

Supporting Information

Amino-assisted synthesis of alkynylthioethers via a visible-light-induced C_(sp)-S^{II} coupling between bromoalkynes and 2,2'-diaminodiarlyldisulfides

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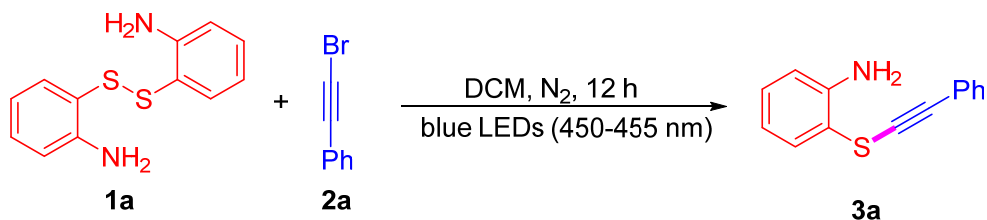
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1. General remarks

All reactions were conducted in clean glassware with magnetic stirring. Chromatographic purification was performed on silica gel (400~500 mesh) or neutral alumina (200-300 mesh) and analytical thin layer chromatography (TLC) on silica gel HG/T2354-2010 GF254 (Qindao), which was detected by fluorescence. ^1H NMR (600 MHz) and ^{13}C NMR (150 MHz) spectra were measured with a Bruker Avance Neo 600 spectrometer with CDCl_3 as solvent and recorded in ppm relative to internal tetramethylsilane standard. NMR data are reported as follows: δ , chemical shift; coupling constants (J are given in Hertz, Hz) and integration. Abbreviations to denote the multiplicity of a particular signal were s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad singlet). High resolution mass spectra were obtained with a Thermo Scientific LTQ Orbitrap XL mass spectrometer (ESI). Cyclic voltammetry (oxidation potential) data was obtained by using Shanghai Chenhua electrochemical workstation. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected.

2. Representative procedure for the synthesis of alkynylthioethers

2.1 Representative procedure for the synthesis of alkynylthioethers in 0.10 mmol scale



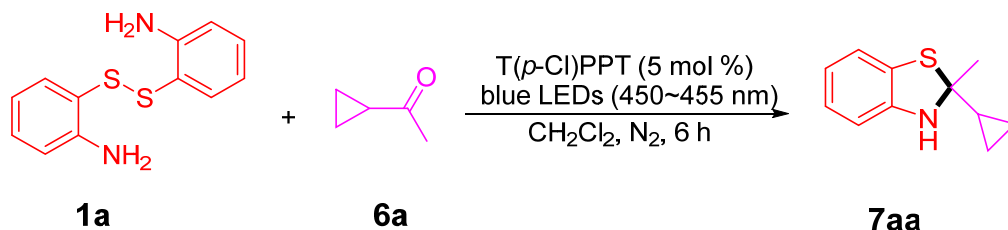
To a solution of 2,2'-diaminodiphenyldisulfide (**1a**, 0.10 mmol) in 4 mL of dichloromethane was added bromoalkyne (**2a**, 0.10 mmol) under nitrogen atmosphere. The reaction mixture was stirred under blue LEDs (450–455 nm) irradiation for 12 h at room temperature. The residue was then purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to give the pure product **3a** in 83% yield.

2.2 Representative procedure for the synthesis of alkynylthioethers in 5.0 mmol scale

2,2'-Diaminodiphenyldisulfide (**1a**, 1.24 g, 5.0 mmol) and bromoalkyne (**2a**, 905 mg, 5.0 mmol) were added in dichloromethane (30.0 mL) under nitrogen atmosphere, and the reaction mixture was stirred under blue LEDs (450–455 nm) irradiation for 48 h at room temperature. The residue was then purified by silica gel column chromatography (petroleum ether/EtOAc = 10:1) to give pure product compound **3aa** (768 mg, 68% yield).

3. Representative procedure General for synthesis of dihydrobenzothiazoles

3.1 Representative procedure for the synthesis of dihydrobenzothiazoles in 0.10 mmol scale

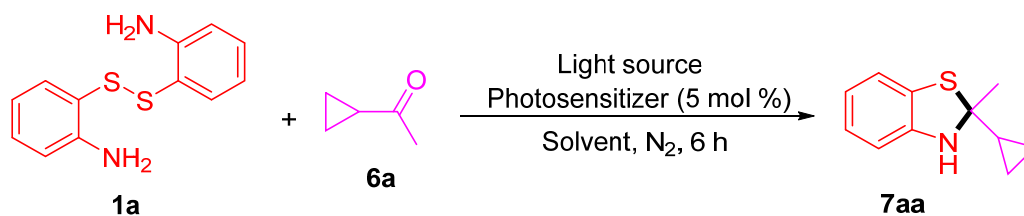


To a solution of 2,2'-diaminodiphenyldisulfide (**1a**, 0.10 mmol) in 2 mL of dichloromethane was added 1-cyclopropylethan-1-one (**6a**, 0.30 mmol) under nitrogen atmosphere, the mixture was stirred for 4 h at room temperature. Subsequently, T(*p*-Cl)PPT (5 mol%) was added to the reaction system and the mixture was stirred under the blue LEDs (450–455 nm) irradiation at room temperature for 6 h. The residue was then purified by column chromatography on neutral alumina (petroleum ether/EtOAc 20:1) to obtain the pure product **7aa** in 67% yield.

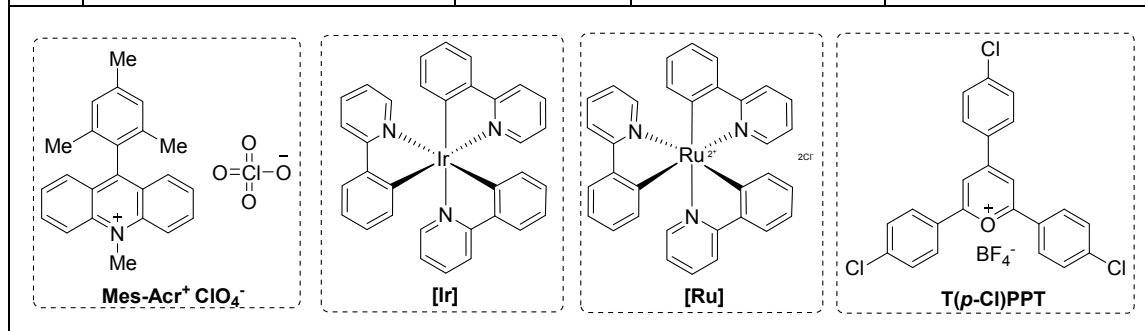
3.1 Representative procedure for the synthesis of dihydrobenzothiazoles in 5.0 mmol scale

To a solution of 2,2'-diaminodiphenyldisulfide (**1a**, 1.24 g, 5.0 mmol) in 20 mL of dichloromethane was added 1-cyclopropylethan-1-one (**6a**, 1.26 g, 15.0 mmol) under nitrogen atmosphere, the mixture was stirred for 8 h at room temperature. Subsequently, T(*p*-Cl)PPT (125 mg, 5 mol%) was added to the reaction system and the mixture was stirred under the blue LEDs (450–455 nm) irradiation at room temperature for 12 h. The residue was then purified by column chromatography on neutral alumina (petroleum ether/EtOAc 20:1) to obtain the pure product **7aa** (516 mg, 54% yield).

4. Optimization conditions for the reaction of 2,2'-diaminodiphenyl disulfide and ketone



Entry	Light source	Solvent	Photosensitizer	Yield ^b (%)
1	blue LED (450–455 nm)	DCM	Mes-Acr ⁺ ClO ₄ ⁻	N.R
2	blue LED (450–455 nm)	DCM	Eosin Y	N.R
3	blue LED (450–455 nm)	DCM	[Ir]	N.R
4	blue LED (450–455 nm)	DCM	T(<i>p</i>-Cl)PPT	67
5	blue LED (450–455 nm)	DCM	[Ru]	ND ^c
6	blue LED (450–455 nm)	DCM	T(<i>p</i> -Cl)PPT	65 ^d
7	blue LED (450–455 nm)	DCM	T(<i>p</i> -Cl)PPT	64 ^e
8	blue LED (450–455 nm)	DCM	T(<i>p</i> -Cl)PPT	52
9	purple LED (380–385 nm)	DCM	T(<i>p</i> -Cl)PPT	ND
10	green LED (480–570 nm)	DCM	T(<i>p</i> -Cl)PPT	ND
11	yellow LED (570–610 nm)	DCM	T(<i>p</i> -Cl)PPT	ND
12	—	DCM	T(<i>p</i> -Cl)PPT	ND
13	blue LED (450–455 nm)	THF	T(<i>p</i> -Cl)PPT	32
14	blue LED (450–455 nm)	DMF	T(<i>p</i> -Cl)PPT	23
15	blue LED (450–455 nm)	CH ₃ CN	T(<i>p</i> -Cl)PPT	27
16	blue LED (450–455 nm)	EtOH	T(<i>p</i> -Cl)PPT	13
17	blue LED (450–455 nm)	DMSO	T(<i>p</i> -Cl)PPT	21



^a Reaction conditions: **1a** (0.1 mmol), **6** (0.3 mmol), T(*p*-Cl)PPT (5 mol%), light source, solvent (2.0 mL), room temperature, N₂ atmosphere, 6 h. ^b Isolated yield. ^c ND = No desired product was detected. ^d The mixture was stirred for 24 h. ^e 10 mol% of T(*p*-Cl)PPT was used.

5. The effect of concentration on the yield of 3a (Figure S1)

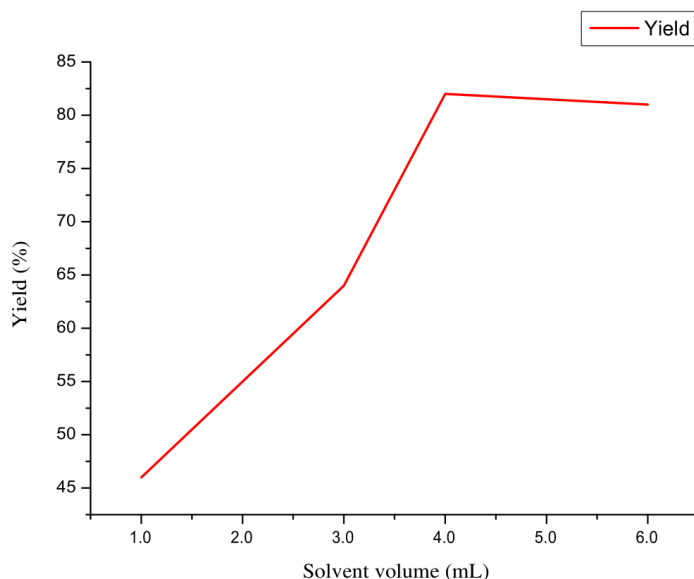
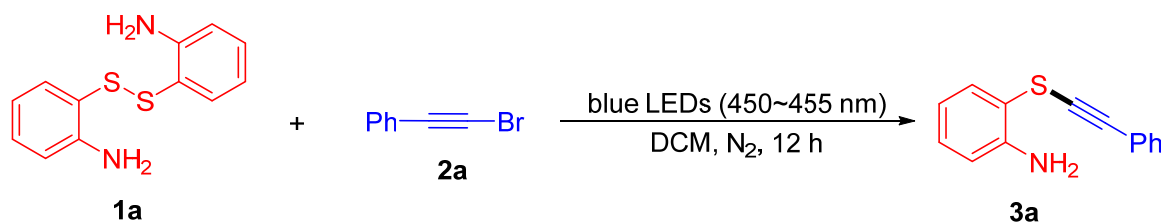


Figure S1. Analysis diagram of the effect of concentration on the product yield^{a,b}

[^a Reaction conditions: **1a** (0.10 mmol), **2a** (0.10 mmol), blue LED (450–455 nm), CH₂Cl₂ (X mL), room temperature, N₂ atmosphere, 12 h. ^b Isolated yield.]

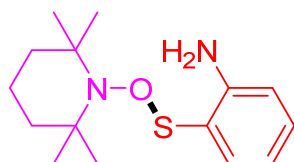
6. Free-radical trapping experiment using TEMPO

To elaborate the reaction clearly and ascertain the coupling reaction initiated by disulfide **1a** or bromoalkyne **2a**, a control experiment was carried out. The coupling reaction was halted when a radical scavenger 2,2,6,6-tetramethyl-1-piperidinyloxy (TEMPO) was added to the reaction system, and this significant suppression implied that a radical process might be involved in the reaction. A free-radical trapping product with TEMPO, 2-(((2,2,6,6-tetramethylpiperidin-1-yl)oxy)thio)aniline was isolated. It believes

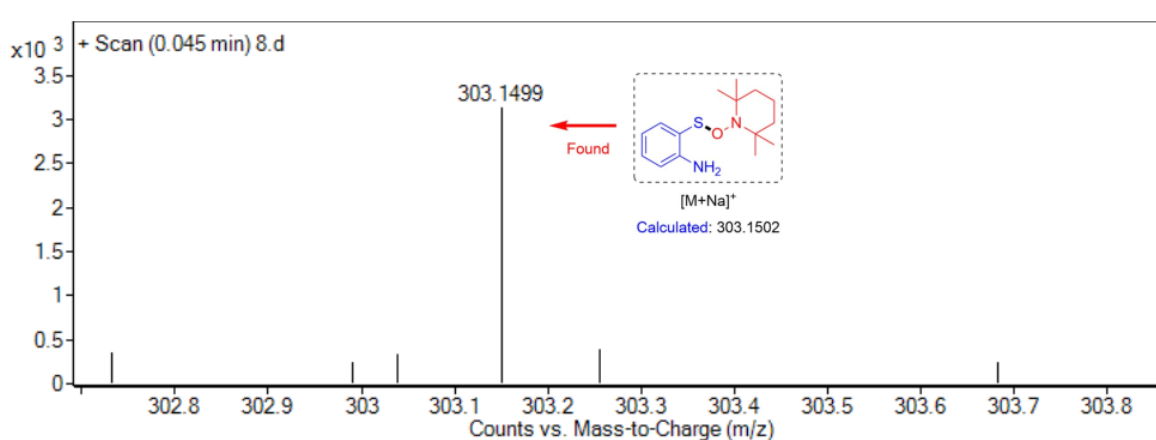
that the transformation was initiated by homolytic cleavage of **1a** under the present reaction conditions.

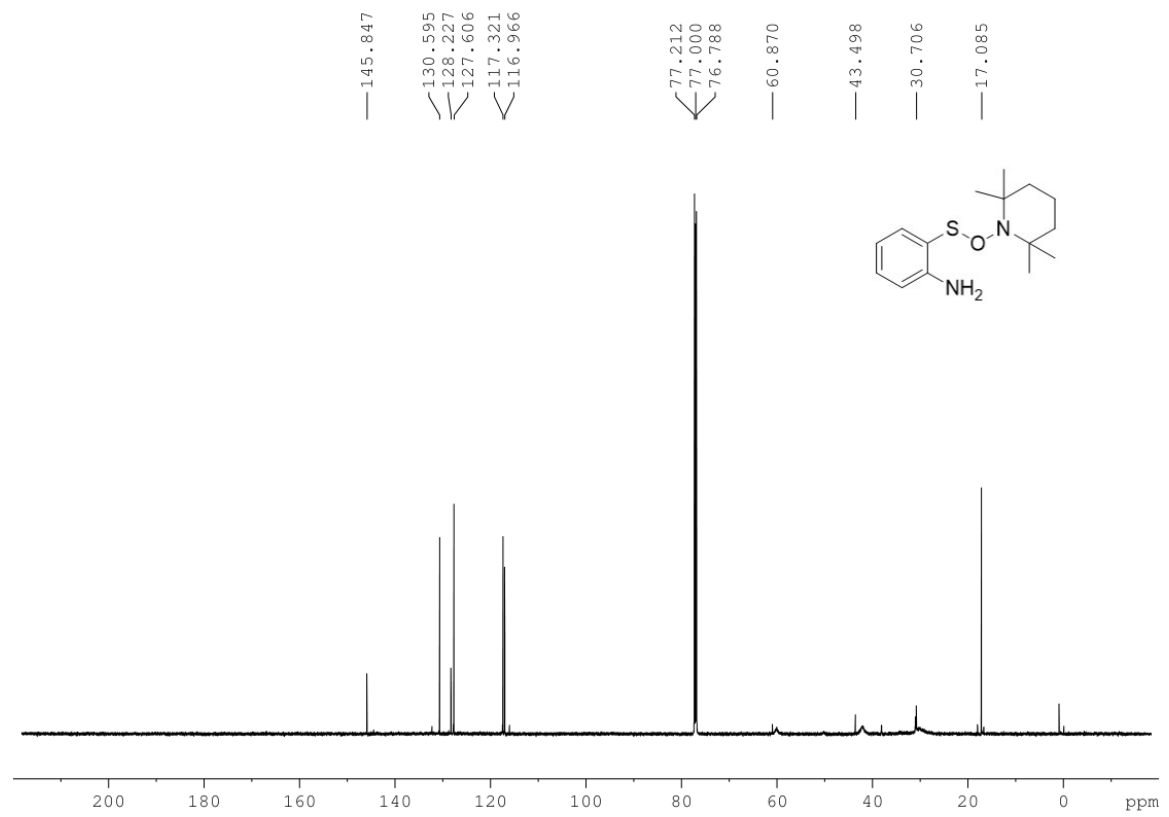
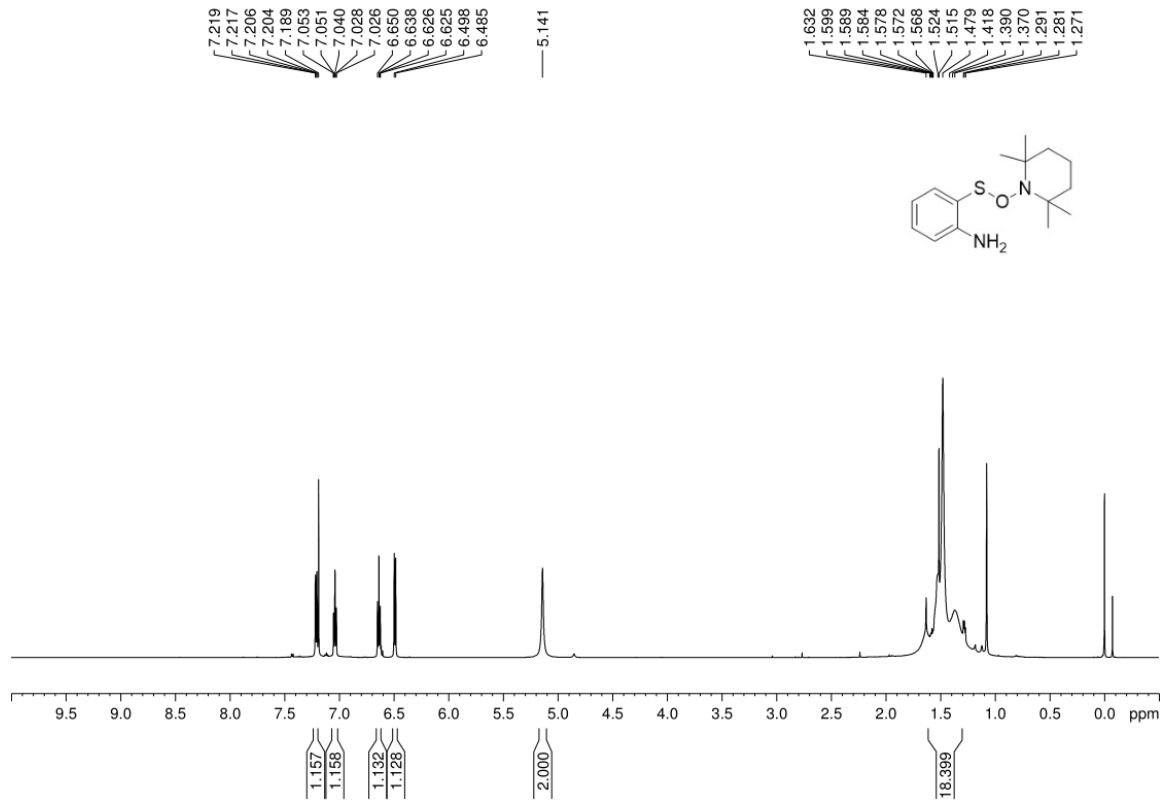


2-(((2,2,6,6-Tetramethylpiperidin-1-yl)oxy)thio)aniline (**4**)



White solid. Mp: 152–154 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.22 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.05 (td, *J* = 7.8, 1.2 Hz, 1H), 6.65–6.62 (m, 1H), 6.50 (d, *J* = 7.8 Hz, 1H), 5.14 (s, 2H), 1.63–1.27 (m, 18H). ¹³C NMR (150 MHz, CDCl₃): δ 145.8, 130.6, 128.2, 127.6, 117.3, 117.0, 60.9, 43.5, 30.7, 17.1. HRMS (ESI) calcd for C₁₅H₂₄N₂OS (M+Na)⁺: 303.1502; Found: 303.1499.





7. Cyclic voltammetry (CV) measurements

(1) Preparation of the samples

(a): Blank control experiment

(b): To a solution of 1,2-diphenyldisulfane (**1a**, 0.30 mmol, 74.4 mg) in 10 mL of dichloromethane under nitrogen atmosphere, and then the mixture was stirred for 4 h at room temperature.

(c): To a solution of 1,2-diphenyldisulfane (**1a**, 0.30 mmol, 74.4 mg) in 10 mL of dichloromethane was added 1-cyclopropylethan-1-one (**6a**, 0.90 mmol, 75.7 mg) under nitrogen atmosphere, and then the mixture was stirred for 4 h at room temperature.

(d): To a solution of 1,2-diphenyldisulfane (**1a**, 0.30 mmol, 74.4 mg) in 10 mL of dichloromethane was added 3-pentanone (**6c**, 0.9 mmol, 77.5 mg) under nitrogen atmosphere, and then the mixture was stirred for 4 h at room temperature.

(2) Cyclic voltammetry measurements

Cyclic voltammetry (CV) measurements were recorded by using Ag/AgCl as the reference electrode, tetrabutylammonium tetrafluoroborate (0.5 mmol, 165 mg) as the electrolyte. The results are summarized in Figure S2.

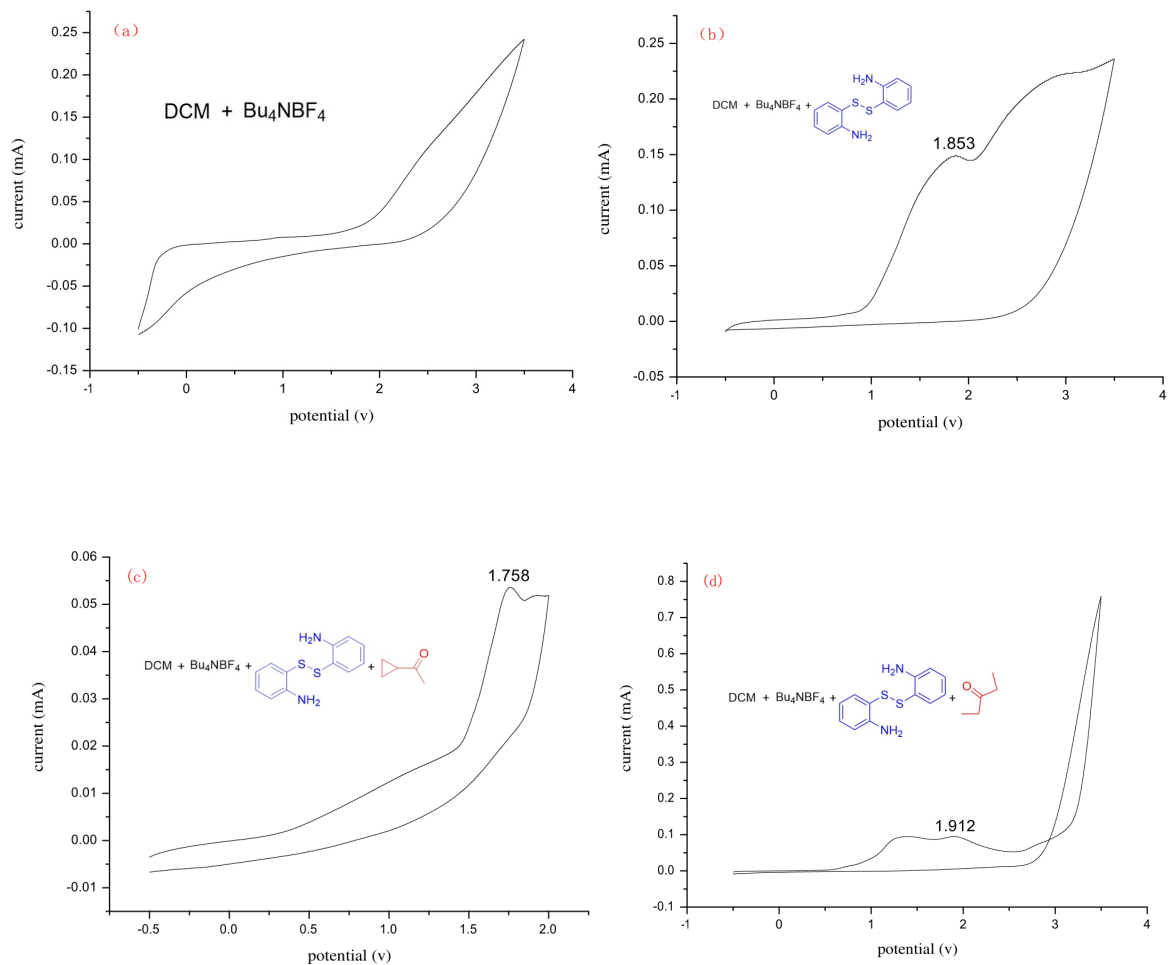
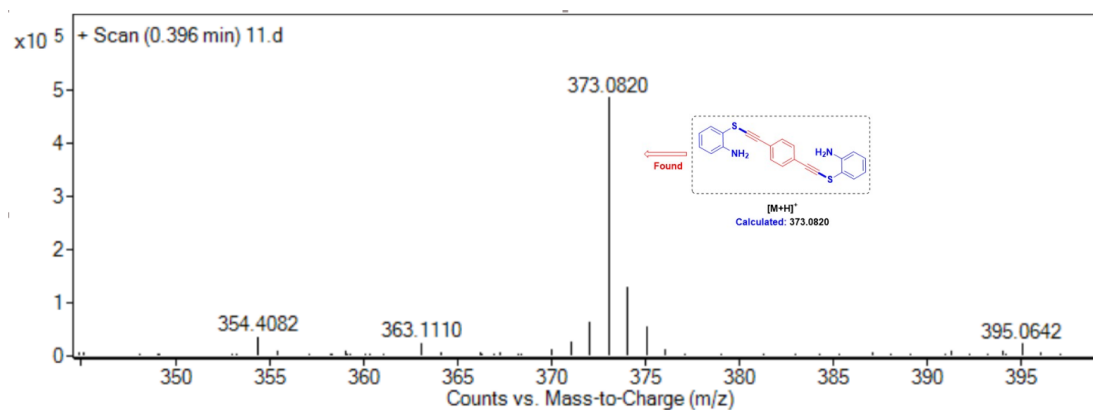


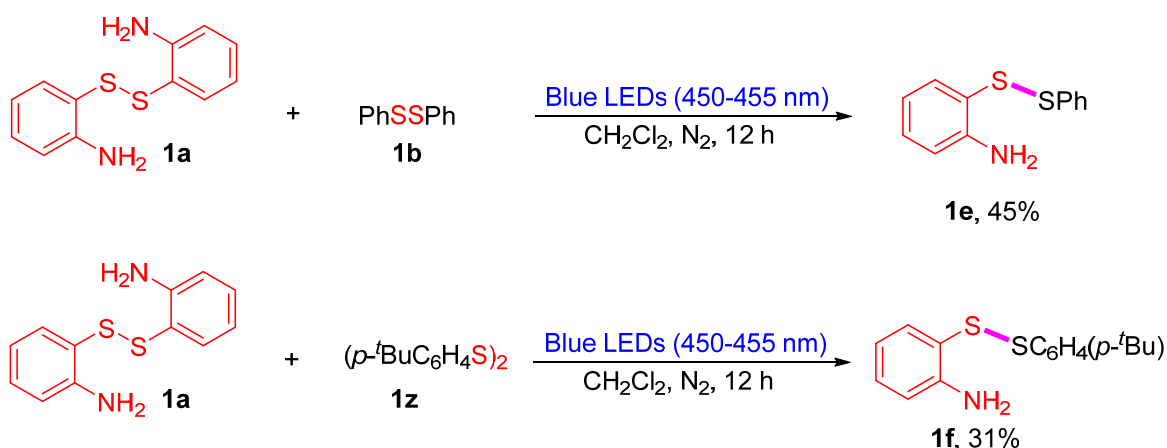
Figure S2. Cyclic voltammetry (CV) measurements

8. HRMS spectrum of 3aw



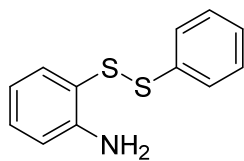
9. The cross-radical-coupling of homolytic cleavage of different disulfides

To elaborate the reaction clearly and ascertain that the coupling reaction is initiated by disulfide **1a** or bromoalkyne **2a**, the cross-radical-couplings of homolytic cleavage of **1a** with **1b/1z** were carried out. To our delight, the corresponding cross-radical-coupling products (**1e** and **1f**) were obtained in 45% and 31% yields, respectively, implying that a radical process might be involved in the reaction and the coupling reaction is initiated by disulfide. In addition, the obtained products (**1e** and **1f**) could be used as substrates for the control experiments.

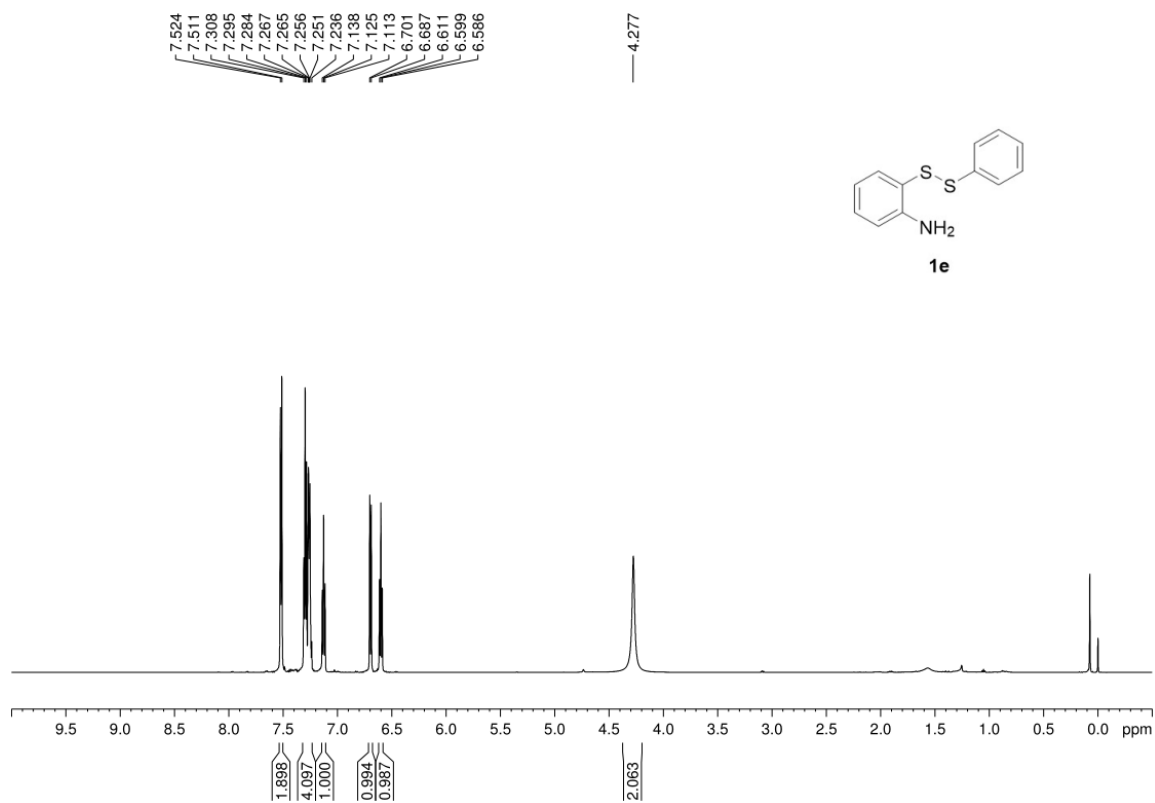


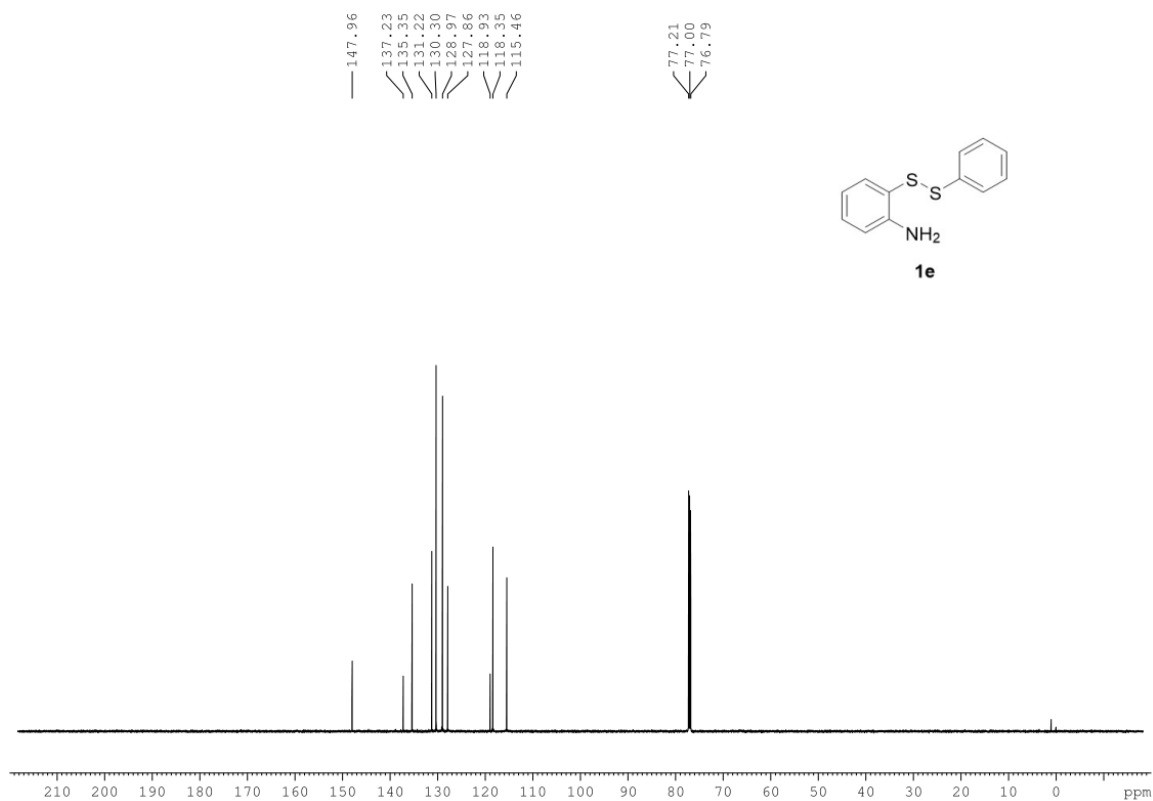
To a solution of 1,2-diphenyldisulfide (**1b**, 0.20 mmol) or 1,2-bis(4-(*tert*-butyl)phenyl)disulfide (**1z**, 0.20 mmol) in 2 mL of dichloromethane was added 2,2'-diaminodiphenyl disulfide (**1a**, 0.2 mmol) under nitrogen atmosphere. The reaction mixture was stirred at room temperature under blue LEDs (450–455 nm) irradiation for 12 h. The residue was then purified by column chromatography on silica gel (petroleum ether/EtOAc = 10:1) to give the pure product.

2-(Phenyldisulfanyl)aniline (1e)

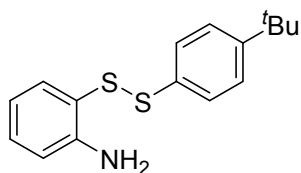


Pale yellow solid. Mp: 72–74 °C. ^1H NMR (600 MHz, CDCl_3): δ 7.52 (d, $J = 7.8$ Hz, 2H), 7.31–7.24 (m, 4H), 7.14 (t, $J = 7.8$ Hz, 1H), 6.70 (d, $J = 8.4$ Hz, 1H), 6.61 (t, $J = 7.2$ Hz, 1H), 4.23 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ 148.0, 137.2, 135.3, 131.2, 130.3, 129.0, 127.9, 118.9, 118.4, 115.5. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{12}\text{NS}_2(\text{M}+\text{H})^+$: 234.0406; Found: 234.0405.

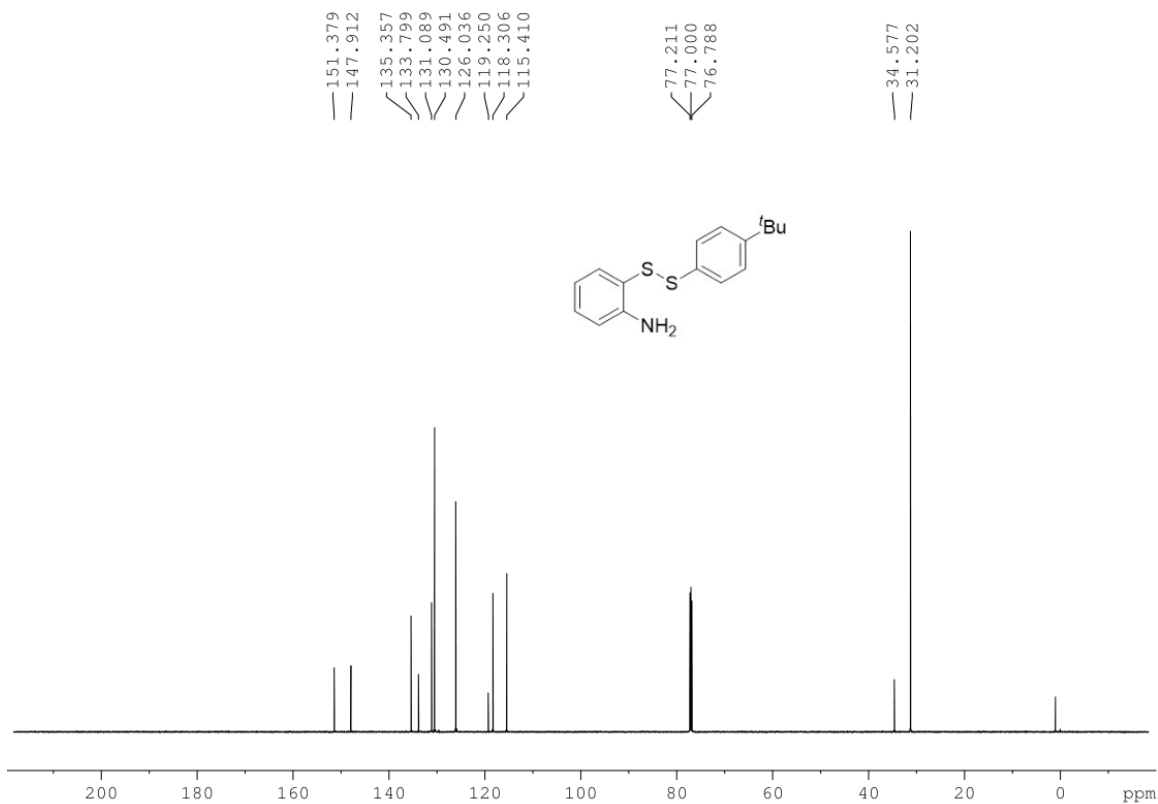
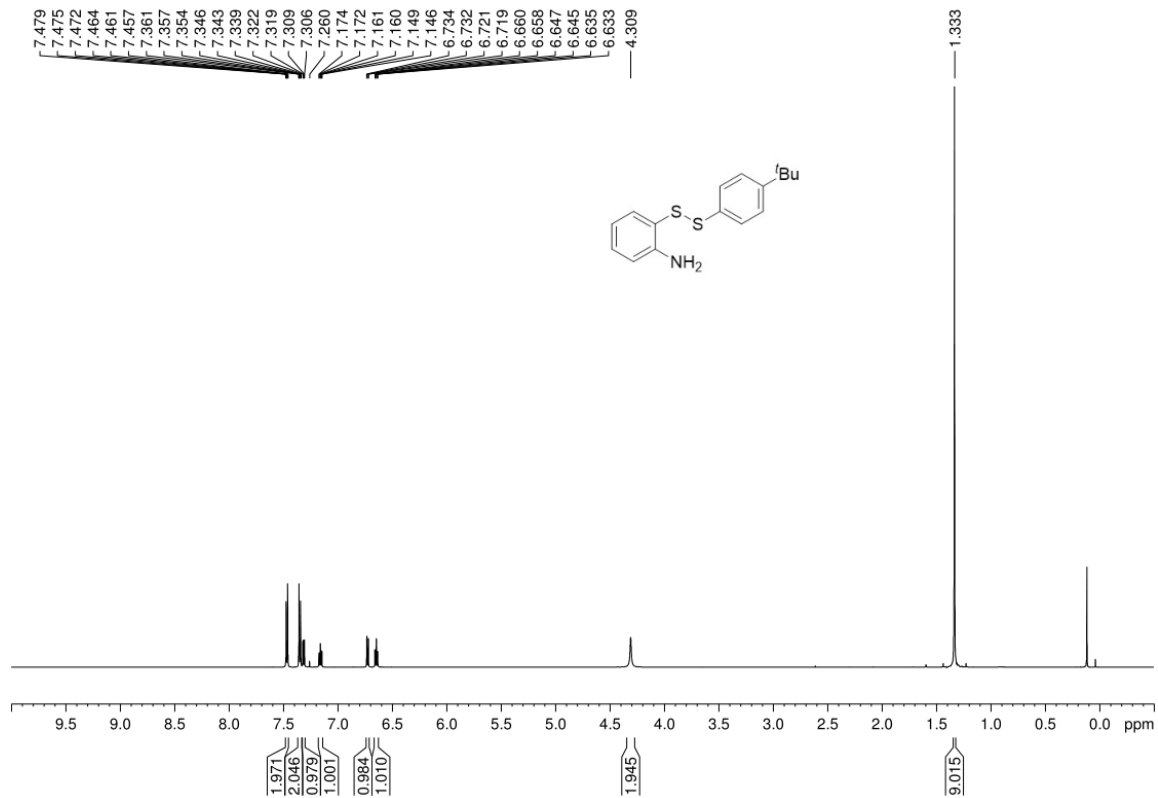




2-((4-(*tert*-Butyl)phenyl)disulfanyl)aniline (**1f**)

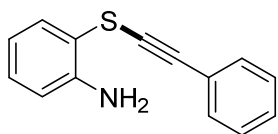


Pale yellow solid. Mp: 87–89 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.48–7.46 (m, 2H), 7.36–7.34 (m, 2H), 7.32 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.17 (td, *J* = 7.5, 1.2 Hz, 1H), 6.73 (dd, *J* = 7.8, 1.2 Hz, 1H), 6.66 (td, *J* = 7.5, 1.2 Hz, 1H), 4.31 (s, 2H), 1.33 (s, 9H). ¹³C NMR (150 MHz, CDCl₃): δ 151.4, 147.9, 135.4, 133.8, 131.1, 130.5, 126.0, 119.3, 118.3, 115.4, 34.6, 31.2. HRMS (ESI) calcd for C₁₆H₂₀NS₂(M+H)⁺ : 290.1032; Found: 290.1034.



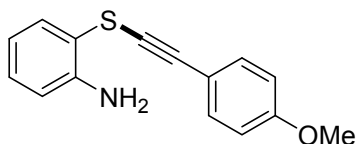
10. Characterization data for the products

2-((Phenylethynyl)thio)aniline (3aa)²



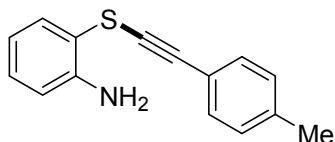
Yellow oil (17 mg, 83% yield). ¹H NMR (600 MHz, CDCl₃): δ 7.53 (d, *J* = 7.8 Hz, 1H), 7.44–7.42 (m, 2H), 7.3–7.29 (m, 3H), 7.61 (t, *J* = 7.8 Hz, 1H), 6.79–6.75 (m, 2H), 4.28 (s, 2H). ¹³C NMR (150 MHz, CDCl₃): δ 146.5, 132.9, 131.6, 130.1, 128.4, 128.3, 123.0, 119.1, 115.9, 114.2, 93.1, 76.7.

2-(((4-Methoxyphenyl)ethynyl)thio)aniline (3ab)²



Yellow solid (20 mg, 78% yield). Mp: 97–99 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.52 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.40–7.38 (m, 2H), 7.17 (td, *J* = 7.5, 1.2 Hz, 1H), 6.83–6.81 (m, 2H), 6.78–6.74 (m, 2H), 4.27 (s, 2H), 3.80 (s, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 159.8, 146.4, 133.6, 132.7, 129.9, 119.0, 115.9, 115.0, 114.6, 113.9, 93.5, 74.6, 55.3.

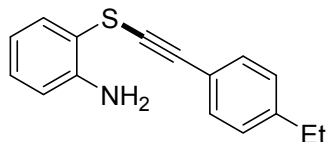
2-((*p*-Tolyethynyl)thio)aniline (3ac)²



Yellow solid (20 mg, 82% yield). Mp: 99–101 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.54 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.35 (d, *J* = 8.4 Hz, 2H), 7.19 (td, *J* = 7.5, 1.2 Hz, 1H), 7.12 (d, *J* = 7.8 Hz, 2H), 6.79–6.75 (m, 2H), 4.27 (s, 2H), 2.35 (s, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 146.4, 138.6, 132.7, 131.7, 130.0, 129.0, 128.9, 119.8,

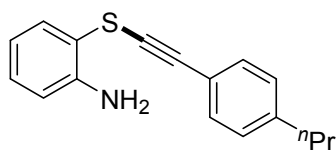
119.0, 115.8, 114.3, 93.6, 75.6, 21.5.

2-(((4-Ethylphenyl)ethynyl)thio)aniline (3ad)



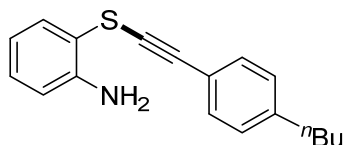
Yellow solid (19 mg, 74% yield). Mp: 103–105 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.52 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.36–7.35 (m, 2H), 7.17 (td, *J* = 7.5, 1.2 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 2H), 6.78–6.74 (m, 2H), 4.25 (s, 2H), 2.65 (q, *J* = 7.8 Hz, 2H), 1.23 (t, *J* = 7.8 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 146.4, 145.0, 132.7, 131.8, 130.0, 127.8, 120.1, 119.1, 115.9, 114.5, 99.7, 75.6, 28.8, 15.3. HRMS (ESI) calcd for C₁₆H₁₆NS (M+H)⁺: 254.0998; Found: 254.0999.

2-(((4-(*n*-Propyl)phenyl)ethynyl)thio)aniline (3ae)



Yellow solid (20 mg, 76% yield). Mp: 103–105 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.53 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.36 (d, *J* = 8.4 Hz, 2H), 7.17–7.14 (m, 1H), 7.11 (d, *J* = 8.4 Hz, 2H), 6.78–6.74 (m, 2H), 4.25 (s, 2H), 2.58 (t, *J* = 7.8 Hz, 2H), 1.65–1.59 (m, 2H), 0.94 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 146.4, 143.5, 132.7, 131.7, 130.0, 128.4, 120.1, 119.1, 115.9, 114.5, 93.7, 75.6, 37.9, 24.3, 13.7. HRMS (ESI) calcd for C₁₇H₁₈NS (M+H)⁺: 268.1155; Found: 268.1154.

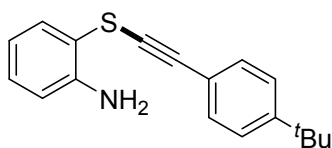
2-(((4-(*n*-Butyl)phenyl)ethynyl)thio)aniline (3af)



Yellow oil (21 mg, 75% yield). ¹H NMR (600 MHz, CDCl₃): δ 7.54 (dd, *J* = 7.8,

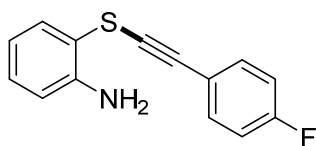
1.2 Hz, 1H), 7.37 (d, $J = 7.8$ Hz, 2H), 7.18 (td, $J = 7.5$, 1.2 Hz, 1H), 7.12 (d, $J = 8.4$ Hz, 2H), 6.78–6.74 (m, 2H), 4.25 (s, 2H), 2.61 (t, $J = 7.8$ Hz, 2H), 1.61–1.56 (m, 2H), 1.37–1.33 (m, 2H), 0.94 (t, $J = 7.8$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 146.4, 143.7, 132.7, 131.7, 130.0, 128.4, 120.0, 119.0, 115.9, 114.4, 93.7, 75.5, 35.5, 33.3, 22.2, 13.9. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{20}\text{NS}$ ($\text{M}+\text{H}$) $^+$: 282.1311; Found: 282.1312.

2-(((4-*tert*-Butyl)phenyl)ethynyl)thio)aniline (3ag)²



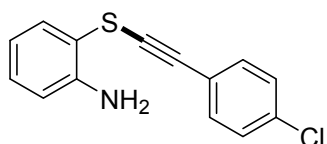
Yellow oil (20 mg, 72% yield). ^1H NMR (600 MHz, CDCl_3): δ 7.53 (dd, $J = 7.8$, 1.2 Hz, 1H), 7.39–7.37 (m, 2H), 7.33–7.31 (m, 2H), 7.17 (td, $J = 7.8$, 1.8 Hz, 1H), 6.78–6.74 (m, 2H), 4.26 (s, 2H), 1.30 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3): δ 151.8, 146.4, 132.6, 131.5, 130.0, 125.3, 119.9, 119.0, 115.9, 114.4, 93.7, 75.5, 34.8, 31.1, 31.1, 31.1.

2-(((4-Fluorophenyl)ethynyl)thio)aniline (3ah)



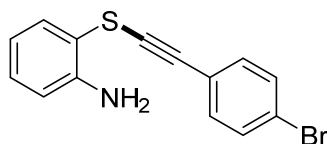
Yellow liquid (15 mg, 60% yield). ^1H NMR (600 MHz, CDCl_3): δ 7.52 (d, $J = 7.8$ Hz, 1H), 7.42–7.40 (m, 2H), 7.19 (t, $J = 7.2$ Hz, 2H), 7.00 (t, $J = 8.4$ Hz, 2H), 6.79–6.75 (m, 2H), 4.28 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ 163.4 ($J = 249$ Hz), 146.5, 133.7 ($J = 8.1$ Hz), 133.0, 130.2, 119.1, 119.0 ($J = 3.3$ Hz), 115.9, 115.6 ($J = 22.4$ Hz), 113.9, 92.1, 76.4. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{11}\text{FNS}$ ($\text{M}+\text{H}$) $^+$: 244.0591; Found: 244.0591.

2-(((4-Chlorophenyl)ethynyl)thio)aniline (3ai)²



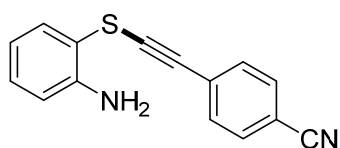
Yellow solid (18 mg, 70% yield). Mp: 95–97 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.52 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.35–7.34 (m, 2H), 7.27–7.26 (m, 2H), 7.20 (td, *J* = 7.8, 1.8 Hz, 1H), 6.79–6.76 (m, 2H), 4.13 (s, 2H). ¹³C NMR (150 MHz, CDCl₃): δ 146.6, 134.4, 133.1, 132.8, 130.4, 128.6, 121.5, 119.1, 115.9, 113.7, 92.4, 78.1.

2-(((4-Bromophenyl)ethynyl)thio)aniline (**3aj**)²



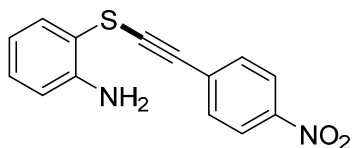
Yellow solid (20 mg, 64% yield). Mp: 97–99 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.51 (d, *J* = 7.8 Hz, 1H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.27–7.26 (m, 2H), 7.19 (t, *J* = 7.2 Hz, 1H), 6.78 (t, *J* = 8.4 Hz, 2H), 4.22 (s, 2H). ¹³C NMR (150 MHz, CDCl₃): δ 146.6, 133.2, 133.0, 131.5, 130.4, 122.6, 121.9, 119.0, 115.9, 113.6, 92.1, 78.3.

4-(((2-Aminophenyl)thio)ethynyl)benzonitrile (**3ak**)²



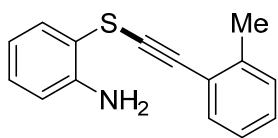
Yellow solid (16 mg, 62% yield). Mp: 141–143 °C. ¹H NMR (600 MHz, CDCl₃): δ 7.56–7.55 (m, 2H), 7.50 (dd, *J* = 8.4, 1.2 Hz, 1H), 7.45–7.44 (m, 2H), 7.19 (td, *J* = 7.8, 1.8 Hz, 1H), 6.79–6.76 (m, 2H), 4.30 (s, 2H). ¹³C NMR (150 MHz, CDCl₃): δ 146.8, 133.5, 131.9, 131.5, 130.8, 127.8, 119.1, 118.4, 115.9, 112.7, 111.1, 91.5, 83.0.

2-(((4-Nitrophenyl)ethynyl)thio)aniline (**3al**)



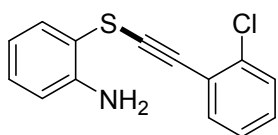
Yellow solid (11 mg, 40% yield). Mp: 109–111 °C. ^1H NMR (600 MHz, CDCl_3): δ 8.15 (d, $J = 8.4$ Hz, 2H), 7.50–7.49 (m, 3H), 7.45 (t, $J = 7.2$ Hz, 1H), 6.79–6.77 (m, 2H), 4.31 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ 146.9, 146.6, 133.6, 131.6, 130.9, 129.8, 123.5, 119.1, 116.0, 112.5, 91.4, 84.4. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{11}\text{N}_2\text{O}_2\text{S}$ ($\text{M}+\text{H}$) $^+$: 271.0536; Found: 271.0536.

2-((*o*-tolylethynyl)thio)aniline (3am)



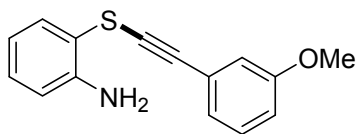
Yellow solid (15 mg, 63% yield). Mp: 104–106 °C. ^1H NMR (600 MHz, CDCl_3): δ 7.56–7.54 (m, 1H), 7.42 (d, $J = 7.2$ Hz, 1H), 7.23–7.17 (m, 3H), 7.14 (t, $J = 7.2$ Hz, 1H), 6.80–6.76 (m, 2H), 4.28 (s, 2H), 2.42 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 146.3, 140.3, 132.7, 131.9, 130.0, 129.4, 128.3, 125.5, 122.8, 119.0, 115.8, 114.5, 92.5, 80.1, 20.7. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{14}\text{NS}$ ($\text{M}+\text{H}$) $^+$: 240.0842; Found: 240.0842.

2-(((2-Chlorophenyl)ethynyl)thio)aniline (3an)²



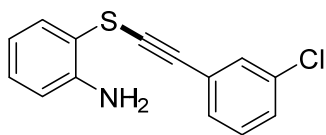
Yellow solid (14 mg, 54% yield). Mp: 97–99 °C. ^1H NMR (600 MHz, CDCl_3): δ 7.56 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.45 (dd, $J = 7.8, 1.8$ Hz, 1H), 7.38 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.24–7.16 (m, 3H), 6.79–6.75 (m, 2H), 4.29 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ 146.6, 135.8, 133.2, 132.9, 130.2, 129.2, 129.2, 126.4, 123.0, 119.1, 116.0, 113.8, 90.3, 82.5.

2-(((3-Methoxyphenyl)ethynyl)thio)aniline (3ao)



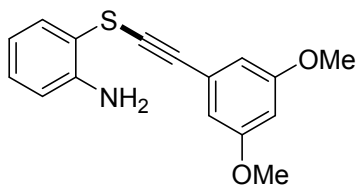
Yellow solid (19 mg, 75% yield). Mp: 107–109 °C. ^1H NMR (600 MHz, CDCl_3): δ 7.52 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.21–7.16 (m, 2H), 7.03–7.01 (m, 1H), 6.95–.94 (m, 1H), 6.87–6.85 (m, 1H), 6.78–6.75 (m, 2H), 4.28 (s, 2H), 3.78 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 159.2, 146.5, 133.0, 130.2, 129.3, 124.2, 123.9, 119.1, 116.3, 115.9, 115.1, 114.0, 93.3, 76.5, 55.3. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{14}\text{NOS}$ ($\text{M}+\text{H}$) $^+$: 256.0791; Found: 256.0791.

2-(((3-Chlorophenyl)ethynyl)thio)aniline (3ap)



Yellow solid (16 mg, 80% yield). Mp: 98–100 °C. ^1H NMR (600 MHz, CDCl_3): δ 7.51–7.50 (m, 1H), 7.40–7.39 (m, 1H), 7.29 (t, $J = 7.8$ Hz, 2H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.20 (td, $J = 7.8, 1.8$ Hz, 1H), 6.78 (t, $J = 7.8$, 2H), 4.06 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ 146.7, 134.1, 133.2, 131.3, 130.4, 129.6, 129.5, 128.5, 124.7, 119.1, 115.9, 113.5, 91.7, 78.7. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{11}\text{ClNS}$ ($\text{M}+\text{H}$) $^+$: 260.0295; Found: 260.0298.

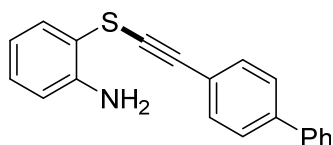
2-(((3,5-Dimethoxyphenyl)ethynyl)thio)aniline (3aq)



Yellow solid (21 mg, 72% yield). Mp: 129–131 °C. ^1H NMR (600 MHz, CDCl_3): δ

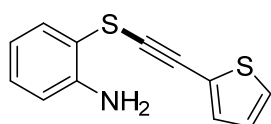
7.53 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.19 (td, $J = 7.8, 1.8$ Hz, 1H), 6.79–6.75 (m, 2H), 6.59 (d, $J = 1.8$ Hz, 2H), 6.44 (t, $J = 1.8$ Hz, 1H), 4.29 (s, 2H), 3.76 (s, 6H). ^{13}C NMR (150 MHz, CDCl_3): δ 160.4, 146.6, 133.0, 130.2, 124.1, 119.0, 115.9, 113.8, 109.3, 101.9, 93.3, 76.4, 55.4, 55.4. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{16}\text{NSO}_2$ ($\text{M}+\text{H}$) $^+$: 286.0896; Found: 286.0896.

2-((1,1'-Biphenyl)-4-ylethynyl)thio)aniline (3ar)



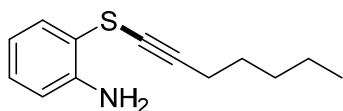
Yellow solid (17 mg, 57% yield). Mp: 142–144 °C. ^1H NMR (600 MHz, CDCl_3): δ 7.59–7.57 (m, 2H), 7.54–7.53 (m, 3H), 7.50–7.49 (m, 2H), 7.45–7.43 (m, 2H), 7.37–7.34 (m, 1H), 7.19 (td, $J = 7.8, 1.8$ Hz, 1H), 6.80–6.76 (m, 2H), 4.29 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ 146.5, 141.1, 140.2, 132.9, 132.1, 130.2, 128.8, 127.7, 127.0, 126.9, 121.9, 119.1, 115.9, 114.2, 93.3, 77.3. HRMS (ESI) calcd for $\text{C}_{20}\text{H}_{16}\text{NS}$ ($\text{M}+\text{H}$) $^+$: 302.0998; Found: 302.0998.

2-((Thiophen-2-ylethynyl)thio)aniline (3as)



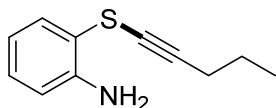
Yellowish brown solid (13 mg, 54% yield). Mp: 53–55 °C. ^1H NMR (600 MHz, CDCl_3): δ 7.41 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.17–7.14 (m, 2H), 7.08 (td, $J = 7.8, 1.8$ Hz, 1H), 6.87–6.85 (m, 1H), 6.68–6.63 (m, 2H), 4.17 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ 146.5, 133.4, 133.0, 130.3, 128.2, 126.9, 123.0, 119.0, 115.9, 113.8, 86.1, 81.1. HRMS (ESI) calcd for $\text{C}_{12}\text{H}_{10}\text{NS}_2$ ($\text{M}+\text{H}$) $^+$: 232.0249; Found: 232.0251.

2-(Hept-1-yn-1-ylthio)aniline (3at)



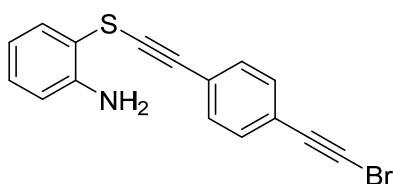
Yellow oil (14 mg, 64% yield). ^1H NMR (600 MHz, CDCl_3): δ 7.45 (dd, $J = 7.2$, 1.2 Hz, 1H), 7.13 (td, $J = 7.8$, 1.2 Hz, 1H), 6.75–6.70 (m, 2H), 4.18 (s, 2H), 2.32 (t, $J = 7.2$ Hz, 2H), 1.55–1.50 (m, 2H), 1.37–1.27 (m, 4H), 0.90 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 146.1, 132.3, 129.6, 118.9, 115.7, 115.1, 95.5, 65.5, 31.0, 28.3, 22.1, 20.1, 13.9. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{18}\text{NS}$ ($\text{M}+\text{H}$) $^+$: 220.1155; Found: 220.1155.

2-(Pent-1-yn-1-ylthio)aniline (3au)



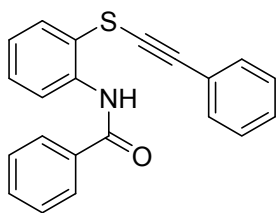
Yellow oil (10 mg, 53% yield). ^1H NMR (600 MHz, CDCl_3): δ 7.47–7.46 (m, 1H), 7.15–7.12 (m, 1H), 6.76–6.72 (m, 2H), 4.21(s, 2H), 2.32 (t, $J = 7.2$ Hz, 2H), 1.59–1.53 (m, 2H), 1.00 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 146.1, 132.3, 129.6, 118.9, 115.7, 115.1, 95.3, 65.7, 22.1, 22.1, 13.5. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{NS}$ ($\text{M}+\text{H}$) $^+$: 192.0842; Found: 192.0843.

2-(((4-(bromoethynyl)phenyl)ethynyl)thio)aniline (3av)



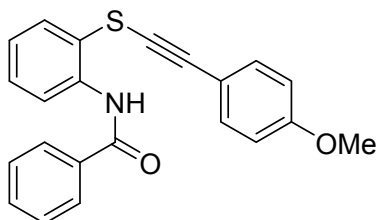
Yellow solid (27 mg, 82% yield). ^1H NMR (600 MHz, CDCl_3): δ 7.51 (dd, $J = 8.4$, 1.2 Hz, 1H), 7.37–7.33 (m, 4H), 6.19 (td, $J = 7.8$, 1.8 Hz, 1H), 6.78–6.75 (m, 2H), 4.27 (s, 2H). ^{13}C NMR (150 MHz, CDCl_3): δ 145.6, 132.1, 130.8, 130.3, 129.4, 122.3, 121.4, 118.1, 114.9, 112.6, 91.7, 78.6, 78.4, 50.9. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{11}\text{BrNS}$ ($\text{M}+\text{H}$) $^+$: 327.9790; Found: 327.9791.

***N*-2-((Phenylethynyl)thio)phenylbenzamide (3ca)**



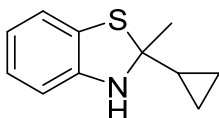
White solid (15 mg, 45% yield). Mp: 122–124 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.82 (s, 1H), 8.44 (d, *J* = 8.4 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.71 (d, *J* = 7.8 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.48–7.44 (m, 3H), 7.36–7.26 (m, 5H), 7.19 (t, *J* = 7.2 Hz, 1H). ¹³C NMR (150 MHz, CDCl₃): δ 165.3, 138.0, 134.6, 132.5, 132.1, 131.8, 130.3, 128.9, 128.8, 128.3, 127.2, 125.0, 122.5, 122.2, 120.8, 94.6, 75.6. HRMS (ESI) calcd for C₂₁H₁₆NSO (M+H)⁺: 330.0947; Found: 330.0942.

***N*-2-(((4-Methoxyphenyl)ethynyl)thio)phenylbenzamide (3da)**



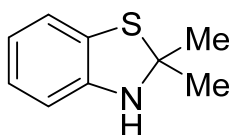
Brown solid (16 mg, 45% yield). Mp: 137–139 °C. ¹H NMR (600 MHz, CDCl₃): δ 8.84 (s, 1H), 8.40 (d, *J* = 7.8 Hz, 1H), 8.01 (d, *J* = 7.8 Hz, 2H), 7.68 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.57 (t, *J* = 7.2 Hz, 1H), 7.48–7.46 (m, 2H), 7.43 (td, *J* = 7.8, 1.2 Hz, 1H), 7.28 (d, *J* = 9.0 Hz, 2H), 7.16–7.13 (m, 1H), 6.78 (d, *J* = 8.4 Hz, 2H), 3.75 (s, 3H). ¹³C NMR (150 MHz, CDCl₃): δ 165.3, 160.2, 137.8, 134.6, 133.7, 132.3, 132.0, 130.1, 128.8, 127.2, 125.0, 122.5, 121.2, 114.1, 113.9, 94.7, 73.7, 55.2. HRMS (ESI) calcd for C₂₂H₁₈NSO₂ (M+H)⁺: 360.1053; Found: 360.1054.

2-Cyclopropyl-2-methyl-2,3-dihydrobenzo[*d*]thiazole (7aa)



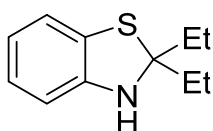
Pale yellow oil (26 mg, 67% yield). ^1H NMR (600 MHz, CDCl_3): δ 7.03 (d, $J = 7.8$ Hz, 1H), 6.91 (td, $J = 7.5$ Hz, 1H), 6.75–6.72 (m, 1H), 7.68 (d, $J = 7.8$ Hz, 1H), 3.88 (s, 1H), 1.68 (s, 3H), 1.37–1.32 (m, 1H), 0.56–0.50 (m, 4H). ^{13}C NMR (150 MHz, CDCl_3): δ 143.5, 125.3, 122.2, 119.1, 118.0, 108.3, 75.8, 27.0, 20.2, -1.7. HRMS (ESI) calcd for $\text{C}_{11}\text{H}_{14}\text{NS}$ ($\text{M}+\text{H}$) $^+$: 192.0842; Found: 192.0842.

2,2-Dimethyl-2,3-dihydrobenzo[d]thiazole (7ab)³



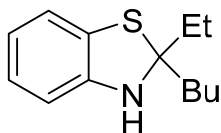
Pale yellow oil (21mg, 64% yield). ^1H NMR (600 MHz, CDCl_3): δ 7.07 (dd, $J = 7.2, 1.2$ Hz, 1H), 6.94 (td, $J = 7.5, 1.2$ Hz, 1H), 6.78 (td, $J = 7.5, 1.2$ Hz, 1H), 7.57 (dd, $J = 7.8, 1.2$ Hz, 1H), 3.98 (s, 1H), 1.73 (s, 6H). ^{13}C NMR (150 MHz, CDCl_3): δ 145.8, 128.5, 125.0, 122.1, 121.0, 111.4, 74.6, 31.6.

2,2-Diethyl-2,3-dihydrobenzo[d]thiazole (7ac)³



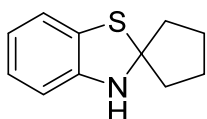
Pale yellow oil (24 mg, 63% yield). ^1H NMR (600 MHz, CDCl_3): δ 7.03 (dd, $J = 7.8, 1.2$ Hz, 1H), 6.89 (td, $J = 7.8, 1.2$ Hz, 1H), 6.71 (td, $J = 7.5, 1.2$ Hz, 1H), 6.60 (dd, $J = 7.8, 0.6$ Hz, 1H), 3.90 (s, 1H), 1.92 (q, $J = 7.2$ Hz, 4H), 1.04 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (150 MHz, CDCl_3): δ 146.6, 127.1, 124.8, 121.6, 120.0, 82.6, 34.5, 9.1.

2-Butyl-2-ethyl-2,3-dihydrobenzo[d]thiazole (7ad)



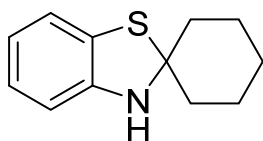
Pale yellow oil (23 mg, 52% yield). ^1H NMR (600 MHz, CDCl_3): δ 6.99 (d, $J = 7.8$ Hz, 1H), 6.87 (t, $J = 7.8$ Hz, 1H), 6.67 (t, $J = 7.8$ Hz, 1H), 6.55 (d, $J = 7.8$ Hz, 1H), 3.82 (s, 1H), 1.87–1.82 (m, 4H), 1.47–1.29 (m, 4H), 1.00 (t, $J = 7.8$ Hz, 3H), 0.91 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3): δ 146.5, 126.9, 124.7, 121.5, 119.8, 82.0, 41.4, 34.8, 26.9, 22.8, 13.9, 9.0. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{20}\text{NS}$ ($\text{M}+\text{H}$) $^+$: 222.1311; Found: 222.1312.

3H-Spiro[benzo[d]thiazole-2,1'-cyclopentane] (3ae)³



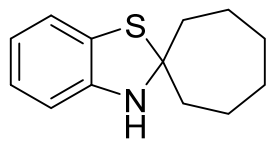
Pale yellow oil (20 mg, 51% yield). ^1H NMR (600 MHz, CDCl_3): δ 7.01 (d, $J = 7.2$ Hz, 1H), 6.93–6.90 (m, 1H), 6.77 (t, $J = 7.2$ Hz, 1H), 6.55 (d, $J = 7.8$ Hz, 1H), 3.81 (s, 1H), 2.22–2.17 (m, 2H), 2.05–2.01 (m, 2H), 1.81–1.78 (m, 4H). ^{13}C NMR (150 MHz, CDCl_3): δ 145.9, 128.1, 124.9, 121.7, 120.6, 110.8, 84.1, 42.5, 22.8.

3H-Spiro[benzo[d]thiazole-2,1'-cyclohexane] (7af)³



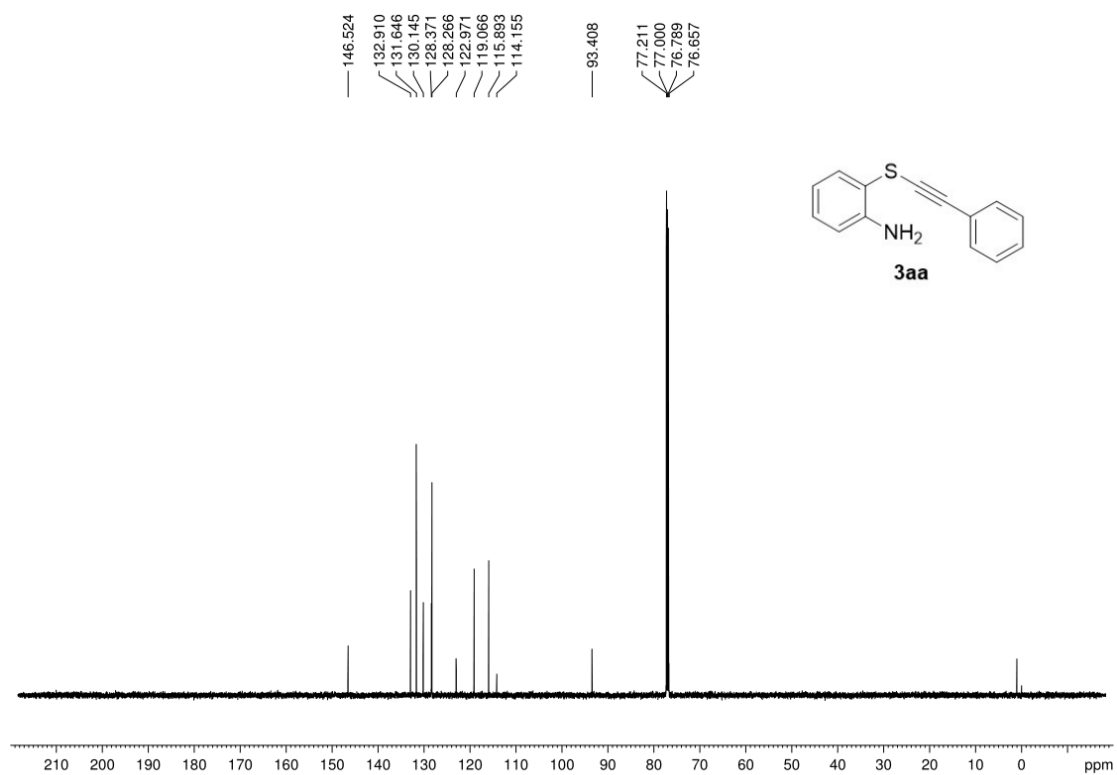
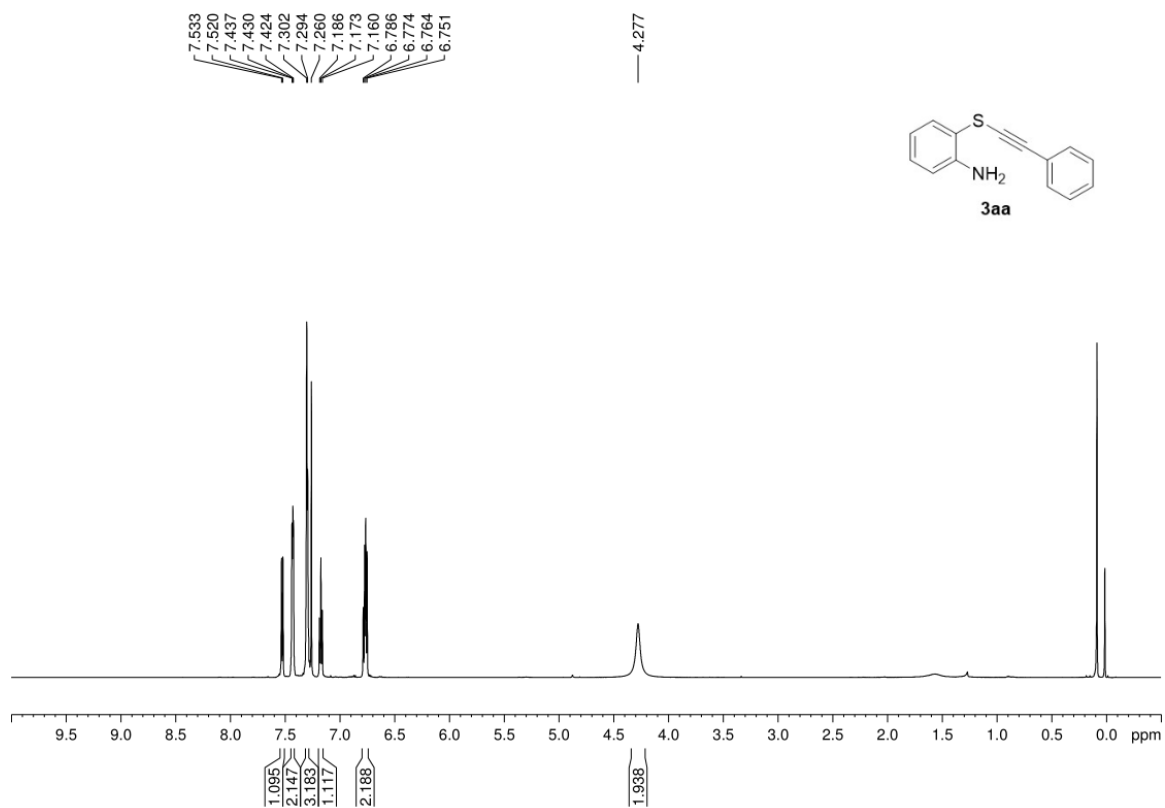
Pale yellow oil (19 mg, 46% yield). ^1H NMR (600 MHz, CDCl_3): δ 7.05 (d, $J = 7.2$ Hz, 1H), 6.91 (td, $J = 7.5, 1.2$ Hz, 1H), 6.74 (t, $J = 7.2$ Hz, 1H), 6.64 (d, $J = 7.8$ Hz, 1H), 3.85 (s, 1H), 2.22–2.20 (m, 2H), 1.77–1.70 (m, 4H), 1.62–1.55 (m, 3H), 1.32–1.26 (m, 1H). ^{13}C NMR (150 MHz, CDCl_3): δ 145.9, 127.1, 124.9, 121.9, 120.4, 110.8, 79.9, 40.9, 24.9, 24.0.

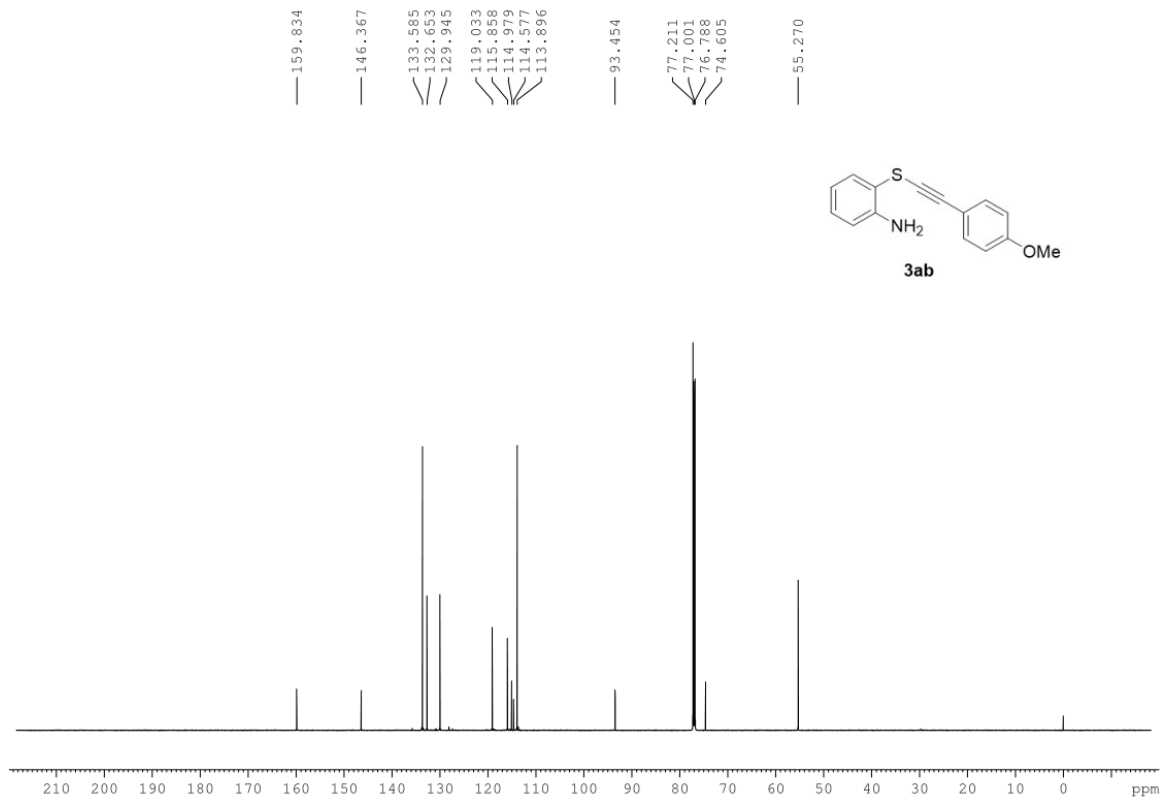
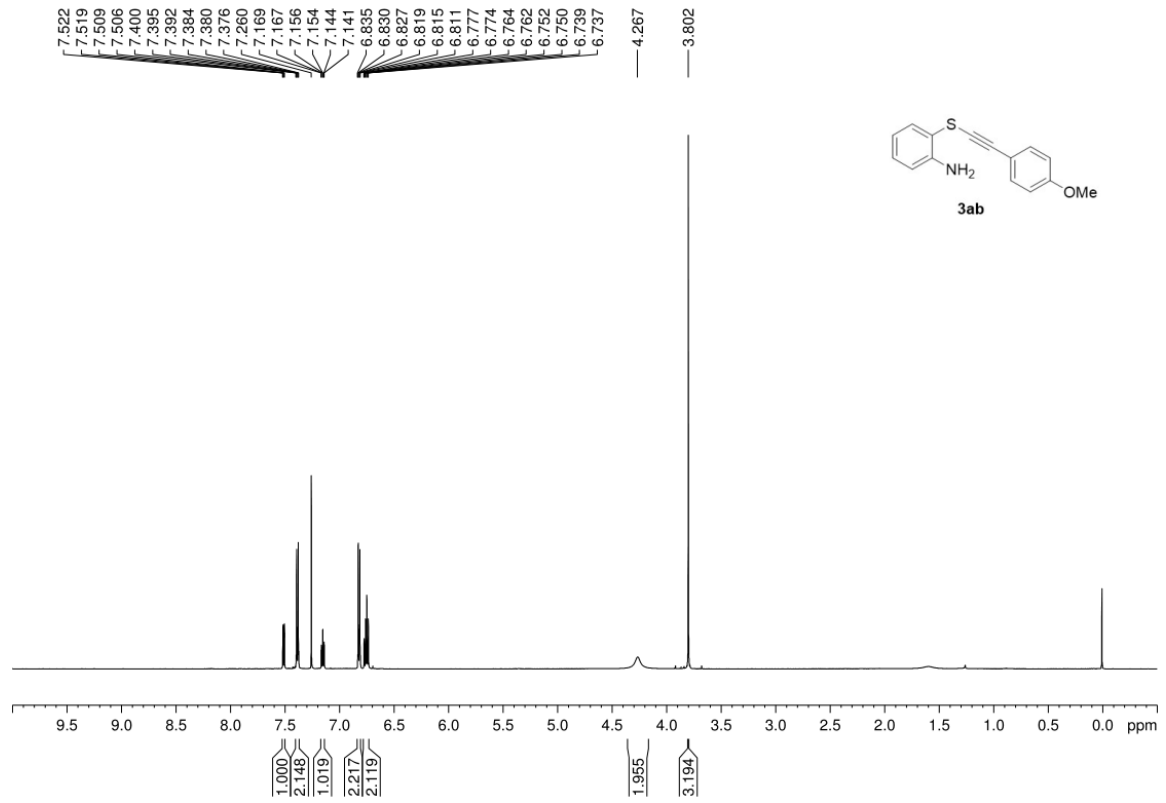
3*H*-Spiro[benzo[d]thiazole-2,1'-cycloheptane] (7ag)

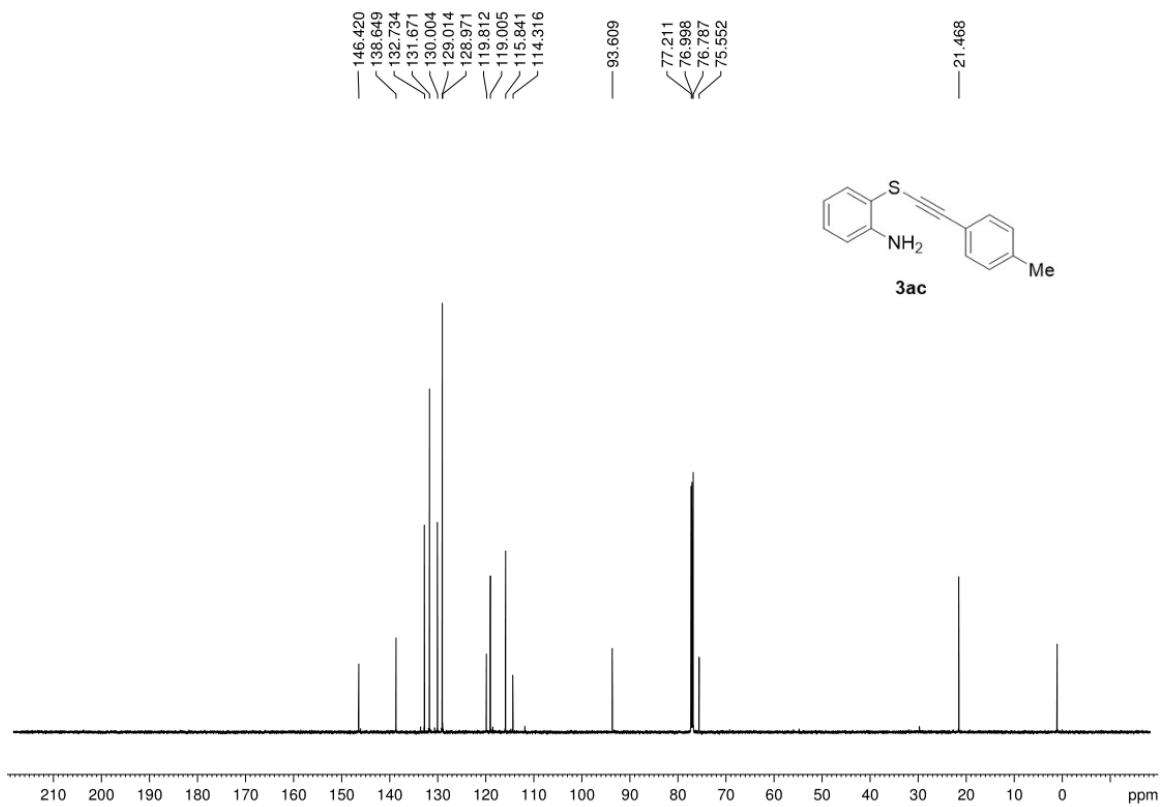
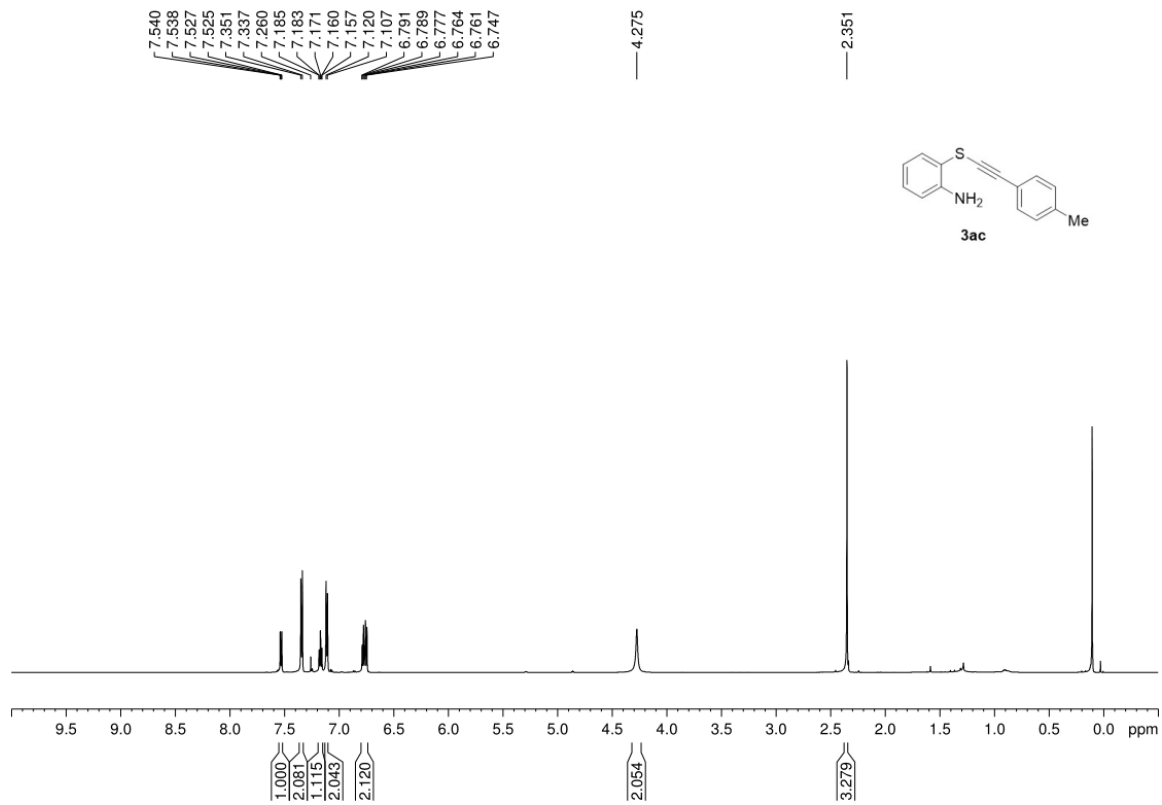


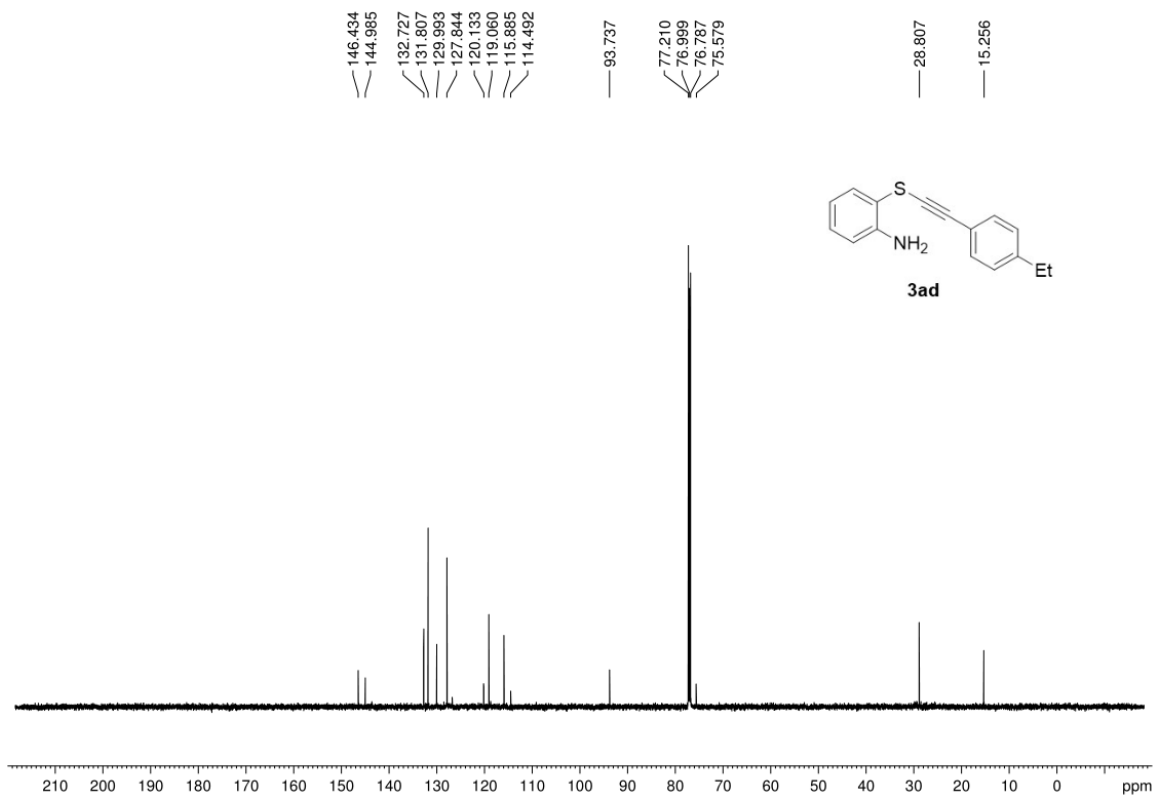
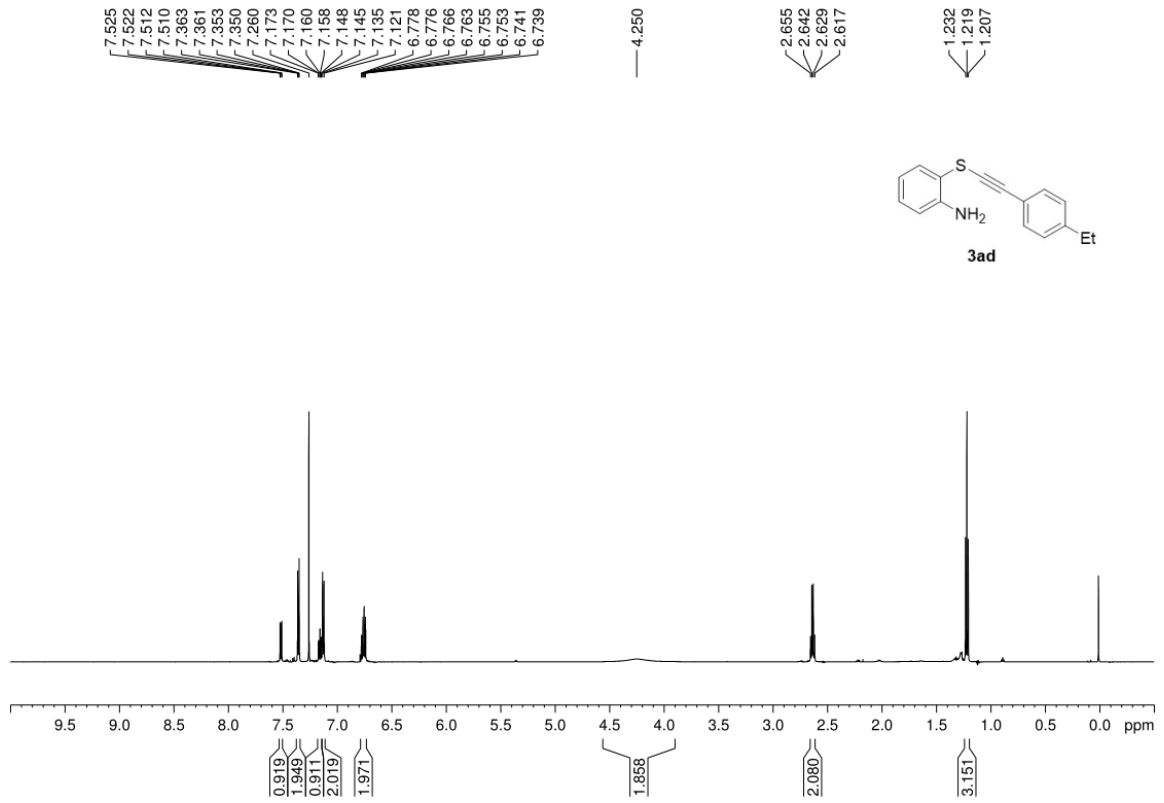
Pale yellow oil (20 mg, 46% yield). ^1H NMR (600 MHz, CDCl_3): δ 7.05 (d, $J = 7.2$ Hz, 1H), 6.91 (td, $J = 7.5, 1.2$ Hz, 1H), 6.75 (td, $J = 7.2, 0.6$ Hz, 1H), 6.65 (d, $J = 7.8$ Hz, 1H), 4.01 (s, 1H), 2.35–2.31 (m, 2H), 2.08–2.04 (m, 2H), 1.66–1.58 (m, 8H). ^{13}C NMR (150 MHz, CDCl_3): δ 145.9, 127.7, 124.9, 122.0, 120.7, 111.2, 83.2, 43.7, 28.1, 22.9. HRMS (ESI) calcd for $\text{C}_{13}\text{H}_{18}\text{NS}$ ($\text{M}+\text{H}$) $^+$: 220.1154; Found: 220.1152.

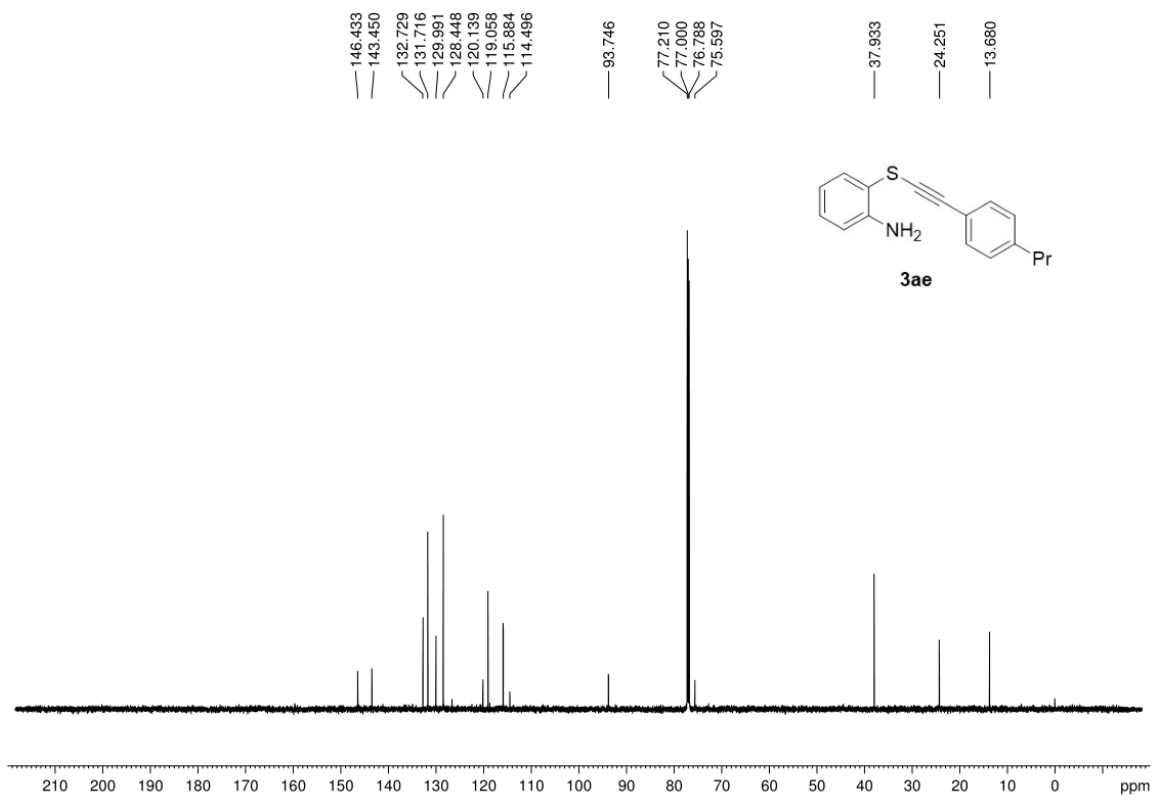
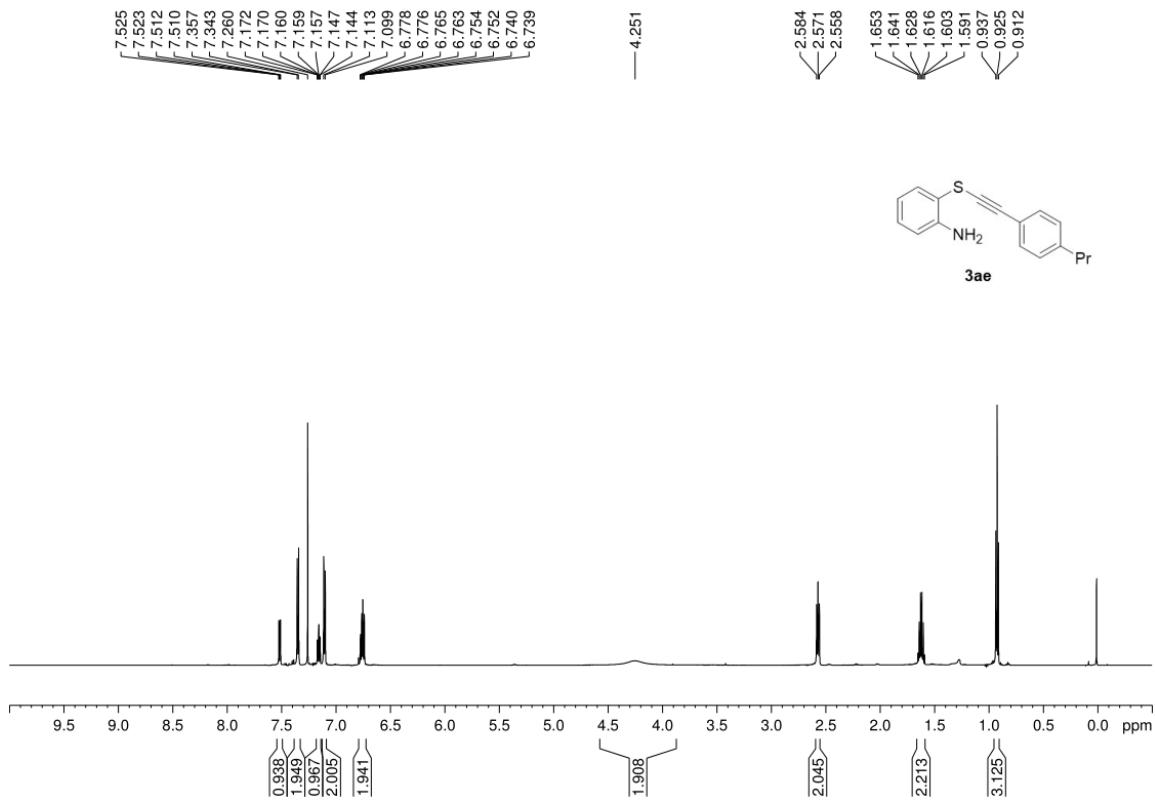
11. ^1H NMR, ^{13}C NMR and HRMS spectra of products and selected starting materials

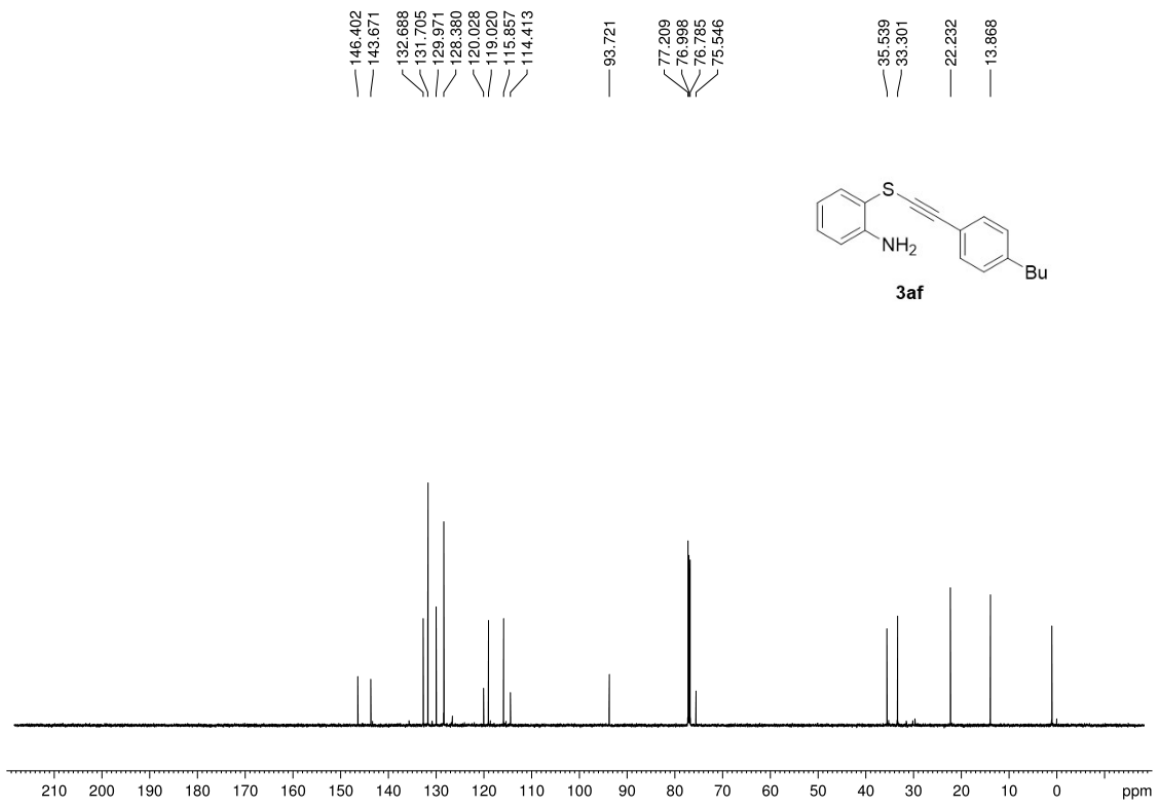
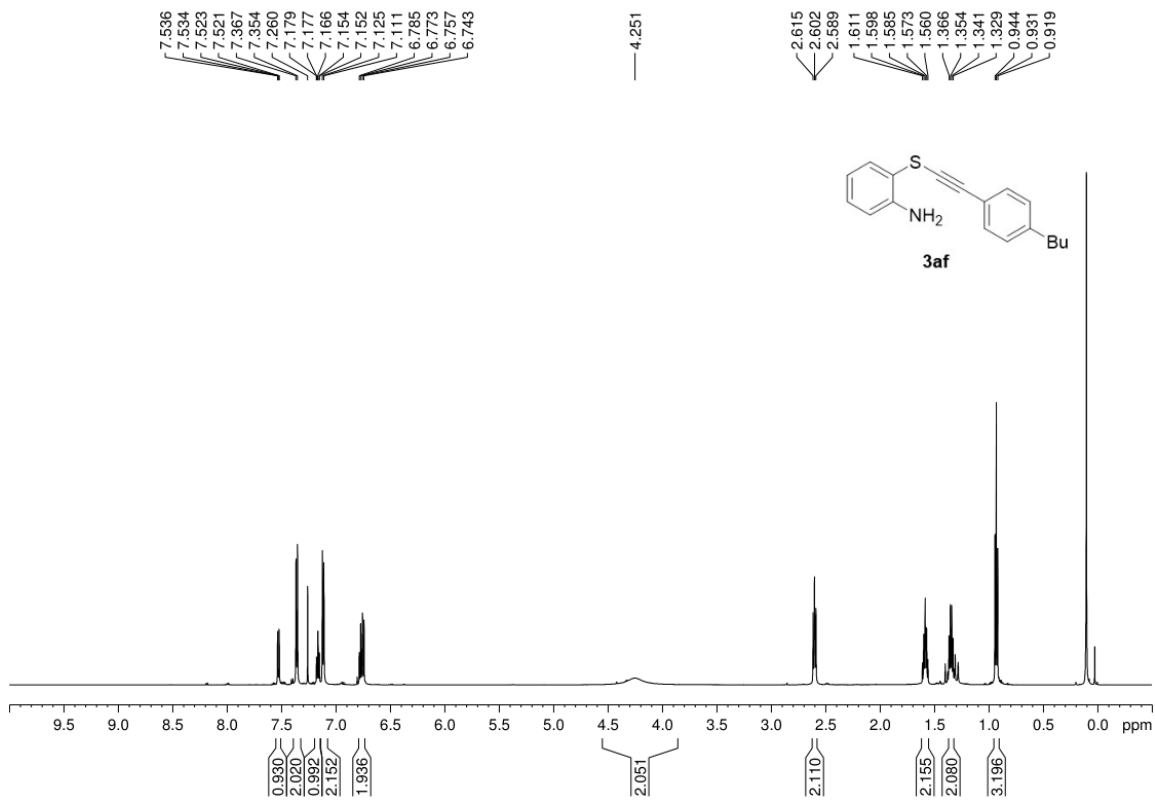


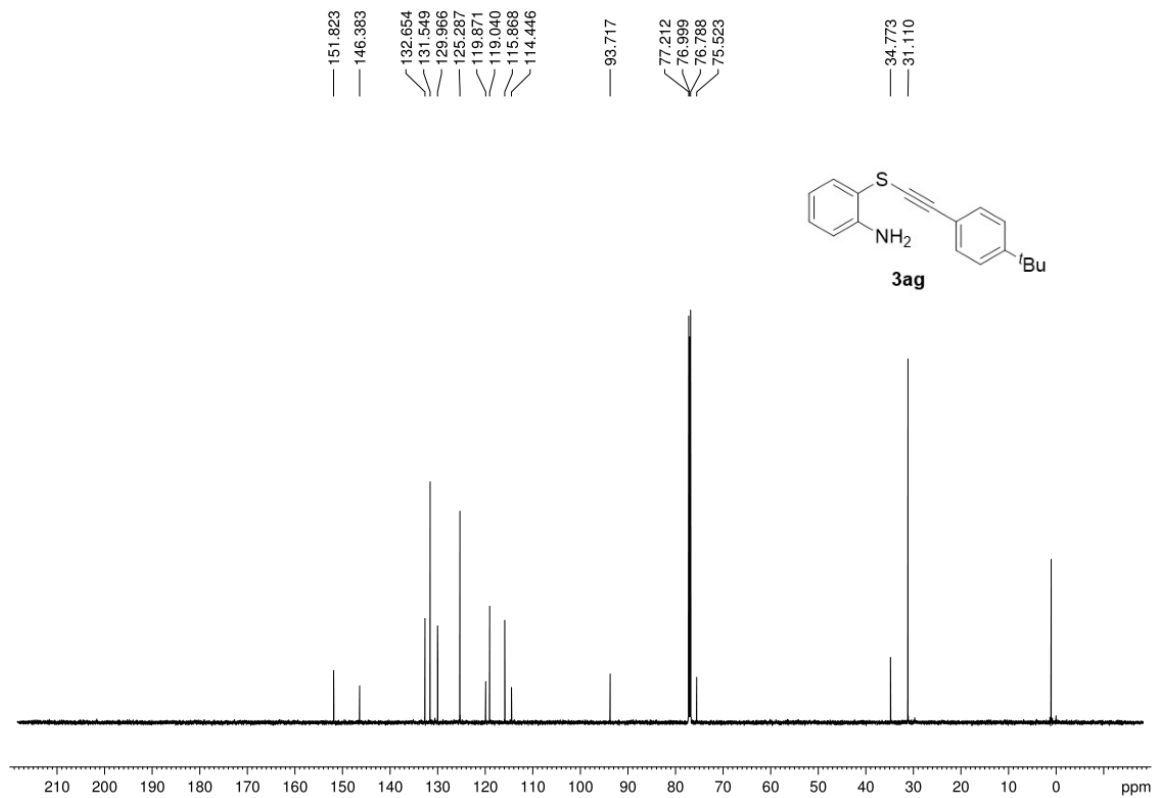
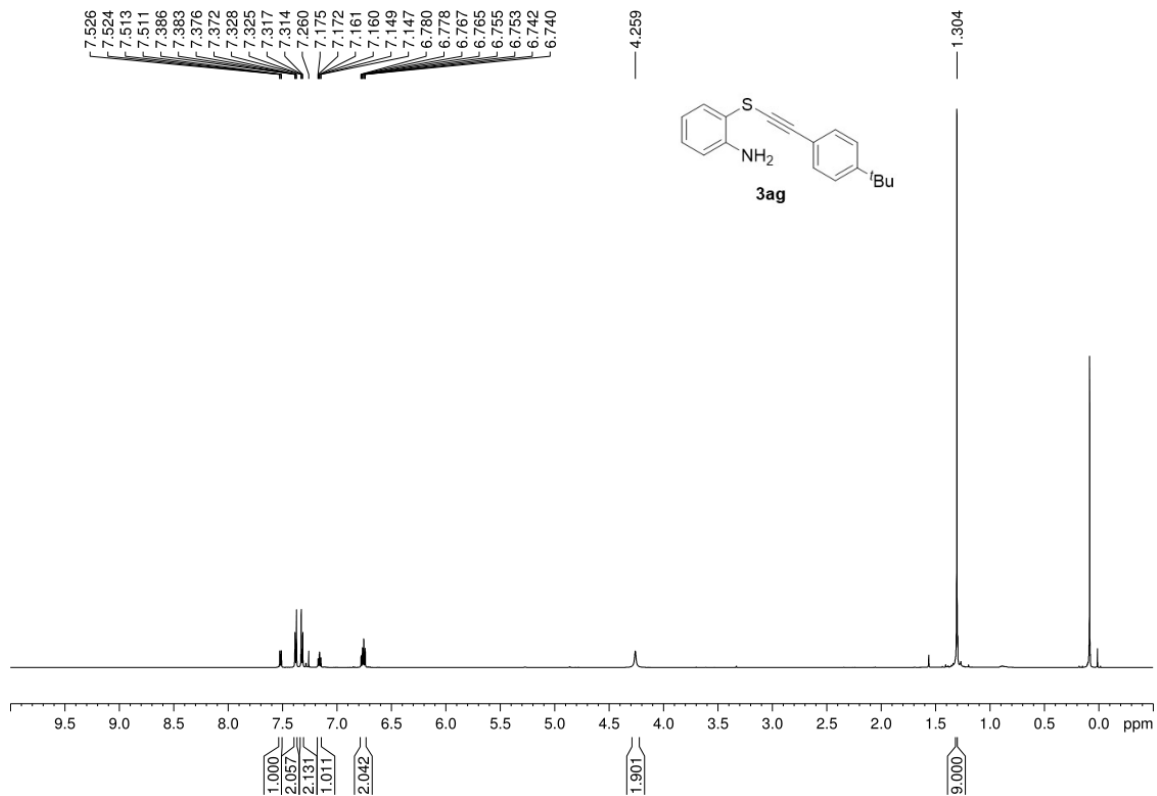


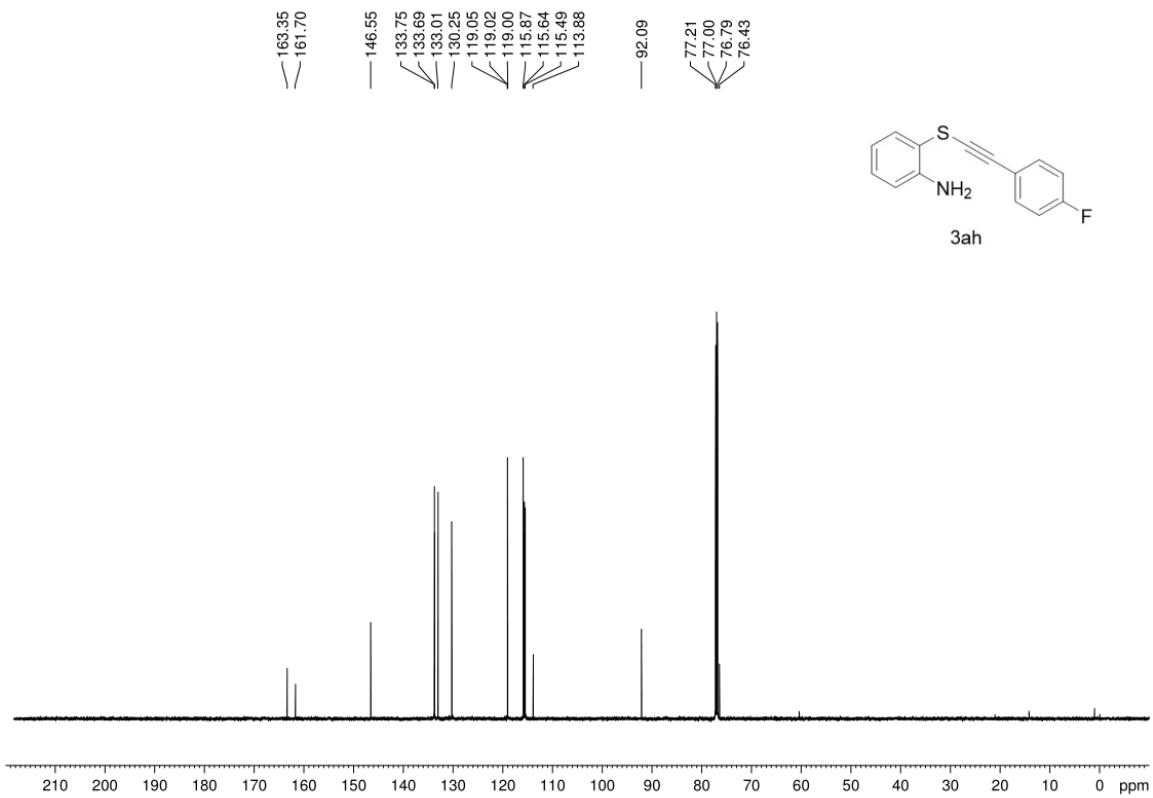
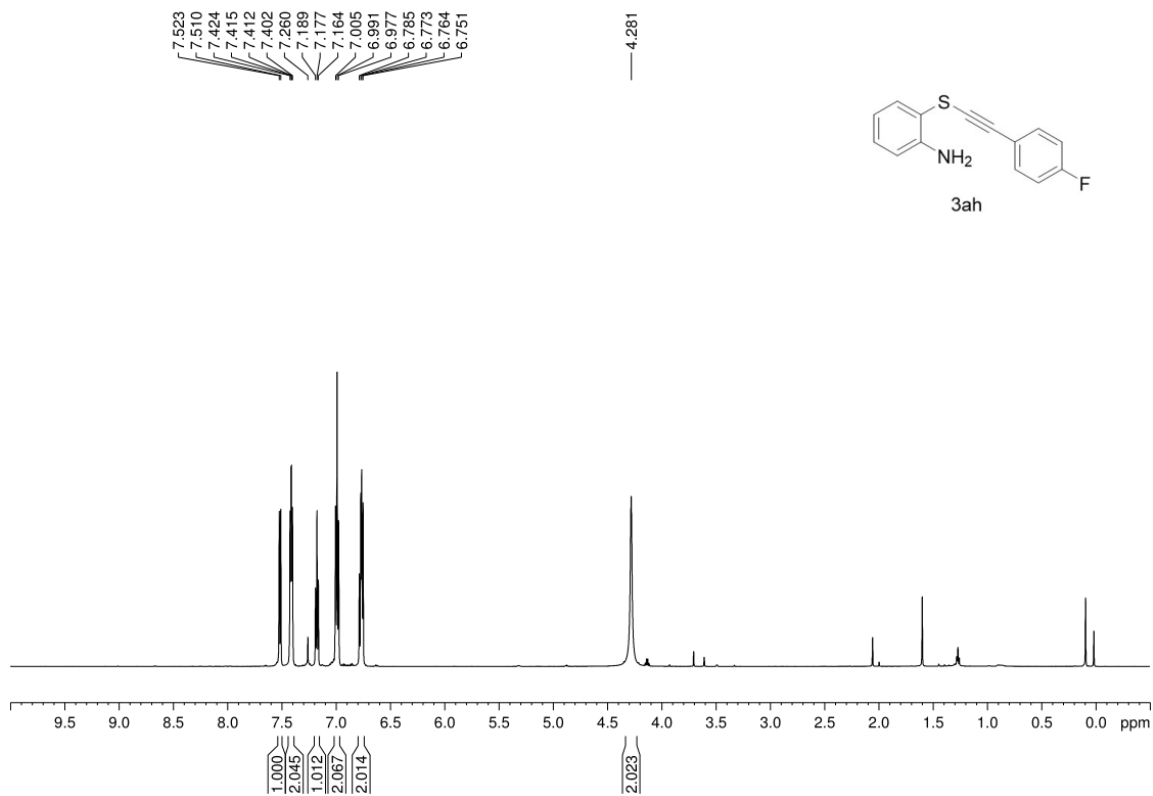


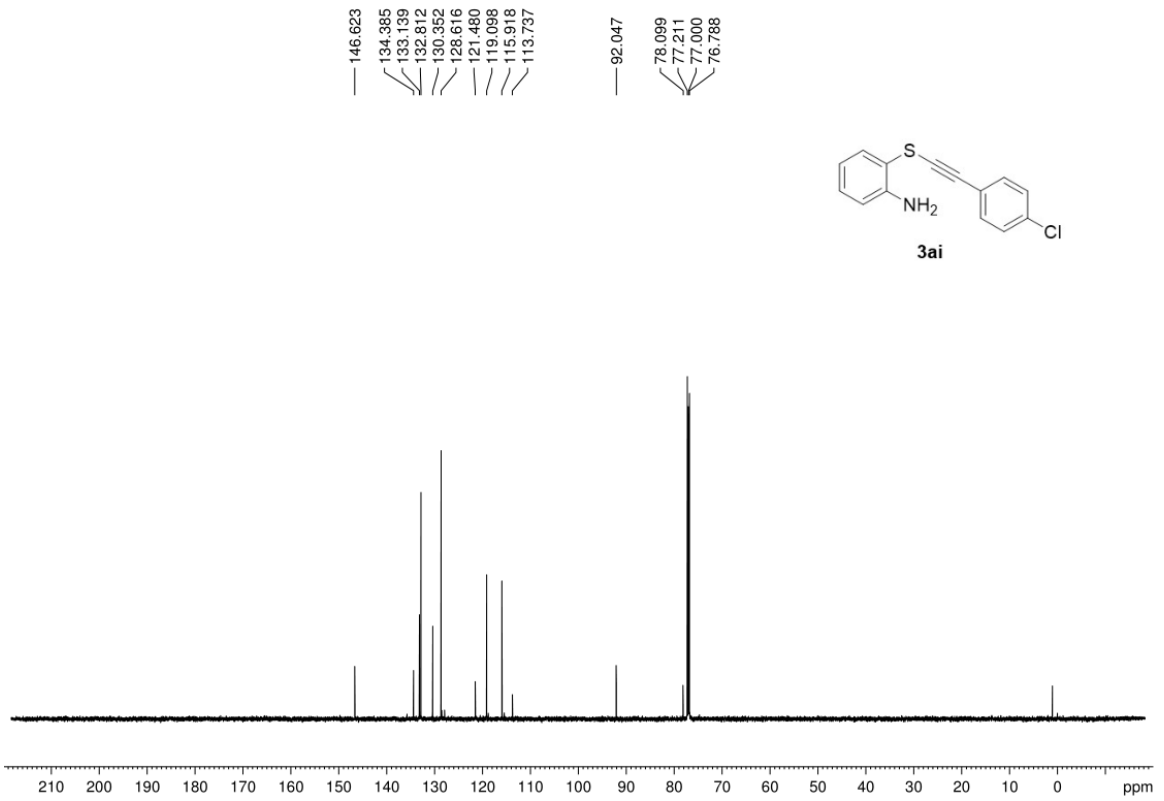
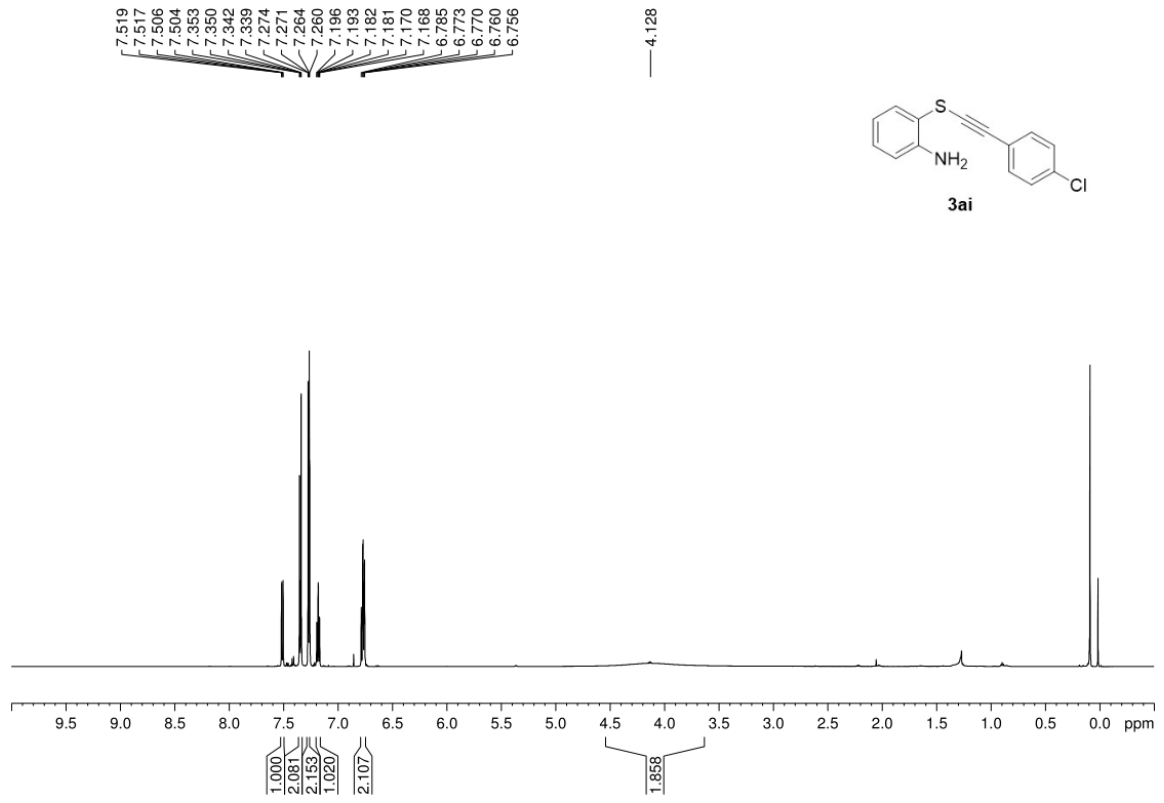


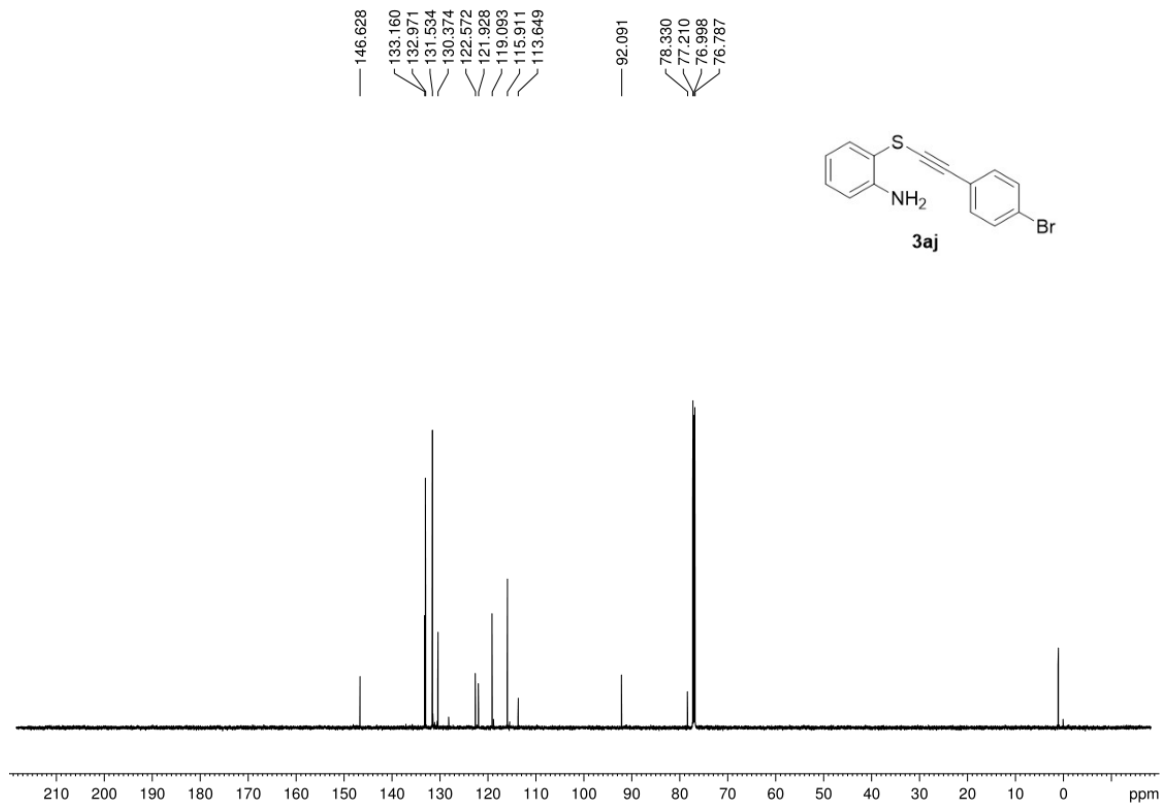
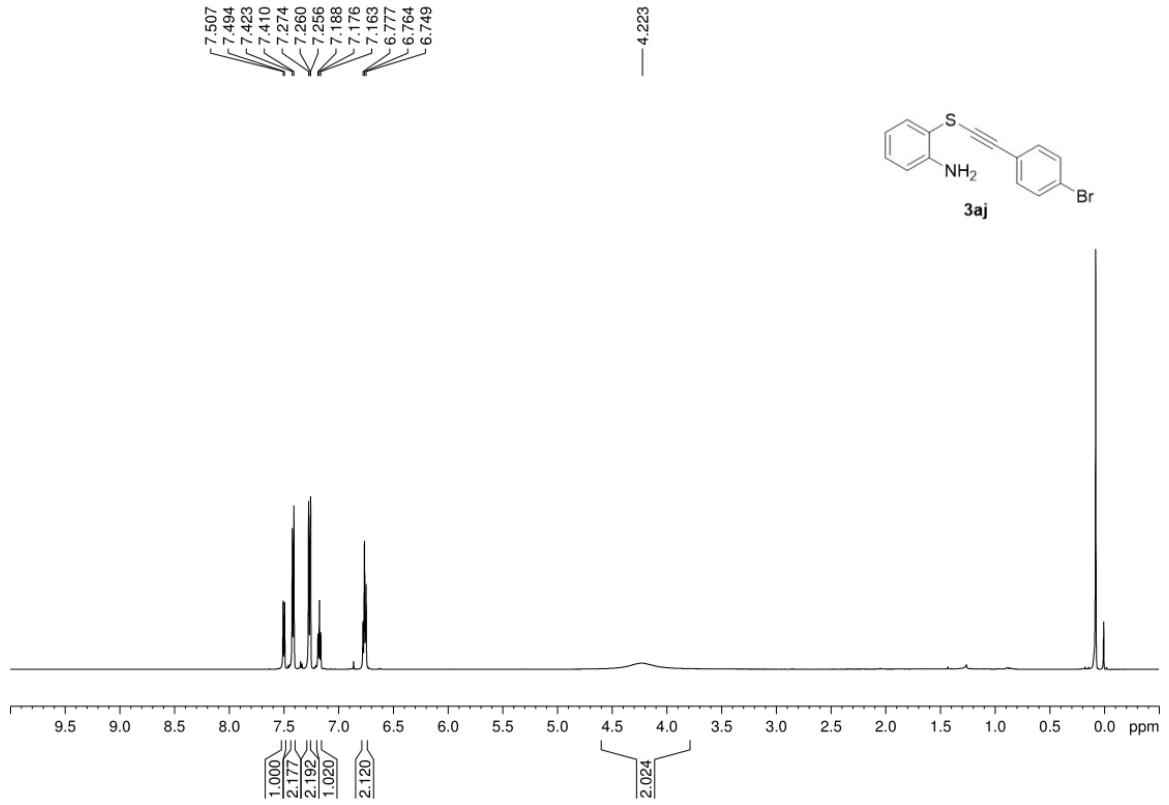


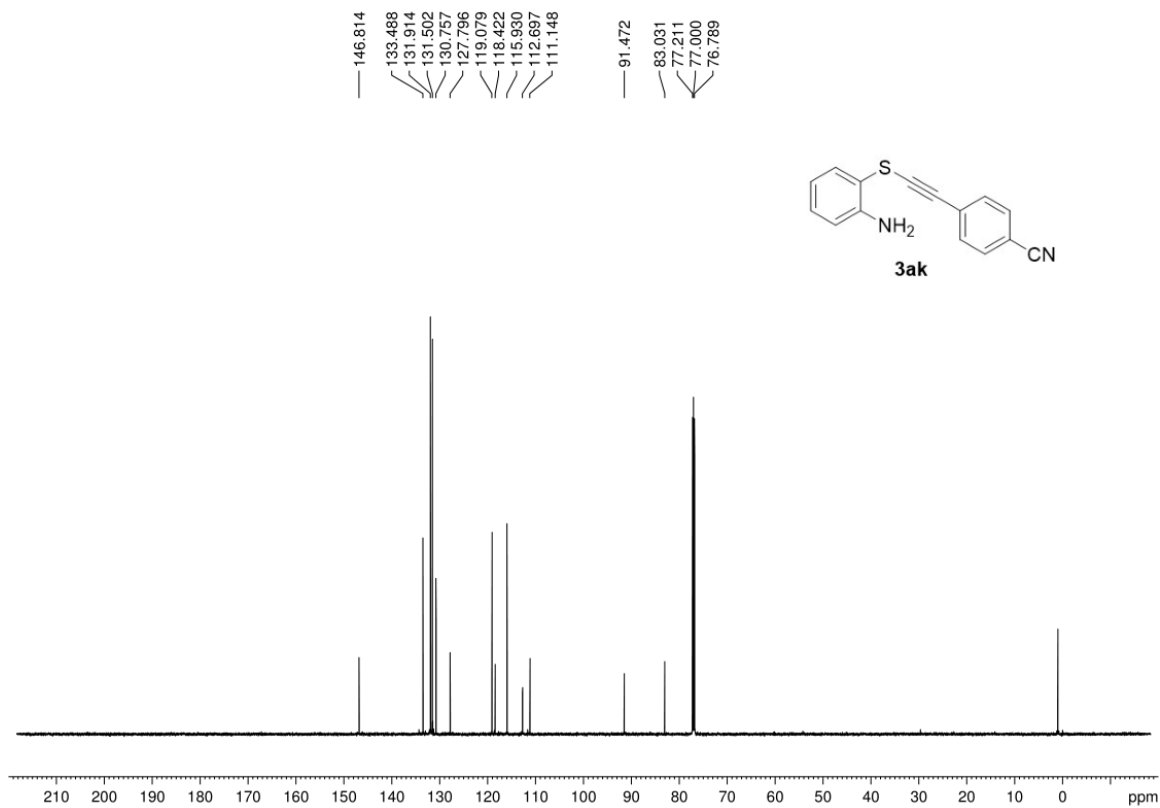
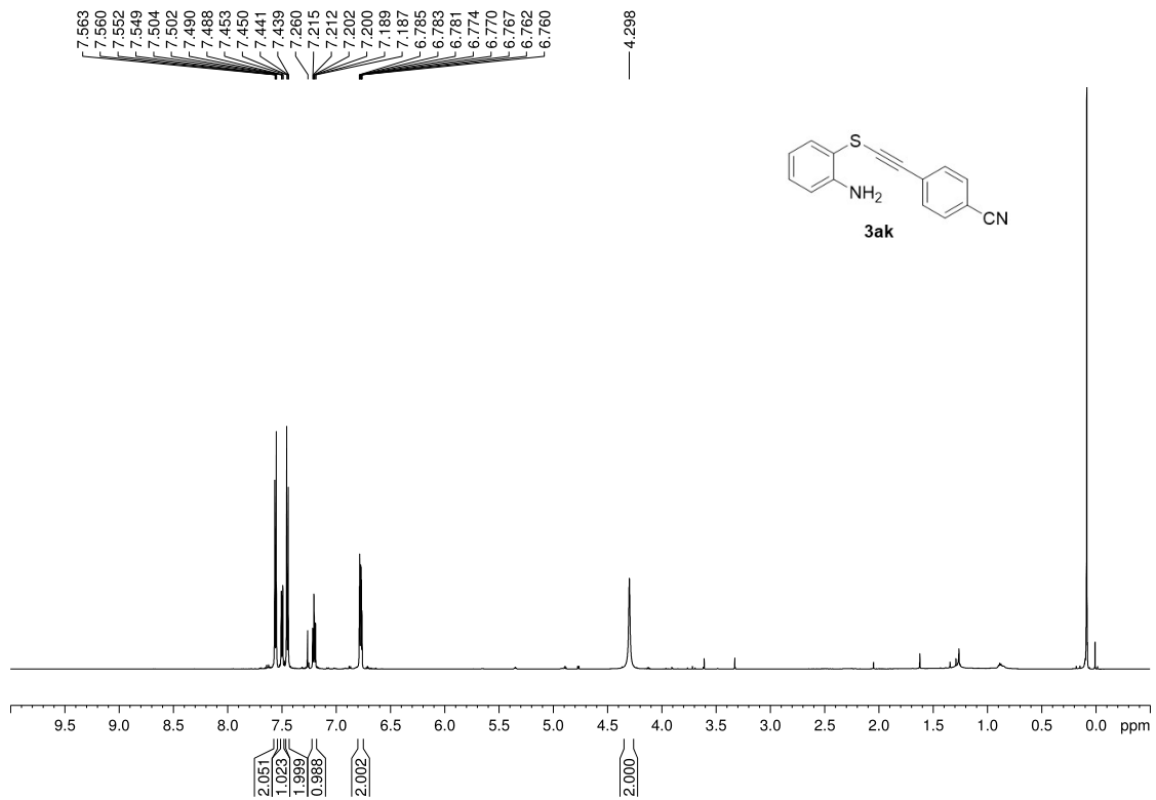


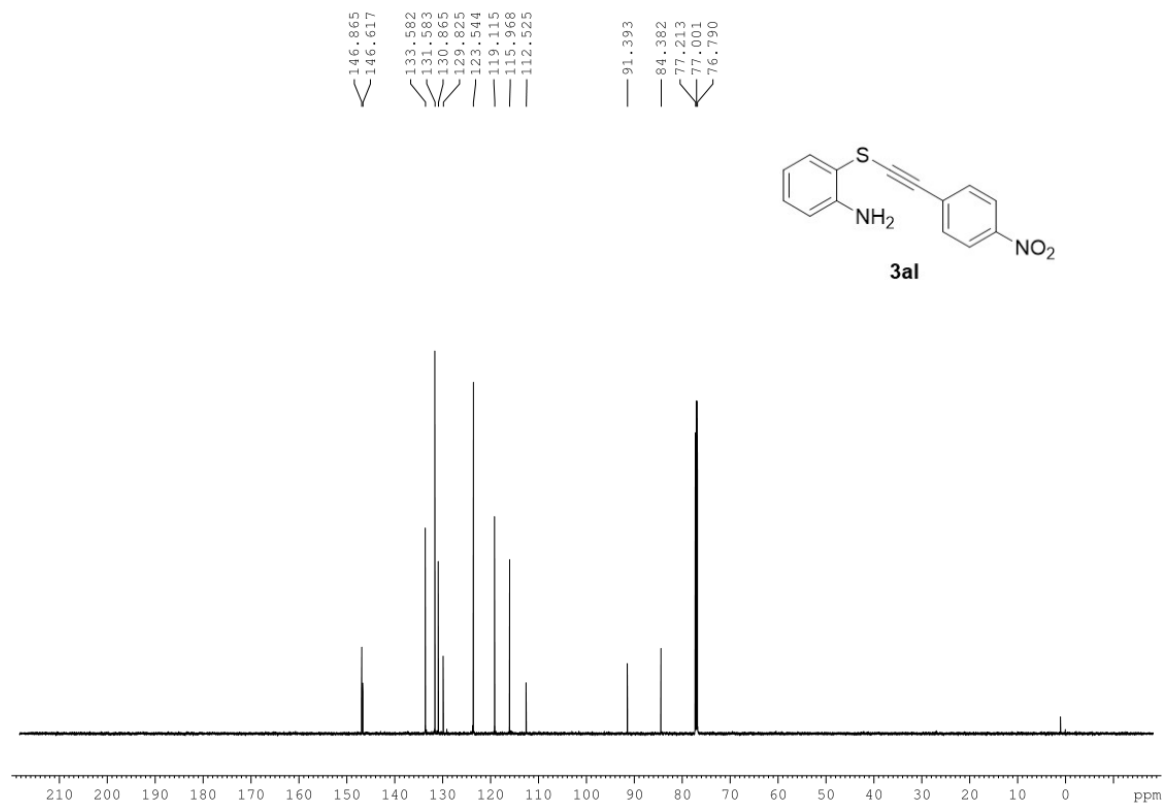
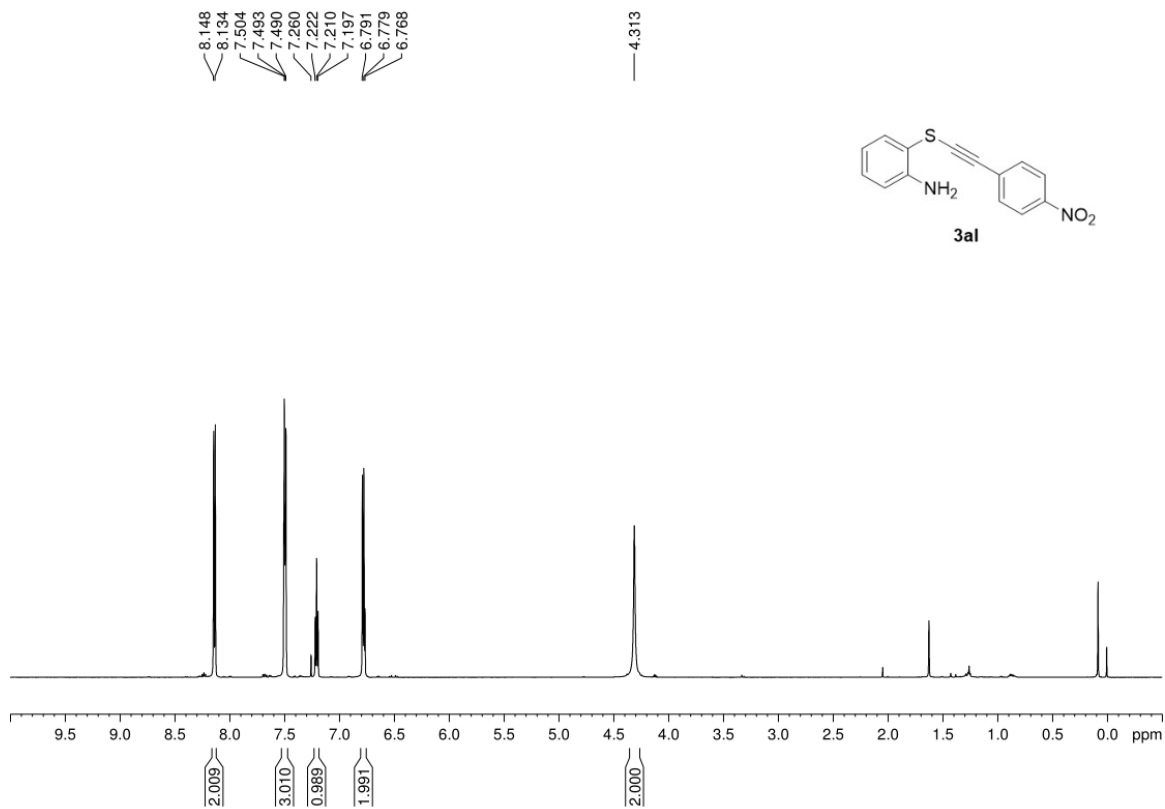


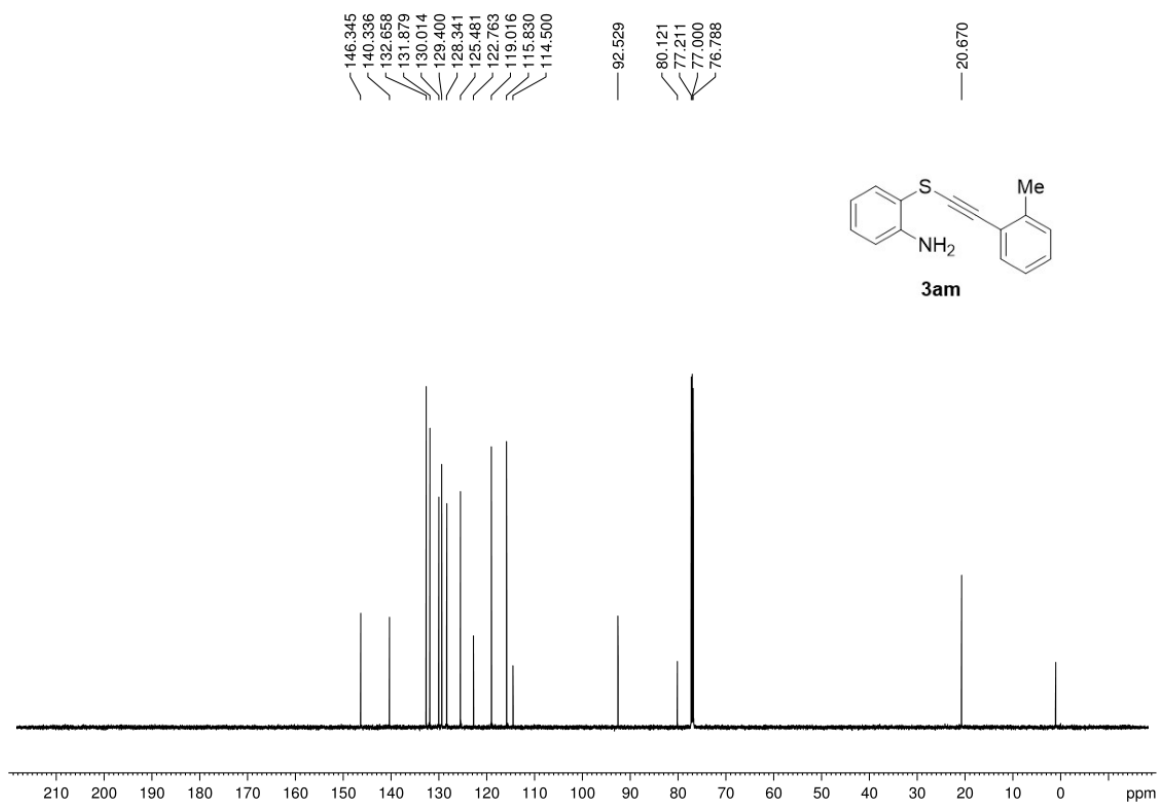
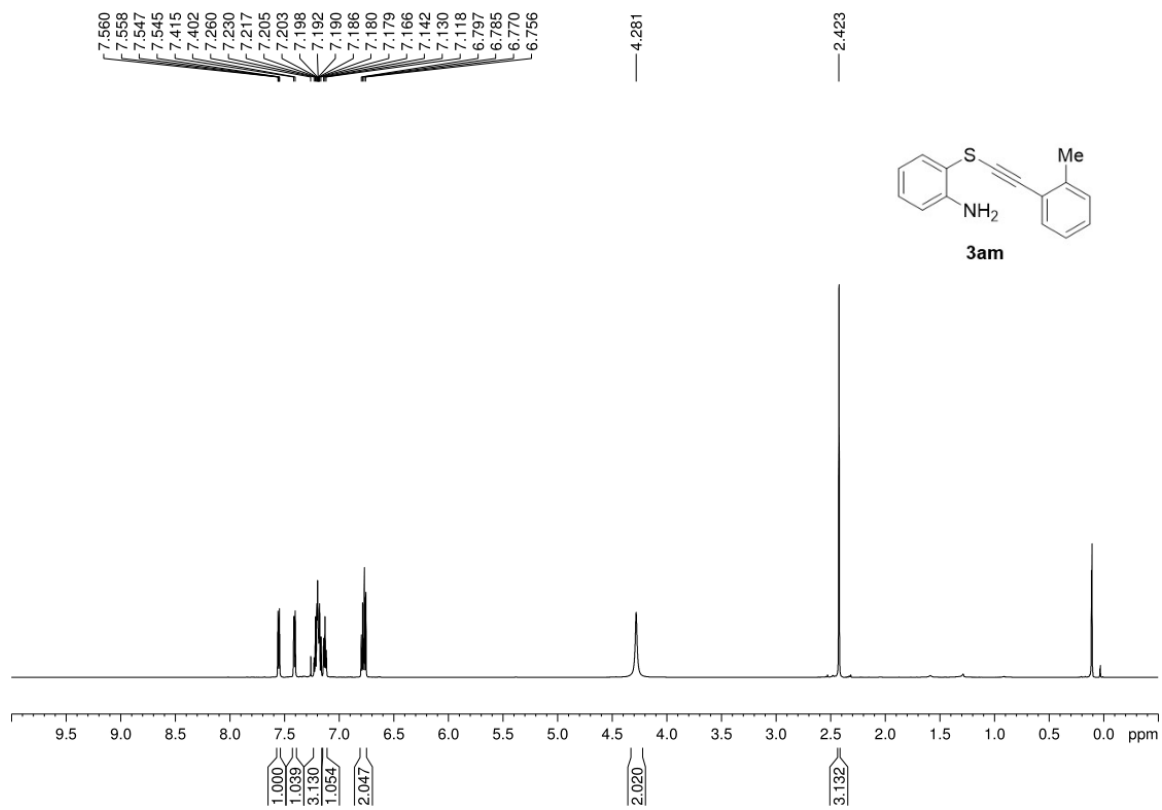




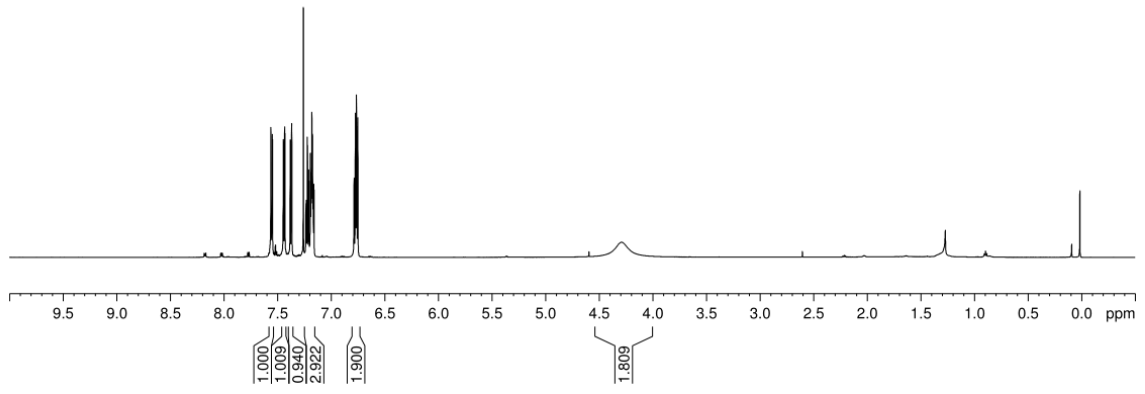
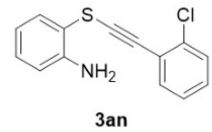




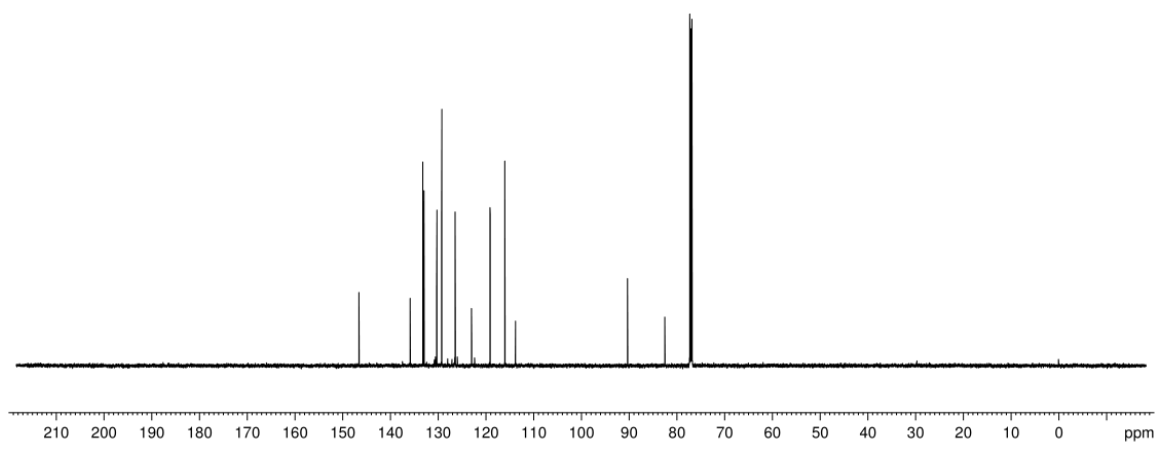
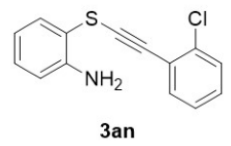


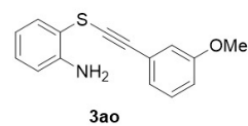
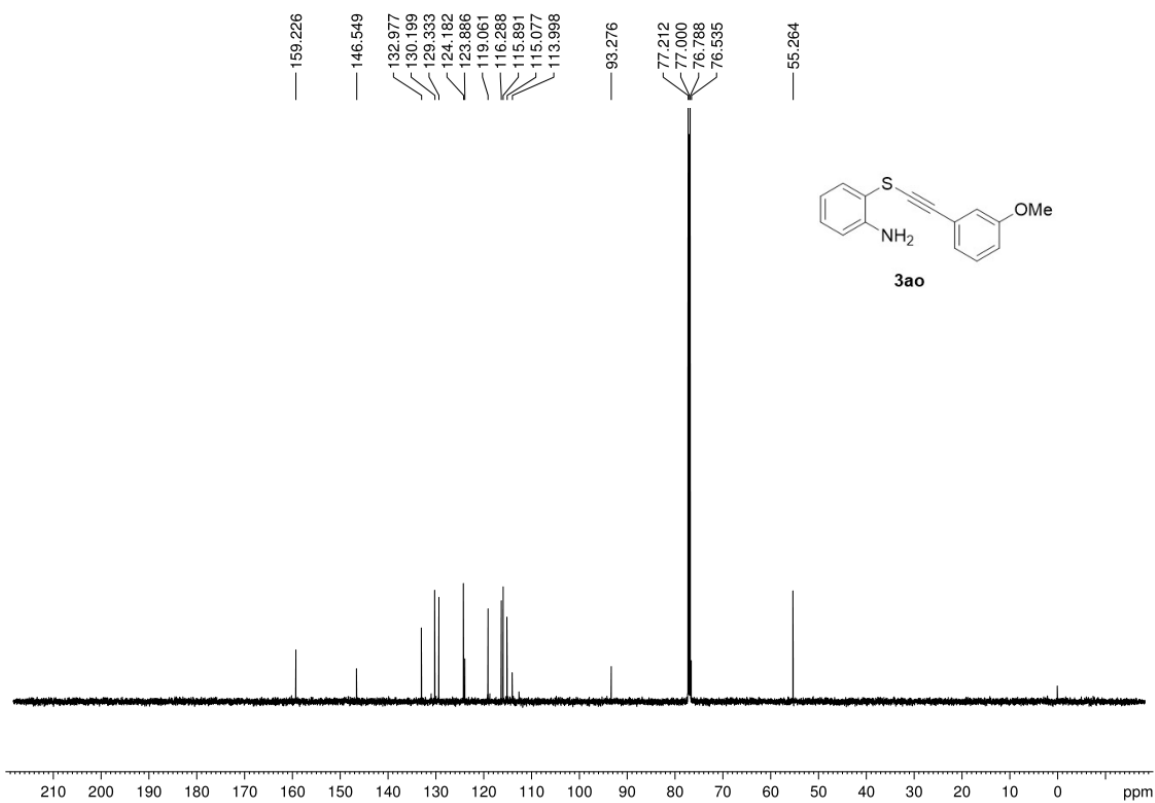
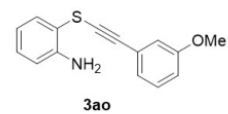
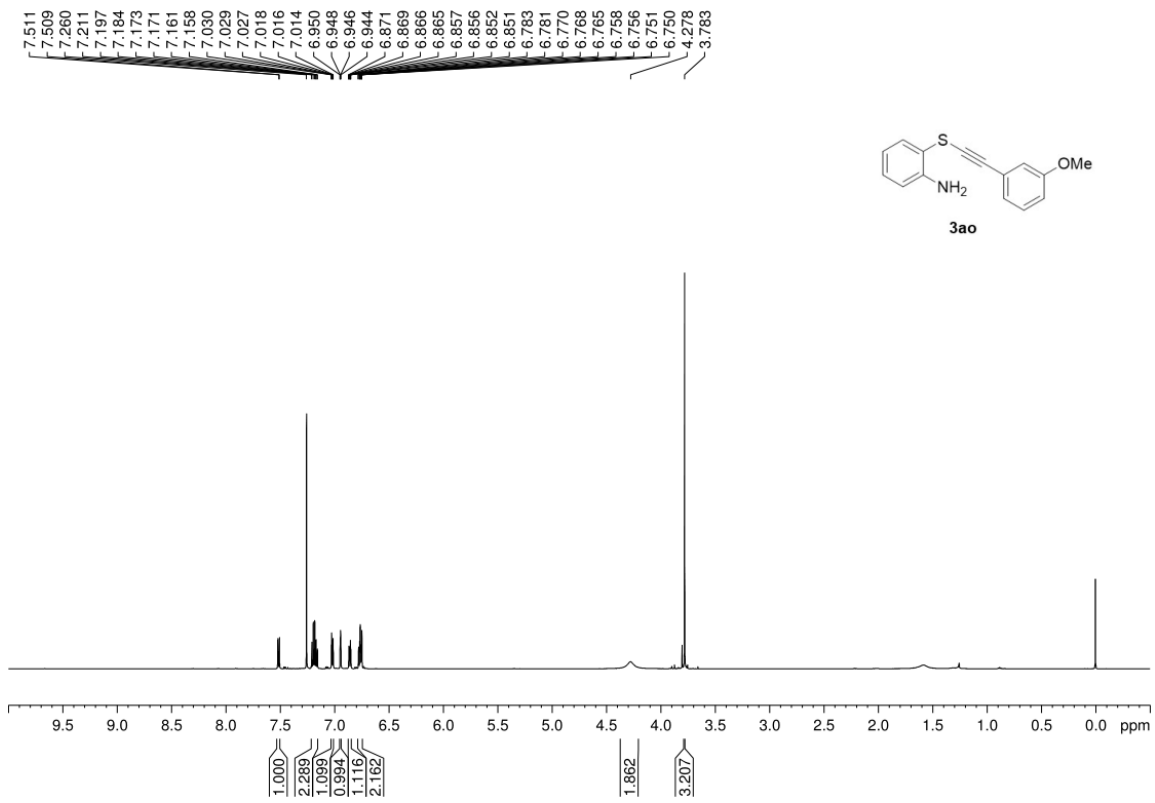


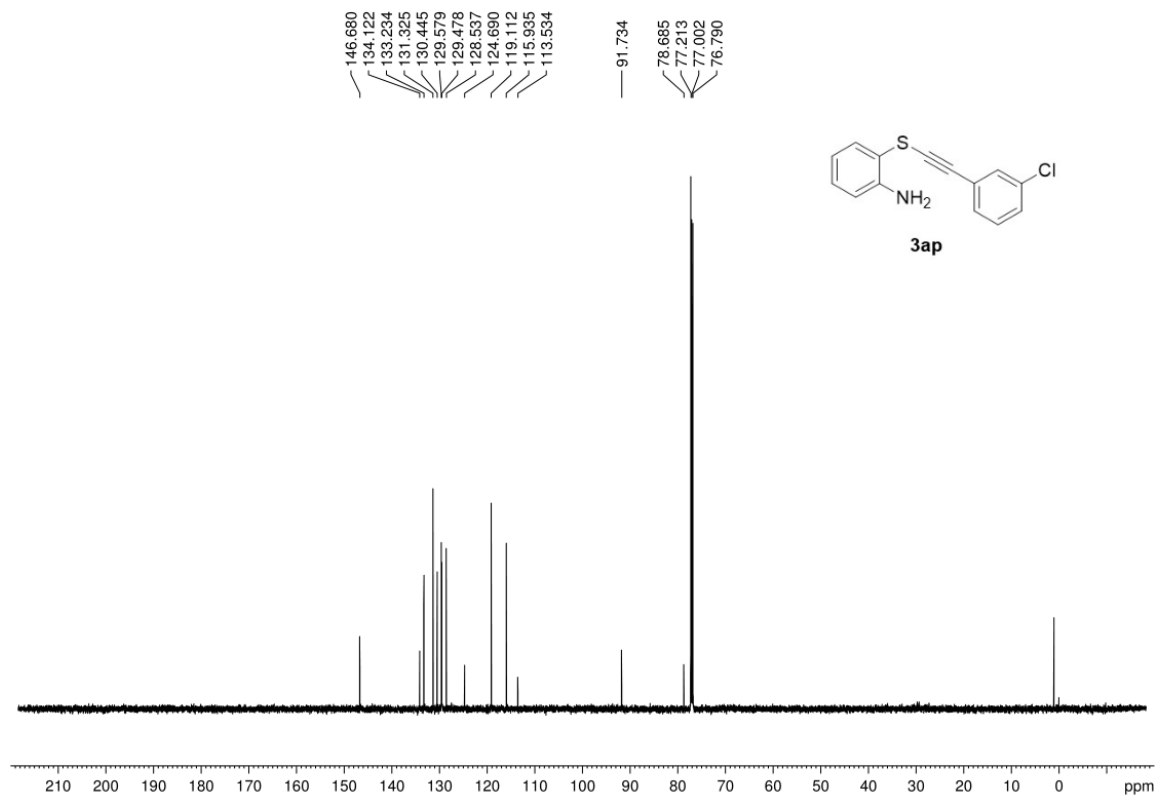
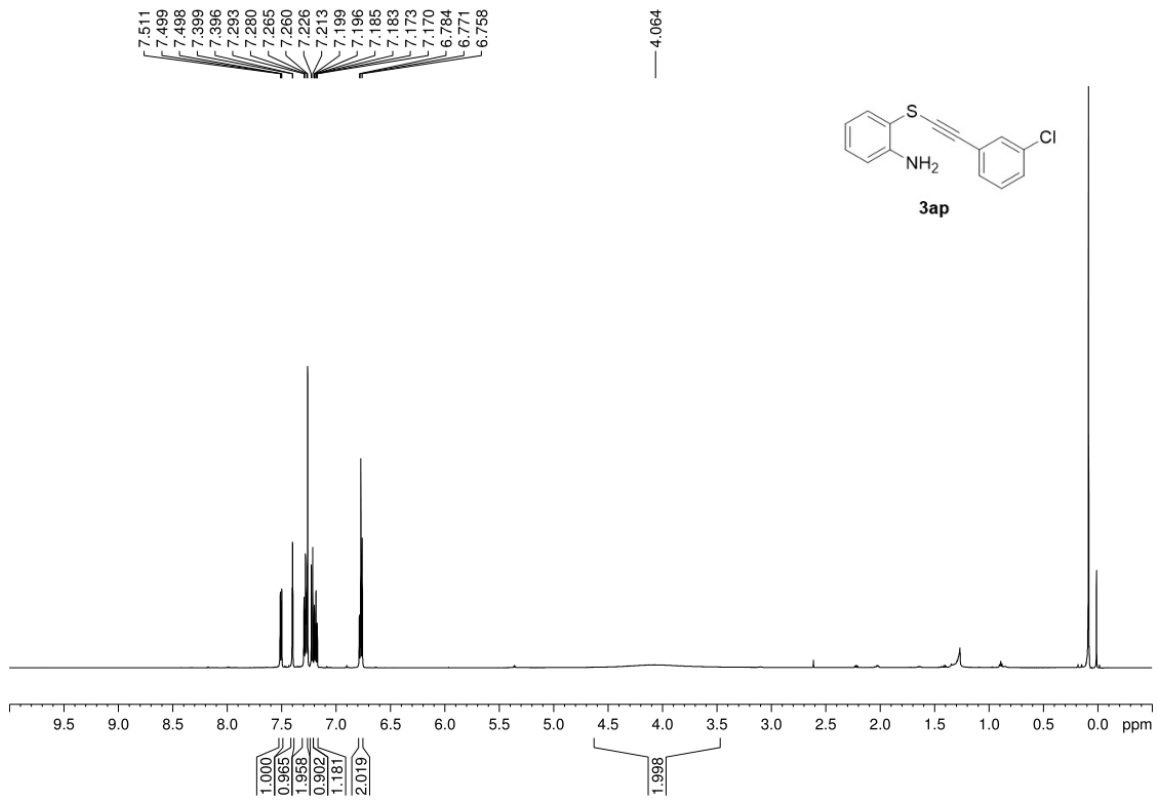
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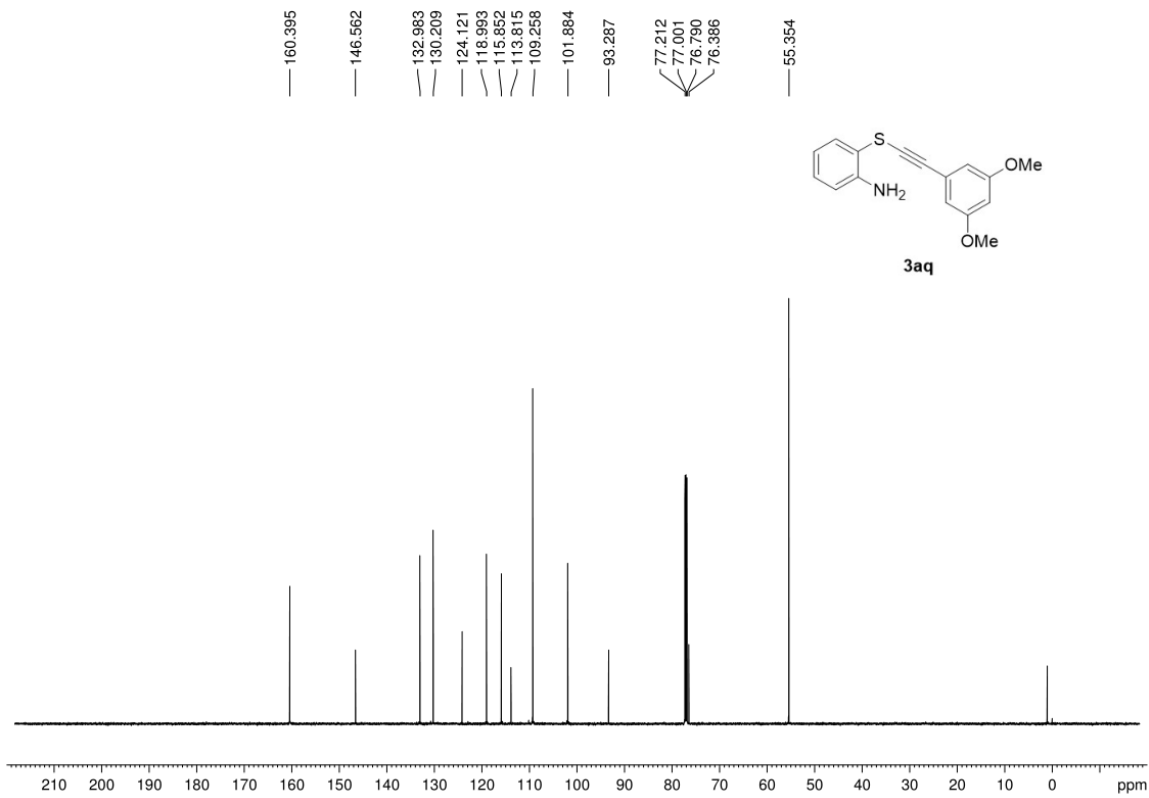
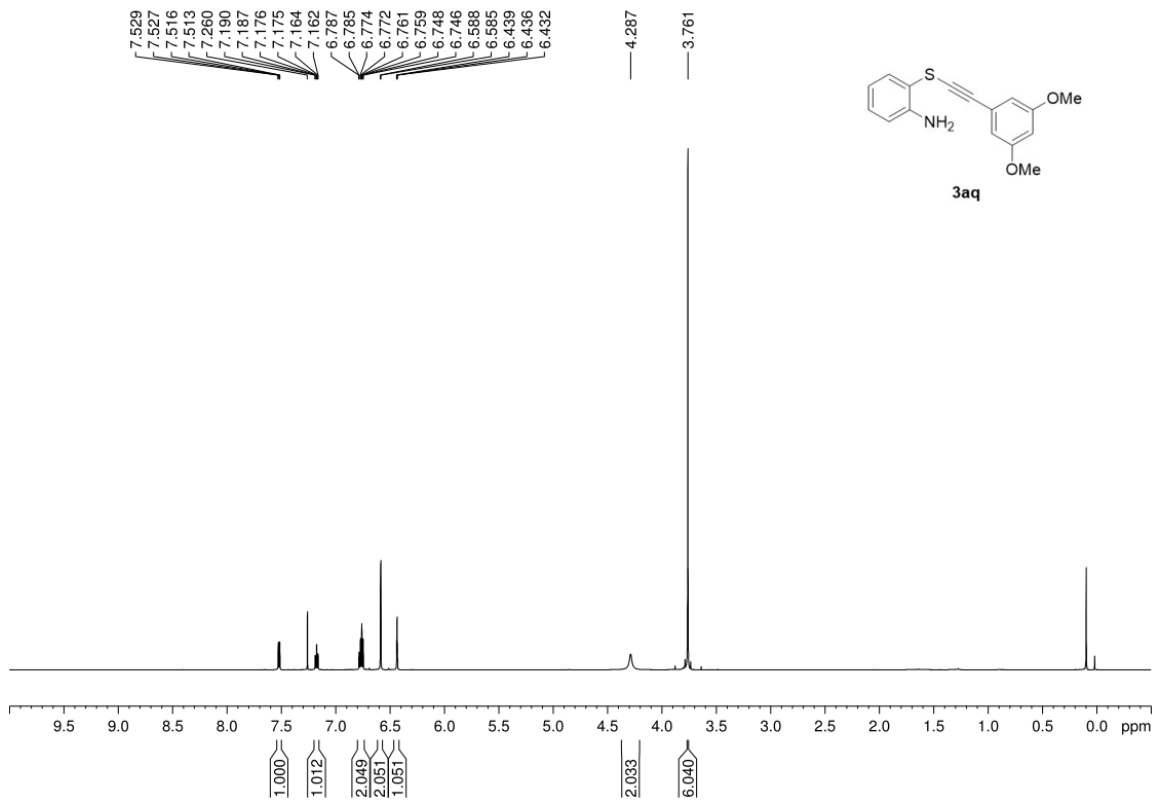


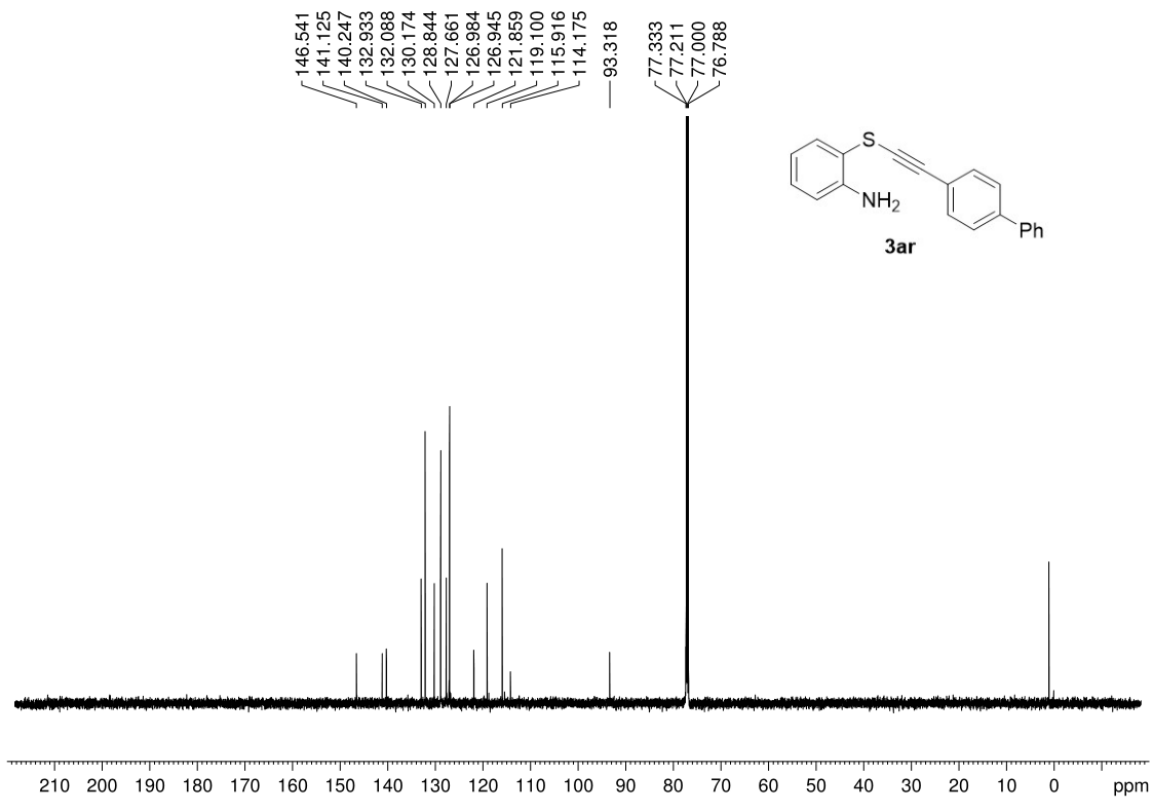
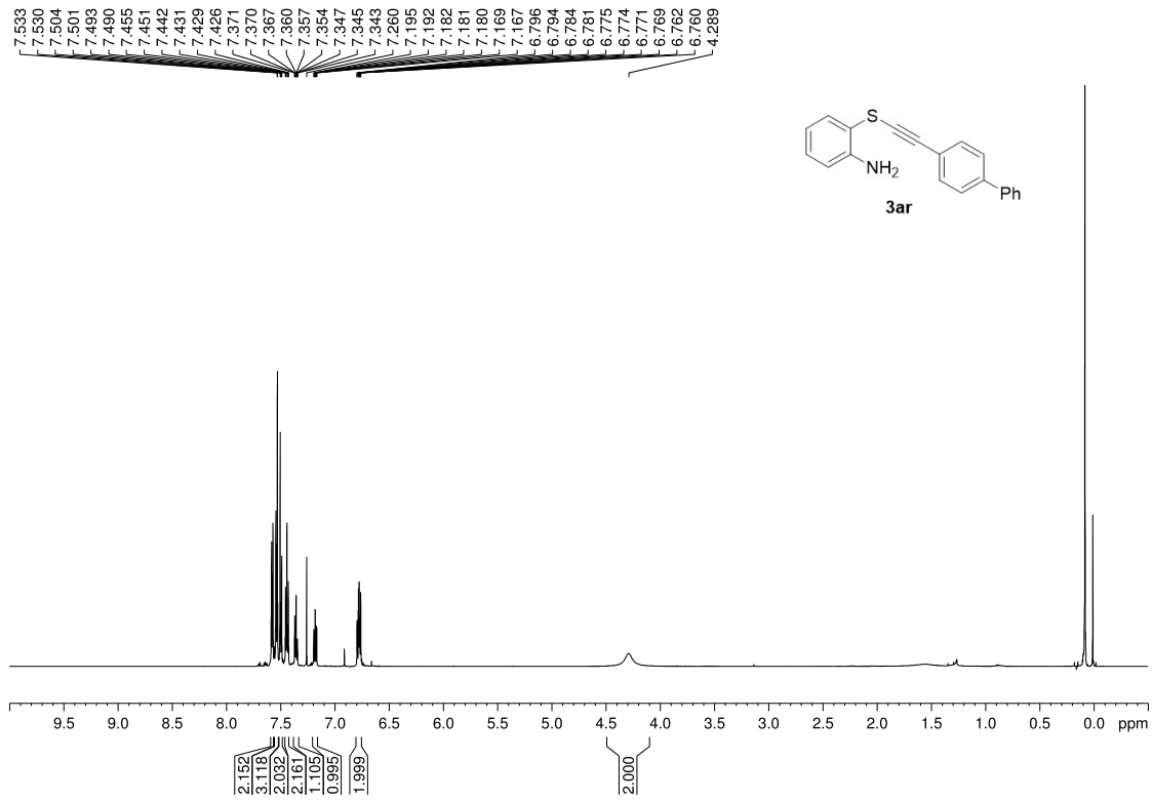
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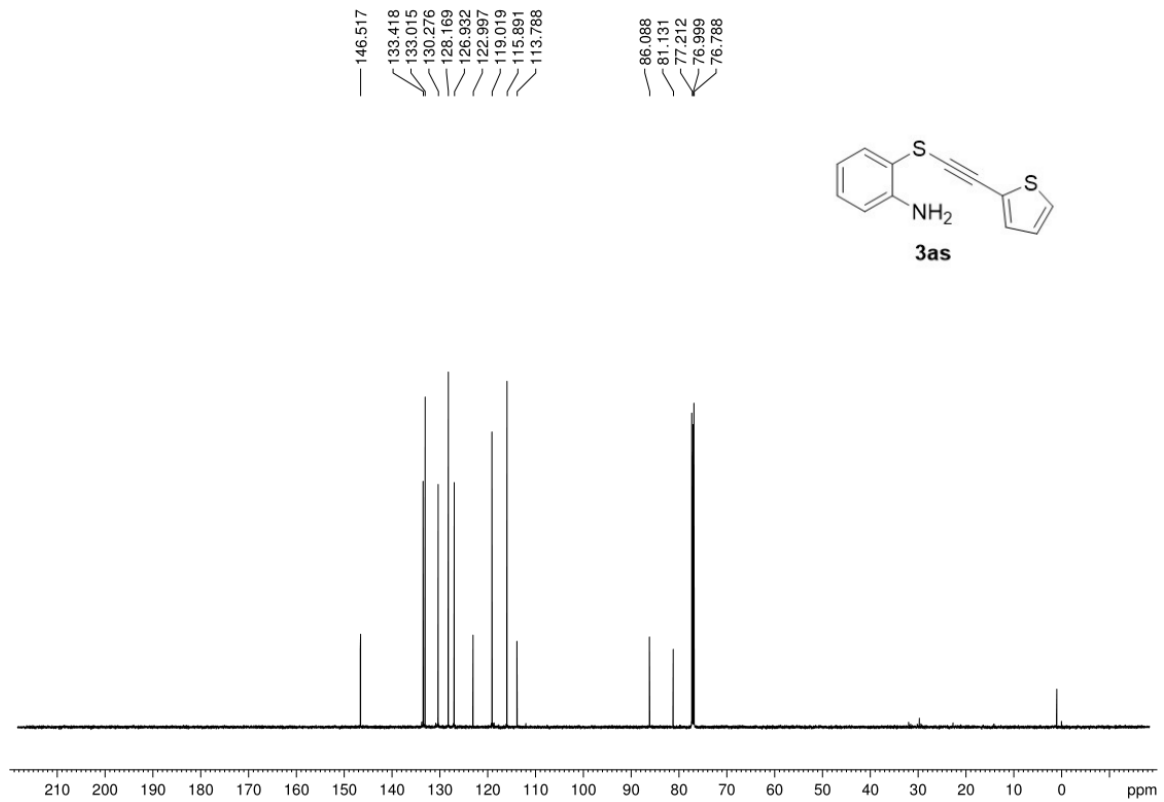
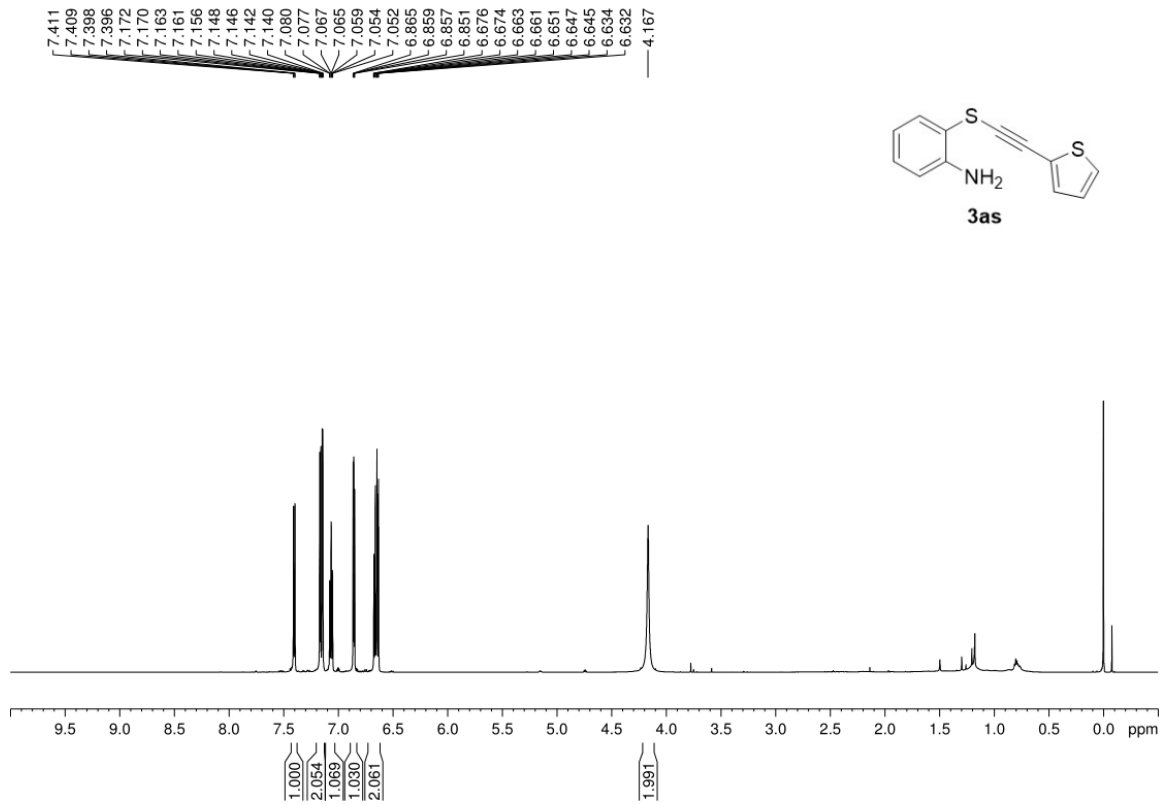


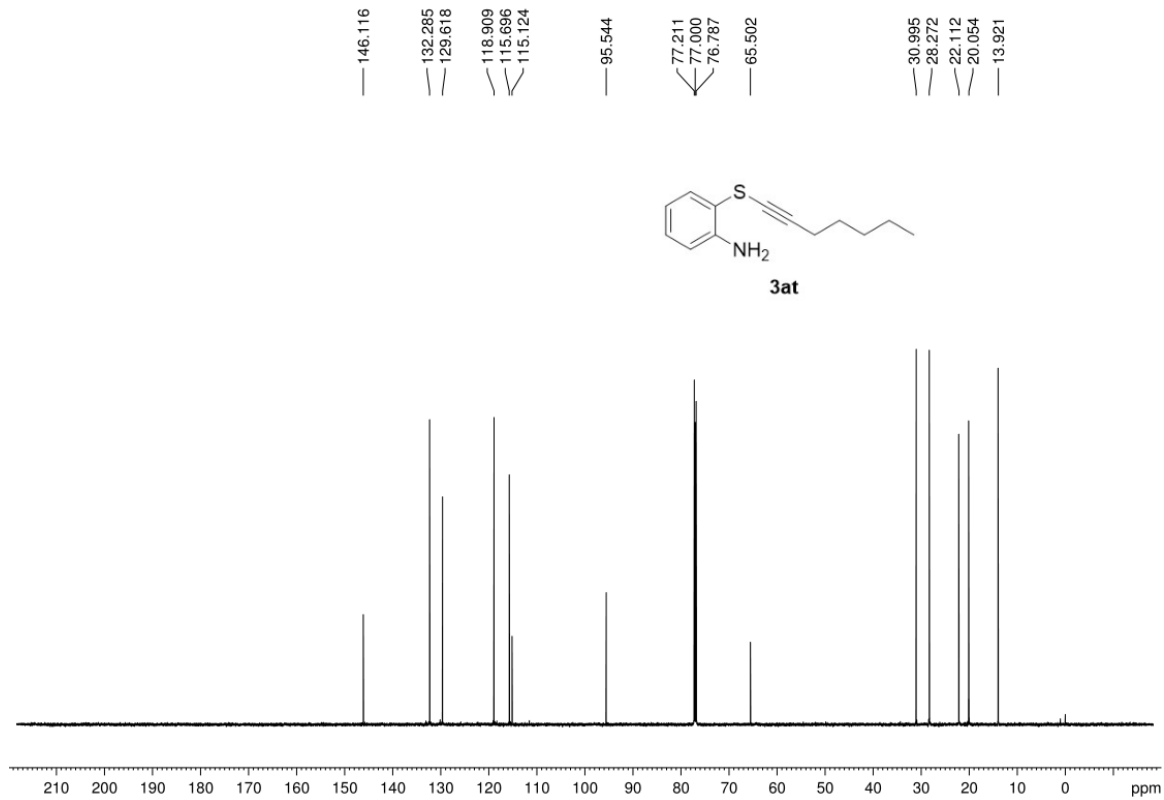
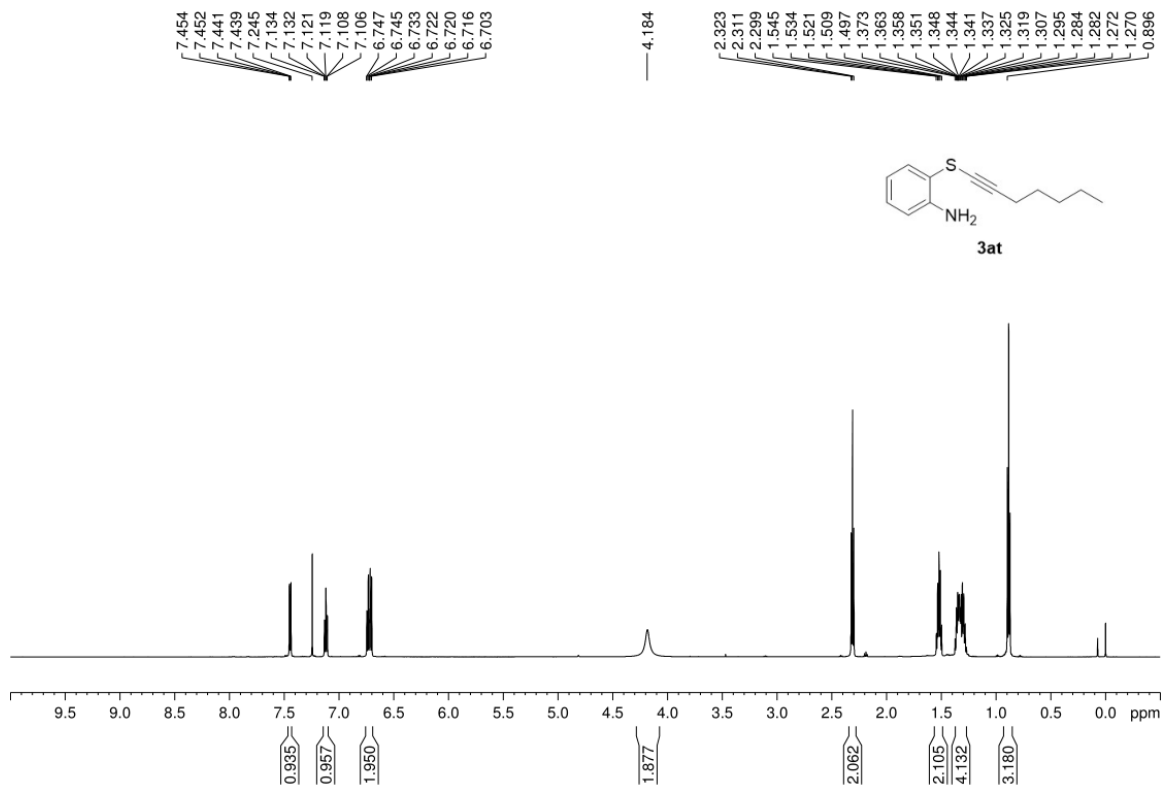


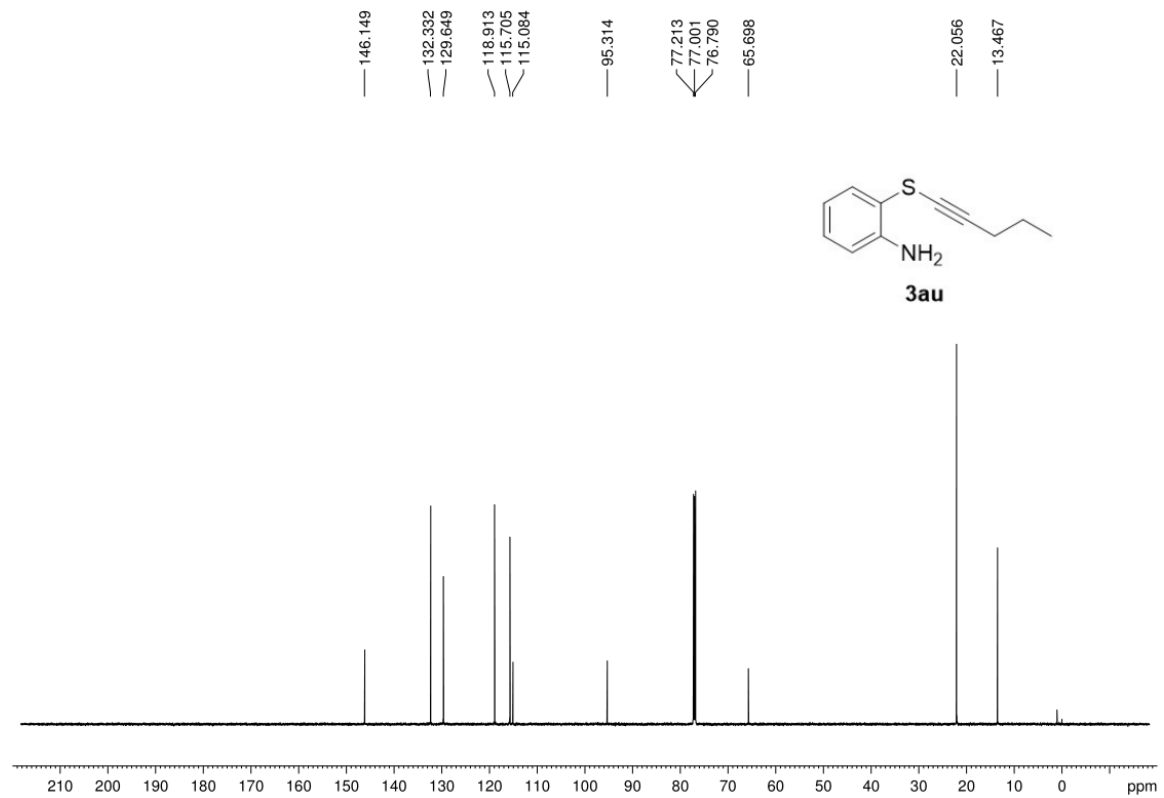
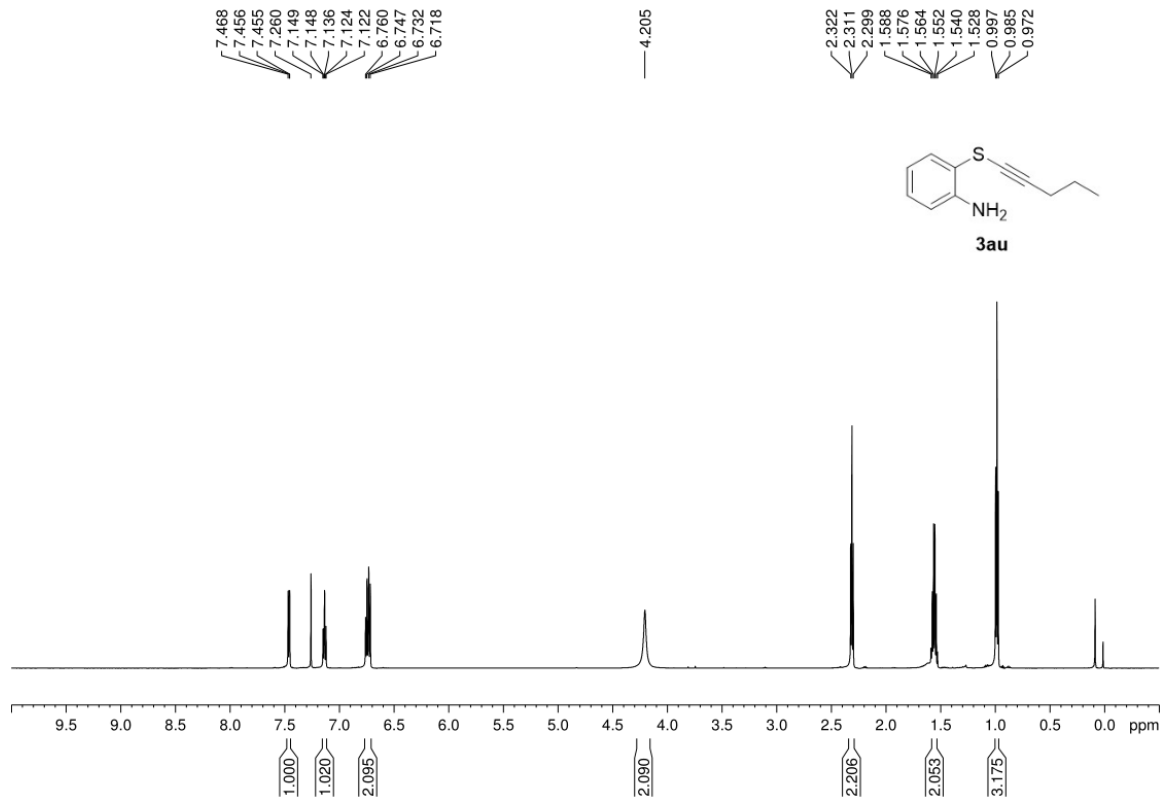


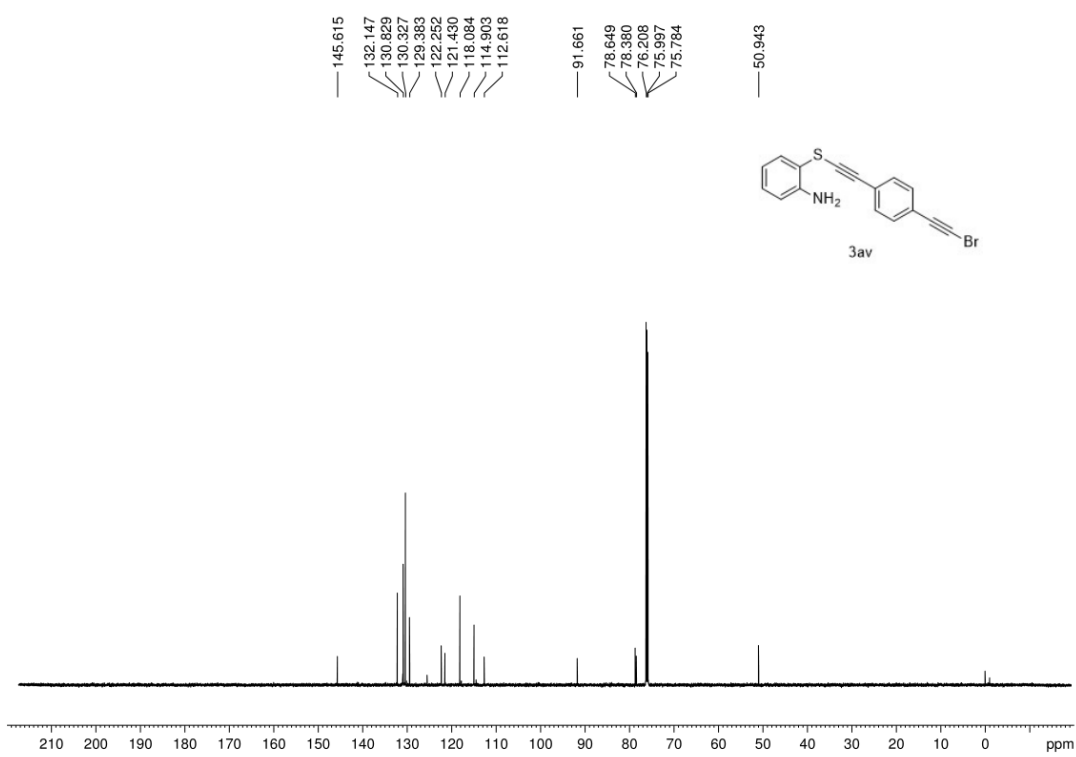
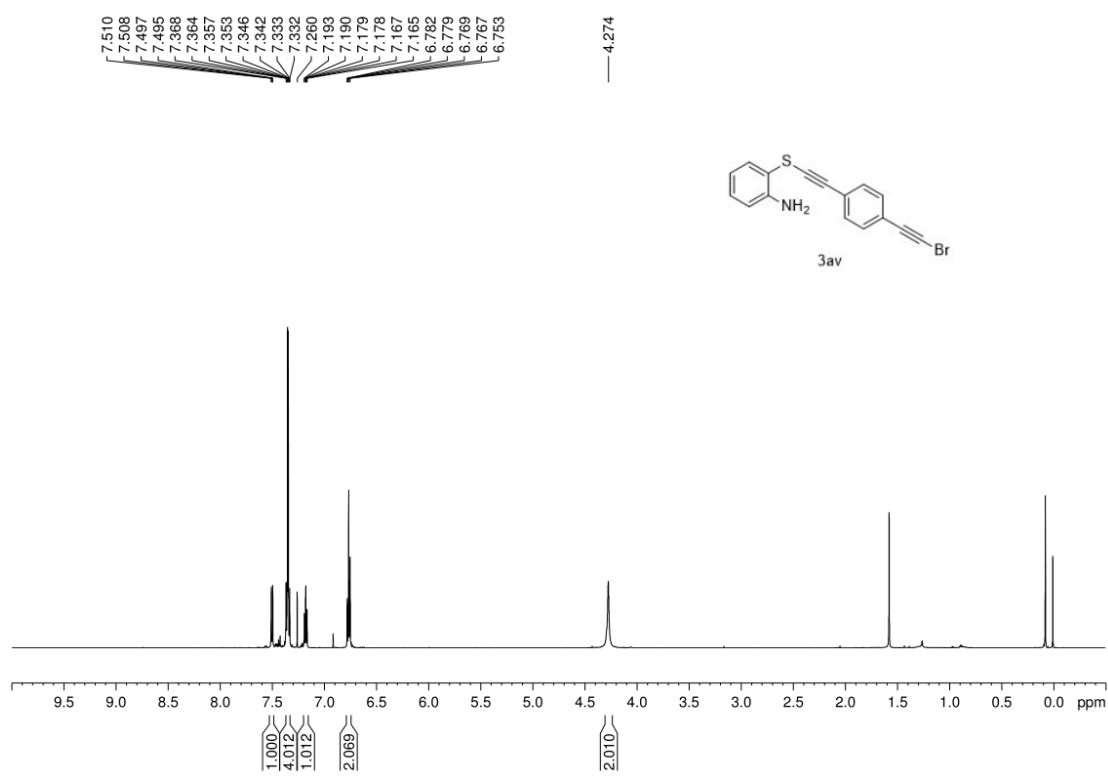


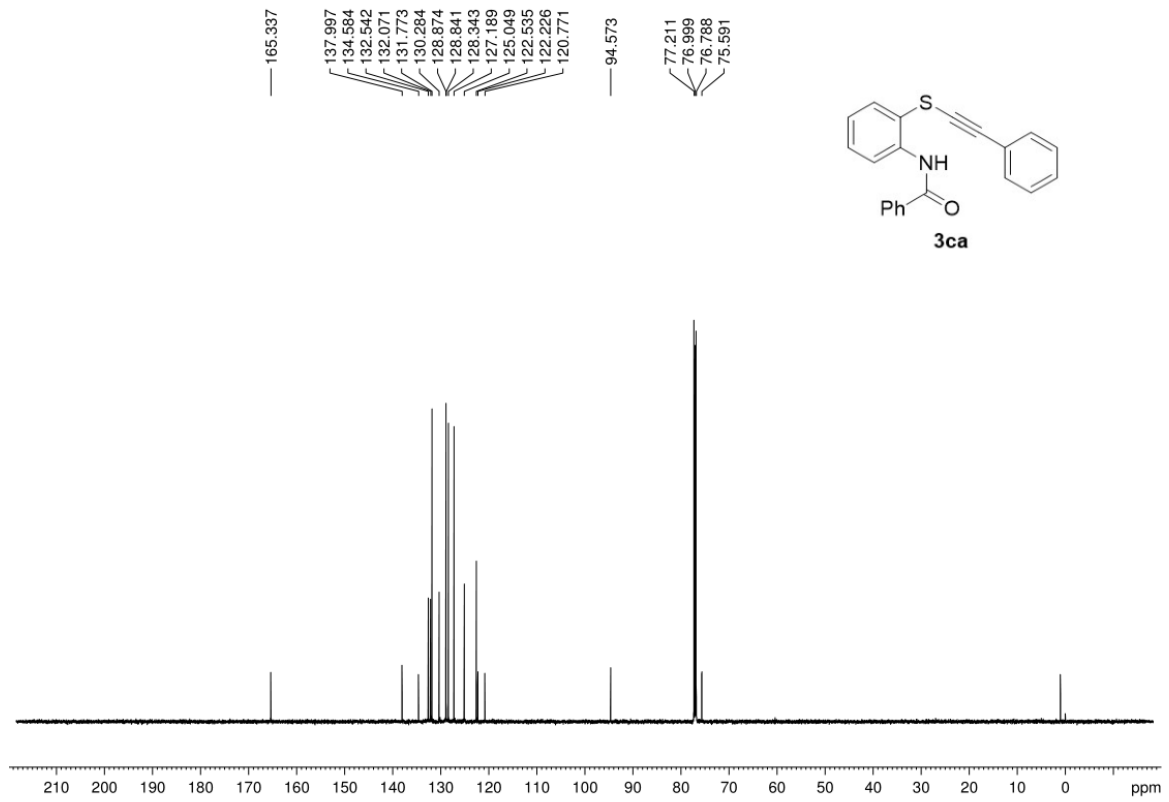
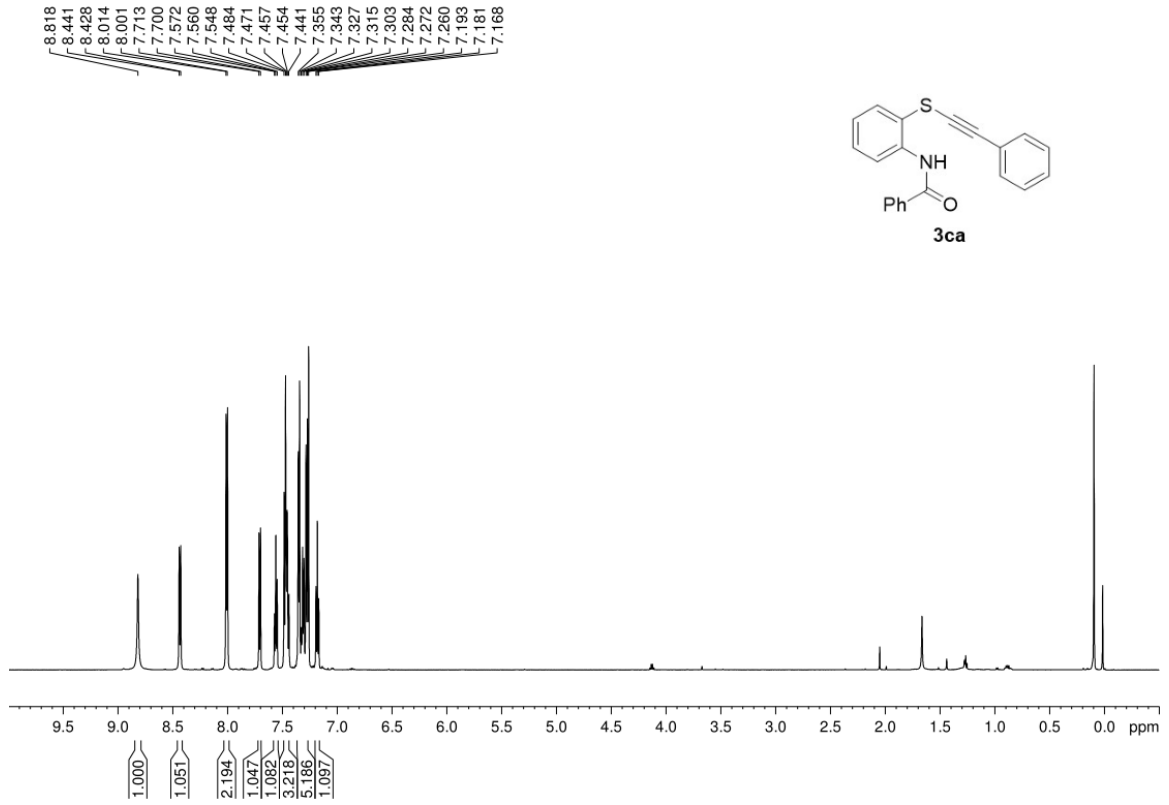


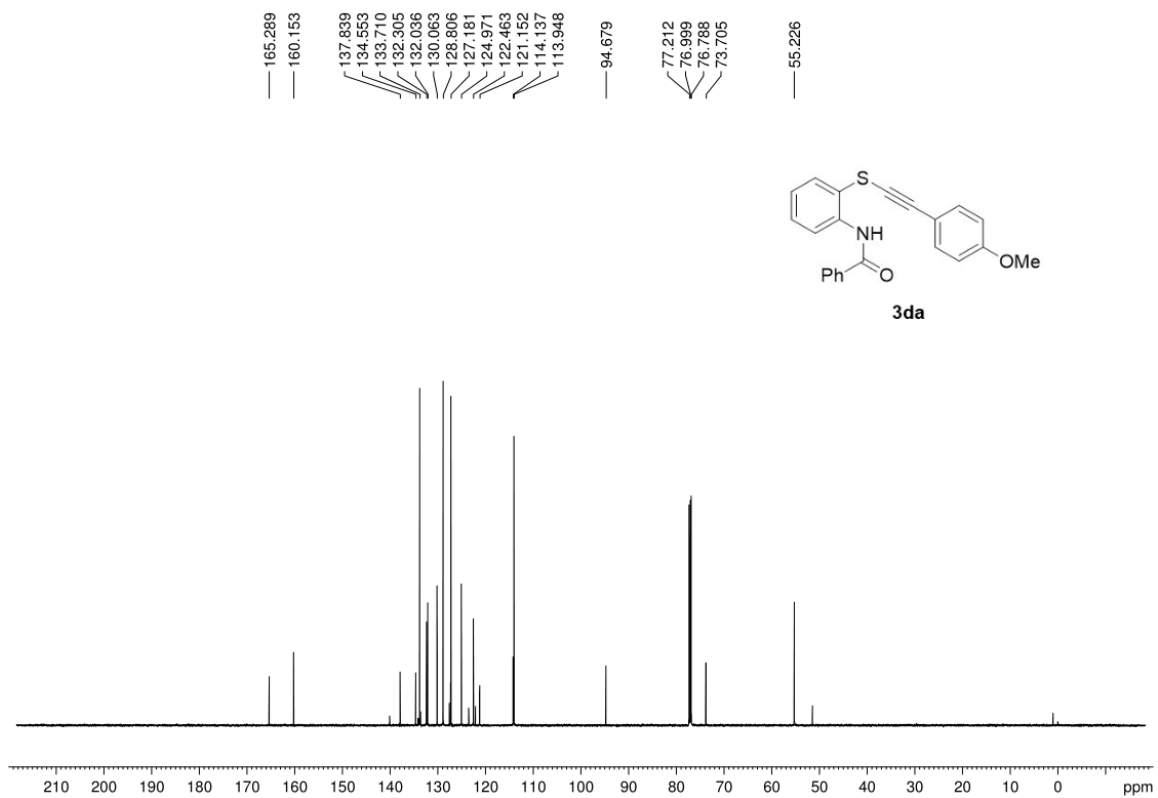
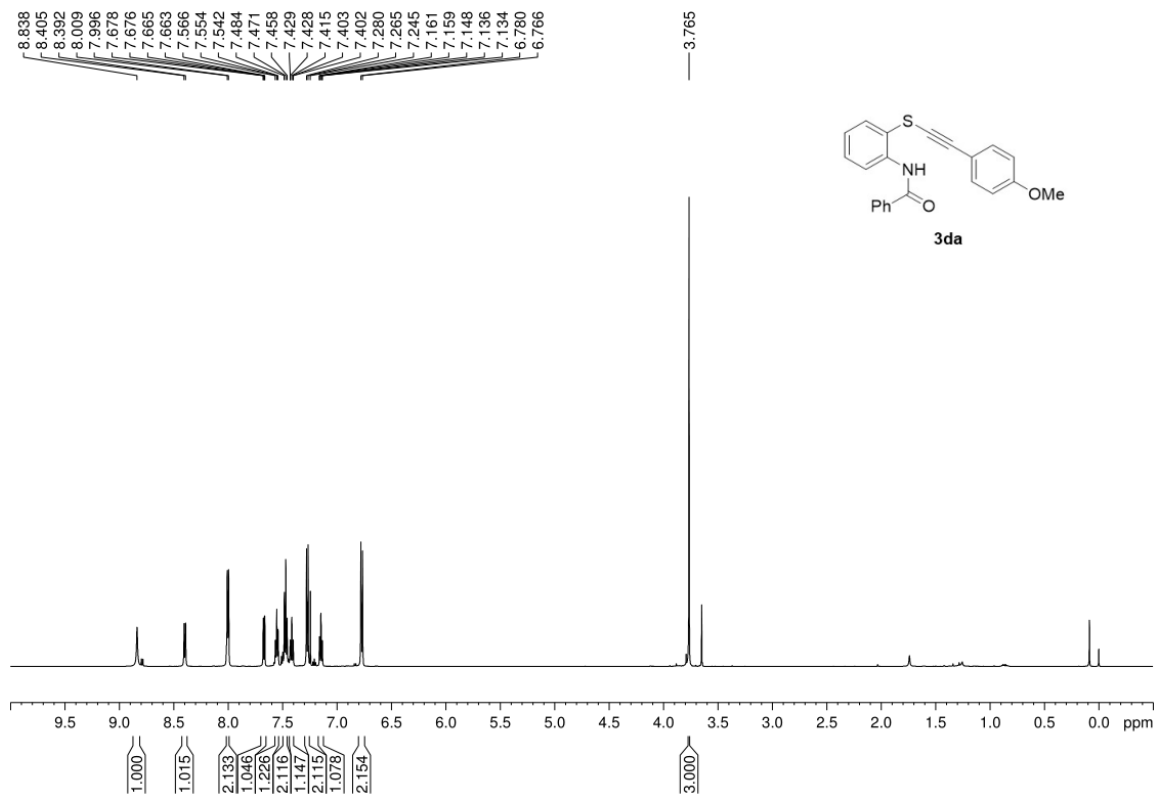


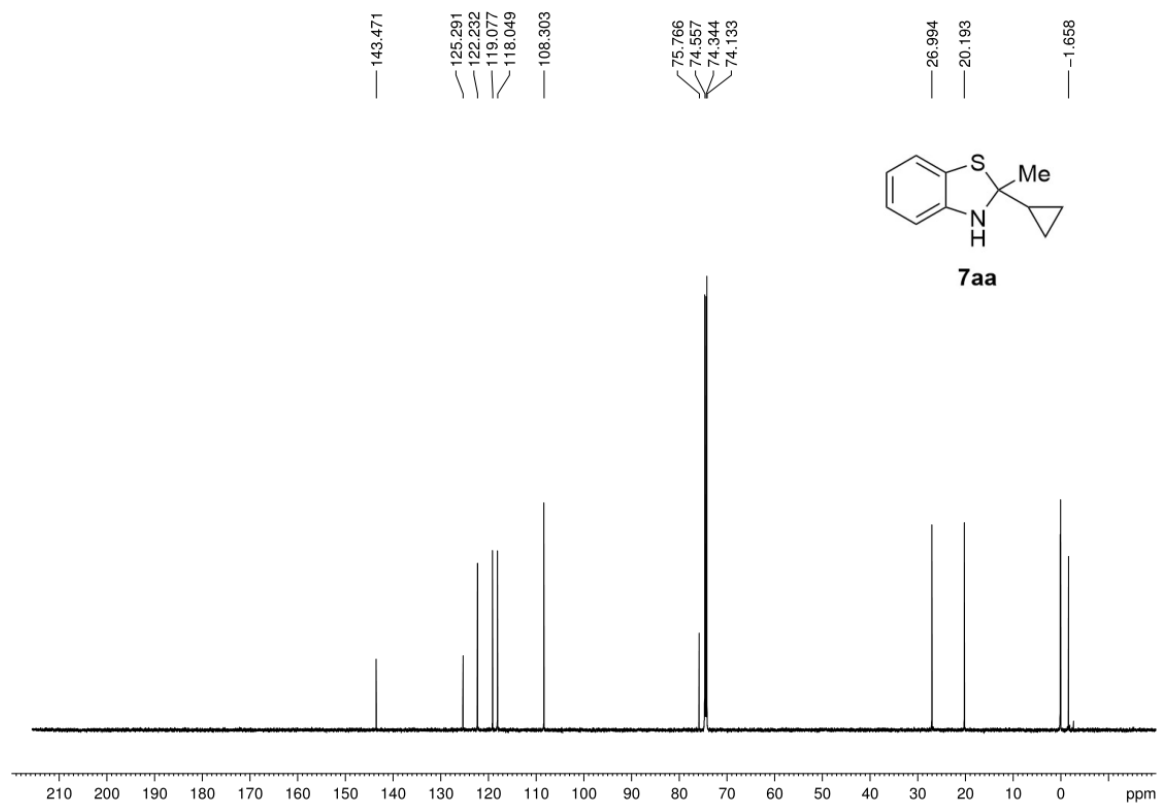
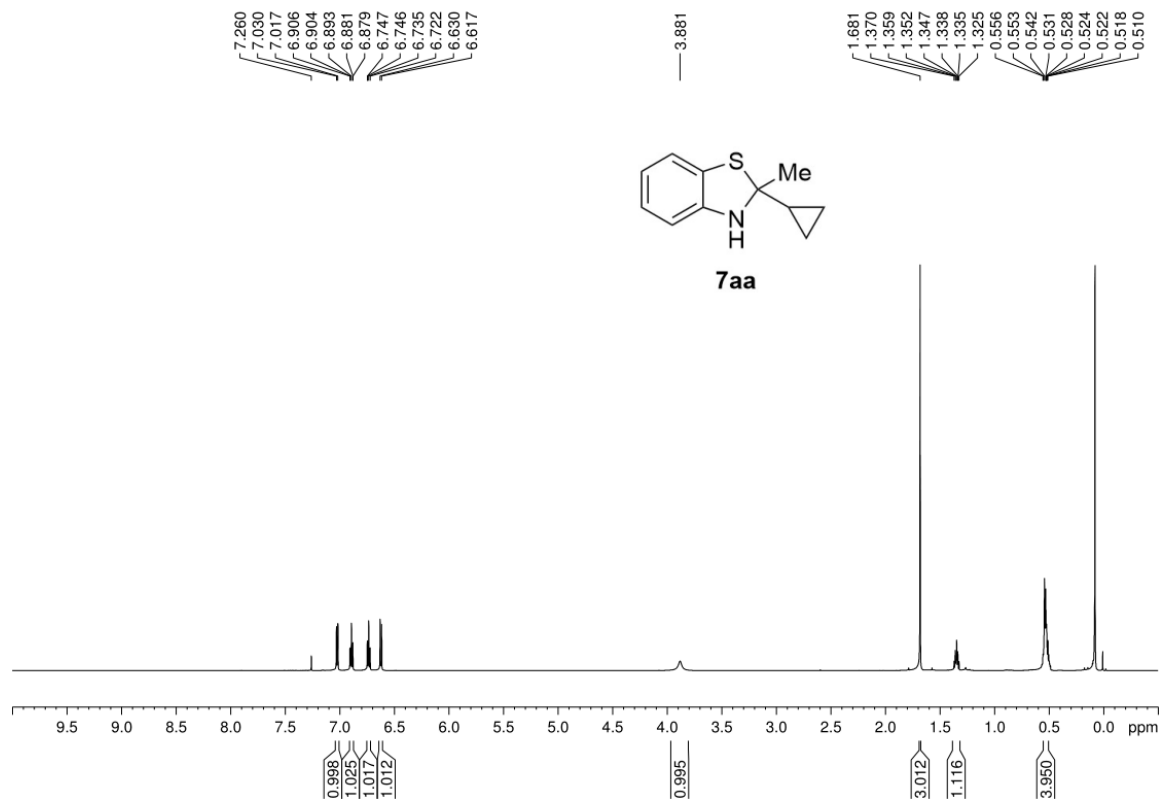


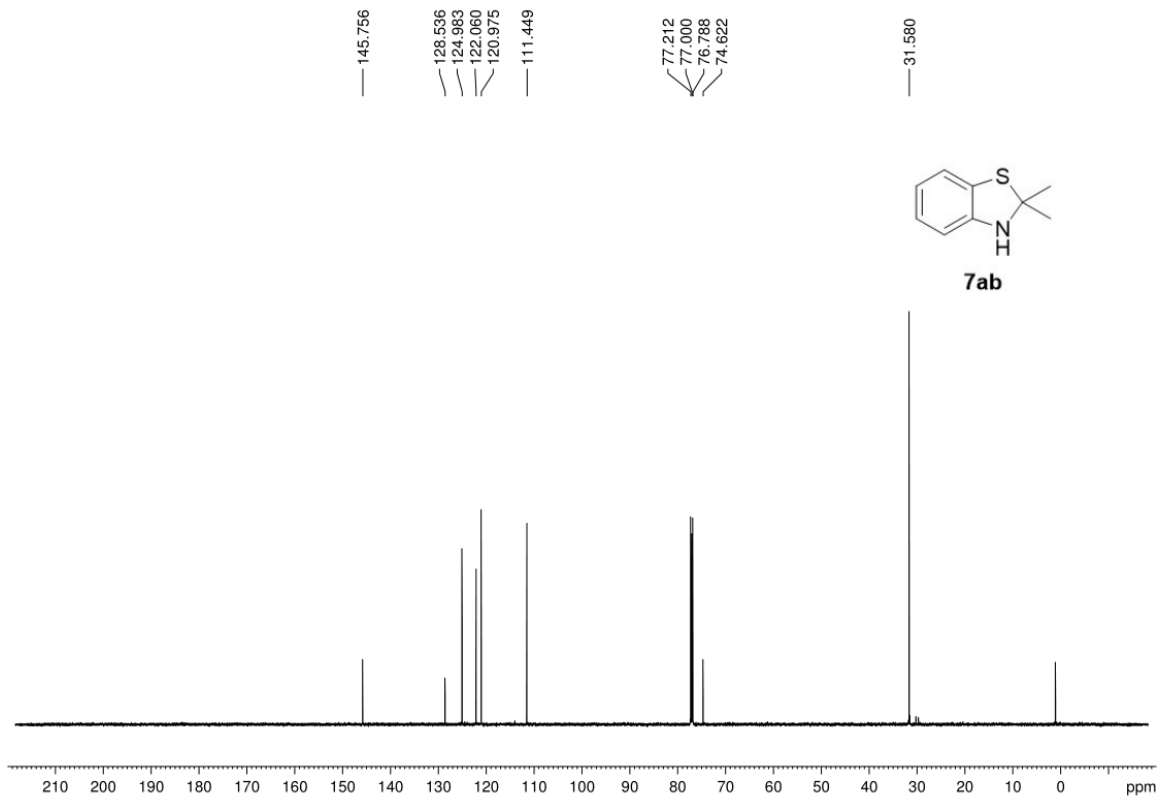
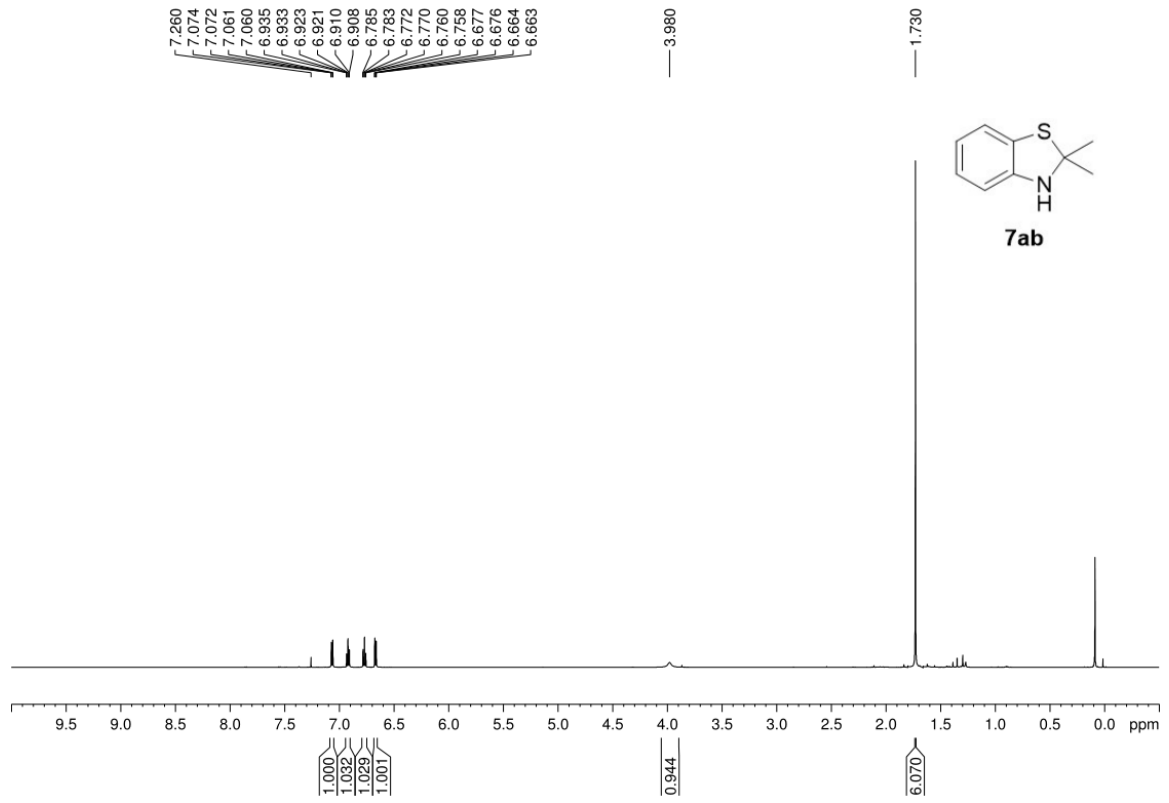


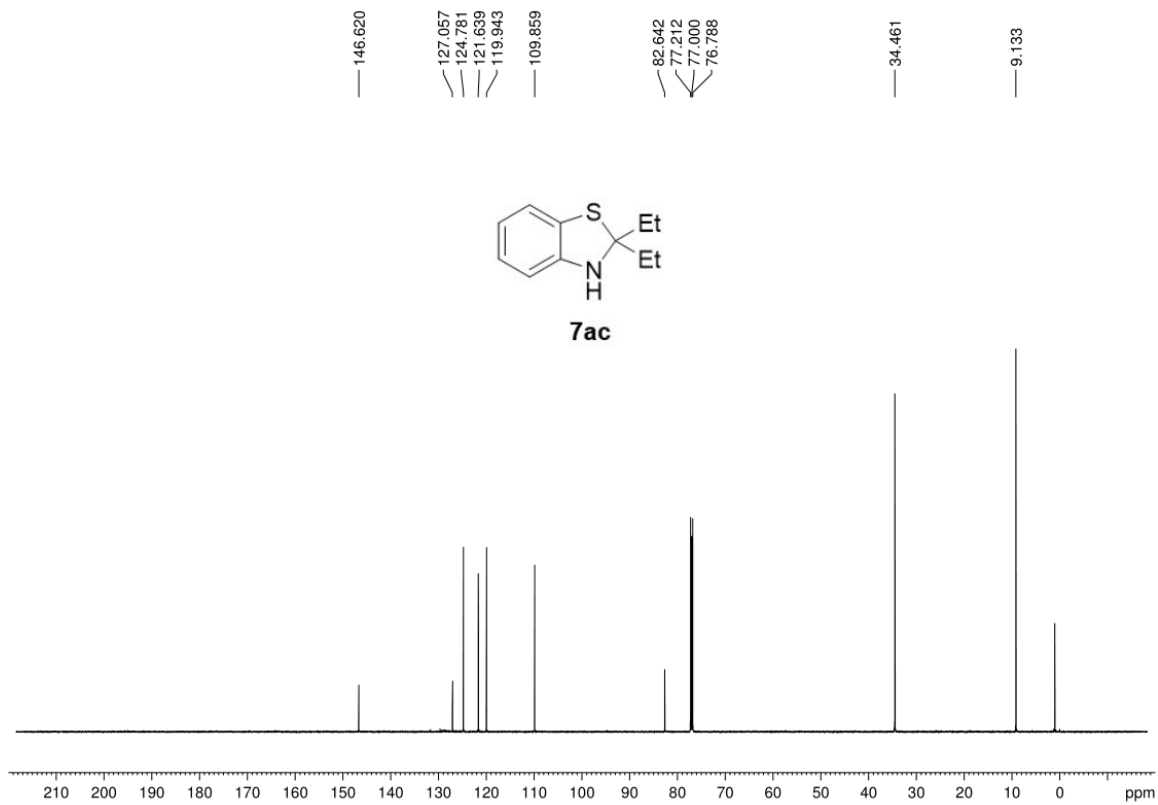
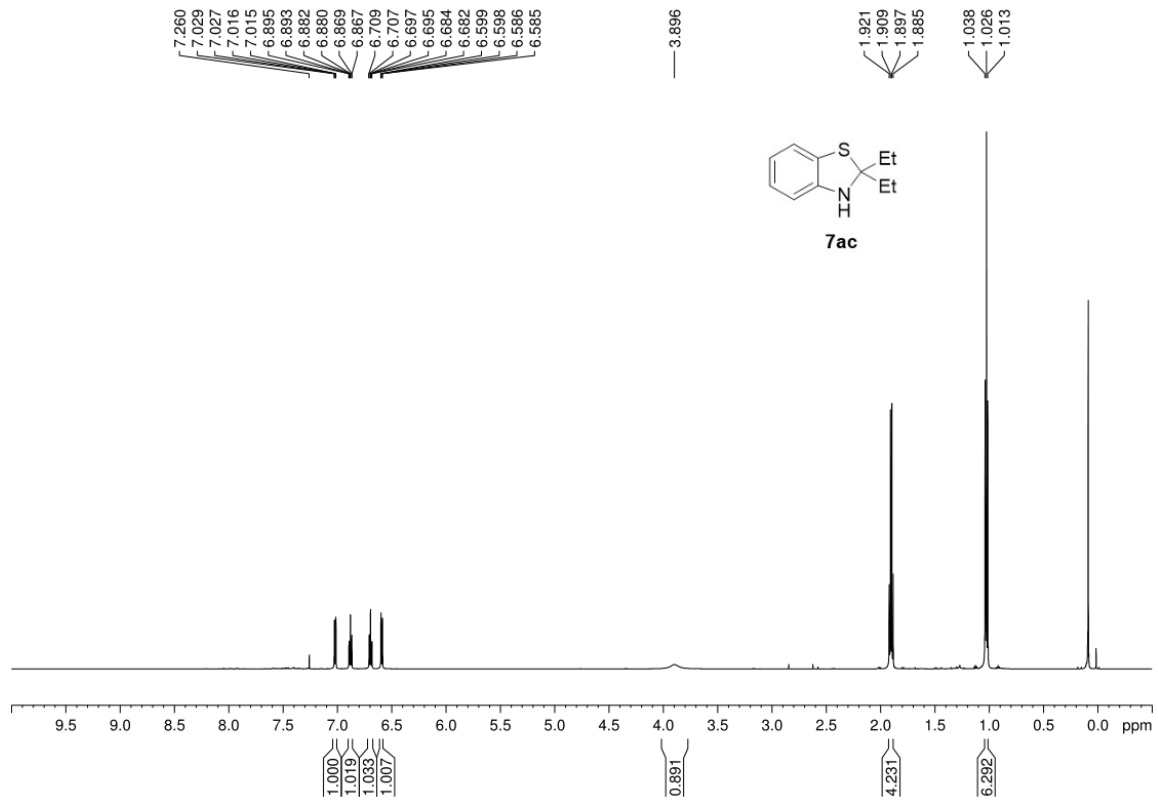


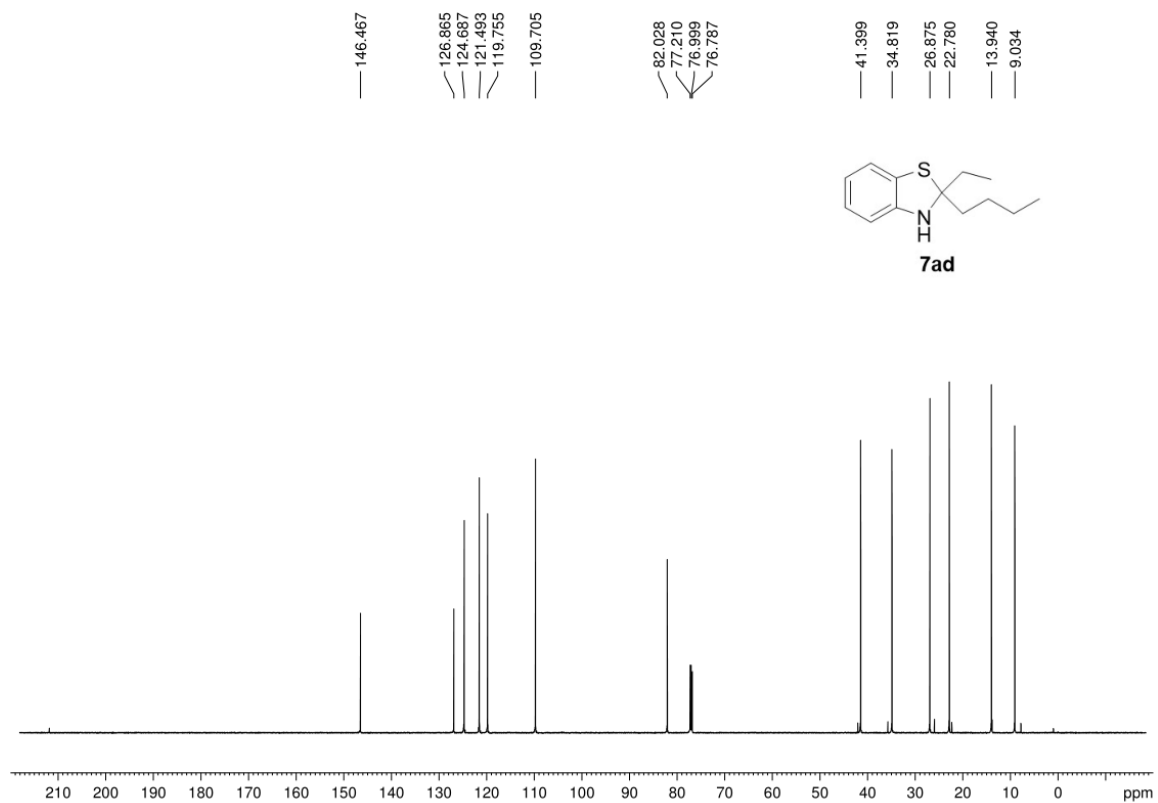
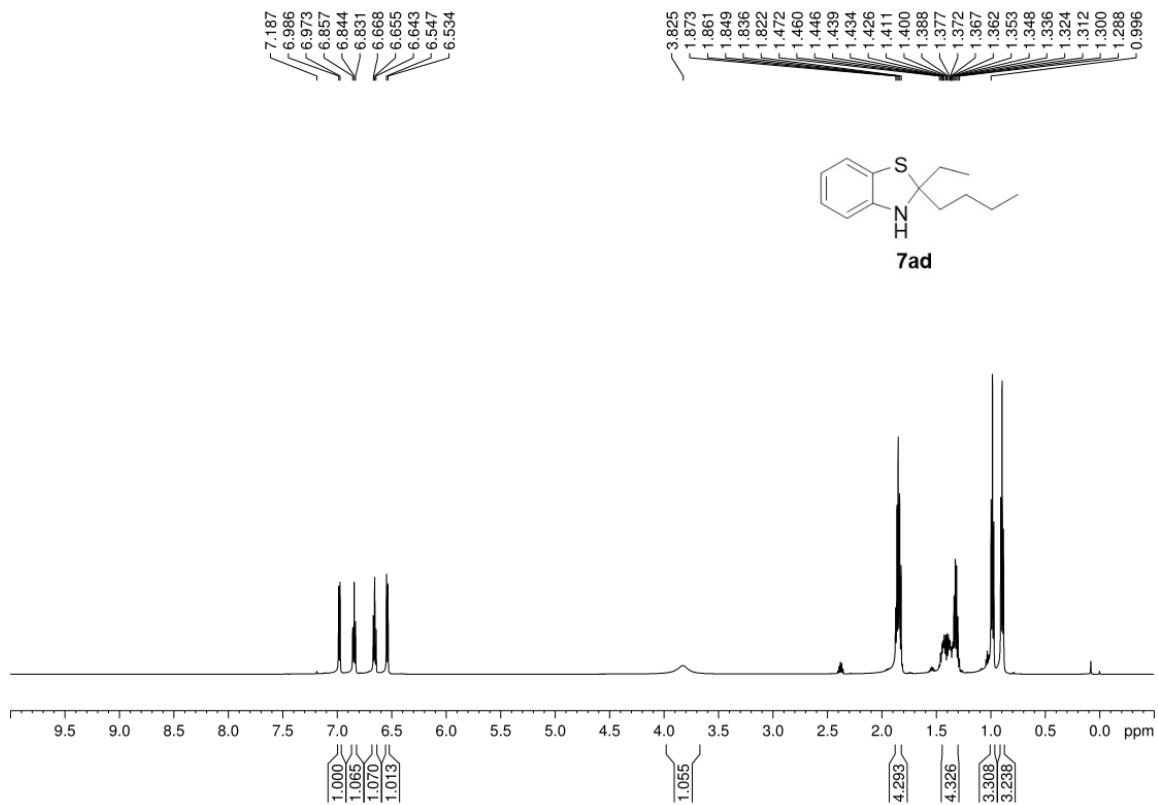


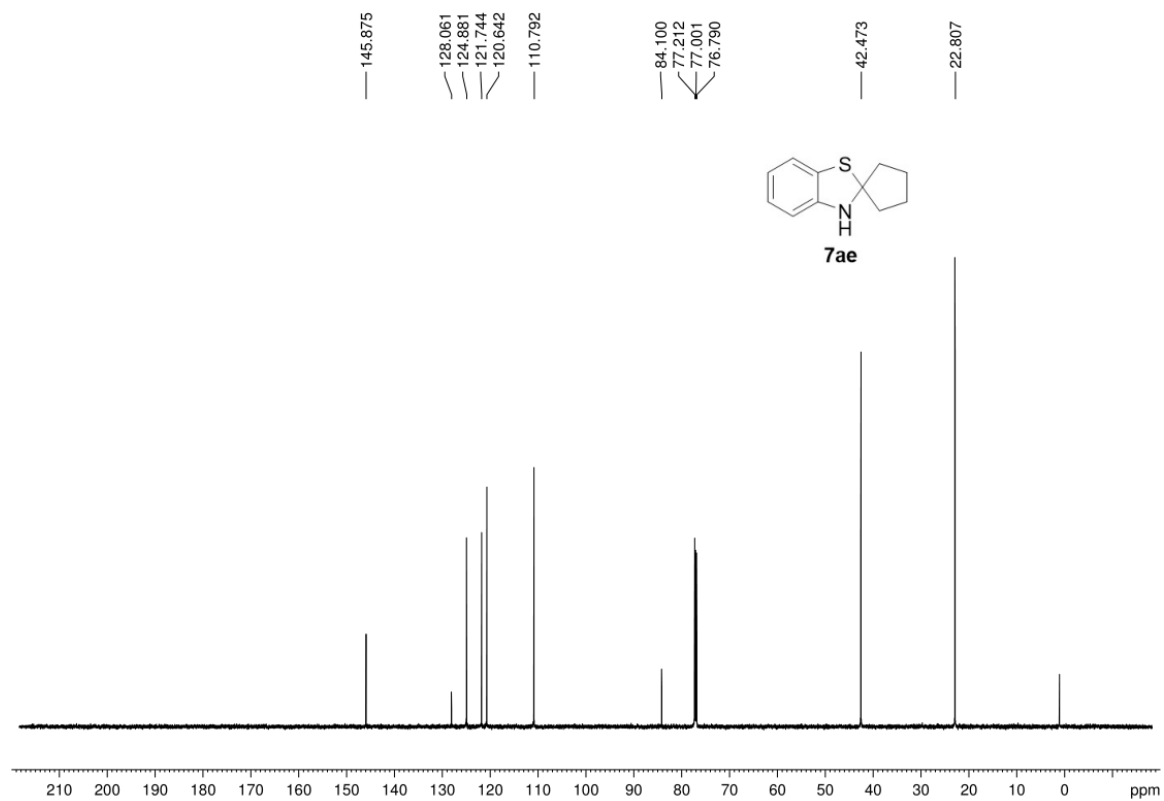
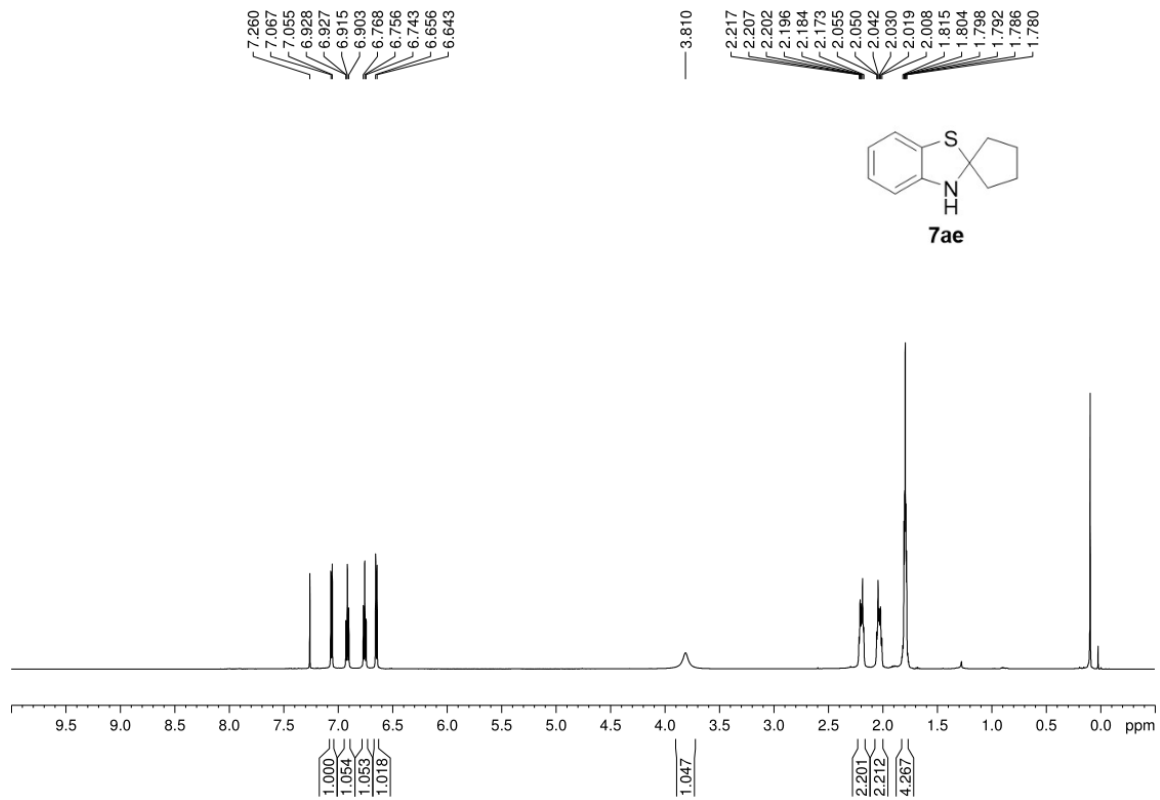


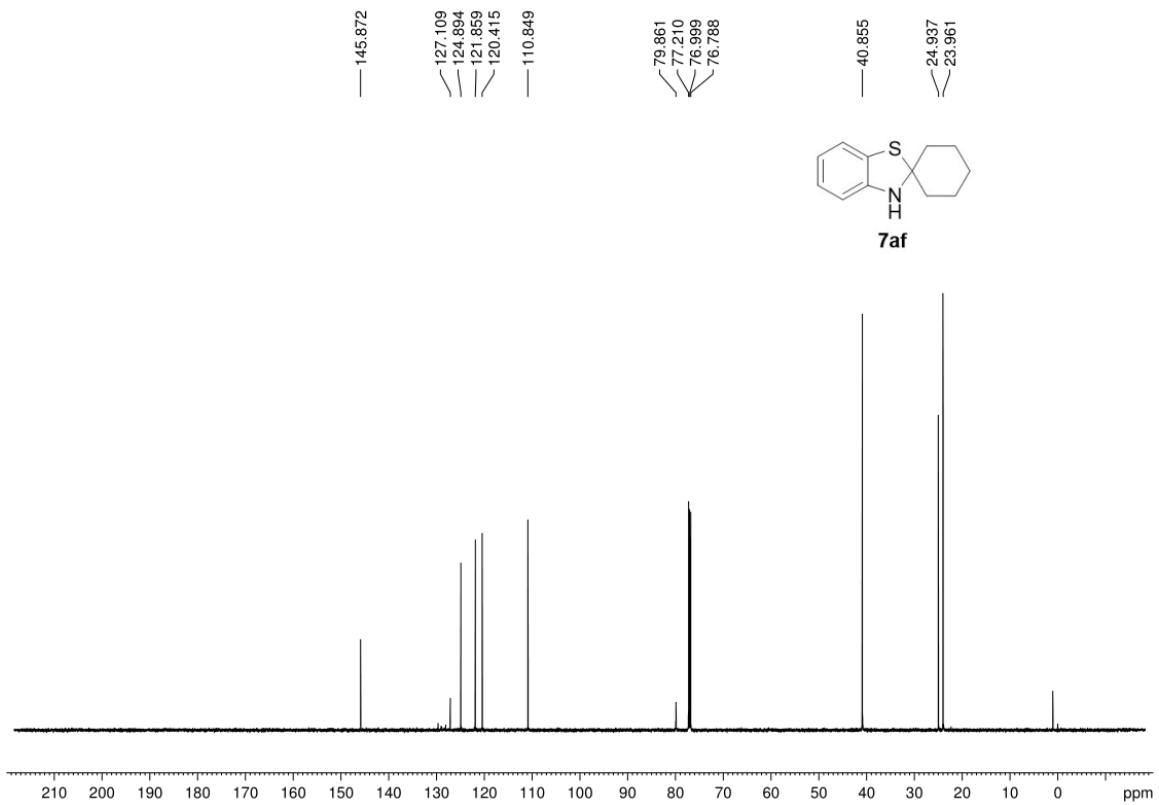
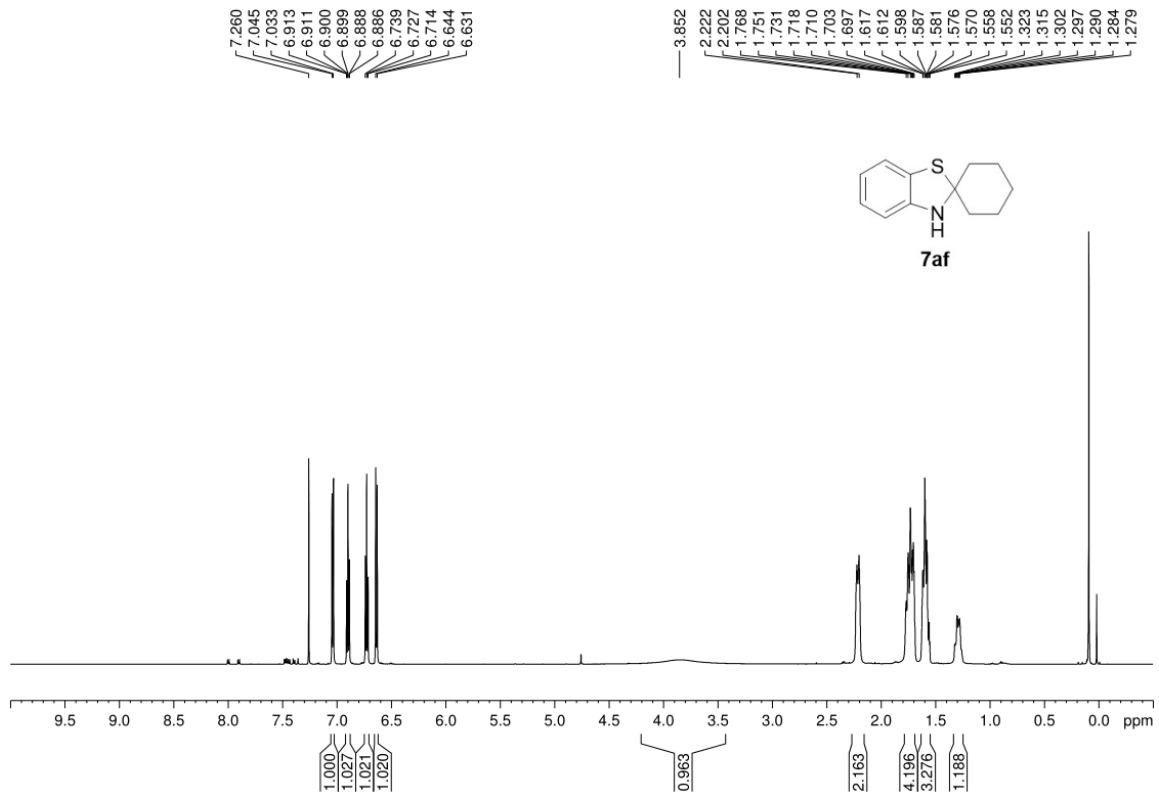


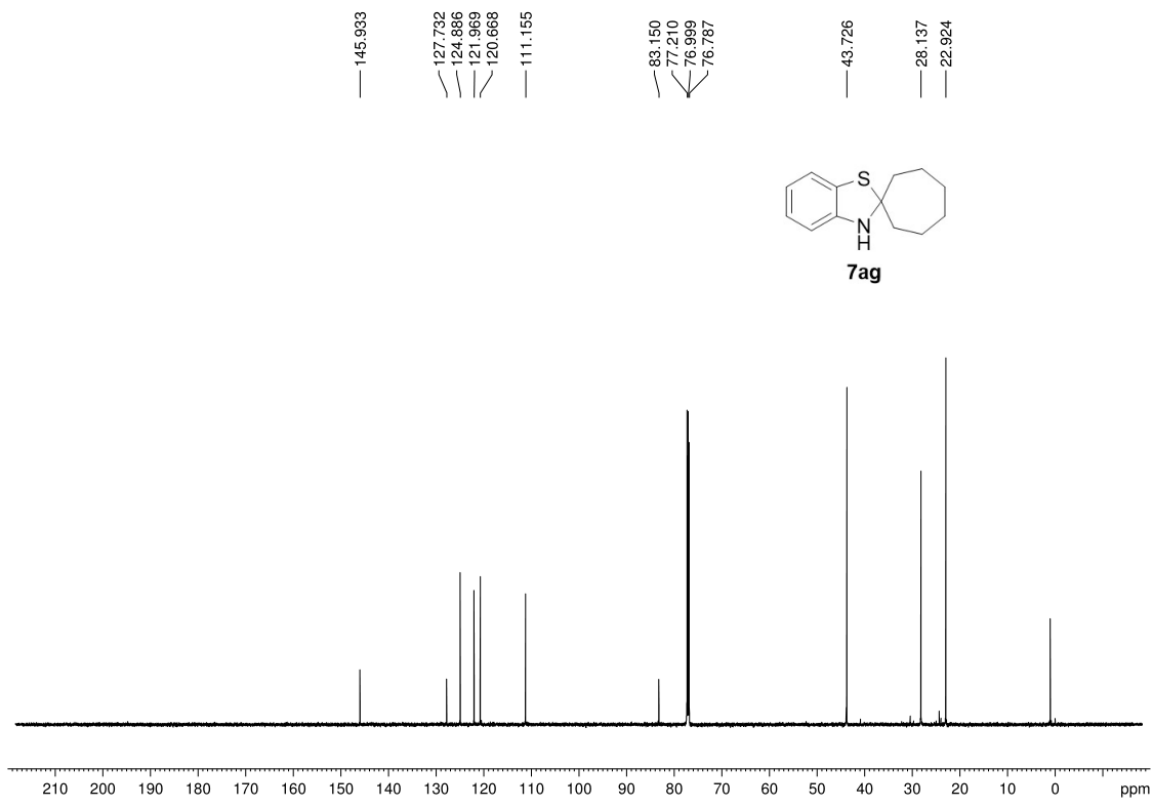
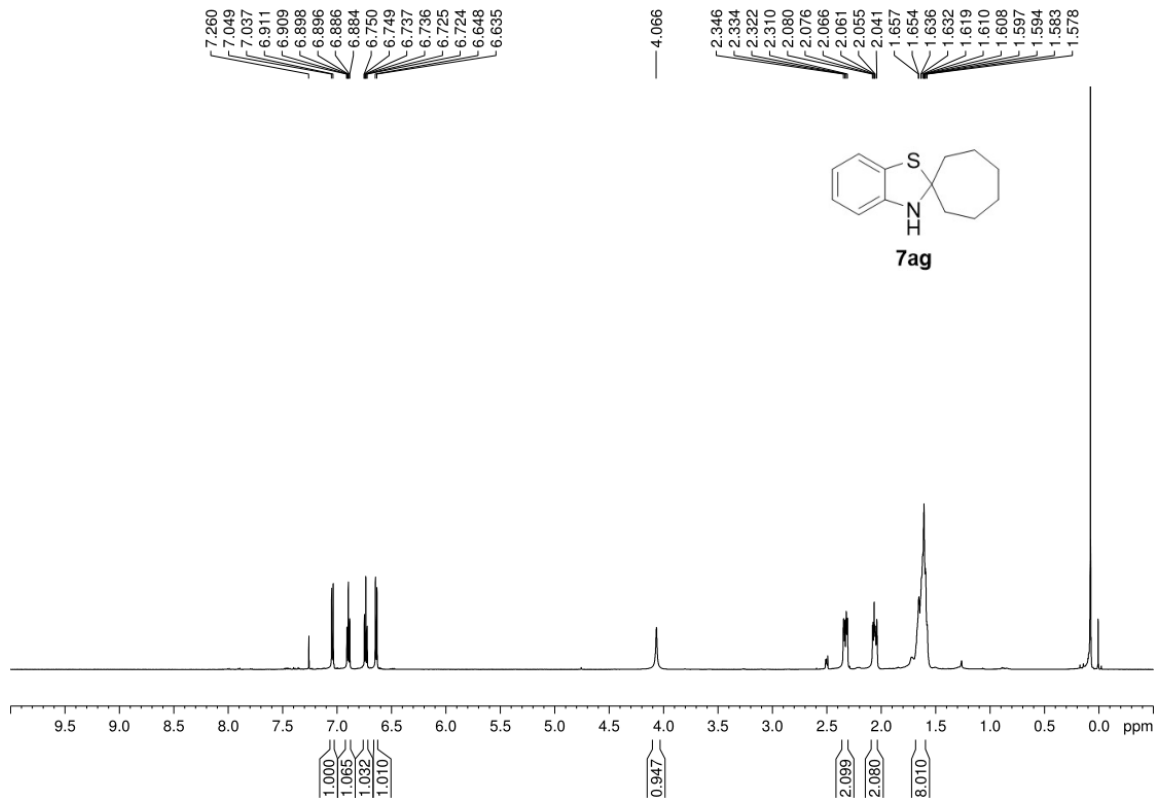












12. References

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2. B. R. Mandapati and A. Ramasamy, *Chem. Commun.*, 2020, **56**, 3781–3784.
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