

# Supporting Information

## Visible-light-induced radical cascade cyclization of 1-(allyloxy)-2-(1-arylviny)benzenes with sulfonyl chlorides for the synthesis of sulfonated benzoxepines

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### General Information:

All reactions were carried out under Ar atmosphere unless otherwise noted. All catalysts, solvents and sulfonyl chlorides were obtained from commercial suppliers. Reactions were monitored by TLC on silica gel plates (GF254), and the analytical thin-layer chromatography (TLC) was performed on precoated, glass-backed silica gel plates. <sup>1</sup>H NMR, <sup>13</sup>C NMR and <sup>19</sup>F NMR spectra were recorded on 400 MHz spectrometer at room temperature. Chemical shifts ( $\delta$ ) are reported in ppm downfield from tetramethylsilane. High resolution mass spectra were obtained on a high-resolution mass spectrometer in the ESI or APCI mode. All substrates **1a-1p** were synthesized according to the literature.<sup>1</sup>

### General procedure for the synthesis of **3**

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1** (0.1 mmol), sulfonyl chlorides **2** (2 equiv, 0.2 mmol), Na<sub>2</sub>CO<sub>3</sub> (2.5 equiv, 0.25 mmol), Eosin Y (2 mol%). The flask was evacuated and backfilled with Ar for 3 times. 1 mL CH<sub>3</sub>CN was added with syringe under Ar. The tube was placed exposed to 12 W Blue LED light at 100°C. After the reaction was finished, the organic solvent was removed under the reduced pressure. The residue was purified by column chromatography (petroleum ether/ethyl acetate, 5:1) to afford the desired products **3**.

### Experimental Procedure for Gram-up Reaction

An oven-dried Schlenk tube (100 mL) was equipped with a magnetic stir bar, **1a** (5 mmol), *p*-tosyl chloride **2a** (2 equiv, 10 mmol), Na<sub>2</sub>CO<sub>3</sub> (2.5 equiv, 12.5 mmol), Eosin Y (2 mol%). The flask was evacuated and backfilled with Ar for 3 times. Then 60 mL CH<sub>3</sub>CN was added under Ar. The tube was placed exposed to 12 W Blue LED light at 100°C. After the reaction was finished, the solvent was concentrated in vacuo and the residue was purified by chromatography on silica gel to afford the corresponding products **3aa** in 82% yield.

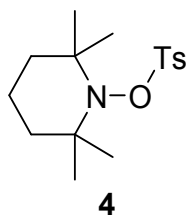
### Trapping experiment with TEMPO

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1a** (0.1 mmol), *p*-tosyl chloride **2a** (2 equiv, 0.2 mmol), Na<sub>2</sub>CO<sub>3</sub> (2.5 equiv, 0.25 mmol), Eosin Y (2 mol%), TEMPO (2.5 equiv, 0.25 mmol). The flask was evacuated and backfilled with Ar for 3 times. Then 1 mL CH<sub>3</sub>CN was added under Ar. The tube was placed exposed to 12 W Blue LED light at 100°C. However, product **3aa** could not be detected, **1a** was almost completely recovered and the intermediate **4** was formed.

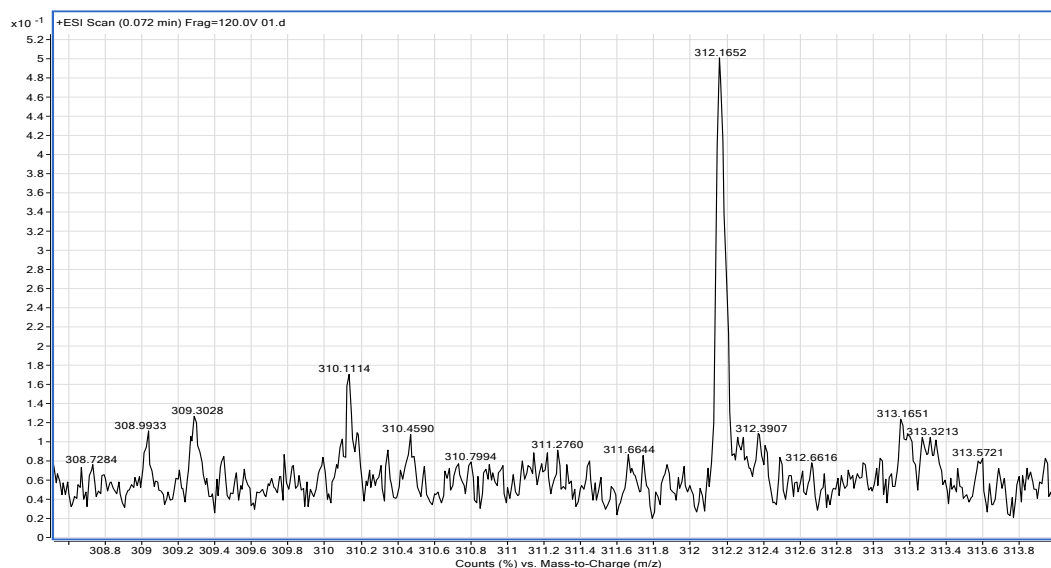
### Trapping experiment with 1,4-dinitrobenzene

An oven-dried Schlenk tube (10 mL) was equipped with a magnetic stir bar, **1a** (0.1 mmol), *p*-tosyl chloride **2a** (2 equiv, 0.2 mmol), Na<sub>2</sub>CO<sub>3</sub> (2.5 equiv, 0.25 mmol), Eosin Y (2 mol%), 1,4-dinitrobenzene (2.5 equiv, 0.25 mmol). The flask was evacuated and backfilled with Ar for 3 times. Then 1 mL CH<sub>3</sub>CN was added under Ar. The tube was placed exposed to 12 W Blue LED light at 100°C. However, no desired product **3aa** was detected, and **1a** was almost completely recovered.

### The HRMS (ESI) for the intermediate 4

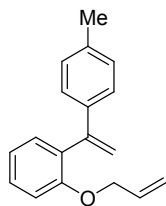


HRMS [4+H]<sup>+</sup>: Calcd: 312.1628; Found: 312.1652.

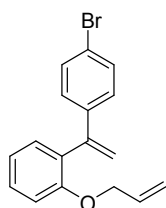


### Reference:

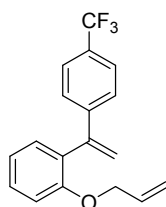
[1] (a) A.-R. Li, H.-M. Chen, P.-Y. Chen, J.-C. Tsai, L.-Y. Chen, E.-C. Wang, Y.-T. Huang, Y.-C. Wei, P.-J. Lu, *J. Chin. Chem. Soc.*, **2008**, *55*, 923-932; (b) N. Wu, R. Li, F. Cui, Y. Pan, *Adv. Synth. Catal.* **2017**, *359*, 2442-2447.



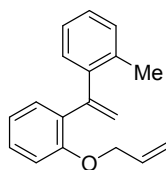
*1-(allyloxy)-2-(1-(p-tolyl)vinyl)benzene (1b)*. Yellow oil;  $R_f = 0.46$  (petroleum ether/ethyl acetate 50:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.31\text{-}7.24$  (m, 2H),  $7.21\text{-}6.83$  (m, 2H),  $7.08\text{-}7.06$  (m, 2H),  $7.00\text{-}6.96$  (m, 2H),  $6.88$  (d,  $J = 8.0$  Hz, 1H),  $5.71\text{-}5.62$  (m, 2H),  $5.28$  (d,  $J = 1.6$  Hz, 1H),  $5.06\text{-}5.01$  (m, 2H),  $4.37\text{-}4.35$  (m, 2H),  $2.33$  (s, 3H) ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 156.0, 147.0, 138.5, 136.9, 133.1, 131.7, 131.3, 128.8, 126.3, 120.8, 116.4, 114.7, 112.8, 69.0, 21.1$  ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{18}\text{H}_{18}\text{O}+\text{Na}^+$ : 273.1250, found 273.1249.



*1-(allyloxy)-2-(1-(4-bromophenyl)vinyl)benzene (1c)*. Yellow oil;  $R_f = 0.48$  (petroleum ether/ethyl acetate 50:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.40\text{-}7.36$  (m, 2H),  $7.33\text{-}7.24$  (m, 2H),  $7.18\text{-}7.14$  (m, 2H),  $7.01\text{-}6.97$  (m, 1H),  $6.87$  (d,  $J = 8.4$  Hz, 1H),  $5.70\text{-}5.60$  (m, 2H),  $5.34$  (d,  $J = 1.4$  Hz, 1H),  $5.06\text{-}4.99$  (m, 2H),  $4.35\text{-}4.33$  (m, 2H) ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 155.9, 146.4, 140.4, 132.8, 131.2, 131.0, 130.8, 129.2, 128.1, 121.1, 120.9, 116.6, 116.0, 112.6, 68.9$  ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{BrO}+\text{H}^+$ : 315.0379, found 315.0388.

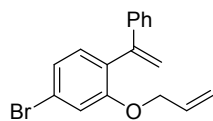


*1-(allyloxy)-2-(1-(4-(trifluoromethyl)phenyl)vinyl)benzene (1d)*. Yellow oil;  $R_f = 0.48$  (petroleum ether/ethyl acetate 50:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.52$  (d,  $J = 8.4$  Hz, 2H),  $7.39$  (d,  $J = 8.4$  Hz, 2H),  $7.34\text{-}7.29$  (m, 2H),  $7.01$  (t,  $J = 7.6$  Hz, 1H),  $6.88$  (d,  $J = 8.0$  Hz, 1H),  $5.71$  (s, 1H),  $5.64\text{-}5.54$  (m, 1H),  $5.44$  (s, 1H),  $5.01\text{-}4.93$  (m, 2H),  $4.31$  (d,  $J = 5.2$  Hz, 2H) ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta = 155.9, 146.5, 145.2, 132.6, 131.2, 130.5, 129.4, 129.1$  (q,  $J = 40.1$  Hz),  $126.7, 124.9$  (q,  $J = 4.7$  Hz),  $124.3$  (q,  $J = 340.3$  Hz),  $121.0, 117.4, 116.7, 112.6, 68.9$  ppm;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta = -62.3$  ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{18}\text{H}_{15}\text{F}_3\text{O}+\text{H}^+$ : 305.1148, found 305.1139.

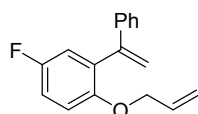


*1-(allyloxy)-2-(1-(o-tolyl)vinyl)benzene (1e)*. Yellow oil;  $R_f = 0.55$  (petroleum ether/ethyl acetate 50:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.22\text{-}7.10$  (m, 6H),  $6.91\text{-}6.83$  (m, 2H),  $5.78\text{-}5.69$  (m, 2H),

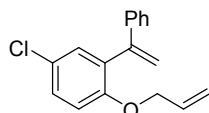
5.35 (d,  $J = 2.4$  Hz, 1H), 5.21-5.10 (m, 2H), 4.38-4.36 (m, 2H), 2.12 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.0, 146.9, 142.9, 135.5, 133.2, 131.4, 130.5, 130.0, 129.4, 128.5, 126.8, 125.3, 120.7, 119.0, 117.0, 112.8, 69.2, 20.4 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{18}\text{H}_{18}\text{O}+\text{H}^+$ : 251.1430, found 251.1425.



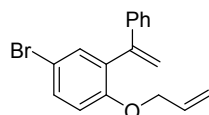
*2-(allyloxy)-4-bromo-1-(1-phenylvinyl)benzene (Ih)*. Yellow oil;  $R_f = 0.50$  (petroleum ether/ethyl acetate 50:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.28$ -7.25 (m, 5H), 7.16-7.11 (m, 2H), 7.00 (s, 1H), 5.68 (s, 1H), 5.64-5.55 (m, 1H), 5.32 (s, 1H), 5.04-4.97 (m, 2H), 4.34-4.32 (m, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.6, 146.4, 140.9, 132.3, 132.2, 130.5, 128.0, 127.4, 126.4, 123.9, 122.0, 116.9, 116.1, 115.9, 69.1 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{BrO}+\text{H}^+$ : 315.0379, found 315.0381.



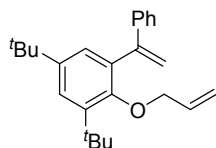
*1-(allyloxy)-4-fluoro-2-(1-phenylvinyl)benzene (Ii)*. Yellow oil;  $R_f = 0.49$  (petroleum ether/ethyl acetate 50:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.29$ -7.24 (m, 5H), 7.04-6.95 (m, 2H), 6.81 (dd,  $J = 8.8$  Hz,  $J = 4.8$  Hz, 1H), 5.69 (d,  $J = 1.2$  Hz, 1H), 5.64-5.55 (m, 1H), 5.35 (d,  $J = 1.6$  Hz, 1H), 5.03-5.00 (m, 2H), 4.29 (d,  $J = 5.2$  Hz, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.3, 155.9, 152.2 ( $J = 3$  Hz), 146.4, 140.8, 133.1 ( $J = 9$  Hz), 132.8, 128.1, 127.4, 126.4, 117.9 ( $J = 3$  Hz), 116.7, 116.2, 114.7 ( $J = 28$  Hz), 114.1, 69.8 ppm;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -123.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{FO}+\text{H}^+$ : 255.1180, found 255.1181.



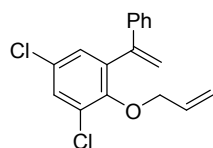
*1-(allyloxy)-4-chloro-2-(1-phenylvinyl)benzene (Ij)*. Yellow solid; mp: 36-37 °C;  $R_f = 0.49$  (petroleum ether/ethyl acetate 50:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.29$ -7.24 (m, 7H), 6.80 (d,  $J = 8.8$  Hz, 1H), 5.69 (d,  $J = 1.6$  Hz, 1H), 5.64-5.55 (m, 1H), 5.33 (d,  $J = 1.2$  Hz, 1H), 5.04-4.96 (m, 2H), 4.32-4.30 (m, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  154.7, 146.2, 140.8, 133.1, 132.5, 130.9, 128.5, 128.1, 127.4, 126.4, 125.7, 116.8, 116.2, 114.0, 69.3 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{ClO}+\text{H}^+$ : 271.0884, found 271.0880.



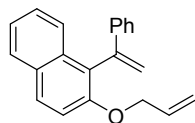
*1-(allyloxy)-4-bromo-2-(1-phenylvinyl)benzene (Ik)*. Yellow solid; mp: 43-45 °C;  $R_f = 0.50$  (petroleum ether/ethyl acetate 50:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.42$ -7.38 (m, 2H), 7.29-7.25 (m, 5H), 6.75 (d,  $J = 8.4$  Hz, 1H), 5.69 (d,  $J = 1.2$  Hz, 1H), 5.64-5.54 (m, 1H), 5.33 (d,  $J = 1.2$  Hz, 1H), 5.07-4.96 (m, 2H), 4.32-4.30 (m, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  155.2, 146.1, 140.7, 133.7, 133.6, 132.5, 131.5, 128.1, 127.4, 126.4, 116.8, 116.3, 114.4, 113.0, 69.2 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{17}\text{H}_{15}\text{BrO}+\text{H}^+$ : 315.0379, found 315.0832.



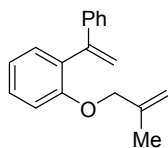
2-(allyloxy)-1,5-di-tert-butyl-3-(1-phenylvinyl)benzene (**II**). Yellow oil;  $R_f = 0.50$  (petroleum ether/ethyl acetate 50:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.34\text{--}7.32$  (m, 3H), 7.29-7.24 (m, 3H), 7.07 (d,  $J = 2.4$  Hz, 1H), 5.75-5.66 (m, 2H), 5.46 (d,  $J = 2.4$  Hz, 1H), 5.10-4.97 (m, 2H), 4.32 (d,  $J = 4.8$  Hz, 2H), 1.38 (s, 9H), 1.30 (s, 9H) ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  153.6, 148.3, 145.0, 142.0, 140.6, 134.3, 134.1, 128.0, 127.5, 127.0, 126.8, 123.6, 115.7, 115.0, 72.4, 35.3, 34.5, 31.2, 30.8 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{25}\text{H}_{32}\text{O} + \text{Na}^+$ : 371.2345, found 371.2352.



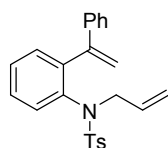
2-(allyloxy)-1,5-dichloro-3-(1-phenylvinyl)benzene (**Im**). Yellow oil;  $R_f = 0.50$  (petroleum ether/ethyl acetate 50:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.38$  (d,  $J = 8.4$  Hz, 1H), 7.32-7.27 (m, 5H), 7.16 (d,  $J = 2.4$  Hz, 1H), 5.81-5.71 (m, 1H), 5.74 (s, 1H), 5.39 (s, 1H), 5.12-5.05 (m, 1H), 4.21 (d,  $J = 6.0$  Hz, 2H), ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.4, 145.4, 140.4, 138.5, 133.0, 129.7, 129.4, 129.3, 129.1, 128.3, 128.0, 126.6, 118.1, 117.3, 74.1 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{17}\text{H}_{14}\text{Cl}_2\text{O} + \text{H}^+$ : 390.1522, found 390.1529.



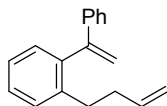
2-(allyloxy)-1-(1-phenylvinyl)naphthalene (**In**). Yellow oil;  $R_f = 0.47$  (petroleum ether/ethyl acetate 50:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.90\text{--}7.88$  (m, 1H), 7.84-7.79 (m, 2H), 7.40-7.30 (m, 5H), 7.26-7.21 (m, 3H), 6.15 (d,  $J = 1.2$  Hz, 1H), 5.83-5.74 (m, 1H), 5.31 (d,  $J = 1.2$  Hz, 1H), 5.22-5.17 (m, 1H), 5.11-5.08 (m, 1H), 6.15 (d,  $J = 28$  Hz, 2H) ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  152.8, 143.3, 140.8, 133.6, 133.4, 129.2, 128.9, 128.2, 127.8, 127.4, 126.5, 126.1, 125.9, 125.3, 123.7, 116.920, 116.866, 115.5, 70.2 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{21}\text{H}_{18}\text{O} + \text{NH}_4^+$ : 304.1696, found 304.1699.



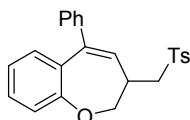
1-((2-methylallyl)oxy)-2-(1-phenylvinyl)benzene (**Io**). Yellow oil;  $R_f = 0.51$  (petroleum ether/ethyl acetate 50:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.32\text{--}7.22$  (m, 7H), 7.00 (t,  $J = 7.2$  Hz, 1H), 6.87 (d,  $J = 8.8$  Hz, 1H), 5.69 (s, 1H), 5.32 (s, 1H), 4.73 (d,  $J = 8.0$  Hz, 2H), 4.24 (s, 2H), 1.44 (s, 3H) ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.1, 147.4, 141.3, 140.7, 131.4, 131.3, 128.9, 128.0, 127.2, 126.4, 120.6, 115.0, 112.048, 119.954, 71.7, 18.9 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{18}\text{H}_{18}\text{O} + \text{Na}^+$ : 273.1250, found 273.1251.



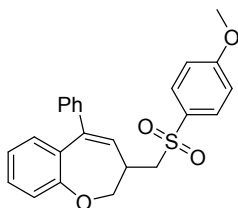
*N*-allyl-4-methyl-*N*-(2-(1-phenylvinyl)phenyl)benzenesulfonamide (**1q**). Yellow oil;  $R_f = 0.48$  (petroleum ether/ethyl acetate 50:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.53$  (d,  $J = 7.6$  Hz, 2H), 7.33 (d,  $J = 4.4$  Hz, 2H), 7.31-7.23 (m, 8H), 6.96 (d,  $J = 7.6$  Hz, 1H), 5.73 (s, 1H), 5.39 (s, 1H), 5.37-5.26 (m, 1H), 4.84-4.75 (m, 2H), 3.8-3.65 (m, 2H), 2.43 (s, 3H) ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  146.7, 143.3, 142.9, 141.3, 137.6, 132.9, 132.0, 129.8, 129.3, 128.2, 128.1, 127.9, 127.6, 127.2, 118.7, 117.5, 53.9, 21.5 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{24}\text{H}_{23}\text{NO}_2\text{S}+\text{H}^+$ : 390.1522, found 390.1529.



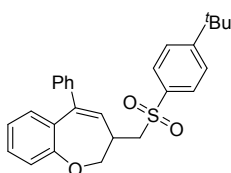
1-(but-3-en-1-yl)-2-(1-phenylvinyl)benzene (**1r**). Yellow oil;  $R_f = 0.46$  (petroleum ether/ethyl acetate 50:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.31$ -7.24 (m, 6H), 7.23-7.21 (m, 3H), 5.77 (d,  $J = 1.2$  Hz, 1H), 5.72-5.62 (m, 1H), 5.20 (d,  $J = 1.6$  Hz, 1H), 4.88-4.82 (m, 2H), 2.49-2.45 (m, 2H), 2.18-2.11 (m, 2H) ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  149.2, 141.3, 140.9, 139.8, 138.3, 130.4, 129.2, 128.3, 127.6, 127.6, 126.5, 125.8, 115.2, 114.5, 35.0, 32.8 ppm. APCI-HRMS:  $m/z$  Calcd for  $\text{C}_{18}\text{H}_{18}+\text{H}^+$ : 235.1481, found 235.1487.



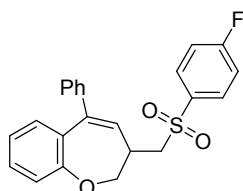
5-phenyl-3-(tosylmethyl)-2,3-dihydrobenzo[*b*]oxepine (**3aa**). Yellow solid; (34.2 mg, 88%); mp: 52-55 °C;  $R_f = 0.40$  (petroleum ether/ethyl acetate 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.83$  (d,  $J = 9.2$  Hz, 2H), 7.31-7.19 (m, 2H), 7.15-7.08 (m, 3H), 7.02-6.91 (m, 4H), 5.90 (d,  $J = 5.2$  Hz, 1H), 4.45 (dd,  $J = 11.2$  Hz,  $J = 6.8$  Hz, 1H), 4.34 (dd,  $J = 11.2$  Hz,  $J = 4.0$  Hz, 1H), 3.87 (s, 3H), 3.31-3.24 (m, 3H) ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.4, 144.9, 142.5, 140.7, 136.5, 131.6, 130.5, 130.1, 130.0, 128.9, 128.7, 128.1, 128.0, 127.3, 123.3, 121.3, 77.8, 58.0, 36.5, 21.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{24}\text{H}_{22}\text{O}_3\text{S}+\text{NH}_4^+$ : 408.1628, found 408.1633.



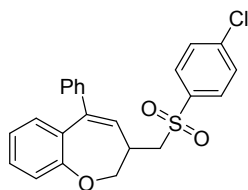
3-(((4-methoxyphenyl)sulfonyl)methyl)-5-phenyl-2,3-dihydrobenzo[*b*]oxepine (**3ab**). Yellow solid; (34.5 mg, 85%); mp: 57-61 °C;  $R_f = 0.41$  (petroleum ether/ethyl acetate 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.83$  (d,  $J = 9.2$  Hz, 2H), 7.31-7.19 (m, 2H), 7.15-7.08 (m, 3H), 7.02-6.91 (m, 4H), 5.90 (d,  $J = 5.2$  Hz, 1H), 4.45 (dd,  $J = 11.2$  Hz,  $J = 6.8$  Hz, 1H), 4.34 (dd,  $J = 11.2$  Hz,  $J = 4.0$  Hz, 1H), 3.87 (s, 3H), 3.31-3.24 (m, 3H) ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  163.9, 158.4, 142.5, 140.7, 131.6, 130.9, 130.6, 130.2, 128.9, 128.7, 128.1, 127.3, 123.4, 121.3, 114.6, 77.9, 58.0, 55.7, 36.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{24}\text{H}_{22}\text{O}_4\text{S}+\text{NH}_4^+$ : 424.1577, found 424.1578.



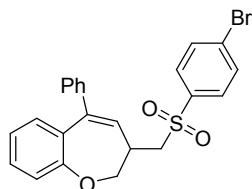
3-(((4-(*tert*-butyl)phenyl)sulfonyl)methyl)-5-phenyl-2,3-dihydrobenzo[*b*]oxepine (**3ac**). Yellow solid; (35.8 mg, 83%); mp: 62-65 °C;  $R_f$  = 0.47 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.83 (d,  $J$  = 8.8 Hz, 2H), 7.56 (d,  $J$  = 8.4 Hz, 2H), 7.31-7.27 (m, 4H), 7.24-7.20 (m, 1H), 7.15-7.08 (m, 3H), 7.01-6.97 (m, 1H), 6.93-6.91 (m, 1H), 5.93 (d,  $J$  = 4.8 Hz, 1H), 4.47 (dd,  $J$  = 11.2 Hz,  $J$  = 3.2 Hz, 1H), 4.36 (dd,  $J$  = 11.2 Hz,  $J$  = 4.0 Hz, 1H), 3.44-3.26 (m, 3H), 1.34 (s, 9H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.4, 157.9, 142.5, 140.8, 136.4, 131.7, 130.6, 130.1, 128.9, 128.7, 128.1, 127.9, 127.3, 126.4, 123.4, 121.3, 78.0, 57.8, 36.5, 35.3, 31.0 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{27}\text{H}_{28}\text{O}_3\text{S}+\text{NH}_4^+$ : 450.2097, found 450.2093.



3-(((4-fluorophenyl)sulfonyl)methyl)-5-phenyl-2,3-dihydrobenzo[*b*]oxepine (**3ad**). Yellow oil; (32.7 mg, 83%);  $R_f$  = 0.42 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.95-7.91 (m, 2H), 7.31-7.29 (m, 3H), 7.25-7.20 (m, 3H), 7.15-7.13 (m, 2H), 7.09 (d,  $J$  = 8.0 Hz, 1H), 7.00-6.91 (m, 2H), 5.93 (d,  $J$  = 4.4 Hz, 1H), 4.48 (dd,  $J$  = 11.2 Hz,  $J$  = 6.4 Hz, 1H), 4.32 (dd,  $J$  = 11.2 Hz,  $J$  = 3.2 Hz, 1H), 3.44-3.26 (m, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  167.1, 164.6, 158.5, 142.5, 141.0, 135.6 (d,  $J$  = 3.7 Hz), 131.8, 130.9, 130.8, 130.2, 129.9, 129.0, 128.7, 128.1, 127.4, 123.4, 121.2, 116.8, 116.6, 77.3, 58.0, 36.6 ppm;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -102.9 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{23}\text{H}_{19}\text{FO}_3\text{S}+\text{NH}_4^+$ : 412.1377, found 412.1370.



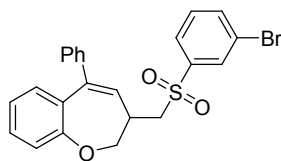
3-(((4-chlorophenyl)sulfonyl)methyl)-5-phenyl-2,3-dihydrobenzo[*b*]oxepine (**3ae**). Yellow solid; (33.6 mg, 82%); mp: 105-109 °C;  $R_f$  = 0.42 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.85 (d,  $J$  = 8.4 Hz, 2H), 7.53 (d,  $J$  = 8.8 Hz, 2H), 7.31-7.30 (m, 3H), 7.24-7.20 (m, 1H), 7.12-7.08 (m, 3H), 7.00-6.96 (m, 1H), 6.93-6.91 (m, 1H), 5.88 (d,  $J$  = 5.2 Hz, 1H), 4.47 (dd,  $J$  = 11.2 Hz,  $J$  = 6.4 Hz, 1H), 4.32 (dd,  $J$  = 11.2 Hz,  $J$  = 4.0 Hz, 1H), 3.23-3.28 (m, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.4, 142.4, 141.0, 140.7, 137.9, 131.8, 130.2, 129.8, 129.7, 129.5, 129.0, 128.7, 128.2, 127.4, 123.4, 121.2, 77.4, 57.9, 36.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{23}\text{H}_{19}\text{ClO}_3\text{S}+\text{NH}_4^+$ : 428.1082, found 428.1083.



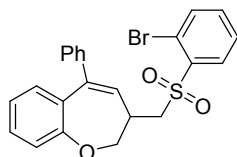
3-(((4-bromophenyl)sulfonyl)methyl)-5-phenyl-2,3-dihydrobenzo[*b*]oxepine (**3af**). Yellow solid; (35.4 mg, 78%); mp: 51-52 °C;  $R_f$  = 0.40 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.77 (d,  $J$  = 8.4 Hz, 2H), 7.70 (d,  $J$  = 8.4 Hz, 2H), 7.33-7.30 (m, 1H), 7.24-7.20 (m, 1H), 7.11-7.08 (m, 3H), 6.98 (t,  $J$  = 7.6 Hz, 1H), 6.92 (d,  $J$  = 8.0 Hz, 1H), 5.87 (d,  $J$  = 4.8 Hz, 1H), 4.47 (dd,  $J$  = 11.2 Hz,  $J$  = 6.4 Hz, 1H), 4.32 (dd,  $J$  = 11.2 Hz,  $J$  = 4.0 Hz, 1H), 3.32-3.27 (m, 3H)



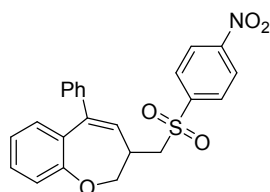
ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.4, 142.4, 141.0, 138.5, 132.7, 131.8, 130.3, 129.8, 129.6, 129.3, 129.0, 128.7, 128.2, 127.4, 123.4, 121.3, 77.4, 57.9, 36.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{23}\text{H}_{19}\text{BrO}_3\text{S}+\text{NH}_4^+$ : 472.0577, found 472.0570.



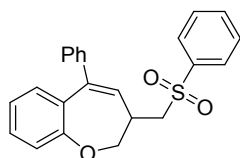
3-(((3-bromophenyl)sulfonyl)methyl)-5-phenyl-2,3-dihydrobenzo[b]oxepine (**3ag**). Yellow solid; (38.1 mg, 84%); mp: 60-65°C;  $R_f$  = 0.39 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.06 (s, 1H), 7.85 (d,  $J$  = 8.0 Hz, 1H), 7.78 (d,  $J$  = 8.0 Hz, 1H), 7.44 (t,  $J$  = 8.0 Hz, 1H), 7.32-7.30 (m, 3H), 7.24-7.20 (m, 1H), 7.16-7.09 (m, 3H), 7.00-6.92 (m, 2H), 5.93 (d,  $J$  = 5.2 Hz, 1H), 4.52-4.47 (m, 1H), 4.35-4.31 (m, 1H), 3.36-3.27 (m, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.5, 142.5, 141.4, 141.1, 137.0, 131.8, 130.9, 130.2, 129.7, 129.0, 128.7, 128.2, 127.4, 126.5, 123.5, 123.4, 121.2, 57.8, 36.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{23}\text{H}_{19}\text{BrO}_3\text{S}+\text{NH}_4^+$ : 472.0577, found 472.0571.



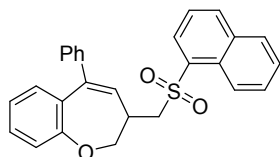
3-(((2-bromophenyl)sulfonyl)methyl)-5-phenyl-2,3-dihydrobenzo[b]oxepine (**3ah**). Yellow solid; (34.5 mg, 76%); mp: 58-62 °C;  $R_f$  = 0.41 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.17-8.15 (m, 1H), 7.77 (d,  $J$  = 8.0 Hz, 1H), 7.53-7.46 (m, 2H), 7.30-7.19 (m, 5H), 7.13-7.08 (m, 3H), 6.97 (t,  $J$  = 7.6 Hz, 1H), 6.90 (d,  $J$  = 7.6 Hz, 1H), 5.94 (d,  $J$  = 5.6 Hz, 1H), 4.50 (dd,  $J$  = 11.2 Hz,  $J$  = 7.2 Hz, 1H), 4.36 (dd,  $J$  = 11.2 Hz,  $J$  = 4.0 Hz, 1H), 3.71 (dd,  $J$  = 14.4 Hz,  $J$  = 6.4 Hz, 1H), 3.58 (dd,  $J$  = 14.4 Hz,  $J$  = 6.4 Hz, 1H), 3.38-3.34 (m, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.2, 142.6, 141.0, 138.7, 135.5, 134.9, 131.9, 131.8, 130.3, 129.9, 129.0, 128.7, 128.2, 128.1, 127.3, 123.3, 121.2, 120.9, 77.5, 55.4, 36.5 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{23}\text{H}_{19}\text{BrO}_3\text{S}+\text{NH}_4^+$ : 472.0577, found 472.0571.



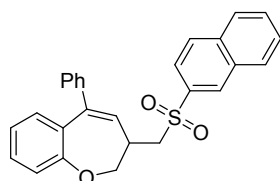
3-(((4-nitrophenyl)sulfonyl)methyl)-5-phenyl-2,3-dihydrobenzo[b]oxepine (**3ai**). Yellow solid; (32.4 mg, 77%); mp: 69-74 °C;  $R_f$  = 0.39 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.37 (d,  $J$  = 8.8 Hz, 2H), 8.11 (d,  $J$  = 8.8 Hz, 2H), 7.32-7.28 (m, 3H), 7.24-7.20 (m, 1H), 7.12-7.08 (m, 3H), 7.00-6.96 (m, 1H), 6.91 (dd,  $J$  = 8.0 Hz,  $J$  = 2.0 Hz, 1H), 5.89 (d,  $J$  = 4.8 Hz, 1H), 4.52 (dd,  $J$  = 11.2 Hz,  $J$  = 4.8 Hz, 1H), 4.30 (dd,  $J$  = 11.2 Hz,  $J$  = 3.6 Hz, 1H), 3.44-3.32 (m, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.6, 150.8, 145.2, 142.6, 141.3, 132.0, 129.7, 129.5, 129.4, 129.1, 128.7, 128.2, 127.5, 124.6, 123.4, 121.2, 76.5, 58.0, 36.9 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{23}\text{H}_{19}\text{NO}_5\text{S}+\text{NH}_4^+$ : 439.1322, found 439.1330.



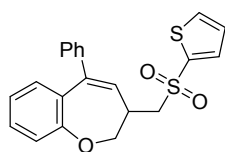
*5-phenyl-3-((phenylsulfonyl)methyl)-2,3-dihydrobenzo[b]oxepine (3aj)*. Yellow solid; (33.5 mg, 89%); mp: 47-49 °C;  $R_f$  = 0.39 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.72 (d,  $J$  = 8.0 Hz, 2H), 7.52-7.46 (m, 2H), 7.37-7.30 (m, 4H), 7.26-7.22 (m, 1H), 7.18-7.14 (m, 2H), 6.97-6.95 (m, 3H), 6.74 (d,  $J$  = 7.6 Hz, 2H), 5.86 (d,  $J$  = 6.0 Hz, 2H), 4.37 (s, 1H), 4.05 (s, 1H), 3.31 (dd,  $J$  = 14.0 Hz,  $J$  = 9.6 Hz, 1H), 3.11 (dd,  $J$  = 14.0 Hz,  $J$  = 4.0 Hz, 1H), 2.97 (s, 1H), 2.45 (s, 3H), 2.23 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.5, 142.5, 140.8, 139.5, 133.9, 131.8, 130.4, 130.1, 129.4, 128.9, 128.7, 128.1, 128.0, 127.3, 123.4, 121.2, 77.6, 57.8, 36.5 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{23}\text{H}_{20}\text{O}_3\text{S}+\text{NH}_4^+$ : 394.1417, found 394.1418.



*3-((naphthalen-1-ylsulfonyl)methyl)-5-phenyl-2,3-dihydrobenzo[b]oxepine (3ak)*. Yellow solid; (30.8 mg, 72%); mp: 75-82 °C;  $R_f$  = 0.39 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.81 (d,  $J$  = 8.4 Hz, 1H), 7.36 (d,  $J$  = 8.0 Hz, 1H), 7.27-7.18 (m, 4H), 7.11-7.09 (m, 2H), 6.73 (d,  $J$  = 2.4 Hz, 1H), 4.33 (dd,  $J$  = 11.2 Hz,  $J$  = 6.0 Hz, 1H), 4.25 (dd,  $J$  = 11.2 Hz,  $J$  = 4.0 Hz, 1H), 3.37-3.26 (m, 3H), 2.46 (s, 3H), 1.40 (s, 9H), 1.13 (s, 9H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.8, 142.8, 141.2, 135.7, 134.8, 134.6, 132.1, 130.9, 130.7, 130.4, 129.7, 129.3, 129.2, 129.1, 129.0, 128.4, 127.6, 124.8, 124.2, 123.6, 121.6, 78.0, 57.8, 36.9 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{27}\text{H}_{22}\text{O}_3\text{S}+\text{NH}_4^+$ : 444.1628, found 444.1619.

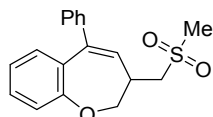


*3-((naphthalen-2-ylsulfonyl)methyl)-5-phenyl-2,3-dihydrobenzo[b]oxepine (3al)*. Yellow solid; (31.9 mg, 75%); mp: 49-54 °C;  $R_f$  = 0.38 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 8.49 (d,  $J$  = 2.0 Hz, 1H), 8.01-7.93 (m, 3H), 7.87 (dd,  $J$  = 8.8 Hz,  $J$  = 2.0 Hz, 1H), 7.71-7.67 (m, 1H), 7.65-7.61 (m, 1H), 7.23-7.16 (m, 1H), 7.10-7.07 (m, 1H), 6.99-6.96 (m, 1H), 6.90-6.88 (m, 1H), 5.86 (d,  $J$  = 4.8 Hz, 1H), 4.50-4.45 (m, 1H), 4.37-4.34 (m, 1H), 3.39-3.32 (m, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.3, 142.3, 140.9, 136.2, 135.3, 132.1, 131.6, 130.5, 129.9, 129.8, 129.4, 128.9, 128.6, 128.012, 127.958, 127.8, 127.2, 123.4, 122.5, 121.3, 77.9, 57.8, 36.5 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{27}\text{H}_{22}\text{O}_3\text{S}+\text{Na}^+$ : 449.1182, found 442.1178.

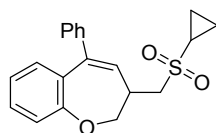


*5-phenyl-3-((thiophen-2-ylsulfonyl)methyl)-2,3-dihydrobenzo[b]oxepine (3am)*. Yellow solid; (24.1 mg, 63%); mp: 46-49 °C;  $R_f$  = 0.42 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.73-7.70 (m, 2H), 7.33-7.30 (m, 3H), 7.24-7.14 (m, 4H), 7.10 (d,  $J$  = 8.0 Hz, 1H),

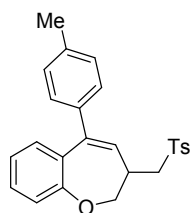
7.00-6.92 (m, 2H), 5.97 (d,  $J = 5.2$  Hz, 1H), 4.48 (dd,  $J = 11.2$  Hz,  $J = 6.8$  Hz, 1H), 4.34 (dd,  $J = 11.2$  Hz,  $J = 4.0$  Hz, 1H), 3.46-3.41 (m, 2H), 3.39-3.30 (m, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.5, 142.6, 141.0, 140.5, 134.3, 134.2, 131.8, 130.4, 129.9, 129.0, 128.7, 128.1, 128.0, 127.4, 123.4, 121.3, 77.5, 59.3, 36.9 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{21}\text{H}_{18}\text{O}_3\text{S}_2+\text{NH}_4^+$ : 400.1036, found 400.1040.



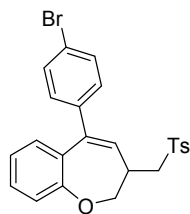
3-((methylsulfonyl)methyl)-5-phenyl-2,3-dihydrobenzo[b]oxepine (**3an**). Yellow solid; (11.3 mg, 36%); mp: 64-68 °C;  $R_f = 0.35$  (petroleum ether/ethyl acetate 3:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.38$ -7.34 (m, 1H), 7.29-7.23 (m, 1H), 7.15-7.13 (m, 1H), 7.03-6.96 (m, 2H), 6.10 (d,  $J = 5.6$  Hz, 1H), 4.57 (dd,  $J = 11.2$  Hz,  $J = 6.4$  Hz, 1H), 4.39 (dd,  $J = 11.2$  Hz,  $J = 4.0$  Hz, 1H), 3.46-3.39 (m, 1H), 3.33-3.23 (m, 1H), 3.00 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.7, 142.8, 141.4, 132.0, 130.030, 129.996, 129.1, 128.8, 128.2, 127.5, 123.4, 121.2, 56.4, 42.1, 36.4 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{18}\text{H}_{18}\text{O}_3\text{S}+\text{NH}_4^+$ : 332.1315, found 332.1309.



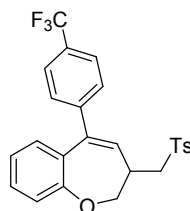
3-((cyclopropylsulfonyl)methyl)-5-phenyl-2,3-dihydrobenzo[b]oxepine (**3ao**). Yellow oil; (23.8 mg, 70%);  $R_f = 0.41$  (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.34$ -7.31 (m, 3H), 7.26-7.21 (m, 3H), 7.11 (d,  $J = 8.0$  Hz, 1H), 7.01-6.94 (m, 2H), 6.11 (d,  $J = 5.2$  Hz, 1H), 4.53 (dd,  $J = 11.2$  Hz,  $J = 7.2$  Hz, 1H), 4.38 (dd,  $J = 11.2$  Hz,  $J = 4.4$  Hz, 1H), 3.47-3.39 (m, 1H), 3.31-3.22 (m, 2H), 2.45-2.38 (m, 1H), 1.08-1.03 (m, 2H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.6, 142.7, 140.9, 131.8, 130.4, 129.0, 128.8, 128.2, 127.4, 123.4, 121.2, 77.6, 55.2, 36.1, 30.4, 4.9 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{20}\text{H}_{20}\text{O}_3\text{S}+\text{NH}_4^+$ : 358.1471, found 358.1468.



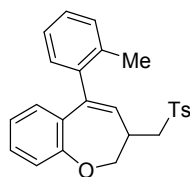
5-(p-tolyl)-3-(tosylmethyl)-2,3-dihydrobenzo[b]oxepine (**3ba**). Yellow solid; (34.7 mg, 86%); mp: 51-55 °C;  $R_f = 0.39$  (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.78$  (d,  $J = 8.0$  Hz, 2H), 7.35 (d,  $J = 8.0$  Hz, 2H), 7.23-7.19 (m, 1H), 7.11-7.07 (m, 3H), 7.03-6.92 (m, 4H), 5.85 (d,  $J = 5.2$  Hz, 1H), 4.44 (dd,  $J = 10.8$  Hz,  $J = 7.2$  Hz, 1H), 4.34 (dd,  $J = 10.8$  Hz,  $J = 4.4$  Hz, 1H), 3.29-3.24 (m, 3H), 2.45 (s, 3H), 2.35 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.3, 144.9, 140.7, 139.6, 137.1, 136.5, 131.6, 130.8, 130.0, 129.5, 128.9, 128.8, 128.6, 128.0, 123.4, 121.3, 78.1, 57.9, 36.4, 21.6, 21.1 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{25}\text{H}_{24}\text{O}_3\text{S}+\text{NH}_4^+$ : 422.1784, found 422.1789.



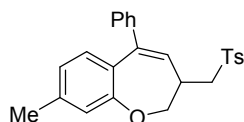
5-(4-bromophenyl)-3-(tosylmethyl)-2,3-dihydrobenzo[b]oxepine (**3ca**). Yellow solid; (37.0 mg, 79%); mp: 49-54 °C;  $R_f$  = 0.41 (petroleum ether/ethyl acetate 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.78 (d,  $J$  = 8.4 Hz, 2H), 7.44-7.40 (m, 2H), 7.35 (d,  $J$  = 8.4 Hz, 2H), 7.25-7.20 (m, 1H), 7.10-7.08 (m, 1H), 7.01-6.97 (m, 1H), 6.90-6.87 (m, 3H), 5.91 (d,  $J$  = 5.2 Hz, 1H), 4.43 (dd,  $J$  = 11.2 Hz,  $J$  = 7.2 Hz, 1H), 4.33 (dd,  $J$  = 11.2 Hz,  $J$  = 4.4 Hz, 1H), 3.32-3.22 (m, 3H), 2.45 (s, 3H) ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.4, 145.0, 141.4, 139.7, 136.5, 131.4, 131.2, 130.5, 130.4, 130.1, 130.0, 129.2, 128.0, 123.5, 121.1, 78.0, 57.8, 36.4, 21.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{24}\text{H}_{21}\text{BrO}_3\text{S}+\text{NH}_4^+$ : 486.0733, found 486.0737.



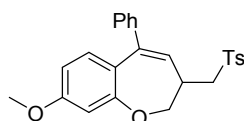
3-(tosylmethyl)-5-(4-(trifluoromethyl)phenyl)-2,3-dihydrobenzo[b]oxepine (**3da**). Yellow solid; (33.4 mg, 73%); mp: 51-55 °C;  $R_f$  = 0.39 (petroleum ether/ethyl acetate 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.78 (d,  $J$  = 8.4 Hz, 2H), 7.44-7.40 (m, 2H), 7.35 (d,  $J$  = 8.4 Hz, 2H), 7.25-7.20 (m, 1H), 7.10-7.08 (m, 1H), 7.01-6.97 (m, 1H), 6.90-6.87 (m, 3H), 5.91 (d,  $J$  = 5.2 Hz, 1H), 4.43 (dd,  $J$  = 11.2 Hz,  $J$  = 7.2 Hz, 1H), 4.33 (dd,  $J$  = 11.2 Hz,  $J$  = 4.4 Hz, 1H), 3.32-3.22 (m, 3H), 2.45 (s, 3H) ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.6, 146.2, 145.1, 139.7, 136.6, 131.6, 131.5, 130.1, 129.8, 129.4, 129.1, 128.1, 125.6 (q,  $J$  = 4.7 Hz), 123.6, 121.5, 77.7, 57.9, 36.7, 21.7 ppm;  $^{19}\text{F NMR}$  (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -62.4 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{25}\text{H}_{21}\text{F}_3\text{O}_3\text{S}+\text{NH}_4^+$ : 476.1502, found 476.1504.



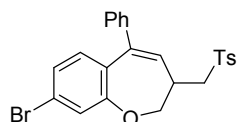
5-(*o*-tolyl)-3-(tosylmethyl)-2,3-dihydrobenzo[b]oxepine (**3ea**). Yellow solid; (33.1 mg, 82%); mp: 44-48 °C;  $R_f$  = 0.41 (petroleum ether/ethyl acetate 5:1);  $^1\text{H NMR}$  (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.81 (d,  $J$  = 8.4 Hz, 2H), 7.35 (d,  $J$  = 8.4 Hz, 2H), 7.23-7.12 (m, 4H), 7.06-7.02 (m, 2H), 6.86-6.82 (m, 1H), 6.66 (dd,  $J$  = 8.0 Hz,  $J$  = 1.6 Hz, 1H), 5.75 (d,  $J$  = 4.8 Hz, 2H), 4.57 (dd,  $J$  = 11.6 Hz,  $J$  = 4.4 Hz, 1H), 4.22 (dd,  $J$  = 11.2 Hz,  $J$  = 3.2 Hz, 1H), 3.48-3.42 (m, 1H), 3.41-3.37 (m, 1H), 3.26-3.22 (m, 1H), 2.44 (s, 3H), 1.96 (s, 3H) ppm;  $^{13}\text{C NMR}$  (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.1, 144.9, 143.0, 139.6, 136.7, 131.4, 131.3, 130.0, 129.9, 129.7, 128.6, 127.909, 127.966, 127.3, 125.7, 123.0, 120.6, 73.4, 58.3, 38.2, 21.6, 19.5 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{25}\text{H}_{24}\text{O}_3\text{S}+\text{NH}_4^+$ : 422.1784, found 422.1789.



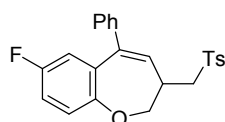
*8-methyl-5-phenyl-3-(tosylmethyl)-2,3-dihydrobenzo[b]oxepine (3fa)*. Yellow solid; (33.5 mg, 83%); mp: 59-61 °C;  $R_f$  = 0.40 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.79 (d,  $J$  = 8.0 Hz, 2H), 7.35 (d,  $J$  = 8.0 Hz, 2H), 7.29-7.27 (m, 3H), 7.11-7.08 (m, 2H), 6.90 (s, 1H), 6.78 (s, 2H), 5.79 (d,  $J$  = 4.8 Hz, 1H), 4.43 (dd,  $J$  = 11.2 Hz,  $J$  = 6.0 Hz, 1H), 4.30 (dd,  $J$  = 11.2 Hz,  $J$  = 3.6 Hz, 1H), 3.31-3.25 (m, 3H), 2.45 (s, 3H), 2.31 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  158.4, 144.9, 142.8, 140.6, 139.3, 136.6, 131.5, 130.0, 129.5, 128.7, 128.0, 127.2, 124.1, 121.7, 77.2, 58.0, 36.8, 21.6, 20.9 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{25}\text{H}_{24}\text{O}_3\text{S}+\text{NH}_4^+$ : 422.1784, found 422.1787.



*8-methoxy-5-phenyl-3-(tosylmethyl)-2,3-dihydrobenzo[b]oxepine (3ga)*. Yellow solid; (34.0 mg, 81%); mp: 47-52 °C;  $R_f$  = 0.41 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.79 (d,  $J$  = 8.0 Hz, 2H), 7.35 (d,  $J$  = 8.0 Hz, 2H), 7.29-7.27 (m, 3H), 7.11-7.09 (m, 2H), 6.80 (d,  $J$  = 8.8 Hz, 1H), 6.64 (d,  $J$  = 2.8 Hz, 1H), 6.51 (dd,  $J$  = 8.8 Hz,  $J$  = 2.8 Hz, 1H), 5.71 (d,  $J$  = 4.8 Hz, 1H), 4.48 (dd,  $J$  = 11.2 Hz,  $J$  = 6.0 Hz, 1H), 4.31 (dd,  $J$  = 11.2 Hz,  $J$  = 3.6 Hz, 1H), 3.79 (s, 3H), 3.36-3.21 (m, 3H), 2.45 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.0, 159.9, 144.9, 143.1, 140.4, 136.6, 132.7, 130.0, 128.8, 128.5, 128.042, 127.994, 127.2, 122.3, 109.5, 106.1, 76.5, 58.0, 55.4, 37.0, 21.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{25}\text{H}_{24}\text{O}_4\text{S}+\text{NH}_4^+$ : 438.1734, found 438.1729.

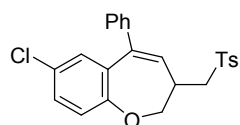


*8-bromo-5-phenyl-3-(tosylmethyl)-2,3-dihydrobenzo[b]oxepine (3ha)*. Yellow solid; (36.9 mg, 79%); mp: 56-60 °C;  $R_f$  = 0.40 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.79 (d,  $J$  = 8.0 Hz, 2H), 7.35 (d,  $J$  = 8.0 Hz, 2H), 7.31-7.29 (m, 3H), 7.26 (s, 1H), 7.11-7.09 (m, 3H), 7.68 (d,  $J$  = 8.4 Hz, 1H), 5.92 (d,  $J$  = 8.8 Hz, 1H), 4.46 (dd,  $J$  = 11.2 Hz,  $J$  = 6.4 Hz, 1H), 4.31 (dd,  $J$  = 11.6 Hz,  $J$  = 3.6 Hz, 1H), 3.32-3.23 (m, 3H), 2.45 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.0, 145.0, 142.2, 140.0, 136.4, 132.8, 130.9, 130.1, 129.3, 128.7, 128.2, 128.0, 127.5, 126.5, 124.5, 121.8, 77.5, 57.7, 36.7, 21.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{24}\text{H}_{21}\text{BrO}_3\text{S}+\text{NH}_4^+$ : 486.0733, found 486.0737.

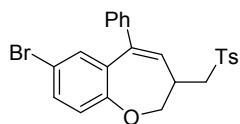


*7-fluoro-5-phenyl-3-(tosylmethyl)-2,3-dihydrobenzo[b]oxepine (3ia)*. Yellow solid; (32.6 mg, 80%); mp: 52-56 °C;  $R_f$  = 0.42 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.79 (d,  $J$  = 8.4 Hz, 2H), 7.36 (d,  $J$  = 8.0 Hz, 2H), 7.31-7.30 (m, 3H), 7.12-7.09 (m, 2H), 7.07-7.03 (m, 1H), 6.93-6.88 (m, 1H), 6.62 (dd,  $J$  = 10.0 Hz,  $J$  = 3.2 Hz, 1H), 5.94 (d,  $J$  = 4.8 Hz, 1H), 4.42 (dd,  $J$  = 11.2 Hz,  $J$  = 6.8 Hz, 1H), 4.32 (dd,  $J$  = 11.2 Hz,  $J$  = 4.0 Hz, 1H), 3.30-3.22 (m, 3H), 2.46 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  159.8, 157.4, 154.3 ( $J$  = 3 Hz), 145.1, 141.7,

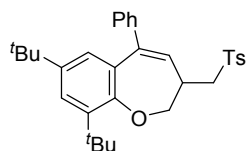
140.1 ( $J = 2$  Hz), 136.5, 132.4 ( $J = 10$  Hz), 131.1, 130.1, 128.6, 128.3, 128.1, 127.7, 122.5 ( $J = 11$  Hz), 117.5 ( $J = 30$  Hz), 115.6 ( $J = 29$  Hz), 78.4, 57.8, 36.4, 21.7 ppm;  $^{19}\text{F}$  NMR (376 MHz,  $\text{CDCl}_3$ ):  $\delta$  -119.3 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{24}\text{H}_{21}\text{FO}_3\text{S}+\text{NH}_4^+$ : 426.1534, found 426.1526.



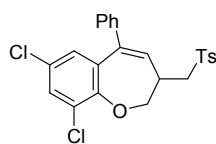
*7-chloro-5-phenyl-3-(tosylmethyl)-2,3-dihydrobenzo[b]oxepine (3ja)*. Yellow solid; (31.4 mg, 74%); mp: 142-146 °C;  $R_f = 0.40$  (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.79$  (d,  $J = 8.4$  Hz, 2H), 7.36 (d,  $J = 8.0$  Hz, 2H), 7.32-7.31 (m, 3H), 7.18-7.16 (m, 1H), 7.11-7.08 (m, 1H), 7.03 (d,  $J = 8.8$  Hz, 1H), 6.90 (d,  $J = 2.8$  Hz, 1H), 5.93 (d,  $J = 4.8$  Hz, 1H), 4.44 (dd,  $J = 11.2$  Hz,  $J = 6.8$  Hz, 1H), 4.32 (dd,  $J = 11.6$  Hz,  $J = 4.0$  Hz, 1H), 3.30-3.22 (m, 3H), 2.46 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.9, 145.1, 141.6, 139.9, 136.4, 132.3, 131.3, 131.0, 128.8, 128.601, 128.579, 128.3, 128.0, 127.7, 122.7, 78.2, 57.6, 36.3, 21.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{24}\text{H}_{21}\text{ClO}_3\text{S}+\text{NH}_4^+$ : 442.1238, found 442.1246.



*7-bromo-5-phenyl-3-(tosylmethyl)-2,3-dihydrobenzo[b]oxepine (3ka)*. Yellow solid; (37.9 mg, 81%); mp: 162-165 °C;  $R_f = 0.40$  (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.79$  (d,  $J = 8.0$  Hz, 2H), 7.36 (d,  $J = 8.0$  Hz, 2H), 7.33-7.30 (m, 4H), 7.11-7.09 (m, 2H), 7.04 (d,  $J = 2.4$  Hz, 1H), 6.97 (d,  $J = 8.8$  Hz, 1H), 5.93 (d,  $J = 4.8$  Hz, 1H), 4.44 (dd,  $J = 11.2$  Hz,  $J = 3.2$  Hz, 1H), 4.33 (dd,  $J = 11.2$  Hz,  $J = 4.0$  Hz, 1H), 3.30-3.21 (m, 3H), 2.46 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  157.4, 145.1, 141.6, 139.8, 136.4, 133.9, 132.8, 131.8, 131.3, 130.1, 128.6, 128.3, 128.0, 127.7, 123.2, 116.2, 78.3, 57.6, 36.3, 31.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{24}\text{H}_{21}\text{BrO}_3\text{S}+\text{NH}_4^+$ : 486.0733, found 486.0727.

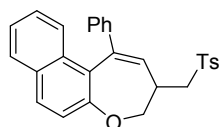


*7,9-di-tert-butyl-5-phenyl-3-(tosylmethyl)-2,3-dihydrobenzo[b]oxepine (3la)*. Yellow solid; (34.1 mg, 68%); mp: 65-69 °C;  $R_f = 0.40$  (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta = 7.81$  (d,  $J = 8.4$  Hz, 1H), 7.36 (d,  $J = 8.0$  Hz, 1H), 7.28 (m, 4H), 7.11-7.09 (m, 2H), 6.73 (d,  $J = 2.4$  Hz, 1H), 4.33 (dd,  $J = 11.2$  Hz,  $J = 6.0$  Hz, 1H), 4.25 (dd,  $J = 11.2$  Hz,  $J = 4.0$  Hz, 1H), 3.37-3.26 (m, 3H), 2.46 (s, 3H), 1.40 (s, 9H), 1.13 (s, 9H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  156.1, 144.9, 144.3, 144.1, 141.5, 140.5, 136.7, 130.2, 130.0, 129.5, 128.8, 128.0, 127.8, 127.5, 127.0, 123.5, 76.2, 58.2, 37.2, 35.2, 34.4, 31.3, 30.7, 21.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{32}\text{H}_{38}\text{O}_3\text{S}+\text{NH}_4^+$ : 520.2880, found 520.2880.

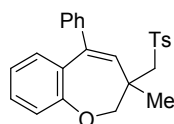


*7,9-dichloro-5-phenyl-3-(tosylmethyl)-2,3-dihydrobenzo[b]oxepine (3ma)*. Yellow solid; (29.8 mg,

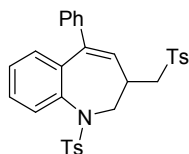
65%); mp: 60-64 °C;  $R_f$  = 0.48 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.78 (d,  $J$  = 8.4 Hz, 2H), 7.38-7.30 (m, 6H), 7.10-7.08 (m, 2H), 6.65 (d,  $J$  = 2.4 Hz, 1H), 6.06 (d,  $J$  = 5.2 Hz, 2H), 4.50-4.40 (m, 1H), 3.32-3.24 (m, 1H), 3.22-3.11 (m, 1H), 2.47 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  151.7, 145.2, 140.5, 139.8, 136.2, 135.1, 131.2, 130.1, 129.2, 129.1, 128.9, 128.4, 128.3, 128.1, 128.0, 80.4, 57.2, 35.3, 21.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{24}\text{H}_{20}\text{Cl}_2\text{O}_3\text{S}+\text{NH}_4^+$ : 476.0848, found 476.0854.



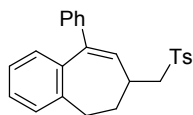
*1-phenyl-3-(tosylmethyl)-3,4-dihydronaphtho[2,1-b]oxepine (3na)*. Yellow solid; (29.5 mg, 67%); mp: 86-90 °C;  $R_f$  = 0.38 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.85-7.81 (m, 2H), 7.69 (d,  $J$  = 8.0 Hz, 2H), 7.37-7.33 (m, 1H), 7.30-7.25 (m, 3H), 7.23-7.17 (m, 5H), 6.94-6.91 (m, 2H), 6.14 (d,  $J$  = 6.4 Hz, 1H), 4.54 (dd,  $J$  = 9.6 Hz,  $J$  = 2.4 Hz, 1H), 4.29 (dd,  $J$  = 11.6 Hz,  $J$  = 9.6 Hz, 1H), 3.10-3.02 (m, 1H), 3.01-2.97 (m, 1H), 2.43-3.22 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  154.0, 145.1, 140.7, 135.7, 132.0, 131.7, 130.6, 130.3, 130.0, 128.5, 128.4, 128.3, 127.4, 127.2, 126.6, 126.5, 125.7, 124.6, 121.9, 83.4, 56.8, 33.9, 21.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{28}\text{H}_{24}\text{O}_3\text{S}+\text{NH}_4^+$ : 458.1784, found 458.1775.



*3-methyl-5-phenyl-3-(tosylmethyl)-2,3-dihydrobenzo[b]oxepine (3oa)*. Yellow oil; (37.2 mg, 92%);  $R_f$  = 0.39 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.77 (d,  $J$  = 8.0 Hz, 2H), 7.31-7.25 (m, 5H), 7.17-7.10 (m, 3H), 7.05-7.02 (m, 1H), 6.89-6.82 (m, 2H), 5.74 (d,  $J$  = 1.6 Hz, 1H), 4.52 (dd,  $J$  = 12.0 Hz,  $J$  = 1.6 Hz, 1H), 3.96 (d,  $J$  = 12.0 Hz, 1H), 3.46-3.41 (m, 2H), 3.42 (q,  $J$  = 44.0 Hz,  $J$  = 14.0 Hz, 2H), 2.40 (s, 3H), 1.49 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  160.1, 144.424, 144.402, 138.5, 137.2, 137.1, 132.7, 129.8, 129.3, 128.6, 128.0, 127.7, 127.6, 126.9, 122.6, 120.3, 77.4, 63.3, 44.6, 23.3, 21.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{25}\text{H}_{24}\text{O}_3\text{S}+\text{NH}_4^+$ : 422.1784, found 422.1785.

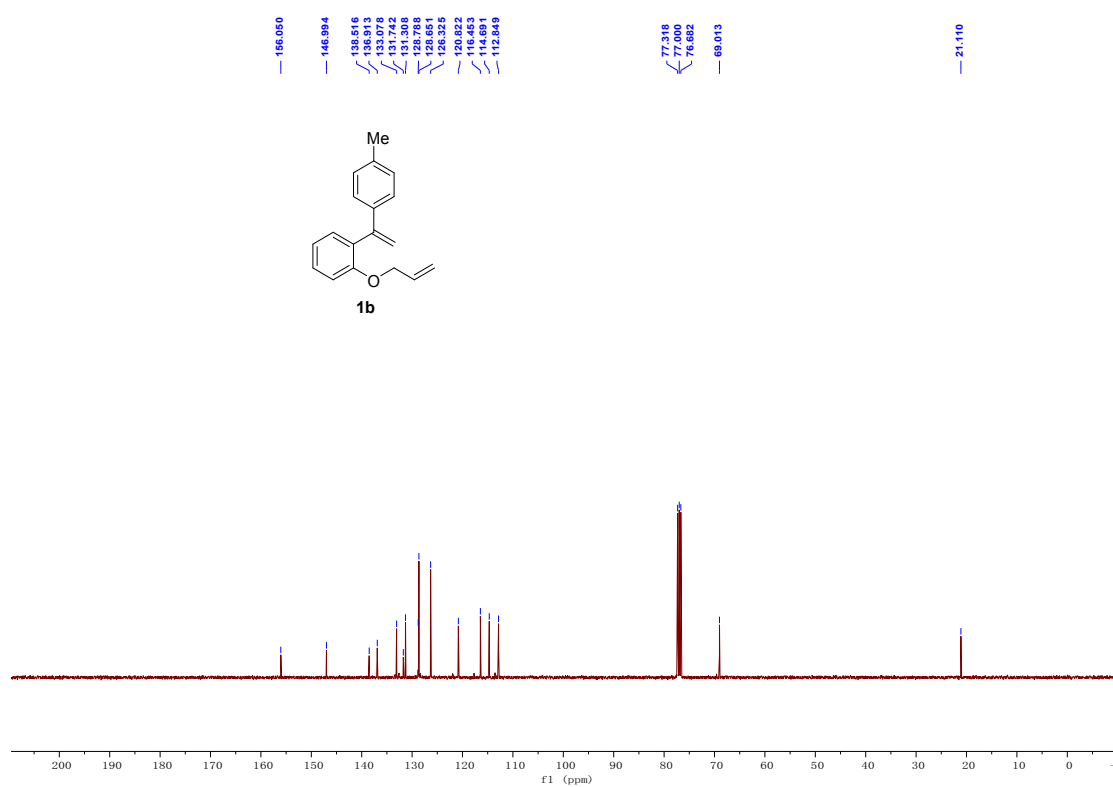
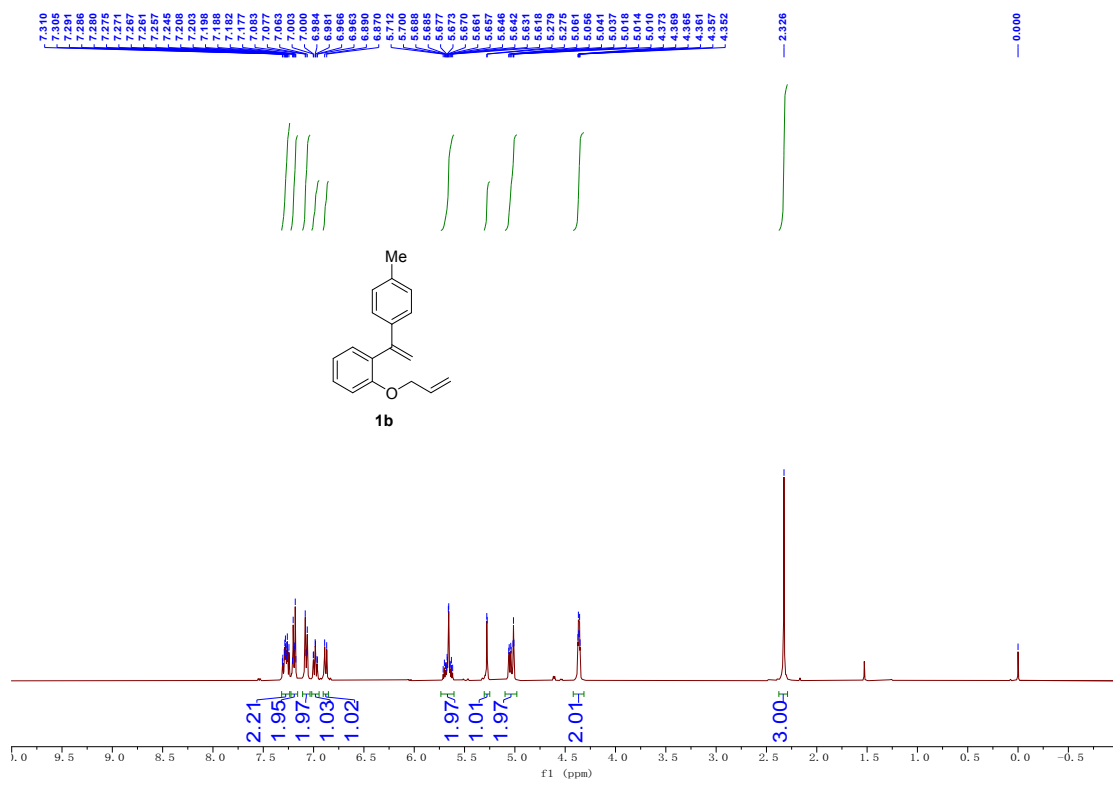


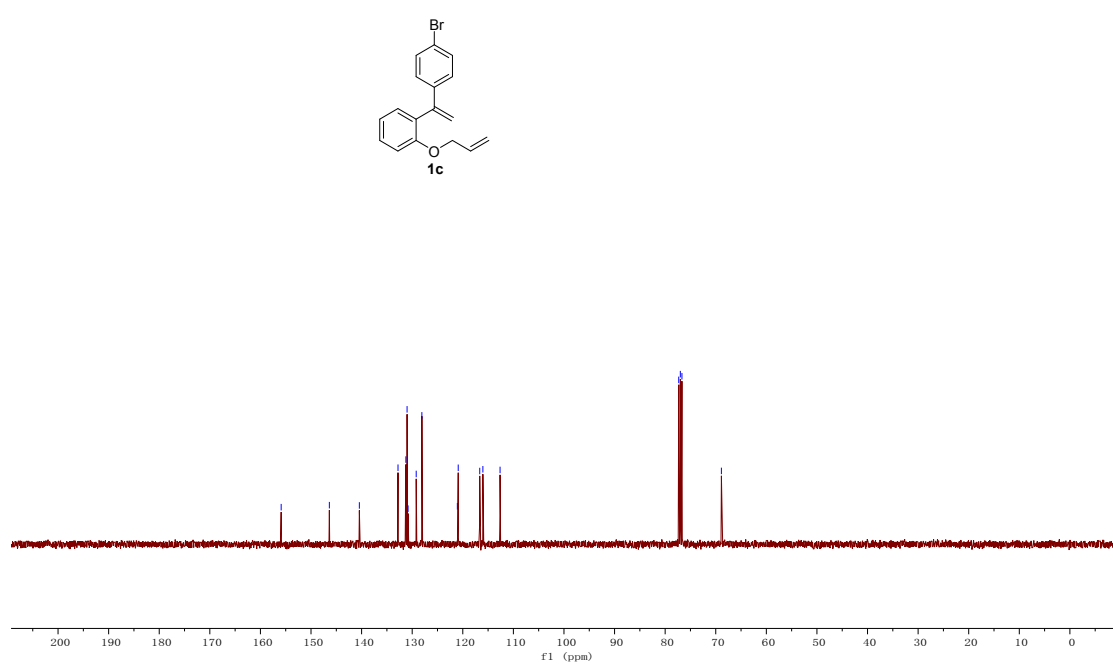
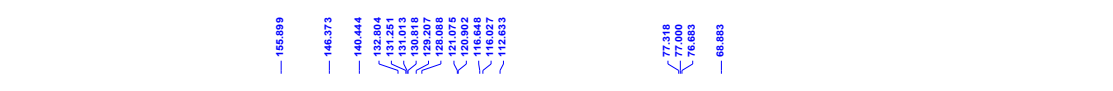
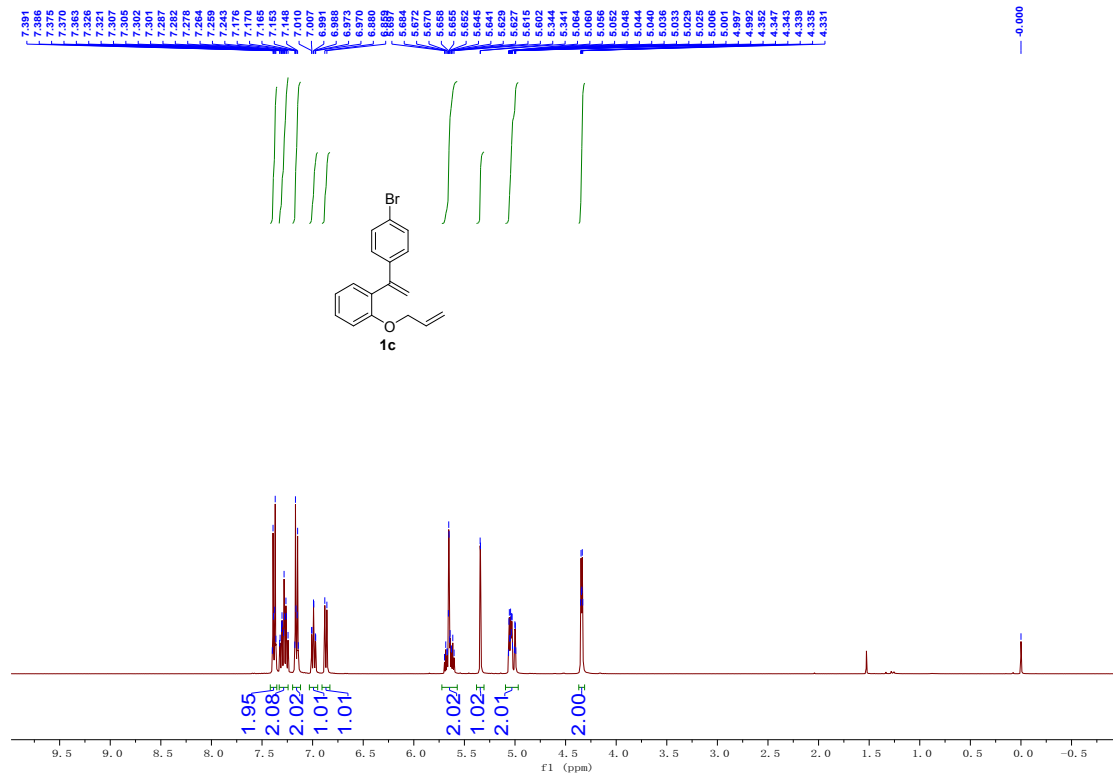
*5-phenyl-1-tosyl-3-(tosylmethyl)-2,3-dihydro-1H-benzo[b]azepine (3qa)*. Yellow solid; (48.3 mg, 89%); mp: 92-96 °C;  $R_f$  = 0.38 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.72 (d,  $J$  = 8.0 Hz, 2H), 7.52-7.46 (m, 2H), 7.37-7.30 (m, 4H), 7.26-7.22 (m, 1H), 7.18-7.14 (m, 2H), 6.97-6.95 (m, 3H), 6.74 (d,  $J$  = 7.6 Hz, 2H), 5.86 (d,  $J$  = 6.0 Hz, 2H), 4.37 (s, 1H), 4.05 (s, 1H), 3.31 (dd,  $J$  = 14.0 Hz,  $J$  = 9.6 Hz, 1H), 3.11 (dd,  $J$  = 14.0 Hz,  $J$  = 4.0 Hz, 1H), 2.97 (s, 1H), 2.45 (s, 3H), 2.23 (s, 3H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  145.1, 143.1, 137.5, 135.9, 130.0, 129.3, 128.7, 128.4, 128.2, 127.8, 127.7, 127.6, 127.2, 77.2, 58.0, 33.4, 21.6, 21.3 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{31}\text{H}_{29}\text{NO}_4\text{S}_2+\text{NH}_4^+$ : 561.1876, found 561.1872.

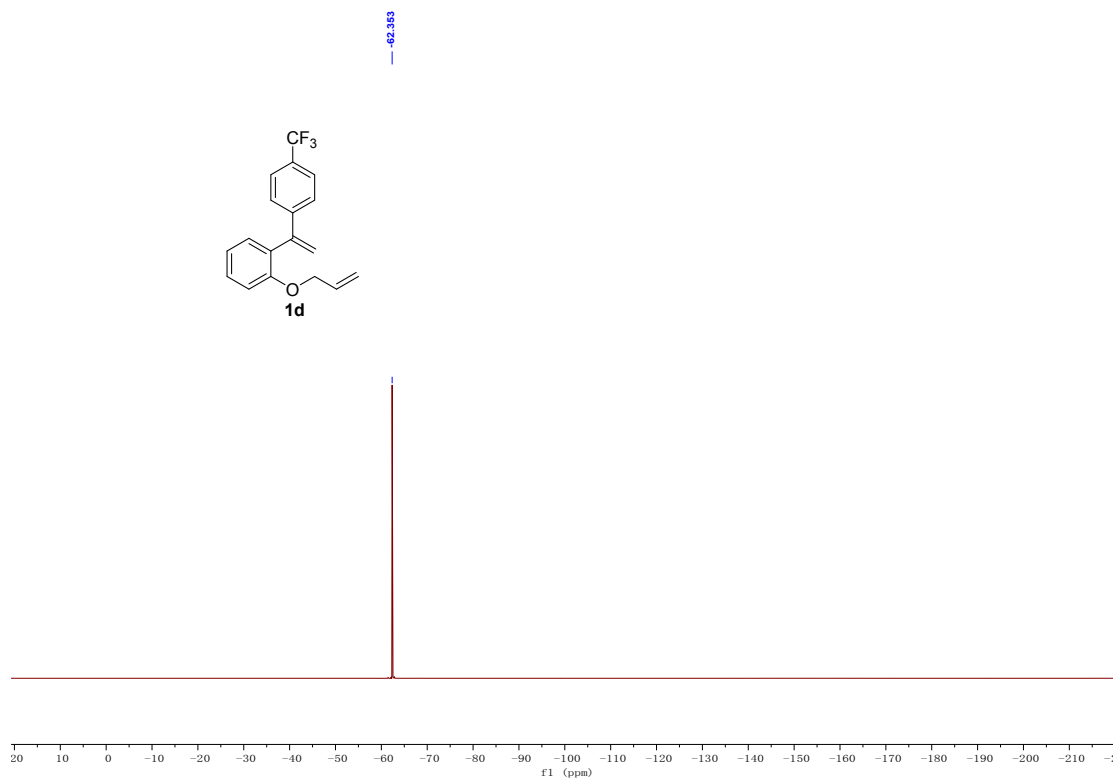
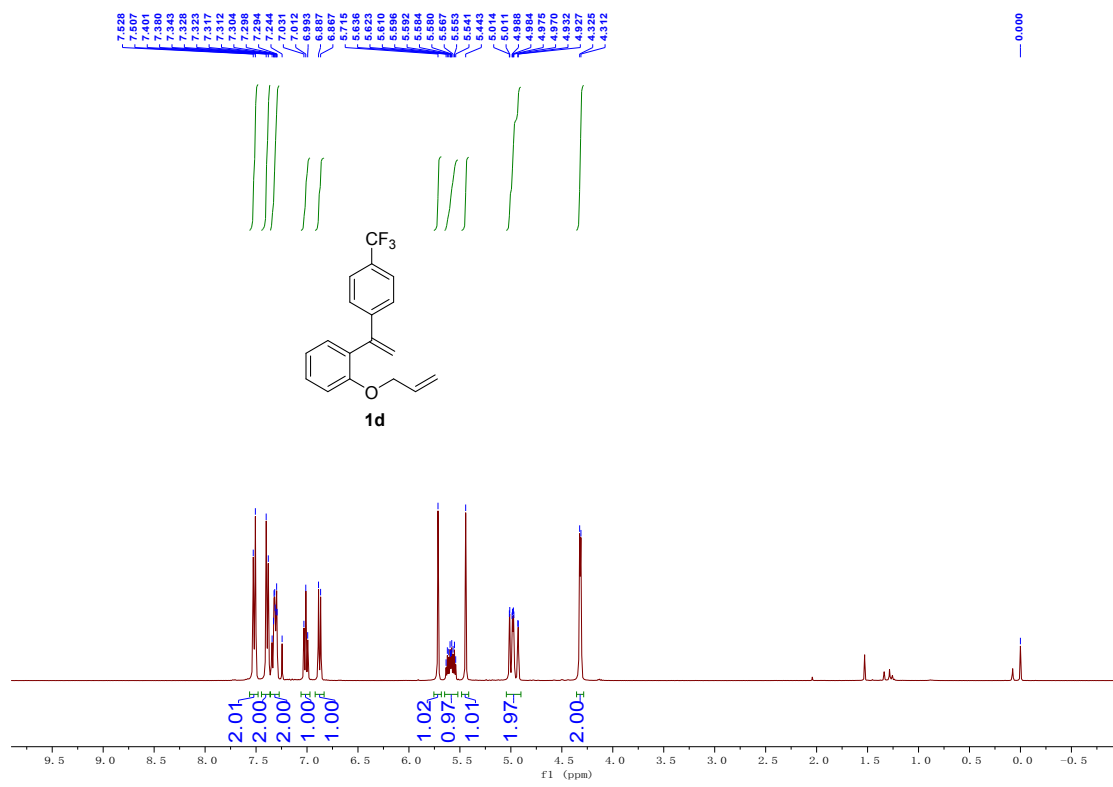


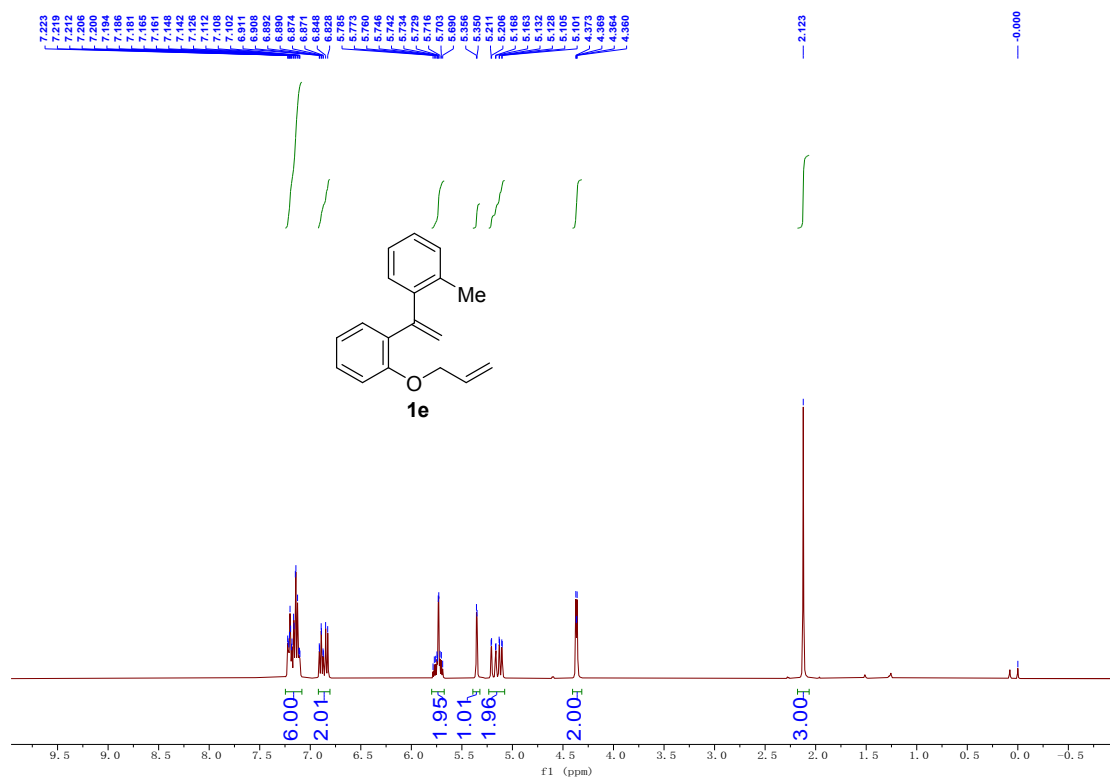
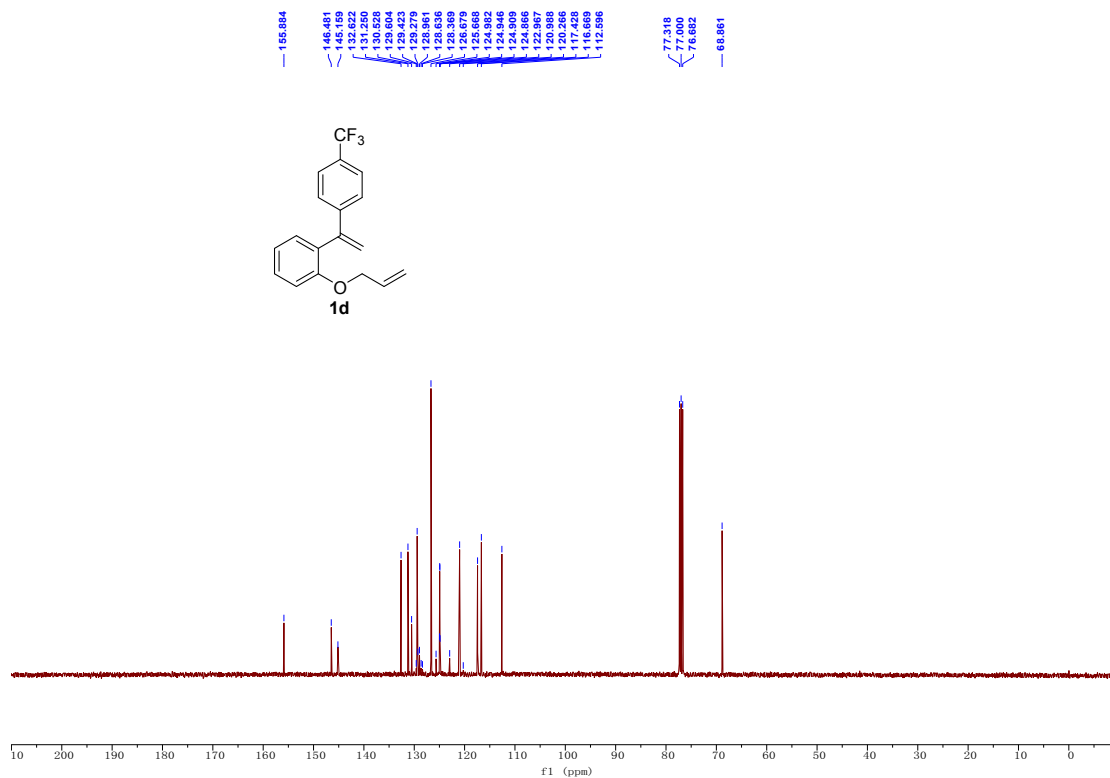
*9-phenyl-7-(tosylmethyl)-6,7-dihydro-5H-benzo[7]annulene (3ra)*. Yellow solid; (25.2 mg, 65%); mp: 51-52 °C;  $R_f$  = 0.41 (petroleum ether/ethyl acetate 5:1);  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  = 7.70 (d,  $J$  = 7.6 Hz, 2H), 7.31-7.22 (m, 8H), 7.07-7.05 (m, 2H), 6.98 (d,  $J$  = 0.8 Hz, 1H), 6.01 (d,  $J$  = 6.4 Hz, 1H), 3.32 (dd,  $J$  = 14.0 Hz,  $J$  = 6.0 Hz, 1H), 3.08 (dd,  $J$  = 14.0 Hz,  $J$  = 3.6 Hz, 1H), 2.72-2.64 (m, 1H), 2.60-2.48 (m, 1H), 2.42 (s, 3H), 2.34-2.25 (m, 1H), 2.02-1.93 (m, 1H) ppm;  $^{13}\text{C}$  NMR (101 MHz,  $\text{CDCl}_3$ ):  $\delta$  144.7, 142.0, 141.2, 141.1, 139.6, 136.3, 129.9, 129.3, 129.2, 128.6, 128.4, 128.1, 128.0, 127.6, 127.4, 126.3, 61.2, 42.2, 32.6, 31.6, 21.6 ppm. ESI-HRMS:  $m/z$  Calcd for  $\text{C}_{25}\text{H}_{24}\text{O}_2\text{S}+\text{Na}^+$ : 411.1389, found 411.1395.

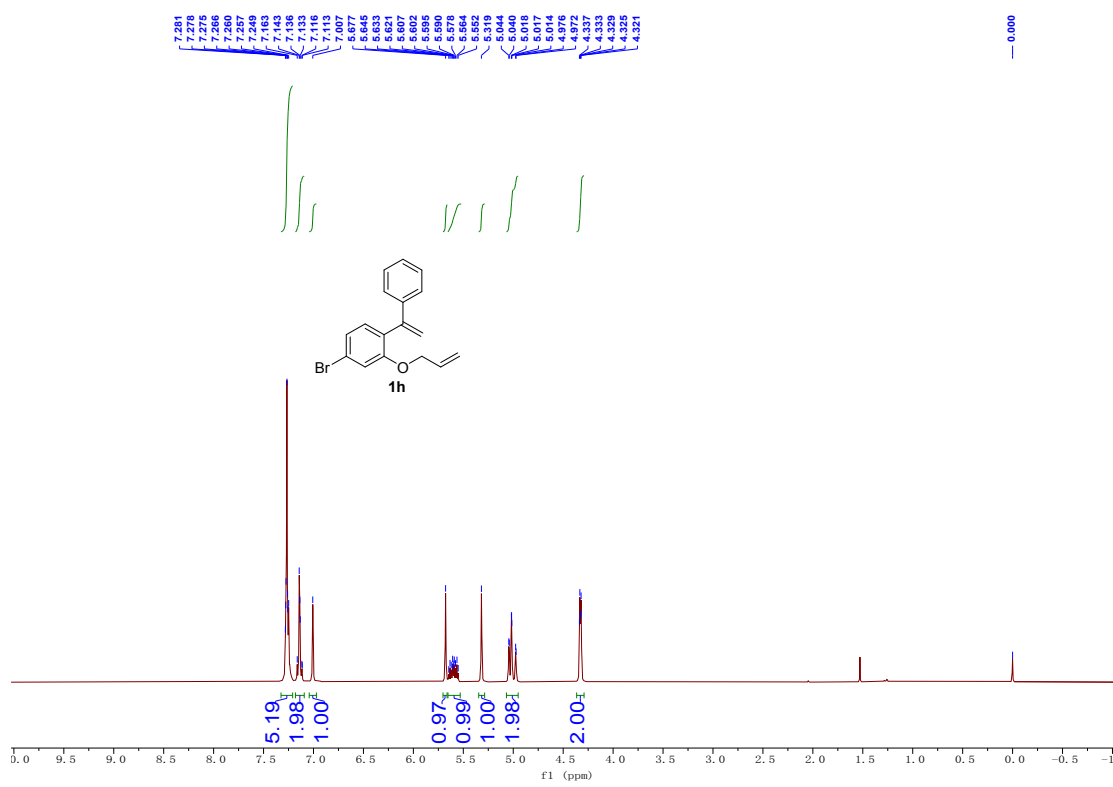
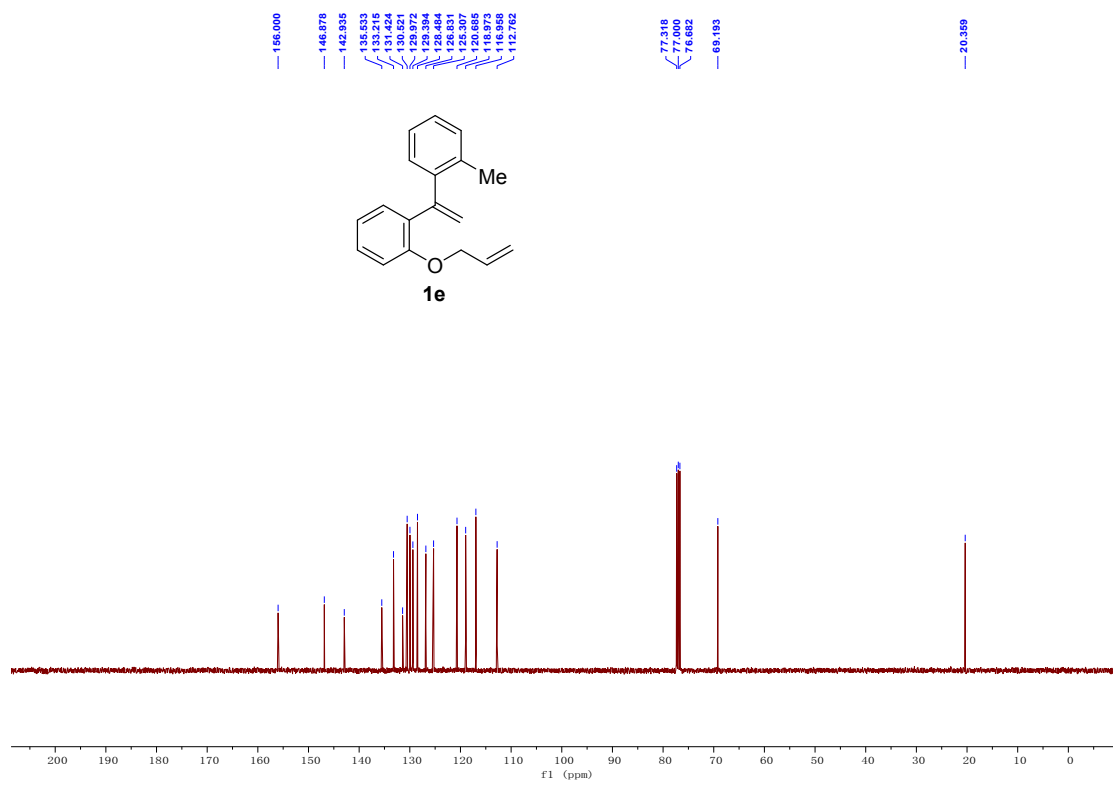


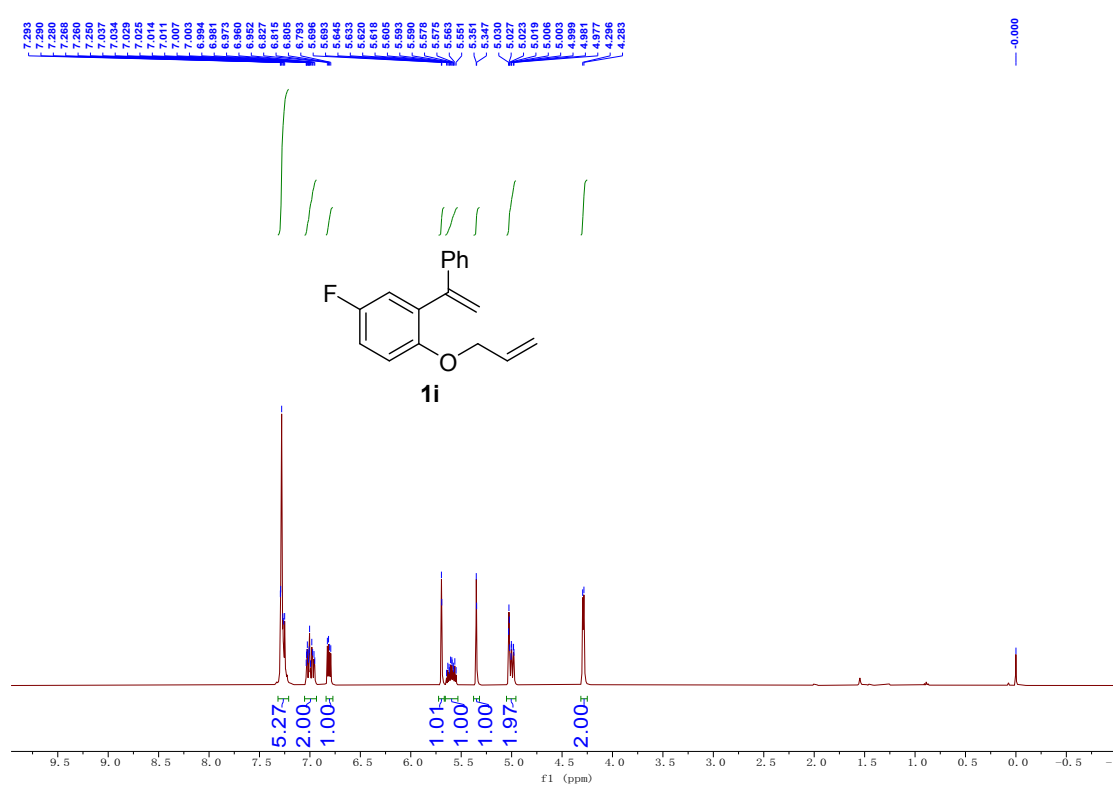
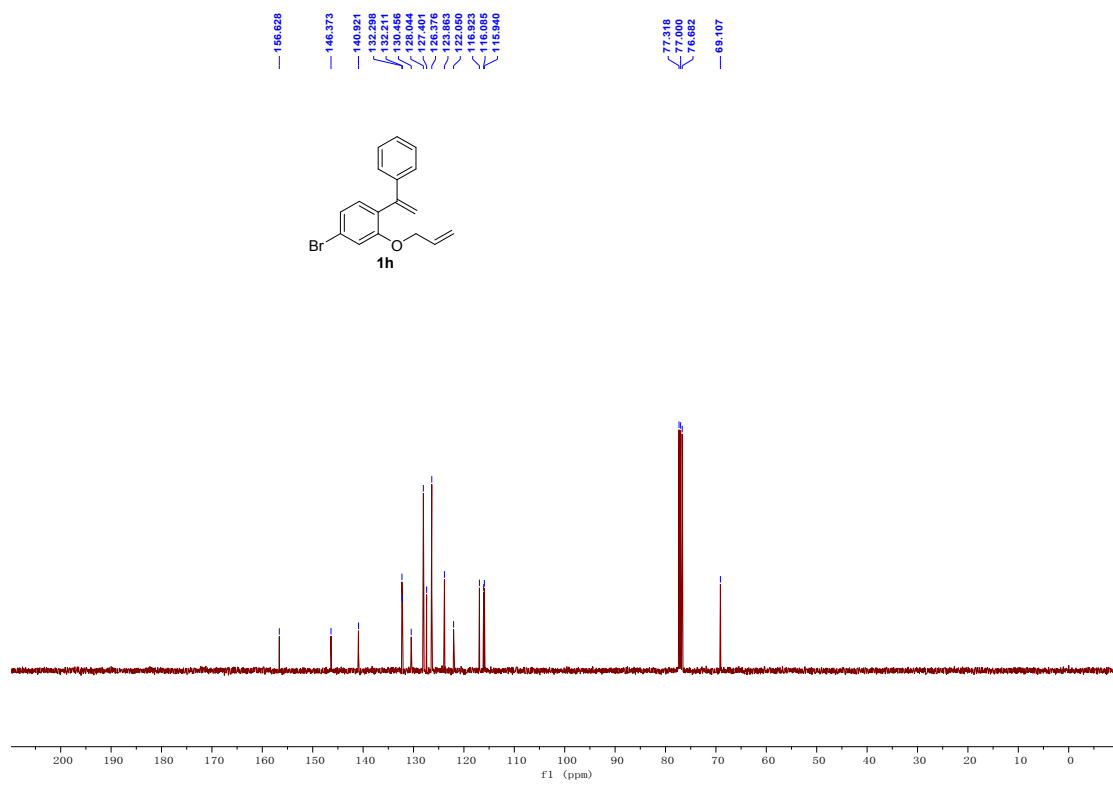


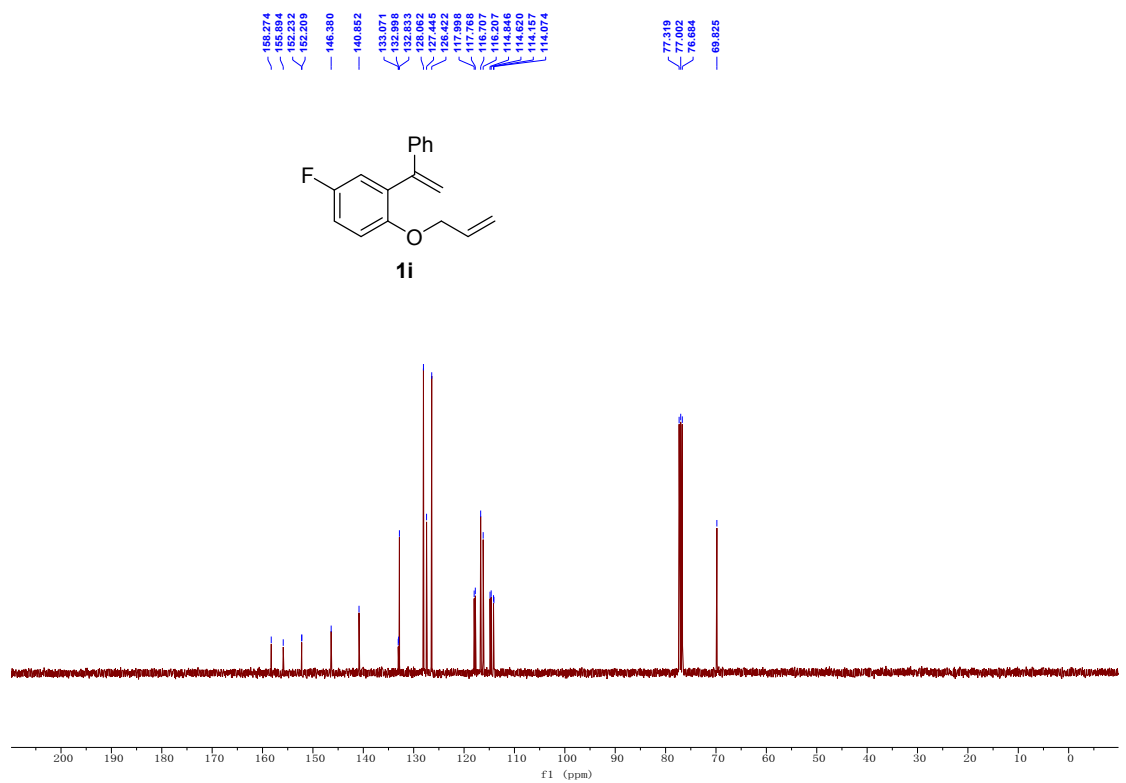
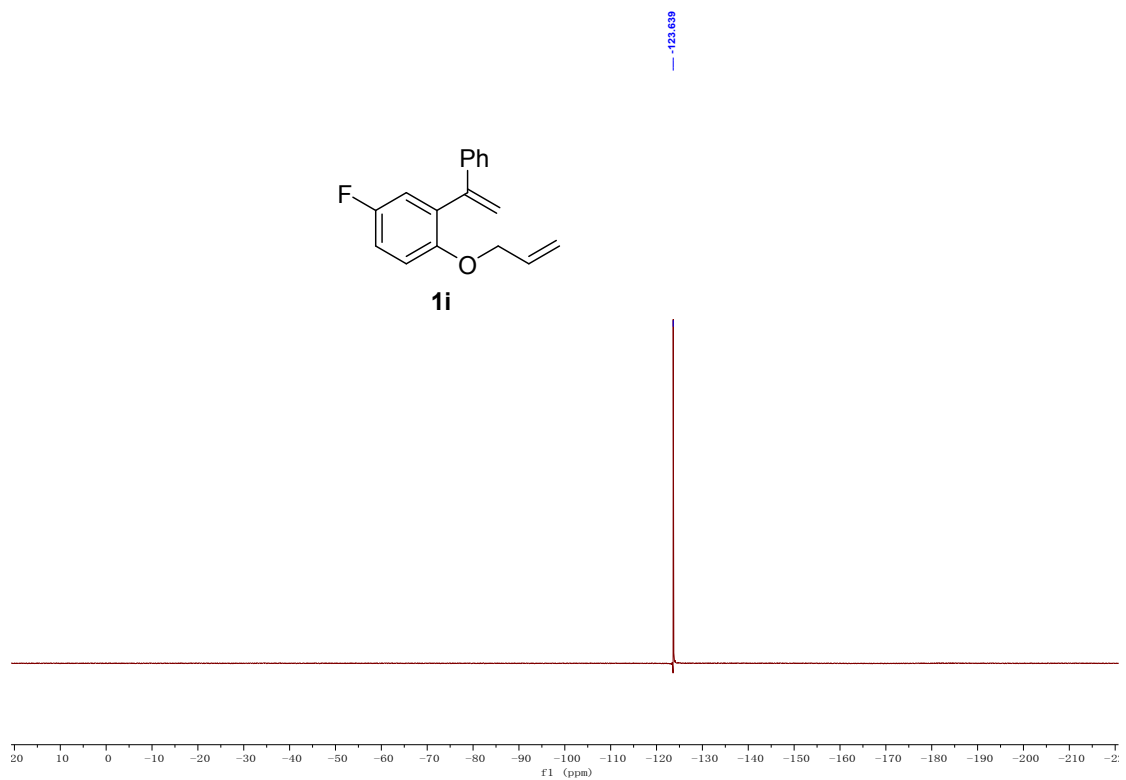


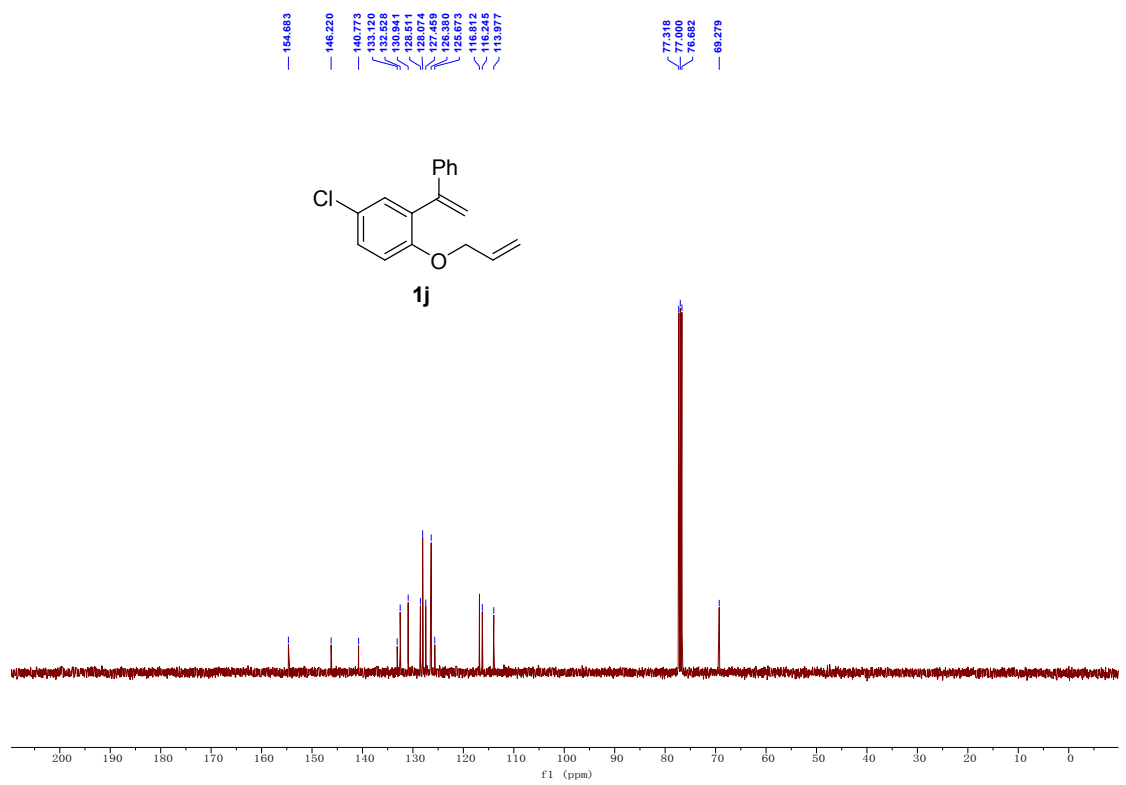
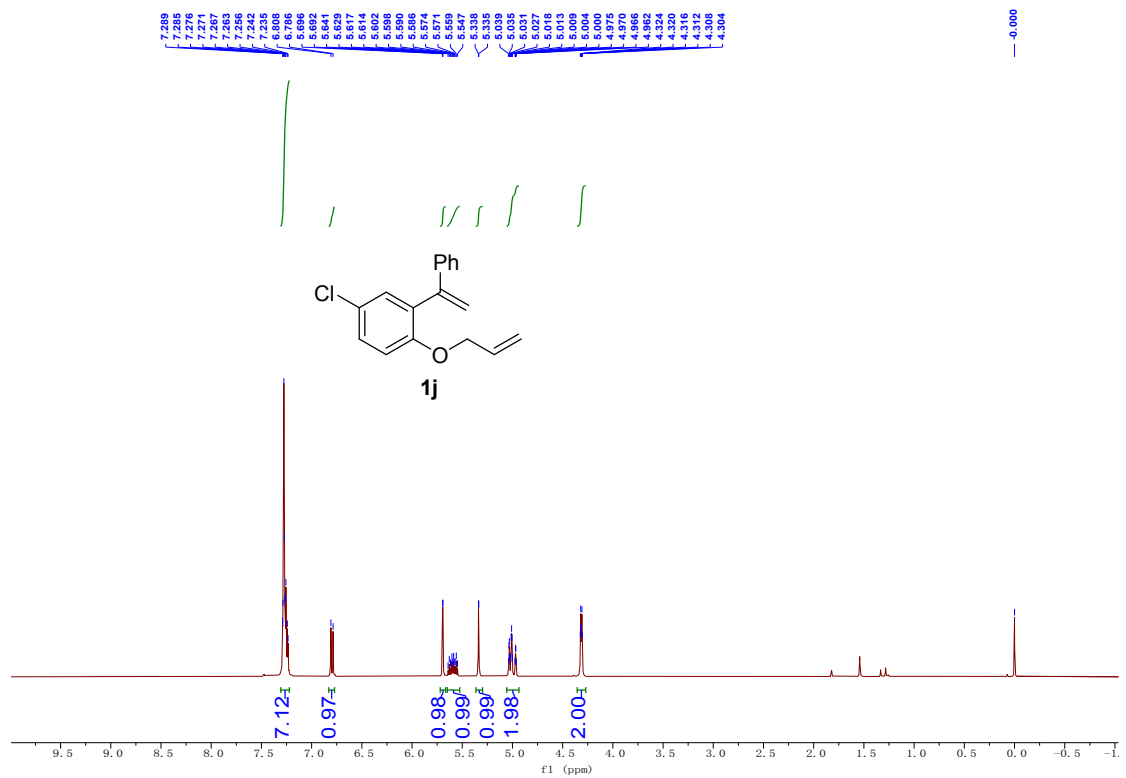




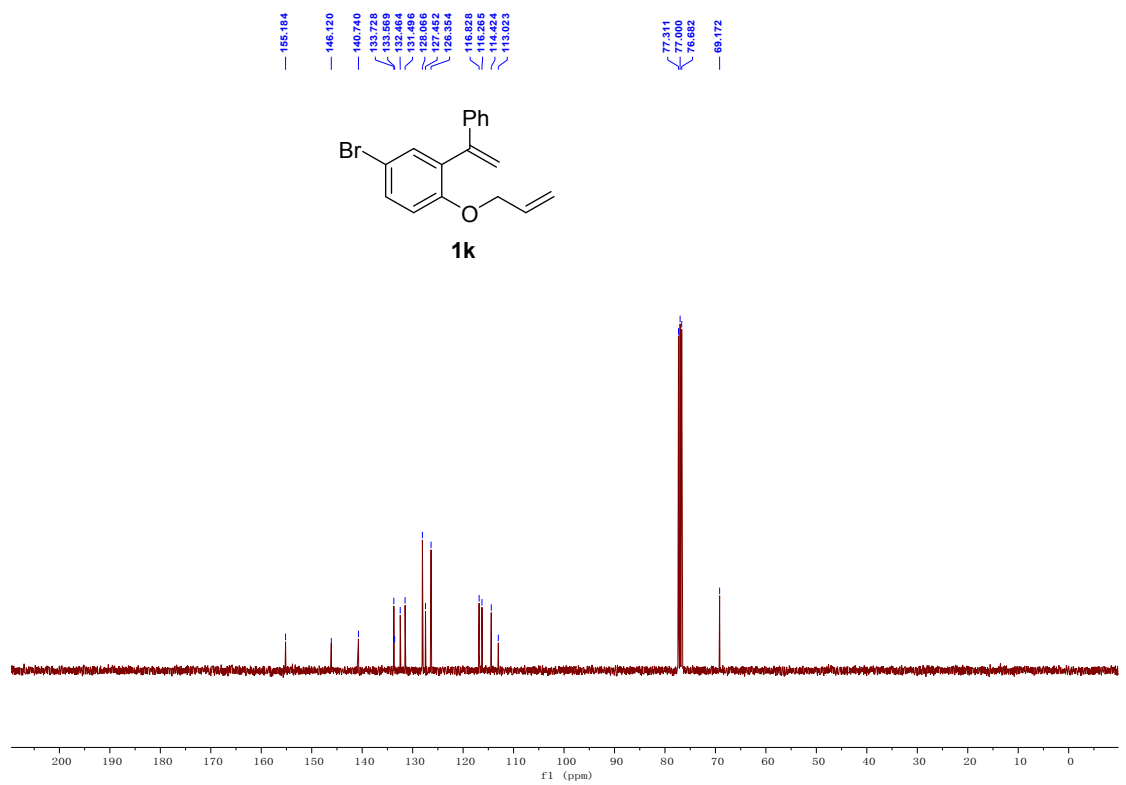
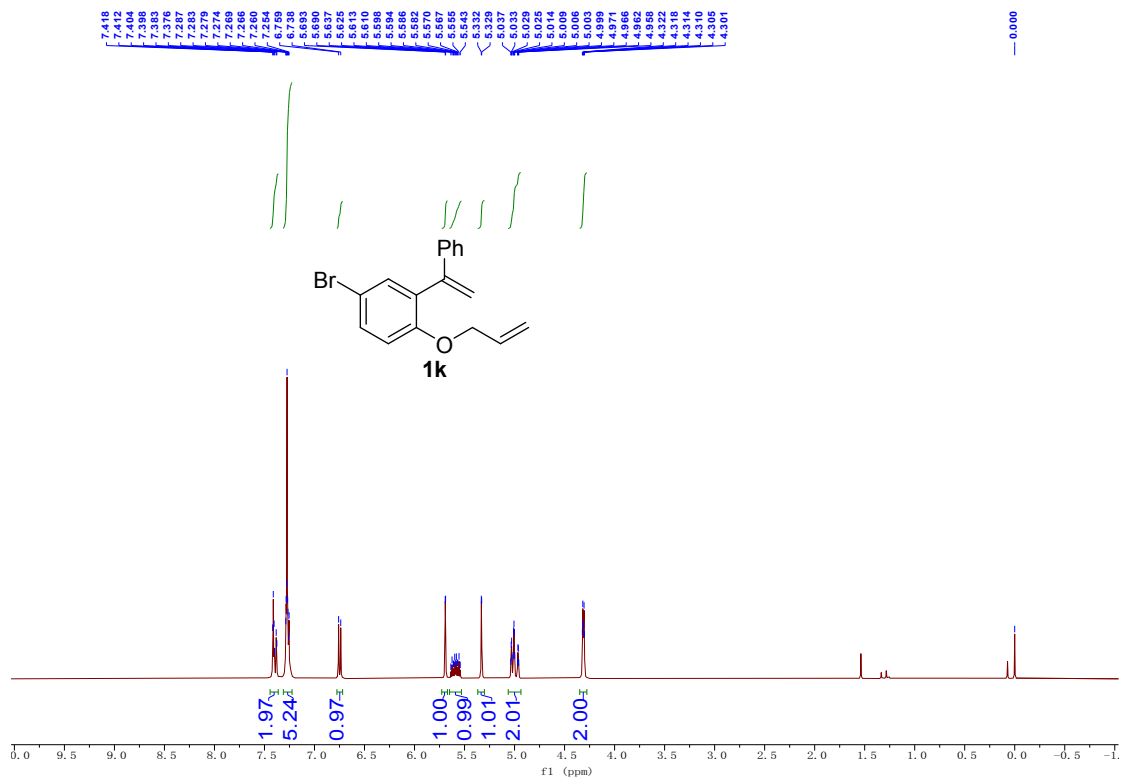


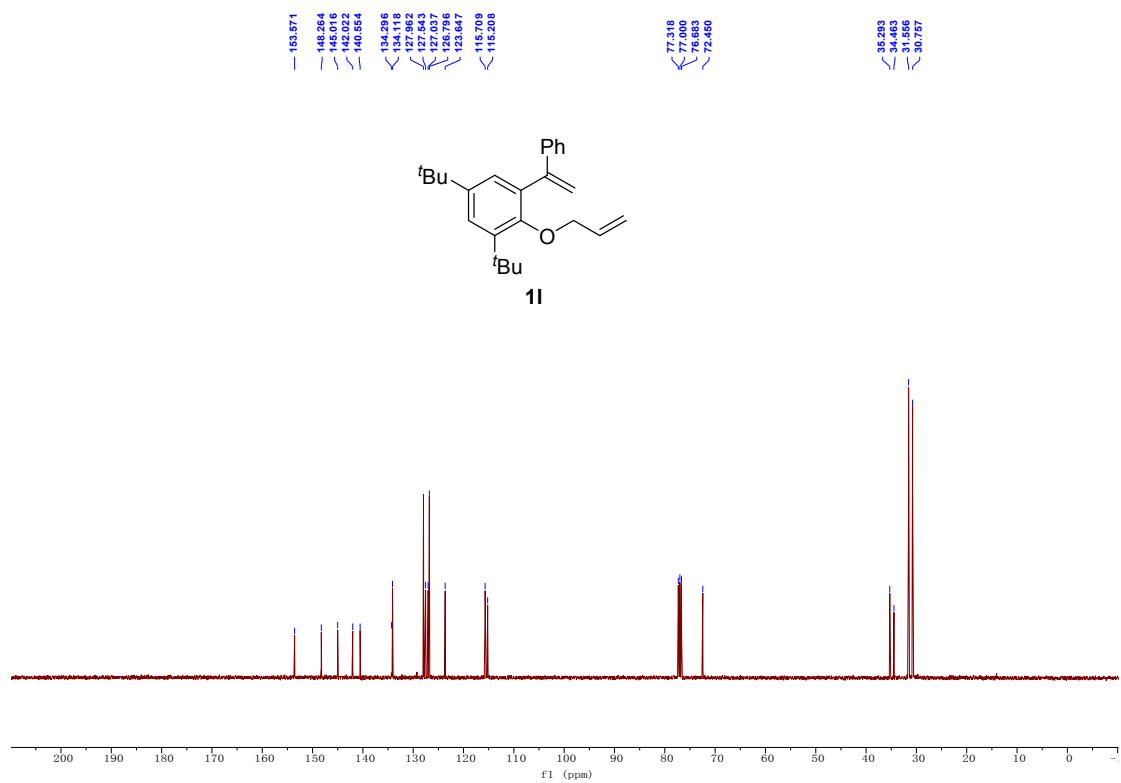
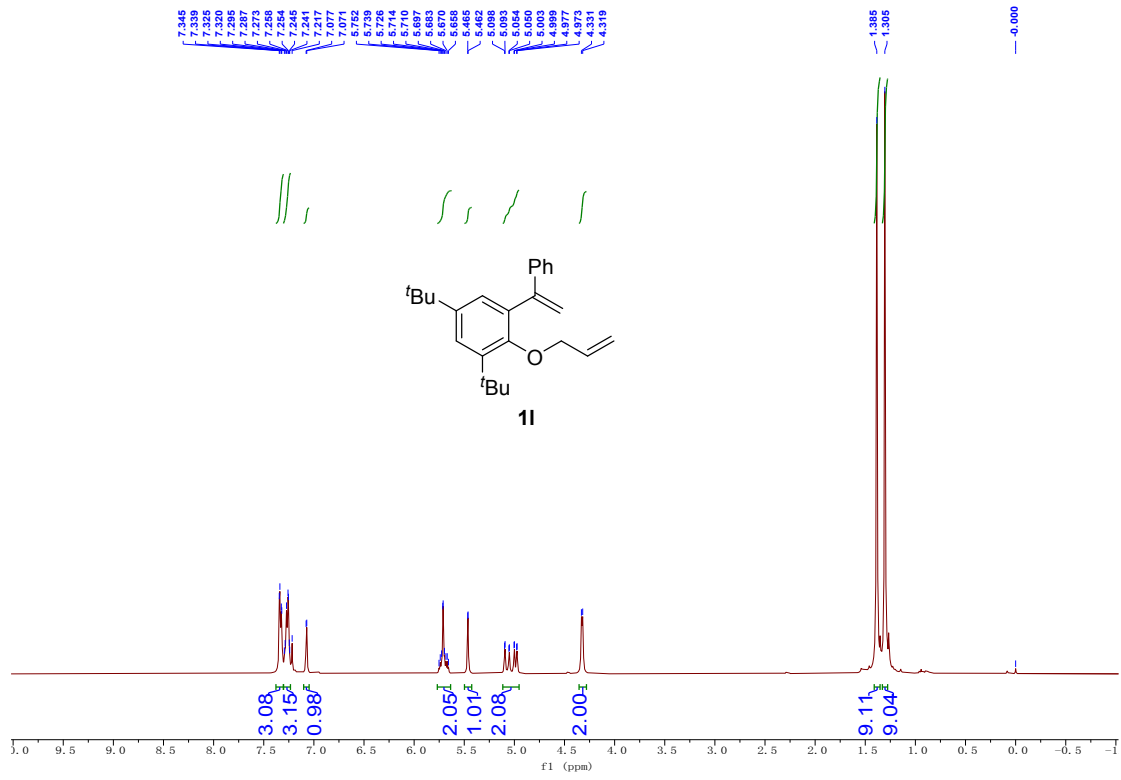


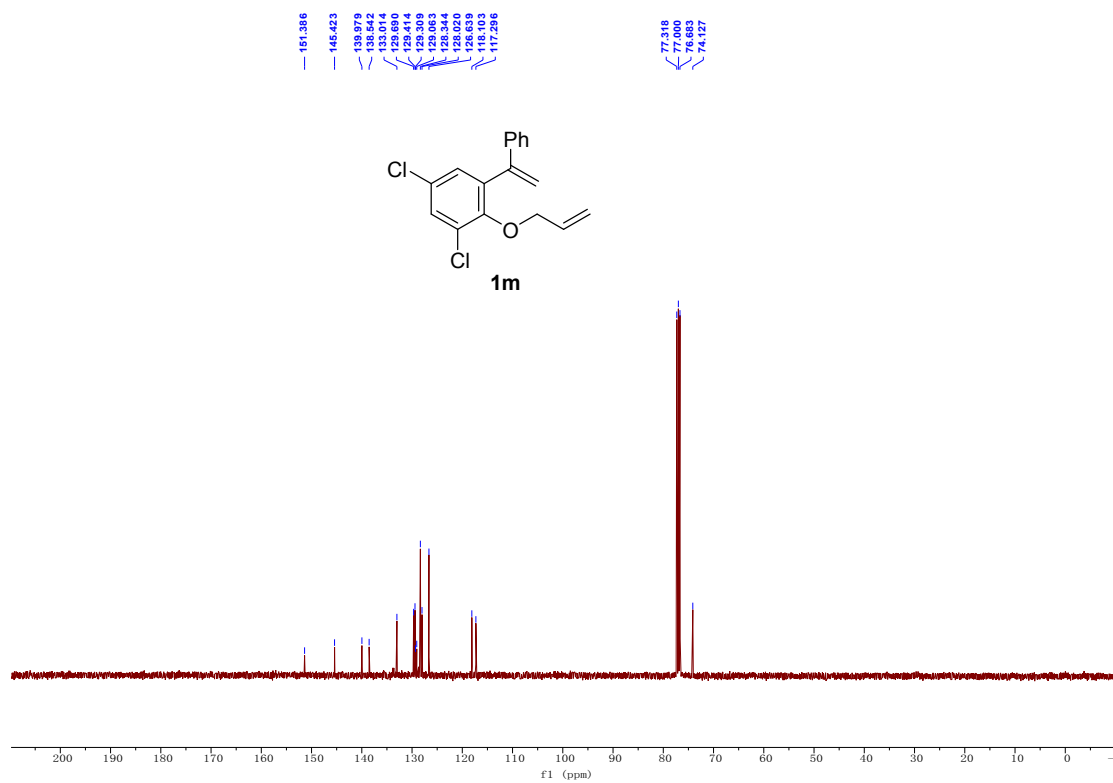
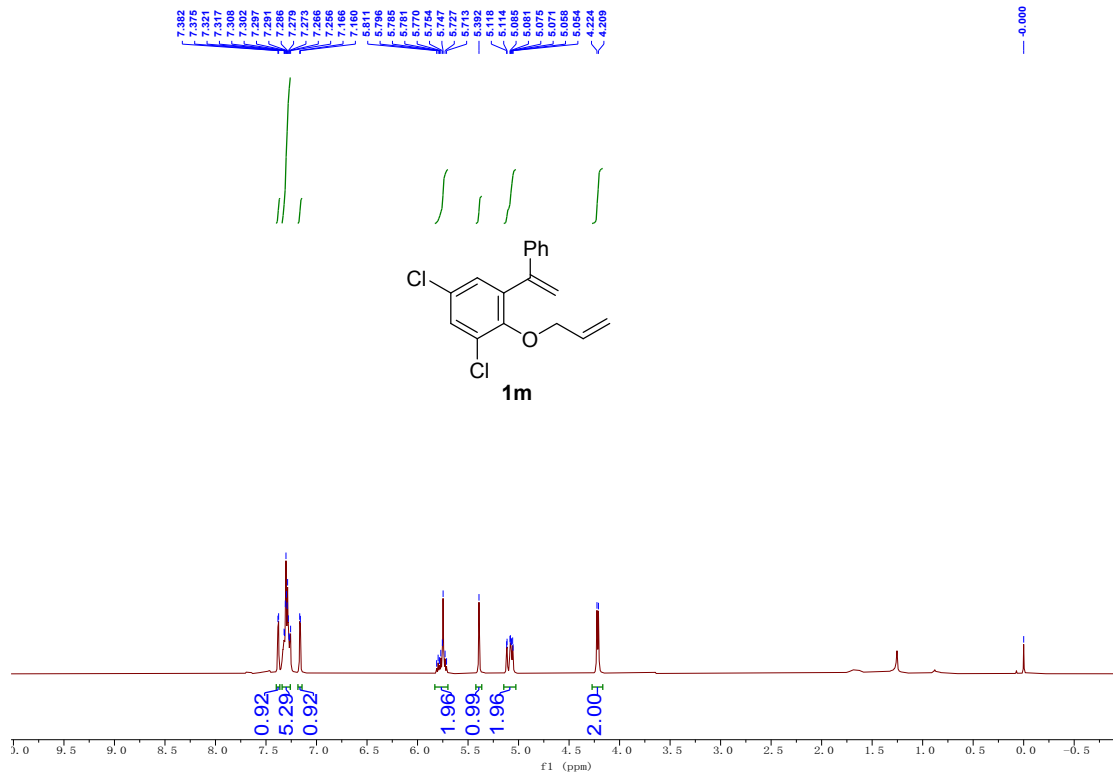


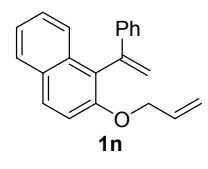
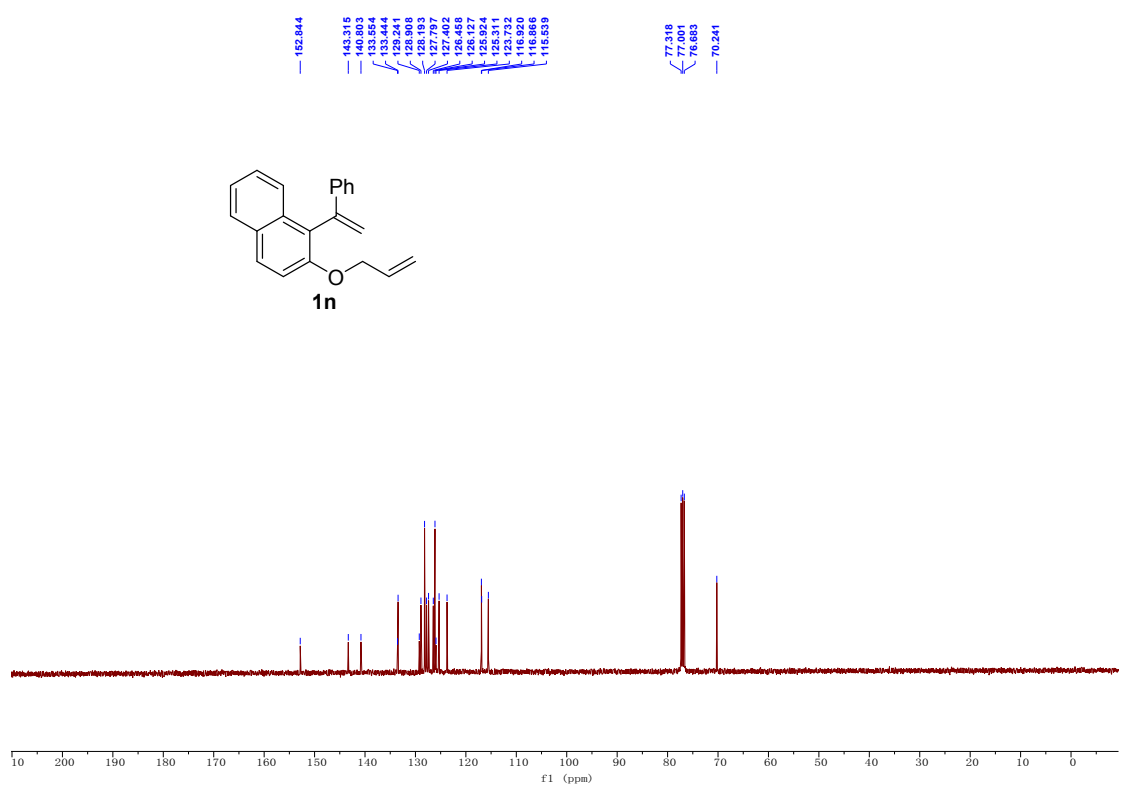
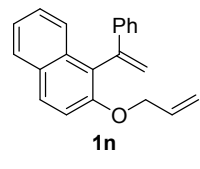
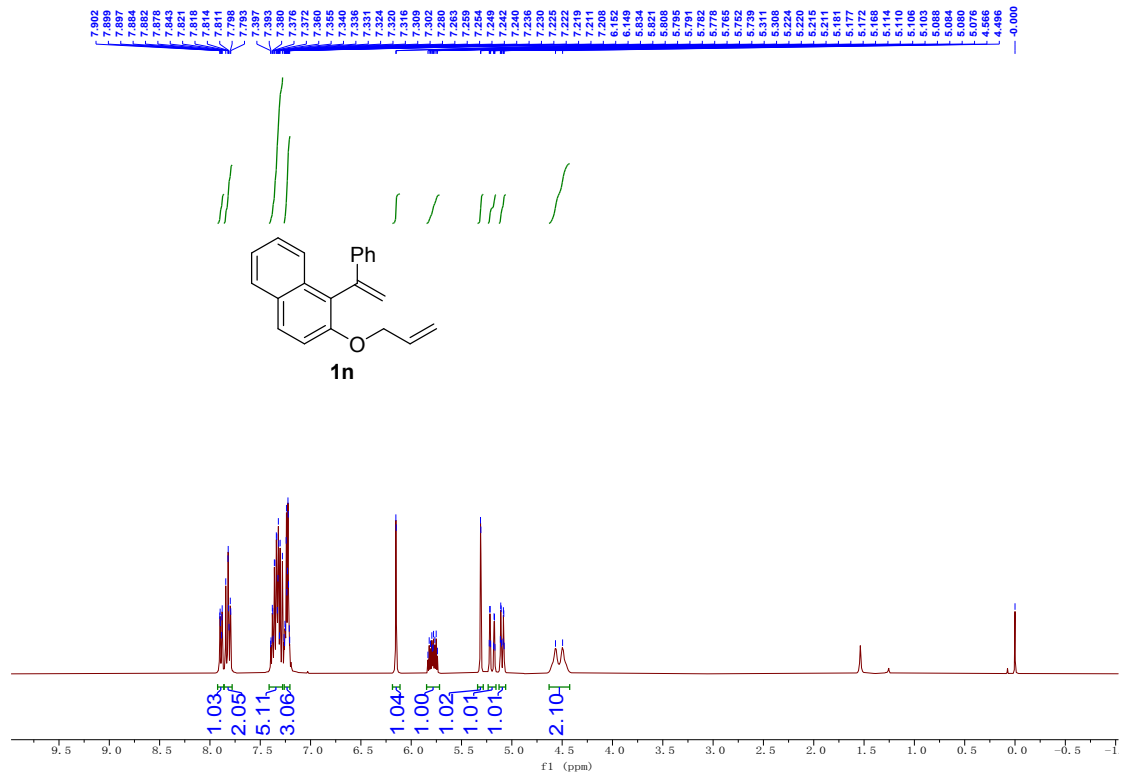


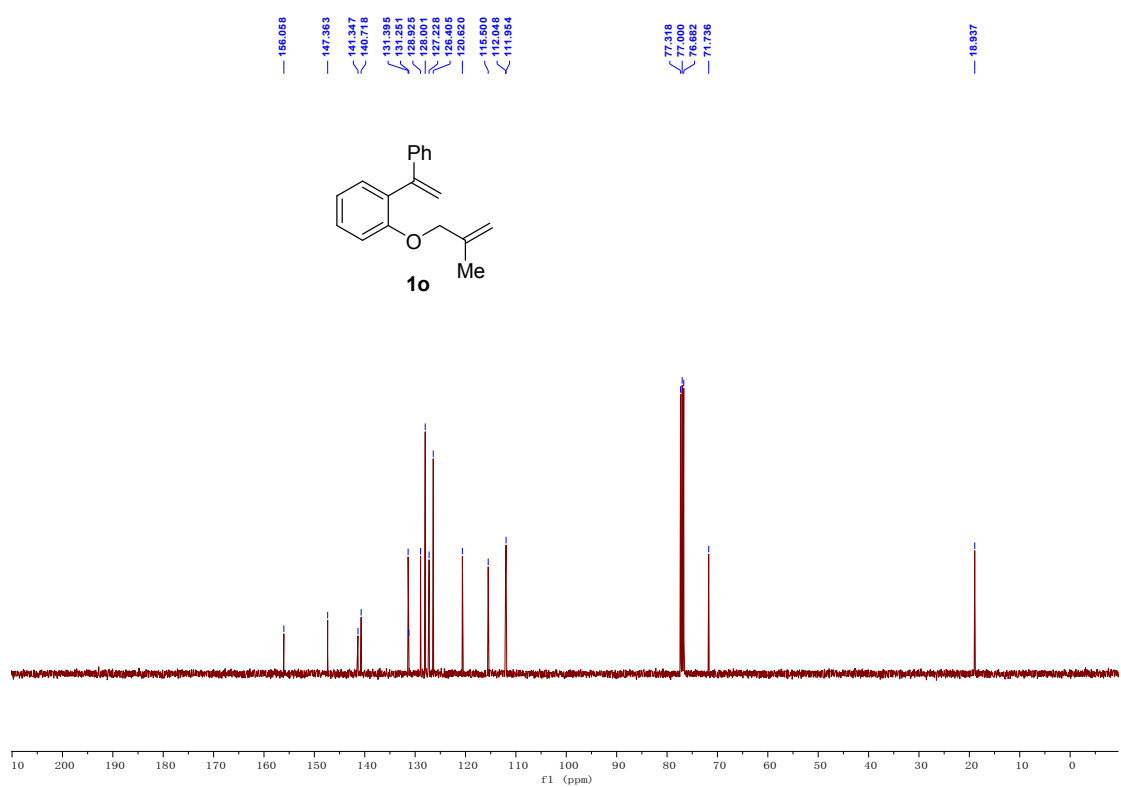
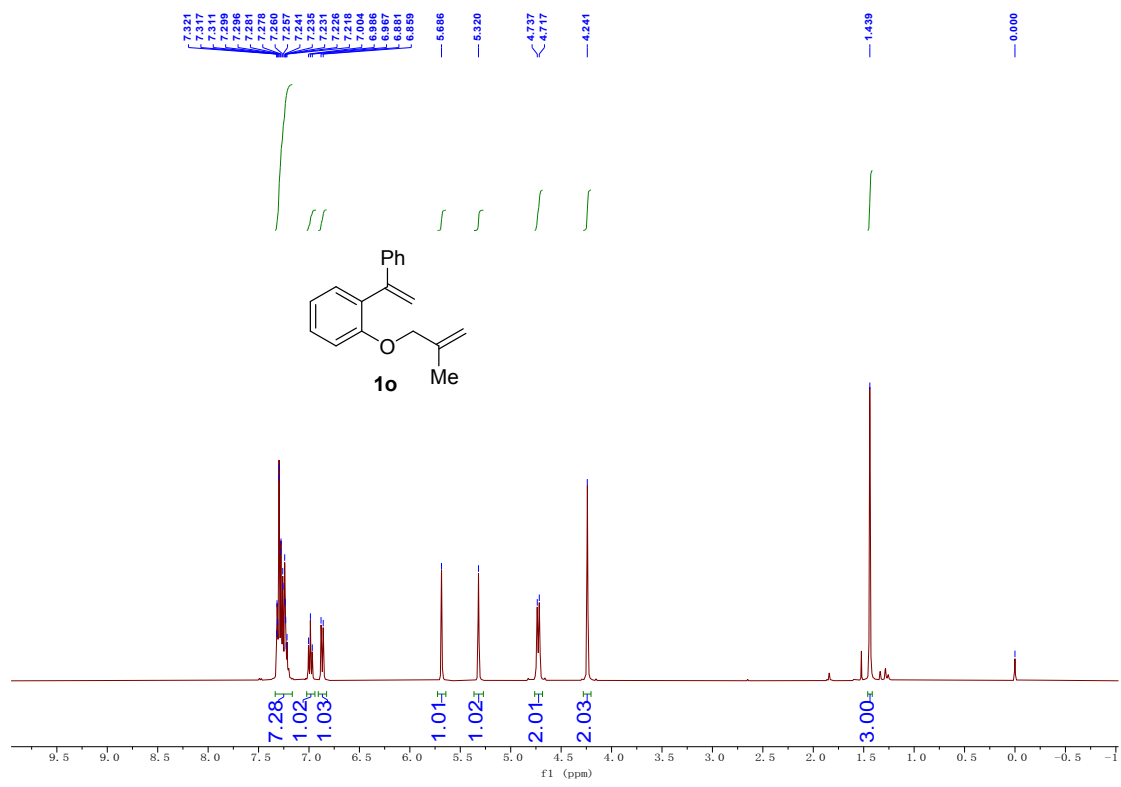


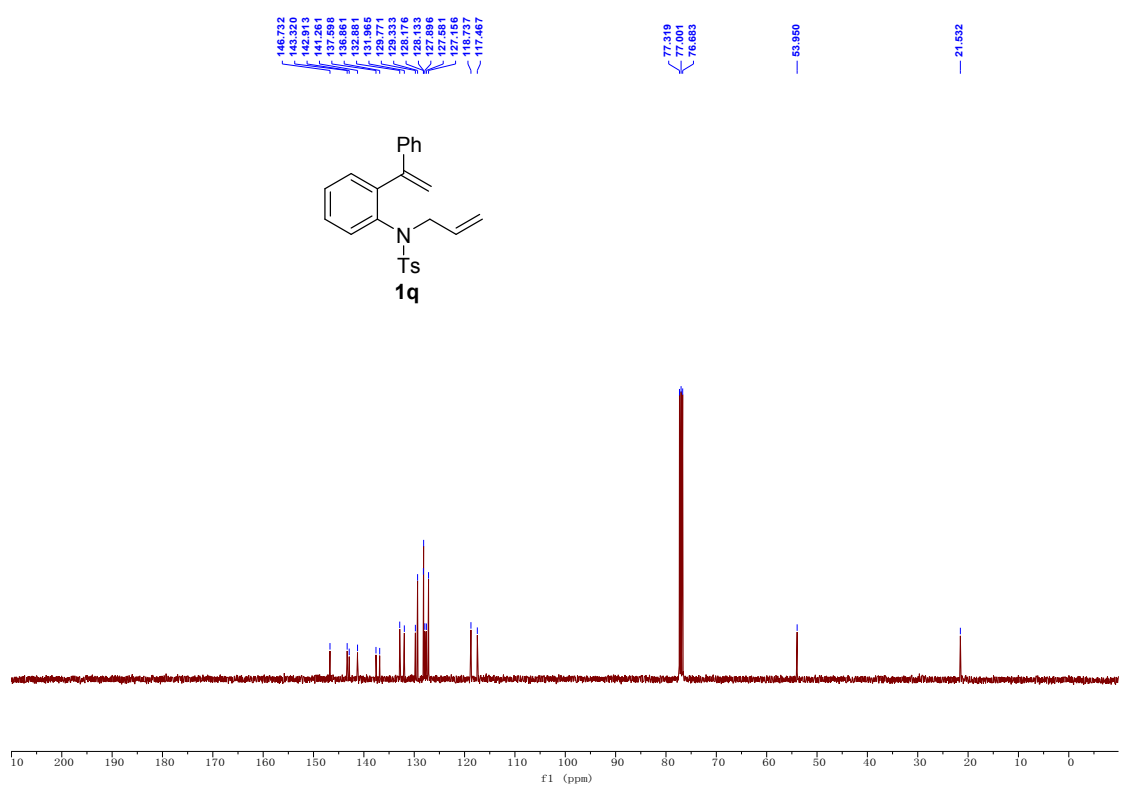
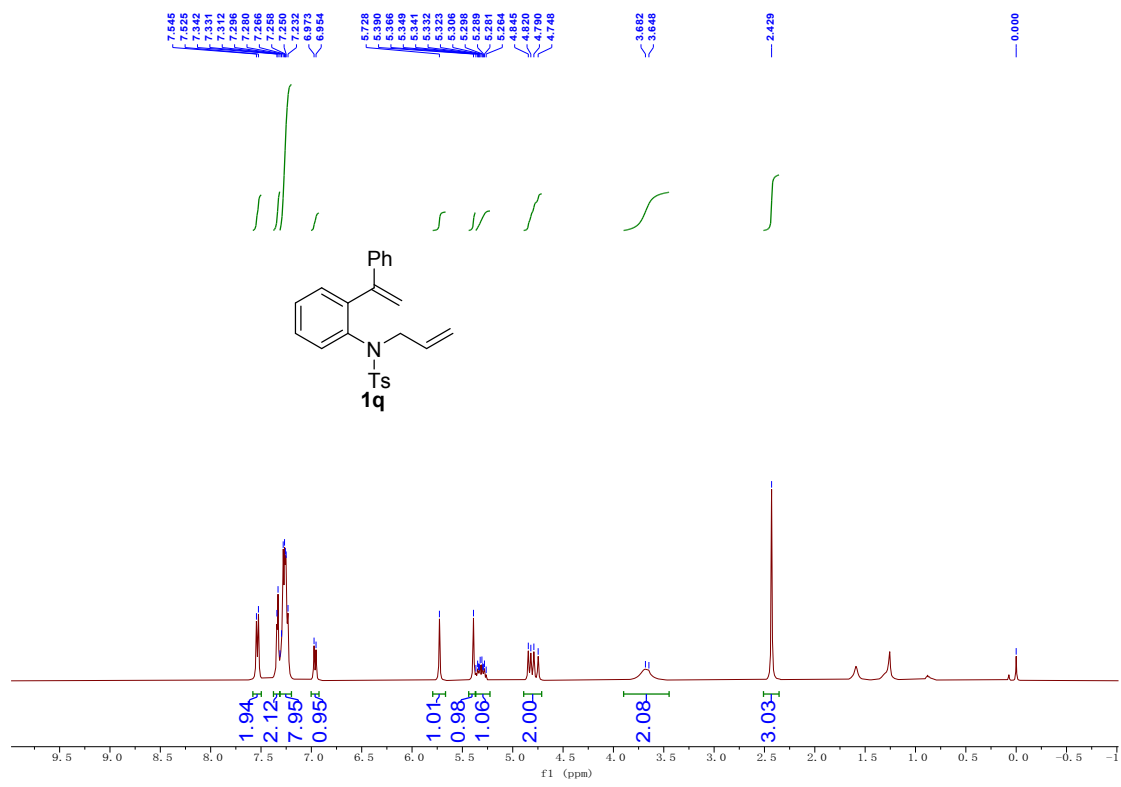


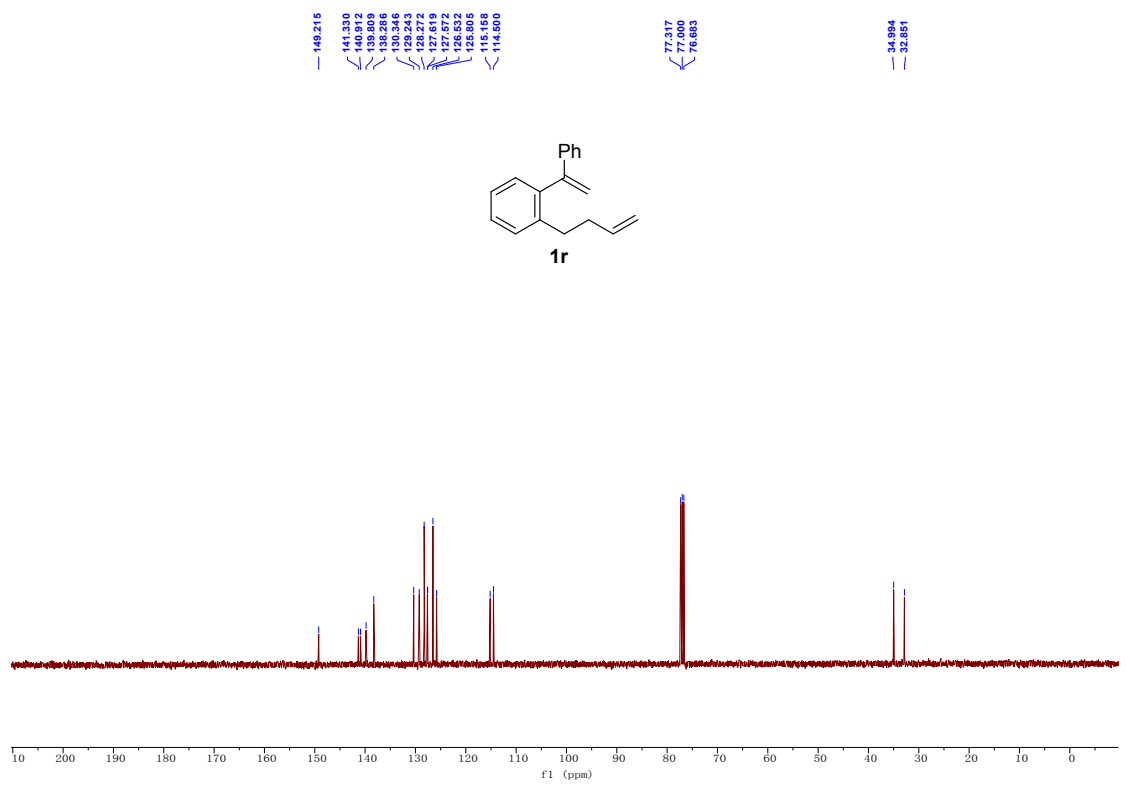
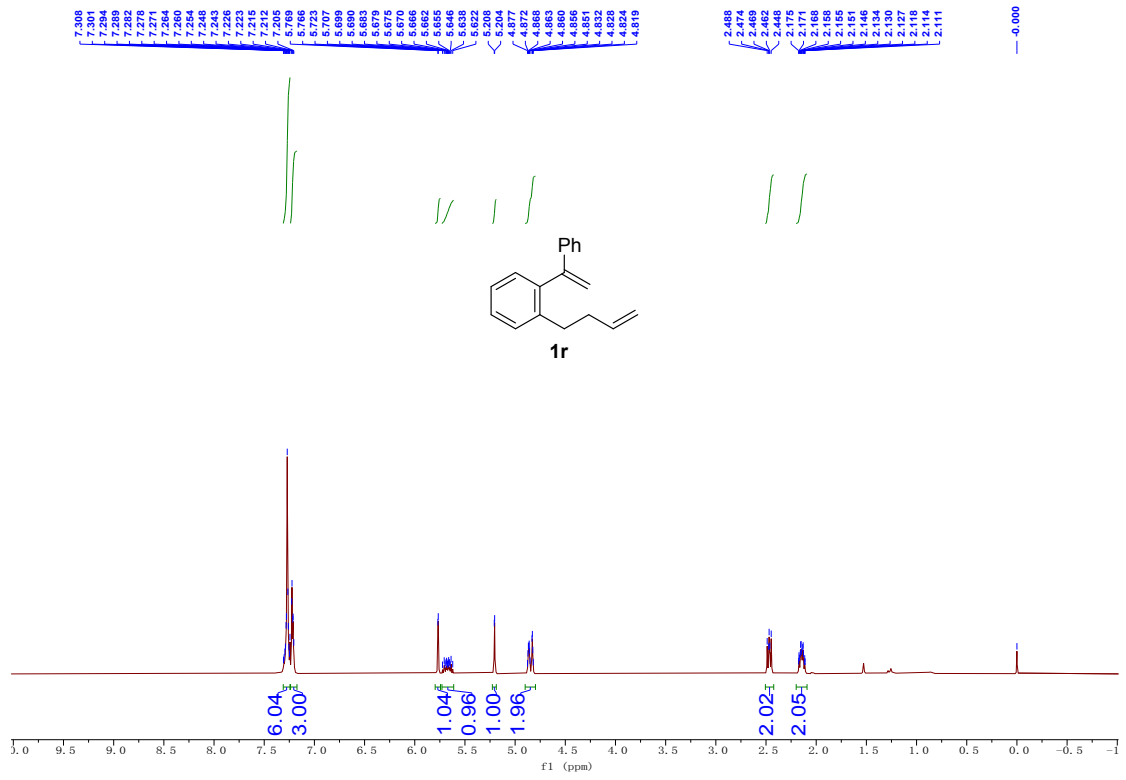


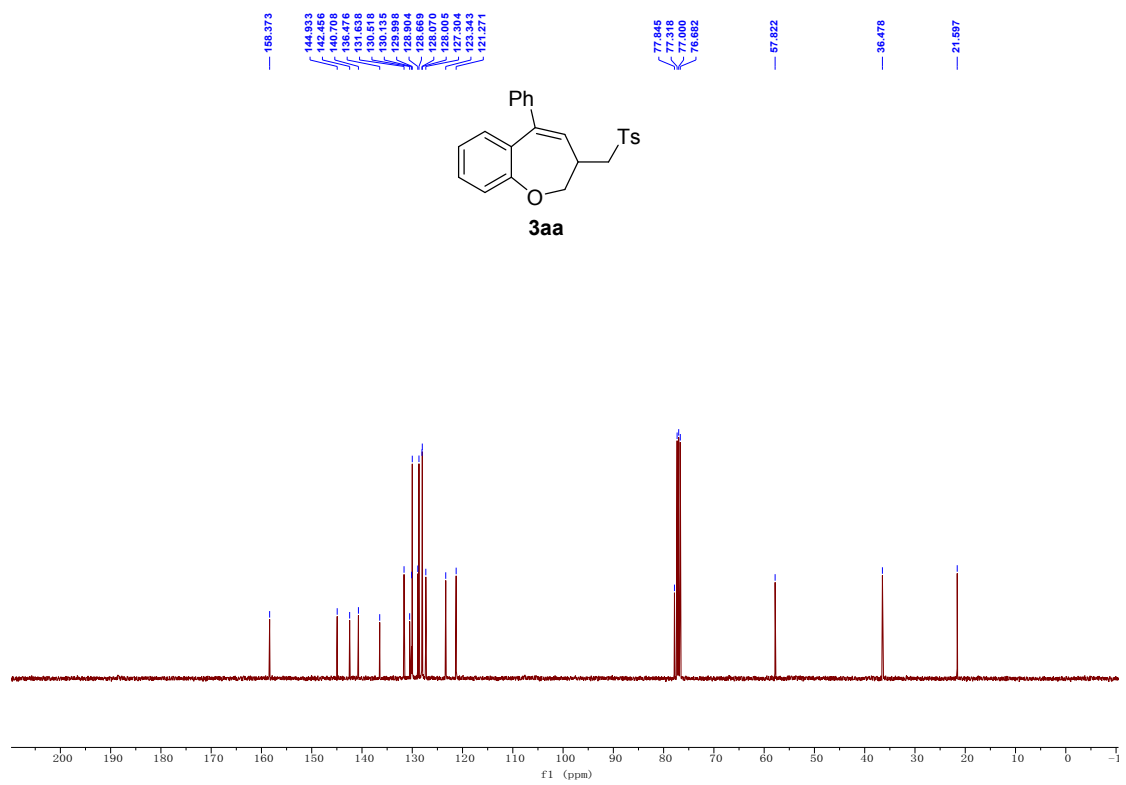
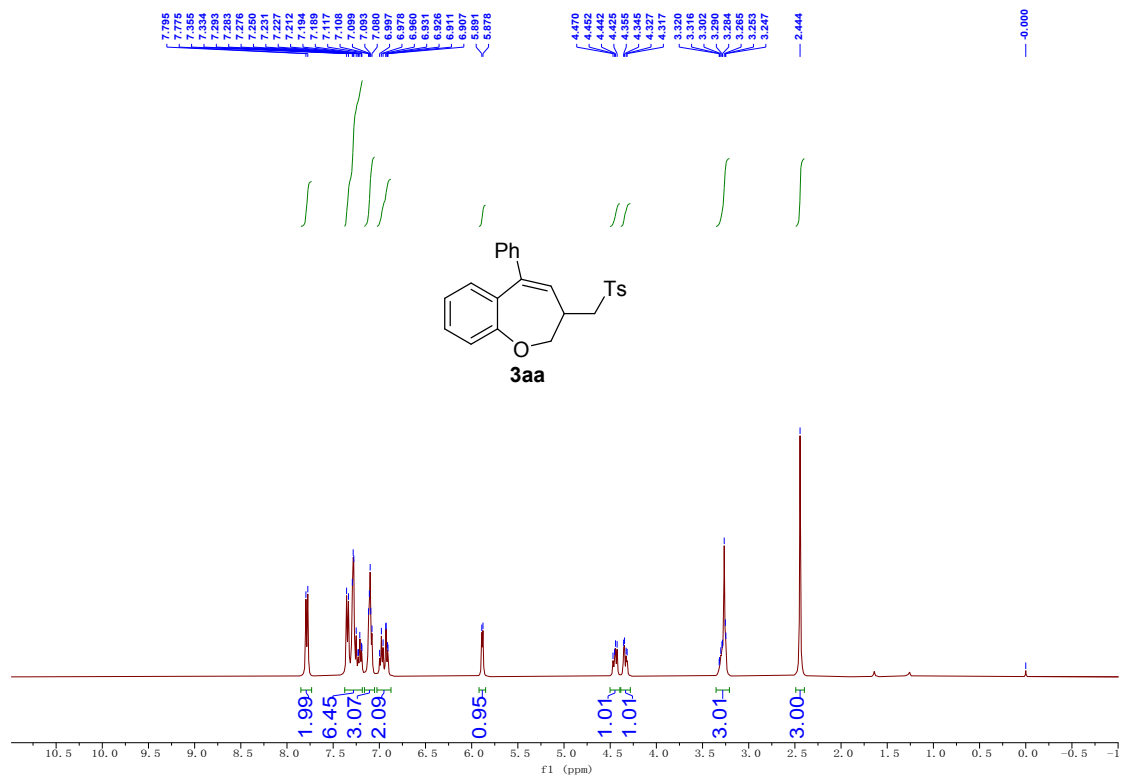




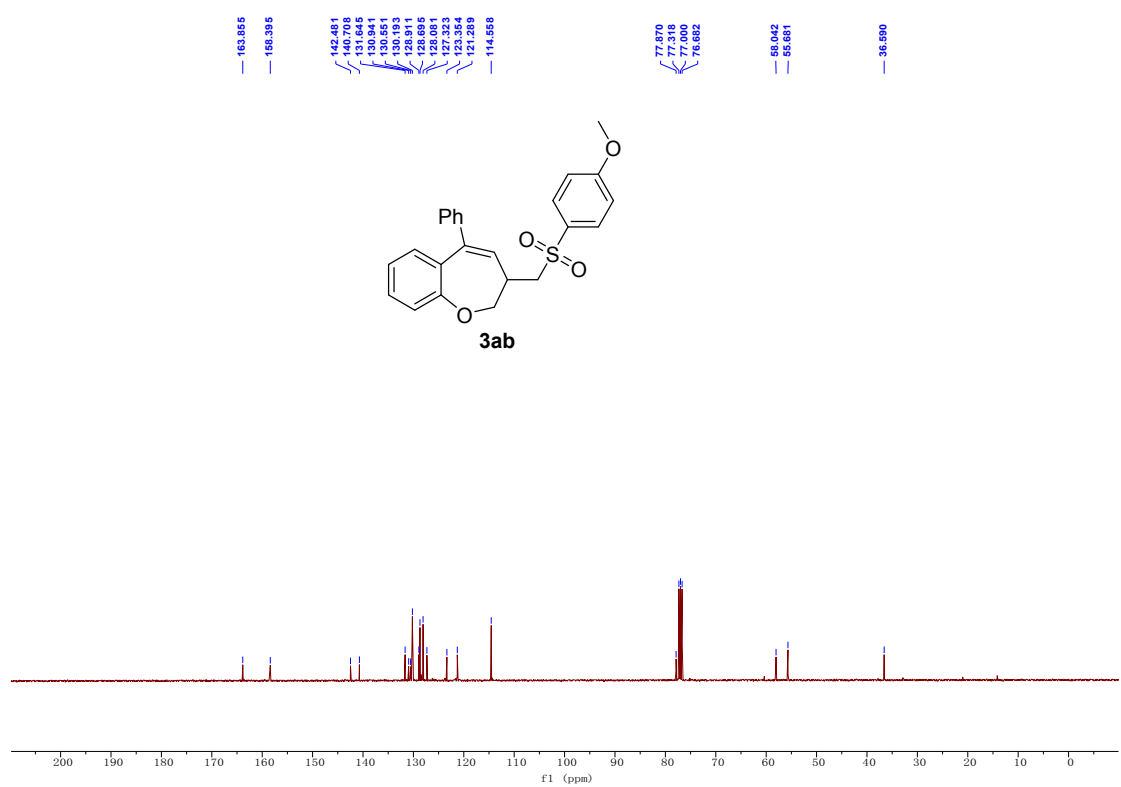
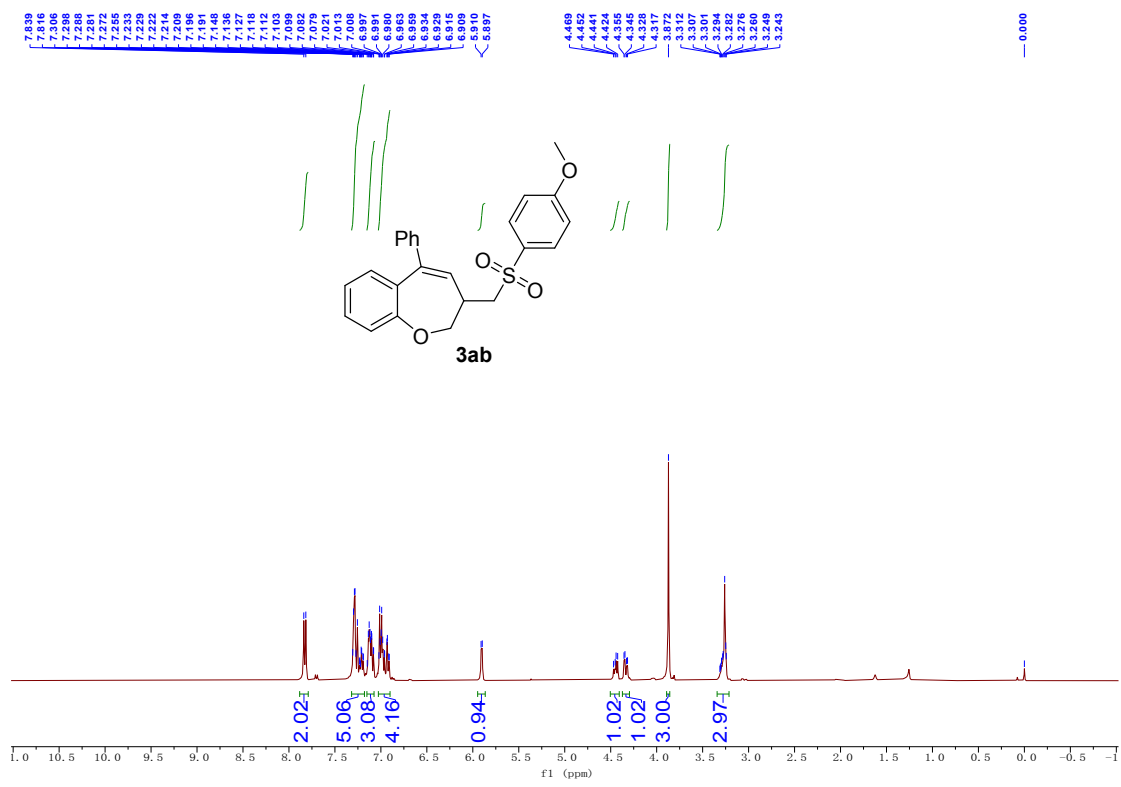


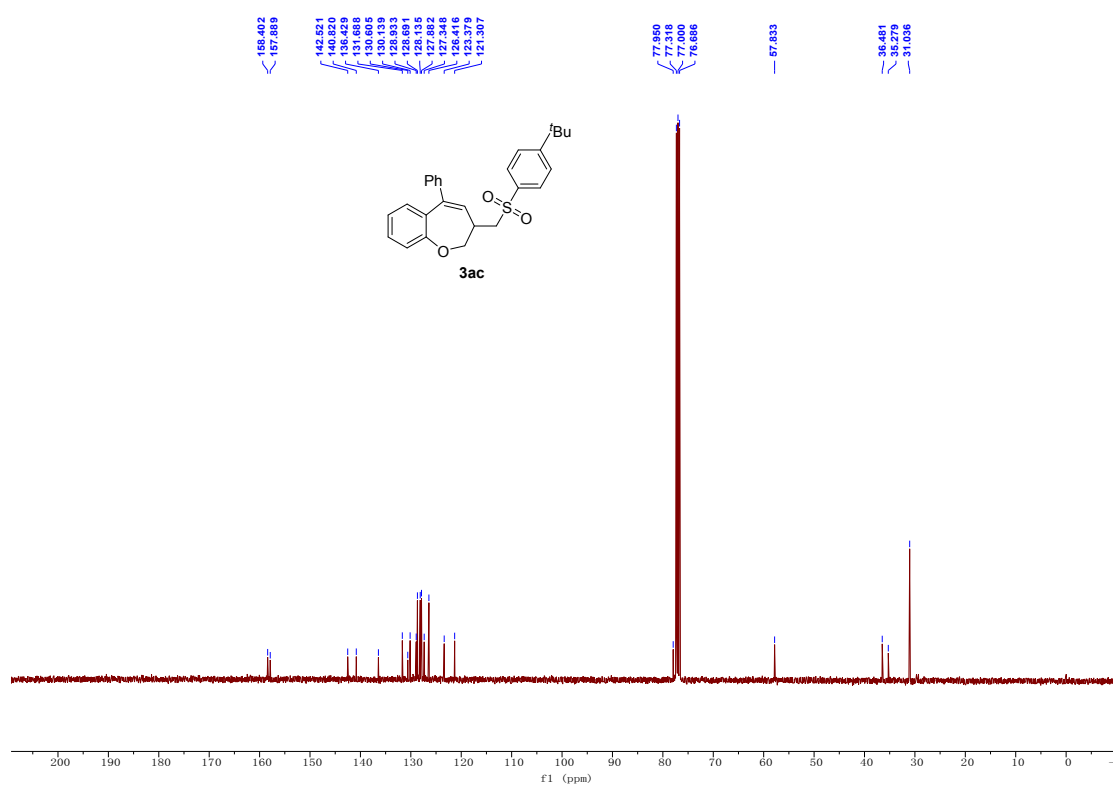
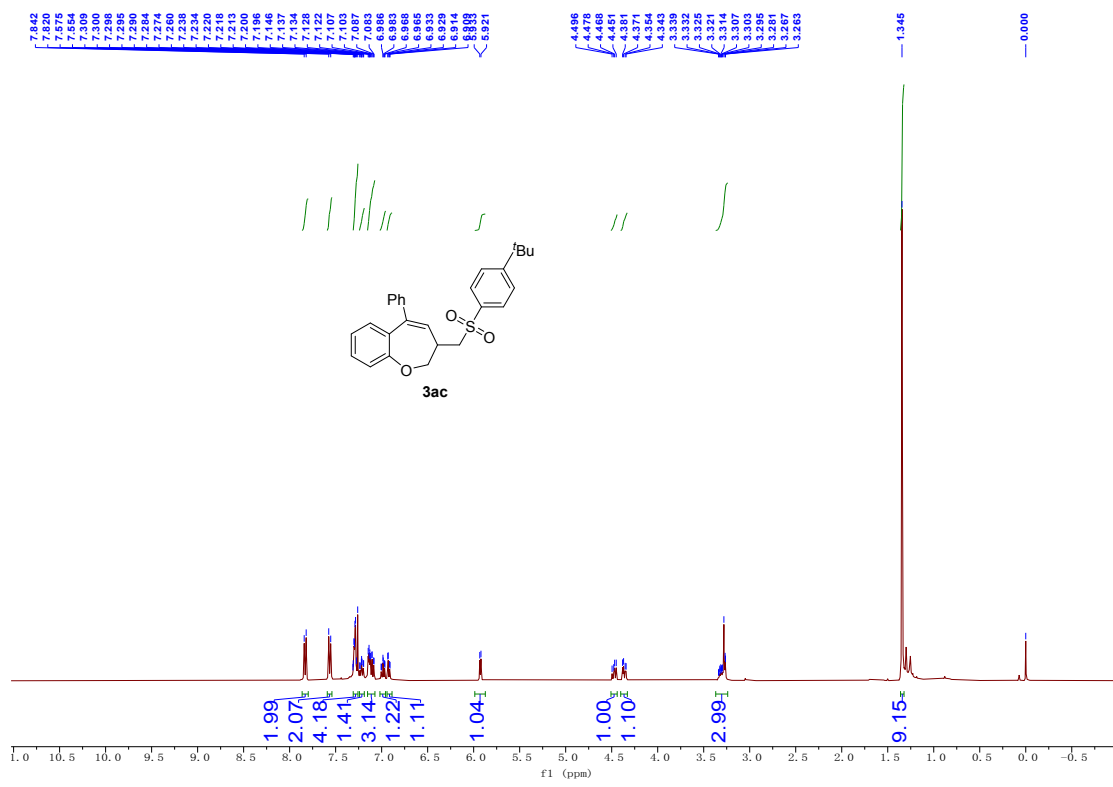


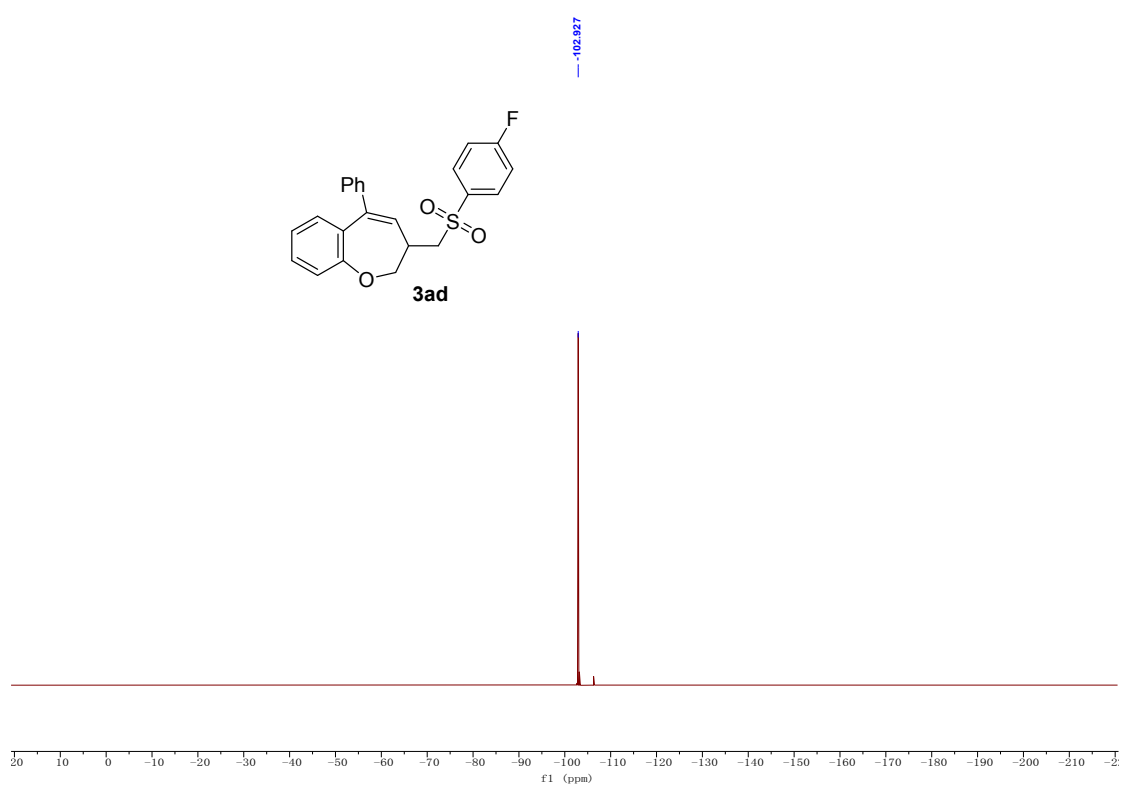
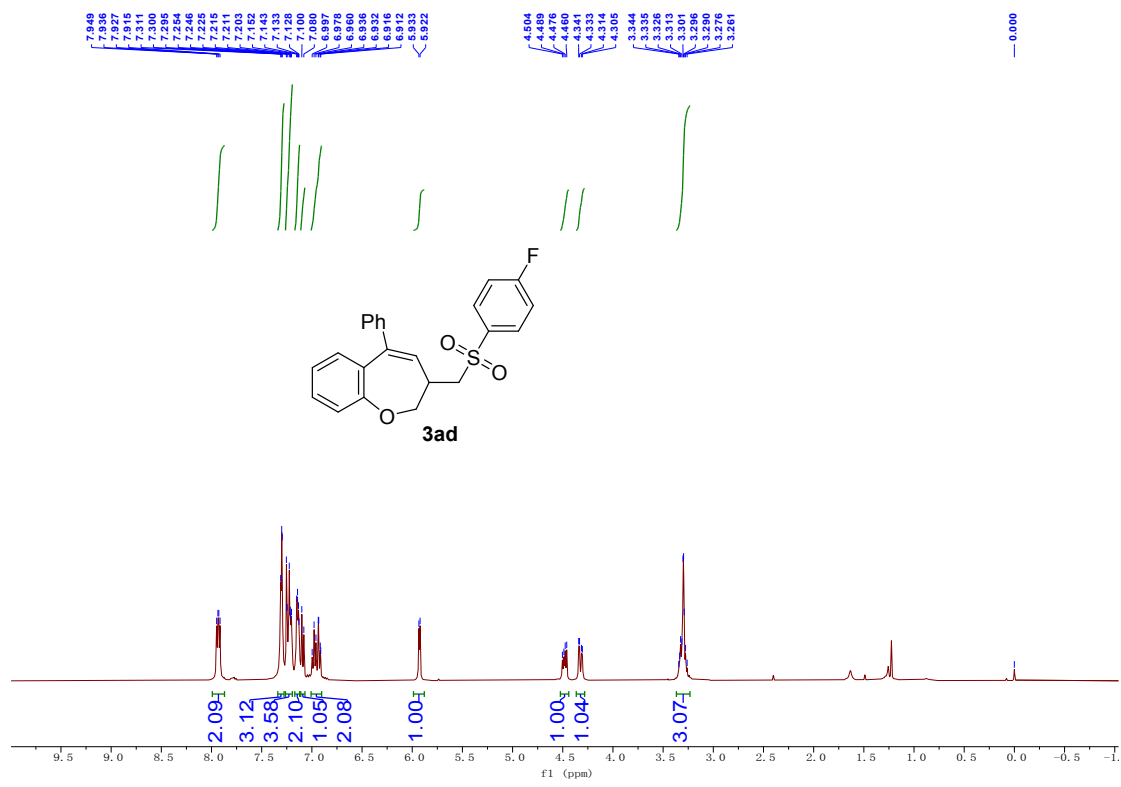


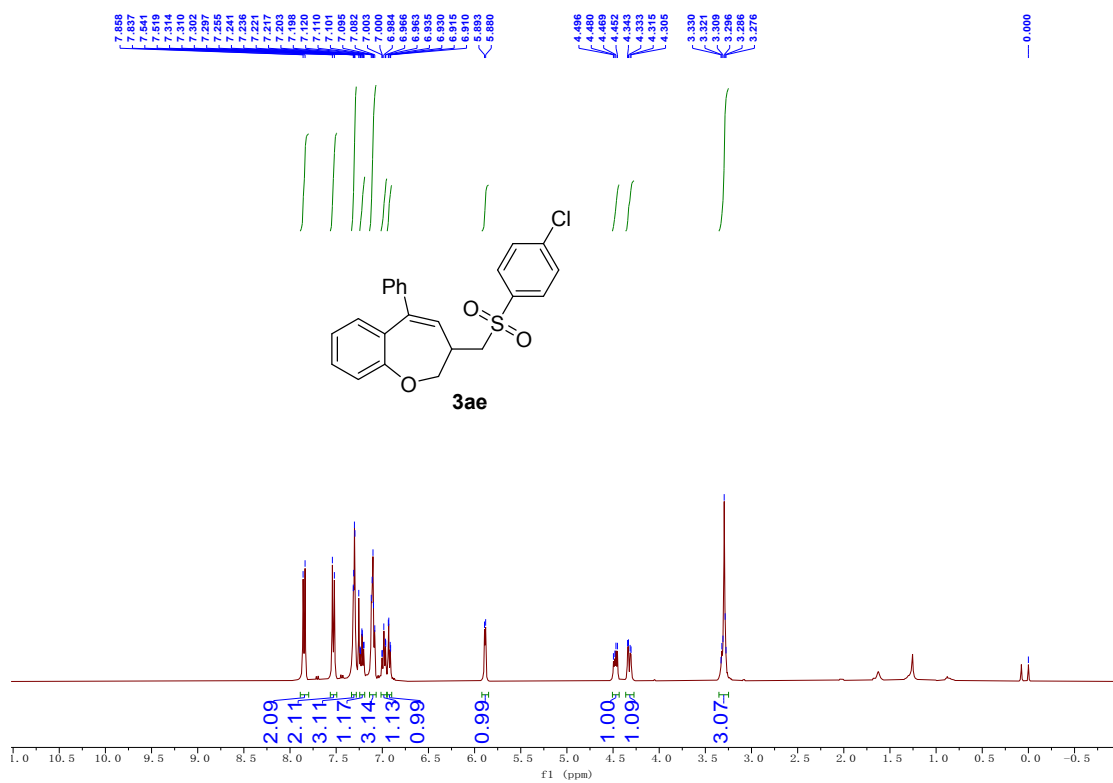
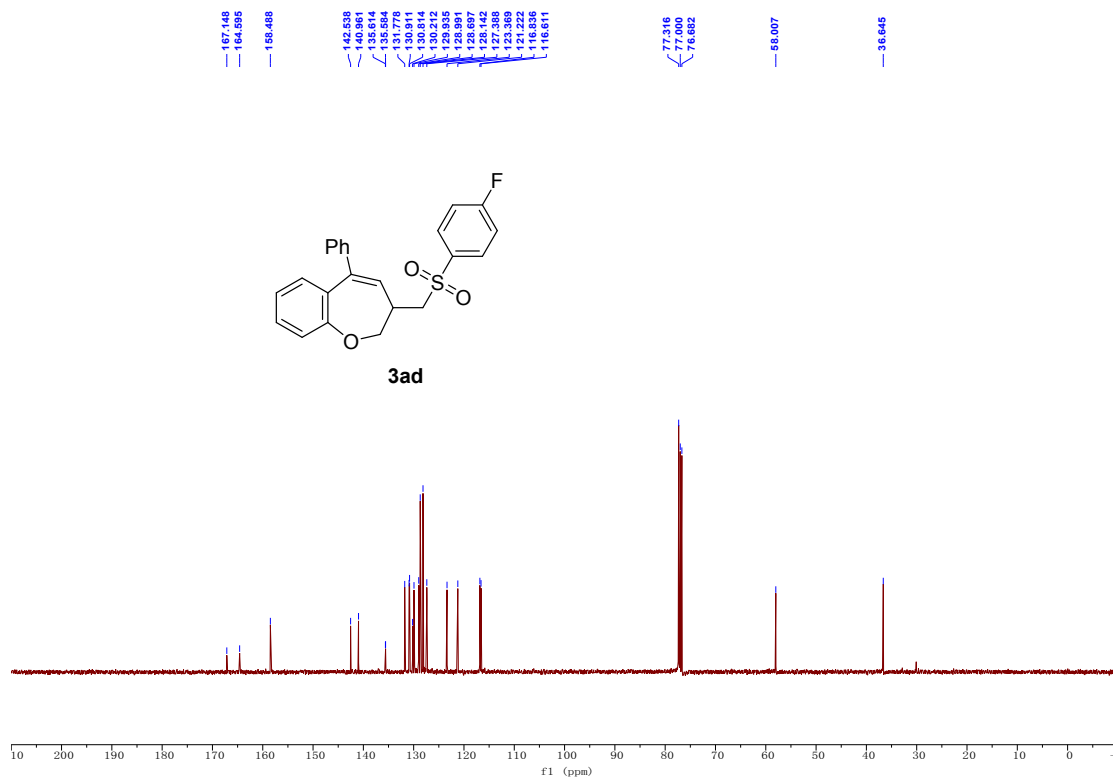


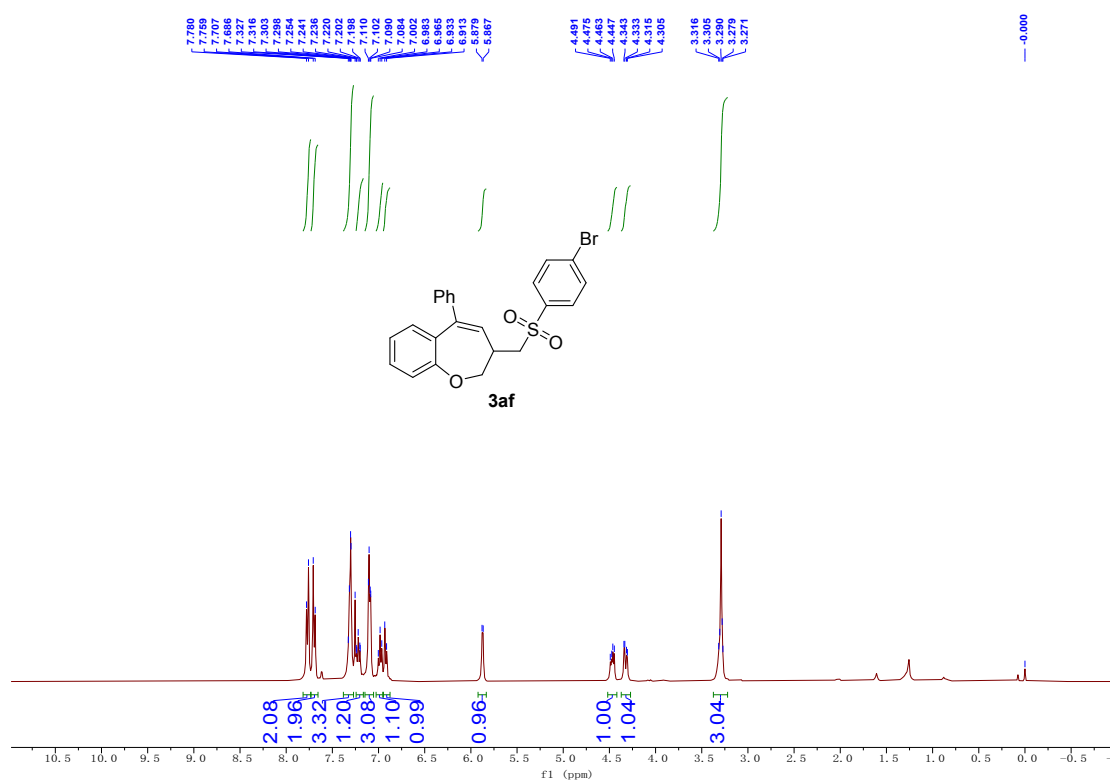
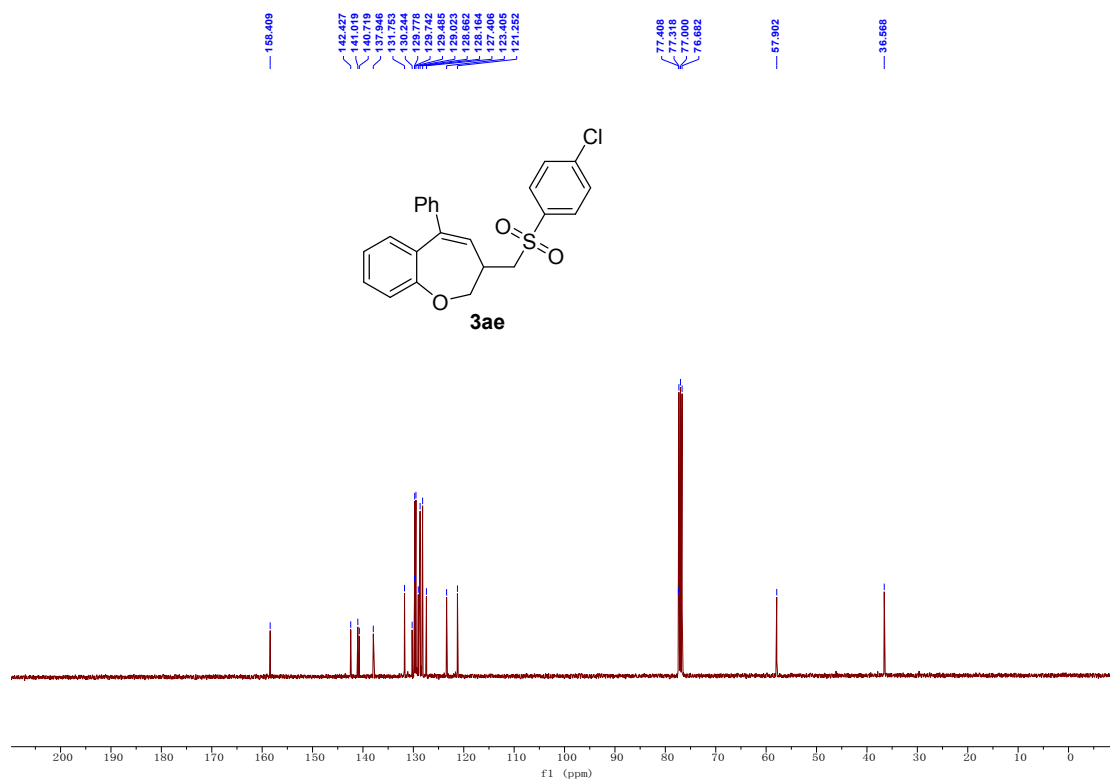


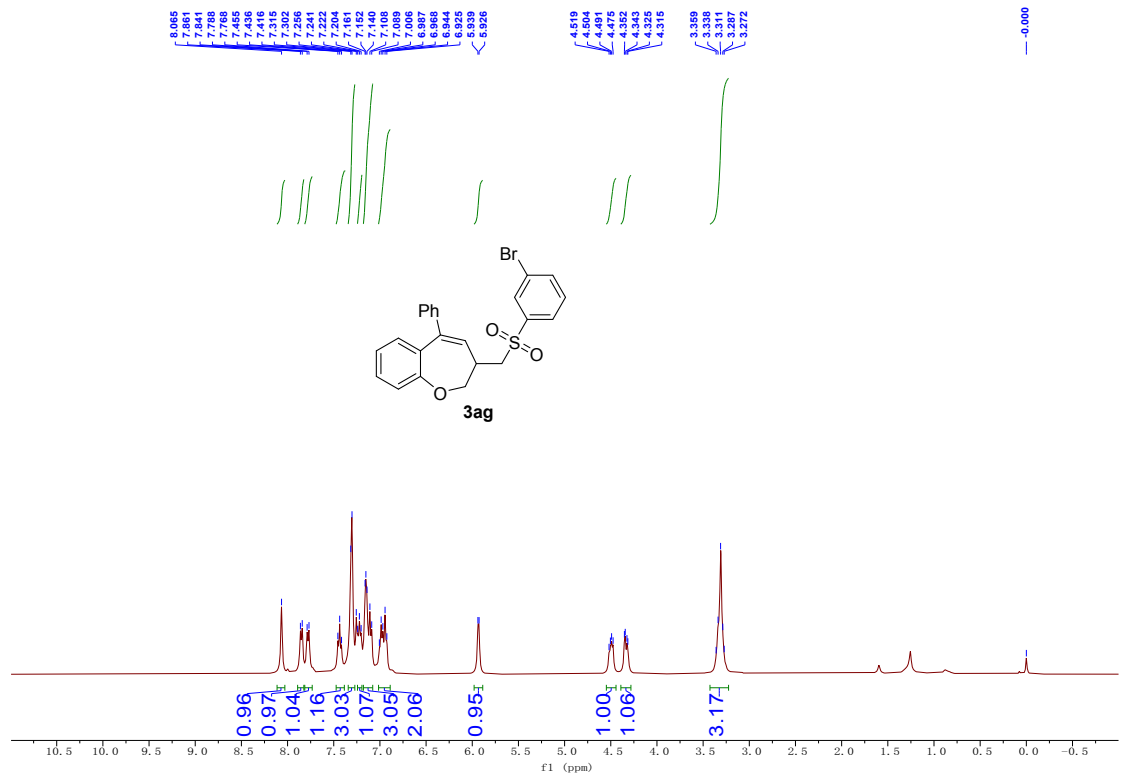
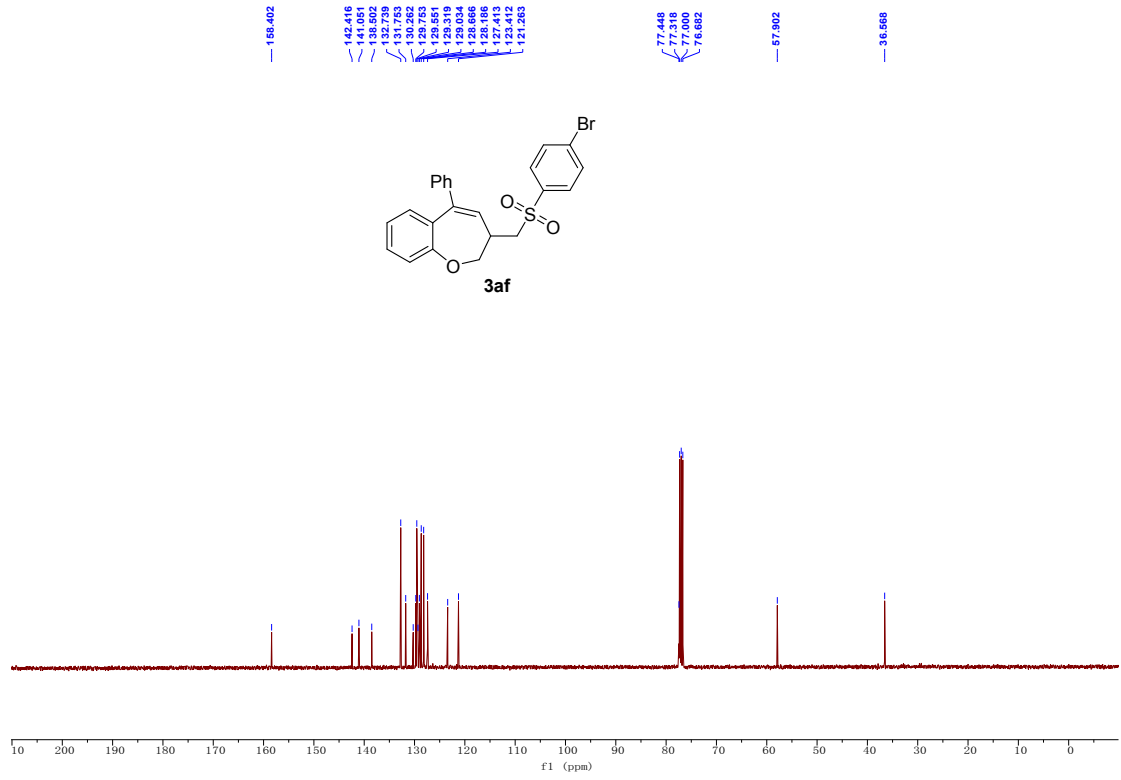


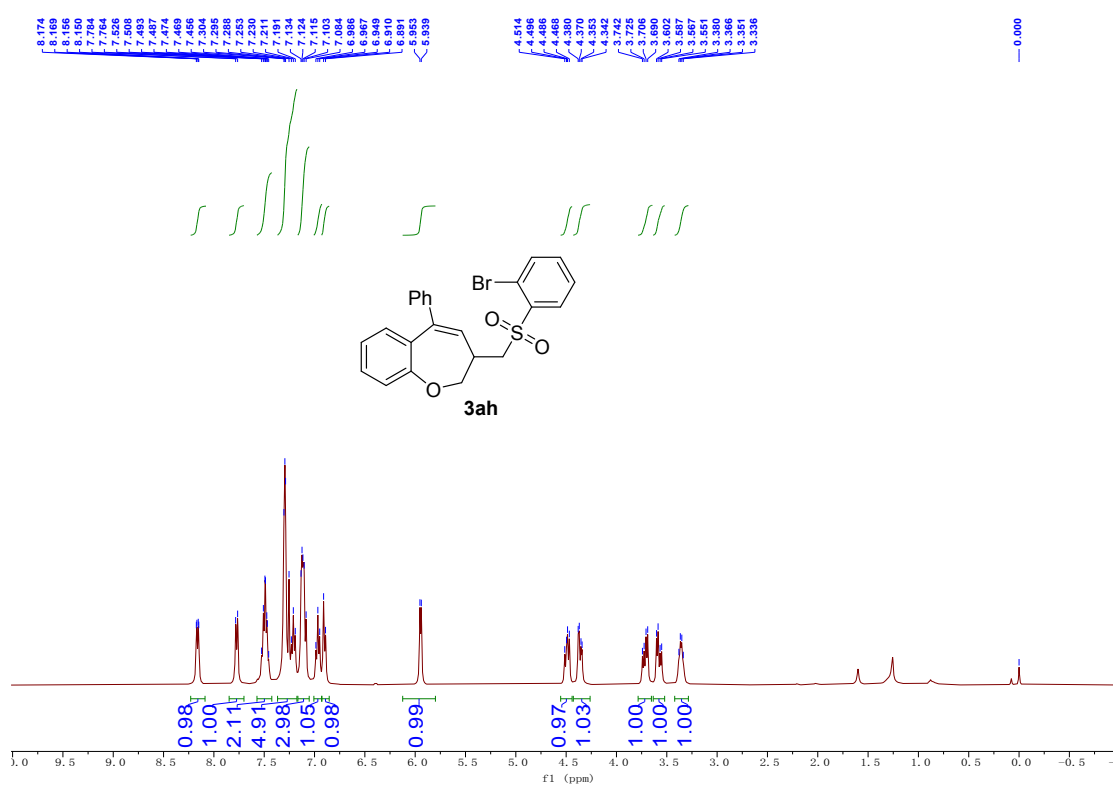
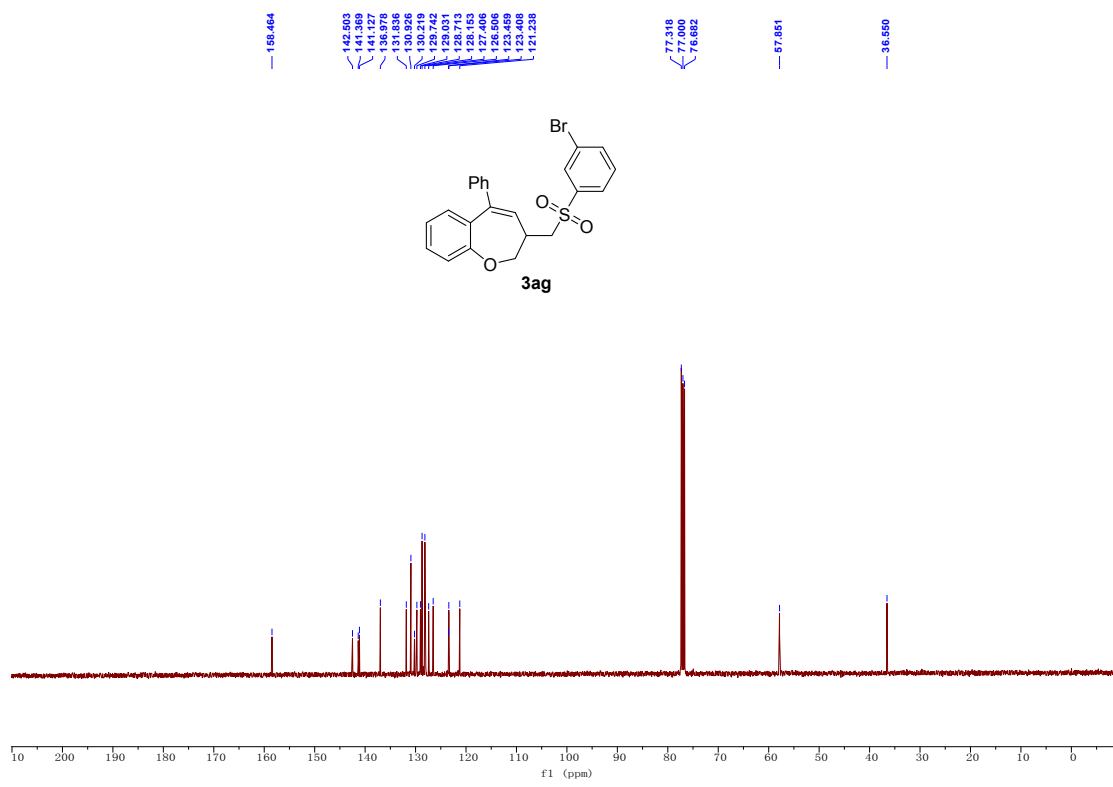


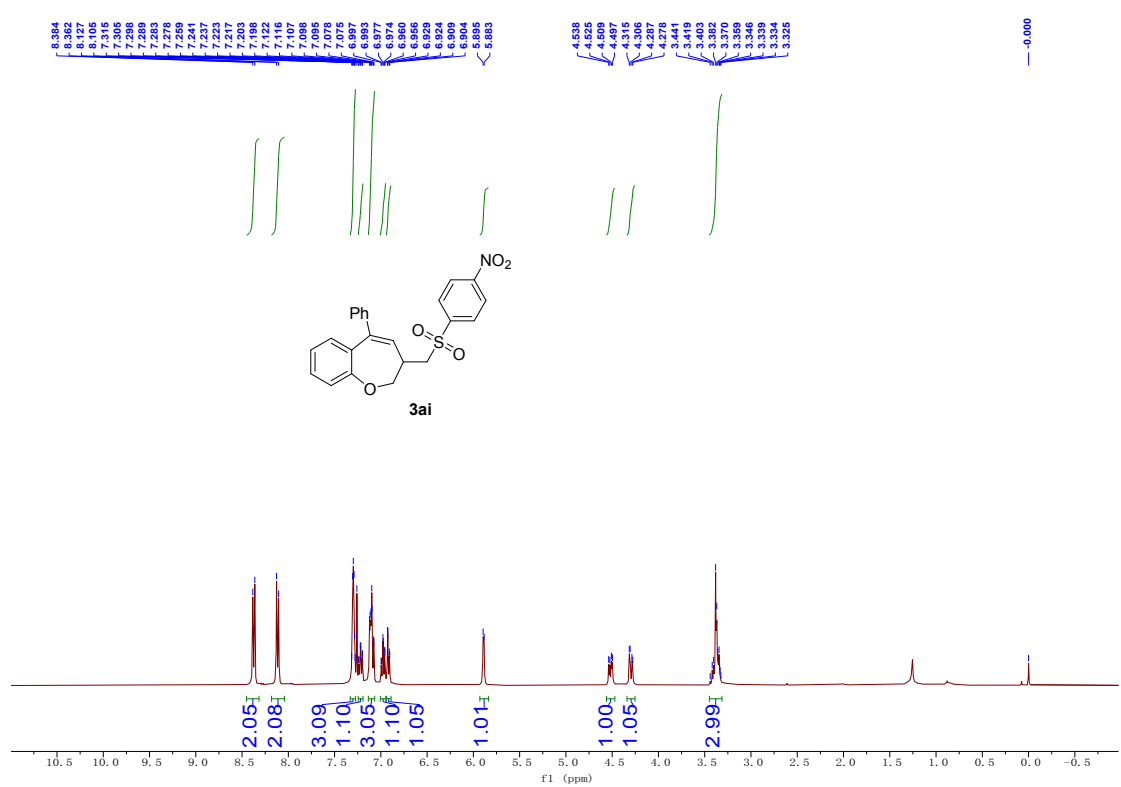
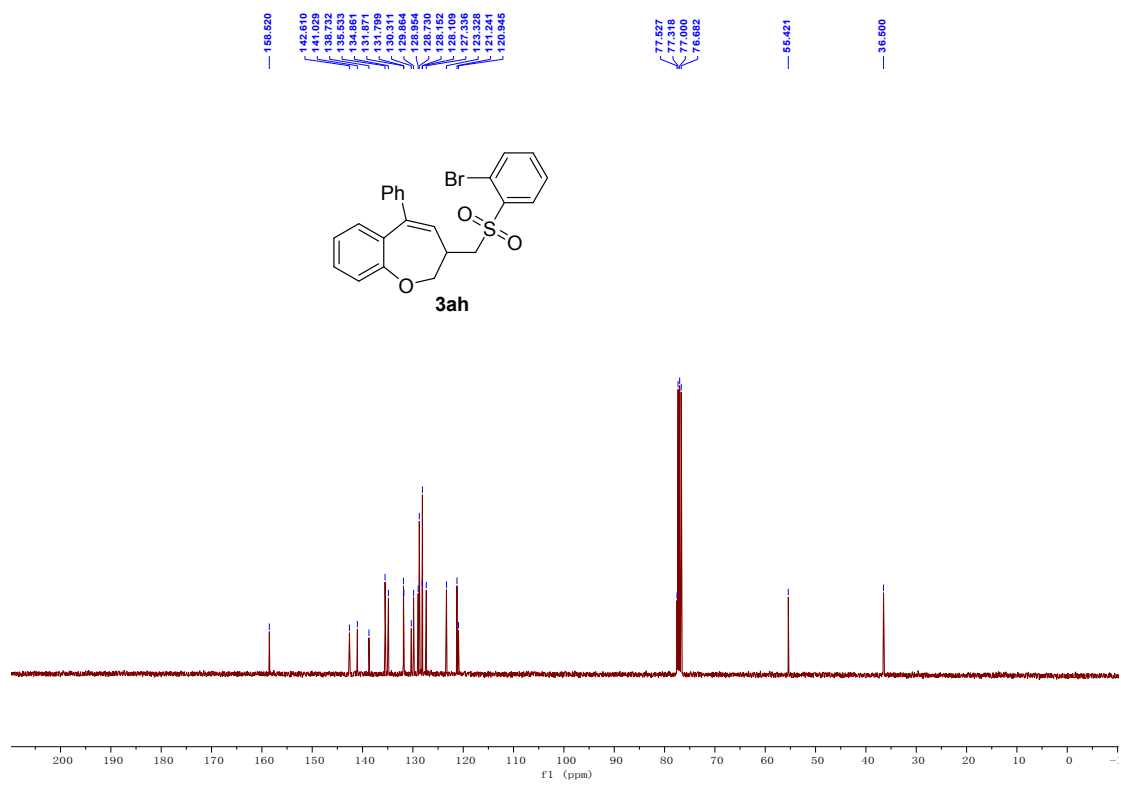




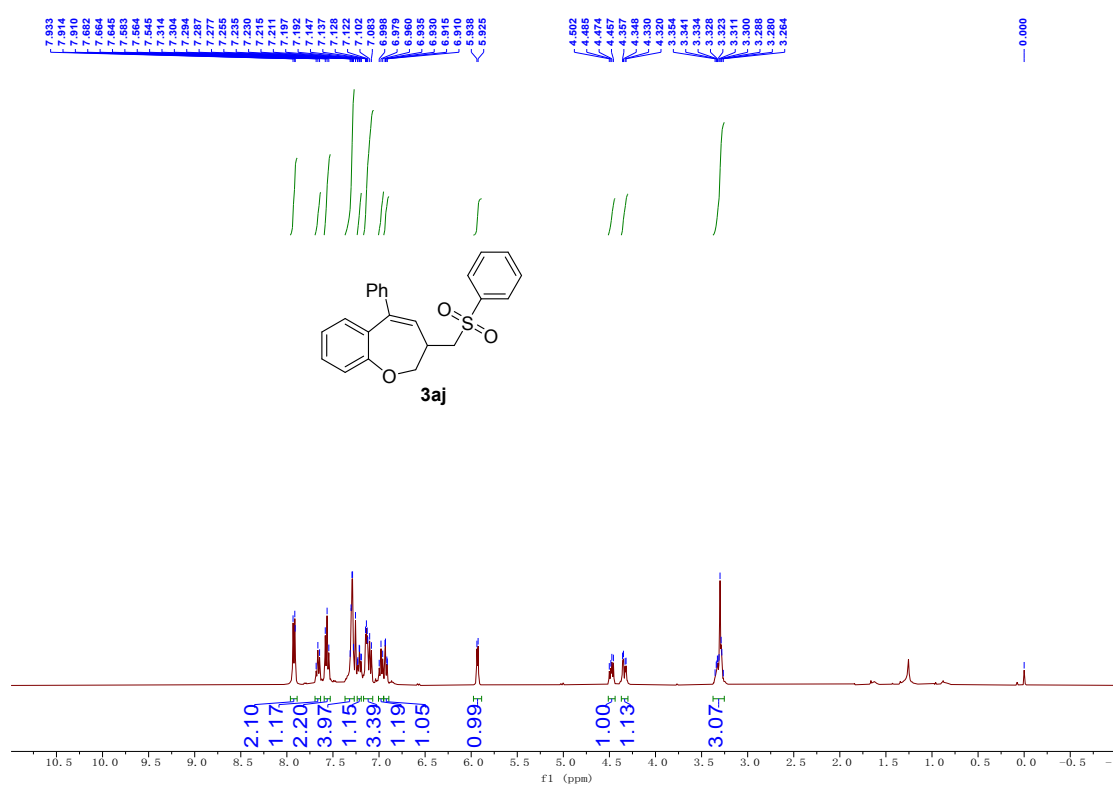
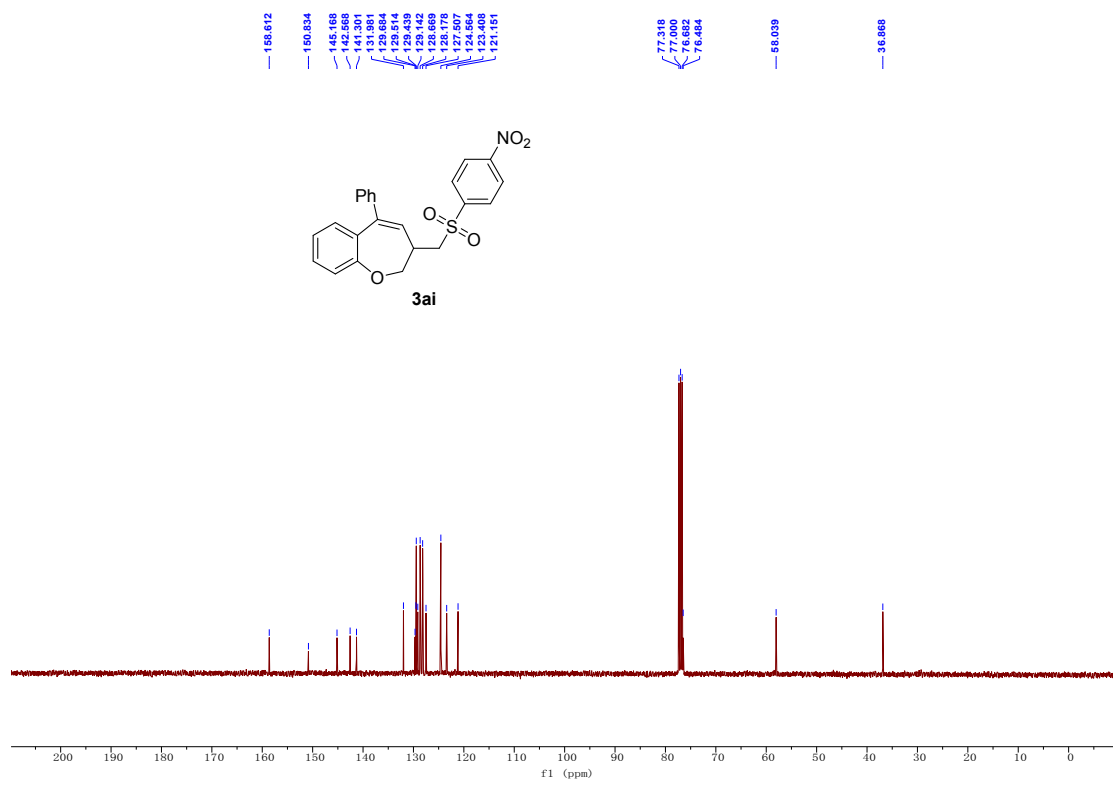


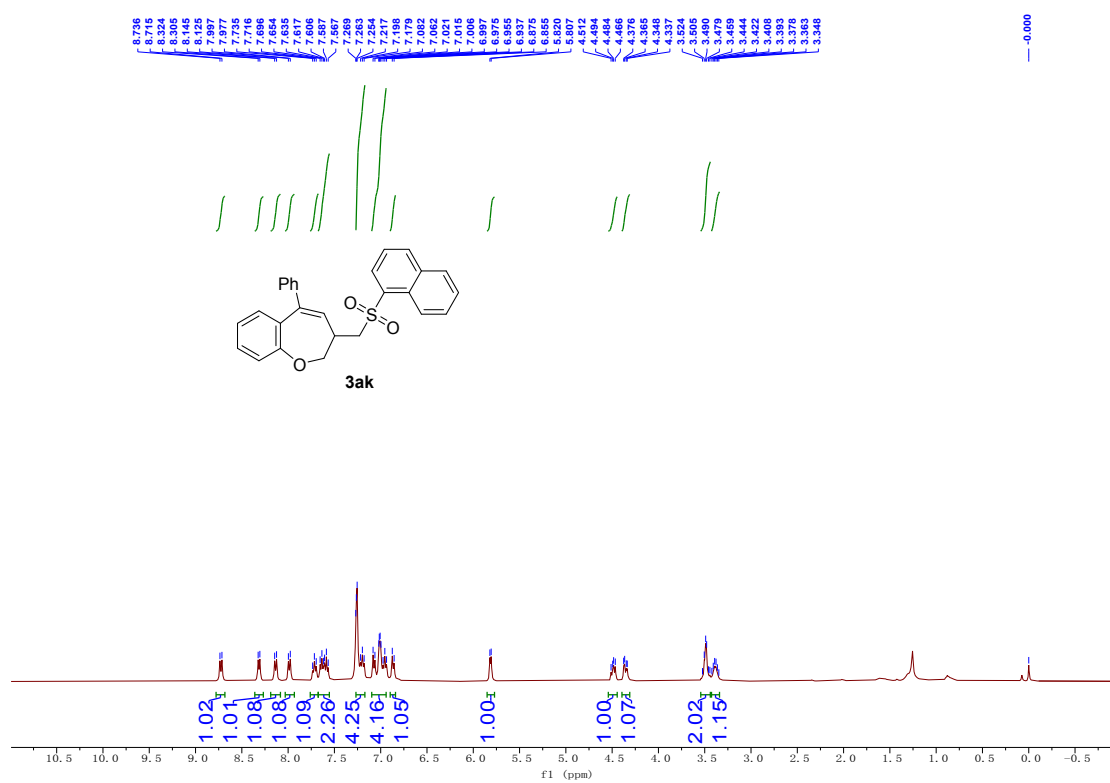
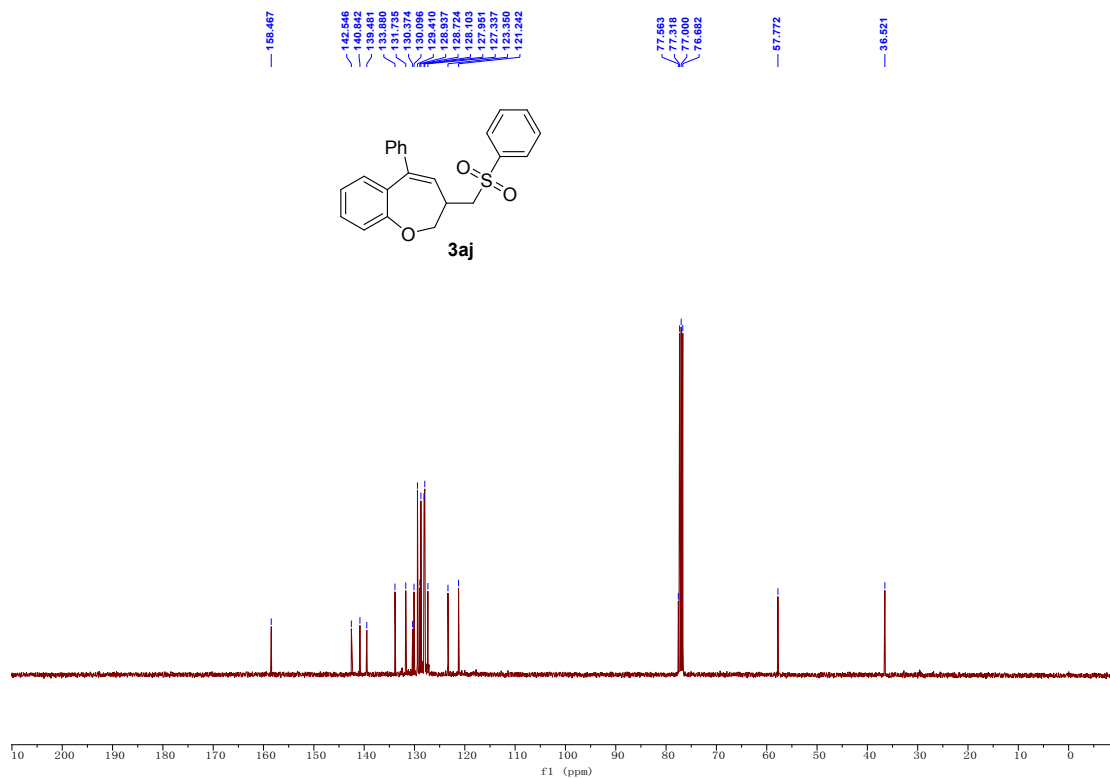


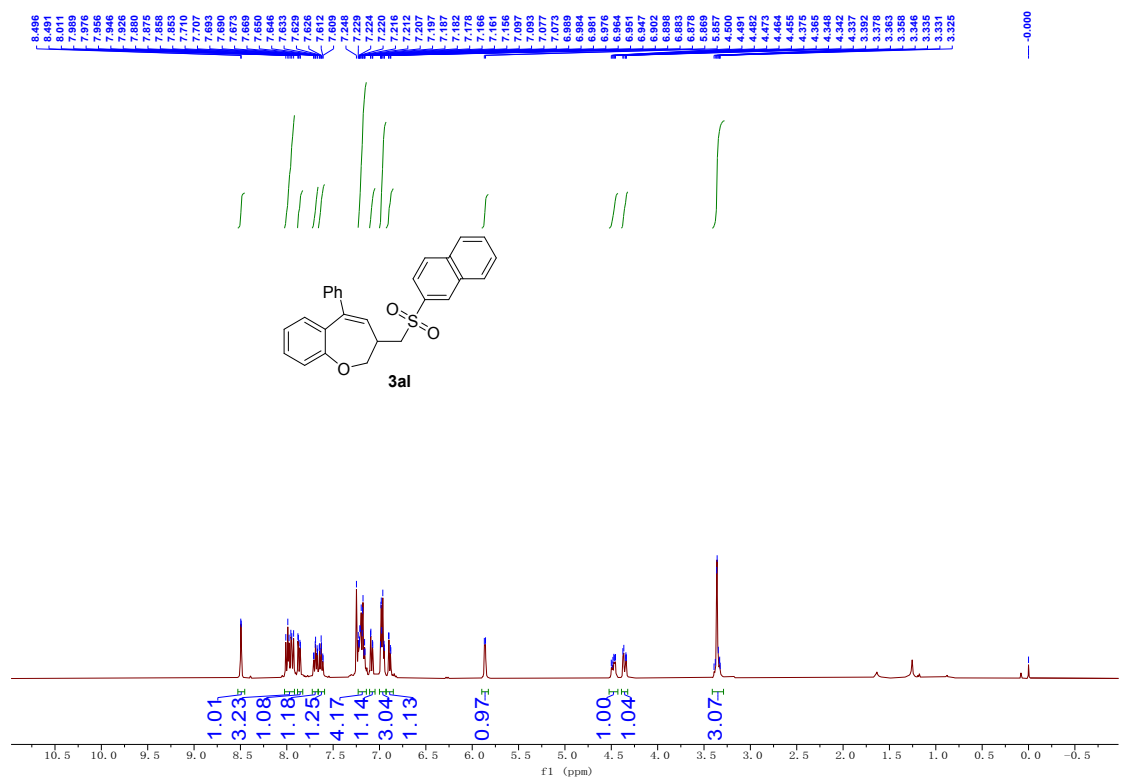
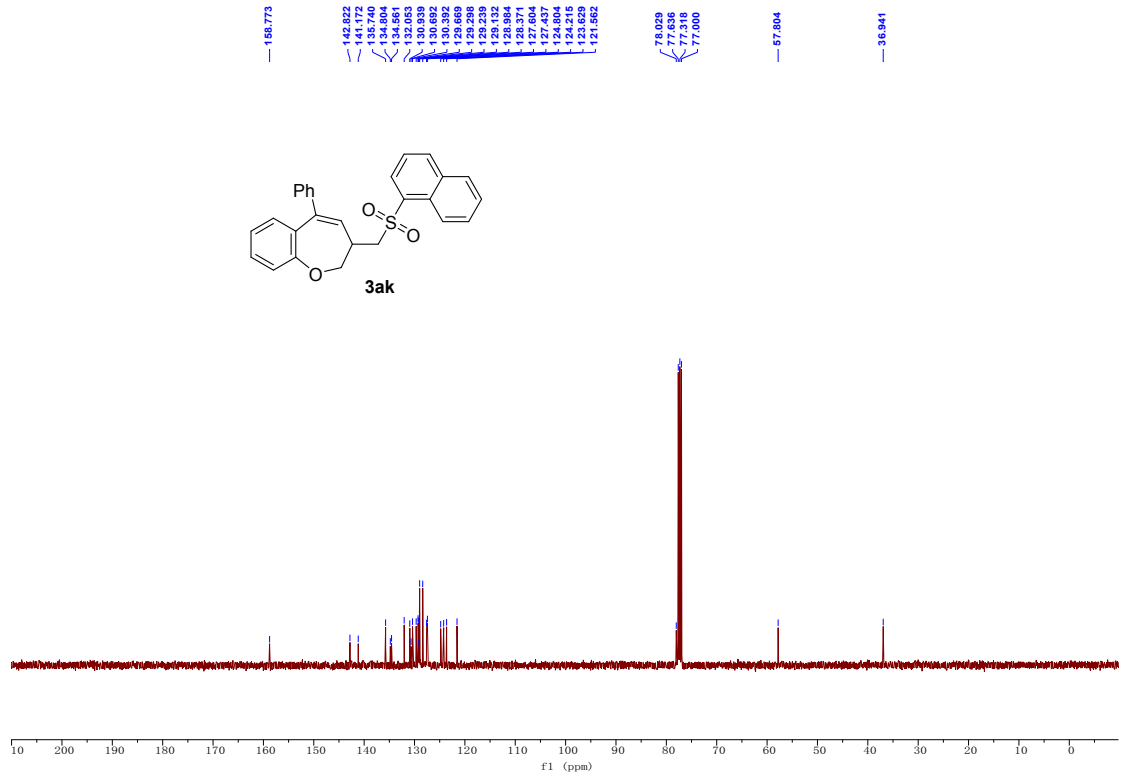


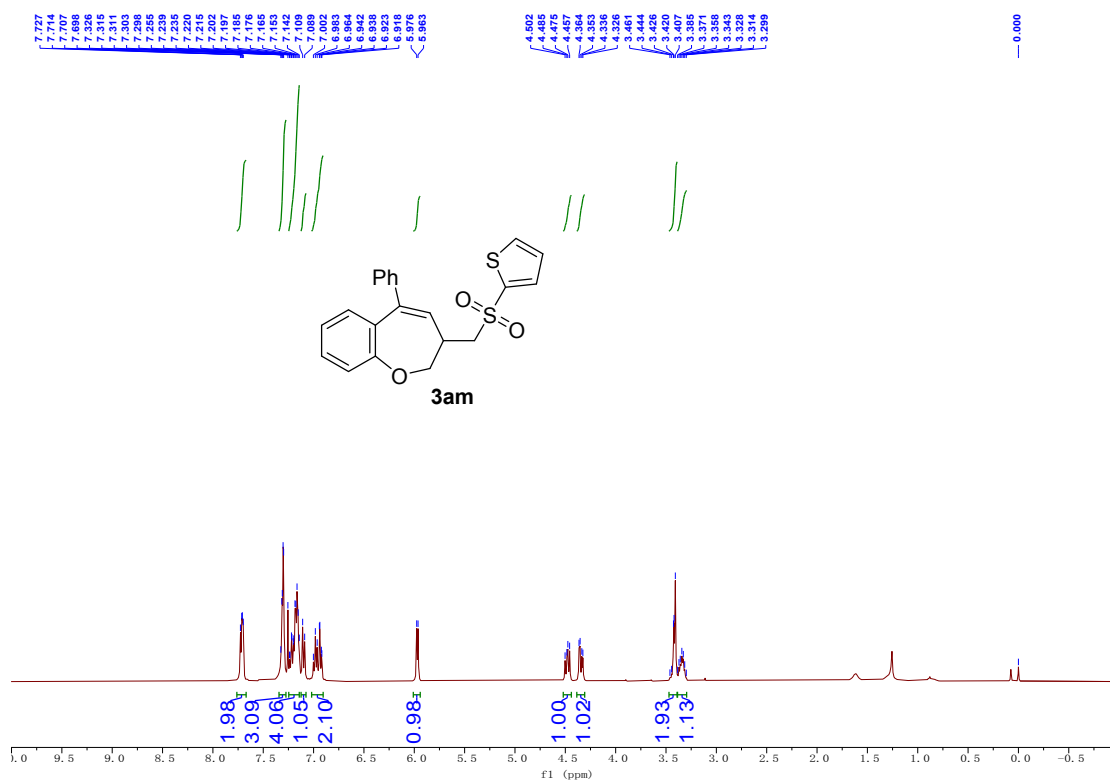
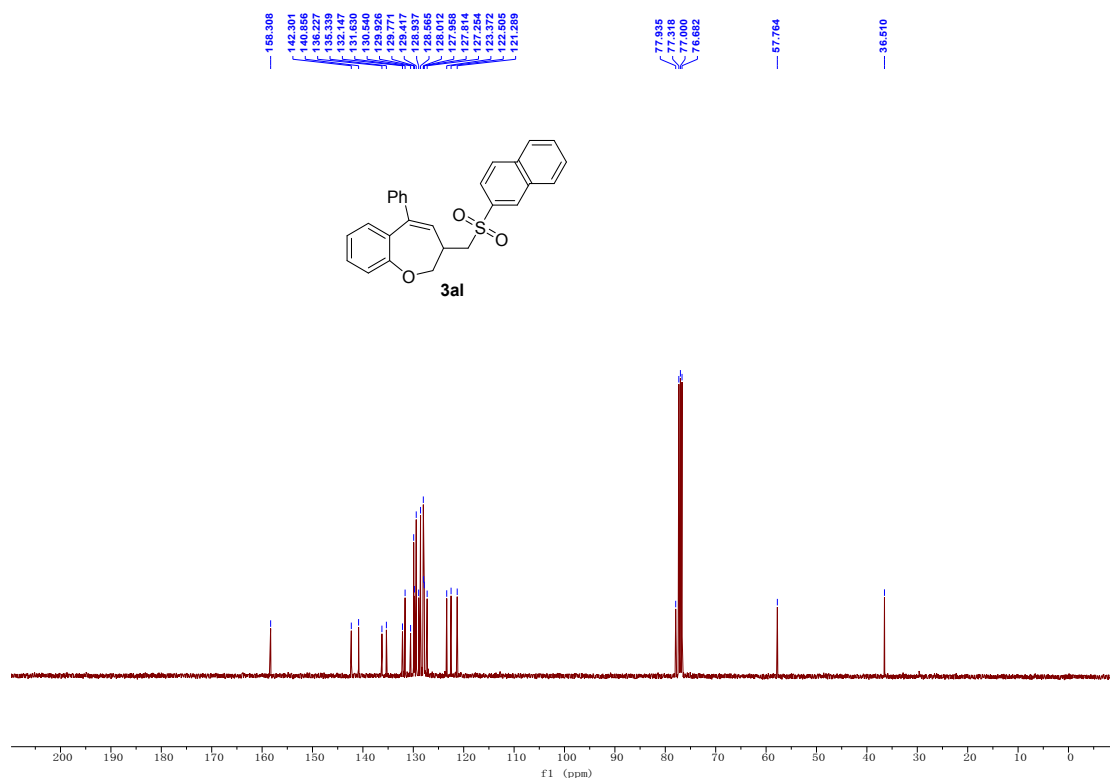


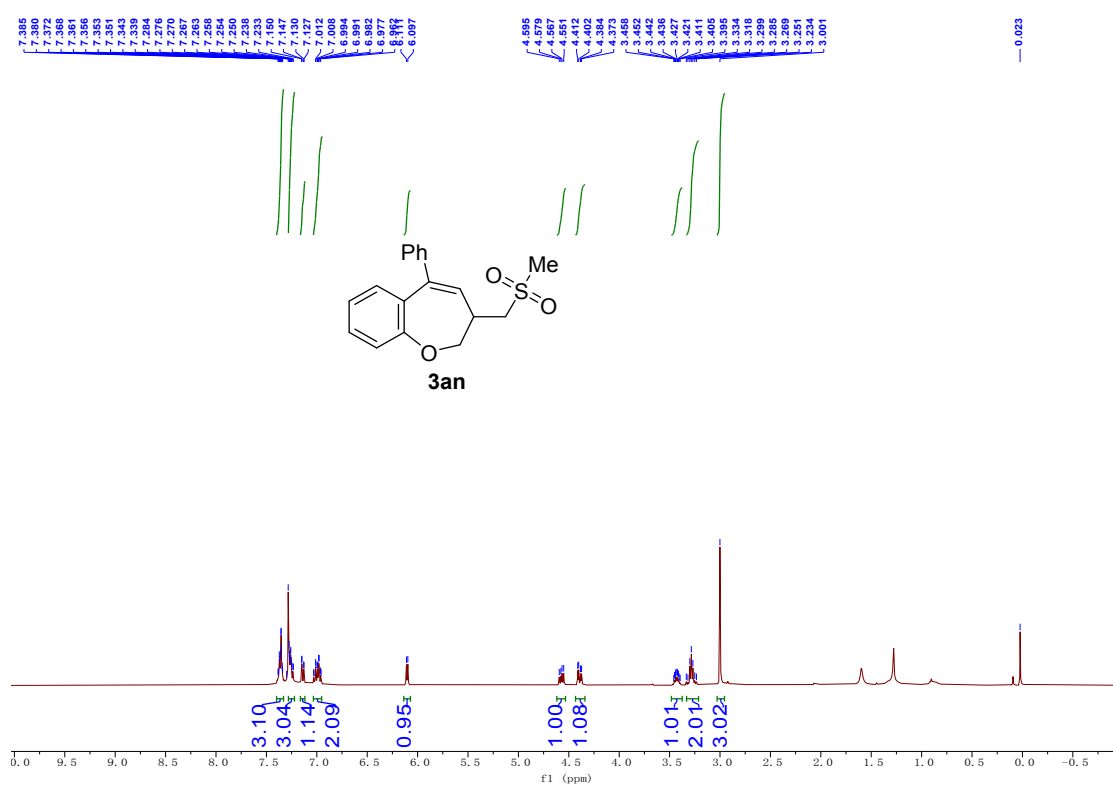
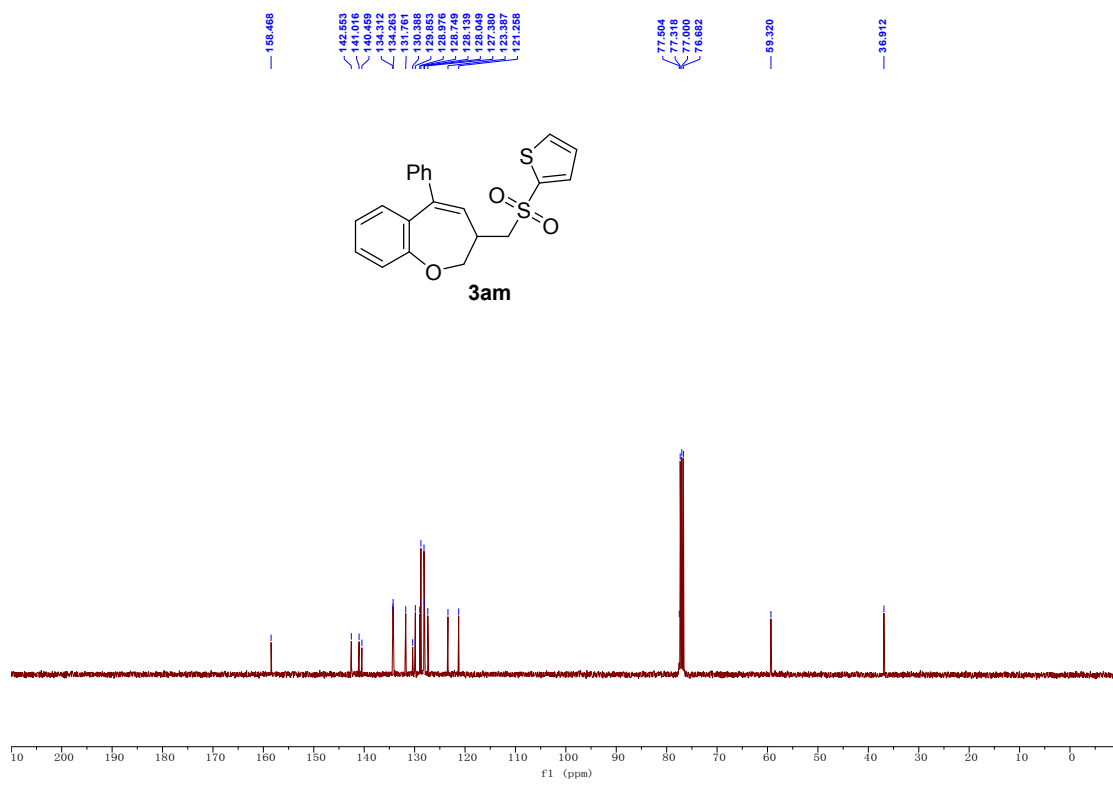


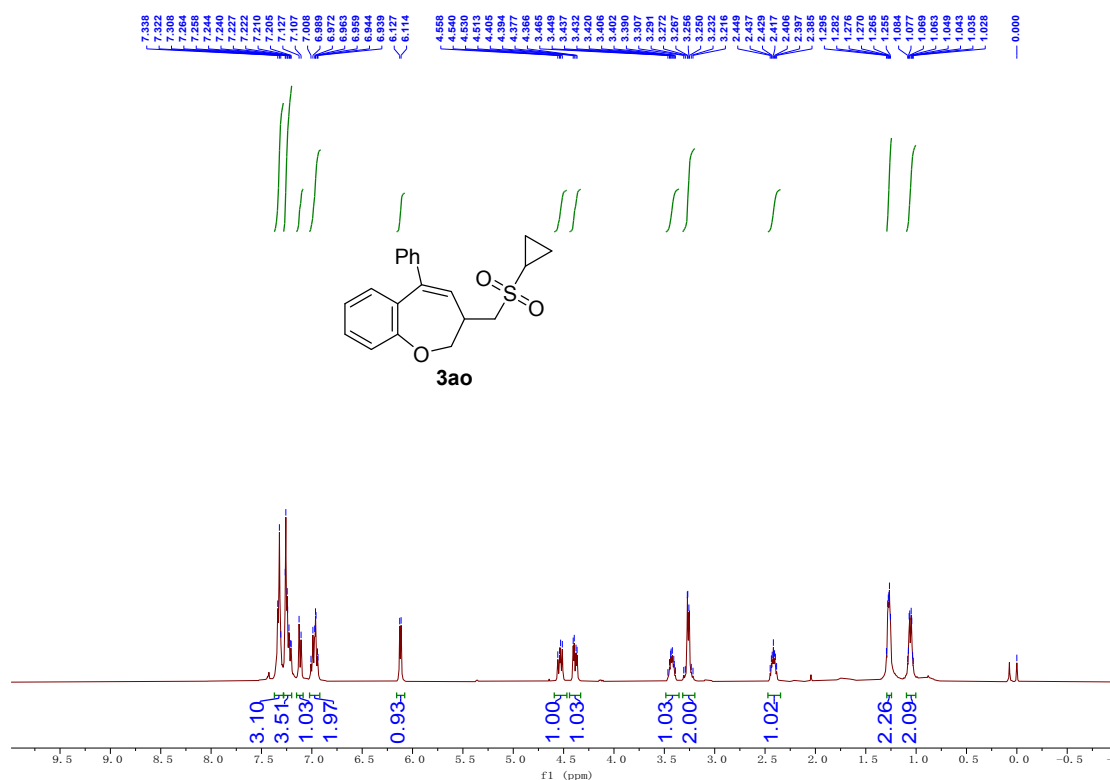
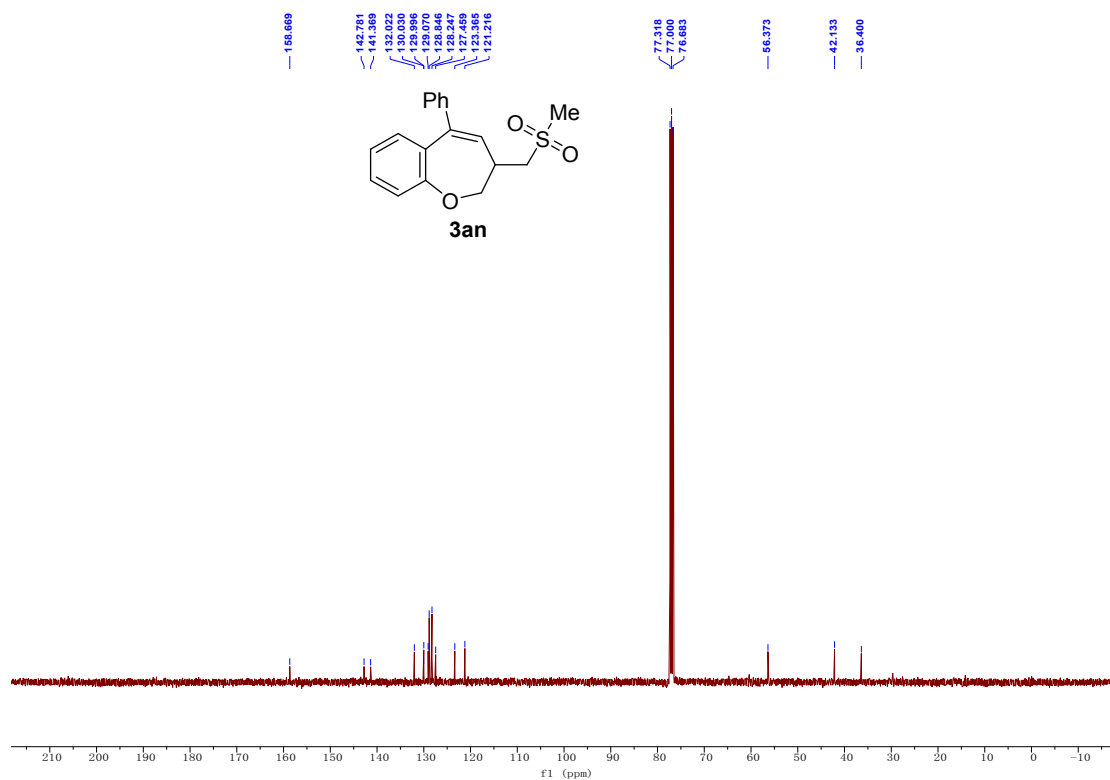


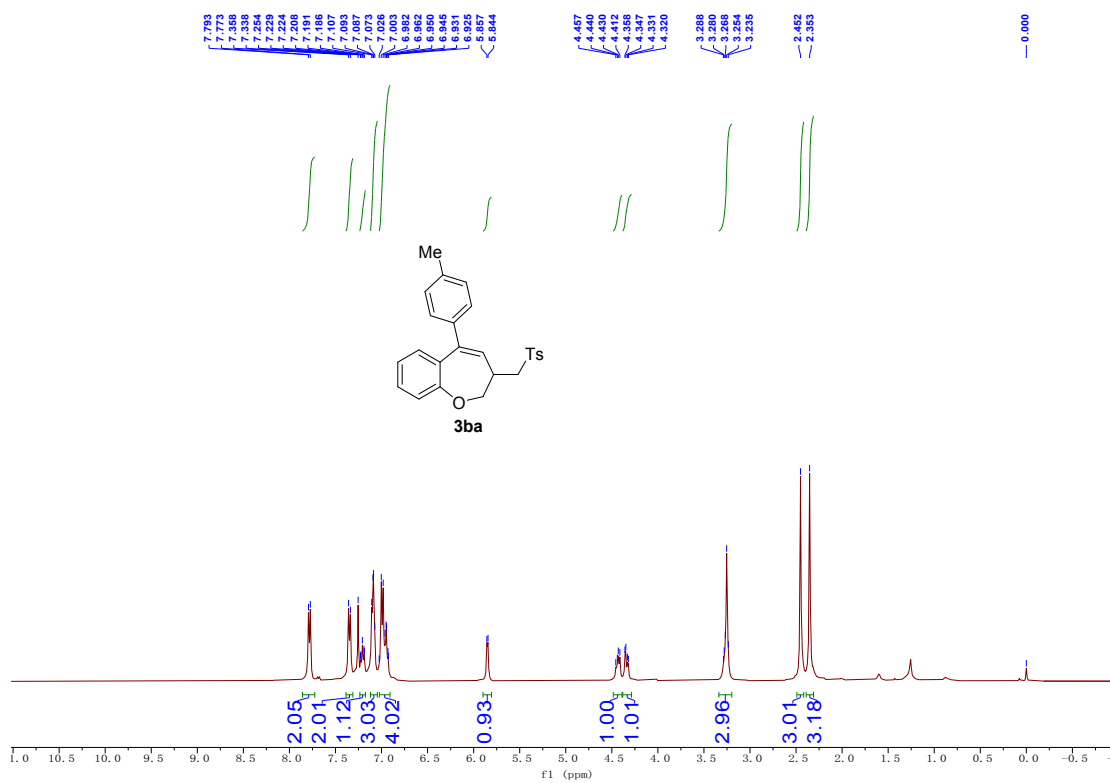
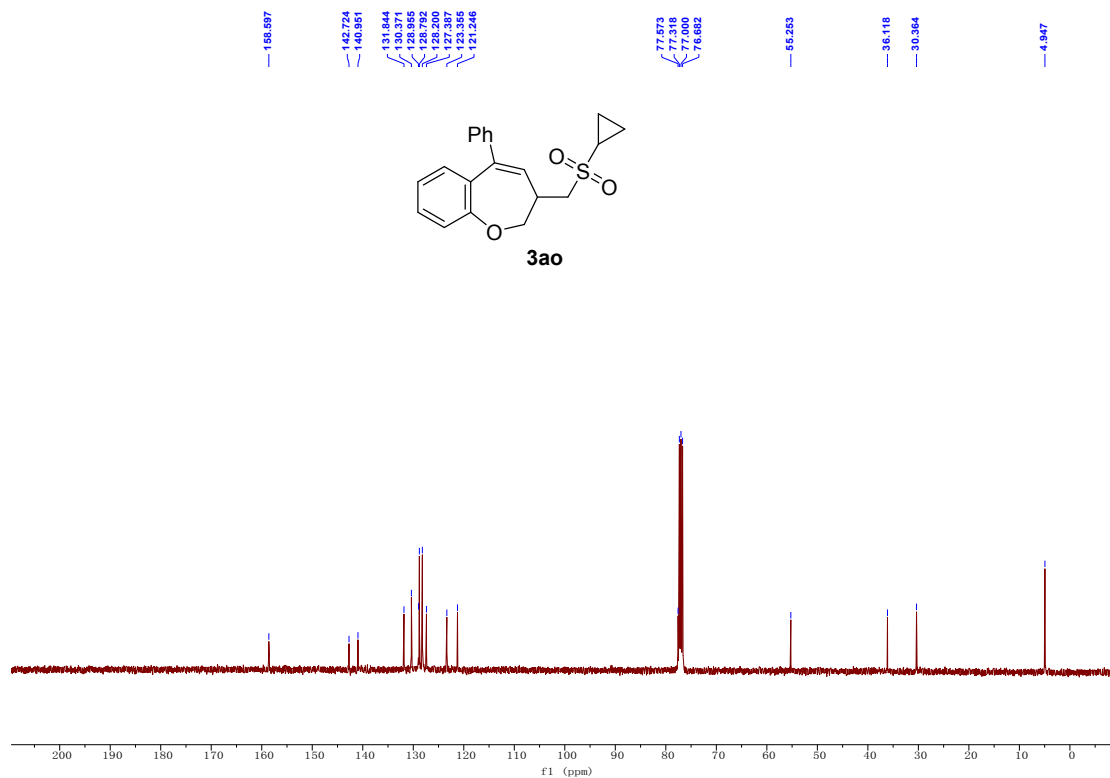


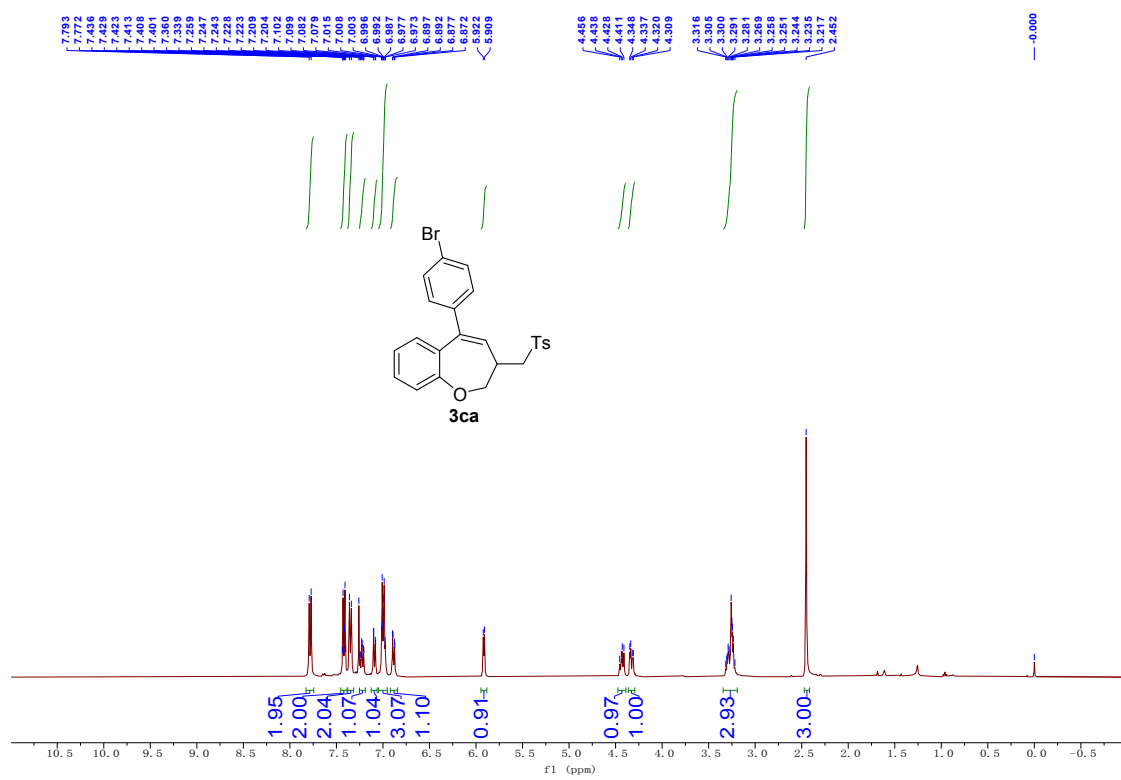
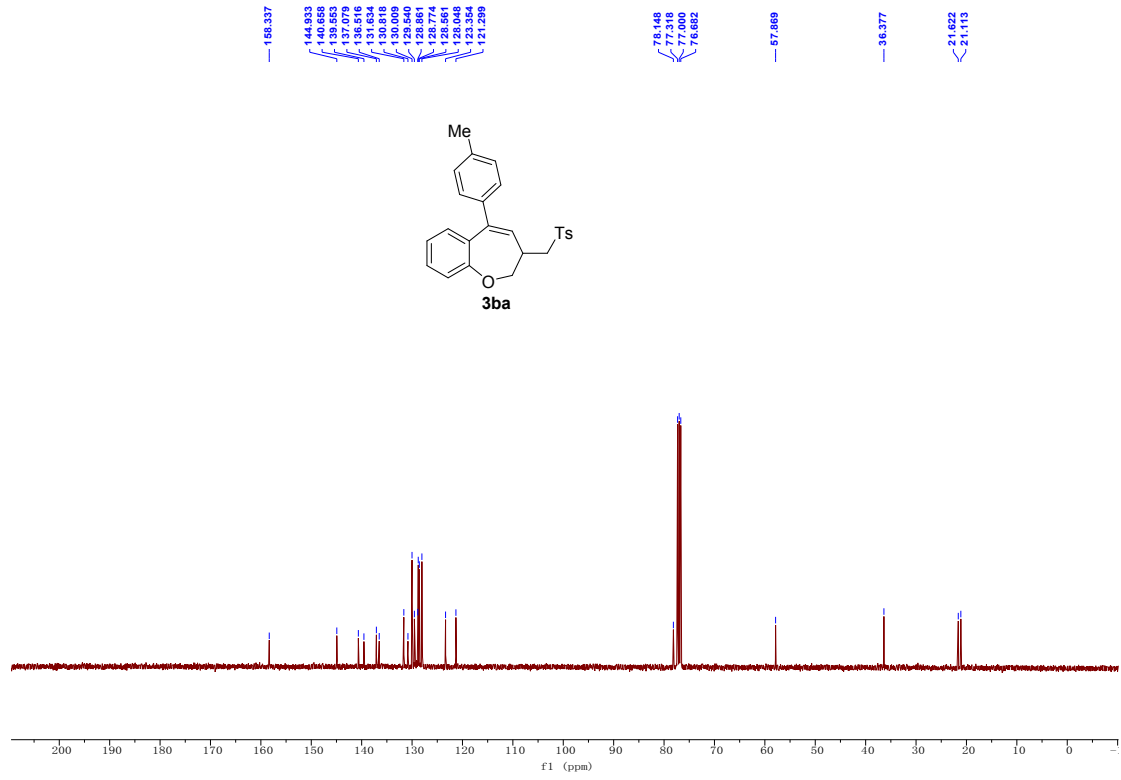




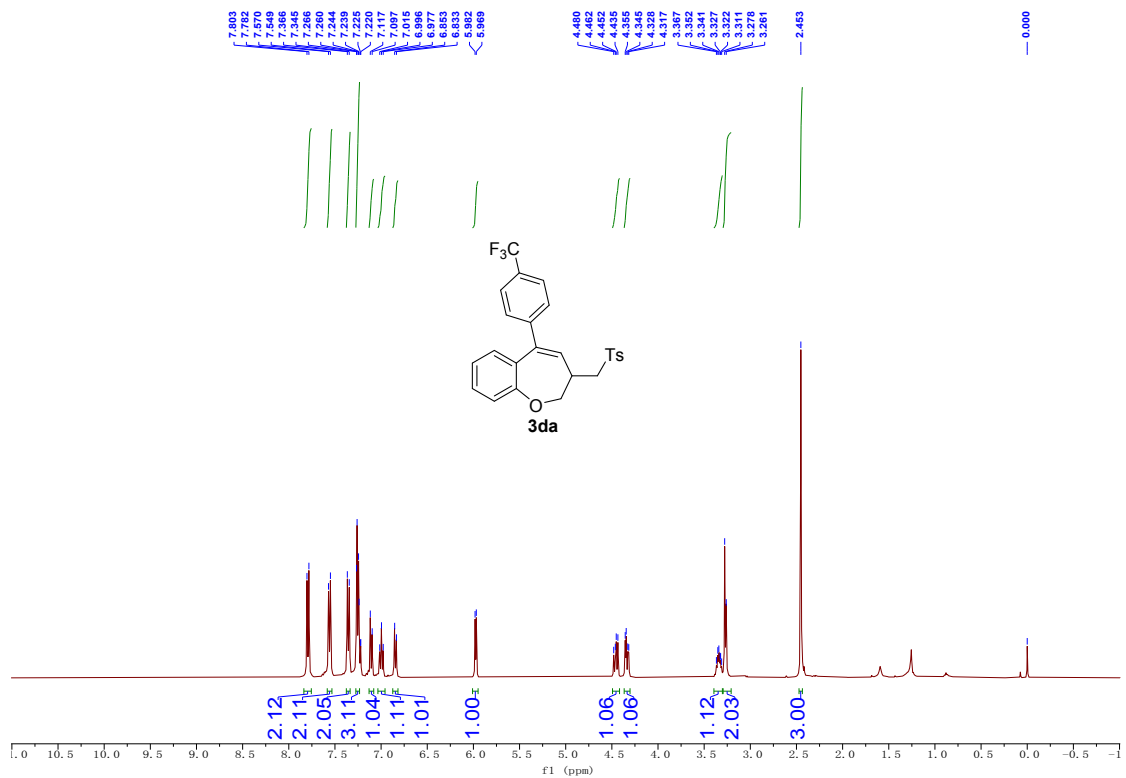
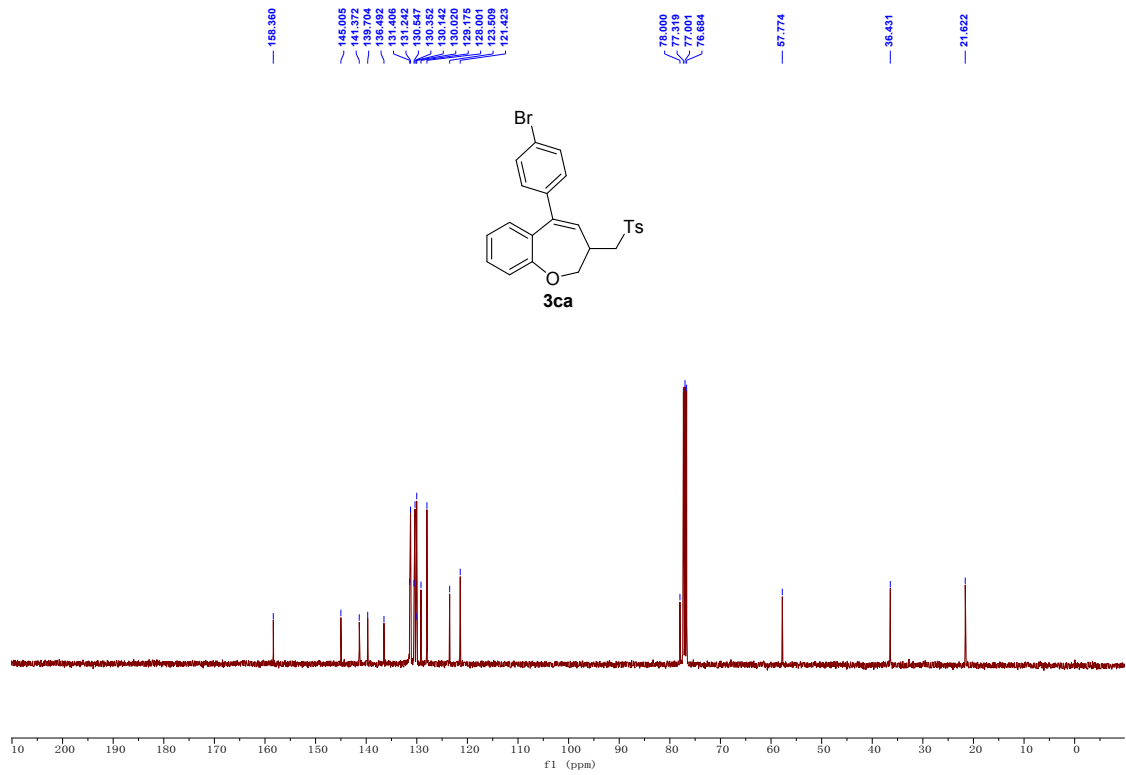


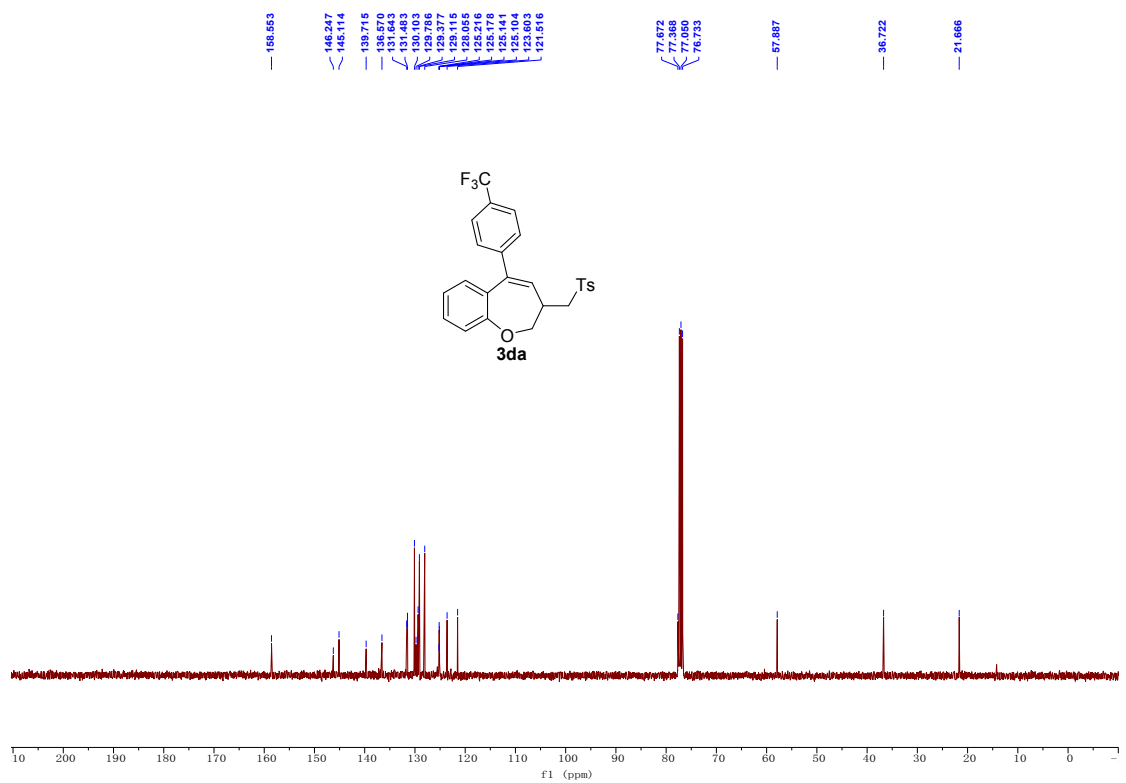
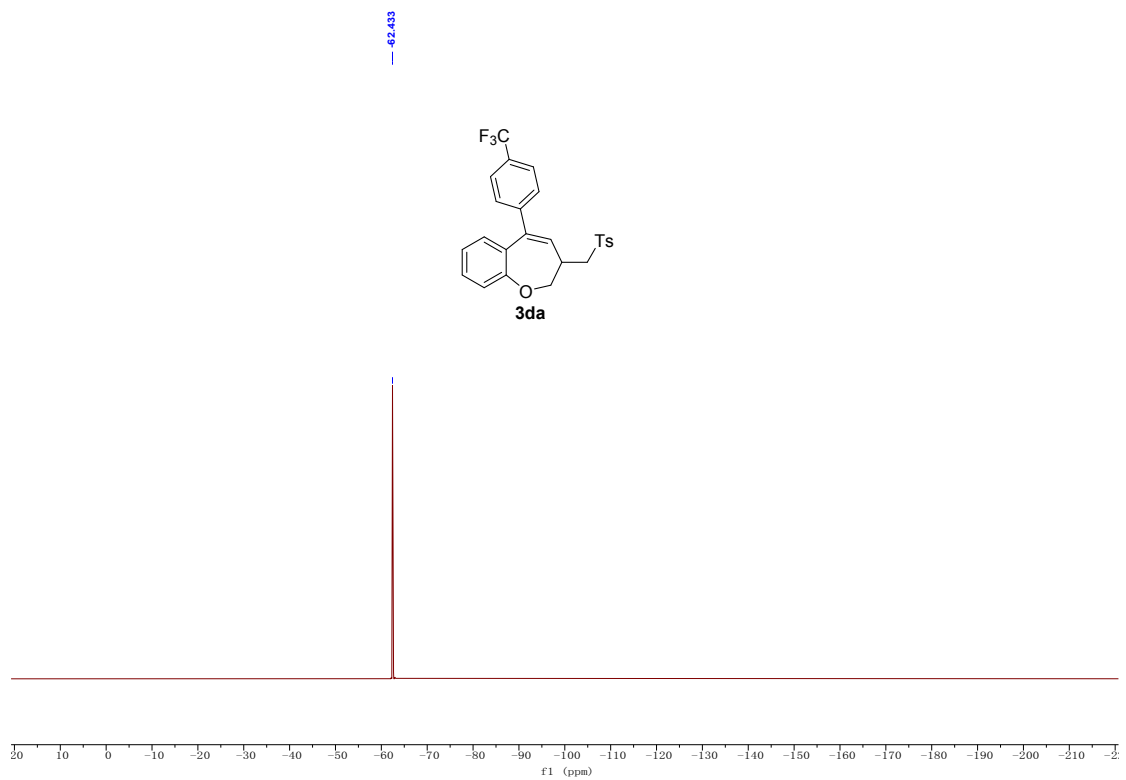


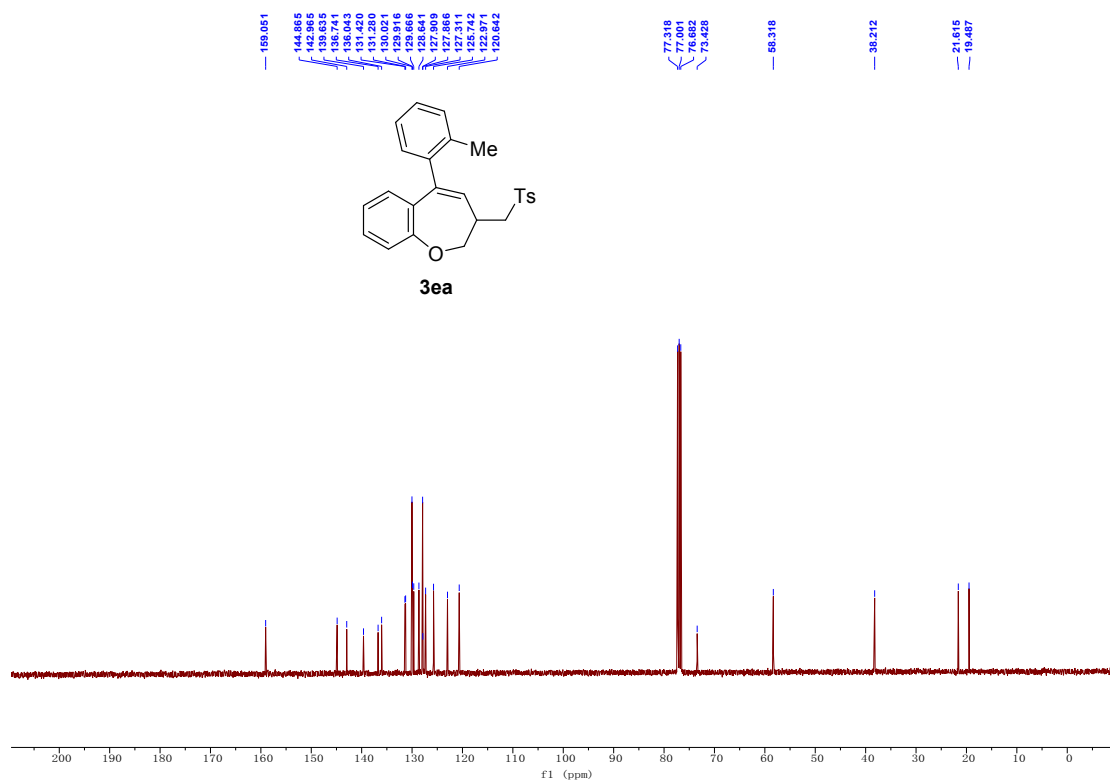
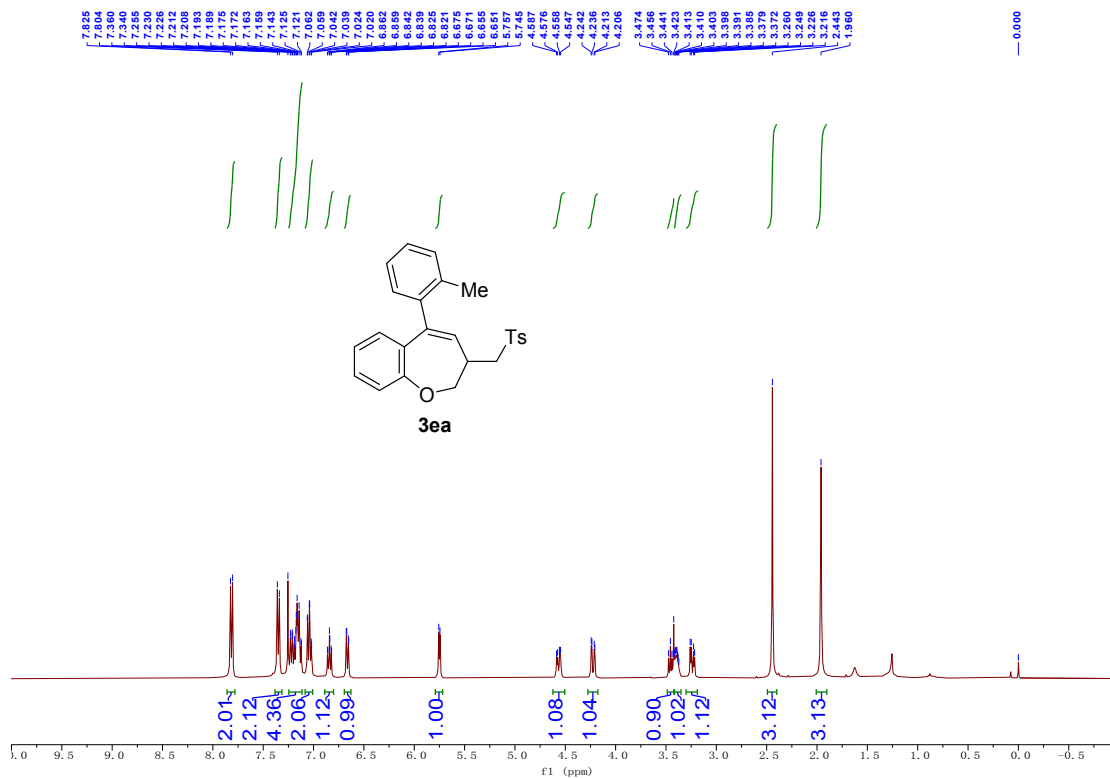


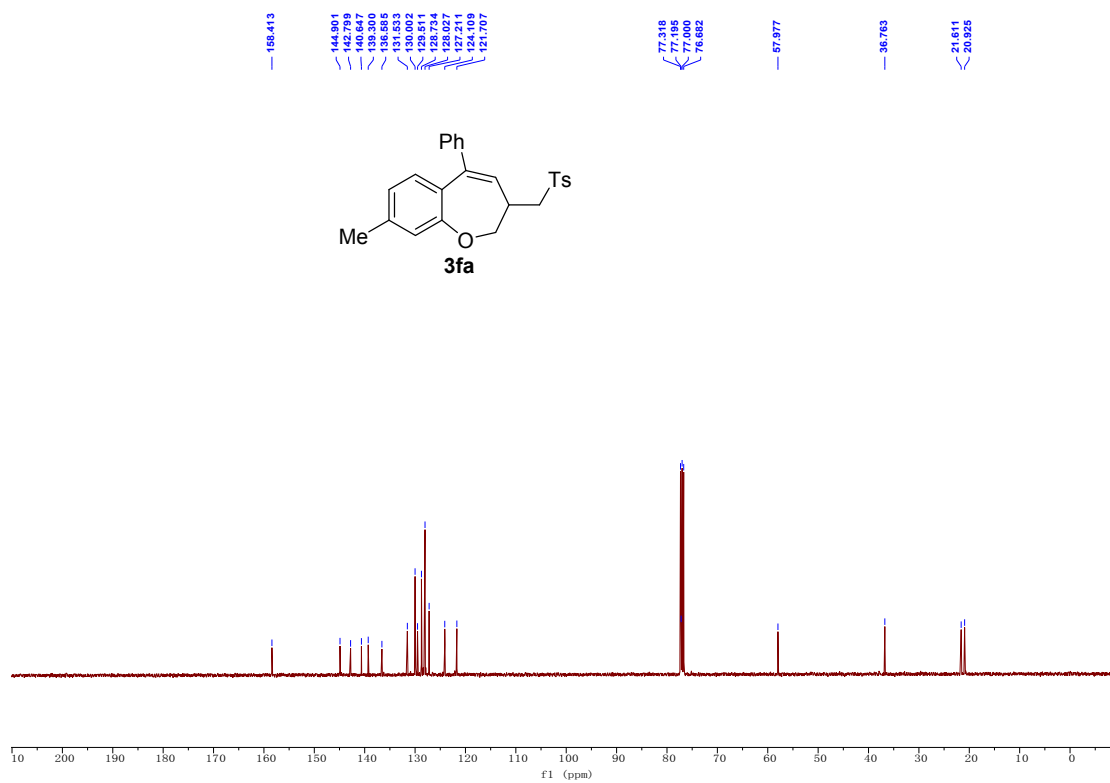
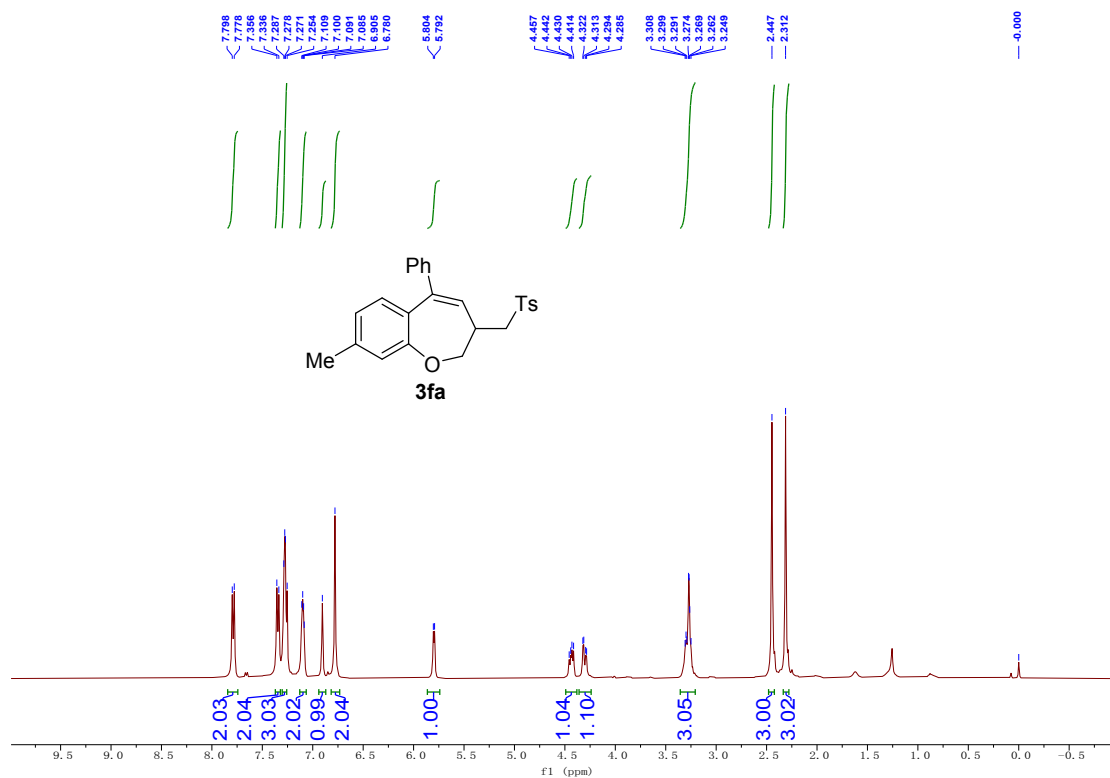


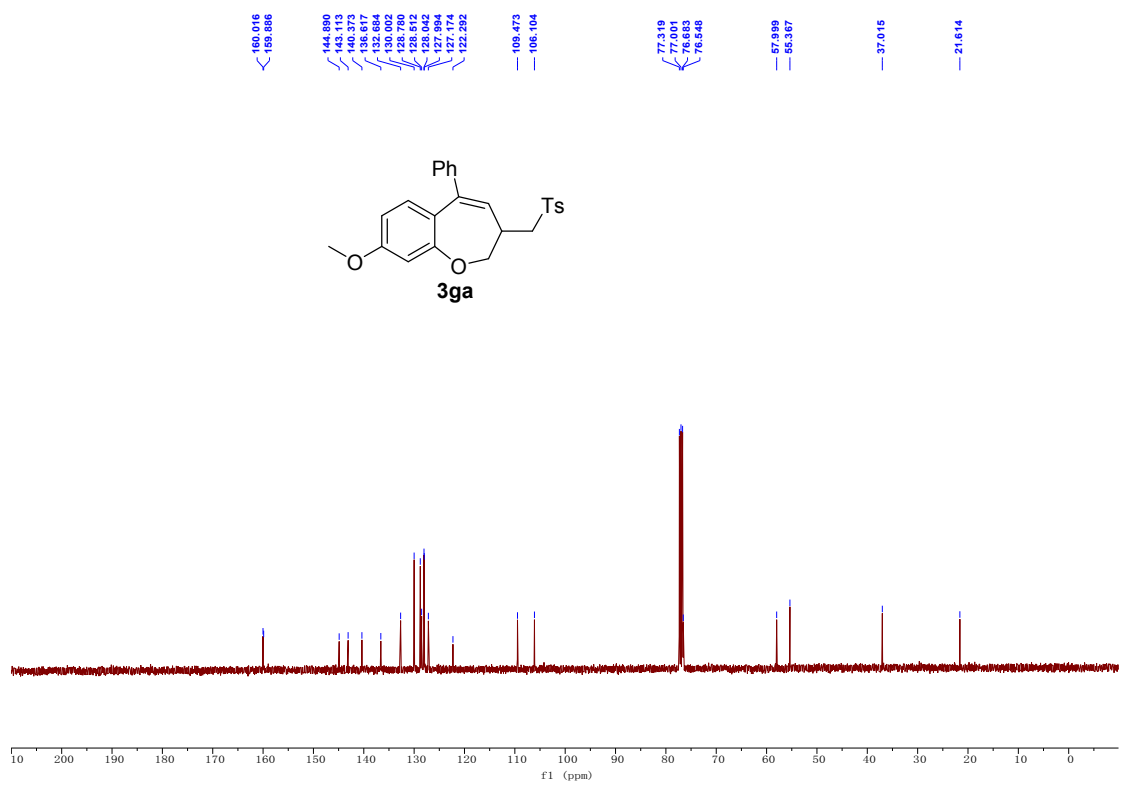
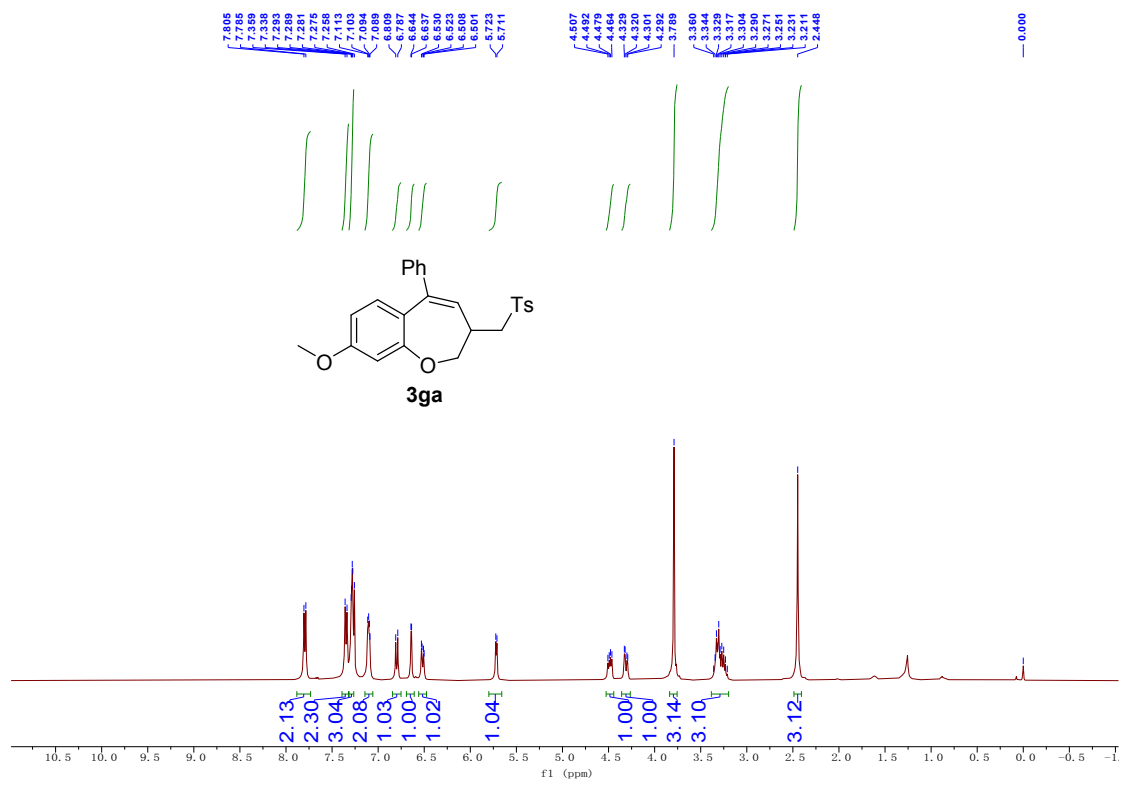


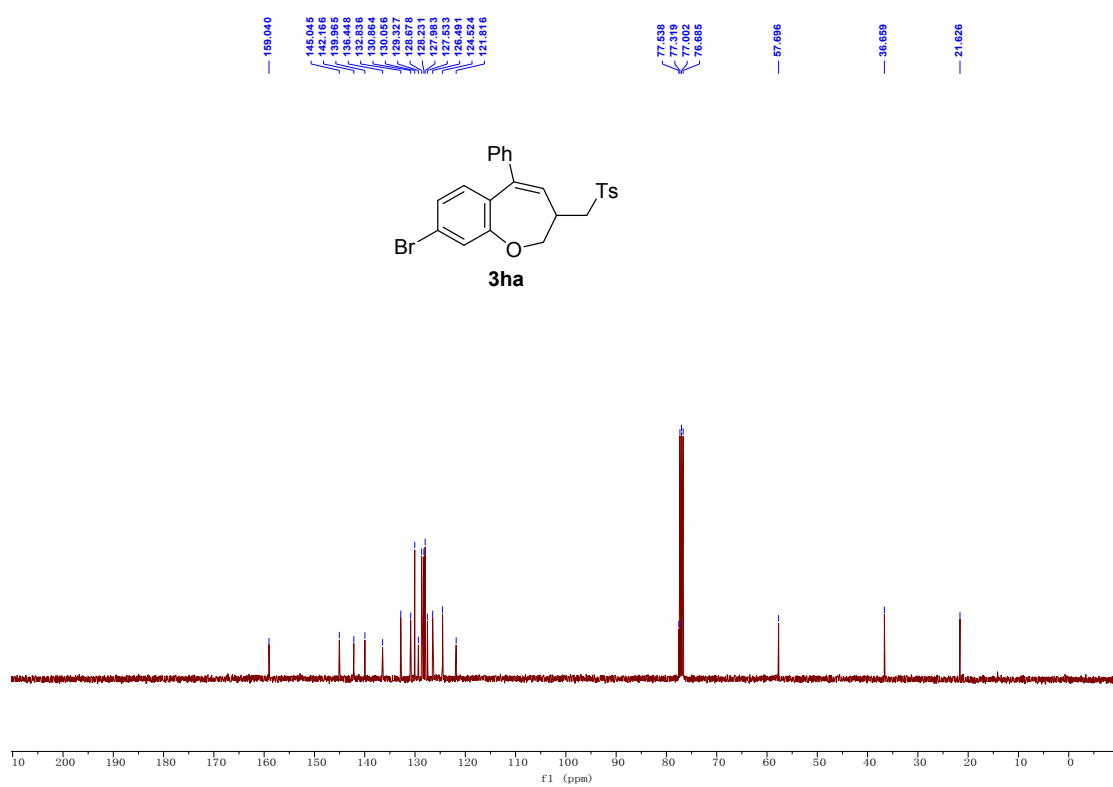
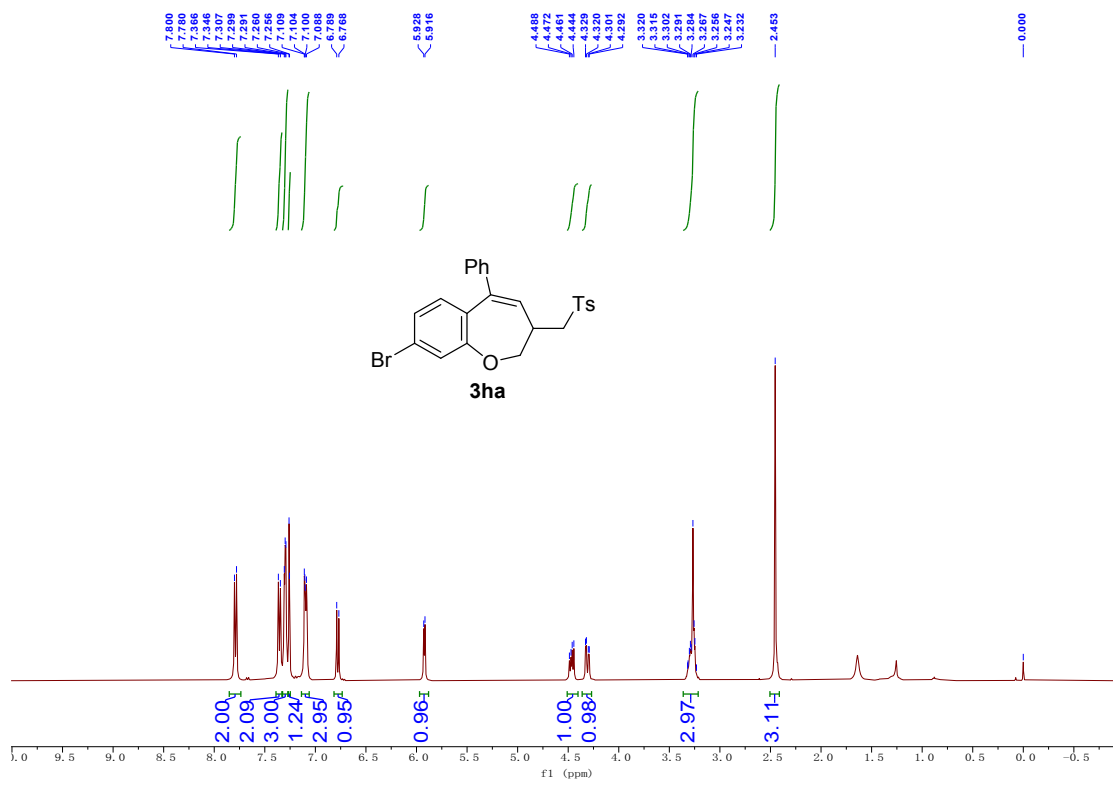


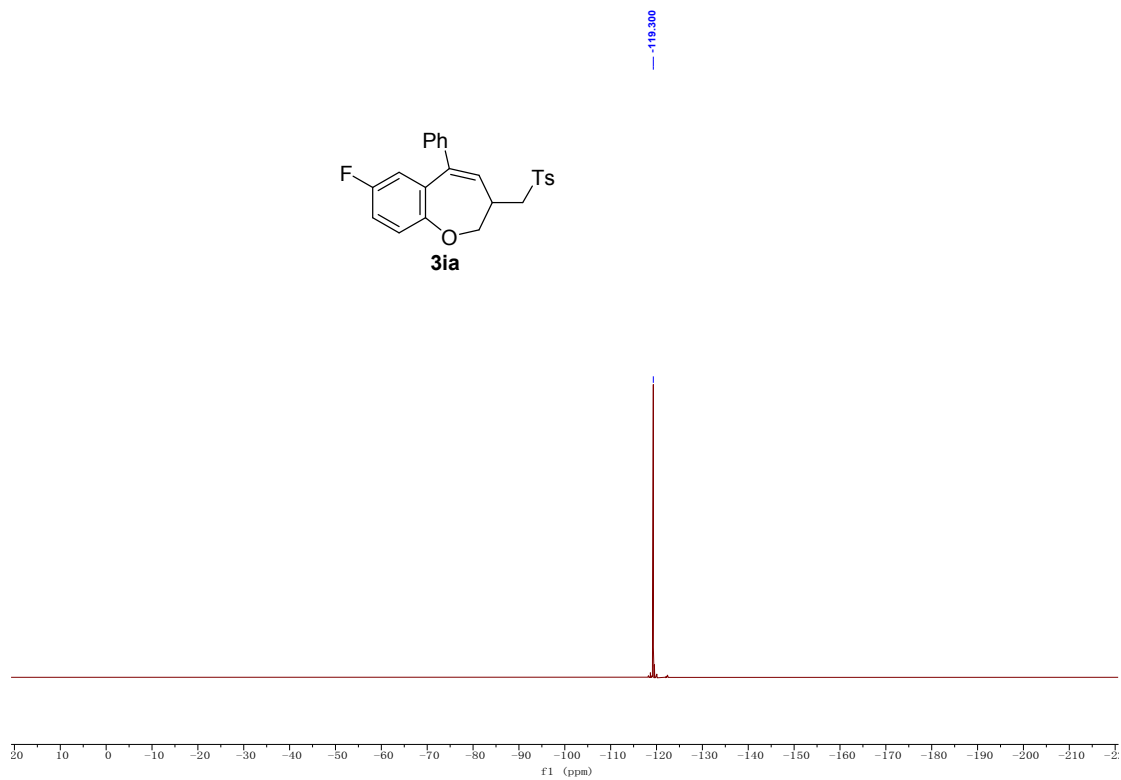
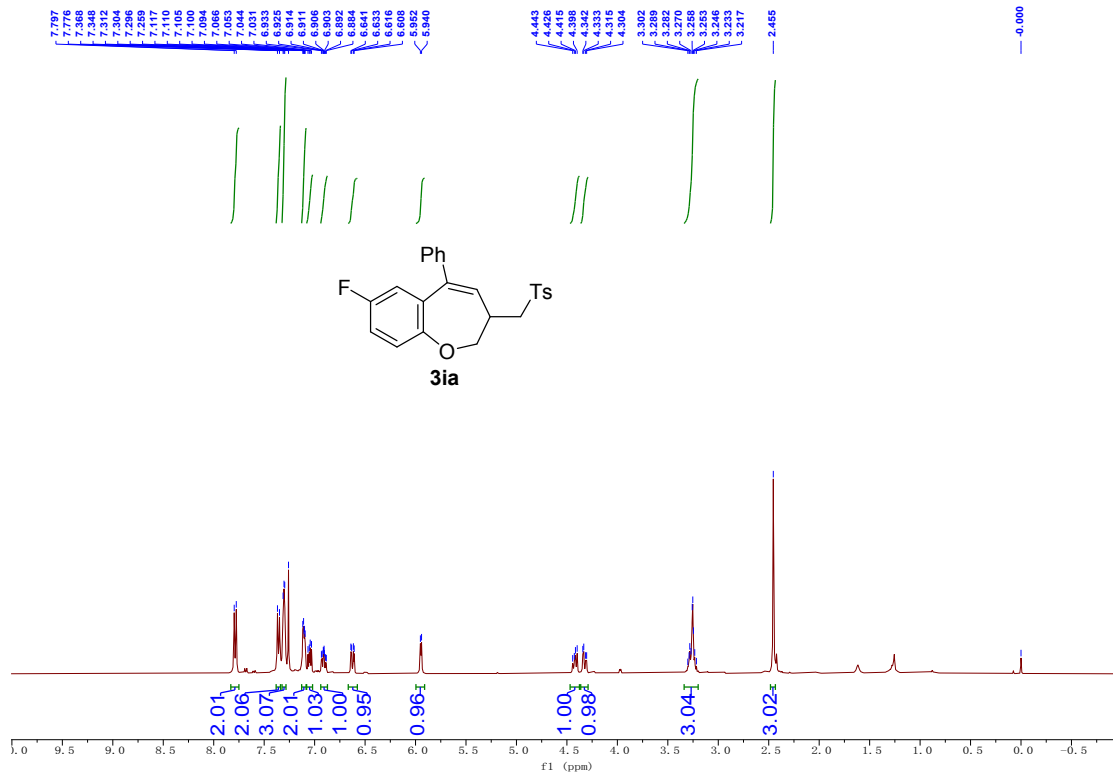


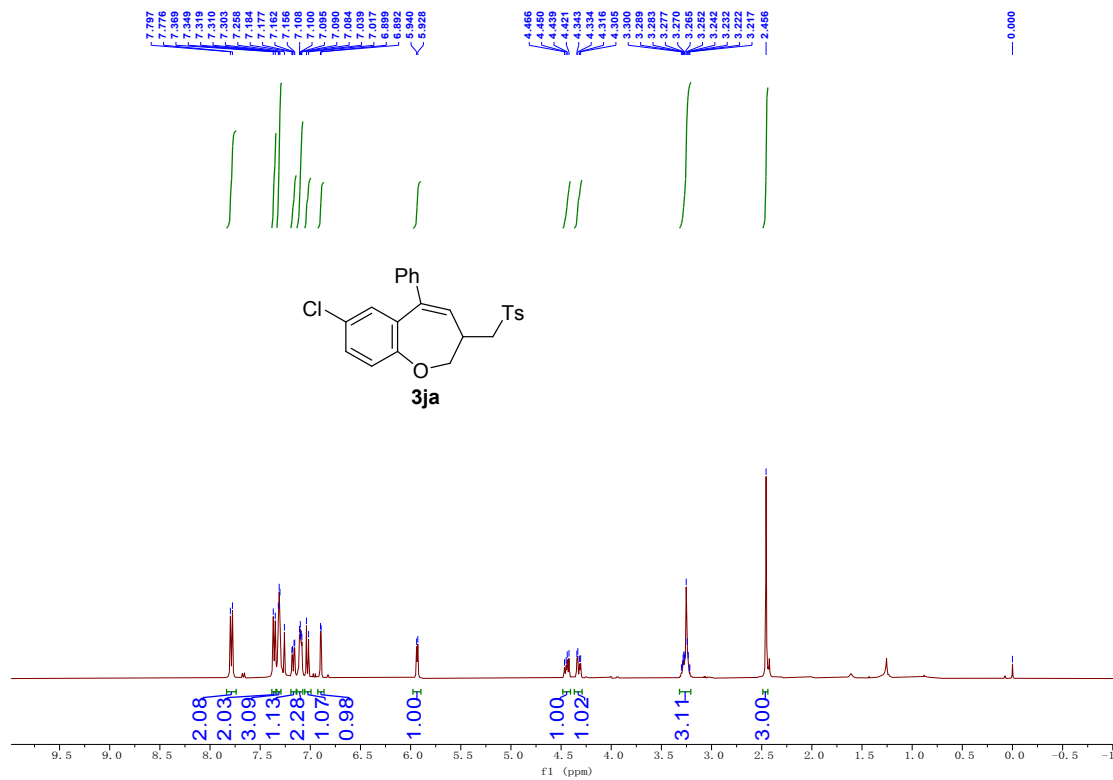
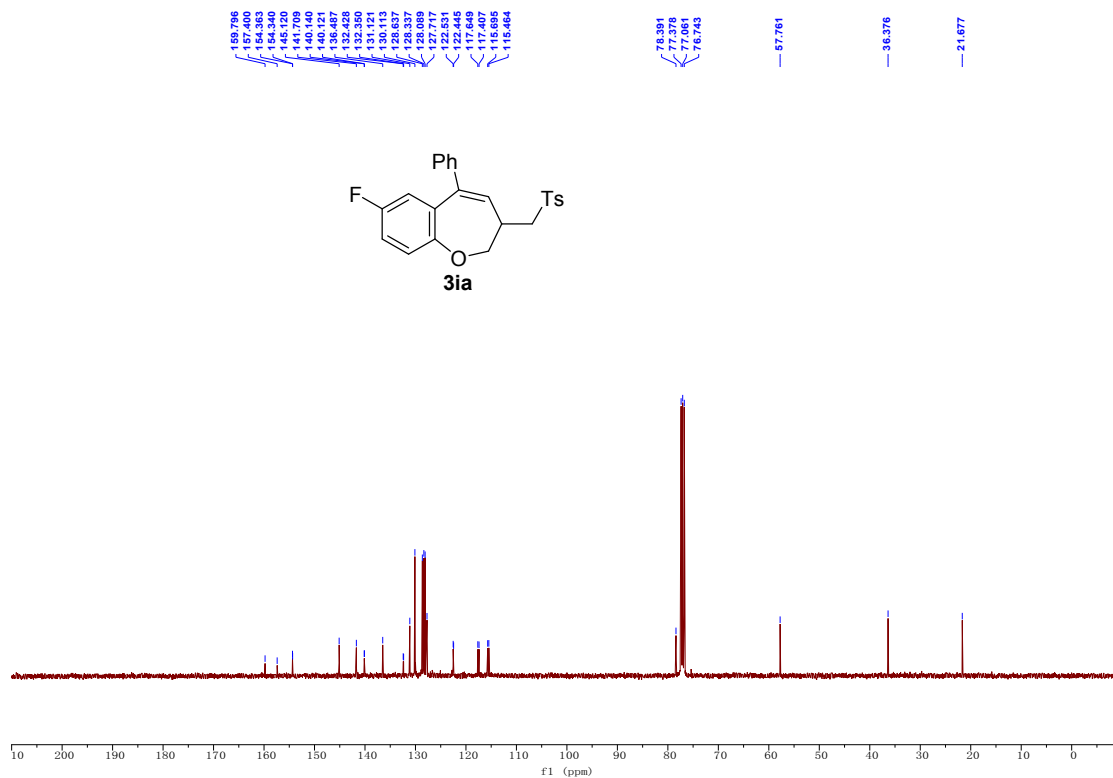




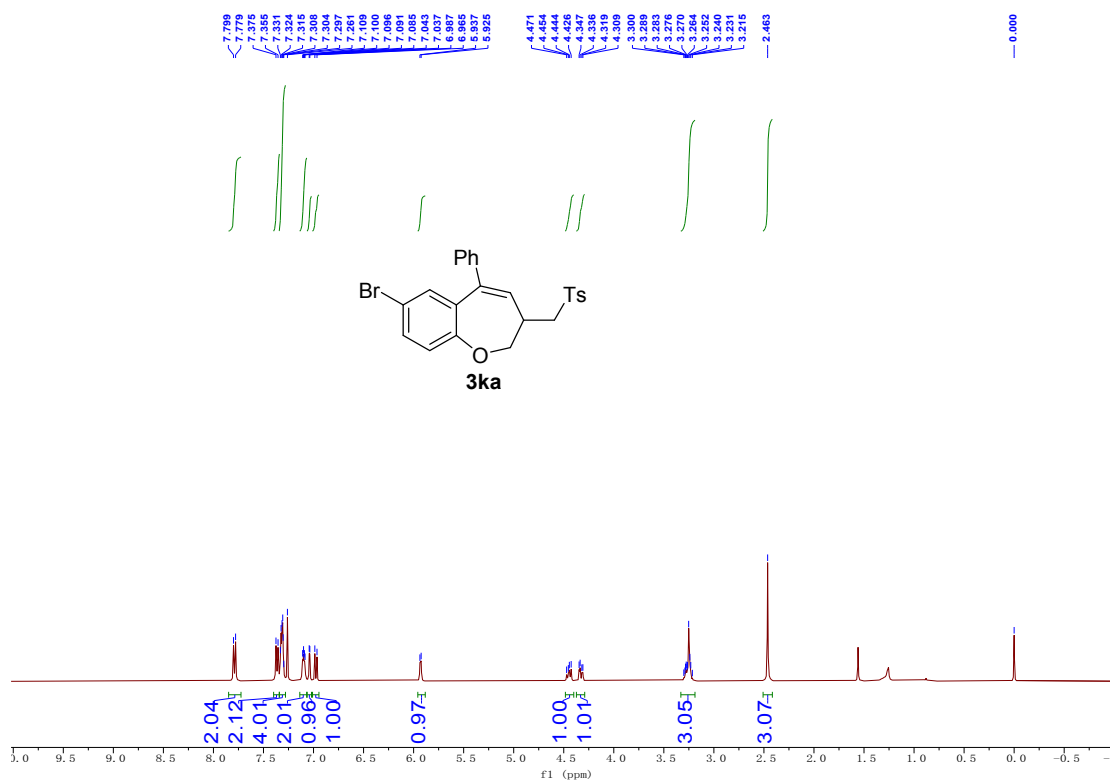
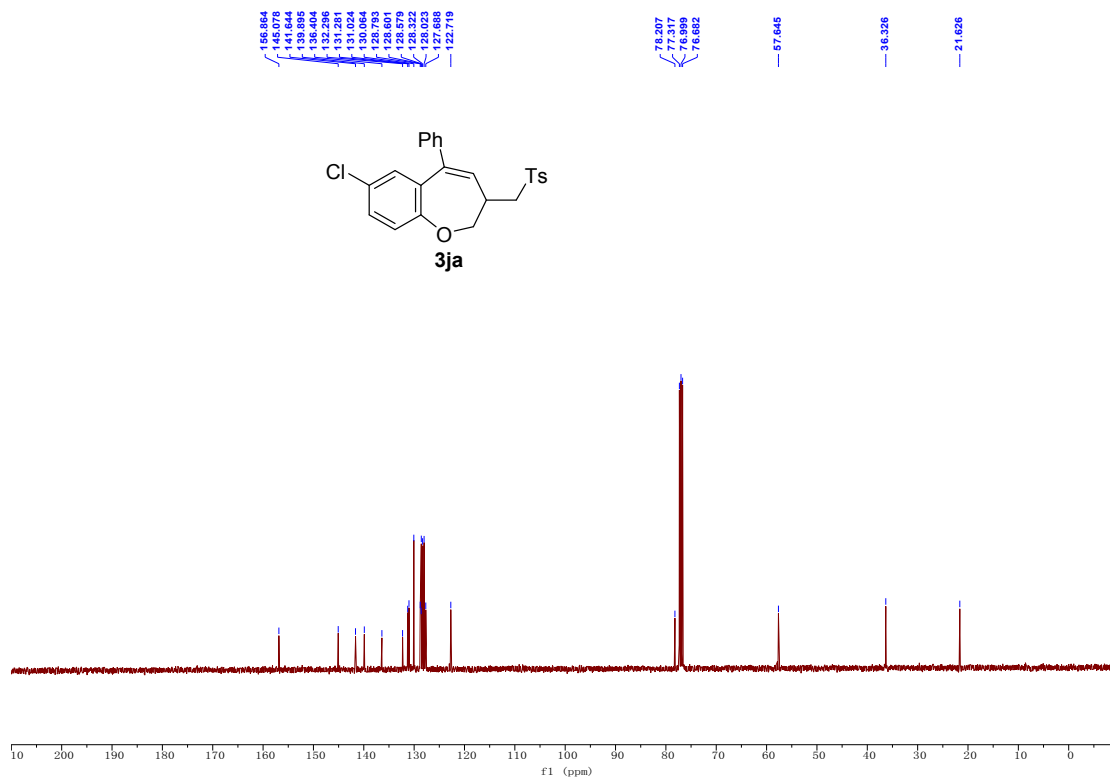


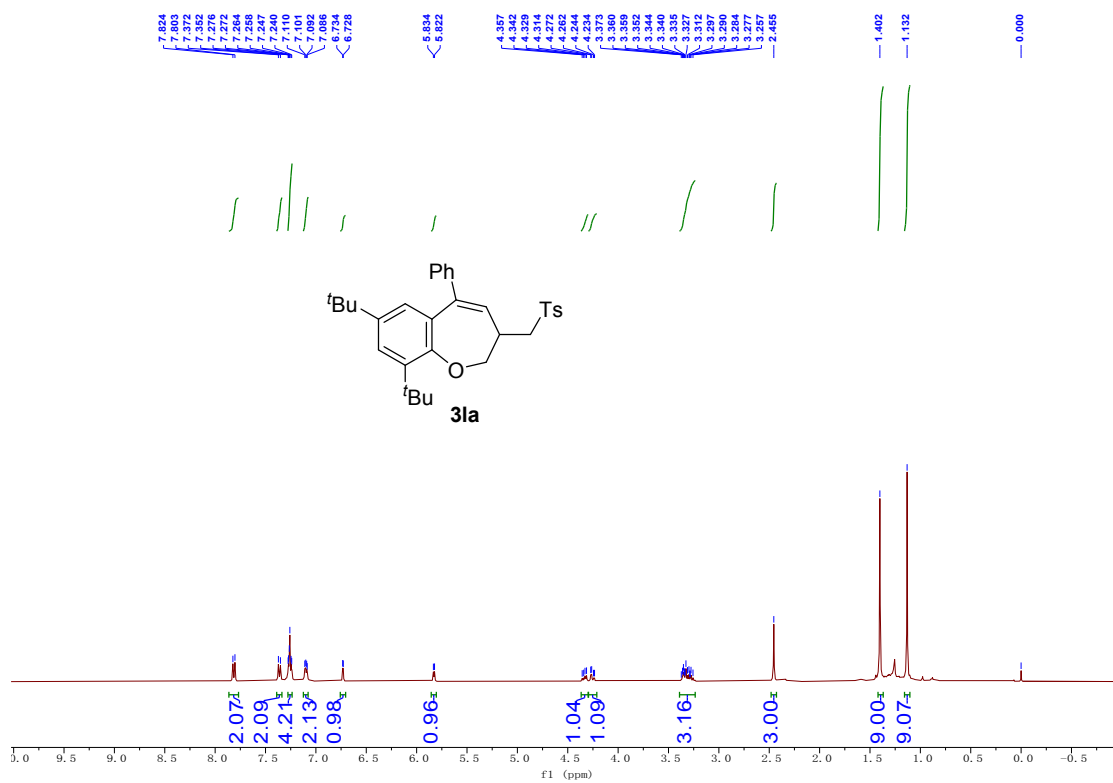
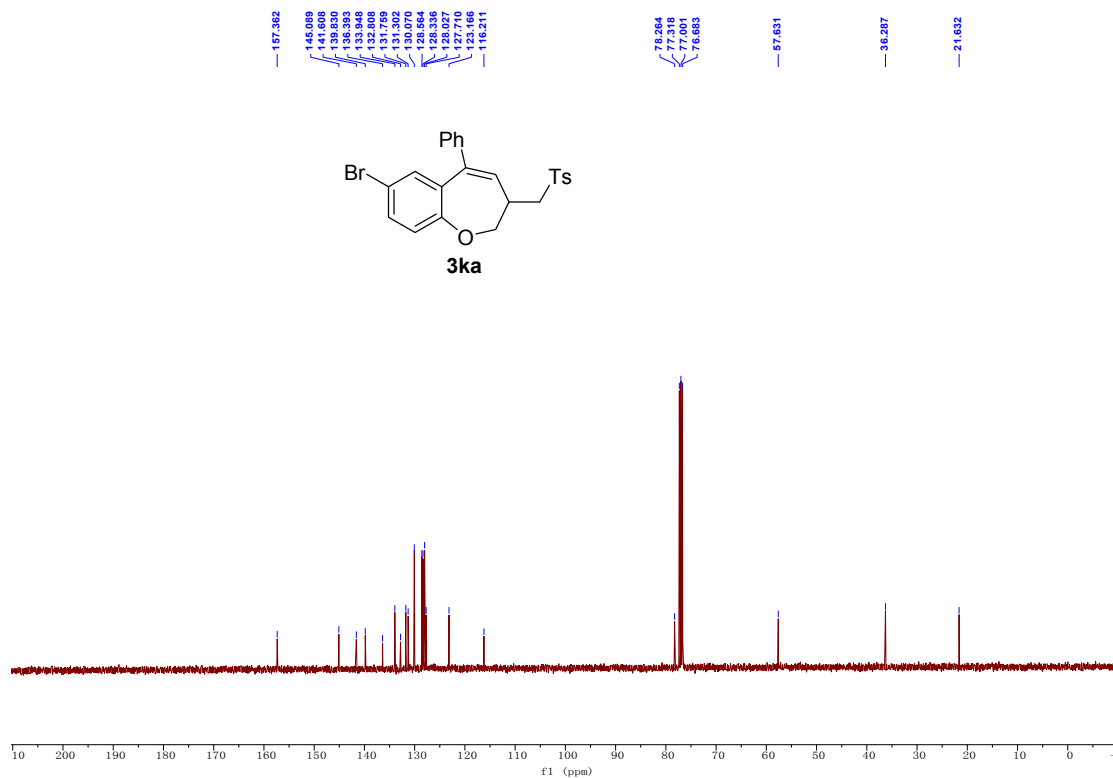


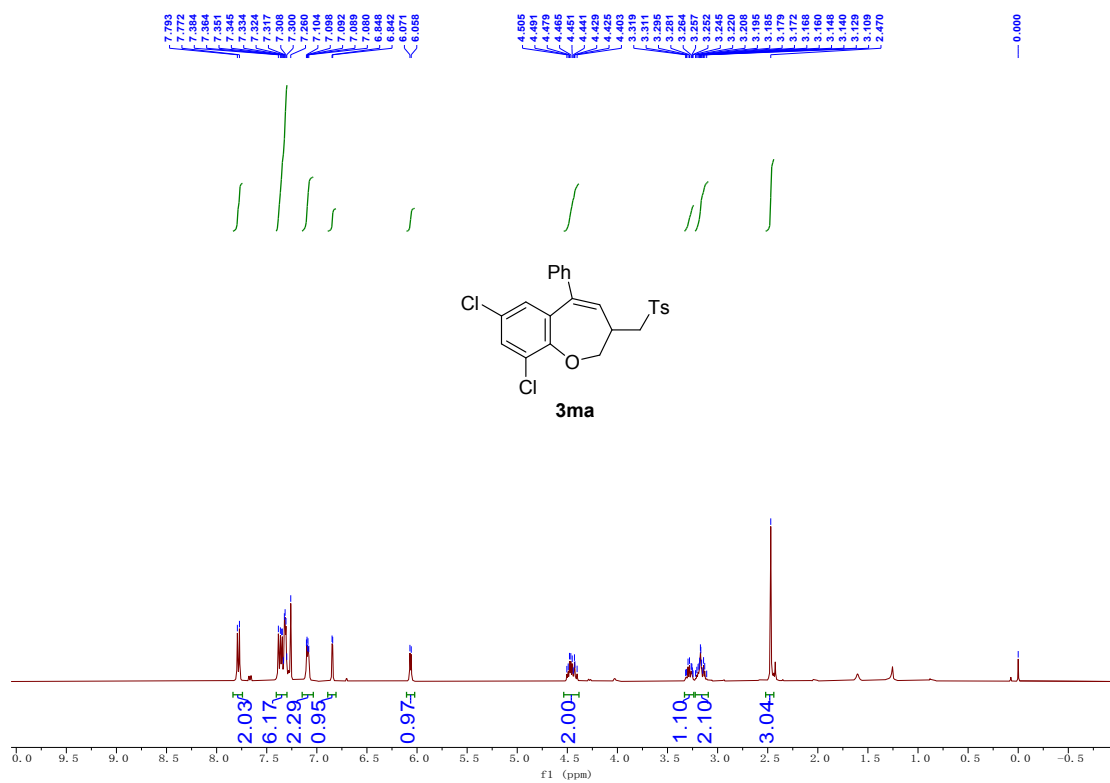
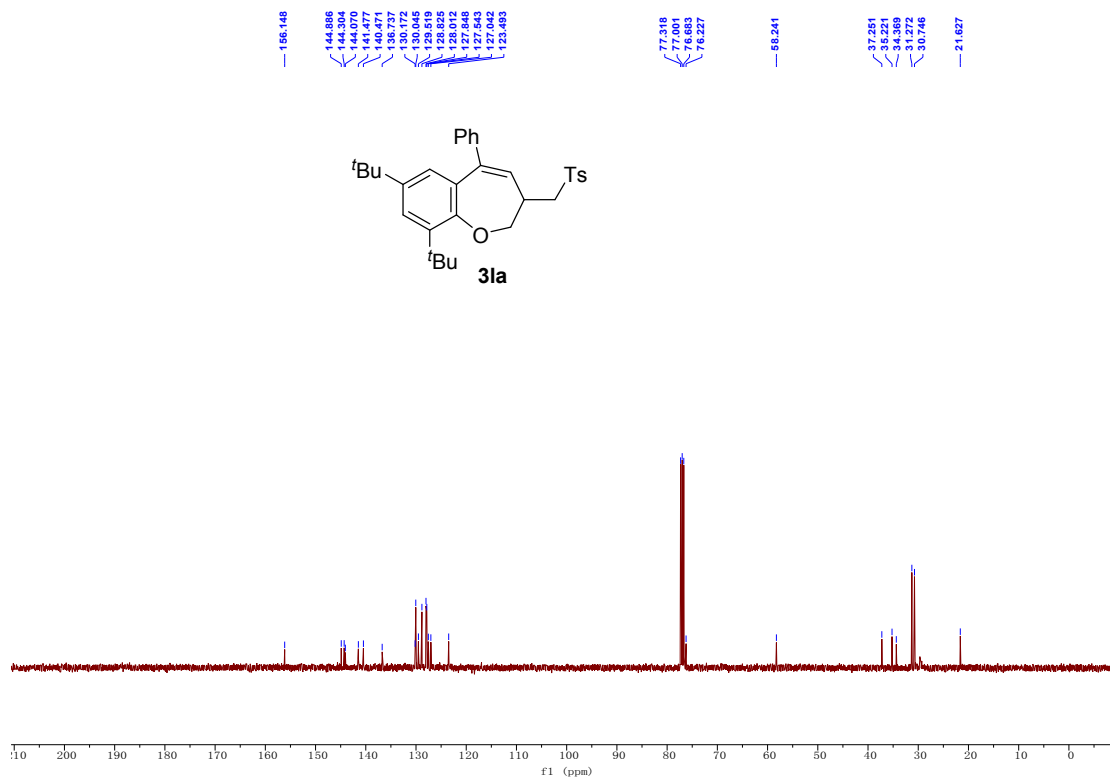


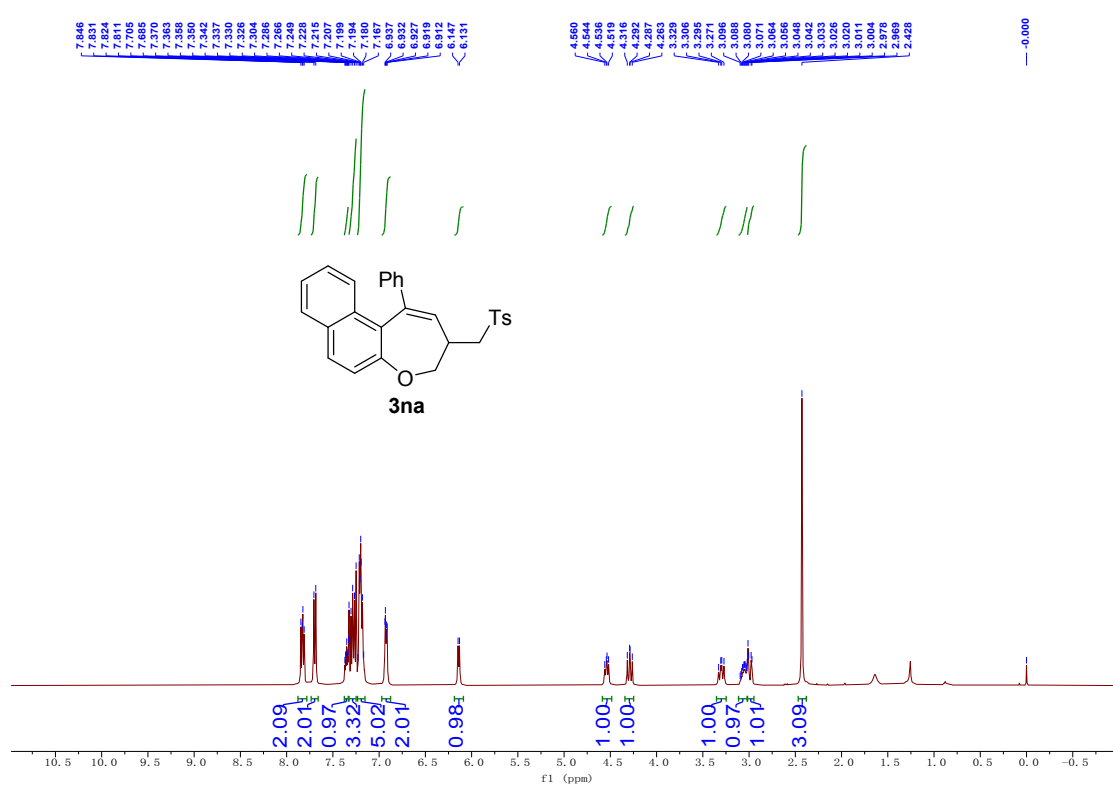
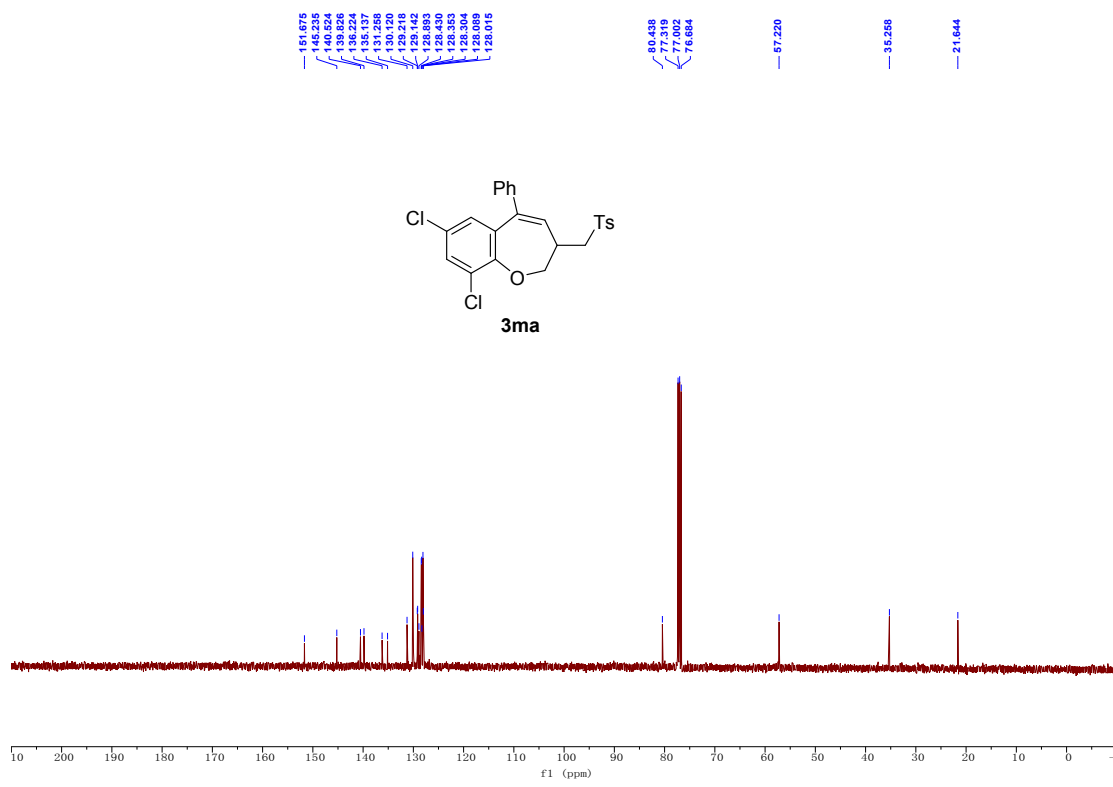


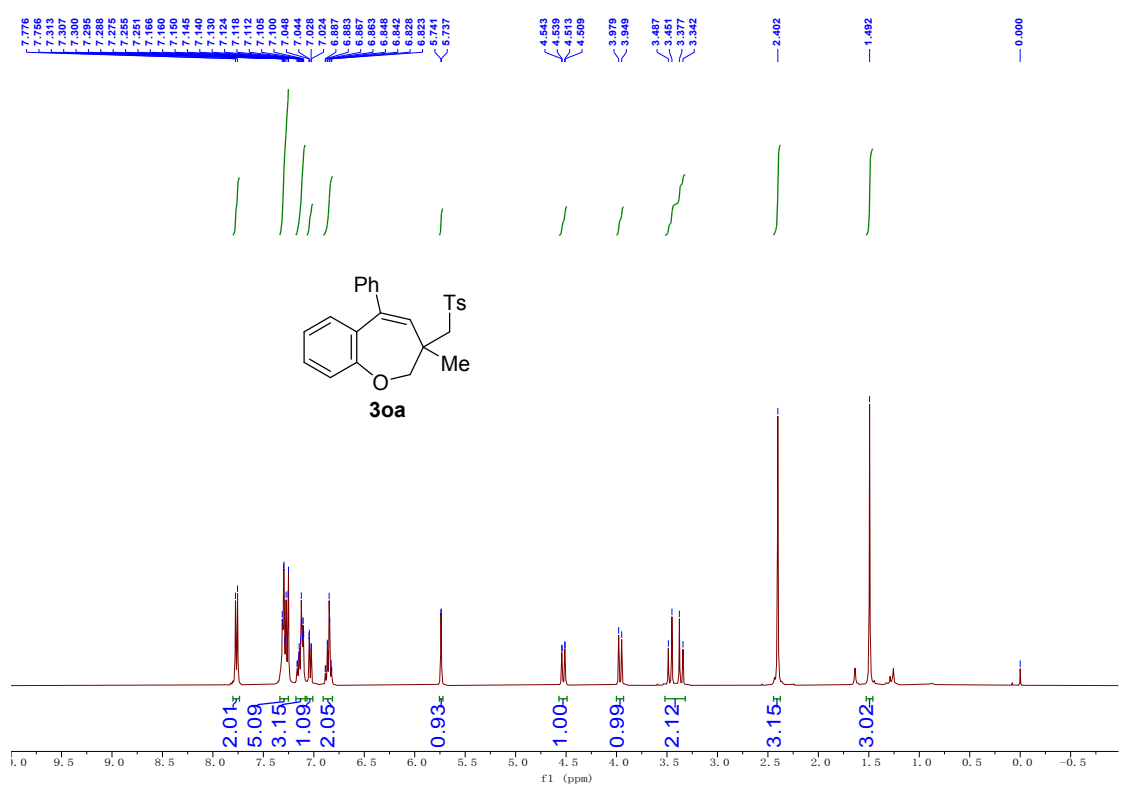
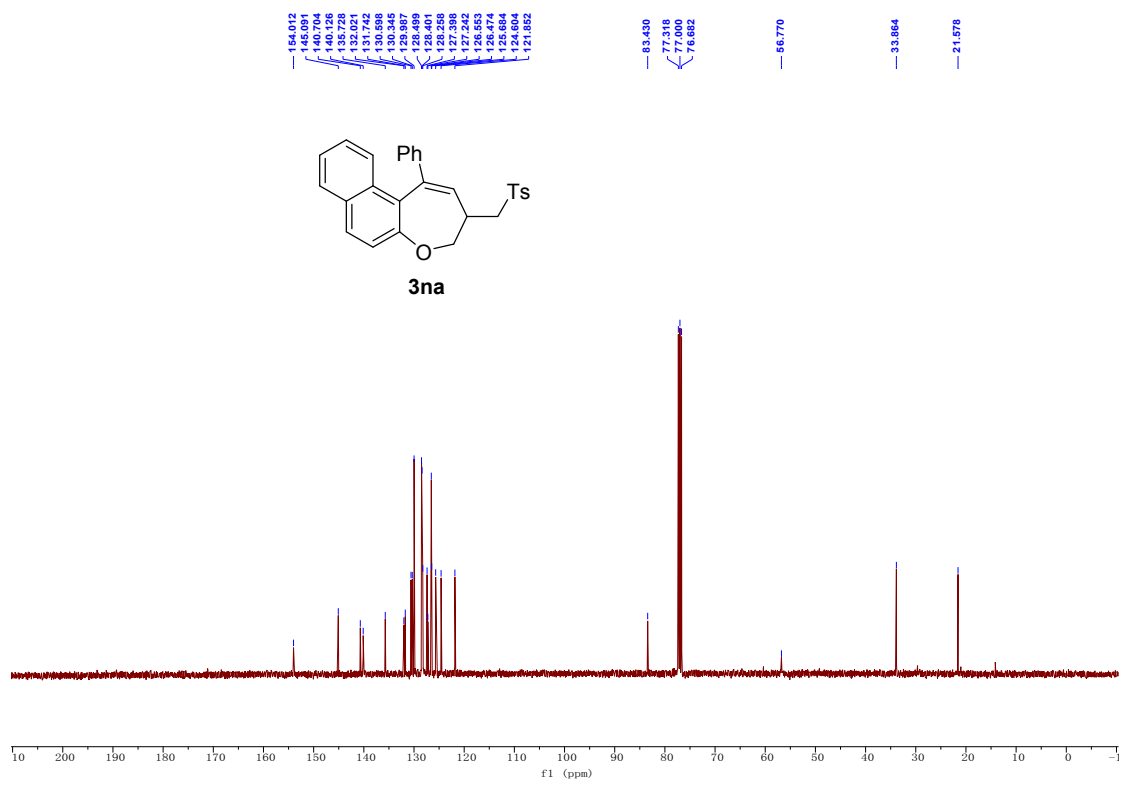


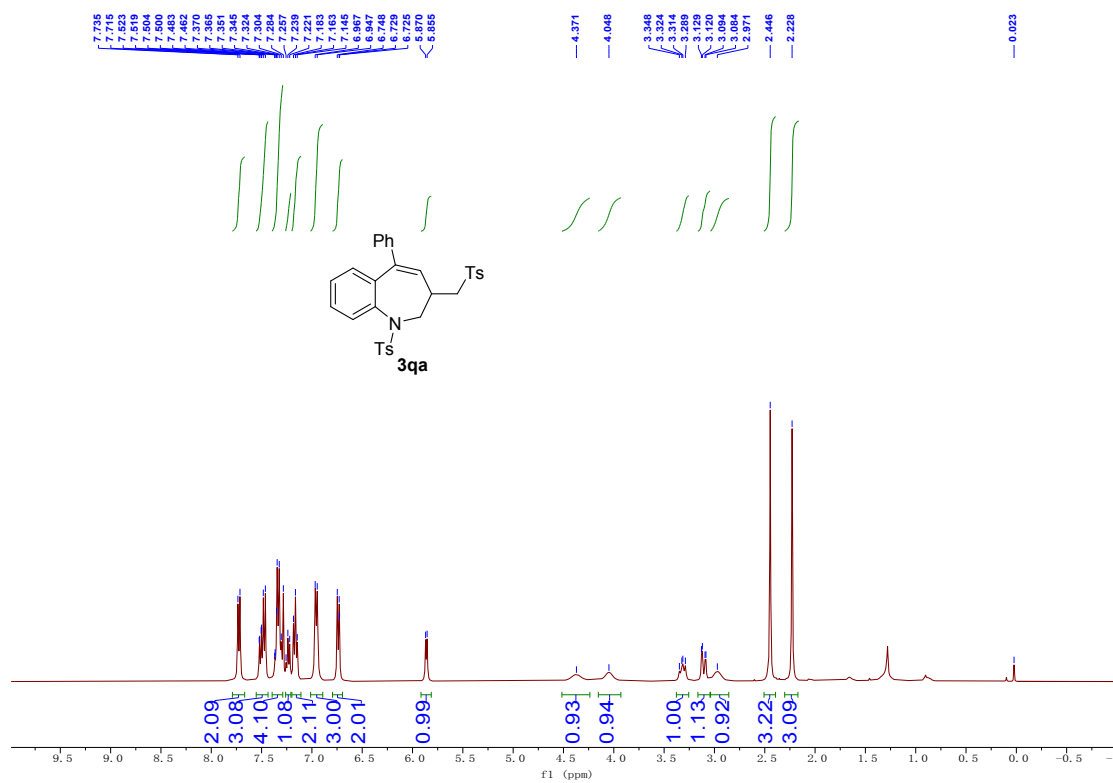
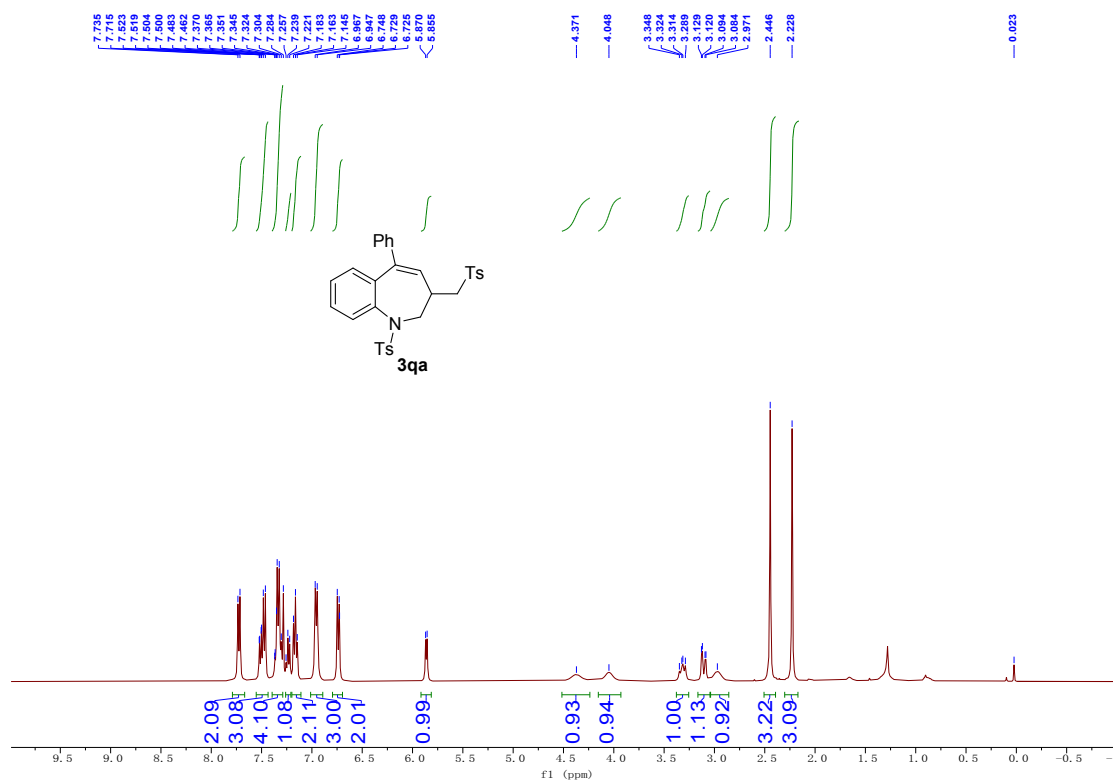
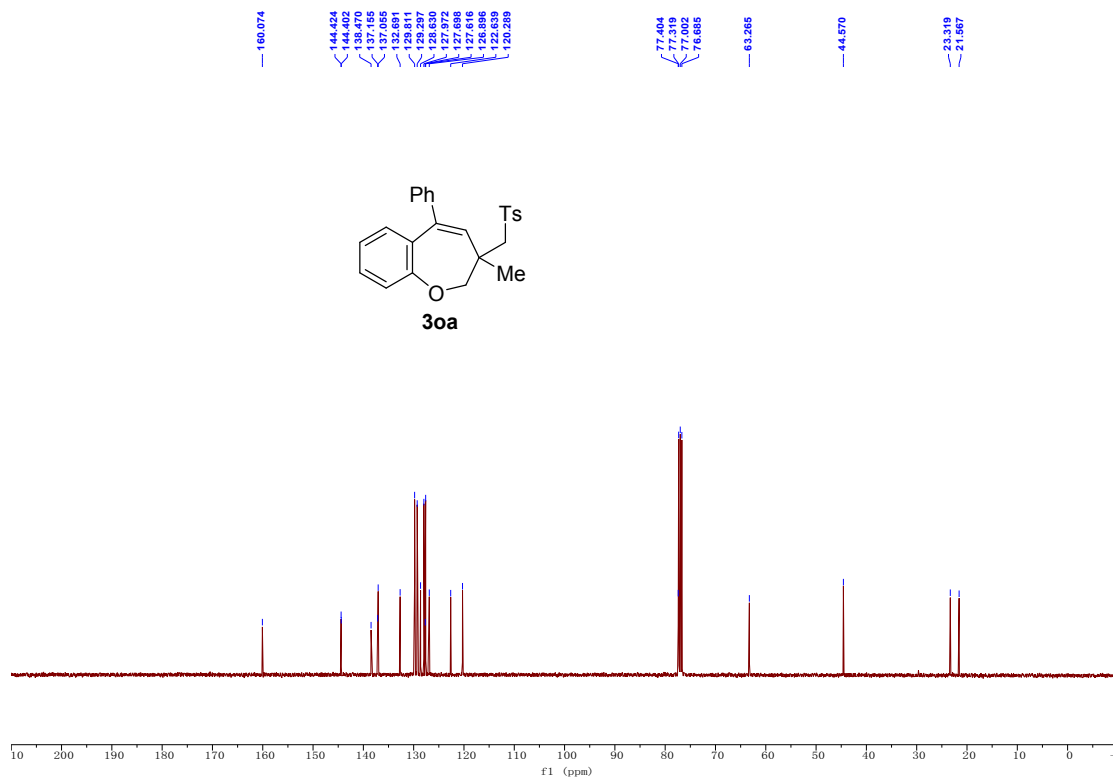


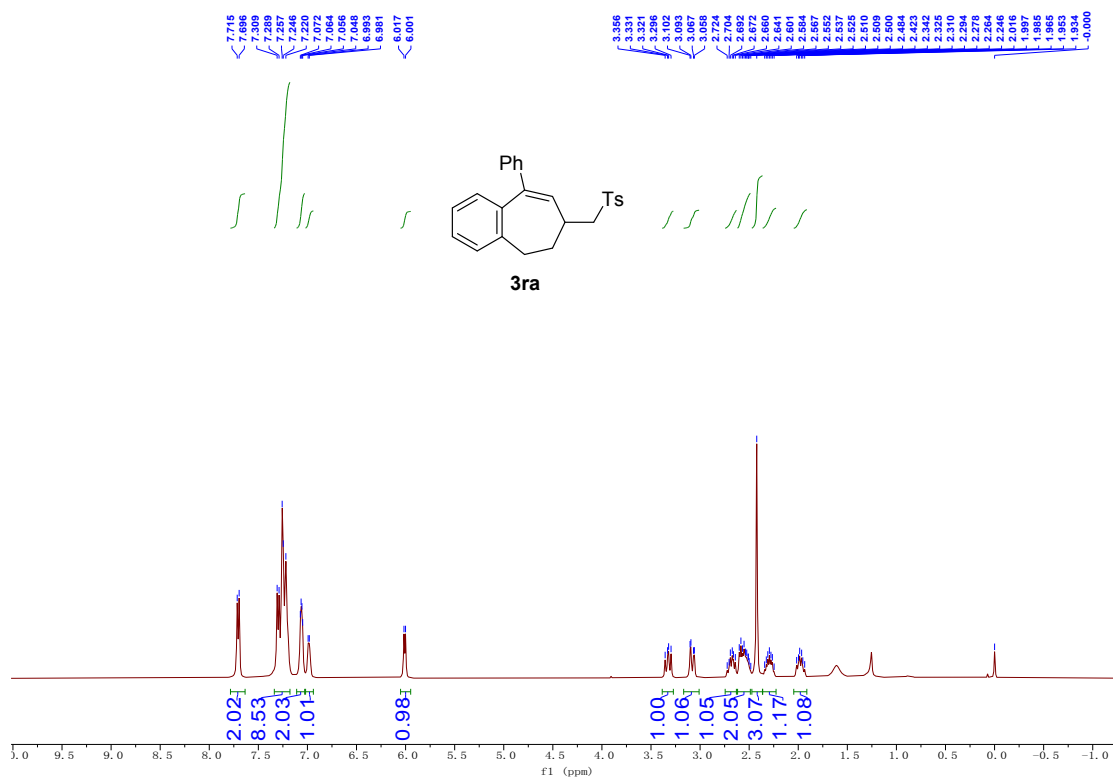
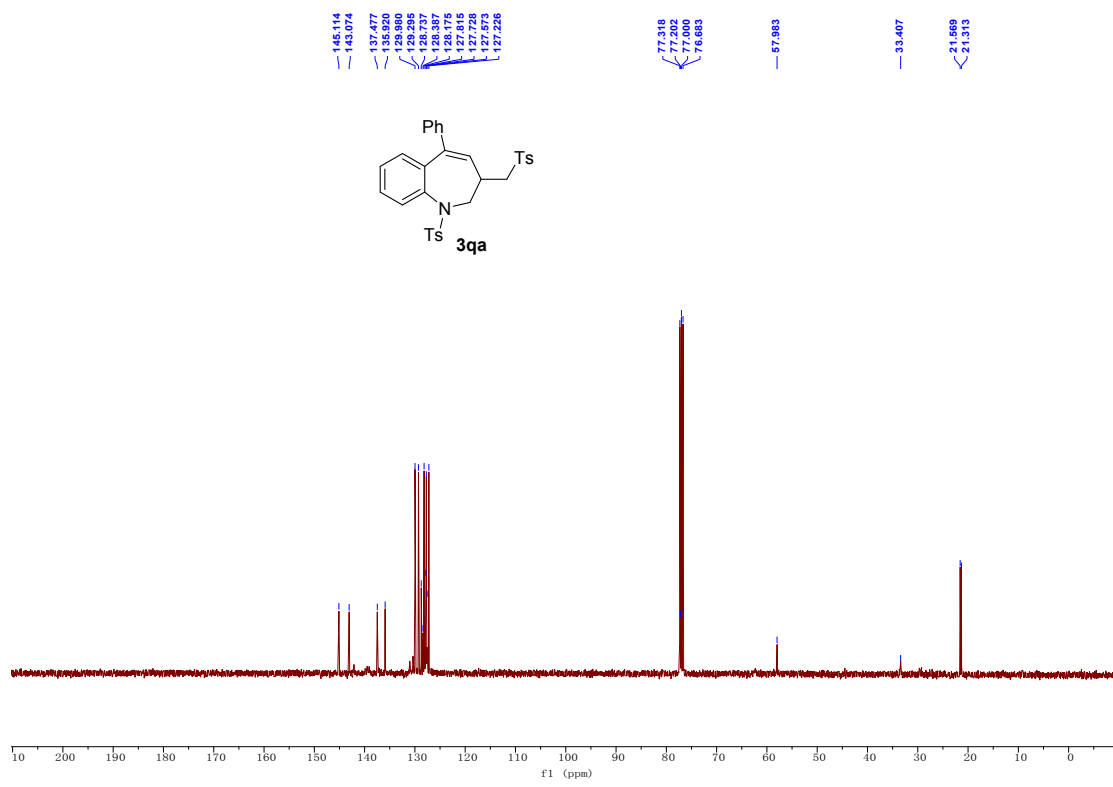


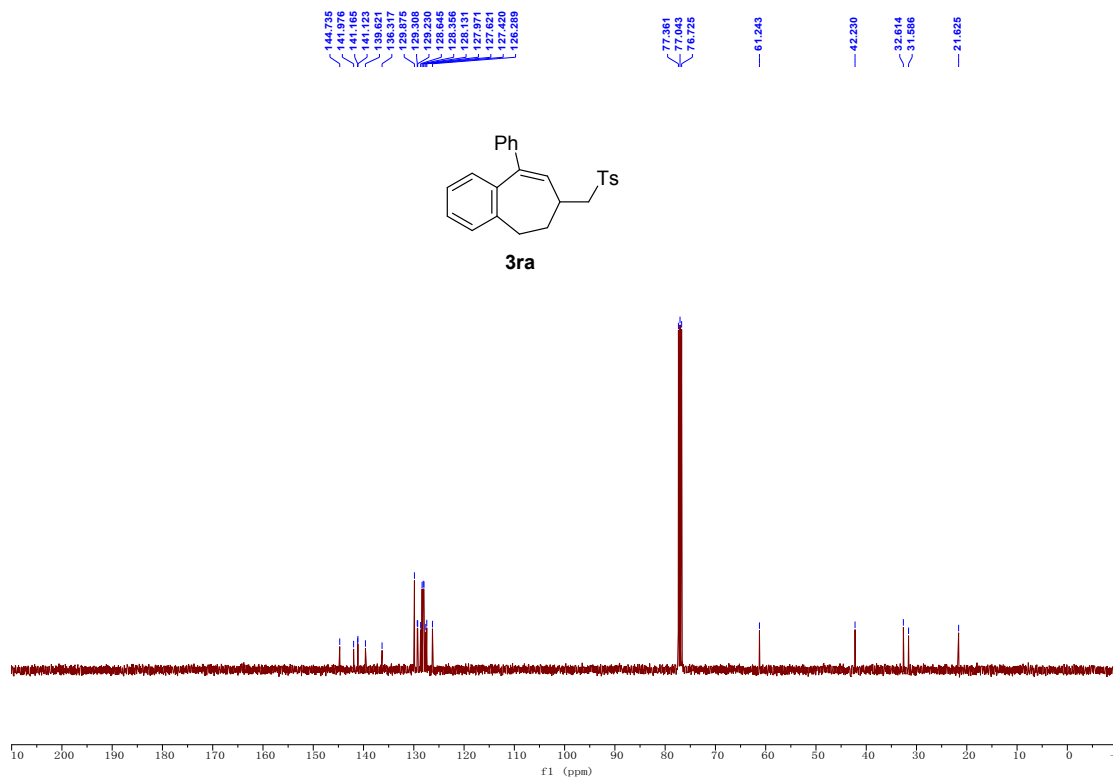




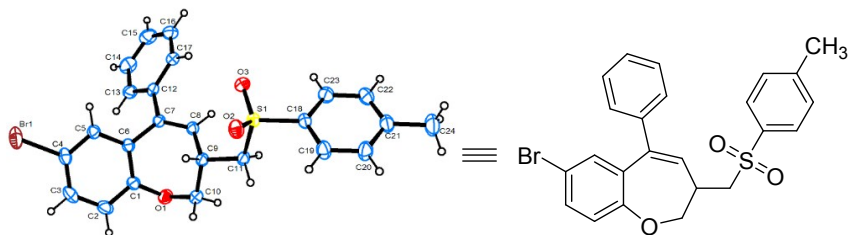












X-ray Crystal Structure of **3ka**, CCDC 2074239.

Thermal ellipsoids are drawn at 30% probability level.

Identification code	<b>3ka</b>
Empirical formula	C <sub>24</sub> H <sub>21</sub> Br O <sub>3</sub> S
Formula weight	469.38
Temperature	293(2)
Wavelength	0.71073 Å
Crystal system, space group	triclinic, P -1
Unit cell dimensions	a = 9.2058(16)Å      alpha = 107.378(2) deg.
	b = 10.3794 Å      beta = 109.996(2) deg
	c = 12.708(2) Å      gamma = 97.756(2) deg.
Volume	1050.2(3) Å <sup>3</sup>
Z	2
Absorption coefficient	2.079
F(000)	480
Theta range for data collection	2.441 to 27.081 deg.
Limiting indices	-11<=h<=11, -13<=k<=13, -16<=l<=16
Absorption correction	multi-scan
Data / parameters	4749 /263
Goodness-of-fit on F <sup>2</sup>	1.033
Final R indices [I>2sigma(I)]	R1 = 0.0380, wR2 = 0.0921
R indices (all data)	R1 = 0.0579, wR2 = 0.0995
Largest diff. peak and hole	0.375 and -0.433 e. Å <sup>-3</sup>