

Supporting Information

C(sp)-C(sp) Lever-Based Targets of Orientational Chirality: Design and Asymmetric Synthesis

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EXPERIMENTAL SECTION

For general Information, all melting points are uncorrected. The NMR spectra were recorded in CDCl₃ on a 400 MHz instrument with TMS as the internal standard. Chemical shifts (δ) are reported in ppm with respect to TMS. Data are represented as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, m = multiplet), coupling constant (J, Hz), and integration. High-resolution mass spectrometry (HRMS) analyses were carried out using a time-of-flight mass spectrometry (TOF-MS) instrument with an electrospray ionization (ESI) source. X-ray crystallographic analysis was performed with a SMART CCD and a P4 diffractometer. All commercially sourced starting materials were used without further purification.

1. General Procedure for the Synthesis of alkynyl precursors 5

The product of **(R,Z)-2-methyl-N-(1-phenylpentylidene)propane-2-sulfinamide (S3)**: was synthesized according to the literature (**Scheme 2**). Ethynyltrimethylsilane was converted into ((trimethylsilyl)ethynyl)lithium precursor *via* the treatment with ⁿBuLi in THF at -78 °C, followed by reacting with (**S5**) to give **(R)-2-methyl-N-((S)-3-phenyl-1-(trimethylsilyl)hept-1-yn-3-yl)propane-2-sulfinamide (S6, 48% yield)**, which was then transformed into **(R)-2-methyl-N-((R)-3-phenylhept-1-yn-3-yl)propane-2-sulfinamide ((R,R)-5a)** by reacting with K₂CO₃ in the presence of MeOH to give a yield of 65%.

2. General Procedure for the Synthesis of Products (R,S-7)

1-bromo-8-(p-tolylethynyl)naphthalene (6a) was prepared by Sonogashira coupling in 74 % chemical yield (**Scheme 3**). With the abovementioned assumption in mind, we explored the reaction of **1-bromo-8-(p-tolylethynyl)naphthalene (6a)** (0.1 mmol) with **(R)-2-methyl-N-((R)-3-phenylhept-1-yn-3-yl)propane-2-sulfinamide ((R,R)-5a)** (0.1 mmol, 1.0 eq), as model substrates, with PdCl₂(PPh₃)₂ (2 mol%) and Cu(I) iodide (5 mol%) as co-catalysts in the presence of Et₃N (2.0 mL), promoted under argon at 50 °C for 24 h, resulted in the product **(R)-2-methyl-N-((S)-3-phenyl-1-(8-(p-tolylethynyl)naphthalen-1-yl)hept-1-yn-3-yl)propane-2-sulfinamide ((R,S)-7a)** in a yield of 68% (**Scheme 5**).

3. General Procedure for the Synthesis of substrates 6

The substrates **6** were prepared according to the reported procedures. Compound **A3**, **A4**, **B3**, **C5** and **D5** are new, while the rest of them have been previously reported, and their characterization data are in agreement with the literature.

A3:

Step 1: A 25 mL clean and dried tube was equipped with a stirring bar and charged with (1S, 2S, 5R)-2-isopropyl-5-methylcyclohexan-1-ol **A1** (3.0 mmol), 4-ethynylbenzoic acid (3.0 mmol, 1.0 eq.) and DMAP (0.6 mmol, 0.2 eq). 15 mL of DCM was then added to the mixture. DCC (3.6 mmol, 1.2 eq) was added slowly to this solution at 0 °C. Next, the mixture was stirred at 25 °C overnight until the reaction completed. After concentration, the crude product was purified *via* flash chromatography on silica gel using PE/EA as an eluent to give the final product **A2** (88% yield, 0.748 g).

Step 2: A mixture of **A2** (2.5 mmol), 1,8-dibromonaphthalene (2.5 mmol, 1.0 eq) and Pd(PPh₃)₂Cl₂ (2 mol %), CuI (5 mol%) in 20 mL Et₃N was stirred for 12 h at 60 °C under argon atmosphere. The resulting mixture was extracted with 50 mL H₂O and 20 mL ethyl acetate for three times. The organic phase was concentrated to a bottle and was dried over MgSO₄. Then, the mixture was filtrated. The crude product was purified by chromatography on silica gel to afford compound **A3** (total 48% yield, 0.703 g). (Figure S1-2 in the Supporting Information)

Product **A4** (total 41% yield, 0.605 g) was obtained through the synthesis method of product **A3**. (Figure S3-4 in the Supporting Information)

B3:

B3 was obtained through the synthesis method of product **A3** (total 36% yield, 0.70 g). (Figure S5-6 in the Supporting Information)

C3:

Step 1: **C1** (5 mmol) was dissolved in 20 mL DCM and the mixture was loaded in an oven-dried flask equipped with a magnetic stir bar. Then, pyridine (10 mmol, 2.0 eq) was added to the flask and the mixture was cooled to 0 °C. Subsequently, TiF_4 (6 mmol, 1.2 eq) was added dropwise to the mixture at 0 °C and the mixture was stirred under room temperature overnight. The mixture was then quenched with NH_4Cl and extracted with DCM. The organic layer was dried over anhydrous MgSO_4 and filtered. The colature was evaporated on a rotary evaporator. The crude product was purified by chromatography on silica gel to afford compound **C2** (88% yield, 1.762 g).

Step 2: A mixture of **C2** (4 mmol), ethynyltrimethylsilane (5.6 mmol, 1.4 eq), triethylamine (4 mL), and $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ (3 mol %) in 20 mL DMF was stirred for 4 h at 90 °C under argon atmosphere. The resulting mixture was extracted with 50 mL H_2O and 20 mL ethyl acetate three times. The organic phase was concentrated to a bottle and was dried over MgSO_4 . Then, the mixture was filtrated. The crude product was purified by chromatography on silica gel to afford compound **C3** (63% yield, 0.879 g).

Step 3: **C3** (2 mmol) was dissolved in 10 mL MeOH and K_2CO_3 (3 mmol, 1.5 eq) was loaded in the mixture, which was stirred at room temperature for 8 h. The reaction process was determined by TLC until the starting material **C3** consumed completely. The mixture was quenched by saturated ammonium chloride solution and extracted with ethyl acetate for three times. The crude product was purified by chromatography on silica gel to afford compound **C4** (47% yield, 0.263 g).

C5 was obtained through the synthesis method of product **A3** (total 25% yield, 0.602 g). (Figure S7-8 in the Supporting Information).

D5:

Step 1: **D1** (7.5 mmol, 1.5 eq) and Cs_2CO_3 (10 mmol, 2.0 eq) were dissolved in DMF. Then the 1-(bromomethyl)-4-iodobenzene (5 mmol, 1.0 eq) was added to the reaction vial and the reaction was reacted at 60 °C overnight. The resulting mixture was cooled to room temperature and filtered. Then the filtrate was extracted with ethyl acetate

and saturated aqueous sodium chloride. The organic phase was concentrated, dried by MgSO₄ and filtered. The crude product was purified by chromatography on silica gel to afford compound **D2** (77% yield, 0.702 g).

D5 was obtained through the synthesis method of product **A3** (total 21% yield, 0.989 g). (Figure S9-10 in the Supporting Information)

(1S, 2S, 5R)-2-isopropyl-5-methylcyclohexyl 4-((8-bromonaphthalen-1-yl)ethynyl)benzoate (A3)

¹H NMR (400 MHz, CDCl₃) δ 8.06 (dd, *J* = 15.0, 8.4 Hz, 2H), 7.98 - 7.84 (m, 4H), 7.65 (dd, *J* = 27.2, 8.4 Hz, 2H), 7.53 - 7.45 (m, 1H), 7.32 (dd, *J* = 15.2, 7.6 Hz, 1H), 5.00 - 4.93 (m, 1H), 2.20 - 2.13 (m, 1H), 2.02 - 1.94 (m, 1H), 1.76 (d, *J* = 12.0 Hz, 2H), 1.61 (d, *J* = 11.6 Hz, 2H), 1.20 - 1.10 (m, 2H), 0.98 - 0.93 (m, 7H), 0.85 - 0.81 (m, 3H).
¹³C NMR (100 MHz, CDCl₃) δ 165.6, 136.1, 135.7, 135.4, 134.1, 132.4, 130.7, 130.4, 130.2, 129.6, 129.2, 128.5, 126.6, 126.5, 125.6, 120.5, 96.9, 93.0, 75.1, 47.3, 41.0, 34.3, 31.5, 26.6, 23.7, 22.0, 20.8, 16.6.

(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-((8-bromonaphthalen-1-yl)ethynyl)benzoate (A4)

¹H NMR (400 MHz, CDCl₃) δ 8.06 (dd, *J* = 15.2, 8.4 Hz, 2H), 7.98 - 7.84 (m, 4H), 7.65 (dd, *J* = 27.2, 8.4 Hz, 2H), 7.53 - 7.45 (m, 1H), 7.32 (dd, *J* = 15.6, 7.6 Hz, 1H), 5.00 - 4.93 (m, 1H), 2.20 - 2.13 (m, 1H), 2.02 - 1.94 (m, 1H), 1.76 (d, *J* = 11.6 Hz, 2H), 1.61 (d, *J* = 11.6 Hz, 2H), 1.20 - 1.10 (m, 2H), 0.98 - 0.93 (m, 7H), 0.85 - 0.81 (m, 3H).
¹³C NMR (100 MHz, CDCl₃) δ 165.6, 136.1, 135.7, 135.4, 134.1, 132.4, 130.7, 130.4, 130.2, 129.6, 129.2, 128.5, 126.6, 126.5, 125.6, 120.5, 96.9, 93.0, 75.1, 47.3, 41.0, 34.3, 31.5, 26.6, 23.7, 22.0, 20.8, 16.6.

(3S,8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((8-bromonaphthalen-1-yl)ethynyl)benzoate (B5)

¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 8.4 Hz, 2H), 7.97 - 7.82 (m, 4H), 7.72 - 7.64 (m, 2H), 7.52 - 7.47 (m, 1H), 7.36 - 7.30 (m, 1H), 5.46 (d, *J* = 3.6 Hz, 1H), 4.94 - 4.85 (m, 1H), 2.61 - 2.46 (m, 3H), 2.15 (s, 3H), 2.11 -

1.94 (m, 4H), 1.80 - 1.50 (m, 9H), 1.33 - 1.16 (m, 4H), 1.10 (s, 3H), 0.67 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 209.4, 165.5, 139.6, 136.1, 135.7, 134.1, 130.6, 130.4, 130.1, 129.5, 129.2, 128.6, 126.6, 125.6, 122.5, 120.5, 100.0, 96.9, 93.1, 74.7, 63.7, 56.9, 50.0, 44.0, 38.8, 38.2, 37.1, 36.7, 31.9, 31.8, 31.5, 27.9, 24.5, 22.9, 21.1, 19.4, 13.2.

(8R,9S,13S,14S)-3-((8-bromonaphthalen-1-yl)ethynyl)-13-methyl-6,7,8,9,11,12,13,14,15,16-decahydro-17H-cyclopenta[a]phenanthren-17-one (C5)

¹H NMR (400 MHz, CDCl₃) δ 7.93 - 7.88 (m, 2H), 7.83 (d, *J* = 8.4 Hz, 2H), 7.49 - 7.41 (m, 2H), 7.37 (s, 1H), 7.34 - 7.29 (m, 2H), 2.99 - 2.93 (m, 2H), 2.57 - 2.44 (m, 2H), 2.39 - 2.32 (m, 1H), 2.20 - 2.00 (m, 4H), 1.69 - 1.48 (m, 7H), 0.95 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 140.3, 136.7, 135.7, 135.6, 133.9, 131.3, 130.6, 129.7, 129.1, 128.3, 126.4, 125.6, 125.4, 121.5, 121.2, 120.7, 97.9, 89.6, 50.6, 48.0, 44.5, 38.0, 35.8, 31.6, 29.2, 26.4, 25.6, 21.6, 13.9.

(S)-6-((4-((8-bromonaphthalen-1-yl)ethynyl)benzyl)oxy)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chromane (D5)

¹H NMR (400 MHz, CDCl₃) δ 7.94 - 7.88 (m, 2H), 7.84 - 7.80 (m, 2H), 7.65 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.46 (t, *J* = 7.6 Hz, 1H), 7.32 - 7.28 (m, 1H), 4.74 (s, 2H), 2.64 - 2.58 (m, 2H), 2.23 (s, 3H), 2.18 (s, 3H), 2.13 (s, 3H), 1.87 - 1.76 (m, 2H), 1.60 - 1.51 (m, 4H), 1.47 - 1.26 (m, 12H), 1.23 - 1.04 (m, 8H), 0.89 - 0.85 (m, 12H). ¹³C NMR (100 MHz, CDCl₃) δ 148.1, 148.0, 138.3, 135.7, 134.0, 131.0, 130.7, 129.9, 129.1, 127.9, 127.6, 126.5, 125.9, 125.6, 123.5, 123.0, 121.0, 120.7, 117.7, 97.7, 90.3, 74.9, 74.3, 40.1, 39.4, 37.5, 37.5, 37.4, 37.3, 32.8, 32.7, 31.5, 28.0, 24.8, 24.5, 23.9, 22.7, 22.6, 21.1, 20.7, 19.8, 19.7, 12.9, 12.0, 11.8.

(R)-2-methyl-N-((S)-3-phenyl-1-(8-(p-tolyethynyl)naphthalen-1-yl)hept-1-yn-3-yl)propane-2-sulfinamide (7a)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), white solid, 36.2 mg, 68 % yield, mp 138.4-139.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 7.2 Hz, 1H), 7.84 - 7.79 (m, 3H), 7.70 (d, *J* = 7.6 Hz, 2H), 7.49 - 7.41 (m, 2H), 7.32 - 7.26 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 3.52 (s, 1H), 2.27 (s, 3H), 2.18 - 2.10 (m, 1H), 1.87 - 1.80 (m, 1H), 1.74 - 1.68 (m, 1H), 1.48 - 1.42 (m, 1H), 1.18 (s, 9H), 1.11 (d, *J* = 6.8 Hz, 1H), 0.99 - 0.94 (m, 1H), 0.74 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 142.6, 137.8, 136.0, 135.2, 134.1, 131.5, 131.3, 129.5, 129.4, 128.8, 128.1, 127.7, 127.0, 125.7, 125.4, 121.0, 120.9, 120.6, 98.1, 96.9, 89.5, 87.6, 61.3, 56.2, 43.3, 29.7, 26.8, 22.6, 22.5, 21.4, 13.9. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₆H₃₈NOS 532.2674; Found 532.2654. [α]_D²⁵ = 10.166 (c = 2.12, CH₂Cl₂).

***(R)*-2-methyl-*N*-((*S*)-3-phenyl-1-(8-(phenylethynyl)naphthalen-1-yl)hept-1-yn-3-yl)propane-2-sulfinamide (7b)**

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 32.0 mg, 62 % yield; ¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 6.8 Hz, 1H), 7.86 - 7.80 (m, 3H), 7.70 (d, *J* = 6.8 Hz, 2H), 7.50 - 7.42 (m, 2H), 7.31 - 7.23 (m, 5H), 7.19 - 7.14 (m, 1H), 7.12 - 7.06 (m, 2H), 3.49 (s, 1H), 2.20 - 2.12 (m, 1H), 1.87 - 1.78 (m, 1H), 1.50 - 1.41 (m, 1H), 1.18 (s, 9H), 1.14 - 1.05 (m, 2H), 1.02 - 0.94 (m, 1H), 0.75 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 142.5, 136.1, 135.2, 134.1, 131.6, 131.2, 129.6, 129.5, 128.2, 128.1, 127.8, 127.7, 127.0, 125.7, 125.4, 123.9, 120.8, 120.5, 98.0, 96.6, 90.2, 87.6, 61.3, 56.2, 43.3, 26.8, 22.7, 22.5, 13.9. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₅H₃₆NOS 518.2518; Found 518.2532. [α]_D²⁵ = 9.544 (c = 1.76, CH₂Cl₂).

***(R)*-*N*-((*S*)-1-(8-((4-ethylphenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7c)**

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 27.2 mg, 48 % yield; ¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 7.2 Hz, 1H), 7.84 - 7.79 (m, 3H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.49 - 7.41 (m, 2H), 7.31 - 7.25 (m, 3H), 7.16 (d, *J* = 8.0 Hz, 2H), 6.92 (d, *J* = 7.6 Hz, 2H), 3.51 (s, 1H), 2.56 (q, *J* = 7.6 Hz,

2H), 2.19 - 2.11 (m, 1H), 1.87 - 1.78 (m, 1H), 1.46 - 1.41 (m, 1H), 1.20 - 1.15 (m, 12H), 1.12 - 1.06 (m, 2H), 0.99 - 0.95 (m, 1H), 0.74 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 142.6, 136.0, 135.1, 134.1, 131.8, 131.6, 131.3, 129.5, 129.34.4, 128.1, 127.7, 127.6, 127.0, 125.7, 125.4, 121.1, 121.0, 120.6, 98.0, 96.9, 89.4, 87.6, 61.3, 56.2, 43.3, 29.7, 28.8, 26.8, 22.7, 22.5, 15.4, 13.9. HRMS (ESI) m/z : $[\text{M}+\text{Na}]^+$ Calcd for $\text{C}_{37}\text{H}_{39}\text{NNaOS}$ 568.2650; Found 568.2630. $[\alpha]_{\text{D}}^{25} = 15.071$ ($c = 1.04$, CH_2Cl_2).

(R)-N-((S)-1-(8-((4-(tert-butyl)phenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7d)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 29.1 mg, 51 % yield; ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, $J = 7.2$ Hz, 1H), 7.84 - 7.79 (m, 3H), 7.68 (d, $J = 7.2$ Hz, 2H), 7.48 - 7.41 (m, 2H), 7.30 - 7.26 (m, 3H), 7.17 (d, $J = 8.0$ Hz, 2H), 7.09 (d, $J = 8.0$ Hz, 2H), 3.46 (s, 1H), 2.21 - 2.12 (m, 1H), 1.86 - 1.76 (m, 1H), 1.46 - 1.40 (m, 1H), 1.26 (s, 9H), 1.17 (s, 9H), 1.12 - 1.05 (m, 2H), 0.99 - 0.94 (m, 1H), 0.74 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 150.9, 142.6, 136.0, 135.1, 134.1, 131.3, 129.5, 129.4, 128.1, 127.7, 127.0, 125.6, 125.4, 125.0, 121.1, 120.9, 120.6, 98.0, 96.8, 89.4, 87.6, 61.2, 56.2, 43.3, 34.6, 31.1, 26.8, 22.7, 22.5, 13.9. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{39}\text{H}_{44}\text{NOS}$ 574.3144; Found 574.3116. $[\alpha]_{\text{D}}^{25} = 12.233$ ($c = 1.18$, CH_2Cl_2).

(R)-N-((S)-1-(8-((4-methoxyphenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7e)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 24.6 mg, 45 % yield; ^1H NMR (400 MHz, CDCl_3) δ 8.02 (d, $J = 7.2$ Hz, 1H), 7.84 - 7.78 (m, 3H), 7.71 (d, $J = 7.6$ Hz, 2H), 7.49 - 7.40 (m, 2H), 7.32 - 7.25 (m, 3H), 7.16 (d, $J = 8.0$ Hz, 2H), 6.61 (d, $J = 8.0$ Hz, 2H), 3.75 (s, 3H), 3.51 (s, 1H), 2.20 - 2.12 (m, 1H), 1.88 - 1.79 (m, 1H), 1.48 - 1.42 (m, 1H), 1.19 (s, 9H), 1.15 - 1.06 (m, 2H), 0.99 - 0.94 (m, 1H), 0.76

(t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.2, 142.6, 136.0, 135.1, 134.1, 133.0, 131.3, 129.5, 129.3, 128.2, 127.7, 127.0, 125.6, 125.4, 121.1, 120.6, 116.2, 113.7, 98.0, 96.6, 88.7, 87.7, 61.3, 56.2, 55.2, 43.3, 29.7, 26.8, 22.7, 22.6, 13.9. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{36}\text{H}_{38}\text{NO}_2\text{S}$ 548.2623; Found 548.2591. $[\alpha]_{\text{D}}^{25} = 15.941$ ($c = 1.23$, CH_2Cl_2).

(R)-N-((S)-1-(8-([1,1'-biphenyl]-4-ylethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7f)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 34.4 mg, 58 % yield; ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, $J = 6.8$ Hz, 1H), 7.88 - 7.82 (m, 3H), 7.71 (d, $J = 7.2$ Hz, 2H), 7.52 (d, $J = 8.0$ Hz, 2H), 7.50 - 7.42 (m, 4H), 7.39 - 7.32 (m, 2H), 7.32 - 7.27 (m, 6H), 3.50 (s, 1H), 2.25 - 2.15 (m, 1H), 1.90 - 1.80 (m, 1H), 1.53 - 1.43 (m, 1H), 1.18 (s, 9H), 1.15 - 1.08 (m, 2H), 1.03 - 0.96 (m, 1H), 0.75 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.6, 140.5, 140.4, 136.1, 135.2, 134.1, 132.0, 131.3, 129.6, 129.6, 128.8, 128.3, 128.2, 127.8, 127.5, 127.0, 126.9, 126.7, 125.7, 125.4, 122.9, 120.8, 120.6, 98.0, 96.4, 90.9, 87.6, 61.2, 56.3, 43.3, 26.9, 22.6, 22.6, 13.9. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{41}\text{H}_{40}\text{NOS}$ 594.2831; Found 594.2823. $[\alpha]_{\text{D}}^{25} = 10.588$ ($c = 1.55$, CH_2Cl_2).

(R)-N-((S)-1-(8-((4-chlorophenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7g)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 20.1 mg, 38 % yield; ^1H NMR (400 MHz, CDCl_3) δ 8.04 (dd, $J = 7.2, 0.8$ Hz, 1H), 7.86 - 7.81 (m, 3H), 7.71 - 7.66 (m, 2H), 7.50 - 7.42 (m, 2H), 7.33 - 7.27 (m, 3H), 7.13 - 7.09 (m, 2H), 7.05 - 7.01 (m, 2H), 3.43 (s, 1H), 2.22 - 2.14 (m, 1H), 1.88 - 1.79 (m, 1H), 1.49 - 1.40 (m, 1H), 1.19 (s, 9H), 1.16 - 1.10 (m, 2H), 1.02 - 0.94 (m, 1H), 0.76 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.4, 136.2, 135.3, 134.1, 133.7, 132.8, 131.2, 129.8, 129.6, 128.3, 128.2, 127.9, 126.9,

125.8, 125.4, 122.4, 120.4, 120.4, 97.9, 95.3, 91.1, 87.6, 61.2, 56.3, 43.3, 26.9, 22.6, 22.6, 13.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{35}ClNOS$ 552.2128; Found 552.2127. $[\alpha]_D^{25} = 10.217$ (c = 0.77, CH_2Cl_2).

(R)-N-((S)-1-(8-((4-bromophenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7h)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 20.8 mg, 35 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, $J = 7.2$ Hz, 1H), 7.83 (d, $J = 8.4$ Hz, 3H), 7.68 (d, $J = 7.6$ Hz, 2H), 7.50 - 7.42 (m, 2H), 7.33 - 7.27 (m, 3H), 7.18 (d, $J = 8.0$ Hz, 2H), 7.04 (d, $J = 8.0$ Hz, 2H), 3.42 (s, 1H), 2.22 - 2.14 (m, 1H), 1.89 - 1.80 (m, 1H), 1.47 - 1.41 (m, 1H), 1.19 (s, 9H), 1.16 - 1.10 (m, 2H), 0.99 - 0.95 (m, 1H), 0.76 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 136.2, 135.2, 134.1, 133.0, 131.2, 129.8, 129.6, 128.2, 127.9, 126.9, 125.8, 125.4, 122.8, 121.9, 120.4, 97.9, 95.4, 91.3, 87.6, 61.2, 56.3, 43.3, 29.7, 26.9, 22.6, 22.6, 13.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{35}H_{35}BrNOS$ 596.1623; Found 596.1606. $[\alpha]_D^{25} = 9.695$ (c = 1.64, CH_2Cl_2).

(R)-N-((S)-1-(8-((4-cyanophenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7i)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 21.7 mg, 40 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 - 8.04 (m, 1H), 7.89 - 7.81 (m, 3H), 7.68 - 7.63 (m, 2H), 7.52 - 7.44 (m, 2H), 7.34 - 7.26 (m, 5H), 7.23 (d, $J = 7.6$ Hz, 2H), 3.34 (s, 1H), 2.24 - 2.15 (m, 1H), 1.88 - 1.78 (m, 1H), 1.51 - 1.42 (m, 1H), 1.19 (s, 9H), 1.17 - 1.09 (m, 2H), 1.00 - 0.92 (m, 1H), 0.76 (t, $J = 7.6$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.3, 136.4, 135.4, 134.0, 132.0, 131.6, 131.1, 130.4, 129.7, 128.7, 128.3, 128.0, 126.8, 126.0, 125.4, 120.3, 119.7, 118.6, 110.7, 97.8, 94.8, 87.6, 61.1, 56.3, 43.5, 26.9, 22.6(9), 22.6(6), 13.9. HRMS (ESI) m/z: $[M+H]^+$ Calcd for $C_{36}H_{35}N_2OS$ 543.2470; Found 543.2469. $[\alpha]_D^{25} = 7.890$ (c = 1.09, CH_2Cl_2).

Methyl 4-((8-((S)-3-(((R)-tert-butylsulfinyl)amino)-3-phenylhept-1-yn-1-yl)naphthalen-1-yl)ethynyl)benzoate (7j)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 33.1 mg, 58 % yield; ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 6.4 Hz, 1H), 7.87 - 7.82 (m, 3H), 7.74 (d, *J* = 8.0 Hz, 2H), 7.69 - 7.65 (m, 2H), 7.48 (dd, *J* = 16.4, 8.0 Hz, 2H), 7.30 - 7.25 (m, 5H), 3.90 (s, 3H), 3.44 (s, 1H), 2.20 - 2.12 (m, 1H), 1.86 - 1.78 (m, 1H), 1.50 - 1.40 (m, 1H), 1.18 (s, 9H), 1.13 - 1.06 (m, 2H), 0.99 - 0.91 (m, 1H), 0.74 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.5, 142.3, 136.2, 135.4, 134.0, 131.4, 131.1(1), 130.1(5), 129.6, 129.2, 128.9, 128.6, 128.3, 127.9, 126.9, 125.9, 125.4, 120.4, 120.2, 98.0, 95.8, 93.4, 87.5, 61.2, 56.3, 52.1, 43.3, 26.9, 22.6, 22.5, 13.9. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₇H₃₈NO₃S 576.2572; Found 576.2571. [α]_D²⁵ = 8.855 (c = 1.66, CH₂Cl₂).

(R)-N-((S)-1-(8-((4-formylphenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7k)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 33.8 mg, 63% yield; ¹H NMR (400 MHz, CDCl₃) δ 9.91 (s, 1H), 8.06 (d, *J* = 7.2 Hz, 1H), 7.88 - 7.82 (m, 3H), 7.66 (d, *J* = 7.6 Hz, 2H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.52 - 7.43 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.28 (d, *J* = 7.2 Hz, 3H), 3.41 (s, 1H), 2.22 - 2.13 (m, 1H), 1.86 - 1.78 (m, 1H), 1.51 - 1.41 (m, 1H), 1.18 (s, 9H), 1.14 - 1.07 (m, 2H), 0.99 - 0.90 (m, 1H), 0.74 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 191.4, 142.3, 136.3, 135.4, 134.9, 134.0, 132.1, 131.1, 130.3, 130.2, 129.7, 129.2, 128.3, 127.9, 126.8, 125.9, 125.4, 120.3, 120.0, 97.9, 95.6, 94.5, 87.6, 61.2, 56.3, 43.4, 26.9, 22.6, 22.5, 13.9. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₆H₃₆NO₂S 546.2467; Found 546.2459. [α]_D²⁵ = 6.962 (c = 1.69, CH₂Cl₂).

(R)-2-methyl-N-((S)-1-(8-((4-nitrophenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)propane-2-sulfinamide (7l)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 25.7 mg, 46 % yield; ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 7.2 Hz, 1H), 7.90 - 7.83 (m, 5H), 7.68 - 7.61 (m, 2H), 7.50 (dd, *J* = 17.6, 8.0 Hz, 2H), 7.30 - 7.25 (m, 5H), 3.35 (s, 1H), 2.24 - 2.14 (m, 1H), 1.89 - 1.79 (m, 1H), 1.51 - 1.41 (m, 1H), 1.20 (s, 9H), 1.17 - 1.07 (m, 2H), 1.01 - 0.92 (m, 1H), 0.76 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 146.4, 142.2, 136.4, 135.5, 134.0, 132.2, 131.5, 131.1, 130.7, 130.5, 129.7, 128.4, 128.0, 126.8, 126.0, 125.4, 123.7, 123.1, 120.3, 119.6, 97.9, 95.7, 94.6, 87.6, 61.1, 56.4, 43.6, 26.9, 22.6, 13.9. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₅H₃₅N₂O₃S 563.2368; Found 563.2360. [α]_D²⁵ = 3.306 (*c* = 1.21, CH₂Cl₂).

(R)-2-methyl-N-((S)-3-phenyl-1-(8-(*m*-tolylethynyl)naphthalen-1-yl)hept-1-yn-3-yl)propane-2-sulfinamide (7m)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 18.1 mg, 34 % yield; ¹H NMR (400 MHz, CDCl₃) δ 8.05 - 8.01 (m, 1H), 7.85 - 7.81 (m, 3H), 7.73 - 7.69 (m, 2H), 7.49 - 7.42 (m, 2H), 7.31 - 7.25 (m, 3H), 7.10 - 7.04 (m, 2H), 7.03 - 6.97 (m, 2H), 3.53 (s, 1H), 2.19 - 2.15 (m, 1H), 2.14 (s, 3H), 2.12 (d, *J* = 4.0 Hz, 1H), 1.86 - 1.77 (m, 1H), 1.47 - 1.40 (m, 1H), 1.17 (s, 9H), 1.13 - 1.06 (m, 2H), 1.00 - 0.94 (m, 1H), 0.74 (t, *J* = 3.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 142.5, 137.6, 136.0, 135.2, 134.1, 132.0, 131.2, 129.5, 128.8, 128.7, 128.2, 128.0, 127.7, 127.0, 125.7, 125.4, 123.7, 120.9, 120.5, 98.0, 96.8, 89.8, 87.6, 61.3, 56.2, 43.3, 29.7, 26.9, 22.6, 22.5, 21.1, 13.9. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₆H₃₈NOS 532.2674; Found 532.2695. [α]_D²⁵ = 15.844 (*c* = 0.64, CH₂Cl₂).

(R)-N-((S)-1-(8-((3-fluorophenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7n)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 29.9 mg, 56 % yield; ^1H NMR (400 MHz, CDCl_3) δ 8.05 (d, J = 7.2 Hz, 1H), 7.83 (d, J = 7.6 Hz, 3H), 7.67 (d, J = 6.4 Hz, 2H), 7.50 - 7.42 (m, 2H), 7.33 - 7.26 (m, 3H), 7.06 - 6.99 (m, 2H), 6.94 - 6.82 (m, 2H), 3.48 (s, 1H), 2.22 - 2.14 (m, 1H), 1.89 - 1.80 (m, 1H), 1.52 - 1.41 (m, 1H), 1.20 (s, 9H), 1.15 - 1.09 (m, 2H), 1.01 - 0.92 (m, 1H), 0.76 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.3, 160.9, 142.3, 136.2, 135.4, 134.0, 131.2, 129.9, 129.6, 129.5, 128.2, 127.9, 127.5(3), 127.5(8), 126.8, 125.8, 125.7, 125.4, 120.4, 120.3, 118.4, 118.2, 115.2, 115.0, 98.0, 95.2(1), 95.2(6), 91.1, 87.5, 61.2, 56.3, 43.3, 26.9, 22.6, 22.5, 13.9. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{35}\text{H}_{35}\text{FNOS}$ 536.2423; Found 536.2415. $[\alpha]_{\text{D}}^{25}$ = 8.067 (c = 1.50, CH_2Cl_2).

(R)-N-((S)-1-(8-((3-chlorophenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7o)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 19.8 mg, 36 % yield; ^1H NMR (400 MHz, CDCl_3) δ 8.07 - 8.03 (m, 1H), 7.86 - 7.81 (m, 3H), 7.70 - 7.65 (m, 2H), 7.50 - 7.43 (m, 2H), 7.30 - 7.26 (m, 3H), 7.24 (s, 1H), 7.16 - 7.09 (m, 2H), 7.02 - 6.98 (m, 1H), 3.49 (s, 1H), 2.22 - 2.13 (m, 1H), 1.89 - 1.80 (m, 1H), 1.50 - 1.41 (m, 1H), 1.21 (s, 9H), 1.17 - 1.10 (m, 2H), 0.99 - 0.91 (m, 1H), 0.76 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.3, 136.2, 135.4, 134.0, 133.9, 131.3, 131.1, 129.9, 129.8, 129.6, 129.2, 128.3, 128.0, 127.9, 126.8, 125.8, 125.6, 125.4, 120.4, 120.3, 98.0, 95.0, 91.4, 87.6, 61.2, 56.3, 43.3, 29.7, 26.9, 22.6, 22.5, 13.9. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{35}\text{H}_{35}\text{ClINOS}$ 552.2128; Found 552.2129. $[\alpha]_{\text{D}}^{25}$ = 7.400 (c = 1.0, CH_2Cl_2).

(R)-2-methyl-N-((S)-3-phenyl-1-(8-((3-(trifluoromethyl)phenyl)ethynyl)naphthalen-1-yl)hept-1-yn-3-yl)propane-2-sulfinamide (7p)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 31.4 mg, 54 % yield; ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, *J* = 7.2 Hz, 1H), 7.87 - 7.83 (m, 3H), 7.68 (d, *J* = 7.6 Hz, 2H), 7.57 (s, 1H), 7.52 - 7.45 (m, 2H), 7.39 (dd, *J* = 13.6, 7.6 Hz, 2H), 7.29 - 7.23 (m, 3H), 7.18 (t, *J* = 8.0 Hz, 1H), 3.49 (s, 1H), 2.20 - 2.13 (m, 1H), 1.89 - 1.81 (m, 1H), 1.51 - 1.42 (m, 1H), 1.20 (s, 9H), 1.12 - 1.06 (m, 2H), 1.01 - 0.93 (m, 1H), 0.73 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 142.2, 136.3, 135.6, 134.8, 134.0, 131.1, 130.8, 130.5, 130.1, 129.6, 128.5, 128.4, 128.2, 128.1(1), 128.1(7), 127.9, 127.0, 126.8, 125.9, 125.4, 125.0, 124.9, 124.3, 120.4, 120.1, 98.0, 94.9, 91.8, 87.6, 61.2, 56.3, 43.3, 26.8, 22.7, 22.6, 22.5, 13.8. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₆H₃₅F₃NOS 586.2391; Found 586.2385. [α]_D²⁵ = 11.361 (c = 1.58, CH₂Cl₂).

methyl 3-((8-((S)-3-(((R)-tert-butylsulfinyl)amino)-3-phenylhept-1-yn-1-yl)naphthalen-1-yl)ethynyl)benzoate (7q)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), white solid, 34.4 mg, 60 % yield, mp 145.6-146.5 °C; ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 7.2 Hz, 1H), 7.99 (s, 1H), 7.87 - 7.81 (m, 4H), 7.65 (d, *J* = 7.6 Hz, 2H), 7.51 - 7.44 (m, 2H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.25 - 7.13 (m, 4H), 3.89 (s, 3H), 3.55 (s, 1H), 2.18 - 2.09 (m, 1H), 1.87 - 1.79 (m, 1H), 1.48 - 1.39 (m, 1H), 1.21 (s, 9H), 1.12 - 1.04 (m, 2H), 1.00 - 0.92 (m, 1H), 0.74 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.3, 142.2, 136.2, 135.7, 135.4, 134.0, 132.7, 131.1, 130.1, 129.9, 129.6, 128.8, 128.1(3), 128.1(1), 127.7, 126.8, 125.8, 125.4, 124.3, 120.4, 120.3, 98.0, 95.4, 91.1, 87.6, 61.3, 56.3, 52.1, 43.5, 26.8, 22.6, 22.5, 13.9. HRMS (ESI) *m/z*: [M+H]⁺ Calcd for C₃₇H₃₈NO₃S 576.2572; Found 576.2564. [α]_D²⁵ = 7.160 (c = 0.25, CH₂Cl₂).

(R)-N-((S)-1-(8-((3-formylphenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7r)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 32.7 mg, 60 % yield; ¹H NMR (400 MHz, CDCl₃) δ 9.70 (s, 1H), 8.05 (d, *J* = 7.2 Hz, 1H), 7.87 - 7.83 (m, 3H), 7.66 (d, *J* = 7.6 Hz, 3H), 7.62 (s, 1H), 7.52 - 7.45 (m, 3H), 7.26 - 7.21 (m, 4H), 3.45 (s, 1H), 2.21 - 2.13 (m, 1H), 1.85 - 1.78 (m, 1H), 1.50 - 1.39 (m, 1H), 1.19 (s, 9H), 1.13 - 1.06 (m, 2H), 1.00 - 0.92 (m, 1H), 0.73 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 191.6, 142.3, 137.2, 136.3, 136.1, 135.4, 134.0, 133.6, 131.2, 130.1, 129.7, 128.7, 128.3, 127.9, 127.6, 126.9, 125.9, 125.4, 125.0, 120.4, 120.2, 97.8, 94.9, 91.7, 87.8, 61.2, 56.3, 43.6, 26.9, 22.6, 22.5, 13.9. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₆H₃₅NNaO₂S 568.2286; Found 568.2293. [α]_D²⁵ = 10.508 (c = 1.64, CH₂Cl₂).

(R)-N-((S)-1-(8-((3-aminophenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7s)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 22.3 mg, 42 % yield; ¹H NMR (400 MHz, CDCl₃) δ 7.98 (dd, *J* = 7.2, 1.2 Hz, 1H), 7.84 - 7.79 (m, 3H), 7.77 - 7.73 (m, 2H), 7.48 - 7.43 (m, 2H), 7.35 - 7.26 (m, 3H), 6.92 - 6.88 (m, 1H), 6.71 (d, *J* = 7.6 Hz, 1H), 6.49 - 6.41 (m, 2H), 3.66 (s, 1H), 2.27 - 2.19 (m, 1H), 1.91 - 1.84 (m, 1H), 1.54 - 1.45 (m, 1H), 1.29 - 1.25 (m, 1H), 1.17 (s, 9H), 1.12 - 1.00 (m, 2H), 0.77 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 146.1, 142.8, 136.0, 135.2, 134.1, 132.1, 131.2, 129.6, 129.4, 129.0, 128.6, 128.4, 128.2, 127.6, 127.2, 125.6, 125.5, 124.5, 121.9, 121.0, 120.5, 117.8, 114.9, 97.8, 97.1, 89.5, 87.8, 61.5, 56.3, 43.6, 27.0, 22.6, 22.6, 13.9. HRMS (ESI) *m/z*: [M+Na]⁺ Calcd for C₃₅H₃₆N₂NaOS 555.2446; Found 555.2462. [α]_D²⁵ = 2.523 (c = 1.07, CH₂Cl₂).

(R)-2-methyl-N-((S)-1-(8-((3-nitrophenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)propane-2-sulfinamide (7t)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 30.3 mg, 54 % yield; ¹H NMR (400 MHz, CDCl₃) δ 8.06 (d, *J* = 7.2 Hz, 1H), 7.99 (s, 1H), 7.95 (d, *J* = 8.4 Hz, 1H), 7.89 - 7.83 (m, 3H),

7.62 (d, $J = 7.6$ Hz, 2H), 7.56 - 7.45 (m, 3H), 7.26 - 7.23 (m, 1H), 7.21 - 7.13 (m, 3H), 3.51 (s, 1H), 2.23 - 2.15 (m, 1H), 1.90 - 1.81 (m, 1H), 1.51 - 1.40 (m, 1H), 1.23 (s, 9H), 1.17 - 1.11 (m, 2H), 1.03 - 0.93 (m, 1H), 0.76 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.7, 142.0, 137.3, 136.5, 135.5, 134.0, 131.1, 130.4, 129.7, 128.8, 128.1, 127.9, 126.6, 126.2, 126.0, 125.7, 125.4, 122.3, 120.3, 119.7, 97.9, 93.9, 92.7, 87.7, 61.2, 56.4, 43.8, 26.9, 22.6, 22.6, 13.9. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{35}\text{H}_{35}\text{N}_2\text{O}_3\text{S}$ 563.2368; Found 563.2360. $[\alpha]_{\text{D}}^{25} = 8.688$ ($c = 1.55$, CH_2Cl_2).

(R)-N-((S)-1-(8-((3-hydroxyphenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7u)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 25.6 mg, 48 % yield; ^1H NMR (400 MHz, CDCl_3) δ 8.14 (s, 1H), 7.89 - 7.79 (m, 4H), 7.64 (d, $J = 7.6$ Hz, 2H), 7.48 - 7.44 (m, 2H), 7.16 (t, $J = 7.6$ Hz, 2H), 7.07 - 7.02 (m, 1H), 6.96 - 6.91 (m, 2H), 6.76 (d, $J = 7.6$ Hz, 1H), 6.63 (dd, $J = 8.0, 2.0$ Hz, 1H), 3.97 (s, 1H), 2.19 - 2.11 (m, 1H), 2.00 - 1.93 (m, 1H), 1.58 - 1.47 (m, 1H), 1.29 (s, 9H), 1.22 - 1.15 (m, 3H), 0.79 (t, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.4, 142.2, 136.4, 134.8, 134.2, 131.5, 129.9, 129.3, 129.0, 128.2, 128.0, 127.5, 126.5, 125.7, 125.5, 124.2, 121.9, 121.0, 120.4, 119.0, 116.0, 97.7, 97.2, 89.3, 88.2, 62.8, 57.0, 45.8, 27.2, 22.7, 22.5, 13.9. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{35}\text{H}_{36}\text{NO}_2\text{S}$ 534.2467; Found 534.2463. $[\alpha]_{\text{D}}^{25} = 9.520$ ($c = 1.28$, CH_2Cl_2).

(R)-2-methyl-N-((S)-3-phenyl-1-(8-(o-tolyethynyl)naphthalen-1-yl)hept-1-yn-3-yl)propane-2-sulfinamide (7v)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 25.0 mg, 48 % yield; ^1H NMR (400 MHz, CDCl_3) δ 8.07 - 8.03 (m, 1H), 7.85 - 7.81 (m, 3H), 7.69 - 7.65 (m, 2H), 7.50 - 7.42 (m, 2H), 7.30 - 7.26 (m, 3H), 7.10 (d, $J = 6.8$ Hz, 3H), 6.89 - 6.83 (m, 1H), 3.54 (s, 1H), 2.46 (s, 3H), 2.14 - 2.06 (m, 1H), 1.86 - 1.78 (m, 1H), 1.43 - 1.36 (m, 1H), 1.19 (s, 9H), 1.09 - 0.98 (m, 1H), 0.74 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100

MHz, CDCl₃) δ 142.6, 140.4, 136.1, 135.1, 134.1, 131.6, 131.1, 129.5(7), 129.5(1), 129.3, 128.1, 127.9, 127.7, 126.9, 125.8, 125.4, 125.3, 123.7, 121.1, 120.6, 98.3, 95.7, 94.2, 87.6, 61.2, 56.3, 43.1, 26.7, 22.6, 22.5, 21.0, 13.9. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₆H₃₈NOS 532.2674; Found 532.2668. $[\alpha]_D^{25} = 12.700$ (c = 1.28, CH₂Cl₂).

(R)-N-((S)-1-(8-((2-chlorophenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7w)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 29.2 mg, 53 % yield; ¹H NMR (400 MHz, CDCl₃) δ 8.09 - 8.04 (m, 1H), 7.94 - 7.89 (m, 1H), 7.87 - 7.81 (m, 2H), 7.69 (d, *J* = 7.6 Hz, 2H), 7.51 - 7.46 (m, 2H), 7.31 - 7.26 (m, 3H), 7.24 - 7.20 (m, 1H), 7.18 - 7.15 (m, 1H), 7.12 - 7.07 (m, 1H), 6.93 - 6.88 (m, 1H), 3.65 (s, 1H), 2.17 - 2.08 (m, 1H), 1.93 - 1.85 (m, 1H), 1.48 - 1.40 (m, 1H), 1.22 (s, 9H), 1.12 - 1.06 (m, 2H), 0.92 - 0.82 (m, 1H), 0.74 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 142.4, 136.2, 136.1, 135.8, 134.0, 133.1, 131.0, 129.9, 129.5, 129.1, 128.8, 128.2, 127.7, 126.9, 126.1, 125.8, 125.4, 123.9, 120.5, 120.4, 98.2, 95.4, 93.5, 87.6, 61.4, 56.3, 43.3, 29.7, 26.8, 22.7, 22.5, 13.9. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₅H₃₅ClNOS 552.2128; Found 552.2132. $[\alpha]_D^{25} = 5.445$ (c = 1.64, CHCl₃).

(R)-2-methyl-N-((S)-3-phenyl-1-(8-((2-(trifluoromethyl)phenyl)ethynyl)naphthalen-1-yl)hept-1-yn-3-yl)propane-2-sulfinamide (7x)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 35.2 mg, 68 % yield; ¹H NMR (400 MHz, CDCl₃) δ 8.08 (d, *J* = 7.2 Hz, 1H), 7.89 (d, *J* = 7.2 Hz, 1H), 7.87 - 7.82 (m, 2H), 7.72 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.0 Hz, 1H), 7.51 - 7.45 (m, 2H), 7.28 - 7.20 (m, 5H), 7.12 - 7.07 (m, 1H), 3.68 (s, 1H), 2.20 - 2.11 (m, 1H), 1.98 - 1.89 (m, 1H), 1.51 - 1.40 (m, 1H), 1.22 (s, 9H), 1.13 - 1.03 (m, 3H), 0.71 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 142.4, 136.4, 135.6, 134.0, 133.5, 131.3, 131.1, 130.9, 130.1, 129.6, 128.2, 127.8, 127.5, 127.0, 125.8, 125.6(4), 125.6(1), 125.5, 122.1, 120.4, 120.3, 98.1, 95.9, 92.7, 87.7, 61.6, 56.3, 43.4,

26.8, 22.6, 22.5, 13.7. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₆H₃₅F₃NOS 586.2391; Found 586.2388. [α]_D²⁵ = 9.234 (c = 1.11, CH₂Cl₂).

(R)-N-((S)-1-(8-((2-aminophenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7y)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 36.2 mg, 68 % yield; ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 7.2 Hz, 1H), 7.85 - 7.81 (m, 3H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.50 - 7.43 (m, 2H), 7.26 - 7.17 (m, 3H), 6.99 - 6.93 (m, 2H), 6.51 (d, *J* = 8.4 Hz, 1H), 6.47 - 6.42 (m, 1H), 4.27 (s, 2H), 3.97 (s, 1H), 2.25 - 2.17 (m, 1H), 1.87 - 1.83 (m, 1H), 1.45 - 1.36 (m, 1H), 1.22 (s, 9H), 1.14 - 1.04 (m, 2H), 1.03 - 0.95 (m, 1H), 0.77 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.8, 142.5, 136.1, 135.2, 134.1, 131.8, 131.2, 129.6, 129.2, 128.0, 127.6, 126.8, 125.7, 125.5, 120.8, 120.5, 117.7, 114.4, 109.1, 98.8, 94.9, 93.6, 87.4, 61.1, 56.3, 43.2, 26.8, 22.7, 22.5, 14.0. HRMS (ESI) m/z: [M+H]⁺ Calcd for C₃₅H₃₅N₂O₃S 563.2368; Found 563.2368. [α]_D²⁵ = 12.210 (c = 1.81, CH₂Cl₂).

(R)-2-methyl-N-((S)-1-(8-((2-nitrophenyl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)propane-2-sulfinamide (7z)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 42.1 mg, 75 % yield; ¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 7.2 Hz, 1H), 7.85 - 7.81 (m, 3H), 7.64 (d, *J* = 7.6 Hz, 2H), 7.50 - 7.43 (m, 2H), 7.26 - 7.17 (m, 3H), 6.99 - 6.93 (m, 2H), 6.51 (d, *J* = 8.4 Hz, 1H), 6.47 - 6.42 (m, 1H), 4.27 (s, 2H), 3.97 (s, 1H), 2.25 - 2.17 (m, 1H), 1.87 - 1.83 (m, 1H), 1.45 - 1.36 (m, 1H), 1.22 (s, 9H), 1.14 - 1.04 (m, 2H), 1.03 - 0.95 (m, 1H), 0.77 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 147.8, 142.5, 136.1, 135.2, 134.1, 131.8, 131.2, 129.6, 129.2, 128.0, 127.6, 126.8, 125.7, 125.5, 120.8, 120.5, 117.7, 114.4, 109.1, 98.8, 94.9, 93.6, 87.4, 61.1, 56.3,

43.2, 26.8, 22.7, 22.5, 14.0. HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{35}H_{35}N_2O_3S$ 563.2368; Found 563.2368. $[\alpha]_D^{25} = 1.110$ ($c = 2.11$, CH_2Cl_2).

(R)-2-methyl-N-((S)-1-(8-(naphthalen-1-ylethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)propane-2-sulfinamide (7aa)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 26.7 mg, 47 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.46 (d, $J = 8.4$ Hz, 1H), 8.08 (d, $J = 7.2$ Hz, 1H), 7.96 (d, $J = 7.2$ Hz, 1H), 7.88 - 7.84 (m, 2H), 7.78 (d, $J = 7.6$ Hz, 1H), 7.69 (d, $J = 8.4$ Hz, 1H), 7.60 - 7.55 (m, 2H), 7.53 - 7.46 (m, 4H), 7.40 (d, $J = 7.2$ Hz, 1H), 7.18 - 7.14 (m, 1H), 7.11 - 7.06 (m, 3H), 3.52 (s, 1H), 2.00 - 1.92 (m, 1H), 1.73 - 1.67 (m, 1H), 1.33 - 1.27 (m, 1H), 1.10 (s, 9H), 0.91 - 0.84 (m, 1H), 0.83 - 0.75 (m, 2H), 0.57 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.4, 136.2, 135.3, 134.1, 133.4, 133.2, 131.2, 130.1, 129.7, 129.5, 128.4, 128.1, 128.0, 127.5, 126.7, 126.7, 126.3, 125.8, 125.5, 125.0, 121.6, 120.9, 120.7, 98.5, 95.0, 94.9, 87.5, 61.2, 56.2, 43.0, 26.6, 22.5, 22.2, 13.7. HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{39}H_{38}NOS$ 568.2674; Found 568.2664. $[\alpha]_D^{25} = 16.321$ ($c = 1.06$, CH_2Cl_2).

(R)-N-((S)-1-(8-(anthracen-9-ylethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7ab)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 40.0 mg, 65 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.72 (d, $J = 8.4$ Hz, 2H), 8.32 (s, 1H), 8.13 (dd, $J = 7.2, 1.2$ Hz, 1H), 8.04 (dd, $J = 7.2, 1.2$ Hz, 1H), 7.95 (d, $J = 8.4$ Hz, 2H), 7.91 - 7.87 (m, 2H), 7.54 - 7.44 (m, 6H), 7.30 - 7.27 (m, 2H), 6.79 - 6.75 (m, 1H), 6.73 - 6.69 (m, 2H), 3.47 (s, 1H), 1.60 - 1.46 (m, 2H), 1.37 - 1.21 (m, 2H), 1.15 (s, 9H), 0.94 - 0.88 (m, 1H), 0.80 - 0.72 (m, 1H), 0.39 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.0, 136.5, 135.2, 134.2, 132.5, 131.2, 131.1, 129.8, 129.5, 128.5, 127.5, 127.4, 126.9, 126.6, 126.1, 126.0, 125.6, 125.5, 121.0, 120.9, 118.4, 101.1,

99.5, 93.9, 87.2, 61.0, 56.3, 42.7, 26.0, 22.7, 21.9, 13.6. HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{43}H_{40}NOS$ 618.2831; Found 618.2821. $[\alpha]_D^{25} = 10.380$ ($c = 1.97$, CH_2Cl_2).

(R)-2-methyl-N-((S)-3-phenyl-1-(8-(thiophen-2-ylethynyl)naphthalen-1-yl)hept-1-yn-3-yl)propane-2-sulfinamide (7ac)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 26.2 mg, 51 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, $J = 6.8$ Hz, 1H), 7.87 - 7.80 (m, 3H), 7.74 (d, $J = 7.2$ Hz, 2H), 7.50 - 7.43 (m, 2H), 7.34 - 7.27 (m, 3H), 7.12 (d, $J = 4.8$ Hz, 1H), 6.78 (d, $J = 6.8$ Hz, 2H), 3.65 (s, 1H), 2.25 - 2.17 (m, 1H), 1.96 - 1.88 (m, 1H), 1.51 - 1.43 (m, 1H), 1.21 (s, 9H), 1.17 - 1.10 (m, 2H), 1.04 (d, $J = 11.6$ Hz, 1H), 0.77 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.5, 136.0, 135.7, 134.0, 131.7, 131.2, 129.9, 129.5, 128.4, 128.2, 127.8, 127.1, 126.9, 126.8, 125.8, 125.4, 124.2, 120.5, 120.4, 98.3, 93.8, 89.8, 87.3, 61.4, 56.3, 43.3, 26.9, 22.7, 22.6, 13.9. HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{33}H_{34}NOS_2$ 524.2082; Found 524.2076. $[\alpha]_D^{25} = 7.608$ ($c = 1.31$, CH_2Cl_2).

(R)-2-methyl-N-((S)-3-phenyl-1-(8-(thiophen-3-ylethynyl)naphthalen-1-yl)hept-1-yn-3-yl)propane-2-sulfinamide (7ad)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 29.2 mg, 56 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, $J = 7.2$ Hz, 1H), 7.82 (d, $J = 8.8$ Hz, 3H), 7.73 (d, $J = 6.8$ Hz, 2H), 7.49 - 7.41 (m, 2H), 7.35 - 7.28 (m, 3H), 7.08 - 7.03 (m, 1H), 7.01 - 6.95 (m, 1H), 6.88 (d, $J = 4.8$ Hz, 1H), 3.51 (s, 1H), 2.26 - 2.17 (m, 1H), 1.91 - 1.81 (m, 1H), 1.52 - 1.42 (m, 1H), 1.20 (s, 9H), 1.18 - 1.11 (m, 2H), 1.02 - 0.94 (m, 1H), 0.77 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 136.0, 135.4, 134.1, 131.3, 130.0, 129.6, 129.5, 128.3, 128.2, 127.8, 127.1, 125.7, 125.4, 124.8, 123.1, 120.7, 120.5, 97.9, 91.8, 89.5, 87.5, 61.2, 56.3, 43.3, 26.9,

22.7, 22.6, 13.9. HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{33}H_{34}NOS_2$ 524.2082; Found 524.2075. $[\alpha]_D^{25} = 9.542$ ($c = 1.31$, CH_2Cl_2).

(R)-N-((S)-1-(8-(((R)-cyclohex-2-en-1-yl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)-2-methylpropane-2-sulfinamide (7ae)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 27.1 mg, 52 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, $J = 7.2$ Hz, 1H), 7.82 - 7.72 (m, 5H), 7.46 - 7.42 (m, 1H), 7.40 - 7.33 (m, 3H), 7.30 (d, $J = 7.2$ Hz, 1H), 5.87 (s, 1H), 3.74 (s, 1H), 2.40 - 2.32 (m, 1H), 2.12 - 2.06 (m, 1H), 2.05 - 1.96 (m, 2H), 1.92 - 1.84 (m, 2H), 1.62 - 1.54 (m, 1H), 1.46 - 1.39 (m, 4H), 1.34 - 1.28 (m, 2H), 1.27 (s, 9H), 1.22 - 1.16 (m, 1H), 0.86 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.6, 135.9, 135.1, 134.6, 134.1, 131.1, 129.5, 129.0, 128.3, 127.8, 127.1, 125.6, 125.4, 121.5, 121.4, 120.5, 98.7, 97.7, 87.7, 87.6, 61.6, 56.3, 43.5, 28.9, 27.0, 25.6, 22.8, 22.7, 22.2, 21.3, 14.0. HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{35}H_{40}NOS$ 522.2831; Found 522.2822. $[\alpha]_D^{25} = 10.236$ ($c = 1.31$, CH_2Cl_2).

(R)-2-methyl-N-((S)-3-phenyl-1-(8-(pyridin-2-ylethynyl)naphthalen-1-yl)hept-1-yn-3-yl)propane-2-sulfinamide (7af)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 24.3 mg, 47 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.34 (dd, $J = 4.8, 0.8$ Hz, 1H), 7.95 - 7.90 (m, 2H), 7.87 - 7.81 (m, 2H), 7.76 - 7.71 (m, 2H), 7.49 - 7.43 (m, 3H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.25 - 7.20 (m, 2H), 7.16 - 7.11 (m, 1H), 7.08 - 7.03 (m, 1H), 5.99 (s, 1H), 2.37 - 2.29 (m, 1H), 2.02 - 1.94 (m, 1H), 1.53 - 1.42 (m, 1H), 1.26 (s, 9H), 1.19 - 1.11 (m, 2H), 1.03 - 0.94 (m, 1H), 0.75 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.2, 143.7, 142.0, 136.1, 135.8, 135.7, 134.0, 131.3, 130.4, 129.5, 127.8, 127.53, 127.5(8), 127.4, 125.7, 125.4, 122.3, 120.7, 119.9, 98.9, 95.0,

90.6, 86.5, 61.6, 56.3, 42.9, 27.0, 23.0, 22.6, 13.9. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{34}H_{34}N_2NaOS$ 541.2290; Found 541.2296. $[\alpha]_D^{25} = 3.154$ ($c = 1.3$, CH_2Cl_2).

(1S,2R,5S)-2-isopropyl-5-methylcyclohexyl 4-((8-((S)-3-(((R)-tert-butylsulfinyl)amino)-3-phenylhept-1-yn-1-yl)naphthalen-1-yl)ethynyl)benzoate (7ag)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 29.4 mg, 42 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, $J = 7.2$ Hz, 1H), 7.84 (d, $J = 6.4$ Hz, 3H), 7.72 (d, $J = 8.0$ Hz, 2H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.51 - 7.43 (m, 2H), 7.28 - 7.23 (m, 5H), 4.95 - 4.87 (m, 1H), 3.42 (s, 1H), 2.20 - 2.10 (m, 2H), 1.97 - 1.89 (m, 1H), 1.86 - 1.78 (m, 1H), 1.74 (d, $J = 11.6$ Hz, 2H), 1.59 - 1.52 (m, 2H), 1.47 - 1.39 (m, 1H), 1.18 (s, 9H), 1.15 - 1.05 (m, 4H), 1.00 (d, $J = 15.2$ Hz, 1H), 0.94 (d, $J = 6.8$ Hz, 6H), 0.91 - 0.85 (m, 1H), 0.82 (d, $J = 6.8$ Hz, 3H), 0.74 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 142.3, 136.2, 135.2, 134.0, 131.4, 131.2, 130.0, 129.6, 129.1, 128.3, 128.2, 127.9, 126.8, 125.8, 125.4, 120.4, 120.3, 98.0, 95.8, 93.1, 87.5, 75.0, 61.1, 56.3, 47.3, 43.3, 41.0, 34.3, 31.5, 29.7, 26.8, 26.7, 23.8, 22.6, 22.5, 22.0, 20.7, 16.7, 13.9. HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{46}H_{54}NO_3S$ 700.3824; Found 700.3831. $[\alpha]_D^{25} = 9.588$ ($c = 2.1$, CH_2Cl_2).

(1S,2S,5R)-2-isopropyl-5-methylcyclohexyl 4-((8-((3S)-3-((tert-butylsulfinyl)amino)-3-phenylhept-1-yn-1-yl)naphthalen-1-yl)ethynyl)benzoate (7ah)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 39.2 mg, 56 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, $J = 7.2$ Hz, 1H), 7.86 - 7.81 (m, 3H), 7.73 (d, $J = 8.0$ Hz, 2H), 7.66 (d, $J = 7.2$ Hz, 2H), 7.51 - 7.43 (m, 2H), 7.29 - 7.23 (m, 5H), 4.94 - 4.87 (m, 1H), 3.40 (s, 1H), 2.21 - 2.10 (m, 2H), 1.97 - 1.89 (m, 1H), 1.87 - 1.78 (m, 1H), 1.77 - 1.71 (m, 3H), 1.61 - 1.52 (m, 2H), 1.48 - 1.38 (m, 1H), 1.17 (s, 9H), 1.15 - 1.05 (m, 4H), 0.99 (d, $J = 10.0$ Hz, 1H), 0.94 (d, $J = 6.8$ Hz, 6H), 0.81 (d, $J = 7.2$ Hz, 3H), 0.73 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 142.4, 136.2, 135.3, 134.0, 131.4, 131.2, 130.0, 129.6, 129.2, 128.4,

128.2, 127.9, 126.8, 125.8, 125.4, 120.4, 120.3, 98.1, 95.8, 93.1, 87.5, 75.0, 61.1, 56.3, 47.3, 43.3, 41.0, 34.3, 31.5, 26.8, 26.7, 23.8, 22.6, 22.5, 22.0, 20.7, 16.7, 13.9. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{46}H_{53}NNaO_3$ 722.3644; Found 722.3658. $[\alpha]_D^{25} = 3.057$ ($c = 1.96$, CH_2Cl_2).

(R)-2-methyl-N-((S)-3-phenyl-1-(8-((4-(((S)-2,5,7,8-tetramethyl-2-((4S,8S)-4,8,12-trimethyltridecyl)chroman-6-yl)oxy)methyl)phenyl)ethynyl)naphthalen-1-yl)hept-1-yn-3-yl)propane-2-sulfinamide (7ai)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 35.4 mg, 37 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, $J = 7.2$ Hz, 1H), 7.88 - 7.82 (m, 3H), 7.71 (d, $J = 7.6$ Hz, 2H), 7.51 - 7.45 (m, 2H), 7.32 - 7.25 (m, 5H), 7.22 (d, $J = 8.0$ Hz, 2H), 4.63 (s, 2H), 3.52 (s, 1H), 2.64 - 2.59 (m, 2H), 2.21 (s, 3H), 2.16 (s, 3H), 2.13 (s, 3H), 1.90 - 1.78 (m, 3H), 1.60 - 1.53 (m, 3H), 1.52 - 1.45 (m, 2H), 1.44 - 1.38 (m, 3H), 1.36 - 1.30 (m, 4H), 1.29 - 1.22 (m, 9H), 1.20 (s, 9H), 1.17 - 1.07 (m, 8H), 0.88 (t, $J = 6.8$ Hz, 12H), 0.77 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.2, 148.0, 142.5, 137.9, 136.1, 135.2, 134.1, 131.6, 131.3, 129.6, 129.5, 128.2, 127.8, 127.8, 127.1, 127.0, 125.8, 125.7, 125.4, 123.2, 123.0, 120.8, 120.6, 117.7, 98.1, 96.6, 90.2, 87.6, 74.9, 74.2, 61.2, 56.3, 43.3, 40.1, 39.4, 37.5, 37.4, 37.3, 32.8, 32.7, 31.4, 28.0, 26.8, 24.8, 24.5, 23.9, 22.7, 22.6, 22.6, 21.1, 20.7, 19.8, 19.7, 13.9, 12.9, 12.0, 11.8. HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{65}H_{86}NO_3S$ 960.6328; Found 960.6335. $[\alpha]_D^{25} = 7.679$ ($c = 1.12$, CH_2Cl_2).

(3S,8R,9S,10S,13S,17S)-17-acetyl-10,13-dimethylhexadecahydro-1H-cyclopenta[a]phenanthren-3-yl 4-((8-((S)-3-(((R)-tert-butylsulfinyl)amino)-3-phenylhept-1-yn-1-yl)naphthalen-1-yl)ethynyl)benzoate (7aj)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 28.4 mg, 33 % yield; ^1H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, $J = 6.8$ Hz, 1H), 7.91 - 7.78 (m, 3H), 7.74 (d, $J = 8.4$ Hz, 2H), 7.69 - 7.62 (m, 2H), 7.51 - 7.43 (m, 2H), 7.28 (d, $J = 7.2$ Hz, 3H), 7.24 (s, 1H), 5.43 (d, $J = 4.0$ Hz, 1H), 4.89 - 4.80 (m, 1H), 3.43 (s, 1H), 2.59 - 2.51 (m, 1H), 2.46 (d, $J = 8.0$ Hz, 2H), 2.13 (s, 3H), 2.10 - 1.93 (m, 4H), 1.83 - 1.64 (m, 5H),

1.61 (s, 6H), 1.59 - 1.40 (m, 5H), 1.30 - 1.21 (m, 6H), 1.19 (s, 9H), 1.15 - 1.09 (m, 2H), 1.08 (s, 3H), 0.90 - 0.82 (m, 1H), 0.73 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 209.5, 165.4, 142.3, 139.6, 136.2, 135.3, 134.0, 131.4, 131.1, 130.0, 129.6, 129.5, 129.2, 128.4, 128.3, 127.9, 126.9, 125.9, 125.4, 122.5, 120.4, 120.2, 98.0, 95.9, 93.2, 87.5, 74.6, 63.7, 61.2, 56.9, 56.3, 49.9, 44.0, 43.3, 38.8, 38.2, 37.1, 36.7, 31.8, 31.5, 27.9, 26.8, 24.5, 22.9, 22.6, 22.5, 21.1, 19.4, 13.9, 13.2. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{57}\text{H}_{68}\text{NO}_4\text{S}$ 862.4869; Found 862.4793. $[\alpha]_{\text{D}}^{25} = 7.596$ ($c = 1.04$, CH_2Cl_2).

(R)-2-methyl-N-((S)-1-(8-(((8R,9S,13S,14S)-13-methyl-17-oxo-7,8,9,11,12,13,14,15,16,17-decahydro-6H-cyclopenta[a]phenanthren-3-yl)ethynyl)naphthalen-1-yl)-3-phenylhept-1-yn-3-yl)propane-2-sulfinamide (7ak)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 29.8 mg, 43 % yield; ^1H NMR (400 MHz, CDCl_3) δ 8.03 - 7.99 (m, 1H), 7.84 - 7.79 (m, 3H), 7.71 (d, $J = 6.8$ Hz, 2H), 7.48 - 7.41 (m, 2H), 7.31 - 7.26 (m, 3H), 7.06 - 7.01 (m, 2H), 6.98 (s, 1H), 3.55 (s, 1H), 2.71 - 2.60 (m, 2H), 2.55 - 2.48 (m, 1H), 2.34 (d, $J = 8.8$ Hz, 1H), 2.22 - 2.10 (m, 3H), 1.97 (d, $J = 2.8$ Hz, 1H), 1.87 - 1.80 (m, 1H), 1.64 - 1.58 (m, 7H), 1.50 - 1.45 (m, 3H), 1.17 (s, 9H), 1.12 - 1.06 (m, 2H), 0.92 (s, 3H), 0.74 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.5, 139.8, 136.2, 136.0, 135.2, 134.1, 131.9, 131.2, 129.5, 129.4, 129.1, 128.1, 127.6, 127.1, 125.7, 125.4, 125.1, 121.3, 121.0, 120.5, 97.9, 96.8, 89.5, 87.7, 61.3, 56.2, 50.5, 47.9, 44.4, 43.3, 38.1, 35.8, 31.6, 29.0, 26.9, 26.3, 25.6, 22.6, 22.5, 21.6, 13.9, 13.8. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{47}\text{H}_{52}\text{NO}_2\text{S}$ 694.3719; Found 694.3711. $[\alpha]_{\text{D}}^{25} = 9.704$ ($c = 1.18$, CH_2Cl_2).

(R)-2-methyl-N-((S)-4-methyl-3-phenyl-1-(8-(phenylethynyl)naphthalen-1-yl)pent-1-yn-3-yl)propane-2-sulfinamide (7ba)

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 24.6 mg, 49 % yield; ^1H NMR (400 MHz, CDCl_3) δ 8.20 - 8.16 (m, 1H), 7.88 - 7.85 (m, 1H), 7.84 - 7.80 (m, 2H), 7.73 - 7.70 (m, 2H),

7.50 - 7.42 (m, 2H), 7.36 - 7.33 (m, 2H), 7.26 - 7.20 (m, 3H), 7.19 - 7.11 (m, 3H), 3.74 (s, 1H), 2.16 - 2.08 (m, 1H), 1.15 (s, 9H), 1.01 (d, $J = 6.8$ Hz, 3H), 0.74 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.0, 136.6, 135.5, 134.1, 131.7, 131.0, 129.6, 129.4, 128.3, 128.0, 127.8, 127.6, 127.4, 125.9, 125.3, 124.2, 120.8, 120.6, 97.17, 96.8, 90.3, 89.0, 65.9, 56.5, 40.1, 22.8, 18.2, 18.1. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{34}\text{H}_{34}\text{NOS}$ 504.2361; Found 504.2359. $[\alpha]_{\text{D}}^{25} = 9.578$ ($c = 0.98$, CH_2Cl_2).

***(R)*-2-methyl-*N*-((*S*)-5-methyl-3-phenyl-1-(8-(phenylethynyl)naphthalen-1-yl)hex-1-yn-3-yl)propane-2-sulfonamide (7bb)**

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 24.3 mg, 47 % yield; ^1H NMR (400 MHz, CDCl_3) δ 8.03 - 7.99 (m, 1H), 7.86 - 7.81 (m, 3H), 7.75 - 7.71 (m, 2H), 7.49 - 7.42 (m, 2H), 7.31 - 7.25 (m, 3H), 7.23 - 7.19 (m, 2H), 7.17 - 7.13 (m, 1H), 7.10 - 7.05 (m, 2H), 3.45 (s, 1H), 2.19 - 2.12 (m, 1H), 1.80 - 1.74 (m, 1H), 1.68 - 1.61 (m, 1H), 1.17 (s, 9H), 0.90 (d, $J = 6.8$ Hz, 3H), 0.49 (d, $J = 6.4$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.5, 135.8, 135.3, 134.1, 131.6, 131.3, 129.6, 129.5, 128.2, 128.1, 127.8, 127.7, 127.1, 125.7, 125.4, 123.9, 120.8, 120.6, 98.1, 96.5, 90.3, 87.6, 61.0, 56.2, 52.1, 24.6, 24.1, 24.0, 22.6. HRMS (ESI) m/z : $[\text{M}+\text{H}]^+$ Calcd for $\text{C}_{35}\text{H}_{36}\text{NOS}$ 518.2518; Found 518.2519. $[\alpha]_{\text{D}}^{25} = 5.422$ ($c = 1.21$, CH_2Cl_2).

***(S)*-2-methyl-*N*-((*R*)-4-methyl-3-phenyl-1-(8-(*p*-tolylethynyl)naphthalen-1-yl)pent-1-yn-3-yl)propane-2-sulfonamide (7bc)**

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), white solid, 28.9 mg, 55 % yield, mp 141.4-142.2 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, $J = 7.2$ Hz, 1H), 7.87 - 7.79 (m, 3H), 7.75 - 7.69 (m, 2H), 7.50 - 7.41 (m, 2H), 7.26 - 7.21 (m, 5H), 6.94 (d, $J = 8.0$ Hz, 2H), 3.73 (s, 1H), 2.28 (s, 3H), 2.17 - 2.10 (m, 1H), 1.15 (s, 9H), 1.01 (d, $J = 6.8$ Hz, 3H), 0.75 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 141.0, 137.9, 136.5, 135.5, 134.1, 131.6, 131.0, 129.5, 129.4, 128.7, 128.4, 127.6, 127.4, 125.9, 125.3, 121.1, 121.0, 120.6, 97.2, 97.1,

89.6, 89.0, 65.9, 56.5, 40.0, 22.8, 21.4, 18.2, 18.1. HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{35}H_{36}NOS$ 518.2518; Found 518.2525. $[\alpha]_D^{25} = 9.238$ ($c = 1.44$, CH_2Cl_2).

***(R)*-2-methyl-N-((R)-4-methyl-3-phenyl-1-(8-(p-tolylethynyl)naphthalen-1-yl)pent-1-yn-3-yl)propane-2-sulfinamide (7bc')**

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), white solid, 30.5 mg, 59 % yield
mp 139.8-140.7 °C; ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, $J = 7.2$ Hz, 1H), 7.83 (dd, $J = 15.6, 7.6$ Hz, 3H), 7.72 (d, $J = 6.8$ Hz, 2H), 7.50 – 7.41 (m, 2H), 7.22 (d, $J = 6.8$ Hz, 4H), 6.94 (d, $J = 7.8$ Hz, 2H), 3.74 (s, 1H), 2.28 (s, 3H), 1.15 (s, 9H), 1.00 (d, $J = 6.8$ Hz, 3H), 0.75 (d, $J = 6.8$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.0, 137.9, 136.5, 135.5, 134.1, 131.6, 131.0, 129.5, 129.4, 128.7, 128.4, 127.6, 127.4, 125.9, 125.3, 121.1, 121.0, 120.6, 97.2, 97.1, 89.6, 89.0, 65.9, 56.5, 40.0, 22.8, 21.4, 18.2, 18.1. HRMS (ESI) m/z : $[M+H]^+$ Calcd for $C_{35}H_{36}NOS$ 518.2518; Found 518.2528. $[\alpha]_D^{25} = -10.233$ ($c = 1.62$, CH_2Cl_2).

***(S)*-2-methyl-N-(3-phenyl-1-(8-(p-tolylethynyl)naphthalen-1-yl)hept-1-yn-3-yl)propane-2-sulfonamide (8a)**

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), colorless oil, 44.2 mg, 81 % yield;
 ^1H NMR (400 MHz, $CDCl_3$) δ 7.98 (dd, $J = 7.2, 1.2$ Hz, 1H), 7.86 – 7.81 (m, 3H), 7.71 (d, $J = 6.8$ Hz, 2H), 7.50 – 7.43 (m, 2H), 7.34 – 7.27 (m, 3H), 7.16 (d, $J = 8.0$ Hz, 2H), 6.93 (d, $J = 7.6$ Hz, 2H), 4.04 (s, 1H), 2.29 (s, 3H), 2.28 – 2.21 (m, 1H), 1.87 – 1.77 (m, 1H), 1.39 (s, 9H), 1.18 – 1.07 (m, 2H), 1.01 – 0.92 (m, 1H), 0.76 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) 142.4, 138.1, 136.0, 135.0, 134.1, 131.5, 131.4, 129.7, 129.5, 129.0, 128.0, 127.6, 126.9, 125.7, 125.5, 120.9, 120.7, 120.5, 96.9, 96.7, 89.5, 87.4, 62.3, 60.3, 42.5, 27.0, 24.4, 22.4, 21.4, 13.9. HRMS (ESI) m/z : $[M+Na]^+$ Calcd for $C_{36}H_{37}NNaO_2S$ 570.2443; Found 570.2435. $[\alpha]_D^{25} = 10.238$ ($c = 2.12$, CH_2Cl_2).

***(S)*-3-phenyl-1-(8-(*p*-tolylethynyl)naphthalen-1-yl)hept-1-yn-3-amine (8b)**

Isolation by column chromatography (petroleum ether/ ethyl acetate= 5/1 v/v), white solid, 38.7 mg, 56 % yield, mp 88.7-89.9 °C; ¹H NMR (400 MHz, CDCl₃) δ 7.89 – 7.82 (m, 4H), 7.76 – 7.71 (m, 2H), 7.51 – 7.45 (m, 2H), 7.38 – 7.33 (m, 2H), 7.32 – 7.28 (m, 1H), 7.24 (d, J = 8.0 Hz, 2H), 7.03 (d, J = 7.6 Hz, 2H), 2.35 (s, 3H), 1.83 – 1.75 (m, 2H), 1.47 – 1.38 (m, 1H), 1.32 – 1.21 (m, 3H), 0.87 (t, J = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) 145.2, 138.3, 135.1, 134.8, 134.2, 131.7, 131.1, 129.5, 129.3, 129.2, 127.9, 127.0, 126.3, 125.5, 125.5, 121.2, 120.9, 120.7, 102.2, 96.6, 89.4, 84.3, 56.4, 45.8, 27.2, 22.8, 21.5, 14.0. HRMS (ESI) m/z: [M+Na]⁺ Calcd for C₃₂H₂₉NNa 450.2198; Found 450.2180. [α]_D²⁵ = 10.444 (c = 1.84, CH₂Cl₂).

2 NMR spectra of Precursors **A3**, **A4**, **B3**, **C5** and **D5**

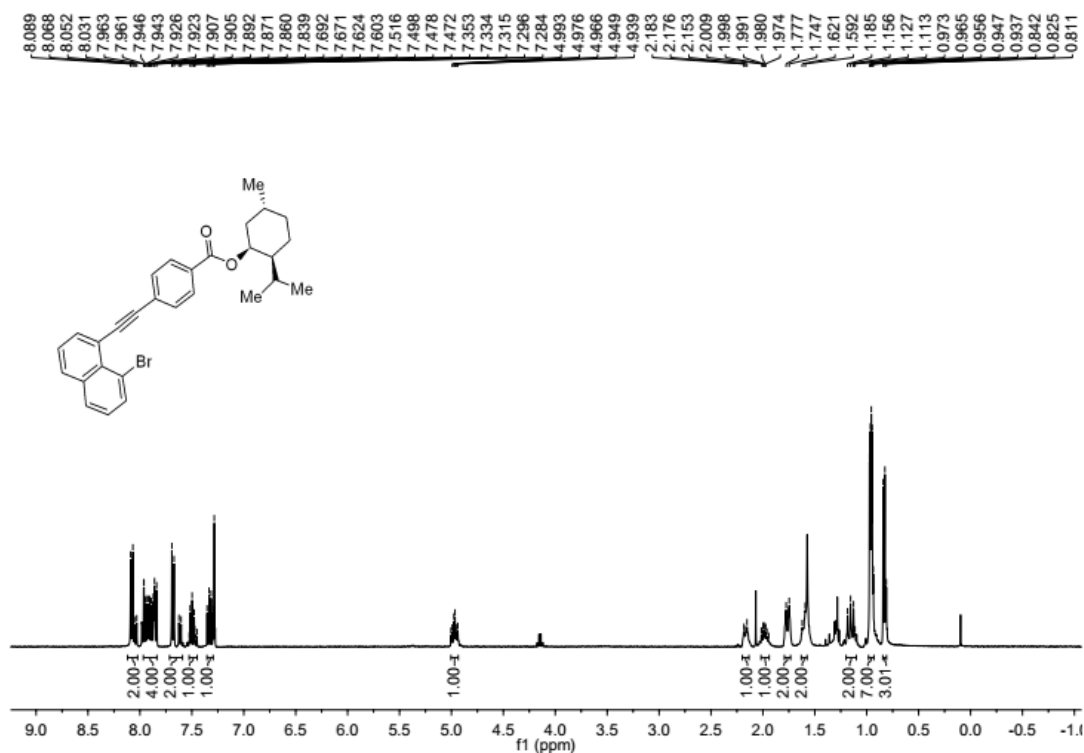


Figure S1. ¹H NMR Spectrum of Precursor A3 (CDCl₃, 400 MHz)

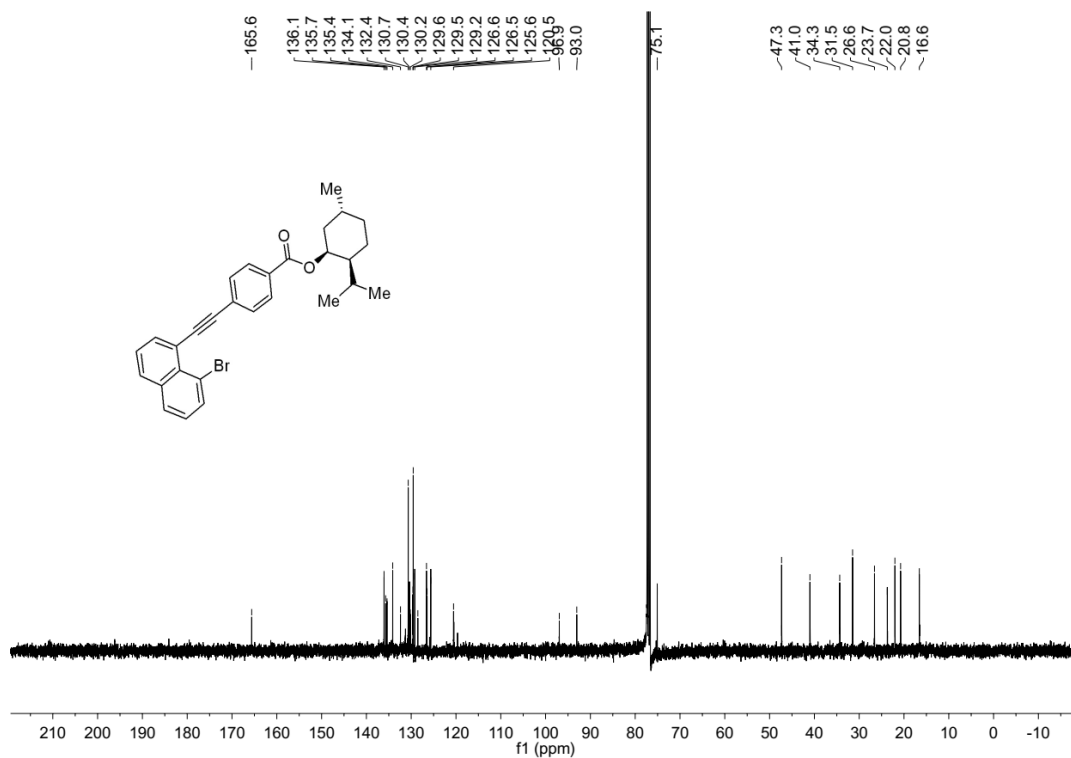


Figure S2. ^{13}C NMR Spectrum of Precursor A3 (CDCl_3 , 100 MHz)

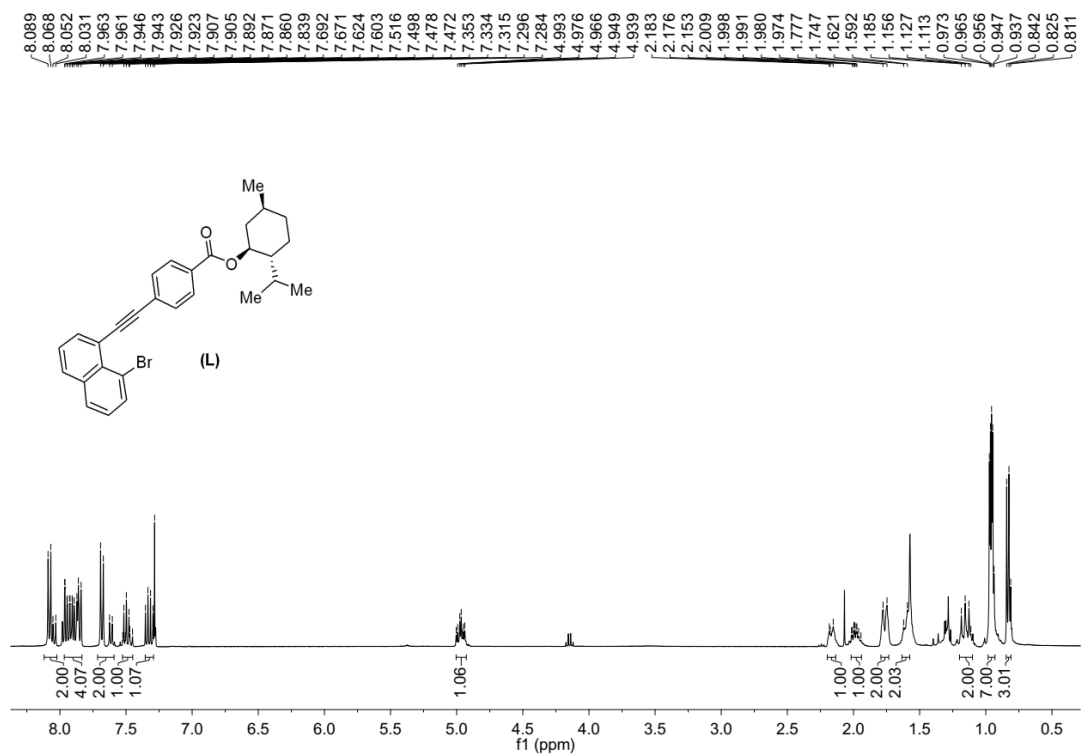


Figure S3. ¹H NMR Spectrum of Precursor A4 (CDCl₃, 400 MHz)

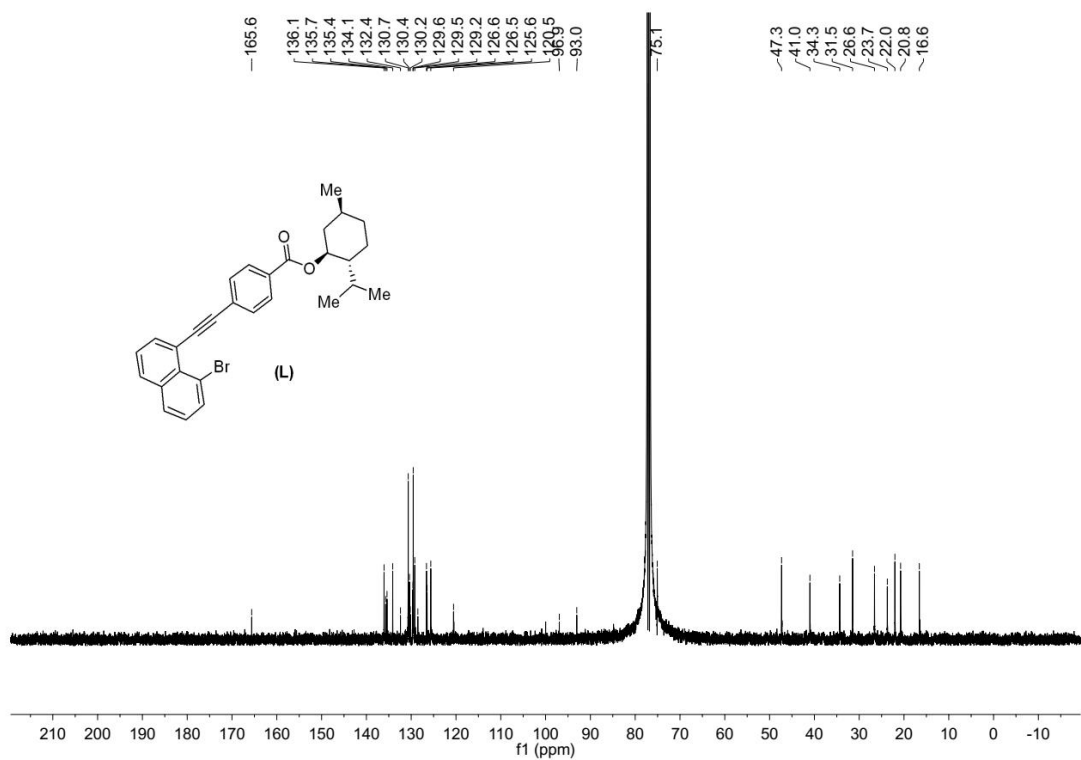


Figure S4. ¹³C NMR Spectrum of Precursor A4 (CDCl₃, 100 MHz)

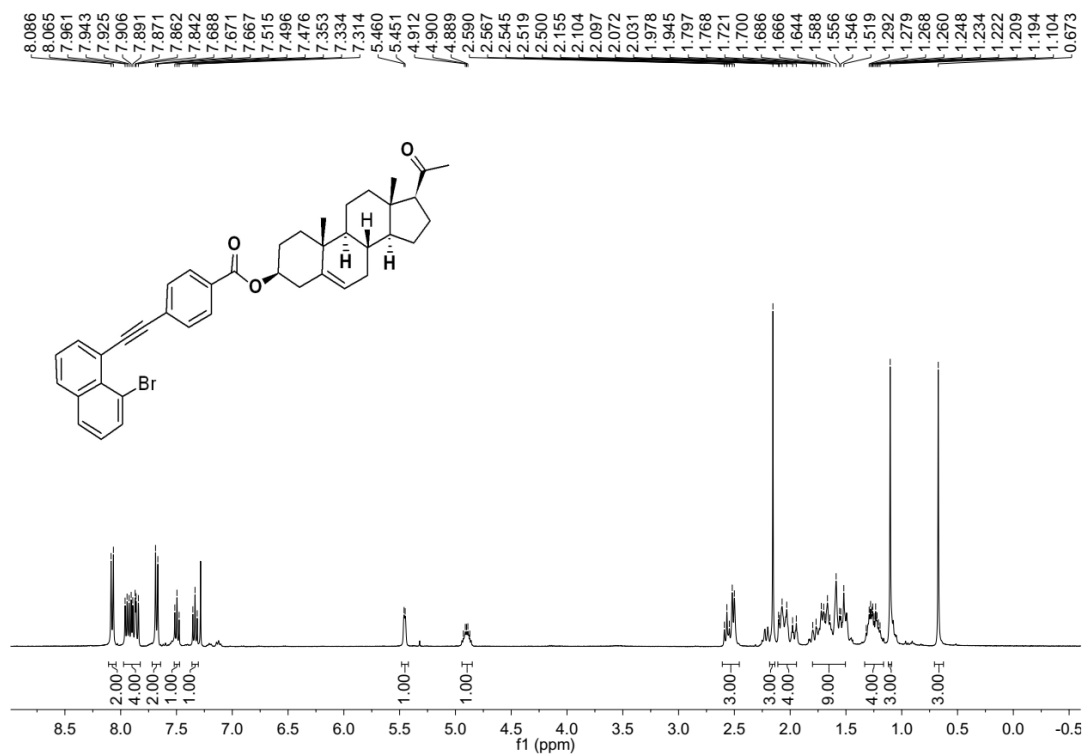


Figure S5. ¹H NMR Spectrum of Precursor B3 (CDCl₃, 400 MHz)

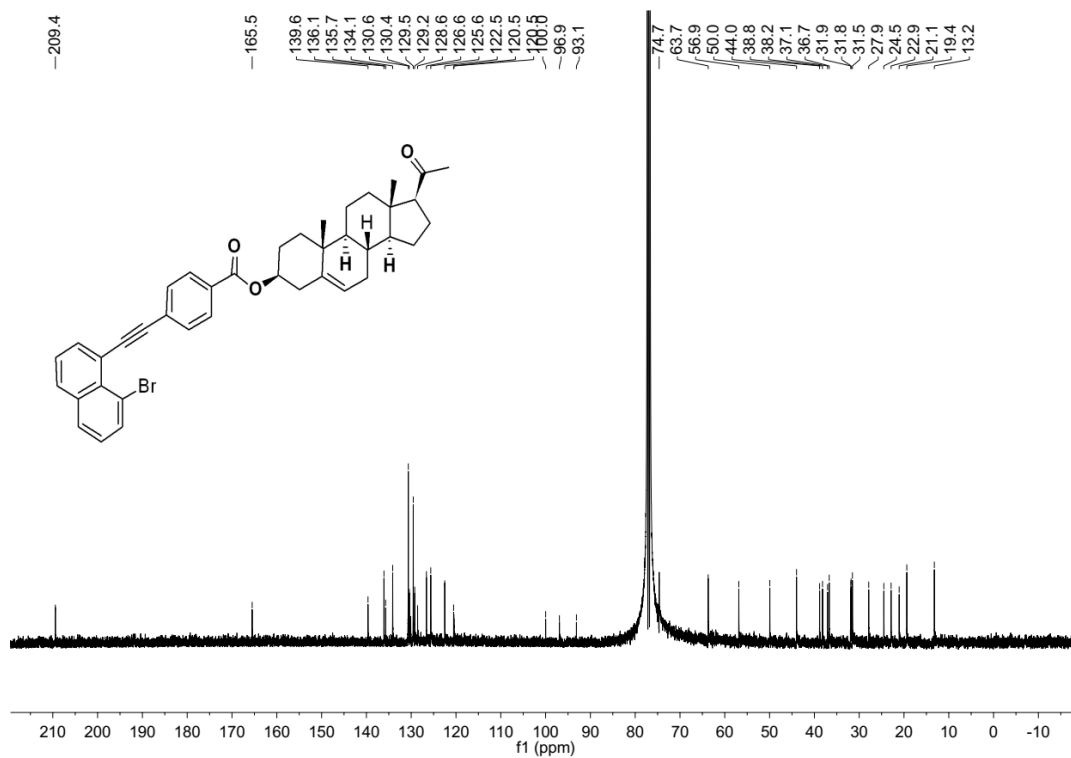


Figure S6. ¹³C NMR Spectrum of Precursor B3 (CDCl₃, 100 MHz)

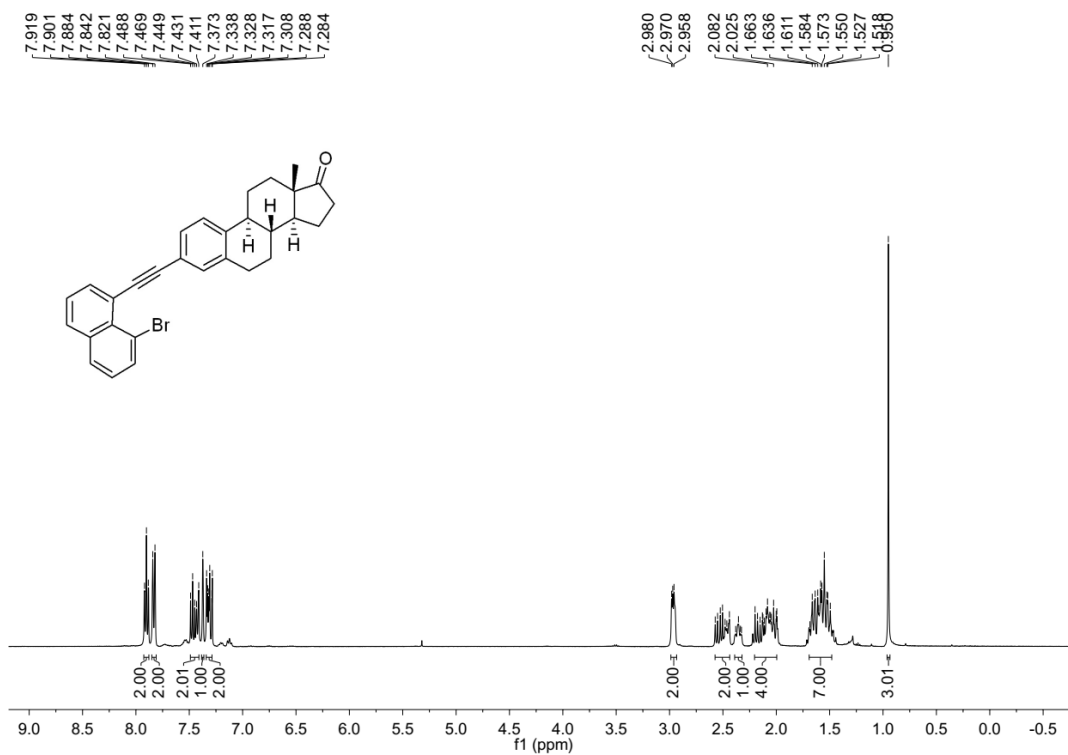


Figure S7. ¹H NMR Spectrum of Precursor C5 (CDCl₃, 400 MHz)

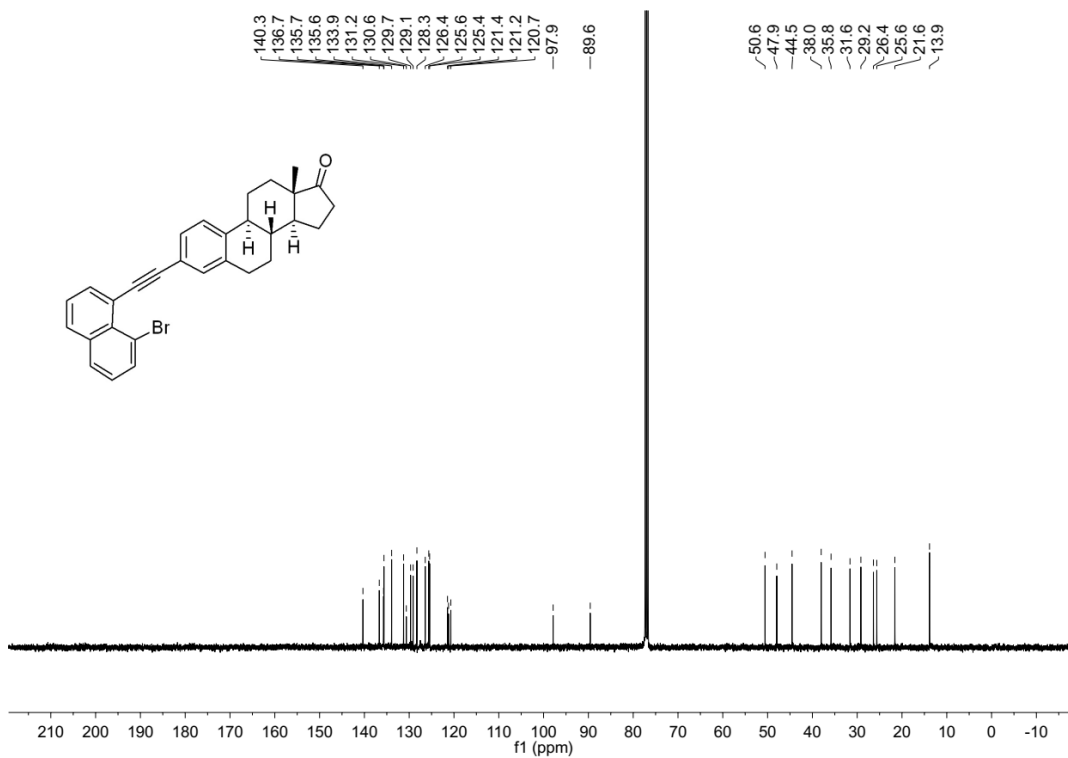


Figure S8. ¹³C NMR Spectrum of Precursor C5 (CDCl₃, 100 MHz)

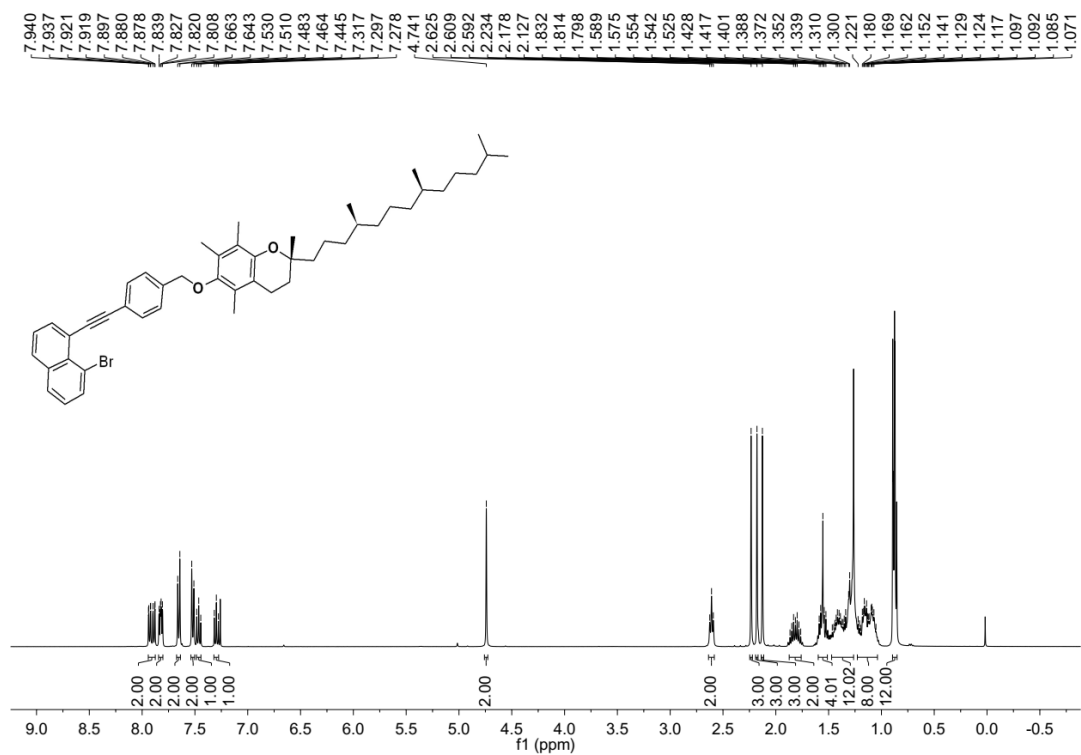


Figure S9. ¹H NMR Spectrum of Precursor D5 (CDCl₃, 400 MHz)

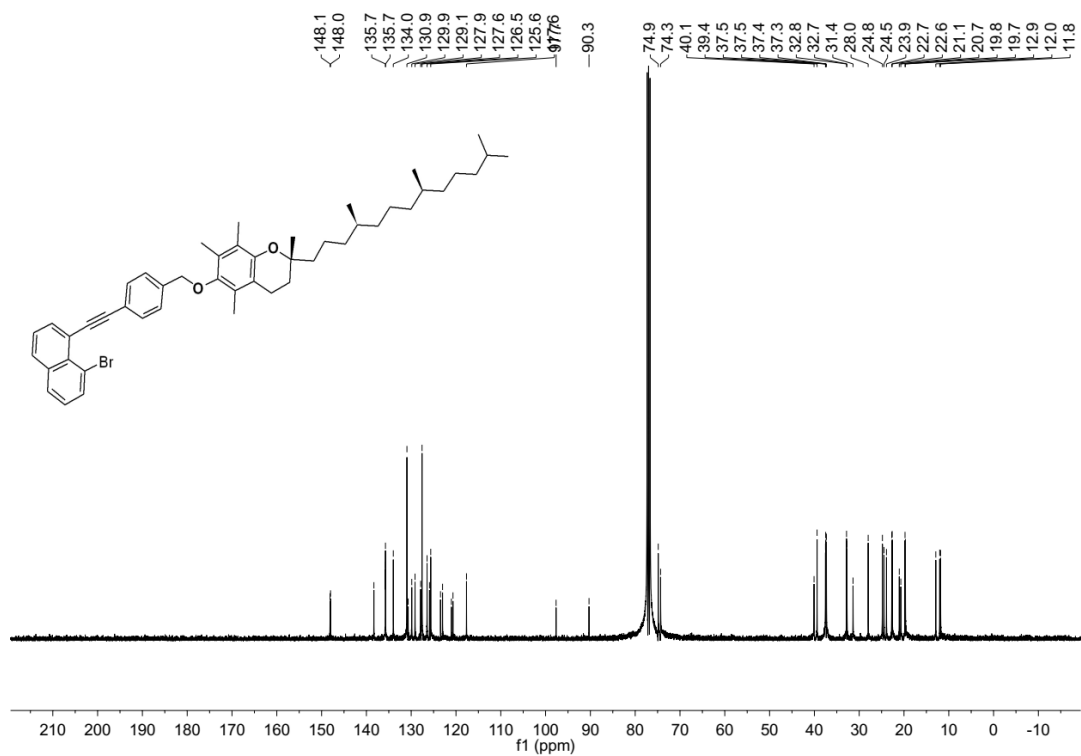


Figure S10. ¹³C NMR Spectrum of Precursor D5 (CDCl₃, 100 MHz)

3 NMR spectra of Compounds 7a-8b

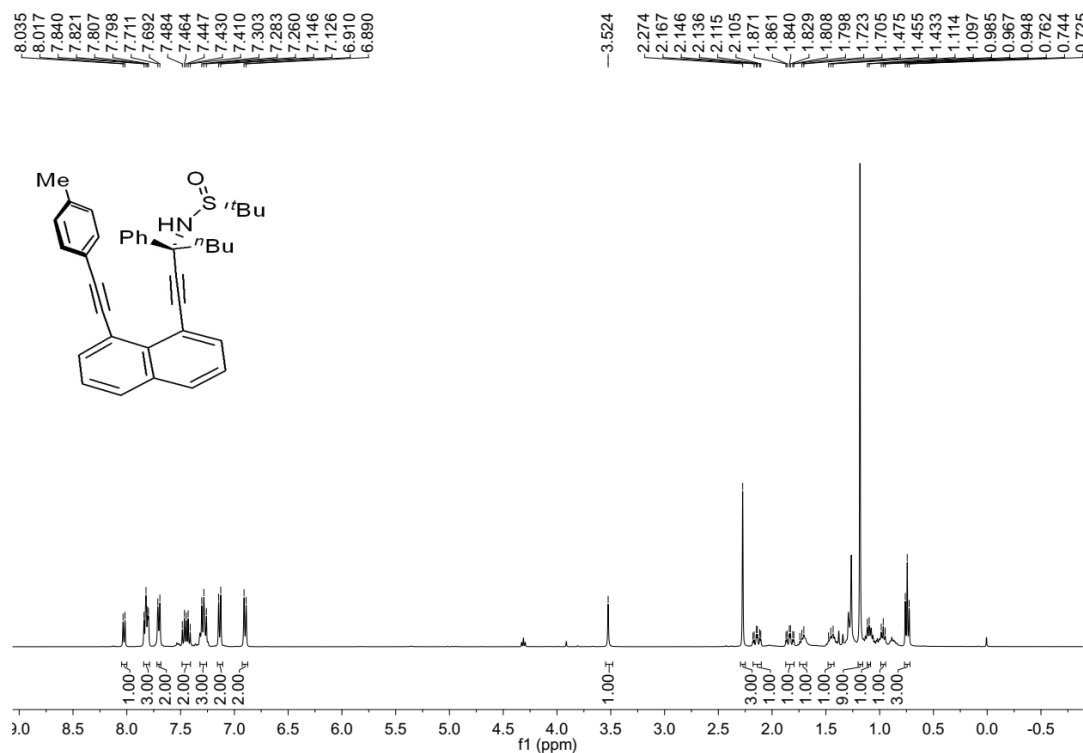


Figure S11. ¹H NMR Spectrum of Compound 7a (CDCl₃, 400 MHz)

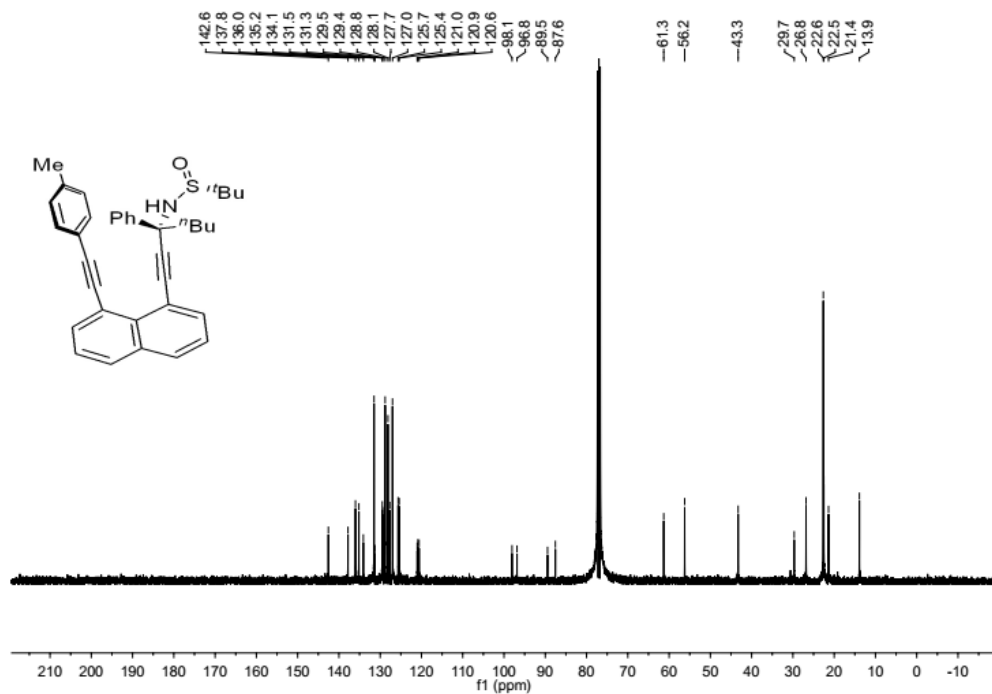


Figure S12. ¹³C NMR Spectrum of Compound 7a (CDCl₃, 100 MHz)

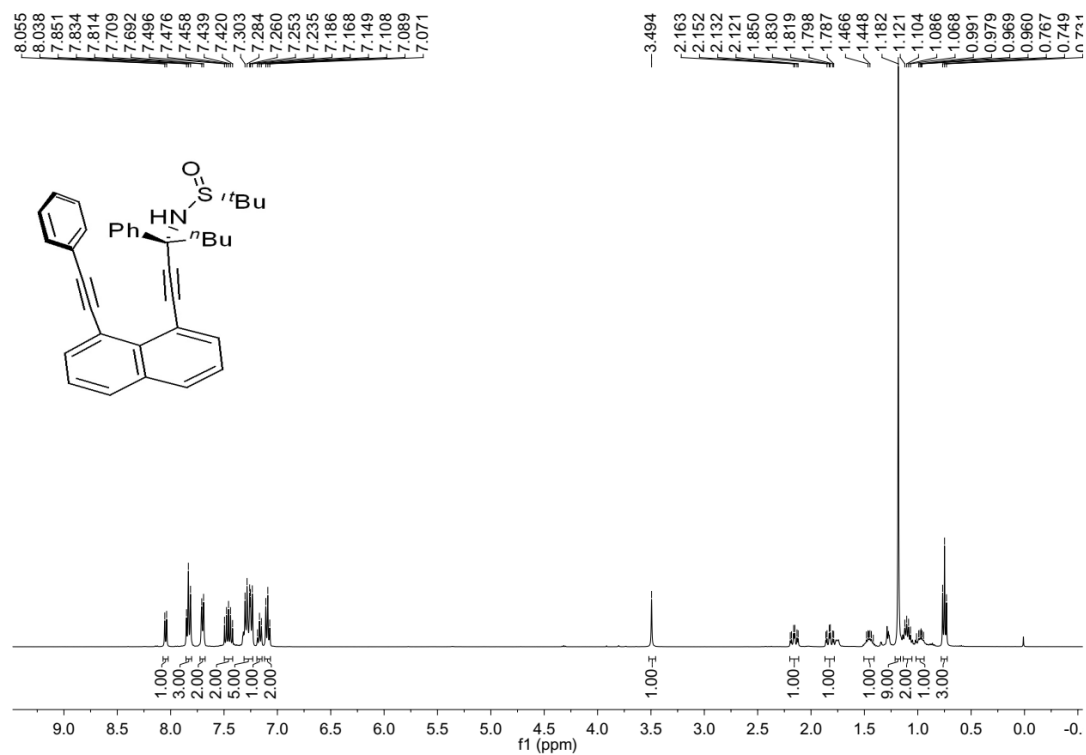


Figure S13. ¹H NMR Spectrum of Compound 7b (CDCl₃, 400 MHz)

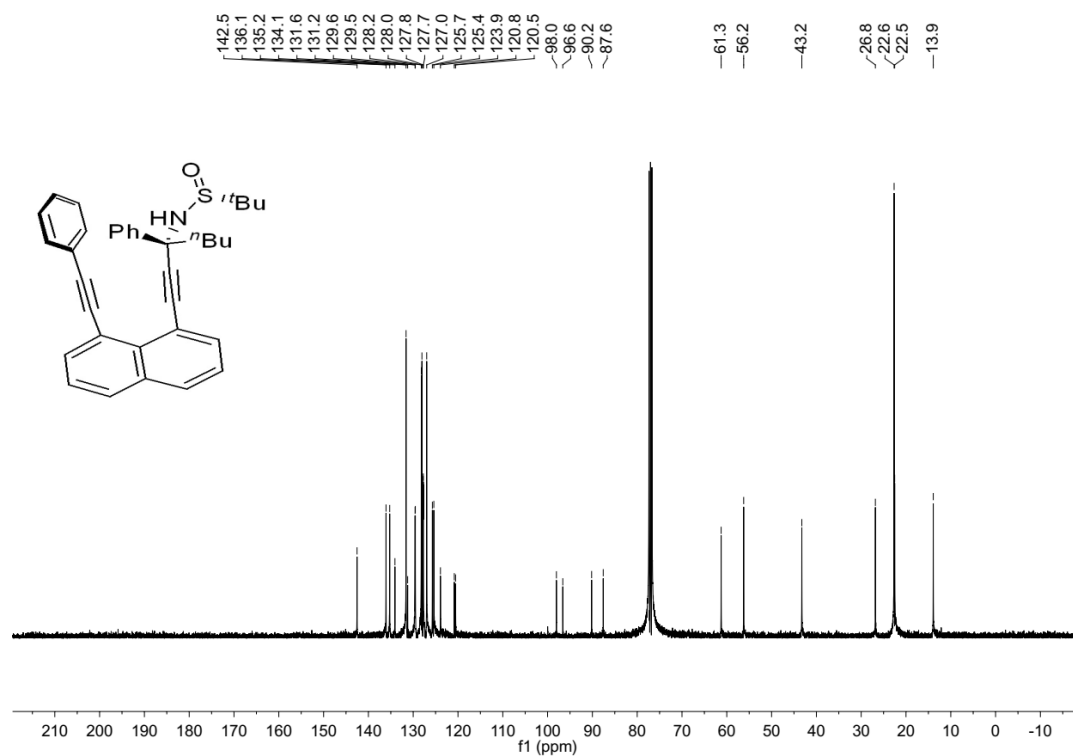


Figure S14. ¹³C NMR Spectrum of Compound 7b (CDCl₃, 100 MHz)

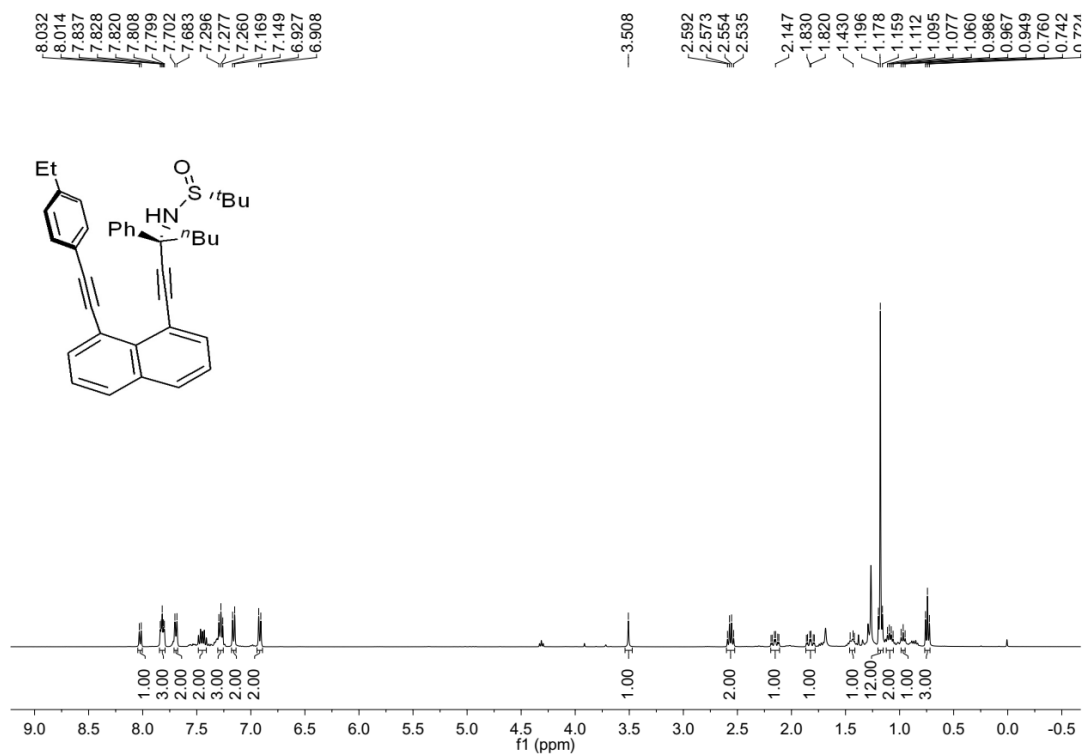


Figure S15. ¹H NMR Spectrum of Compound 7c (CDCl₃, 400 MHz)

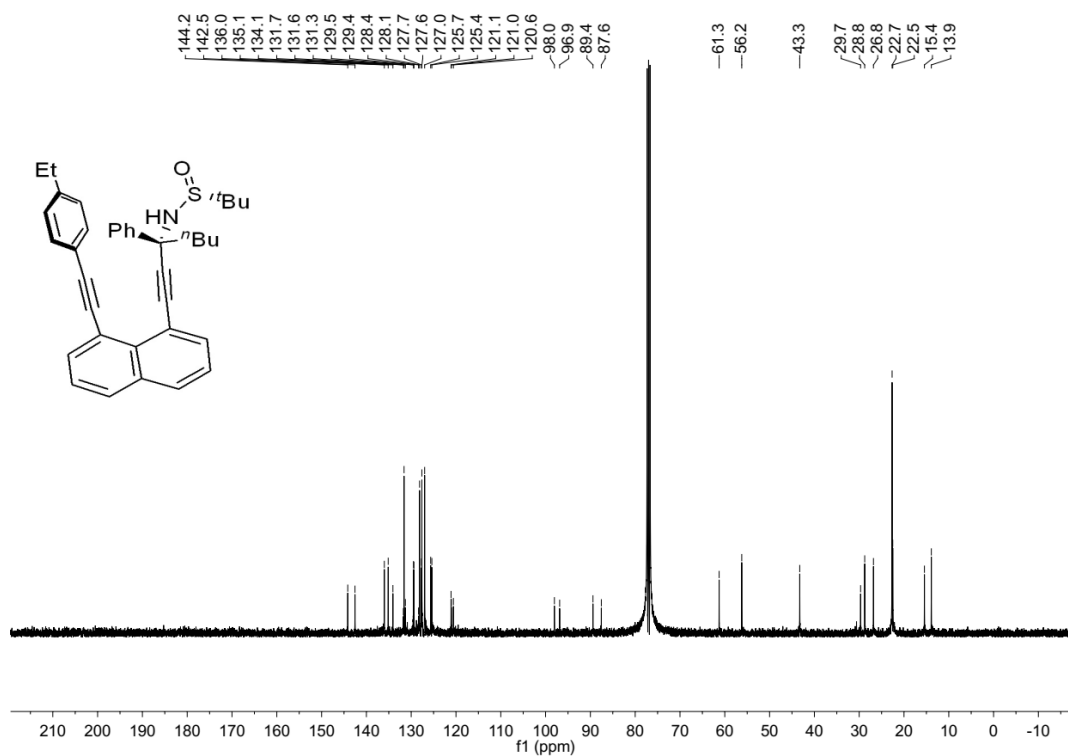


Figure S16. ¹³C NMR Spectrum of Compound 7c (CDCl₃, 100 MHz)

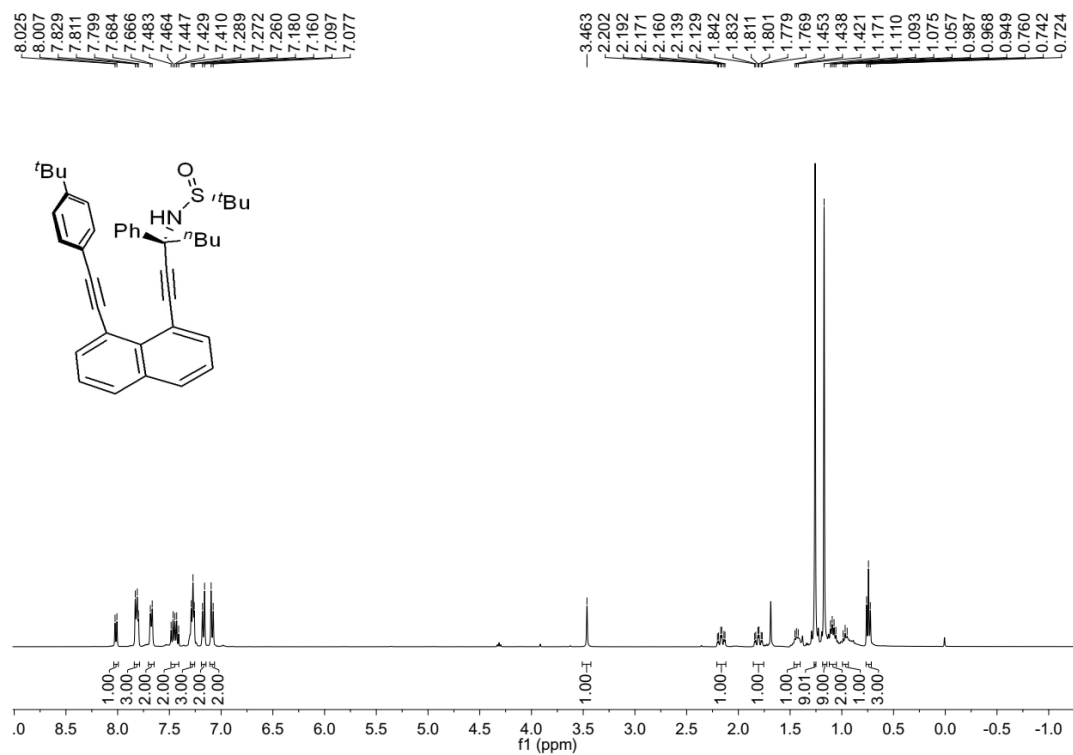


Figure S17. ¹H NMR Spectrum of Compound 7d (CDCl₃, 400 MHz)

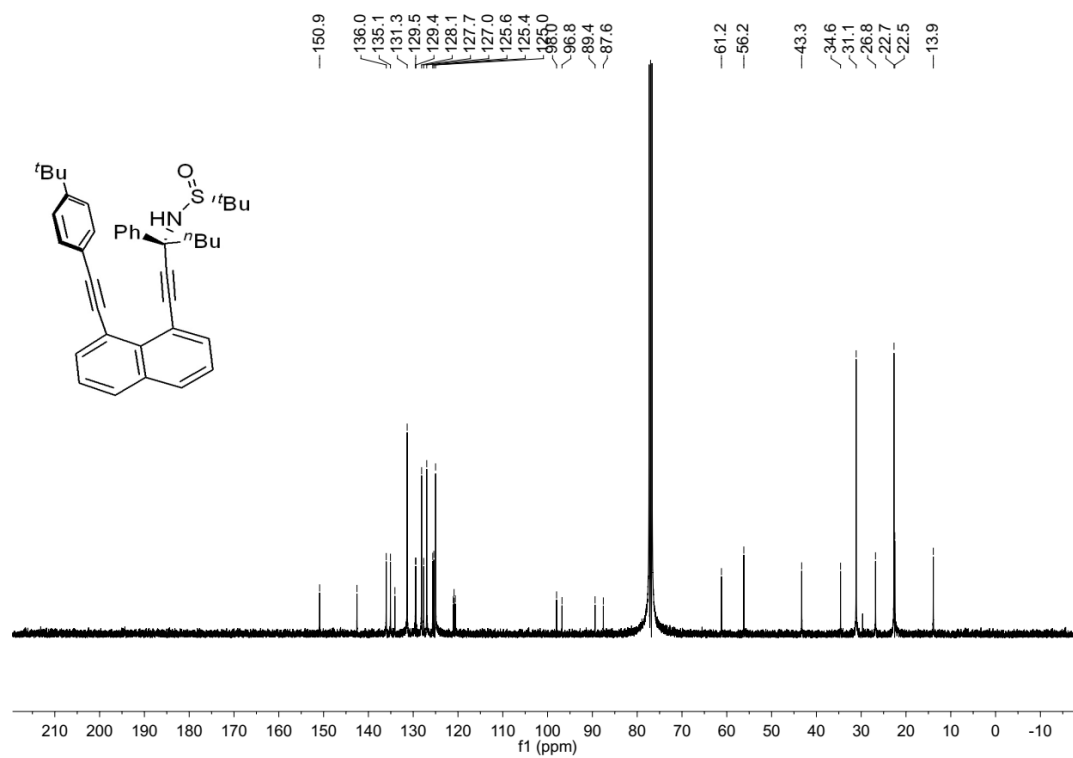


Figure S18. ¹³C NMR Spectrum of Compound 7d (CDCl₃, 100 MHz)

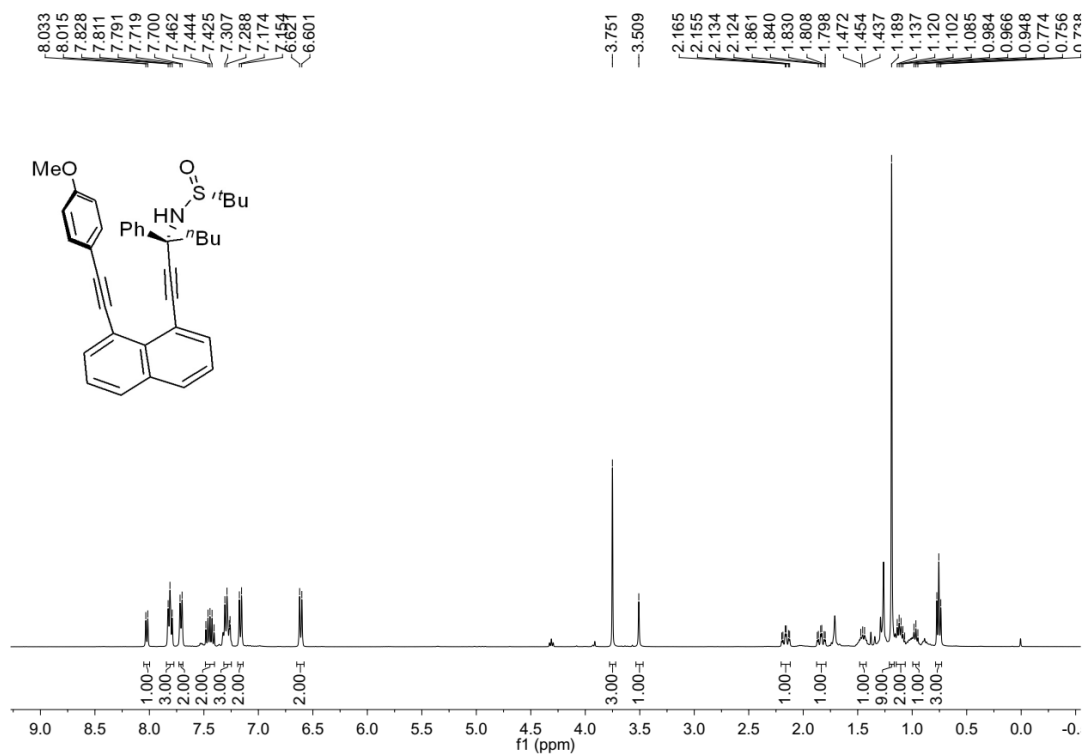


Figure S19. ¹H NMR Spectrum of Compound 7e (CDCl₃, 400 MHz)

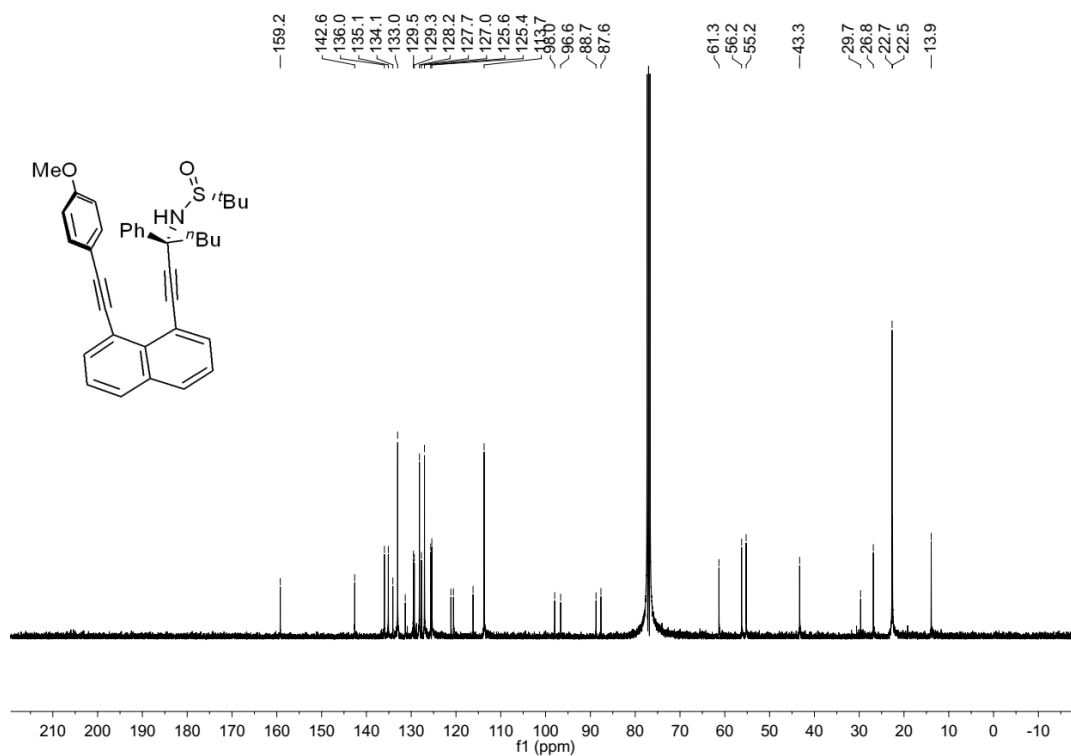


Figure S20. ¹³C NMR Spectrum of Compound 7e (CDCl₃, 100 MHz)

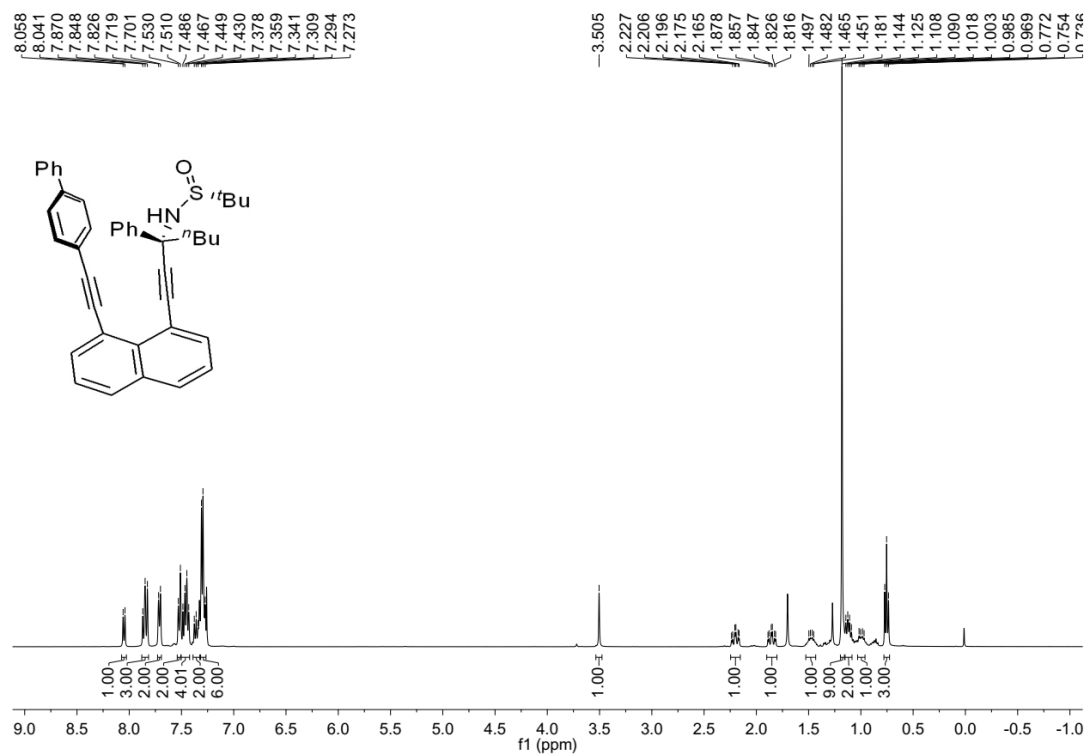


Figure S21. ¹H NMR Spectrum of Compound 7f (CDCl₃, 400 MHz)

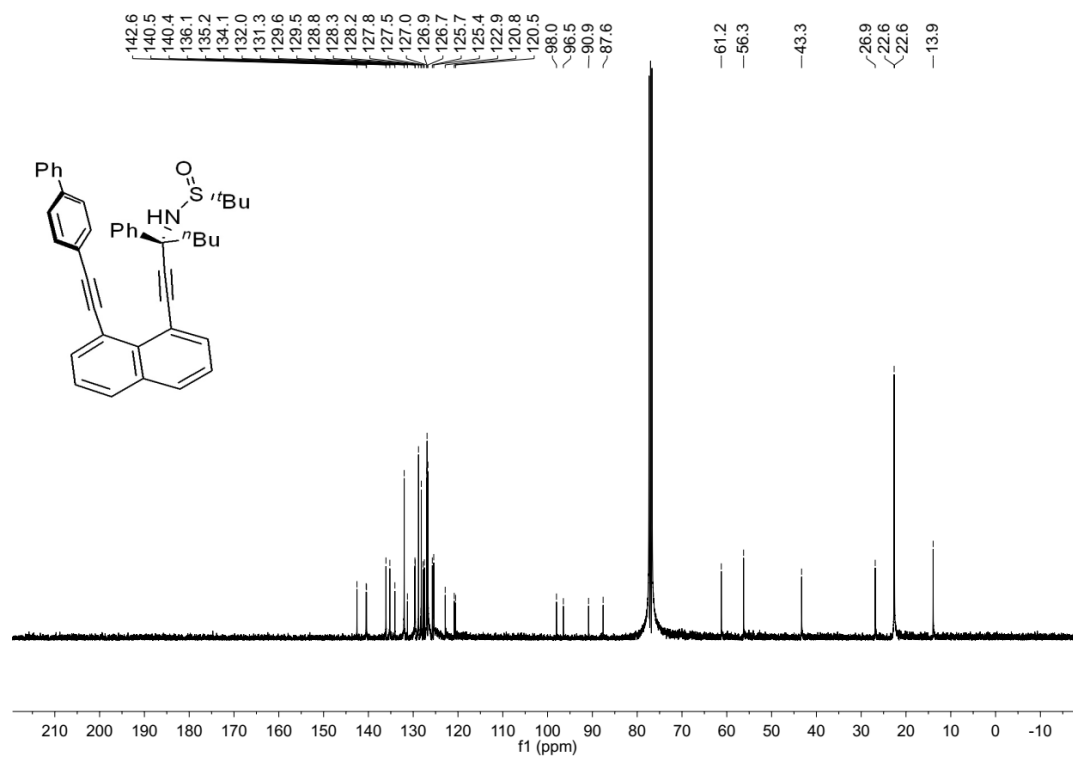


Figure S22. ¹³C NMR Spectrum of Compound 7f (CDCl₃, 100 MHz)

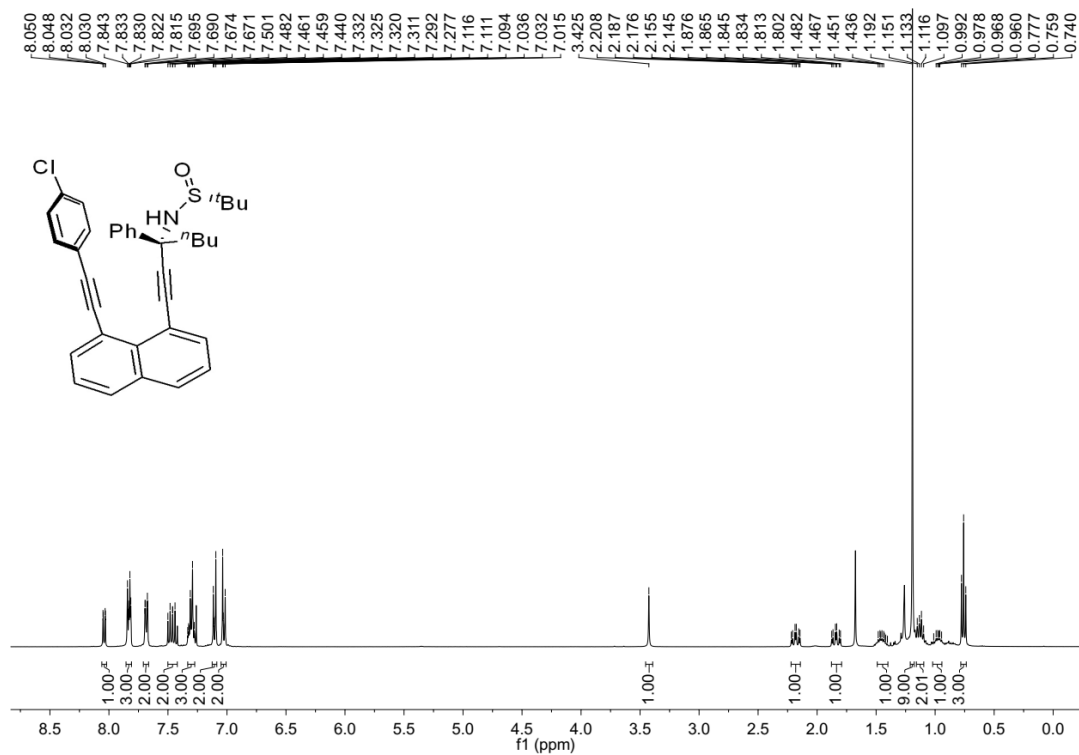


Figure S23. ¹H NMR Spectrum of Compound 7g (CDCl₃, 400 MHz)

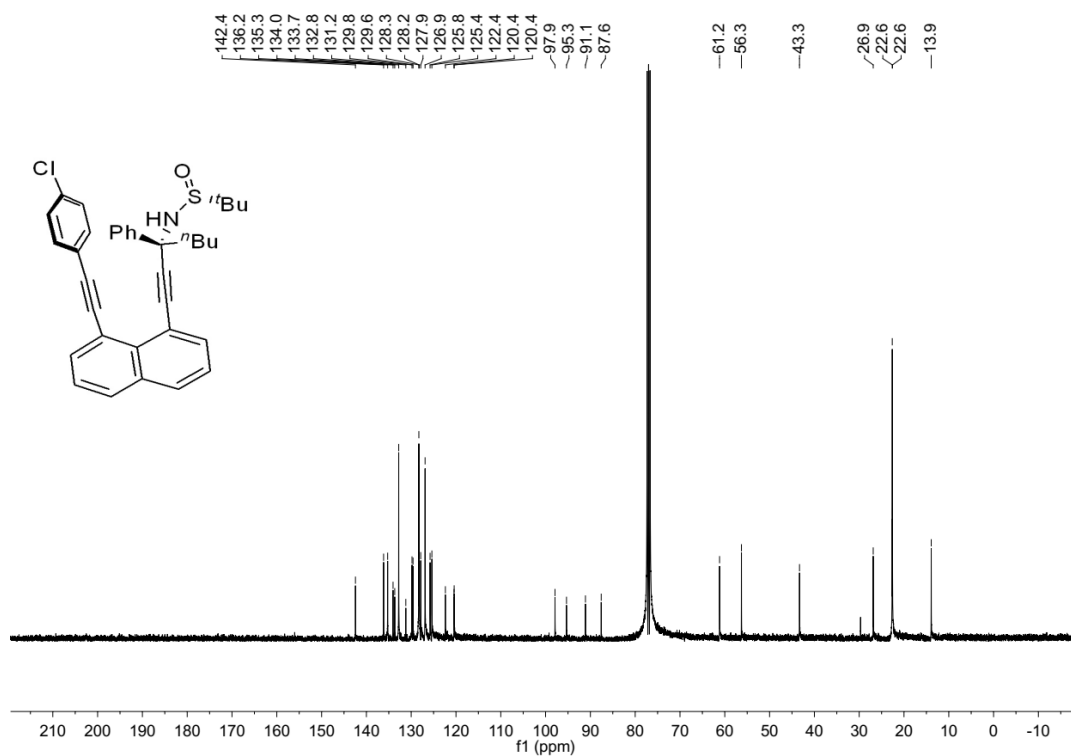


Figure S24. ¹³C NMR Spectrum of Compound 7g (CDCl₃, 100 MHz)

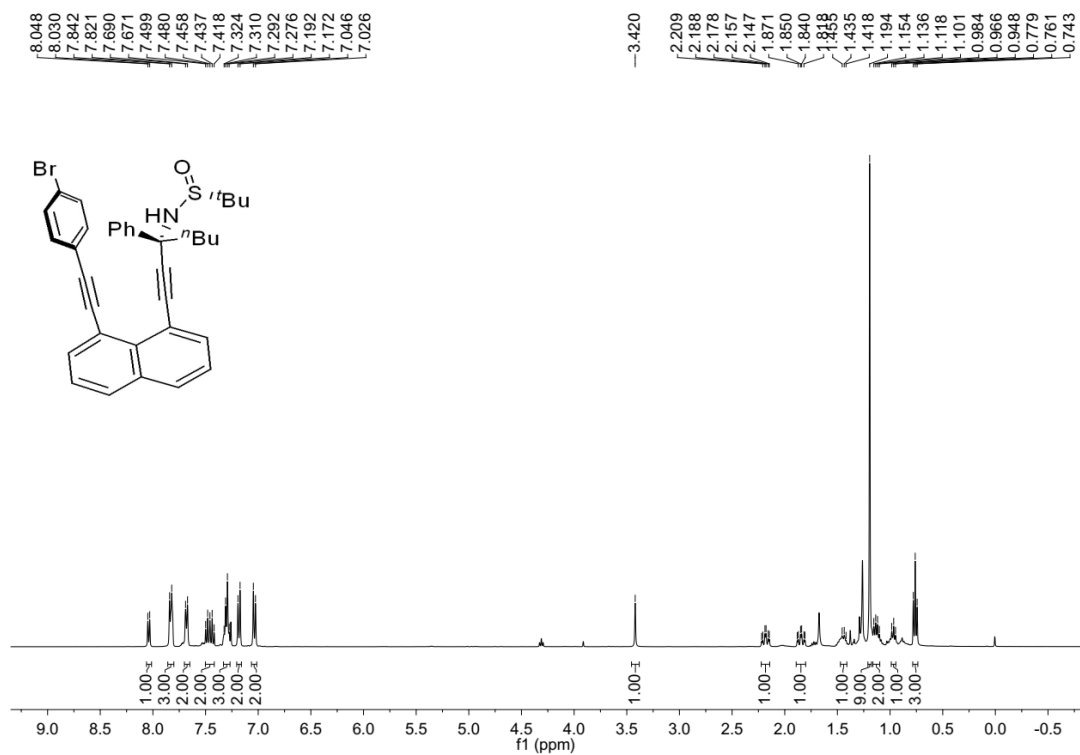


Figure S25. ¹H NMR Spectrum of Compound 7h (CDCl₃, 400 MHz)

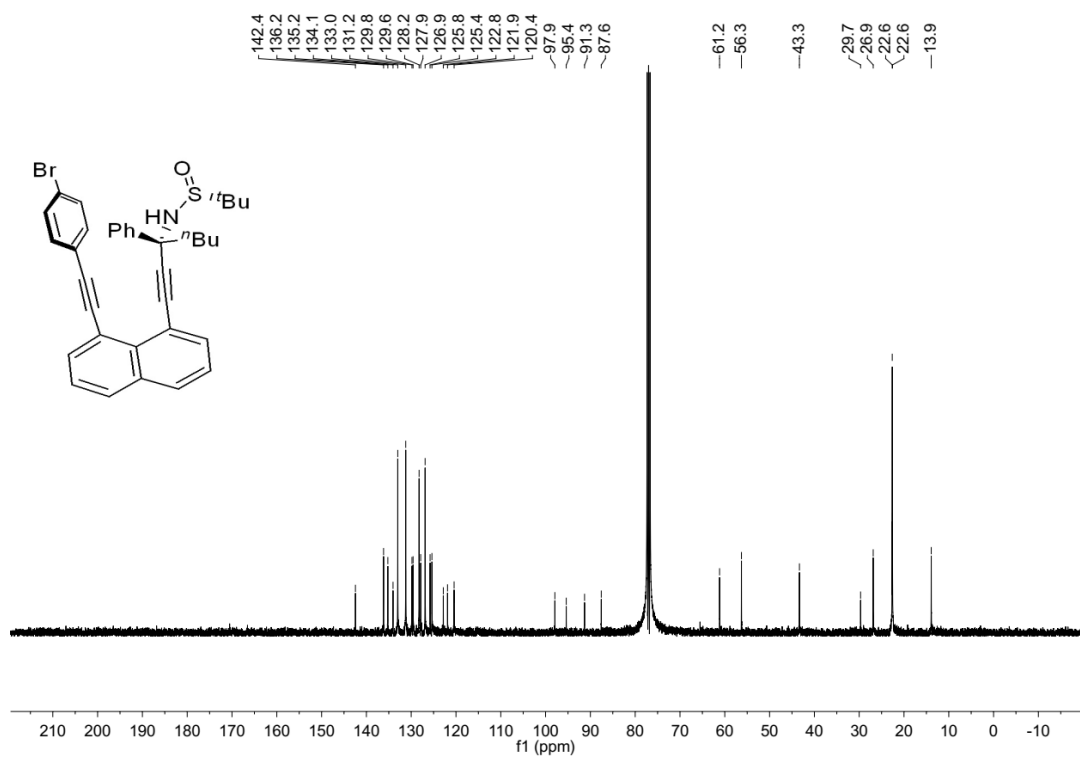


Figure S26. ¹³C NMR Spectrum of Compound 7h (CDCl₃, 100 MHz)

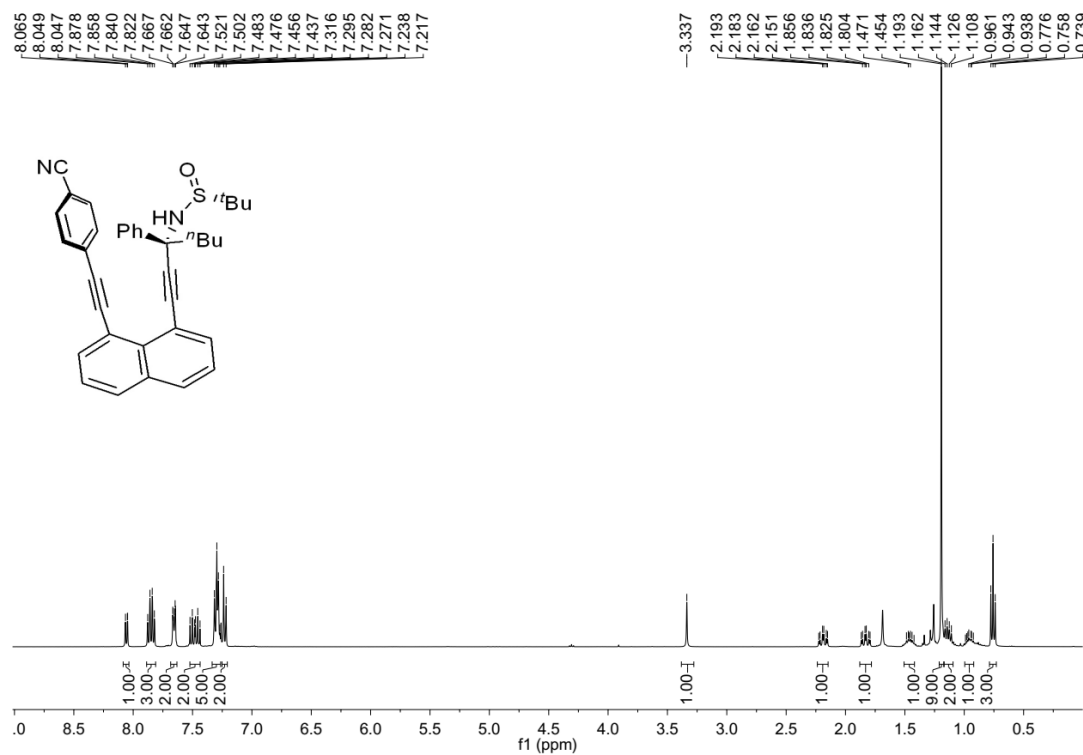


Figure S27. ¹H NMR Spectrum of Compound 7i (CDCl₃, 400 MHz)

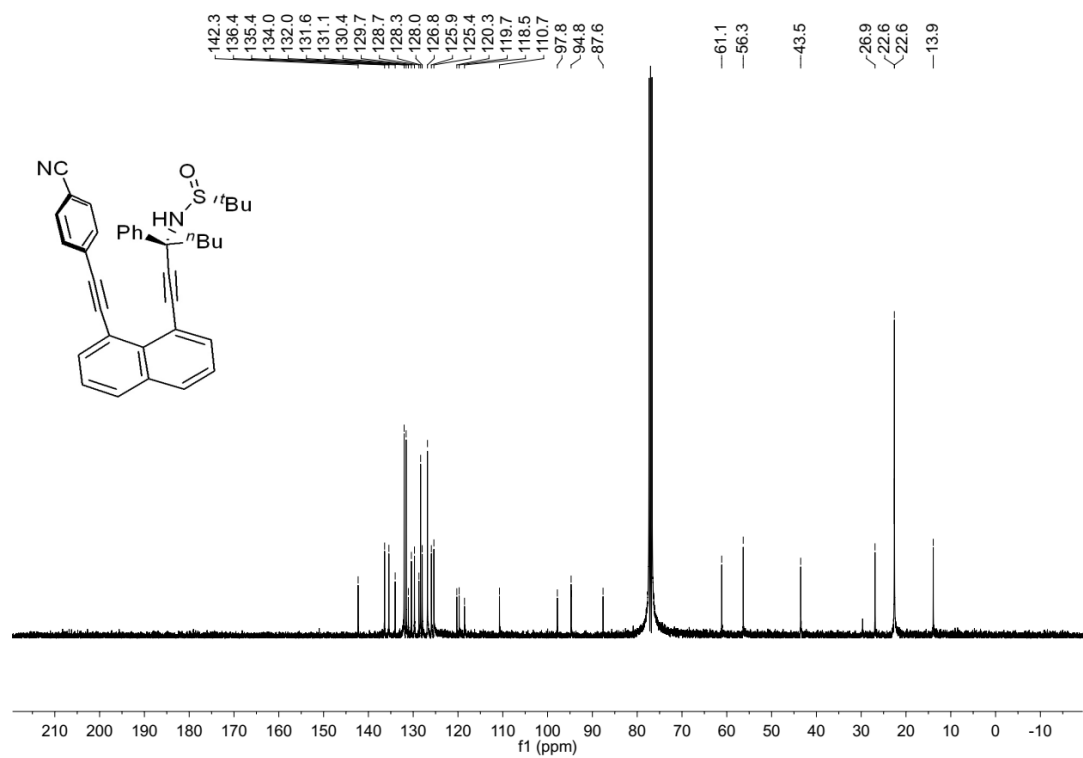


Figure S28. ¹³C NMR Spectrum of Compound 7i (CDCl₃, 100 MHz)

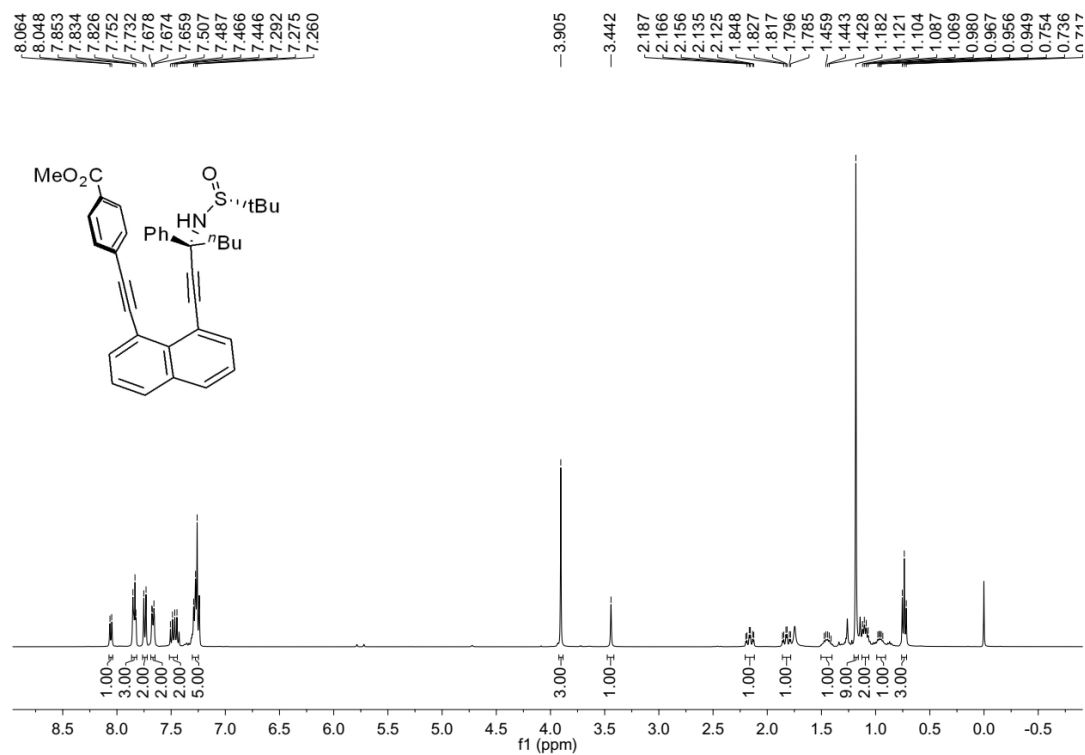


Figure S29. ¹H NMR Spectrum of Compound 7j (CDCl₃, 400 MHz)

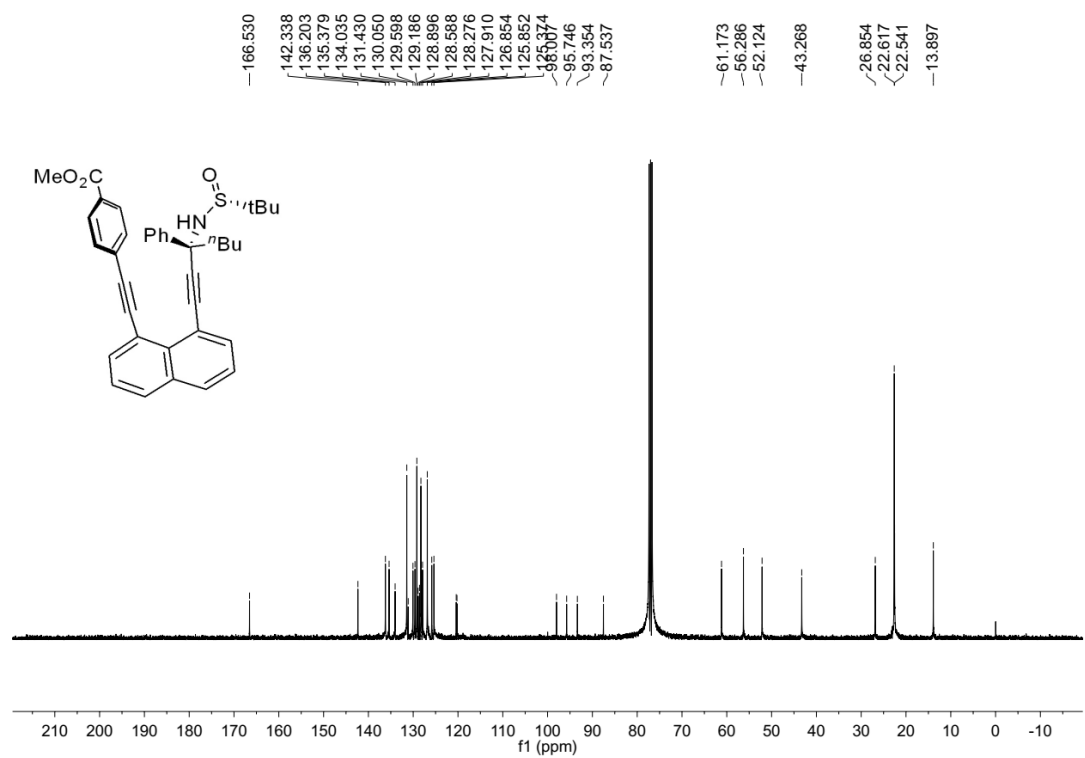


Figure S30. ¹³C NMR Spectrum of Compound 7j (CDCl₃, 100 MHz)

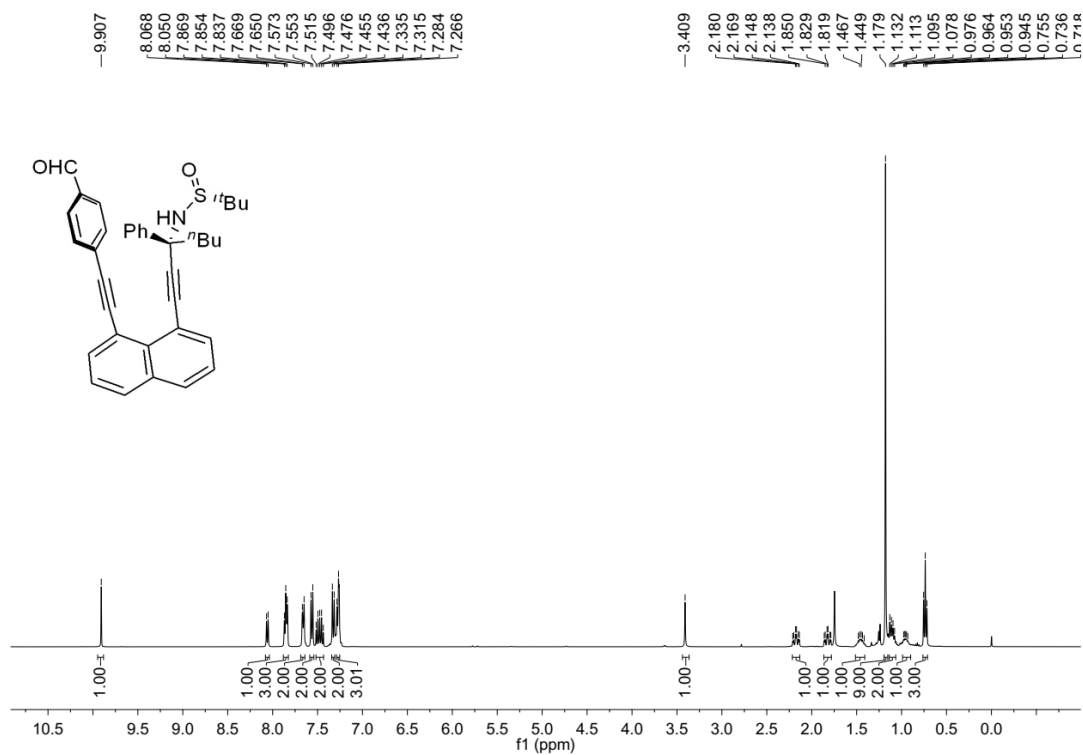


Figure S31. ¹H NMR Spectrum of Compound 7k (CDCl₃, 400 MHz)

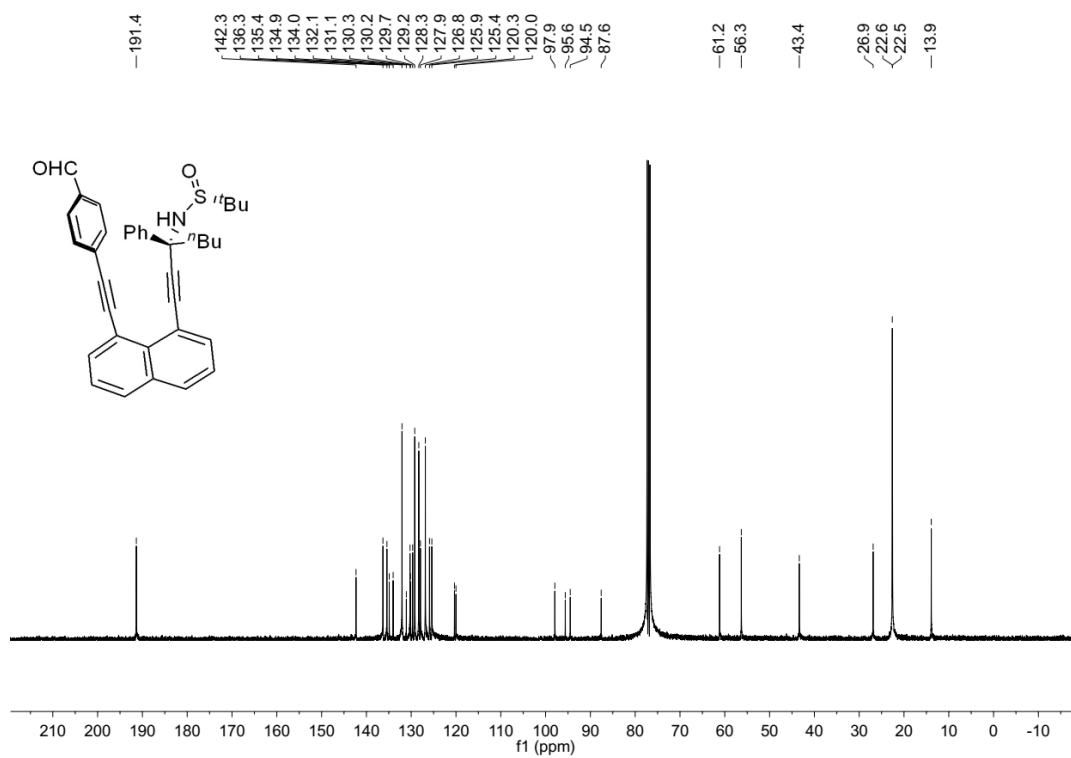


Figure S32. ¹³C NMR Spectrum of Compound 7k (CDCl₃, 100 MHz)

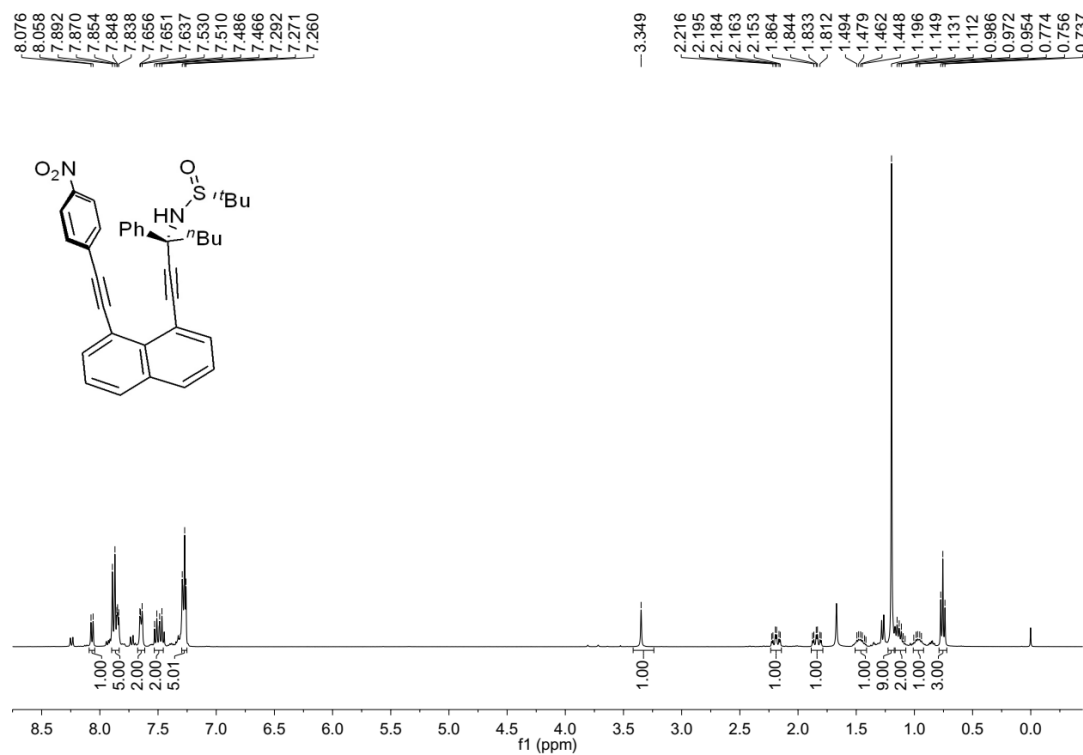


Figure S33. ¹H NMR Spectrum of Compound 7l (CDCl₃, 400 MHz)

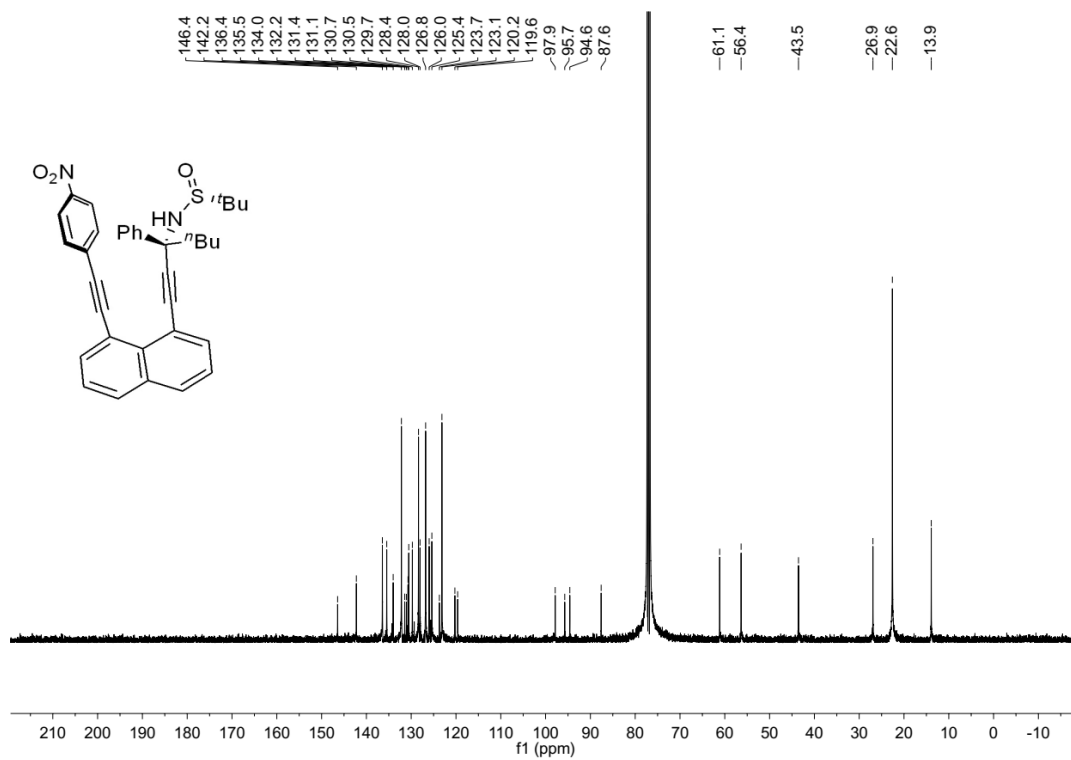


Figure S34. ¹³C NMR Spectrum of Compound 7l (CDCl₃, 100 MHz)

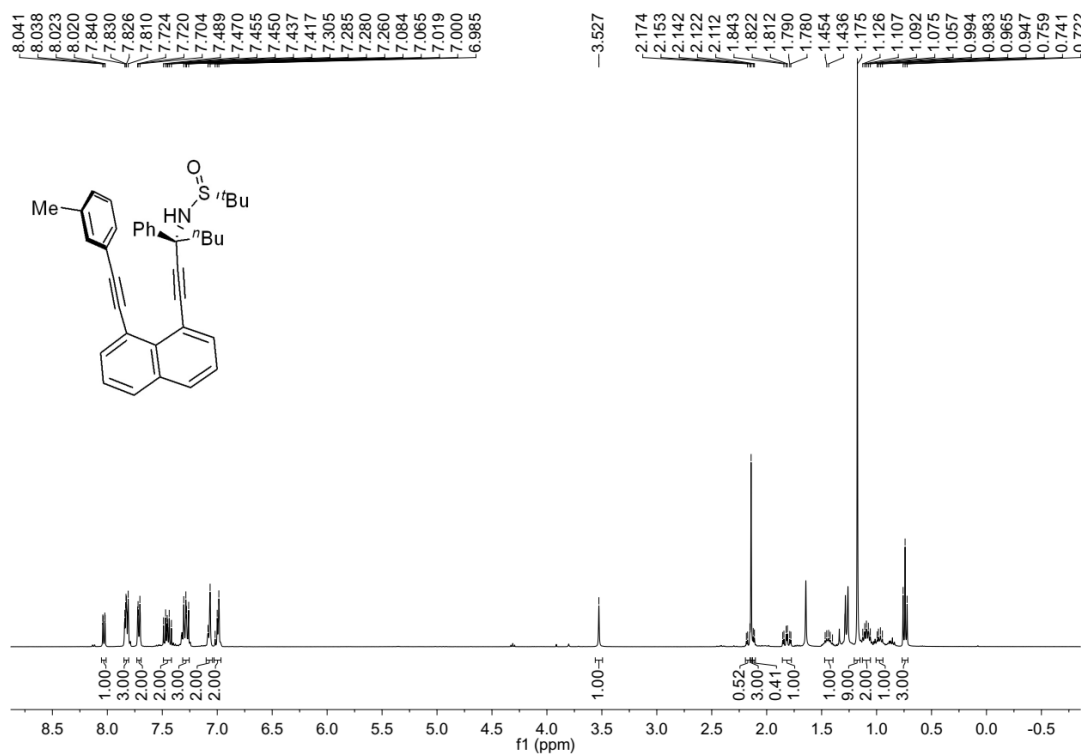


Figure S35. ¹H NMR Spectrum of Compound 7m (CDCl₃, 400 MHz)

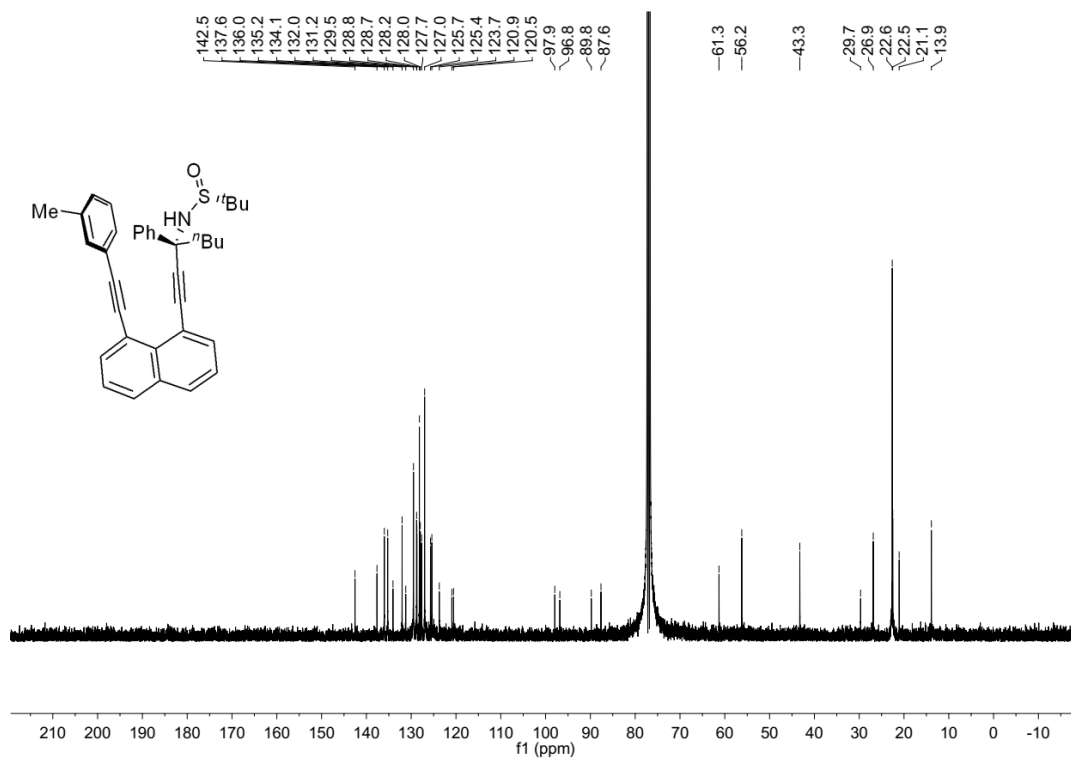


Figure S36. ¹³C NMR Spectrum of Compound 7m (CDCl₃, 100 MHz)

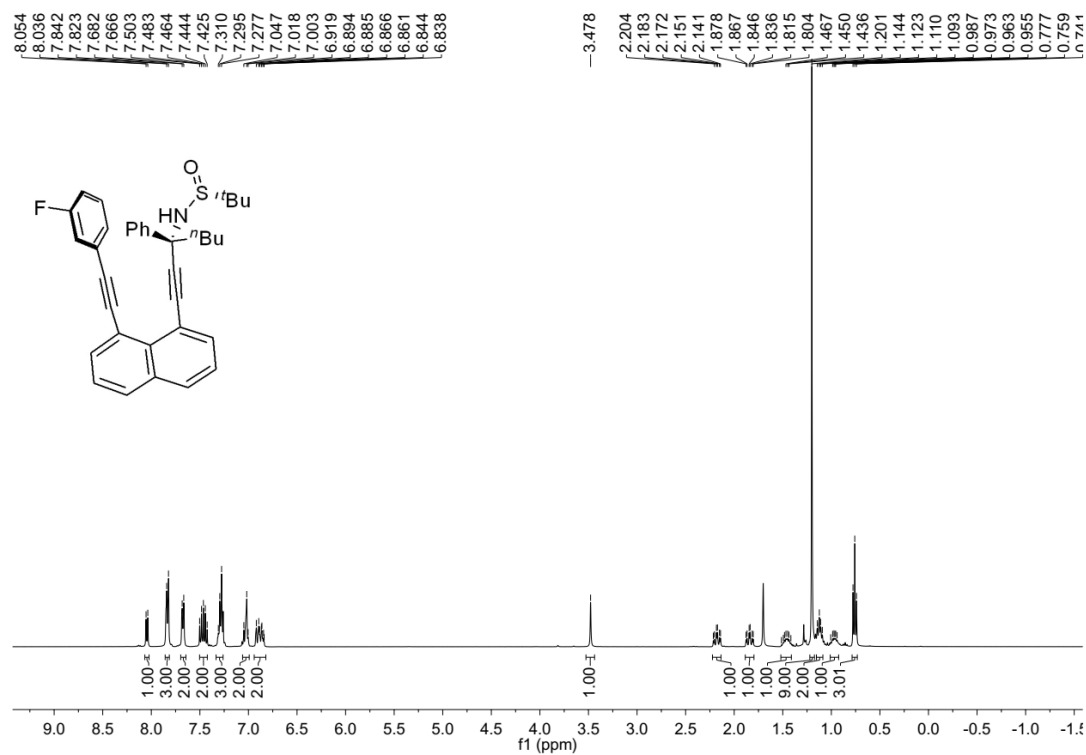


Figure S37. ¹H NMR Spectrum of Compound 7n (CDCl₃, 400 MHz)

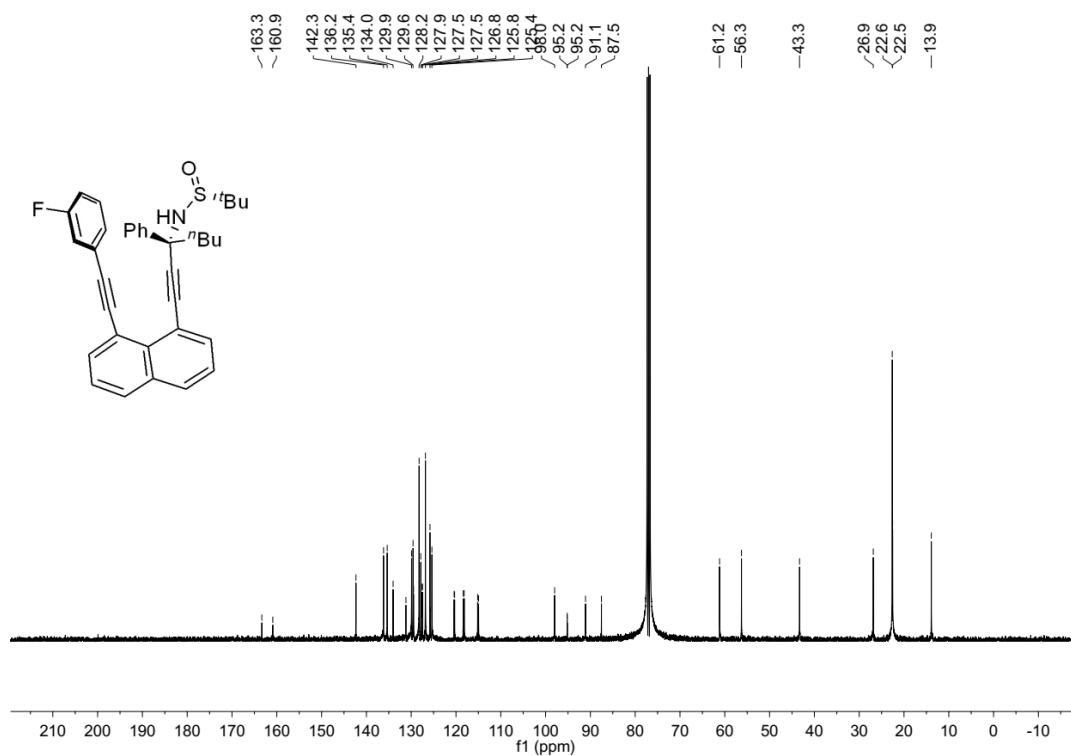


Figure S38. ¹³C NMR Spectrum of Compound 7n (CDCl₃, 100 MHz)

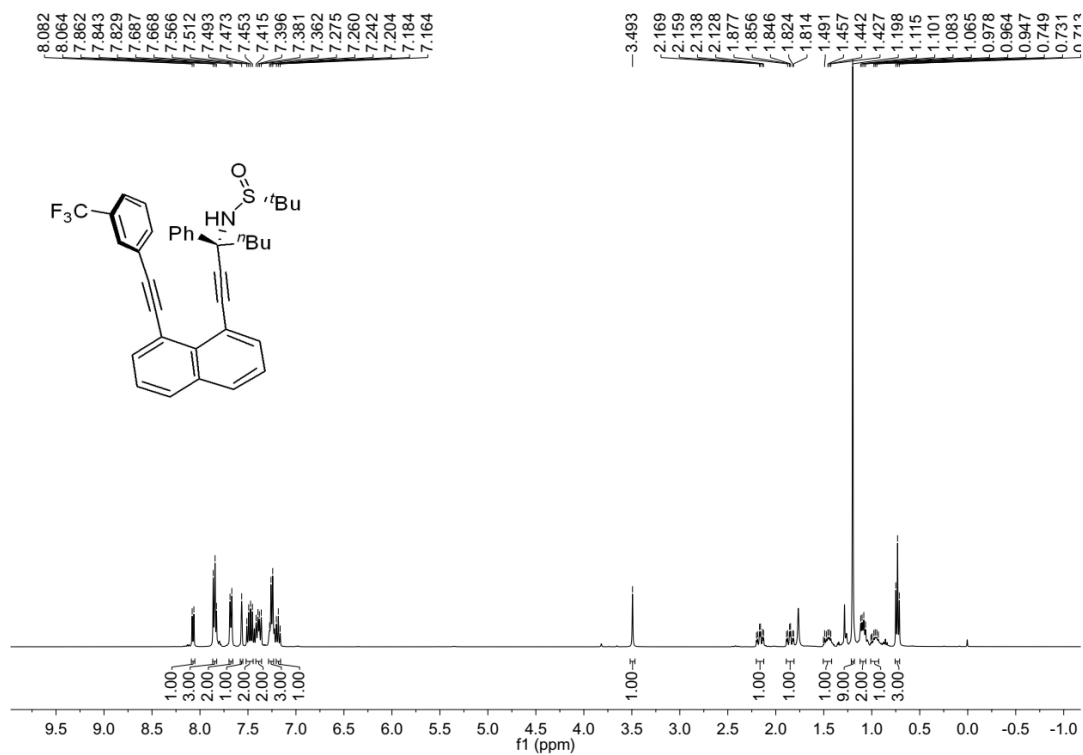


Figure S41. ¹H NMR Spectrum of Compound 7p (CDCl₃, 400 MHz)

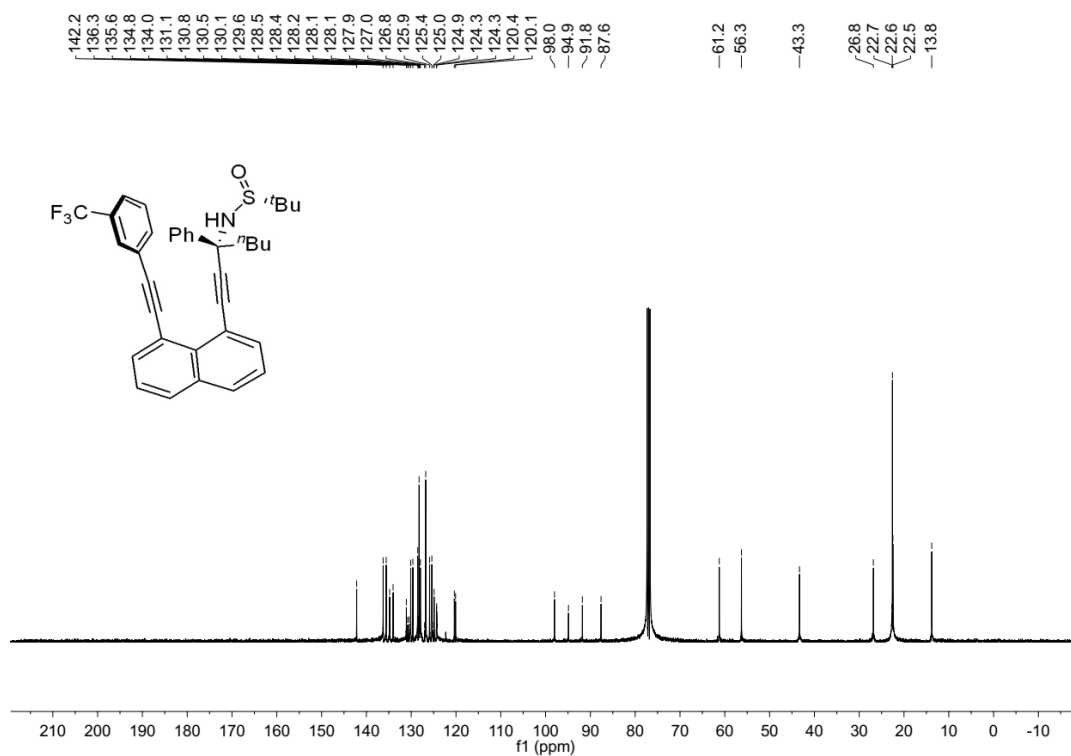


Figure S42. ¹³C NMR Spectrum of Compound 7p (CDCl₃, 100 MHz)

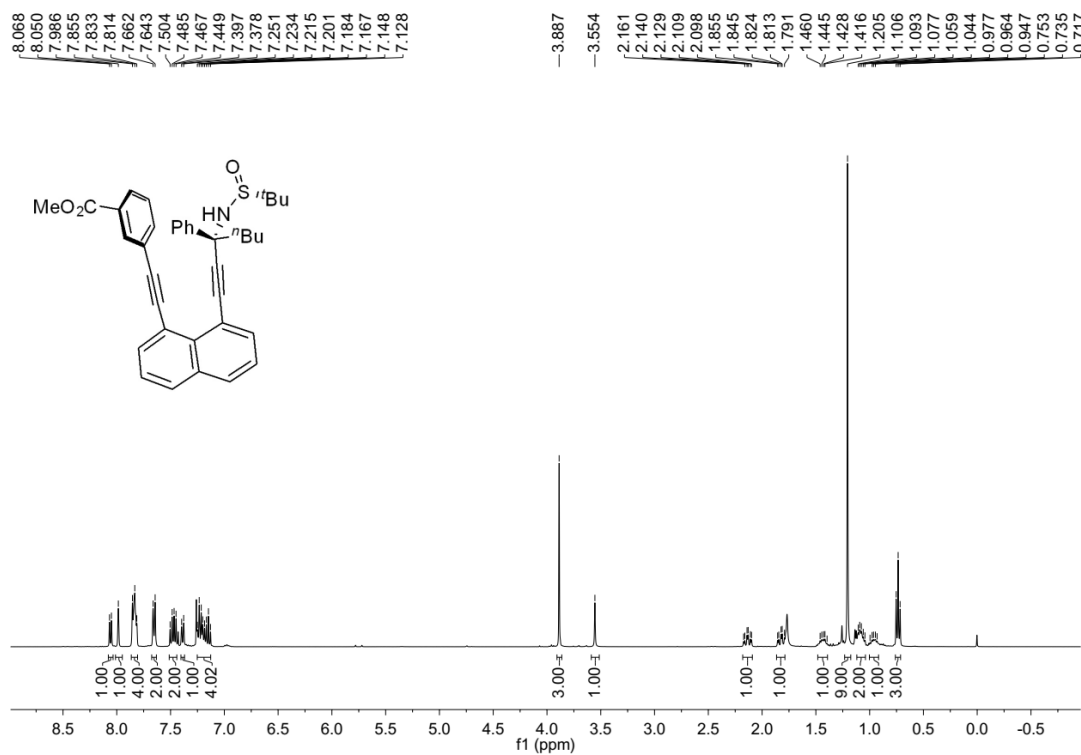


Figure S43. ¹H NMR Spectrum of Compound 7q (CDCl₃, 400 MHz)

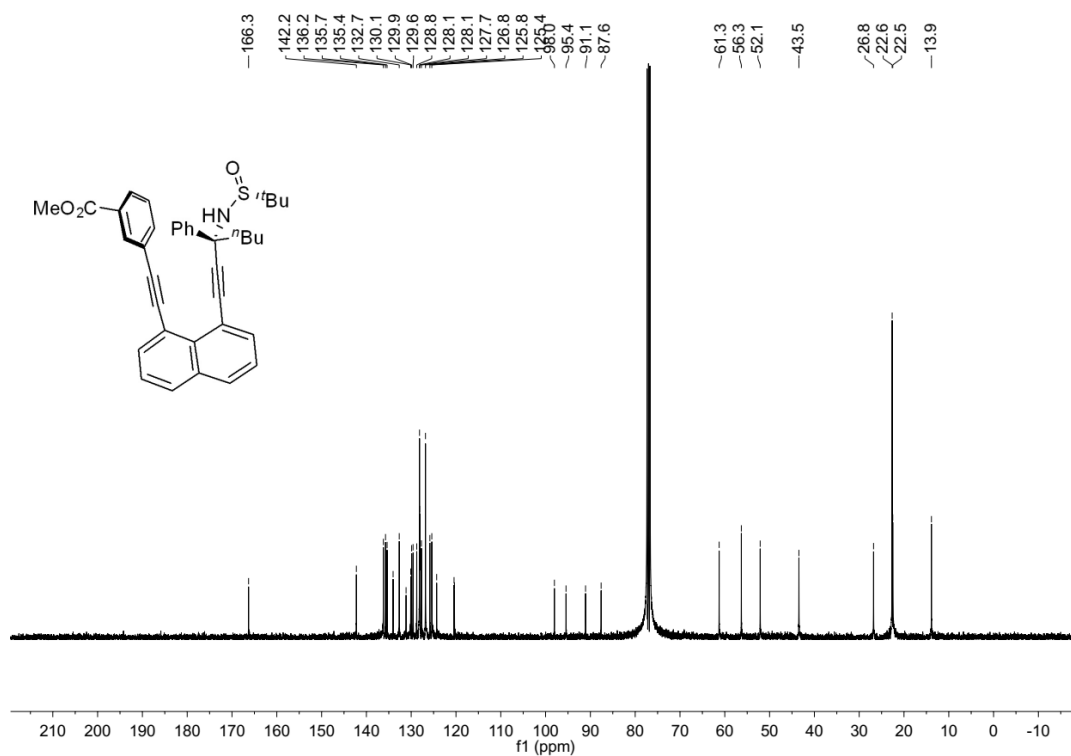


Figure S44. ¹³C NMR Spectrum of Compound 7q (CDCl₃, 100 MHz)

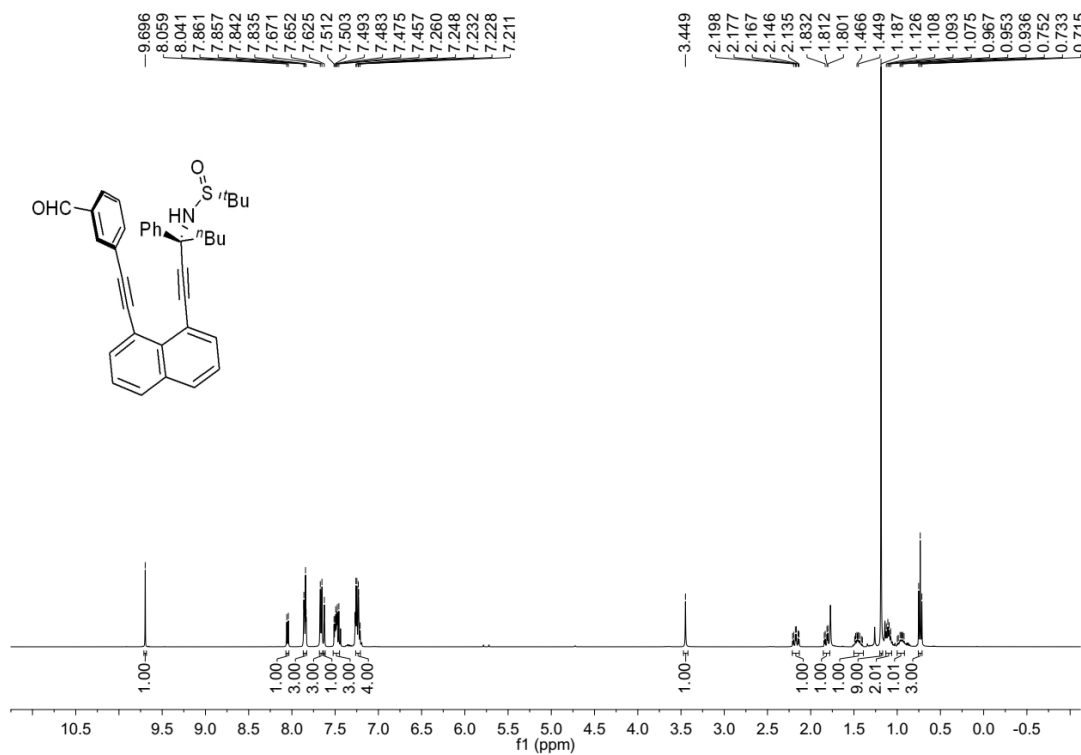


Figure S45. ¹H NMR Spectrum of Compound 7r (CDCl₃, 400 MHz)

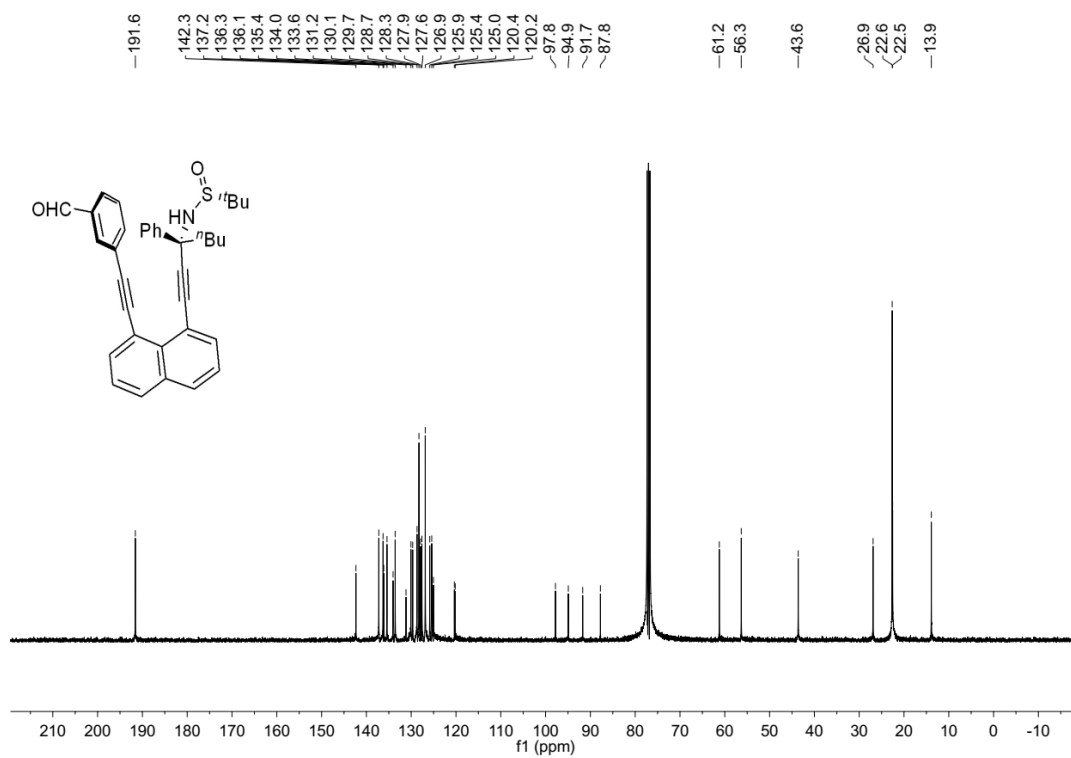


Figure S46. ¹³C NMR Spectrum of Compound 7r (CDCl₃, 100 MHz)

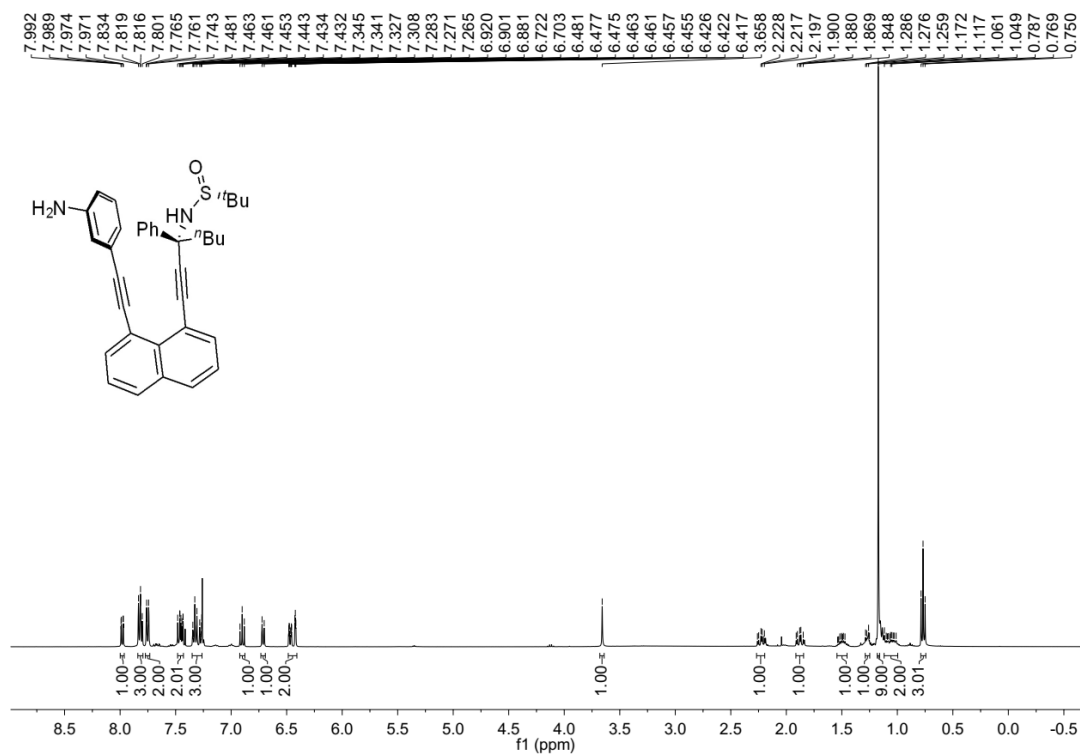


Figure S47. ¹H NMR Spectrum of Compound 7s (CDCl₃, 400 MHz)

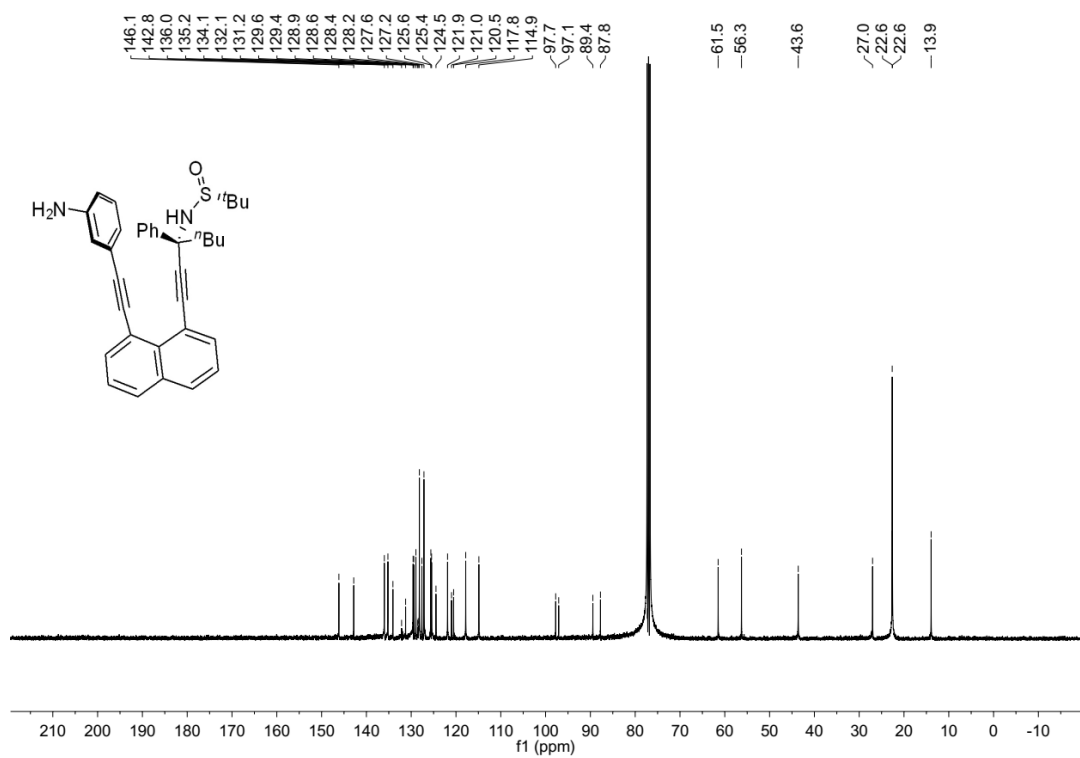


Figure S48. ¹³C NMR Spectrum of Compound 7s (CDCl₃, 100 MHz)

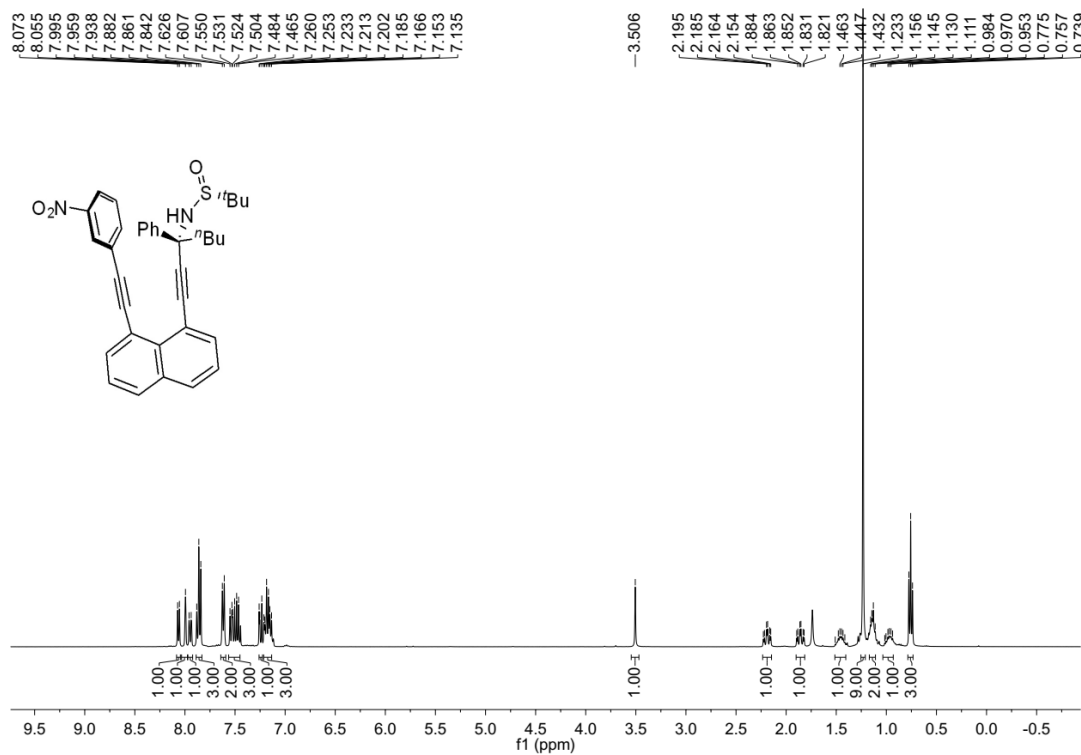


Figure S49. ¹H NMR Spectrum of Compound 7t (CDCl₃, 400 MHz)

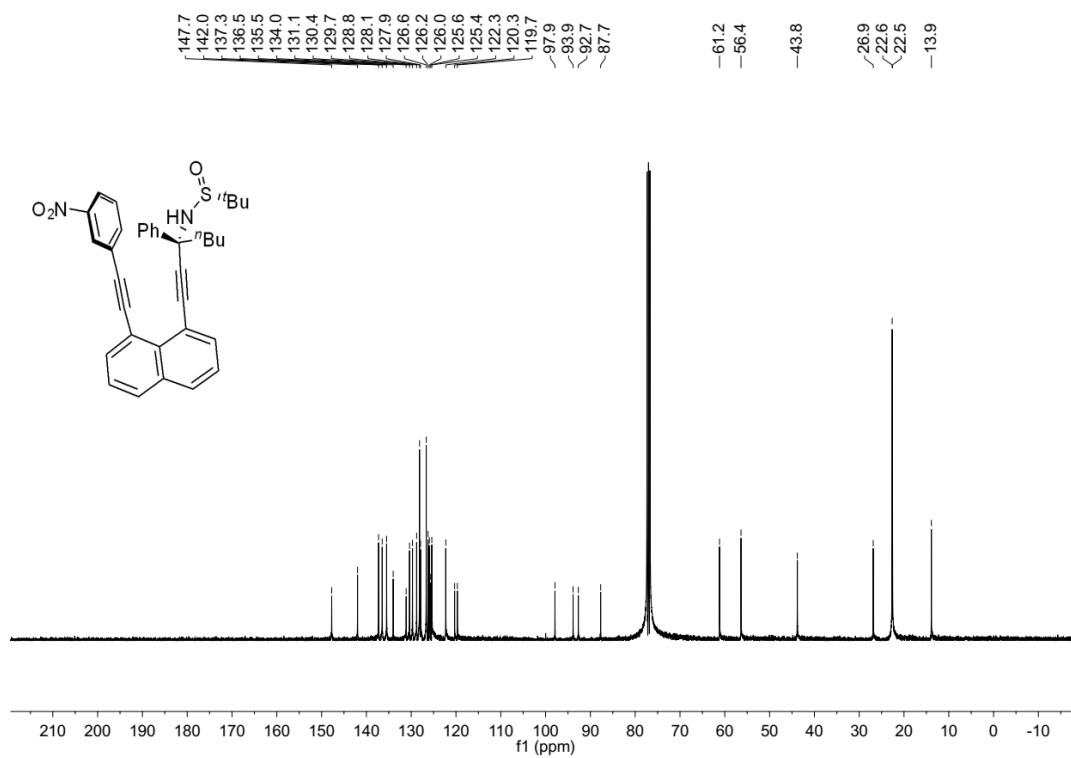


Figure S50. ¹³C NMR Spectrum of Compound 7t (CDCl₃, 100 MHz)

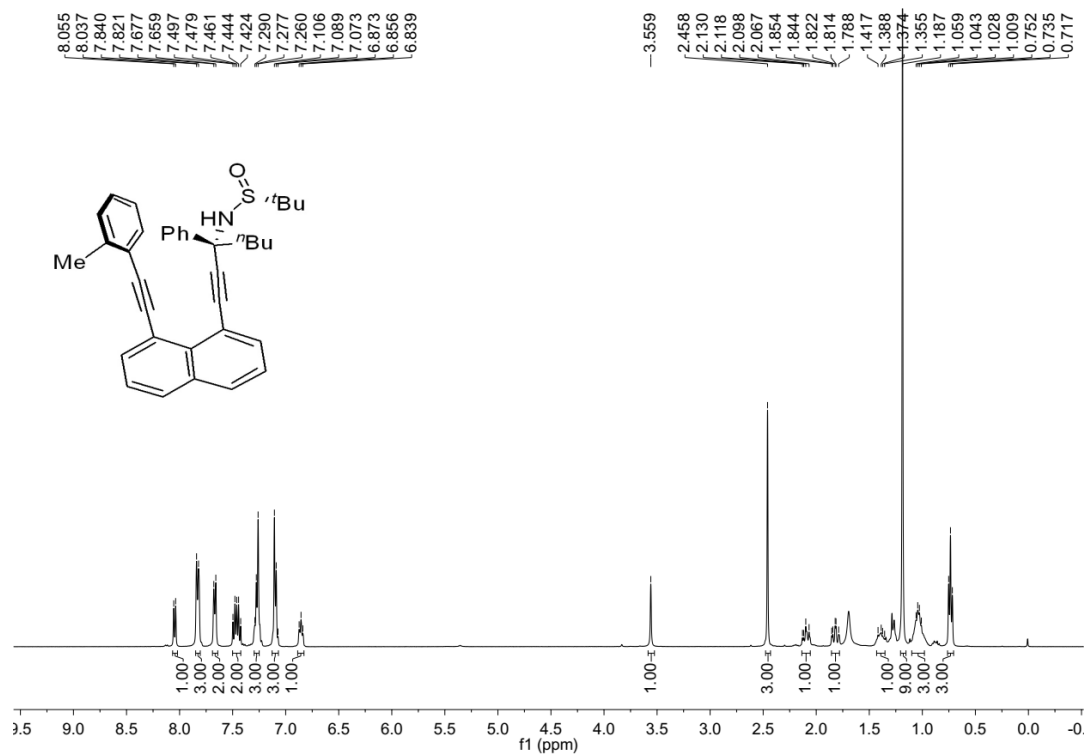


Figure S53. ¹H NMR Spectrum of Compound 7v (CDCl₃, 400 MHz)

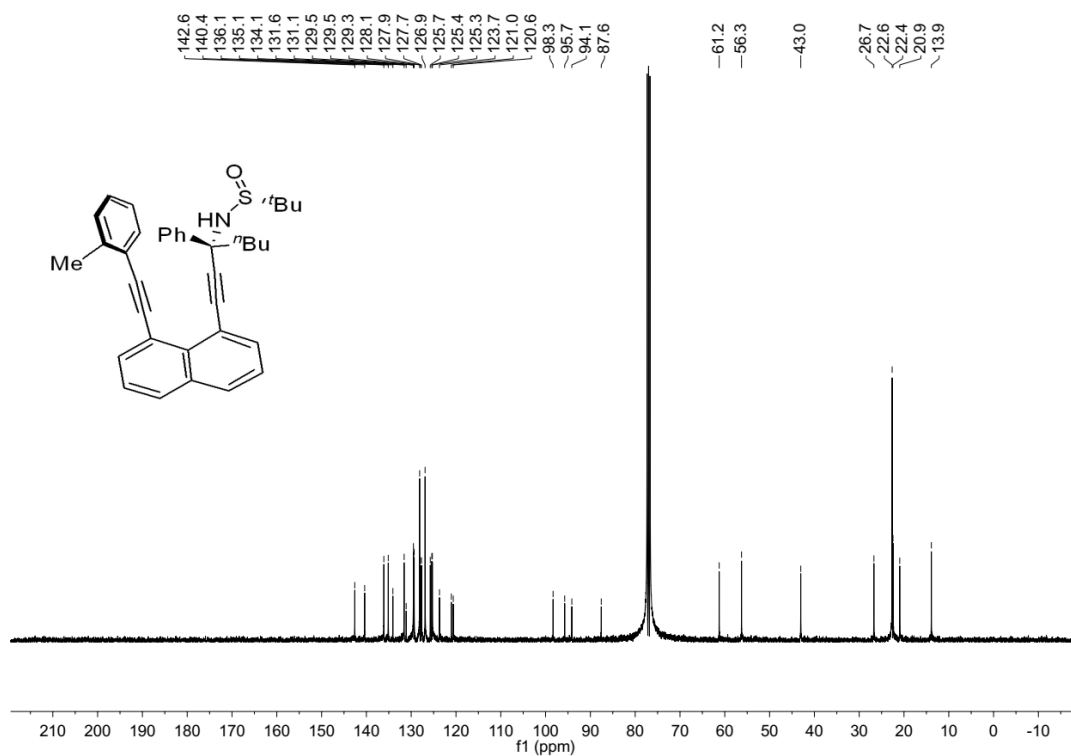


Figure S54. ¹³C NMR Spectrum of Compound 7v (CDCl₃, 100 MHz)

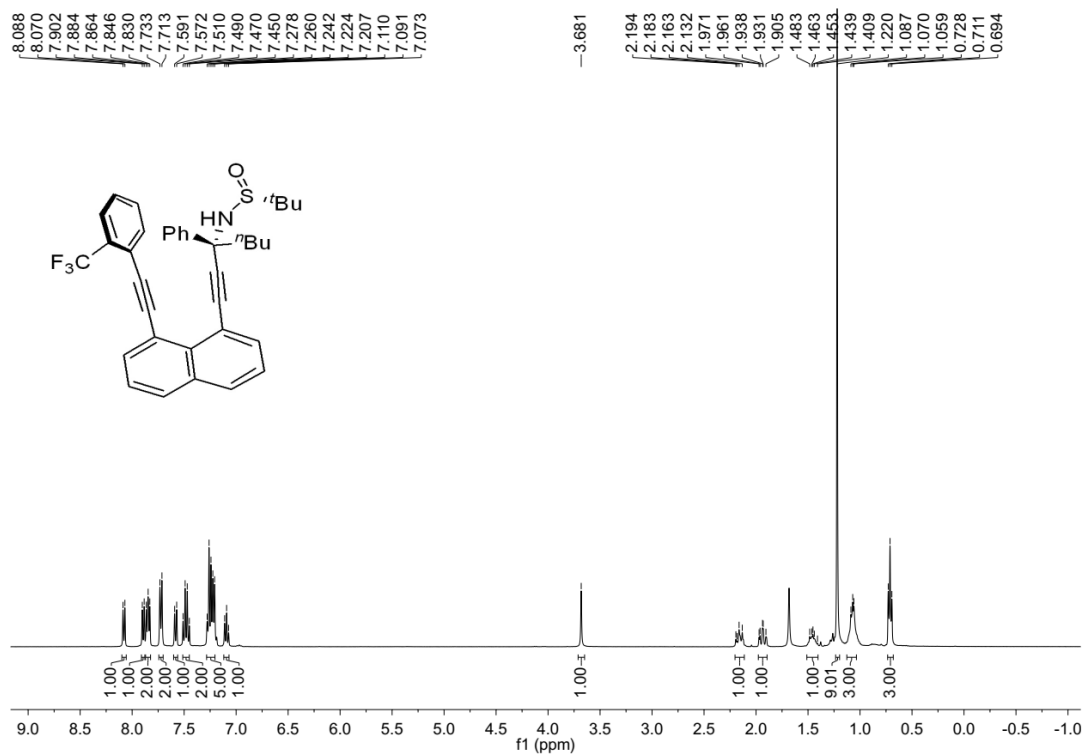


Figure S57. ¹H NMR Spectrum of Compound 7x (CDCl₃, 400 MHz)

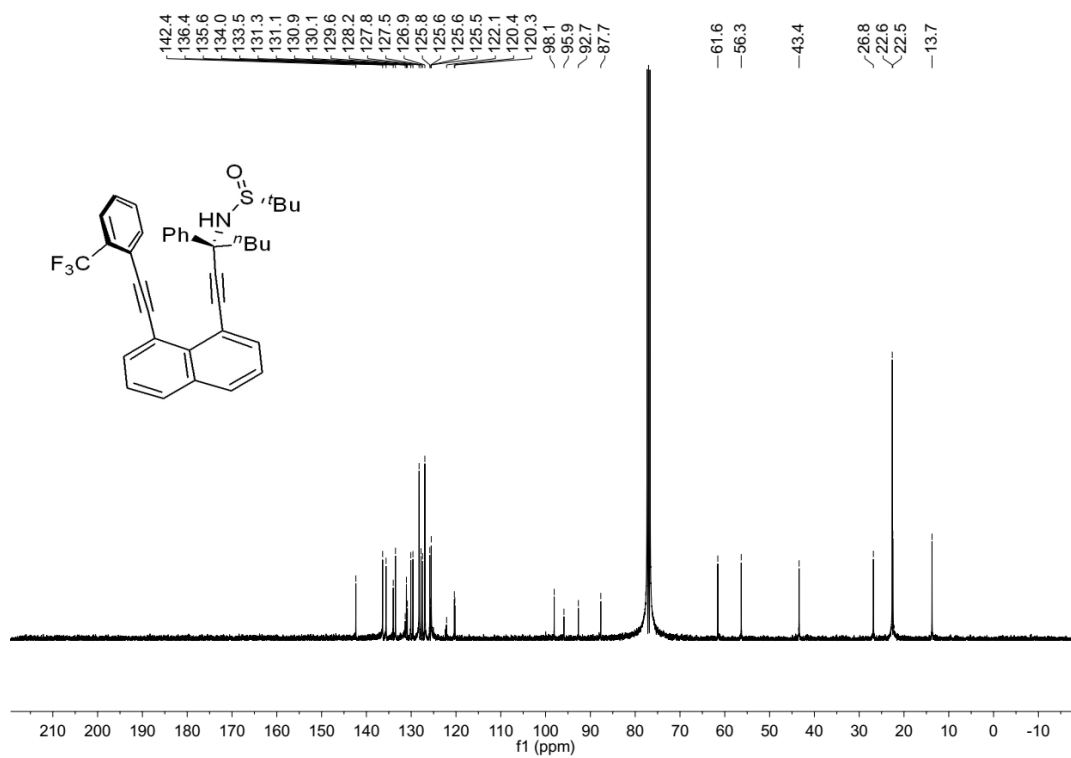


Figure S58. ¹³C NMR Spectrum of Compound 7x (CDCl₃, 100 MHz)

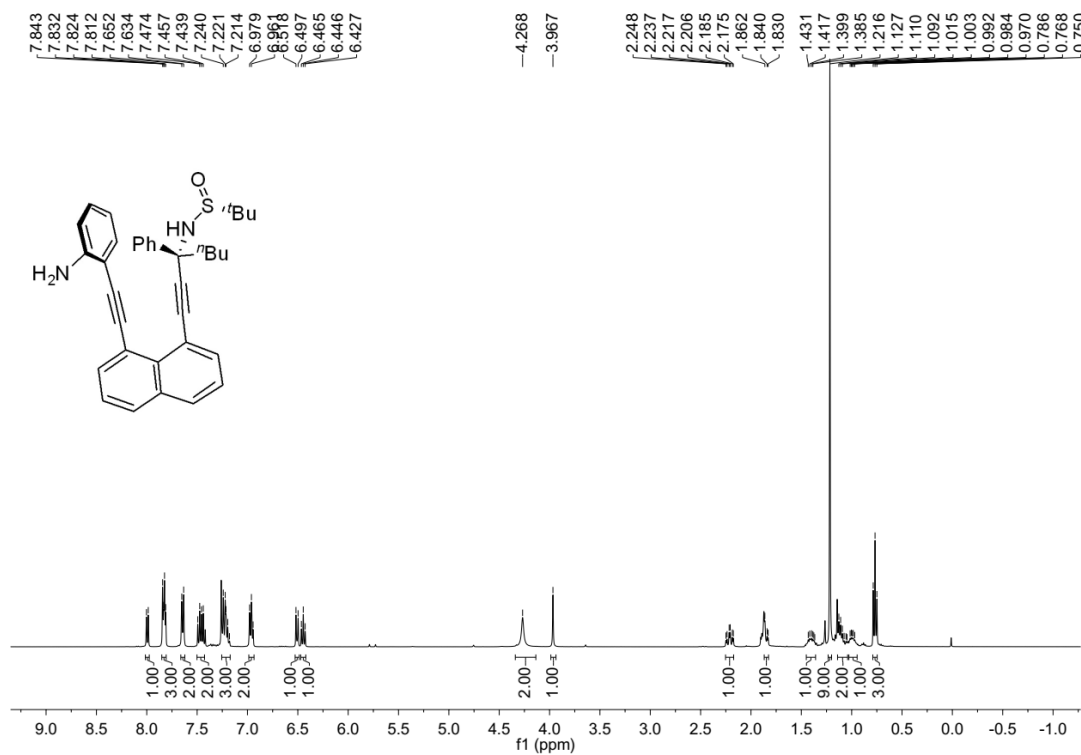


Figure S59. ¹H NMR Spectrum of Compound 7y (CDCl₃, 400 MHz)

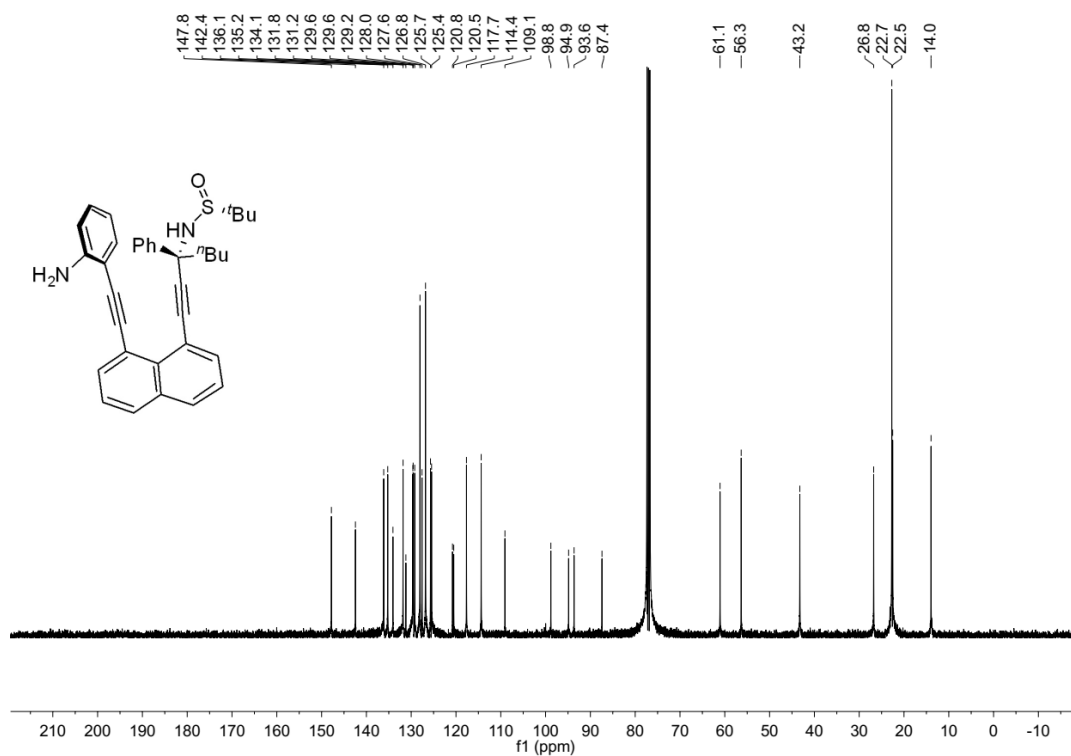


Figure S60. ¹³C NMR Spectrum of Compound 7y (CDCl₃, 100 MHz)

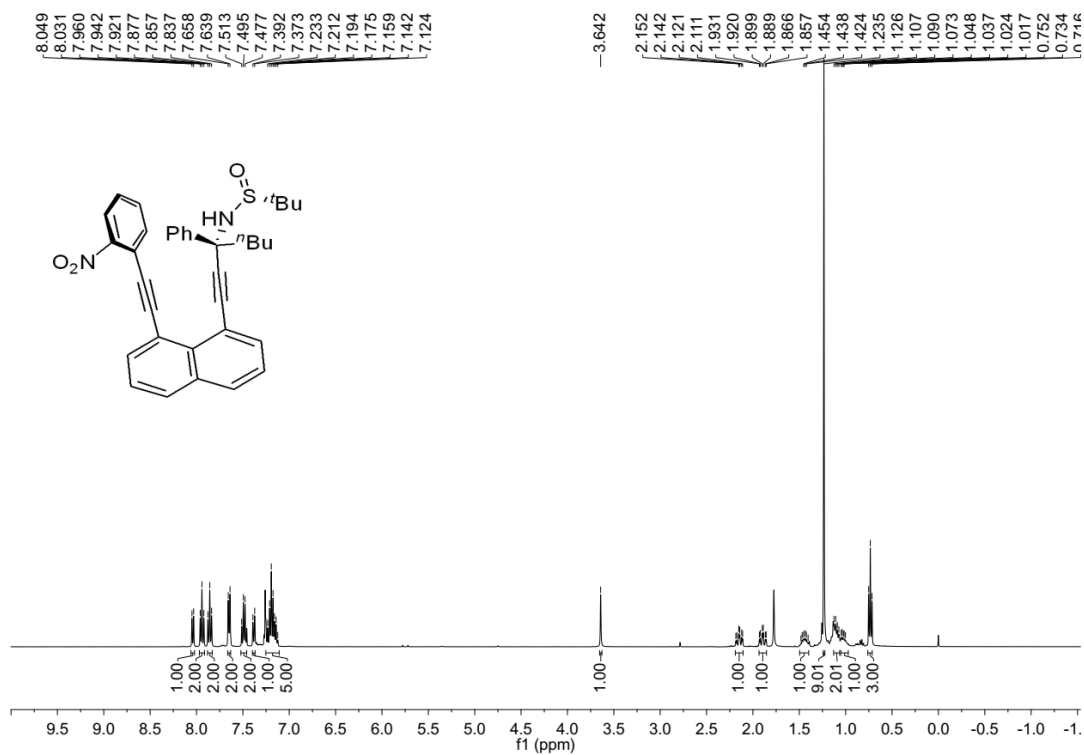


Figure S61. ¹H NMR Spectrum of Compound 7z (CDCl₃, 400 MHz)

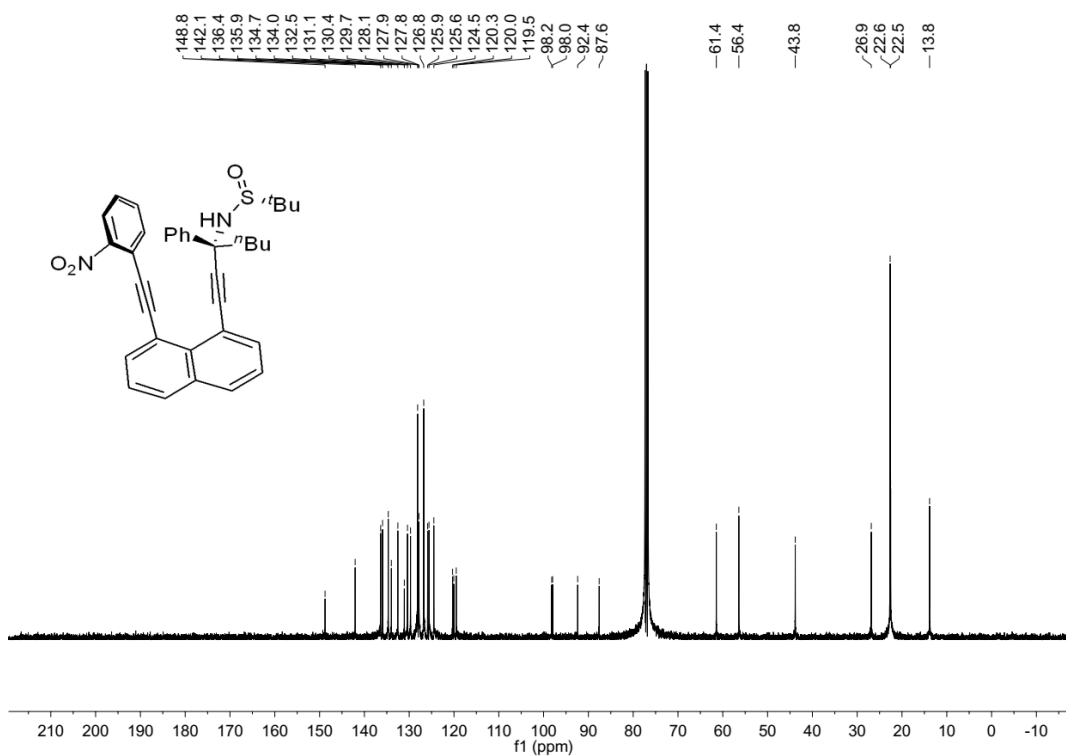


Figure S62. ¹³C NMR Spectrum of Compound 7z (CDCl₃, 100 MHz)

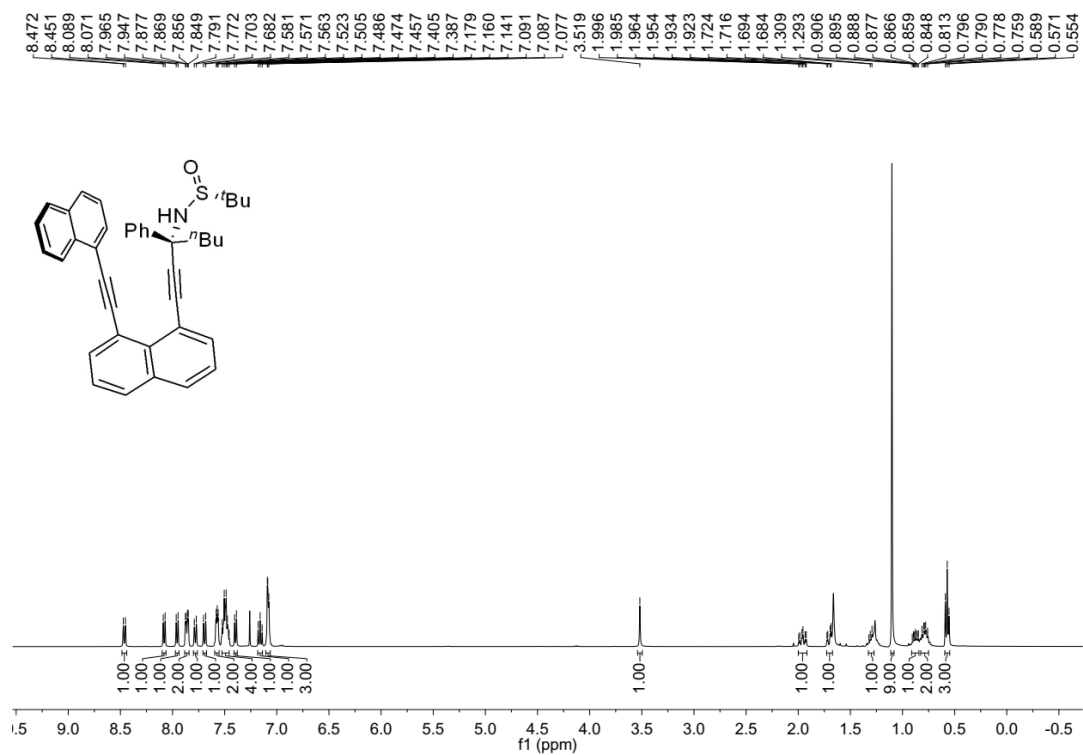


Figure S63. ¹H NMR Spectrum of Compound 7aa (CDCl₃, 400 MHz)

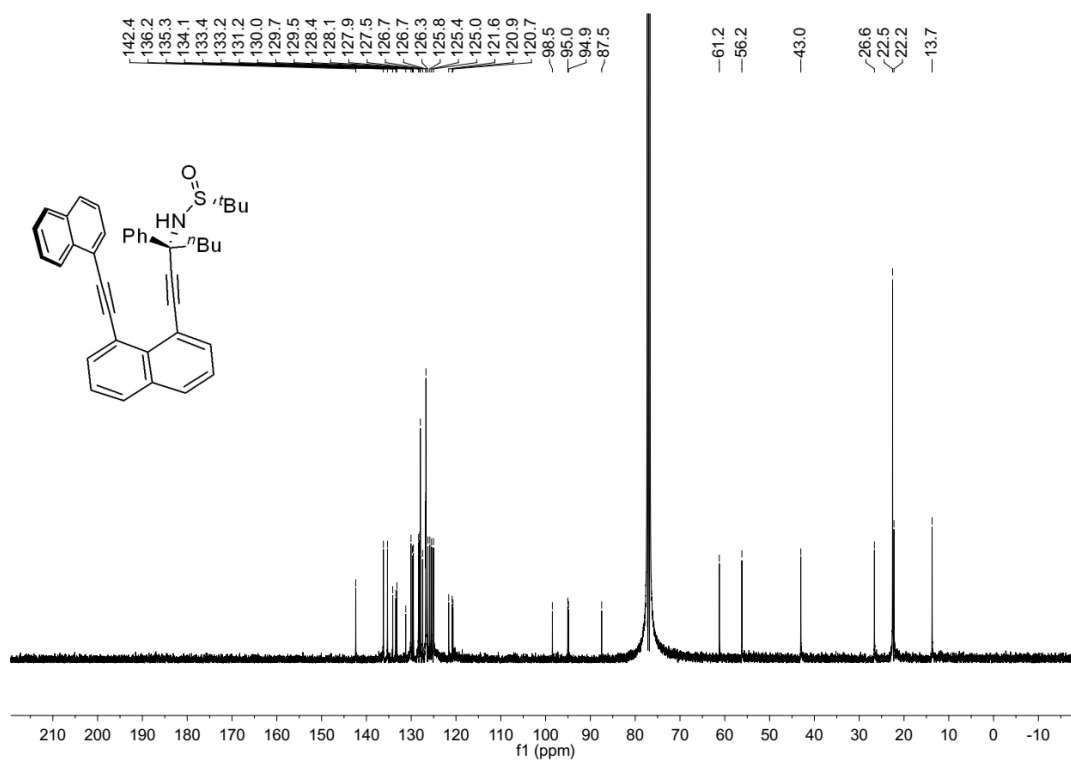


Figure S64. ¹³C NMR Spectrum of Compound 7aa (CDCl₃, 100 MHz)

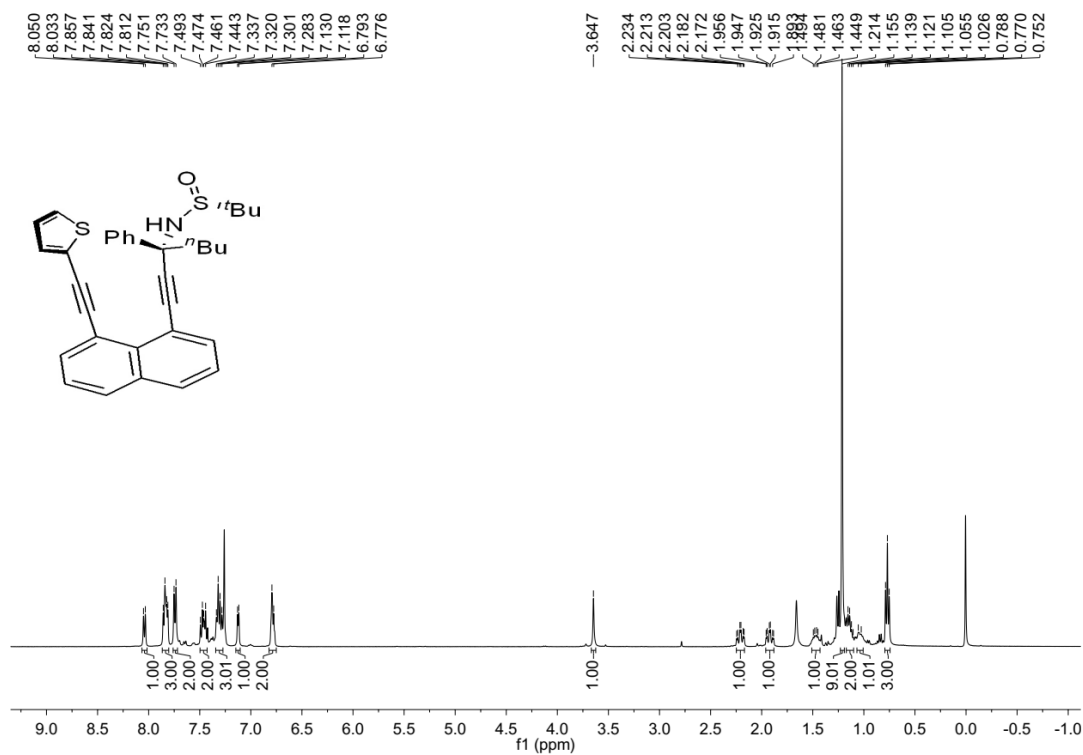


Figure S67. ¹H NMR Spectrum of Compound 7ac (CDCl₃, 400 MHz)

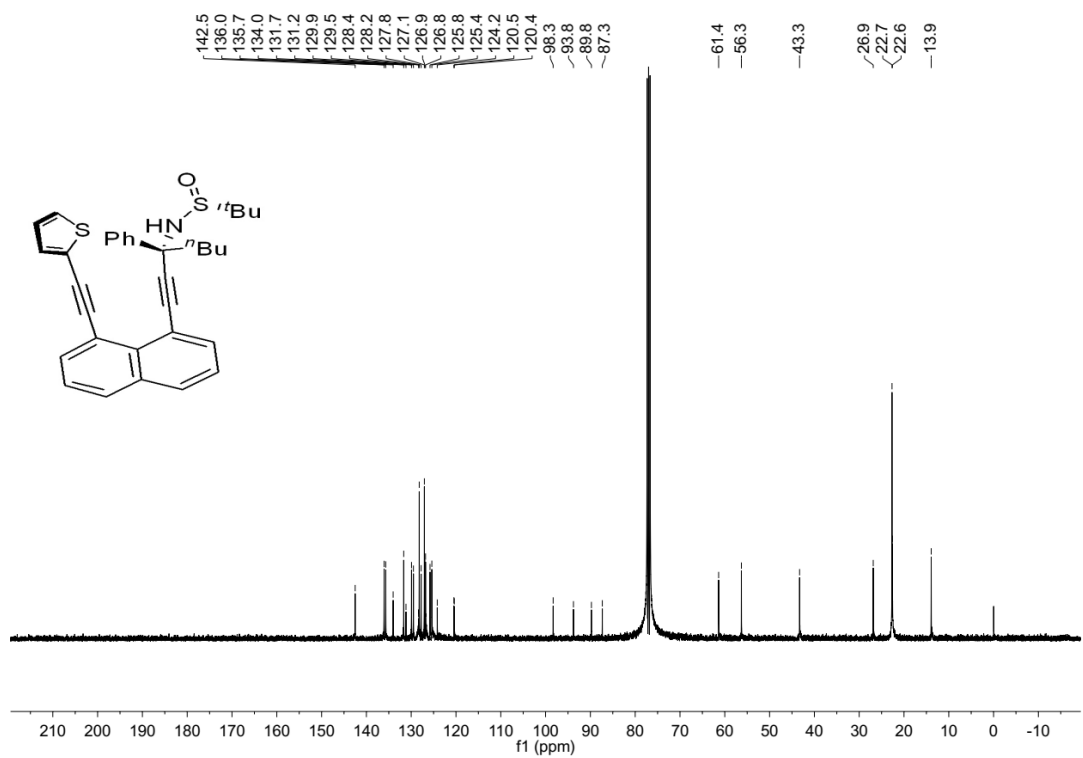
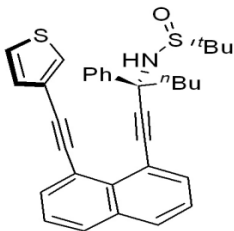


Figure S68. ¹³C NMR Spectrum of Compound 7ac (CDCl₃, 100 MHz)



Chemical structure of compound 10: C#Cc1ccc2c(c1)c(c3ccccc3S2)C#Cc4ccccc4C#Cc5ccccc5S6

¹³C NMR spectrum (CDCl₃) of compound 10. The x-axis represents the chemical shift in ppm, ranging from -10 to 210. The spectrum shows several sharp peaks corresponding to the carbon atoms in the molecule.

Chemical shift values (ppm) labeled on the spectrum:

- 142.6
- 136.0
- 135.4
- 134.1
- 131.3
- 130.0
- 129.6
- 129.5
- 128.3
- 128.2
- 127.8
- 127.0
- 126.7
- 125.4
- 124.8
- 123.1
- 120.7
- 120.5
- 97.9
- 91.8
- 89.5
- 87.5
- 61.2
- 56.3
- 43.3
- 26.9
- 22.7
- 22.6
- 13.9

S62

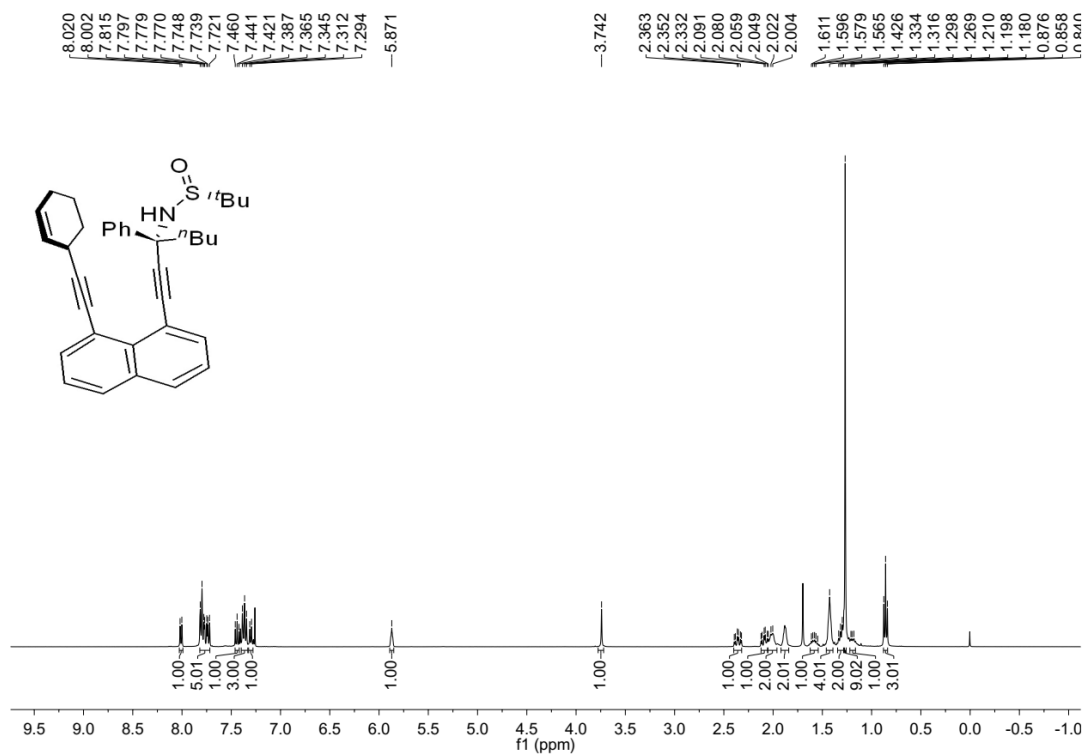


Figure S71. ¹H NMR Spectrum of Compound 7ae (CDCl₃, 400 MHz)

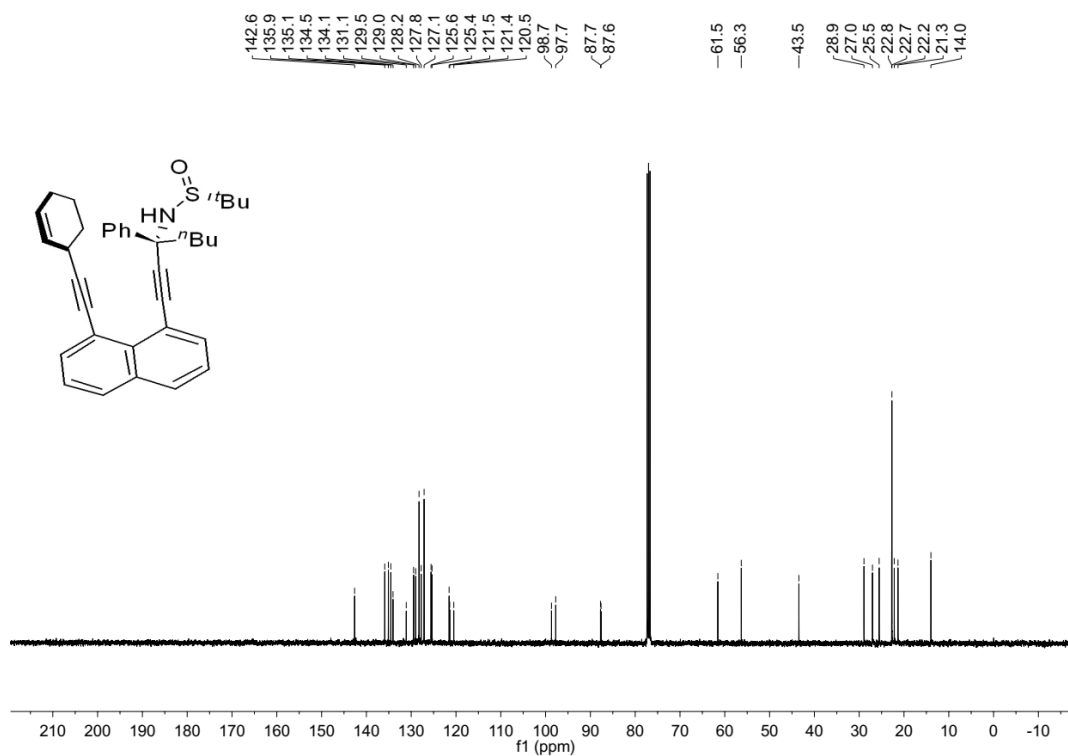


Figure S72. ¹³C NMR Spectrum of Compound 7ae (CDCl₃, 100 MHz)

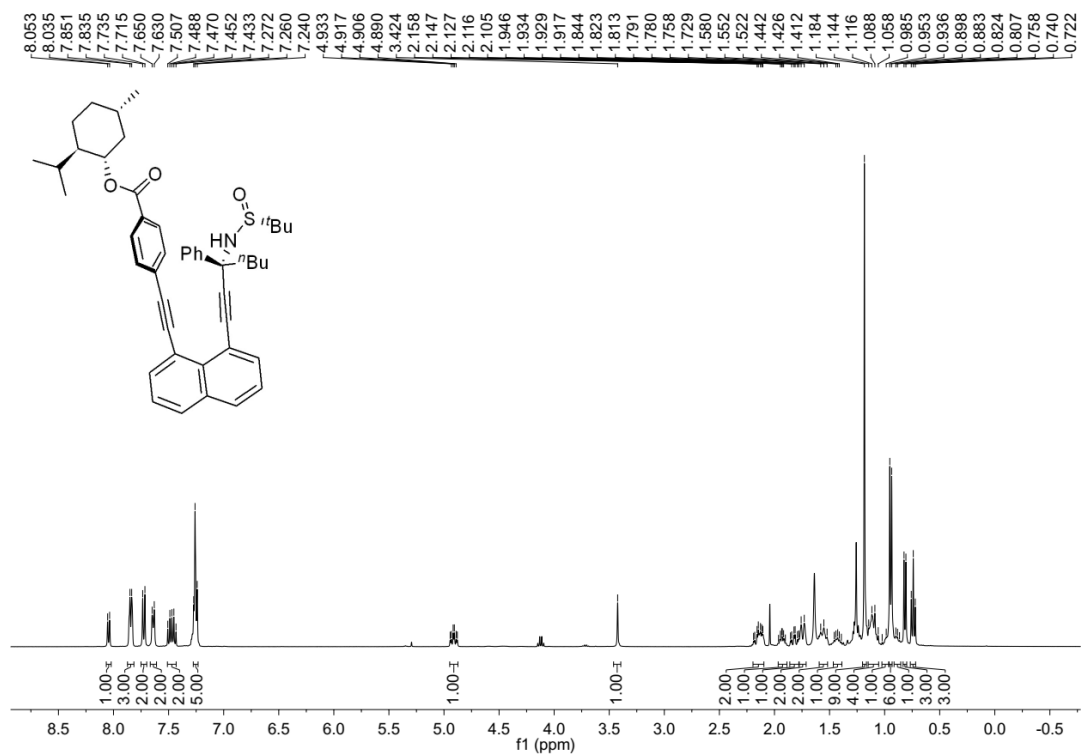


Figure S75. ¹H NMR Spectrum of Compound 7ag (CDCl₃, 400 MHz)

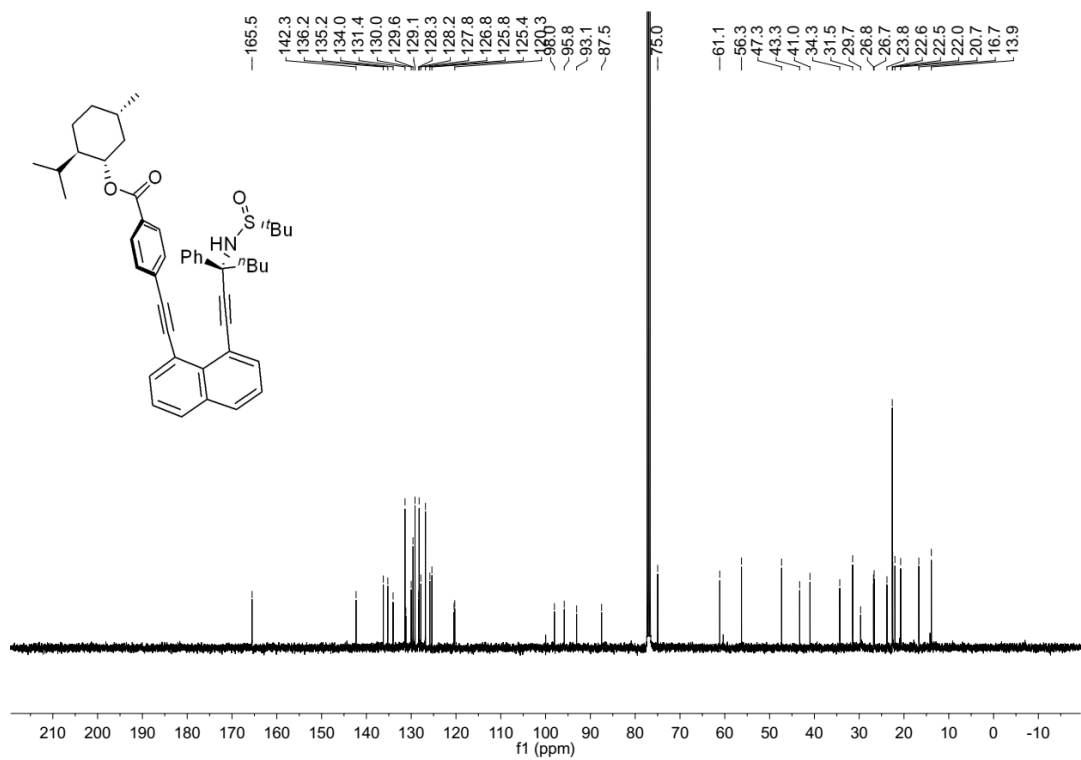


Figure S76. ¹³C NMR Spectrum of Compound 7ag (CDCl₃, 100 MHz)

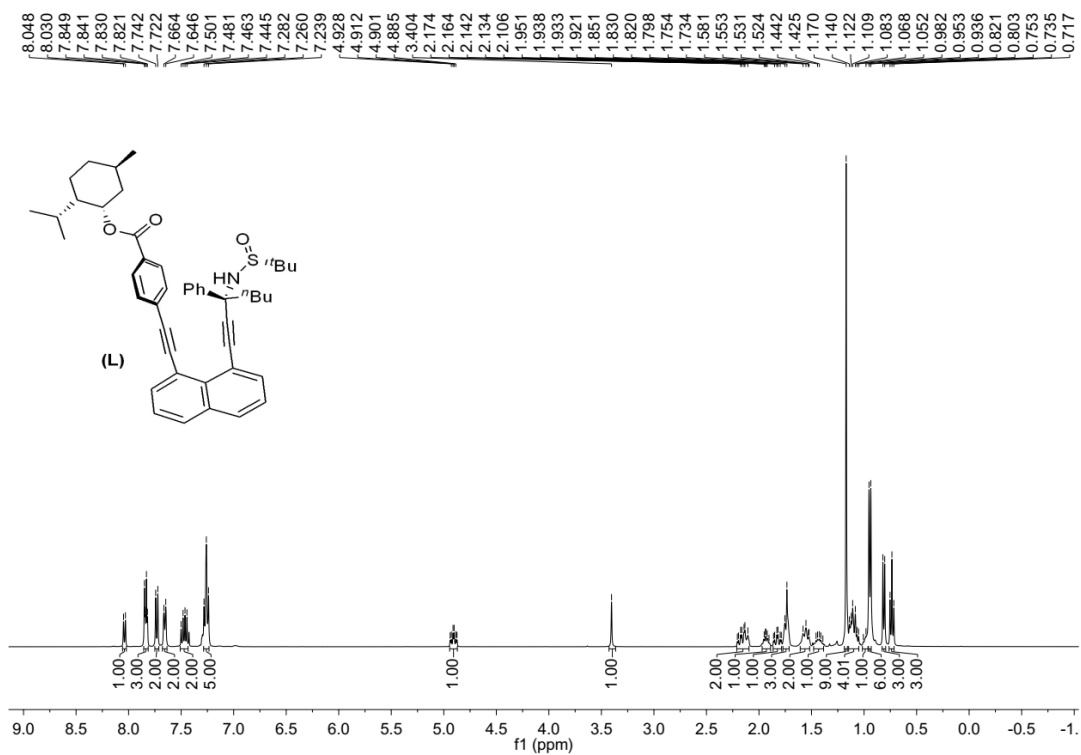


Figure S77. ¹H NMR Spectrum of Compound 7ah (CDCl₃, 400 MHz)

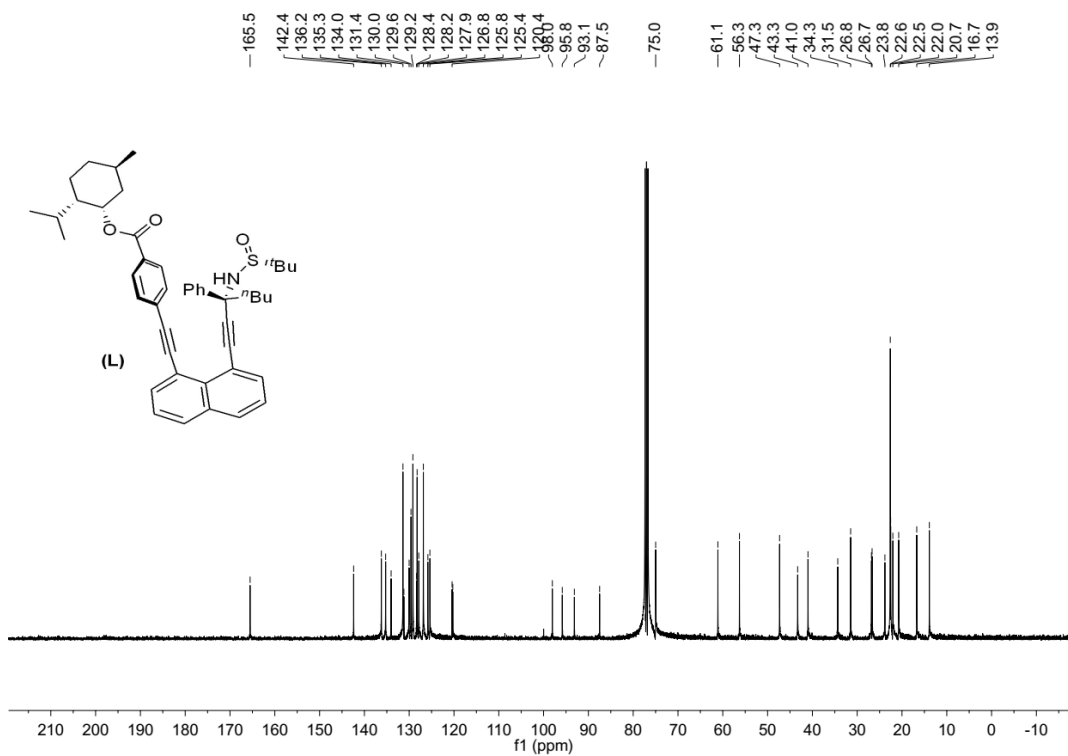
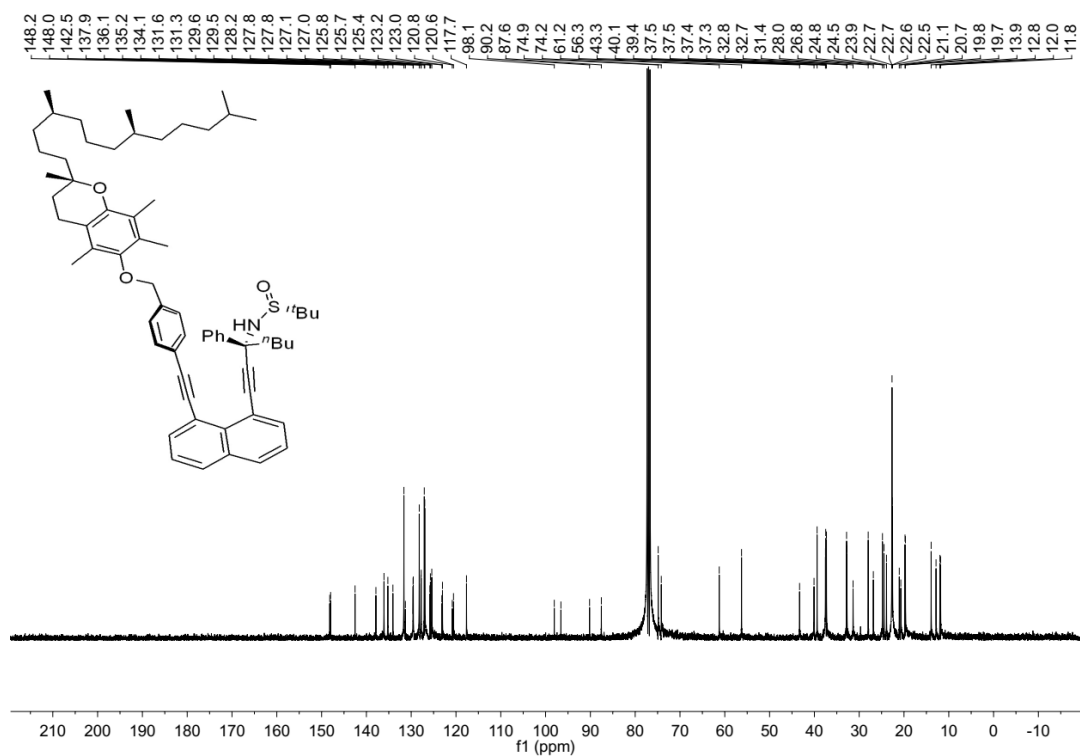
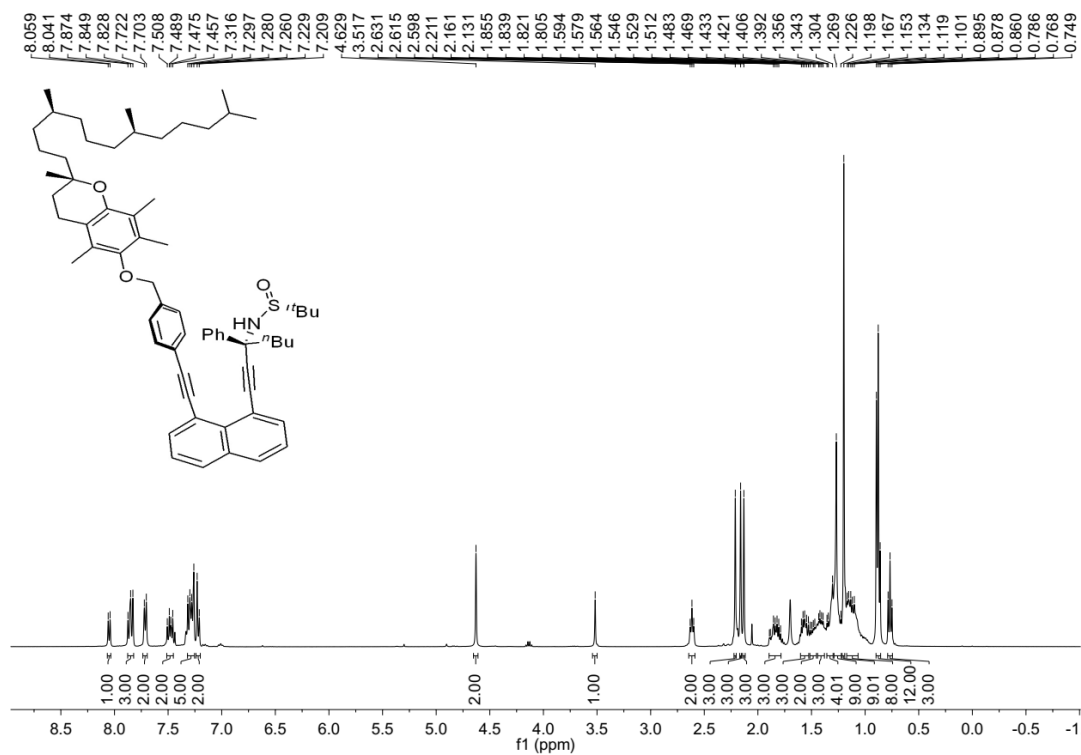
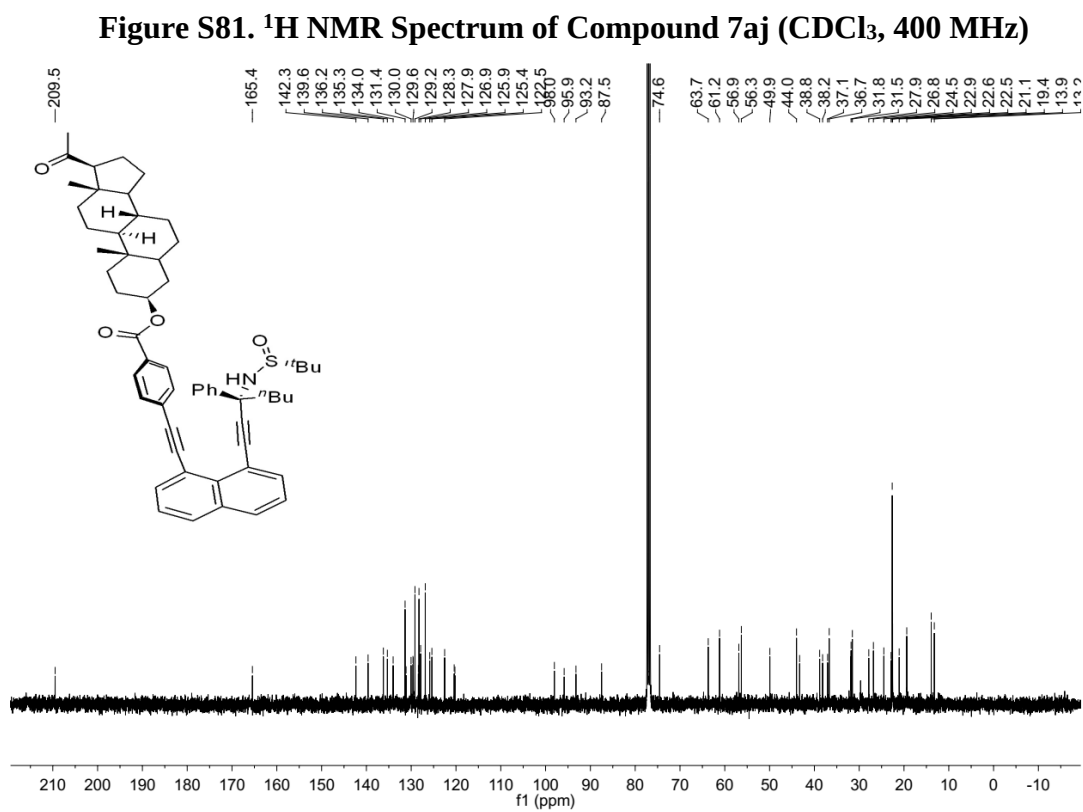
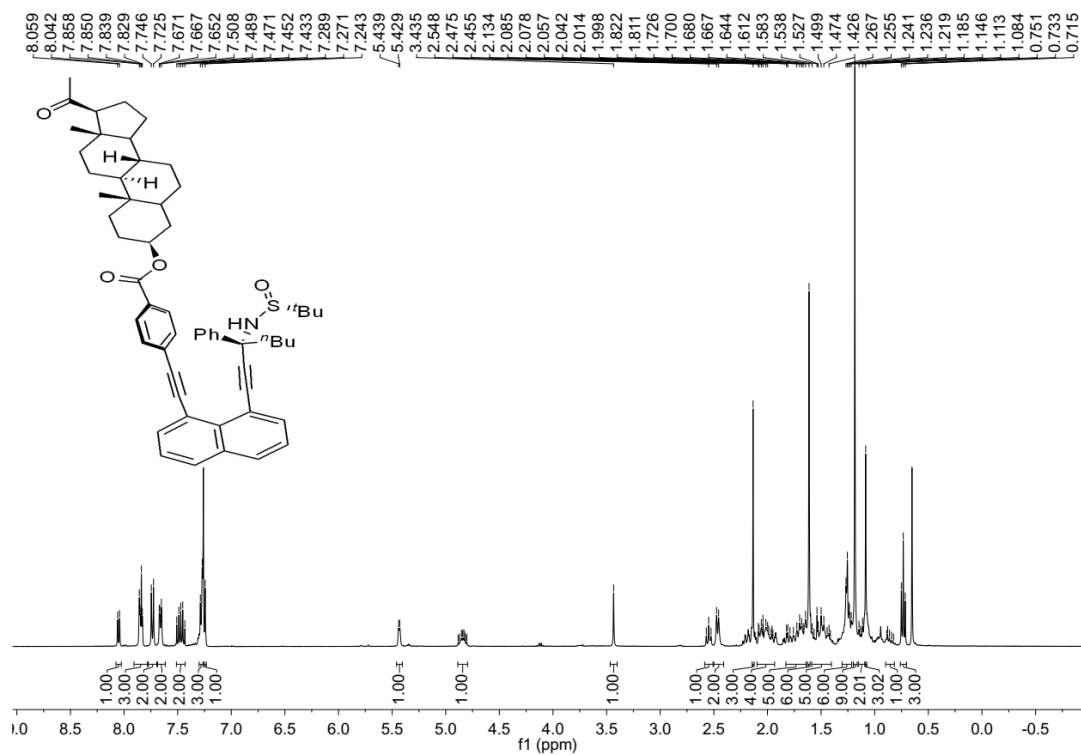


Figure S78. ¹³C NMR Spectrum of Compound 7ah (CDCl₃, 100 MHz)





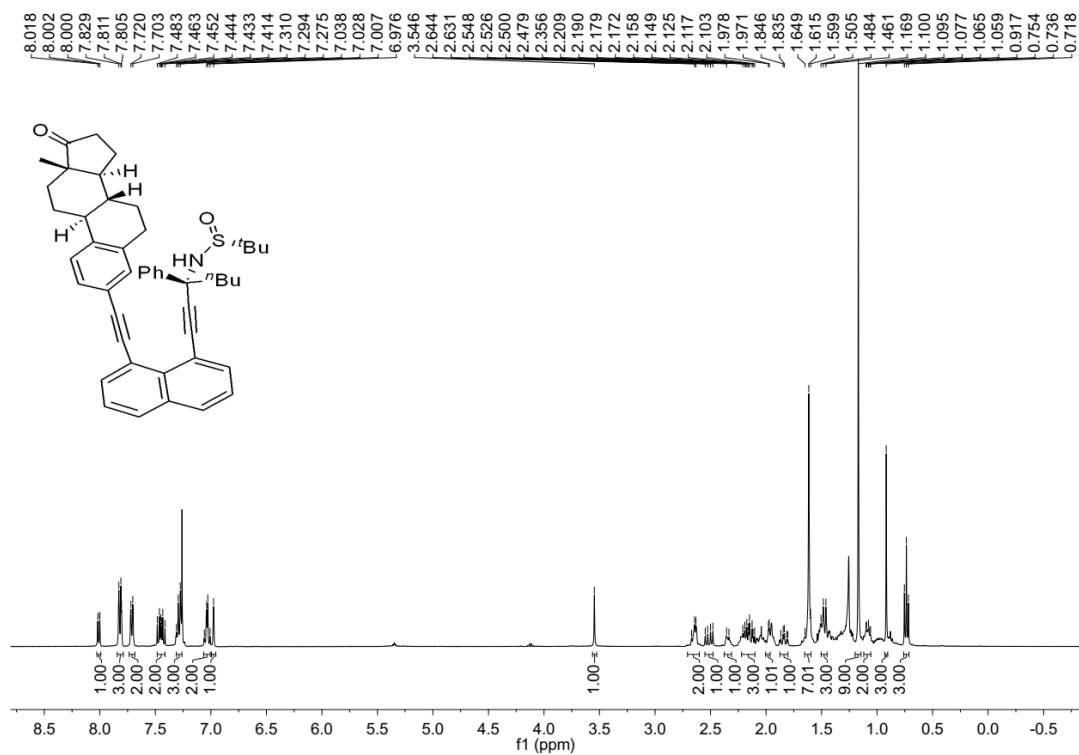


Figure S83. ¹H NMR Spectrum of Compound 7ak (CDCl₃, 400 MHz)

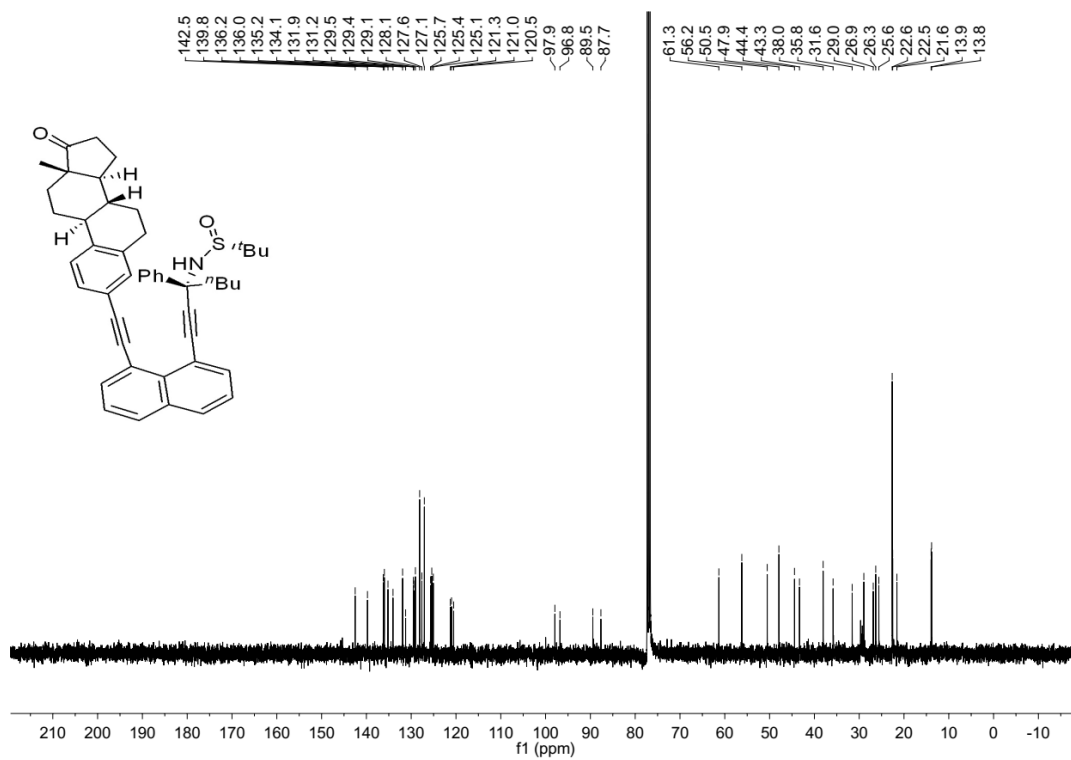


Figure S84. ¹³C NMR Spectrum of Compound 7ak (CDCl₃, 100 MHz)

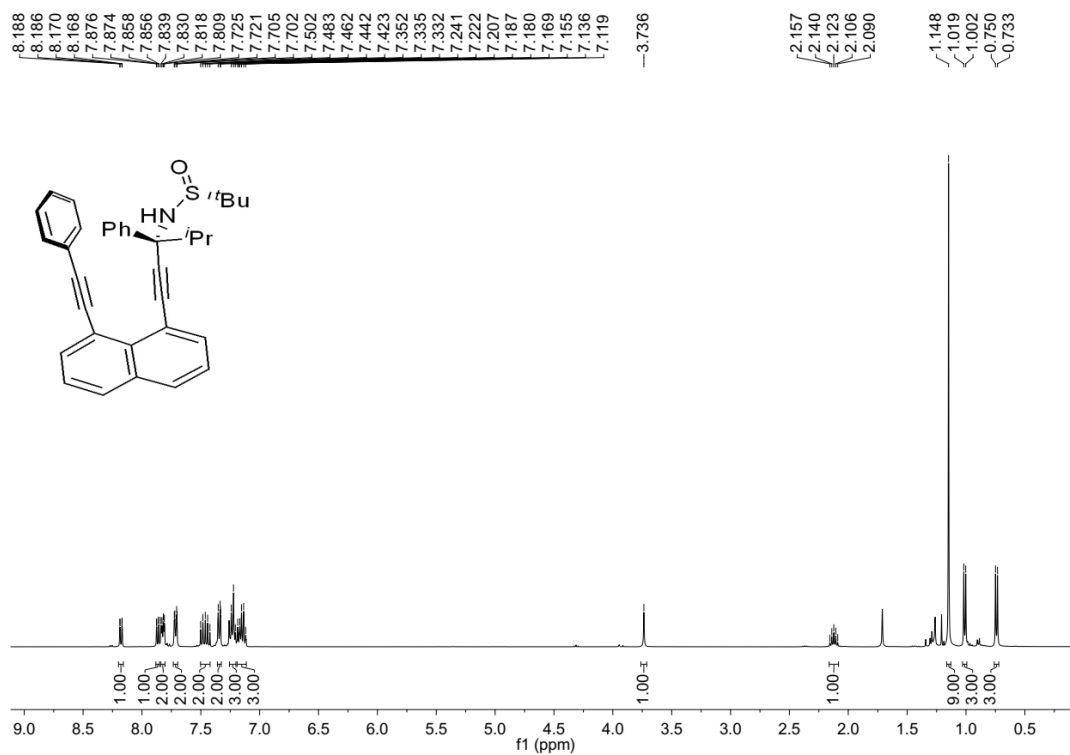


Figure S85. ¹H NMR Spectrum of Compound 7ba (CDCl₃, 400 MHz)

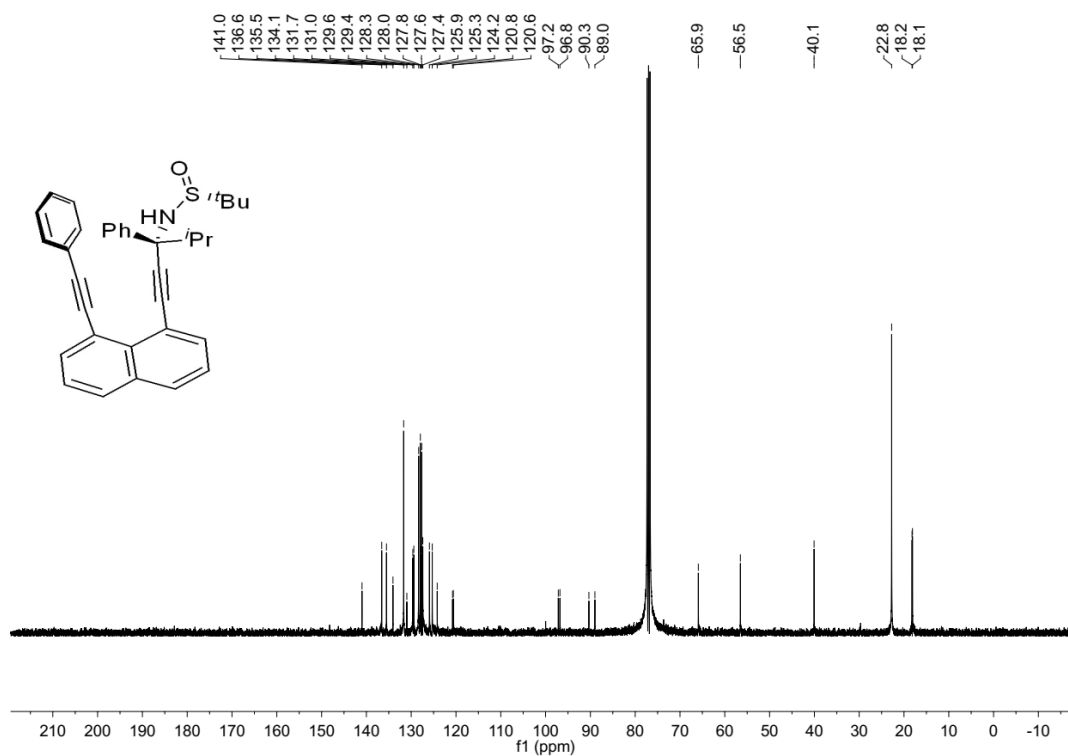


Figure S86. ¹³C NMR Spectrum of Compound 7ba (CDCl₃, 100 MHz)

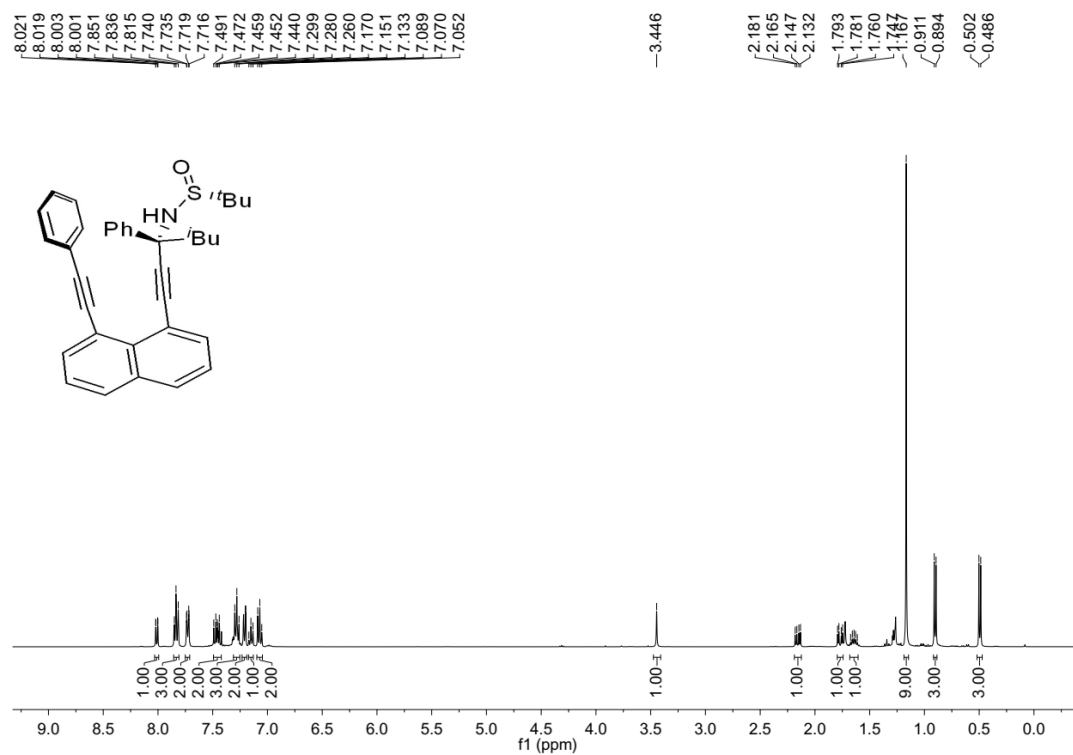


Figure S87. ¹H NMR Spectrum of Compound 7bb (CDCl₃, 400 MHz)

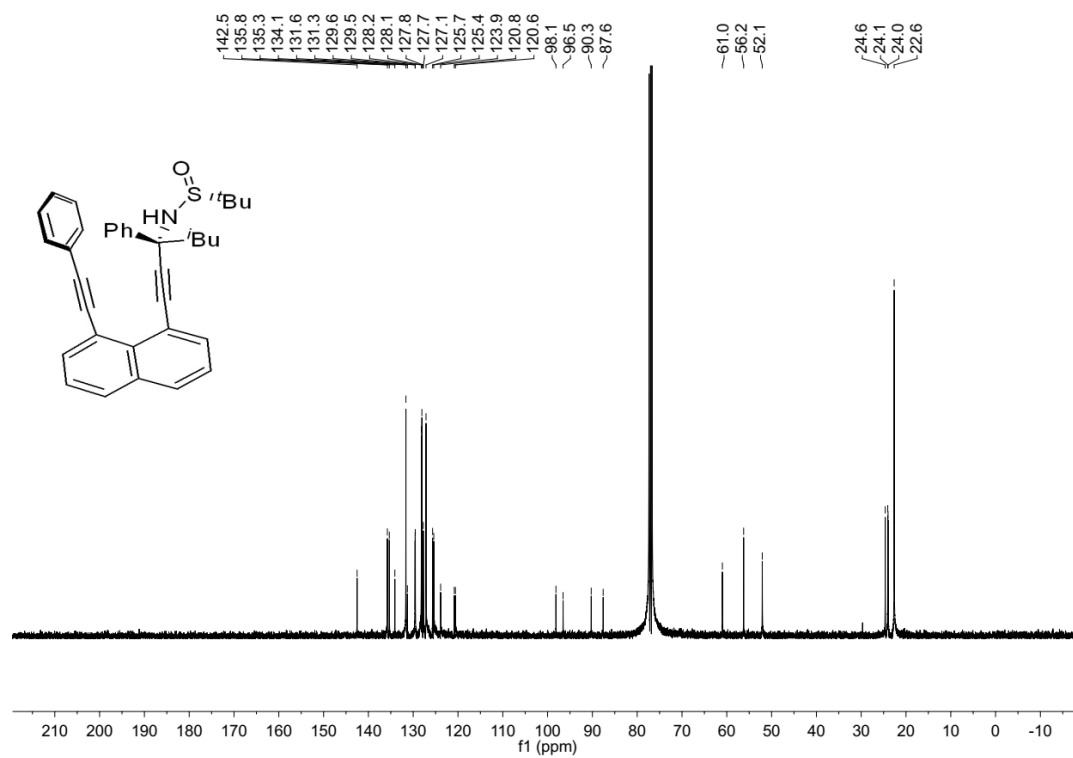


Figure S88. ¹³C NMR Spectrum of Compound 7bb (CDCl₃, 100 MHz)

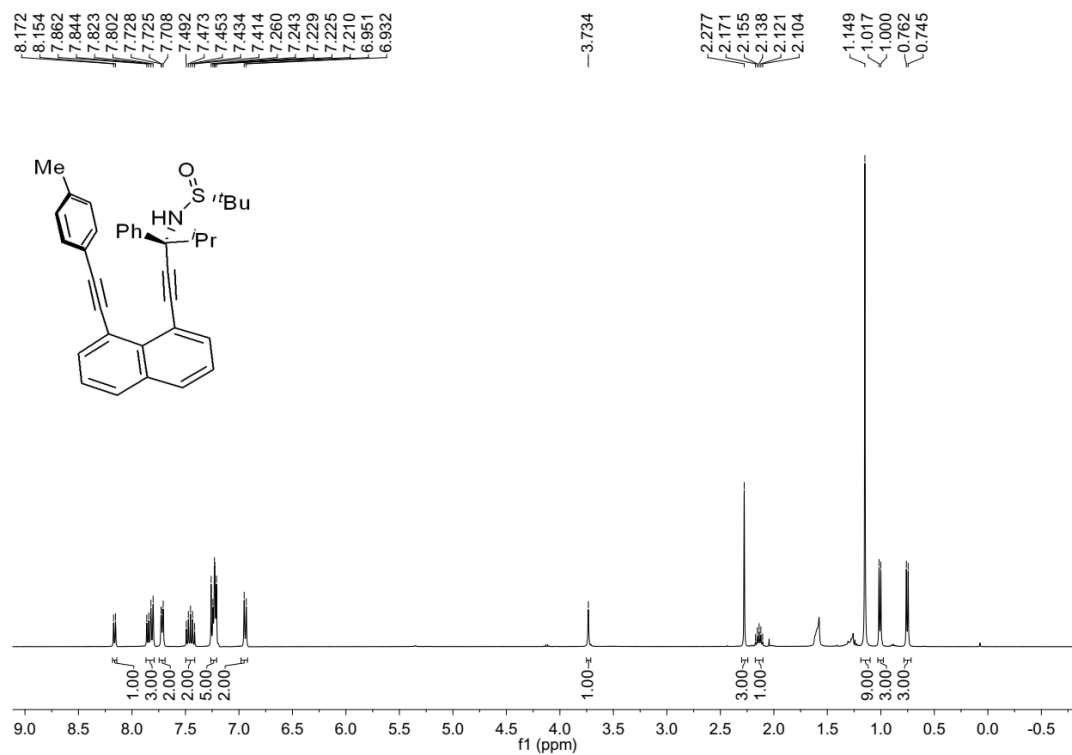


Figure S89. ¹H NMR Spectrum of Compound 7bc (CDCl₃, 400 MHz)

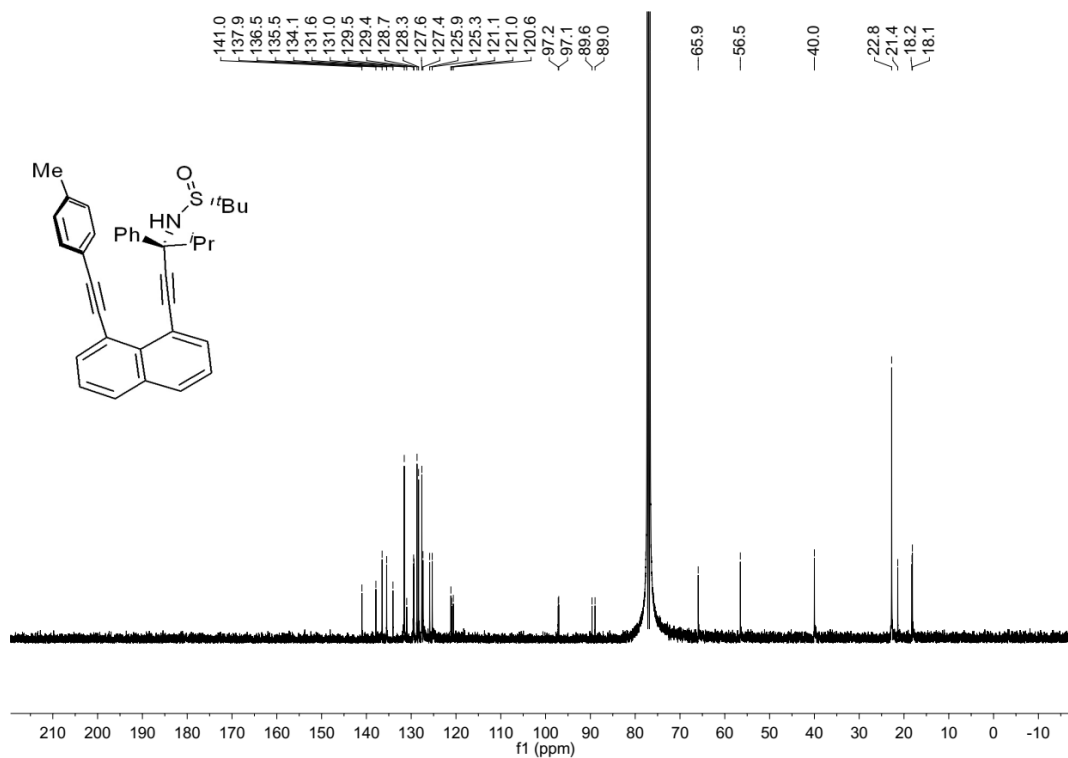


Figure S90. ¹³C NMR Spectrum of Compound 7bc (CDCl₃, 100 MHz)

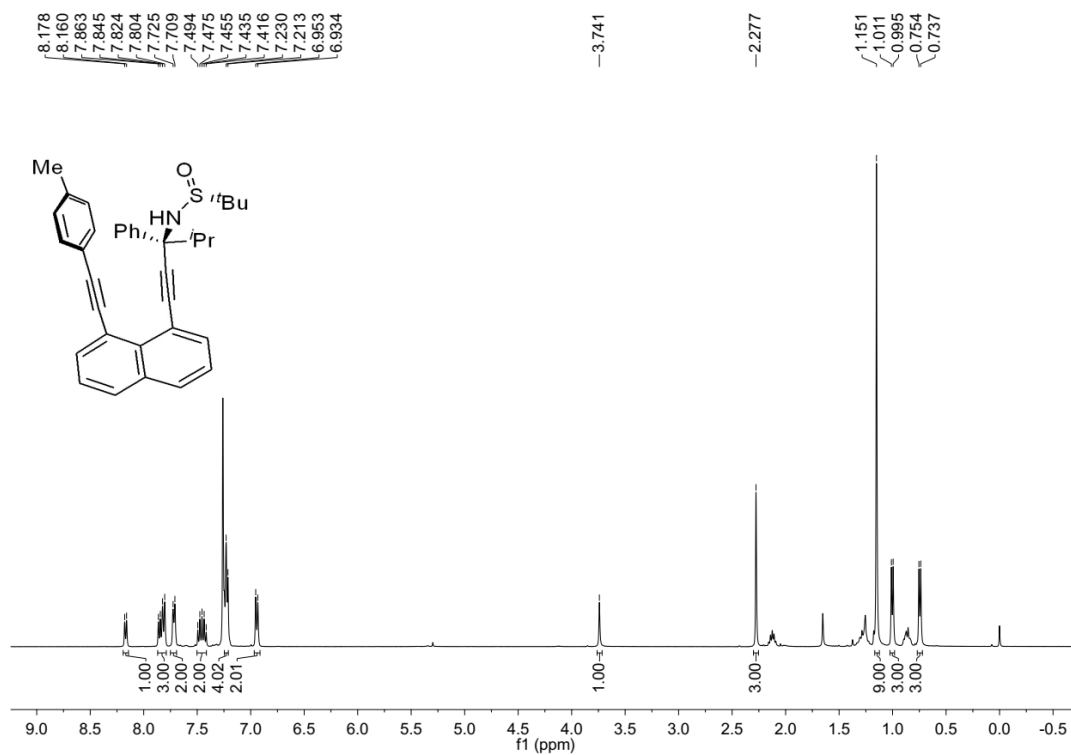


Figure S91. ¹H NMR Spectrum of Compound 7bc' (CDCl₃, 400 MHz)

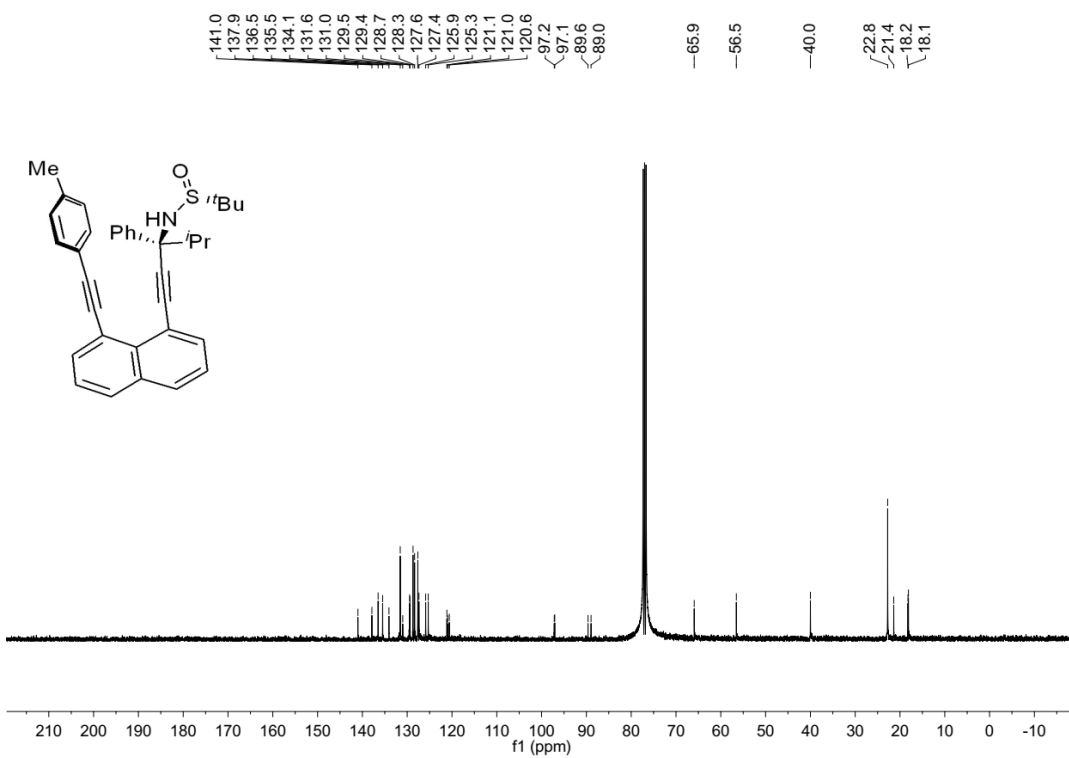


Figure S92. ¹³C NMR Spectrum of Compound 7bc' (CDCl₃, 100 MHz)

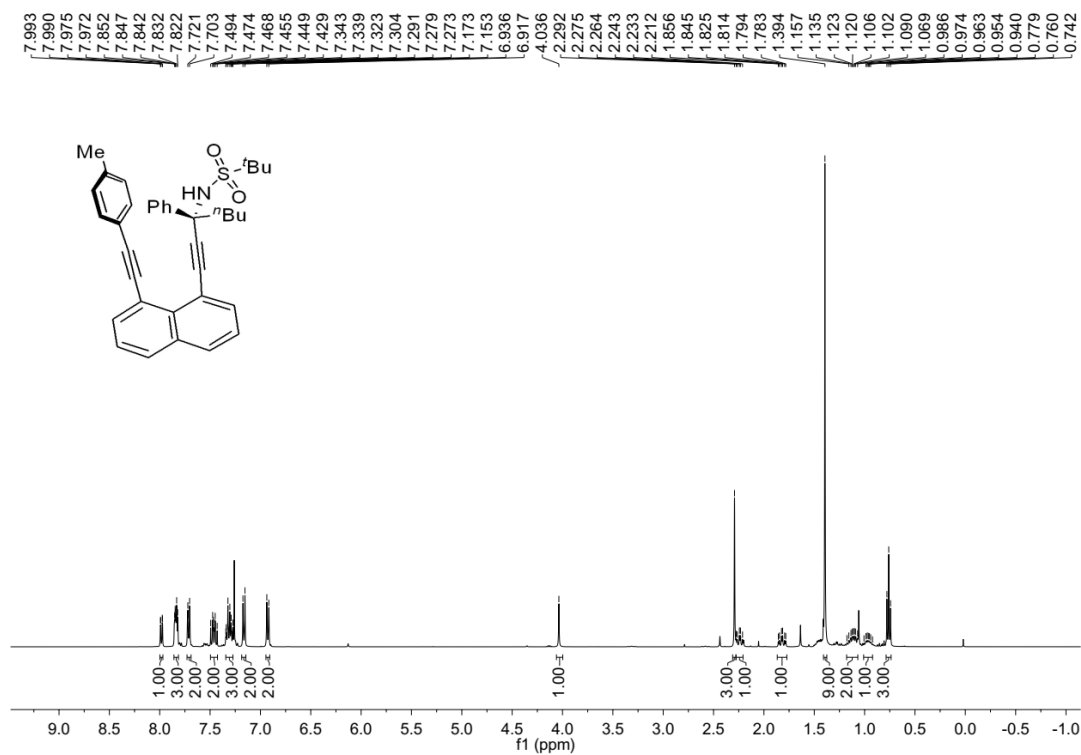


Figure S93. ¹H NMR Spectrum of Compound 8a (CDCl₃, 400 MHz)

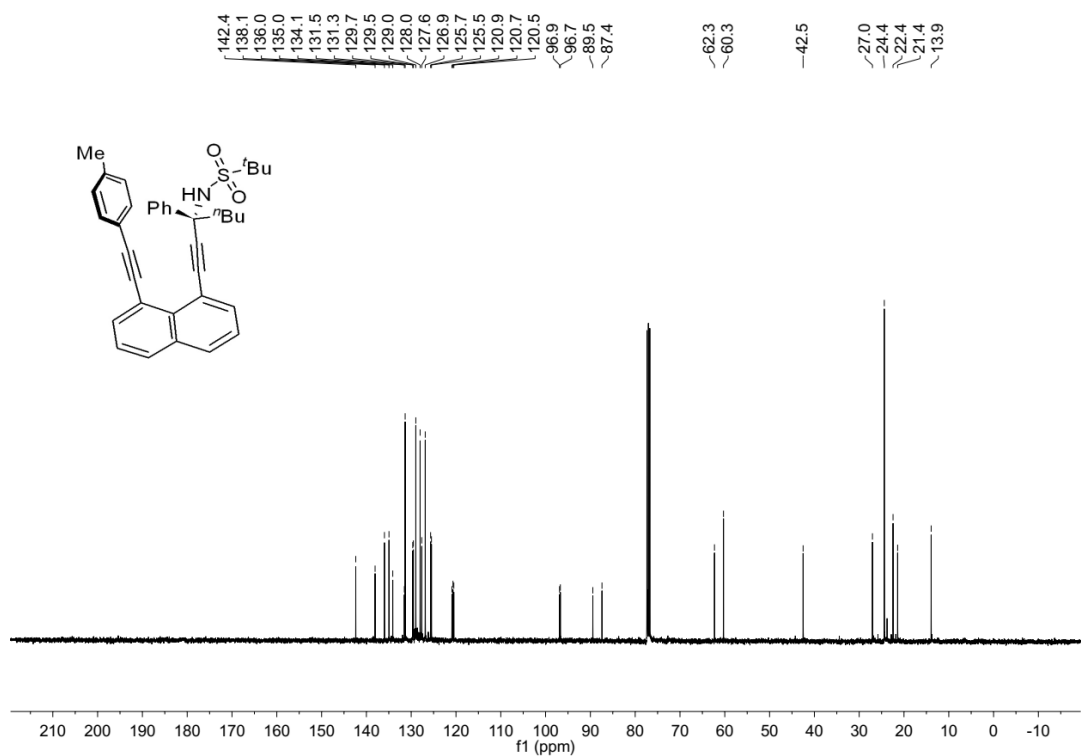


Figure S94. ¹³C NMR Spectrum of Compound 8a (CDCl₃, 100 MHz)

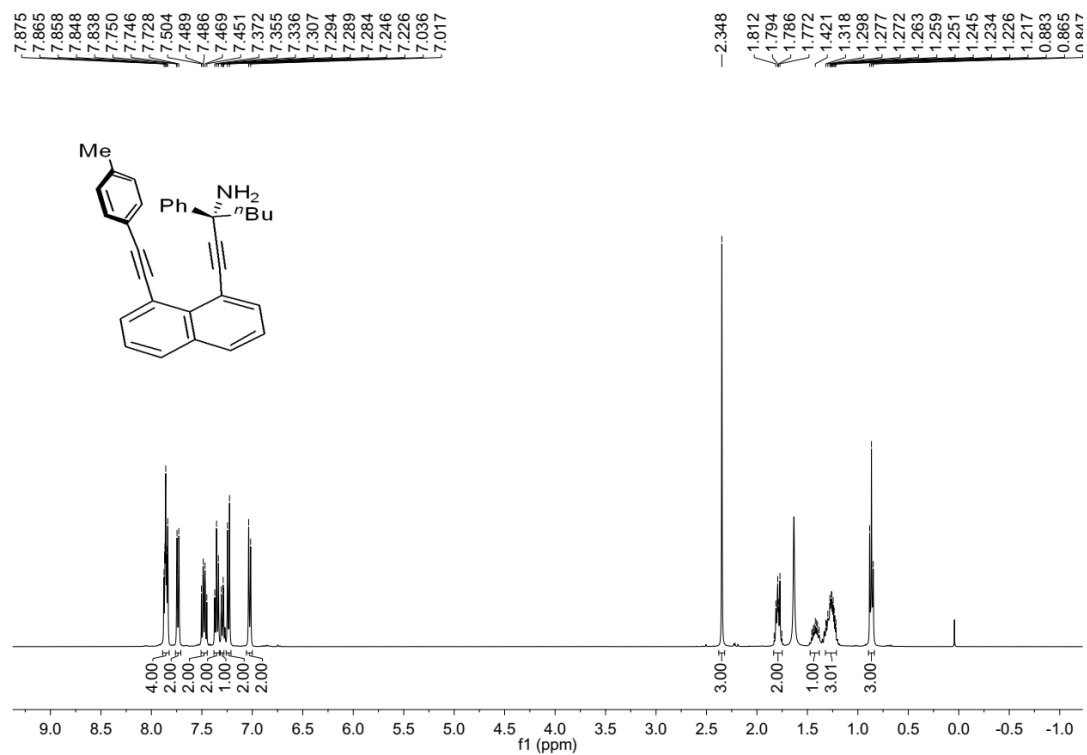


Figure S95. ¹H NMR Spectrum of Precursor 8b (CDCl₃, 400 MHz)

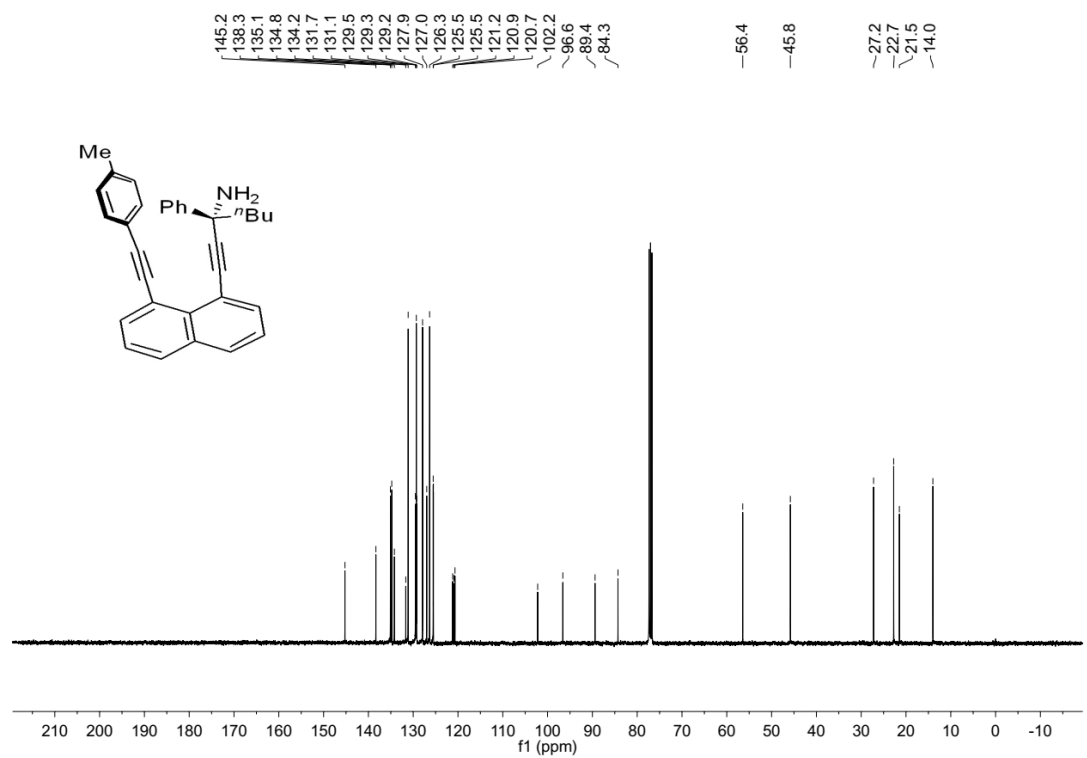
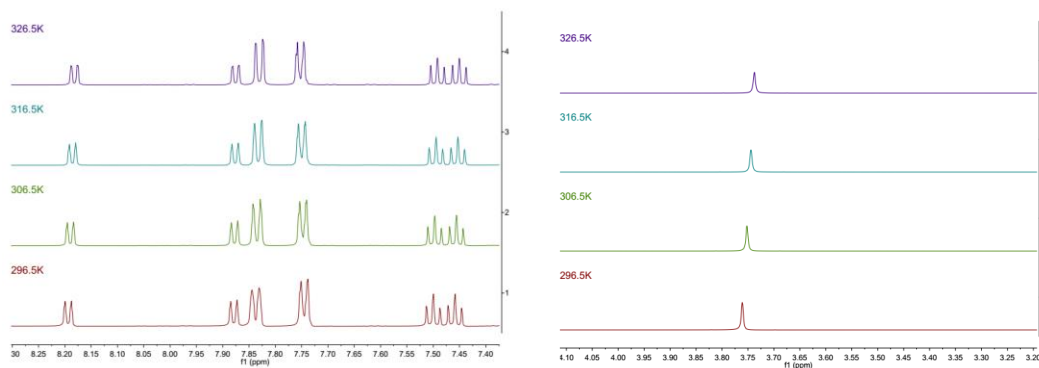


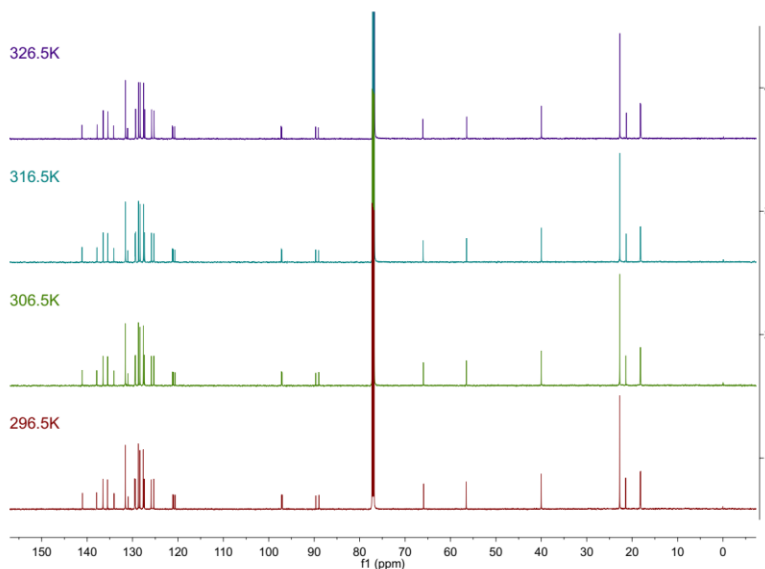
Figure S96. ¹³C NMR Spectrum of Precursor 8b (CDCl₃, 100 MHz)

4 VT NMR of Compound **7bc**



¹H VT-NMR spectra of **7bc in CDCl₃.**

(The spectra above were acquired in 10-degree increments between 25 °C and 55 °C.)



¹³C VT-NMR spectra of **7bc in CDCl₃.**

(The spectra above were acquired in 10-degree increments between 25 °C and 55 °C.)

According to DFT studies, when increasing the temperature, one of the conformations of **7bc-2**, **7bc-3** may be observed. In **7bc-3**, the isopropyl group is closer to the left aromatic ring and may be subject to the shielding effect of this aromatic ring, leading to a lower field shift in the H chemical shift of isopropyl group. After undergoing **VT-NMR**, we can clearly see that whether it is the chemical shift of H or the chemical shift of C, all peaks remain consistent, indicating that the structure shown in the **7bc** is the most stable isomer.

5 X-ray Single-crystal Data for Compound **7bc** and **7bc'**

Table S1 Crystal data and structure refinement of **7bc**.

Identification code	CCDC 2303102
Empirical formula	C ₃₅ H ₃₅ NOS
Formula weight	517.70
Temperature/K	298(2)
Crystal system	trigonal
Space group	P3 ₂
a/Å	13.6015(14)
b/Å	13.6015(14)
c/Å	13.3008(15)
$\alpha/^\circ$	90.00
$\beta/^\circ$	90.00
$\gamma/^\circ$	120.00
Volume/Å ³	2131.0(4)
Z	3
$\rho_{\text{calc}}/\text{g}/\text{cm}^3$	1.210
μ/mm^{-1}	0.142
F(000)	828.0
Crystal size/mm ³	0.4 × 0.11 × 0.1
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/ $^\circ$	4.62 to 50.04
Index ranges	-16 ≤ h ≤ 11, -16 ≤ k ≤ 16, -15 ≤ l ≤ 15
Reflections collected	10359
Independent reflections	4970 [R_{int} = 0.0681, R_{sigma} = 0.1029]

Data/restraints/parameters	4970/1/378
Goodness-of-fit on F^2	1.013
Final R indexes [$I \geq 2\sigma(I)$]	$R_1 = 0.0592$, $wR_2 = 0.1188$
Final R indexes [all data]	$R_1 = 0.0938$, $wR_2 = 0.1299$
Largest diff. peak/hole / $e \text{ \AA}^{-3}$	0.17/-0.24
Flack parameter	0.03(10)

Table S2 Crystal data and structure refinement of **7bc'**.

Identification code	CCDC 2303103
Empirical formula	$C_{35}H_{35}NOS$
Formula weight	517.70
Temperature/K	298(2)
Crystal system	trigonal
Space group	$P3_1$
$a/\text{\AA}$	13.5845(12)
$b/\text{\AA}$	13.5845(12)
$c/\text{\AA}$	13.2817(11)
$\alpha/^\circ$	90.00
$\beta/^\circ$	90.00
$\gamma/^\circ$	120.00
Volume/ $\text{\AA}^3$	2122.6(3)
Z	3
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.215
μ/mm^{-1}	0.143
F(000)	828.0

Crystal size/mm ³	0.3 × 0.22 × 0.14
Radiation	MoK α (λ = 0.71073)
2 Θ range for data collection/°	4.62 to 50.04
Index ranges	-15 ≤ h ≤ 16, -14 ≤ k ≤ 16, -15 ≤ l ≤ 15
Reflections collected	10284
Independent reflections	4799 [R_{int} = 0.0386, R_{sigma} = 0.0549]
Data/restraints/parameters	4799/1/350
Goodness-of-fit on F^2	1.092
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0445, wR_2 = 0.0959
Final R indexes [all data]	R_1 = 0.0703, wR_2 = 0.1122
Largest diff. peak/hole / e Å ⁻³	0.15/-0.26
Flack parameter	-0.06(9)