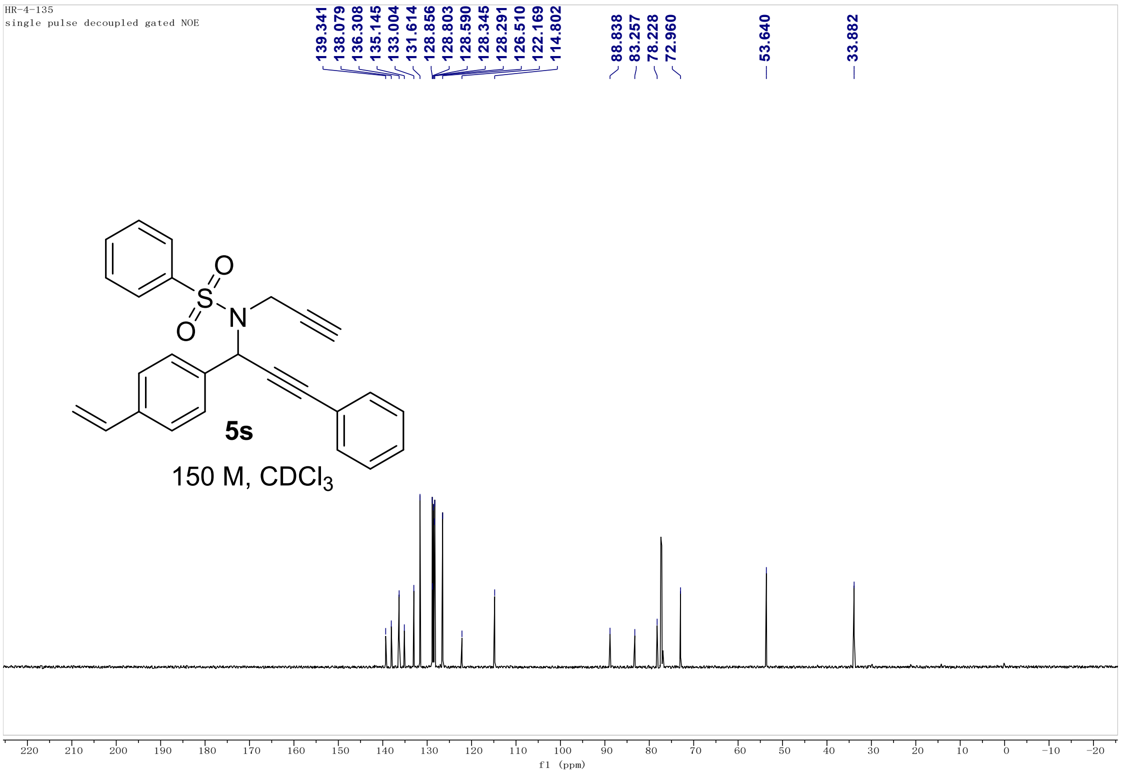

8.044
8.042
8.039
8.030
8.027
7.597
7.594
7.587
7.584
7.558
7.545
7.502
7.500
7.491
7.489
7.476
7.309
7.297
7.274
7.271
7.264
7.261
7.255
7.252
7.248
7.241
7.180
7.178
7.175
7.170
7.166
7.163
6.262
4.137
4.102
3.761
3.726
2.487
1.913
1.909
1.905
O
S
O
N
S
3s
600 M, CDCl3
2.08
2.01
1.16
2.04
1.13
4.31
2.07
1.00
1.08
1.03
3.03
0.98
f1 (ppm)

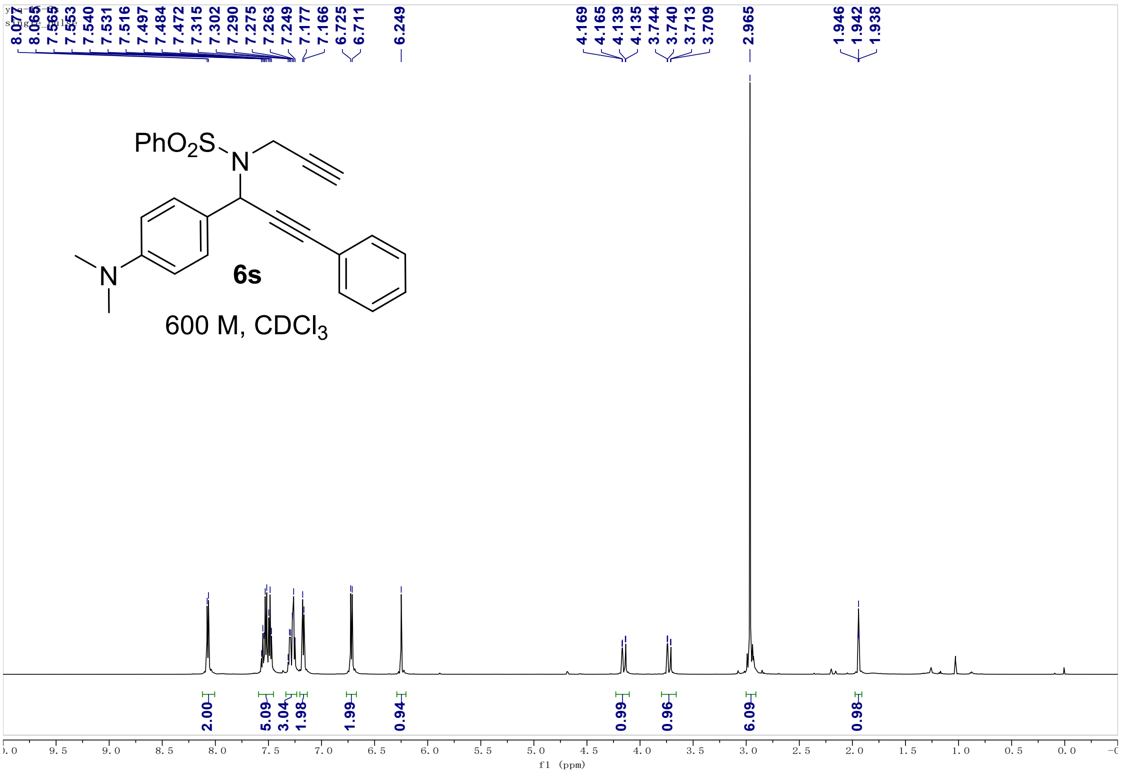

hr-2-52
single pulse decoupled gated NOE
139.480
139.237
133.008
132.288
131.587
128.842
128.828
128.330
128.279
126.295
122.102
88.798
83.126
78.168
72.917
53.429
33.782
15.661
O
S
O
N
S
3s
150 M, CDCl3
f1 (ppm)

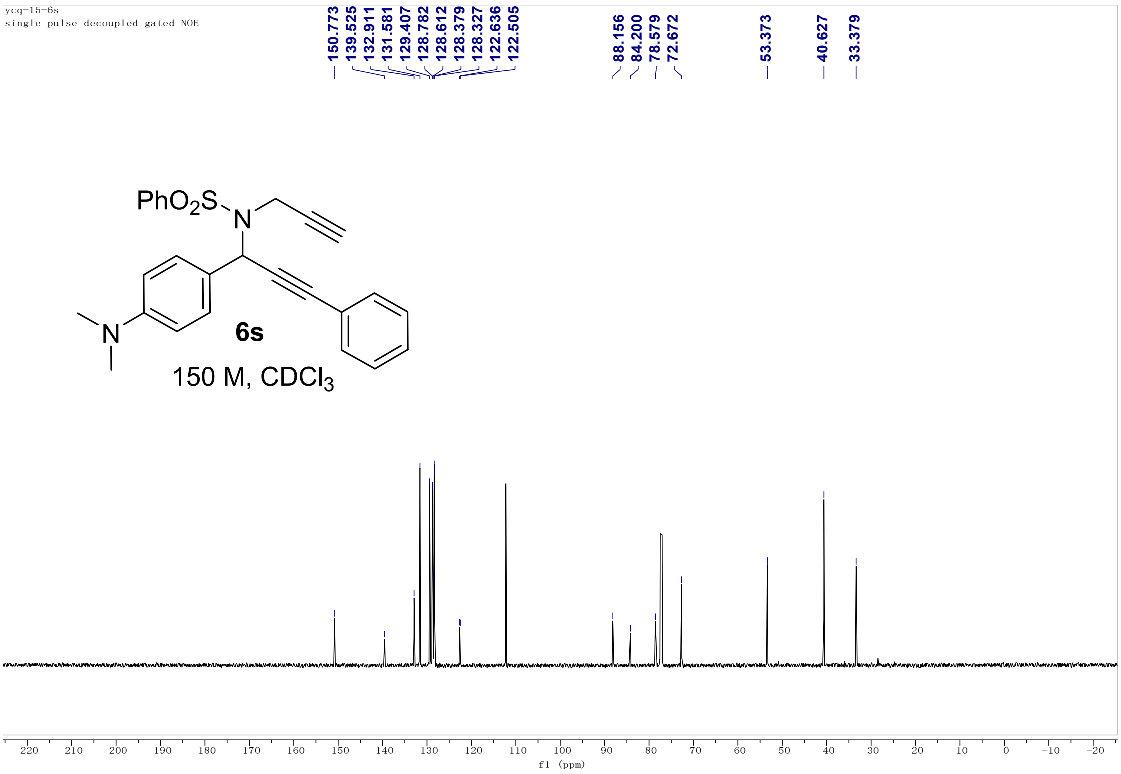

hr-ome-r1
single_pulse
8.067 8.065 8.053 8.051 7.618 7.617 7.615 7.606 7.603 7.602 7.564 7.551 7.511 7.510 7.509 7.507 7.499 7.497 7.484 7.483 7.318 7.306 7.303 7.288 7.286 7.284 7.277 7.274 7.273 7.262 7.260 7.202 7.200 7.197 7.188 7.186 6.930 6.926 6.919 6.915 6.280 4.157 4.153 4.126 4.122 3.825 3.782 3.778 3.751 3.747 1.936 1.932
O
S
O
N
O
4s
600 M, $CDCl_3$
2.01 2.04 1.05 2.07 1.06 1.96 2.02 2.07 0.99 1.00 3.15 1.06 0.96
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)

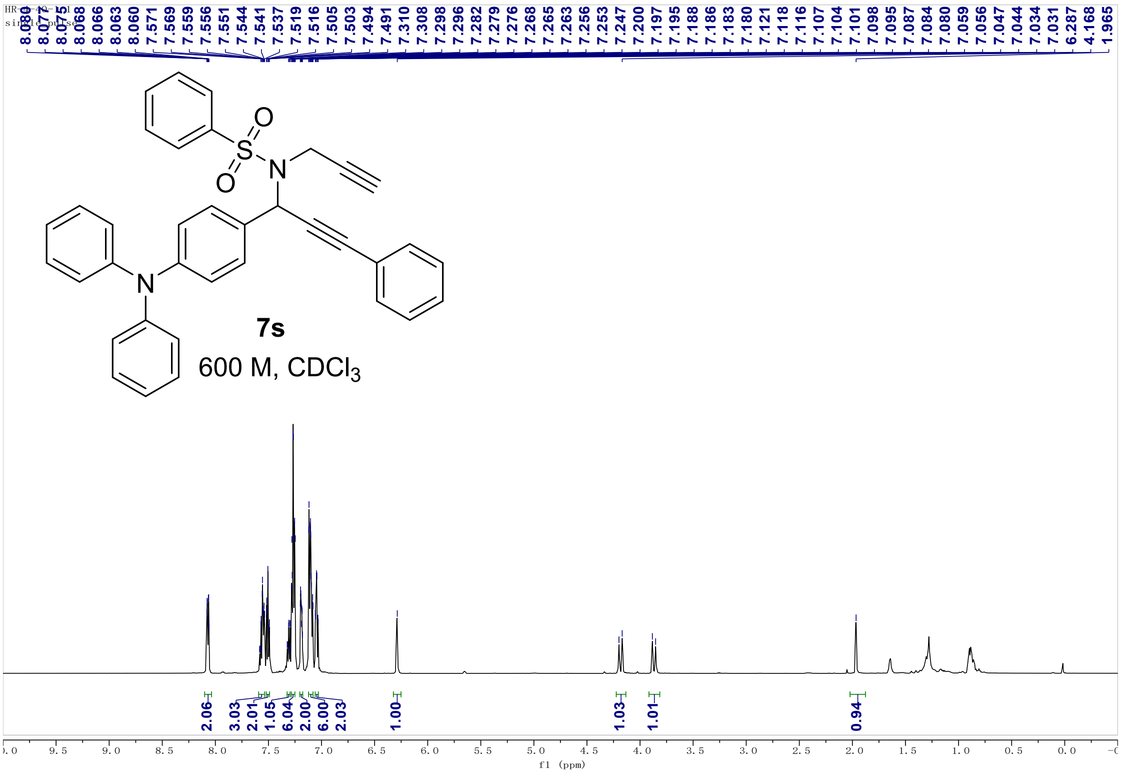

HR-OME-R1
single pulse decoupled gated NOE
159.982 139.392 132.942 131.589 129.716 128.813 128.739 128.275 127.632 122.241 113.998 88.560 83.620 78.360 72.736 55.452 53.315 33.610
O
S
O
N
O
4s
150 M, $CDCl_3$
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

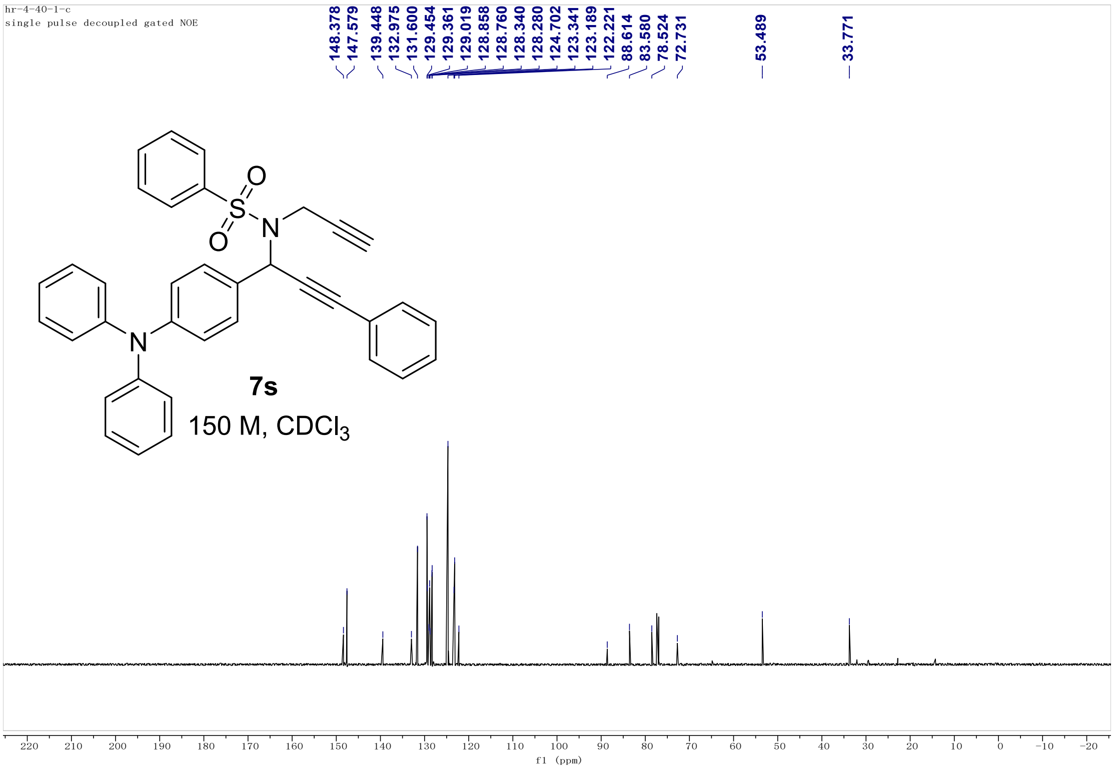

8.066 8.063 8.061 8.060 8.052 8.051 8.049 7.663 7.662 7.649 7.648 7.563 7.551 7.510 7.509 7.506 7.498 7.495 7.483 7.482 7.442 7.439 7.431 7.428 7.318 7.306 7.288 7.287 7.285 7.277 7.275 7.274 7.263 7.261 7.248 7.210 7.208 7.205 7.196 7.194 6.727 6.310 5.804 5.803 5.775 5.774 5.299 5.298 5.281 5.280 4.166 4.162 4.135 4.131 3.793 3.789 3.762 3.758 1.925 1.921 1.917
5s
600 M, CDCl3
1.96 2.00 1.04 2.05 2.00 1.09 2.05 2.01 0.95 1.00 0.96 0.96 1.03 1.01 0.93
f1 (ppm)

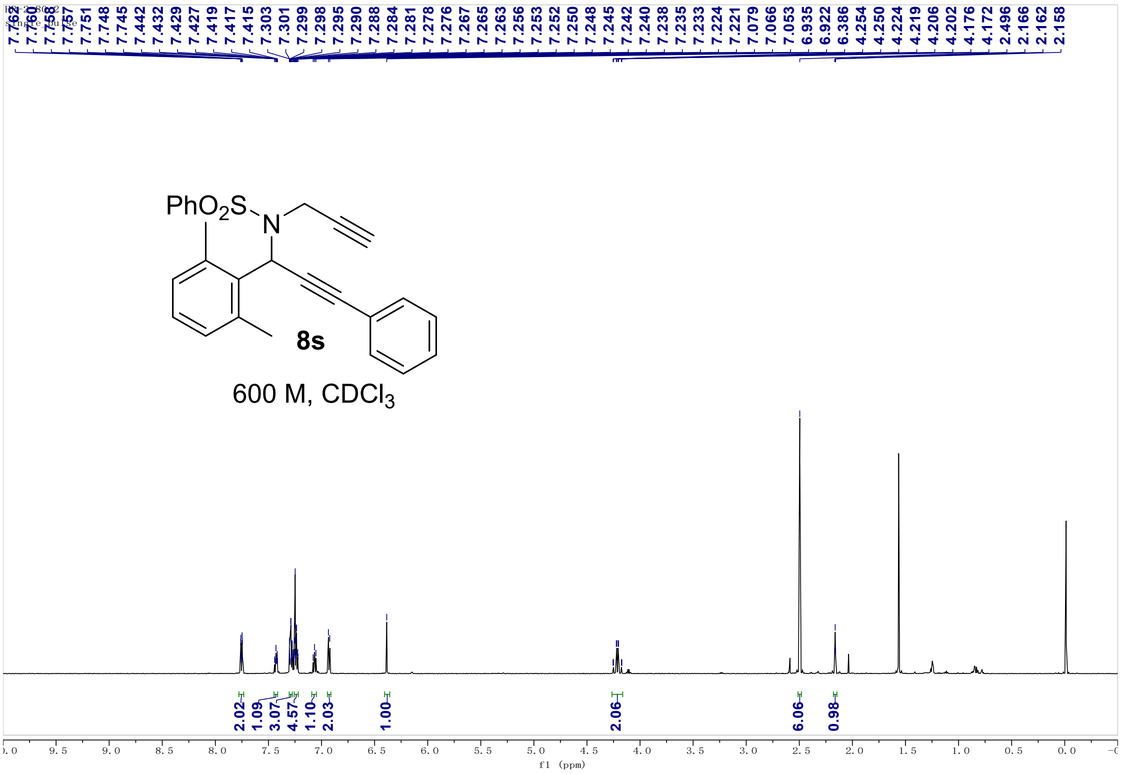

HR-4-135
single pulse decoupled gated NOE
139.341 138.079 136.308 135.145 133.004 131.614 128.856 128.803 128.590 128.345 128.291 126.510 122.169 114.802
88.838 83.257 78.228 72.960
53.640
33.882
5s
150 M, CDCl3
f1 (ppm)

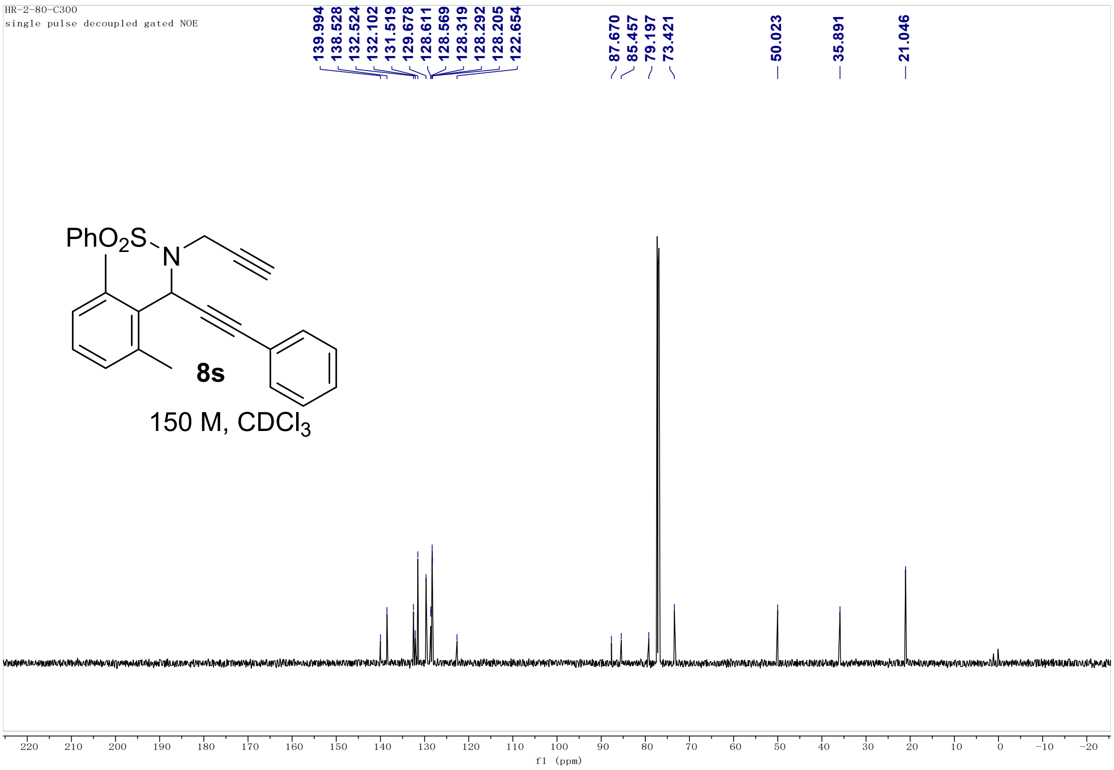

8.077
8.065
7.565
7.553
7.540
7.531
7.516
7.497
7.484
7.472
7.315
7.302
7.290
7.275
7.263
7.249
7.177
7.166
6.725
6.711
6.249
4.169
4.165
4.139
4.135
3.744
3.740
3.713
3.709
2.965
1.946
1.942
1.938
PhO2S
N
N
6s
600 M, CDCl3
2.00
5.09
3.04
1.98
1.99
0.94
0.99
0.96
6.09
0.98
f1 (ppm)

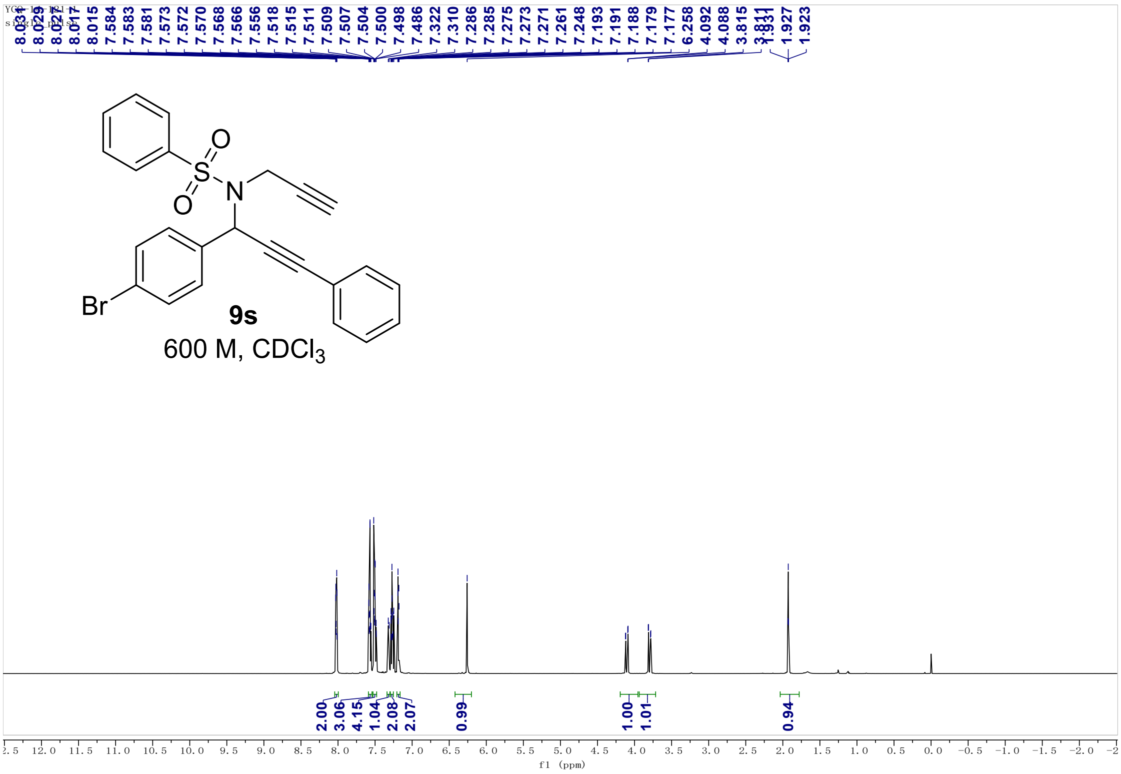

ycq-15-6s
single pulse decoupled gated NOE
150.773
139.525
132.911
131.581
129.407
128.782
128.612
128.379
128.327
122.636
122.505
88.156
84.200
78.579
72.672
53.373
40.627
33.379
PhO2S
N
N
6s
150 M, CDCl3
f1 (ppm)

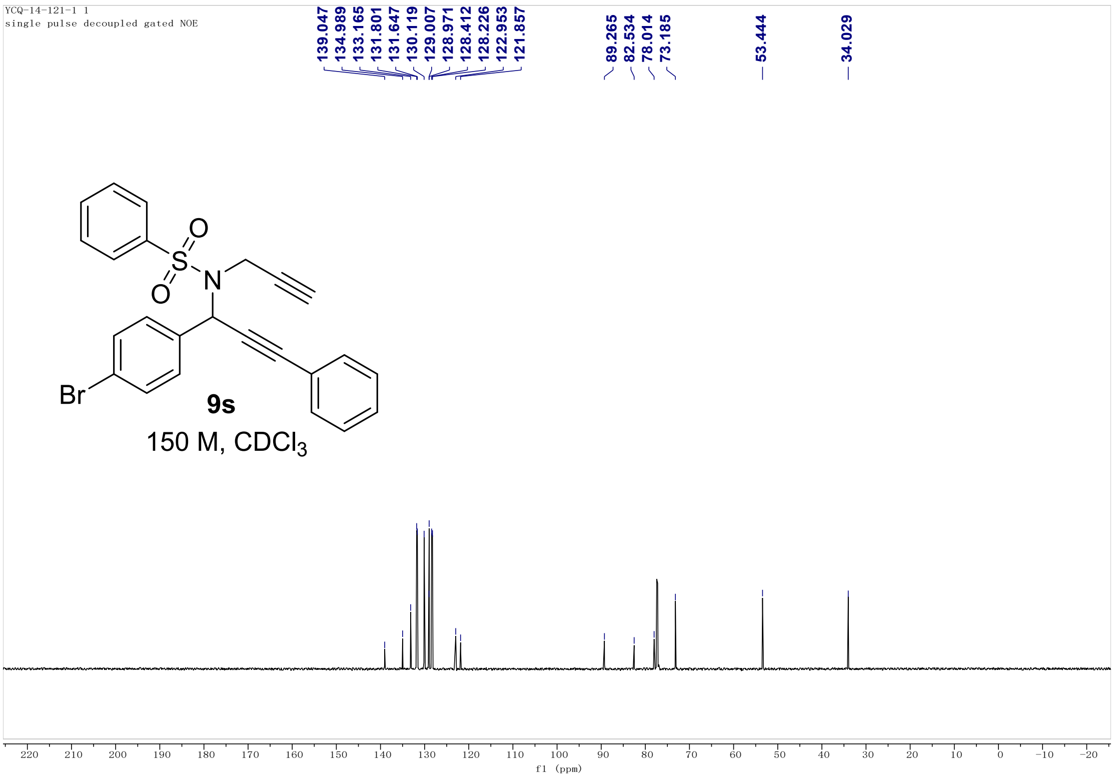

7s
600 M, CDCl3
2.06
3.03
2.01
1.05
6.04
2.00
6.00
2.03
1.00
1.03
1.01
0.94
f1 (ppm)

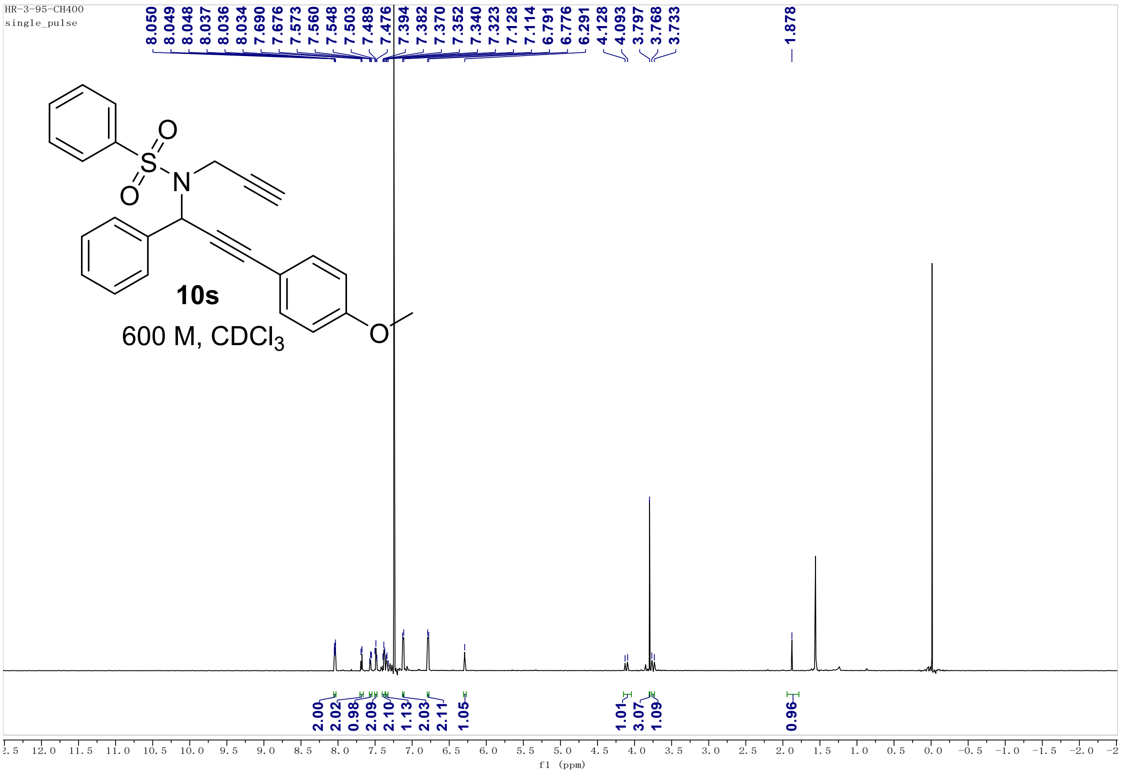

hr-4-40-1-c
single pulse decoupled gated NOE
148.378
147.579
139.448
132.975
131.600
129.454
129.361
129.019
128.858
128.760
128.340
128.280
124.702
123.341
123.189
122.221
88.614
83.580
78.524
72.731
53.489
33.771
7s
150 M, CDCl3
f1 (ppm)

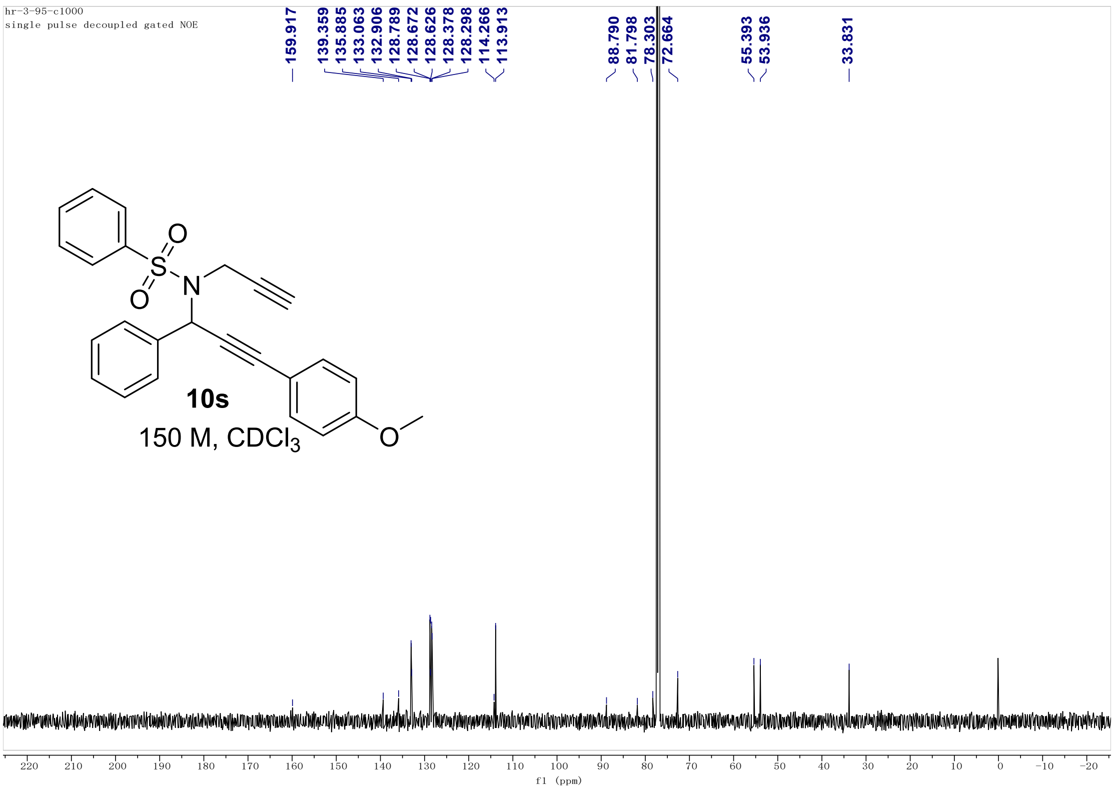

7.762
7.760
7.758
7.757
7.751
7.748
7.745
7.442
7.432
7.429
7.427
7.419
7.417
7.415
7.303
7.301
7.299
7.298
7.295
7.290
7.288
7.284
7.281
7.278
7.276
7.267
7.265
7.263
7.256
7.253
7.252
7.250
7.248
7.245
7.242
7.240
7.238
7.235
7.233
7.224
7.221
7.079
7.066
7.053
6.935
6.922
6.386
4.254
4.250
4.224
4.219
4.206
4.202
4.176
4.172
2.496
2.166
2.162
2.158
PhO2S
N
8s
600 M, CDCl3
2.02
1.09
3.07
4.57
1.10
2.03
1.00
2.06
6.06
0.98
f1 (ppm)

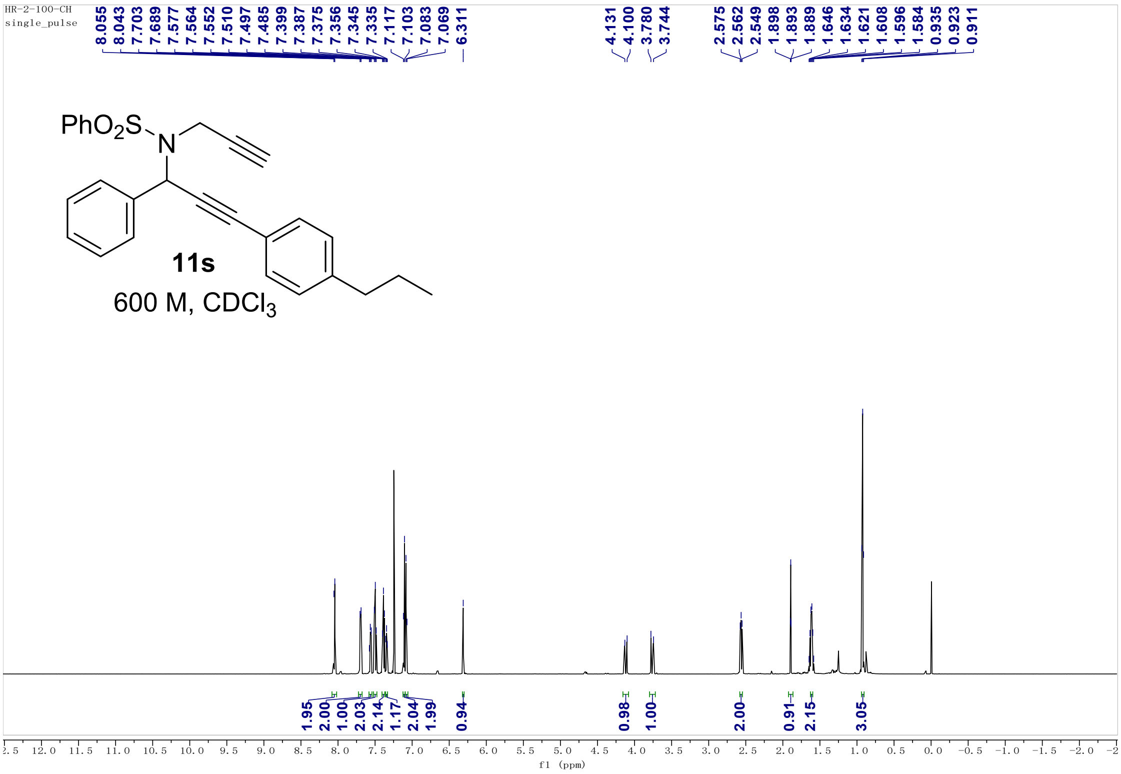

HR-2-80-C300
single pulse decoupled gated NOE
139.994
138.528
132.524
132.102
131.519
129.678
128.611
128.569
128.319
128.292
128.205
122.654
87.670
85.457
79.197
73.421
50.023
35.891
21.046
PhO2S
N
8s
150 M, CDCl3
f1 (ppm)

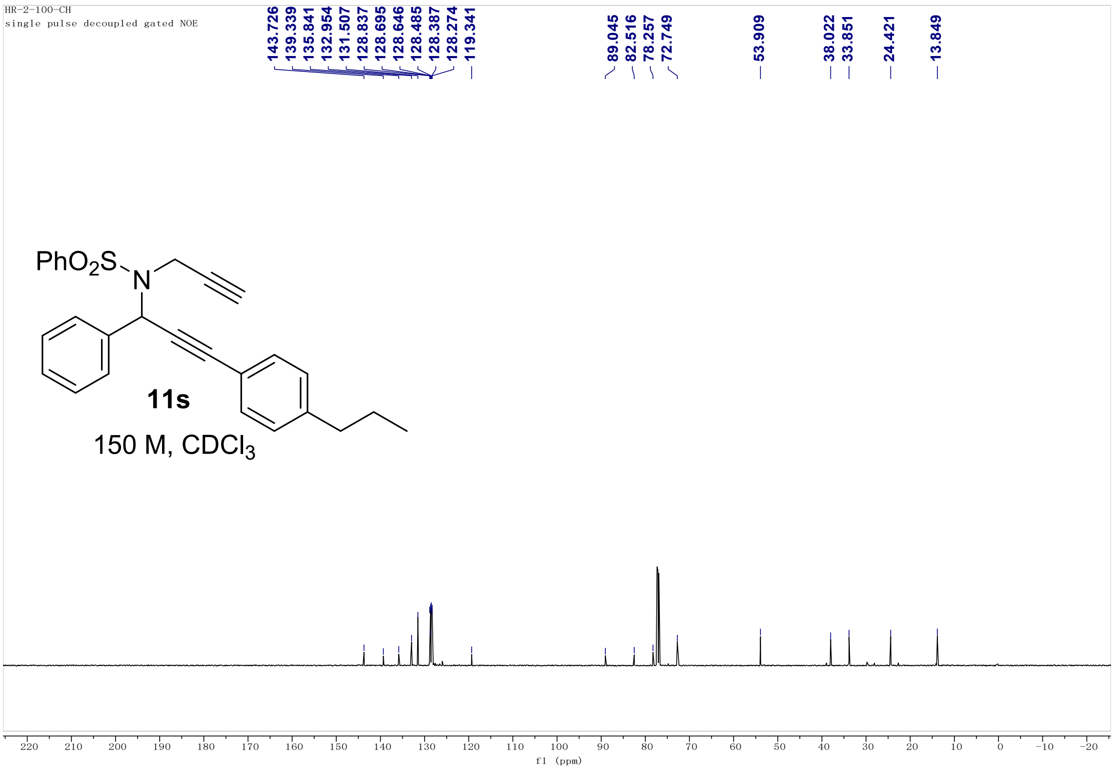


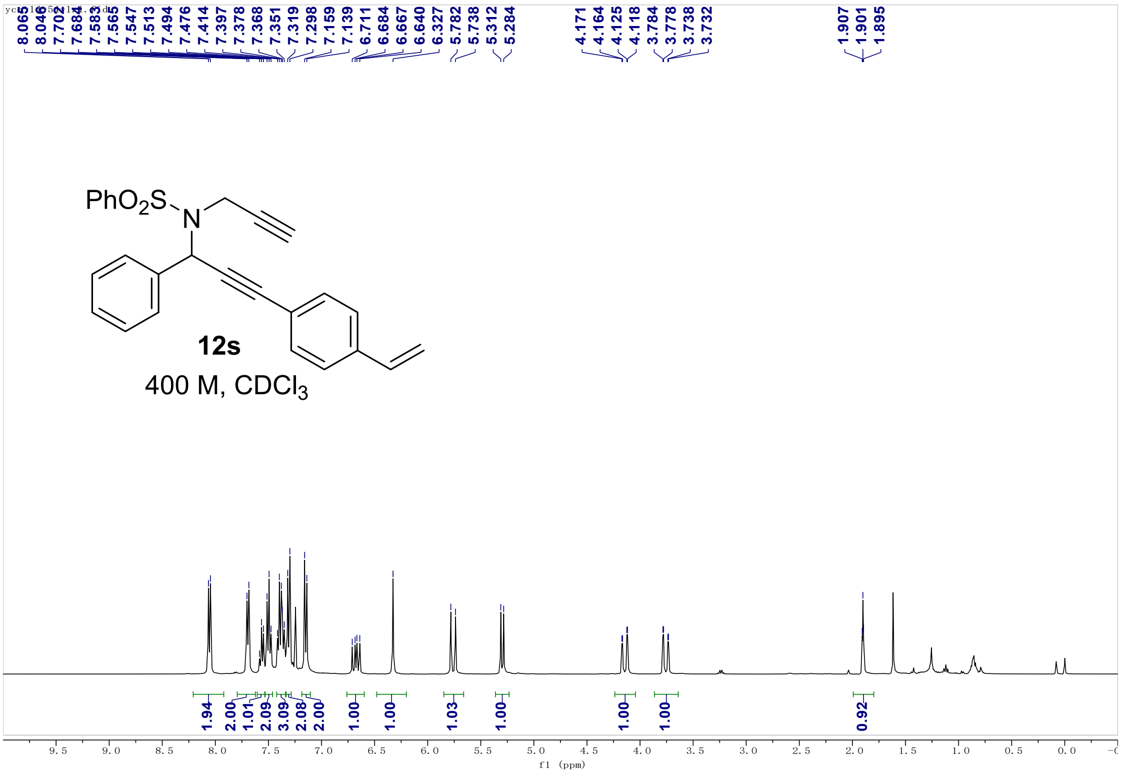



HR-3-95-CH400
single_pulse
8.050
8.049
8.048
8.037
8.036
8.034
7.690
7.676
7.573
7.560
7.548
7.503
7.489
7.476
7.394
7.382
7.370
7.352
7.340
7.323
7.128
7.114
6.791
6.776
6.291
4.128
4.093
3.797
3.768
3.733
1.878
10s
600 M, CDCl3
2.00
2.02
0.98
2.09
2.10
1.13
2.03
2.11
1.05
1.01
3.07
1.09
0.96
f1 (ppm)

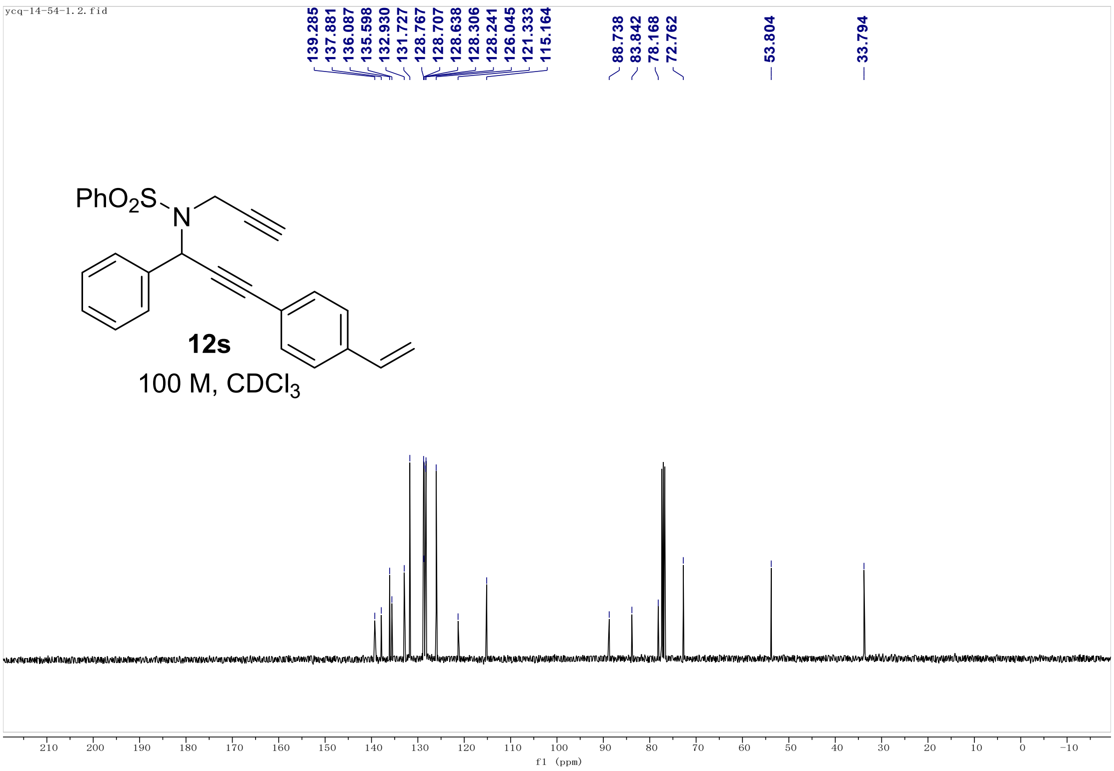

hr-3-95-c1000
single pulse decoupled gated NOE
159.917
139.359
135.885
133.063
132.906
128.789
128.672
128.626
128.378
128.298
114.266
113.913
88.790
81.798
78.303
72.664
55.393
53.936
33.831
10s
150 M, CDCl3
f1 (ppm)


HR-2-100-CH
single_pulse
PhO2S
N
11s
600 M, CDCl3
f1 (ppm)

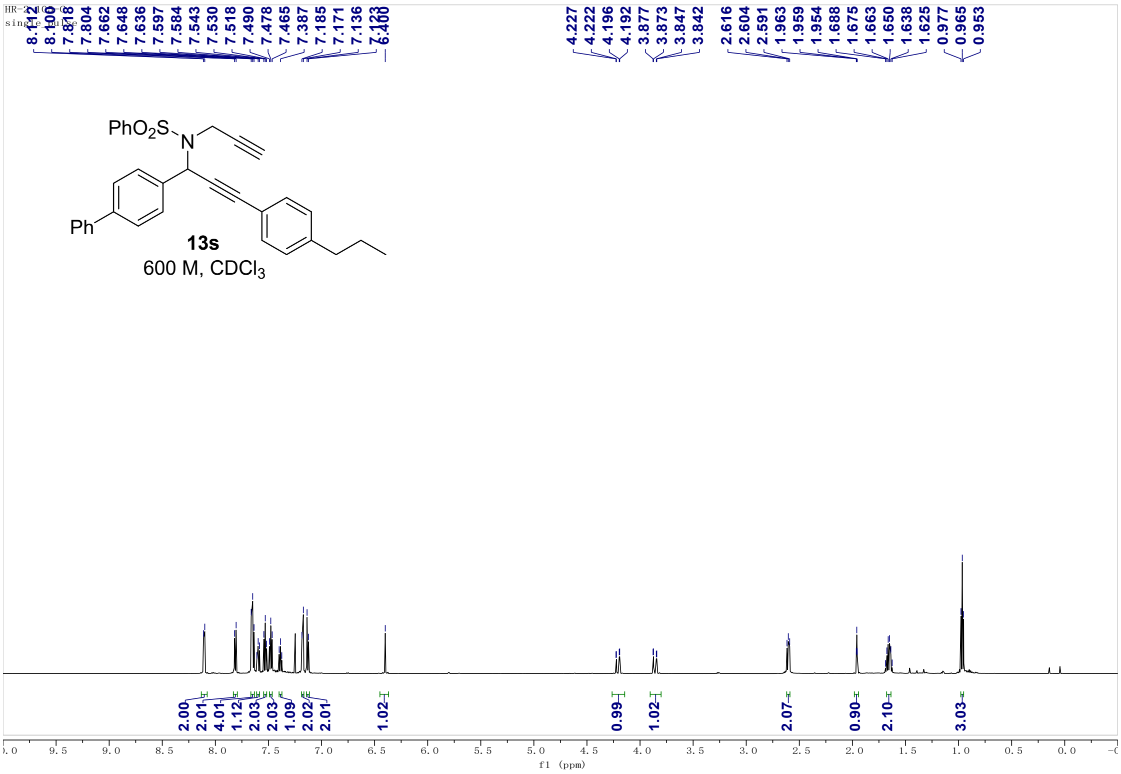

HR-2-100-CH
single pulse decoupled gated NOE
PhO2S
N
11s
150 M, CDCl3
f1 (ppm)

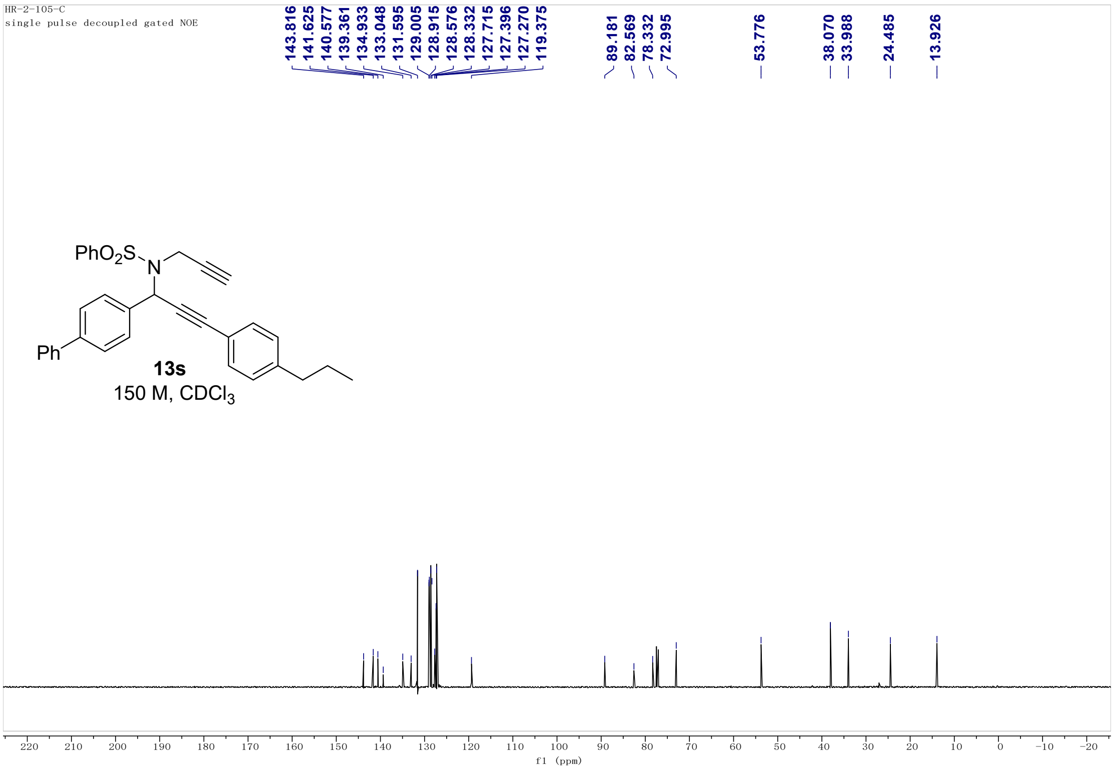


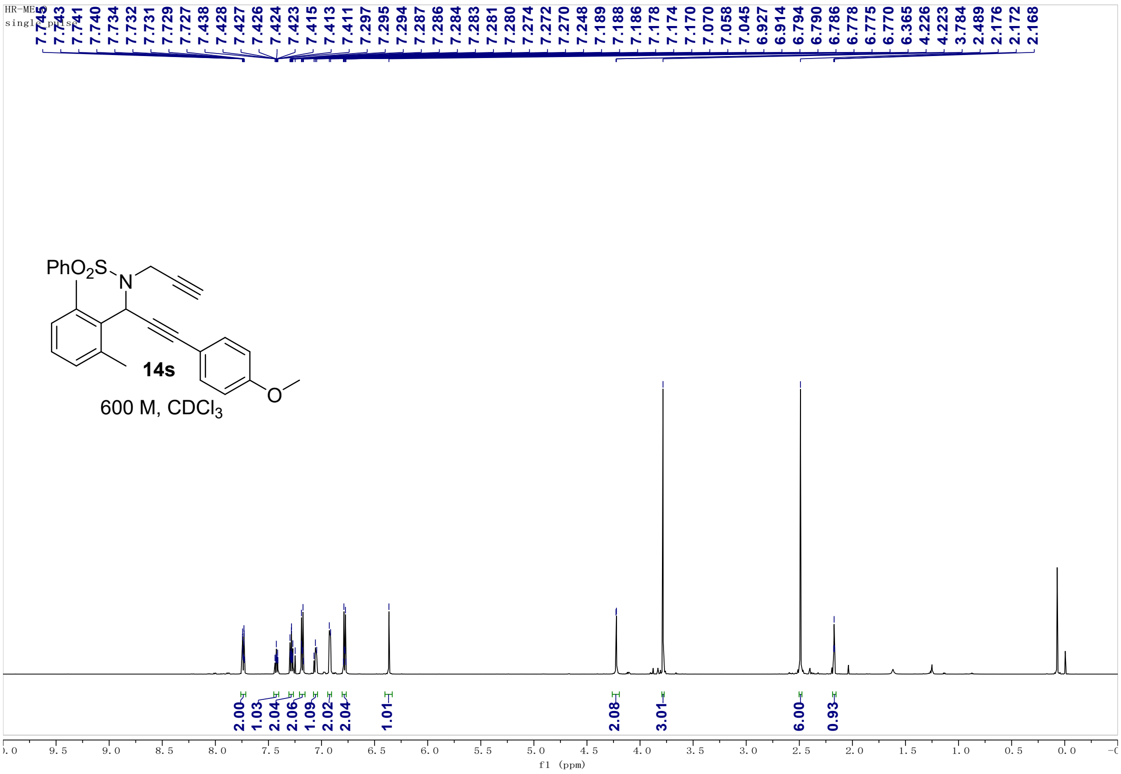
PhO2S
N
12s
400 M, CDCl3

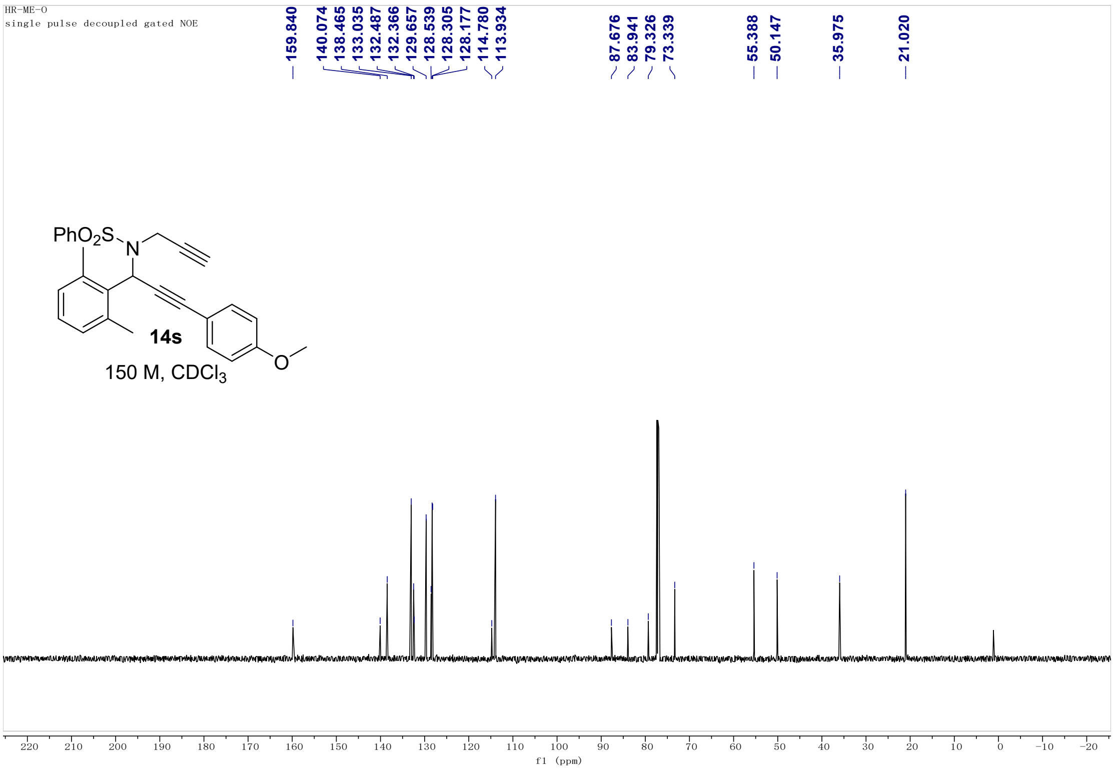


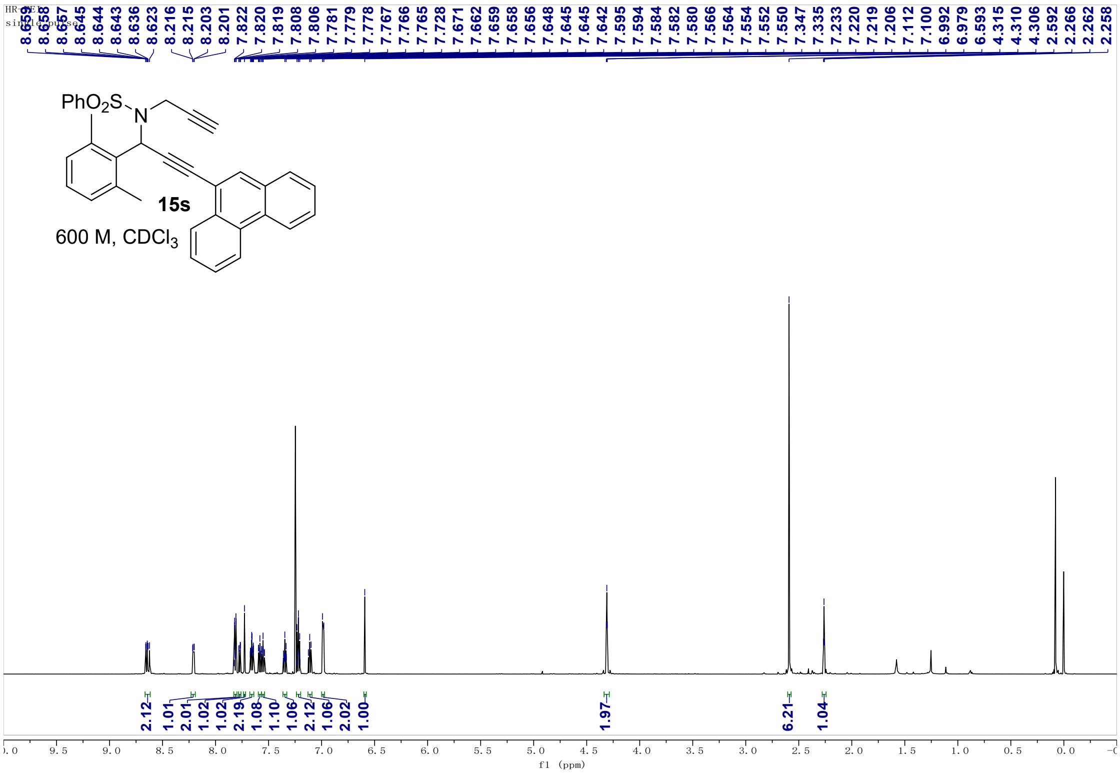
PhO2S
N
12s
100 M, CDCl3

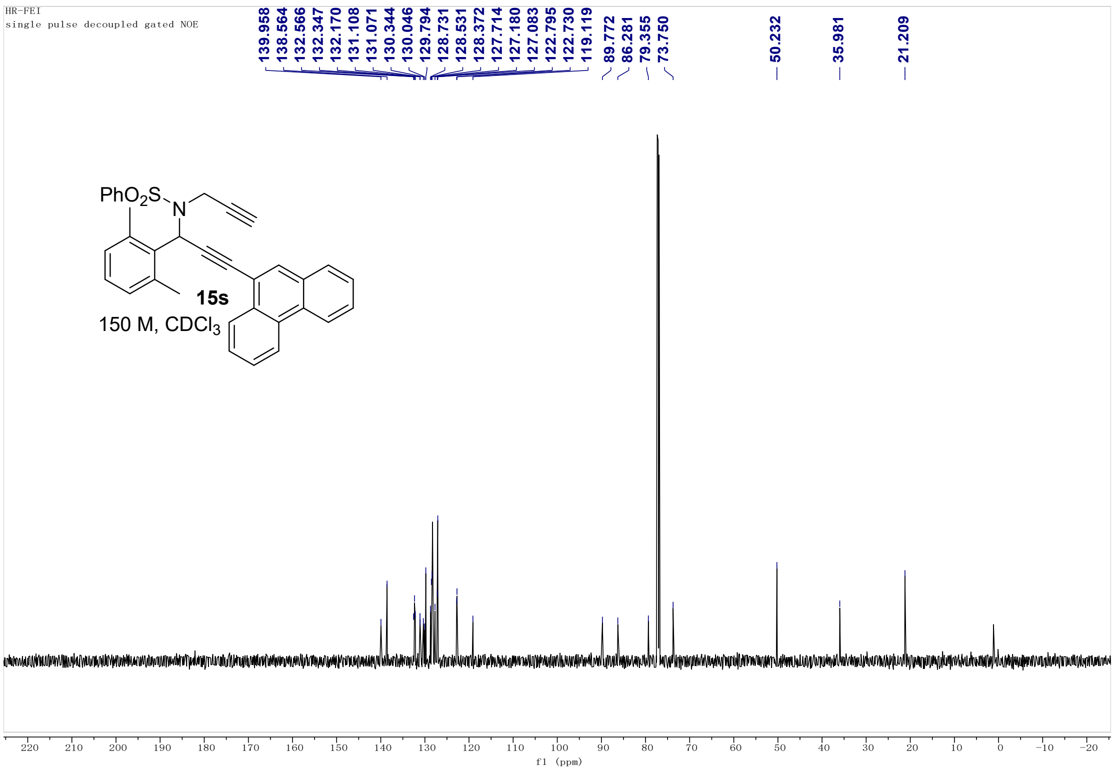

8.112
8.100
7.818
7.804
7.662
7.648
7.636
7.597
7.584
7.543
7.530
7.518
7.490
7.478
7.465
7.387
7.185
7.171
7.136
7.123
6.400
4.227
4.222
4.196
4.192
3.877
3.873
3.847
3.842
2.616
2.604
2.591
1.963
1.959
1.954
1.688
1.675
1.663
1.650
1.638
1.625
0.977
0.965
0.953
PhO2S
N
Ph
13s
600 M, CDCl3
2.00
2.01
4.01
1.12
2.03
2.03
1.09
2.02
2.01
1.02
0.99
1.02
2.07
0.90
2.10
3.03
f1 (ppm)

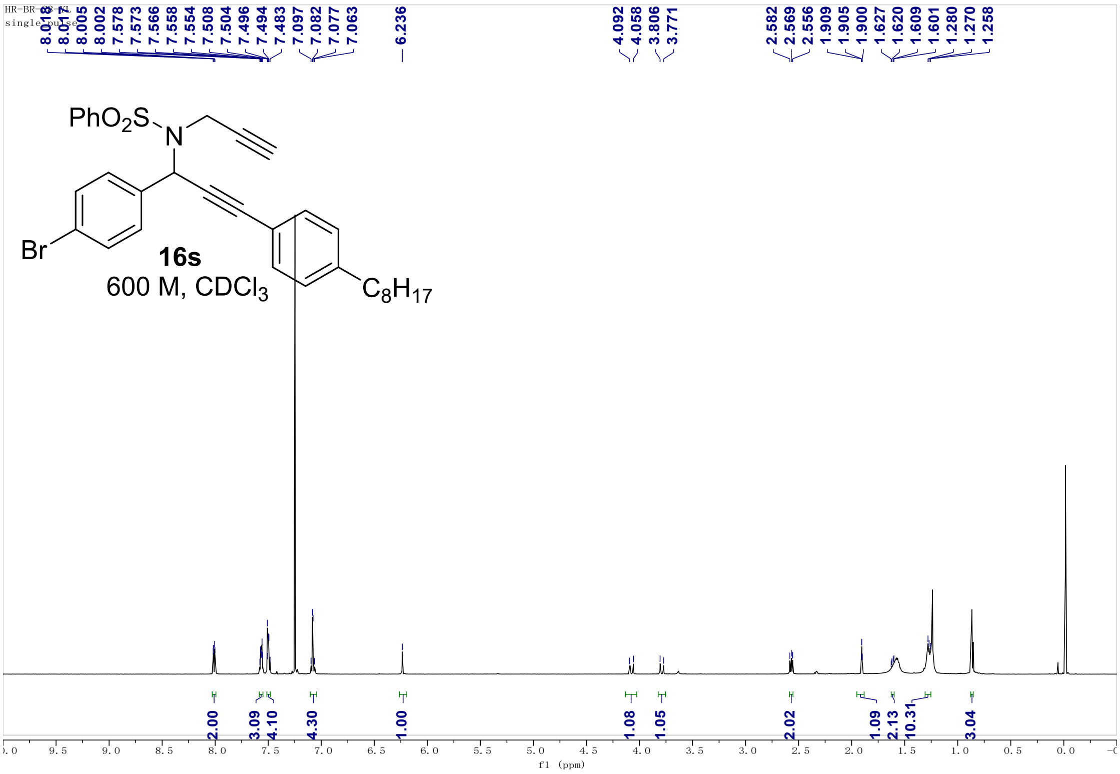

HR-2-105-C
single pulse decoupled gated NOE
143.816
141.625
140.577
139.361
134.933
133.048
131.595
129.005
128.915
128.576
128.332
127.715
127.396
127.270
119.375
89.181
82.569
78.332
72.995
53.776
38.070
33.988
24.485
13.926
PhO2S
N
Ph
13s
150 M, CDCl3
f1 (ppm)

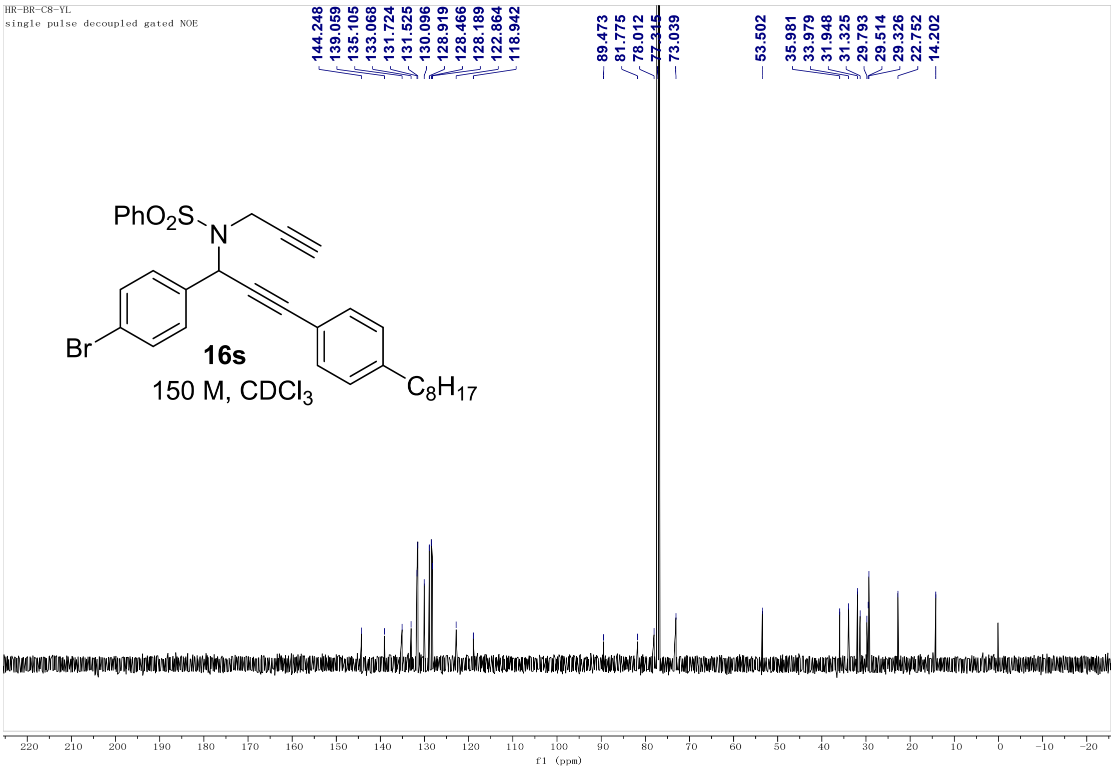


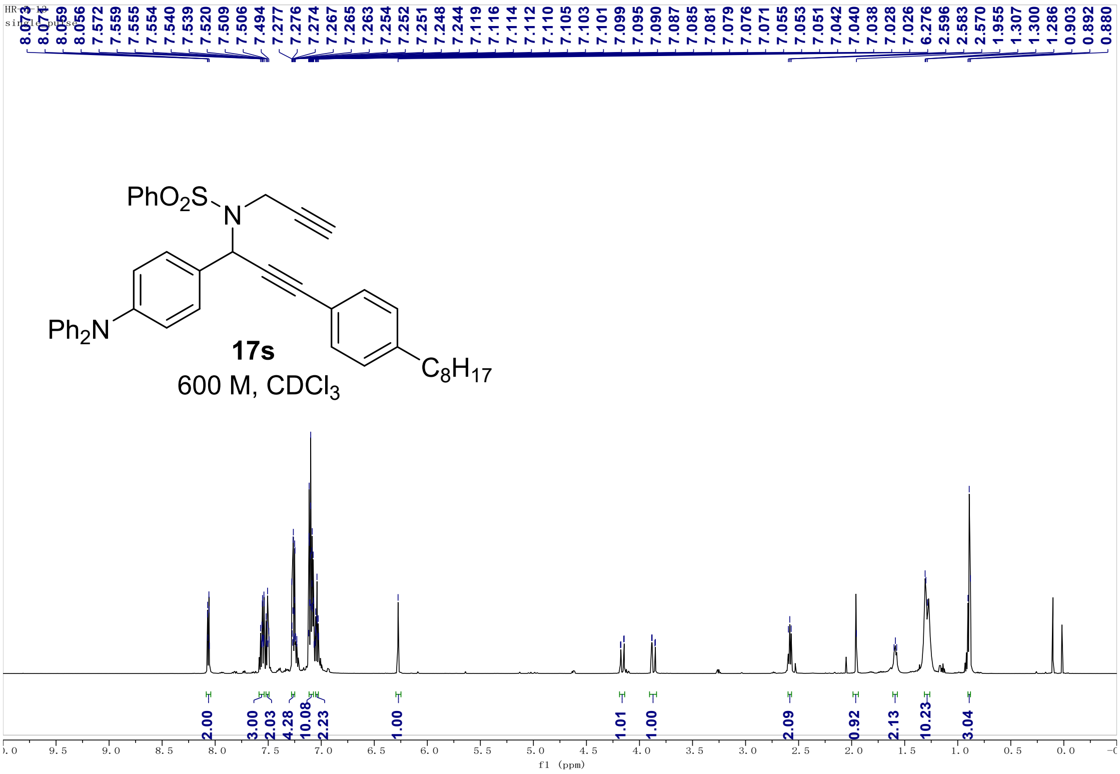



15s
600 M, CDCl3
f1 (ppm)

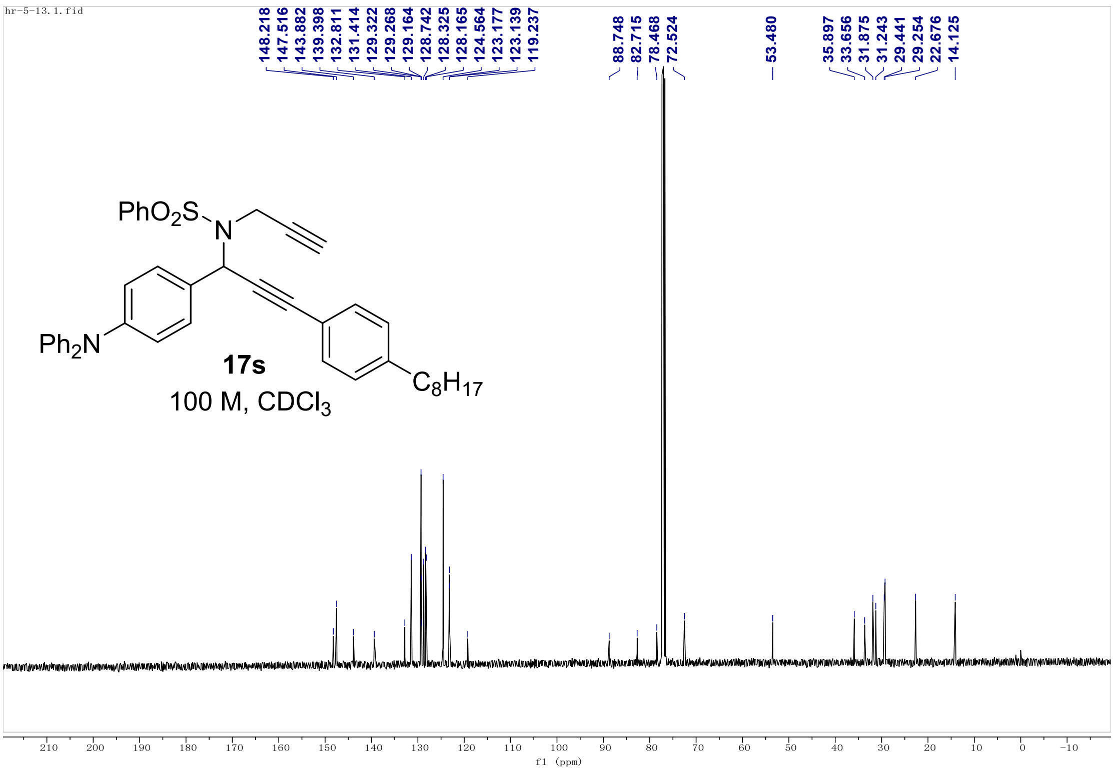

HR-FEI
single pulse decoupled gated NOE
15s
150 M, CDCl3
f1 (ppm)


HR-BR-C8-YL
single pulse
8.018
8.017
8.005
8.002
7.578
7.573
7.566
7.558
7.554
7.508
7.504
7.496
7.494
7.483
7.097
7.082
7.077
7.063
6.236
4.092
4.058
3.806
3.771
2.582
2.569
2.556
1.909
1.905
1.900
1.627
1.620
1.609
1.601
1.280
1.270
1.258
PhO2S
N
Br
16s
600 M, CDCl3
C8H17
2.00
3.09
4.10
4.30
1.00
1.08
1.05
2.02
1.09
2.13
10.31
3.04
f1 (ppm)

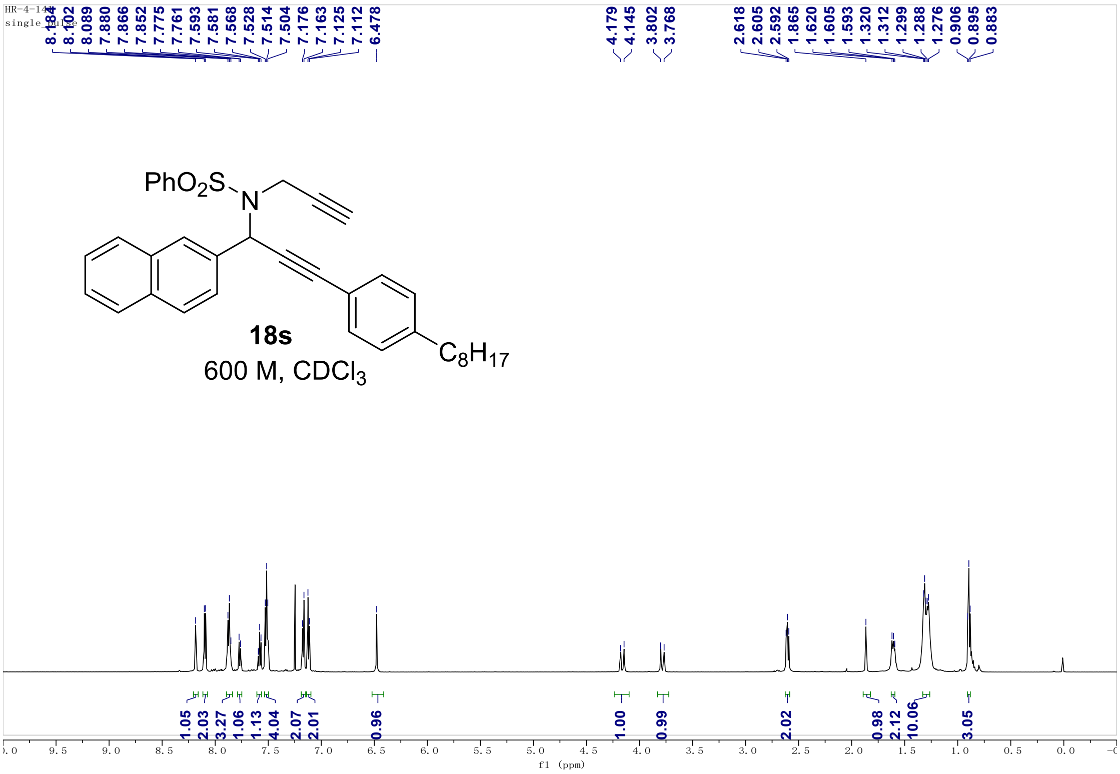

HR-BR-C8-YL
single pulse decoupled gated NOE
144.248
139.059
135.105
133.068
131.724
131.525
130.096
128.919
128.466
128.189
122.864
118.942
89.473
81.775
78.012
77.315
73.039
53.502
35.981
33.979
31.948
31.325
29.793
29.514
29.326
22.752
14.202
PhO2S
N
Br
16s
150 M, CDCl3
C8H17
f1 (ppm)



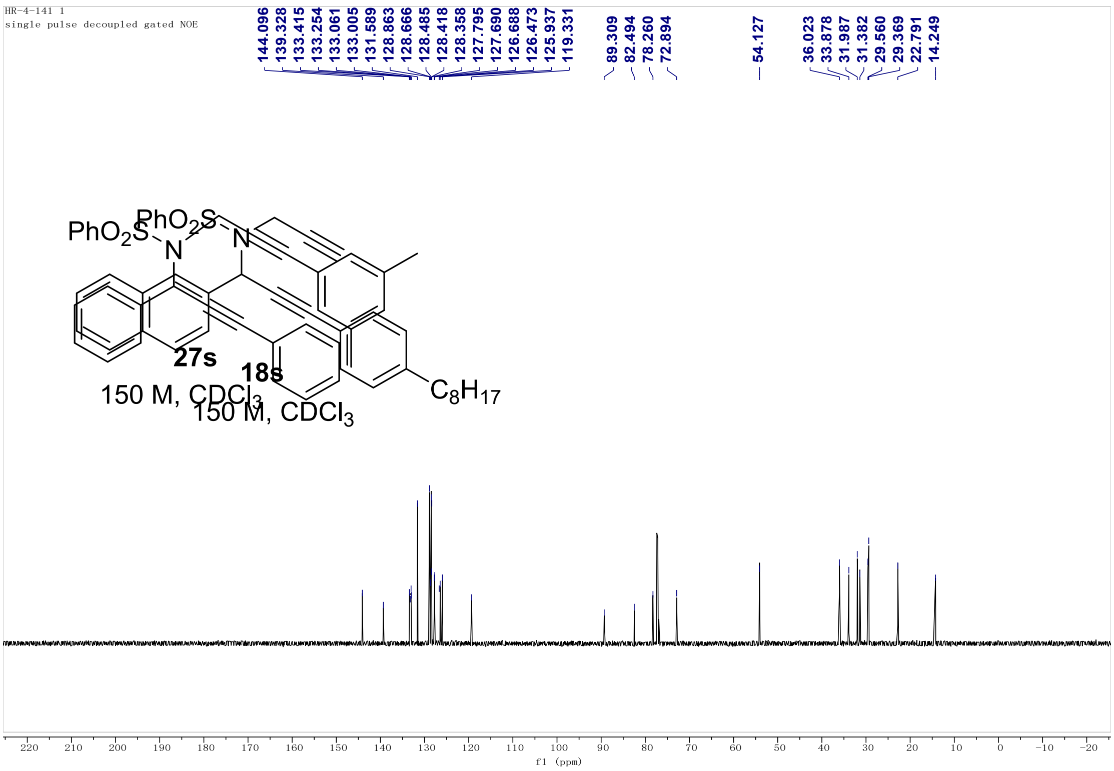
PhO2S
N
Ph2N
17s
600 M, CDCl3
C8H17
f1 (ppm)



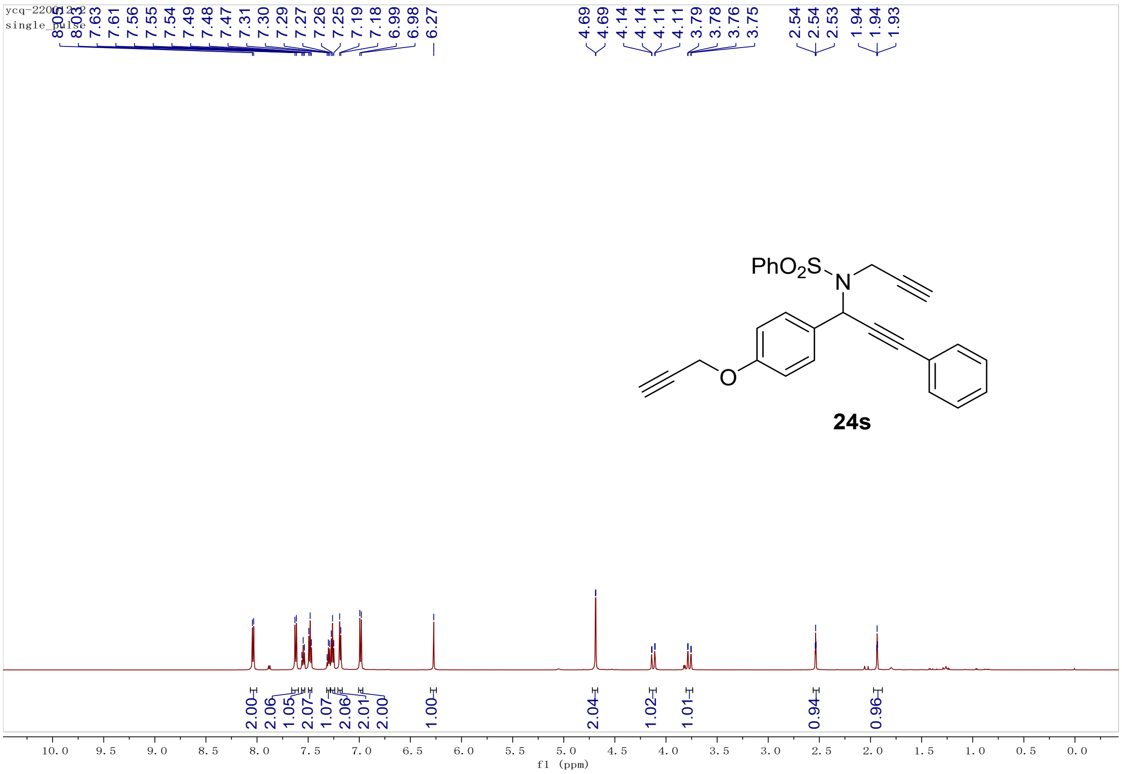
hr-5-13.1.fid
148.218
147.516
143.882
139.398
132.811
131.414
129.322
129.268
129.164
128.742
128.325
128.165
124.564
123.177
123.139
119.237
88.748
82.715
78.468
72.524
53.480
35.897
33.656
31.875
31.243
29.441
29.254
22.676
14.125
PhO2S
N
Ph2N
17s
100 M, CDCl3
C8H17
f1 (ppm)

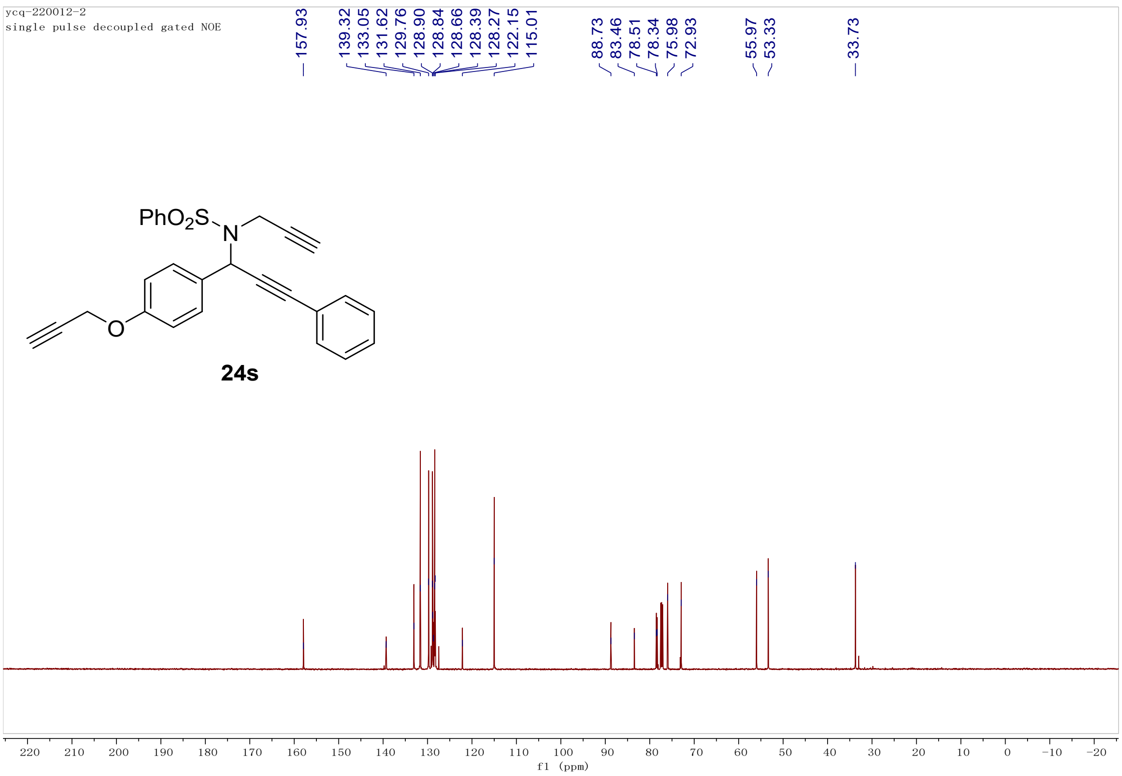


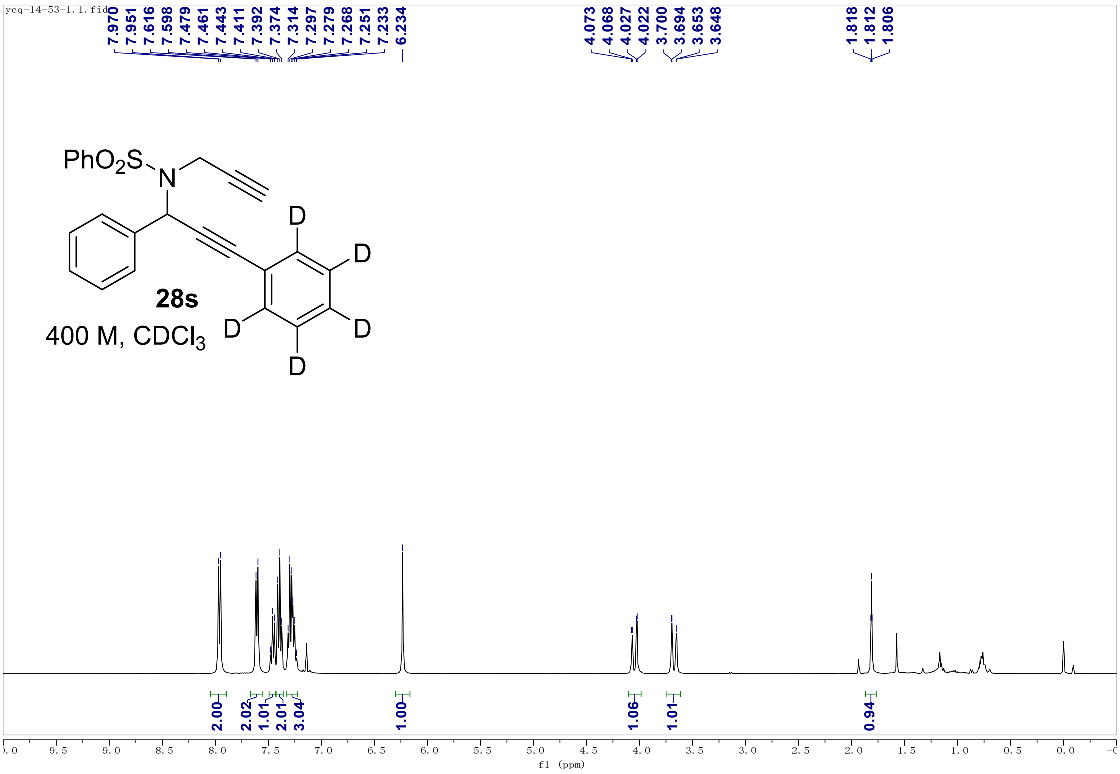
HR-4-141
single pulse
8.184
8.102
8.089
7.880
7.866
7.852
7.775
7.761
7.593
7.581
7.568
7.528
7.514
7.504
7.176
7.163
7.125
7.112
6.478
4.179
4.145
3.802
3.768
2.618
2.605
2.592
1.865
1.620
1.605
1.593
1.320
1.312
1.299
1.288
1.276
0.906
0.895
0.883
PhO2S
N
18s
600 M, CDCl3
C8H17
1.05
2.03
3.27
1.06
1.13
4.04
2.07
2.01
0.96
1.00
0.99
2.02
0.98
2.12
10.06
3.05
f1 (ppm)

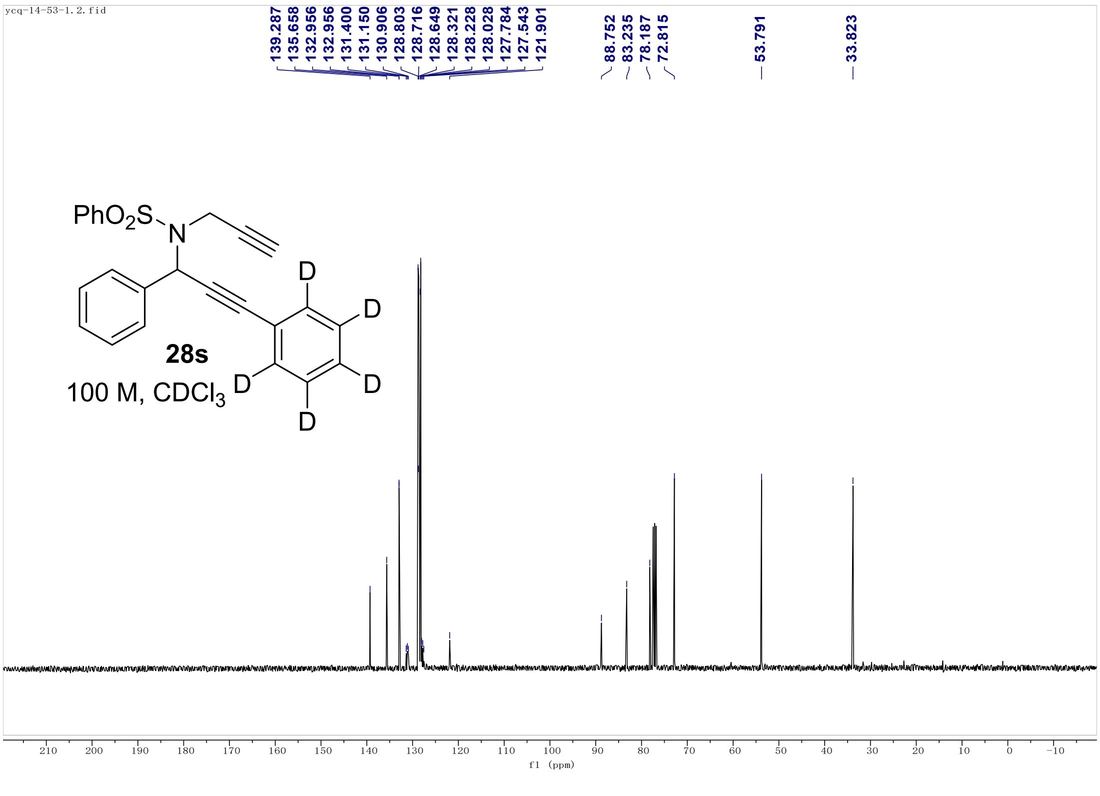


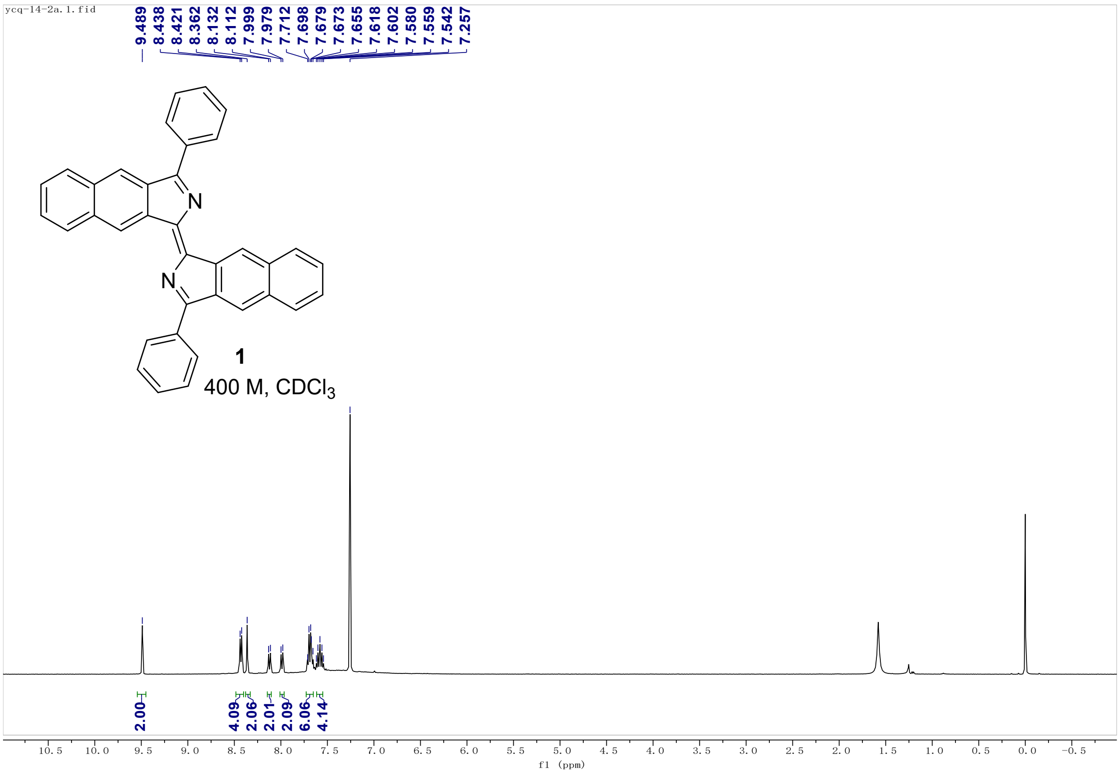
HR-4-141 1
single pulse decoupled gated NOE
144.096
139.328
133.415
133.254
133.061
133.005
131.589
128.863
128.666
128.485
128.418
128.358
127.795
127.690
126.688
126.473
125.937
119.331
89.309
82.494
78.260
72.894
54.127
36.023
33.878
31.987
31.382
29.560
29.369
22.791
14.249
PhO2S
N
27s
18s
150 M, CDCl3
C8H17
f1 (ppm)

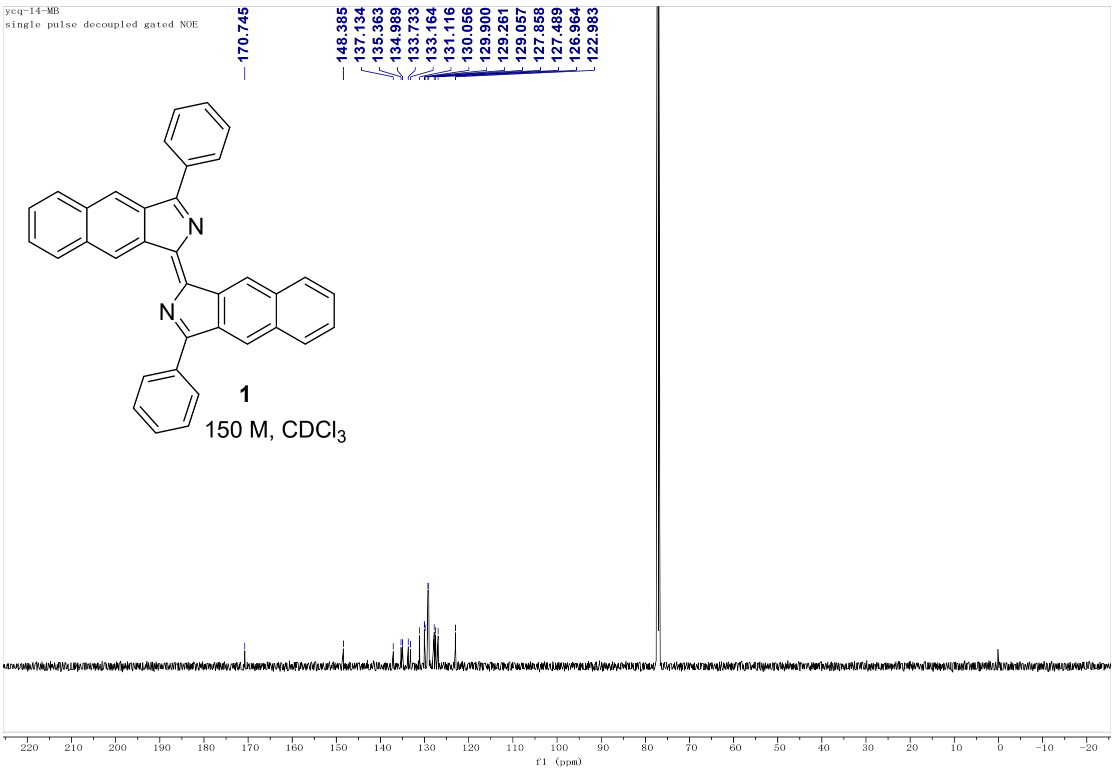

ycq-220012-2
single_pulse
8.05 8.03 7.63 7.61 7.56 7.55 7.54 7.49 7.48 7.47 7.31 7.30 7.29 7.27 7.26 7.25 7.19 7.18 6.99 6.98 6.27
4.69 4.69 4.14 4.14 4.11 4.11 3.79 3.78 3.76 3.75
2.54 2.54 2.53 1.94 1.94 1.93
PhO2S
N
O
24s
2.00 2.06 1.05 2.07 1.07 2.06 2.01 2.00 1.00 2.04 1.02 1.01 0.94 0.96
f1 (ppm)

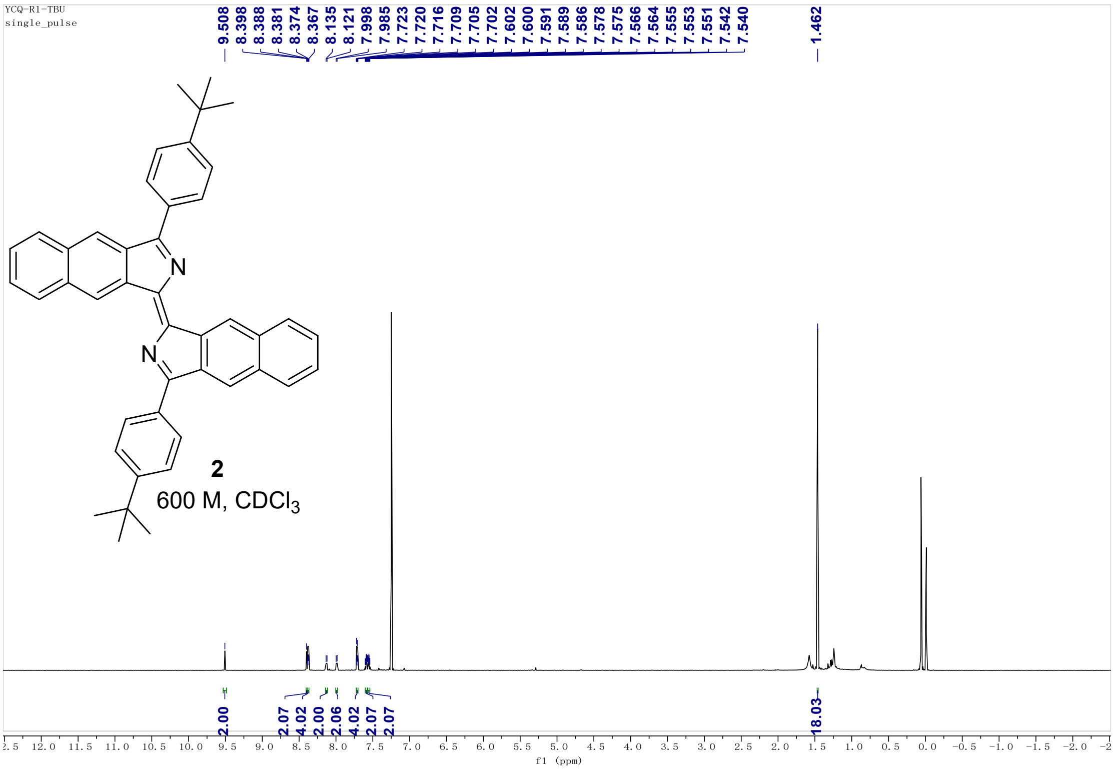

ycq-220012-2
single pulse decoupled gated NOE
157.93
139.32 133.05 131.62 129.76 128.90 128.84 128.66 128.39 128.27 122.15 115.01
88.73 83.46 78.51 78.34 75.98 72.93
55.97 53.33
33.73
PhO2S
N
O
24s
f1 (ppm)

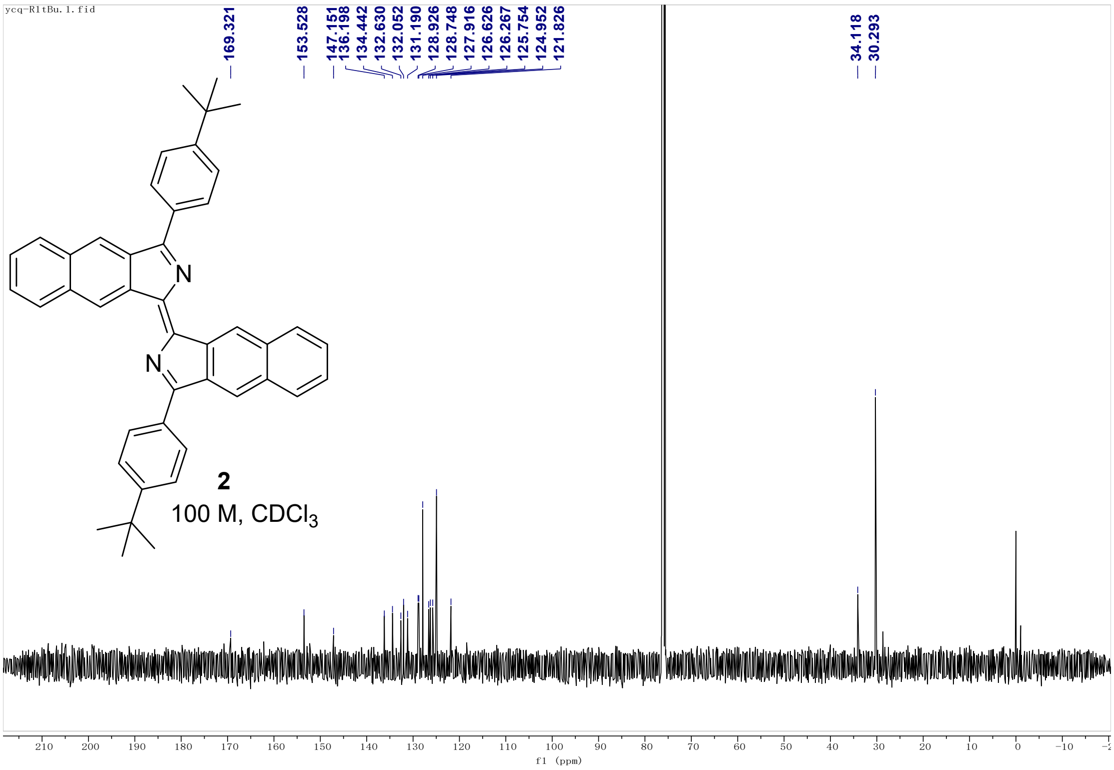

ycq-14-53-1.1.fid
7.970
7.951
7.616
7.598
7.479
7.461
7.443
7.411
7.392
7.374
7.314
7.297
7.279
7.268
7.251
7.233
6.234
4.073
4.068
4.027
4.022
3.700
3.694
3.653
3.648
1.818
1.812
1.806
PhO2S
N
D
D
D
D
D
28s
400 M, CDCl3
2.00
2.02
1.01
2.01
3.04
1.00
1.06
1.01
0.94
f1 (ppm)

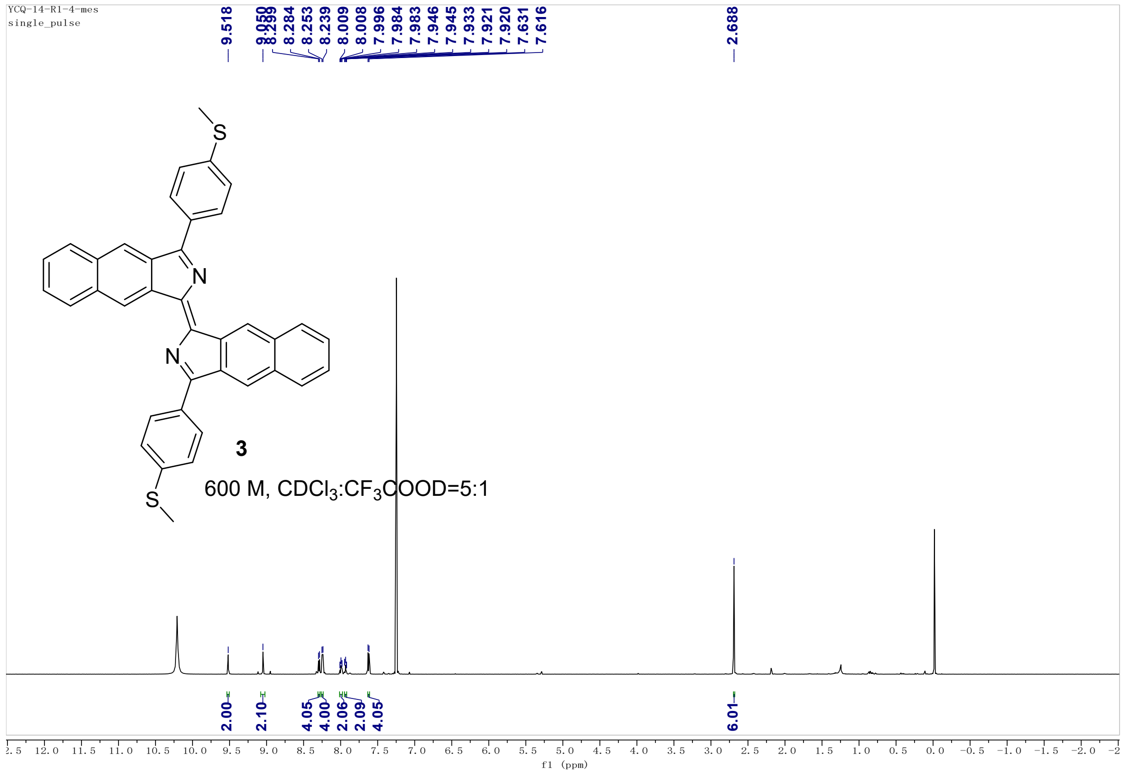

ycq-14-53-1.2.fid
139.287
135.658
132.956
132.956
131.400
131.150
130.906
128.803
128.716
128.649
128.321
128.228
128.028
127.784
127.543
121.901
88.752
83.235
78.187
72.815
53.791
33.823
PhO2S
N
D
D
D
D
D
28s
100 M, CDCl3
f1 (ppm)

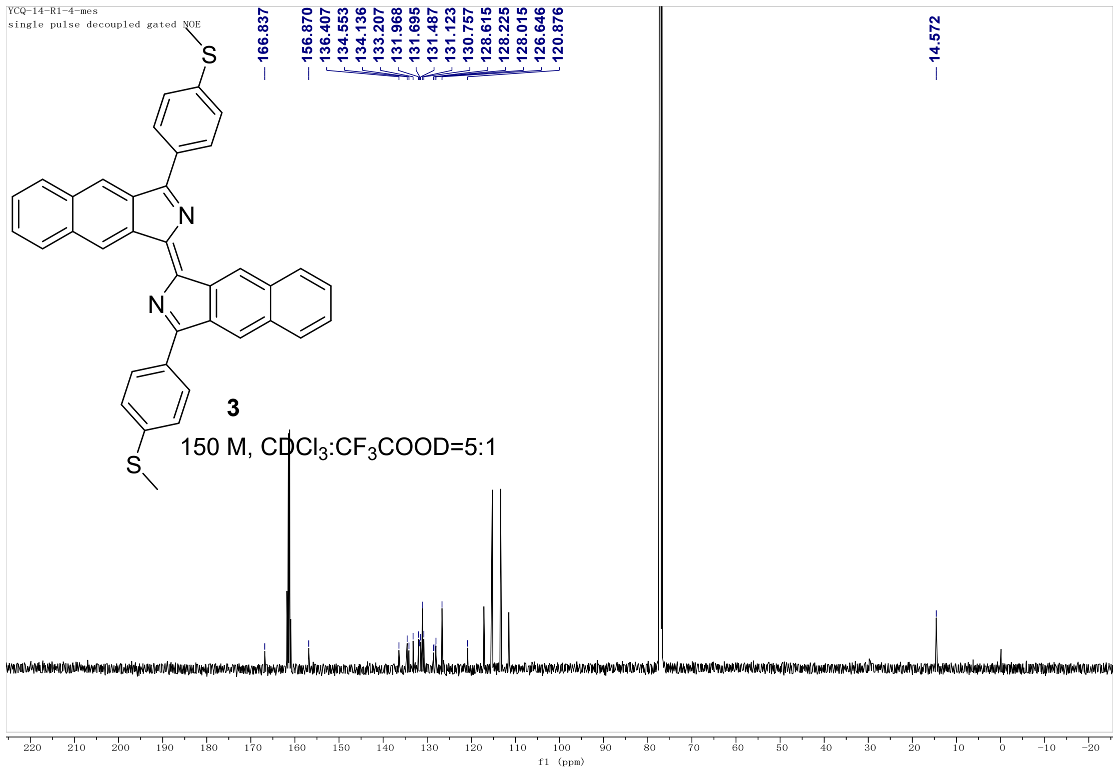

ycq-14-2a.1.fid
9.489
8.438
8.421
8.362
8.132
8.112
7.999
7.979
7.712
7.698
7.679
7.673
7.655
7.618
7.602
7.580
7.559
7.542
7.257
N
N
1
400 M, $CDCl_3$
2.00
4.09
2.06
2.01
2.09
6.06
4.14
f1 (ppm)

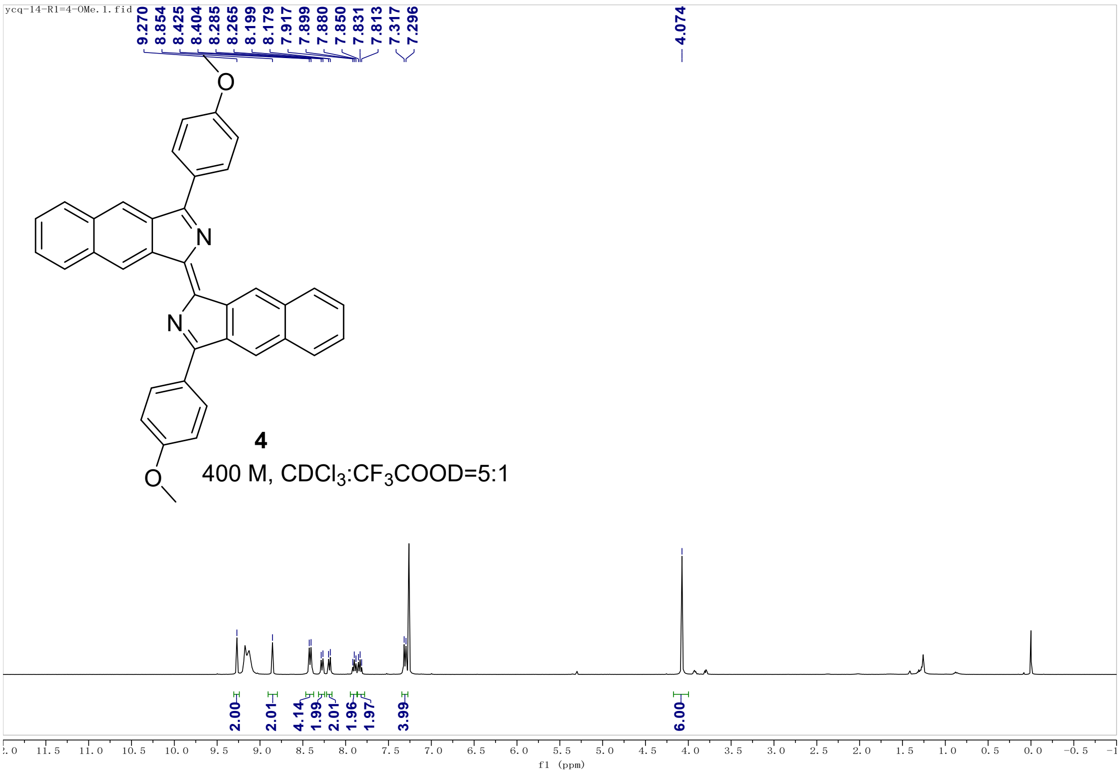

ycq-14-MB
single pulse decoupled gated NOE
170.745
148.385
137.134
135.363
134.989
133.733
133.164
131.116
130.056
129.900
129.261
129.057
127.858
127.489
126.964
122.983
N
N
1
150 M, $CDCl_3$
f1 (ppm)

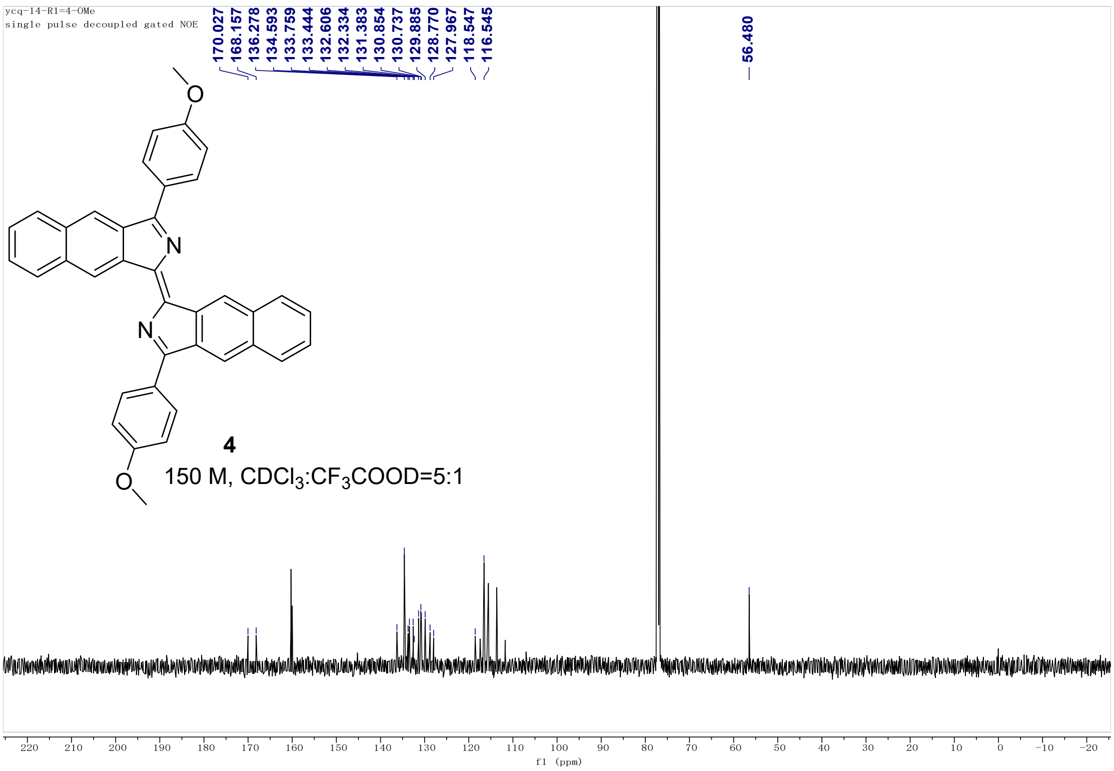

YCQ-R1-TBU
single_pulse
9.508
8.398
8.388
8.381
8.374
8.367
8.135
8.121
7.998
7.985
7.723
7.720
7.716
7.709
7.705
7.702
7.602
7.600
7.591
7.589
7.586
7.578
7.575
7.566
7.564
7.555
7.553
7.551
7.542
7.540
1.462
N
N
2
600 M, $CDCl_3$
2.00
2.07
4.02
2.00
2.06
4.02
2.07
2.07
18.03
f1 (ppm)

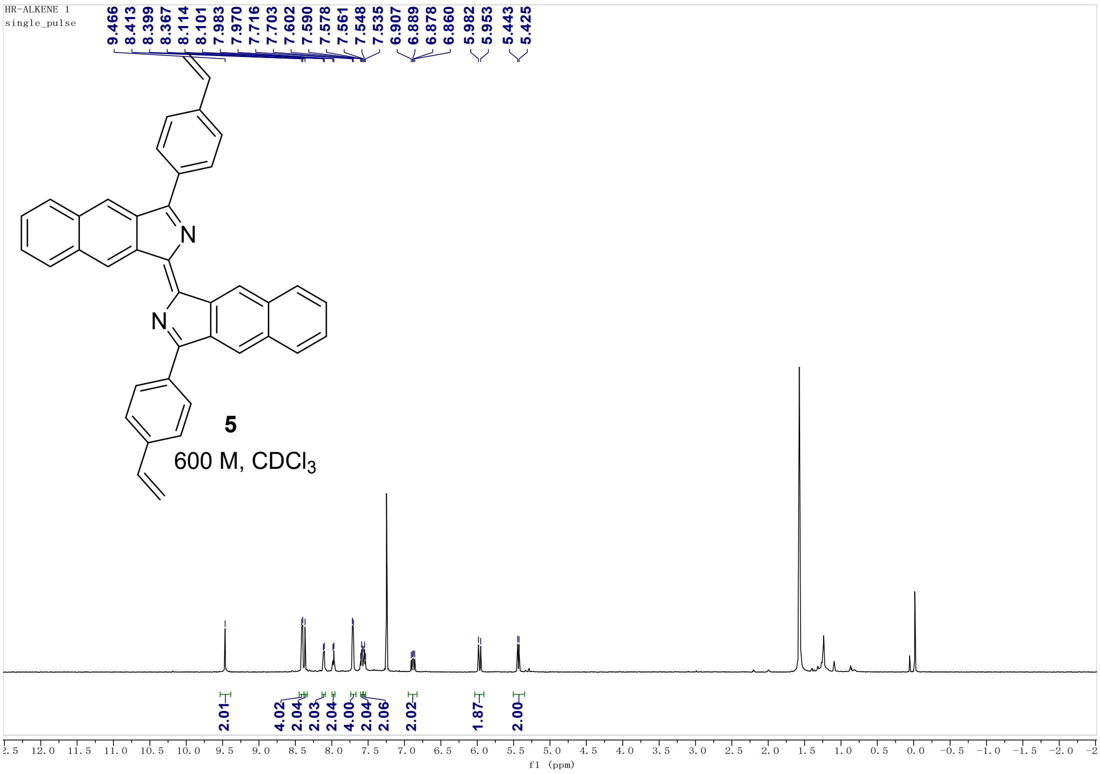

ycq-R1tBu.1.fid
169.321
153.528
147.151
136.198
134.442
132.630
132.052
131.190
128.926
128.748
127.916
126.626
126.267
125.754
124.952
121.826
34.118
30.293
N
N
2
100 M, $CDCl_3$
f1 (ppm)

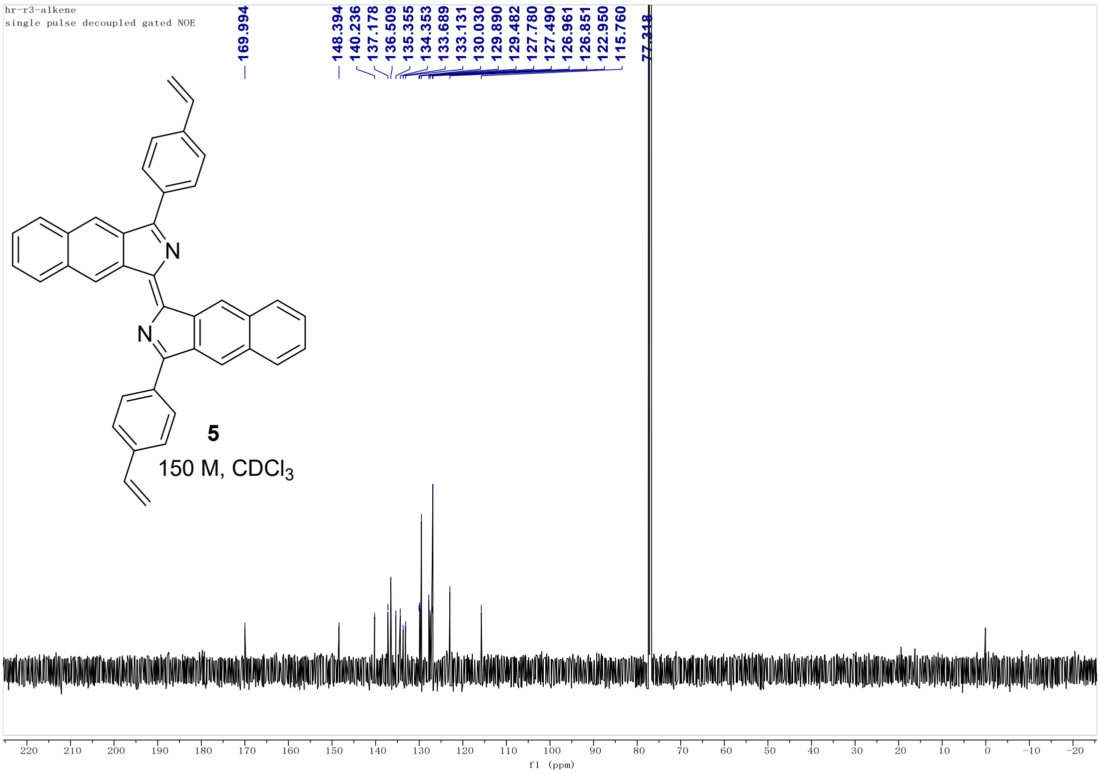

YCQ-14-R1-4-mes
single_pulse
9.518
9.050
8.284
8.253
8.239
8.009
8.008
7.996
7.984
7.983
7.946
7.945
7.933
7.921
7.920
7.631
7.616
2.688
3
600 M, CDCl3:CF3COOD=5:1
2.00
2.10
4.05
4.00
2.06
2.09
4.05
6.01
f1 (ppm)

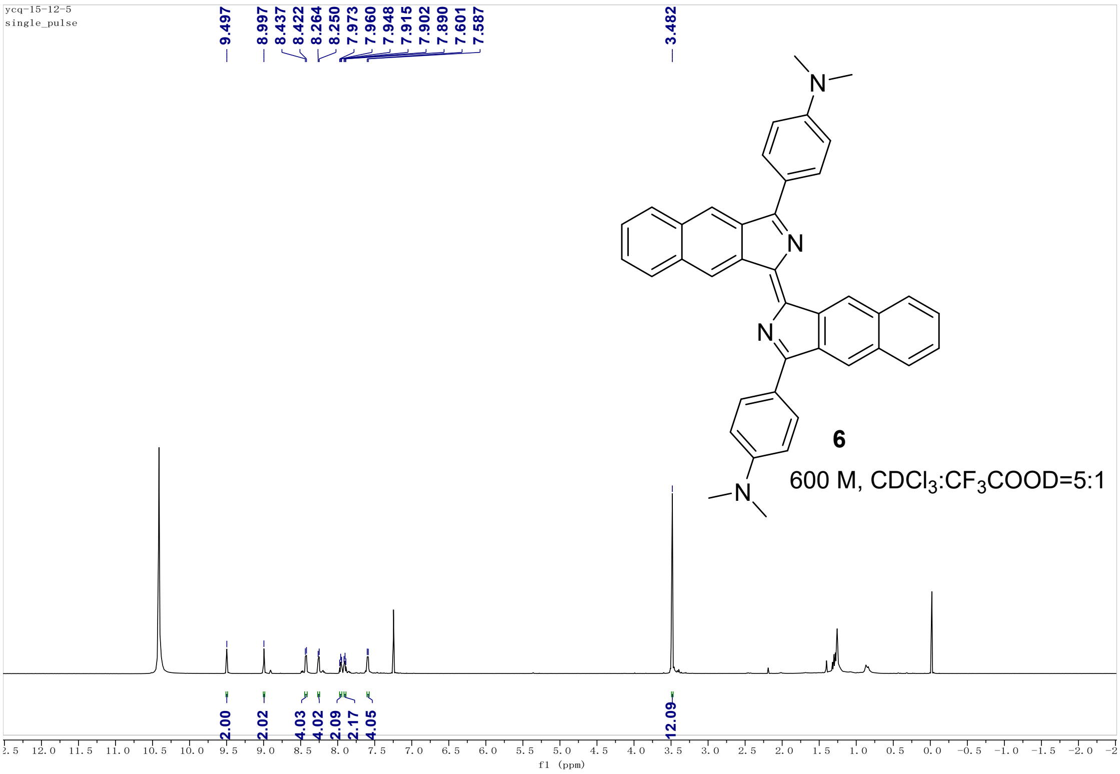

YCQ-14-R1-4-mes
single pulse decoupled gated NOE
166.837
156.870
136.407
134.553
134.136
133.207
131.968
131.695
131.487
131.123
130.757
128.615
128.225
128.015
126.646
120.876
14.572
3
150 M, CDCl3:CF3COOD=5:1
f1 (ppm)

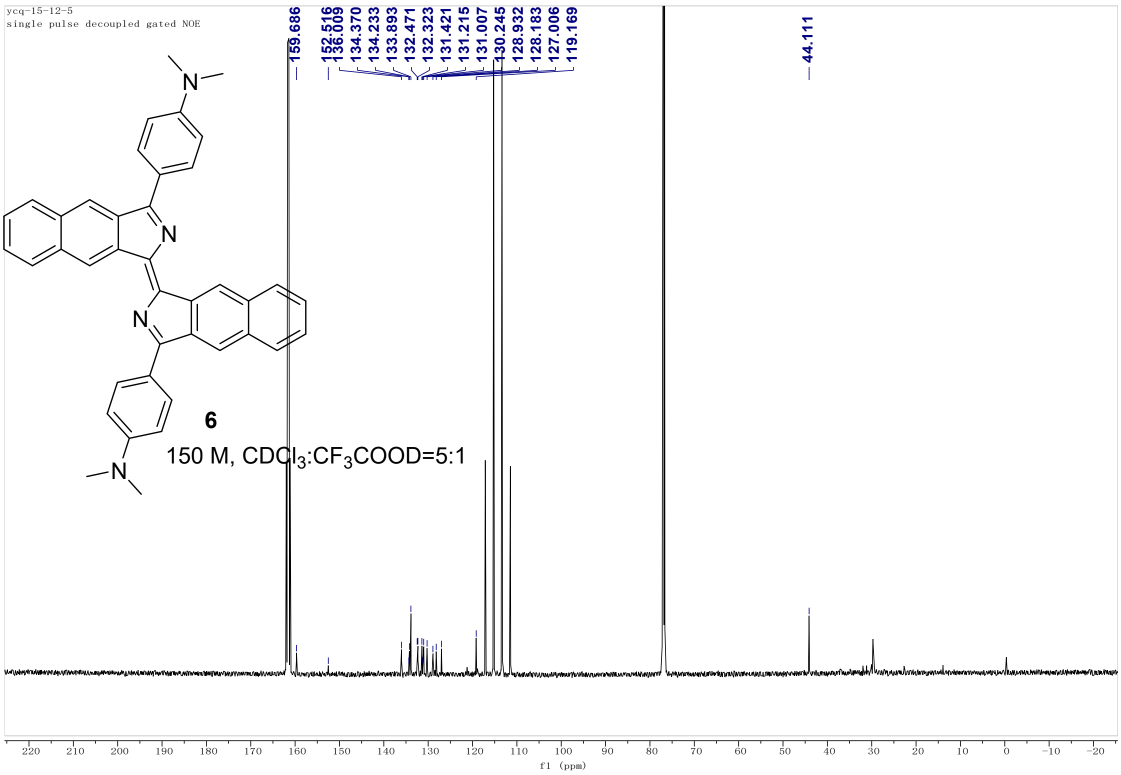

ycq-14-R1=4-OMe.1.fid
9.270
8.854
8.425
8.404
8.285
8.265
8.199
8.179
7.917
7.899
7.880
7.850
7.831
7.813
7.317
7.296
4.074
N
N
O
O
4
400 M, CDCl3:CF3COOD=5:1
2.00
2.01
4.14
1.99
2.01
1.96
1.97
3.99
6.00
f1 (ppm)

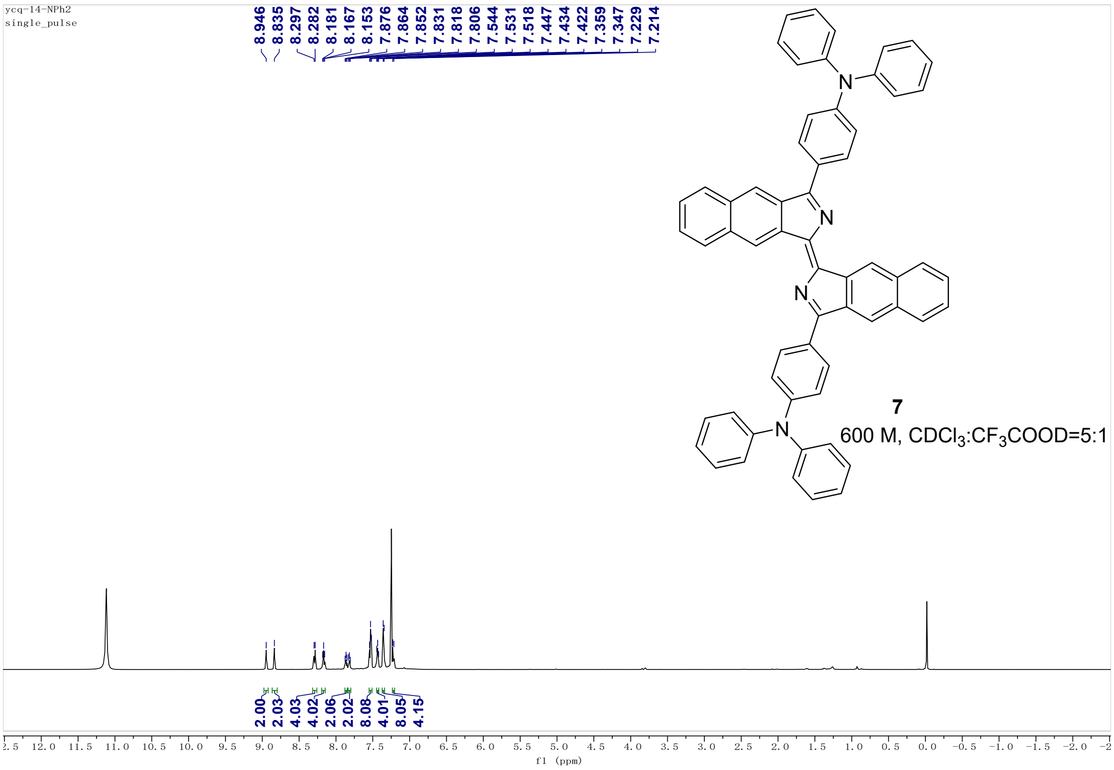

ycq-14-R1=4-OMe
single pulse decoupled gated NOE
170.027
168.157
136.278
134.593
133.759
133.444
132.606
132.334
131.383
130.854
130.737
129.885
128.770
127.967
118.547
116.545
56.480
N
N
O
O
4
150 M, CDCl3:CF3COOD=5:1
f1 (ppm)

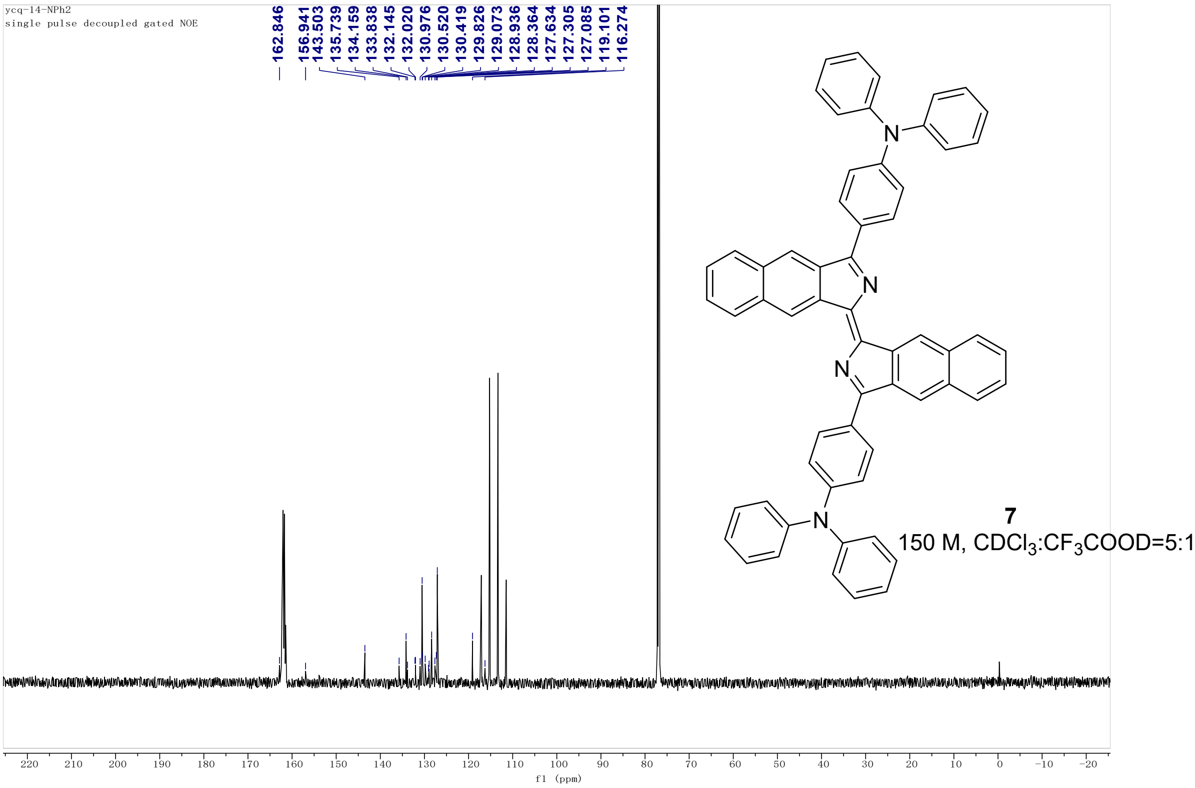

HR-ALKENE 1
single_pulse
9.466
8.413
8.399
8.367
8.114
8.101
7.983
7.970
7.716
7.703
7.602
7.590
7.578
7.561
7.548
7.535
6.907
6.889
6.878
6.860
5.982
5.953
5.443
5.425
N
N
5
600 M, CDCl3
2.01
4.02
2.04
2.03
2.04
4.00
2.04
2.06
2.02
1.87
2.00
f1 (ppm)

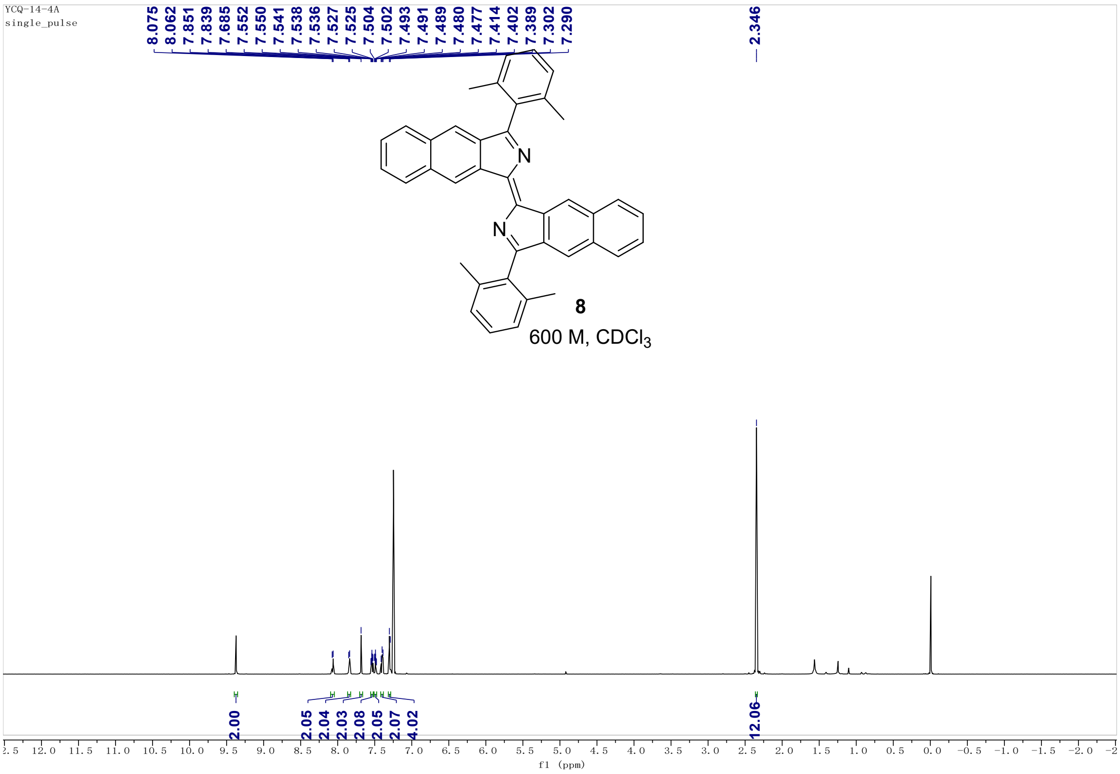

hr-r3-alkene
single pulse decoupled gated NOE
169.994
148.394
140.236
137.178
136.509
135.355
134.353
133.689
133.131
130.030
129.890
129.482
127.780
127.490
126.961
126.851
122.950
115.760
77.318
N
N
5
150 M, CDCl3
f1 (ppm)

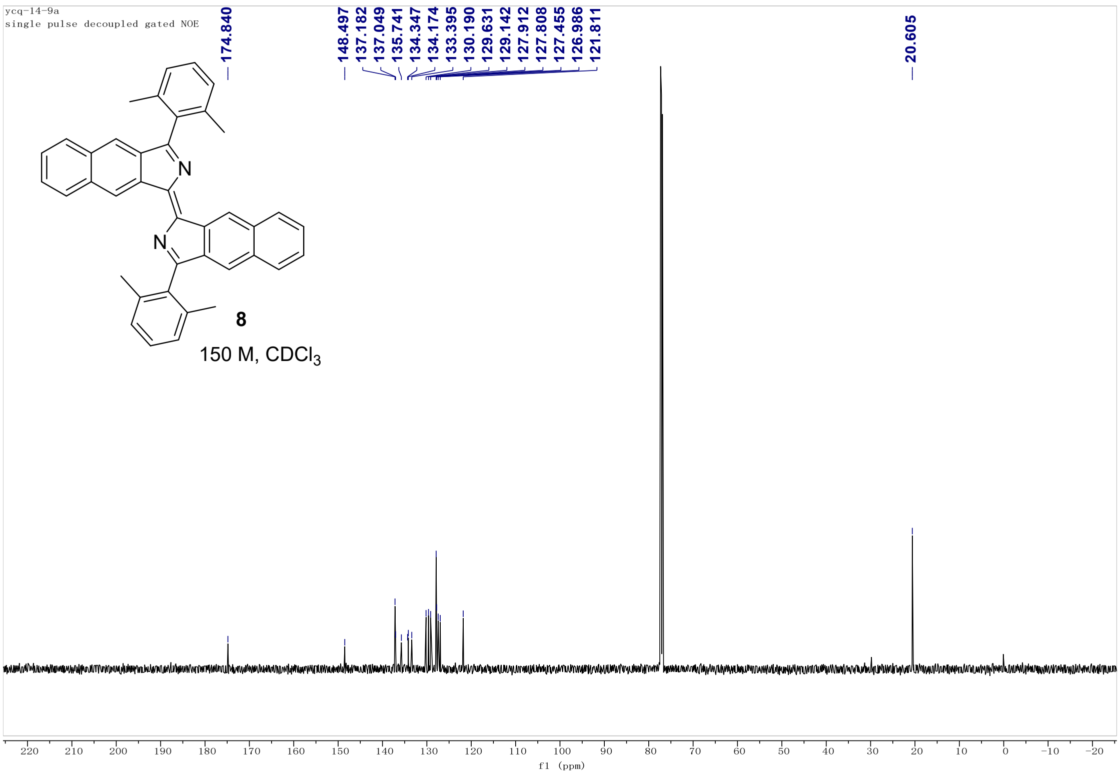

ycq-15-12-5
single_pulse
9.497
8.997
8.437
8.422
8.264
8.250
7.973
7.960
7.948
7.915
7.902
7.890
7.601
7.587
3.482
N
N
N
N
6
600 M, $CDCl_3:CF_3COOD$=5:1
2.00
2.02
4.03
4.02
2.09
2.17
4.05
12.09
f1 (ppm)

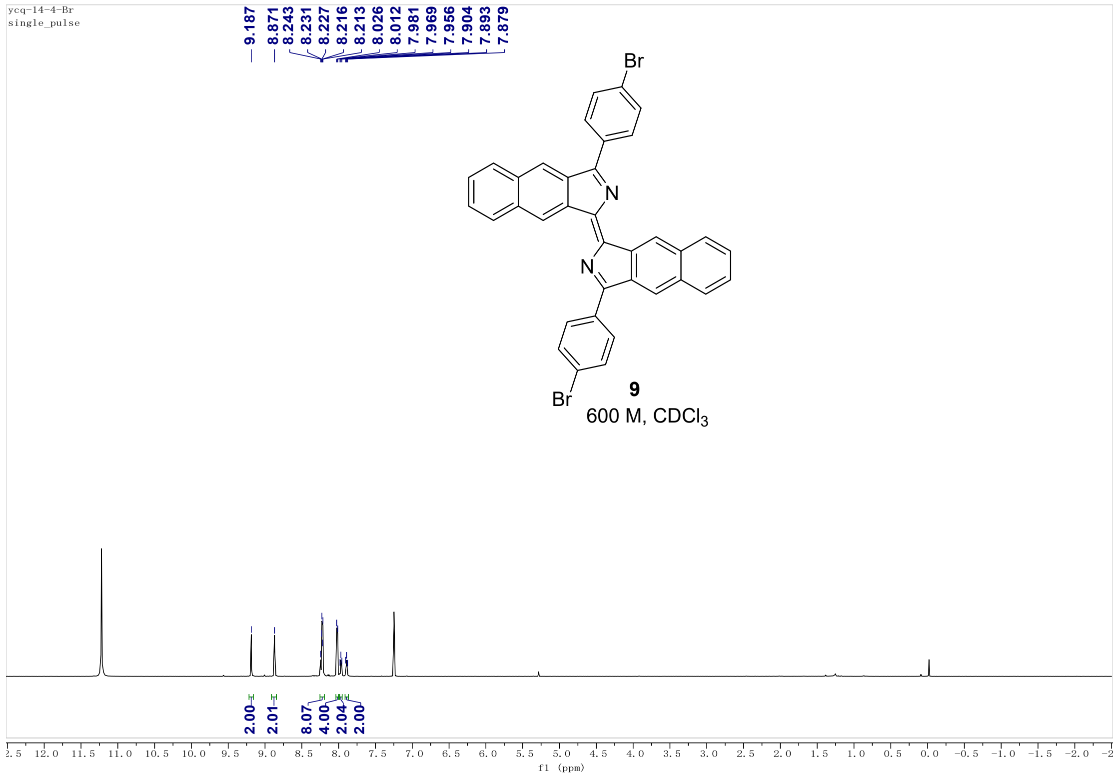

ycq-15-12-5
single pulse decoupled gated NOE
159.686
152.516
136.009
134.370
134.233
133.893
132.471
132.323
131.421
131.215
131.007
130.245
128.932
128.183
127.006
119.169
44.111
N
N
N
N
6
150 M, $CDCl_3:CF_3COOD$=5:1
f1 (ppm)

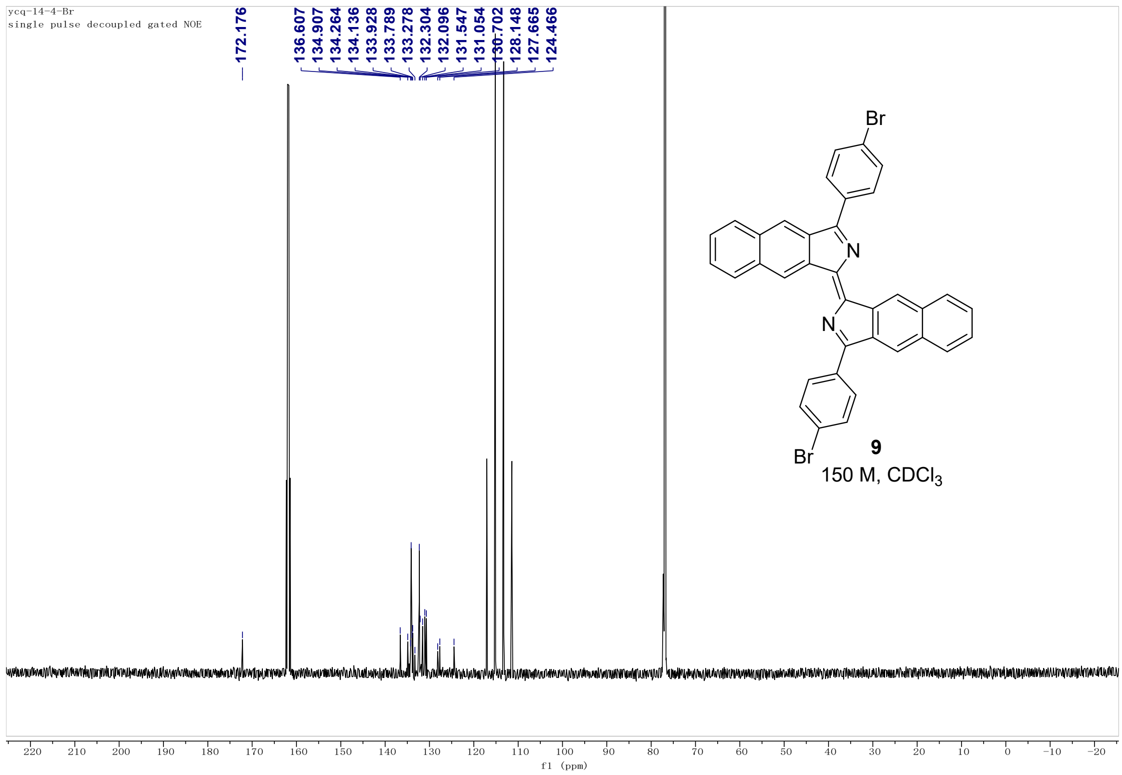

ycq-14-NPh2
single_pulse
8.946
8.835
8.297
8.282
8.181
8.167
8.153
7.876
7.864
7.852
7.831
7.818
7.806
7.544
7.531
7.518
7.447
7.434
7.422
7.359
7.347
7.229
7.214
N
N
N
N
7
600 M, $CDCl_3$:CF_3COOD=5:1
2.00
2.03
4.03
4.02
2.06
2.02
8.08
4.01
8.05
4.15
f1 (ppm)

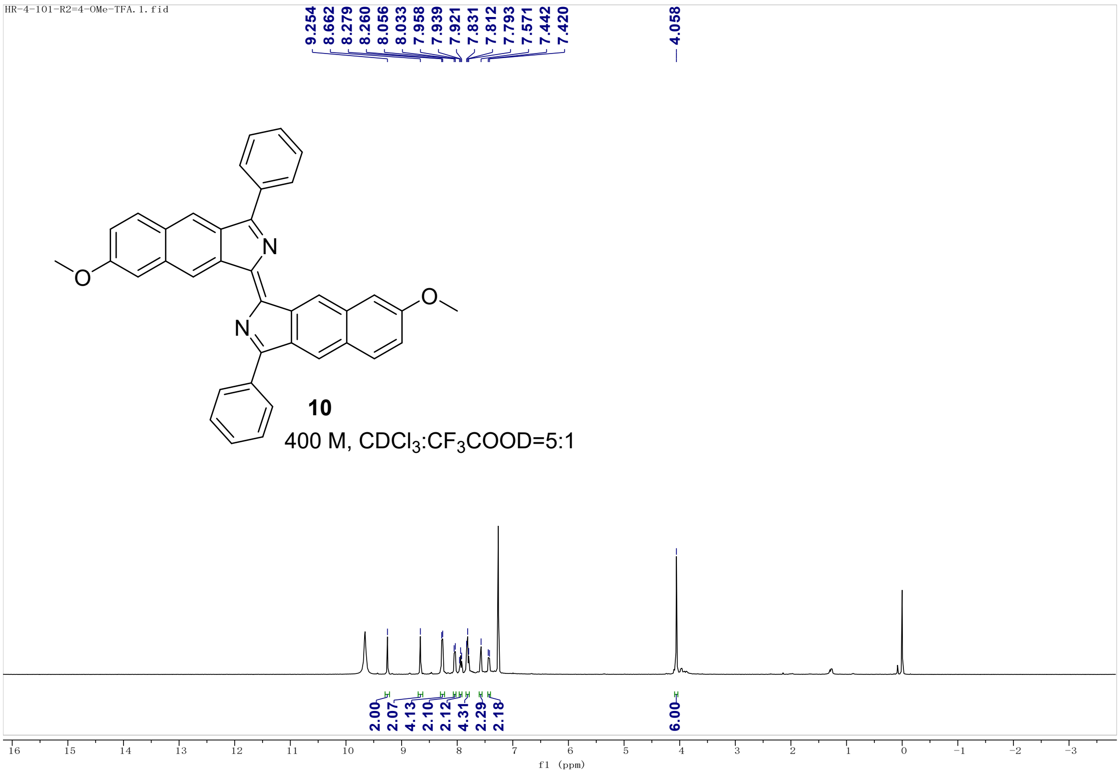

ycq-14-NPh2
single pulse decoupled gated NOE
162.846
156.941
143.503
135.739
134.159
133.838
132.145
132.020
130.976
130.520
130.419
129.826
129.073
128.936
128.364
127.634
127.305
127.085
119.101
116.274
N
N
N
N
7
150 M, $CDCl_3$:CF_3COOD=5:1
f1 (ppm)


YCQ-14-4A
single_pulse
8
600 M, CDCl$_3$
f1 (ppm)

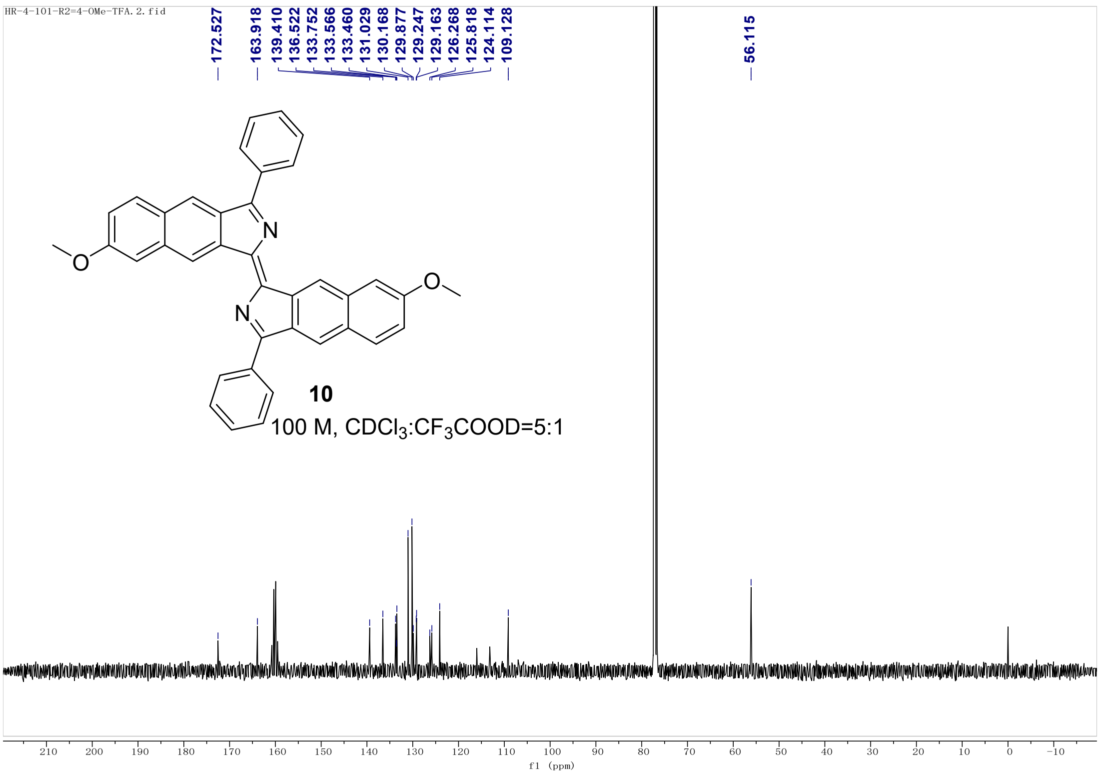

ycq-14-9a
single pulse decoupled gated NOE
8
150 M, CDCl$_3$
f1 (ppm)


ycq-14-4-Br
single_pulse
9.187
8.871
8.243
8.231
8.227
8.216
8.213
8.026
8.012
7.981
7.969
7.956
7.904
7.893
7.879
Br
N
N
Br
9
600 M, CDCl3
2.00
2.01
8.07
4.00
2.04
2.00
f1 (ppm)

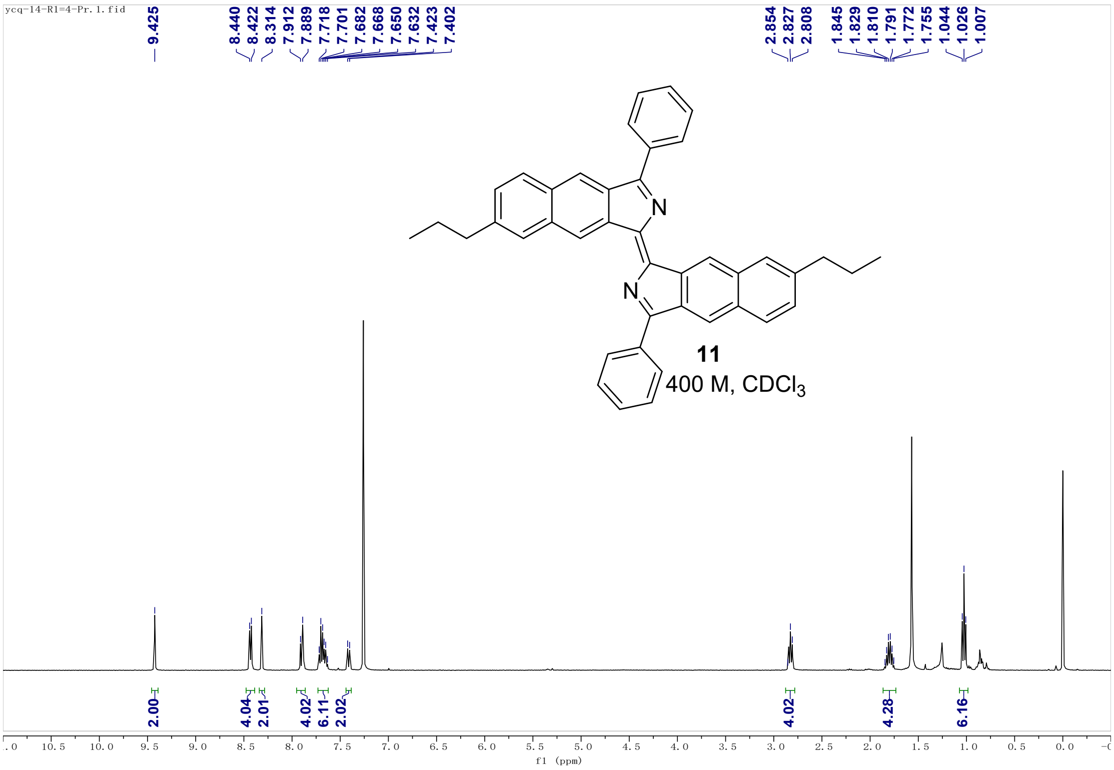

ycq-14-4-Br
single pulse decoupled gated NOE
172.176
136.607
134.907
134.264
134.136
133.928
133.789
133.278
132.304
132.096
131.547
131.054
130.702
128.148
127.665
124.466
Br
N
N
Br
9
150 M, CDCl3
f1 (ppm)

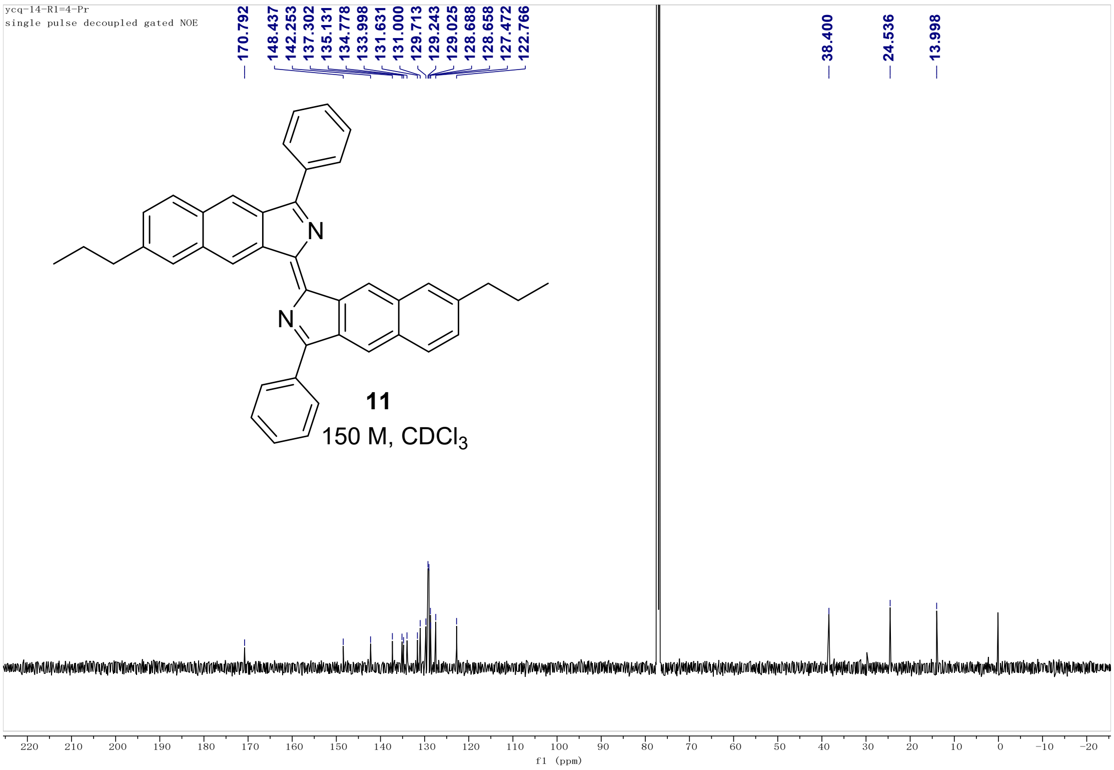


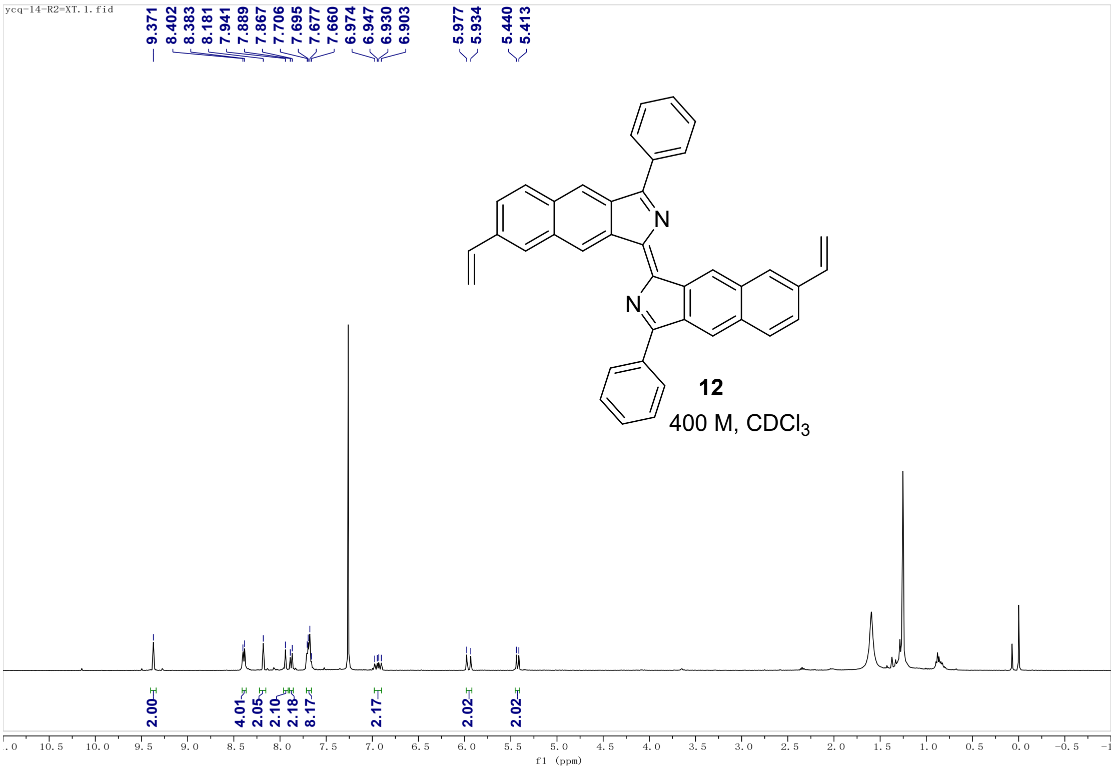
HR-4-101-R2=4-OMe-TFA.1.fid
9.254
8.662
8.279
8.260
8.056
8.033
7.958
7.939
7.921
7.831
7.812
7.793
7.571
7.442
7.420
4.058
10
400 M, CDCl3:CF3COOD=5:1
2.00
2.07
4.13
2.10
2.12
4.31
2.29
2.18
6.00
f1 (ppm)

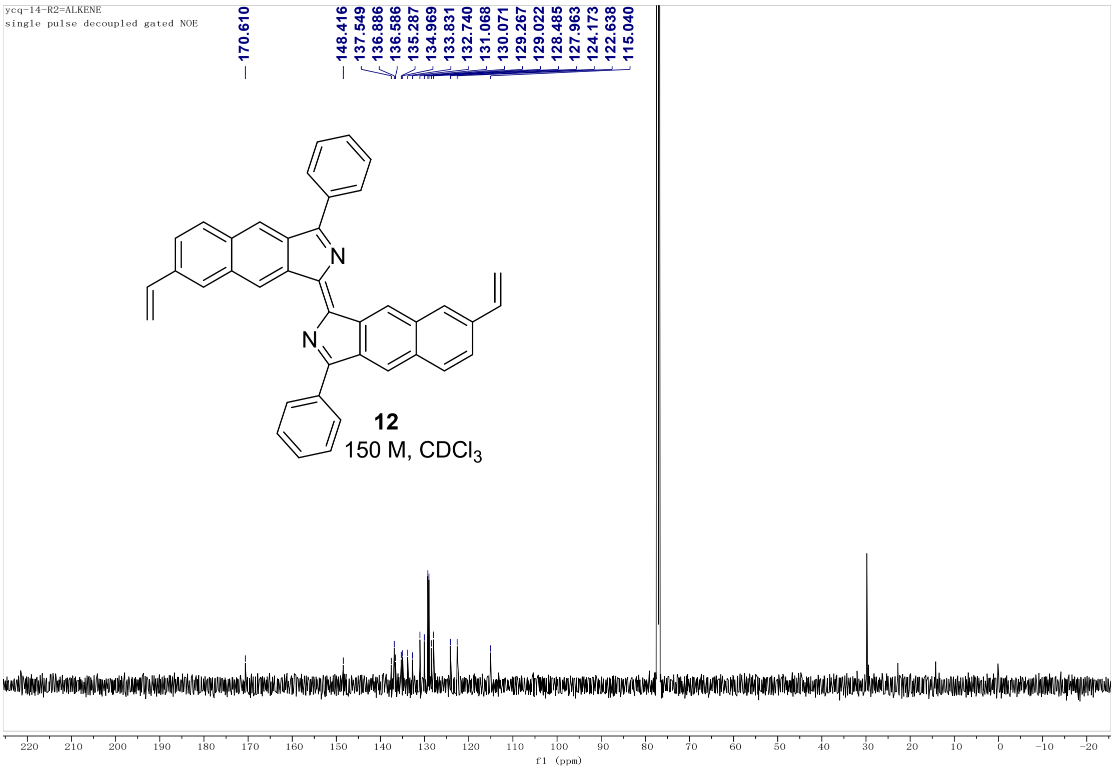


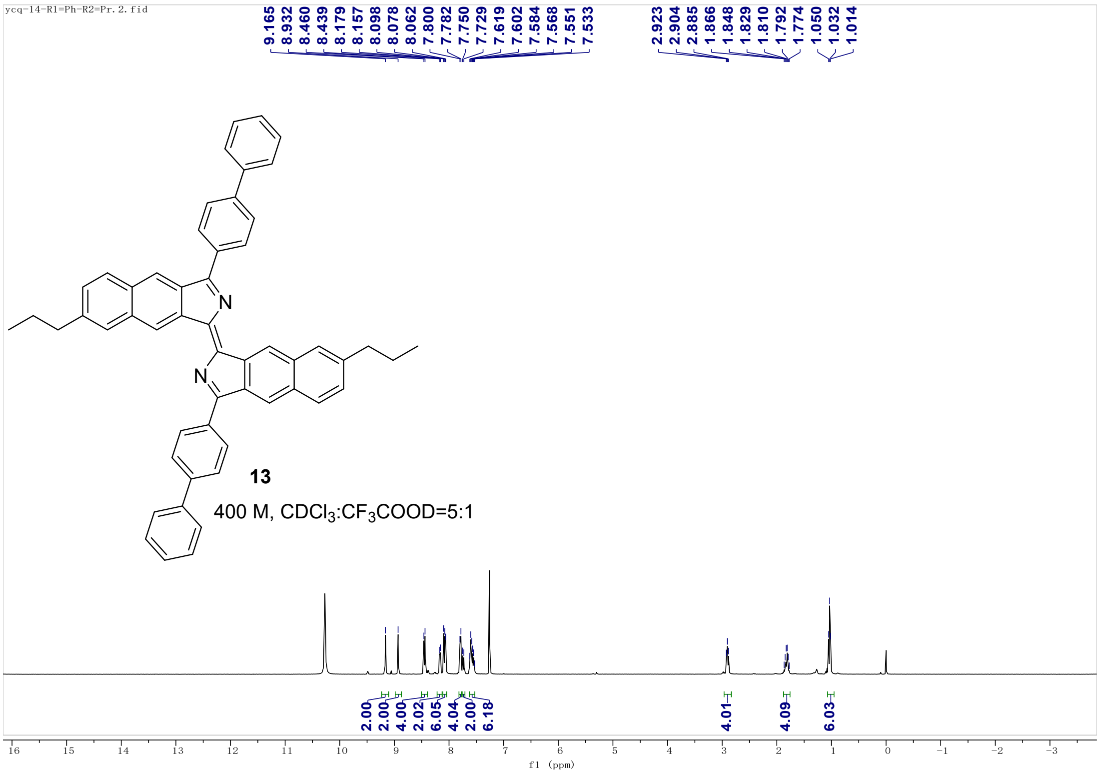
HR-4-101-R2=4-OMe-TFA.2.fid
172.527
163.918
139.410
136.522
133.752
133.566
133.460
131.029
130.168
129.877
129.247
129.163
126.268
125.818
124.114
109.128
56.115
10
100 M, CDCl3:CF3COOD=5:1
f1 (ppm)

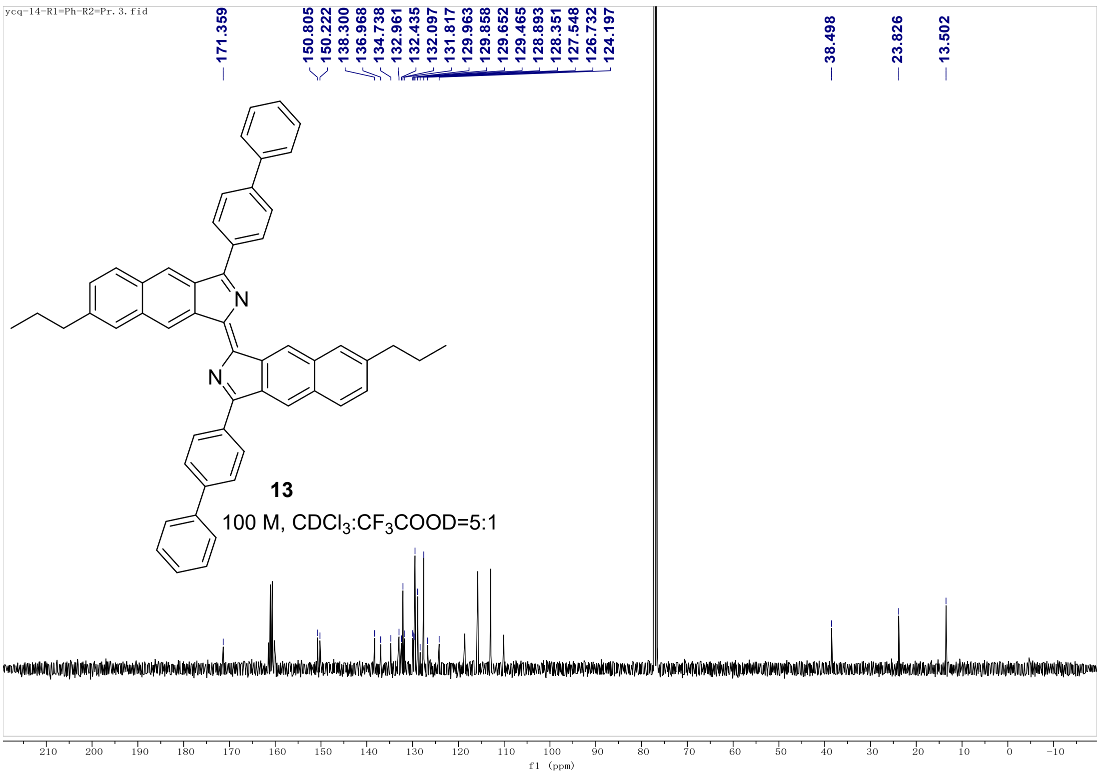

ycq-14-R1=4-Pr.1.fid
9.425
8.440
8.422
8.314
7.912
7.889
7.718
7.701
7.682
7.668
7.650
7.632
7.423
7.402
2.854
2.827
2.808
1.845
1.829
1.810
1.791
1.772
1.755
1.044
1.026
1.007
N
N
11
400 M, CDCl3
2.00
4.04
2.01
4.02
6.11
2.02
4.02
4.28
6.16
f1 (ppm)

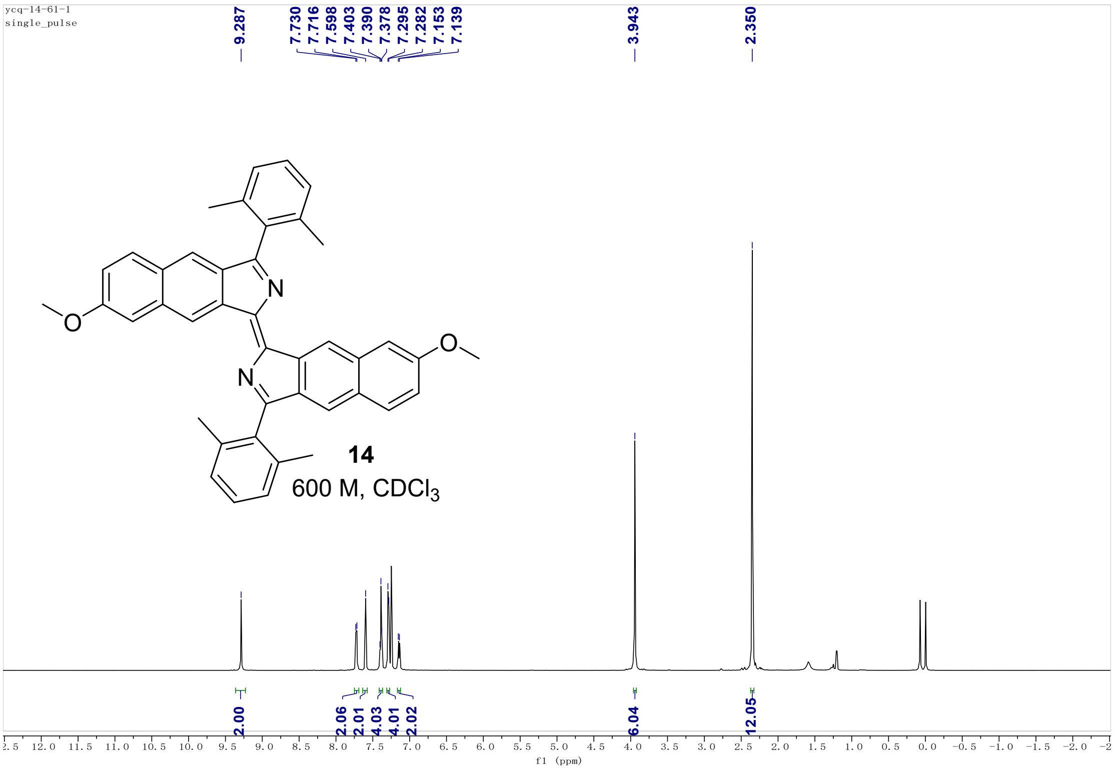

ycq-14-R1=4-Pr
single pulse decoupled gated NOE
170.792
148.437
142.253
137.302
135.131
134.778
133.998
131.631
131.000
129.713
129.243
129.025
128.688
128.658
127.472
122.766
38.400
24.536
13.998
N
N
11
150 M, CDCl3
f1 (ppm)

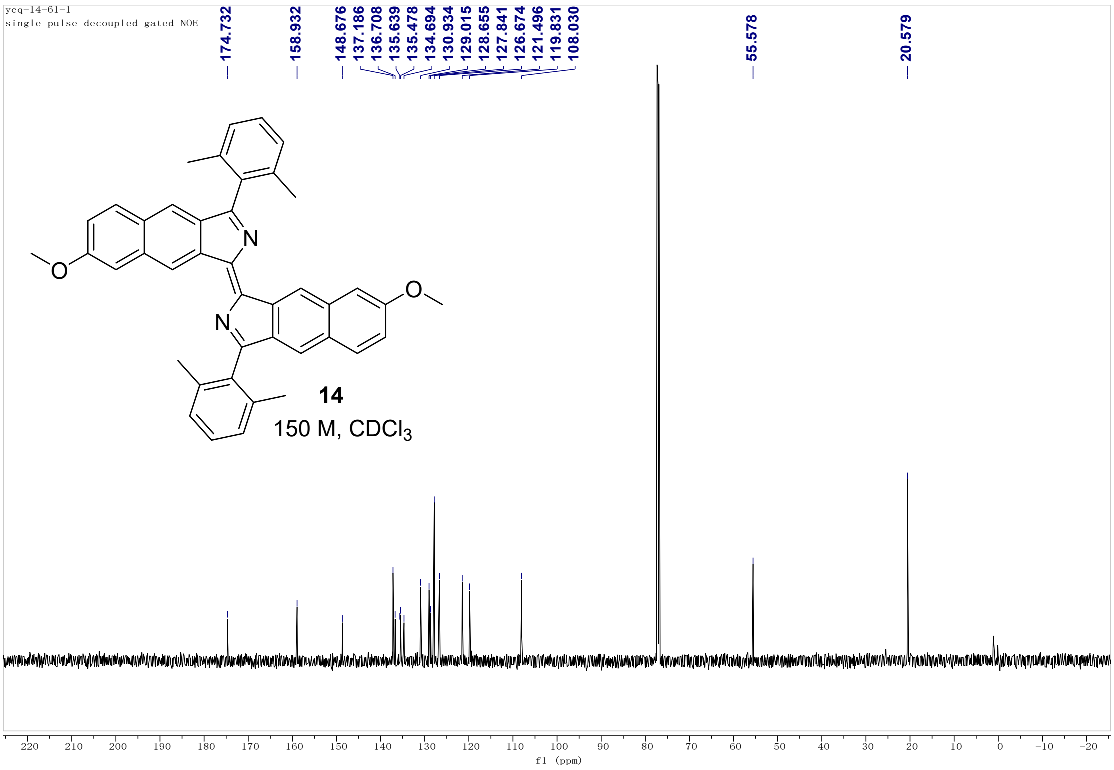

ycq-14-R2=XT.1.fid
9.371
8.402
8.383
8.181
7.941
7.889
7.867
7.706
7.695
7.677
7.660
6.974
6.947
6.930
6.903
5.977
5.934
5.440
5.413
N
N
12
400 M, CDCl3
2.00
4.01
2.05
2.10
2.18
8.17
2.17
2.02
2.02
f1 (ppm)

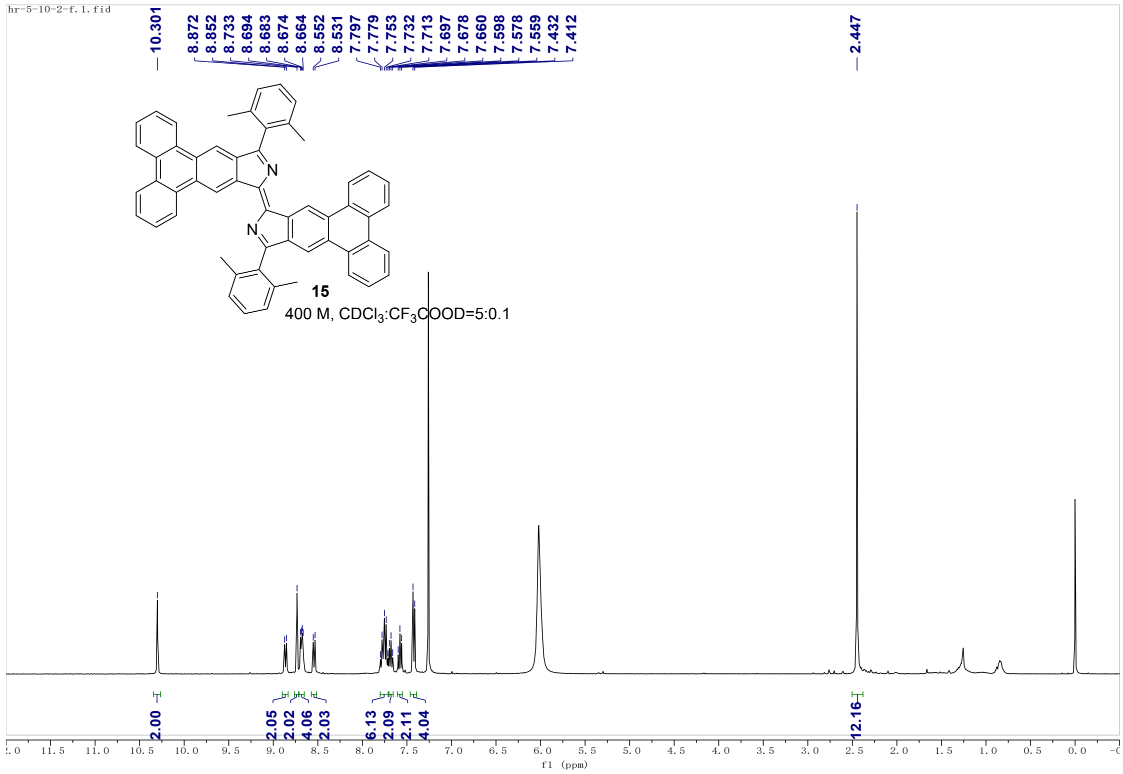

ycq-14-R2=ALKENE
single pulse decoupled gated NOE
170.610
148.416
137.549
136.886
136.586
135.287
134.969
133.831
132.740
131.068
130.071
129.267
129.022
128.485
127.963
124.173
122.638
115.040
N
N
12
150 M, CDCl3
f1 (ppm)

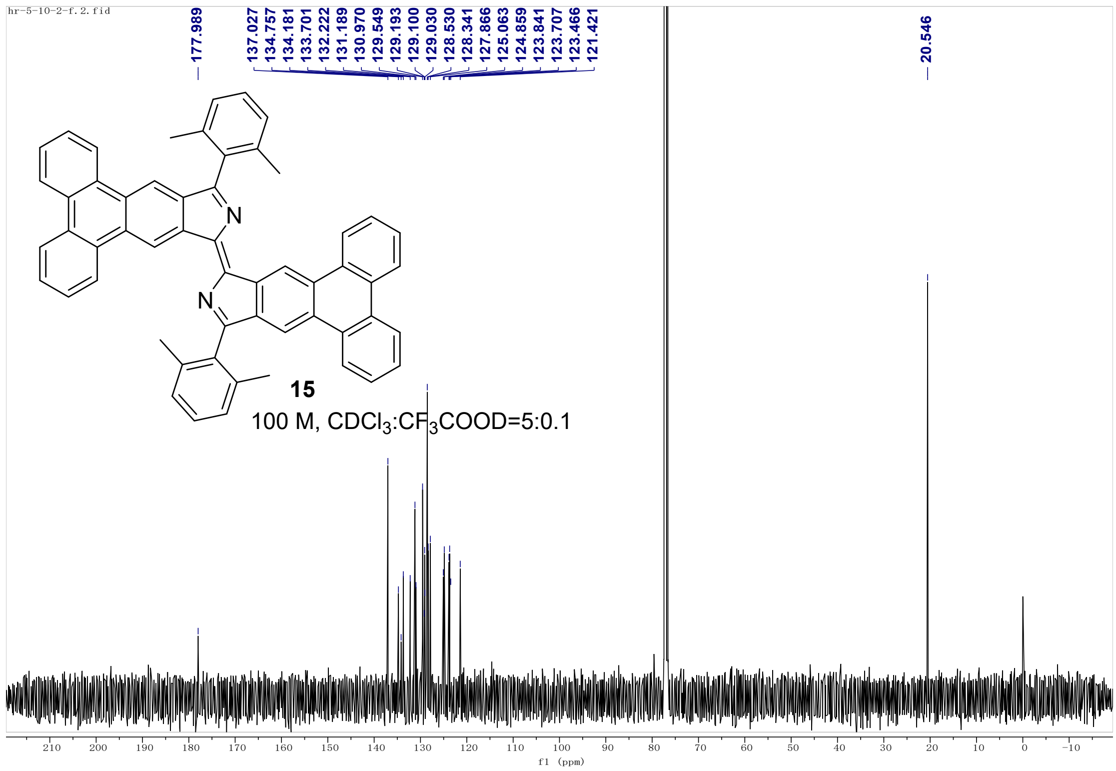

ycq-14-R1=Ph-R2=Pr.2.fid
9.165
8.932
8.460
8.439
8.179
8.157
8.098
8.078
8.062
7.800
7.782
7.750
7.729
7.619
7.602
7.584
7.568
7.551
7.533
2.923
2.904
2.885
1.866
1.848
1.829
1.810
1.792
1.774
1.050
1.032
1.014
N
N
13
400 M, $CDCl_3$:CF_3COOD=5:1
2.00
2.00
4.00
2.02
6.05
4.04
2.00
6.18
4.01
4.09
6.03
f1 (ppm)

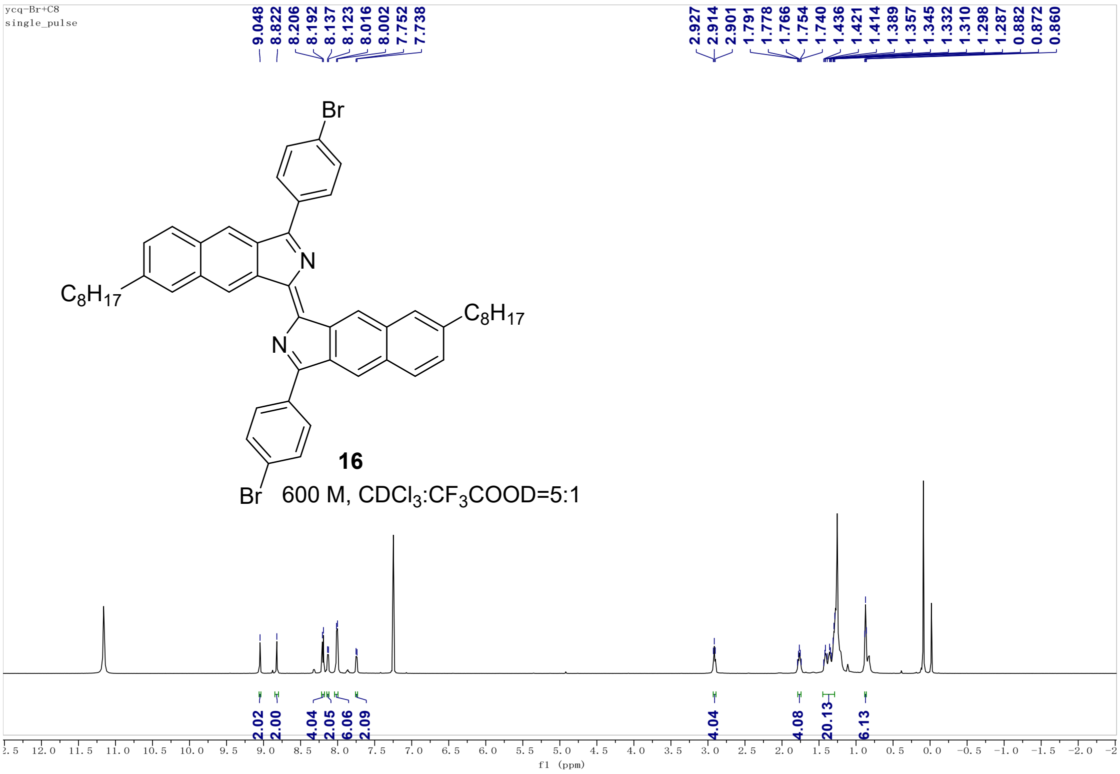

ycq-14-R1=Ph-R2=Pr.3.fid
171.359
150.805
150.222
138.300
136.968
134.738
132.961
132.435
132.097
131.817
129.963
129.858
129.652
129.465
128.893
128.351
127.548
126.732
124.197
38.498
23.826
13.502
N
N
13
100 M, $CDCl_3$:CF_3COOD=5:1
f1 (ppm)

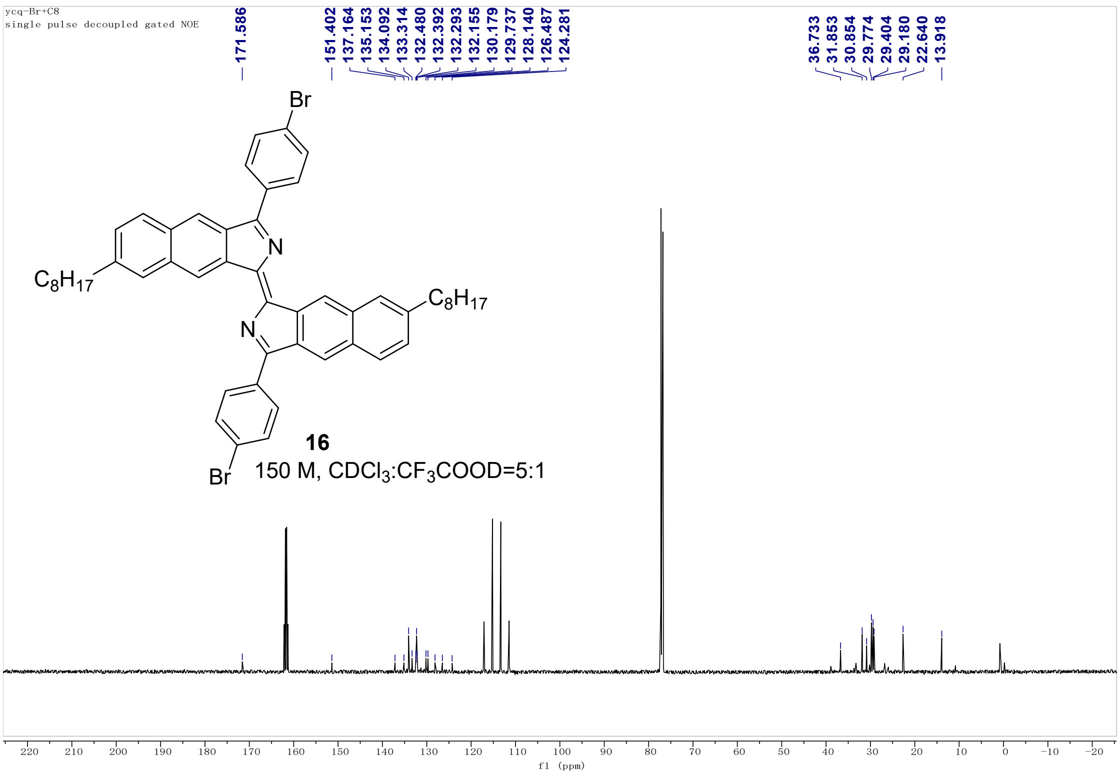

ycq-14-61-1
single_pulse
9.287
7.730
7.716
7.598
7.403
7.390
7.378
7.295
7.282
7.153
7.139
3.943
2.350
N
O
14
600 M, CDCl3
2.00
2.06
2.01
4.03
4.01
2.02
6.04
12.05
f1 (ppm)

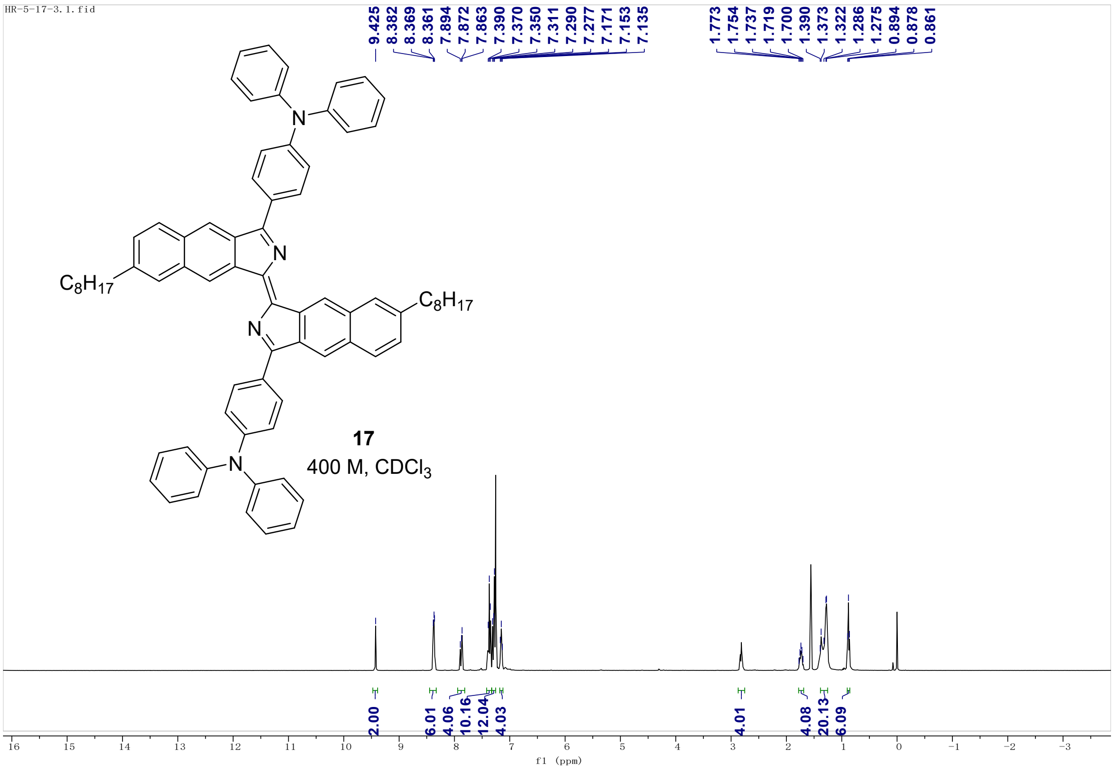

ycq-14-61-1
single pulse decoupled gated NOE
174.732
158.932
148.676
137.186
136.708
135.639
135.478
134.694
130.934
129.015
128.655
127.841
126.674
121.496
119.831
108.030
55.578
20.579
N
O
14
150 M, CDCl3
f1 (ppm)


hr-5-10-2-f.1.fid
10.301
8.872 8.852 8.733 8.694 8.683 8.674 8.664 8.552 8.531 7.797 7.779 7.753 7.732 7.713 7.697 7.678 7.660 7.598 7.578 7.559 7.432 7.412
2.447
N
N
15
400 M, CDCl3:CF3COOD=5:0.1
2.00
2.05 2.02 4.06 2.03
6.13 2.09 2.11 4.04
12.16
f1 (ppm)

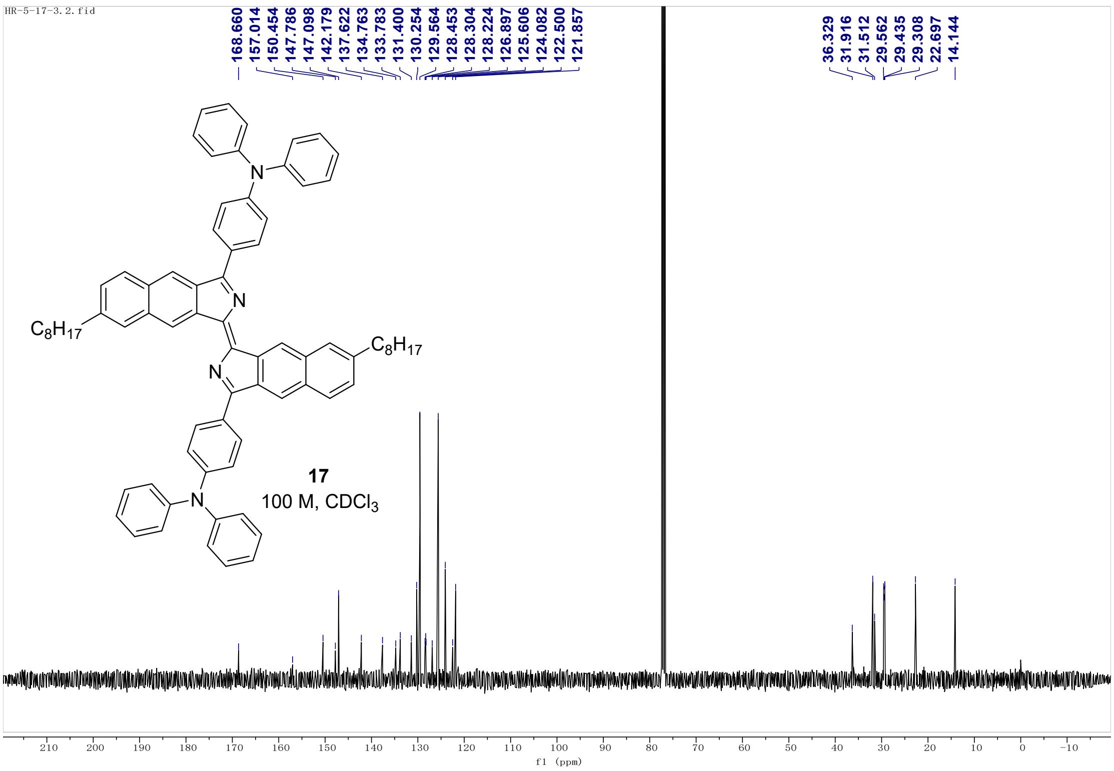

hr-5-10-2-f.2.fid
177.989
137.027 134.757 134.181 133.701 132.222 131.189 130.970 129.549 129.193 129.100 129.030 128.530 128.341 127.866 125.063 124.859 123.841 123.707 123.466 121.421
20.546
N
N
15
100 M, CDCl3:CF3COOD=5:0.1
f1 (ppm)


ycq-Br+C8
single_pulse
16
600 M, CDCl3:CF3COOD=5:1
f1 (ppm)

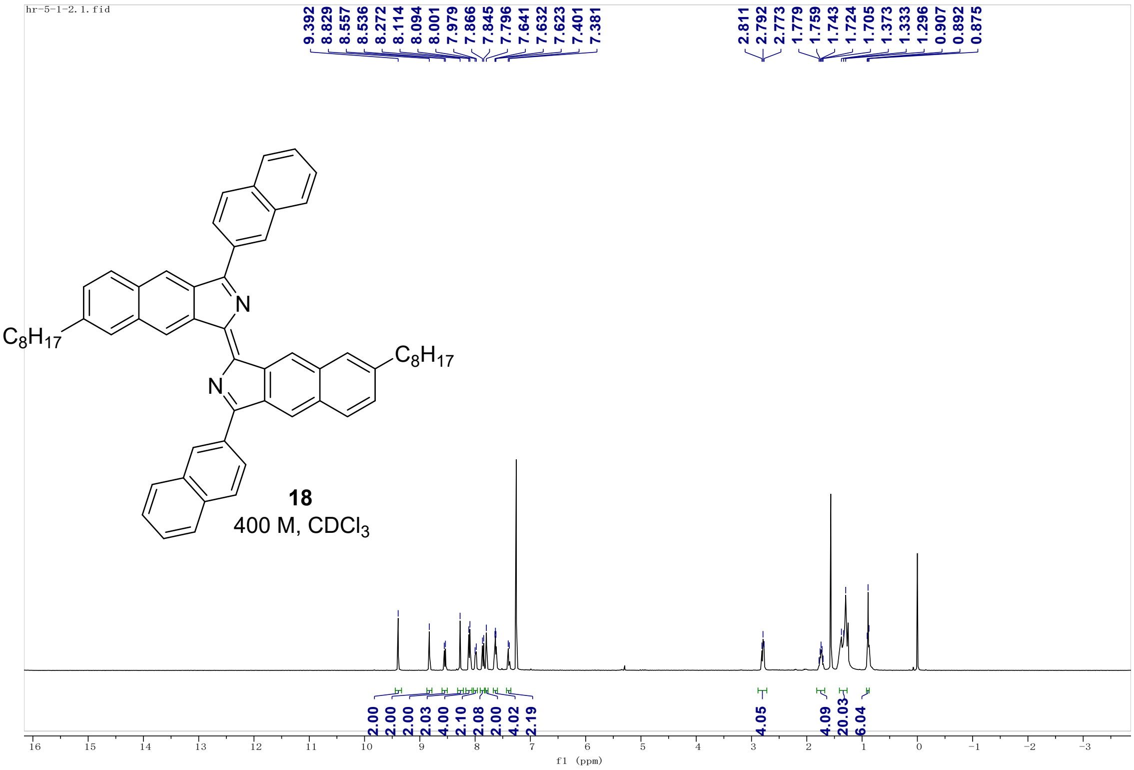

ycq-Br+C8
single pulse decoupled gated NOE
16
150 M, CDCl3:CF3COOD=5:1
f1 (ppm)

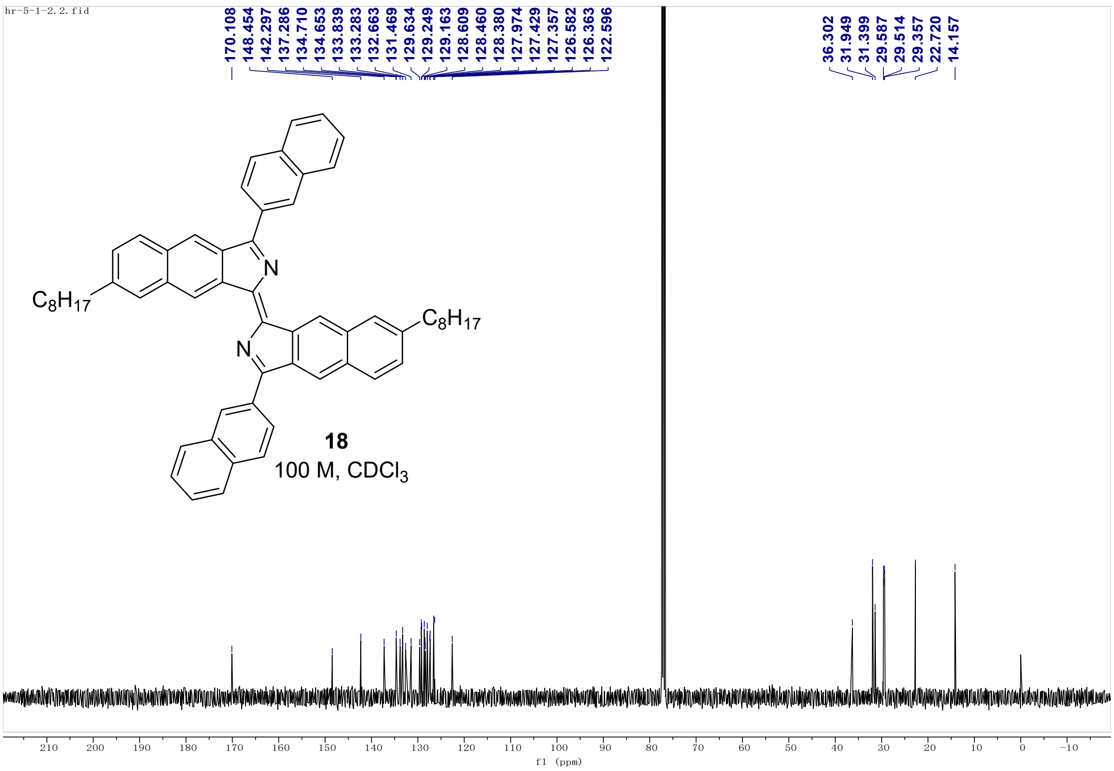


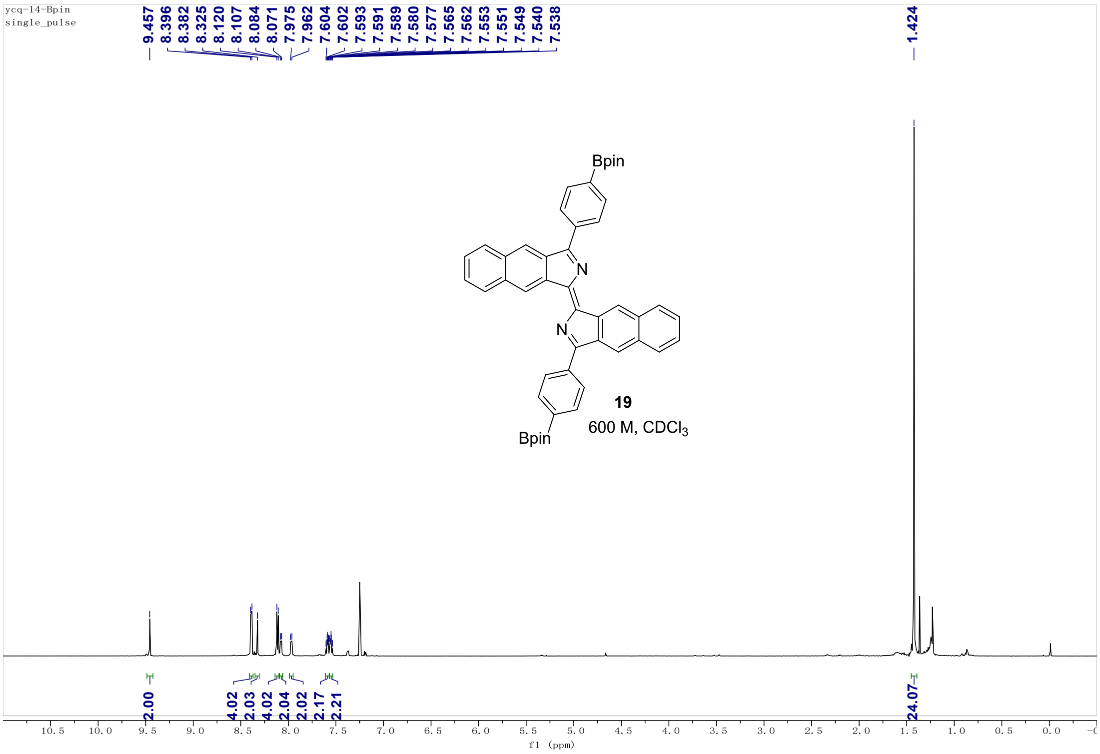
17
400 M, $CDCl_3$

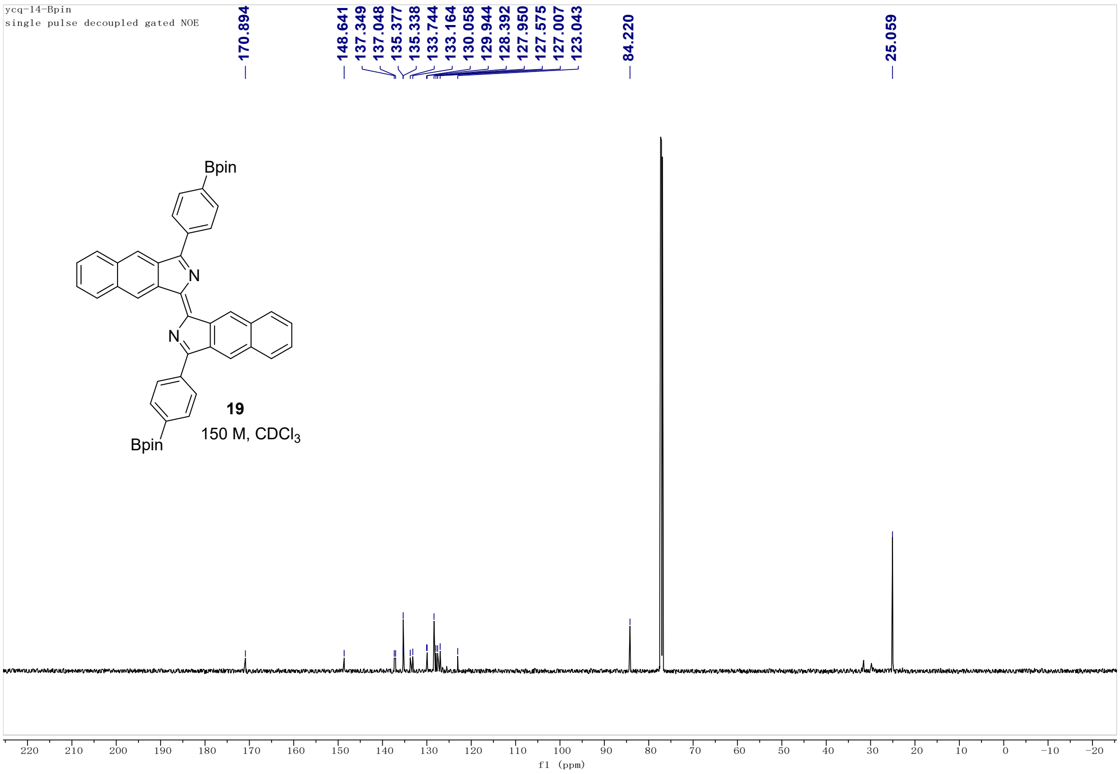


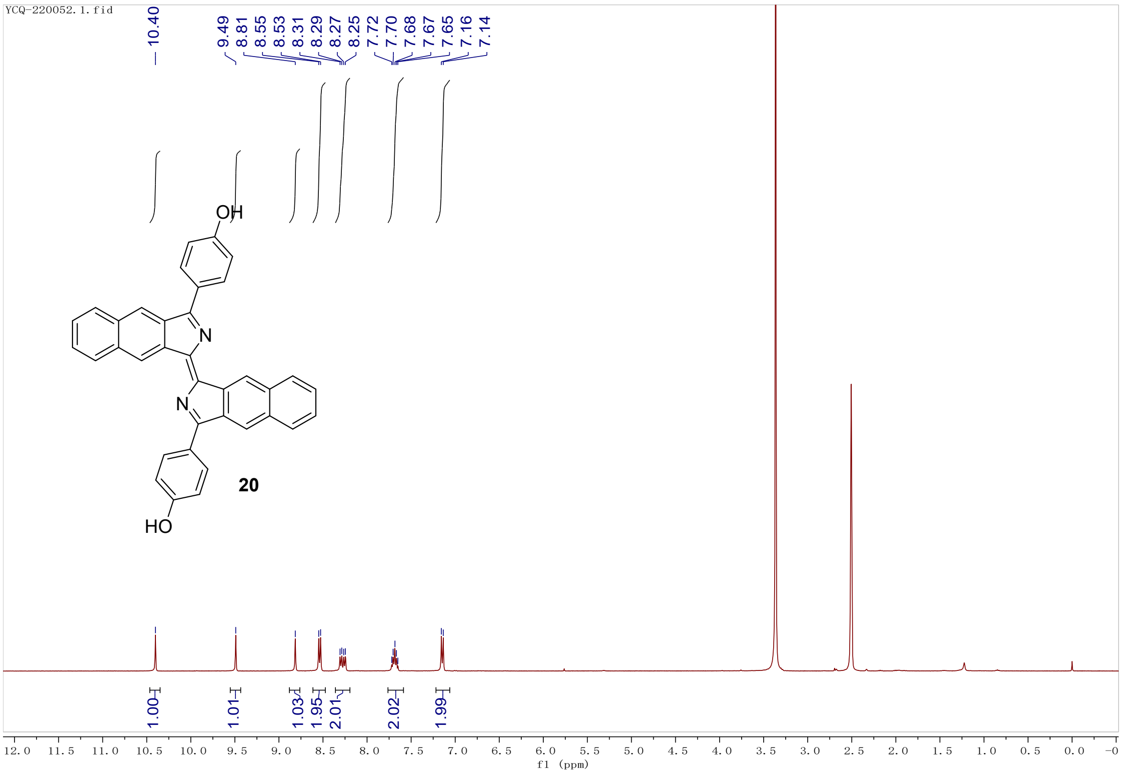
17
100 M, $CDCl_3$

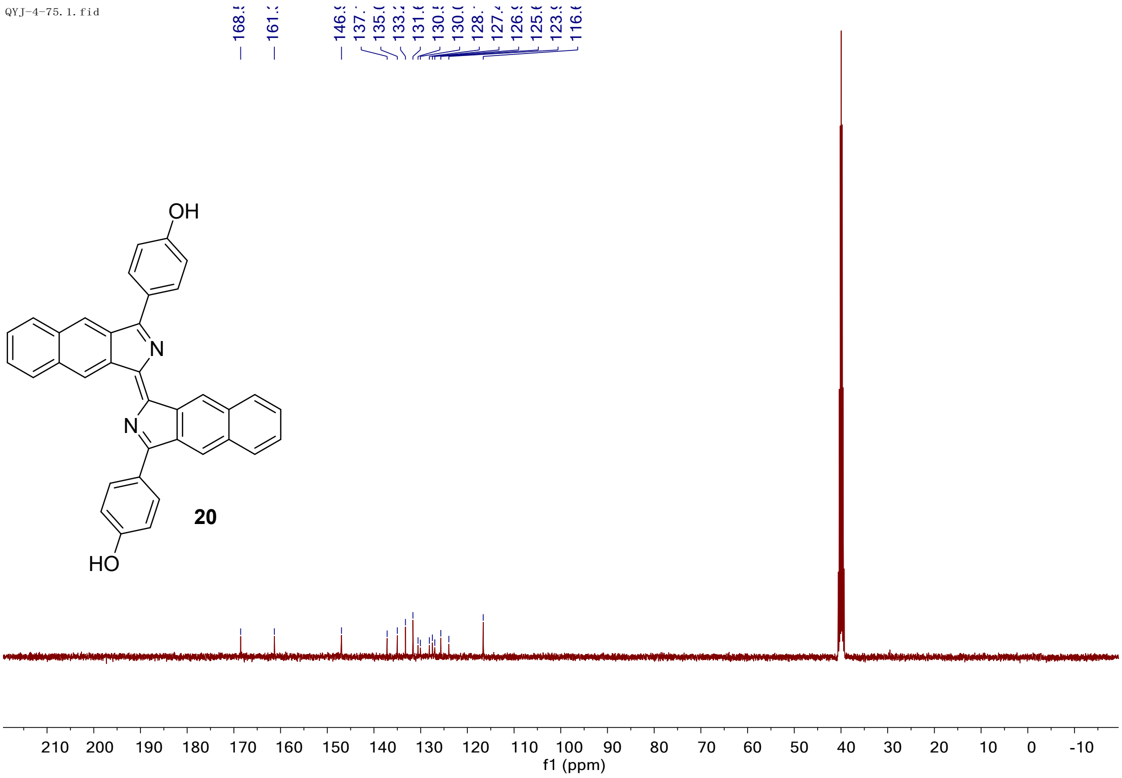

hr-5-1-2.1.fid
9.392
8.829
8.557
8.536
8.272
8.114
8.094
8.001
7.979
7.866
7.845
7.796
7.641
7.632
7.623
7.401
7.381
2.811
2.792
2.773
1.779
1.759
1.743
1.724
1.705
1.373
1.333
1.296
0.907
0.892
0.875
N
N
C8H17
C8H17
18
400 M, CDCl3
2.00
2.00
2.00
2.03
4.00
2.10
2.08
2.00
4.02
2.19
4.05
4.09
20.03
6.04
f1 (ppm)

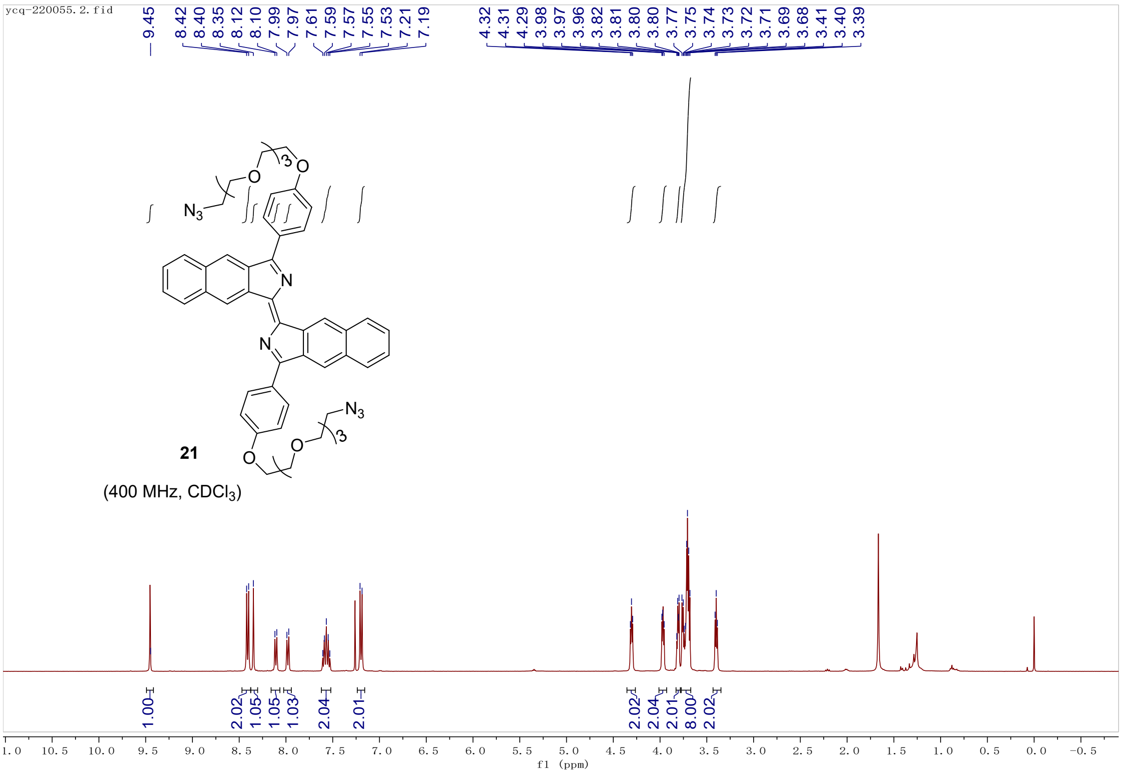

hr-5-1-2.2.fid
170.108
148.454
142.297
137.286
134.710
134.653
133.839
133.283
132.663
131.469
129.634
129.249
129.163
128.609
128.460
128.380
127.974
127.429
127.357
126.582
126.363
122.596
36.302
31.949
31.399
29.587
29.514
29.357
22.720
14.157
N
N
C8H17
C8H17
18
100 M, CDCl3
f1 (ppm)

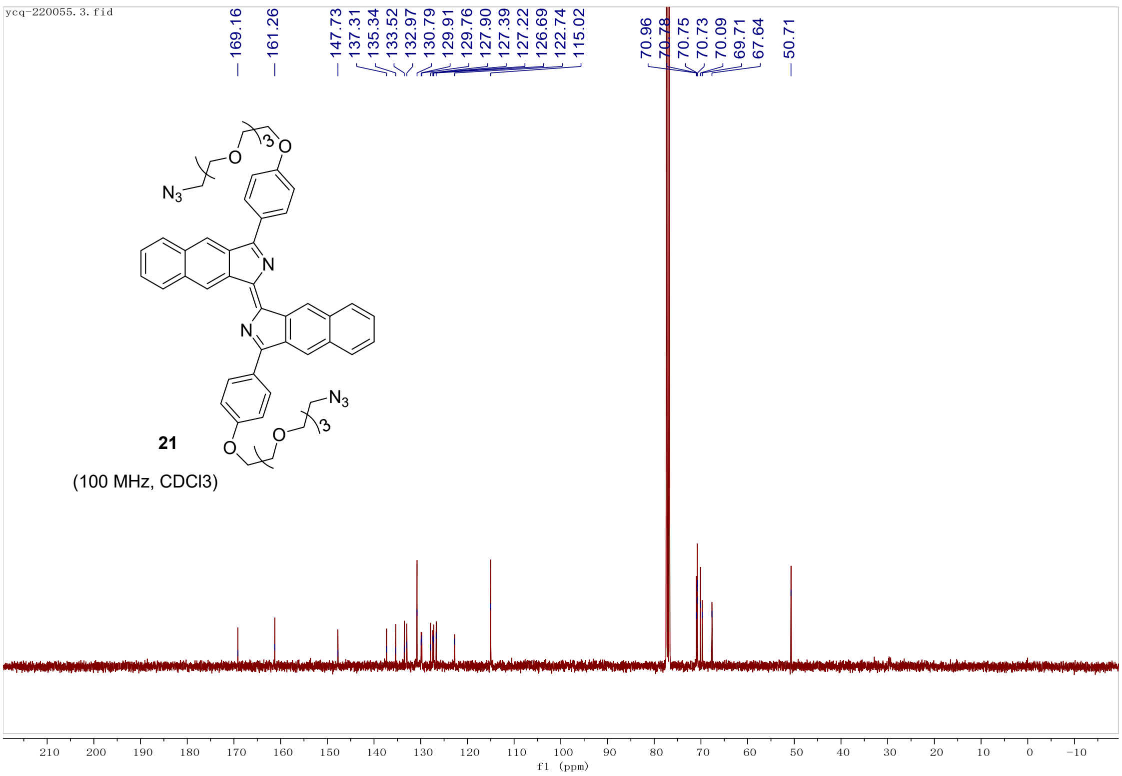

ycq-14-Bpin
single_pulse
9.457
8.396
8.382
8.325
8.120
8.107
8.084
8.071
7.975
7.962
7.604
7.602
7.593
7.591
7.589
7.580
7.577
7.565
7.562
7.553
7.551
7.549
7.540
7.538
1.424
Bpin
N
N
Bpin
19
600 M, $CDCl_3$
2.00
4.02
2.03
4.02
2.04
2.02
2.17
2.21
24.07
f1 (ppm)

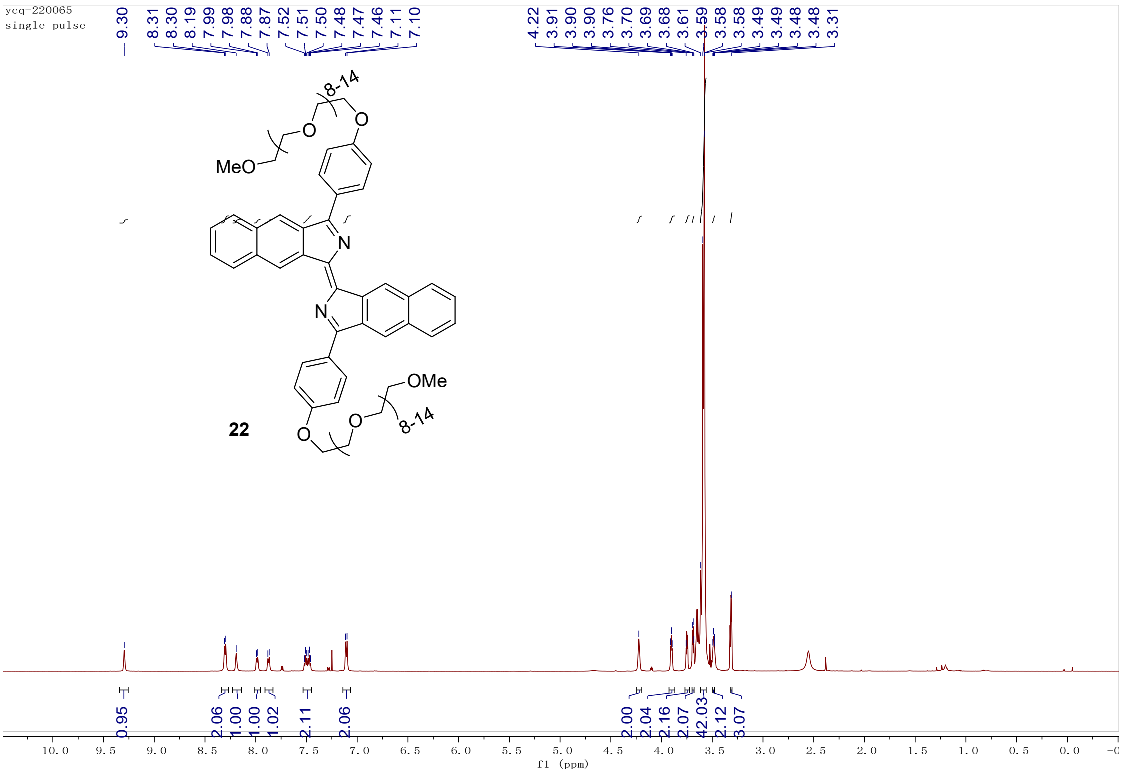

ycq-14-Bpin
single pulse decoupled gated NOE
170.894
148.641
137.349
137.048
135.377
135.338
133.744
133.164
130.058
129.944
128.392
127.950
127.575
127.007
123.043
84.220
25.059
Bpin
N
N
Bpin
19
150 M, $CDCl_3$
f1 (ppm)

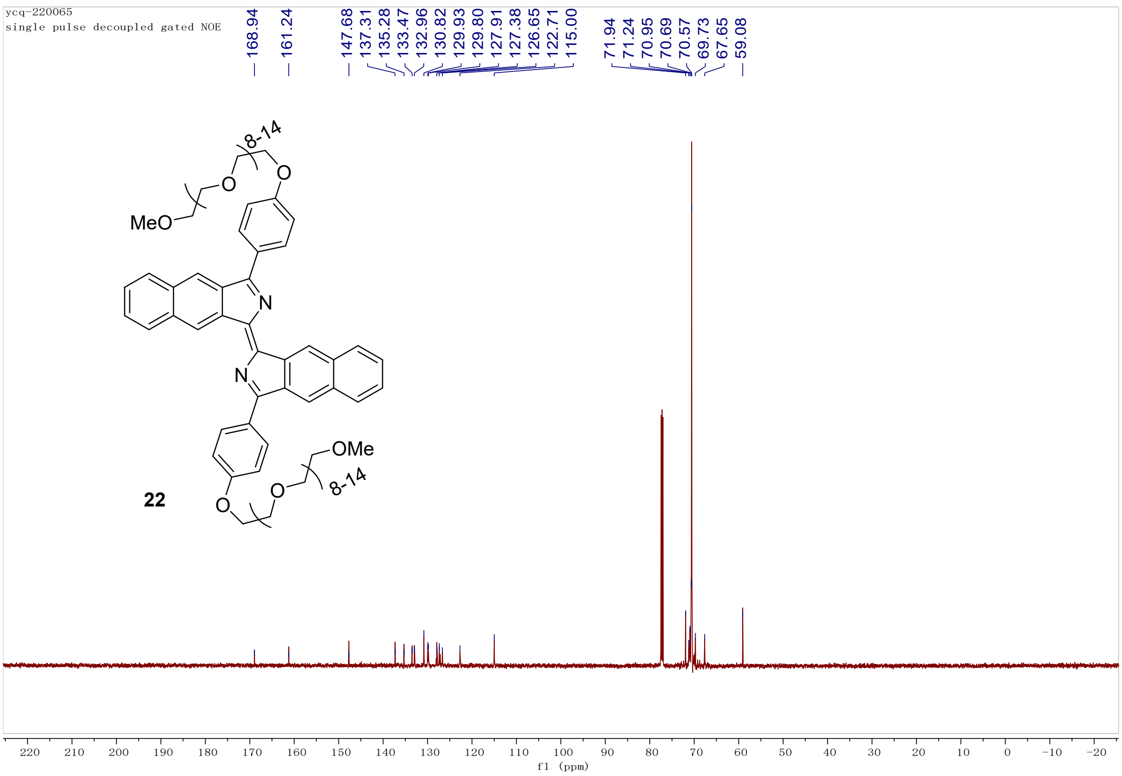

YCQ-220052.1.fid
10.40
9.49
8.81
8.55
8.53
8.31
8.29
8.27
8.25
7.72
7.70
7.68
7.67
7.65
7.16
7.14
OH
N
N
20
HO
1.00
1.01
1.03
1.95
2.01
2.02
1.99
f1 (ppm)

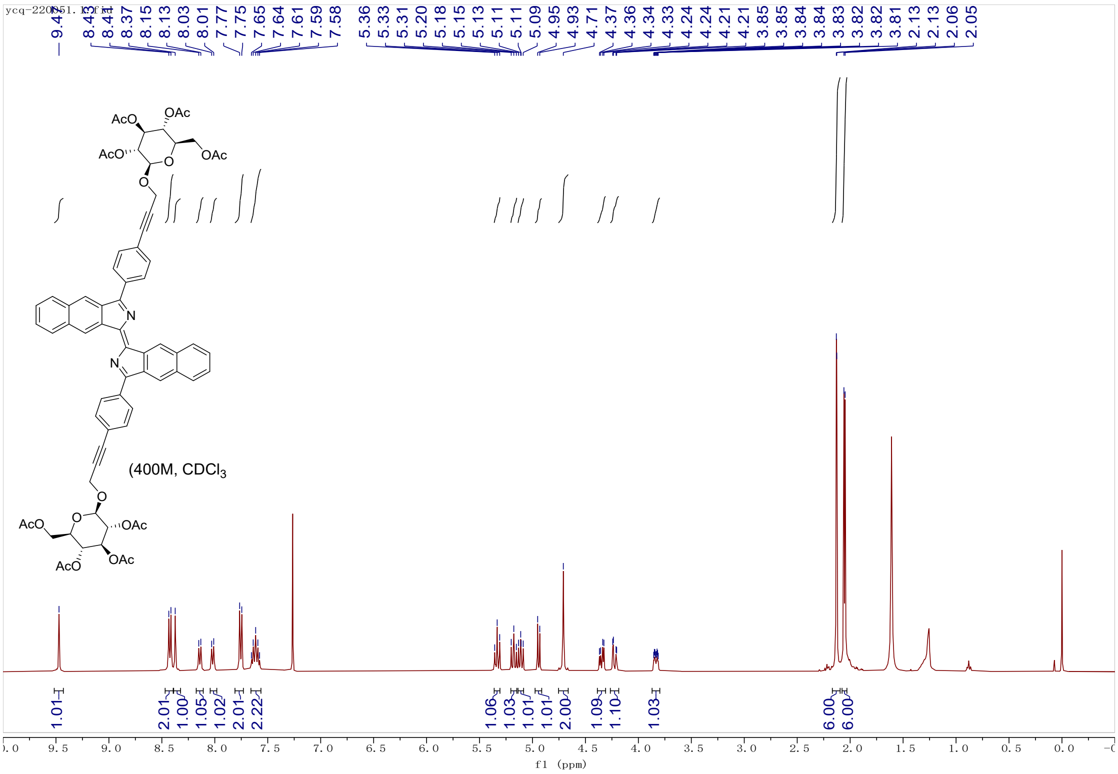

QYJ-4-75.1.fid
OH
N
N
20
HO
f1 (ppm)

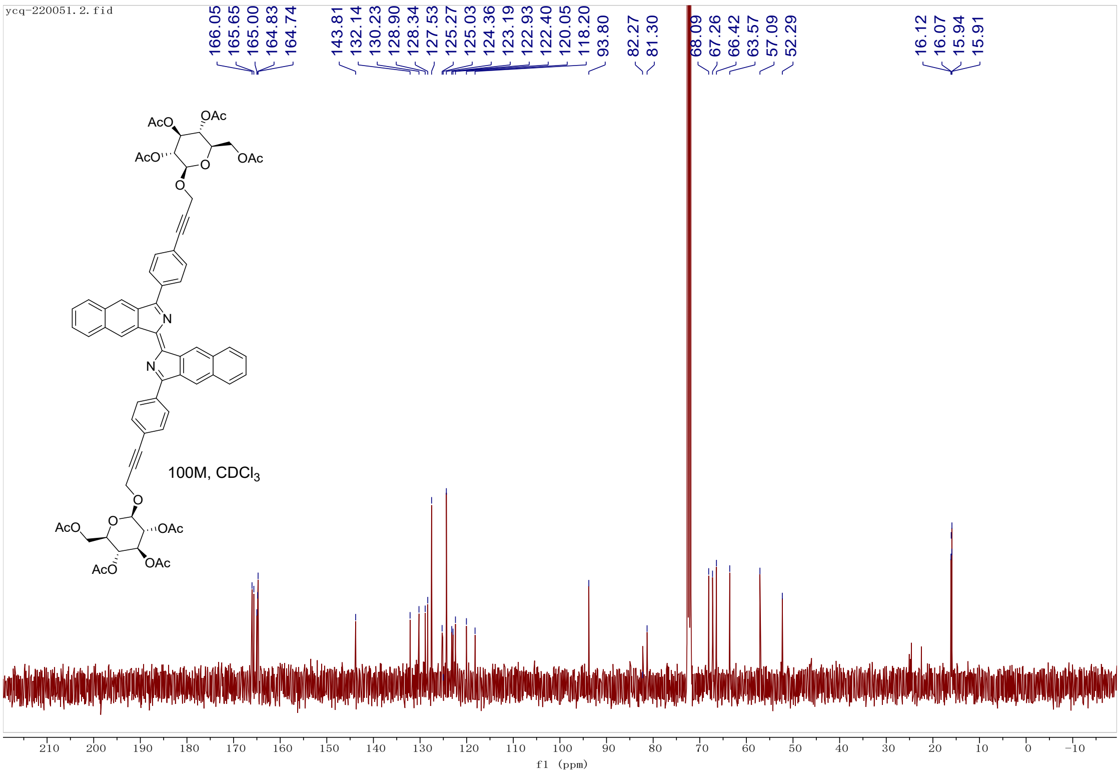

ycq-220055.2.fid
9.45
8.42 8.40 8.35 8.12 8.10 7.99 7.97 7.61 7.59 7.57 7.55 7.53 7.21 7.19
4.32 4.31 4.29 3.98 3.97 3.96 3.82 3.81 3.80 3.80 3.77 3.75 3.74 3.73 3.72 3.71 3.69 3.68 3.41 3.40 3.39
21
(400 MHz, CDCl3)
1.00 2.02 1.05 1.05 1.03 2.04 2.01 2.02 2.04 2.01 8.00 2.02
f1 (ppm)

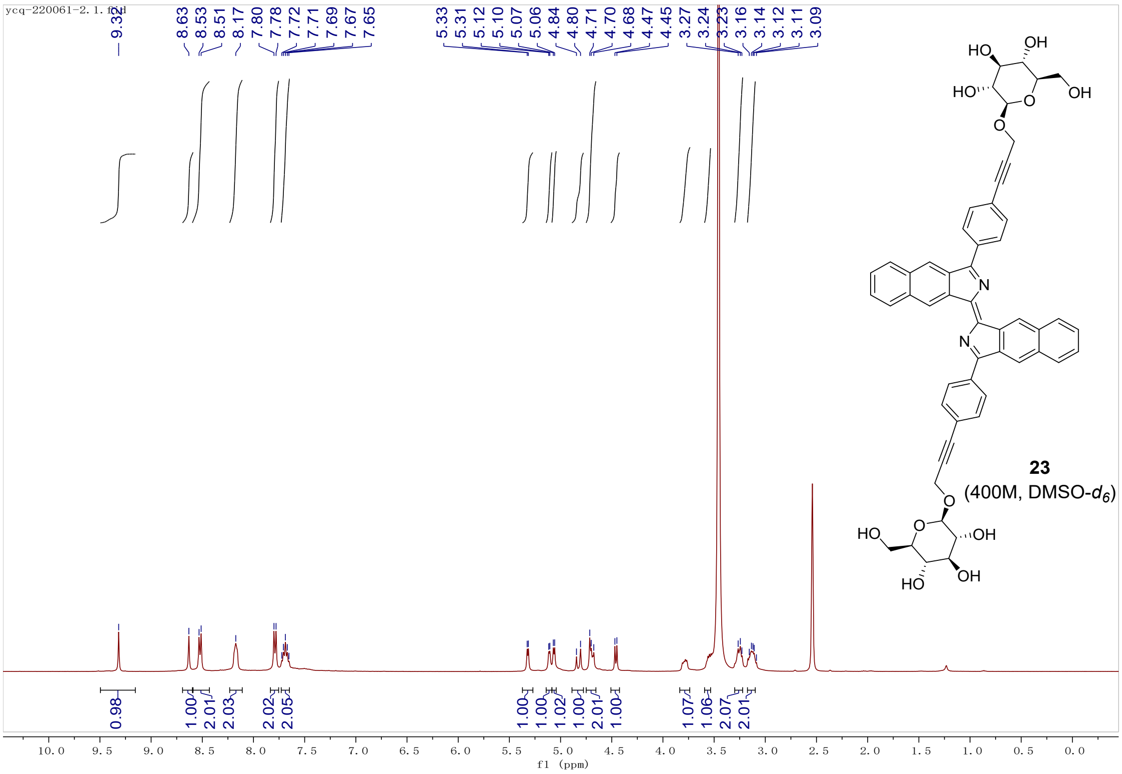

ycq-220055.3.fid
169.16
161.26
147.73 137.31 135.34 133.52 132.97 130.79 129.91 129.76 127.90 127.39 127.22 126.69 122.74 115.02
70.96 70.78 70.75 70.73 70.09 69.71 67.64
50.71
21
(100 MHz, CDCl3)
f1 (ppm)

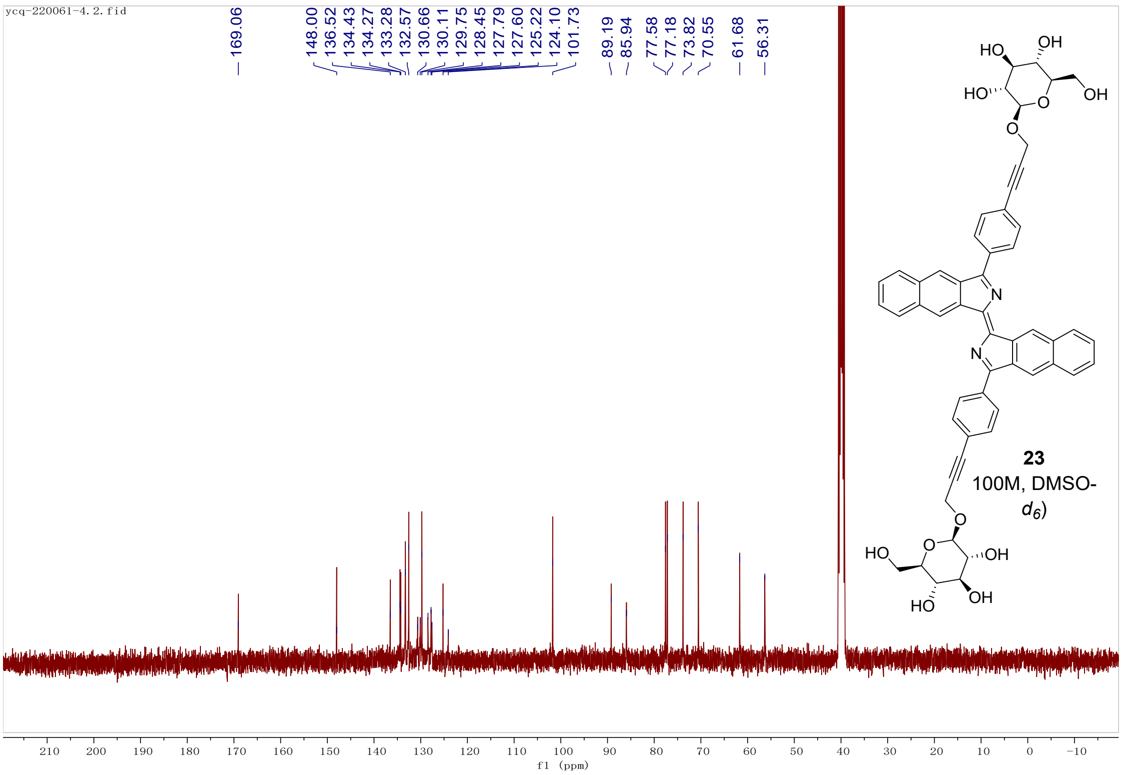

ycq-220065
single_pulse
22
MeO
OMe
8-14
f1 (ppm)

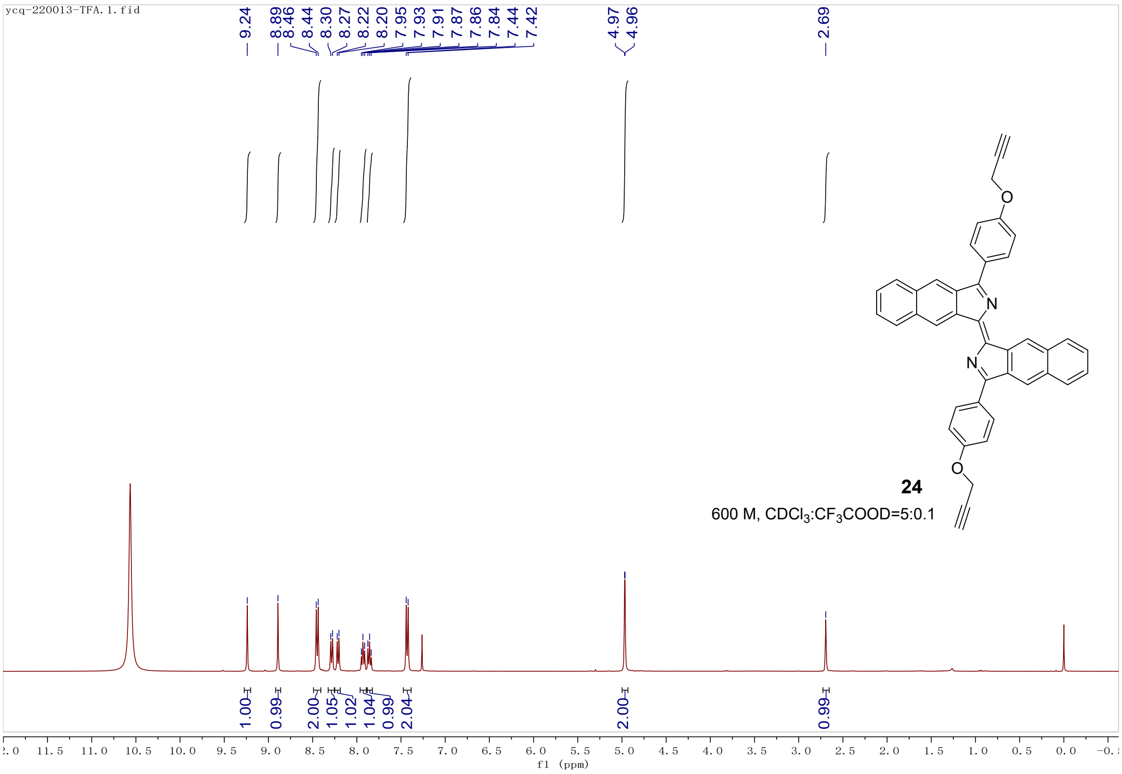

ycq-220065
single pulse decoupled gated NOE
22
MeO
OMe
8-14
f1 (ppm)

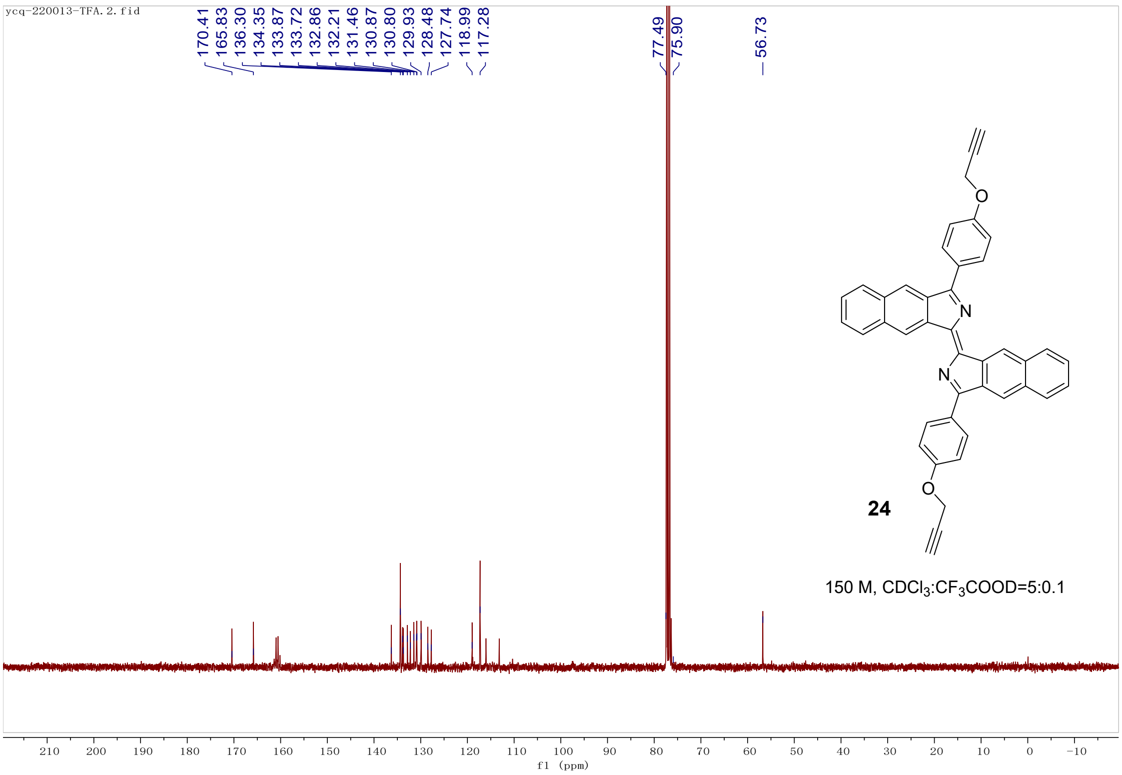

ycq-220051
8.43 8.41 8.37 8.15 8.13 8.03 8.01 7.77 7.75 7.65 7.64 7.61 7.59 7.58 5.36 5.33 5.31 5.20 5.18 5.15 5.13 5.11 5.11 5.09 4.95 4.93 4.71 4.37 4.36 4.34 4.33 4.24 4.24 4.21 3.85 3.85 3.84 3.84 3.83 3.82 3.82 3.81 2.13 2.06 2.05
AcO
OAc
AcO
O
OAc
O
N
N
O
AcO
O
OAc
AcO
OAc
(400M, CDCl3
1.01 2.01 1.00 1.05 1.02 2.01 2.22 1.06 1.03 1.01 1.01 2.00 1.09 1.10 1.03 6.00 6.00
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)

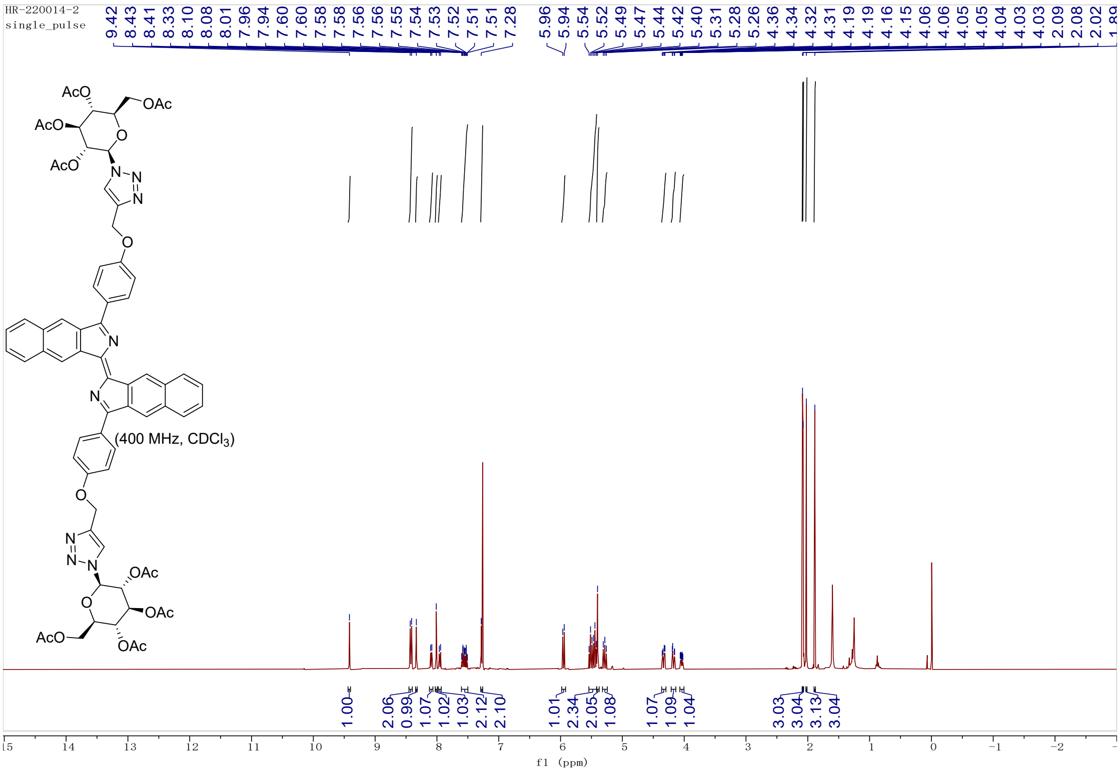

ycq-220051.2.fid
166.05 165.65 165.00 164.83 164.74 143.81 132.14 130.23 128.90 128.34 127.53 125.27 125.03 124.36 123.19 122.93 122.40 120.05 118.20 93.80 82.27 81.30 68.09 67.26 66.42 63.57 57.09 52.29 16.12 16.07 15.94 15.91
AcO
OAc
AcO
O
OAc
O
N
N
O
AcO
O
OAc
AcO
OAc
100M, CDCl3
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

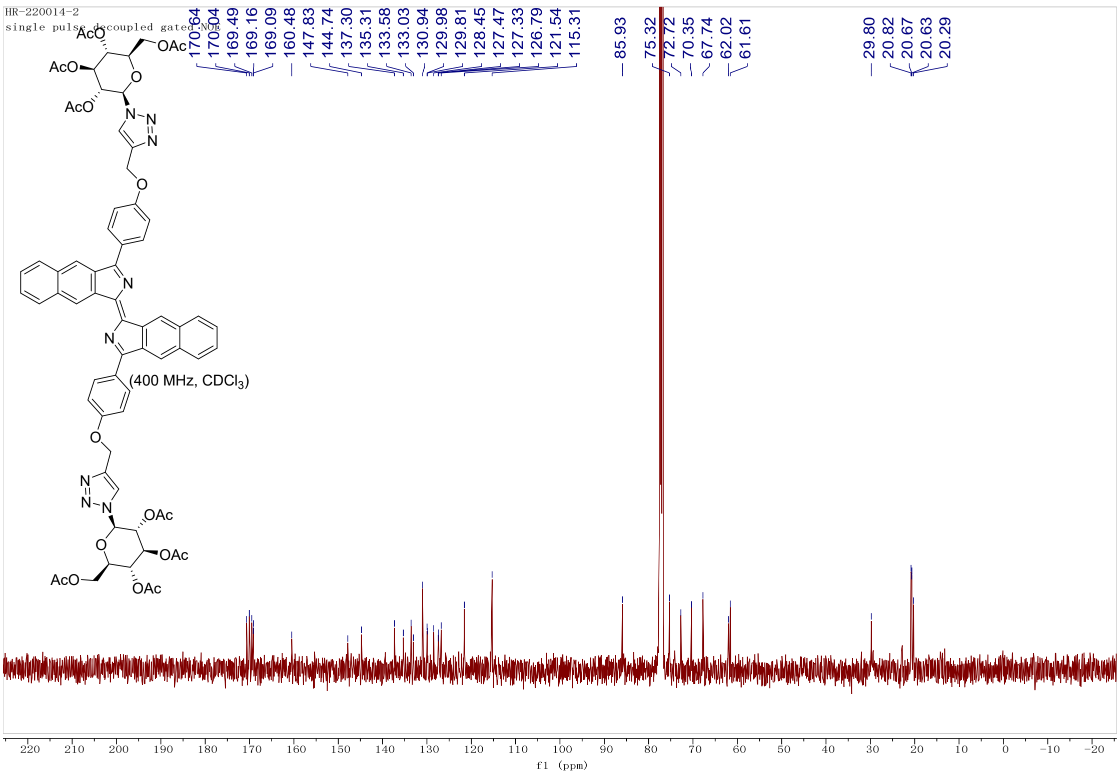

ycq-220061-2.1.fid
9.32
8.63
8.53
8.51
8.17
7.80
7.78
7.72
7.71
7.69
7.67
7.65
5.33
5.31
5.12
5.10
5.07
5.06
4.84
4.80
4.71
4.70
4.68
4.47
4.45
3.27
3.24
3.23
3.16
3.14
3.12
3.11
3.09
0.98
1.00
2.01
2.03
2.02
2.05
1.00
1.00
1.02
1.00
2.01
1.00
1.07
1.06
2.07
2.01
HO
OH
HO
O
OH
O
N
N
O
HO
O
OH
HO
OH
23
(400M, DMSO-d_6)
f1 (ppm)

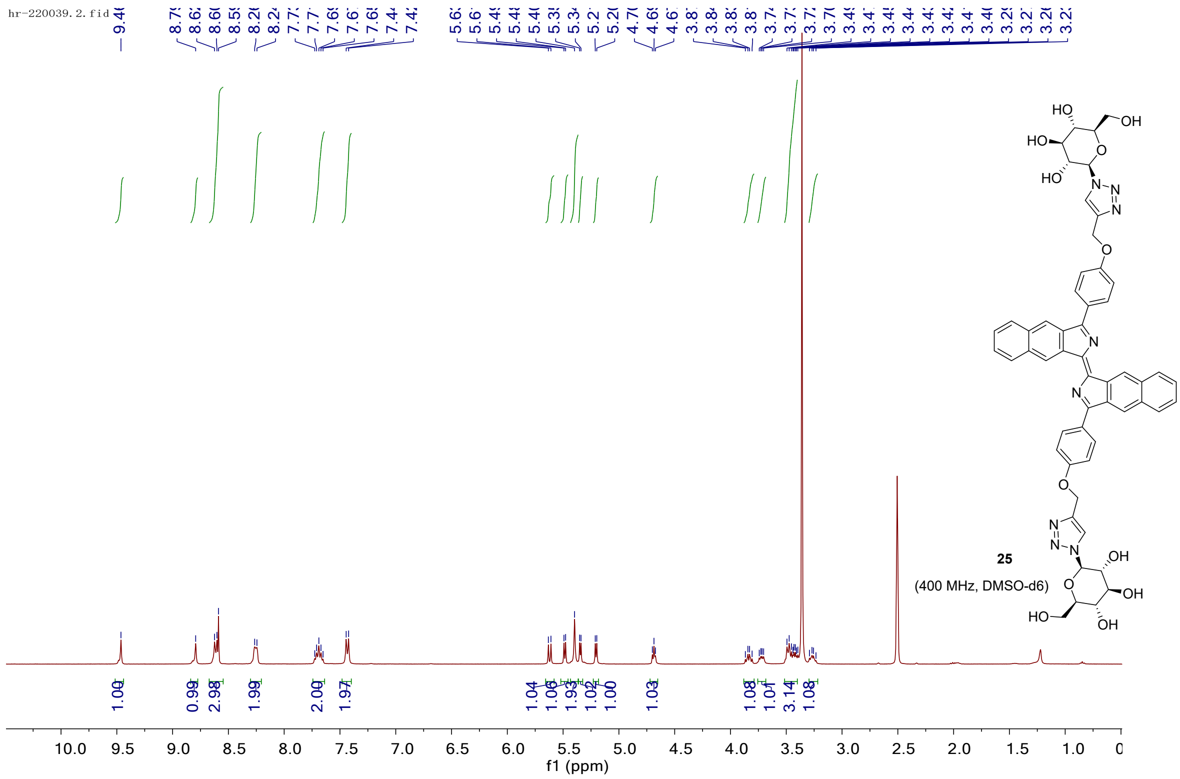

ycq-220061-4.2.fid
169.06
148.00
136.52
134.43
134.27
133.28
132.57
130.66
130.11
129.75
128.45
127.79
127.60
125.22
124.10
101.73
89.19
85.94
77.58
77.18
73.82
70.55
61.68
56.31
HO
OH
HO
O
OH
O
N
N
O
HO
O
OH
HO
OH
23
100M, DMSO-d_6)
f1 (ppm)

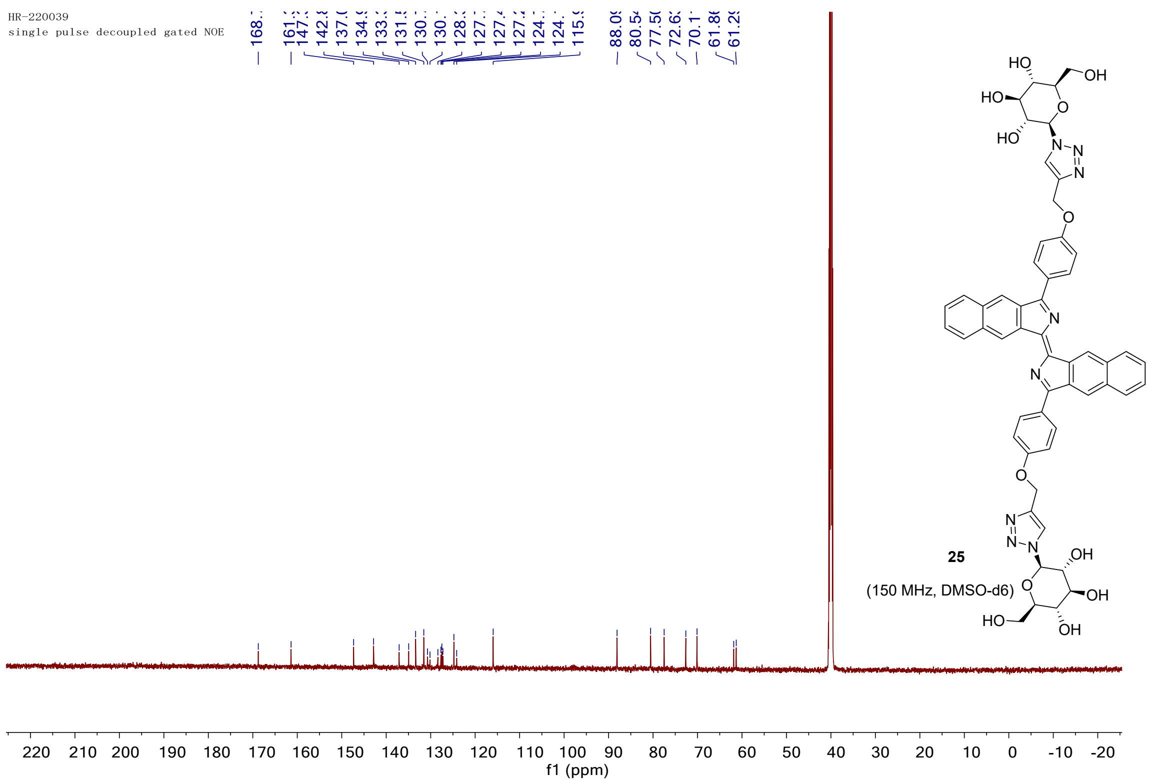

ycq-220013-TFA.1.fid
9.24
8.89
8.46
8.44
8.30
8.27
8.22
8.20
7.95
7.93
7.91
7.87
7.86
7.84
7.44
7.42
4.97
4.96
2.69
24
600 M, CDCl3:CF3COOD=5:0.1
1.00
0.99
2.00
1.05
1.02
1.04
0.99
2.04
2.00
0.99
f1 (ppm)

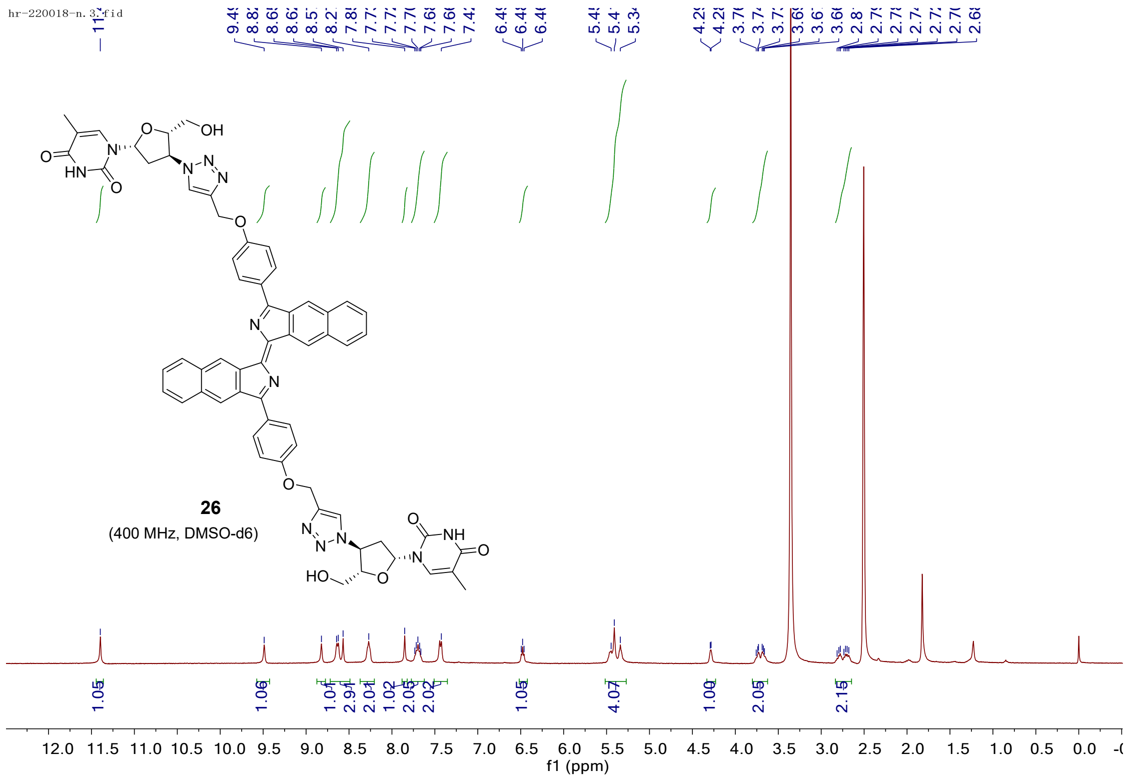

ycq-220013-TFA.2.fid
170.41
165.83
136.30
134.35
133.87
133.72
132.86
132.21
131.46
130.87
130.80
129.93
128.48
127.74
118.99
117.28
77.49
75.90
56.73
24
150 M, CDCl3:CF3COOD=5:0.1
f1 (ppm)

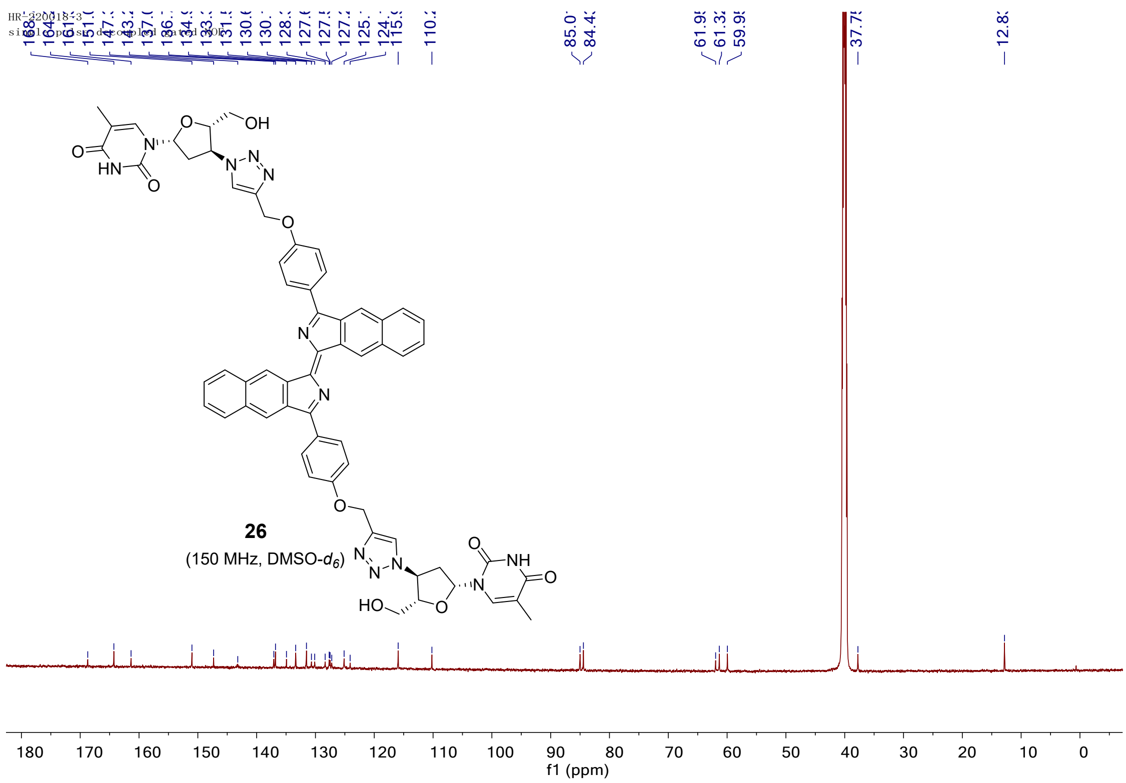


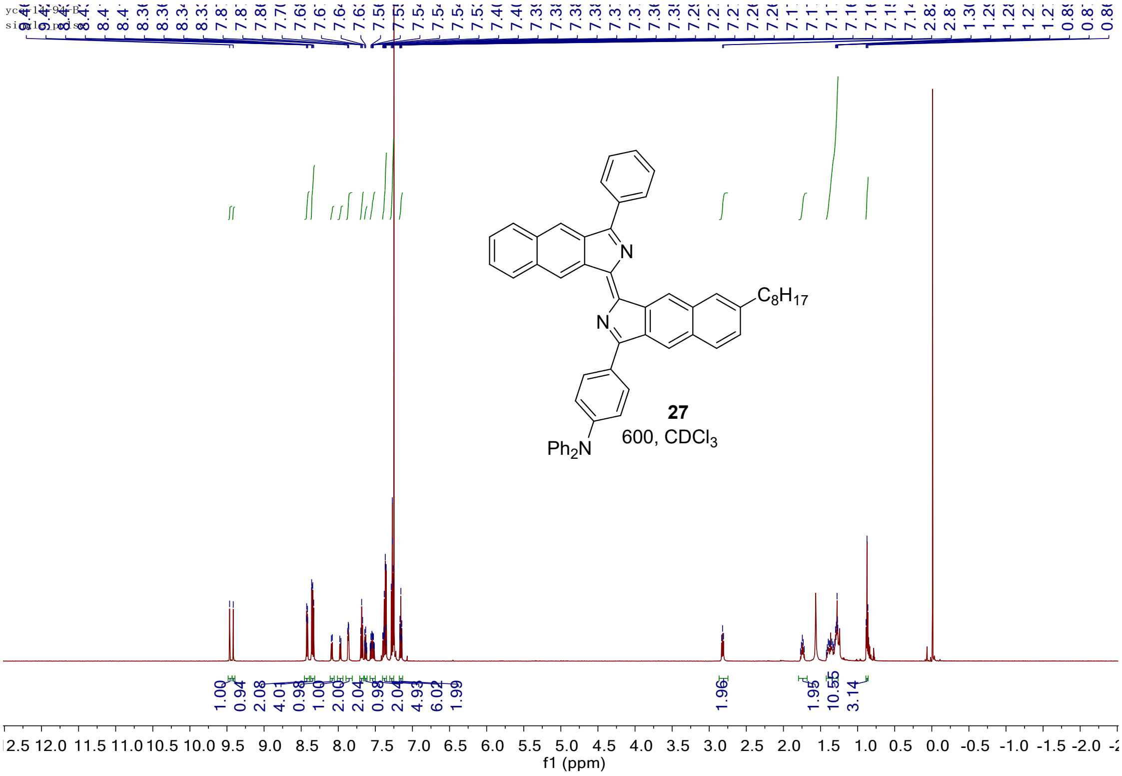


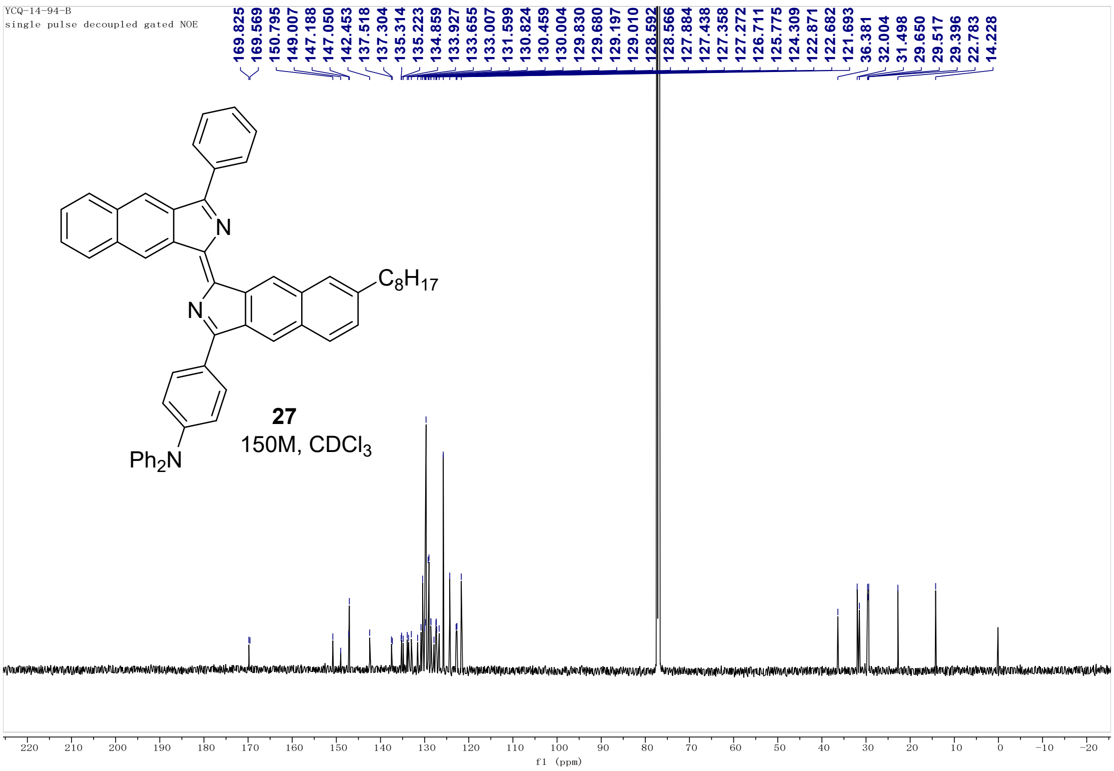

hr-220039.2.fid
25
(400 MHz, DMSO-d6)
f1 (ppm)

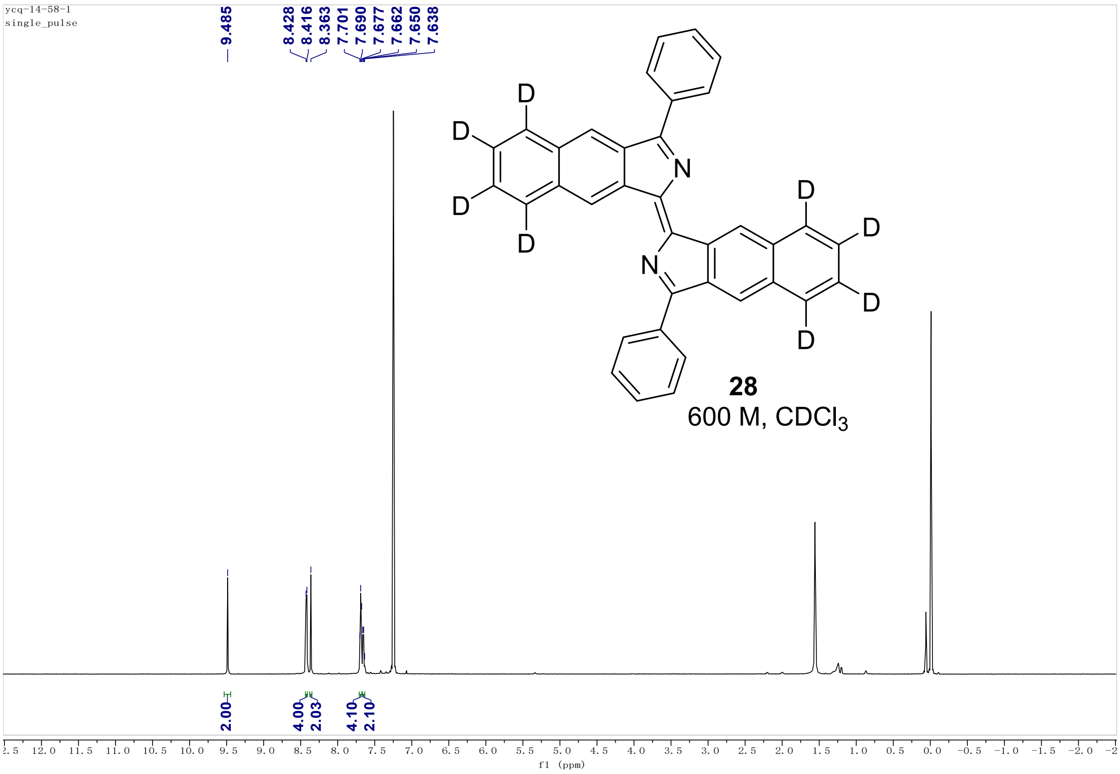

HR-220039
single pulse decoupled gated NOE
25
(150 MHz, DMSO-d6)
f1 (ppm)

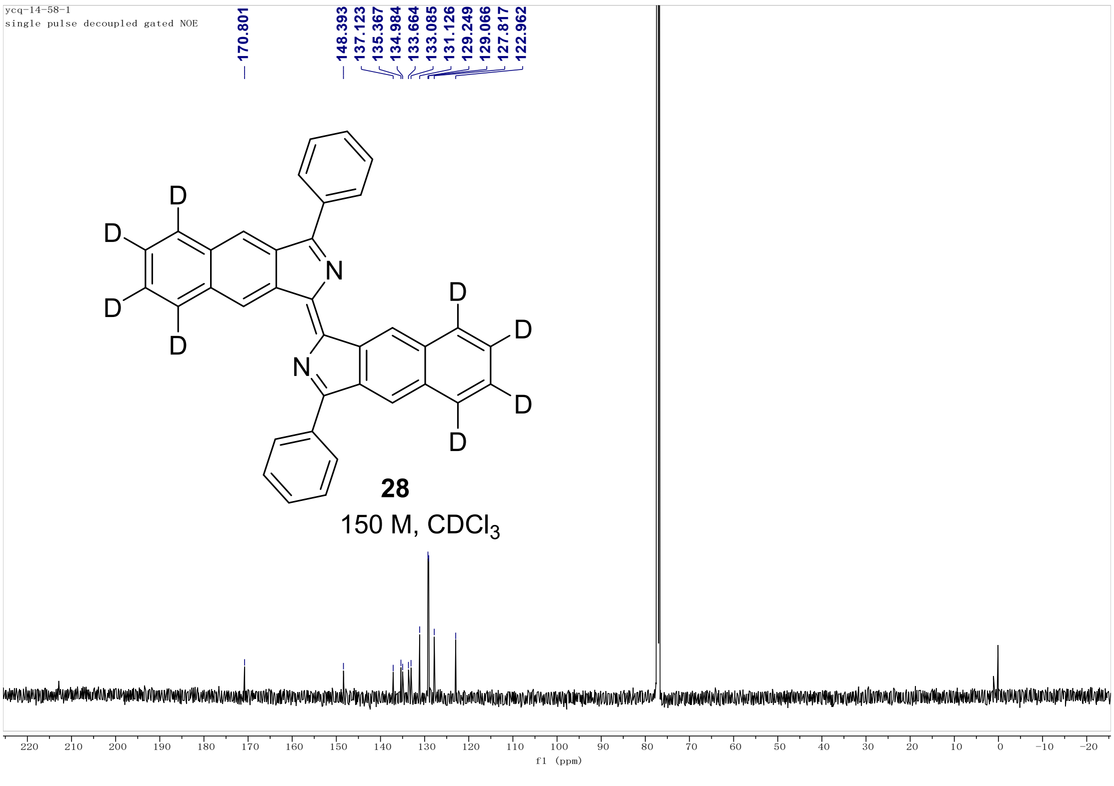

26
(400 MHz, DMSO-d6)
f1 (ppm)

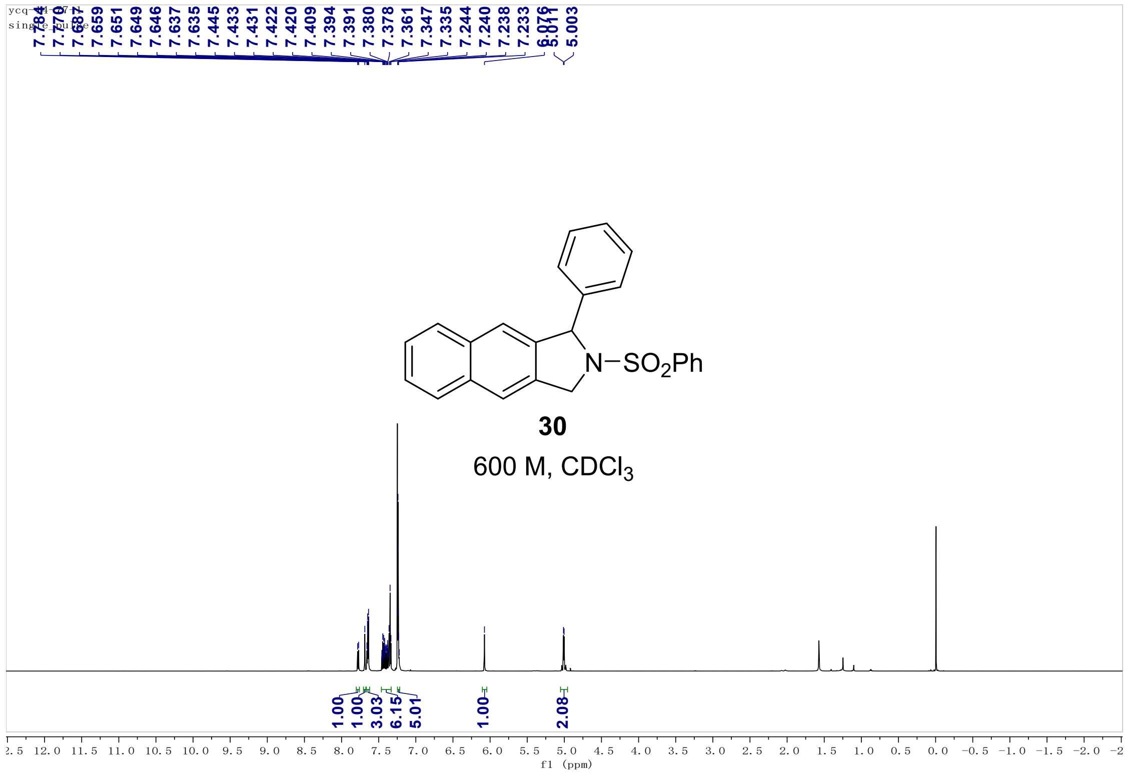

26
(150 MHz, DMSO-d_6)
f1 (ppm)

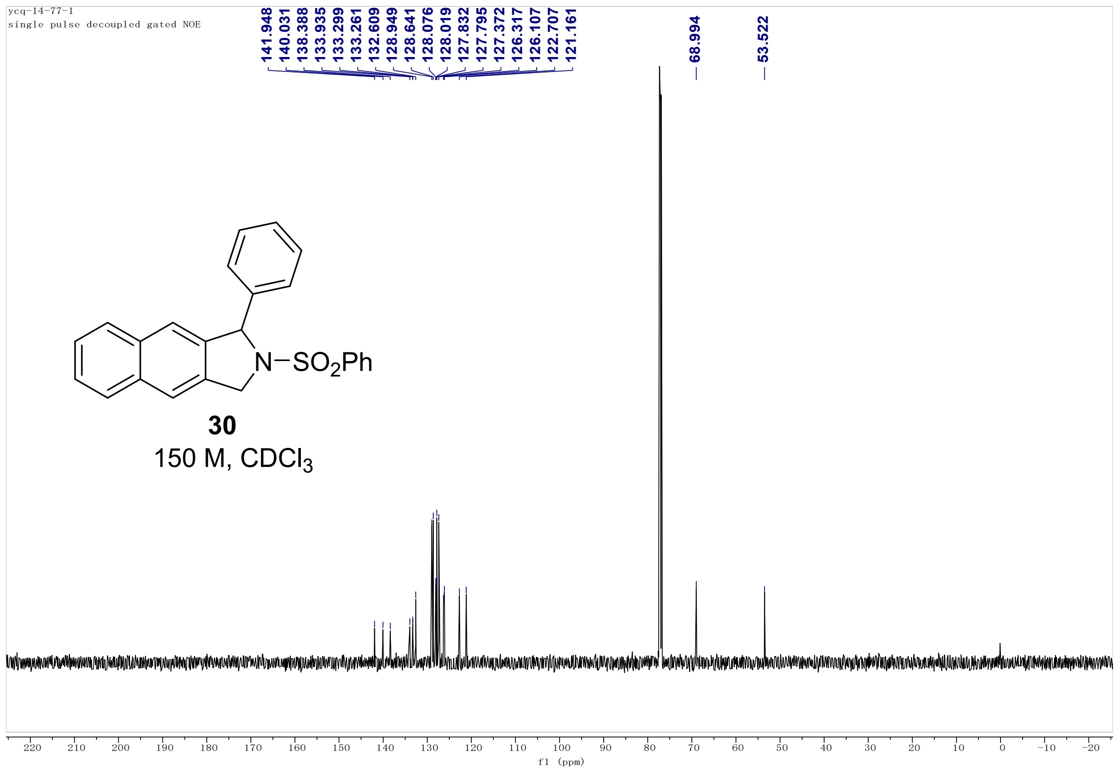

27
600, CDCl3
f1 (ppm)

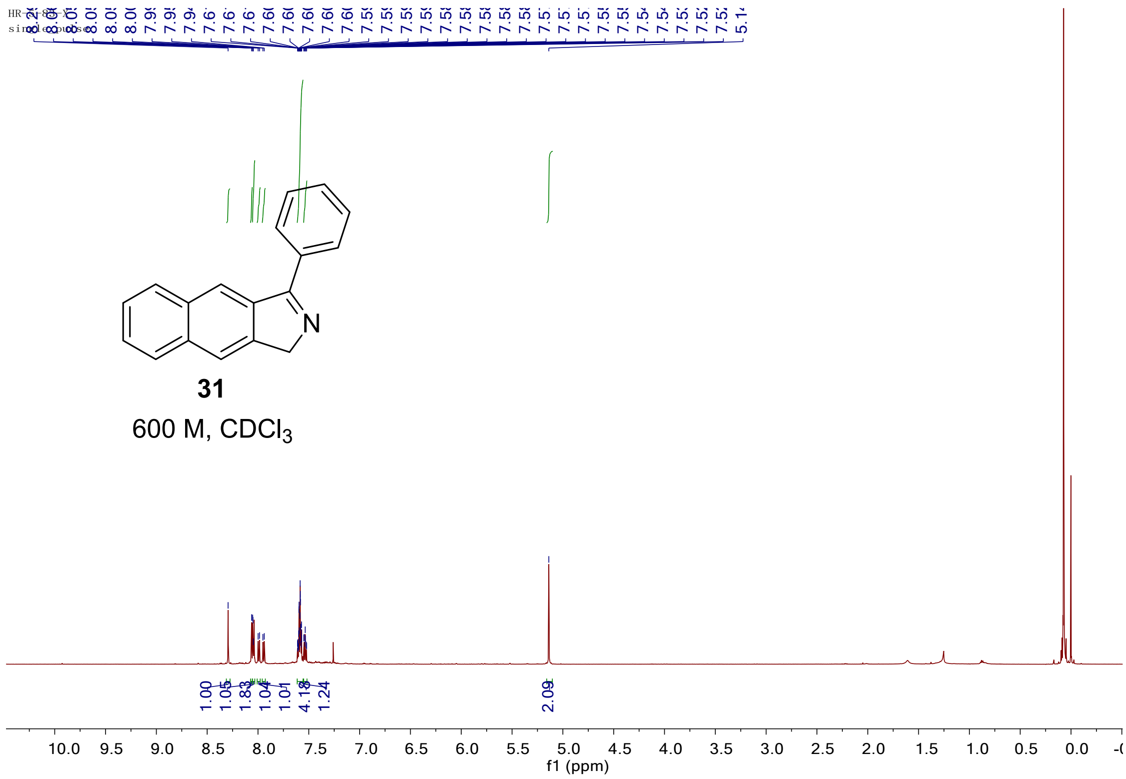

YCQ-14-94-B
single pulse decoupled gated NOE
169.825
169.569
150.795
149.007
147.188
147.050
142.453
137.518
137.304
135.314
135.223
134.859
133.927
133.655
133.007
131.599
130.824
130.459
130.004
129.830
129.680
129.197
129.010
128.592
128.566
127.884
127.438
127.358
127.272
126.711
125.775
124.309
122.871
122.682
121.693
36.381
32.004
31.498
29.650
29.517
29.396
22.783
14.228
27
150M, CDCl3
f1 (ppm)


ycq-14-58-1
single_pulse
9.485
8.428
8.416
8.363
7.701
7.690
7.677
7.662
7.650
7.638
D
N
28
600 M, CDCl3
2.00
4.00
2.03
4.10
2.10
f1 (ppm)

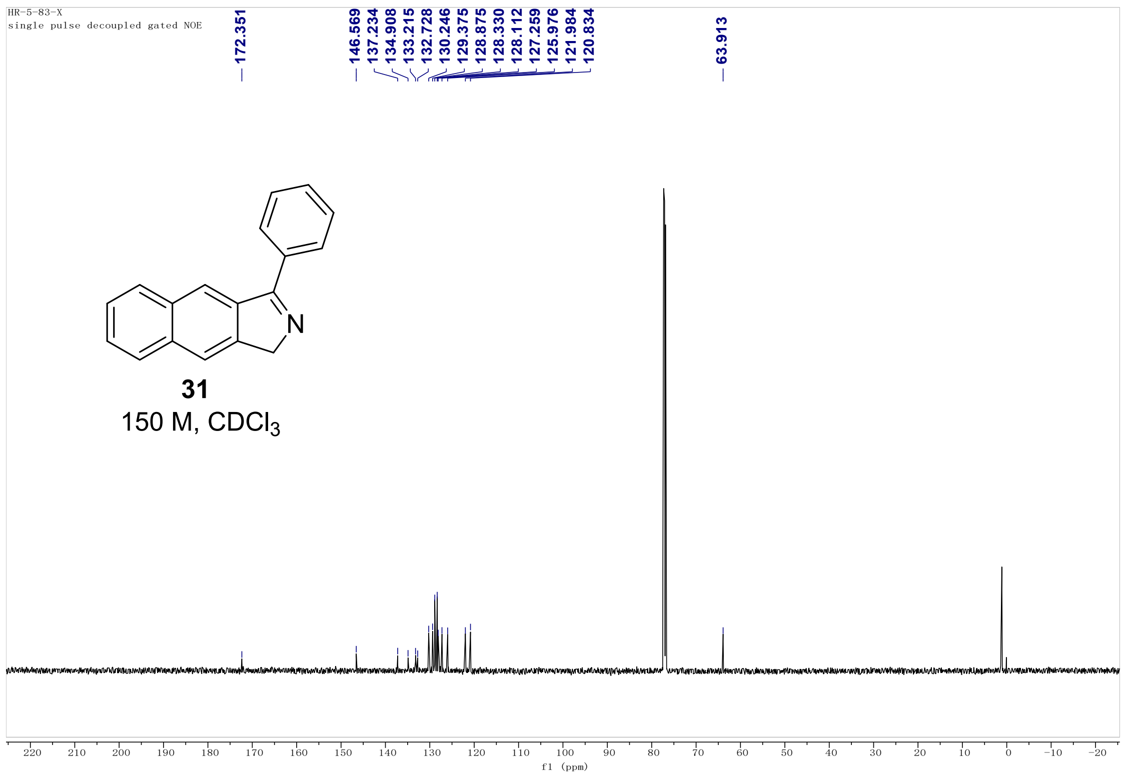

ycq-14-58-1
single pulse decoupled gated NOE
170.801
148.393
137.123
135.367
134.984
133.664
133.085
131.126
129.249
129.066
127.817
122.962
D
N
28
150 M, CDCl3
f1 (ppm)


ycq-14-77
single pulse
7.784 7.770 7.687 7.659 7.651 7.649 7.646 7.637 7.635 7.445 7.433 7.431 7.422 7.420 7.409 7.394 7.391 7.380 7.378 7.361 7.347 7.335 7.244 7.240 7.238 7.233 6.076 5.011 5.003
N−SO2Ph
30
600 M, CDCl3
1.00 1.00 3.03 6.15 5.01 1.00 2.08
f1 (ppm)


ycq-14-77-1
single pulse decoupled gated NOE
141.948 140.031 138.388 133.935 133.299 133.261 132.609 128.949 128.641 128.076 128.019 127.832 127.795 127.372 126.317 126.107 122.707 121.161
68.994
53.522
N−SO2Ph
30
150 M, CDCl3
f1 (ppm)



31
600 M, $CDCl_3$
f1 (ppm)



HR-5-83-X
single pulse decoupled gated NOE
172.351
146.569
137.234
134.908
133.215
132.728
130.246
129.375
128.875
128.330
128.112
127.259
125.976
121.984
120.834
63.913
31
150 M, $CDCl_3$
f1 (ppm)

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