*Supporting Information for*

# gem-Dialkylthio Vinylallenes: Alkylthio-Regulated Reactivity and Application in the Divergent Synthesis of Pyrroles and Thiophenes

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## Contents

Table of contents .....S1

**I.** General information.....S2

**II.** Synthesis and spectra data of vinylallenes **2a** and **2b1**.....S2-S6

**III.** Synthesis and spectra data of pyrroles **3a**.....S6-S15

**IV.** Synthesis and spectra data of thiophenes **3c**.....S15-S18

**V.** Crystallography of **3a8, 3a26** and **3c2**……..……S19-S22

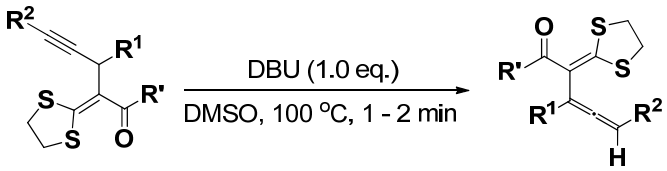
**VI.** Computational details.....S23-S27

# I. General information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. $^{1}$H-NMR and $^{13}$C-NMR spectra were recorded at 25 ºC on a Varian 500 MHz and 125 MHz, respectively, and TMS was used as internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on Bruck microTof by using ESI method.

# II. Synthesis and spectra data of dialkylthio vinylallenes **2a** and **2b1**

**Table S1** Synthesis of dialkylthio vinylallenes.



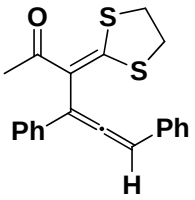

**1a1** **2a1**

| Entry | Yield (%)[a] | Entry | Yield (%) [a] |
|---|---|---|---|
| **2a1** | 95 | **2a7** | 97 |
| **2a2** | 95 | **2a8** | 94 |
| **2a3** | 96 | **2a9** | 96 |
| **2a4** | 93 | **2a10** | 98 |
| **2a5** | 97 | **2a11** | 98 |
| **2a6** | 95 | **2b1** | 91 |

[a] Isolated yield.

**Typical synthetic procedure** (with **2a1** as an example): To the mixture of **1a1** (350 mg, 1.0 mmol) in DMSO (1.0 mL) was added 1,8-diazabicyclo[5.4.0.]undec-7-ene (DBU) (0.152 mL, 1.0 mmol) in one portion at room temperature. The reaction mixture was heated to 100 °C and stirred for 1-2 min, until the substrate **1a1** was consumed as indicated by TLC. The resulting mixture was cooled to room temperature and poured into ice-water (50 mL) under stirring. The precipitated solid was collected by filtration, washed with water (3 × 10 mL), and dried in vacuo to afford the crude product, which was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate = 15 : 1, V/V) to give **2a1** (332 mg, 95%).

**Figure S1. 2a1** can be prepared on a multigram-scale in a one-pot operation and is stable under ambient conditions.




(**2a1**) Yellowish solid, m.p. 132-133 $^{o}$C; **$^{1}$H-NMR** (500 MHz, $CDCl_3$) δ 7.43-7.36 (m, 4H), 7.35-7.30 (m, 4H), 7.27-7.23 (m, 2H), 6.64 (s, 1H), 3.50-3.41 (m, 2H), 3.31-3.23 (m, 2H), 2.21 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 207.2, 193.5, 166.0, 134.3, 133.2, 128.9, 128.8, 127.7, 127.5, 127.4, 126.0, 119.3, 111.0, 97.9, 39.6, 35.5, 27.8; **HRMS** (ESI) m/z calculated for $C_{21}H_{19}OS_2$ $[M+H]^+$: 351.0877, found 351.0883.

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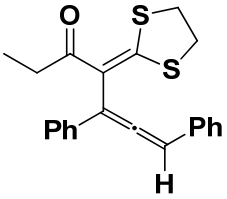


(**2a2**) Yellow solid, m.p. 90-91 $^{o}$C; **$^{1}$H-NMR** (500 MHz, $CDCl_3$) δ 7.43-7.41 (m, 2H), 7.39-7.37 (m, 2H), 7.35-7.32 (m, 4H), 7.27-7.23 (m, 2H), 6.63 (s, 1H), 3.49-3.41 (m, 2H), 3.31-3.23 (m, 2H), 2.62-2.48 (m, 2H), 1.04 (t, J=7.5 Hz, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) 207.3, 196.3, 165.4, 134.3, 133.2, 128.8, 128.7, 127.7, 127.5, 127.4, 126.0, 119.0, 110.5, 97.9, 39.5, 35.4, 32.8, 8.3; **HRMS** (ESI) m/z calculated for $C_{22}H_{21}OS_2$ $[M+H]^+$: 365.1034, found 365.1038.

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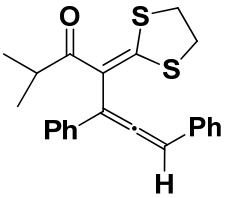


(**2a3**) White solid, m.p. 117-118 $^{o}$C; **$^{1}$H-NMR** (500 MHz, $CDCl_3$) δ 7.44-7.40 (m, 2H), 7.39-7.36 (m, 2H), 7.33 (t, *J* = 7.5 Hz, 4H), 7.28-7.22 (m, 2H), 6.65 (s, 1H), 3.49-3.41 (m, 2H), 3.31-3.23 (m, 2H), 3.11-3.01 (m, 1H), 1.00 (dd, *J* = 6.5 Hz, 6H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 207.3, 200.3, 166.8, 134.6, 133.2, 128.8, 128.7, 127.8, 127.58, 127.5, 126.0, 118.5, 110.7, 98.1, 39.6, 36.2, 35.4, 19.7, 19.1; **HRMS** (ESI) m/z calculated for $C_{23}H_{23}OS_2$ $[M+H]^+$: 379.1190, found 379.1188.

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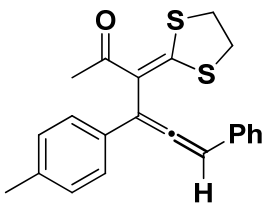

(**2a4**) Yellow solid, m.p. 98-99 °C. **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.42-7.38 (m, 2H), 7.35-7.30 (m, 2H), 7.28-7.21 (m, 3H), 7.14 (d, *J* = 8.0 Hz, 2H), 6.62 (s, 1H), 3.49-3.40 (m, 2H), 3.30-3.22 (m, 2H), 2.34 (s, 3H), 2.21 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 206.8, 193.6, 165.8, 137.7, 133.3, 131.1, 129.6, 128.7, 127.4, 127.3, 125.9, 119.4, 110.8, 97.8, 39.6, 35.5, 27.8, 21.1; **HRMS** (ESI) m/z calculated for $C_{22}H_{21}OS_2$ $[M+H]^+$: 365.1034, found 365.1037.

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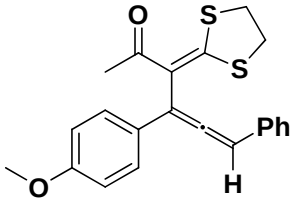


(**2a5**) White solid, m.p. 108-109 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.44-7.40 (m, 2H), 7.37-7.30 (m, 4H), 7.27-7.23 (m, 1H), 6.91-6.87 (m, 2H), 6.62 (s, 1H), 3.81 (s, 3H), 3.49-3.42 (m, 2H), 3.31-3.24 (m, 2H), 2.23 (s, 1H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 206.5, 193.6, 165.7, 159.3, 133.5, 128.7, 127.4, 127.3, 127.2, 126.3, 119.5, 114.3, 110.5, 97.8, 55.2, 39.6, 35.5, 27.7; **HRMS** (ESI) m/z calculated for $C_{22}H_{21}O_2S_2$ $[M+H]^+$: 381.0983, found 381.0985.

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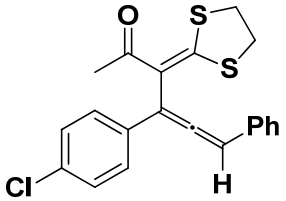


(**2a6**) White solid, m.p. 153-154 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.53-7.49 (m, 2H), 7.48-7.43 (m, 2H), 7.43-7.41 (m, 4H), 7.39-7.35 (m, 1H), 6.77 (s, 1H), 3.60-3.53 (m, 2H), 3.43-3.37 (m, 2H), 2.32 (s, 1H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 207.1, 193.1, 166.5, 133.4, 132.7, 129.0, 128.8, 127.7, 127.4,127.2, 118.7, 110.0, 98.2, 39.6, 35.5, 27.7; **HRMS** (ESI) m/z calculated for $C_{21}H_{18}ClOS_2$ $[M+H]^+$: 385.0488, found 385.0487.

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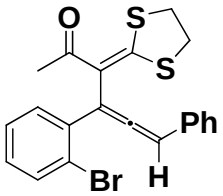


(**2a7**) Yellow solid, m.p. 231-232 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.65-7.61 (m, 1H), 7.46-7.42 (m, 2H), 7.35 (t, *J* = 7.5 Hz, 2H), 7.29-7.23 (m, 3H), 7.14-7.09 (m, 1H), 6.50 (s, 1H), 3.50-3.39 (m, 2H), 3.34-3.28 (m, 2H), 2.18 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 207.2, 193.6, 166.1, 135.0, 134.2, 132.5, 129.4, 128.8, 128.5, 128.3, 127.59, 127.5, 122.5, 121.1, 109.5, 97.7, 39.5, 35.6, 27.9.

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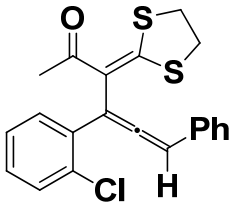


(**2a8**) Pale-yellow solid, m.p. 108-109 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.43 (t, *J* = 7.5 Hz, 3H), 7.34 (t, *J* = 7.5 Hz, 2H), 7.27-7.17 (m, 4H), 6.46 (s, 1H), 3.49-3.39 (m, 2H), 3.34-3.28 (m, 2H), 2.18 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 207.8, 193.4, 166.0, 133.3, 133.0, 132.7, 130.8, 129.2, 128.6, 128.5, 128.0, 127.4, 127.0, 121.0, 107.7, 97.0, 39.6, 35.6, 27.8; **HRMS** (ESI) m/z calculated for $C_{21}H_{18}ClOS_2$ $[M+H]^+$: 385.0488, found 385.0487.

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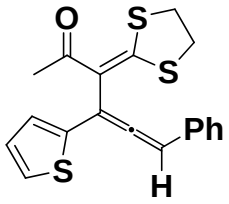


(**2a9**) White solid, m.p. 135-136 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.40 (d, *J* = 8.0 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.27-7.21 (m, 2H), 6.99-6.96 (m, 1H), 6.90 (d, *J* = 3.5 Hz, 1H), 6.63 (s, 1H), 3.47-3.41 (m, 2H), 3.31-3.24 (m, 2H), 2.28 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 206.2, 193.1, 166.6, 139.3, 132.9, 128.7, 127.8, 127.6, 125.7, 124.7, 119.5, 106.3, 98.1, 39.6, 35.6, 27.5; **HRMS** (ESI) m/z calculated for $C_{20}H_{21}OS_3$ $[M+H]^+$: 373.0755, found 373.0753.

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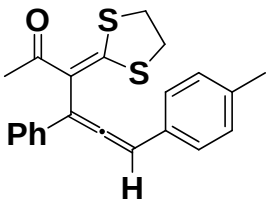


(**2a10**) White solid, m.p. 182-183 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.26 (d, *J* = 7.5 Hz, 2H), 7.22-7.17 (m, 4H), 7.12 (t, *J* = 7.5 Hz, 1H), 7.02 (d, *J* = 7.5 Hz, 2H), 6.51 (s, 1H), 3.27 (t, *J* = 6.0 Hz, 2H), 3.09 (t, *J* = 6.0 Hz, 2H), 2.21 (s, 3H), 2.09 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 206.8, 193.2, 165.8, 137.2, 134.2, 129.9, 129.3, 128.7, 127.5, 127.1, 125.8, 119.2, 110.6, 97.6, 39.4, 35.3, 27.6, 21.0; **HRMS** (ESI) m/z calculated for $C_{22}H_{21}OS_2$ $[M+H]^+$: 365.1034, found 365.1037.

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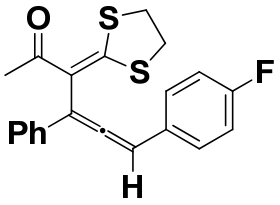


(**2a11**) Brown solid, m.p. 233-234 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ7.31-7.40 (m, 6H), 7.26 (t, *J* = 6.5 Hz, 1H), 7.02 (t, *J* = 8.5 Hz, 2H), 6.61 (s, 1H), 3.45 (t, *J* = 6.5 Hz, 2H), 3.27 (t, *J* = 6.5 Hz, 2H), 2.17 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125

MHz) δ 206.8, 193.4, 166.0, 163.1, 163.1 ($^1J_{CF}$ = 247.0 Hz), 161.1 ($^1J_{CF}$ = 247.0 Hz), 134.1, 129.1 ($^4J_{CF}$ = 3.2 Hz), 128.96 ($^3J_{CF}$ = 8.1 Hz), 128.9, 128.8 ($^3J_{CF}$ = 8.1 Hz), 127.8, 126.0, 119.2, 115.8 ($^2J_{CF}$ = 21.8 Hz), 115.7 ($^2J_{CF}$ = 21.8 Hz), 111.1, 96.9, 39.6, 35.5, 27.7; **HRMS** (ESI) m/z calculated for $C_{21}H_{18}FOS_2$ $[M+1]^+$: 369.0783 found: 369.0784.

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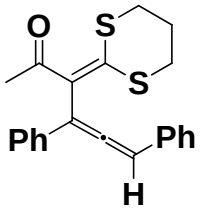


(**2b1**) White solid, m.p. 153-154 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.42 (d, *J* = 7.5 Hz, 2H), 7.38-7.29 (m, 6H), 7.27-7.22 (m, 2H), 6.63 (s, 1H), 2.98-2.81 (m, 4H), 2.20 (s, 3H), 2.18-2.15 (m, 2H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 207.8, 194.0, 161.7, 134.4, 133.2, 128.8, 128.7, 127.6, 127.5, 127.4, 125.9, 109.1, 97.7, 29.8, 29.0, 23.9; **HRMS** (ESI) m/z calculated for $C_{22}H_{21}OS_2$ $[M+H]^+$: 365.1034, found 365.1038.

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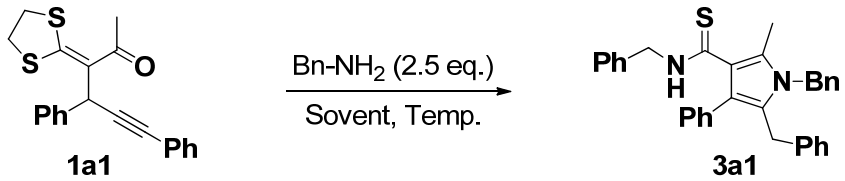
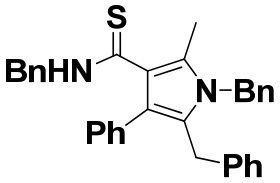
## **III.** Synthesis and spectra data of pyrroles **3a**

**Table S2** Condition optimization.




| Entry | Solvent | Temp. (°C) | Time (h) | Yield (%) [a] |
|---|---|---|---|---|
| 1 | DMSO | 100 | 5 | 85 |
| 2 | DMSO | 80 | 12 | 80 |
| 3 | DMSO | 60 | 12 | Trace |
| 4 | 1,4-Dioxane | 100 | 12 | 70 |
| 5 | Toluene | 100 | 12 | 62 |
| 6 | Methanol | 100 | 12 | NR |

[a] Isolated yield.




(**3a1**) White solid, m.p. 144-145 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.35-7.30 (m, 4H), 7.29-7.23 (m, 4H), 7.22-7.18 (m, 3H), 7.18-7.12 (m, 3H), 6.97 (d, *J* = 7.0 Hz, 2H), 6.87 (d, *J* = 7.0 Hz, 2H), 6.83 (t, *J* = 4.0 Hz, 1H), 6.74 (d, *J* = 7.0 Hz, 2H), 4.84 (s, 2H), 4.63 (d, *J* = 4.0 Hz, 2H), 3.78 (s, 2H), 2.57 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 193.1, 139.1, 136.9, 136.1, 134.9, 133.5, 129.9, 128.8, 128.5, 128.0, 127.7, 127.5, 127.3, 127.1, 126.7, 126.3, 125.5, 122.5, 120.3, 50.4, 47.2, 30.2, 11.8; **HRMS** (ESI) m/z calculated for $C_{33}H_{31}N_2S$ $[M+H]^+$: 487.2208, found 487.2203.

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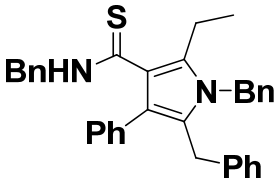


(**3a2**) White solid, m.p. 148-149 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.34-7.27 (m, 6H), 7.27-7.23 (m, 2H), 7.23-7.17 (m, 3H), 7.17-7.12 (m, 3H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.87 (d, *J* = 7.0 Hz, 3H), 6.73 (d, *J* = 7.5 Hz, 2H), 4.86 (s, 2H), 4.64 (d, *J* = 4.5 Hz, 2H), 3.72 (s, 2H), 3.09 (q, *J* = 7.5 Hz, 2H), 1.14 (t, *J* = 7.5 Hz, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 193.3, 139.1, 139.0, 137.4, 136.2, 134.9, 129.9, 128.7, 128.5, 128.0, 127.6, 127.5, 127.2, 126.9, 126.6, 126.2, 125.4, 122.0, 120.4, 50.3, 46.9, 30.1, 18.3, 15.0; **HRMS** (ESI) m/z calculated for $C_{34}H_{33}N_2S$ $[M+H]^+$: 501.2326, found 501.2330.

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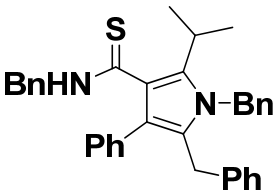


(**3a3**) White solid, m.p. 110-111 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.36-7.31 (m, 4H), 7.31-7.27 (m, 3H), 7.24-7.19 (m, 4H), 7.19-7.13 (m, 3H), 6.97-6.92 (m, 3H), 6.84 (d, *J* = 8.5 Hz, 2H), 6.71 (d, *J* = 7.0 Hz, 2H), 4.93 (s, 2H), 4.62 (d, *J* = 4.5 Hz, 2H), 3.93-3.82 (m, 1H), 3.69 (s, 2H), 1.31 (d, *J* = 7.5 Hz, 6H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 195.5, 139.5, 139.4, 137.9, 136.1, 135.1, 129.5, 128.7, 128.62, 128.6, 128.5, 128.2, 127.7, 127.1, 126.7, 126.4, 126.2, 125.4, 123.2, 120.8, 50.8, 48.0, 30.2, 25.6, 21.9; **HRMS** (ESI) m/z calculated for $C_{34}H_{33}N_2S$ $[M+H]^+$: 513.2364, found 513.2361.

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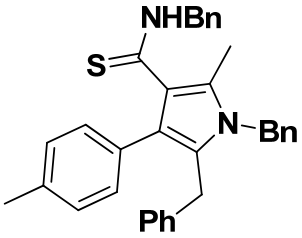


(**3a4**) White solid, m.p. 164-165 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.24-7.12 (m, 9H), 7.09 (d, *J* = 7.5 Hz, 2H), 6.96 (d, *J* = 7.0 Hz, 2H), 6.87 (d, *J* = 7.0 Hz, 3H), 6.76 (d, *J* = 7.5 Hz, 2H), 4.84 (s, 2H), 4.63 (d, d, *J* = 4.5 Hz, 2H), 3.76 (s, 2H), 2.58 (s 3H), 2.34 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 192.9, 139.1, 137.0, 136.4, 136.2, 133.6, 131.8, 129.8, 129.4, 128.7, 128.5, 128.4, 128.1, 127.7, 127.5, 127.2, 127.0, 126.2, 125.5, 122.3, 120.2, 50.3, 47.2, 30.1, 21.1, 11.9; **HRMS** (ESI) m/z calculated for $C_{34}H_{33}N_2S$ $[M+H]^+$: 501.2364, found 501.2365.

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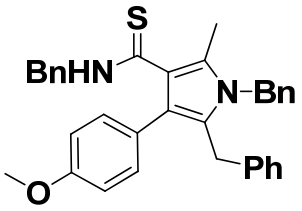


(**3a5**) Pale-yellow solid, m.p. 157-158 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.31-7.27 (m, 2H), 7.25-7.16 (m, 8H), 7.16-7.13 (m, 1H), 6.95 (d, *J* = 7.5 Hz, 2H), 6.90 (t, *J* = 4.5 Hz, 1H), 6.87 (d, *J* = 7.5 Hz, 2H), 6.81 (d, *J* = 8.0 Hz, 4H), 4.84 (s, 2H), 4.64 (d, *J* = 4.5 Hz, 2H), 3.79 (s, 3H), 3.74 (s, 2H), 2.59 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 192.9, 158.6, 139.1, 137.0, 136.2, 133.6, 131.0, 128.7, 128.5, 128.4, 128.1, 127.7, 127.5, 127.2, 127.1, 127.0, 126.2, 125.5, 122.3, 119.7, 114.2, 55.1, 50.3, 47.2, 30.1, 11.9; **HRMS** (ESI) m/z calculated for $C_{34}H_{33}N_2OS$ $[M+H]^+$: 517.2314, found 517.2320.

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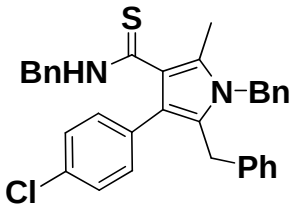


(**3a6**) White solid, m.p. 208-209 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.27-7.19 (m, 10H), 7.15 (t, *J* = 7.5 Hz, 1H), 6.93 (d, *J* = 7.5 Hz, 2H), 6.85 (d, *J* = 7.5 Hz, 2H), 6.81 (d, *J* = 6.5 Hz, 2H), 6.75 (t, *J* = 4.5 Hz, 1H), 4.84 (s, 2H), 4.64 (d, *J* = 4.5 Hz, 2H), 3.75 (s, 2H), 2.55 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 192.9, 138.7, 136.8, 135.9, 133.5, 133.4, 132.7, 131.1, 128.9, 128.8, 128.66, 128.6, 128.1, 127.8, 127.6, 127.3, 127.2, 126.4, 125.5, 122.5, 119.0, 50.4, 47.2, 30.1, 11.7; **HRMS** (ESI) m/z calculated for $C_{33}H_{30}ClN_2S$ $[M+H]^+$: 521.1818, found 521.1821.

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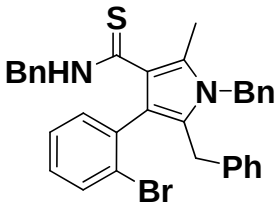


(**3a7**) White solid, m.p. 105-106 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ7.48 (dd, *J* = 8.0, 0.5 Hz, 1H), 7.34 (dd, *J* = 7.5, 1.0 Hz, 1H), 7.32-7.28 (m, 2H), 7.28-7.24 (m, 1H), 7.23-.7.16 (m, 6H), 7.16-7.11 (m, 1H), 7.11-7.06 (m, 1H), 6.94 (d, *J* = 7.0 Hz, 2H), 6.88 (d, *J* = 7.0 Hz, 3H), 6.81 (d, *J* = 7.0 Hz, 2H), 4.85 (AB, *J* = 17.5 Hz, 2H), 4.71 (dd, *J* = 15.0, 5.5 Hz, 1H), 4.56 (dd, *J* = 15.0, 4.0 Hz, 1H), 3.59 (s, 2H), 2.57 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 192.8, 138.5, 137.0, 136.2, 136.0, 133.4, 132.84, 132.8, 129.0, 128.8, 128.5, 128.4, 128.1, 127.9, 127.7, 127.5, 127.3, 126.3, 126.0, 125.4, 122.4, 119.4, 50.2, 47.1, 30.5, 11.9; **HRMS** (ESI) m/z calculated for $C_{33}H_{30}BrN_2S$ $[M+H]^+$: 565.1313, found 567.1292.

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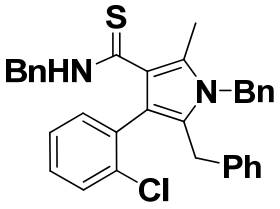


(**3a8**) White solid, m.p. 117-118 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.33 (dd, *J* =6.0, 3.5 Hz, 1H), 7.31-7.27 (m, 3H), 7.25-7.19 (m, 2H), 7.19-7.14 (m, 6H), 7.14-7.10 (m, 1H), 6.94 (d, *J* = 7.5 Hz, 2H), 6.86 (d, *J* = 7.0 Hz, 3H), 6.82 (d, *J* = 7.0 Hz, 2H), 4.86 (AB, *J* = 17.5 Hz, 2H), 4.70 (dd, *J* = 15.0, 5.5 Hz, 1H), 4.60 (dd, *J* = 15.0, 4.0 Hz, 1H), 3.62 (AB, *J* = 17.0 Hz, 2H), 2.57 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 192.7, 138.4, 136.8, 135.9, 135.0, 133.9, 133.3, 132.6, 129.5, 128.7, 128.4, 128.3, 127.9, 127.7, 127.4, 127.1, 126.9, 126.1, 125.2, 122.5, 117.2, 50.1, 47.0, 30.3, 11.8; **HRMS** (ESI) m/z calculated for $C_{33}H_{30}ClN_2S$ $[M+H]^+$: 521.1818, found 521.1815.

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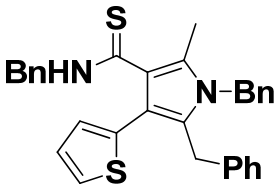


(**3a9**) White solid, m.p. 142-143 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.29 (t, *J* = 7.5 Hz, 2H), 7.25-7.23 (m, 4H), 7.21 (t, *J* = 7.5 Hz, 3H), 7.18-7.13 (m, 2H), 6.98 (d, *J* = 7.5 Hz, 2H), 6.96-6.92 (m, 3H), 6.91 (d, *J* = 3.5 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 2H), 4.85 (s, 2H), 4.70 (d, *J* = 4.5 Hz, 2H), 3.80 (s, 2H), 2.56 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 192.5, 138.6, 136.2, 136.0, 133.8, 129.2, 128.8, 128.6, 128.5, 128.2, 127.8, 127.68, 127.6, 127.4, 127.3, 126.3, 126.1, 125.5, 122.9, 111.9, 50.5, 47.3, 30.3, 12.0; **HRMS** (ESI) m/z calculated for $C_{31}H_{29}N_2S_2$ $[M+H]^+$: 493.1772, found 493.1772.

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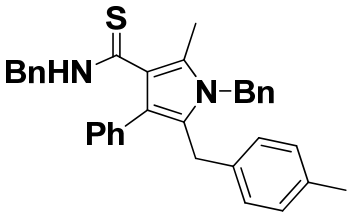


(**3a10**) Yellow solid, m.p. 142-143 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.33-7.27 (m, 6H), 7.26-7.22 (m, 2H), 7.18 (d, *J* = 7.5 Hz, 1H), 7.15 (t, *J* = 7.5 Hz, 2H), 7.01 (d, *J* = 8.0 Hz, 2H), 6.89-6.81 (m, 5H), 6.73 (d, *J* = 7.0 Hz, 2H), 4.84 (s, 2H), 4.62 (d, *J* = 5.0 Hz, 2H), 3.73 (s, 2H), 2.57 (s, 3H), 2.27 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 193.1, 137.0, 136.1, 135.9, 135.7, 134.9, 133.4, 129.9, 129.2, 128.7, 128.5, 128.0, 127.6, 127.5, 127.3, 127.2, 126.6, 125.5, 122.4, 120.1, 50.3, 47.1, 29.7, 20.9, 11.7; **HRMS** (ESI) m/z calculated for $C_{34}H_{33}N_2S$ $[M+H]^+$: 501.2364, found 501.2367.

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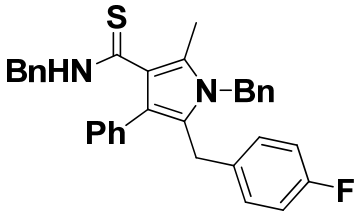


(**3a11**) White solid, m.p. 116-117 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.34-7.29 (m, 4H), 7.29-7.25 (m, 3H), 7.23 (d, *J* = 7.0 Hz, 1H), 7.21-7.17 (m, 1H), 7.15 (t, *J* = 7.5 Hz, 2H), 6.91-6.82 (m, 7H), 6.73 (d, *J* = 7.0 Hz, 2H), 4.84 (s, 2H), 4.62 (d, *J* = 4.5 Hz, 2H), 3.74 (s, 2H), 2.57 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 193.0, 162.2 ($^1J_{CF}$ = 244.7 Hz), 160.3 ($^1J_{CF}$ = 244.7 Hz), 136.7, 134.7, 134.57 ($^4J_{CF}$ = 3.0 Hz), 134.5 ($^4J_{CF}$ = 3.0 Hz), 133.4, 129.8, 129.1 ($^3J_{CF}$ = 8.0 Hz), 129.0 ($^3J_{CF}$ = 8.0 Hz), 128.77, 128.7, 128.4, 127.9, 127.5, 127.2, 126.9, 126.7, 125.4, 122.5, 120.2, 115.3 ($^2J_{CF}$ = 21.4 Hz), 115.1 ($^2J_{CF}$ = 21.4 Hz), 50.3, 47.1, 29.3, 11.7; **HRMS** (ESI) m/z calculated for $C_{33}H_{30}FN_2S$ $[M+H]^+$: 505.2114, found 505.2109.

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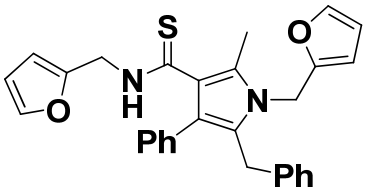


(**3a12**) Yellow solid, m.p. 153-154 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.32 (s, 1H), 7.29-7.22 (m, 6H), 7.17 (t, *J* = 7.5 Hz, 3H), 7.04 (d, *J* = 7.0 Hz, 2H), 6.82 (s, 1H), 6.27 (s, 1H), 6.18 (s, 1H), 6.02 (s, 1H), 5.87 (s, 1H), 4.74 (s, 2H), 4.66, (d, *J* = 4.0 Hz, 2H), 4.00 (s, 2H), 2.68 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 193.0, 149.8, 149.3, 142.4, 142.1, 139.1, 134.4, 133.7, 129.7, 128.64, 128.6, 127.8, 126.9, 126.6, 126.3, 122.2, 120.3, 110.3, 110.2, 107.85, 107.8, 42.5, 40.8, 30.1, 11.9; **HRMS** (ESI) m/z calculated for $C_{29}H_{27}N_2O_2S$ $[M+H]^+$: 467.1793, found 467.1792.

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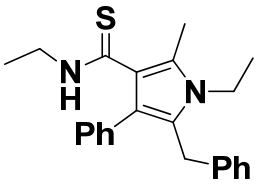

(**3a13**) Pale-yellow solid, m.p. 154-155 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.35-7.28, (m, 4H), 7.27-7.22 (m, 3H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 2H), 6.50 (s, 1H), 3.93 (s, 2H), 3.69 (q, *J* = 7.0 Hz, 2H), 3.51-3.46 (m, 2H), 2.64 (s, 3H), 1.04 (t, *J* = 7.0 Hz, 3H), 0.74 (t, *J* = 7.0 Hz, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 192.7, 139.5, 135.0, 132.5, 129.9, 128.6, 128.5, 127.8, 126.6, 126.29, 126.2, 122.3, 119.8, 40.2, 38.8, 30.3, 15.4, 12.5, 11.7; **HRMS** (ESI) m/z calculated for $C_{23}H_{27}N_2S$ $[M+H]^+$: 363.1895, found 363.1893.

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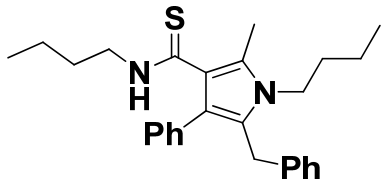


(**3a14**) Yellow solid, m.p. 97-98 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.35-7.28 (m, 4H), 7.28-7.22 (m, 3H), 7.18 (t, *J* = 7.0 Hz, 1H), 7.05 (d, *J* = 7.5 Hz, 2H), 6.59 (s, 1H), 3.92 (s, 2H), 3.58 (t, *J* = 8.0 Hz, 2H), 3.51-3.43 (m, 2H), 2.62 (s, 3H), 1.42-1.32 (m, 2H), 1.25-1.16 (m, 2H), 1.13-1.04 (m, 2H), 0.81 (t, *J* = 7.5 Hz, 3H), 0.74 (t, *J* = 7.0 Hz, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 192.8, 139.5, 135.1, 132.6, 129.9, 128.6, 128.5, 127.8, 126.6, 126.5, 126.2, 122.3, 119.6, 45.2, 44.1, 32.4, 30.4, 29.6, 20.1, 19.8, 13.7, 13.6, 11.8; **HRMS** (ESI) m/z calculated for $C_{27}H_{35}N_2S$ $[M+H]^+$: 419.2521, found, 419.2518.

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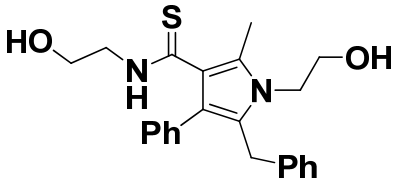


(**3a15**) Yellow solid, m.p. 206-207 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.38-7.30 (m, 4H), 7.29-7.24 (m, 3H), 7.19 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 3H), 3.99 (s, 2H), 3.81 (t, *J* = 6.0 Hz, 2H), 3.70 (dd, *J* = 5.5, 5.5 Hz, 2H), 3.61 (dd, *J* = 5.5, 5.5 Hz, 2H), 3.43 (dd, *J* = 5.5, 5.5 Hz, 2H), 2.65 (s, 3H), 1.88 (t, *J* = 5.5 Hz, 1H), 1.15 (t, *J* = 5.5 Hz, 1H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 194.2, 139.3, 135.1, 132.7, 129.8, 128.6, 128.5, 127.8, 127.2, 126.6, 126.3, 123.1, 119.9, 61.5, 60.5, 47.2, 46.0, 30.2, 11.9; **HRMS** (ESI) m/z calculated for $C_{23}H_{27}N_2O_2S$ $[M+H]^+$: 395.1793, found 395.1794.

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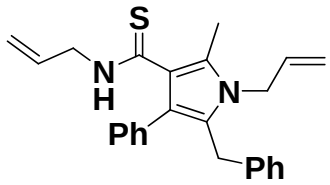


(**3a16**) Yellow solid, m.p. 104-105 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.36-7.28 (m, 4H), 7.28-7.22 (m, 3H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.5 Hz, 2H), 6.62 (s, 1H), 5.74-5.63 (m, 1H), 5.49-5.46 (m, 1H), 5.09 (d, *J* = 10.5 Hz, 1H), 4.93 (d, *J* = 10.5 Hz, 1H), 4.82 (t, *J* = 16.0 Hz, 2H), 4.24 (d, *J* = 2.0 Hz, 2H), 4.10 (t, *J* = 5.5 Hz, 2H), 3.90 (s, 2H), 2.59 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 193.1, 139.2, 134.8, 133.4, 132.7, 131.9, 129.8, 128.6, 128.5, 127.8, 126.7, 126.2,

122.3, 119.9, 117.7, 116.4, 48.0, 46.2, 30.1, 11.6; **HRMS** (ESI) m/z calculated for $C_{25}H_{27}N_2S$ $[M+H]^+$: 387.1895, found 387.1892.

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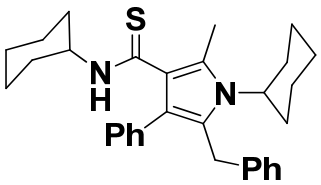


(**3a17**) White solid, m.p. 180-181 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.34-7.28 (m, 4H), 7.26-7.20 (m, 3H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.52 (d, *J* = 8.0 Hz, 1H), 4.32-4.22 (m, 1H), 3.90 (s, 2H), 3.87-3.78 (m, 1H), 2.71 (s, 3H), 1.93-1.77 (m, 2H), 1.73-1.65 (m, 4H), 1.61-1.42 (m, 6H), 1.30-1.18 (m, 2H), 1.13-0.91 (m, 4H), 0.73-0.61 (m, 2H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 191.7, 139.9, 135.4, 131.8, 129.9, 128.5, 128.3, 127.9, 127.1, 126.5, 126.1, 124.0, 119.2, 57.5, 53.1, 31.7, 31.1, 31.0, 26.4, 25.3, 25.2, 24.3, 13.9; **HRMS** (ESI) m/z calculated for $C_{31}H_{39}N_2S$ $[M+H]^+$: 471.2834, found 471.2830.

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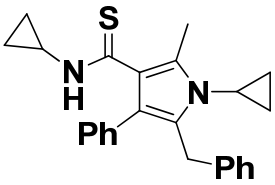


(**3a18**) White solid, m.p. 172-173 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.34-7.30 (m, 2H), 7.28-7.21 (m, 5H), 7.16 (t, *J* = 7.5 Hz, 1H), 7.04 (d, *J* = 7.0 Hz, 2H), 6.50 (d, *J* = 4.0 Hz, 1H), 4.01 (s, 2H), 3.14-3.07 (m, 1H), 2.70 (s, 3H), 2.52-2.44 (m, 1H), 0.95-0.88 (m, 4H), 0.70-0.64 (m, 2H), 0.01- -0.03 (m, 2H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 194.5, 139.9, 135.6, 134.9, 129.8, 128.9, 128.5, 128.3, 127.8, 126.8, 125.9, 121.9, 119.3, 30.8, 27.6, 26.7, 13.2, 8.2, 6.8; **HRMS** (ESI) m/z calculated for $C_{25}H_{27}N_2S$ $[M+H]^+$: 387.1895, found 387.1897.

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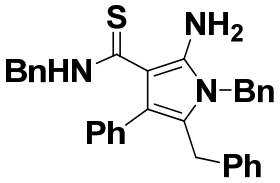


(**3a19**) Yellow solid, m.p. 103-104 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.31 (t, *J* = 7.0 Hz, 3H), 7.29-7.26 (m, 2H), 7.23-7.17 (m, 7H), 7.16-7.11 (m, 2H), 7.04-6.95 (m, 4H), 6.92-6.86 (m, 2H), 6.78 (t, *J* = 5.0 Hz, 1H), 6.28 (s, 2H), 4.73 (s, 2H), 4.65 (d, *J* = 5.0 Hz, 2H), 3.67 (s, 2H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 186.9, 147.3, 139.0, 136.7, 135.8, 134.9, 130.6, 129.0, 128.9, 128.5, 128.4, 127.8, 127.7, 127.5, 127.2, 126.3, 125.9, 122.2, 117.9, 102.3, 48.7, 46.0, 29.7; **HRMS** (ESI) m/z calculated for $C_{32}H_{28}N_3S$ $[M-H]^+$: 486.2004, found 486.2005.

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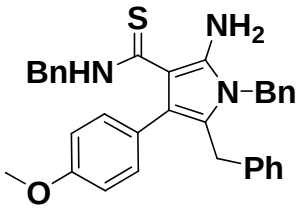


(**3a20**) Pale-yellow solid, m.p. 159-160 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.32-7.25 (m, 3H), 7.23-7.16 (m, 7H), 7.13 (t, *J* = 7.5 Hz, 1H), 7.04-6.96 (m, 4H), 6.96-6.91 (m, 2H), 6.89 (t, *J* = 4.5 Hz, 1H), 6.69 (d, *J* = 7.0 Hz, 2H), 6.30 (s, 2H), 4.72 (s, 2H), 4.65 (d, *J* = 4.5 Hz, 2H), 3.70 (s, 3H), 3.64 (s, 2H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 186.7, 159.0, 147.2, 139.0, 136.8, 135.8, 131.7, 129.0, 128.5, 128.3, 128.0, 127.73, 127.7, 127.2, 126.7, 126.3, 125.9, 122.3, 117.4, 114.2, 102.3, 55.0, 48.8, 45.9, 29.7; **HRMS** (ESI) m/z calculated for $C_{33}H_{30}N_3OS$ $[M-H]^+$: 516.2110, found 516.2109.

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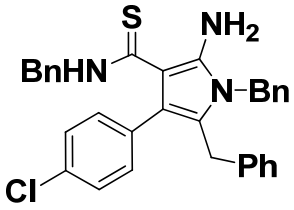


(**3a21**) Pale-yellow solid, m.p. 162-163 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.35-7.26 (m, 3H), 7.25-7.22 (m, 3H), 7.22-7.19 (m, 4H), 7.17-7.11 (m, 3H), 6.98 (d, *J* = 7.0 Hz, 4H), 6.94-6.88 (m, 2H), 6.59 (t, *J* = 4.5 Hz, 1H), 6.25 (s, 2H), 4.73 (s, 2H), 4.65 (d, *J* = 4.5 Hz, 2H), 3.65 (s, 2H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 186.7, 147.3, 138.6, 136.5, 135.6, 133.6, 133.4, 131.8, 129.0, 128.6, 128.5, 127.9, 127.8, 127.64, 127.6, 126.5, 125.8, 122.4, 116.6, 102.7, 49.0, 46.0, 29.6; **HRMS** (ESI) m/z calculated for $C_{32}H_{27}ClN_3S$ $[M-H]^+$: 520.1618, found 520.1621.

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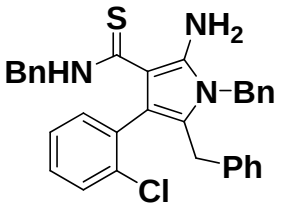


(**3a22**) White solid, m.p. 208-209 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.35-7.28 (m, 4H), 7.28-7.25 (m, 1H), 7.23-7.19 (m, 2H), 7.19-7.16 (m, 4H), 7.15-7.09 (m, 1H), 7.08-7.03 (m, 2H), 7.01 (d, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 7.5 Hz, 2H), 6.95-6.91 (m, 2H), 6.51 (t, *J* = 4.5 Hz, 1H), 6.28 (s, 2H), 4.74 (s, 2H), 4.68 (dd, *J* = 14.5, 4.5 Hz, 1H), 4.59 (dd, *J* = 14.5, 4.5 Hz, 1H), 3.58 (AB, *J* = 17.0 Hz, 2H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 187.0, 147.3, 138.5, 136.6, 135.7, 135.6, 133.8, 132.8, 130.0, 129.3, 129.0, 128.5, 128.4, 127.9, 127.8, 127.7, 127.2, 127.0, 126.3, 125.7, 122.5, 114.8, 102.4, 48.9, 45.8, 29.9; **HRMS** (ESI) m/z calculated for $C_{32}H_{29}ClN_3S$ $[M+H]^+$: 522.1771, found 522.1772.

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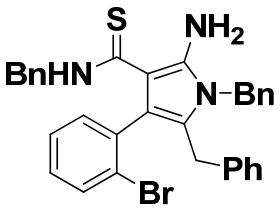


(**3a23**) White solid, m.p. 237-238 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.42 (dd, *J* = 8.0, 1.0 Hz, 1H), 7.36-7.26 (m, 5H), 7.22-7.17 (m, 4H), 7.16-7.11, (m, 2H), 7.05-6.98 (m, 4H), 6.98-6.92 (m, 3H), 6.49 (t, *J* = 4.5 Hz, 1H), 6.27 (s, 2H), 4.75 (s, 2H), 4.70-4.57 (m, 2H), 3.60 (AB, *J* = 17.0 Hz, 2H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 187.0, 147.2, 138.5, 136.6, 136.0, 135.7, 133.2, 132.8, 129.5, 129.1, 128.5, 128.4, 128.0, 127.8, 127.75, 127.7, 126.5, 126.4, 125.8, 122.4, 116.9, 102.3, 49.0, 45.8, 30.0; **HRMS** (ESI) m/z calculated for $C_{32}H_{29}BrN_3S$ $[M+H]^+$: 566.1266, found 566.1268.

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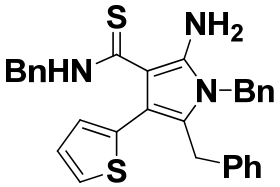


(**3a24**) White solid, m.p. 108-109 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.32-7.26 (m, 3H), 7.25-7.20 (m, 6H), 7.19-7.12 (m, 2H), 7.06-7.01 (m, 4H), 6.98-6.92 (m, 3H), 6.82-6.78 (m, 1H), 6.32 (s, 2H), 4.73 (s, 2H), 4.70 (d, *J* = 5.0 Hz, 2H), 3.72 (s, 2H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 186.7, 147.5, 138.5, 136.8, 135.8, 135.4, 129.2, 129.0, 128.6, 128.4, 128.0, 127.88, 127.8, 127.4, 127.3, 126.4, 125.9, 125.0, 108.9, 102.4, 48.8, 46.1, 29.9; **HRMS** (ESI) m/z calculated for $C_{30}H_{27}N_3S_2$ $[M+H]^+$: 493.1646, found 493.1644.

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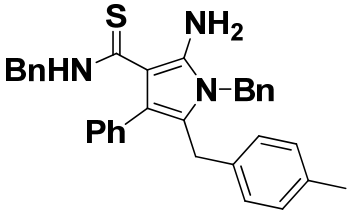


(**3a25**) Pale-yellow solid, m.p. 129-130 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.33-7.27 (m, 5H), 7.22-7.14 (m, 6H), 7.03-6.97 (m, 4H), 6.91-6.87 (d, *J* = 7.5 Hz, 4H), 6.78 (t, *J* = 5.0 Hz, 1H), 6.28 (s, 2H), 4.73 (s, 2H), 4.65 (d, *J* = 5.0 Hz, 2H), 3.62 (s, 2H), 2.27 (s, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 186.8, 147.3, 136.9, 135.94, 135.9, 135.8, 135.0, 130.7, 129.2, 129.0, 128.8, 128.4, 127.9, 127.7, 127.6, 127.5, 127.2, 125.9, 122.5, 117.8, 102.3, 48.7, 46.0, 29.3, 20.9; **HRMS** (ESI) m/z calculated for $C_{33}H_{32}N_3S$ $[M+H]^+$: 502.2317, found 503.2320.

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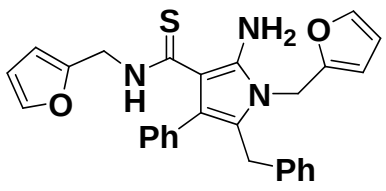

(**3a26**) White solid, m.p. 159-160 °C. **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.34-7.32 (m, 1H), 7.31-7.28 (m, 2H), 7.28-7.25 (m, 2H), 7.25-7.21 (m, 3H), 7.21-7.14 (m, 2H), 7.07 (d, *J* = 7.5 Hz, 2H), 6.75 (s, 1H), 6.64 (s, 2H), 6.25-6.16 (m, 2H), 5.90 (d, *J* = 3.0 Hz, 1H), 5.82 (d, *J* = 3.0 Hz, 1H), 4.68-4.64 (m, 4H), 3.80 (s, 2H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 186.8, 149.9, 149.3, 147.6, 142.6, 141.9, 138.9, 134.7, 130.5, 128.8, 128.6, 127.9, 127.5, 126.4, 121.8, 118.0, 110.5, 110.0, 108.2, 107.3, 102.2, 41.3, 39.4, 29.7; **HRMS** (ESI) m/z calculated for $C_{28}H_{24}N_3O_2S$ $[M-H]^+$: 466.1593, found 466.1594.

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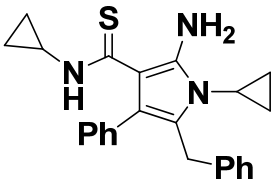


(**3a27**) Yellow solid, m.p. 137-138 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 9.34 (s, 1H), 7.58 (s, 1H), 7.42-7.33 (m, 3H), 7.32-7.26 (m, 4H), 7.21 (t, *J* = 7.5 Hz, 1H), 7.10 (d, *J* = 7.5 Hz, 2H), 6.31 (d, *J* = 1.5 Hz, 1H), 3.70 (s, 2H), 3.07-3.00 (m, 1H), 2.51-2.44 (m, 1H), 0.73-0.68 (m, 2H), 0.67-0.60 (m, 4H), 0.03- -0.03 (m, 2H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 187.0, 149.5, 138.9, 135.0, 130.6, 128.8, 128.6, 128.1, 127.6, 126.5, 119.8, 117.5, 99.8, 31.1, 29.6, 26.5, 23.3, 7.1, 6.8; **HRMS** (ESI) m/z calculated for $C_{24}H_{26}N_3S$ $[M+H]^+$: 388.1847, found 388.1847.

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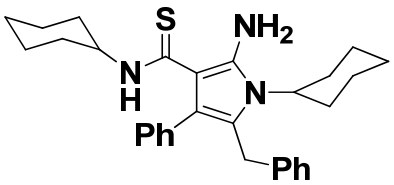


(**3a28**) Yellow liquid; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.41-7.35 (m, 4H), 7.35-7.30 (m, 1H), 7.23 (d, *J* = 7.5 Hz, 2H), 7.16 (t, *J* = 7.0 Hz, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 6.51 (s, 2H), 6.45 (d, *J* = 8.5 Hz, 1H), 4.36-4.26 (m, 1H), 3.74-3.66 (m, 3H), 1.95-1.81 (m, 2H), 1.78-1.67 (m, 4H), 1.56 (s, 1H), 1.52-1.33 (m, 5H), 1.29-1.19 (m, 2H), 1.11-0.91 (m, 4H), 0.71-0.58 (m, 2H); **HRMS** (ESI) m/z calculated for $C_{28}H_{24}N_3O_2S$ $[M-H]^+$: 470.2634, found 470.2635.

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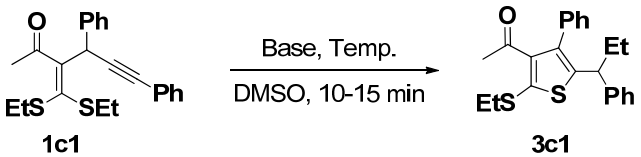
## **V.** Synthesis and spectra data of thiophenes **3c**

**Table S3** Condition optimization.




1c1 3c1

| Entry | Base | Temp. (°C) | Yield (%)[a] |
|---|---|---|---|
| 1 | $BnNH_2$ | 100 | 68 |

| | | | |
|---|---|---|---|
| 2 | $BnNH_2$ | RT | Trace |
| 3 | DBU | RT | 88 |
| 4 | $K_2CO_3$ | RT | 0 |
| 5 | KO*t*Bu | RT | 0 |

[a] Isolated yield.

**Typical synthetic procedure** (with **3c1** as an example): To the mixture of 1c1 (380 mg, 1.0 mmol) in DMSO (1.0 mL) was added 1,8-diazabicyclo [5.4.0.]undec-7-ene (DBU) (0.152 mL, 1.0 mmol) in one portion at room temperature. The substrate **1c1** was consumed as indicated by TLC. The resulting mixture was poured into water (50 mL) under stirring. The combined organic layers were dried over $MgSO_4$, filtered, and the solvent was removed by rotary evaporation. The crude product was purified by flash chromatography (silica gel, petroleum ether : ethyl acetate = 15 : 1, V/V) to give **3c1** (330 mg, 88 %).

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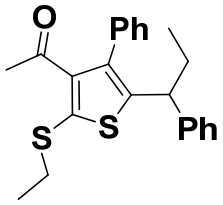


(**3c1**) yellow liquid; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.41-7.37 (m, 3H), 7.27-7.22 (m, 2H), 7.19-7.14 (m, 3H), 7.10-7.07 (m, 2H), 3.82 (t, *J* = 7.5 Hz, 1H), 3.01 (q, *J* = 7.5 Hz, 2H), 2.01-1.92 (m, 2H), 1.79 (s, 3H), 1.39 (t, *J* = 7.5 Hz, 3H), 0.82 (t, *J* = 7.5 Hz, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 195.9, 144.0, 143.8, 138.7, 136.5, 129.9, 129.7, 128.6, 128.5, 128.4, 127.8, 127.4, 126.4, 46.5, 30.7, 30.5, 30.2, 13.8, 12.5; **HRMS** (ESI) m/z calculated for $C_{23}H_{25}OS_2$ $[M+H]^+$: 381.1347, found 381.1345.

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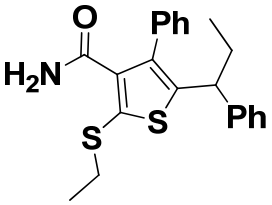


(**3c2**) White solid, m.p. 125-126 °C; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.43-7.35 (m, 3H), 7.24 (t, *J* = 7.5 Hz, 2H), 7.21-7.14 (m, 3H), 7.07 (d, *J* = 7.5 Hz, 2H), 5.60 (s, 1H), 5.29 (s, 1H), 3.79 (t, *J* = 7.5Hz, 1H), 2.98 (q, *J* = 7.5 Hz, 2H), 2.01-1.91 (m, 2H), 1.37 (t, *J* = 7.5 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 165.9, 145.0, 143.7, 140.2, 138.0, 135.6, 133.1, 129.8, 128.6, 128.3, 128.0, 127.3, 126.3, 46.6, 30.7, 30.6, 14.0, 12.5; **HRMS** (ESI) m/z calculated for $C_{22}H_{24}NOS_2$ $[M+H]^+$: 382.1299, found 382.1302.

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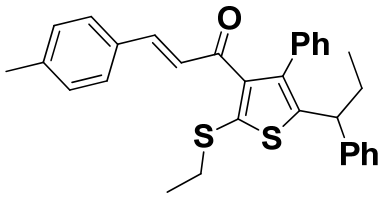


(**3c3**) Yellow liquid; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.42-7.33 (m, 4H), 7.26 (t, *J* = 7.5 Hz, 2H), 7.23-7.19 (m, 2H), 7.19-7.13 (m, 3H), 7.04 (d, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 6.38 (d, *J* = 15.5 Hz, 1H), 3.96 (t, *J* = 7.5 Hz, 1H), 3.00 (q, *J* = 7.5 Hz, 2H), 2.29 (s, 3H), 2.05-1.96 (m, 2H), 1.36 (t, *J* = 7.5 Hz, 3H), 0.84 (t, *J* = 7.5 Hz, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 188.1, 144.6, 143.8, 143.0, 142.8, 140.3, 139.9, 138.7, 136.2, 132.1, 130.0, 129.2, 128.5, 128.4, 128.1, 127.6, 127.4, 126.3, 125.1, 46.5, 30.9, 30.7, 21.3, 13.9, 12.5; **HRMS** (ESI) m/z calculated for $C_{32}H_{33}OS_2$ $[M+H]^+$: 497.1973, found 497.1973.

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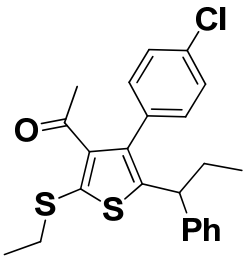


(**3c4**) Yellow liquid; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 13.7 (d, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.18 (t, *J* = 7.5 Hz, 1H), 7.12-7.04 (m, 4H), 3.75 (t, *J* = 7.5 Hz, 1H), 3.00 (q, *J* = 7.5 Hz, 2H), 2.01-1.93 (m, 2H), 1.85 (s, 3H), 1.39 (t, *J* = 7.5 Hz, 3H), 0.82 (t, *J* = 7.5 Hz, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 195.6, 144.7, 144.4, 143.6, 138.5, 137.3, 134.9, 133.9, 131.2, 128.7, 128.5, 127.3, 126.5, 46.6, 30.8, 30.3, 13.7, 12.6; **HRMS** (ESI) m/z calculated for $C_{23}H_{24}ClOS_2$ $[M+H]^+$: 415.0957, found 415.0955.

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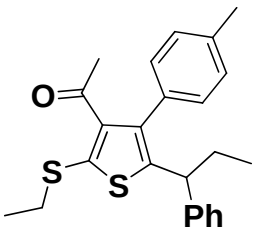


(**3c5**) Yellow liquid; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.28-7.23 (m, 2H), 7.21 (d, *J* = 7.5 Hz, 2H), 7.19-7.15 (m, 1H), 7.12 (d, *J* = 7.5 Hz, 2H), 7.05 (d, *J* = 7.0 Hz, 2H), 3.83 (t, 7.5 Hz, 1H), 2.99 (q, *J* = 7.5 Hz, 2H), 2.40 (s, 3H), 2.02-1.93 (m, 2H), 1.80 (s, 3H), 1.39 (t, *J* = 7.5 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 195.9, 144.8, 143.8, 143.6, 138.7, 138.2, 137.4, 133.3, 129.7, 129.0, 128.3, 127.3, 126.3, 46.3, 30.6, 30.5, 29.9, 21.2, 13.6, 12.5; **HRMS** (ESI) m/z calculated for $C_{24}H_{27}OS_2$ $[M+H]^+$: 395.1503, found 395.1506.

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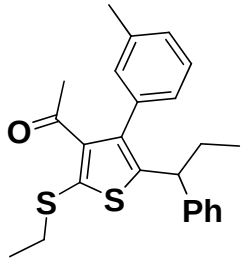


(**3c6**) Yellow liquid; **$^{1}$H-NMR** (500 MHz, $CDCl_3$) δ 7.31-7.26 (m, 2H), 7.25-7.22 (m, 1H), 7.21-7.15 (m, 2H), 7.10 (d, *J* = 7.5 Hz, 2H), 6.99-6.88 (m, 2H), 3.81 (t, *J* = 7.5 Hz, 1H), 2.99 (q, *J* = 7.5 Hz, 2H), 2.34 (s, 3H), 2.01-1.93 (m, 2H), 1.80 (s, 3H), 1.39 (t, *J* = 7.5 Hz, 3H), 0.82 (t, *J* = 7.5 Hz, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 196.1, 144.0, 143.8, 138.9, 138.0, 136.4, 130.6, 128.5, 128.4, 128.2, 127.4, 127.0, 126.7, 126.3, 126.0, 46.6, 30.7, 30.5, 30.2, 21.3, 13.8, 12.5; **HRMS** (ESI) m/z calculated for $C_{24}H_{27}OS_2$ $[M+H]^+$: 395.1503, found 395.1508.

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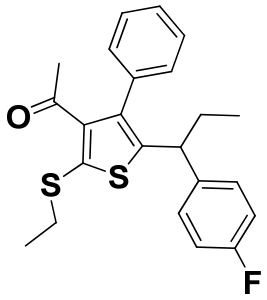


(**3c7**) Yellow liquid; **$^{1}$H-NMR** (500 MHz, $CDCl_3$) δ 7.42-7.35 (m, 3H), 7.16-7.10 (m, 2H), 7.04-6.99 (m, 2H), 6.95-6.90 (m, 2H), 3.80 (t, *J* = 8.0 Hz, 1H), 3.01 (q, *J* = 7.5 Hz, 2H), 2.00-1.89 (m, 2H), 1.79 (s, 3H), 1.40 (t, *J* = 7.5 Hz, 3H), 0.82 (t, *J* = 7.5 Hz, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 195.8, 162.3 ($^{1}J_{CF}$ = 244.7 Hz), 160.3 ($^{1}J_{CF}$ = 244.7 Hz), 144.9, 143.5, 139.59 ($^{4}J_{CF}$ = 3.2 Hz), 139.5 ($^{4}J_{CF}$ = 3.2 Hz), 138.8, 138.4, 136.4, 129.8, 128.8 ($^{3}J_{CF}$ = 8.0 Hz), 128.7 ($^{3}J_{CF}$ = 8.0 Hz), 128.5, 127.9, 115.2 ($^{2}J_{CF}$ = 21.3 Hz), 115.1 ($^{2}J_{CF}$ = 21.3 Hz), 45.7, 30.7, 30.5, 30.1, 13.7, 12.5; **HRMS** (ESI) m/z calculated for $C_{23}H_{24}FOS_2$ $[M+H]^+$: 399.1253, found 399.1250.

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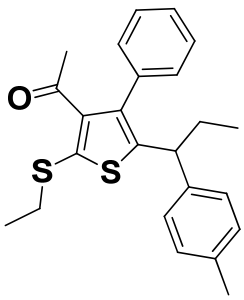


(**3c8**) Yellow liquid; **$^{1}$H-NMR** (500 MHz, $CDCl_3$) δ 7.42-7.35 (m, 3H), 7.17 (d, *J* = 6.0 Hz, 2H), 7.06 (d, *J* = 7.5 Hz, 2H), 7.00 (d, *J* = 8.0 Hz, 2H), 3.79 (t, *J* = 7.5 Hz, 1H), 3.00 (q, *J* = 7.5 Hz, 2H), 2.29 (s, 3H), 2.01-1.90 (m, 2H), 1.78 (s, 3H), 1.38 (t, *J* = 7.5 Hz, 3H), 0.80 (t, *J* = 7.0 Hz, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 195.8, 144.6, 144.2, 140.8, 138.5,

138.4, 136.5, 135.8, 129.9, 129.0, 128.3, 127.7, 127.1, 46.0, 30.7, 30.4, 30.0, 20.9, 13.7, 12.5; **HRMS** (ESI) m/z calculated for $C_{24}H_{27}OS_2$ $[M+H]^+$: 395.1503, found 395.1505.

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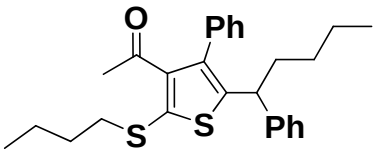



(**3c9**) Yellow liquid; **$^1$H-NMR** (500 MHz, $CDCl_3$) δ 7.42-7.37 (m, 3H), 7.25 (t, *J* = 7.5 Hz, 2H), 7.20-7.13 (m, 3H), 7.10 (d, *J* = 7.5 Hz, 2H), 3.90 (t, *J* = 7.5 Hz, 3H), 2.99 (t, *J* = 7.5 Hz, 2H), 1.97-1.90 (m, 2H), 1.77 (s, 3H), 1.76-1.70 (m, 2H), 1.54-1.46 (m, 2H), 1.27-1.16 (m, 3H), 1.16-1.05 (m, 1H), 0.95 (t, *J* = 7.5 Hz, 3H), 0.81 (t, *J* = 7.5 Hz, 3H); **$^{13}$C-NMR** ($CDCl_3$, 125 MHz) δ 195.7, 145.6, 144.0, 143.8, 138.6, 137.9, 136.5, 129.9, 128.5, 128.4, 127.8, 127.3, 126.3, 44.6, 37.4, 35.6, 30.5, 30.4, 29.8, 22.3, 22.0, 13.8, 13.6; **HRMS** (ESI) m/z calculated for $C_{27}H_{33}OS_2$ $[M+H]^+$: 437.1973, found 437.1971.

## **V.** Crystallography of **3a8**, **3a26** and **3c2**

Single-crystal X-ray diffraction data for the each compound were collected at room temperature on a Oxford Diffraction Gemini R Ultra diffractometer, the X-ray generator using Mo-Kα (λ = 0.71073 Å) radiation with a ω scan technique. The crystal structures were solved by direct method of SHELXS-97 and refined by full-matrix least-squares techniques using the SHELXL-97 program.[1] Non-hydrogen atoms were refined anisotropic, and hydrogen atoms of the ligands were refined as rigid groups. Basic information of crystal parameters and structure refinement are listed in Table S4-S6.

Reference

1) (*a*) G. M. Sheldrick, *SHELXS-97, Program for Solution of Crystal Structures, University of Göttingen,* Germany, 1997; (*b*) G. M. Sheldrick, *SHELXL-97, Program for Refinement of Crystal Structures, University of Göttingen,* Germany, 1997.

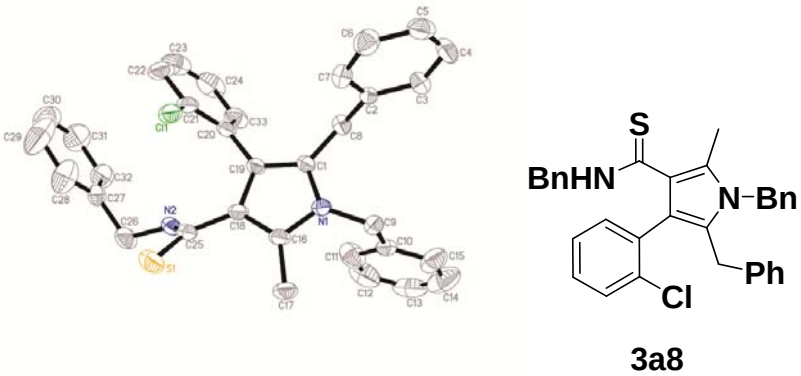
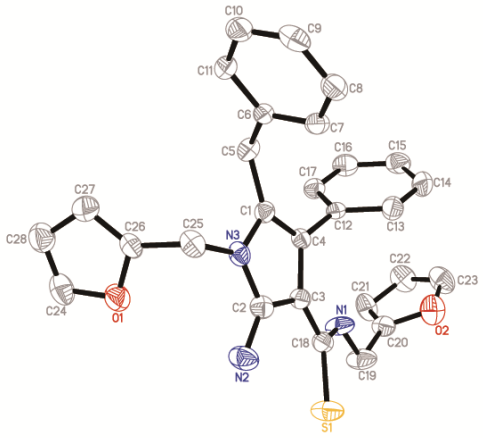
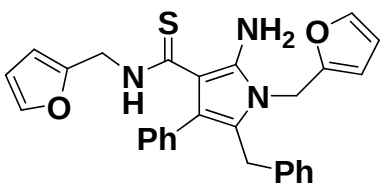



Fig. S1 ORTEP plot of **3a8** with 30% probability displacement ellipsoids

**Table S4** Crystal data and structure refinement.

| | |
|---|---|
| Empirical formula | $C_{33}H_{28}N_2SCl$ |
| Formula weight | 520.08 |
| Temperature | 293(2) K |
| Crystal system | Orthorhombic |
| Space group | Pna21 |
| Unit cell dimensions | a = 13.0268(10) Å |
| | b = 26.8385(14) Å |
| | c =7.9778(6) Å |
| | alpha = 90 ° |
| | beta = 90 ° |
| | gamma = 90 ° |
| Volume | 2789.2(3) $Å^3$ |
| Z | 4 |
| Calculated density | 1.239 $Mg/m^3$ |
| Absorption coefficient | 0.236 $mm^{-1}$ |
| F(000) | 1092 |
| Flack | -0.07(12) |
| Crystal size | 0.34 x 0.19 x 0.14 mm |
| Theta range for data collection | 2.76 to 25.02 deg. |
| Reflections collected / unique | 16740 / 4413 [R(int) = 0.0529] |
| Data / restraints / parameters | 4413 / 1 / 347 |
| Goodness-of-fit on $F^2$ | 1.050 |
| Final R indices [I>2sigma(I)] | R1 = 0.0643, wR2 = 0.1306 |
| R indices (all data) | R1 = 0.1087, wR2 = 0.1492 |




**3a26**

Fig. S2 ORTEP plot of **3a26** with 30% probability displacement ellipsoids

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

| | |
|---|---|
| Empirical formula | $C_{28}H_{25}N_3O_2S$ |
| Formula weight | 467.57 |
| Temperature | 293(2) K |
| Crystal system | Monoclinic |
| Space group | P21/c |
| Unit cell dimensions | a = 13.366(5) Å |
| | b = 10.267(5) Å |
| | c = 18.288(5) Å |
| | alpha = 90 ° |
| | beta = 108.205 ° |
| | gamma = 90 ° |
| Volume | 2384.0(16) $Å^3$ |
| Z | 4 |
| Calculated density | 1.252 $Mg/m^3$ |
| Absorption coefficient | 1.303 $mm^{-1}$ |
| F(000) | 984 |
| Crystal size | 0.31 x 0.21 x 0.17 mm |
| Theta range for data collection | 3.07 to 25.03 deg. |
| Reflections collected / unique | 8506 / 4175 [R(int) = 0.0710] |
| Data / restraints / parameters | 4175 / 1 / 331 |
| Goodness-of-fit on $F^2$ | 1.016 |
| Final R indices [I>2sigma(I)] | R1 = 0.0707, wR2 = 0.1000 |
| R indices (all data) | R1 = 0.1697, wR2 = 0.1282 |

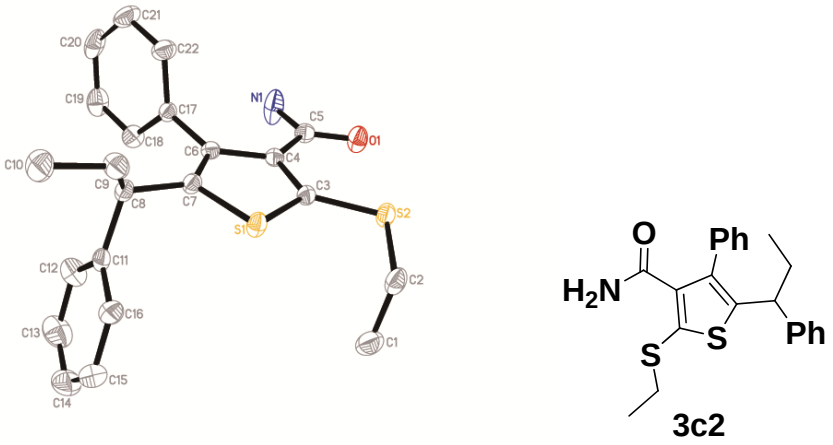


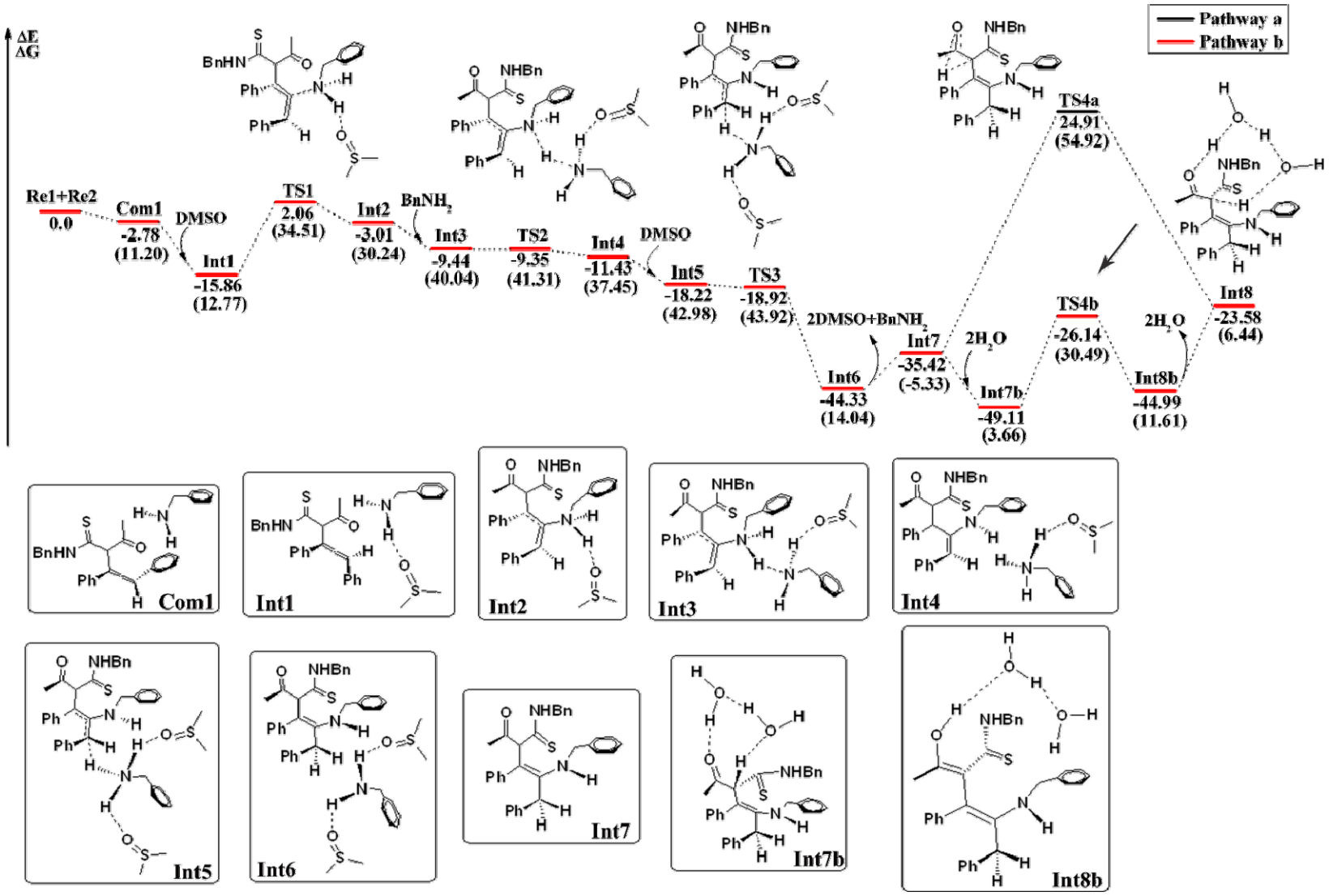

Fig. S3 ORTEP plot of **3c2** with 30% probability displacement ellipsoids

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

| | |
|---|---|
| Empirical formula | $C_{22}H_{23}NOS_2$ |
| Formula weight | 381.53 |
| Temperature | 293(2) K |
| Crystal system | Monoclinic, |
| Space group | P 21/c |
| Unit cell dimensions | a = 10.307(5) Å |
| | b = 7.191(5) Å |
| | c = 27.329(5) Å |
| | alpha = 90 ° |
| | beta = 97.666(5) ° |
| | gamma = 90 ° |
| Volume | 2007.5(17) $Å^3$ |
| Z | 4 |
| Calculated density | 1.262 $Mg/m^3$ |
| Absorption coefficient | 0.276 $mm^{-1}$ |
| F(000) | 808 |
| Crystal size | 0.26 x 0.21 x 0.17 mm |
| Theta range for data collection | 3.38 to 29.21 deg. |
| Reflections collected / unique | 8391 / 4622 [R(int) = 0.0278] |
| Data / restraints / parameters | 4622 / 0 / 235 |
| Goodness-of-fit on $F^2$ | 1.033 |
| Final R indices [I>2sigma(I)] | R1 = 0.0465, wR2 = 0.0981 |
| R indices (all data) | R1 = 0.0746, wR2 = 0.1113 |

**VI.** Computational details.

All of the DFT calculations were performed with the Gaussian 09 suite of programs.[2] B3LYP[3] method and the 6-31G**[4] basis set were used for the geometry optimization of all the minima and transition states. Frequency analysis were carried out at the same level of theory to check the stationary points to be real minima or saddle points, and to evaluate its zero-point vibration energy (ZPVE). The energetic and geometric results for the mechanism are given in Figures S2, S3, and S4 the relative energies (ΔE, ΔG) are listed with respect to the reactants (**Re1**+**Re2**) for all the species. (**Re1** is gem-dialkylthio vinylallene, **Re2** is benzylamine).



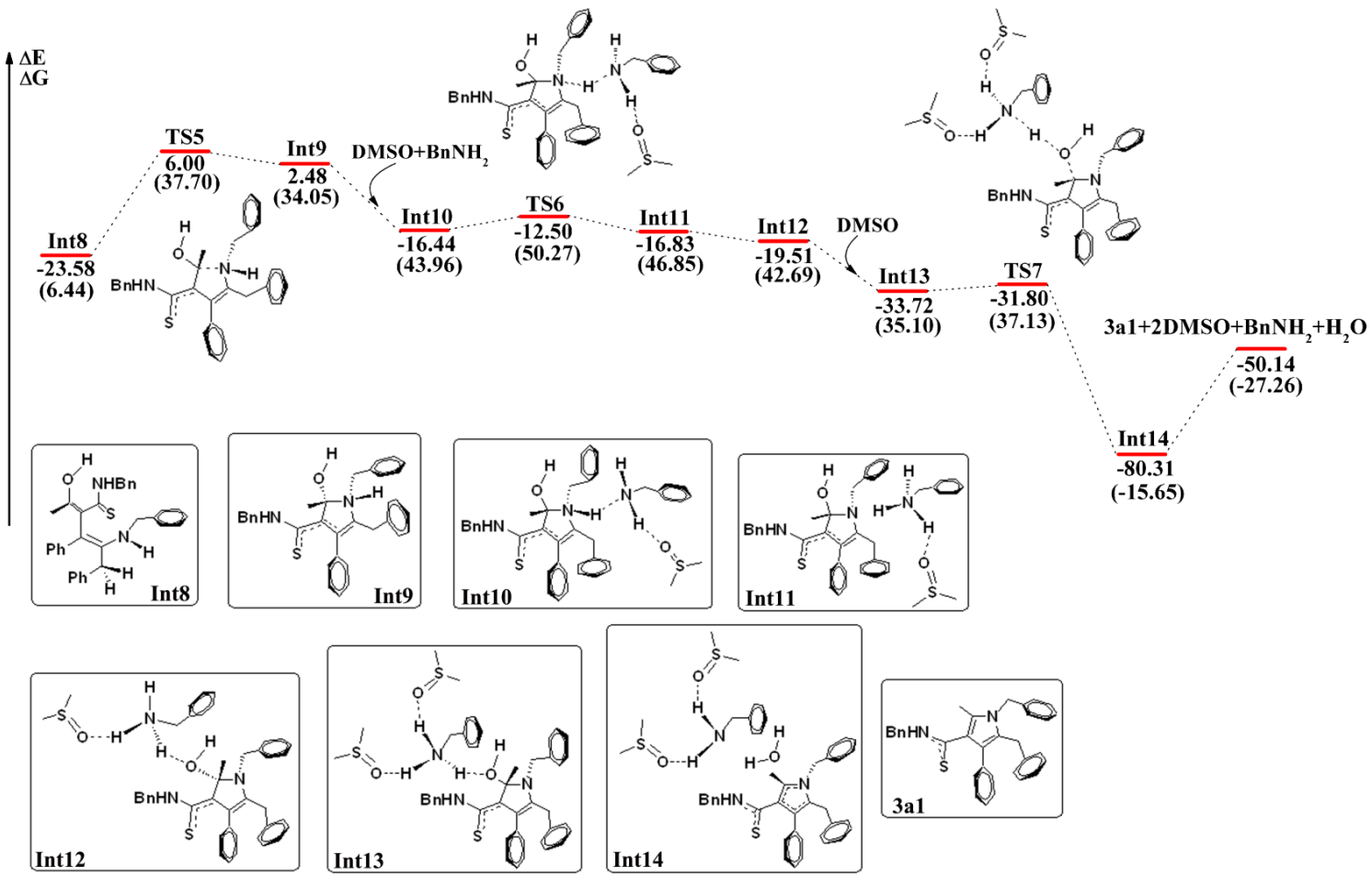



**Figure S2** The two calculated reaction pathways (intramolecualr hydrogen shift, in black and water-assisted intramolecualr hydrogen shift, in red) in gas phase. Relative energies (ΔE) and free energies (ΔG, in parenthesis) are given in kcal/mol.

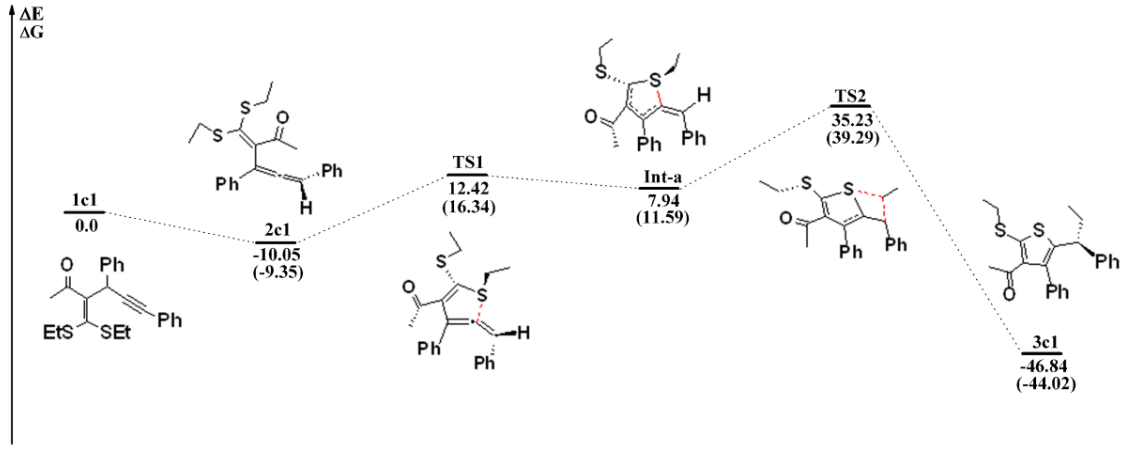
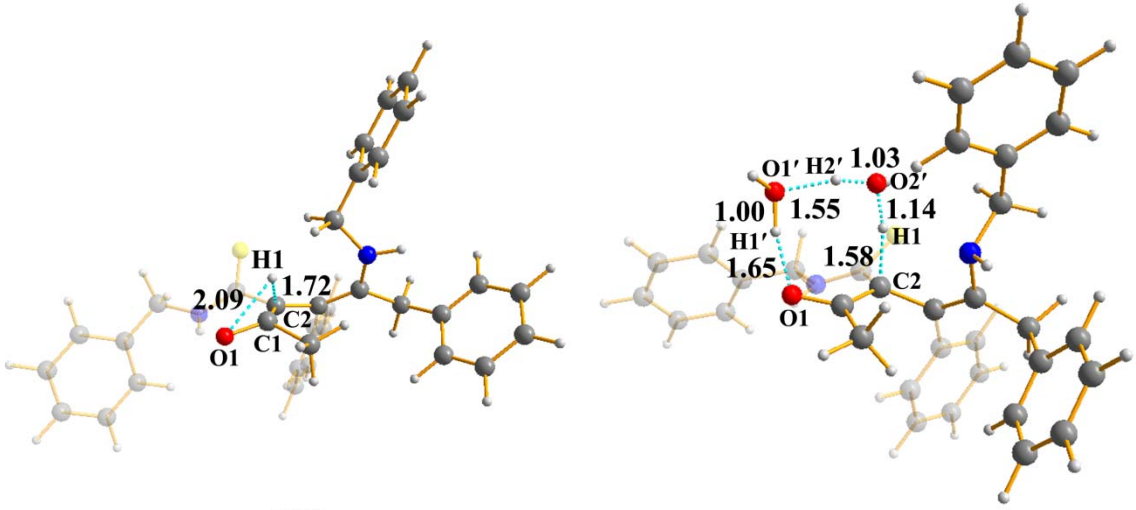



**Figure S3** The calculated reaction pathways of the title reaction in gas phase. Relative energies (ΔE) and free energies (ΔG, in parenthesis) are given in kcal/mol.



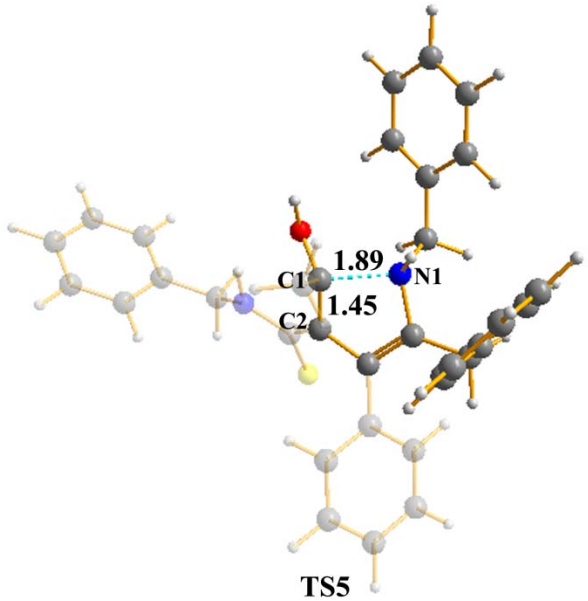




**Figure S4** The B3LYP/6-31G** optimized geometry of **TS4a**, **TS4b** and **TS5** in gas phase.

Reference

2) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.;

Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, Jr., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09; Gaussian, Inc., Wallingford CT, **2009**.

3) (a) Becke, A. D. *J. Chem. Phys*. **1993**, *98*, 5648-5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785-789.

4) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*; Wiley: New York, 1986.

*Supporting Information for*

# gem-Dialkylthio Vinylallenes: Alkylthio-Regulated Reactivity and Application in the Divergent Synthesis of Pyrroles and Thiophenes

Zhongxue Fang,[a] Haiyan Yuan,[a] Ying Liu,[a] Zixun Tong,[a] Huiqin Li,[a] Jin Yang,[a] Badru-Deen Barry,[a] Jianquan Liu,[a] Peiqiu Liao,[a] Jingping Zhang,[a]* Qun Liu,[a]* Xihe Bi[a,b]*

[a] Department of Chemistry, Northeast Normal University, Changchun 130024, China. [b] State Key Laboratory and Institute of Elemento-organic Chemistry, Nankai University, TianJin 300071, China.

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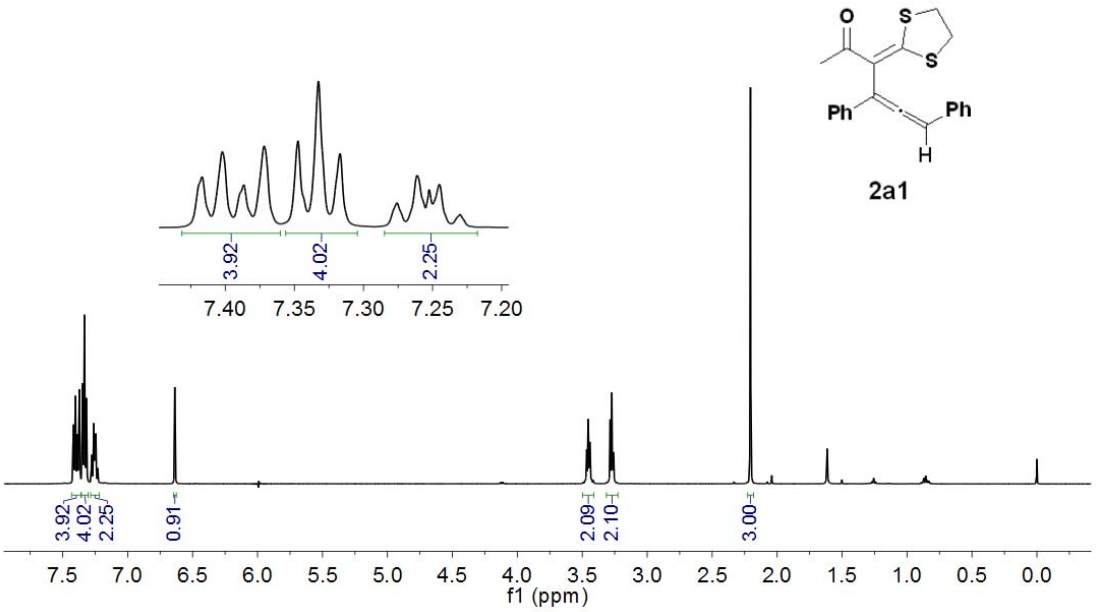
## Contents

Table of contents .....S1

**Copies of $^{1}$H- and $^{13}$C-NMR spectra**.....S2-S50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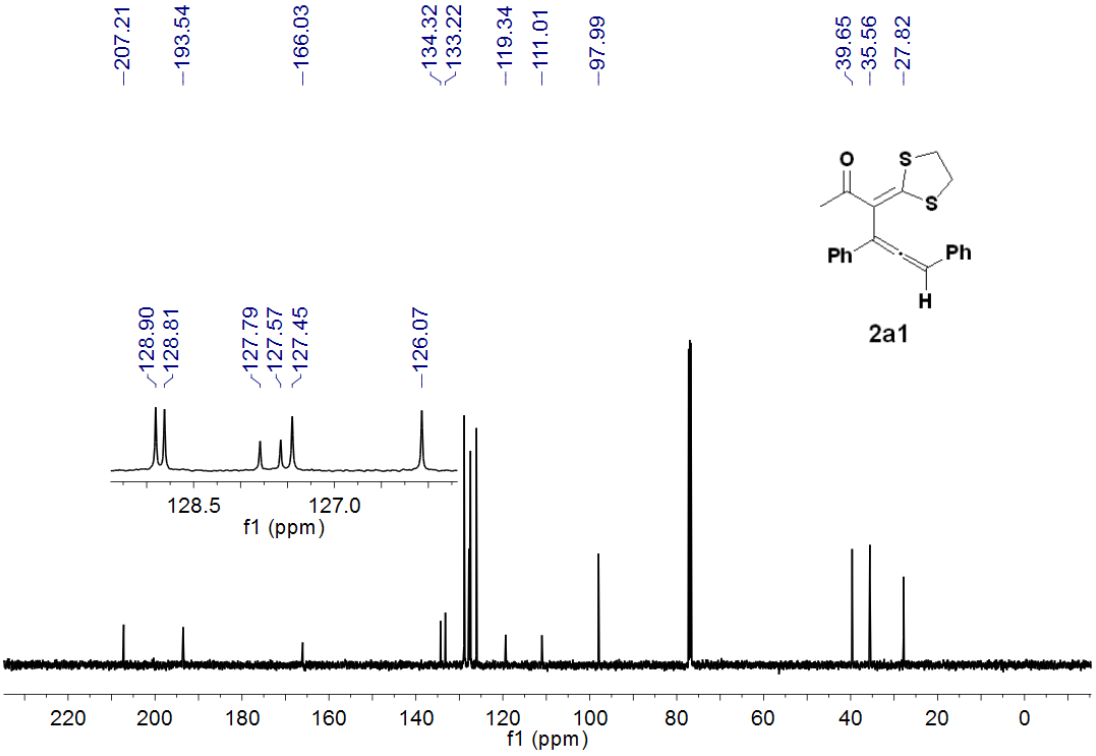
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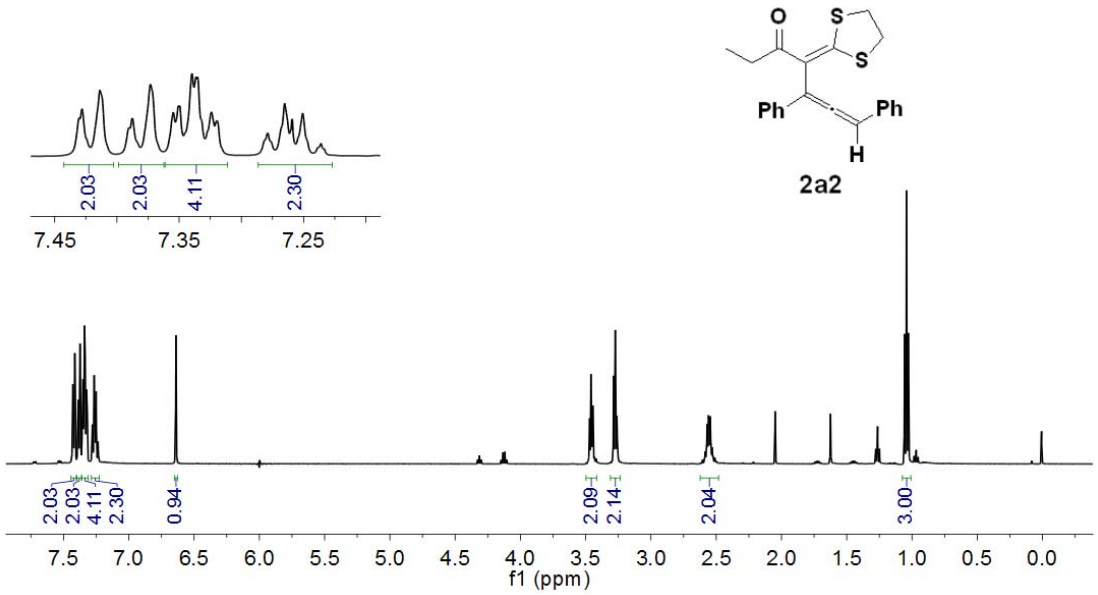
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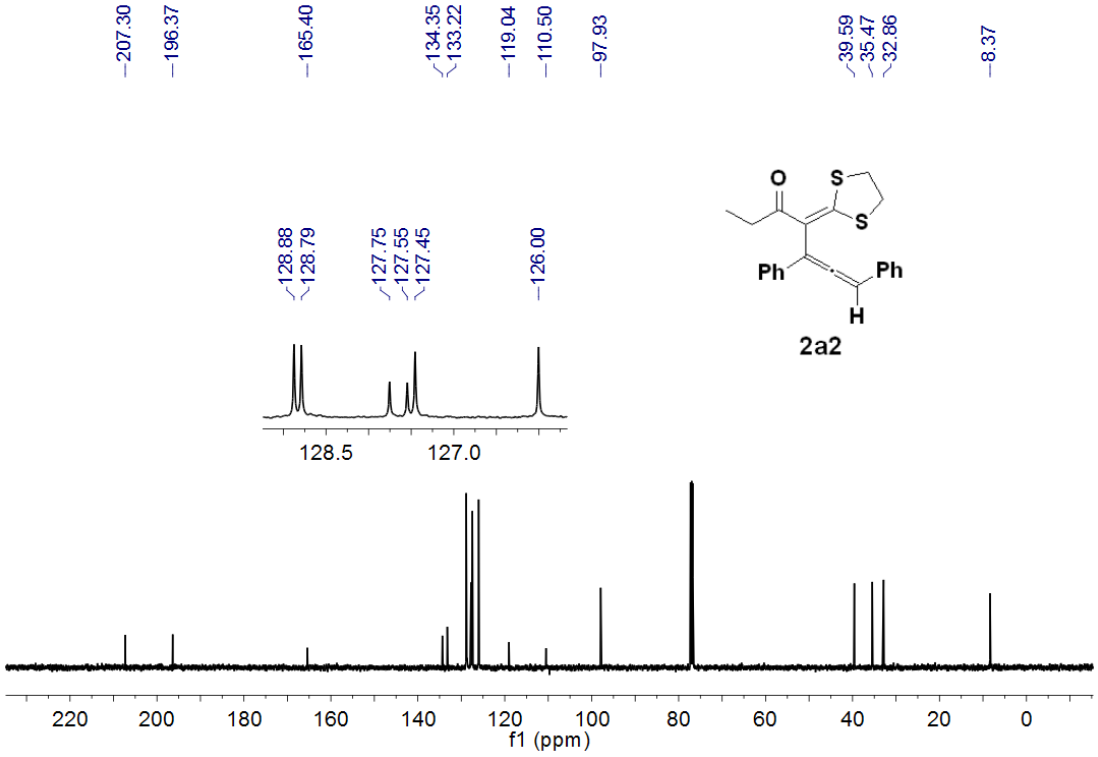
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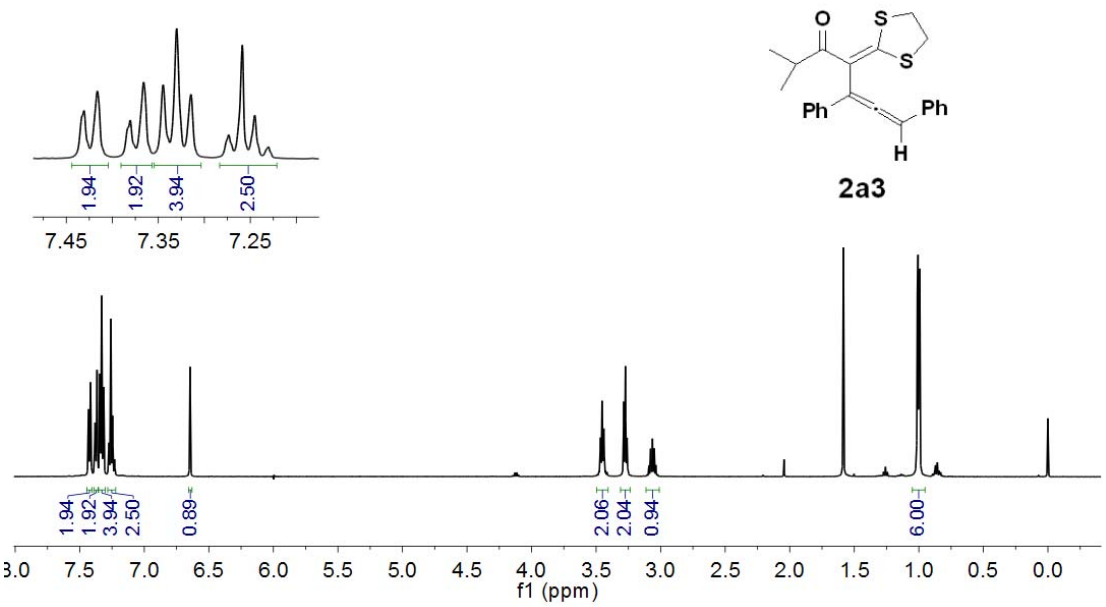
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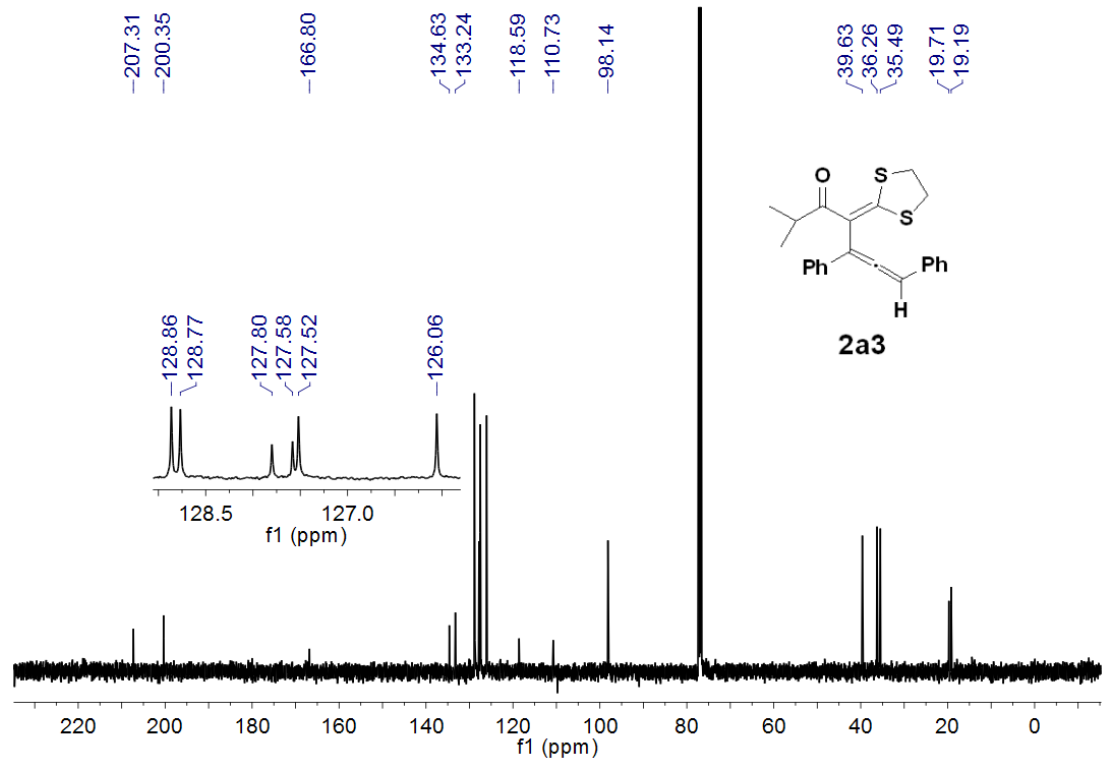
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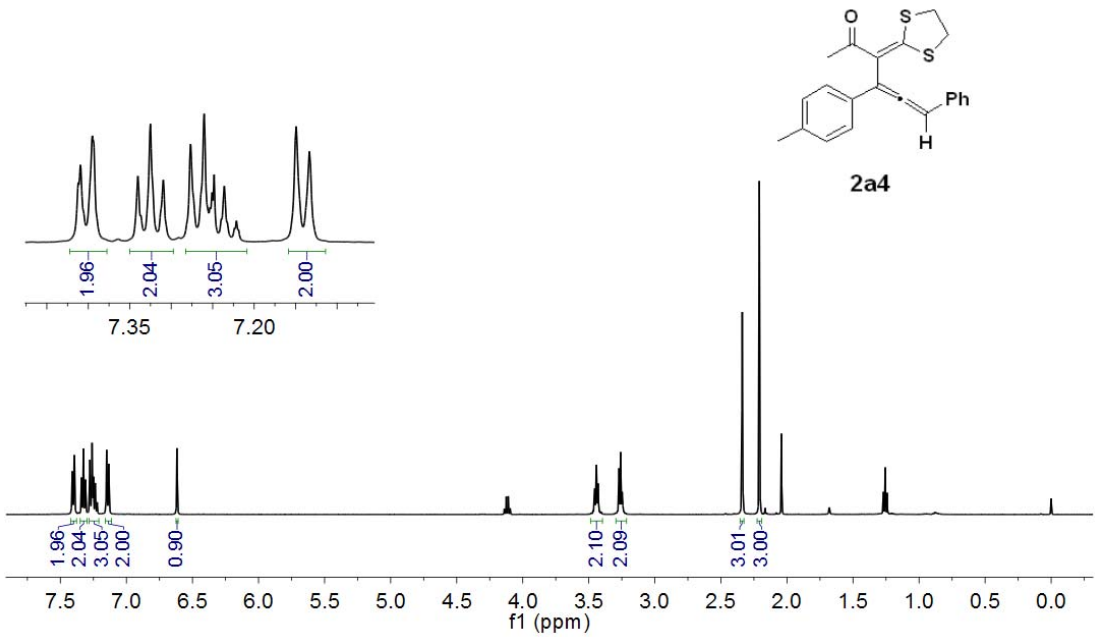
f1 (ppm)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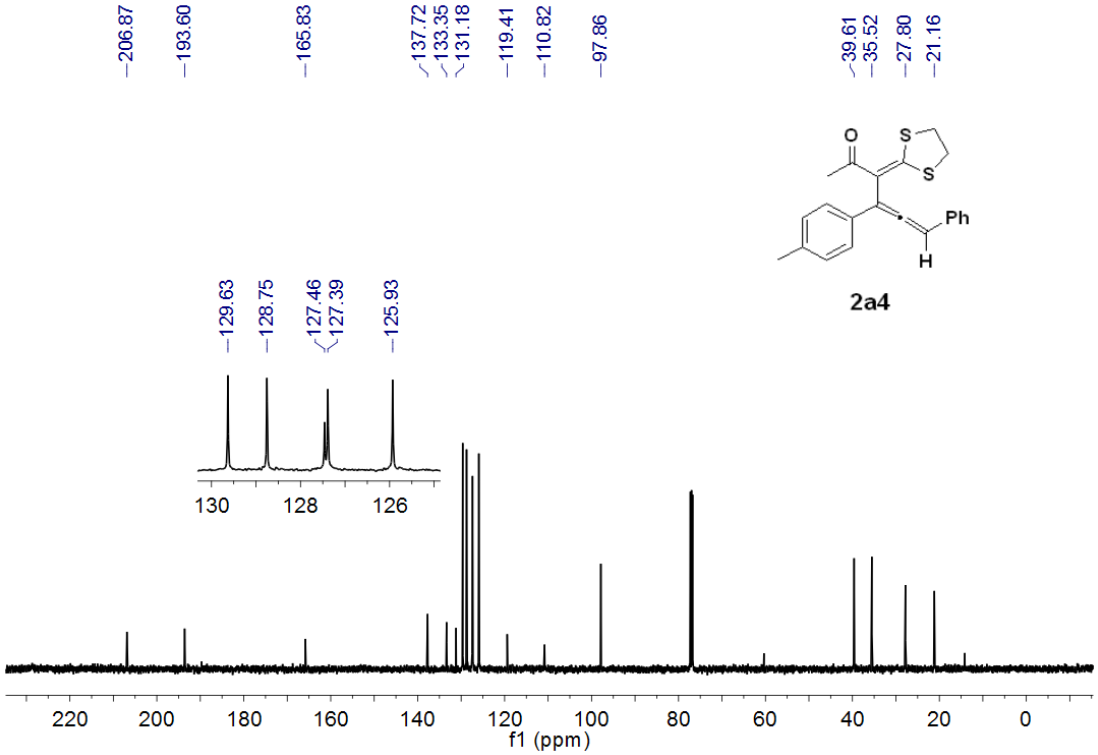
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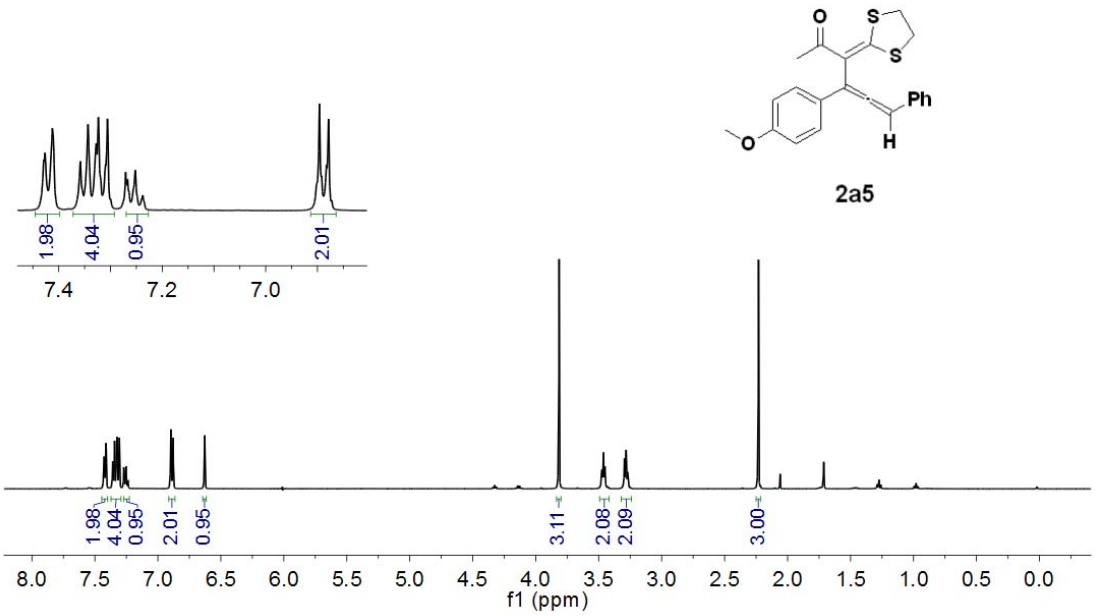
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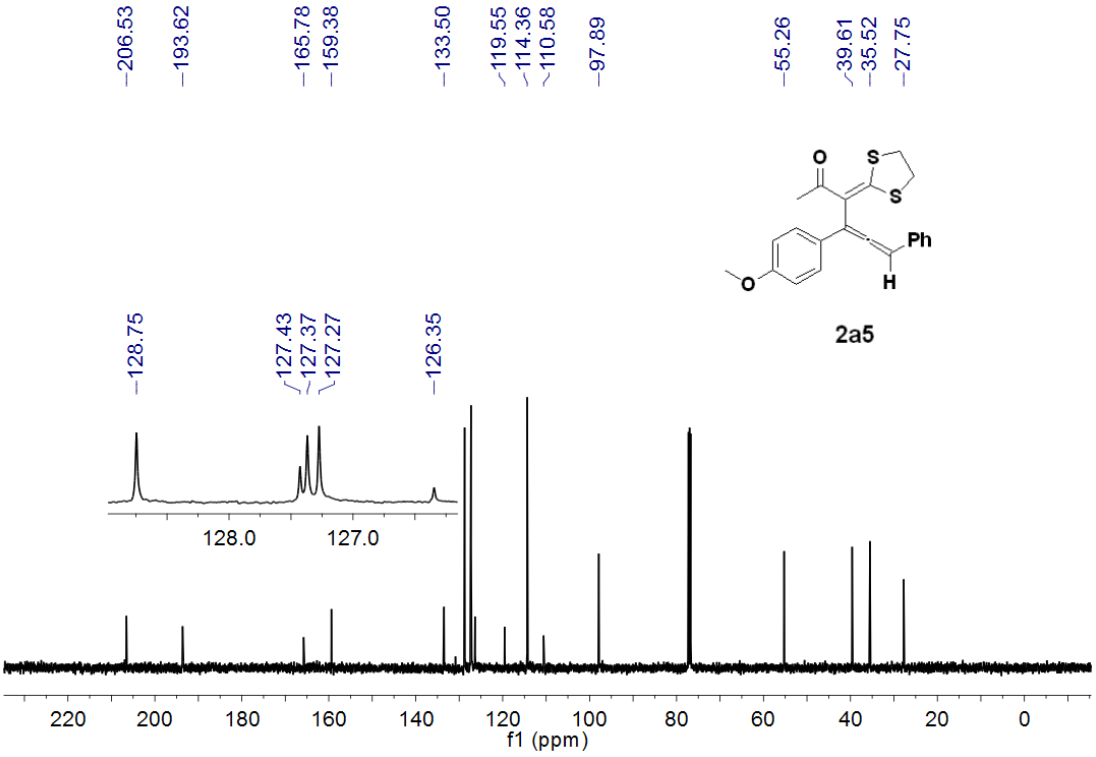
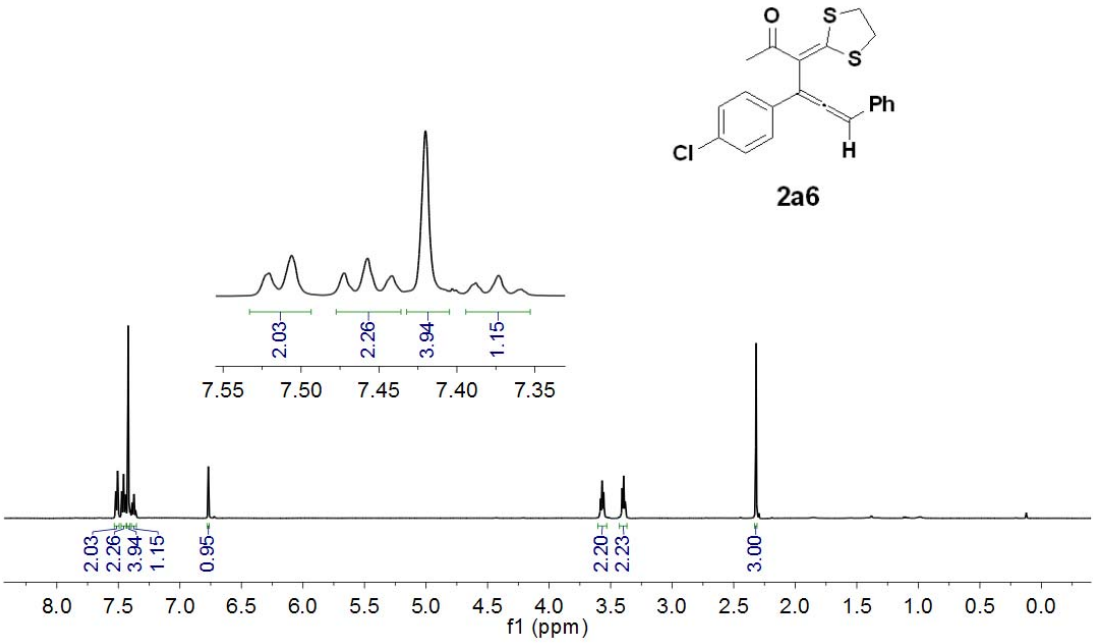
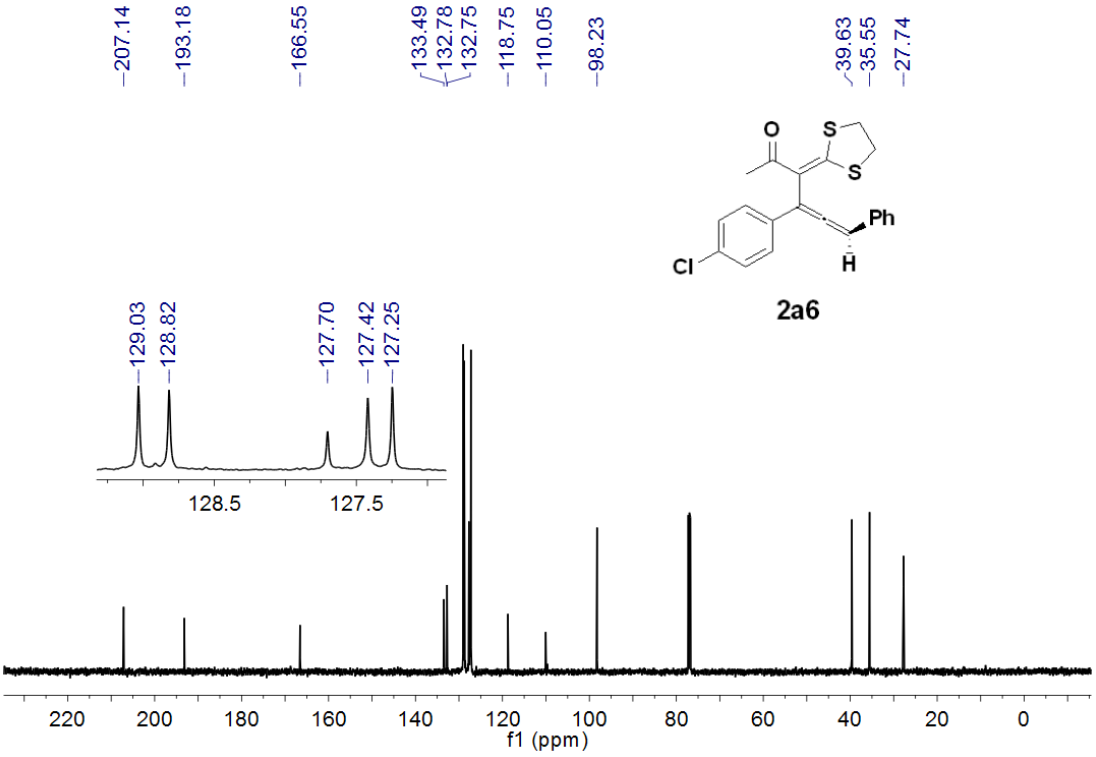
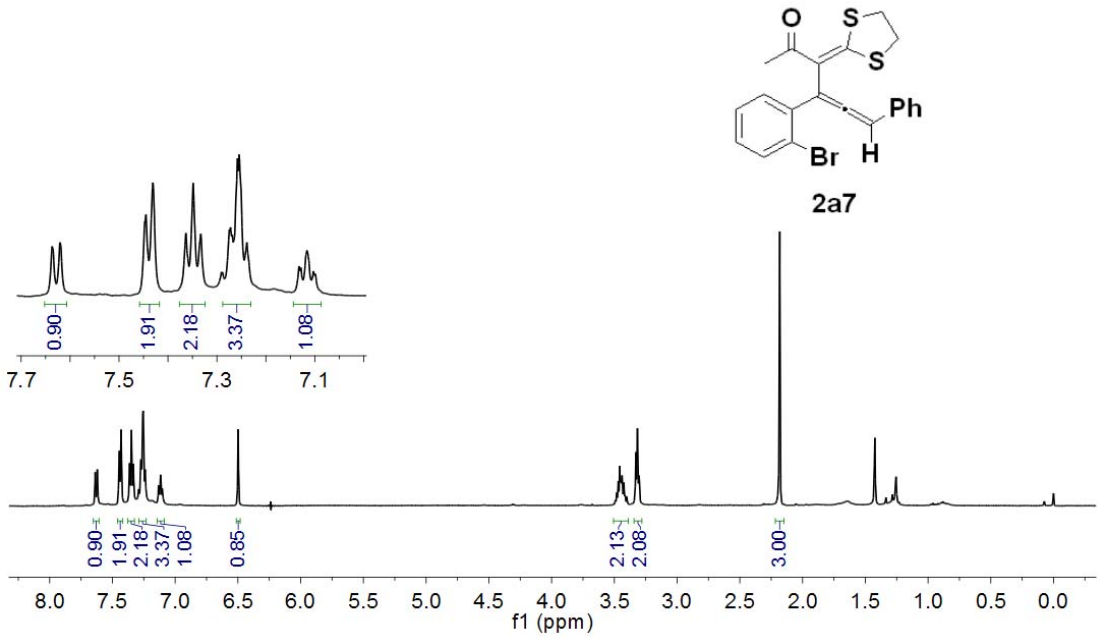
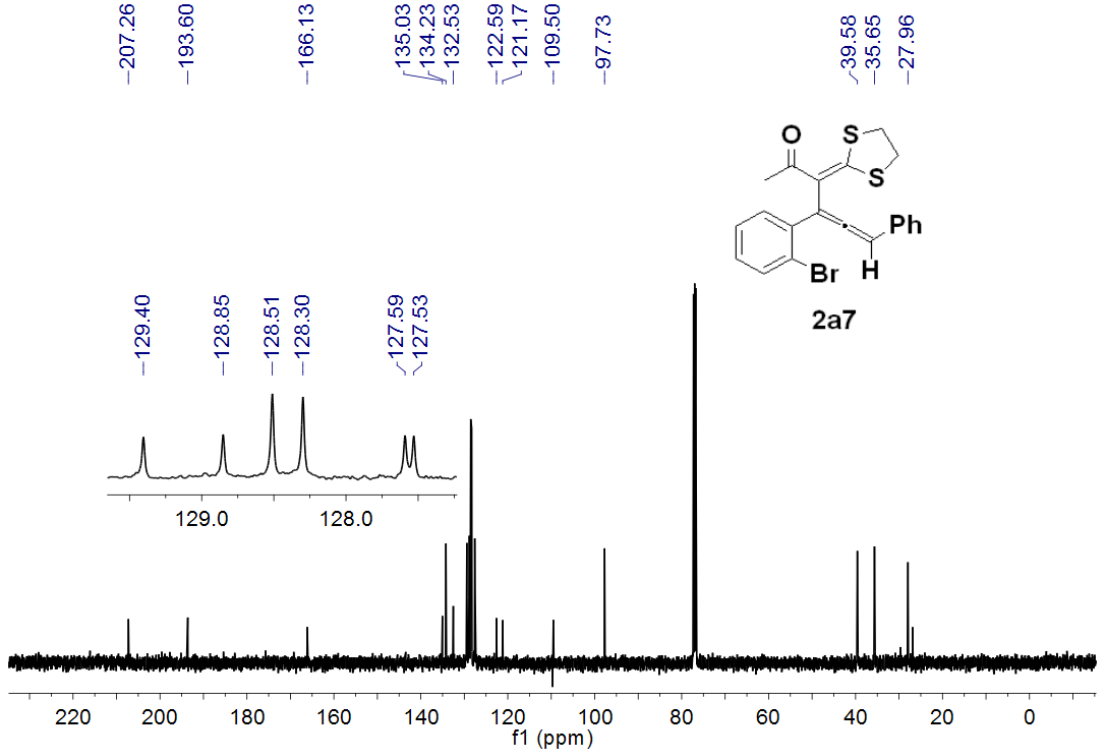
2a5
1.98
4.04
0.95
2.01
7.4
7.2
7.0
1.98
4.04
0.95
2.01
0.95
3.11
2.08
2.09
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

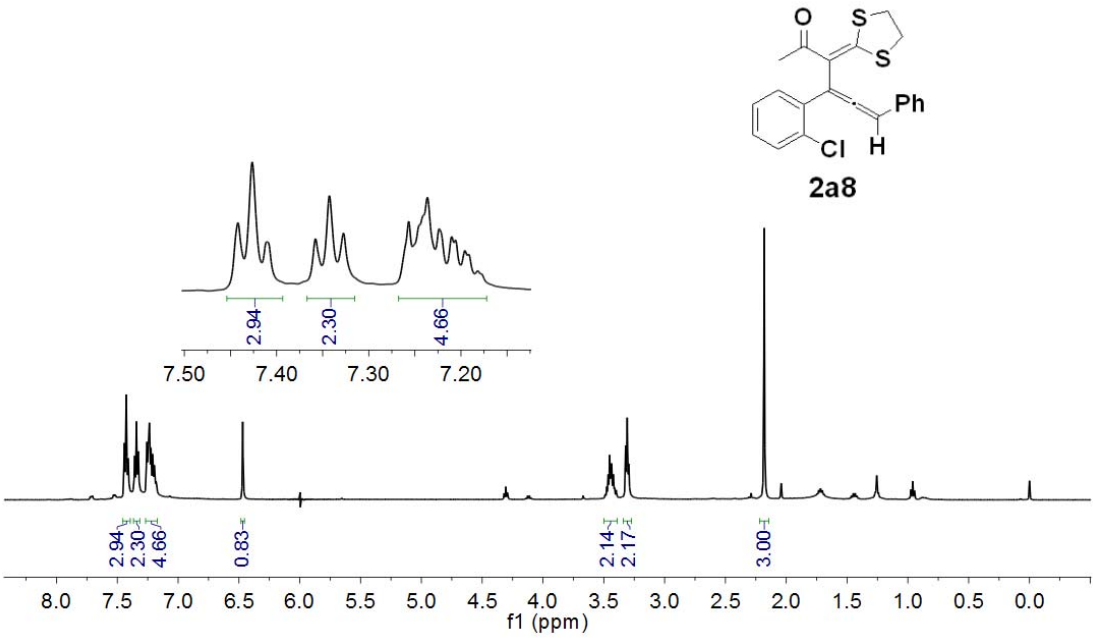

206.53
193.62
165.78
159.38
133.50
119.55
114.36
110.58
97.89
55.26
39.61
35.52
27.75
O
S
S
Ph
O
H
2a5
128.75
127.43
127.37
127.27
126.35
128.0
127.0
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

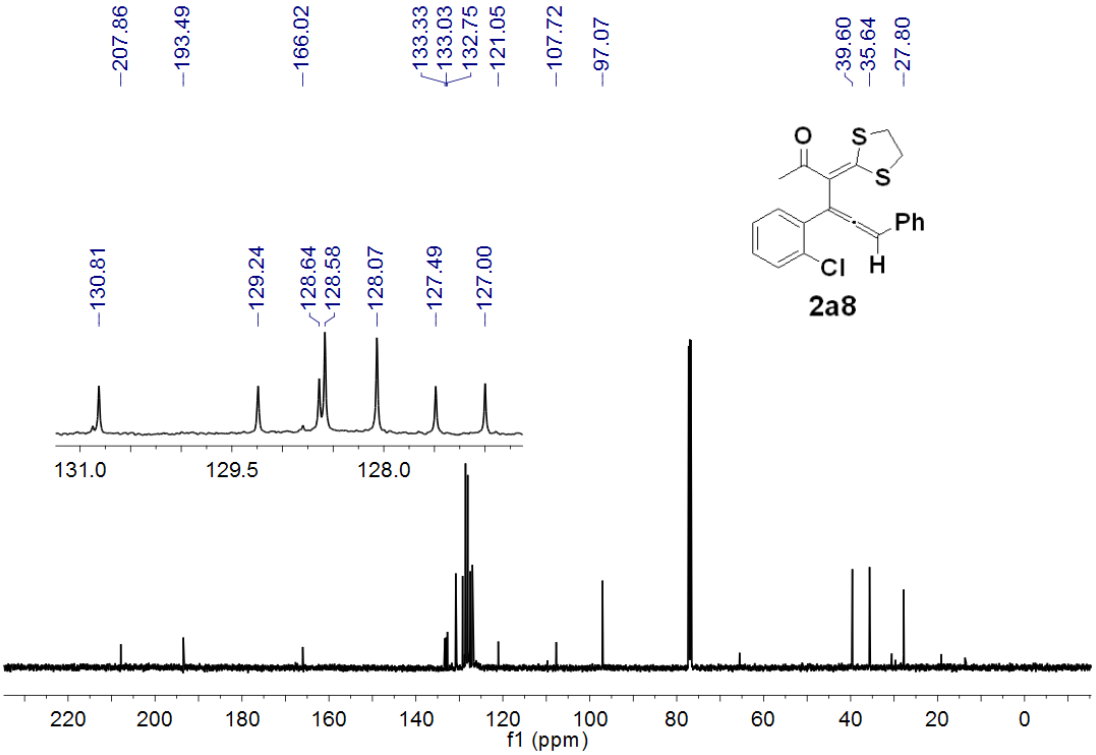

O
S
S
Ph
Cl
H
2a6
2.03
2.26
3.94
1.15
7.55
7.50
7.45
7.40
7.35
2.03
2.26
3.94
1.15
0.95
2.20
2.23
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

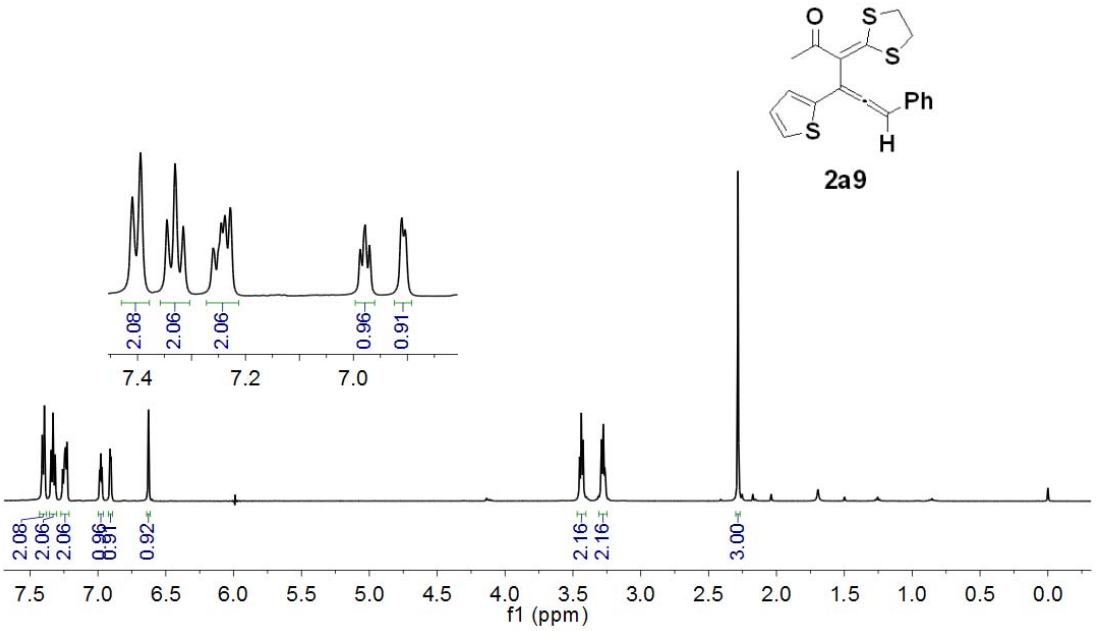

207.14
193.18
166.55
133.49
132.78
132.75
118.75
110.05
98.23
39.63
35.55
27.74
O
S
S
Ph
Cl
H
2a6
129.03
128.82
127.70
127.42
127.25
128.5
127.5
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

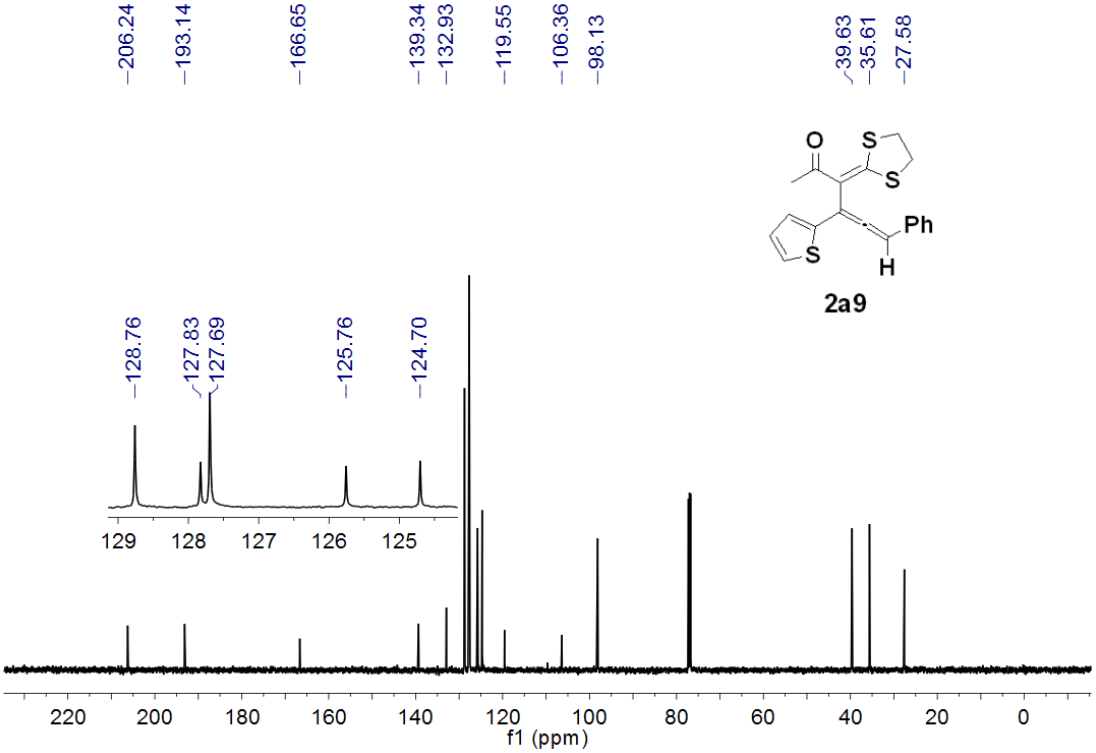

O
S
S
Ph
Br
H
2a7
0.90
1.91
2.18
3.37
1.08
7.7
7.5
7.3
7.1
0.90
1.91
2.18
3.37
1.08
0.85
2.13
2.08
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


207.26
193.60
166.13
135.03
134.23
132.53
122.59
121.17
109.50
97.73
39.58
35.65
27.96
O
S
S
Ph
Br
H
2a7
129.40
128.85
128.51
128.30
127.59
127.53
129.0
128.0
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


O
S
S
Ph
Cl
H
2a8
2.94
2.30
4.66
7.50
7.40
7.30
7.20
0.83
2.14
2.17
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


207.86
193.49
166.02
133.33
133.03
132.75
121.05
107.72
97.07
39.60
35.64
27.80
O
S
S
Ph
Cl
H
2a8
130.81
129.24
128.64
128.58
128.07
127.49
127.00
131.0
129.5
128.0
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


O
S
S
Ph
S
H
2a9
2.08
2.06
2.06
0.96
0.91
7.4
7.2
7.0
2.08
2.06
2.06
0.96
0.91
0.92
2.16
2.16
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)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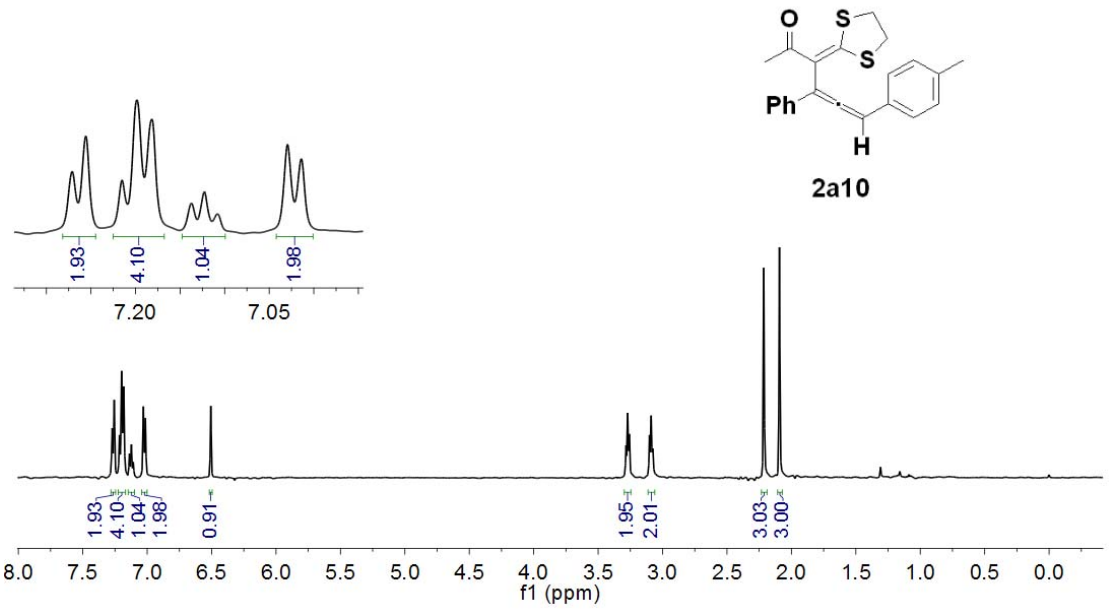
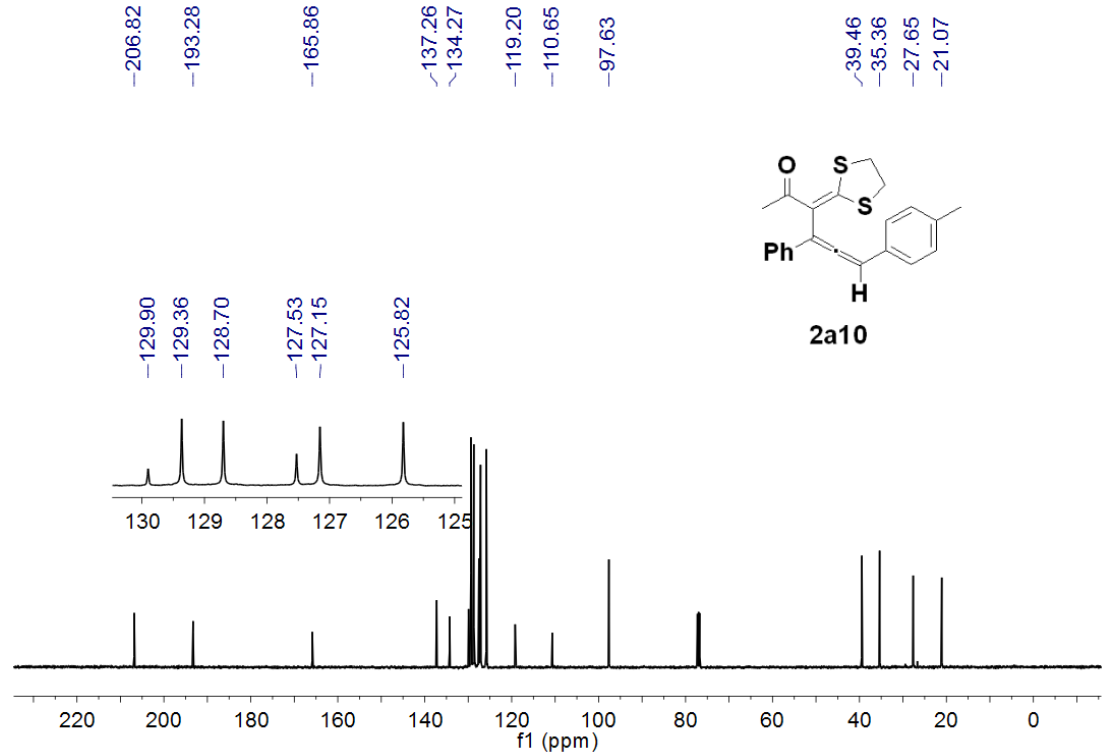
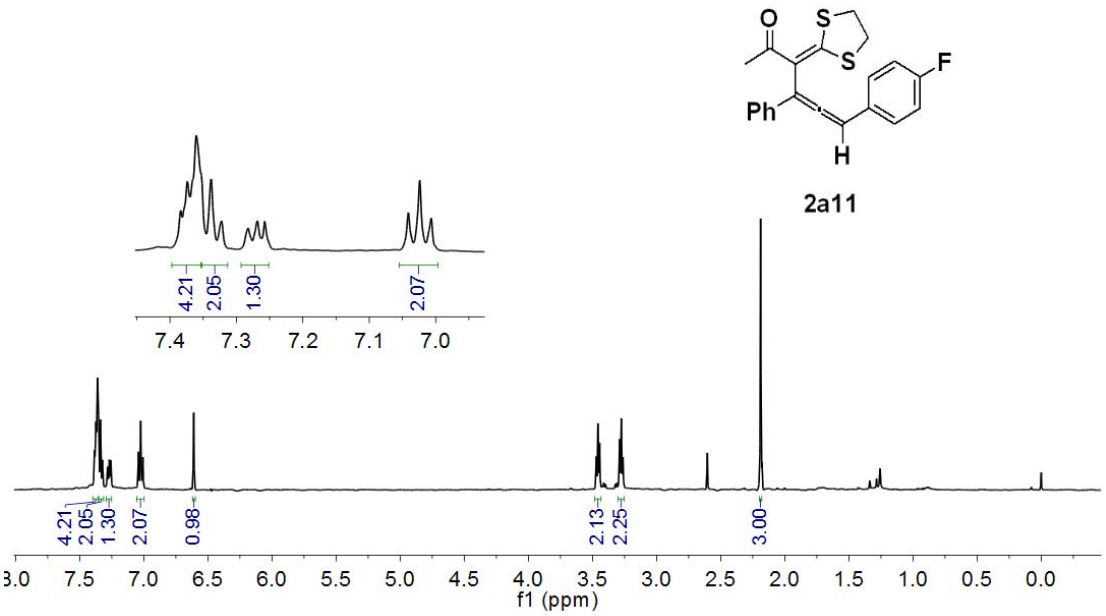
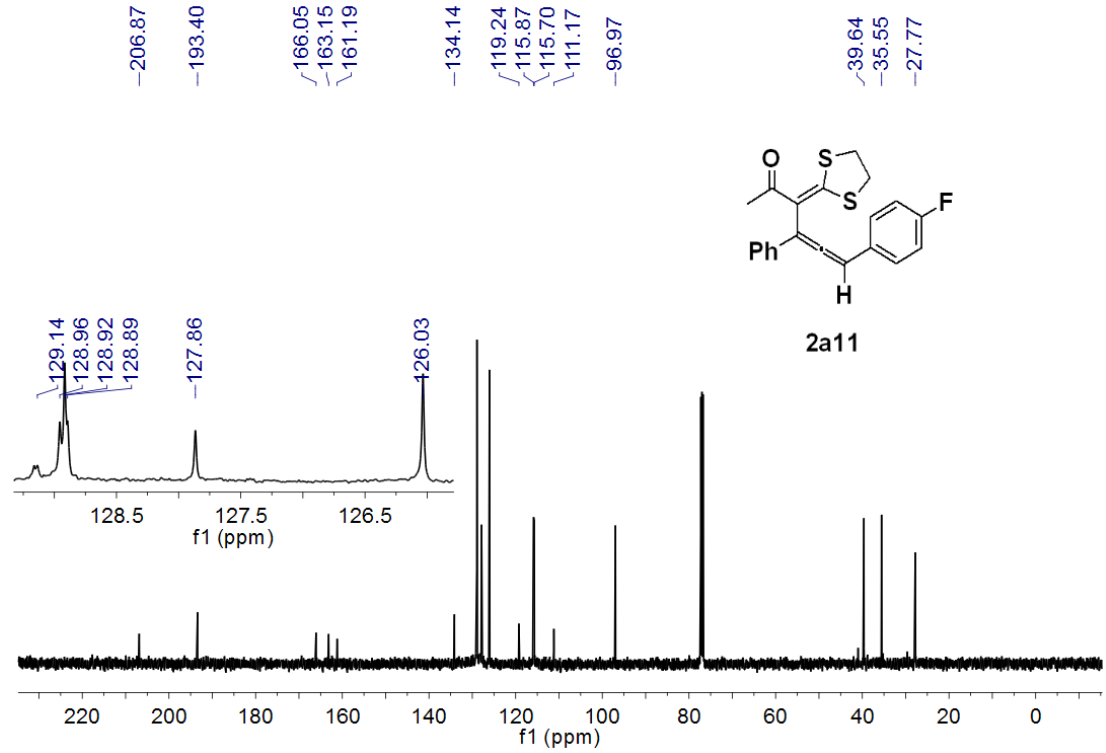
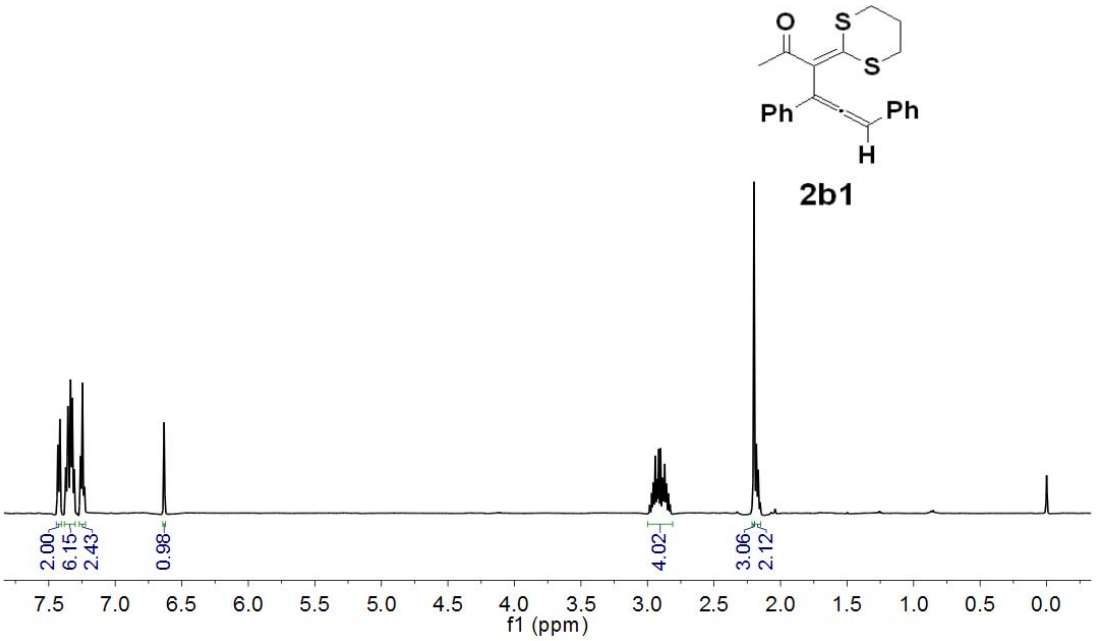
193.14
166.65
139.34
132.93
119.55
106.36
98.13
39.63
35.61
27.58
O
S
S
Ph
S
H
2a9
128.76
127.83
127.69
125.76
124.70
129 128 127 126 125
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

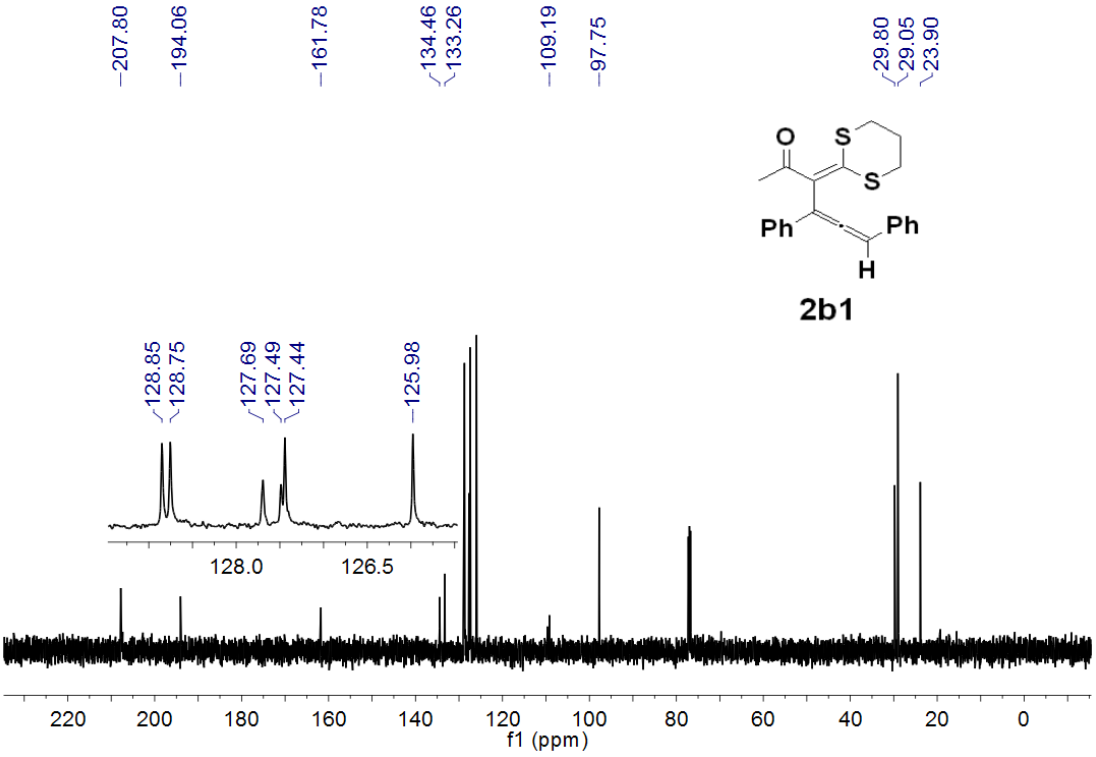

O
S
S
Ph
H
2a10
1.93
4.10
1.04
1.98
7.20
7.05
1.93
4.10
1.04
1.98
0.91
1.95
2.01
3.03
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

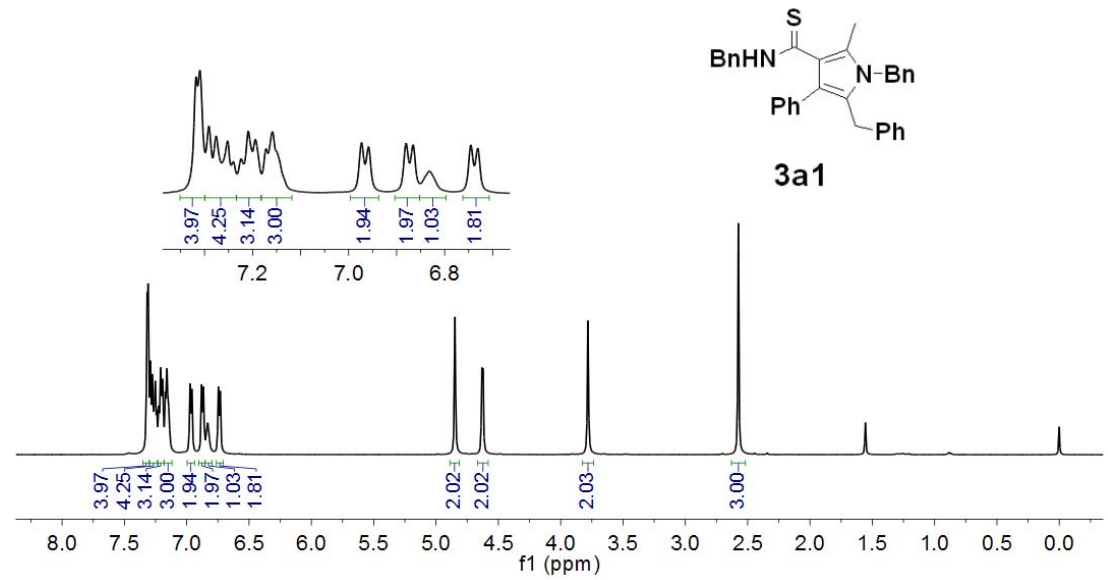

206.82
193.28
165.86
137.26
134.27
119.20
110.65
97.63
39.46
35.36
27.65
21.07
O
S
S
Ph
H
2a10
129.90
129.36
128.70
127.53
127.15
125.82
130 129 128 127 126 125
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

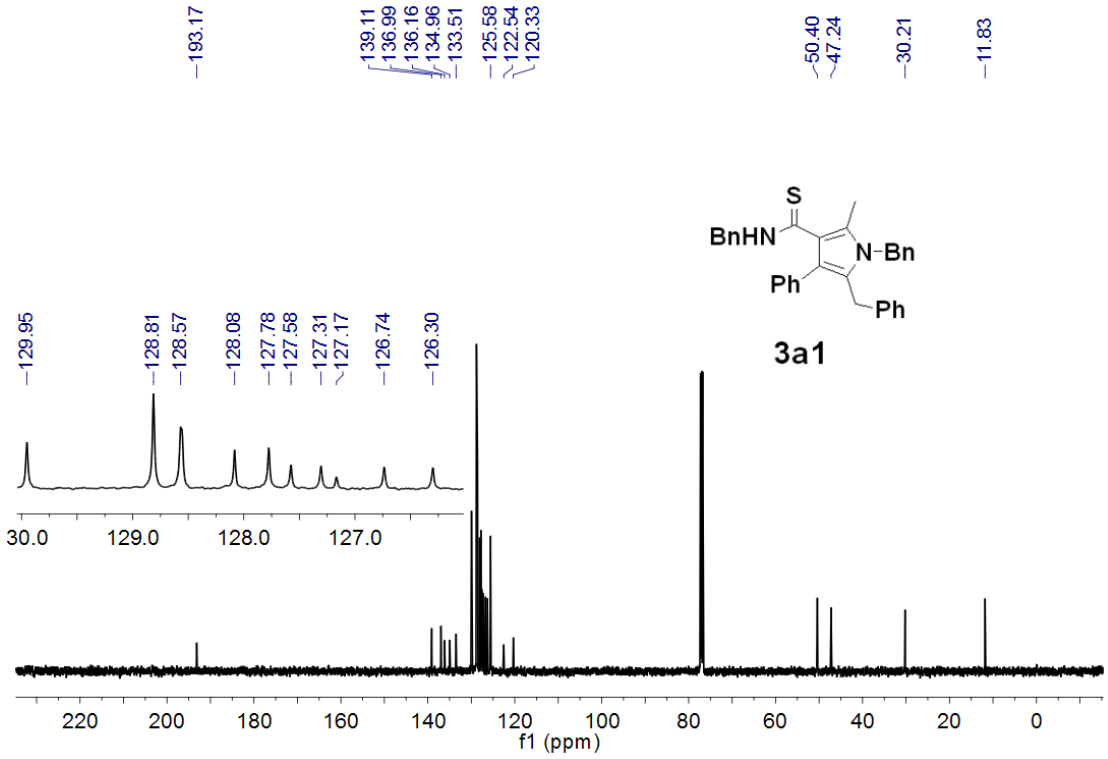

O
S
S
F
Ph
H
2a11
4.21
2.05
1.30
2.07
7.4
7.3
7.2
7.1
7.0
4.21
2.05
1.30
2.07
0.98
2.13
2.25
3.00
f1 (ppm)

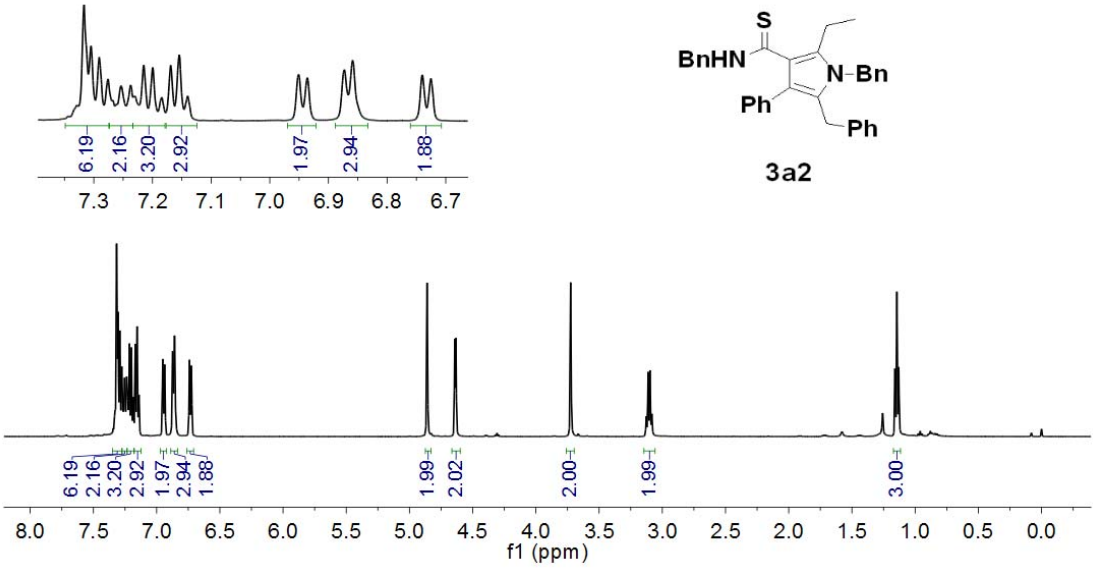

206.87
193.40
166.05
163.15
161.19
134.14
119.24
115.87
115.70
111.17
96.97
39.64
35.55
27.77
O
S
S
F
Ph
H
2a11
129.14
128.96
128.92
128.89
127.86
126.03
128.5
127.5
126.5
f1 (ppm)
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

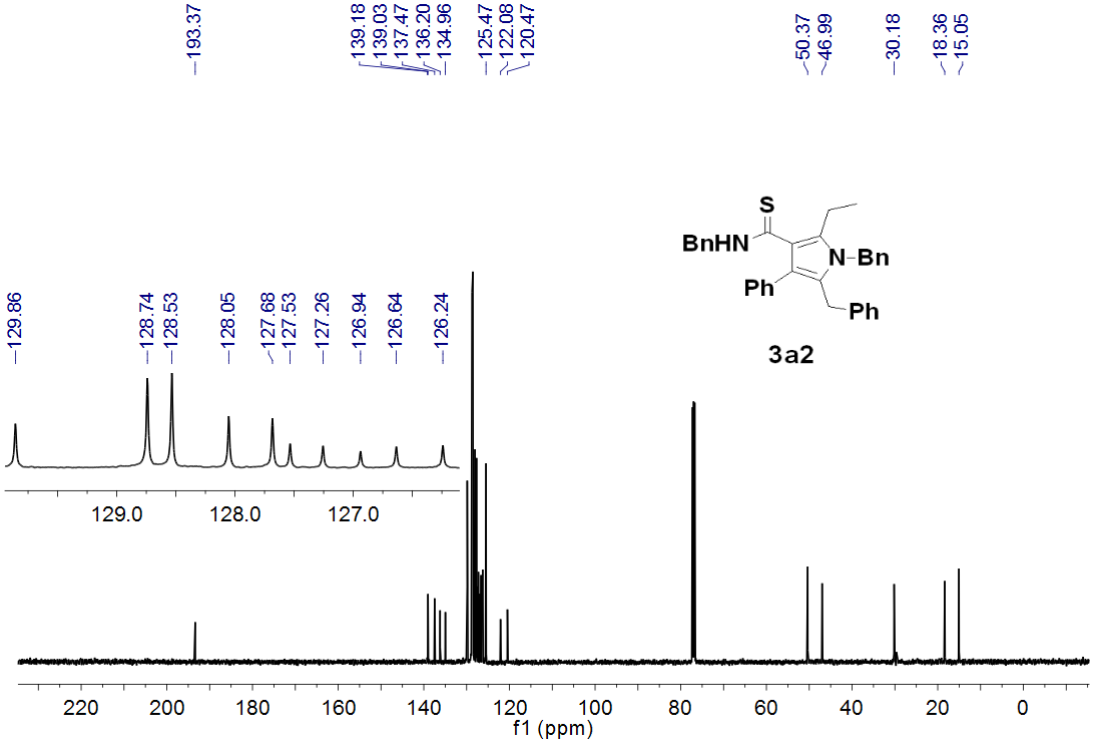

O
S
S
Ph
Ph
H
2b1
2.00
6.15
2.43
0.98
4.02
3.06
2.12
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

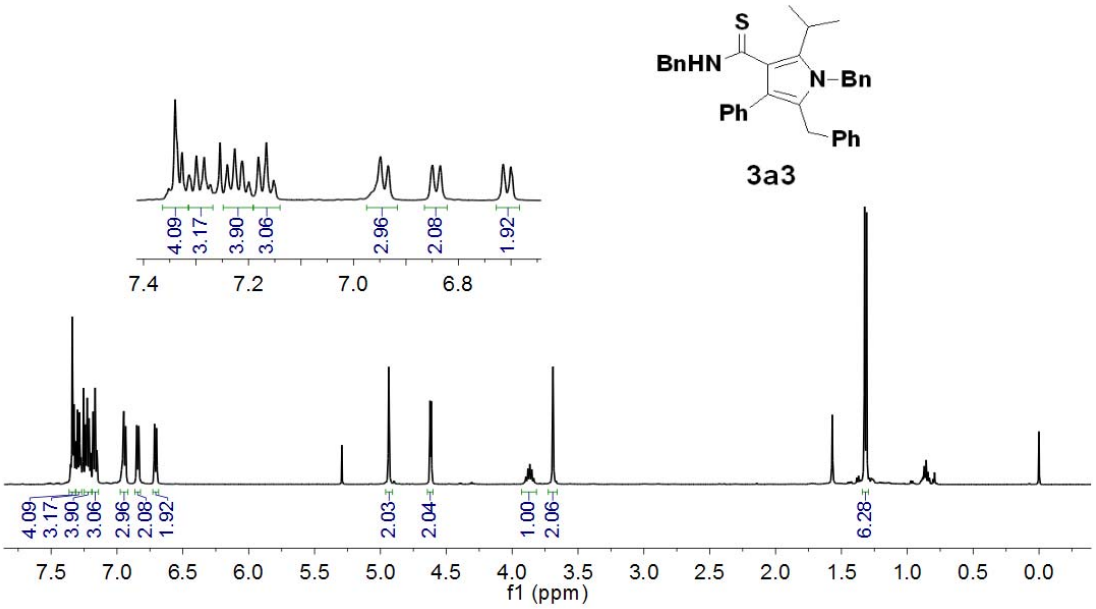

207.80
194.06
161.78
134.46
133.26
109.19
97.75
29.80
29.05
23.90
O
S
S
Ph
Ph
H
2b1
128.85
128.75
127.69
127.49
127.44
125.98
128.0
126.5
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

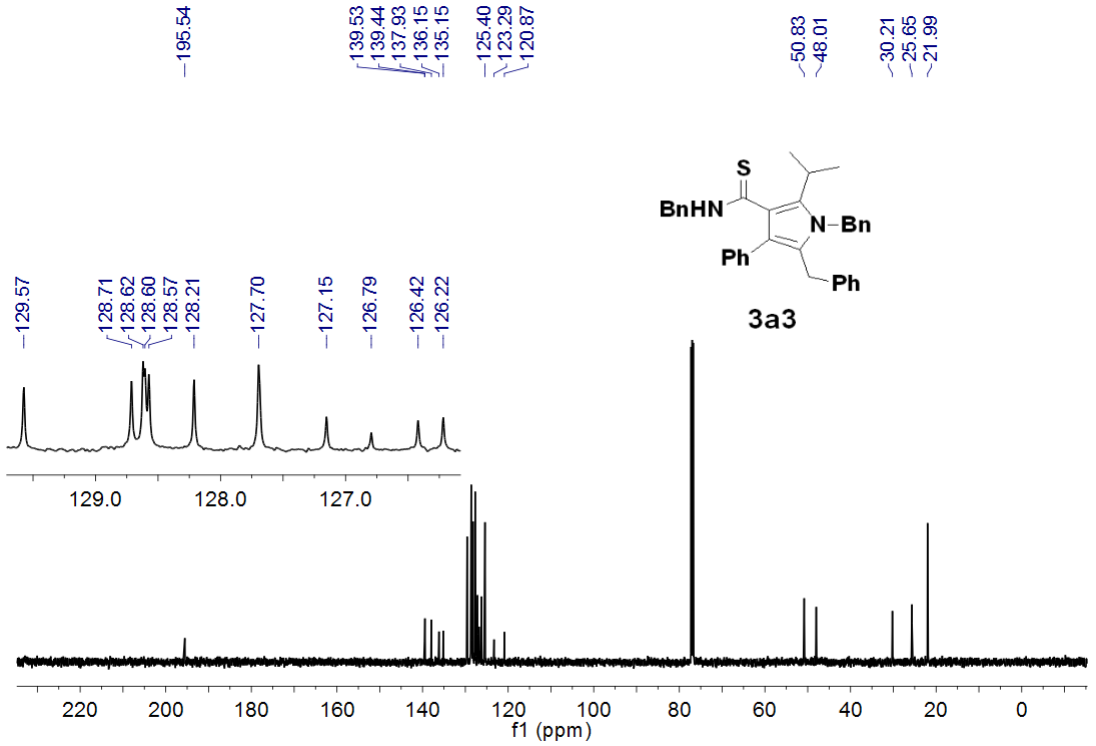

S
BnHN
N-Bn
Ph
Ph
3a1
3.97
4.25
3.14
3.00
1.94
1.97
1.03
1.81
7.2
7.0
6.8
2.02
2.02
2.03
3.00
f1 (ppm)

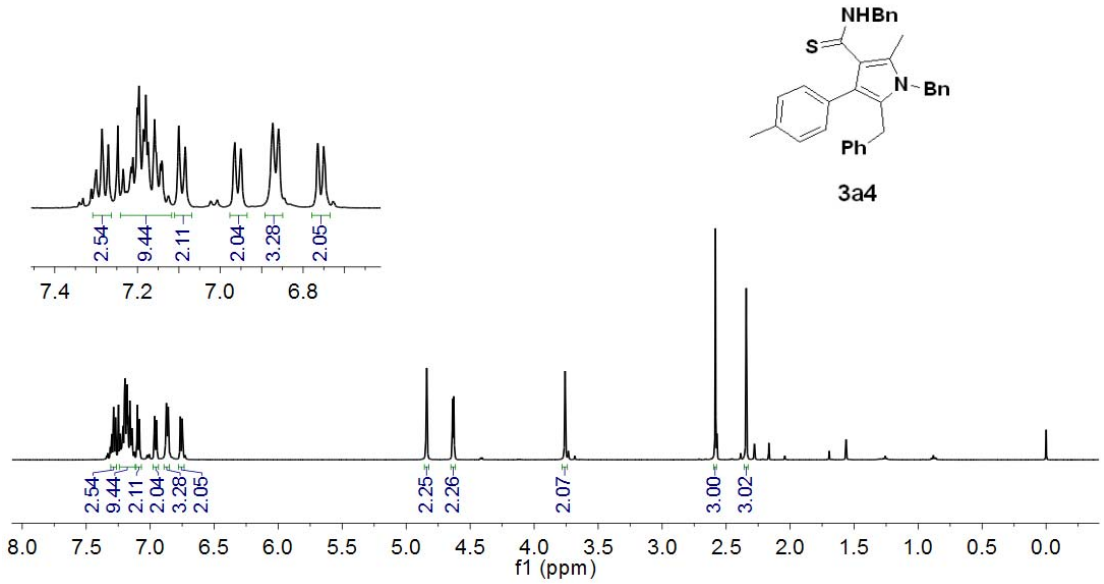

193.17
139.11
136.99
136.16
134.96
133.51
125.58
122.54
120.33
50.40
47.24
30.21
11.83
S
BnHN
N-Bn
Ph
Ph
3a1
129.95
128.81
128.57
128.08
127.78
127.58
127.31
127.17
126.74
126.30
30.0
129.0
128.0
127.0
f1 (ppm)

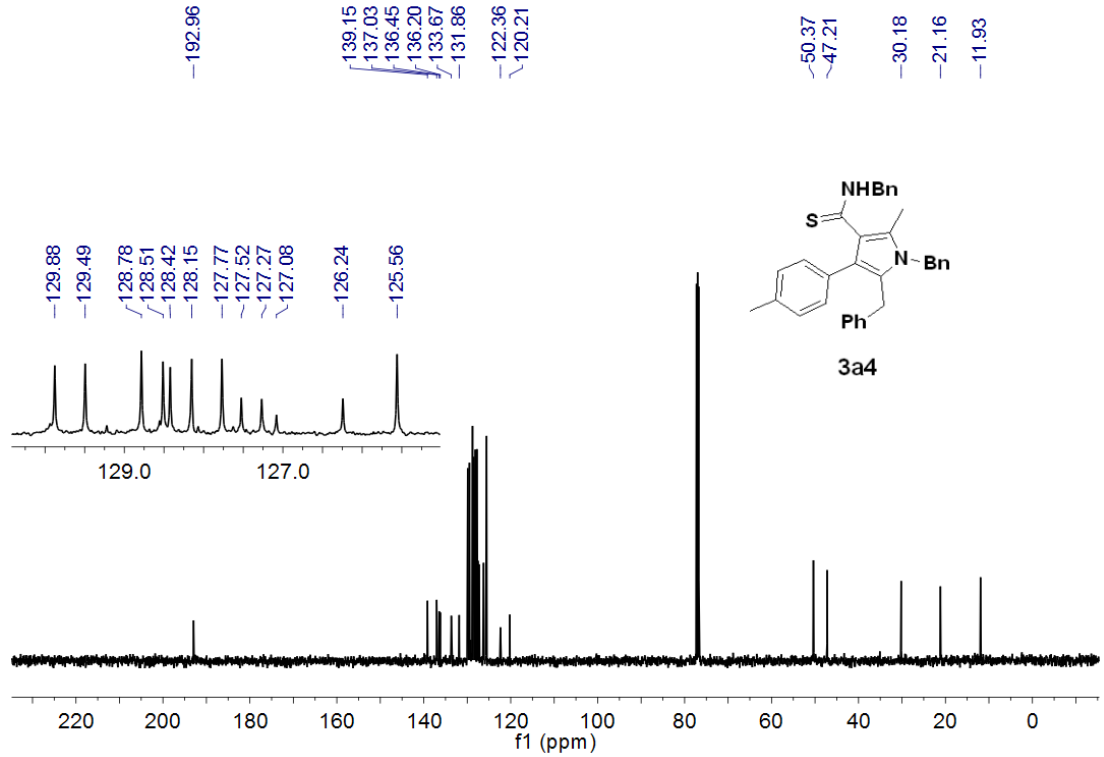

S
BnHN
N-Bn
Ph
Ph
3a2
6.19
2.16
3.20
2.92
1.97
2.94
1.88
1.99
2.02
2.00
1.99
3.00
f1 (ppm)

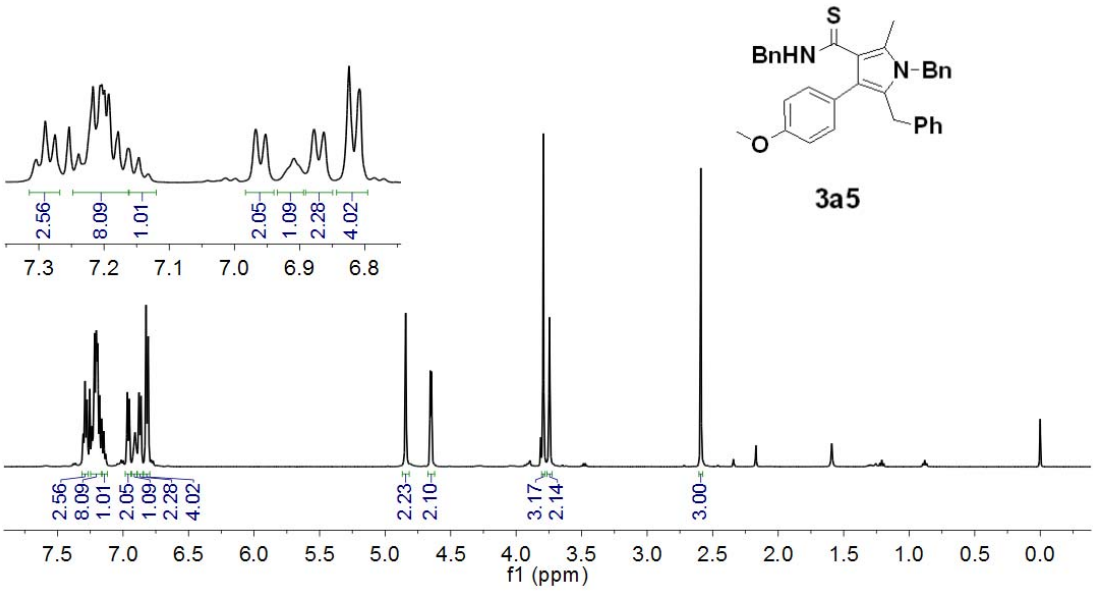

193.37
139.18
139.03
137.47
136.20
134.96
125.47
122.08
120.47
50.37
46.99
30.18
18.36
15.05
S
BnHN
N-Bn
Ph
Ph
3a2
129.86
128.74
128.53
128.05
127.68
127.53
127.26
126.94
126.64
126.24
f1 (ppm)

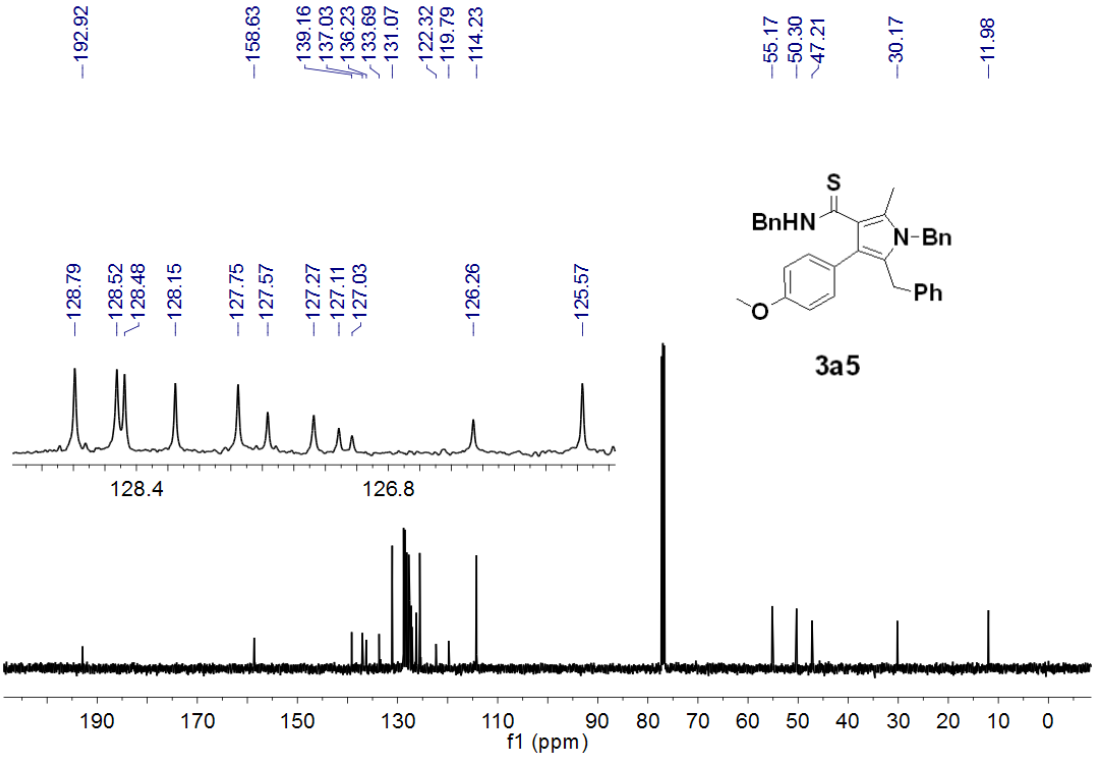

S
BnHN
N–Bn
Ph
Ph
3a3
4.09
3.17
3.90
3.06
2.96
2.08
1.92
2.03
2.04
1.00
2.06
6.28
f1 (ppm)

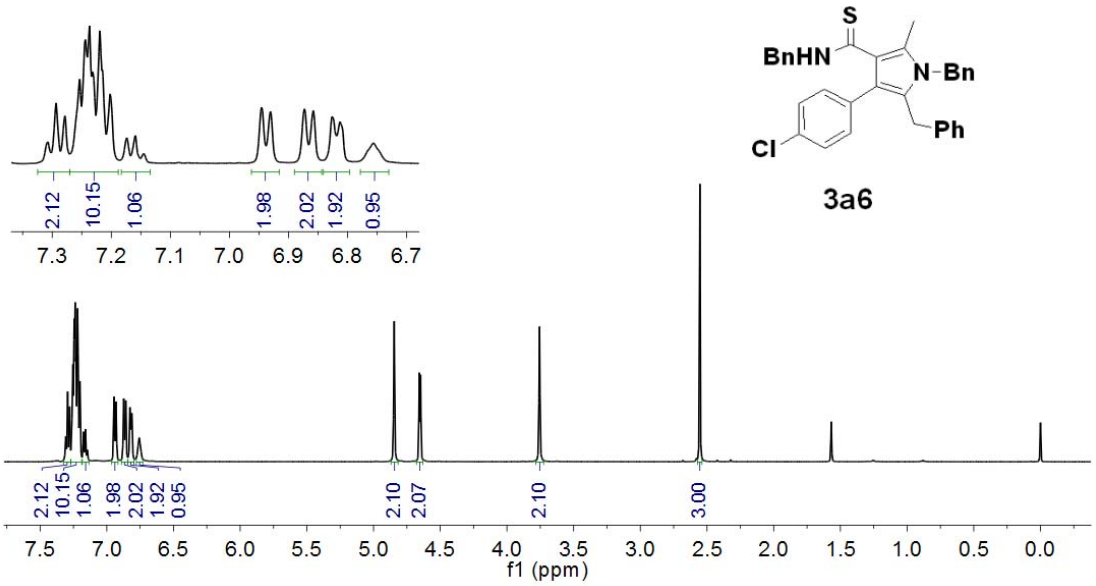

195.54
139.53
139.44
137.93
136.15
135.15
125.40
123.29
120.87
50.83
48.01
30.21
25.65
21.99
S
BnHN
N–Bn
Ph
Ph
3a3
129.57
128.71
128.62
128.60
128.57
128.21
127.70
127.15
126.79
126.42
126.22
f1 (ppm)

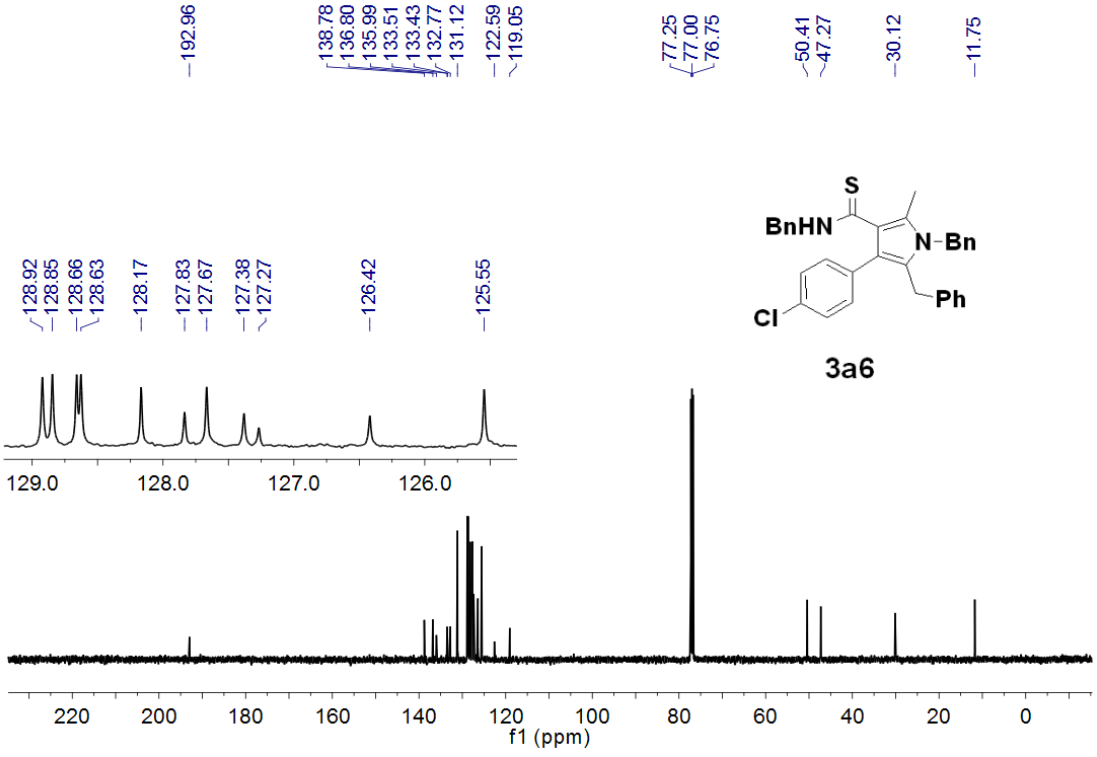

NHBn
S
N
Bn
Ph
3a4
2.54
9.44
2.11
2.04
3.28
2.05
2.25
2.26
2.07
3.00
3.02
f1 (ppm)

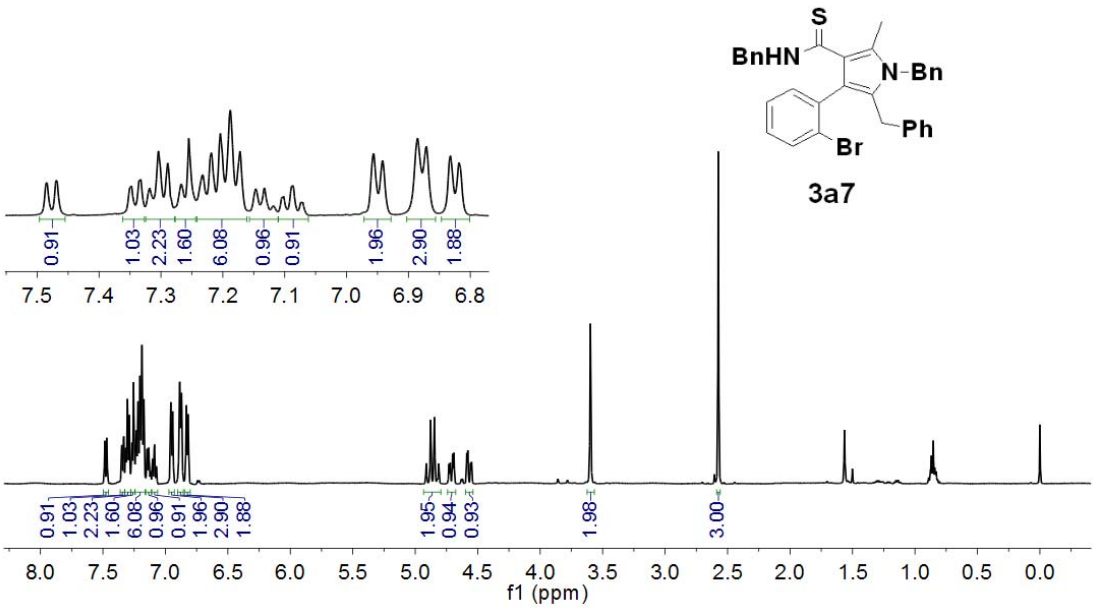

192.96
139.15
137.03
136.45
136.20
133.67
131.86
122.36
120.21
50.37
47.21
30.18
21.16
11.93
NHBn
S
N
Bn
Ph
3a4
129.88
129.49
128.78
128.51
128.42
128.15
127.77
127.52
127.27
127.08
126.24
125.56
f1 (ppm)

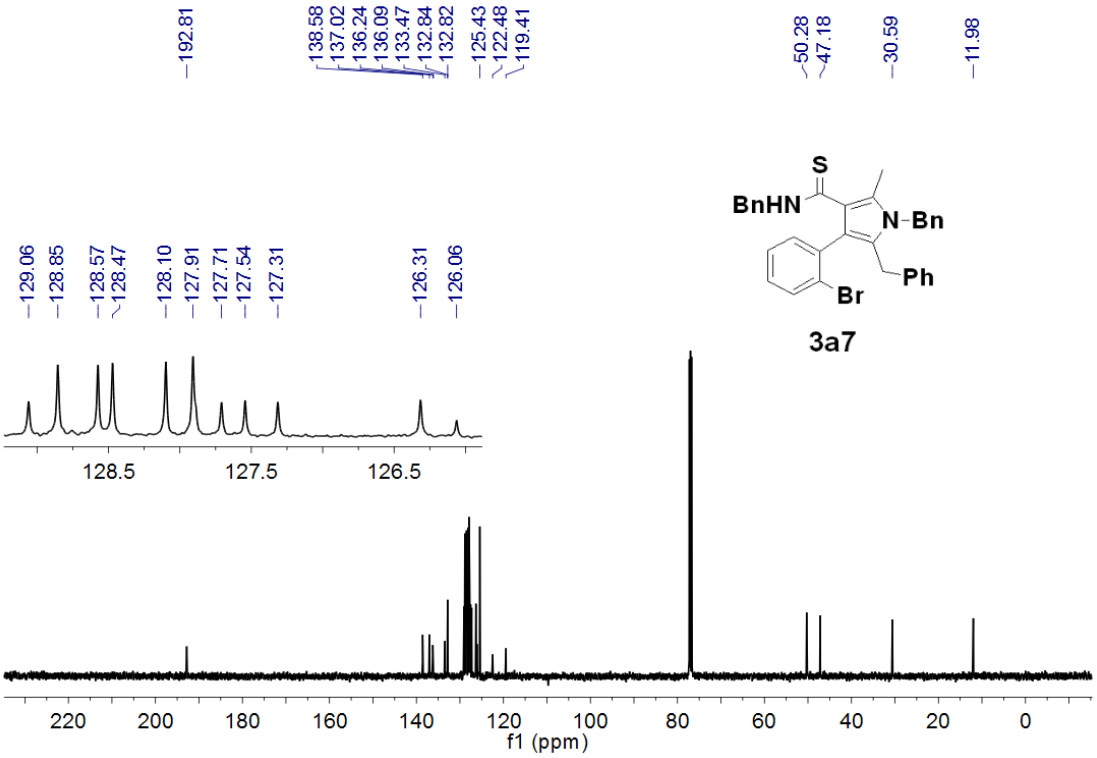

S
BnHN
N-Bn
Ph
O
3a5
2.56
8.09
1.01
2.05
1.09
2.28
4.02
2.23
2.10
3.17
2.14
3.00
f1 (ppm)

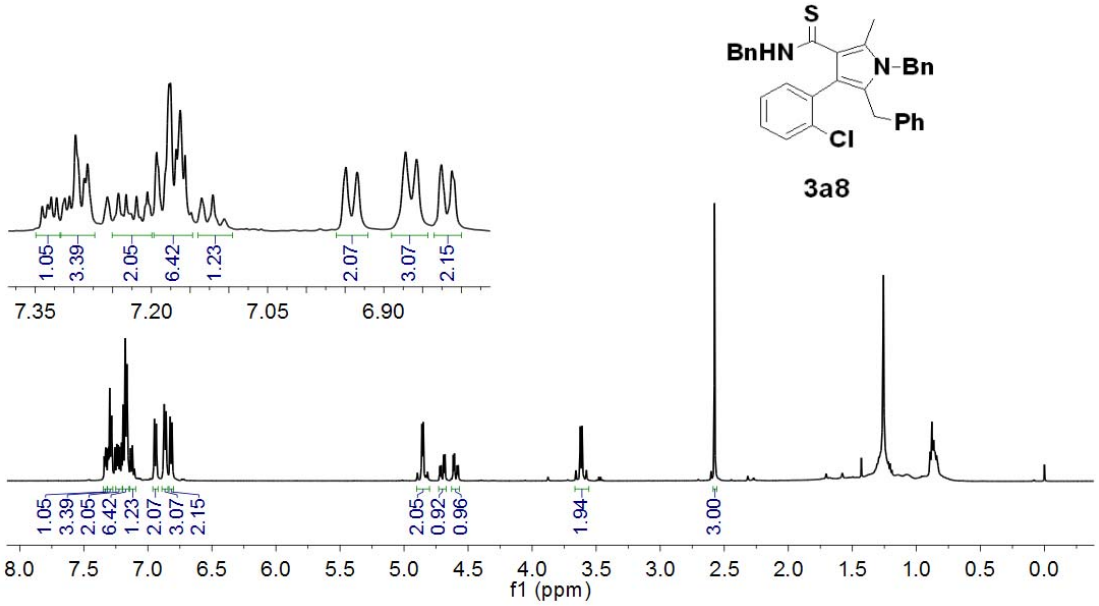

192.92
158.63
139.16
137.03
136.23
133.69
131.07
122.32
119.79
114.23
55.17
50.30
47.21
30.17
11.98
S
BnHN
N-Bn
Ph
O
3a5
128.79
128.52
128.48
128.15
127.75
127.57
127.27
127.11
127.03
126.26
125.57
f1 (ppm)

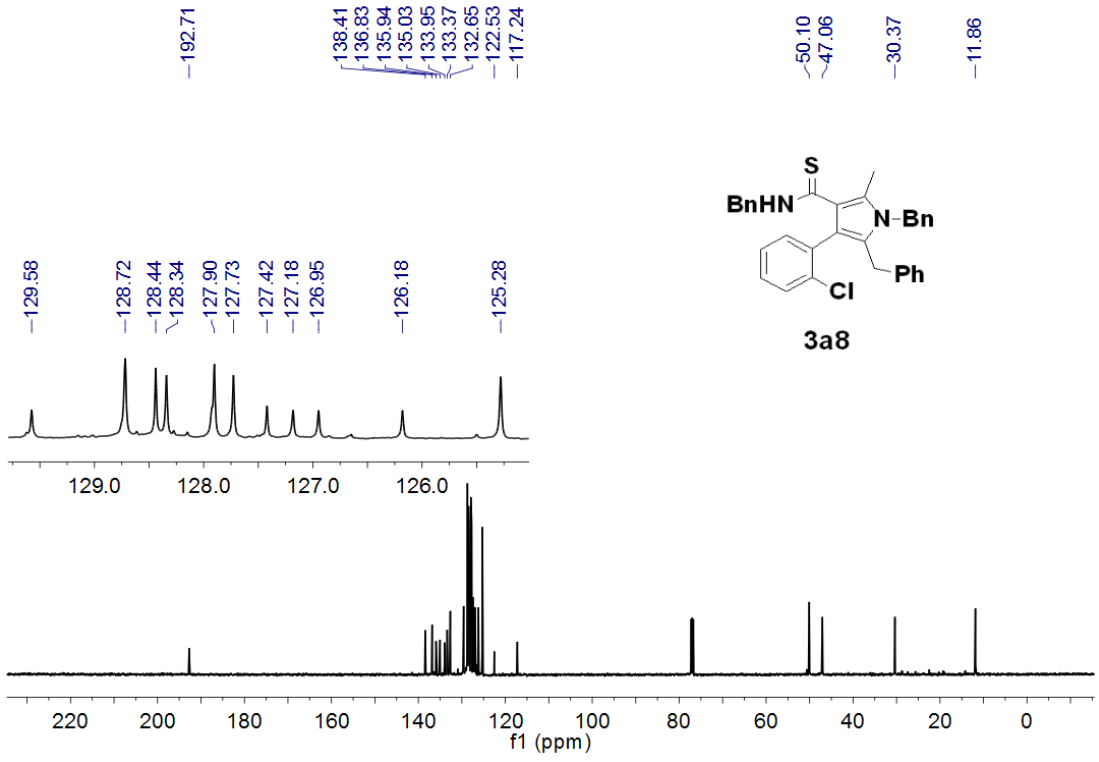

S
BnHN
N-Bn
Ph
Cl
3a6
2.12
10.15
1.06
1.98
2.02
1.92
0.95
2.10
2.07
2.10
3.00
f1 (ppm)

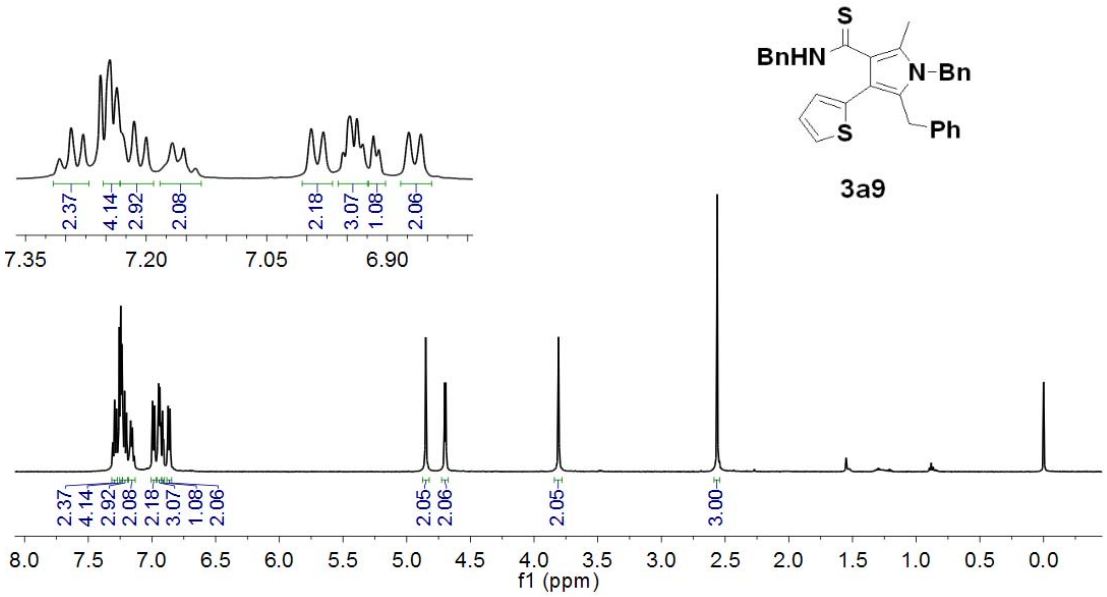

192.96
138.78
136.80
135.99
133.51
133.43
132.77
131.12
122.59
119.05
77.25
77.00
76.75
50.41
47.27
30.12
11.75
128.92
128.85
128.66
128.63
128.17
127.83
127.67
127.38
127.27
126.42
125.55
S
BnHN
N-Bn
Ph
Cl
3a6
f1 (ppm)

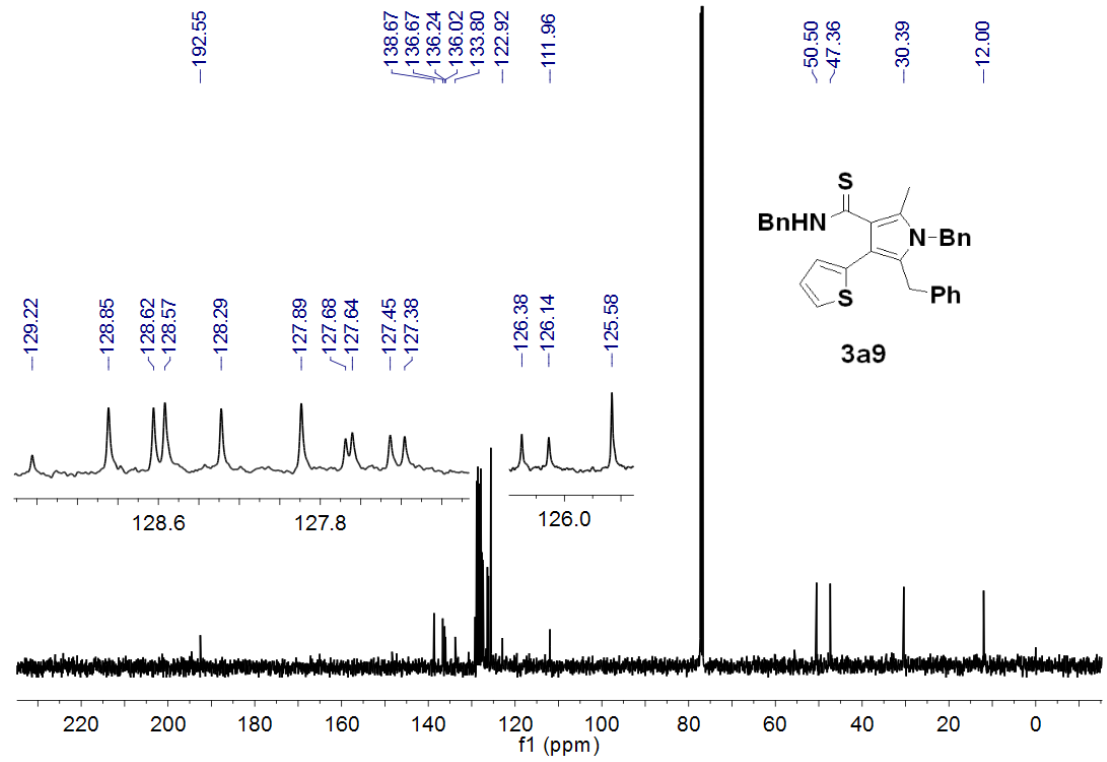


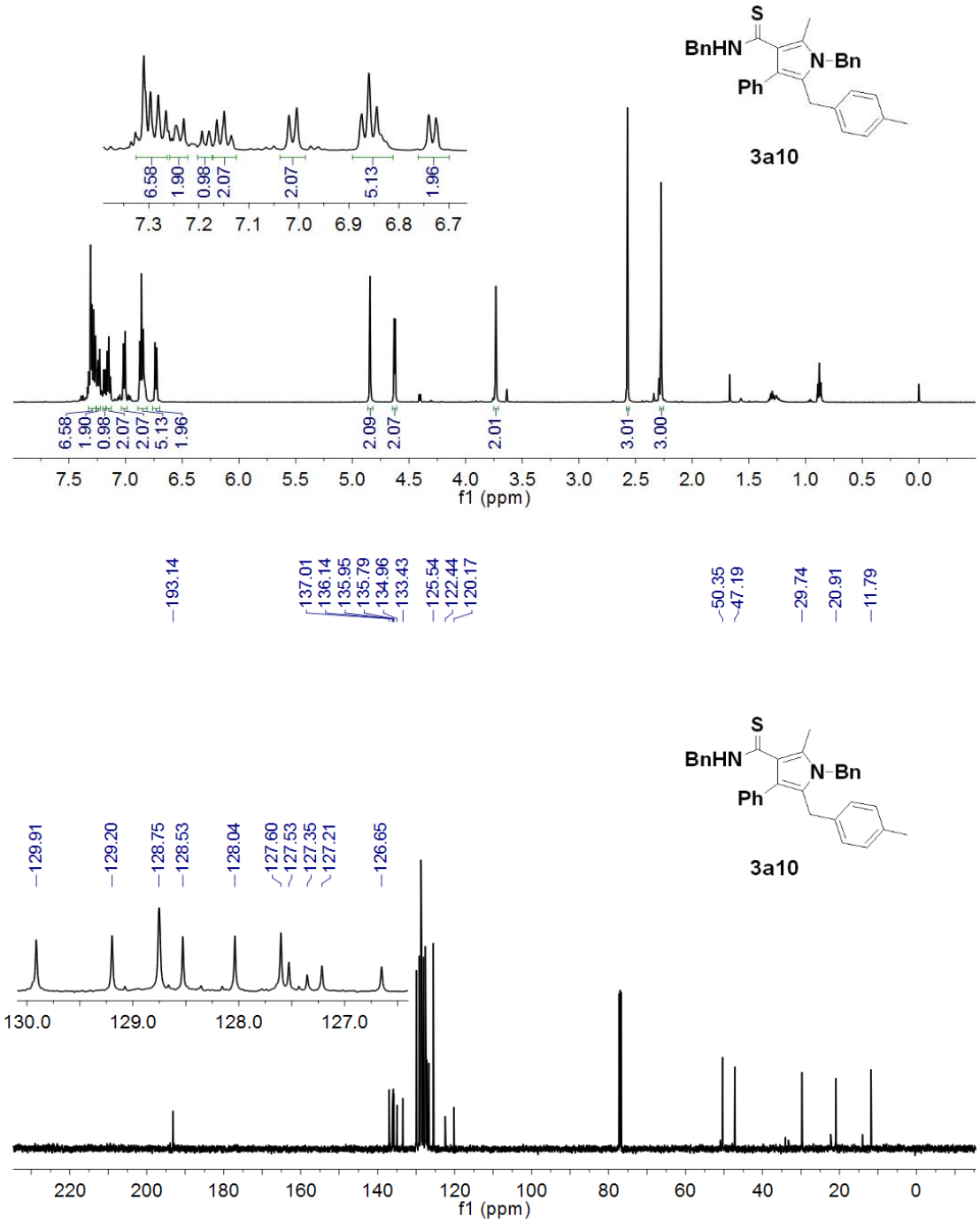



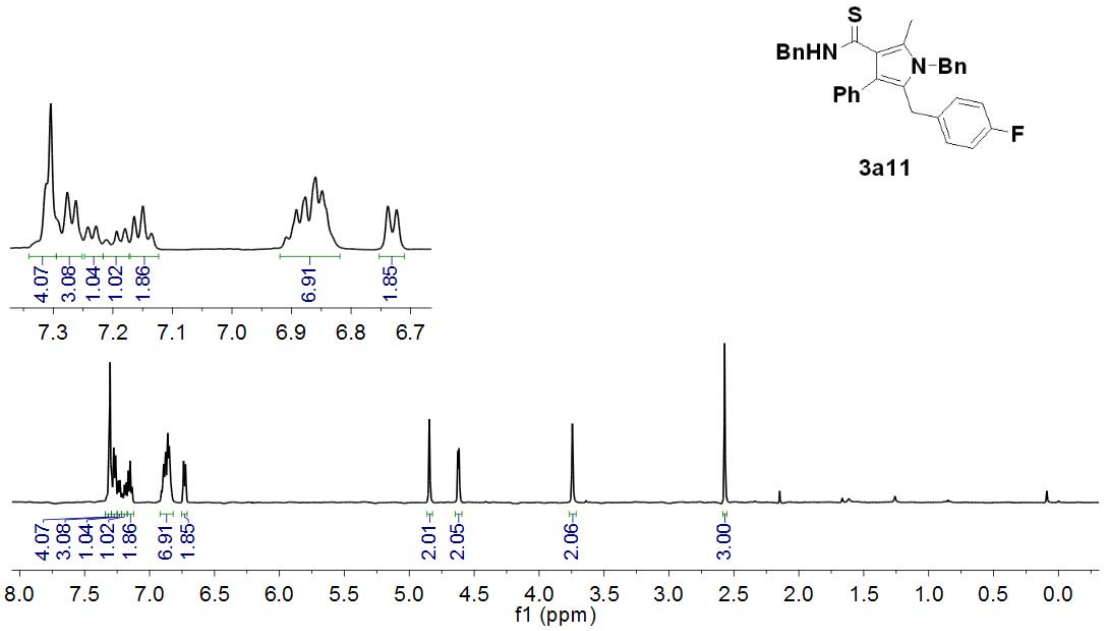

S
BnHN
N-Bn
Ph
Cl
3a8
1.05
3.39
2.05
6.42
1.23
2.07
3.07
2.15
2.05
0.92
0.96
1.94
3.00
f1 (ppm)

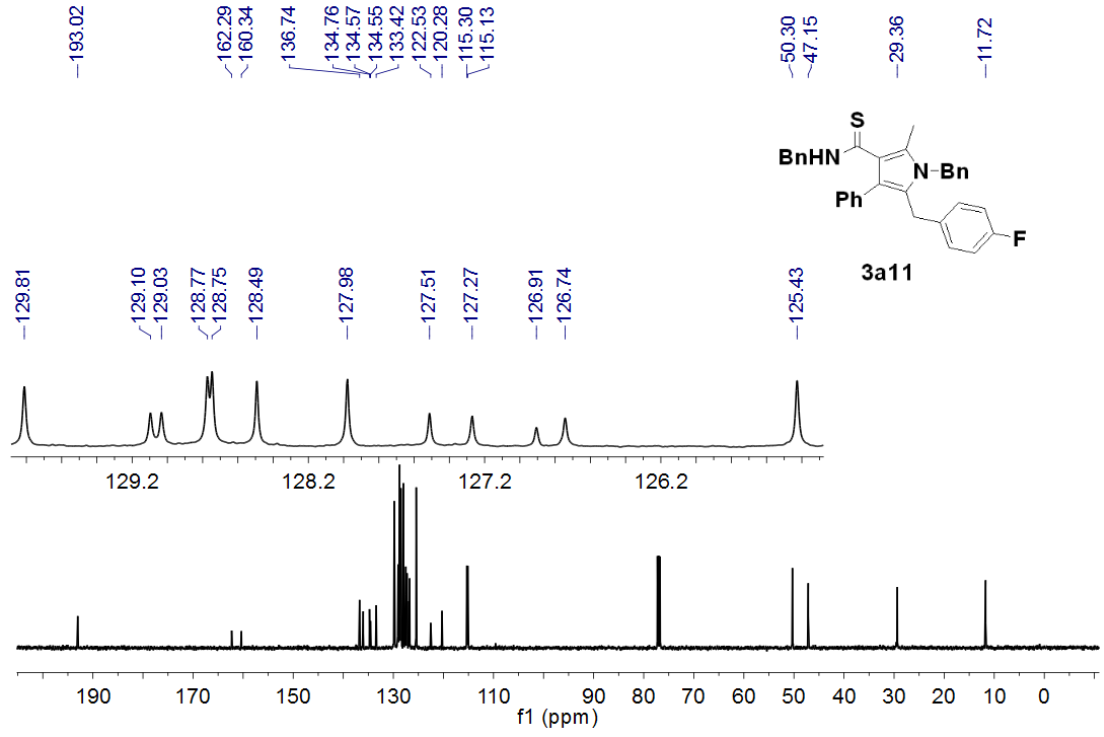

192.71
138.41
136.83
135.94
135.03
133.95
133.37
132.65
122.53
117.24
50.10
47.06
30.37
11.86
S
BnHN
N-Bn
Ph
Cl
3a8
129.58
128.72
128.44
128.34
127.90
127.73
127.42
127.18
126.95
126.18
125.28
f1 (ppm)

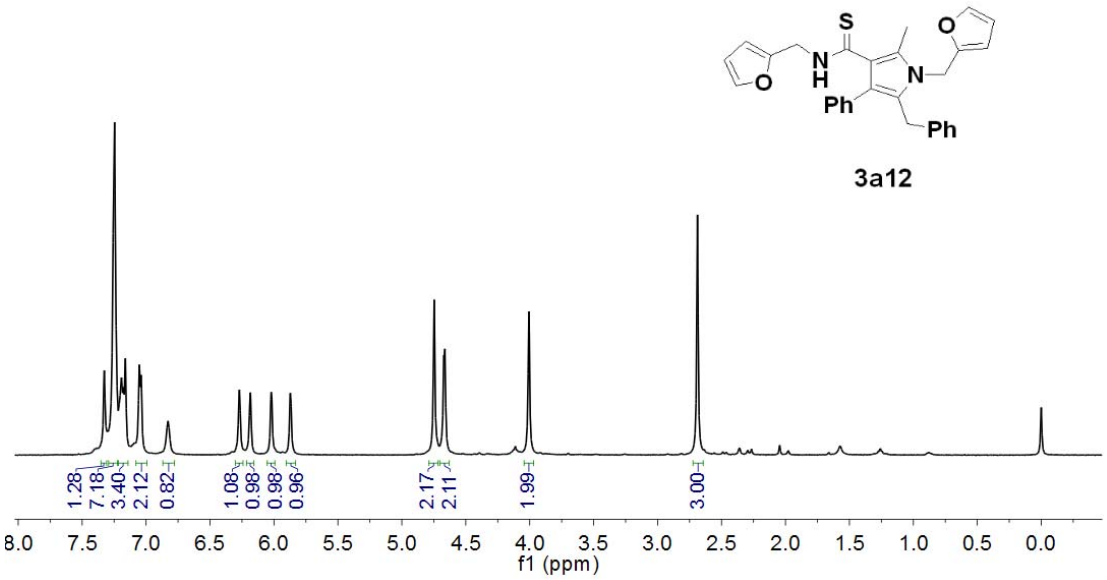

S
BnHN
N-Bn
S
Ph
3a9
2.37
4.14
2.92
2.08
2.18
3.07
1.08
2.06
2.05
2.06
2.05
3.00
7.35
7.20
7.05
6.90
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

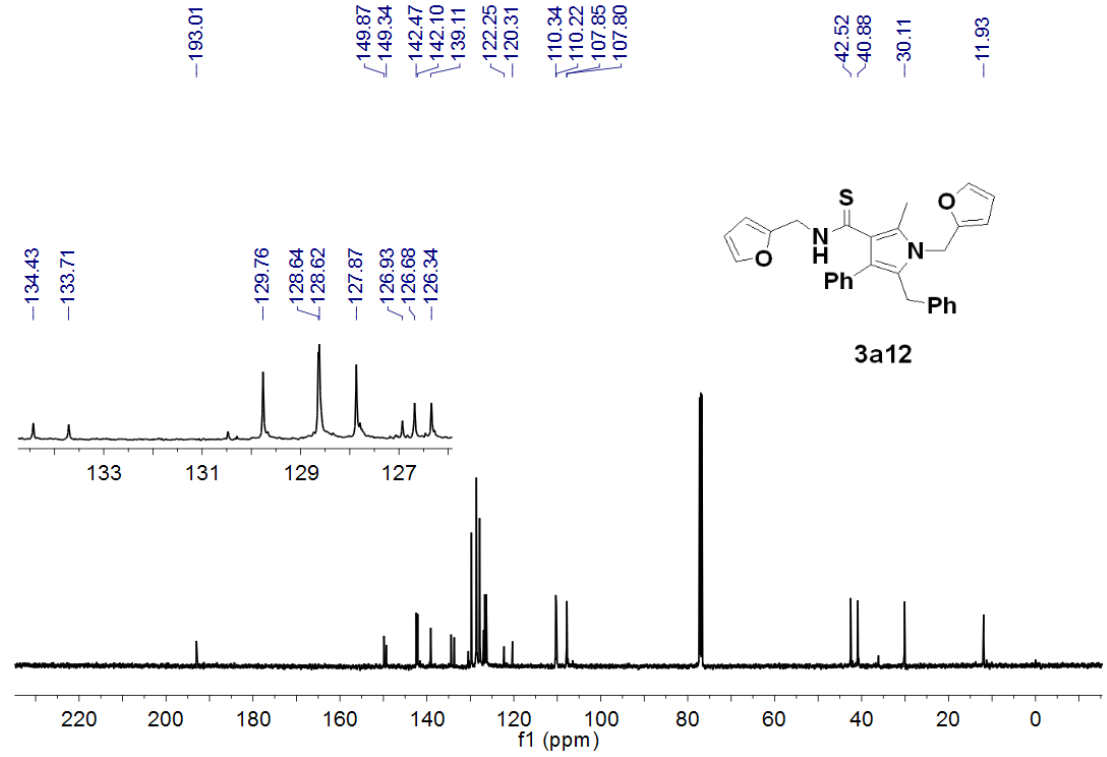

192.55
138.67
136.67
136.24
136.02
133.80
122.92
111.96
50.50
47.36
30.39
12.00
S
BnHN
N-Bn
S
Ph
3a9
129.22
128.85
128.62
128.57
128.29
127.89
127.68
127.64
127.45
127.38
126.38
126.14
125.58
128.6
127.8
126.0
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

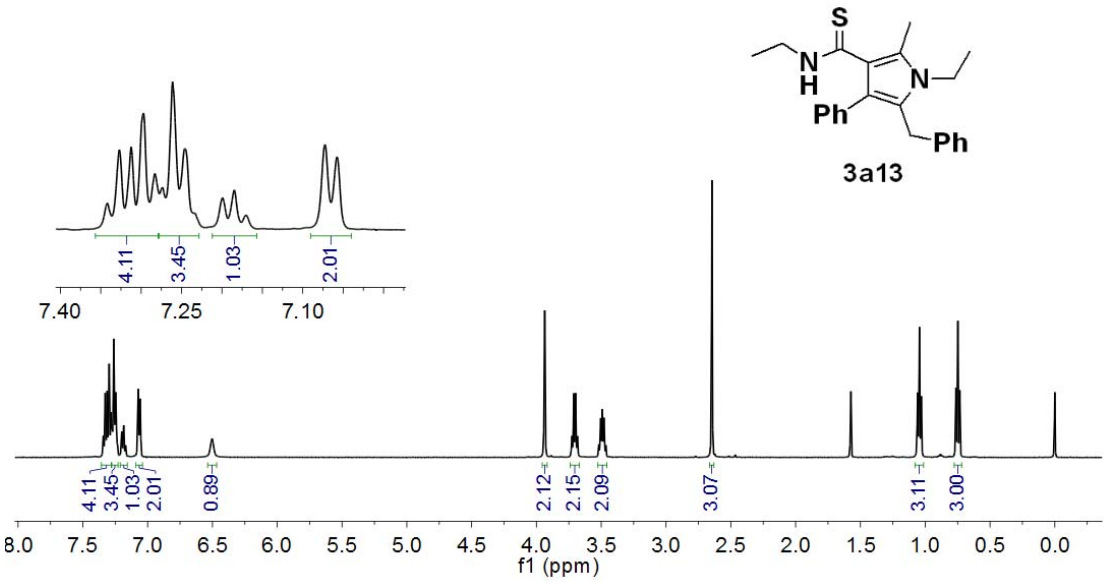

S
BnHN
N-Bn
Ph
3a10
6.58
1.90
0.98
2.07
2.07
5.13
1.96
2.09
2.07
2.01
3.01
3.00
f1 (ppm)
193.14
137.01
136.14
135.95
135.79
134.96
133.43
125.54
122.44
120.17
50.35
47.19
29.74
20.91
11.79
129.91
129.20
128.75
128.53
128.04
127.60
127.53
127.35
127.21
126.65

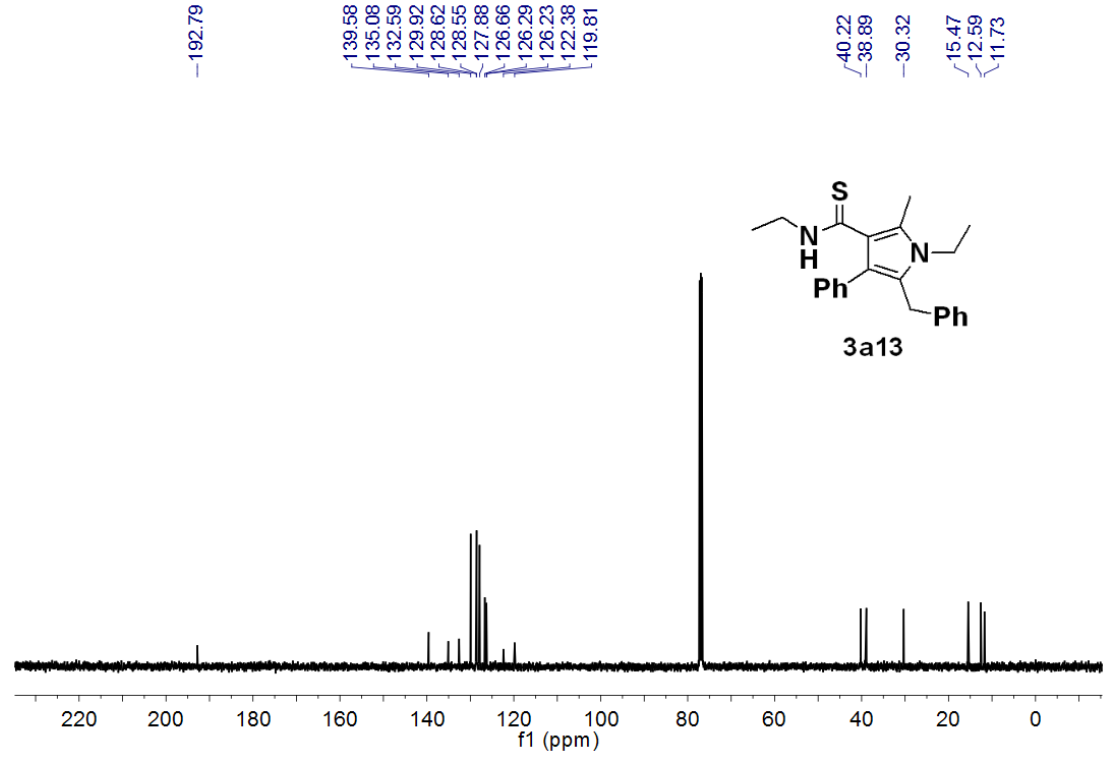

S
BnHN
N-Bn
Ph
F
3a11
4.07
3.08
1.04
1.02
1.86
6.91
1.85
2.01
2.05
2.06
3.00
f1 (ppm)

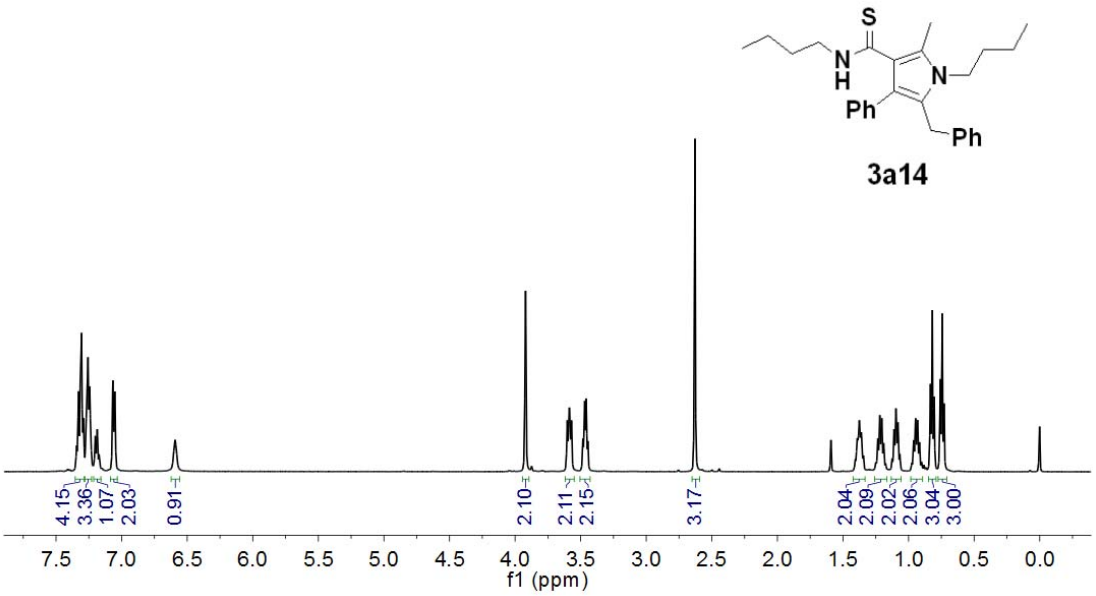

193.02
162.29
160.34
136.74
134.76
134.57
134.55
133.42
122.53
120.28
115.30
115.13
50.30
47.15
29.36
11.72
S
BnHN
N-Bn
Ph
F
3a11
129.81
129.10
129.03
128.77
128.75
128.49
127.98
127.51
127.27
126.91
126.74
125.43
f1 (ppm)

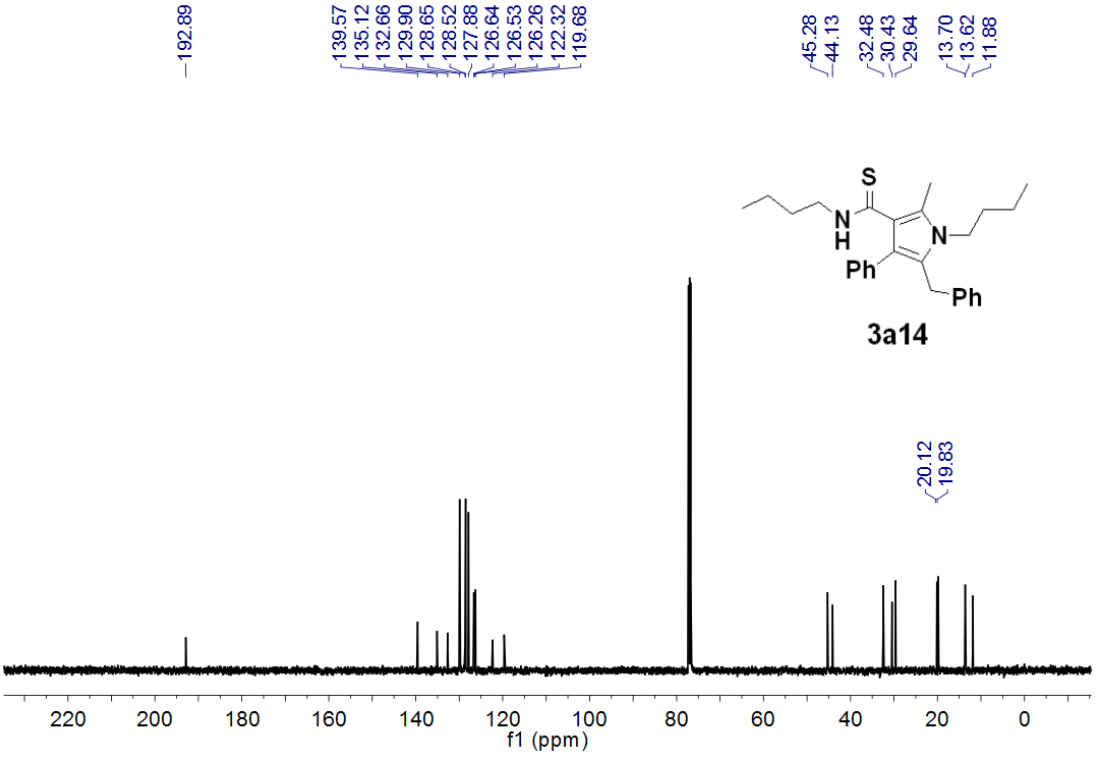

S
O
N
H
O
N
Ph
Ph
3a12
1.28
7.18
3.40
2.12
0.82
1.08
0.98
0.98
0.96
2.17
2.11
1.99
3.00
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

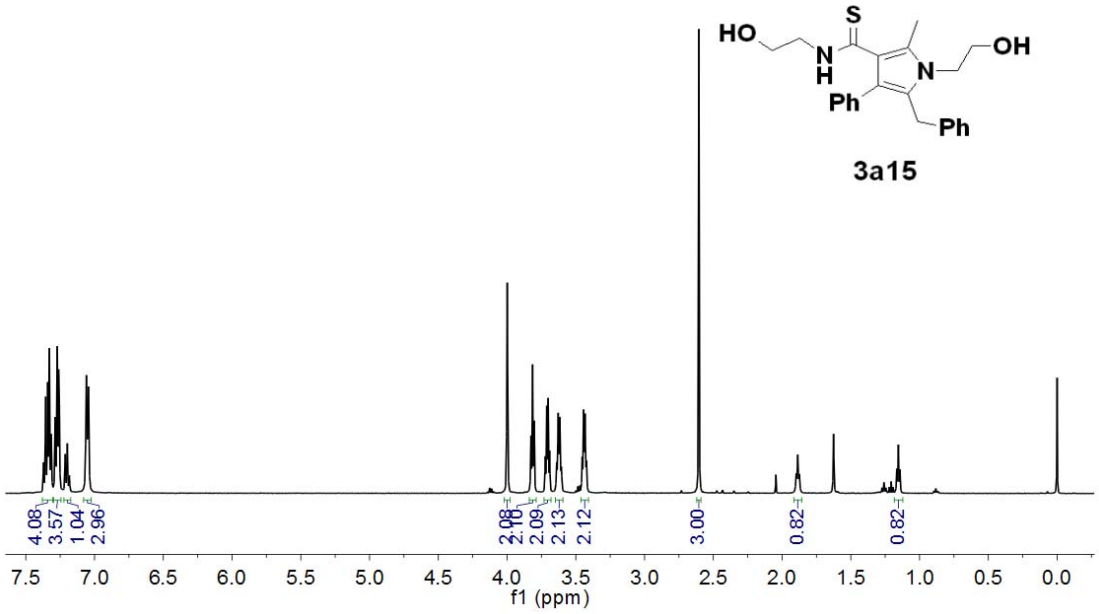

193.01
149.87
149.34
142.47
142.10
139.11
122.25
120.31
110.34
110.22
107.85
107.80
42.52
40.88
30.11
11.93
S
O
N
H
O
N
Ph
Ph
3a12
134.43
133.71
129.76
128.64
128.62
127.87
126.93
126.68
126.34
133 131 129 127
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

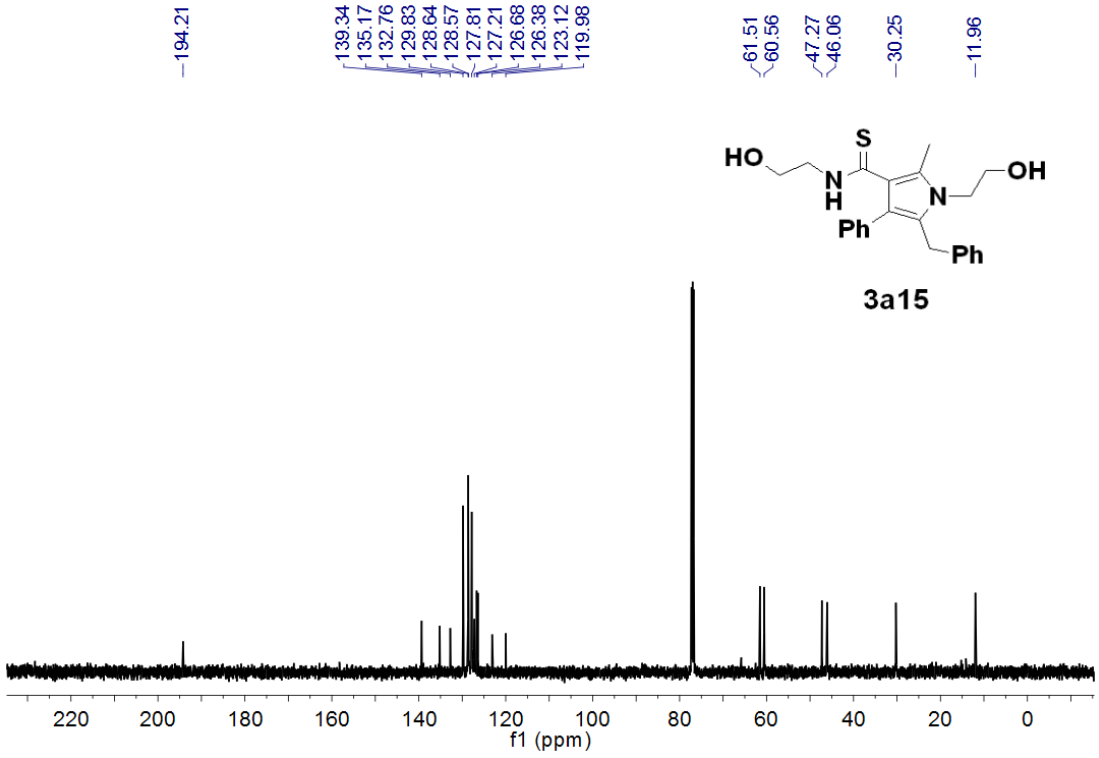

S
N
H
Ph
N
Ph
3a13
4.11
3.45
1.03
2.01
7.40
7.25
7.10
4.11
3.45
1.03
2.01
0.89
2.12
2.15
2.09
3.07
3.11
3.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

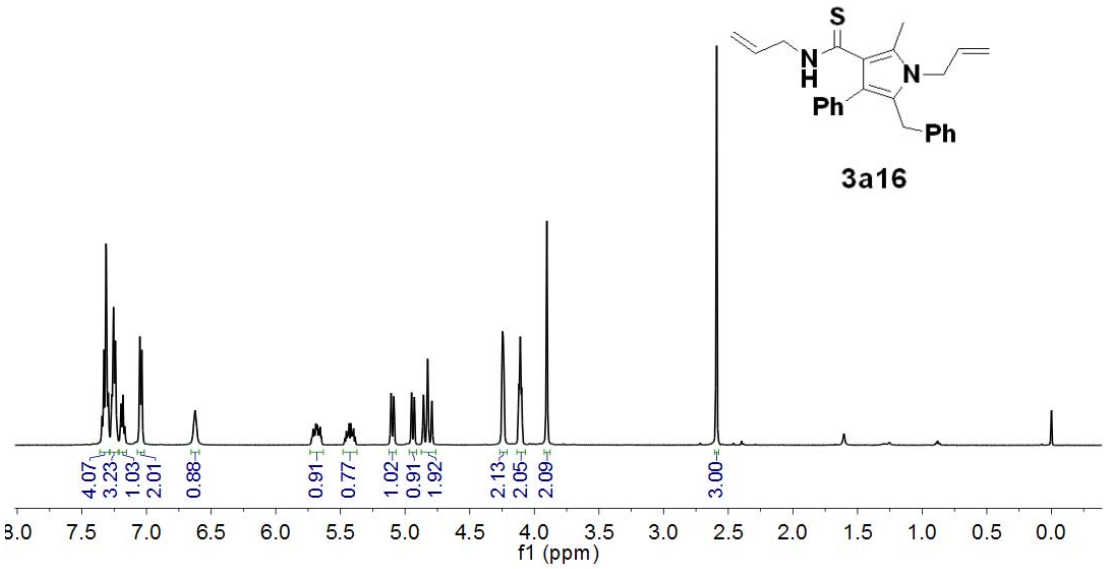

192.79
139.58
135.08
132.59
129.92
128.62
128.55
127.88
126.66
126.29
126.23
122.38
119.81
40.22
38.89
30.32
15.47
12.59
11.73
S
N
H
Ph
N
Ph
3a13
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

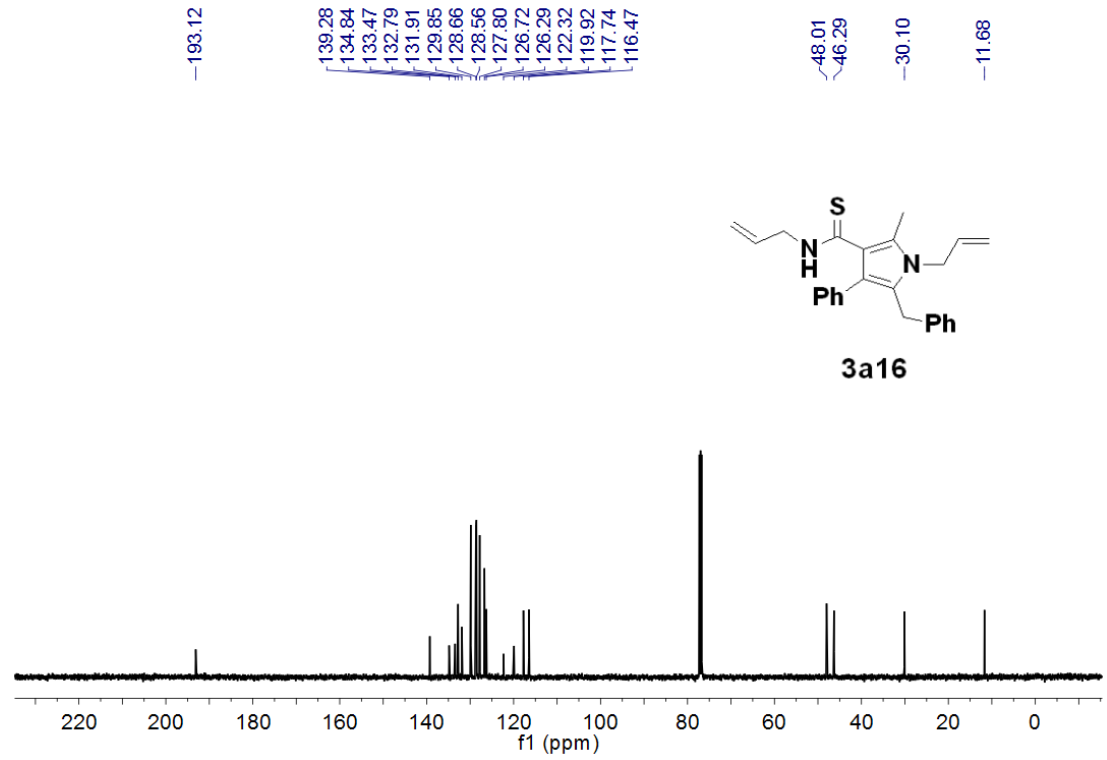

S
N
H
N
Ph
Ph
3a14
4.15
3.36
1.07
2.03
0.91
2.10
2.11
2.15
3.17
2.04
2.09
2.02
2.06
3.04
3.00
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

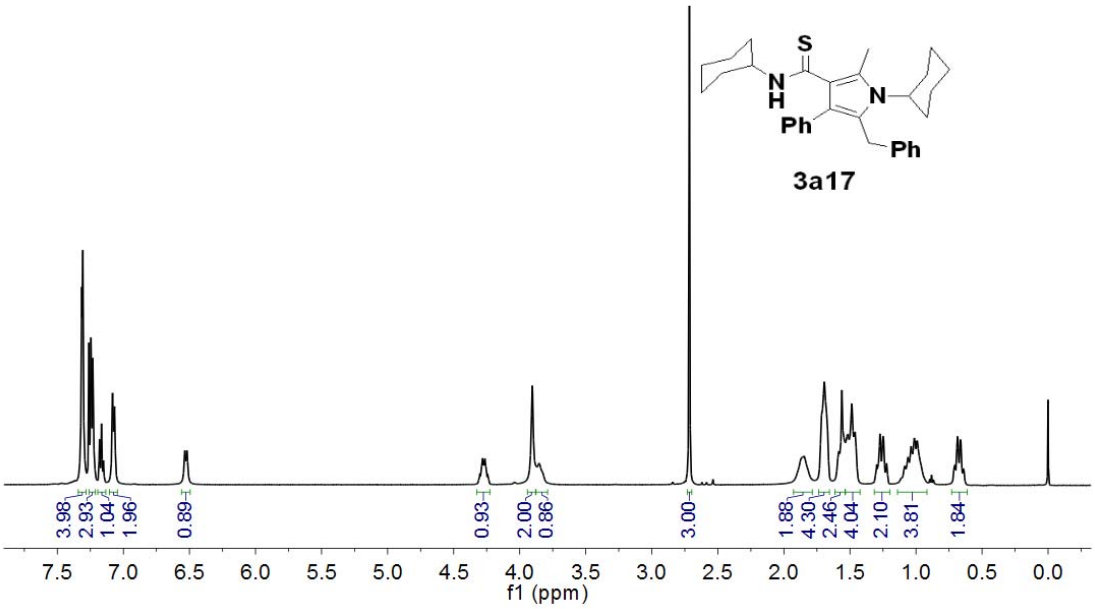

192.89
139.57
135.12
132.66
129.90
128.65
128.52
127.88
126.64
126.53
126.26
122.32
119.68
45.28
44.13
32.48
30.43
29.64
13.70
13.62
11.88
S
N
H
N
Ph
Ph
3a14
20.12
19.83
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

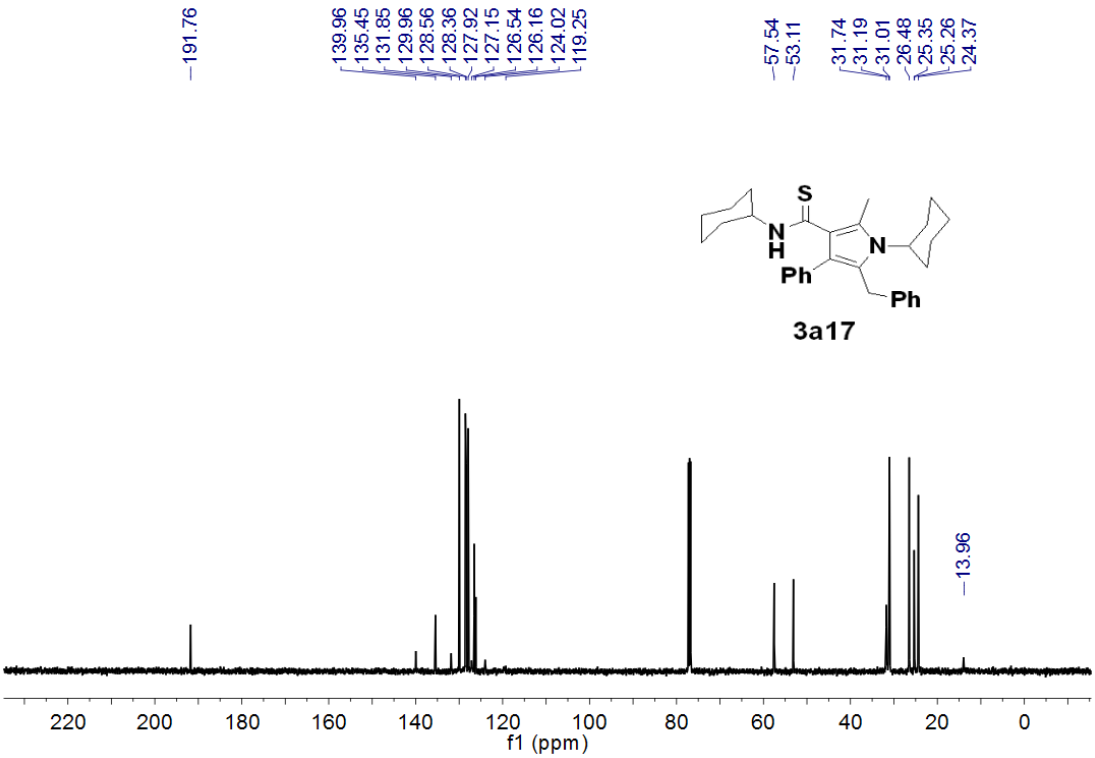

HO
S
N
H
OH
N
Ph
Ph
3a15
4.08
3.57
1.04
2.96
2.08
2.10
2.09
2.13
2.12
3.00
0.82
0.82
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

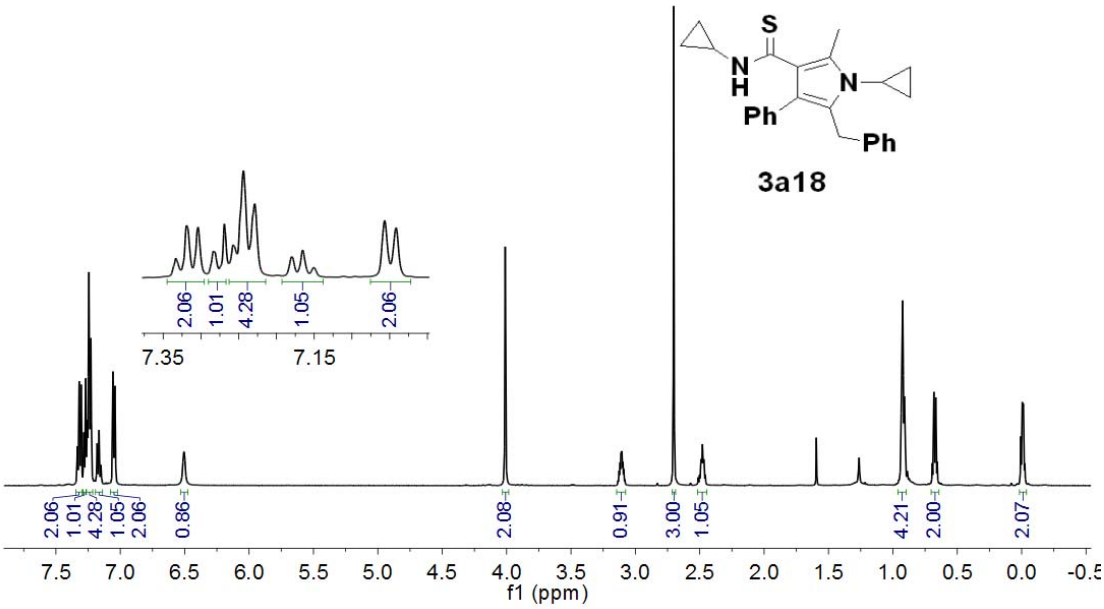

194.21
139.34
135.17
132.76
129.83
128.64
128.57
127.81
127.21
126.68
126.38
123.12
119.98
61.51
60.56
47.27
46.06
30.25
11.96
HO
S
N
H
OH
N
Ph
Ph
3a15
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

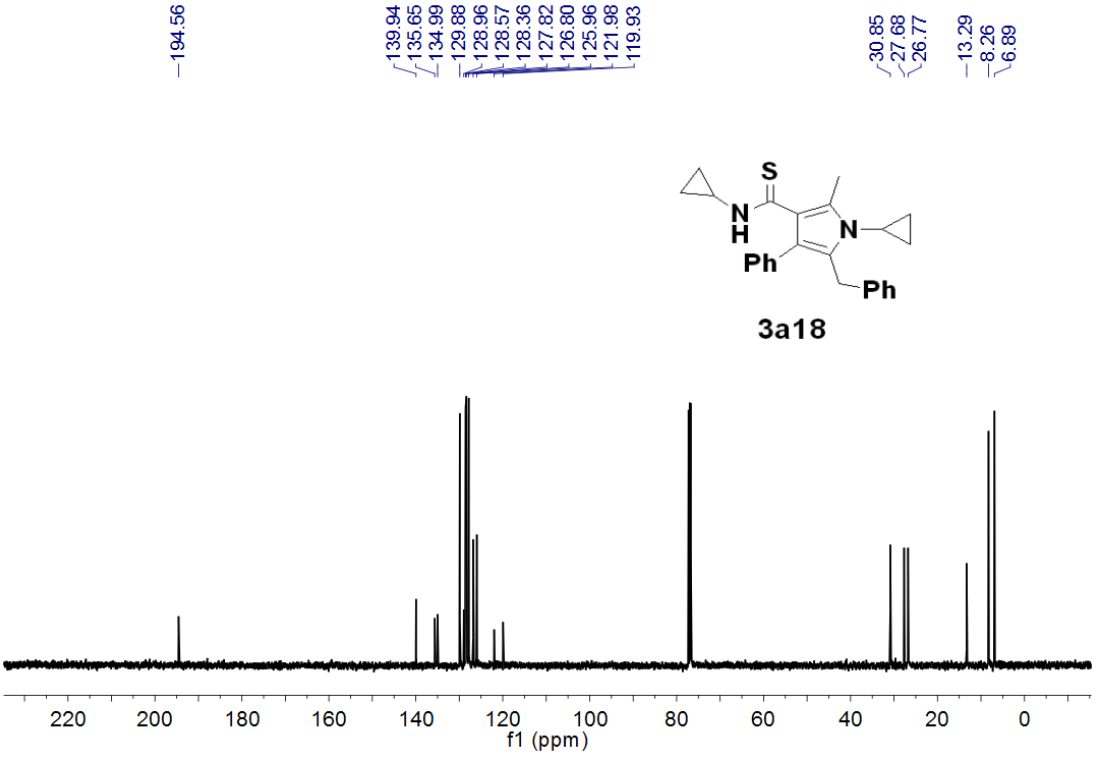

S
N
H
Ph
N
Ph
3a16
4.07
3.23
1.03
2.01
0.88
0.91
0.77
1.02
0.91
1.92
2.13
2.05
2.09
3.00
f1 (ppm)

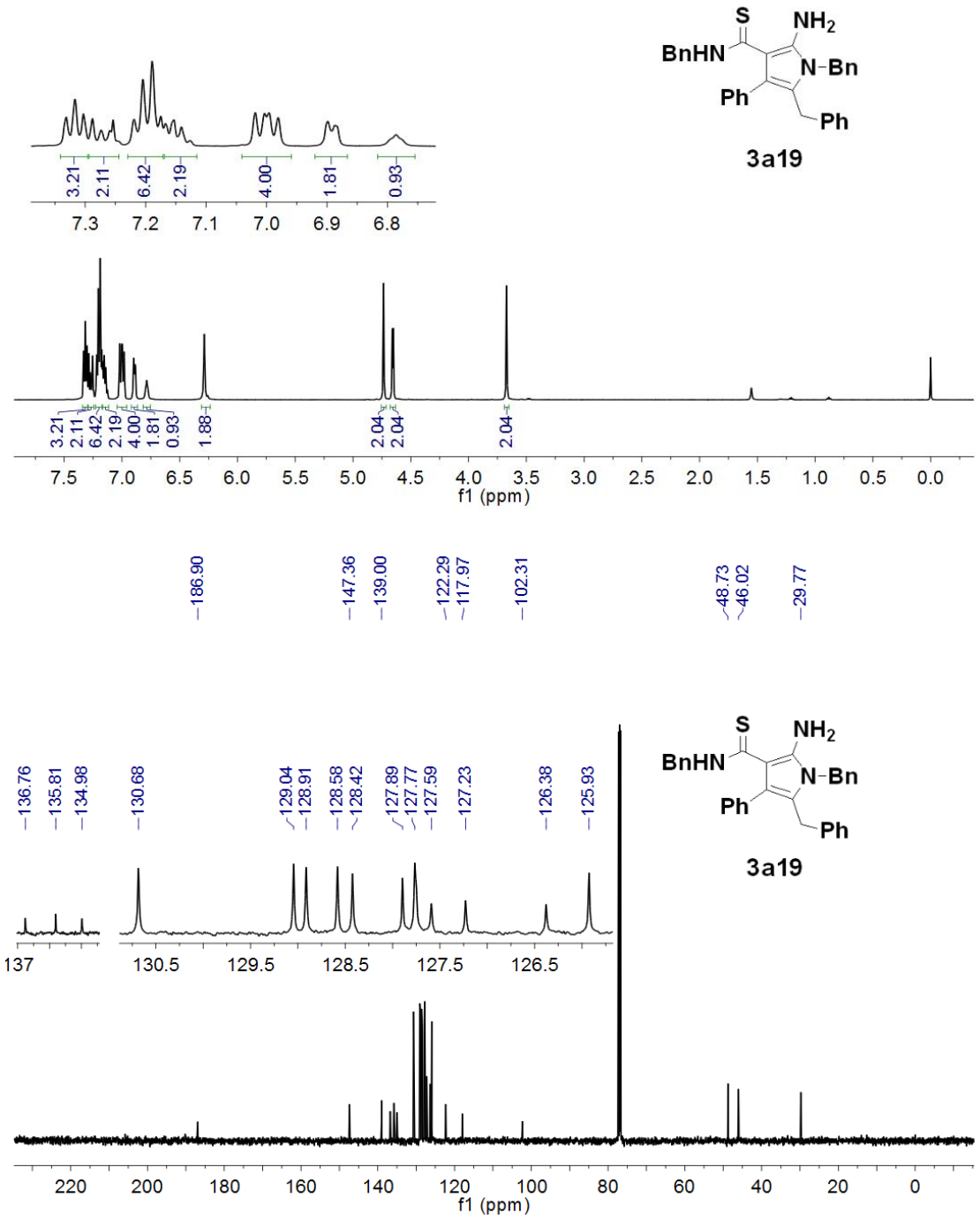

193.12
139.28
134.84
133.47
132.79
131.91
129.85
128.66
128.56
127.80
126.72
126.29
122.32
119.92
117.74
116.47
48.01
46.29
30.10
11.68
S
N
H
Ph
N
Ph
3a16
f1 (ppm)

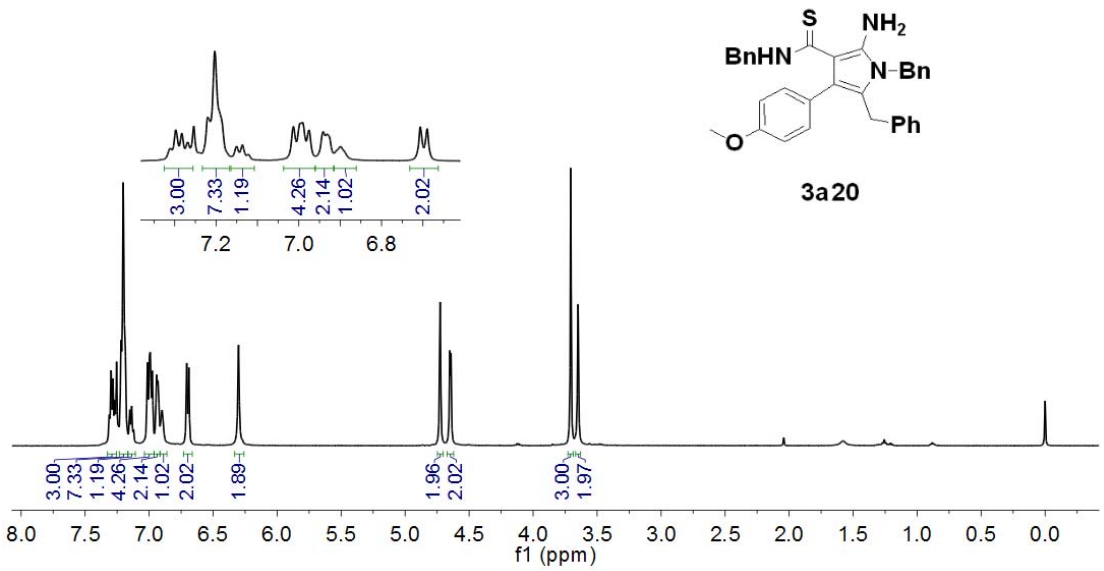

S
N
H
Ph
N
Ph
3a17
3.98
2.93
1.04
1.96
0.89
0.93
2.00
0.86
3.00
1.88
4.30
2.46
4.04
2.10
3.81
1.84
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

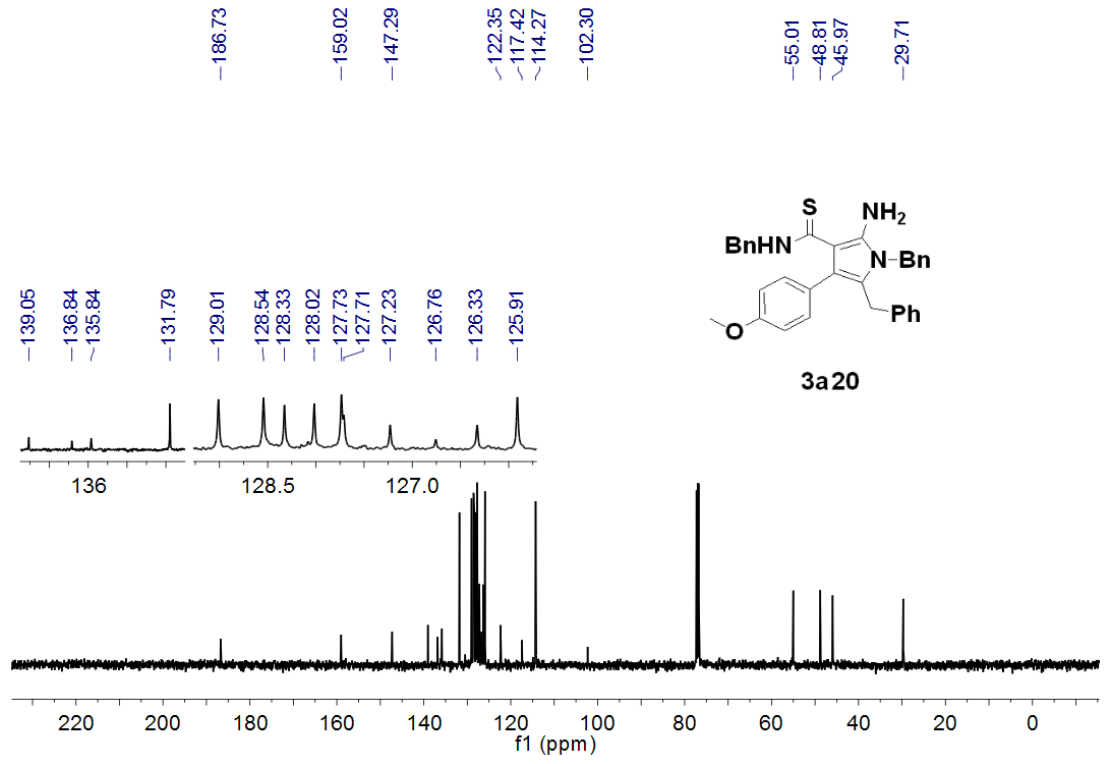

191.76
139.96
135.45
131.85
129.96
128.56
128.36
127.92
127.15
126.54
126.16
124.02
119.25
57.54
53.11
31.74
31.19
31.01
26.48
25.35
25.26
24.37
S
N
H
Ph
N
Ph
3a17
13.96
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

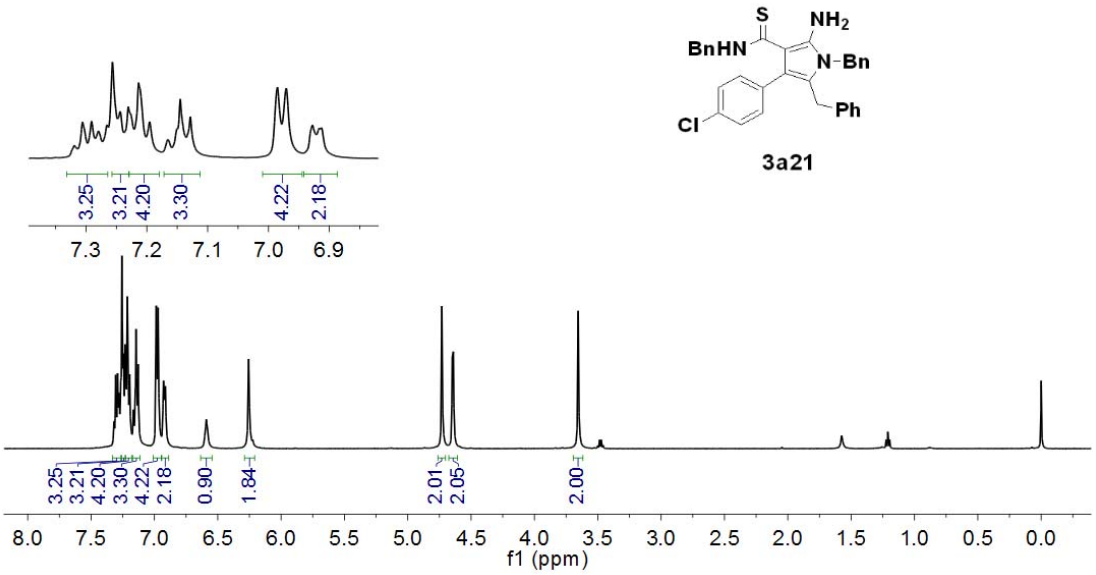

S
N
H
N
Ph
Ph
3a18
2.06
1.01
4.28
1.05
2.06
7.35
7.15
2.06
1.01
4.28
1.05
2.06
0.86
2.08
0.91
3.00
1.05
4.21
2.00
2.07
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

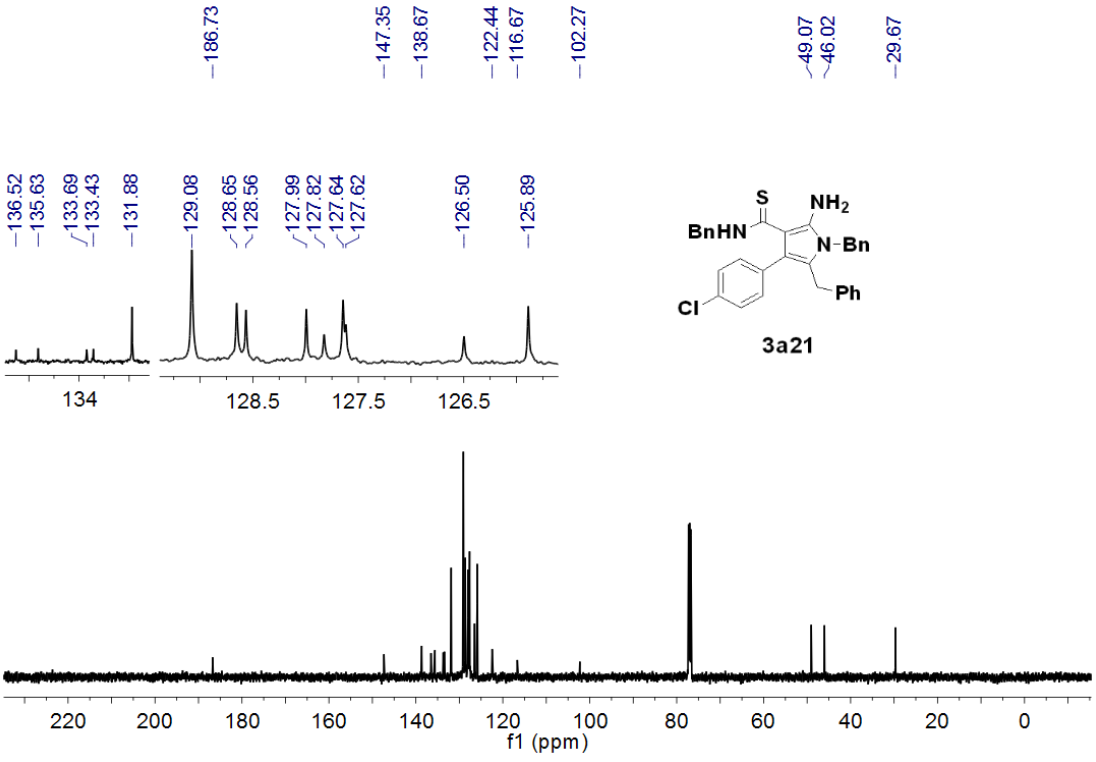

194.56
139.94
135.65
134.99
129.88
128.96
128.57
128.36
127.82
126.80
125.96
121.98
119.93
30.85
27.68
26.77
13.29
8.26
6.89
S
N
H
N
Ph
Ph
3a18
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

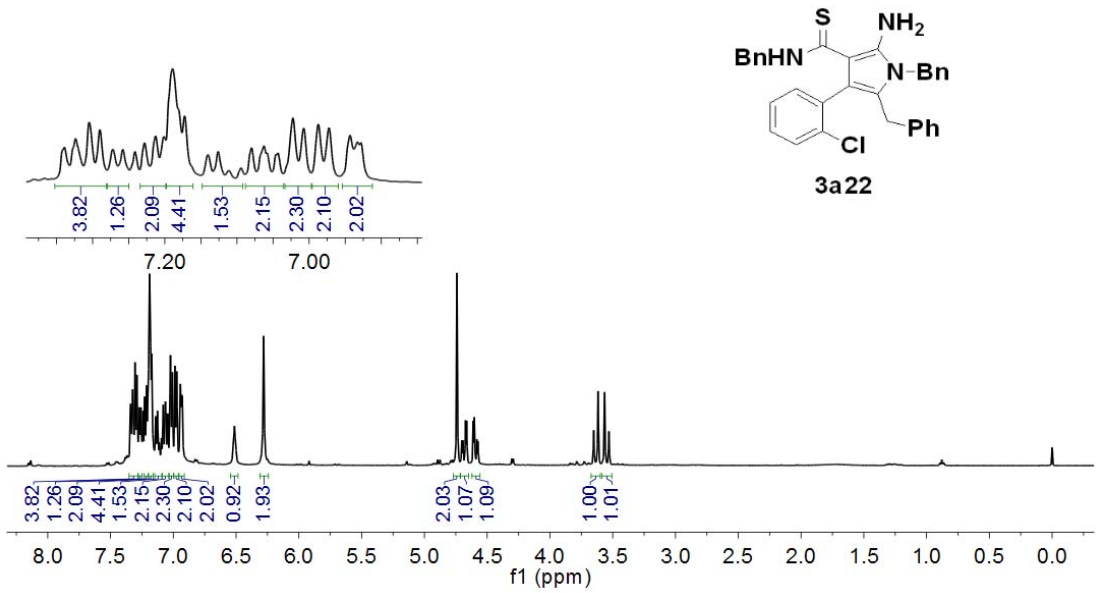


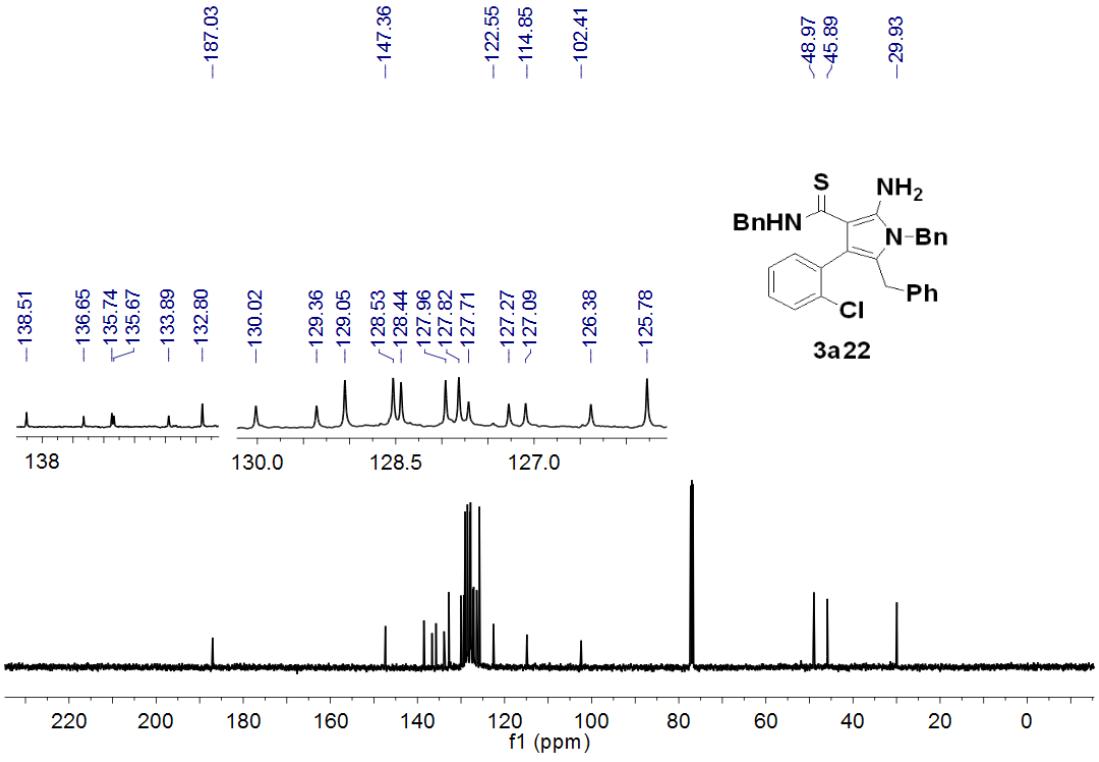

S
NH2
BnHN
N-Bn
Ph
O
3a20
3.00
7.33
1.19
4.26
2.14
1.02
2.02
1.89
1.96
2.02
3.00
1.97
f1 (ppm)

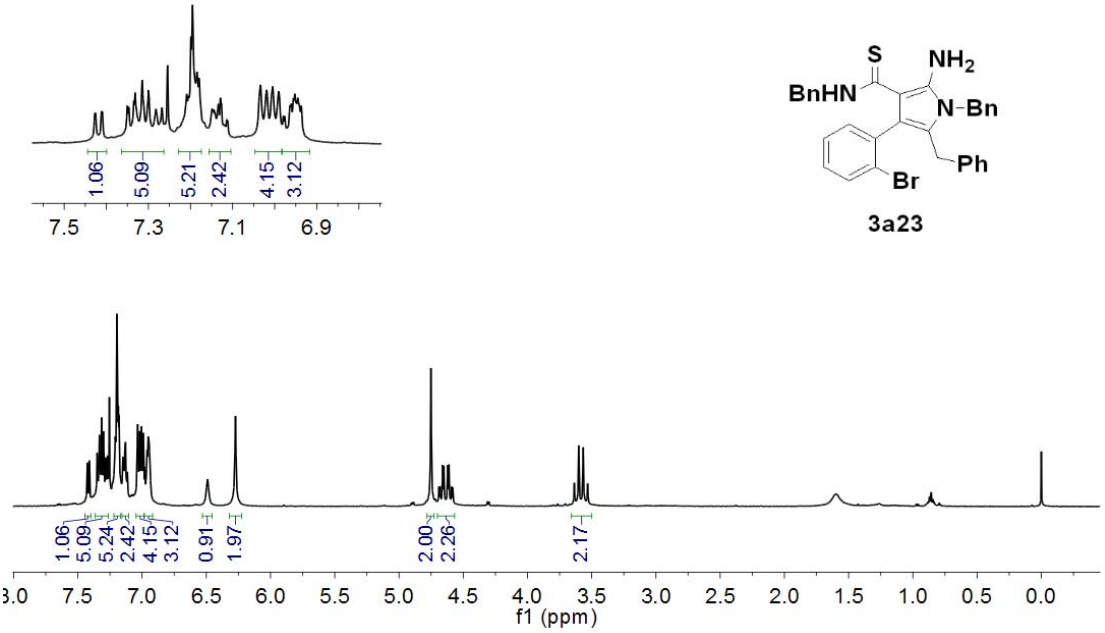

186.73
159.02
147.29
122.35
117.42
114.27
102.30
55.01
48.81
45.97
29.71
S
NH2
BnHN
N-Bn
Ph
O
3a20
139.05
136.84
135.84
131.79
129.01
128.54
128.33
128.02
127.73
127.71
127.23
126.76
126.33
125.91
f1 (ppm)

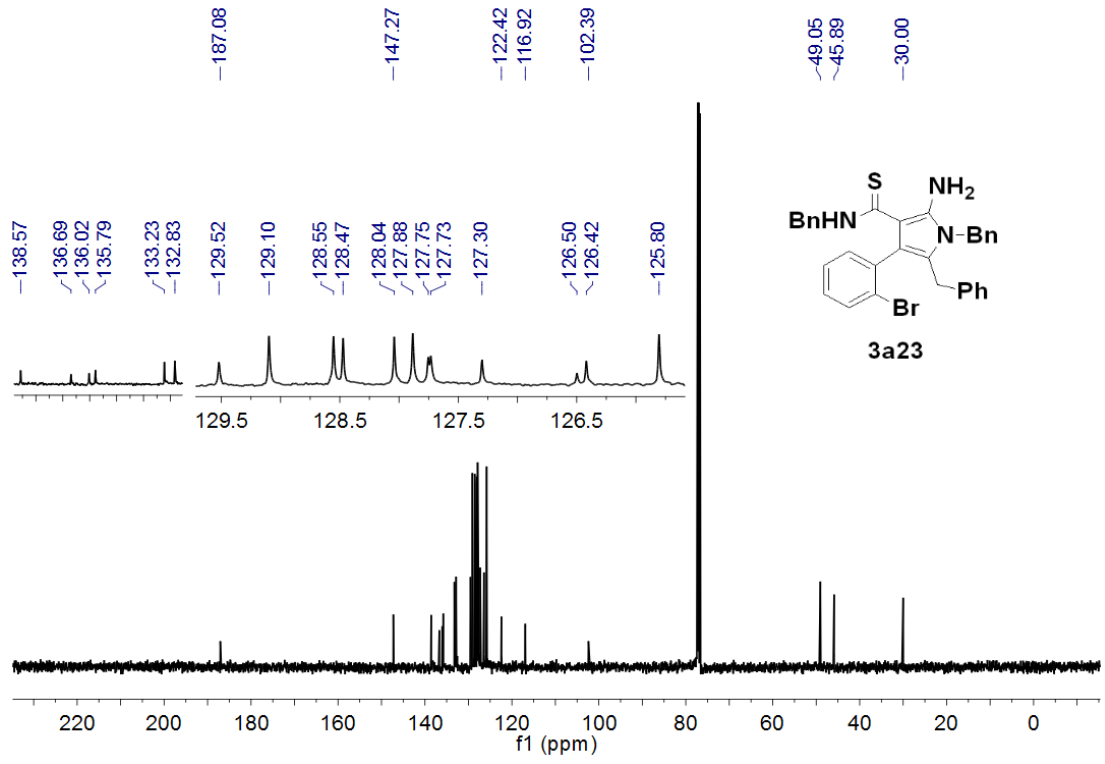

S
NH2
BnHN
N-Bn
Ph
Cl
3a21
3.25
3.21
4.20
3.30
4.22
2.18
0.90
1.84
2.01
2.05
2.00
f1 (ppm)

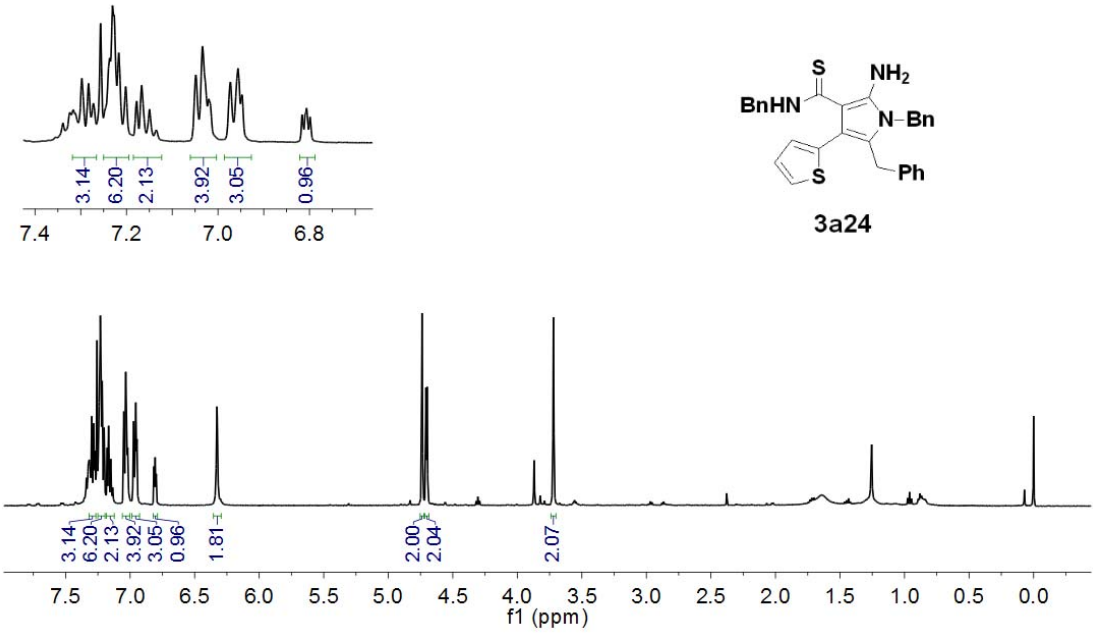

186.73
147.35
138.67
122.44
116.67
102.27
49.07
46.02
29.67
136.52
135.63
133.69
133.43
131.88
129.08
128.65
128.56
127.99
127.82
127.64
127.62
126.50
125.89
S
NH2
BnHN
N-Bn
Ph
Cl
3a21
f1 (ppm)

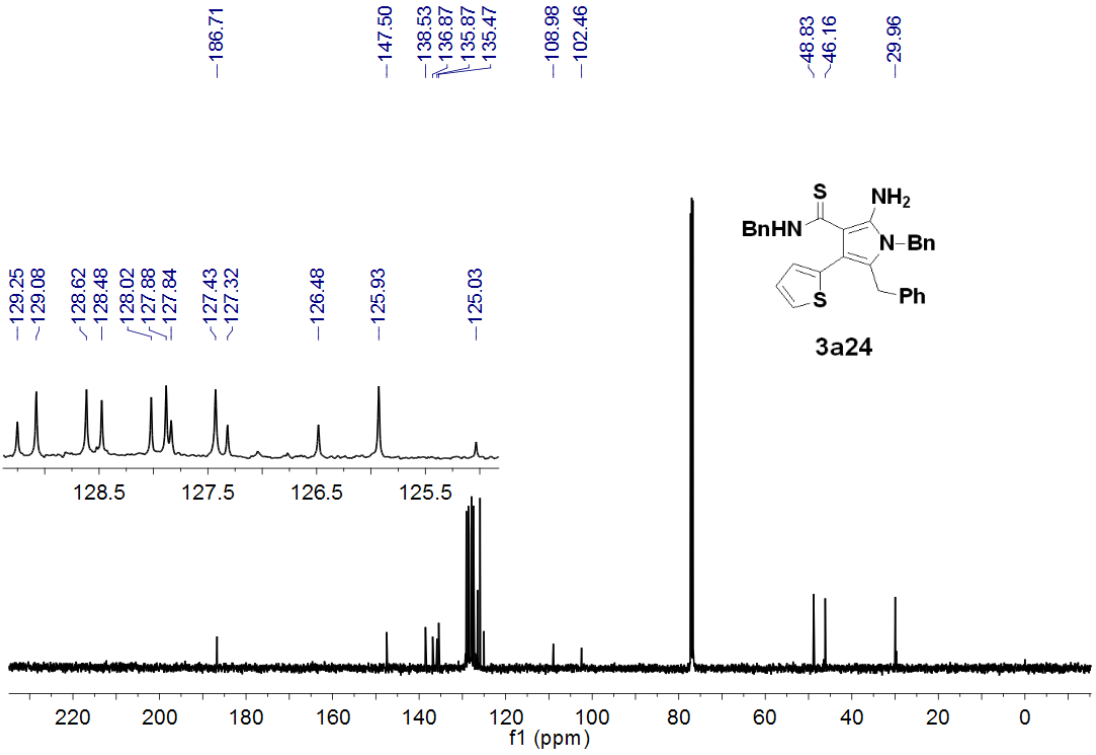


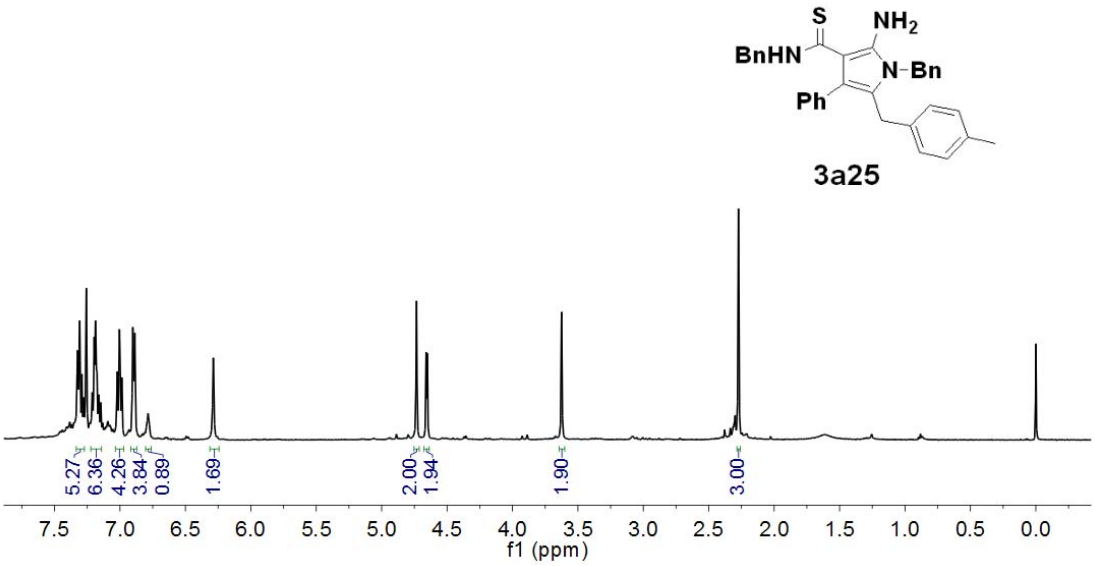



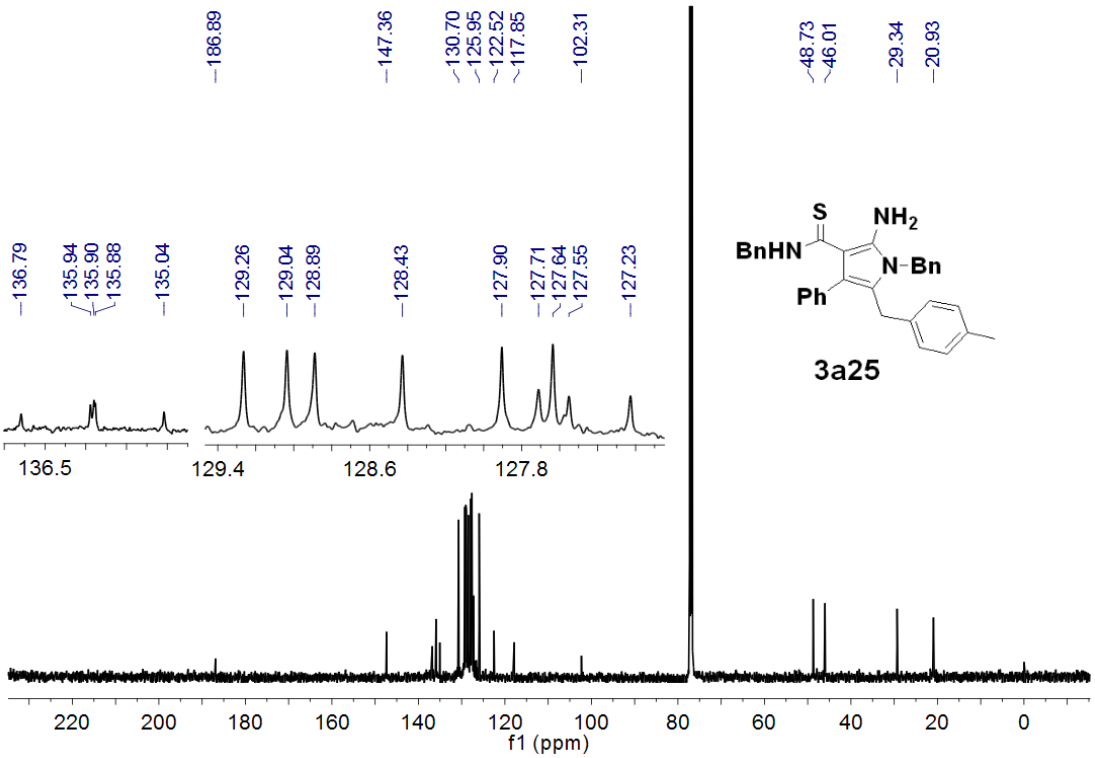

1.06
5.09
5.21
2.42
4.15
3.12
7.5
7.3
7.1
6.9
S
NH2
BnHN
N-Bn
Ph
Br
3a23
1.06
5.09
5.24
2.42
4.15
3.12
0.91
1.97
2.00
2.26
2.17
f1 (ppm)

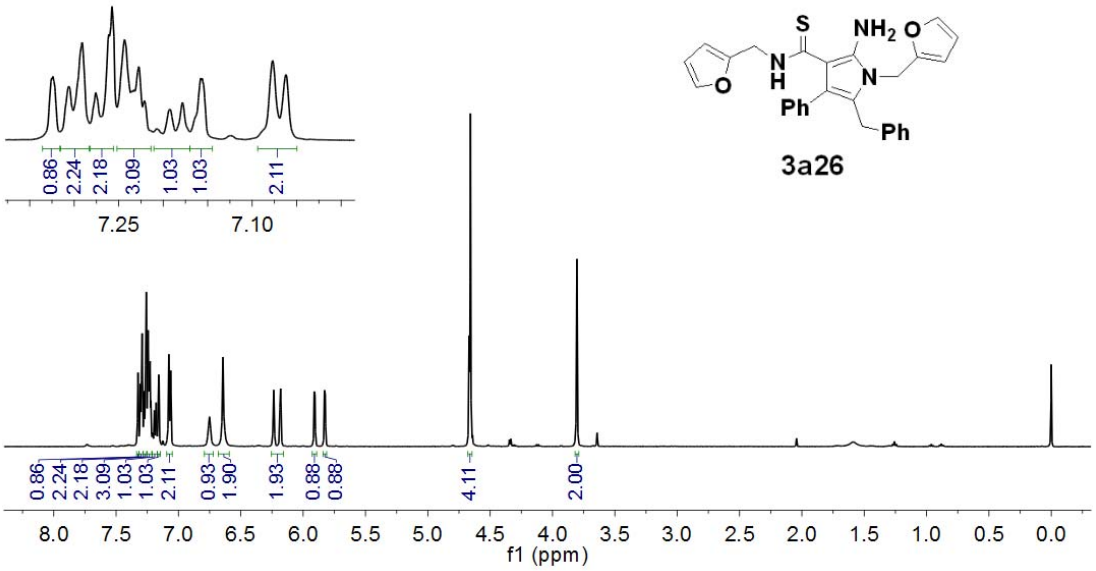

187.08
147.27
122.42
116.92
102.39
49.05
45.89
30.00
138.57
136.69
136.02
135.79
133.23
132.83
129.52
129.10
128.55
128.47
128.04
127.88
127.75
127.73
127.30
126.50
126.42
125.80
129.5
128.5
127.5
126.5
S
NH2
BnHN
N-Bn
Ph
Br
3a23
f1 (ppm)

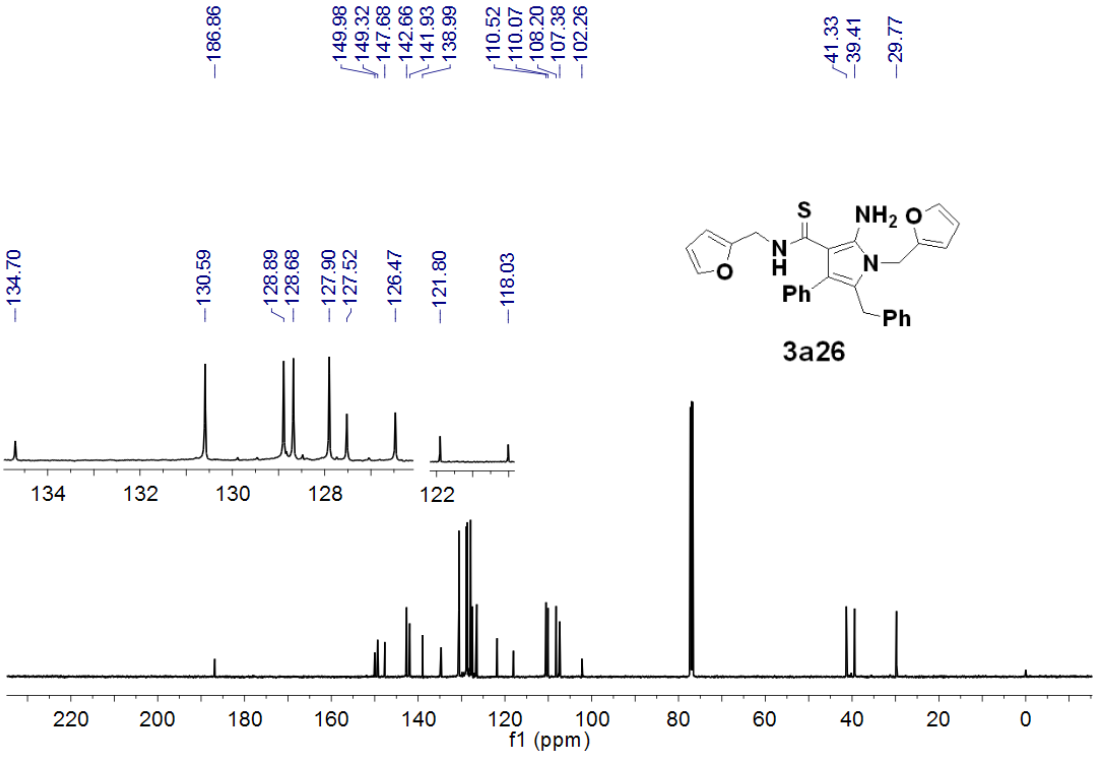

3.14
6.20
2.13
3.92
3.05
0.96
7.4
7.2
7.0
6.8
S
NH2
BnHN
N–Bn
Ph
S
3a24
1.81
2.00
2.04
2.07
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

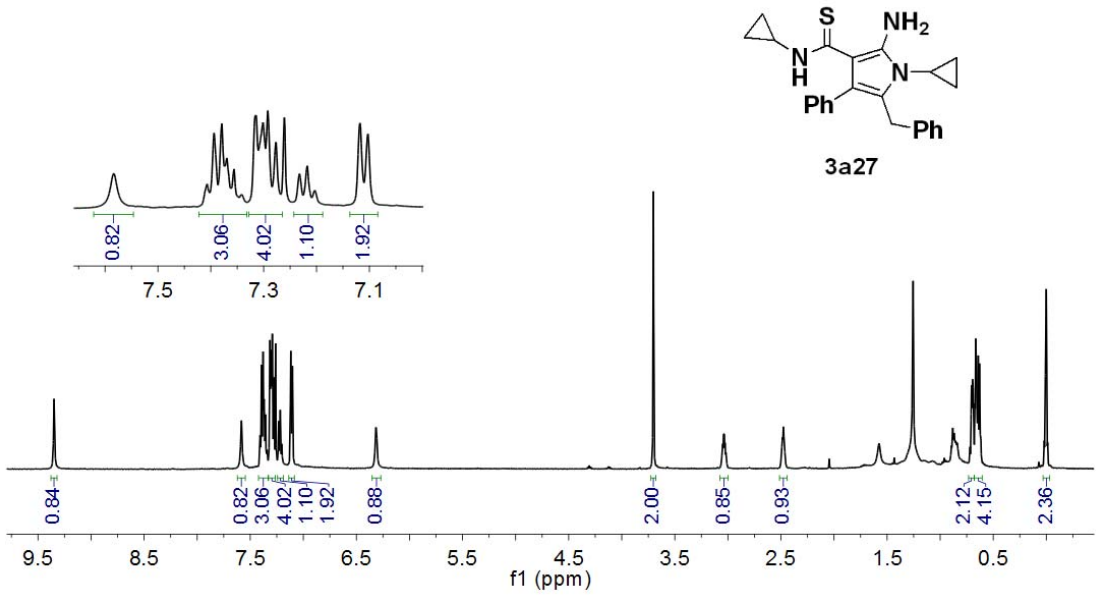

186.71
147.50
138.53
136.87
135.87
135.47
108.98
102.46
48.83
46.16
29.96
129.25
129.08
128.62
128.48
128.02
127.88
127.84
127.43
127.32
126.48
125.93
125.03
128.5
127.5
126.5
125.5
S
NH2
BnHN
N–Bn
Ph
S
3a24
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

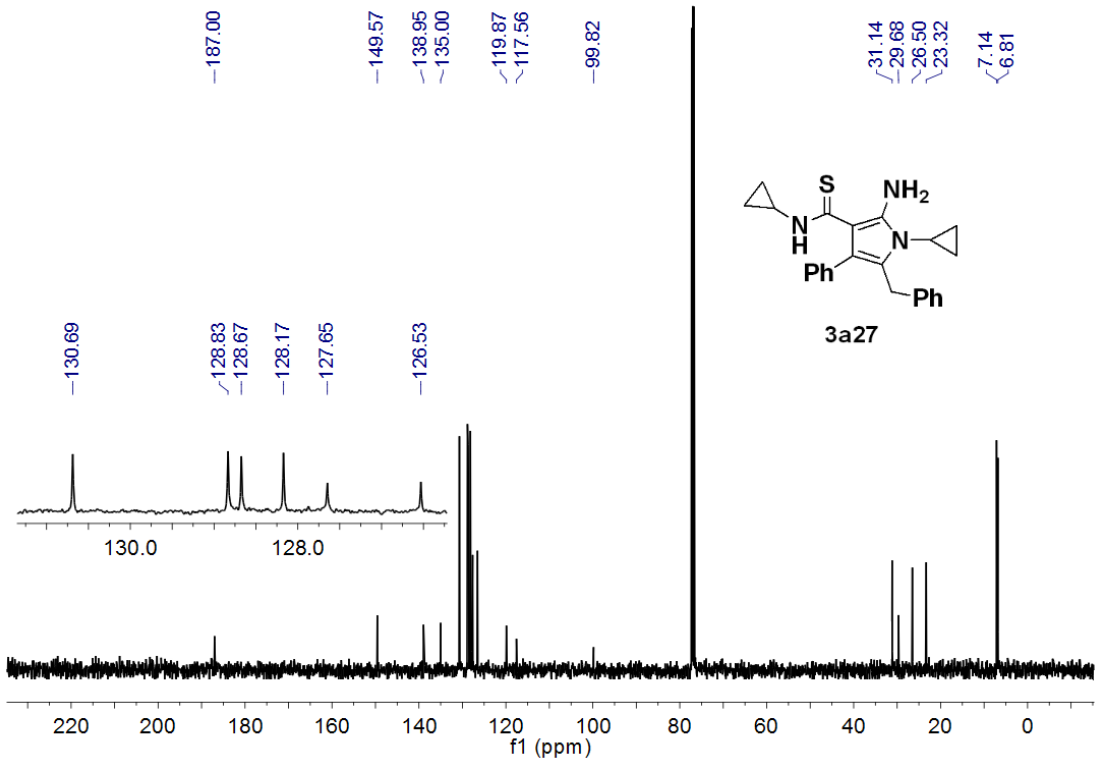


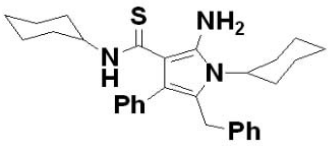





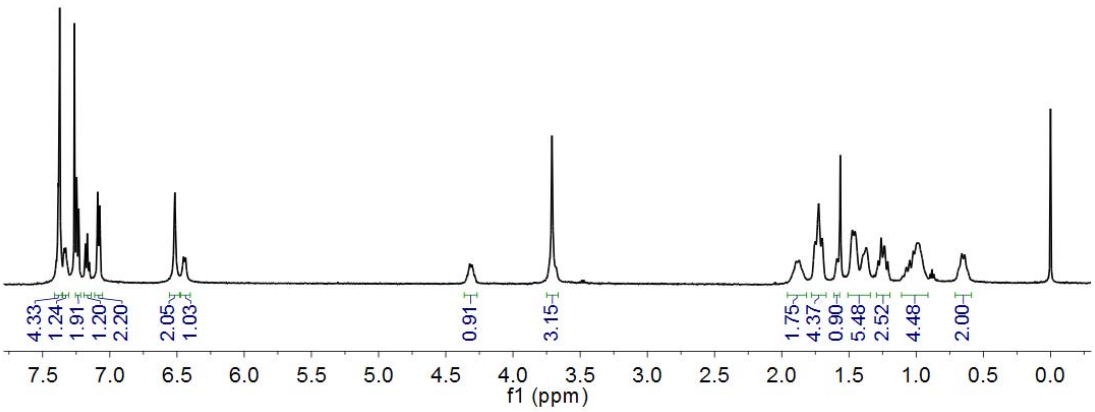



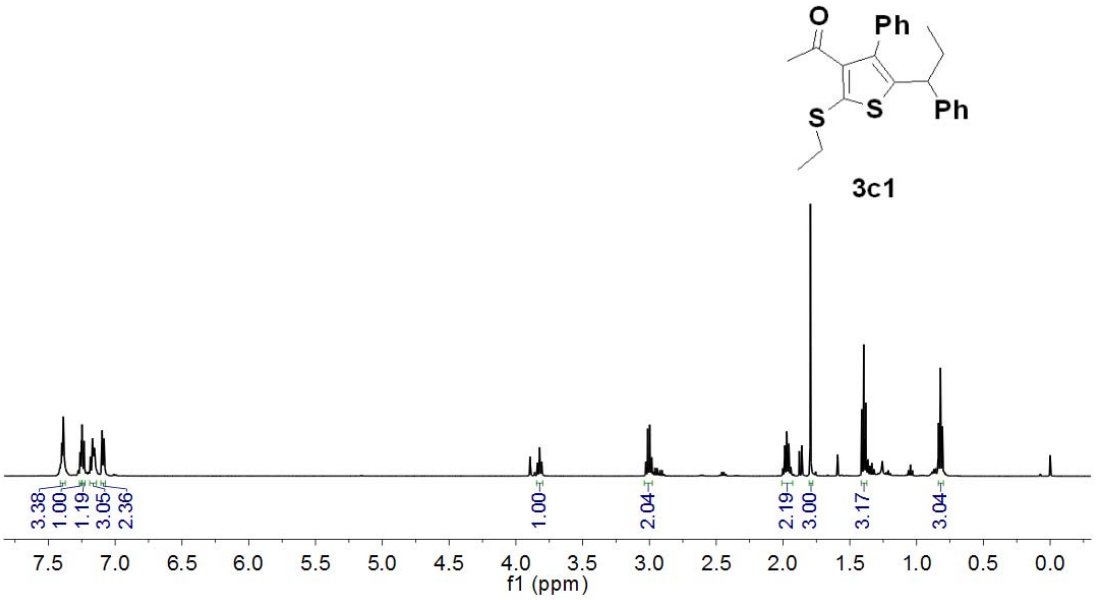

S
NH2
N
H
N
Ph
Ph
3a27
0.82
3.06
4.02
1.10
1.92
7.5
7.3
7.1
0.84
0.82
3.06
4.02
1.10
1.92
0.88
2.00
0.85
0.93
2.12
4.15
2.36
9.5
8.5
7.5
6.5
5.5
4.5
3.5
2.5
1.5
0.5
f1 (ppm)

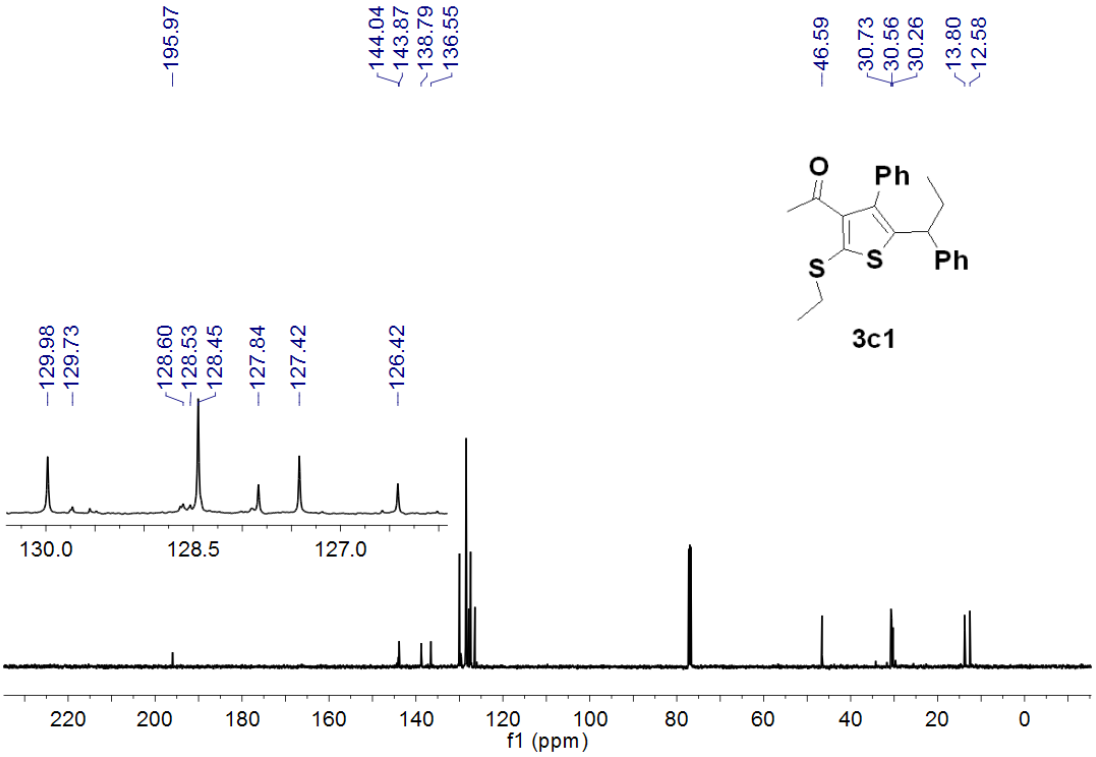

187.00
149.57
138.95
135.00
119.87
117.56
99.82
31.14
29.68
26.50
23.32
7.14
6.81
S
NH2
N
H
N
Ph
Ph
3a27
130.69
128.83
128.67
128.17
127.65
126.53
130.0
128.0
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

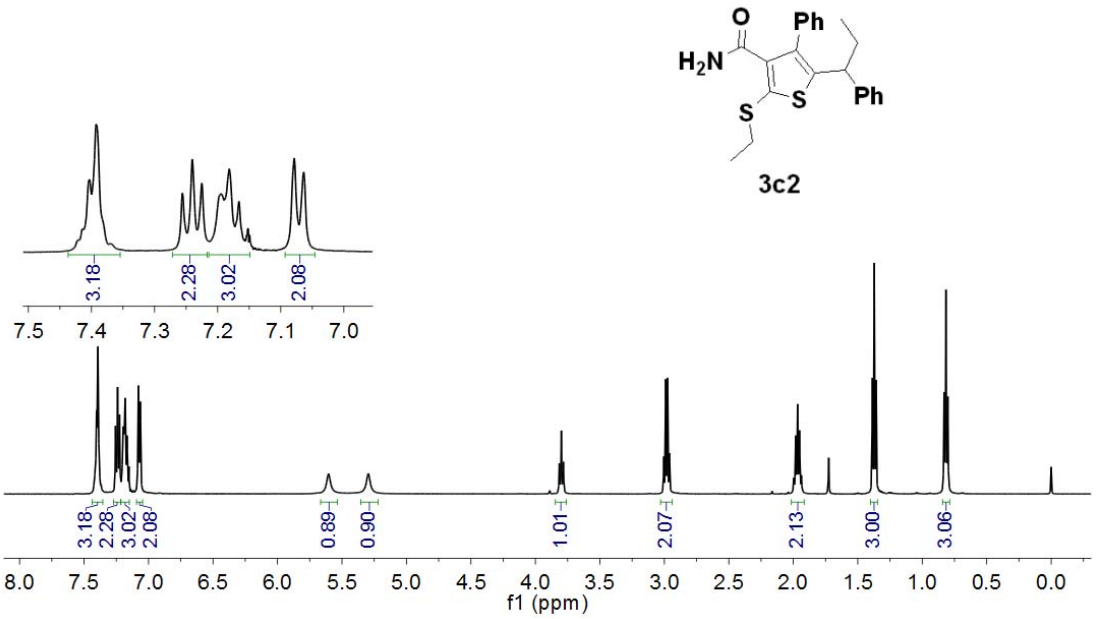

S
NH2
N
H
N
Ph
Ph

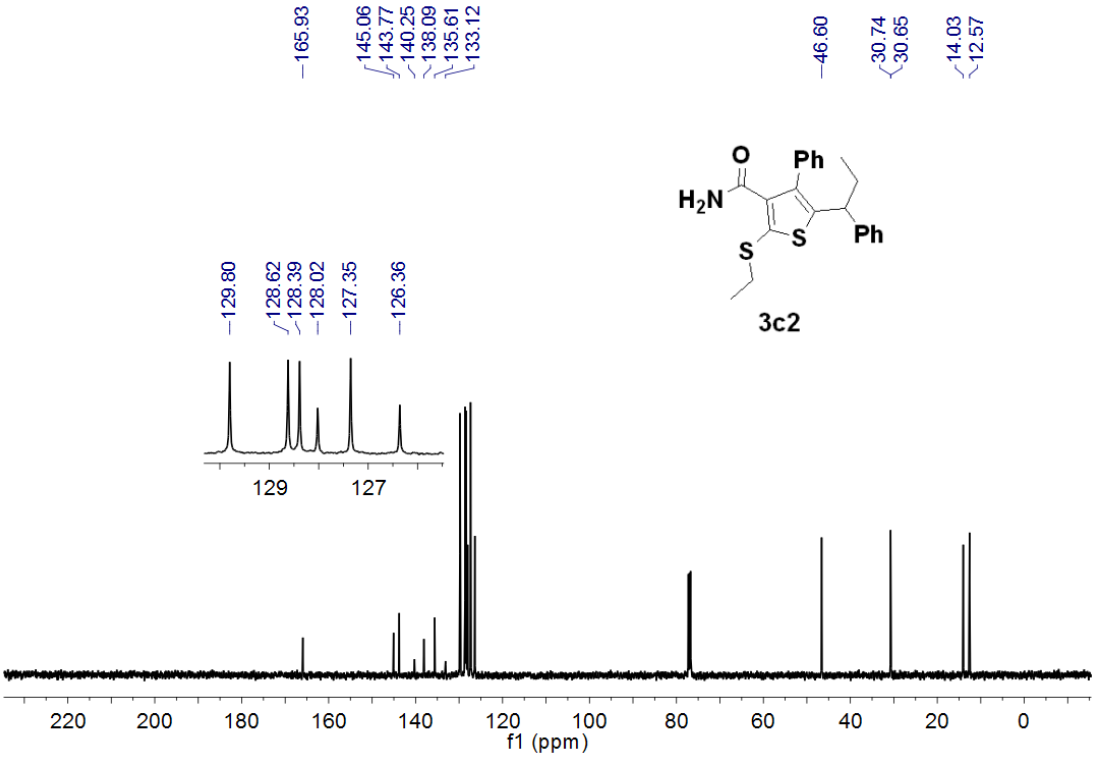
3a28

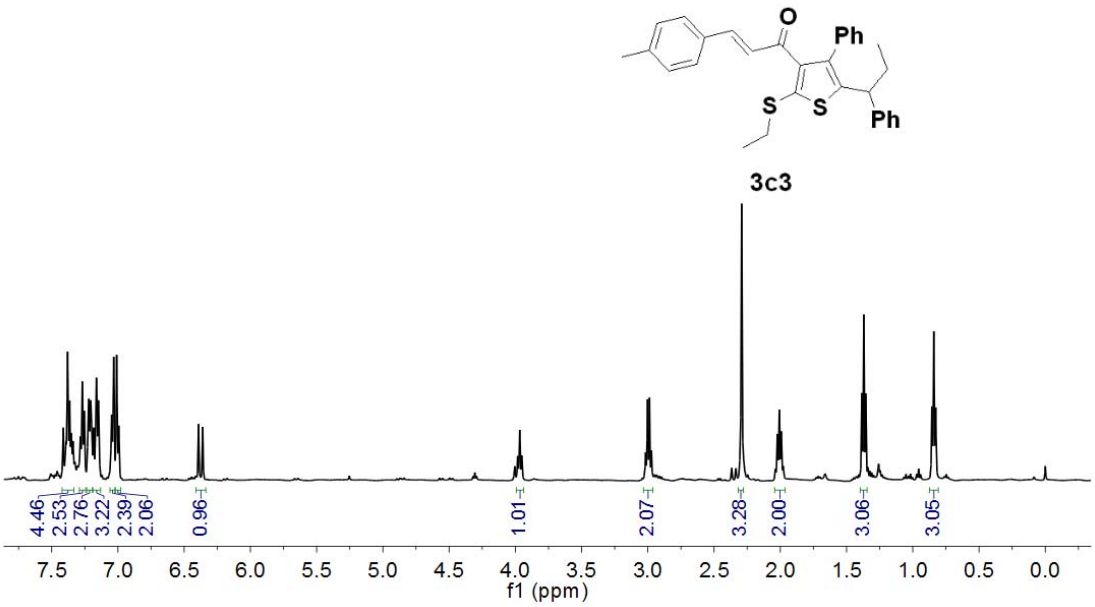

4.33
1.24
1.91
1.20
2.20
2.05
1.03
0.91
3.15
1.75
4.37
0.90
5.48
2.52
4.48
2.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

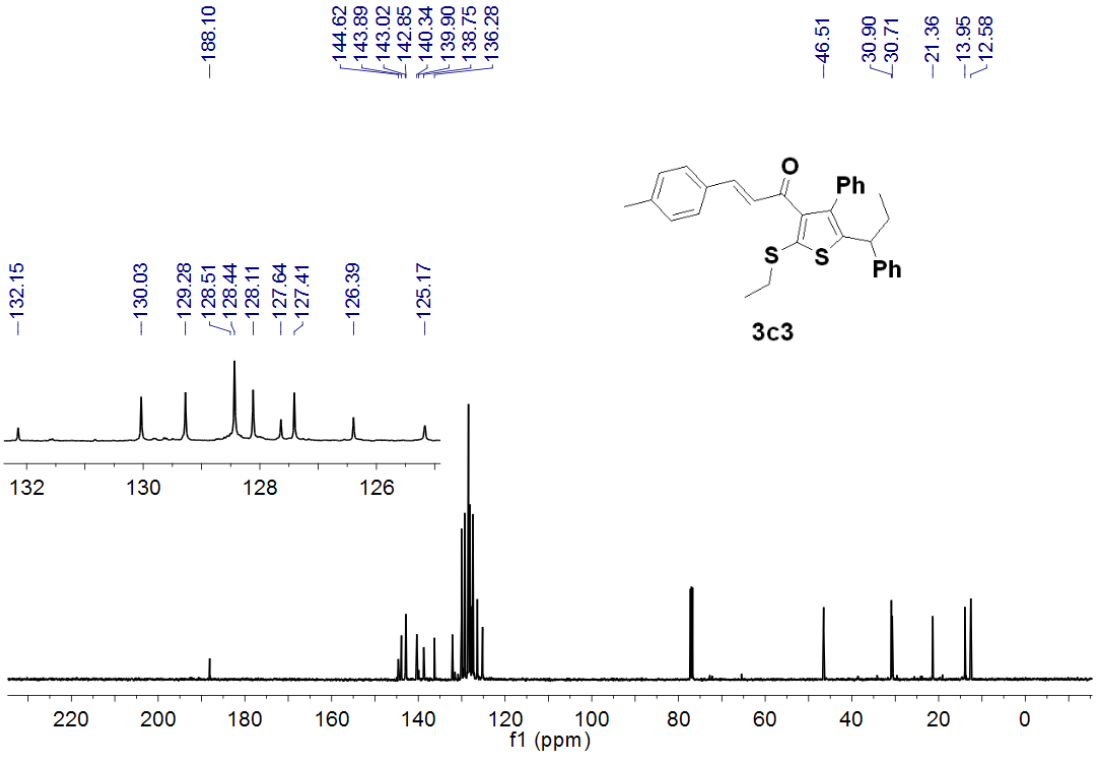

O
Ph
S
S
Ph
3c1
3.38
1.00
1.19
3.05
2.36
1.00
2.04
2.19
3.00
3.17
3.04
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

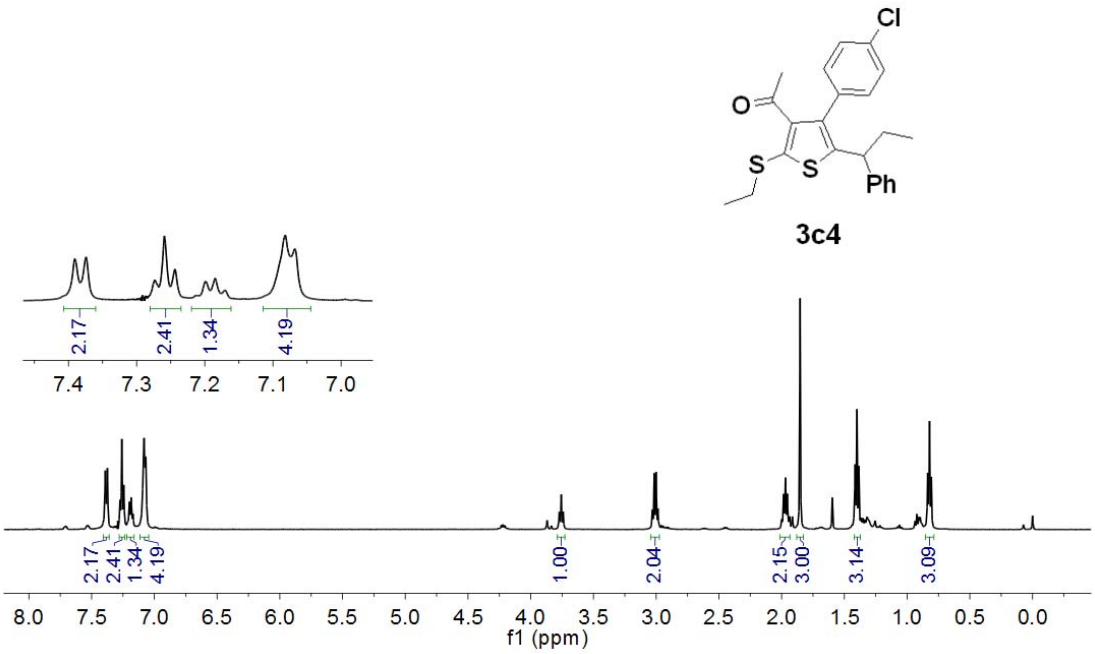

195.97
144.04
143.87
138.79
136.55
46.59
30.73
30.56
30.26
13.80
12.58
O
Ph
S
S
Ph
3c1
129.98
129.73
128.60
128.53
128.45
127.84
127.42
126.42
130.0 128.5 127.0
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

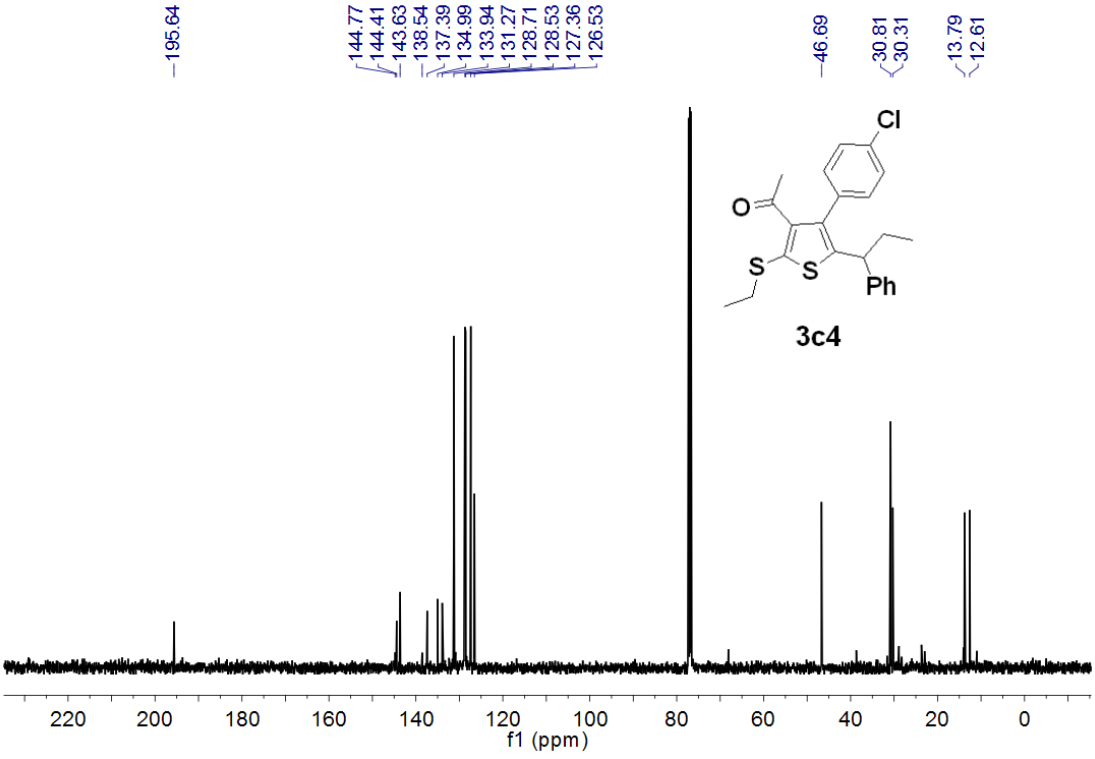

O
Ph
H2N
S
S
Ph
3c2
3.18
2.28
3.02
2.08
7.5 7.4 7.3 7.2 7.1 7.0
3.18
2.28
3.02
2.08
0.89
0.90
1.01
2.07
2.13
3.00
3.06
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

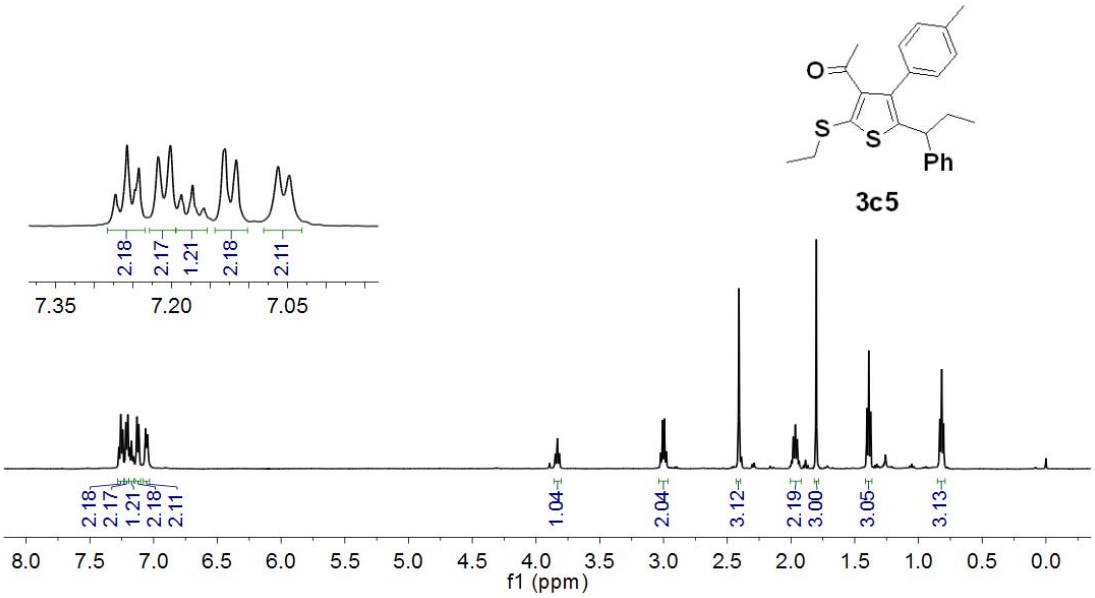

165.93
145.06
143.77
140.25
138.09
135.61
133.12
46.60
30.74
30.65
14.03
12.57
O
Ph
H2N
S
S
Ph
3c2
129.80
128.62
128.39
128.02
127.35
126.36
129
127
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

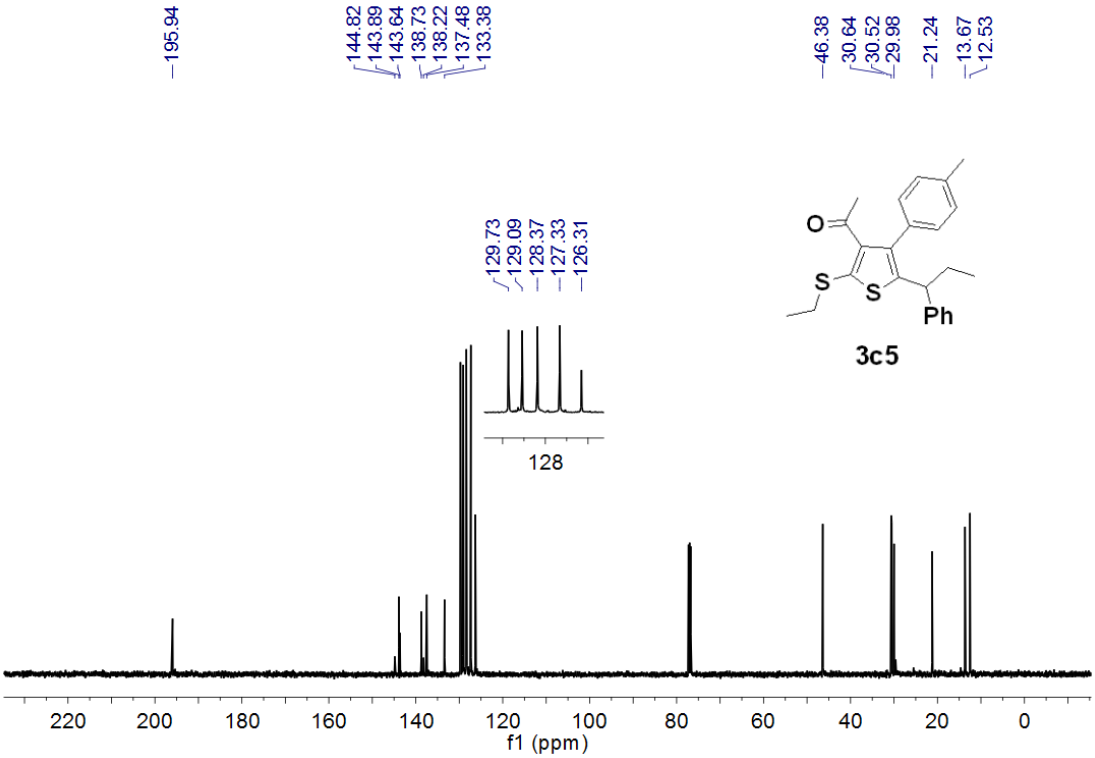

O
Ph
S
S
Ph
3c3
4.46
2.53
2.76
3.22
2.39
2.06
0.96
1.01
2.07
3.28
2.00
3.06
3.05
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

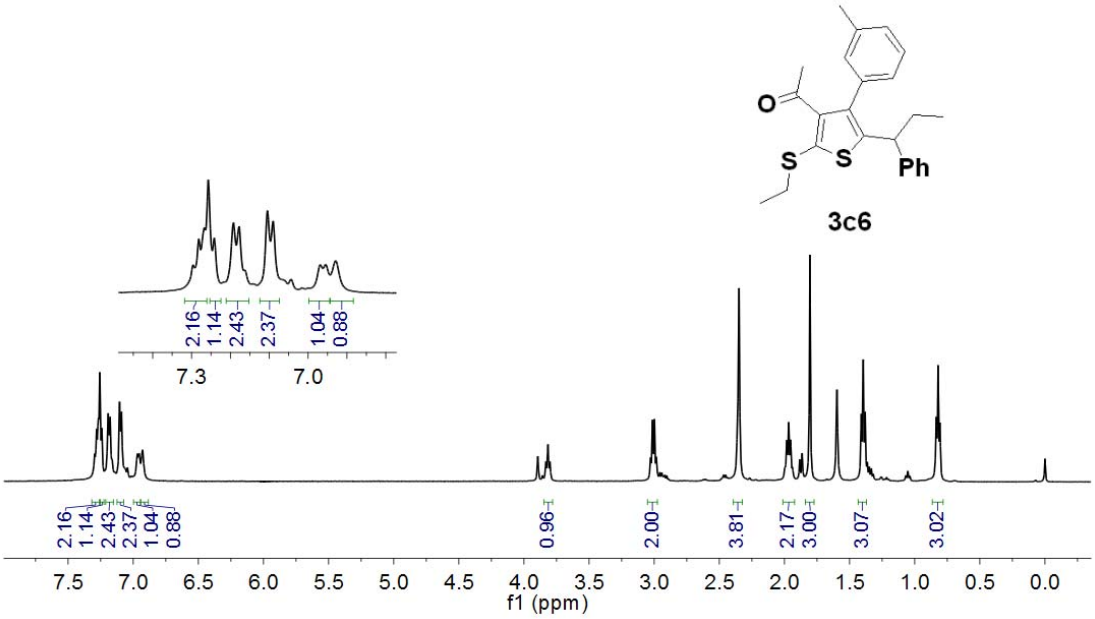

188.10
144.62
143.89
143.02
142.85
140.34
139.90
138.75
136.28
46.51
30.90
30.71
21.36
13.95
12.58
O
Ph
S
S
Ph
3c3
132.15
130.03
129.28
128.51
128.44
128.11
127.64
127.41
126.39
125.17
132 130 128 126
220 200 180 160 140 120 100 80 60 40 20 0
f1 (ppm)

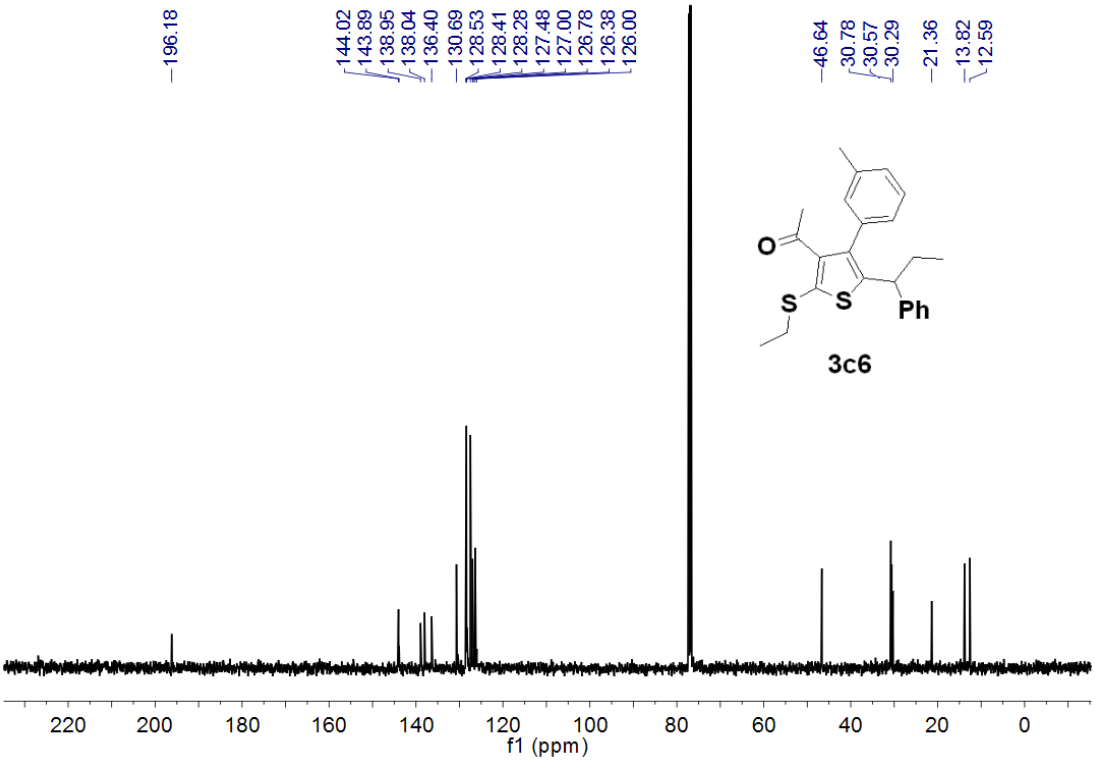


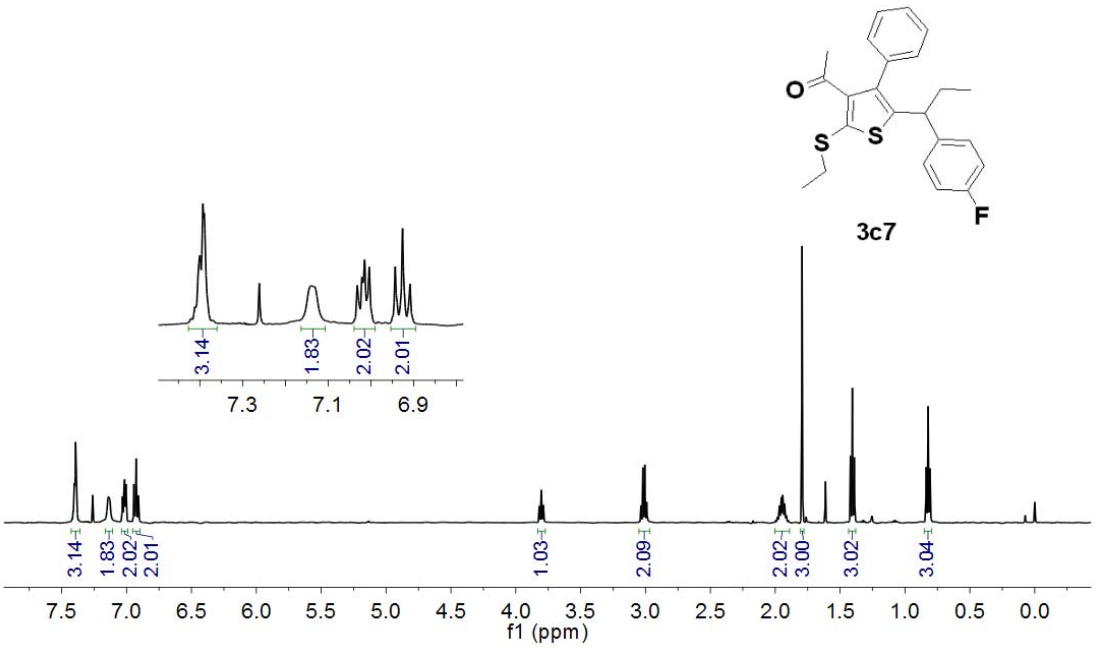



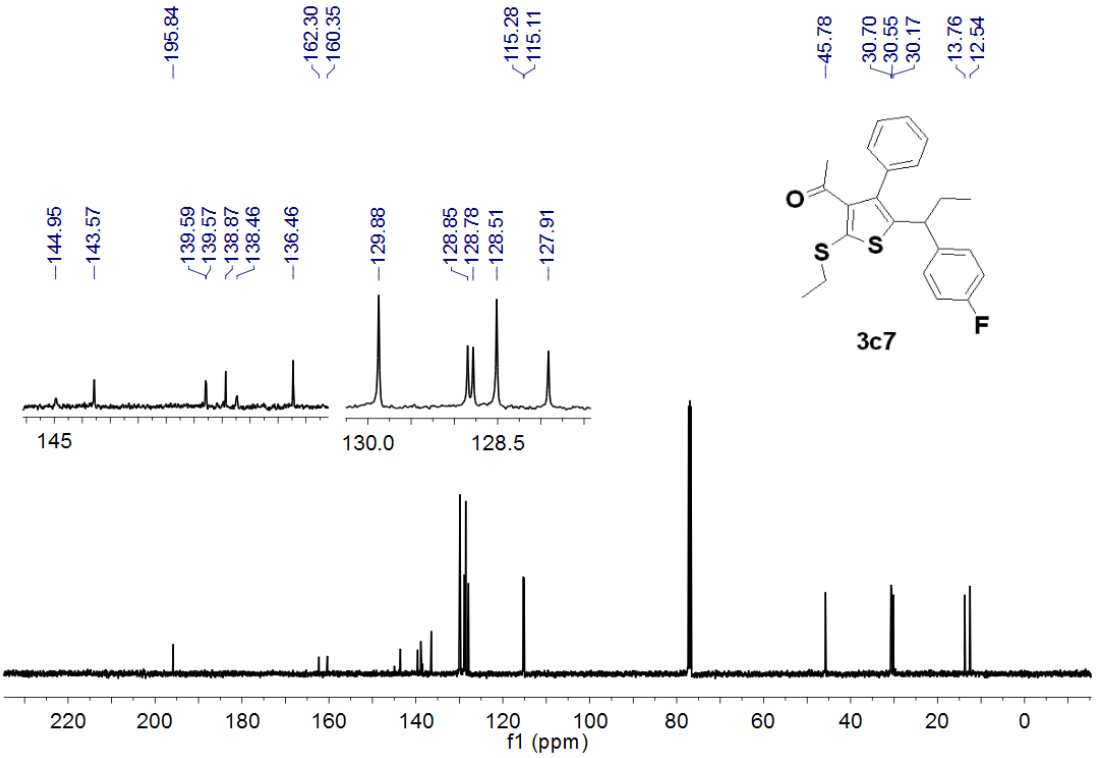

O
S
S
Ph
3c5
2.18
2.17
1.21
2.18
2.11
7.35
7.20
7.05
1.04
2.04
3.12
2.19
3.00
3.05
3.13
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

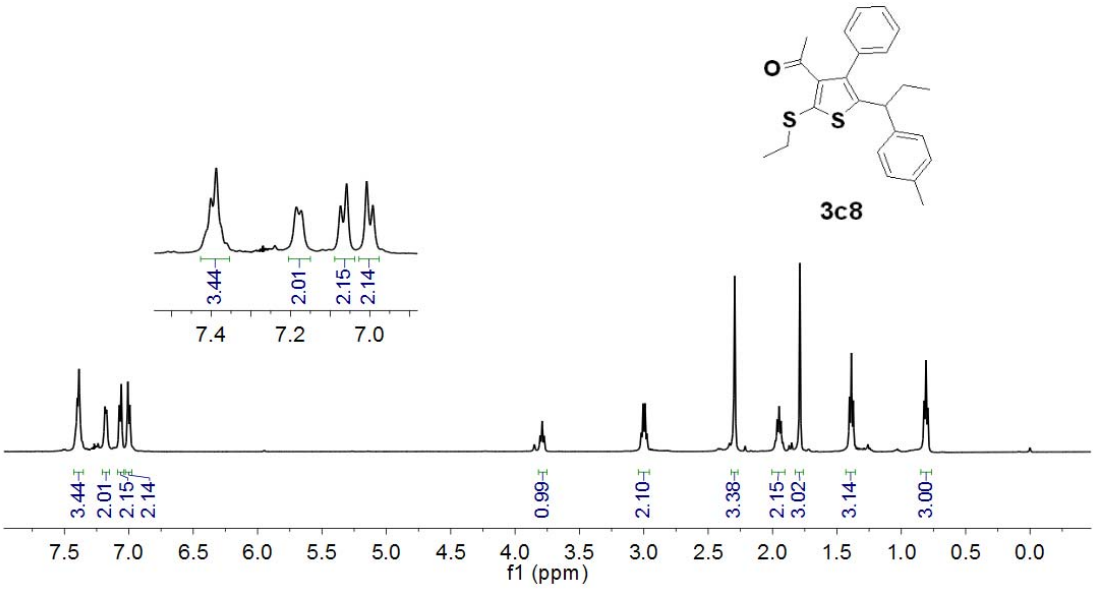

195.94
144.82
143.89
143.64
138.73
138.22
137.48
133.38
46.38
30.64
30.52
29.98
21.24
13.67
12.53
129.73
129.09
128.37
127.33
126.31
128
O
S
S
Ph
3c5
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

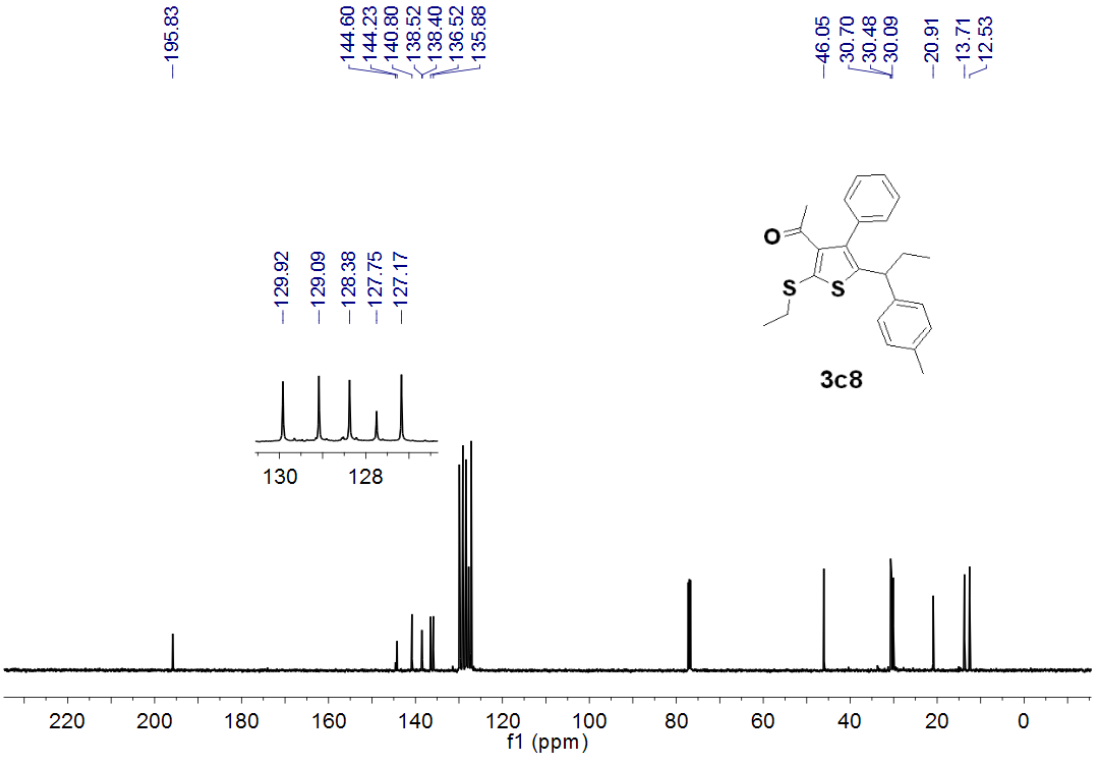

O
S
S
Ph
3c6
2.16
1.14
2.43
2.37
1.04
0.88
7.3
7.0
0.96
2.00
3.81
2.17
3.00
3.07
3.02
f1 (ppm)

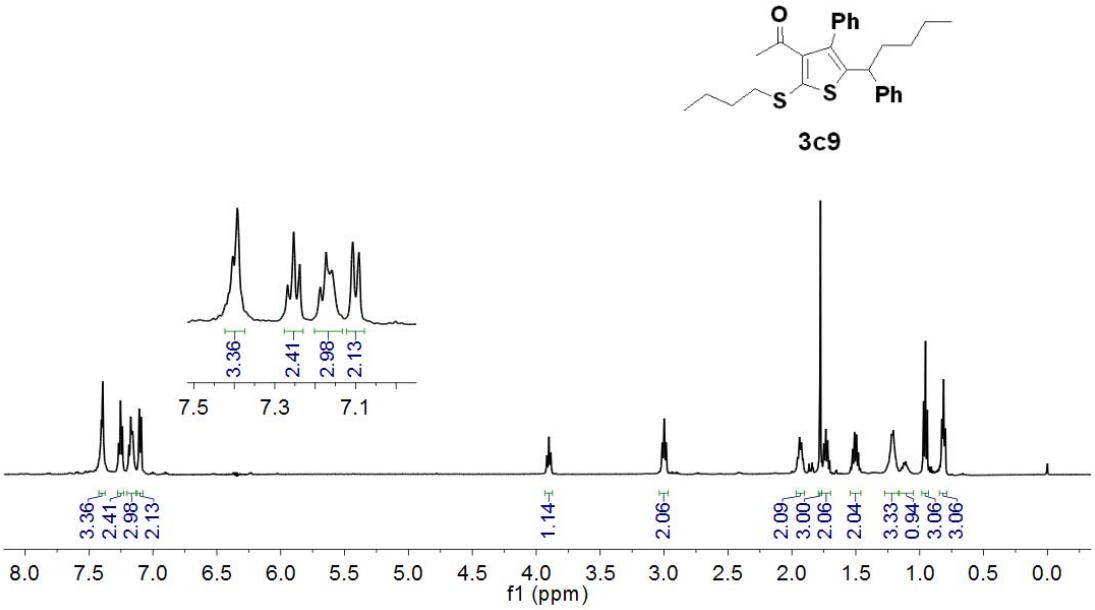

196.18
144.02
143.89
138.95
138.04
136.40
130.69
128.53
128.41
128.28
127.48
127.00
126.78
126.38
126.00
46.64
30.78
30.57
30.29
21.36
13.82
12.59
O
S
S
Ph
3c6
f1 (ppm)

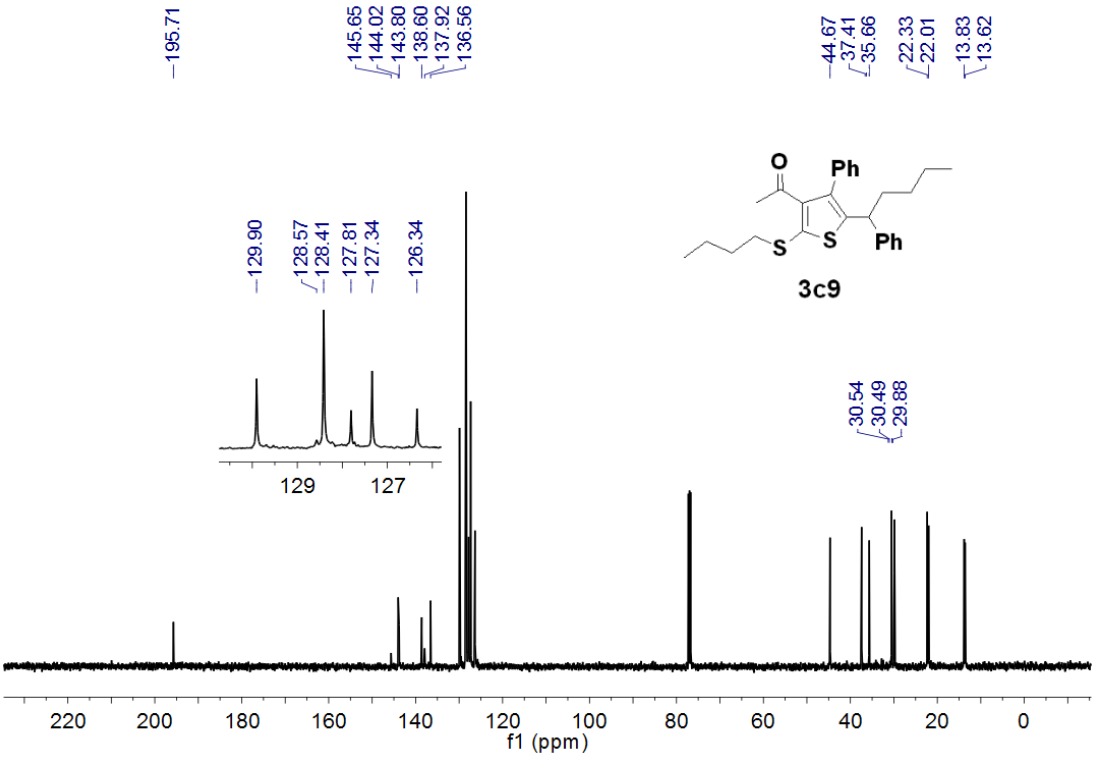



O
S
S
3c8
3.44
2.01
2.15
2.14
7.4
7.2
7.0
3.44
2.01
2.15
2.14
0.99
2.10
3.38
2.15
3.02
3.14
3.00
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


195.83
144.60
144.23
140.80
138.52
138.40
136.52
135.88
46.05
30.70
30.48
30.09
20.91
13.71
12.53
129.92
129.09
128.38
127.75
127.17
O
S
S
3c8
130
128
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)


O
Ph
S
S
Ph
3c9
3.36
2.41
2.98
2.13
7.5
7.3
7.1
1.14
2.06
2.09
3.00
2.06
2.04
3.33
0.94
3.06
3.06
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


195.71
145.65
144.02
143.80
138.60
137.92
136.56
44.67
37.41
35.66
22.33
22.01
13.83
13.62
O
Ph
S
S
Ph
3c9
129.90
128.57
128.41
127.81
127.34
126.34
129
127
30.54
30.49
29.88
220
200
180
160
140
120
100
80
60
40
20
0
f1 (ppm)

5)