

Electronic Supplementary Information

TM-Free Full Utilization of S Atoms: Synthesis of Thioethers from Disulfides and Quaternary Ammonium Salts

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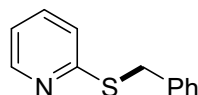
1. General Information

Unless otherwise noted, all chemicals were purchased and used without further purification. All reactions were carried out in sealed Schlenk tubes under air and then monitored by TLC and/or GC-MS. All products were purified by column chromatography on silica gel using petroleum ether and ethyl acetate as the eluent. ^1H and ^{13}C NMR spectra were measured on a JNM-ECZ600R/S₃ (Jeol, Japan) (600 and 150 MHz for ^1H and ^{13}C NMR, respectively) using CDCl_3 as the solvent. Chemical shifts for ^1H and ^{13}C NMR were referred to internal Me_4Si (0 ppm) as the standard. Mass spectra were measured on an Agilent GC-MS-7890A/5975C Plus spectrometer (EI). Infrared spectra were measured on an Infrared spectroscopy combined with infrared microscopy (Thermo Fisher Nicoletis5). HRMS were recorded on a LC-TOF spectrometer (Xevo G2-XS QToF) using ESI techniques.

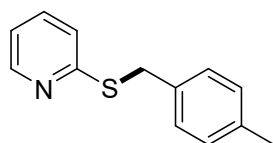
2. Typical Procedure for TM-free synthesis of thioethers from disulfides and quaternary ammonium salts.

A mixture of 1,2-di(pyridin-2-yl)disulfane **1a** (0.375mmol), benzyl trimethyl ammonium chloride **2a** (0.50 mmol, 1.0 equiv), NaOH (1.0 mmol, 2.0 equiv.) and EtOH (1 mL) was sealed in a 10 mL Schlenk heated under air at 130 °C for 12 h. After the reaction mixture was cooled to room temperature, the reaction mixture was then analyzed by TLC/GC-MS and purified by flash column chromatography on silica gel using ethyl acetate and petroleum ether (0~ 1/10) as the eluent, giving **3aa** in 87% isolated yield.

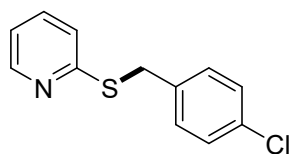
3. Typical Procedure and Characterization of the Products



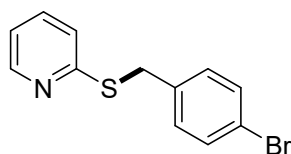
2-(Benzylthio)pyridine (3aa) Colorless oil. , 87.4 mg, 87% yield, ¹H NMR (600 MHz, CDCl₃) δ 8.44 (d, *J* = 4.2 Hz, 1H), 7.42 (ddd, *J* = 13.8, 9.6, 4.2 Hz, 3H), 7.28 (t, *J* = 7.2 Hz, 2H), 7.22 (t, *J* = 7.2 Hz, 1H), 7.13 (d, *J* = 8.4 Hz, 1H), 7.00 – 6.90 (m, 1H), 4.43 (s, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 158.9, 149.5, 138.1, 136.1, 129.1, 128.6, 127.2, 122.2, 119.7, 34.5. This compound was known: Jia, X.; Yu, L.; Liu, J.; Xu, Q.; Sickert, M.; Chen, L.; Lautens, M. *Green Chem.* **2014**, *16*, 3444.



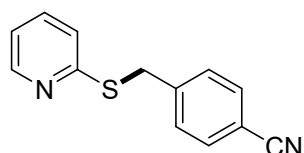
2-((4-Methylbenzyl)thio)pyridine (3ab). Colorless oil. 88.2 mg, 82% yield, ¹H NMR (600 MHz, CDCl₃) δ 8.48 (s, 1H), 7.57 – 7.38 (m, 1H), 7.32 (s, 2H), 7.22 – 7.09 (m, 3H), 7.03 – 6.95 (m, 1H), 4.43 (s, 2H), 2.34 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ 159.1, 149.5, 136.9, 136.0, 134.8, 129.3, 129.0, 122.1, 119.6, 34.3, 21.2. This compound was known: Ma, X.; Yu, J.; Yan, R.; Yan, M.; Xu, Q. *J. Org. Chem.* **2019**, *84*, 11294.



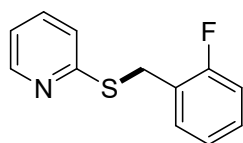
2-((4-Chlorobenzyl)thio)pyridine (3ac). Colorless oil. 97.5 mg, 83% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.44 (d, $J = 4.8$ Hz, 1H), 7.451 – 7.42 (m, 1H), 7.34 (d, $J = 8.4$ Hz, 2H), 7.25 (t, $J = 5.4$ Hz, 2H), 7.14 (d, $J = 7.8$ Hz, 1H), 6.99 (dd, $J = 7.2, 5.4$ Hz, 1H), 4.40 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 158.3, 149.5, 136.9, 136.1, 132.9, 130.4, 128.7, 122.3, 119.8, 33.6. This compound was known: Wang, Q.; Zhu, B.; Yang, G.; Ma, X.; Xu, Q. *Chin. J. Org. Chem.* **2021**, 41, 1193.



2-((4-bromobenzyl)thio)pyridine (3ad). Colorless oil. 120 mg, 86% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.43 (d, $J = 4.2$ Hz, 1H), 7.48 – 7.39 (m, 1H), 7.41 – 7.33 (m, 2H), 7.27 (d, $J = 8.4$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 1H), 7.04 – 6.88 (m, 1H), 4.37 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 158.2, 149.5, 137.5, 136.2, 131.6, 130.8, 122.3, 121.0, 119.9, 33.7. This compound was known: Ma, X.; Yu, L.; Su, C.; Yang, Y.; Li, H.; Xu, Q. *Adv. Synth. Catal.* **2017**, 359, 1649.

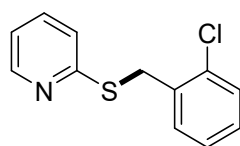


2-((4-cyanobenzyl)thio)pyridine (3ae). Colorless oil. 90.4 mg, 80% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.45 (ddd, $J = 5.4, 1.8, 0.6$ Hz, 1H), 7.76 – 7.41 (m, 5H), 7.20 – 7.13 (m, 1H), 7.03 (ddd, $J = 7.2, 4.8, 1.2$ Hz, 1H), 4.48 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.3, 149.5, 144.5, 136.3, 132.3, 129.8, 122.4, 120.1, 119.0, 110.8, 33.7. This compound was known: Ma, X.; Yan, X.; Zhu, Y.; Niu, S.; Wang, Y. *Chin. J. Org. Chem.* **2023**, 43, 2136.

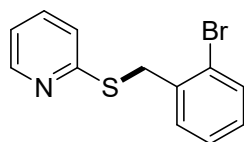


2-((2-Fluorobenzyl)thio)pyridine (3af). Colorless oil. 95.3 mg, 87% yield, ^1H NMR

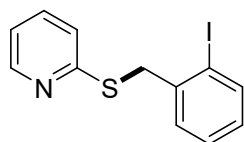
(600 MHz, CDCl₃) δ 8.46 (dd, J = 4.8, 1.8 Hz, 1H), 7.50 – 7.38 (m, 2H), 7.23 – 7.18 (m, 1H), 7.16 (d, J = 8.4 Hz, 1H), 7.09 – 7.03 (m, 2H), 7.00 – 6.96 (m, 1H), 4.48 (s, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 161.1 (d, J = 247.1 Hz), 158.4 (s), 149.5 (s), 136.1 (s), 131.2 (d, J = 3.9 Hz), 129.0 (d, J = 8.4 Hz), 125.4 (d, J = 15.1 Hz), 124.1 (d, J = 3.7 Hz), 122.3 (s), 119.8 (s), 115.4 (d, J = 21.5 Hz), 27.4 (d, J = 2.7 Hz). This compound was known: Ma, X.; Yan, X.; Zhu, Y.; Niu, S.; Wang, Y. *Chin. J. Org. Chem.* **2023**, 43, 2136.



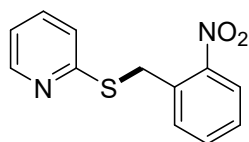
2-((2-Chlorobenzyl)thio)pyridine (3ag). Colorless oil. 99.9mg, 85% yield, ¹H NMR (600 MHz, CDCl₃) δ 8.46 (d, J = 4.8 Hz, 1H), 7.52 (dd, J = 6.0, 3.0 Hz, 1H), 7.48 – 7.39 (m, 1H), 7.39 – 7.32 (m, 1H), 7.15 (ddd, J = 16.2, 9.6, 6.6 Hz, 3H), 6.97 (dd, J = 7.2, 5.4 Hz, 1H), 4.57 (s, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 158.4, 149.4, 136.1, 136.0, 134.4, 131.1, 129.6, 128.6, 126.9, 122.4, 119.8, 31.9. This compound was known: Ma, X.; Yu, L.; Su, C.; Yang, Y.; Li, H.; Xu, Q. *Adv. Synth. Catal.* **2017**, 359, 1649.



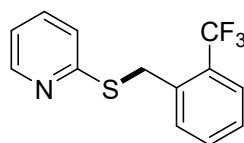
2-((2-bromobenzyl)thio)pyridine (3ah). Colorless oil. 125.5 mg, 90% yield, ¹H NMR (600 MHz, CDCl₃) δ 8.50 – 8.37 (m, 1H), 7.64 – 7.50 (m, 2H), 7.49 – 7.41 (m, 1H), 7.24 – 7.16 (m, 1H), 7.15 (dd, J = 8.4, 1.2 Hz, 1H), 7.12 – 7.03 (m, 1H), 7.02 – 6.94 (m, 1H), 4.58 (s, 2H); ¹³C NMR (150 MHz, CDCl₃) δ 158.3, 149.4, 137.8, 136.1, 132.9, 131.2, 128.8, 127.5, 124.8, 122.4, 119.7, 34.6. IR: ν 3045, 1577, 1555, 1467, 1451, 1439, 1412, 1121, 1087, 1044, 1024, 754, 731 cm⁻¹. HRMS (ESI) for C₁₃H₁₁BrNS (M+H)⁺ Calcd: 278.9714; found: 278.9716.



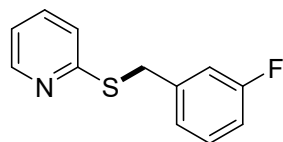
2-((2-iodobenzyl)thio)pyridine (3ai). Colorless oil. 153.7 mg, 94% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.46 (d, $J = 4.8$ Hz, 1H), 7.83 (d, $J = 8.4$ Hz, 1H), 7.53 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.50 – 7.41 (m, 1H), 7.24 (dd, $J = 10.8, 4.2$ Hz, 1H), 7.15 (d, $J = 8.4$ Hz, 1H), 6.99 (dd, $J = 6.6, 4.8$ Hz, 1H), 6.95 – 6.86 (m, 1H), 4.56 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 158.2, 149.5, 141.0, 139.6, 136.1, 130.5, 128.9, 128.4, 122.4, 119.8, 100.9, 39.5. This compound was known: Ma, X.; Yan, X.; Zhu, Y.; Niu, S.; Wang, Y. *Chin. J. Org. Chem.* **2023**, *43*, 2136.



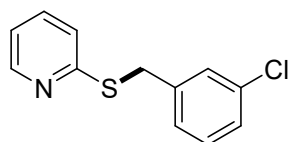
2-((2-nitrobenzyl)thio)pyridine (3aj). Brown oil. 51.7 mg, 42% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.42 (dd, $J = 4.8, 1.8$ Hz, 1H), 8.04 – 7.91 (m, 1H), 7.73 (dd, $J = 7.8, 1.2$ Hz, 1H), 7.54 – 7.48 (m, 1H), 7.48 – 7.41 (m, 1H), 7.39 – 7.32 (m, 1H), 7.13 (d, $J = 8.4$ Hz, 1H), 7.02 – 6.92 (m, 1H), 4.79 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.6, 149.3, 148.9, 136.1, 134.9, 133.2, 132.5, 128.0, 124.9, 122.3, 119.8, 30.5. IR: ν 2983, 2934, 1734, 1673, 1609, 1558, 1524, 1453, 1372, 1239, 1043, 762, 723 cm^{-1} . HRMS (ESI) for $\text{C}_{13}\text{H}_{11}\text{F}_3\text{NS}$ ($\text{M}+\text{H}$) $^+$ Calcd: 247.0574; found: 247.0556.



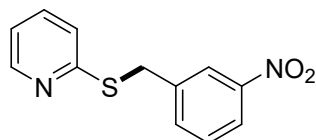
2-((2-(trifluoromethyl)benzyl)thio)pyridine (3ak). Colorless oil. 117 mg, 87% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.47 (ddd, $J = 4.8, 1.8, 0.6$ Hz, 1H), 7.65 (dd, $J = 27.6, 7.8$ Hz, 2H), 7.51 – 7.40 (m, 2H), 7.32 (t, $J = 7.8$ Hz, 1H), 7.18 – 7.11 (m, 1H), 7.00 (ddd, $J = 7.2, 4.8, 1.2$ Hz, 1H), 4.67 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 158.2 (s), 149.5 (s), 137.2 (s), 136.2 (s), 132.2 (s), 131.6 (s), 128.6 (d, $J = 30.2$ Hz), 127.3 (s), 126.1 (q, $J = 5.4$ Hz), 124.5 (d, $J = 274.0$ Hz), 122.1 (s), 119.9 (s), 30.3 (s). This compound was known: Ma, X.; Zhu, Y.; Yan, S.; Chen, Y.; Chang X. *J. Org. Chem.* **2024**, *89*, 18235.



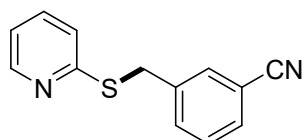
2-((3-fluorobenzyl)thio)pyridine (3al). Colorless oil. 93.1 mg, 85% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.47 (ddd, $J = 4.8, 1.8, 0.6$ Hz, 1H), 7.53 – 7.44 (m, 1H), 7.30 – 7.21 (m, 1H), 7.21 – 7.12 (m, 3H), 7.03 – 6.99 (m, 1H), 6.96 – 6.90 (m, 1H), 4.44 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 162.9 (d, $J = 245.7$ Hz), 158.2 (s), 149.5 (s), 141.0 (d, $J = 7.3$ Hz), 136.2 (s), 130.0 (d, $J = 8.4$ Hz), 124.7 (d, $J = 2.3$ Hz), 122.3 (s), 119.9 (s), 116.0 (d, $J = 21.8$ Hz), 114.1 (d, $J = 21.2$ Hz), 33.8 (s). This compound was known: Ma, X.; Zhu, Y.; Yan, S.; Chen, Y.; Chang X. *J. Org. Chem.* **2024**, 89, 18235.



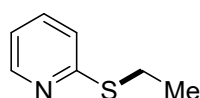
2-((3-Chlorobenzyl)thio)pyridine (3am). Colorless oil. 101.1 mg, 86% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.51 – 8.37 (m, 1H), 7.45 (s, 1H), 7.41 (s, 1H), 7.30 – 7.26 (m, 2H), 7.21 – 7.17 (m, 2H), 7.14 (d, $J = 8.4$ Hz, 1H), 6.99 (dd, $J = 6.0, 0.6$ Hz, 1H), 4.40 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 158.1, 149.5, 140.5, 136.2, 134.2, 129.8, 129.2, 127.3, 127.3, 122.3, 119.9, 33.7. This compound was known: Tresoldi, G.; Schiavo, S. L.; Lanza, S.; Cardiano, P. *Eur. J. Inorg. Chem.* **2002**, 2002, 181.



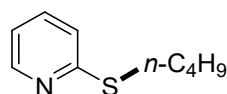
2-((3-nitrobenzyl)thio)pyridine (3an). Brown oil. 83.6 mg, 68% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.60 – 8.40 (m, 1H), 8.31 (s, 1H), 8.07 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.76 (d, $J = 7.8$ Hz, 1H), 7.58 – 7.37 (m, 2H), 7.17 (d, $J = 8.4$ Hz, 1H), 7.06 – 6.88 (m, 1H), 4.51 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.2, 149.6, 148.3, 141.1, 136.3, 135.3, 129.4, 124.1, 122.4, 122.2, 120.1, 33.3. This compound was known: Ma, X.; Zhu, Y.; Yan, S.; Chen, Y.; Chang X. *J. Org. Chem.* **2024**, 89, 18235.



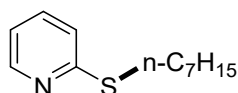
2-((3-cyanobenzyl)thio)pyridine (3ao). Colorless oil. 93.8mg, 83% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.46 (d, $J = 4.2$ Hz, 1H), 7.73 (s, 1H), 7.66 (d, $J = 7.8$ Hz, 1H), 7.50 (dd, $J = 12.6, 7.2$ Hz, 2H), 7.39 (t, $J = 7.8$ Hz, 1H), 7.17 (d, $J = 7.8$ Hz, 1H), 7.10 – 6.96 (m, 1H), 4.46 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 157.4, 149.5, 140.5, 136.3, 133.6, 132.6, 130.7, 129.2, 122.4, 120.1, 118.9, 112.5, 33.2. IR: ν 3047, 2229, 1576, 1556, 1481, 1453, 1413, 1121, 800, 757, 683 cm^{-1} HRMS (ESI) for $\text{C}_{13}\text{H}_{11}\text{F}_3\text{NS}$ ($\text{M}+\text{H}$) $^+$ Calcd: 227.0624; found: 227.0626.



2-(Ethylthio)pyridine (3ap). Colorless oil. 55.6 mg, 80% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.47 – 8.29 (m, 1H), 7.51 – 7.42 (m, 1H), 7.16 (d, $J = 8.4$ Hz, 1H), 7.04 – 6.83 (m, 1H), 3.17 (q, $J = 7.2$ Hz, 2H), 1.38 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.5, 149.5, 135.9, 122.2, 119.3, 24.5, 14.7. 13. This compound was known: Heinz, B.; Balkenhohl, M.; Knochel, P. *Synthesis*. **2019**, 51, 4452.

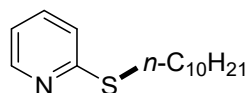


2-(Butylthio)pyridine (3aq). Colorless oil. 68.5 mg, 82% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.42 (d, $J = 4.8$ Hz, 1H), 7.51 – 7.42 (m, 1H), 7.16 (d, $J = 8.4$ Hz, 1H), 6.96 (dd, $J = 7.2, 5.4$ Hz, 1H), 3.31 – 3.02 (m, 2H), 1.75 – 1.64 (m, 2H), 1.53 – 1.40 (m, 2H), 0.94 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.7, 149.5, 135.9, 122.2, 119.3, 31.5, 29.9, 22.2, 13.8. This compound was known: Nath, D.; Skilbeck, M. C.; Coldham, I.; Fleming, F. F. *Org. Lett.* **2014**, 16, 62.

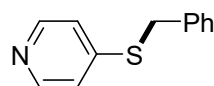


2-(Heptylthio)pyridine (3ar). Colorless oil. 86.8 mg, 83% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.42 (d, $J = 4.8$ Hz, 1H), 7.51 – 7.42 (m, 1H), 7.16 (d, $J = 7.8$ Hz, 1H), 6.96 (dd, $J = 7.2, 5.4$ Hz, 1H), 3.42 – 2.81 (m, 2H), 1.70 (t, $J = 7.8$ Hz, 2H), 1.49 – 1.38 (m, 2H), 1.35 – 1.15 (m, 6H), 0.88 (t, $J = 7.2$ Hz, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.7, 149.5, 135.8, 122.2, 119.2, 31.8, 30.2, 29.4, 29.0, 29.0, 22.7, 14.2. This compound was known: Ma, X.; Yan, X.; Zhu, Y.; Niu, S.; Wang, Y. *Chin. J. Org.*

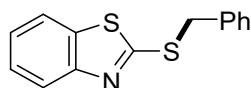
Chem. 2023, 43, 2136.



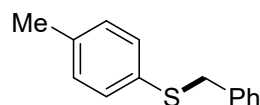
2-(Decylthio)pyridine (3as). Colorless oil. 103 mg, 82% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.42 (d, $J = 4.2$ Hz, 1H), 7.56 – 7.38 (m, 1H), 7.16 (d, $J = 8.4$ Hz, 1H), 7.04 – 6.89 (m, 1H), 3.30 – 3.01 (m, 2H), 1.70 (dd, $J = 15.0, 7.8$ Hz, 2H), 1.50 – 1.38 (m, 2H), 1.32 – 1.21 (m, 12H), 0.88 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.7, 149.5, 135.8, 122.2, 119.2, 32.0, 30.2, 29.6, 29.6, 29.4, 29.4, 29.3, 29.0, 22.8, 14.2. This compound was known: Ma, X.; Yu, L.; Su, C.; Yang, Y.; Li, H.; Xu, Q. *Adv. Synth. Catal.* **2017**, 359, 1649.



4-(Benzylthio)pyridine (3ba). Colorless oil. 82.4 mg, 82% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.36 (d, $J = 3.6$ Hz, 2H), 7.38 (d, $J = 6.6$ Hz, 2H), 7.33 (t, $J = 6.6$ Hz, 2H), 7.28 – 7.24 (m, 1H), 7.10 (d, $J = 4.2$ Hz, 2H), 4.19 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 149.4, 149.1, 135.6, 128.9, 128.8, 127.8, 120.8, 35.7. This compound was known: Ma, X.; Yan, X.; Zhu, Y.; Niu, S.; Wang, Y. *Chin. J. Org. Chem.* **2023**, 43, 2136.

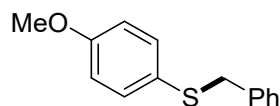


2-(Benzylthio)benzo[d]thiazole (3ca). Colorless oil. 102.8 mg, 80% yield, ^1H NMR (600 MHz, CDCl_3) δ 7.90 (d, $J = 8.4$ Hz, 1H), 7.75 (d, $J = 8.4$ Hz, 1H), 7.50 – 7.39 (m, 3H), 7.30 (ddd, $J = 25.8, 16.8, 12.0$ Hz, 4H), 4.61 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 166.5, 153.2, 136.2, 135.4, 129.2, 128.8, 127.9, 126.2, 124.4, 121.6, 121.1, 37.8. This compound was known: Kumar, D.; Mishra, B. B.; Tiwari, V. K. *J. Org. Chem.* **2014**, 79, 251.

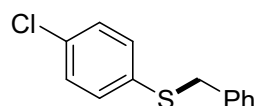


Benzyl(p-tolyl)sulfane (3da). White solid. 39 – 40 °C. 96.3 mg, 90% yield, ^1H NMR (600 MHz, CDCl_3) δ 7.29 – 7.25 (m, 4H), 7.21 (d, $J = 8.4$ Hz, 3H), 7.06 (d, $J = 8.4$ Hz,

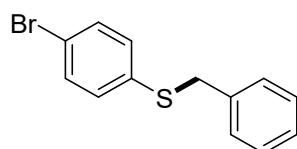
2H), 4.07 (s, 2H), 2.31 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 137.9, 136.7, 132.6, 130.8, 129.7, 128.9, 128.5, 127.1, 39.9, 21.1. This compound was known: Li, F.; Wang, D.; Chen, H.; He, Z.; Zhou, L.; Zeng, Q. *Chem. Commun.* **2020**, 56, 13029.



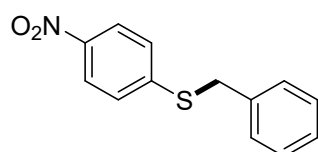
Benzyl(4-methoxyphenyl)sulfane (3ea). White solid. 38 – 40 °C. 95.5 mg, 83% yield, ^1H NMR (600 MHz, CDCl_3) δ 7.26 (t, J = 7.8 Hz, 4H), 7.23 – 7.17 (m, 3H), 6.82 – 6.77 (m, 2H), 3.99 (s, 2H), 3.78 (s, 3H); ^{13}C NMR (150 MHz, CDCl_3) δ 159.3, 138.2, 134.2, 129.0, 128.5, 127.1, 126.1, 114.5, 55.4, 41.3. This compound was known: Li, F.; Wang, D.; Chen, H.; He, Z.; Zhou, L.; Zeng, Q. *Chem. Commun.* **2020**, 56, 13029.



Benzyl(4-chlorophenyl)sulfane (3fa). White solid. 42 – 43 °C. 101.8 mg, 87% yield, ^1H NMR (600 MHz, CDCl_3) δ 7.31 – 7.22 (m, 5H), 7.20 (s, 4H), 4.07 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 137.2, 134.8, 132.6, 131.5, 129.0, 128.9, 128.6, 127.4, 39.4. This compound was known: Li, F.; Wang, D.; Chen, H.; He, Z.; Zhou, L.; Zeng, Q. *Chem. Commun.* **2020**, 56, 13029.

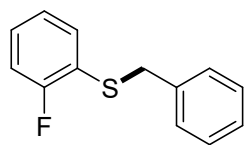


Benzyl(4-bromophenyl)sulfane (3ga). yellow solid. 52 – 53 °C. 118.1 mg, 85% yield, ^1H NMR (600 MHz, CDCl_3) δ 7.35 (d, J = 8.4 Hz, 2H), 7.32 – 7.21 (m, 5H), 7.14 (d, J = 8.4 Hz, 2H), 4.08 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 137.1, 135.5, 131.9, 131.6, 128.9, 128.6, 127.4, 120.4, 39.2. This compound was known: Li, Y.; Pu, J.; Jiang, X. *Org. Lett.* **2014**, 16, 2692.

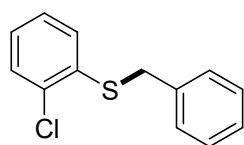


Benzyl(4-nitrophenyl)sulfane (3ha). Yellowish solid. 111 – 113 °C. 98 mg, 80%

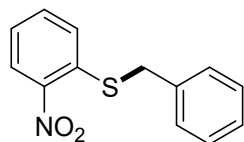
yield, ^1H NMR (600 MHz, CDCl_3) δ 8.12 (d, $J = 8.4$ Hz, 2H), 7.52 – 7.25 (m, 7H), 4.27 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 147.1, 145.0, 135.0, 128.9, 128.8, 127.9, 126.7, 124.0, 37.1. This compound was known: Li, F.; Wang, D.; Chen, H.; He, Z.; Zhou, L.; Zeng, Q. *Chem. Commun.* **2020**, 56, 13029.



Benzyl(2-fluorophenyl)sulfane (3ia). Colorless oil. 89.4 mg, 82% yield, ^1H NMR (600 MHz, CDCl_3) δ 7.39 – 7.09 (m, 7H), 7.07 – 6.95 (m, 2H), 4.08 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 161.76 (d, $J = 245.1$ Hz), 137.30 (s), 133.06 (s), 128.97 (s), 128.90 (s), 128.60 (s), 127.38 (s), 124.48 (d, $J = 2.9$ Hz), 122.85 (d, $J = 17.6$ Hz), 115.72 (d, $J = 22.2$ Hz), 38.47 (s). This compound was known: Li, Y.; Pu, J.; Jiang, X. *Org. Lett.* **2014**, 16, 2692.

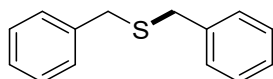


Benzyl(2-chlorophenyl)sulfane (3ja). Colorless oil. 101.8 mg, 87% yield, ^1H NMR (600 MHz, CDCl_3) δ 7.38 – 7.32 (m, 3H), 7.30 (dd, $J = 10.6, 4.8$ Hz, 2H), 7.24 (ddd, $J = 9.0, 7.2, 3.6$ Hz, 2H), 7.95 – 7.13 (m, 1H), 7.12 – 7.06 (m, 1H), 4.14 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 136.4, 135.8, 133.7, 129.7, 129.2, 129.0, 128.7, 127.5, 127.2, 126.9, 37.5. This compound was known: Grover, J.; Prakash, G.; Teja, C.; Lahiri, G. K.; Maiti, D., *Green Chem.* **2023**, 25, 3431.

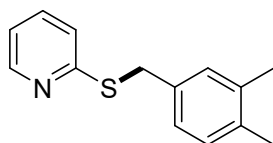


Benzyl(2-nitrophenyl)sulfane (3ka). yellow solid. 82 – 84 °C. 99.2 mg, 81% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.25 (dd, $J = 8.4, 1.8$ Hz, 1H), 7.55 (ddd, $J = 8.4, 7.2, 1.2$ Hz, 1H), 7.48 (dd, $J = 8.4, 1.2$ Hz, 1H), 7.46 – 7.43 (m, 2H), 7.40 – 7.35 (m, 2H), 7.32 (d, $J = 7.2$ Hz, 1H), 7.30 – 7.26 (m, 1H), 4.23 (s, 2H); ^{13}C NMR (150 MHz, CDCl_3) δ 145.7, 137.9, 135.1, 133.6, 129.2, 128.9, 127.9, 127.0, 126.2, 124.8, 37.7. This compound was known: Zhang, X.; Lu, G. P.; Cai, C. *Green chem.* **2016**, 18,

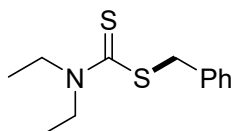
6143.



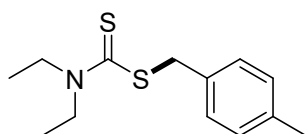
Dibenzylsulfane (3la). White solid. 48 – 49 °C. 85.6 mg, 80% yield, ^1H NMR (600 MHz, CDCl_3) δ 7.36 – 7.29 (m, 8H), 7.29 – 7.24 (m, 2H), 3.62 (s, 4H); ^{13}C NMR (150 MHz, CDCl_3) δ 138.2, 129.1, 128.6, 127.1, 35.7. This compound was known: Yang, Y.; Ye, Z.; Zhang, X.; Zhou, Y.; Ma, X.; Cao, H.; Li, H.; Yu, L.; Xu, Q. *Org. Biomol. Chem.* **2017**, *15*, 9638.



2-((3,4-dimethylbenzyl)thio)pyridine (3ma). Colorless oil. 91.6mg, 80% yield, ^1H NMR (600 MHz, CDCl_3) δ 8.49 – 8.40 (m, 1H), 7.48 – 7.37 (m, 1H), 7.17 (s, 1H), 7.15 – 7.10 (m, 2H), 7.04 (d, $J = 7.8$ Hz, 1H), 6.97 – 6.92 (m, 1H), 4.37 (s, 2H), 2.21 (d, $J = 4.8$ Hz, 6H). ^{13}C NMR (150 MHz, CDCl_3) δ 159.3, 149.5, 136.9, 136.1, 135.6, 135.1, 130.4, 129.9, 126.5, 122.1, 119.6, 34.4, 19.9, 19.6. This compound was known: Balzarini, J.; Stevens, M.; Andrei, G.; Snoeck, R.; Strunk, R.; Pierce, J. B.; Lacadie, J.A.; De Clercq, E.; Pannecouque, C. *Helv. Chim. Acta.* 2002, *85*, 2961.

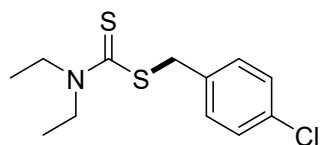


Benzyl diethylcarbamdithioate (5a). Yellow oil. 105.2 mg, 88% yield, ^1H NMR (600 MHz, CDCl_3) δ 7.38 (d, $J = 7.2$ Hz, 2H), 7.30 (t, $J = 7.8$ Hz, 2H), 7.25 (t, $J = 7.2$ Hz, 1H), 4.54 (s, 2H), 4.13 – 3.89 (m, 2H), 3.85 – 3.48 (m, 2H), 1.27 (dd, $J = 16.9, 7.2$ Hz, 6H). ^{13}C NMR (150 MHz, CDCl_3) 195.3, 136.1, 129.5, 128.7, 127.6, 49.6, 46.8, 42.3, 12.6, 11.7. This compound was known: Dutta, S.; Saha, A. *Tetrahedron Lett.* **2020**, *61*, 152382.

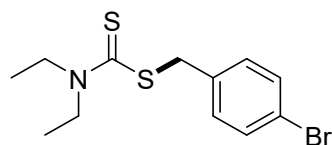


4-methylbenzyl diethylcarbamdithioate (5b). Yellow oil. 122.7 mg, 97% yield, ^1H

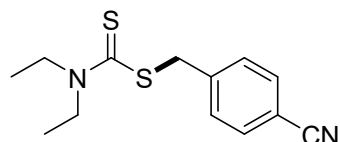
NMR (600 MHz, CDCl_3) δ 7.27 (d, $J = 7.8$ Hz, 2 H), 7.12 (d, $J = 7.8$ Hz, 2 H), 4.49 (s, 2 H), 4.03 (q, $J = 7.2$ Hz, 2 H), 3.71 (q, $J = 7.2$ Hz, 2 H), 2.33 (s, 3 H), 1.27 (dt, $J = 12.0, 7.2$ Hz, 6 H). ^{13}C NMR (150 MHz, CDCl_3) δ 195.5, 137.3, 132.8, 129.4, 129.4, 49.5, 46.8, 42.2, 21.3, 12.6, 11.7. This compound was known: Peng, H. Y.; Dong, Z. B. *Eur. J. Org. Chem.* **2019**, 5, 949.



4-chlorobenzyl diethylcarbamodithioate (5c). Yellow oil. 102.4 mg, 75% yield, ^1H NMR (600 MHz, CDCl_3) δ 7.30 (dd, $J = 32.4, 8.2$ Hz, 4 H), 4.52 (s, 2 H), 4.04 (q, $J = 7.2$ Hz, 2 H), 3.72 (q, $J = 7.2$ Hz, 2 H), 1.28 (dd, $J = 11.4, 6.6$ Hz, 6 H). ^{13}C NMR (150 MHz, CDCl_3) δ 194.8, 135.0, 133.3, 130.8, 128.8, 49.7, 46.9, 41.3, 12.6, 11.7. This compound was known: Peng, H. Y.; Dong, Z. B. *Eur. J. Org. Chem.* **2019**, 5, 949.

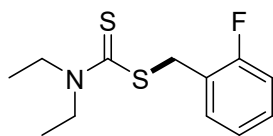


4-bromobenzyl diethylcarbamodithioate (5d). Yellow oil. 98.3 mg, 62% yield, ^1H NMR (600 MHz, CDCl_3) δ 7.46 – 7.38 (m, 2 H), 7.29 – 7.25 (m, 2 H), 4.50 (s, 2 H), 4.03 (q, $J = 7.2$ Hz, 2 H), 3.72 (q, $J = 7.2$ Hz, 2 H), 1.28 (td, $J = 7.2, 4.2$ Hz, 6 H). ^{13}C NMR (150 MHz, CDCl_3) δ 194.8, 135.6, 131.7, 131.1, 121.4, 49.7, 46.9, 41.3, 12.6, 11.7. This compound was known: Peng, H. Y.; Dong, Z. B. *Eur. J. Org. Chem.* **2019**, 5, 949.

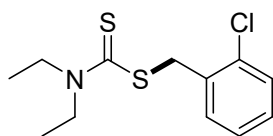


4-cyanobenzyl diethylcarbamodithioate (5e). Yellow oil. 89.8 mg, 68% yield, ^1H NMR (600 MHz, CDCl_3) δ 7.59 (d, $J = 8.4$ Hz, 2 H), 7.51 (d, $J = 8.4$ Hz, 2 H), 4.63 (s, 2 H), 4.03 (t, $J = 6.0$ Hz, 2 H), 3.74 (q, $J = 7.2$ Hz, 2 H), 1.30 – 1.27 (m, 6 H). ^{13}C NMR (150 MHz, CDCl_3) δ 194.0, 142.8, 132.3, 130.1, 118.9, 111.1, 50.1, 47.0, 41.1, 12.6, 11.6. This compound was known: Peng, H. Y.; Dong, Z. B. *Eur. J. Org. Chem.*

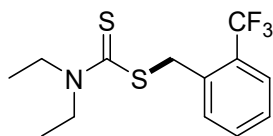
2019, 5, 949.



2-fluorobenzyl diethylcarbamodithioate (5f). Yellow oil. 109.2 mg, 85% yield, ^1H NMR (600 MHz, CDCl_3) δ 7.52 – 7.46 (m, 1 H), 7.26 – 7.23 (m, 1 H), 7.07 (dt, J = 18.0, 8.4 Hz, 2 H), 4.60 (s, 2 H), 4.04 (q, J = 7.2 Hz, 2 H), 3.72 (q, J = 7.2 Hz, 2 H), 1.28 (dd, J = 12.6, 6.0 Hz, 6 H). ^{13}C NMR (150 MHz, CDCl_3) δ 195.0 (s), 131.7 (d, J = 3.6 Hz), 129.4 (d, J = 8.2 Hz), 124.3 (d, J = 3.1 Hz), 115.6 (s), 115.4 (s), 49.7 (s), 46.8 (s), 35.1 (s), 12.6 (s), 11.7 (s). This compound was known: G.A.; Gallinger, T.L.; Mäder, P.; Lange-Grünweller, K.; Haerberlein, S.; Grünweller, A.; Grevelding, C.G.; Schlitzer, M. *Eur. J. Med. Chem.* **2022**, 242, 114641.

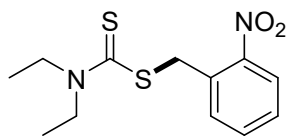


2-chlorobenzyl diethylcarbamodithioate (5g). Yellow oil. 125.6 mg, 92% yield, ^1H NMR (600 MHz, CDCl_3) δ 7.61 – 7.52 (m, 1 H), 7.40 – 7.33 (m, 1 H), 7.24 – 7.17 (m, 2 H), 4.69 (s, 2 H), 4.04 (q, J = 7.2 Hz, 2 H), 3.72 (q, J = 7.2 Hz, 2 H), 1.28 (dt, J = 11.4, 6.0 Hz, 6 H). ^{13}C NMR (150 MHz, CDCl_3) δ 195.0, 134.6, 134.5, 131.7, 129.6, 129.0, 127.0, 49.7, 46.9, 39.7, 12.6, 11.7. This compound was known: Peng, H. Y.; Dong, Z. B. *Eur. J. Org. Chem.* **2019**, 5, 949.

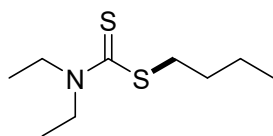


2-(trifluoromethyl)benzyl diethylcarbamodithioate (5h). Yellow oil. 138.2 mg, 90% yield, ^1H NMR (600 MHz, CDCl_3) δ 7.71 (d, J = 7.8 Hz, 1 H), 7.64 (d, J = 7.8 Hz, 1 H), 7.50 (t, J = 7.8 Hz, 1 H), 7.36 (t, J = 7.8 Hz, 1 H), 4.81 (s, 2 H), 4.06 (q, J = 7.2 Hz, 2 H), 3.73 (q, J = 7.2 Hz, 2 H), 1.29 (dt, J = 17.4, 7.2 Hz, 6 H). ^{13}C NMR (150 MHz, CDCl_3) δ 194.9 (s), 135.6 (s), 132.2 (s), 132.1 (s), 129.0 (d, J = 30.1 Hz), 127.6 (s), 126.0 (d, J = 5.6 Hz), 124.3 (d, J = 273.6 Hz), 50.0 (s), 46.9 (s), 38.3 (s), 12.6 (s), 11.7 (s). IR: ν 2978, 2935, 1487, 1454, 1417, 1315, 1268, 1207, 1116, 766, 736 cm^{-1} .

HRMS (ESI) for $C_{13}H_{17}F_3NS_2$ ($M+H$)⁺ Calcd: 308.0755; found: 308.0775.

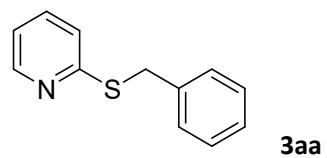


2-nitrobenzyl diethylcarbamodithioate (5i). Yellow oil. 102.2 mg, 72% yield, 1H NMR (600 MHz, $CDCl_3$) δ 8.00 (dd, $J = 8.4, 1.2$ Hz, 1 H), 7.92 – 7.81 (m, 1 H), 7.55 (m, $J = 9.0, 6.6, 2.4$ Hz, 1 H), 7.48 – 7.37 (m, 1 H), 5.00 (s, 2 H), 4.02 (q, $J = 7.2$ Hz, 2 H), 3.72 (q, $J = 7.2$ Hz, 2 H), 1.26 (t, $J = 7.2$ Hz, 6 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 194.5, 148.6, 133.5, 133.5, 133.0, 128.5, 125.0, 50.1, 46.9, 38.5, 12.6, 11.6. This compound was known: Rennar, G.A.; Gallinger, T.L.; Mäder, P.; Lange-Grünweller, K.; Haeberlein, S.; Grünweller, A.; Grevelding, C.G.; Schlitzer, M. *Eur. J. Med. Chem.* **2022**, 242, 114641.

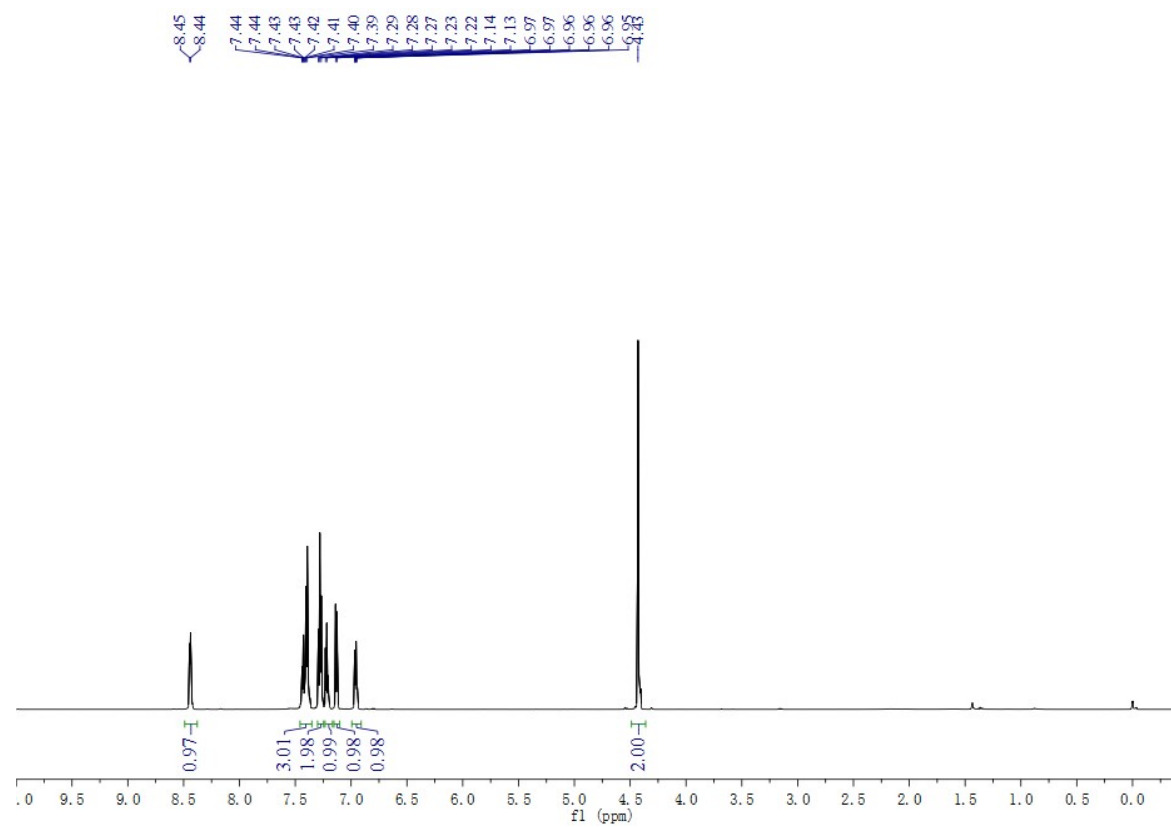


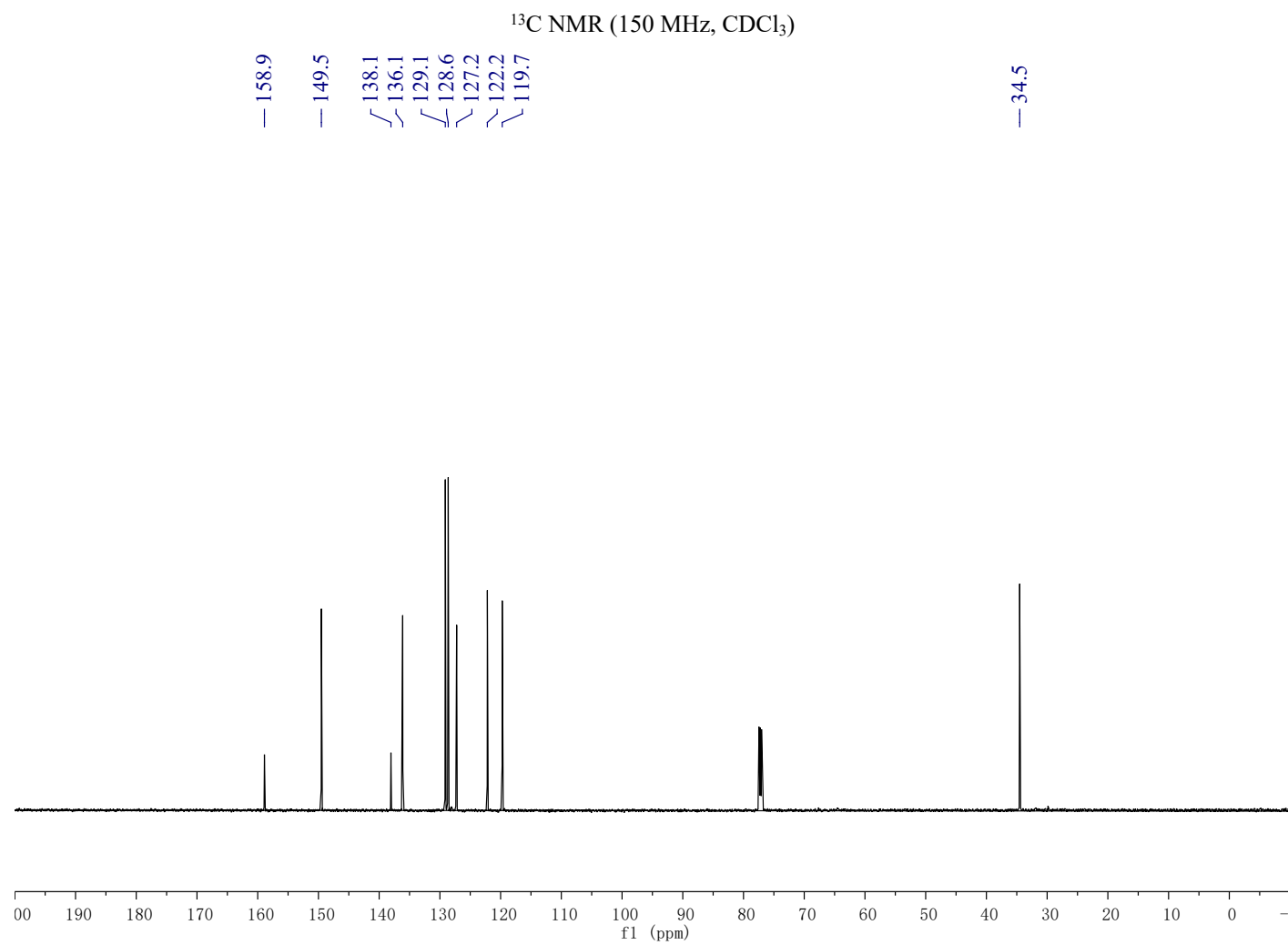
butyl diethylcarbamodithioate (5j). Yellow oil. 51.3 mg, 50% yield, 1H NMR (600 MHz, $CDCl_3$) δ 4.03 (q, $J = 7.2$ Hz, 2 H), 3.75 (q, $J = 7.2$ Hz, 2 H), 3.30 – 3.26 (m, 2 H), 1.74 – 1.64 (m, 2 H), 1.51 – 1.40 (m, 2 H), 1.28 (dt, $J = 11.4, 7.2$ Hz, 6 H), 0.95 (t, $J = 7.2$ Hz, 3 H). ^{13}C NMR (150 MHz, $CDCl_3$) δ 196.1, 49.4, 46.7, 37.1, 30.8, 22.3, 13.8, 12.5, 11.7. This compound was known: Azizi, N.; Aryanasab, F.; Saidi, M. R. *Org. Lett.* **2006**, 8, 5275.

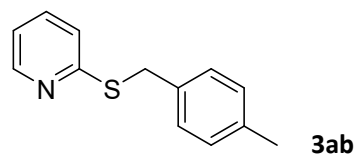
4. Copies of the ^1H , ^{13}C NMR and IR Spectra of the Products



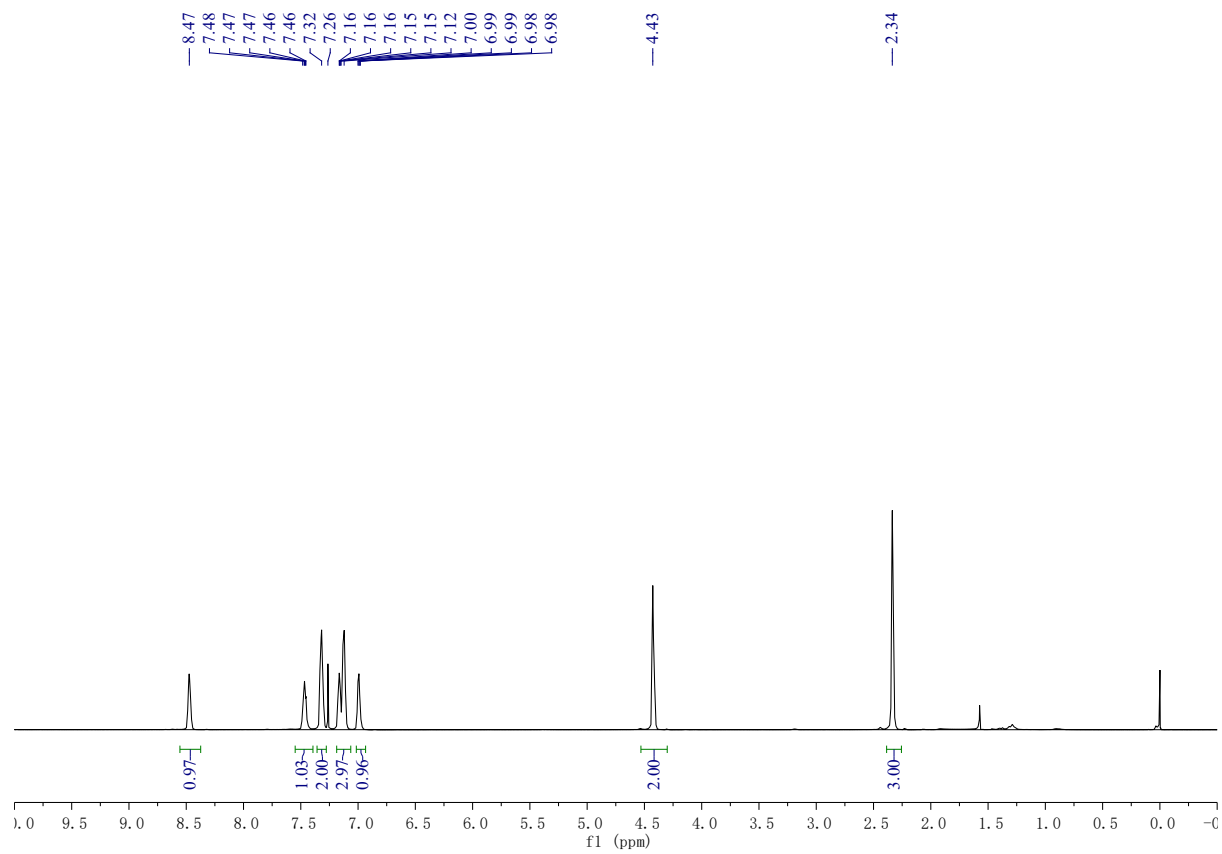
^1H NMR (600 MHz, CDCl_3)

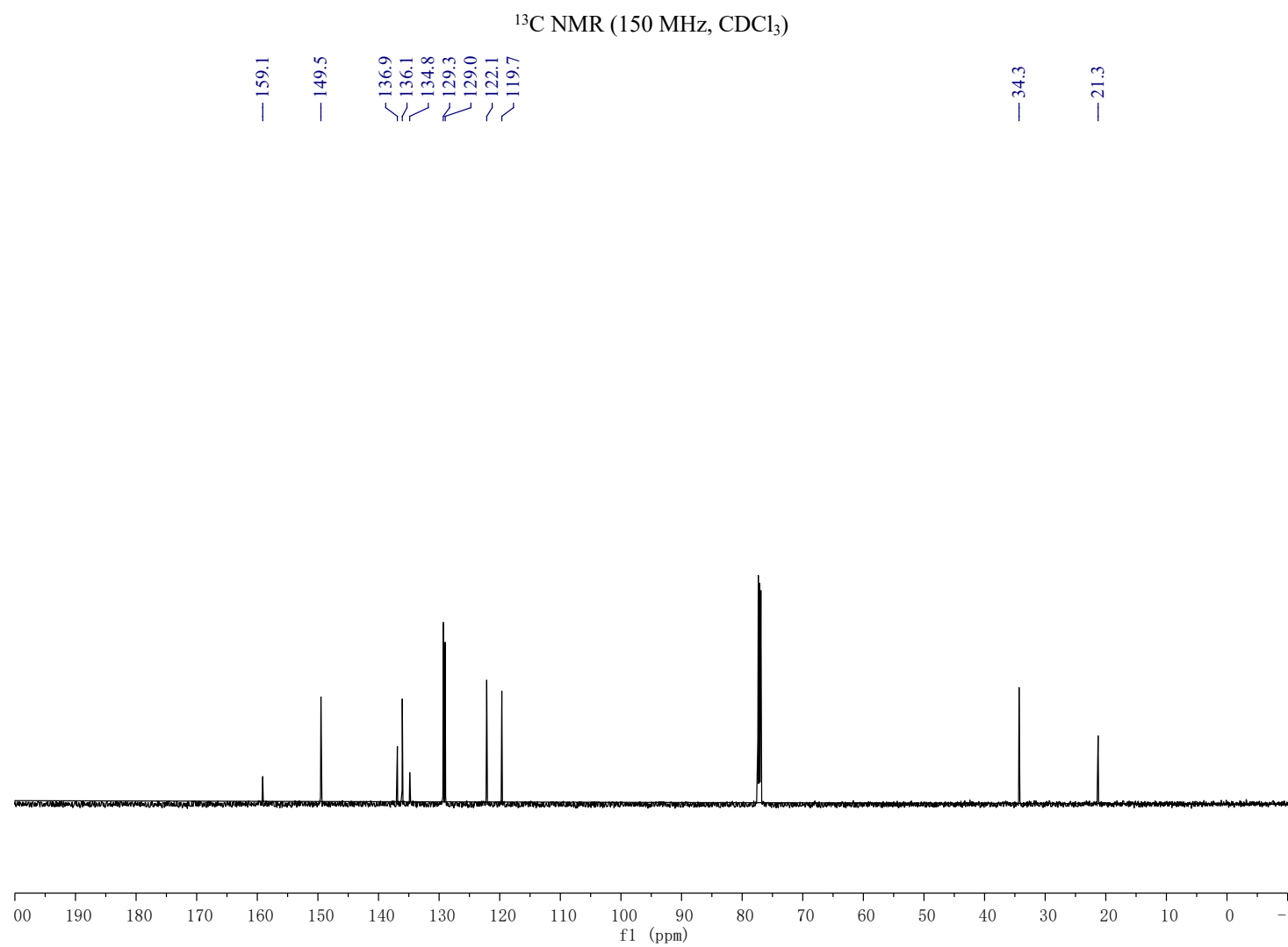


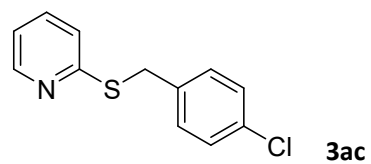




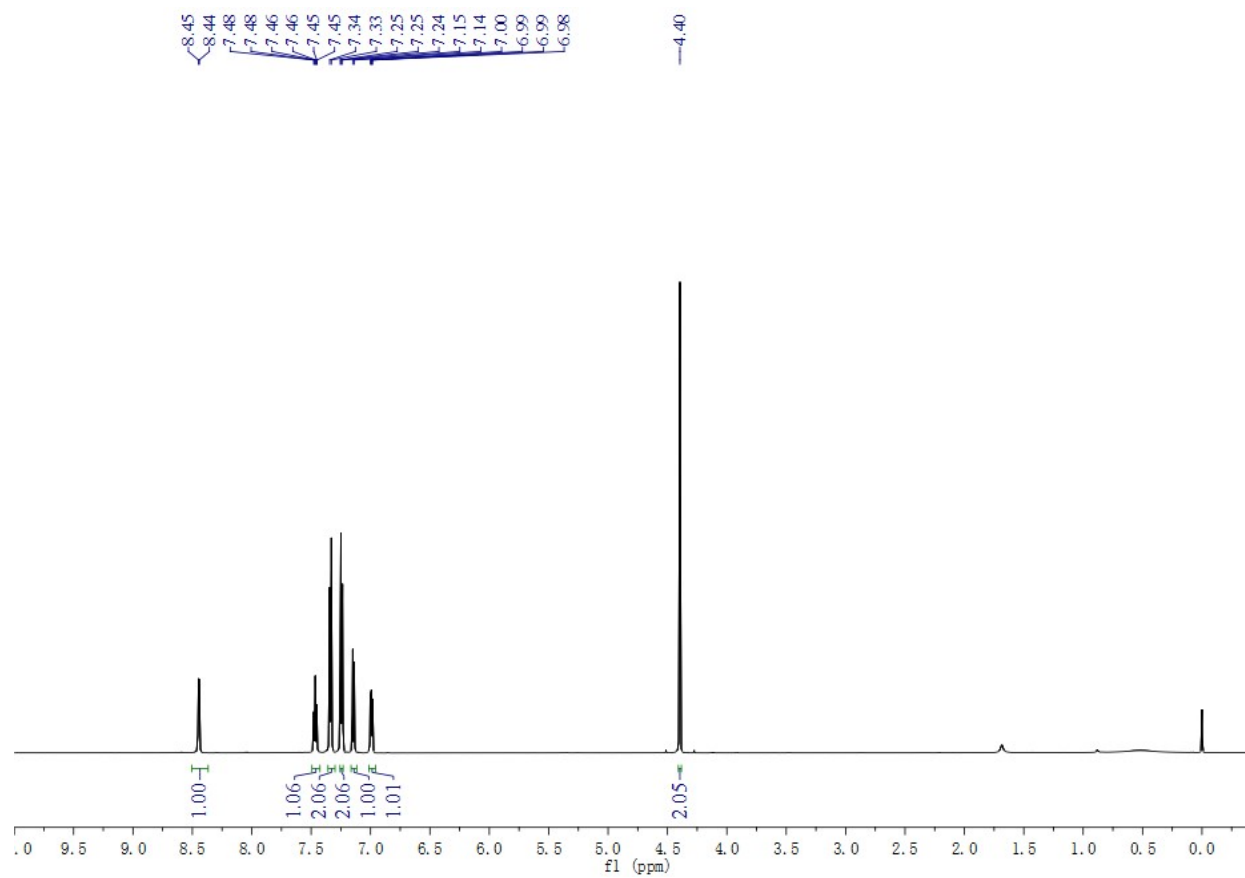
^1H NMR (600 MHz, CDCl_3)

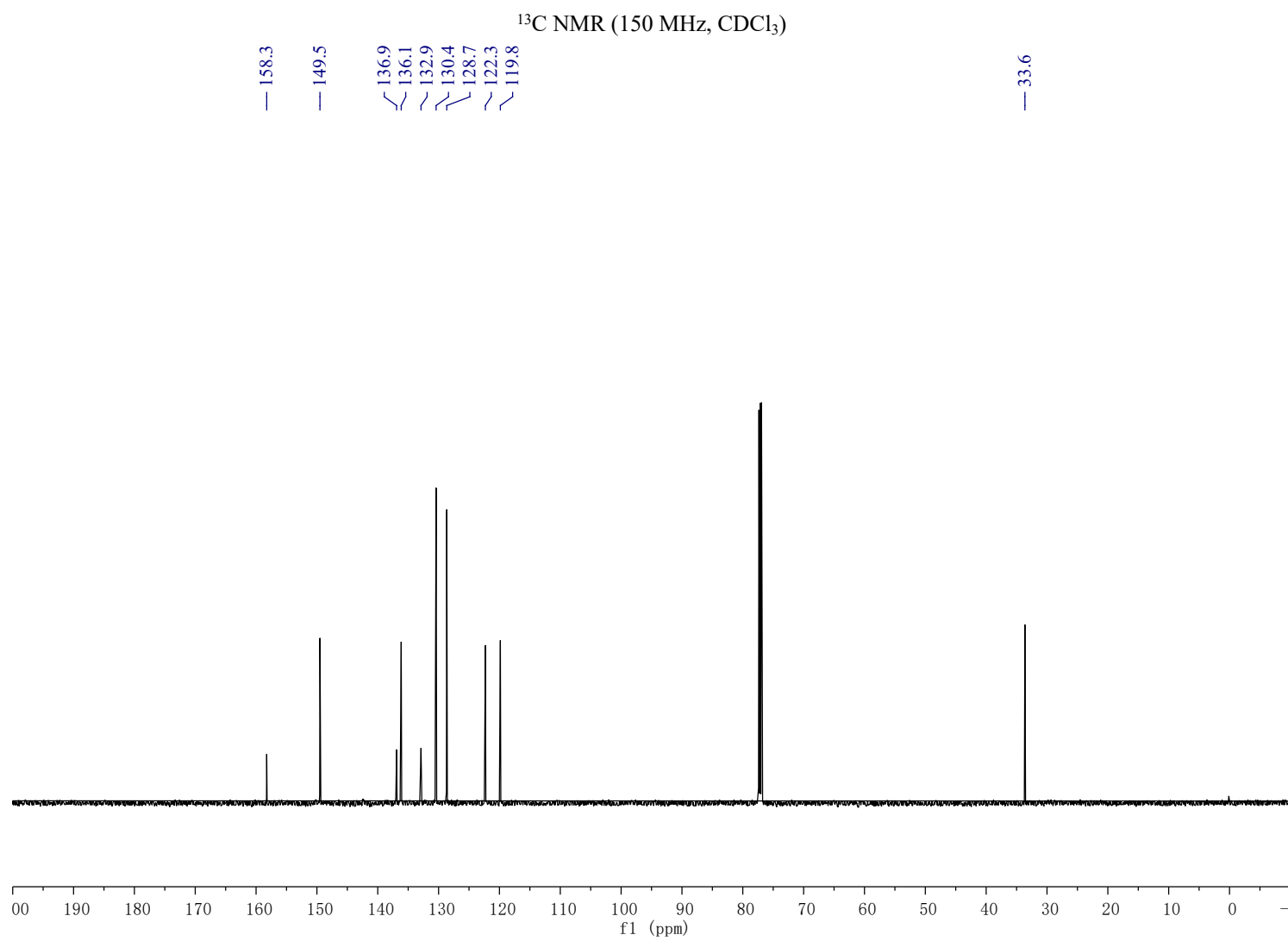


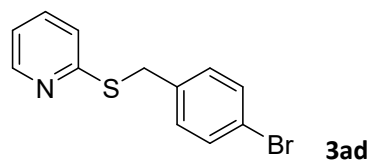




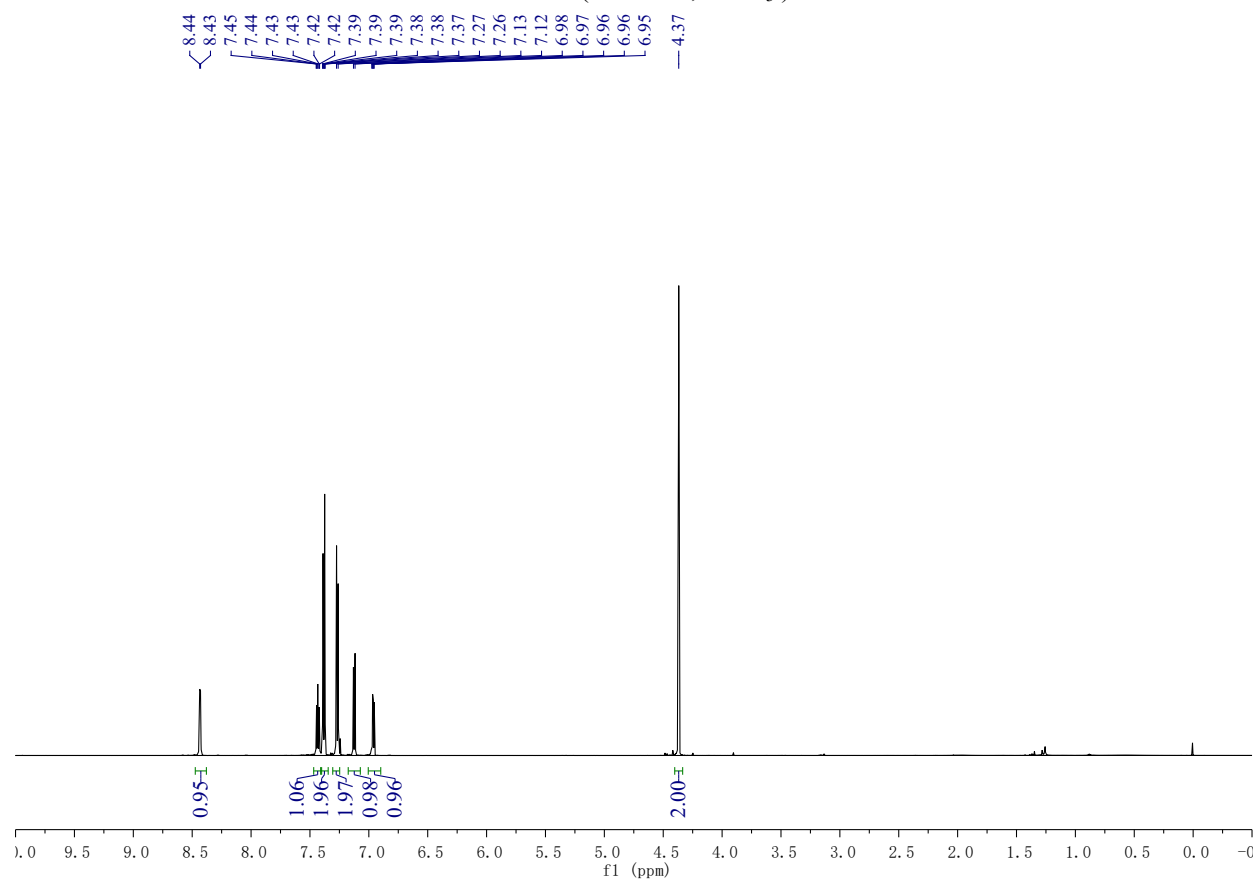
^1H NMR (600 MHz, CDCl_3)

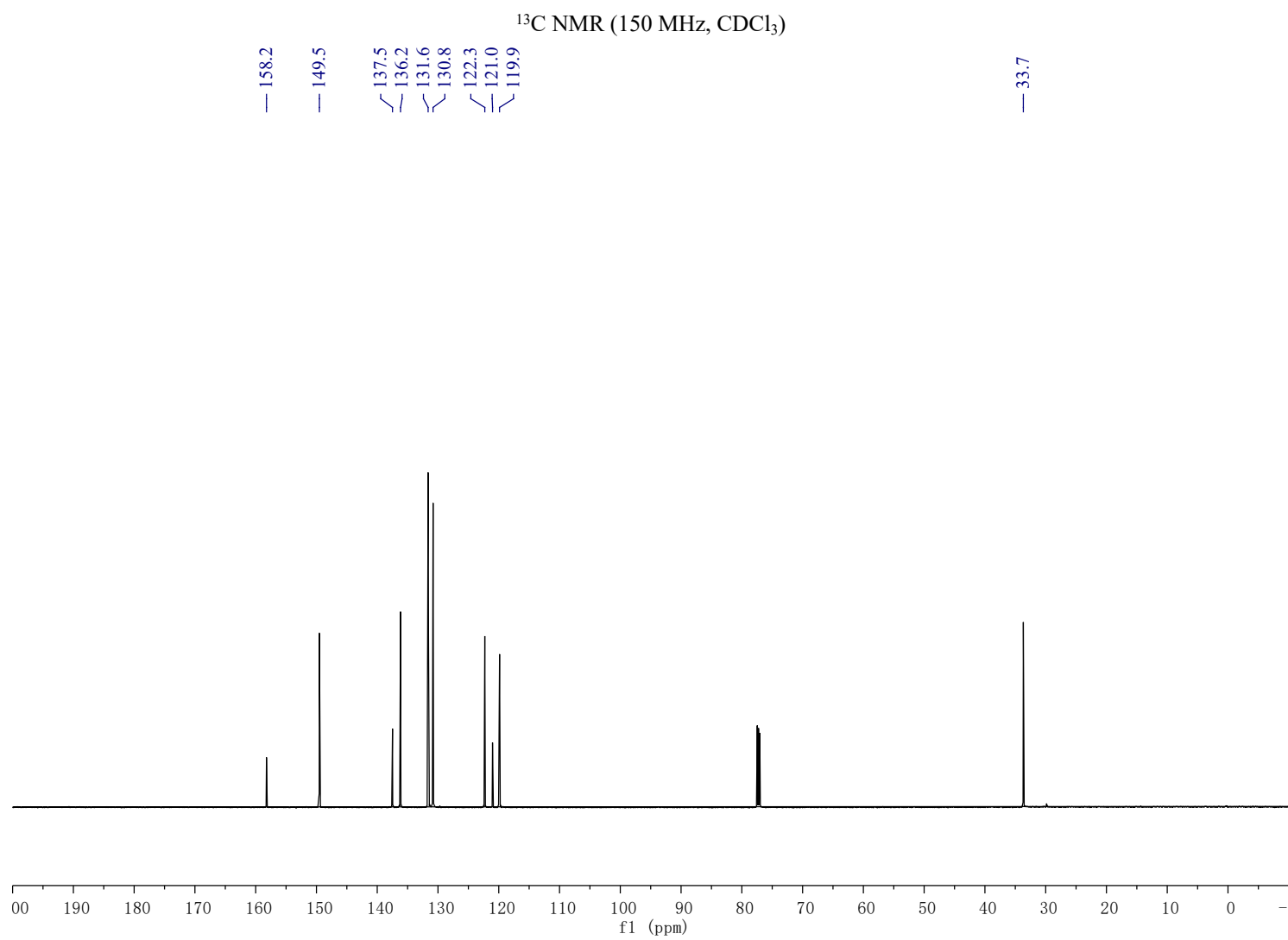


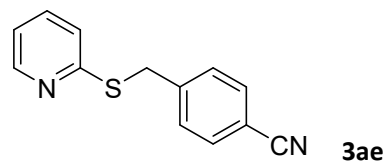




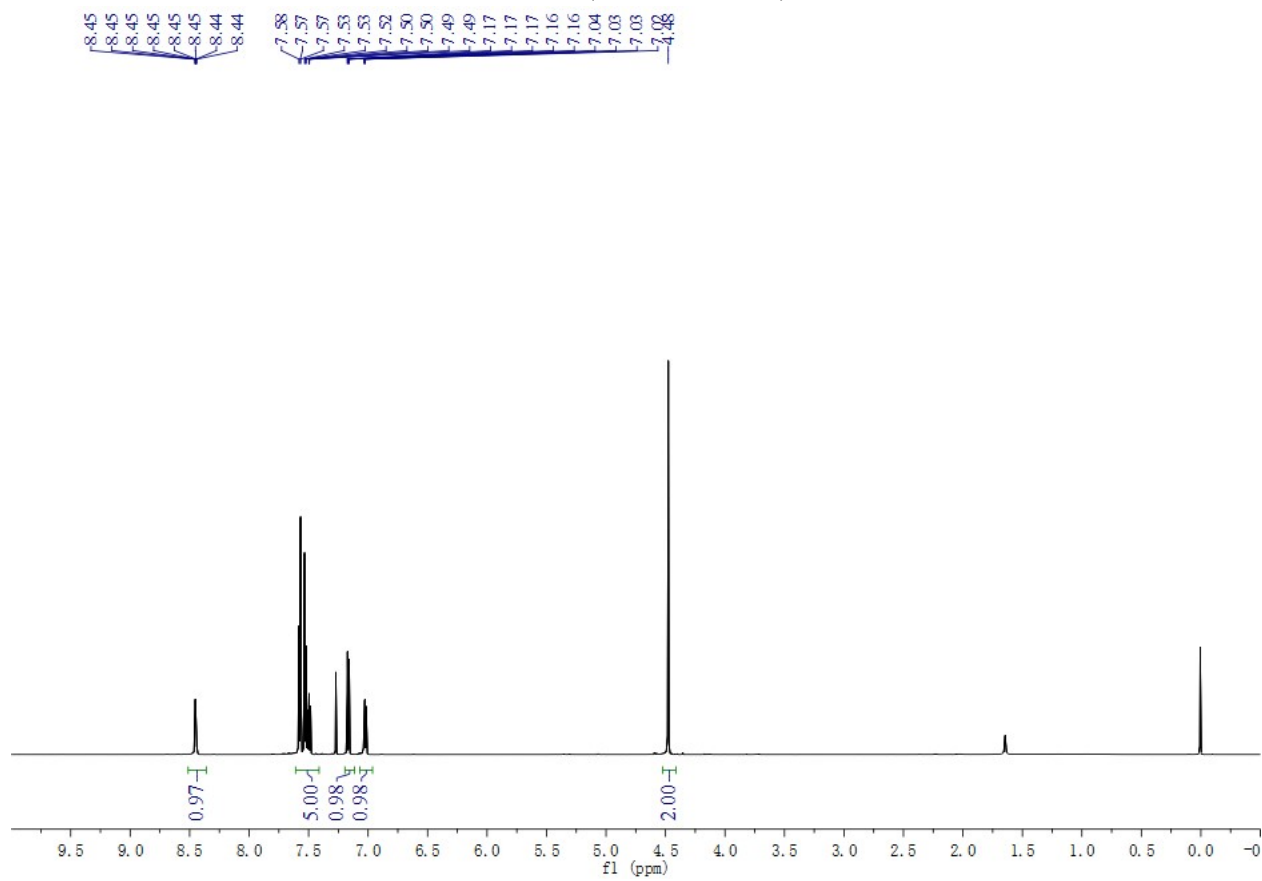
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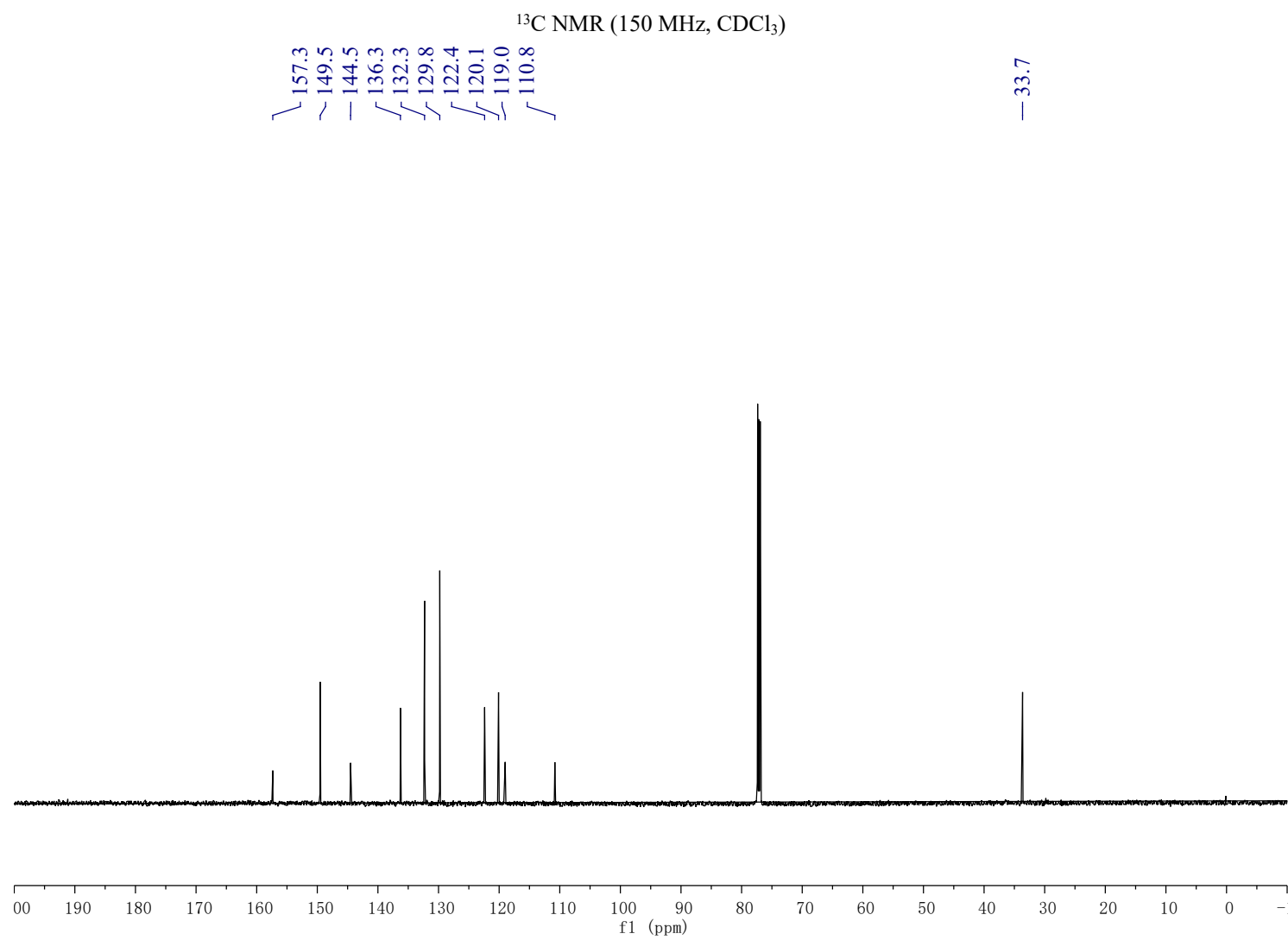


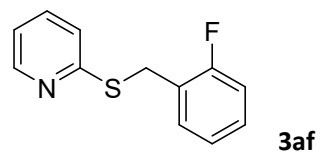




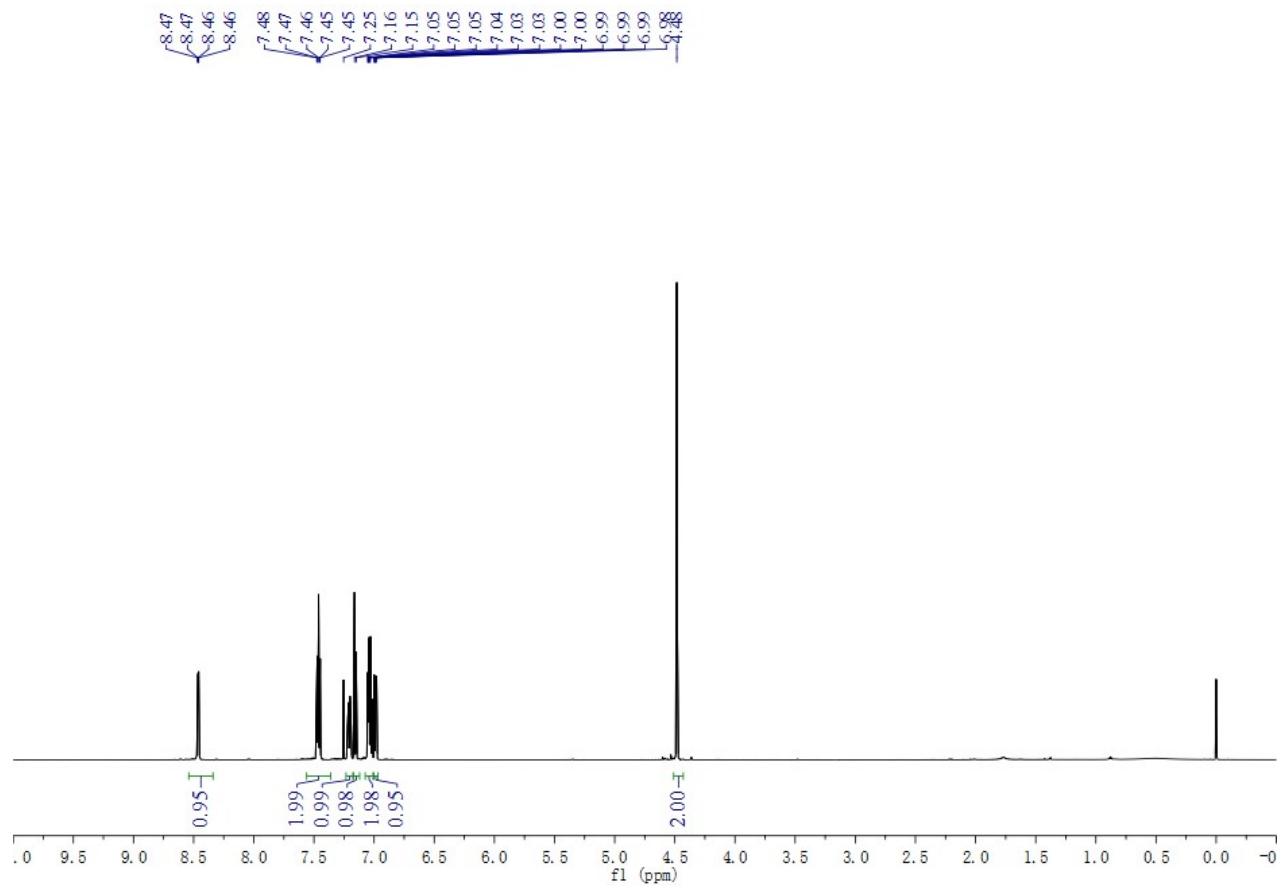
^1H NMR (600 MHz, CDCl_3)



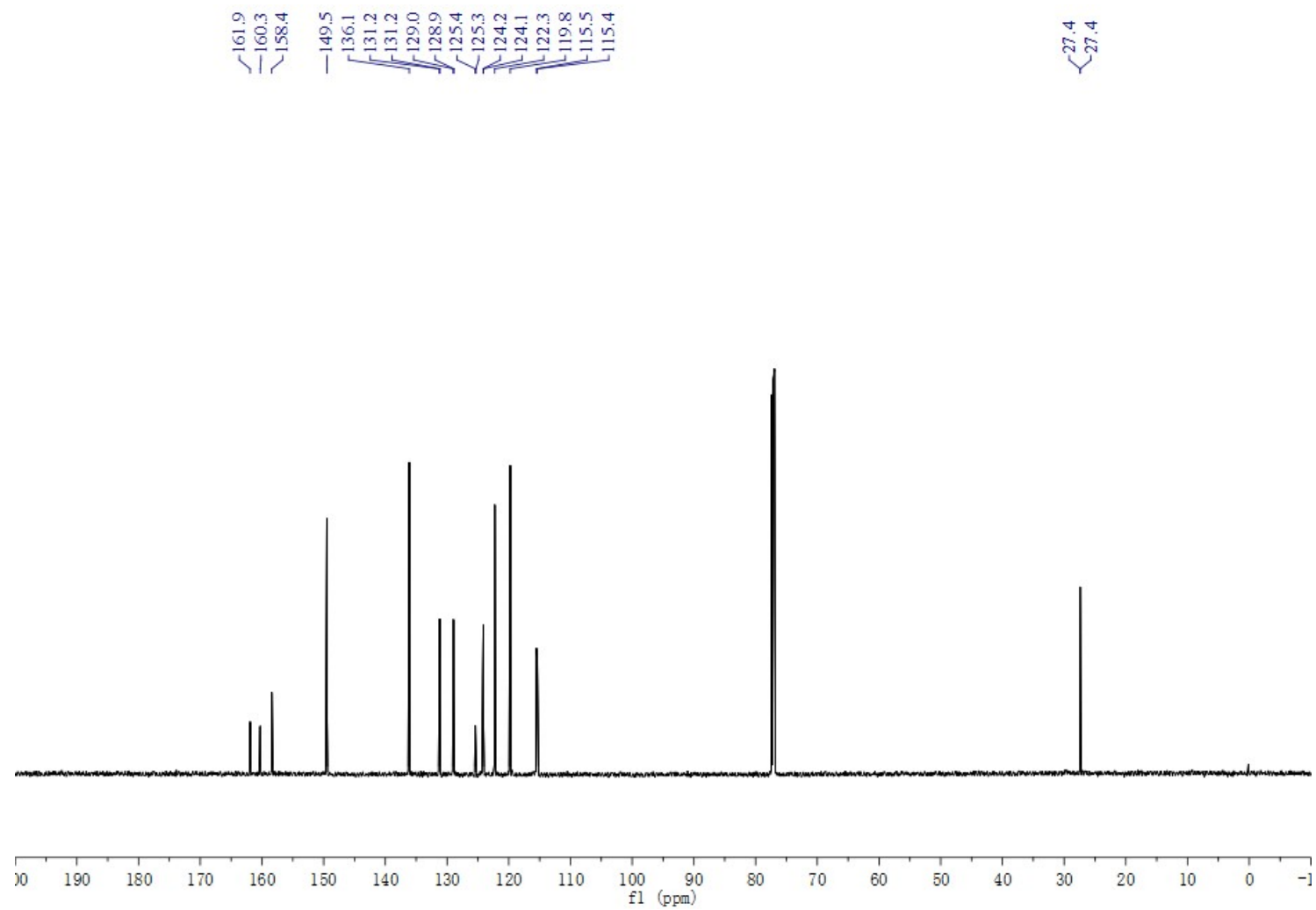


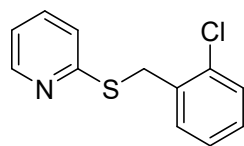


^1H NMR (600 MHz, CDCl_3)



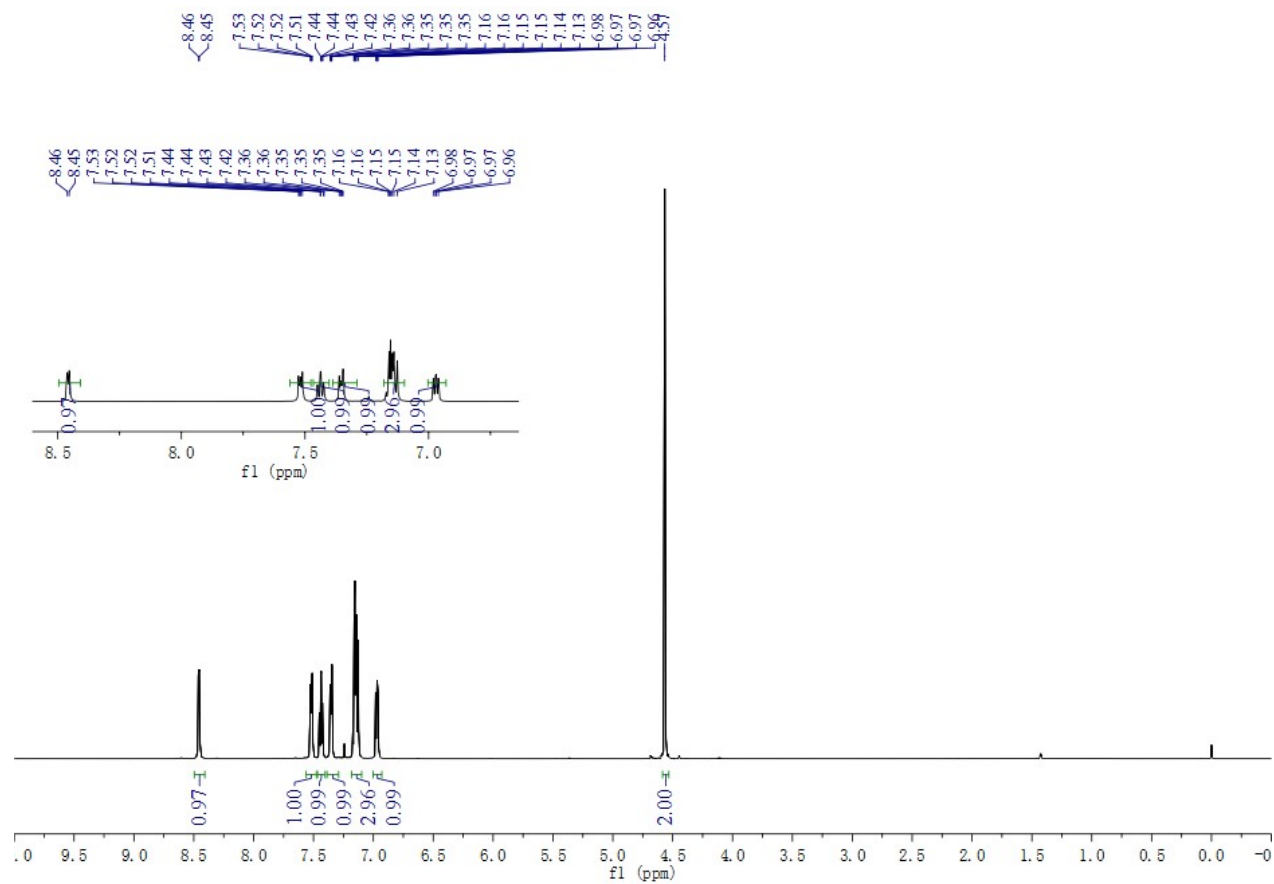
^{13}C NMR (150 MHz, CDCl_3)

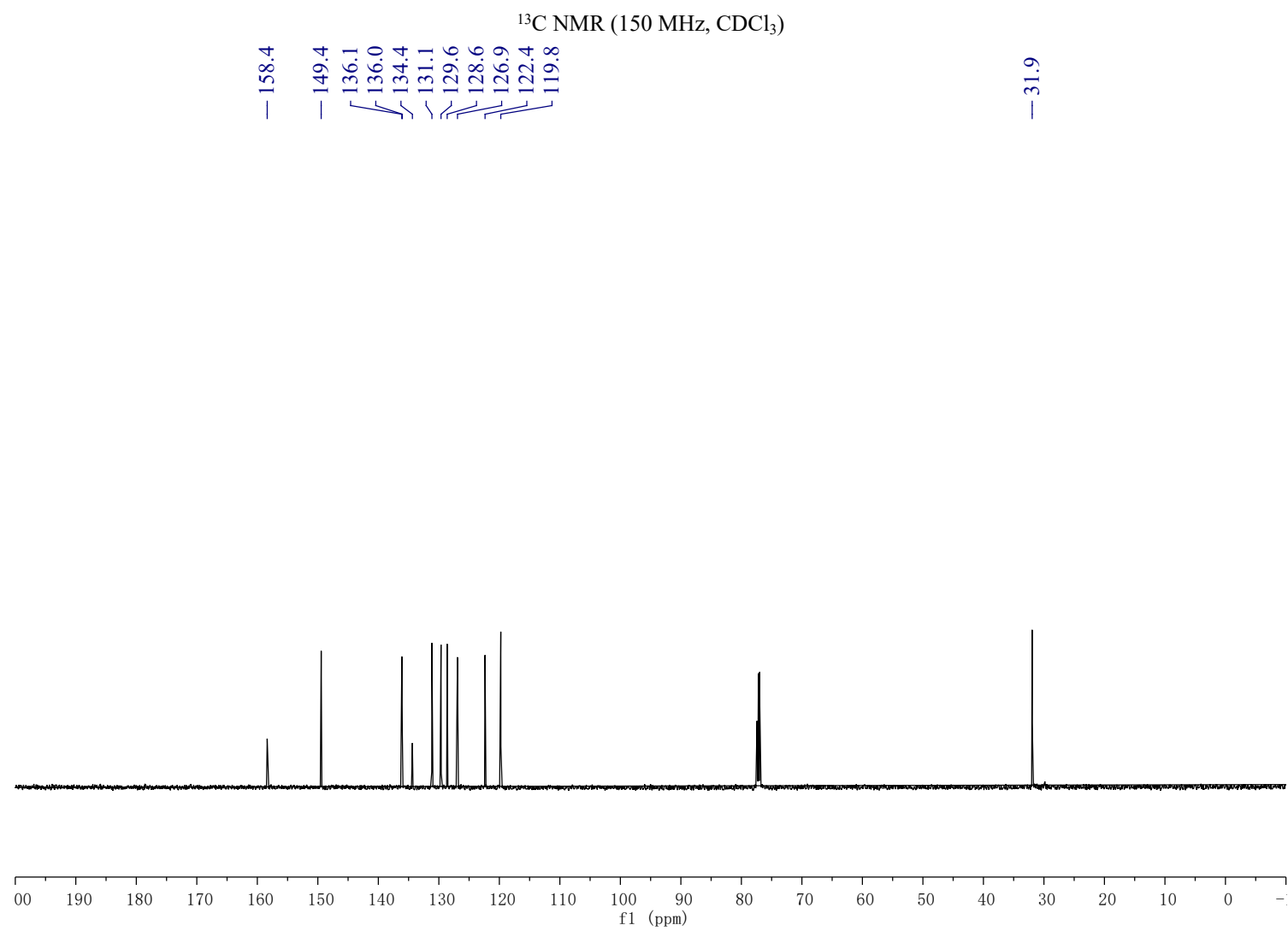


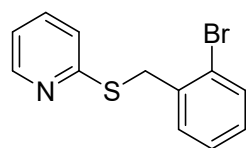


3ag

^1H NMR (600 MHz, CDCl_3)

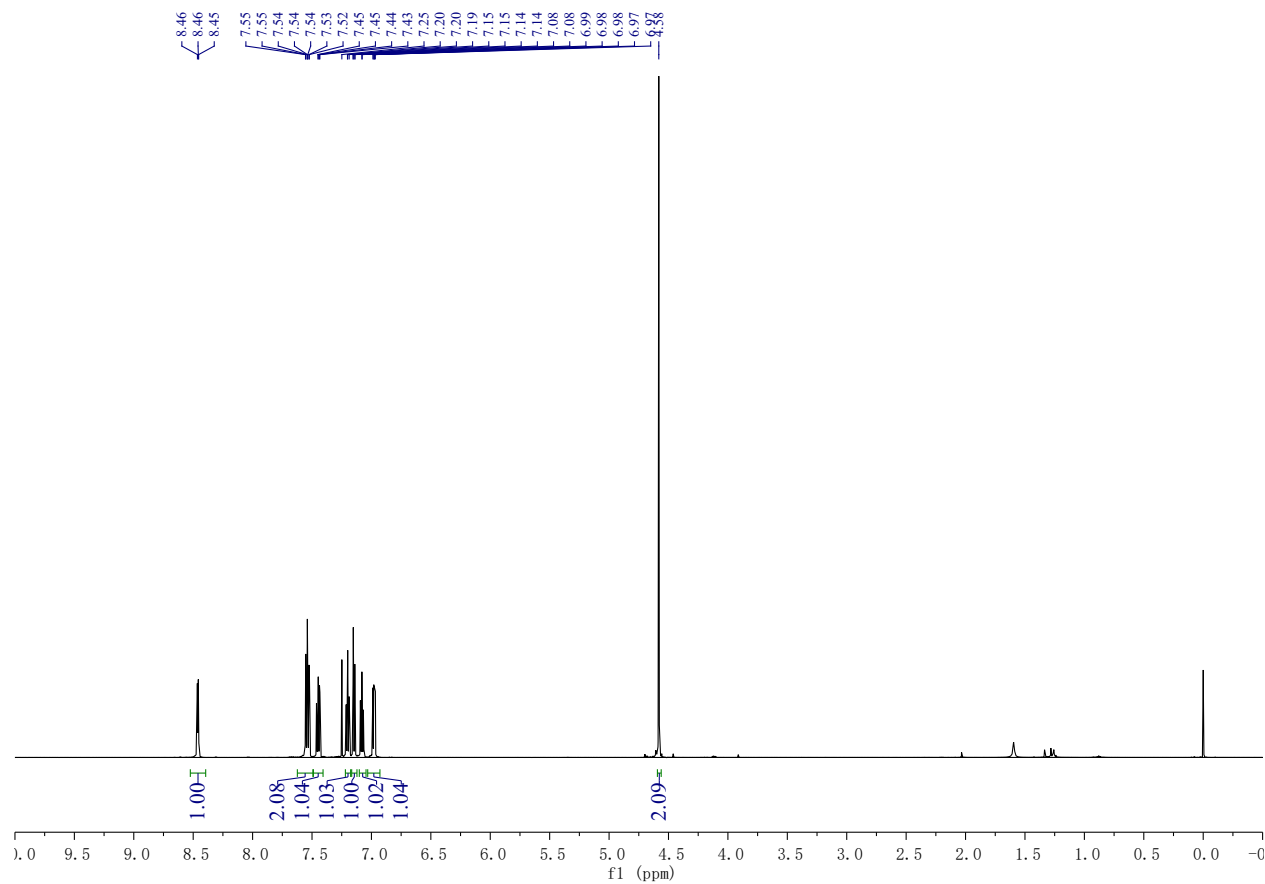


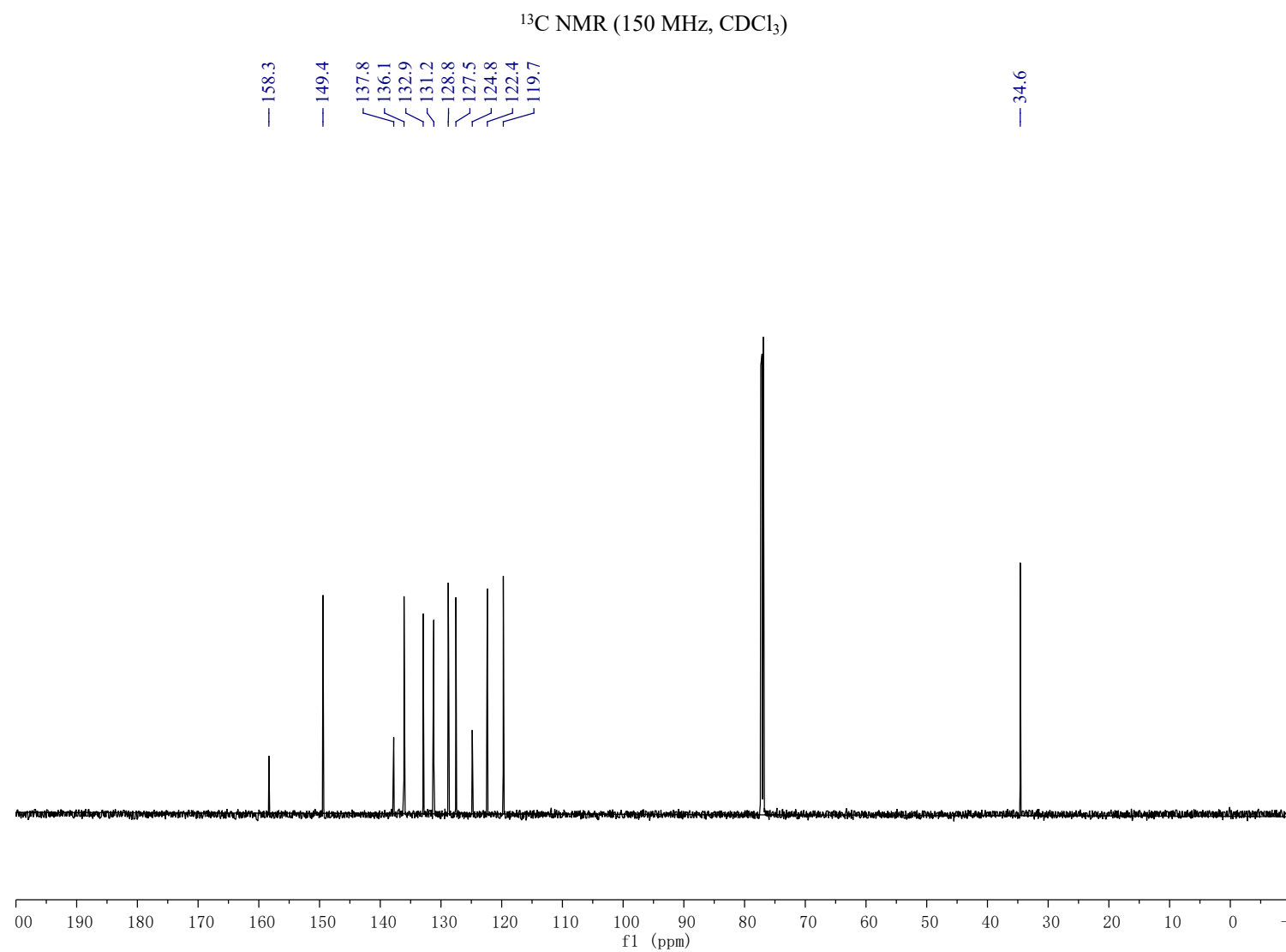




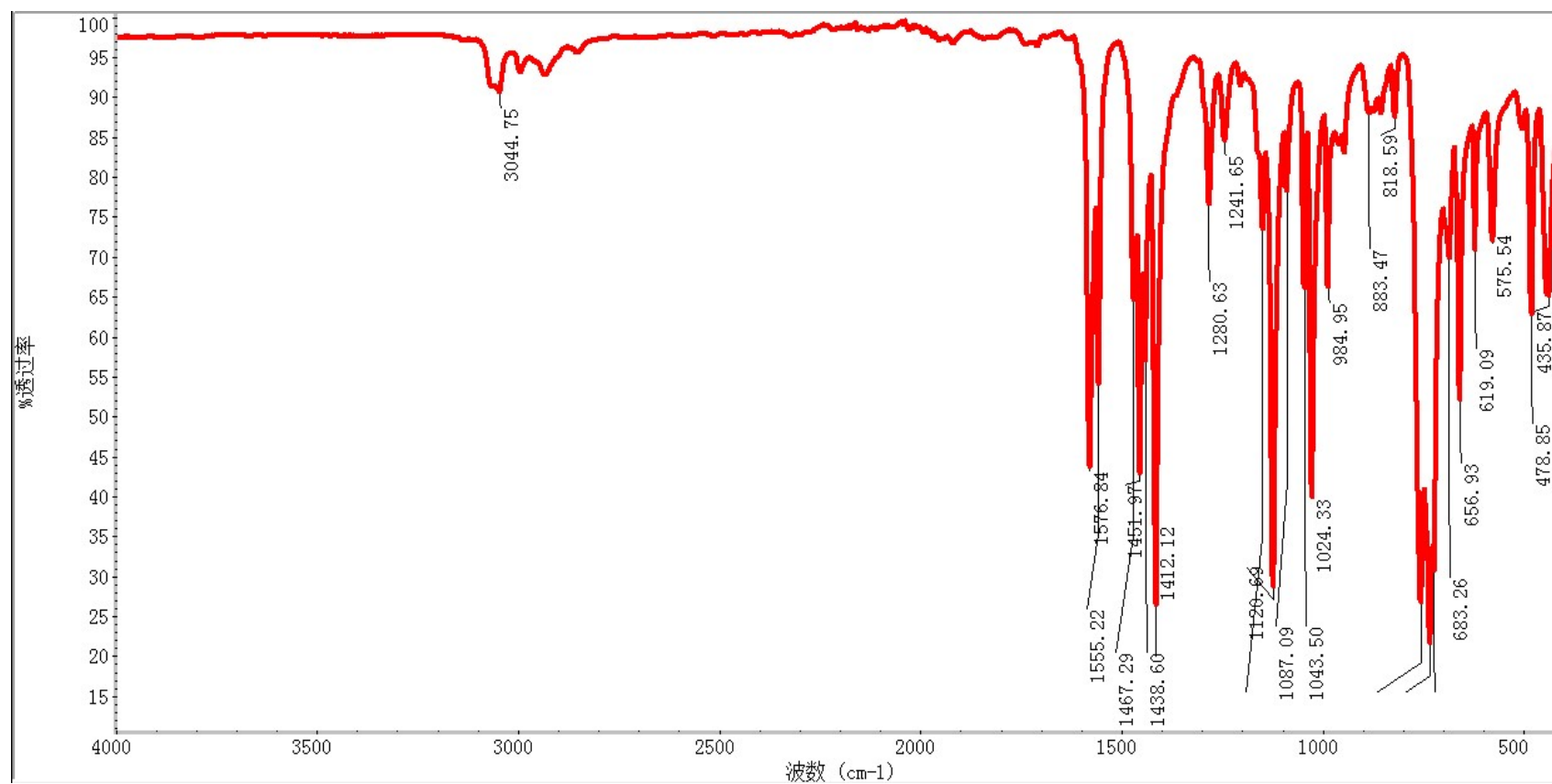
3ah

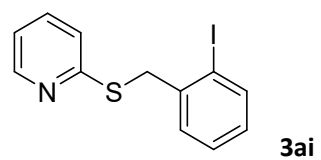
^1H NMR (600 MHz, CDCl_3)



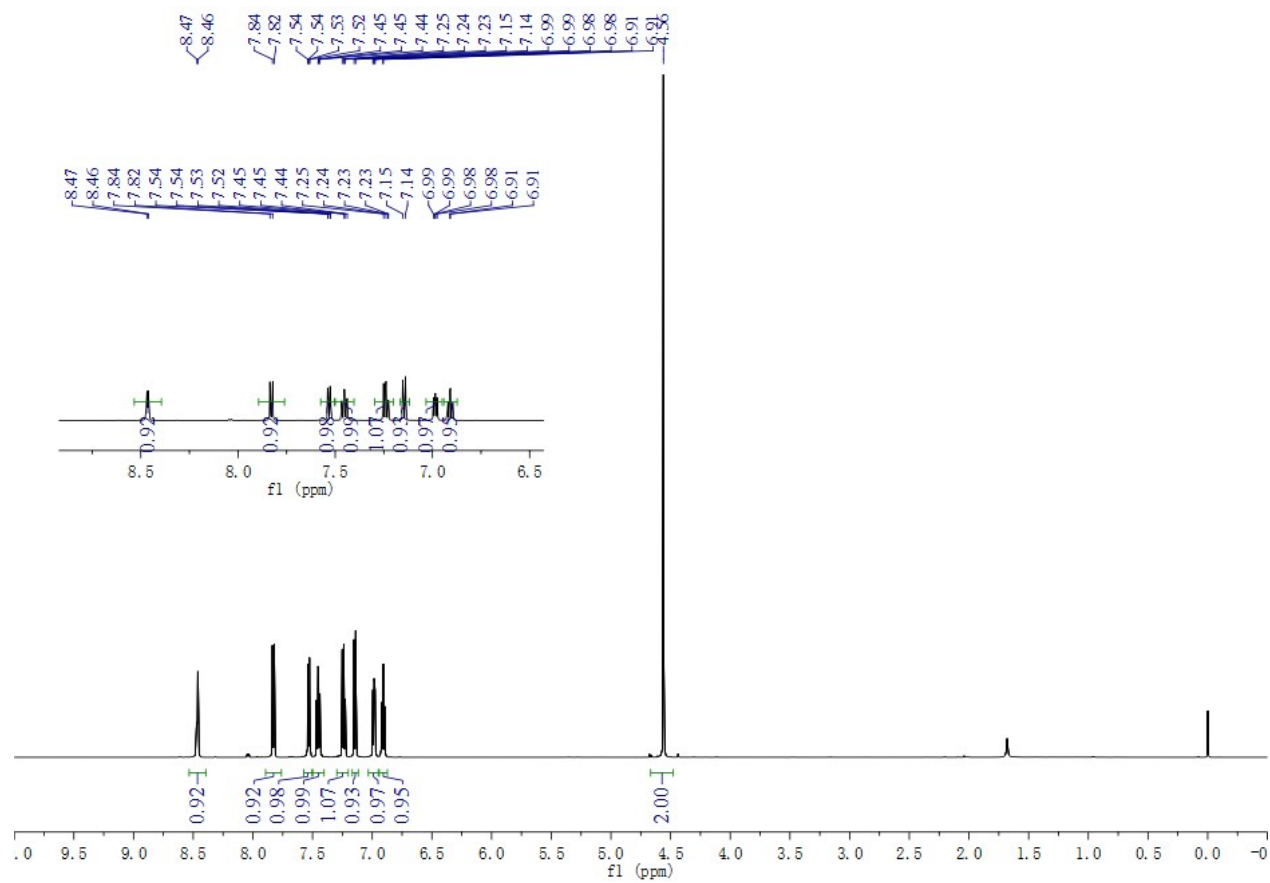


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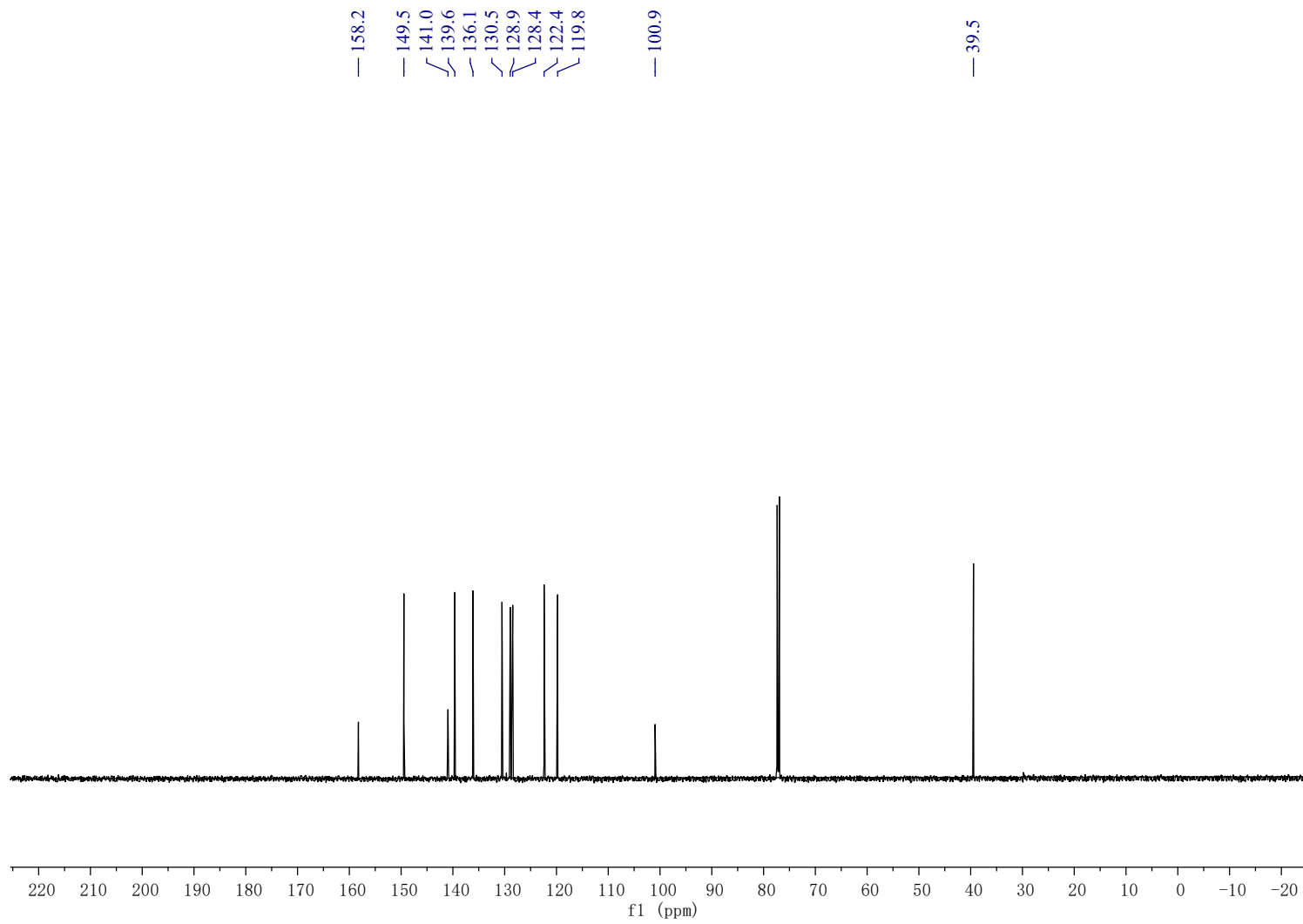


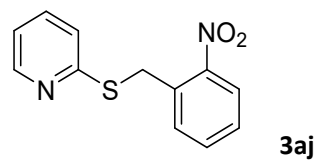


^1H NMR (600 MHz, CDCl_3)

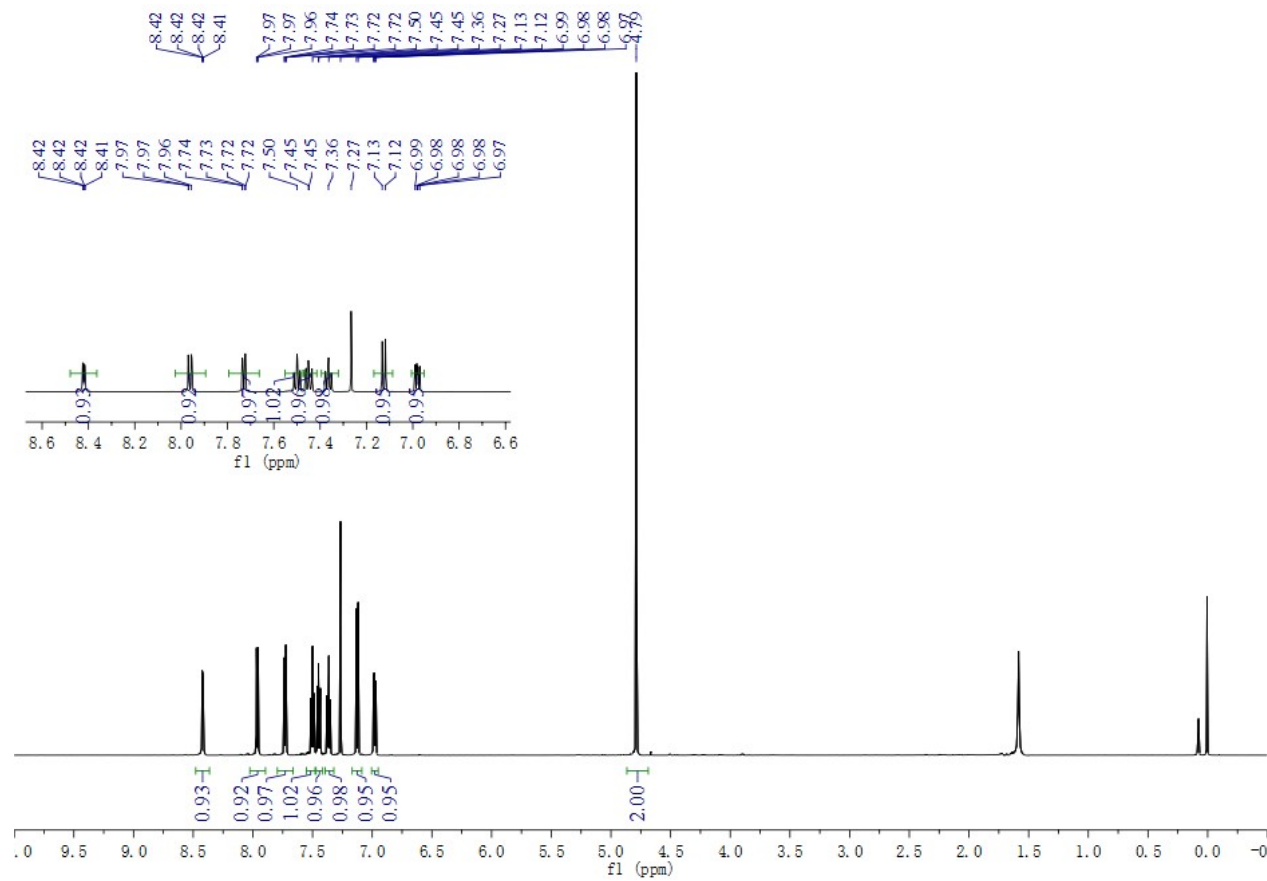


^{13}C NMR (150 MHz, CDCl_3)

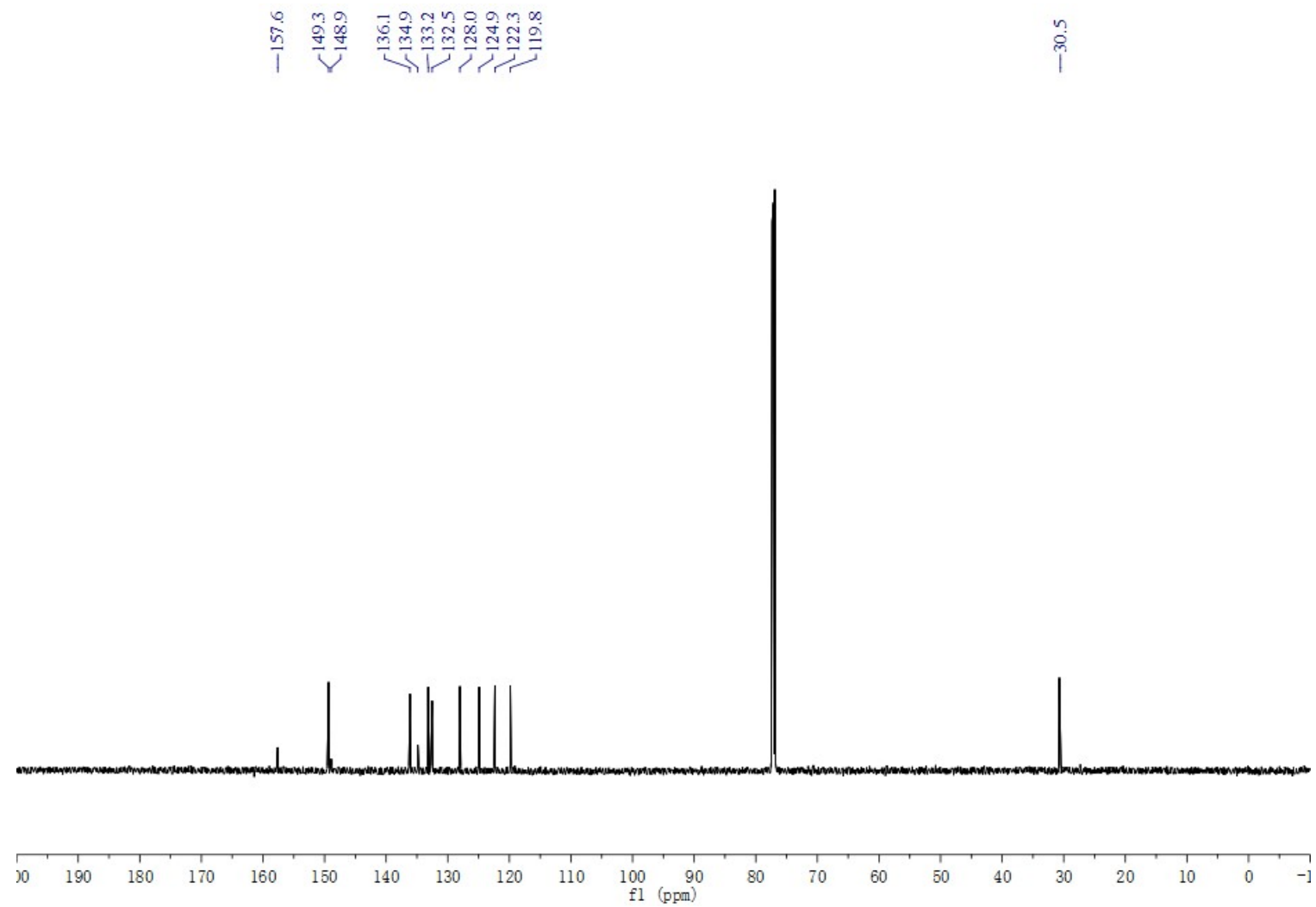




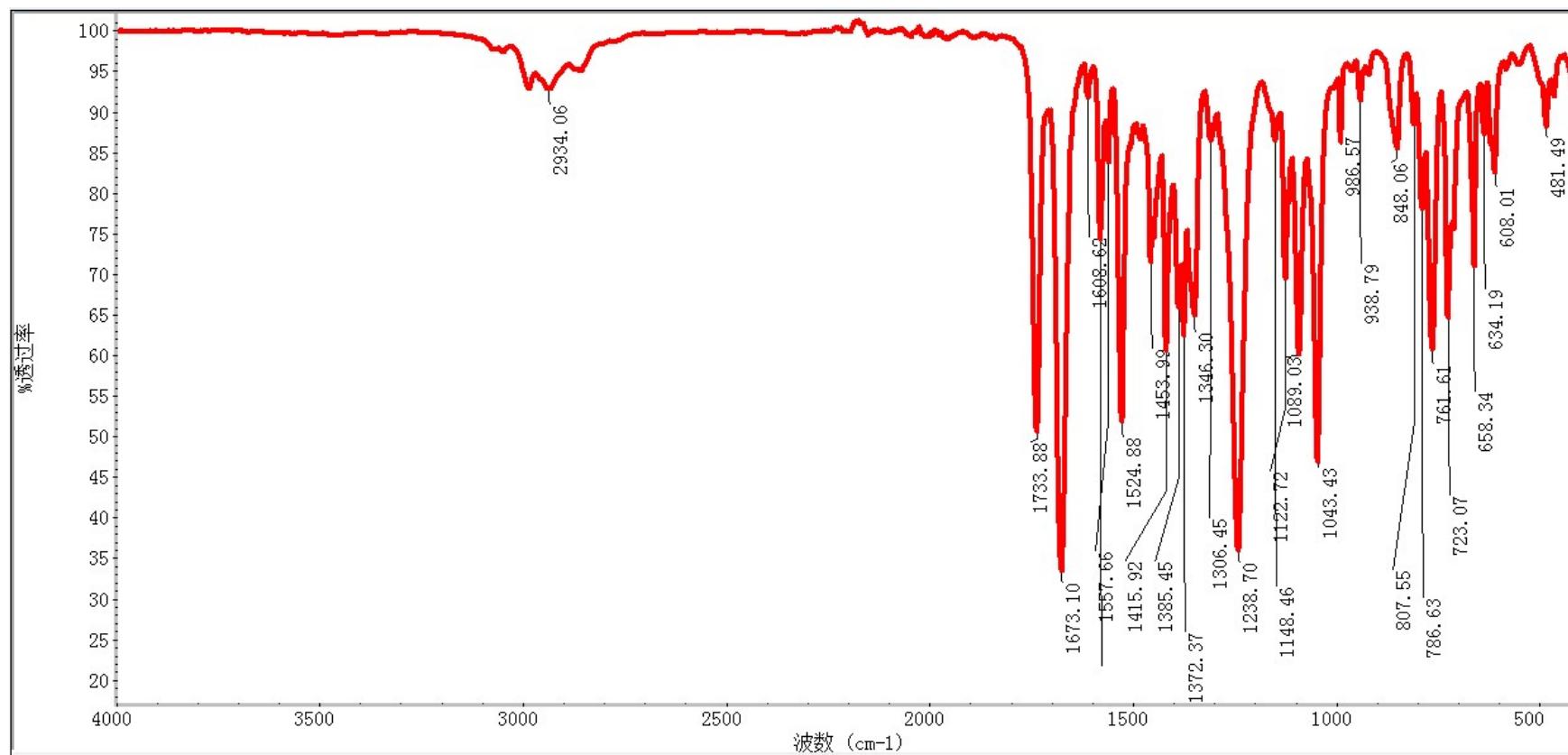
^1H NMR (600 MHz, CDCl_3)

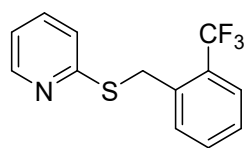


^{13}C NMR (150 MHz, CDCl_3)



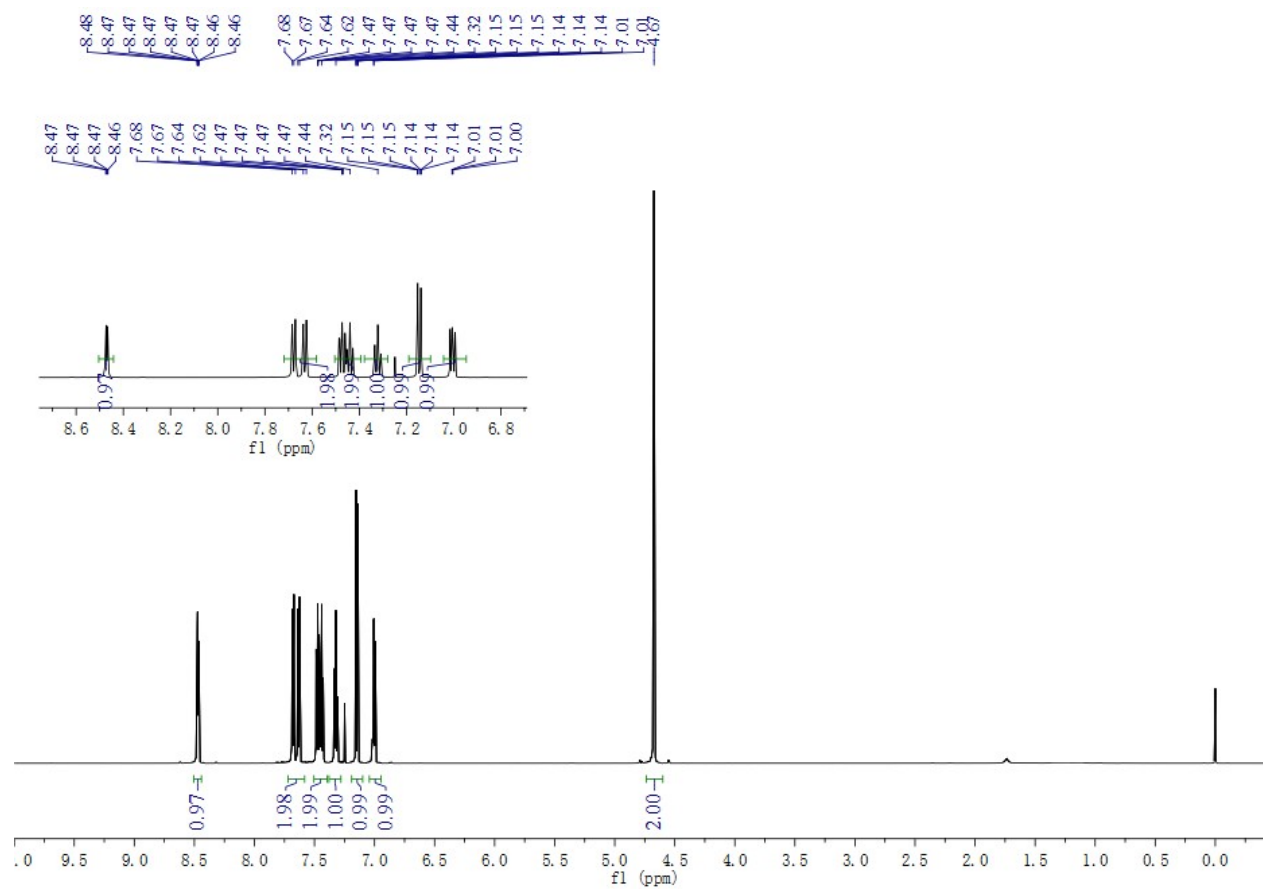
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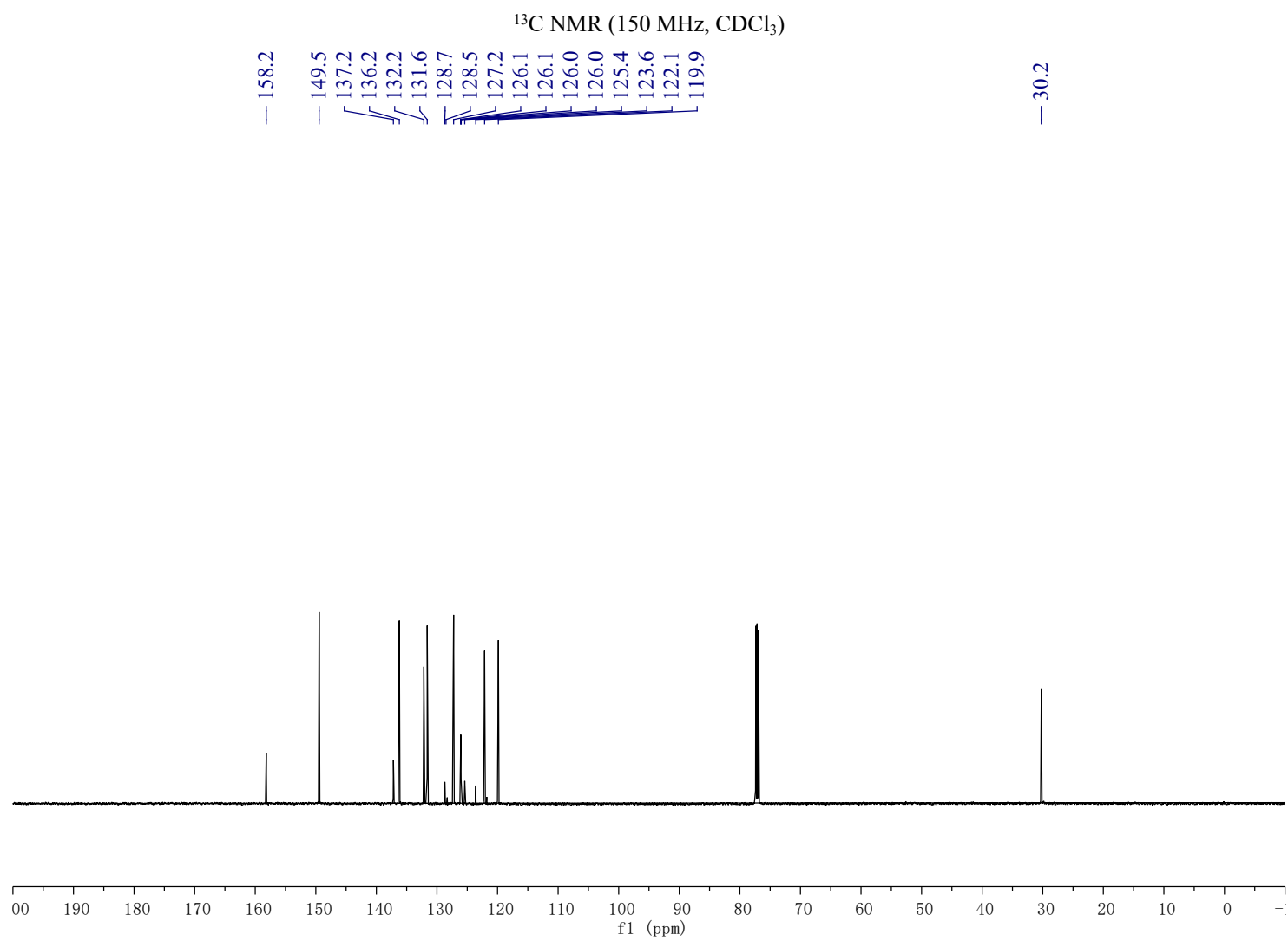


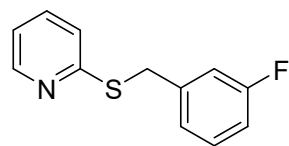


3ak

^1H NMR (600 MHz, CDCl_3)

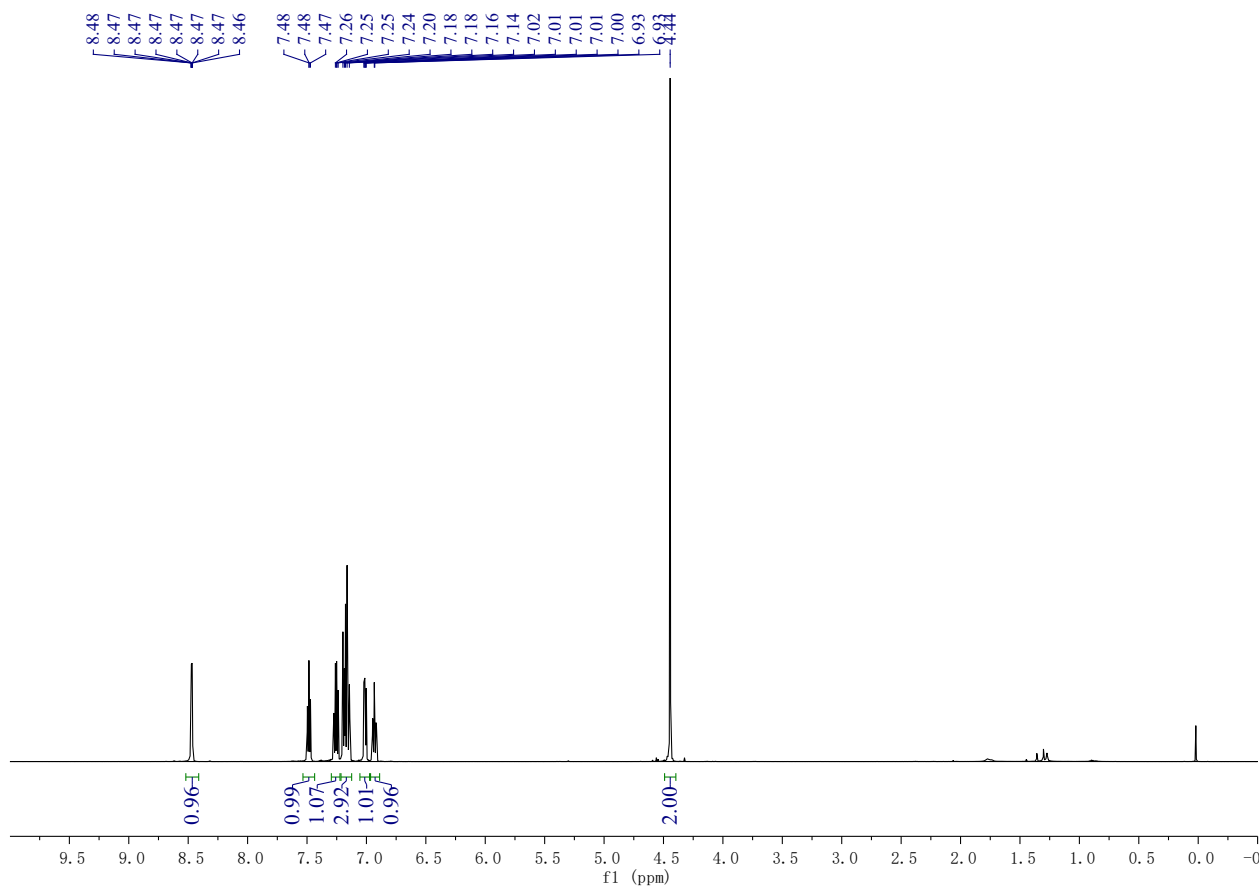


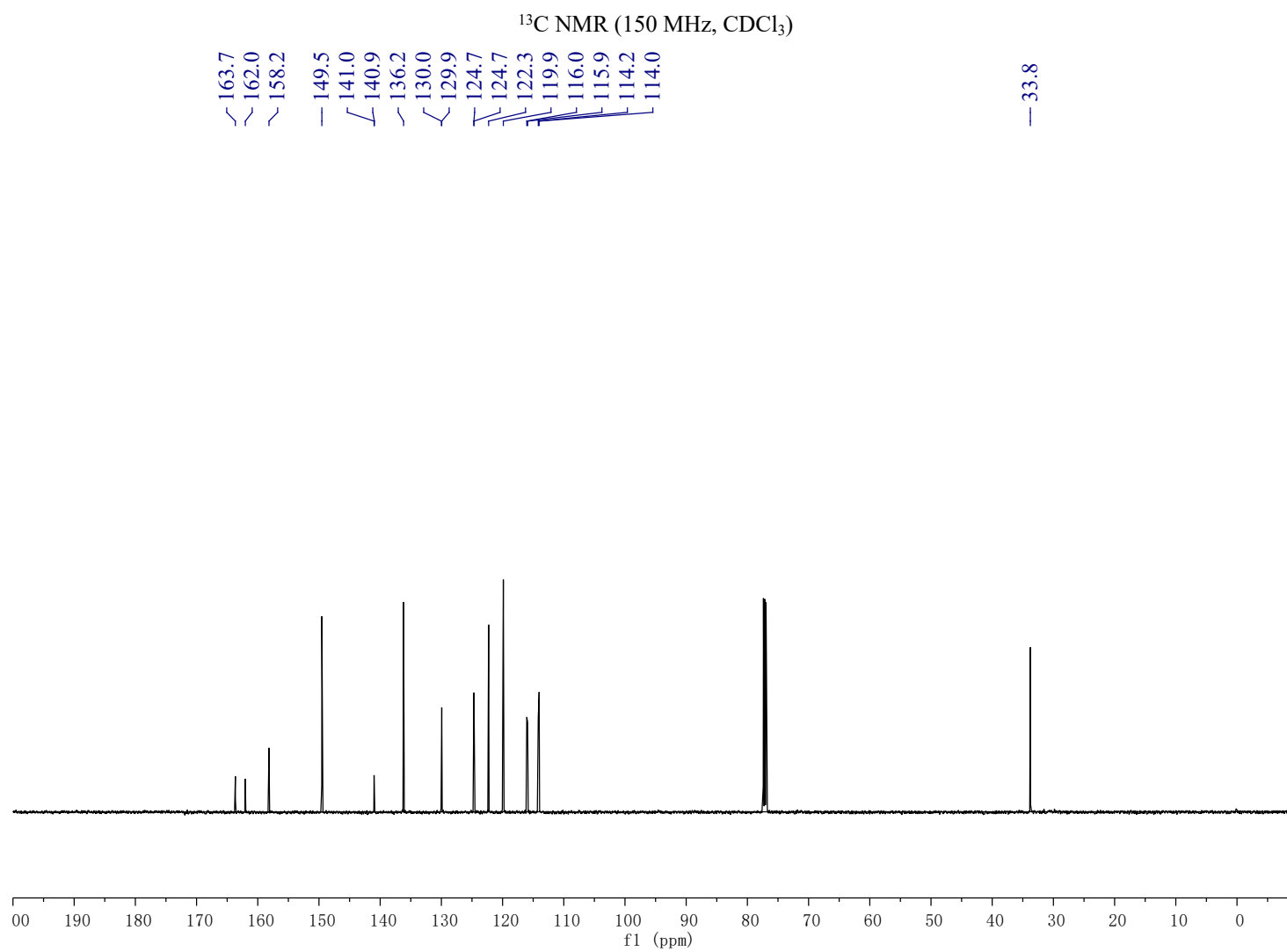


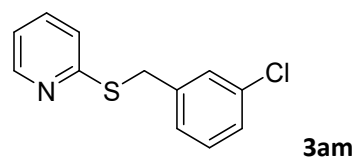


3al

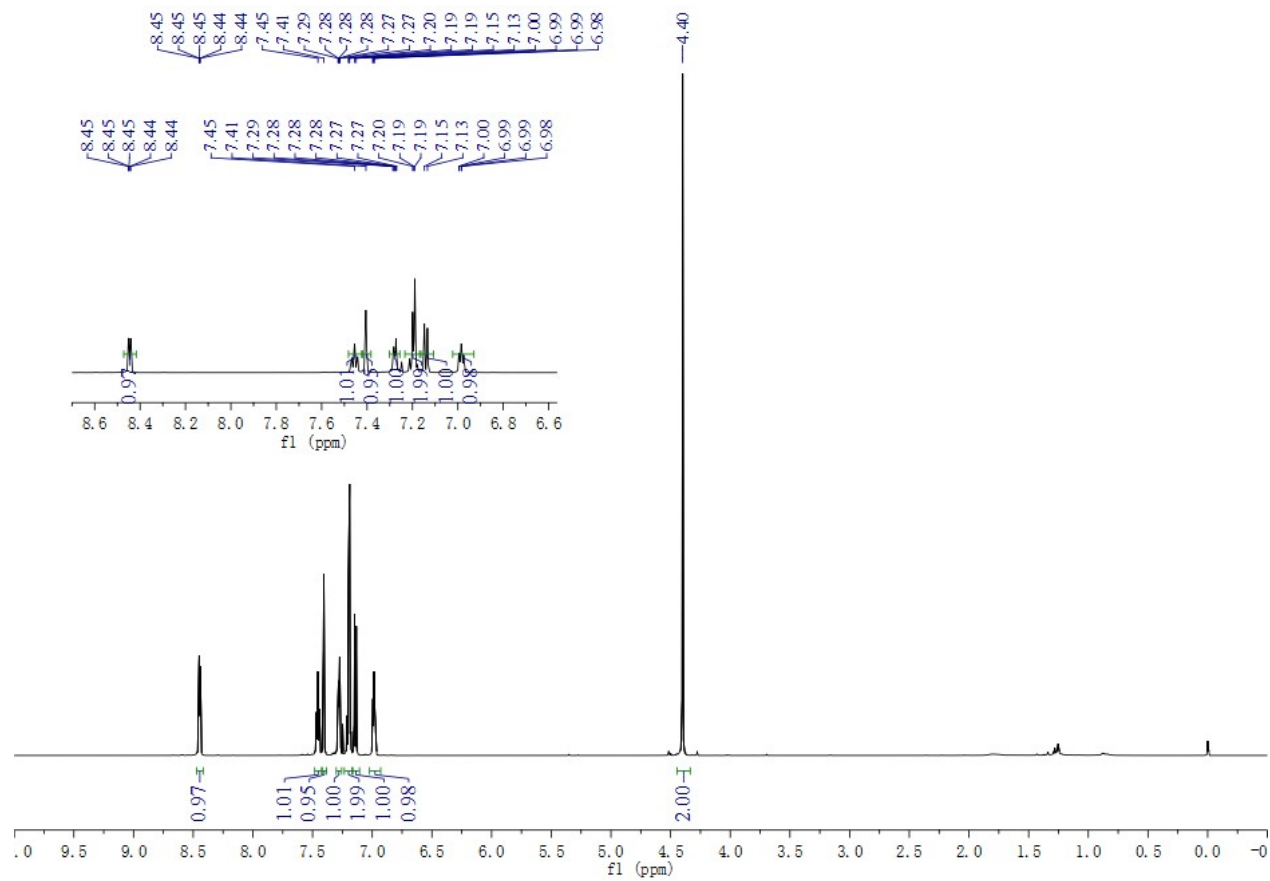
^1H NMR (600 MHz, CDCl_3)



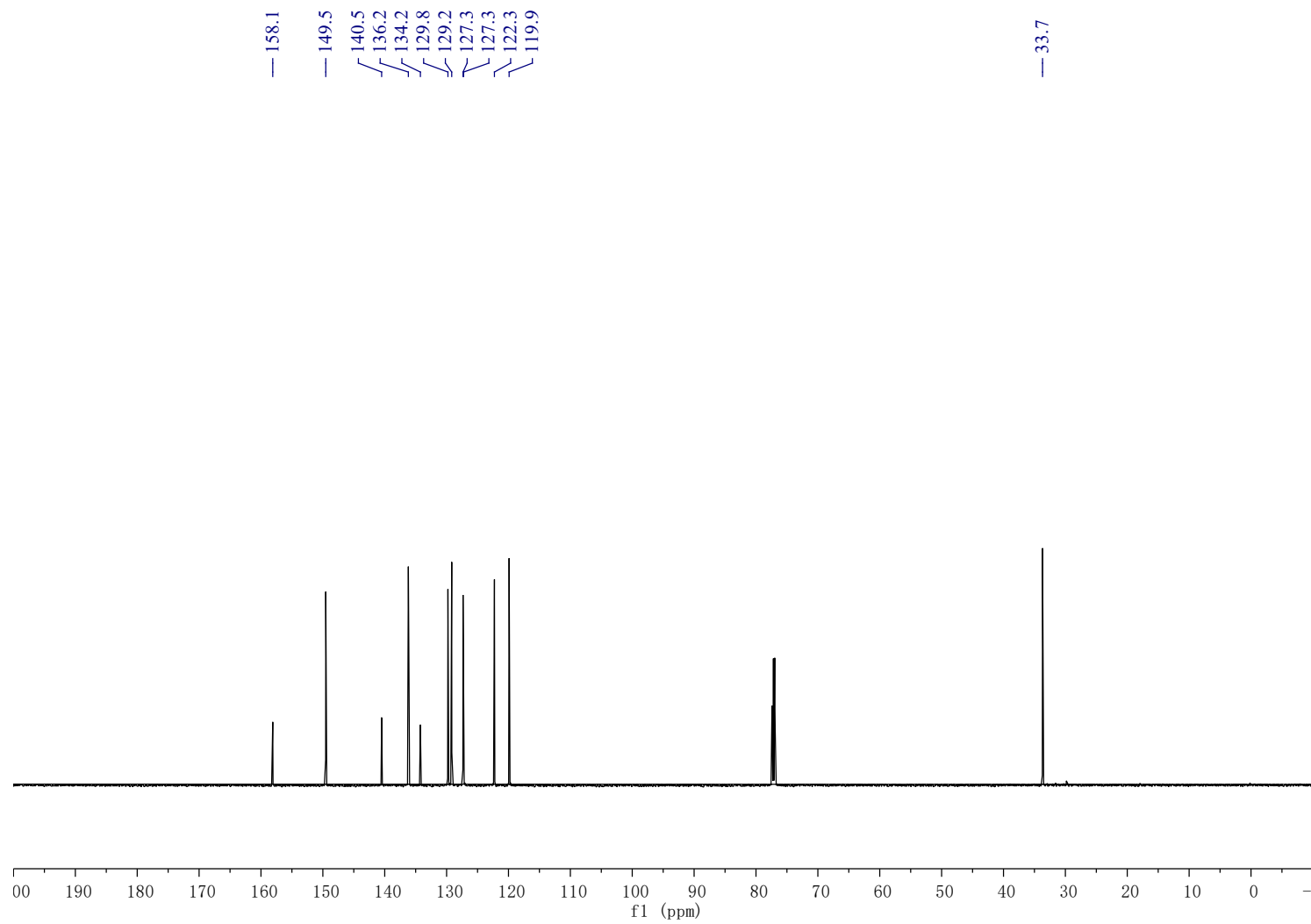


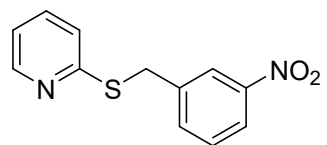


^1H NMR (600 MHz, CDCl_3)



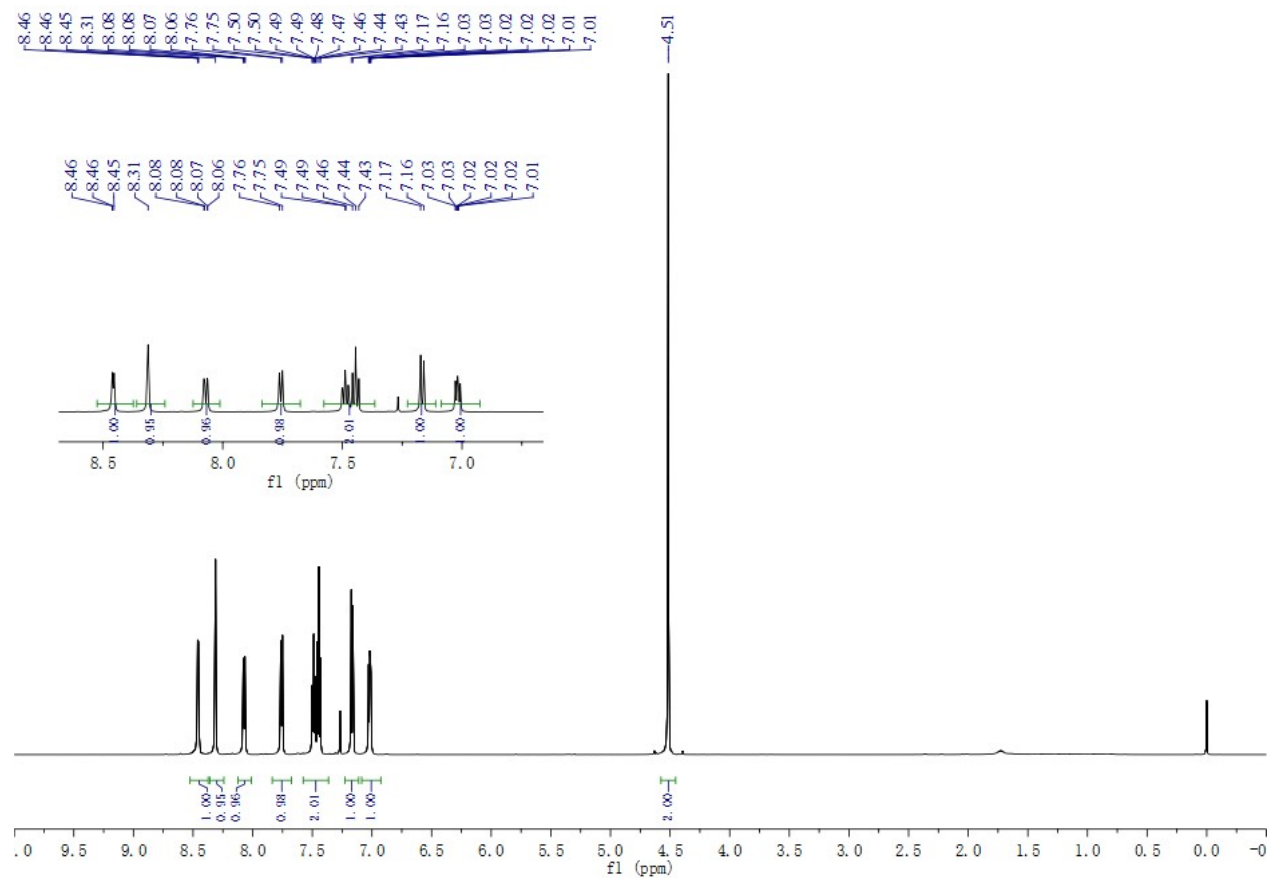
^{13}C NMR (150 MHz, CDCl_3)

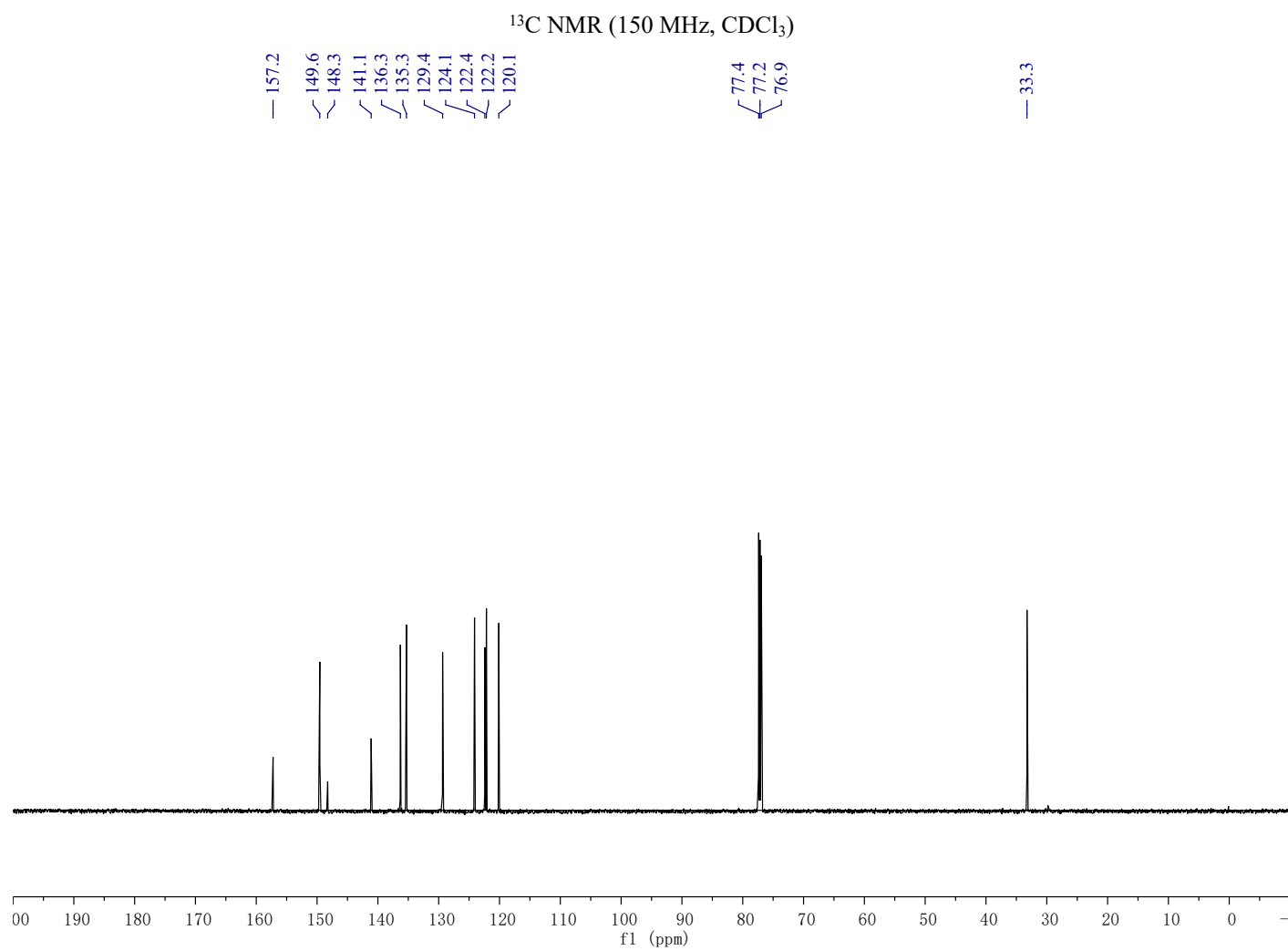


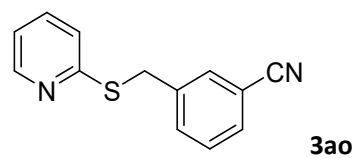


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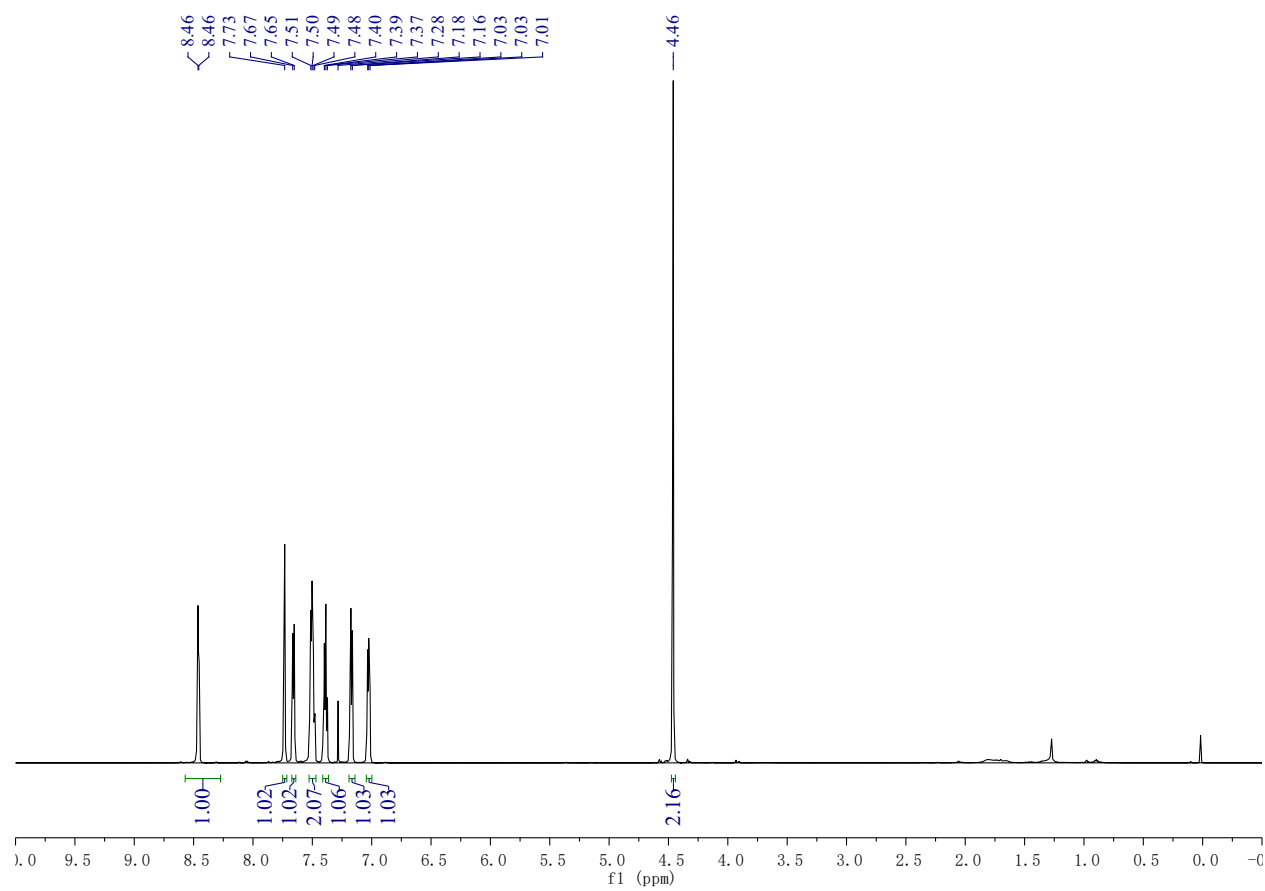
^1H NMR (600 MHz, CDCl_3)

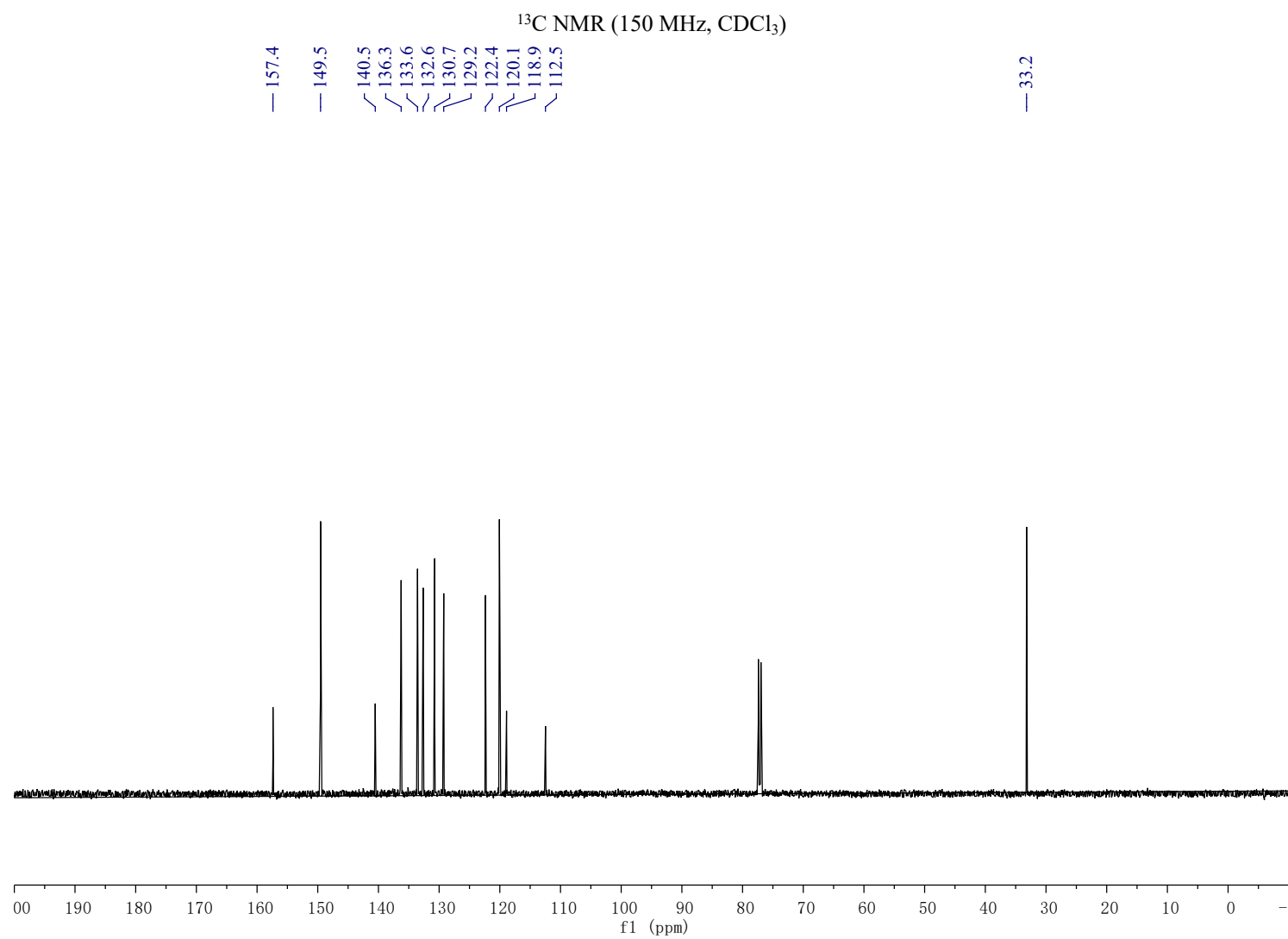


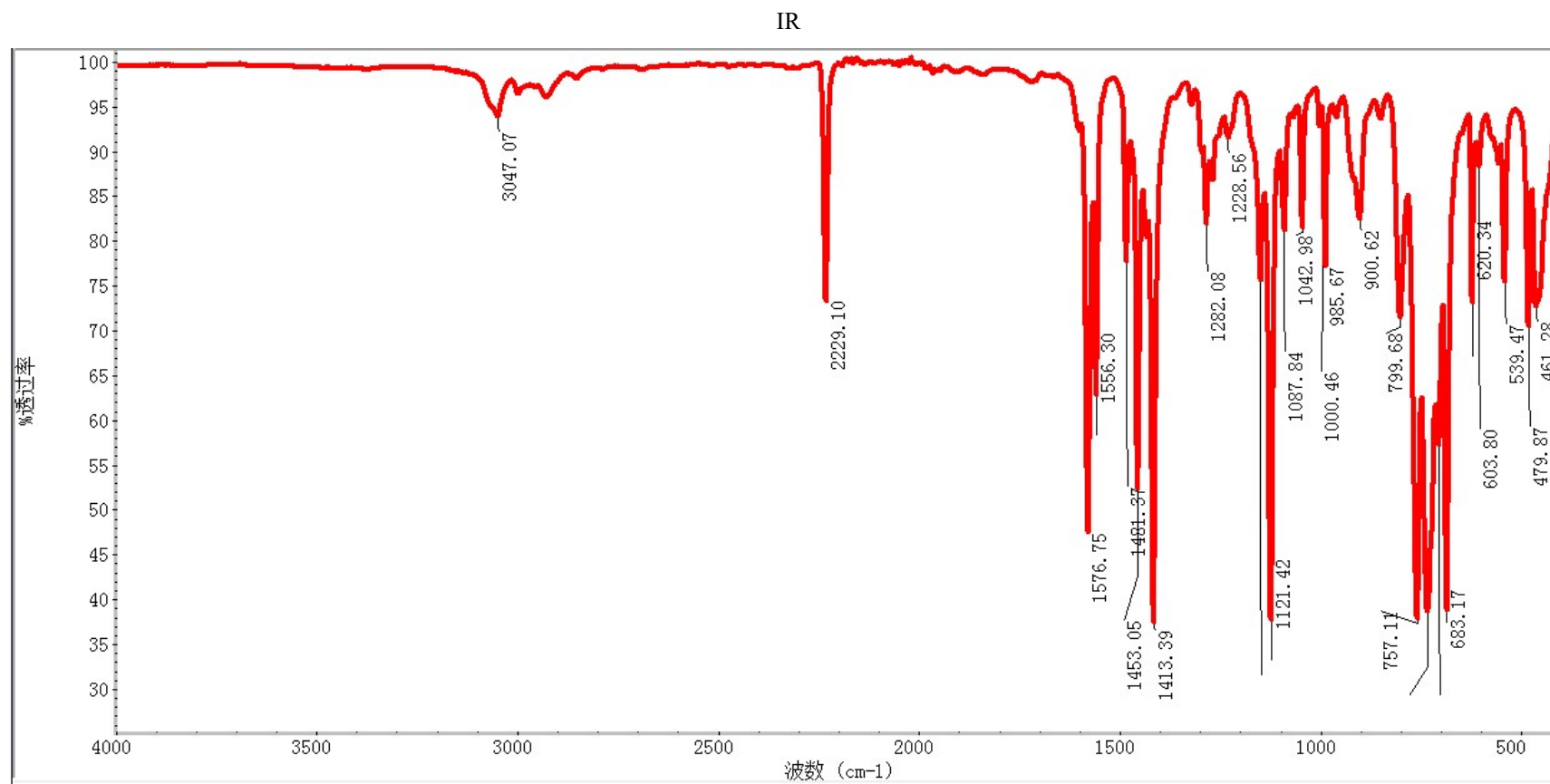


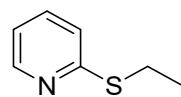


^1H NMR (600 MHz, CDCl_3)



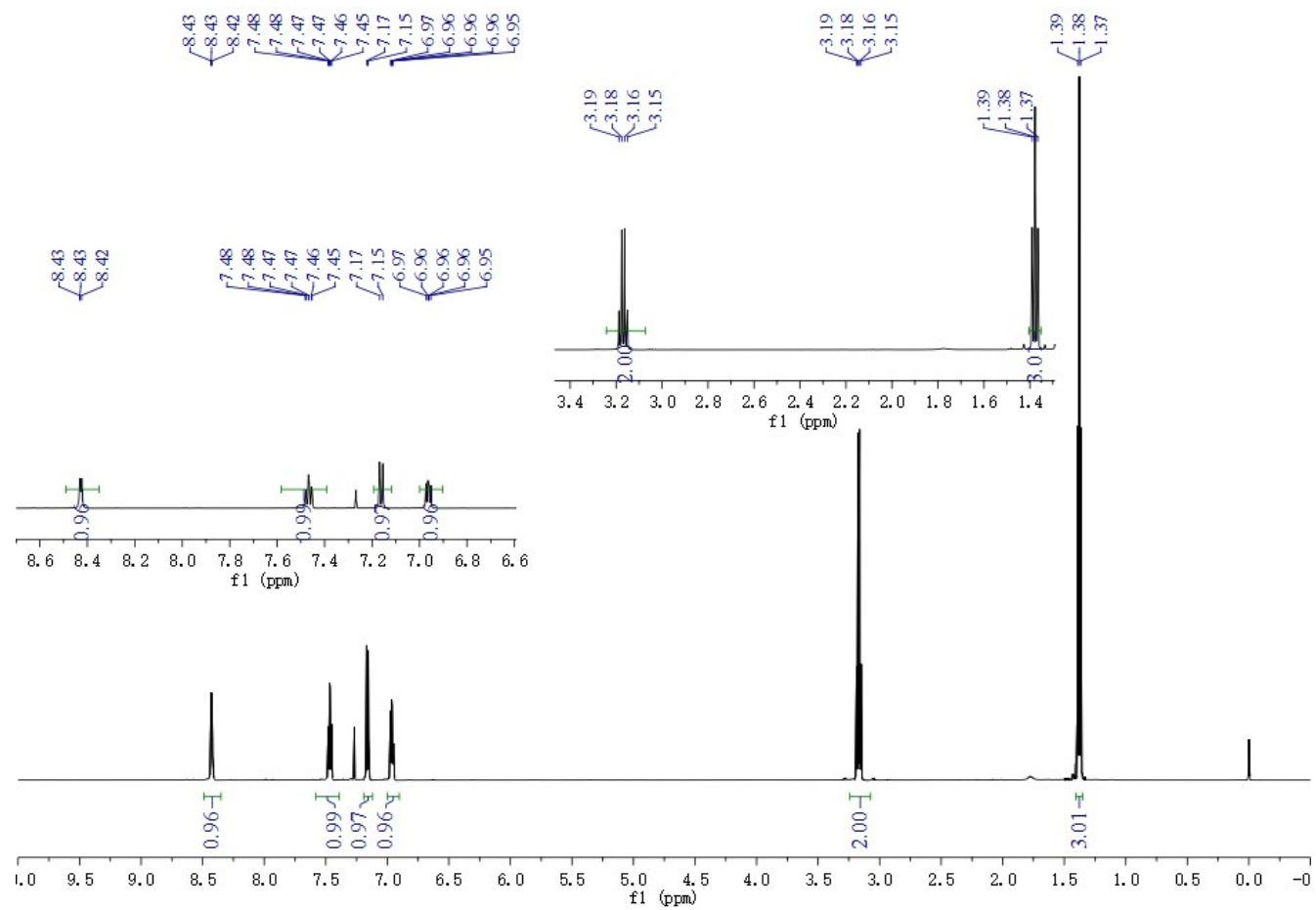


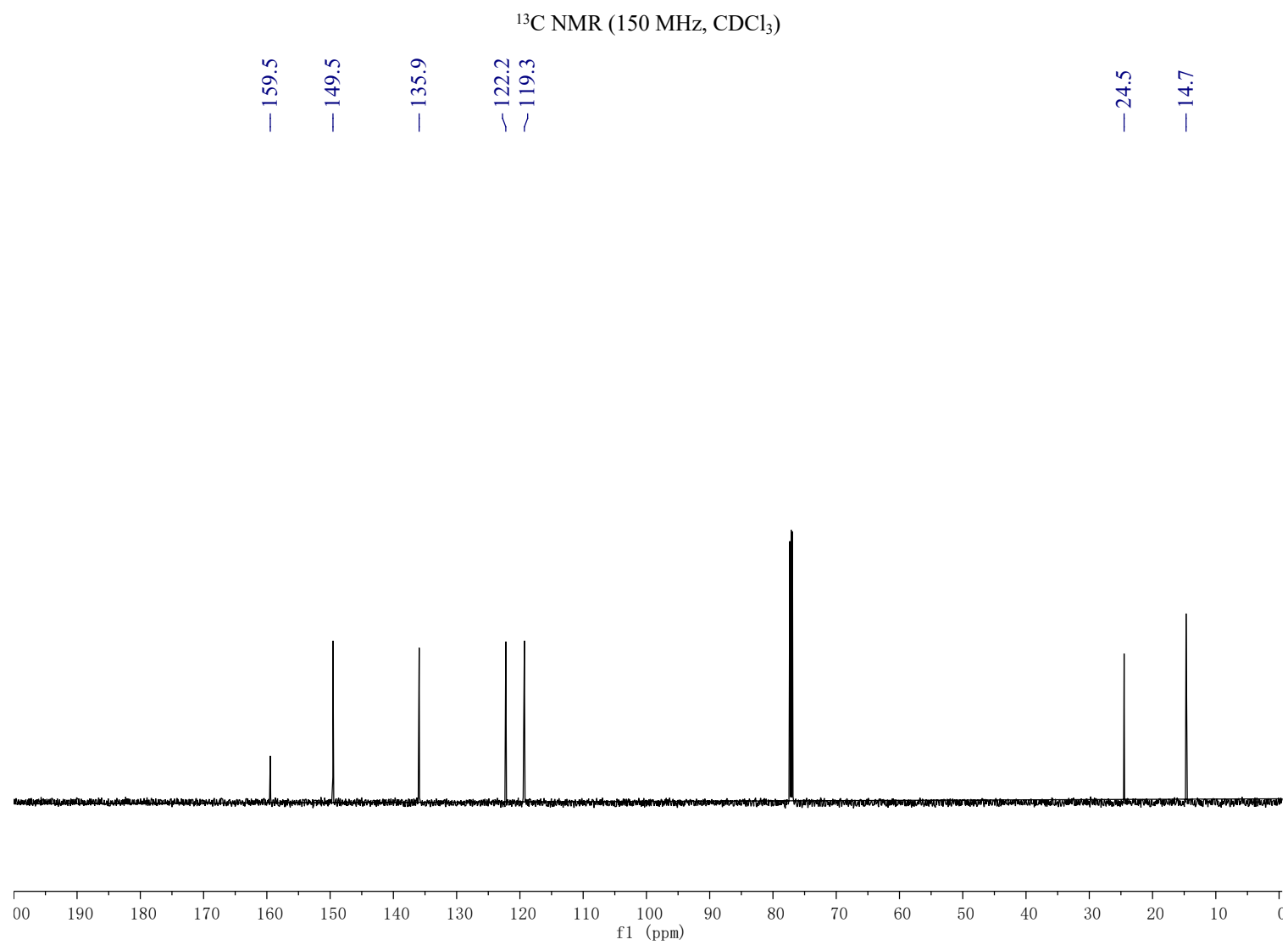




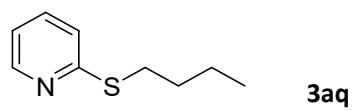
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¹H NMR (600 MHz, CDCl₃)

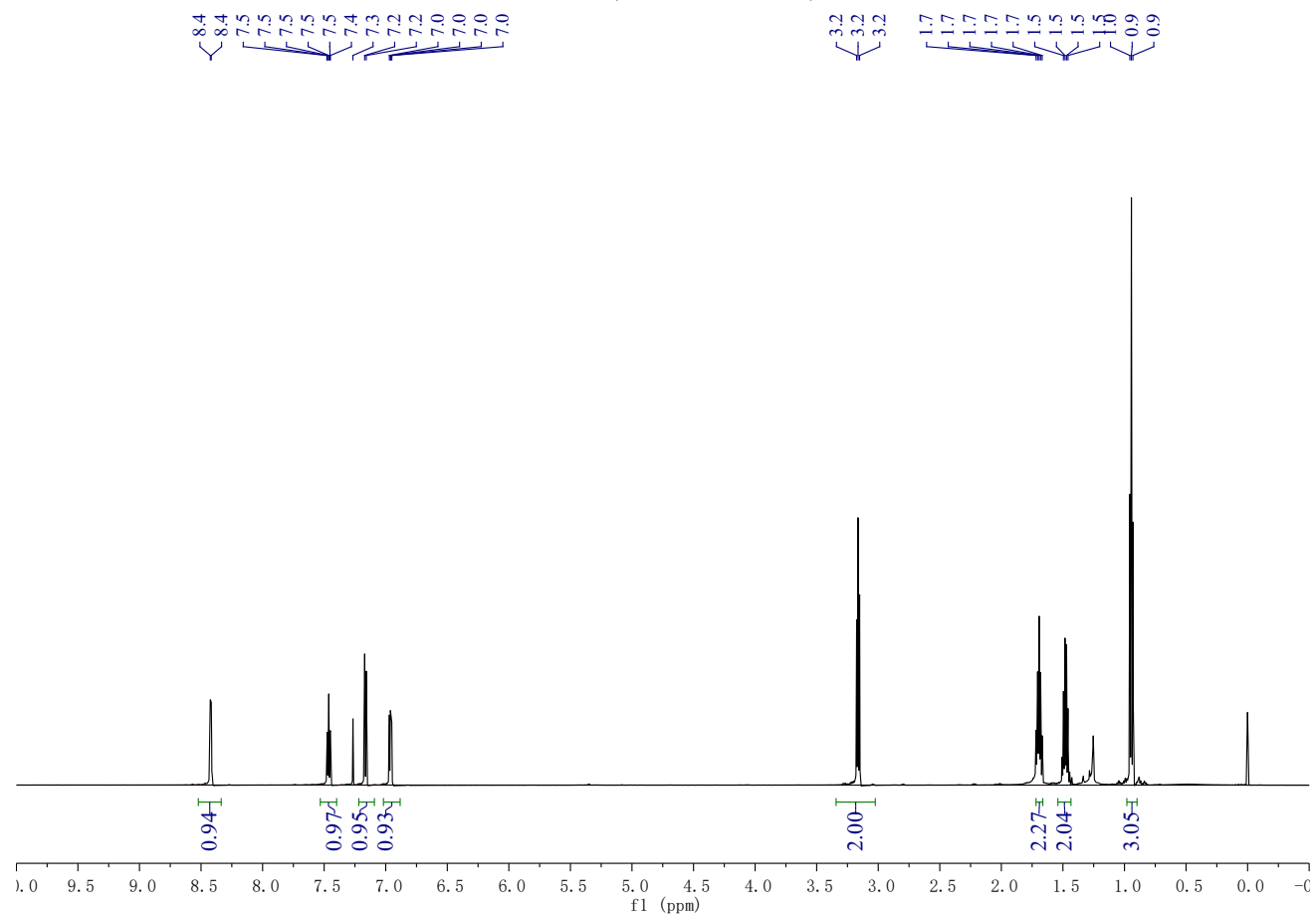


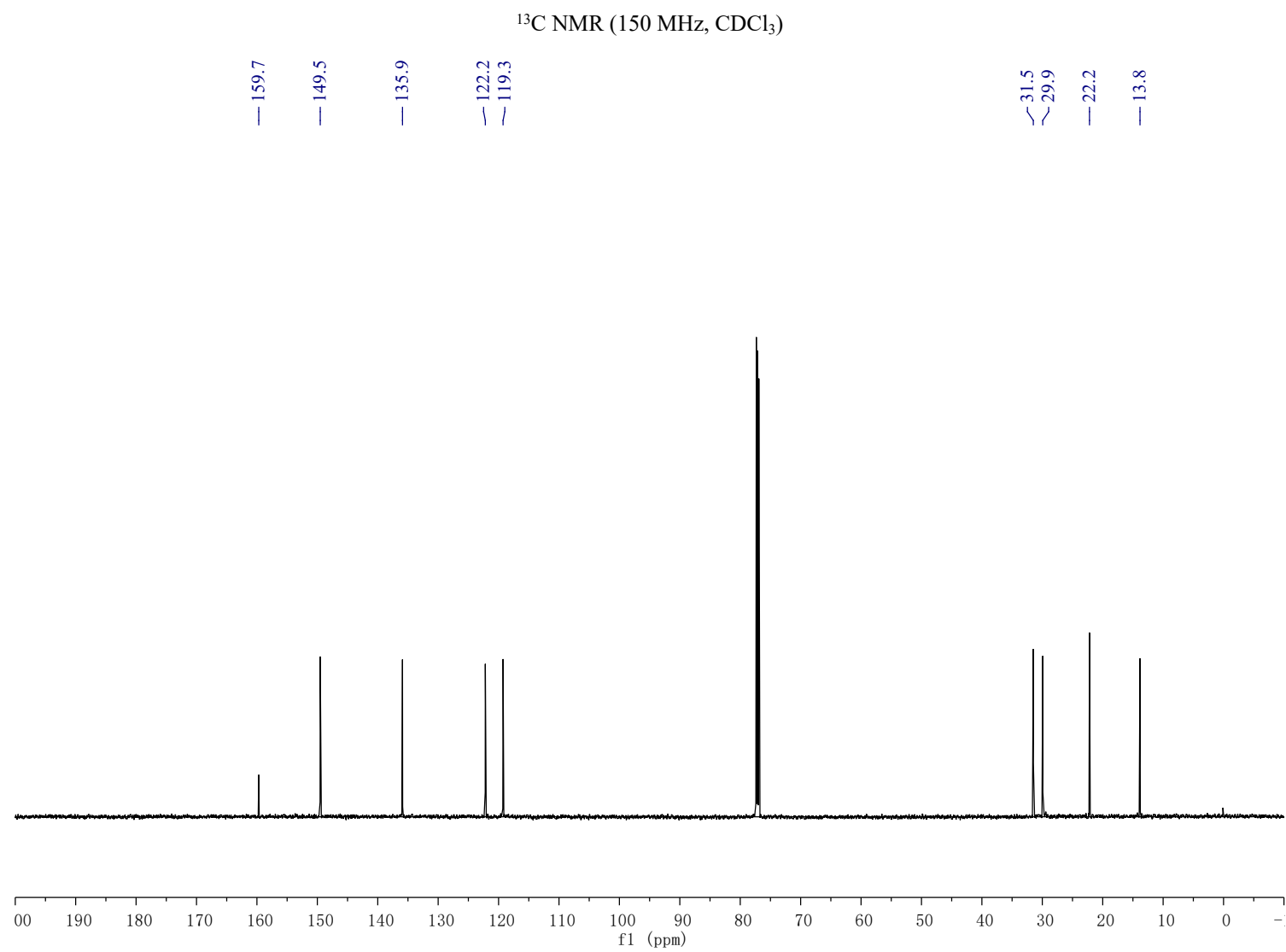


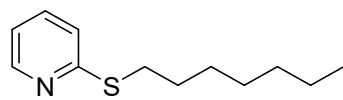
S-50



^1H NMR (600 MHz, CDCl_3)

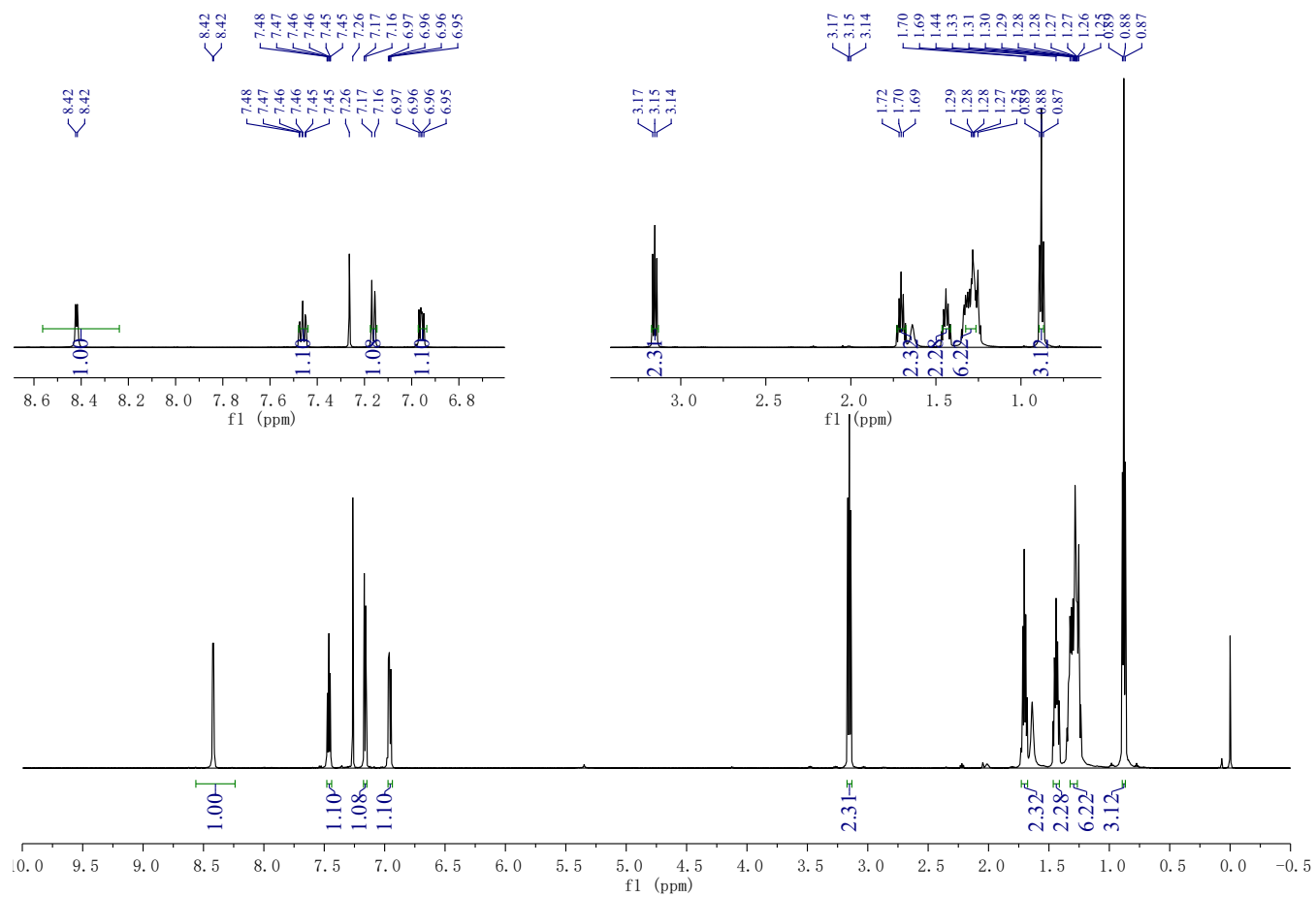


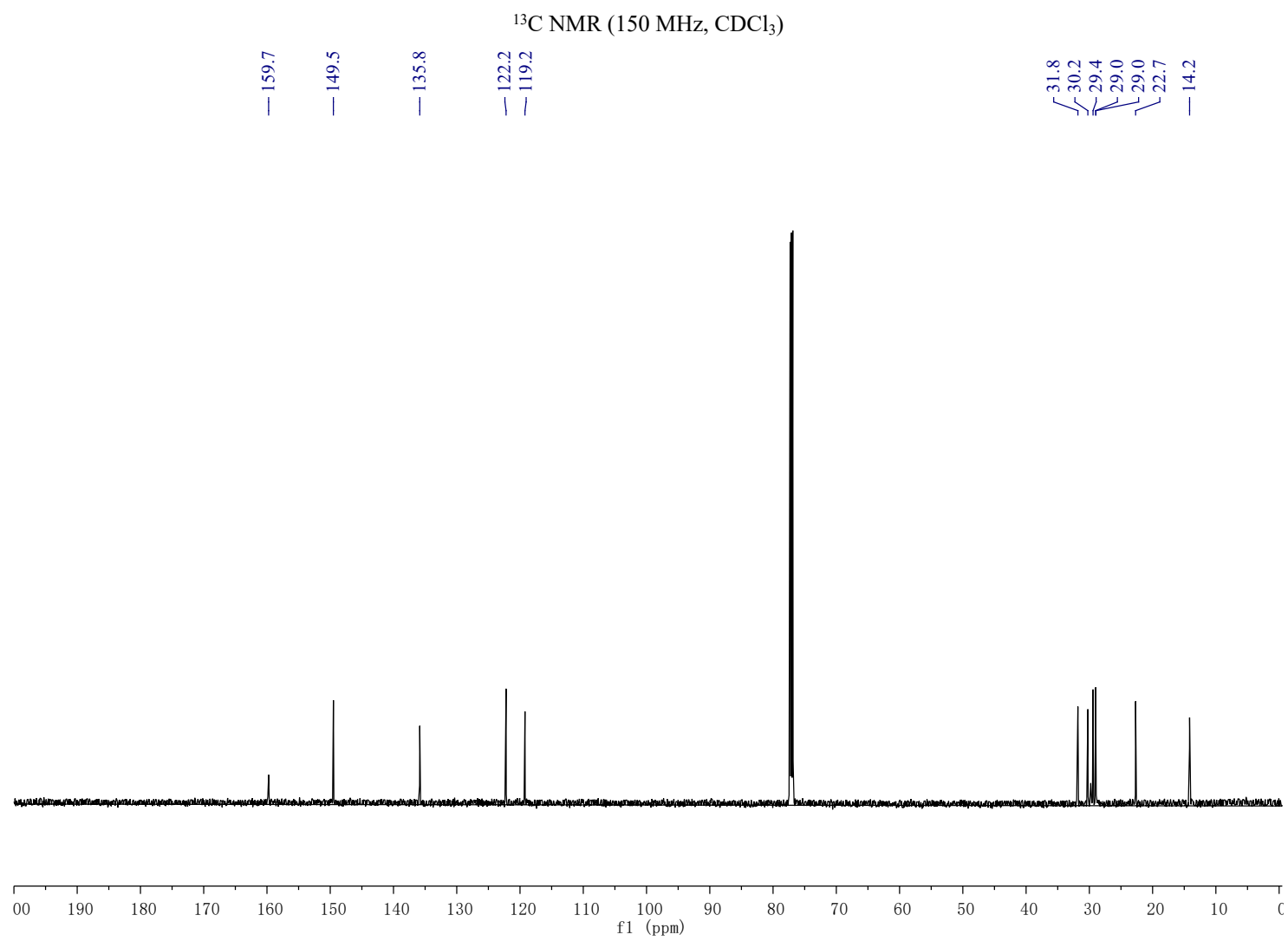


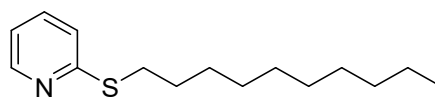


3ar

^1H NMR (600 MHz, CDCl_3)

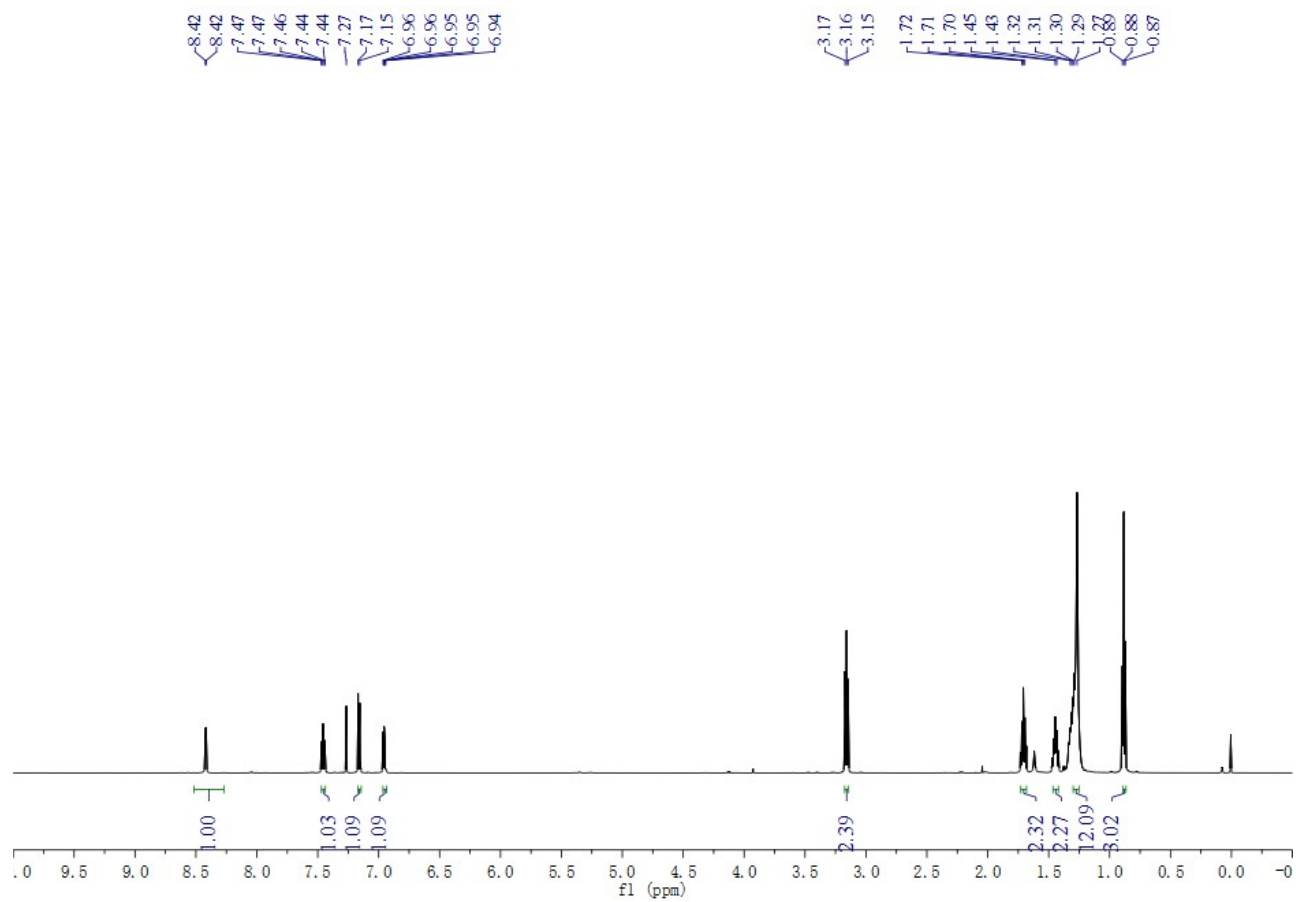


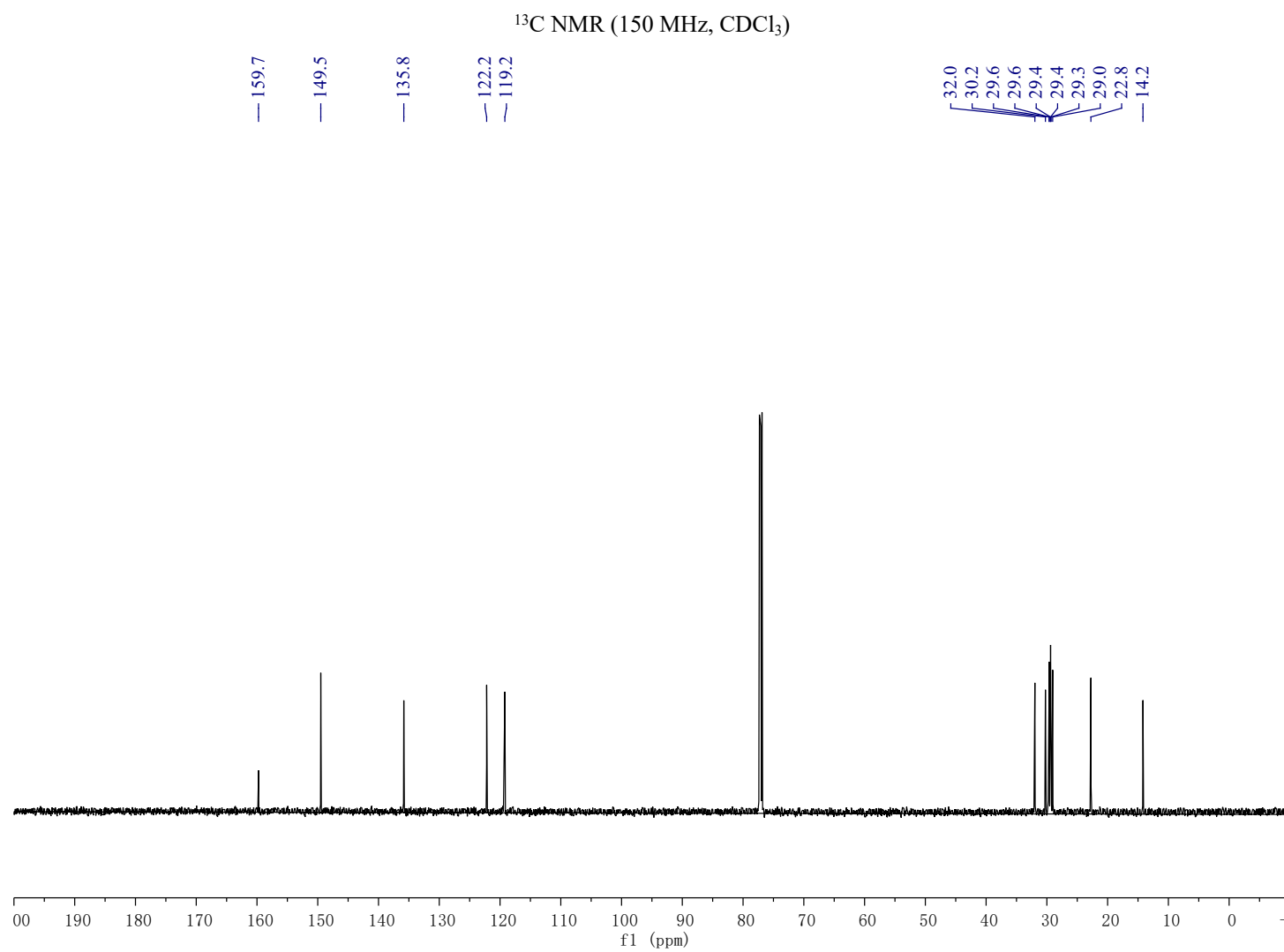


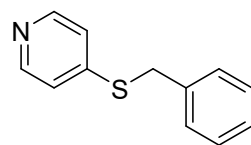


3as

^1H NMR (600 MHz, CDCl_3)

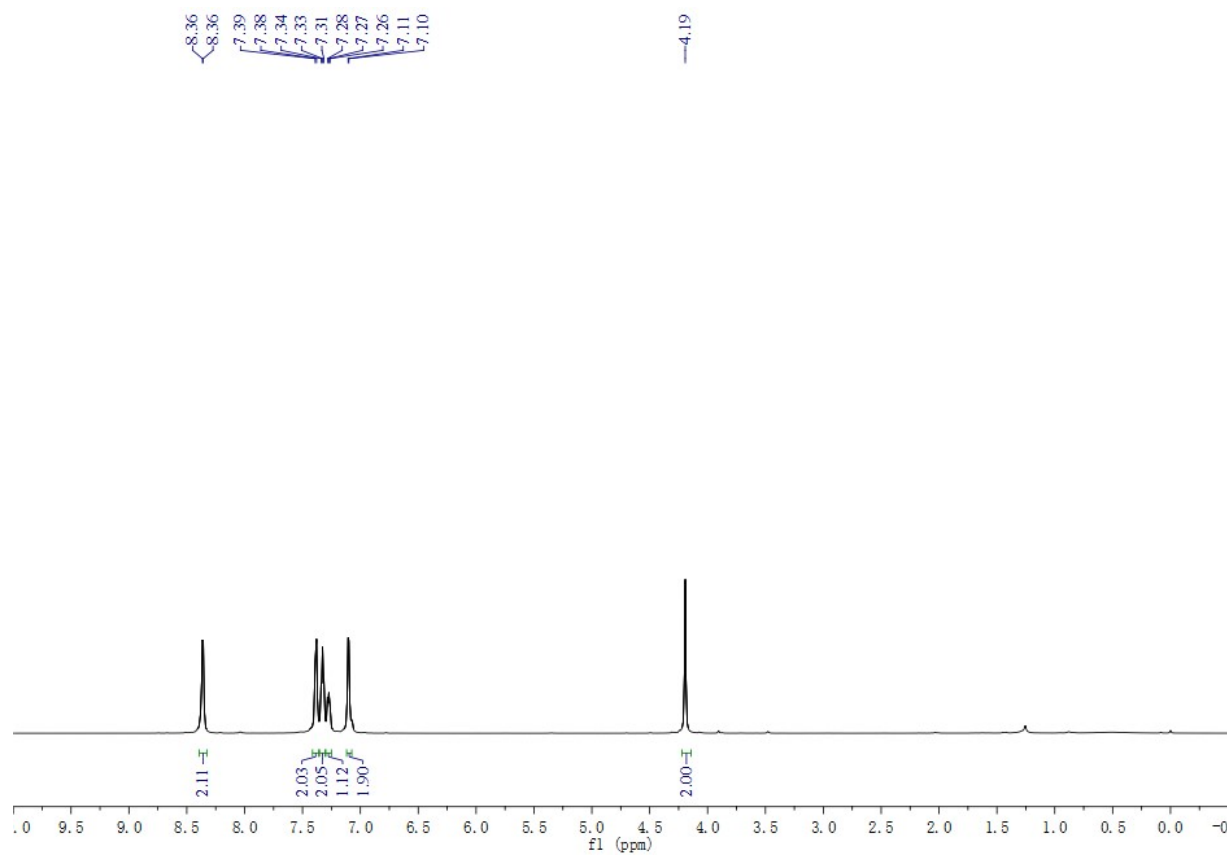


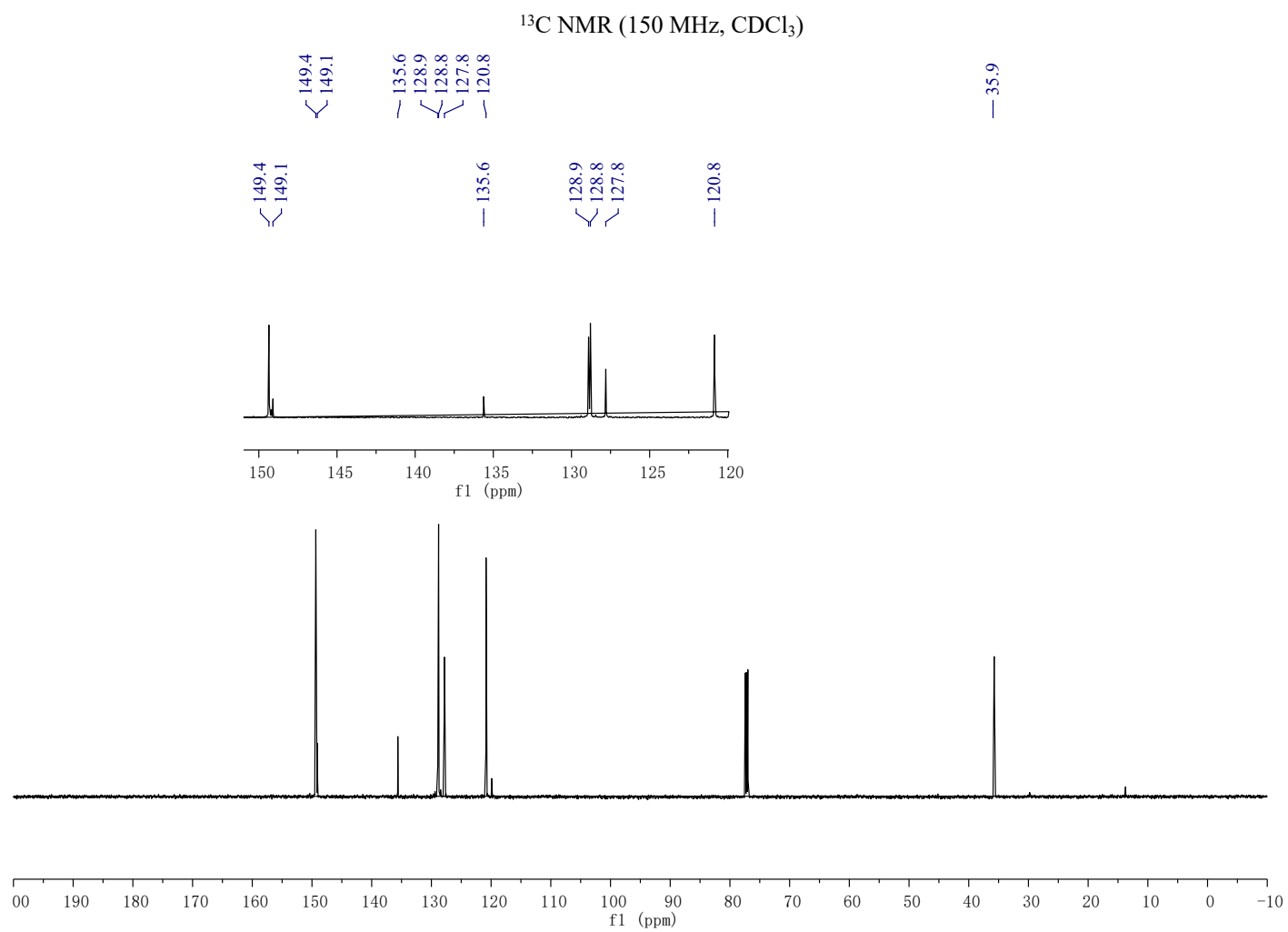


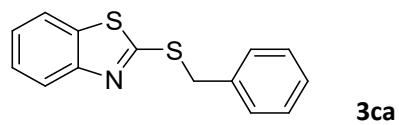


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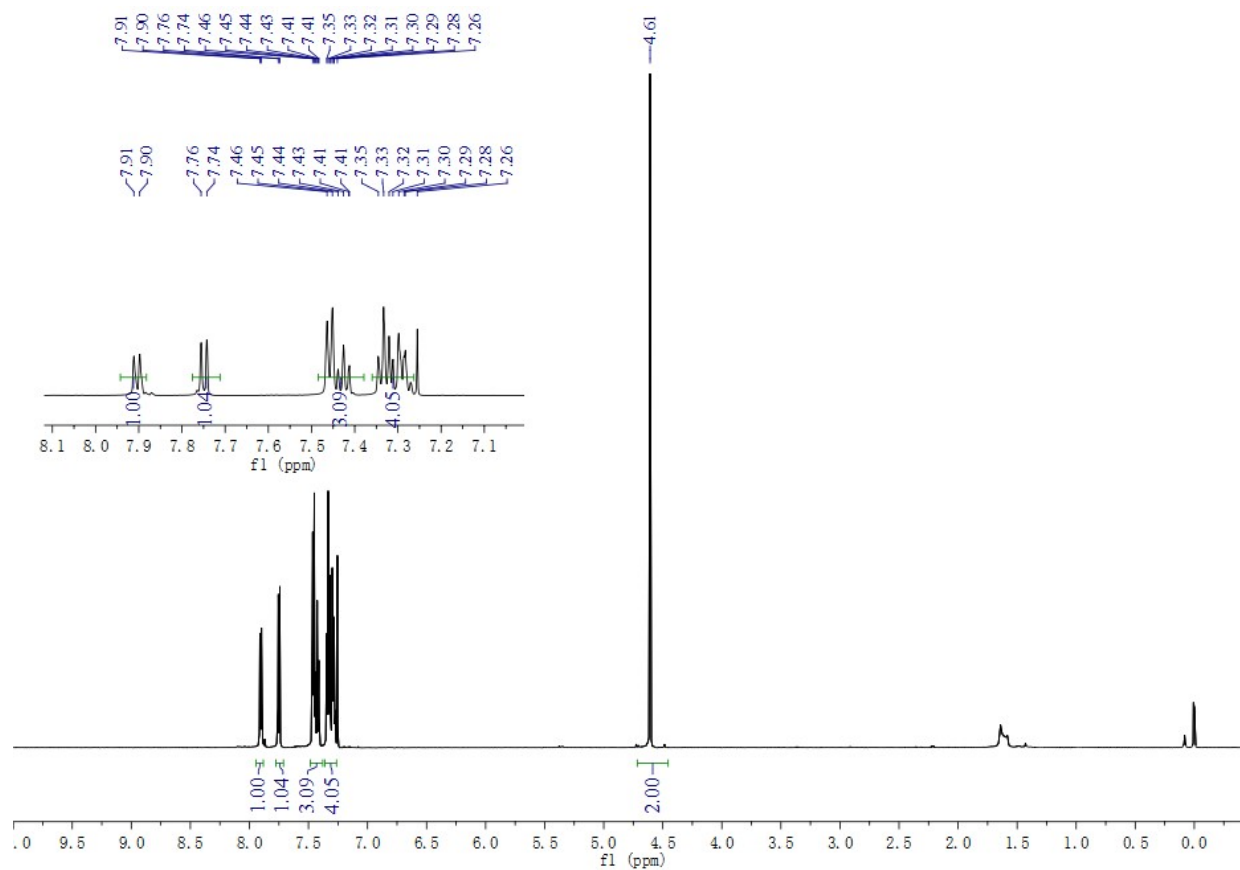
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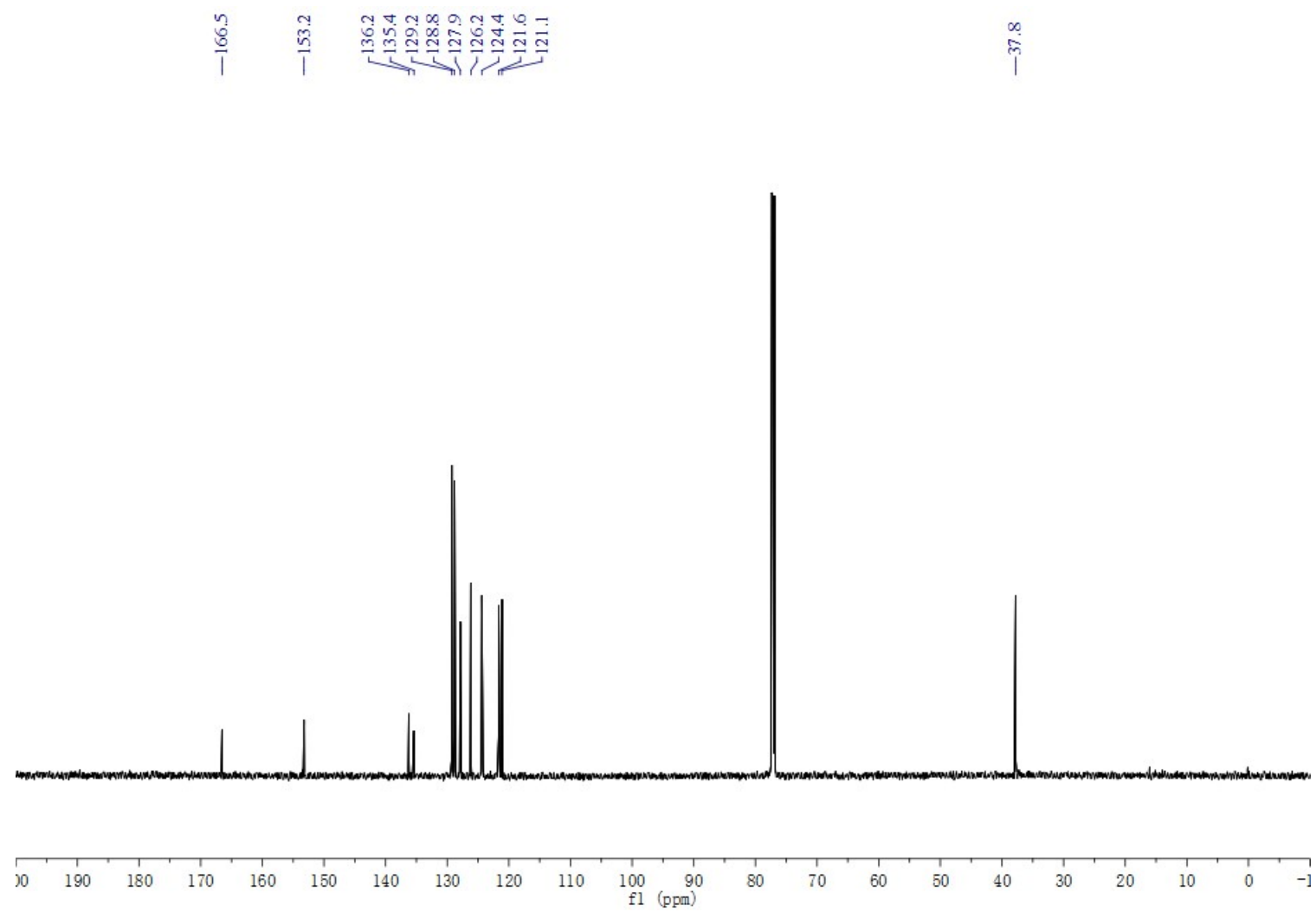


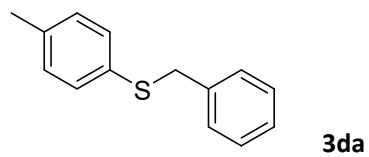


^1H NMR (600 MHz, CDCl_3)

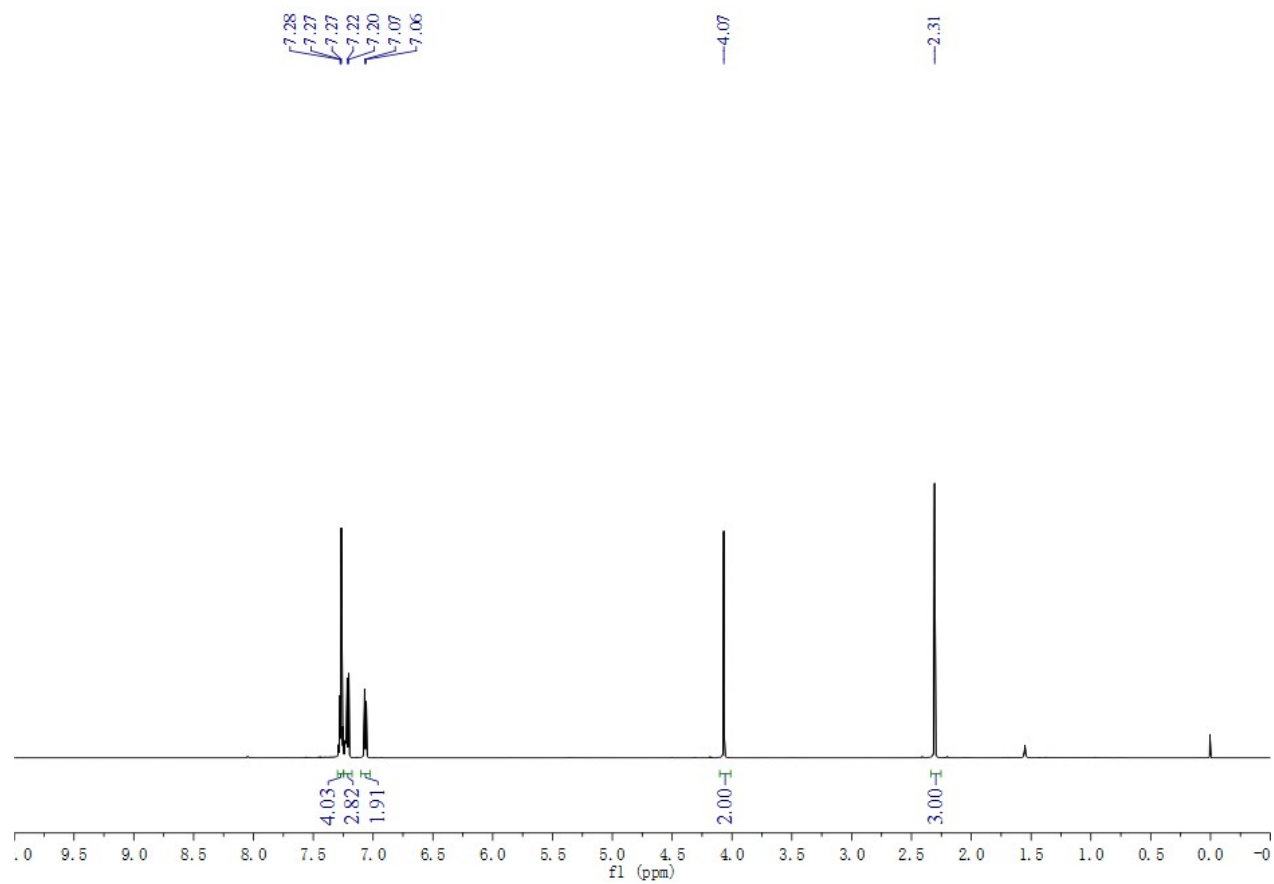


^{13}C NMR (150 MHz, CDCl_3)

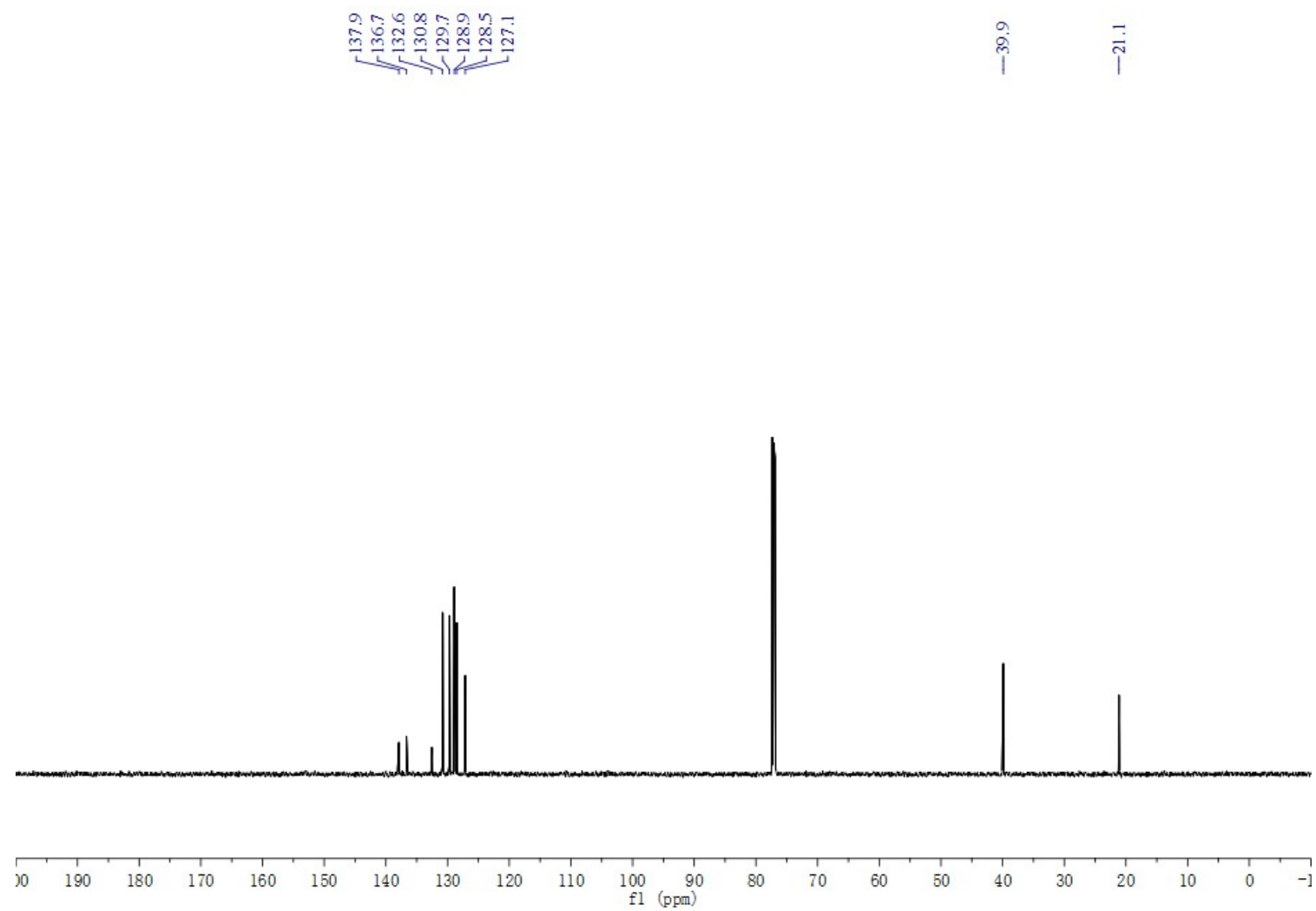


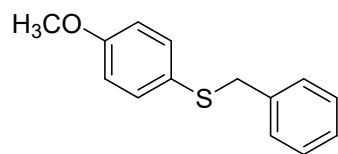


^1H NMR (600 MHz, CDCl_3)



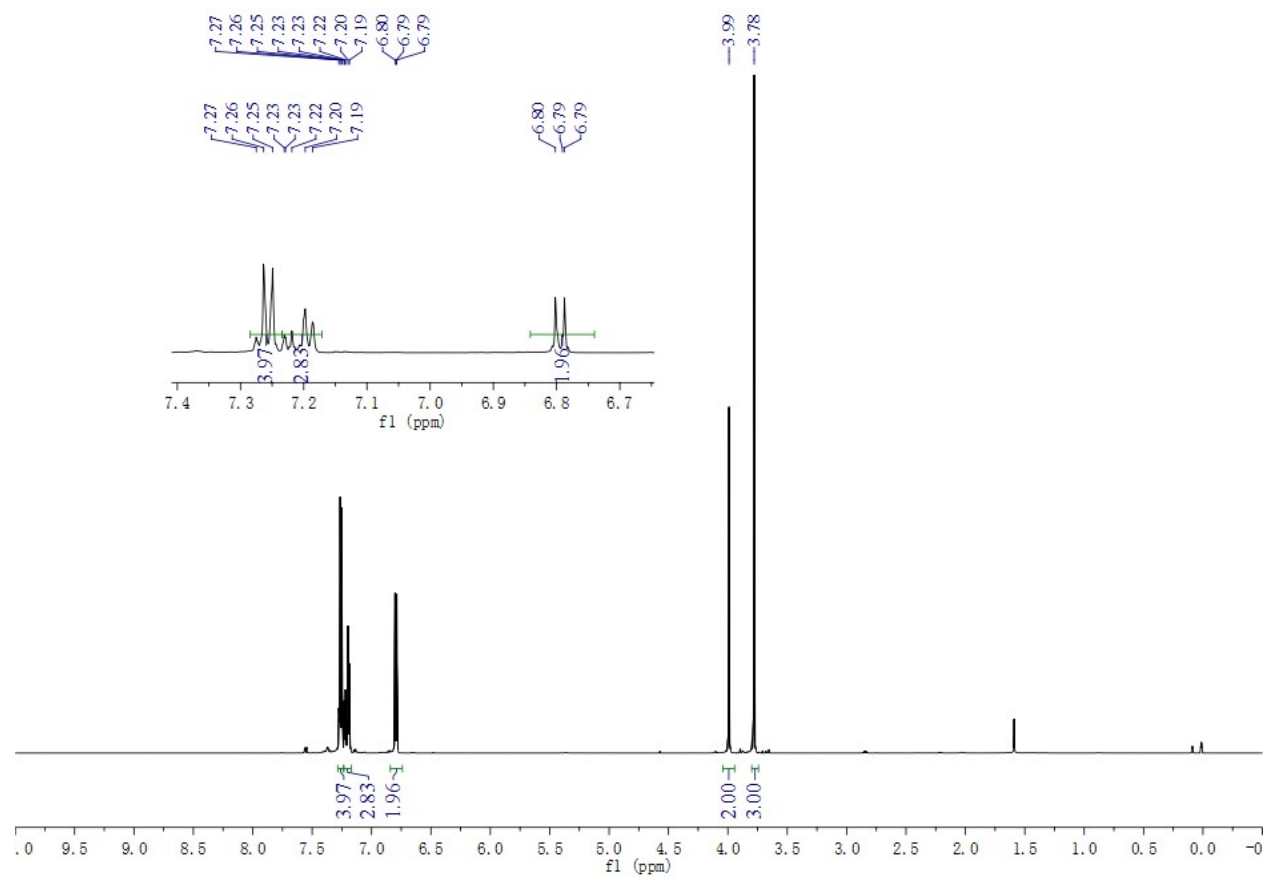
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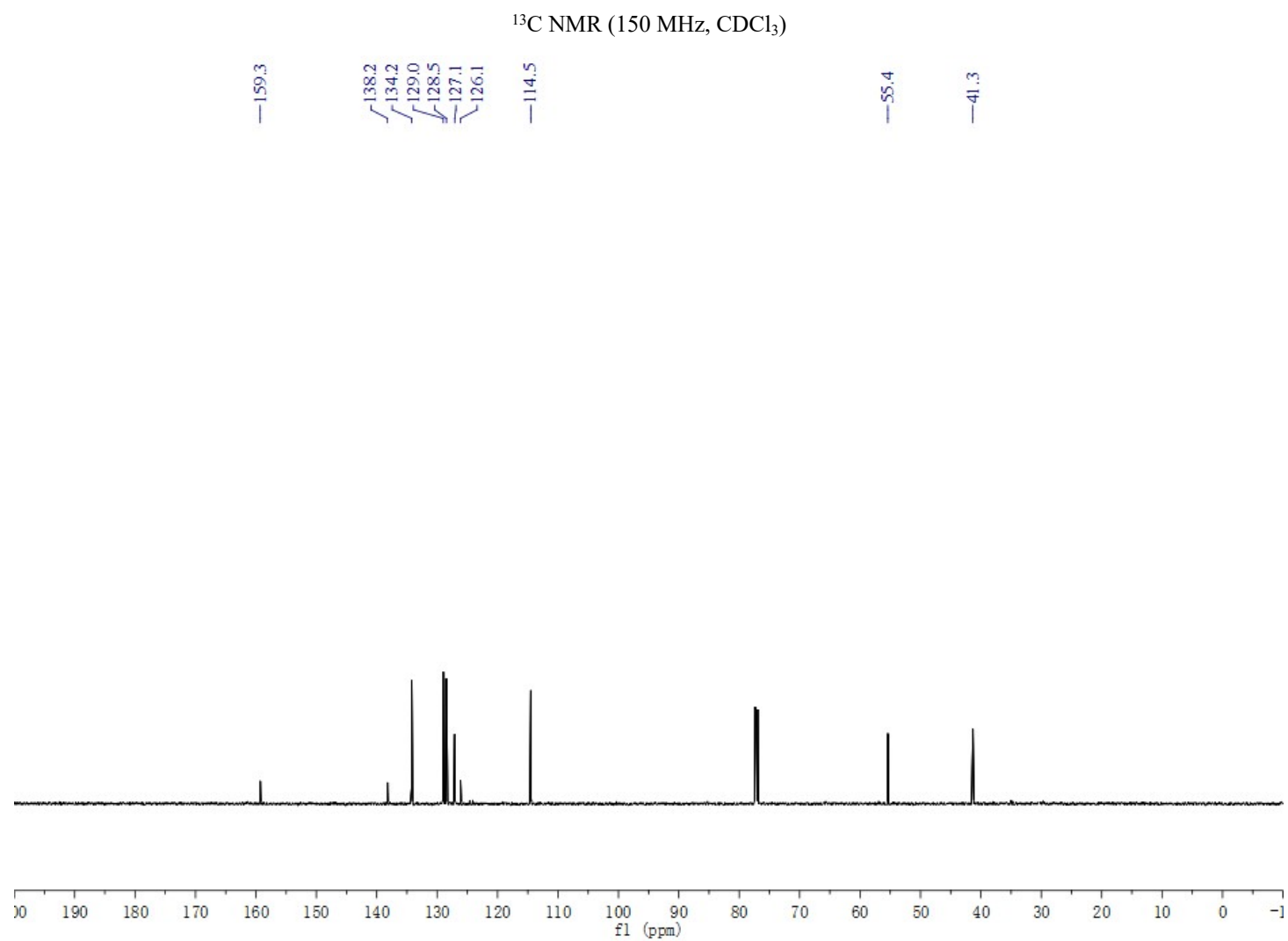


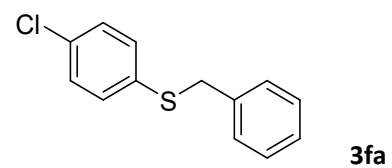


3ea

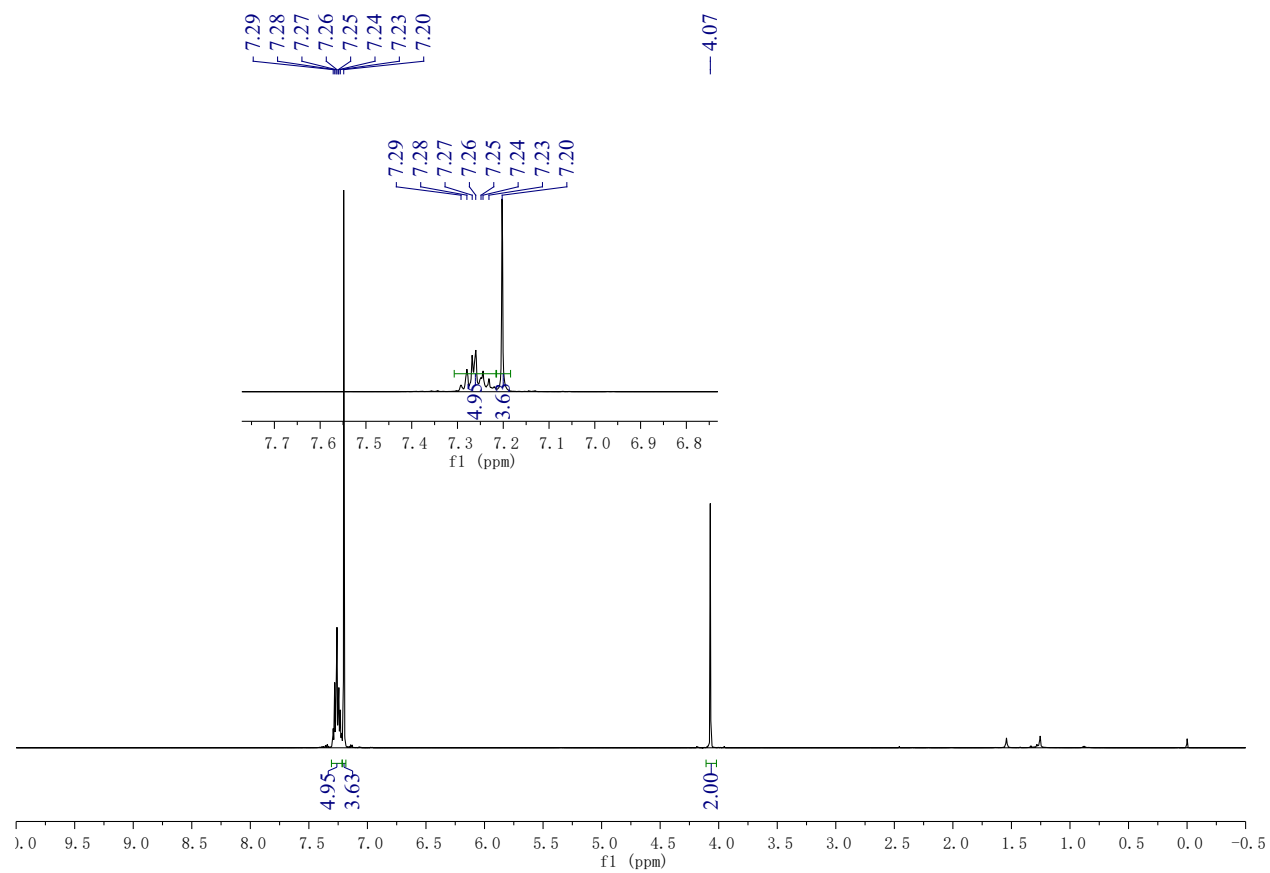
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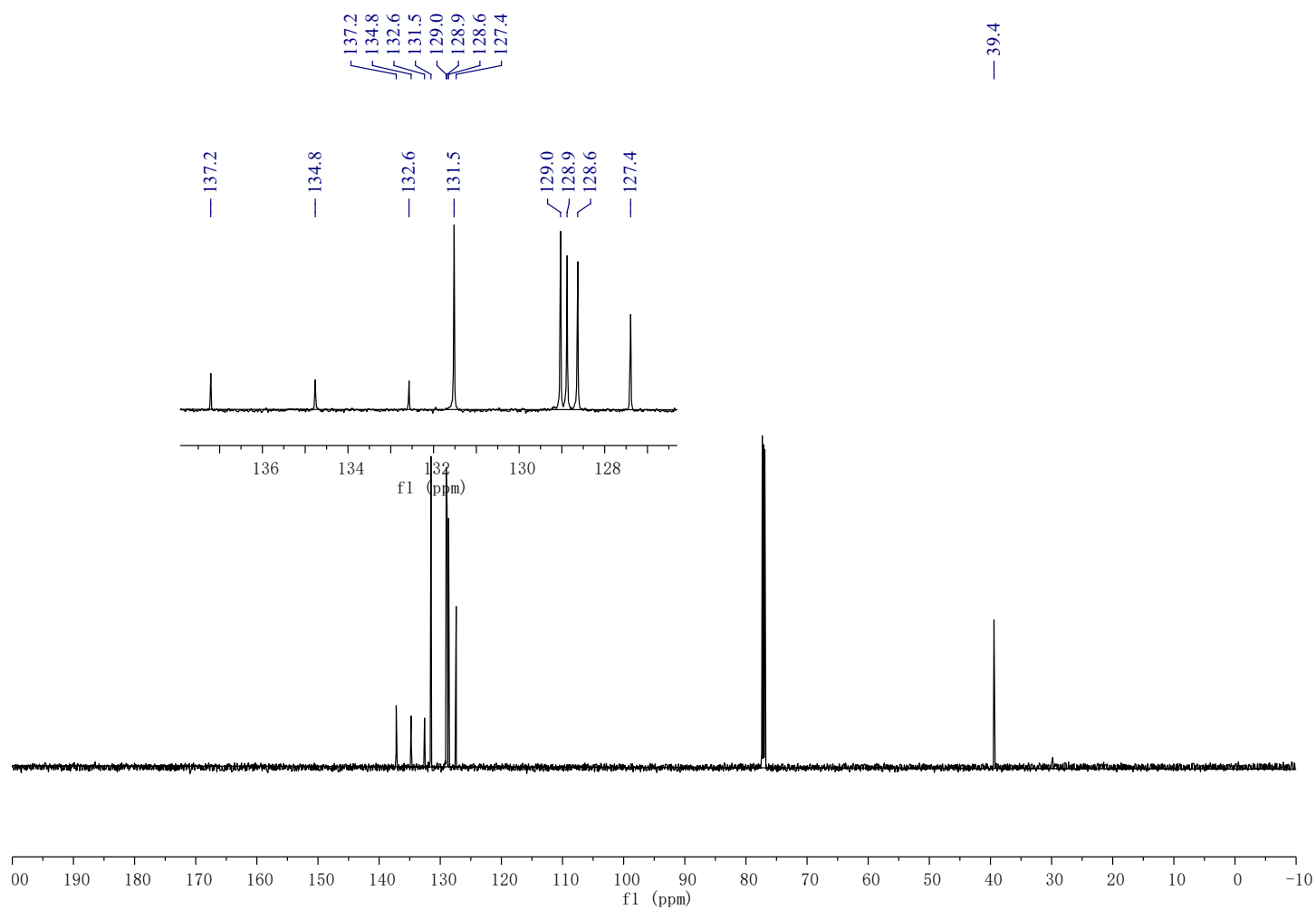


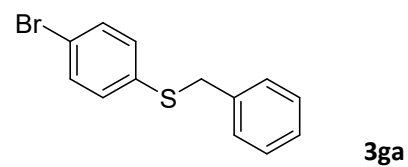


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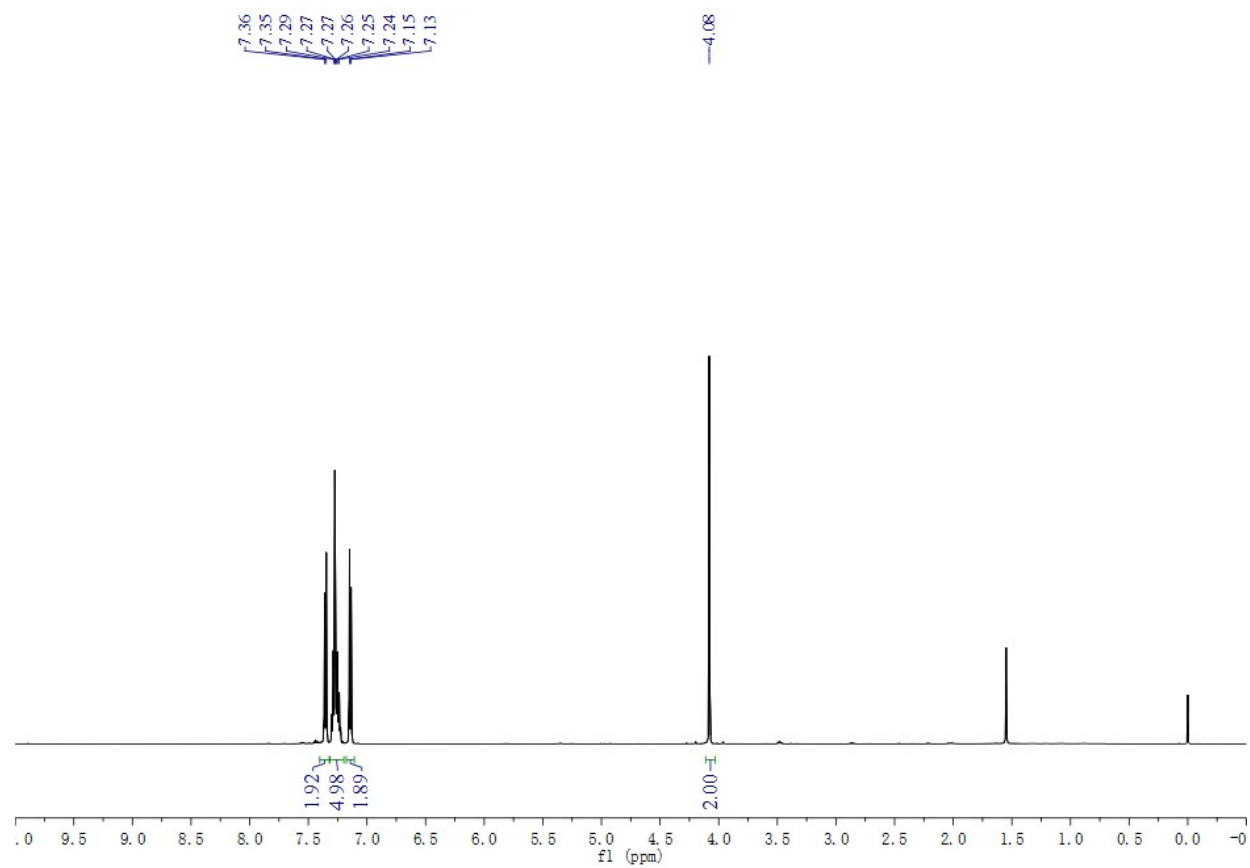


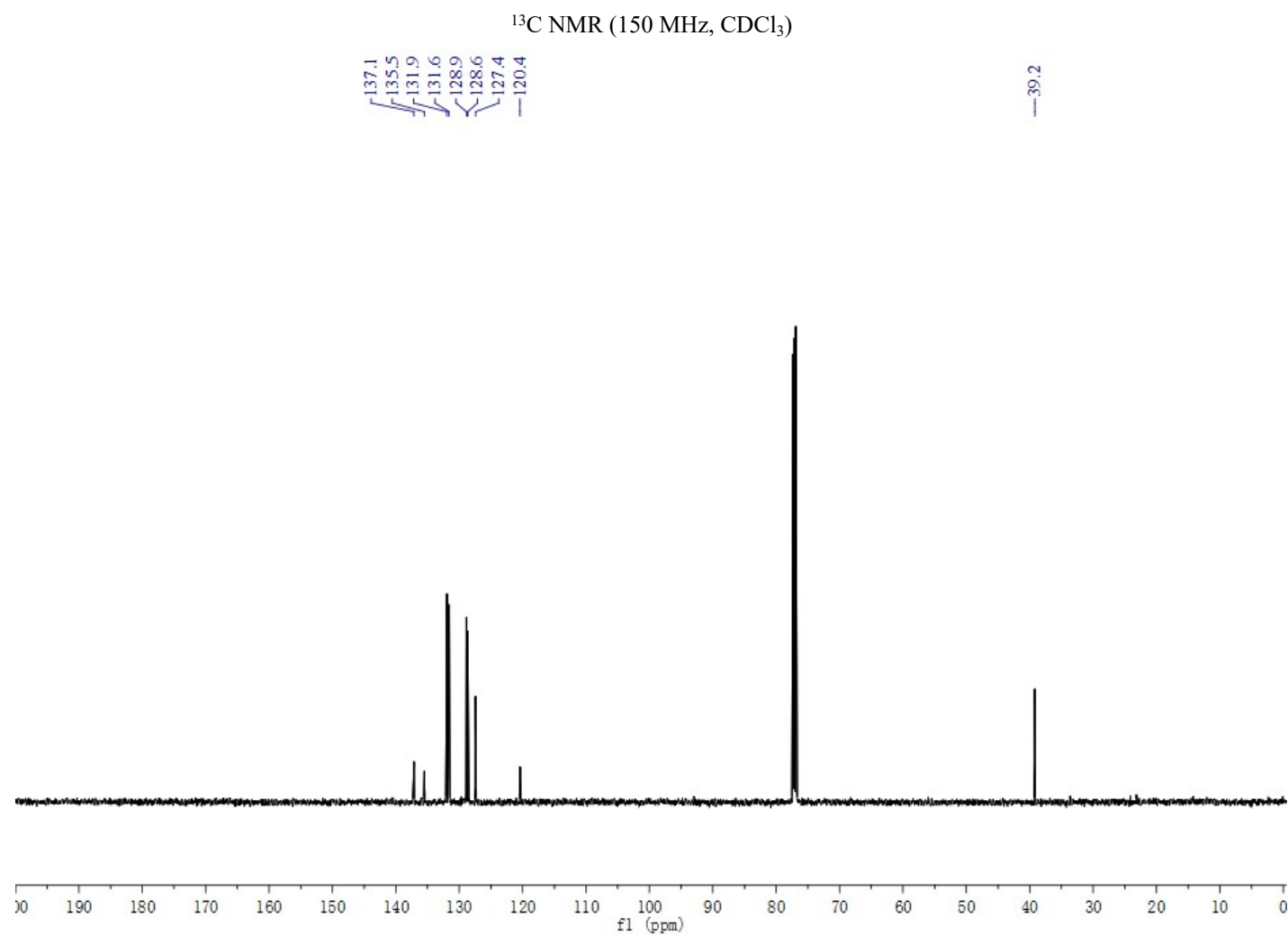
^{13}C NMR (150 MHz, CDCl_3)

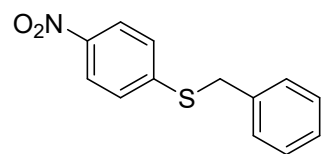




^1H NMR (600 MHz, CDCl_3)

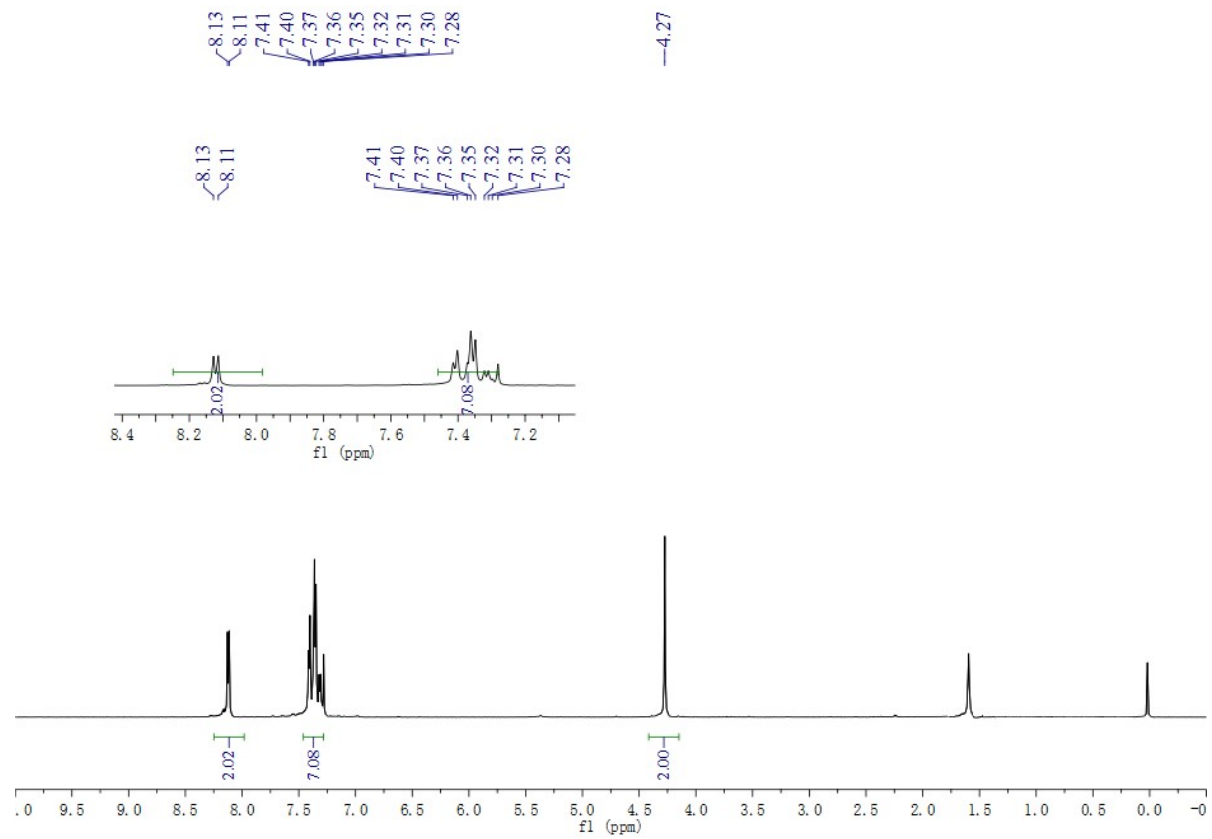




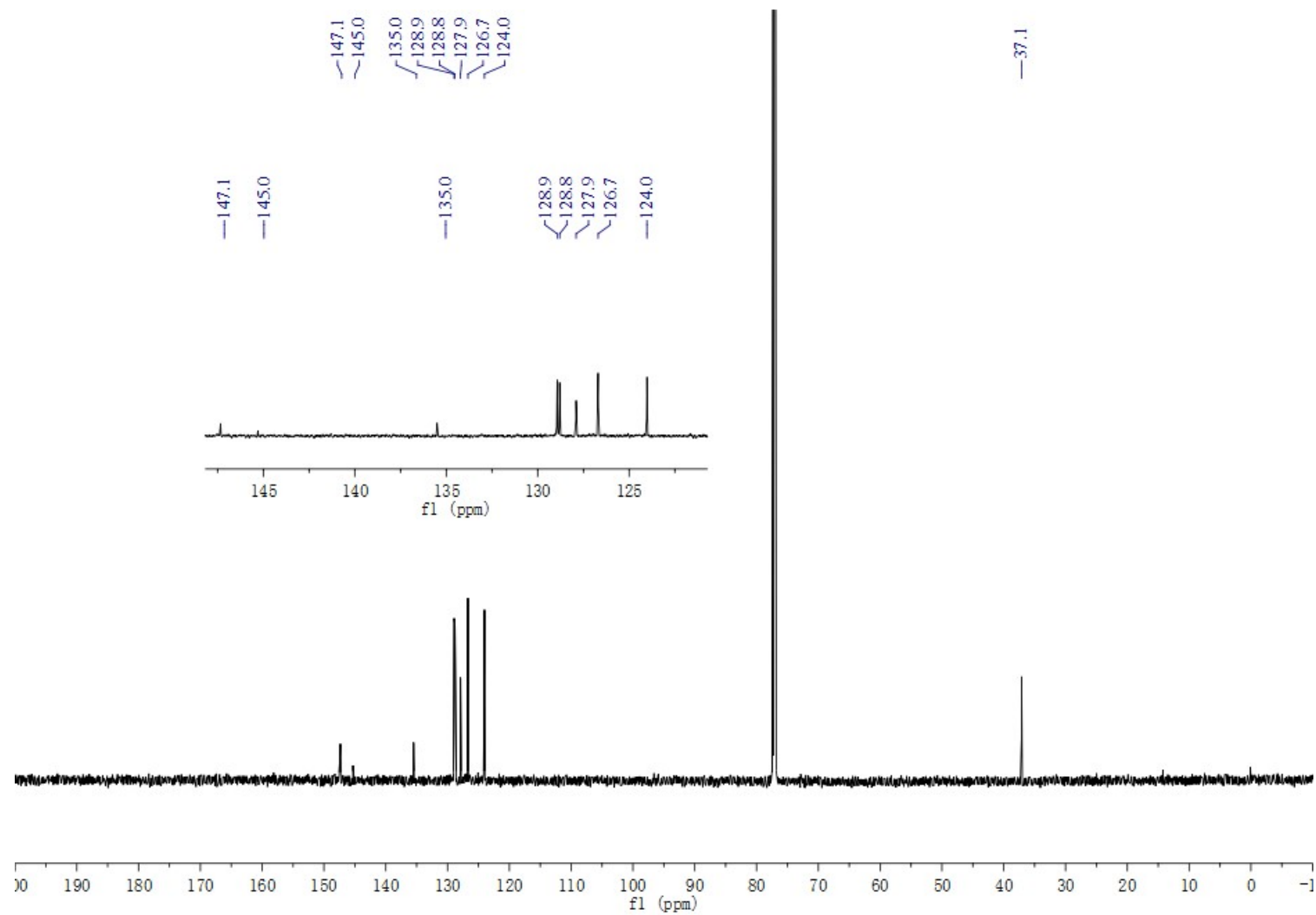


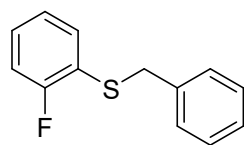
3ha

^1H NMR (600 MHz, CDCl_3)



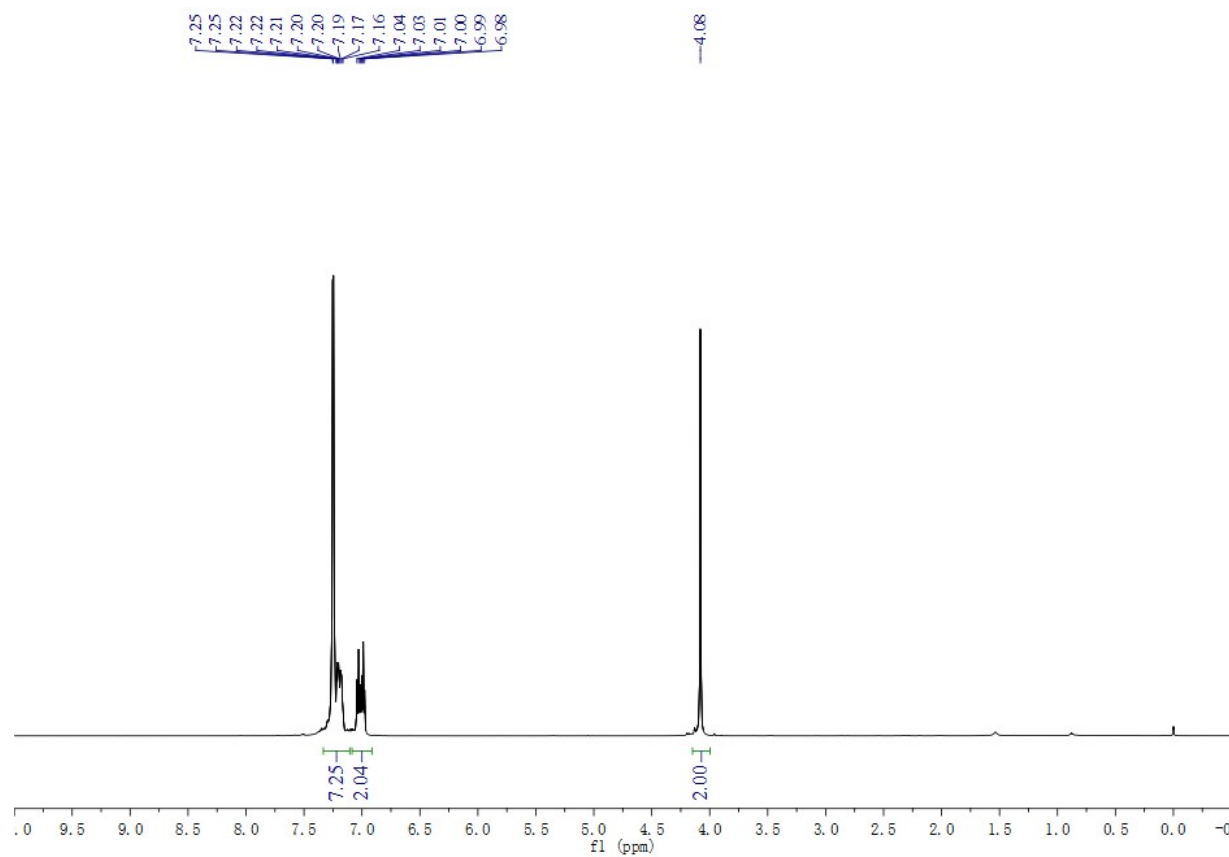
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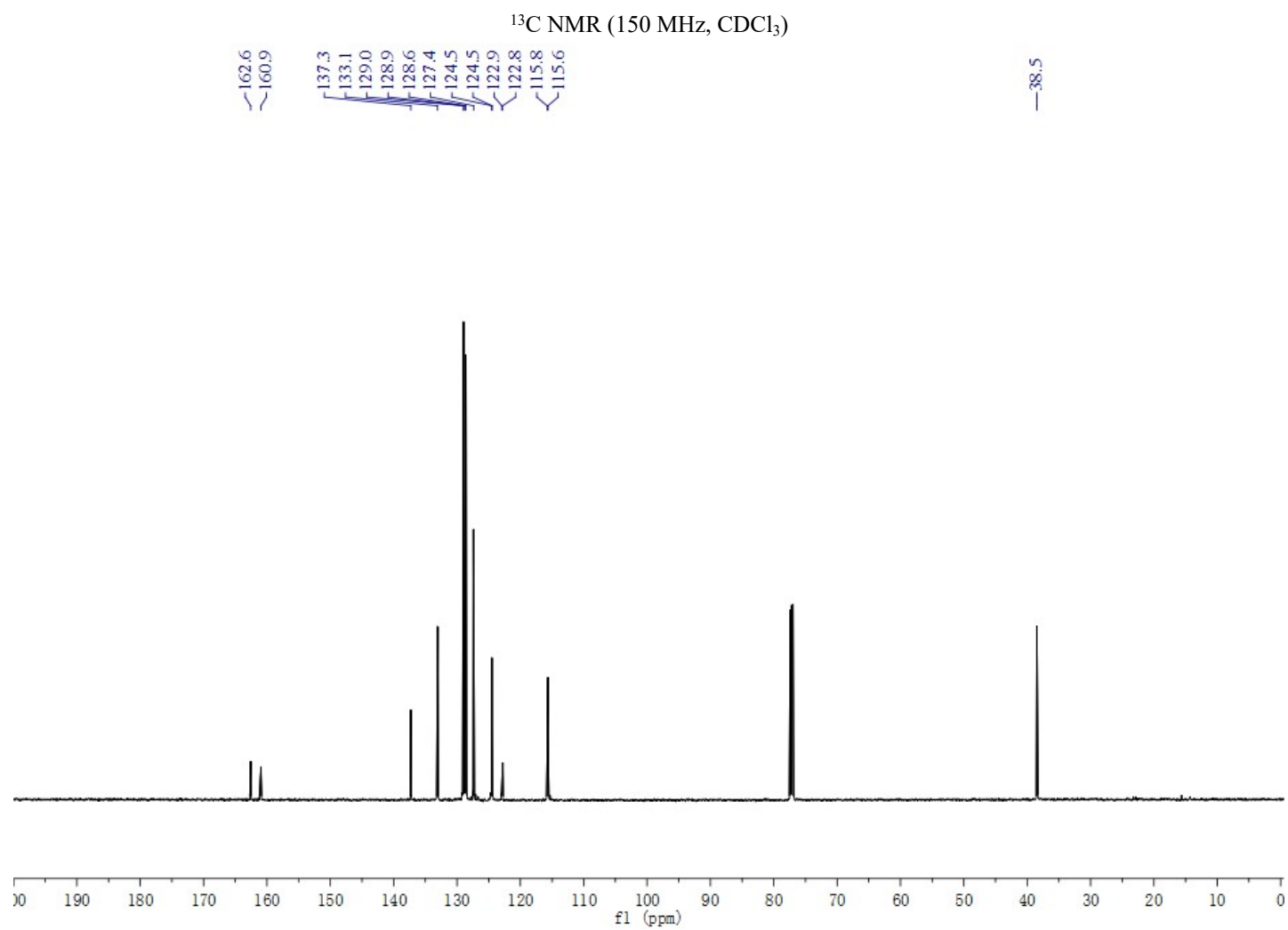


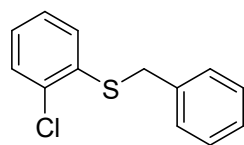


3ia

^1H NMR (600 MHz, CDCl_3)

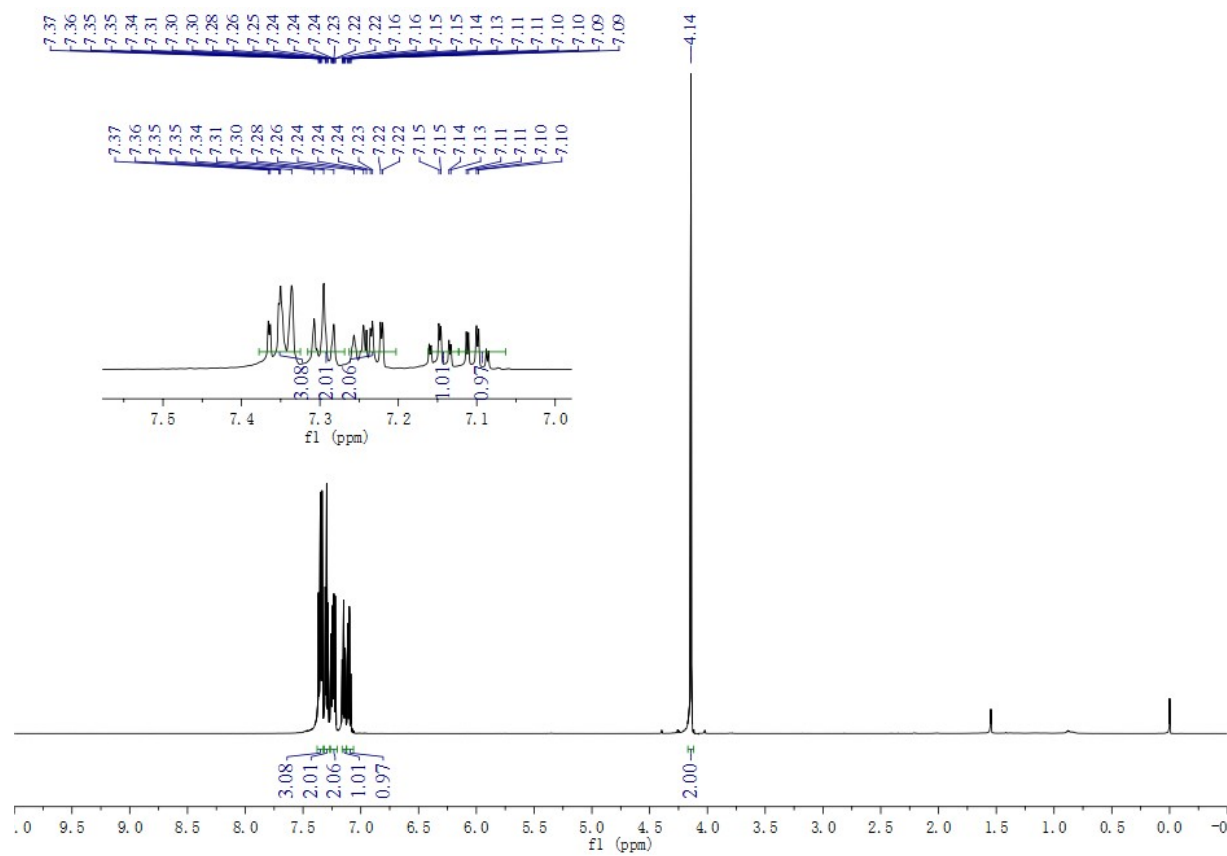


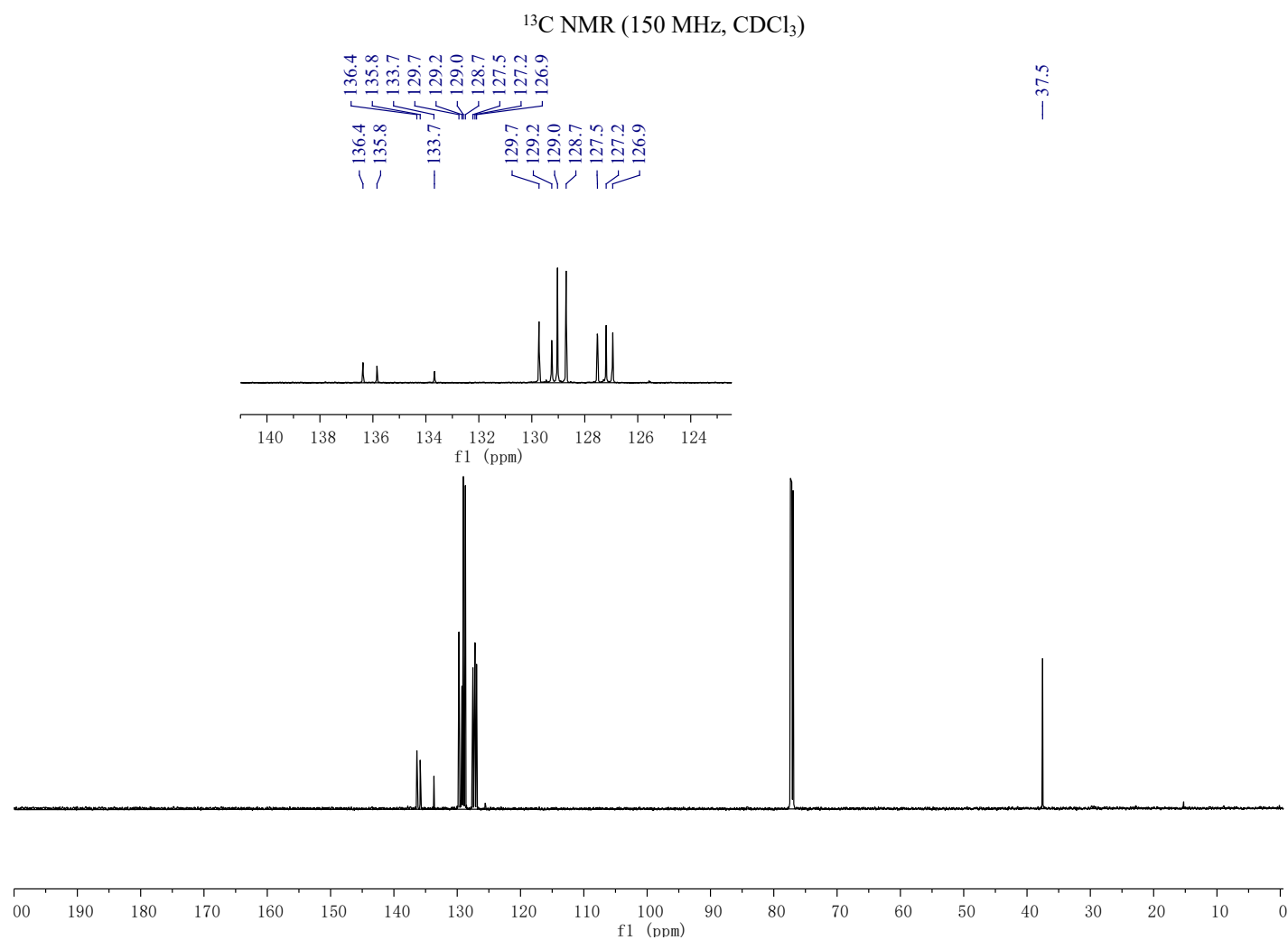


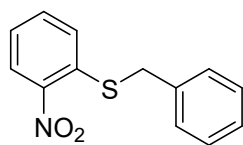


3ja

^1H NMR (600 MHz, CDCl_3)

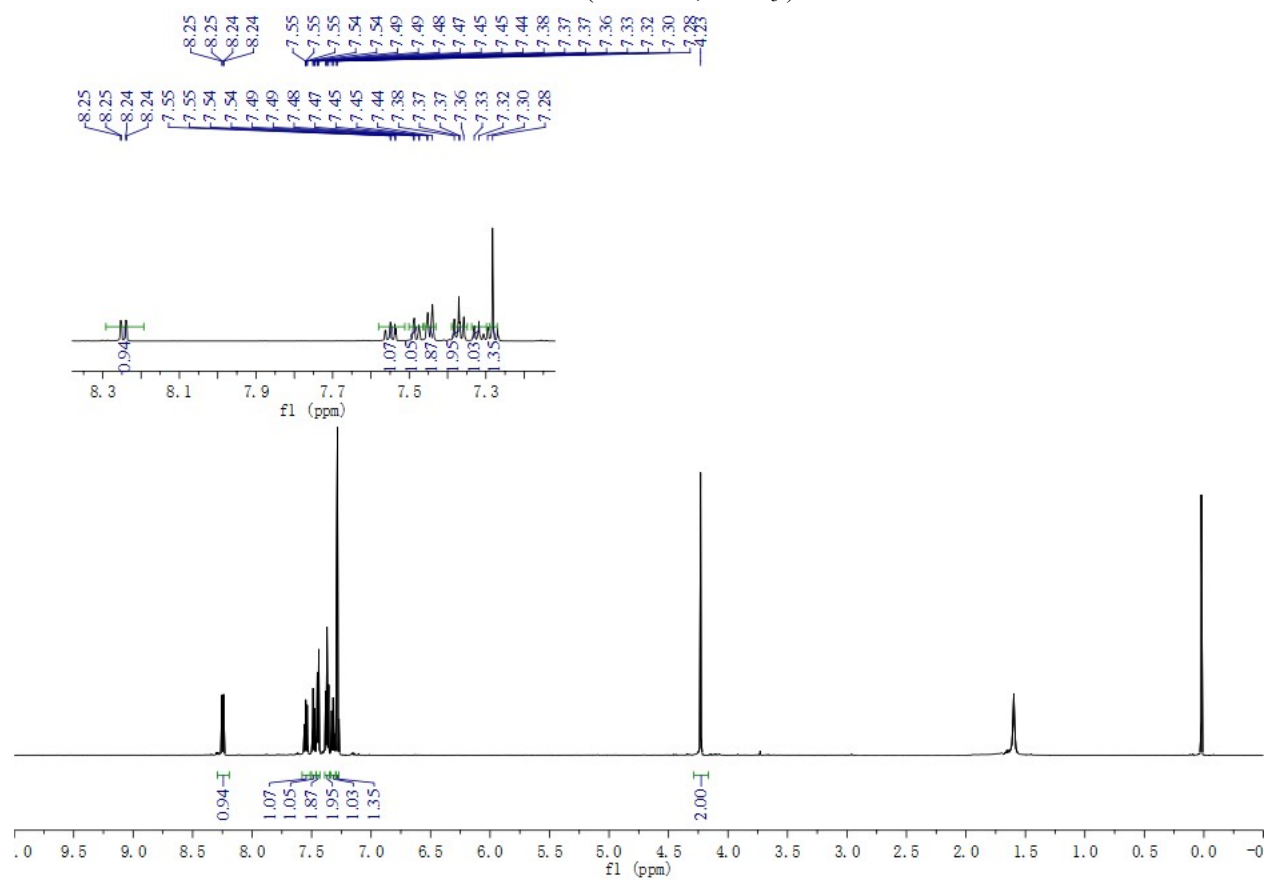


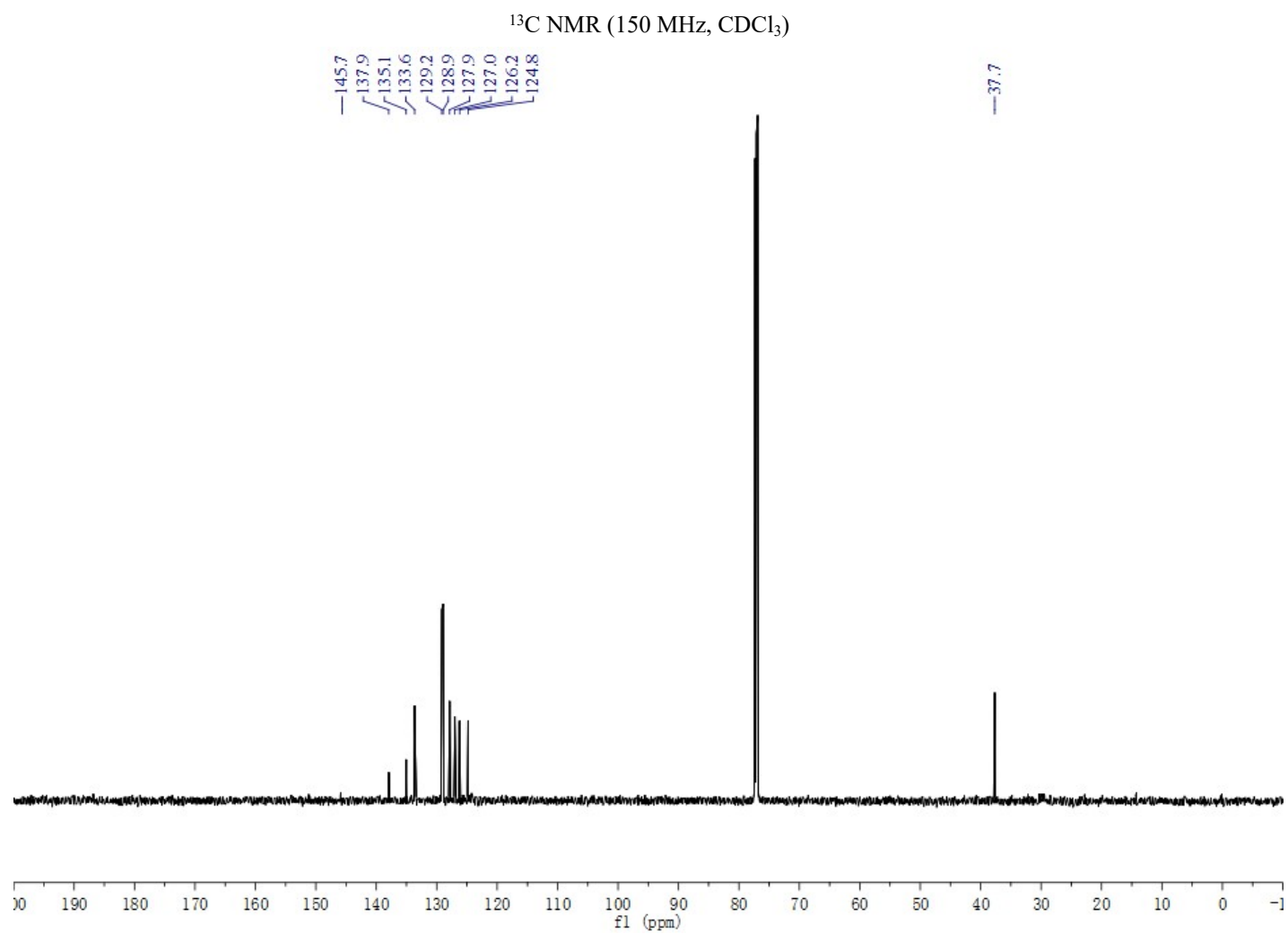


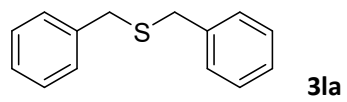


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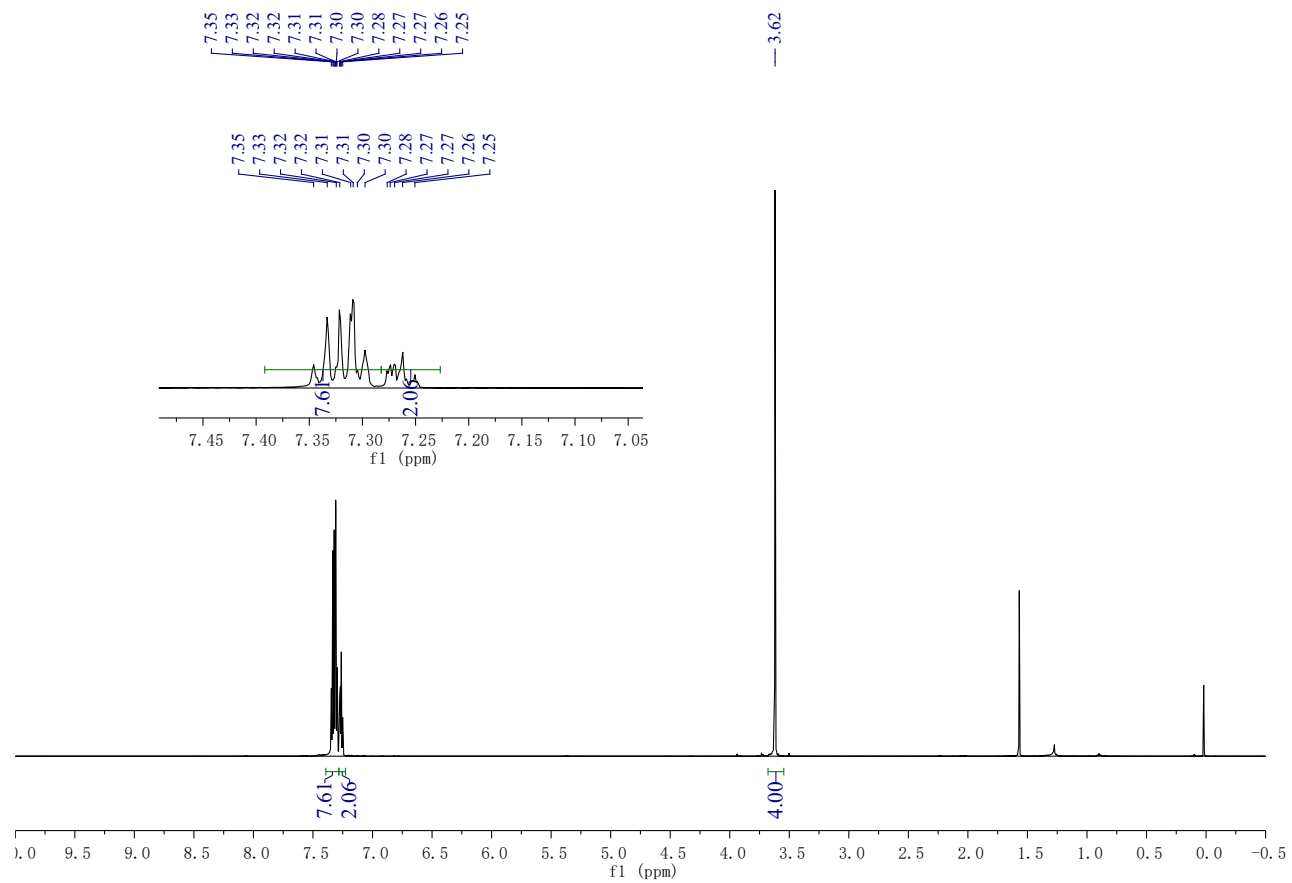
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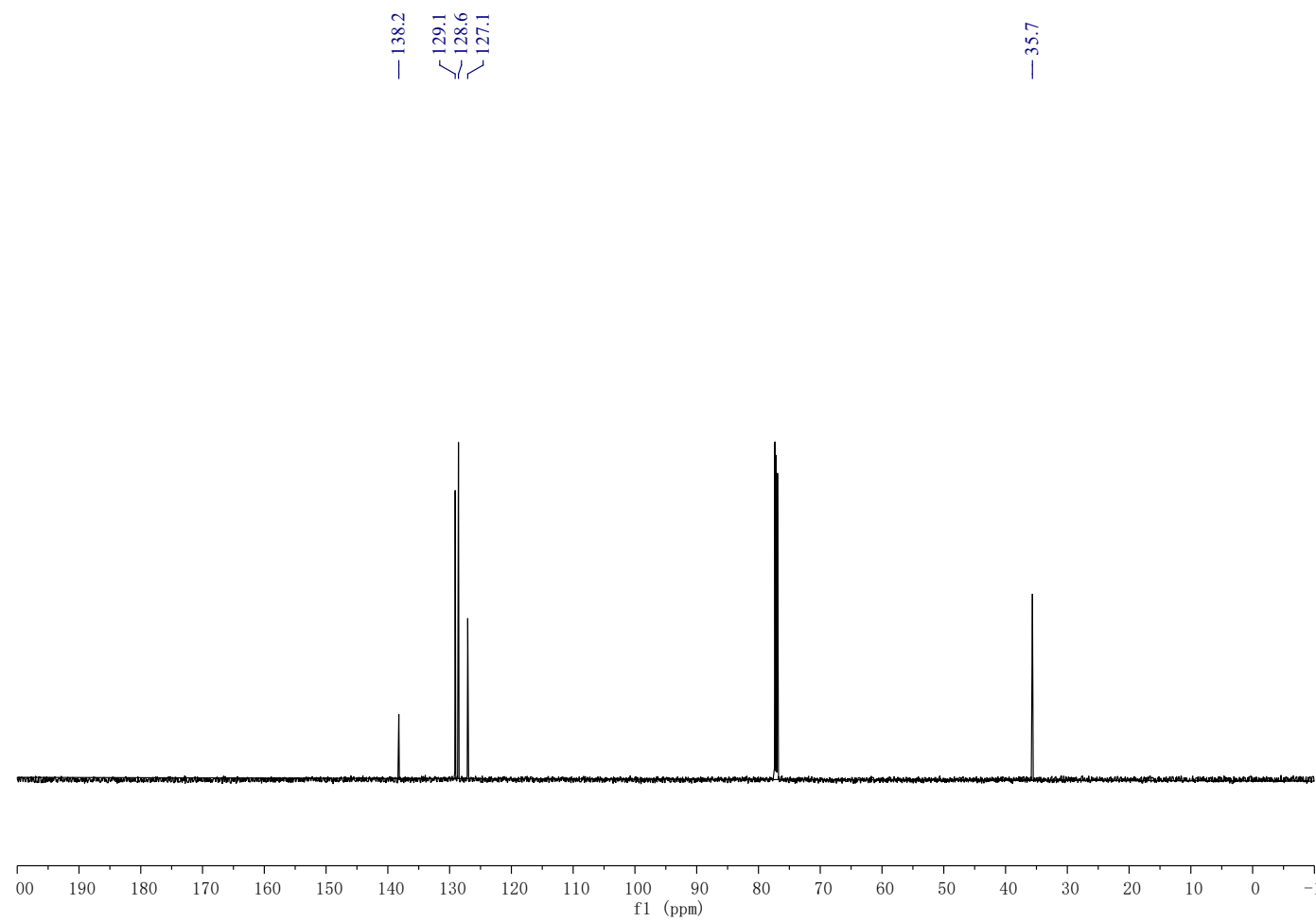


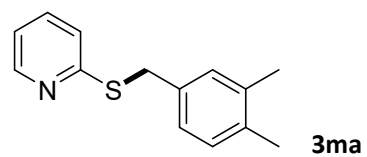


^1H NMR (600 MHz, CDCl_3)

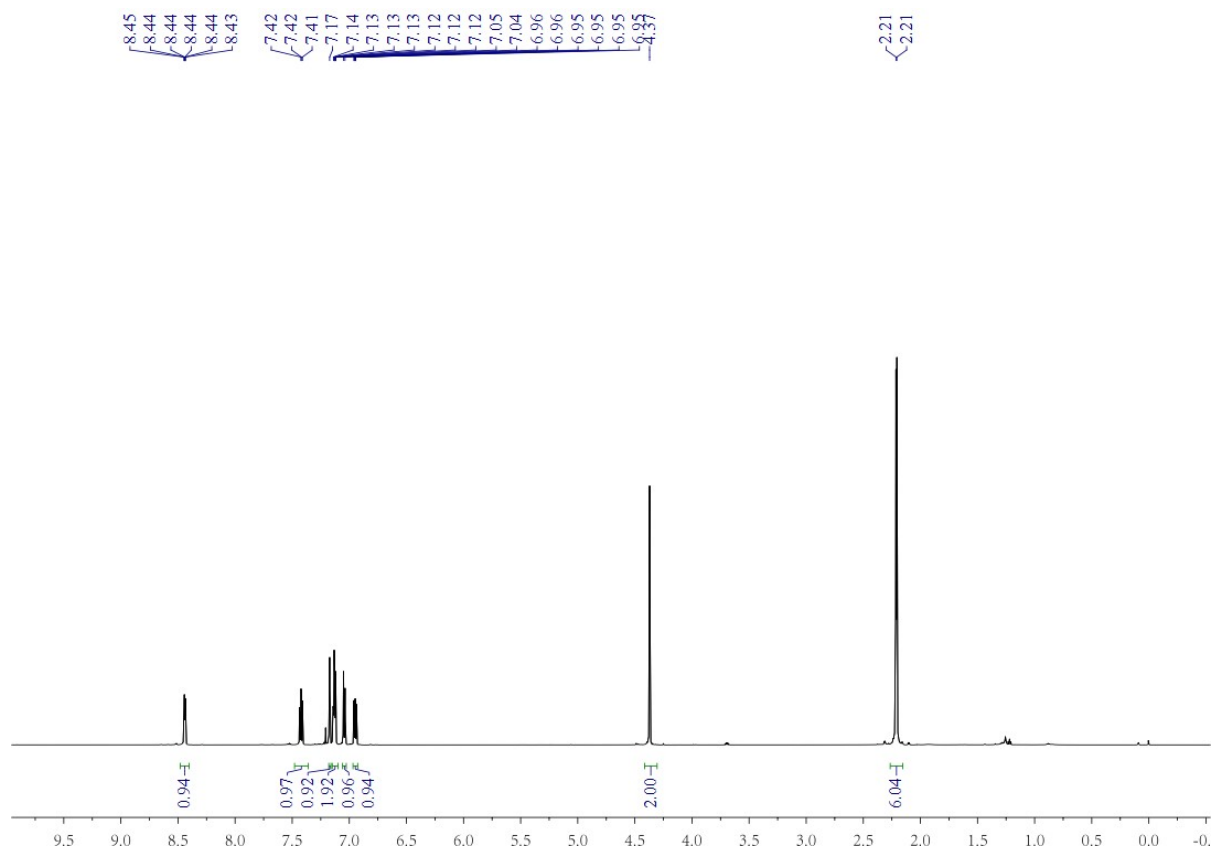


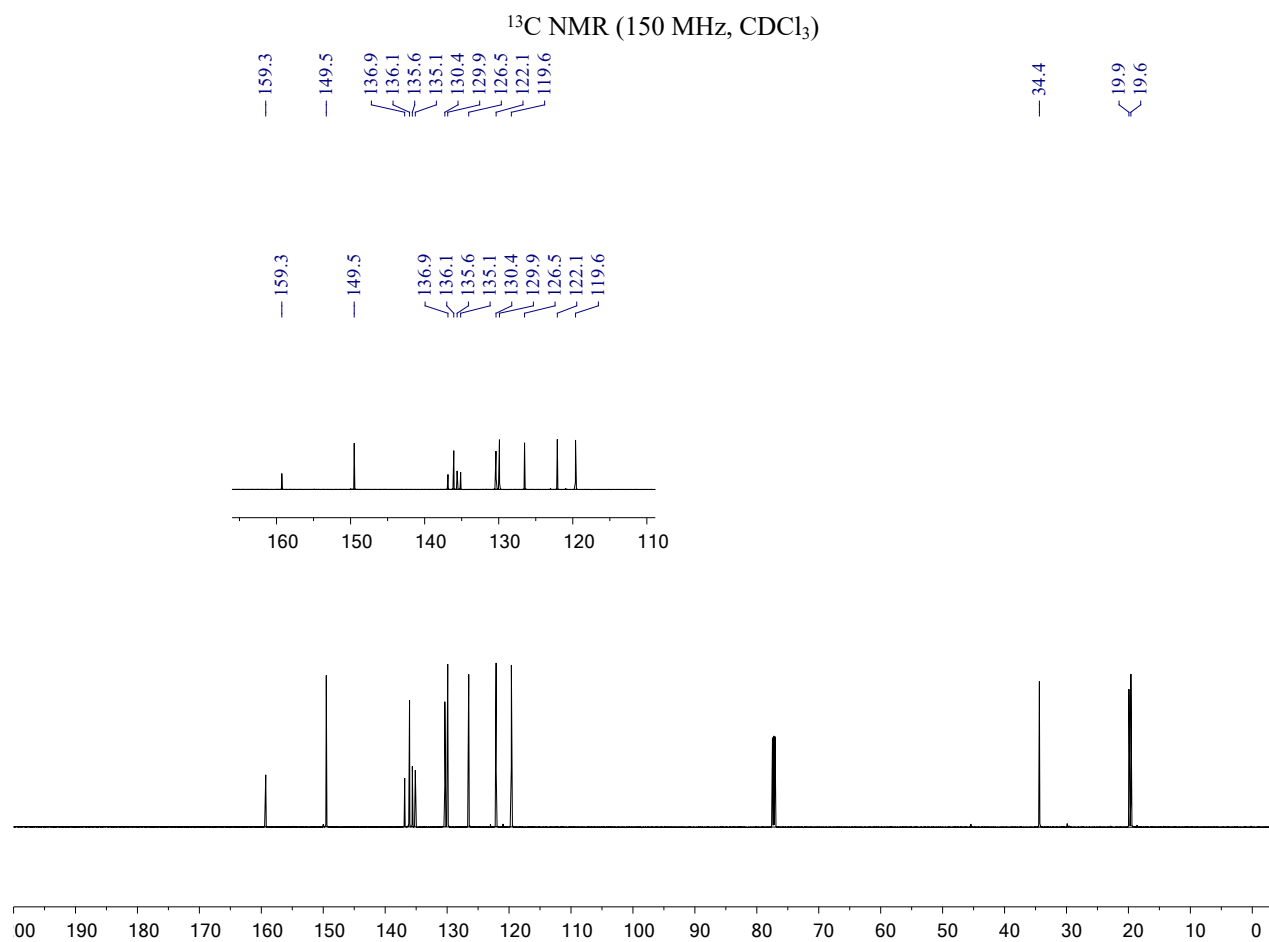
^{13}C NMR (150 MHz, CDCl_3)

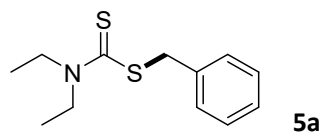




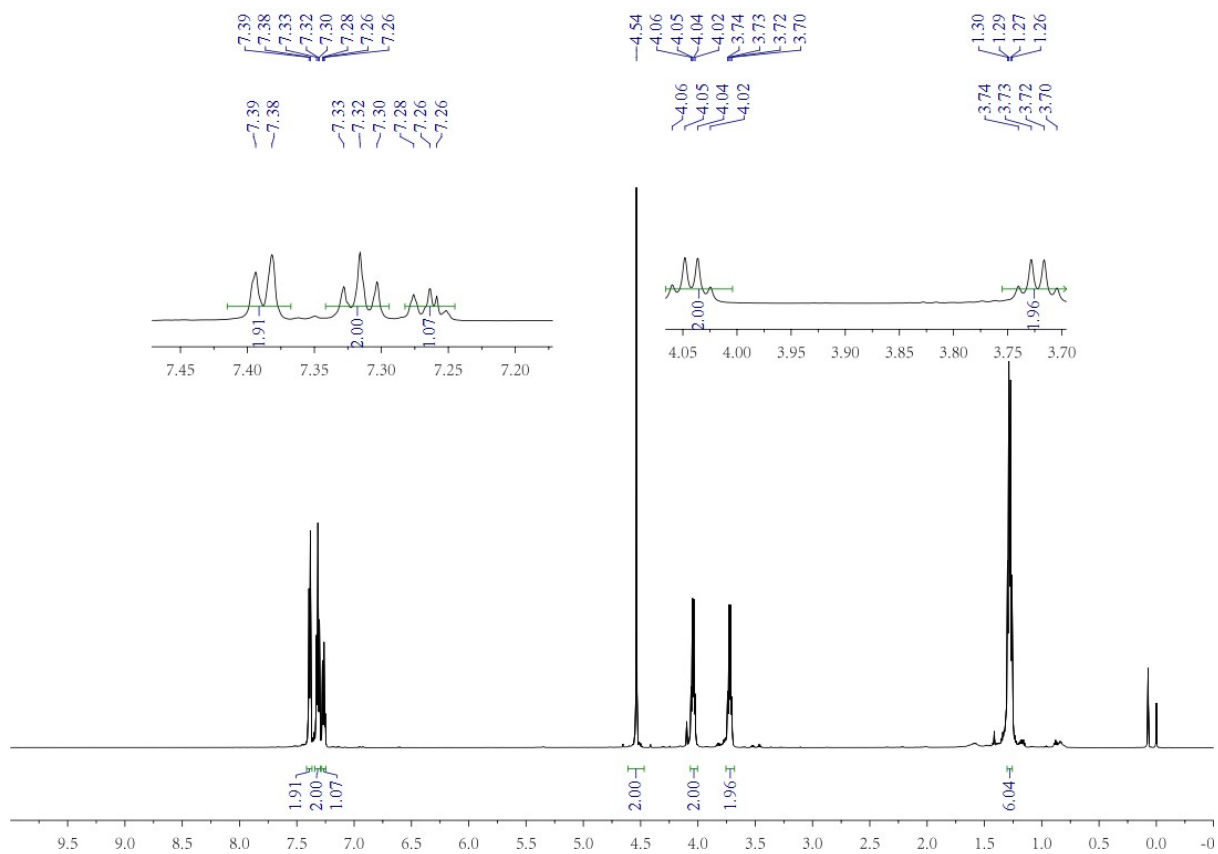
^1H NMR (600 MHz, CDCl_3)



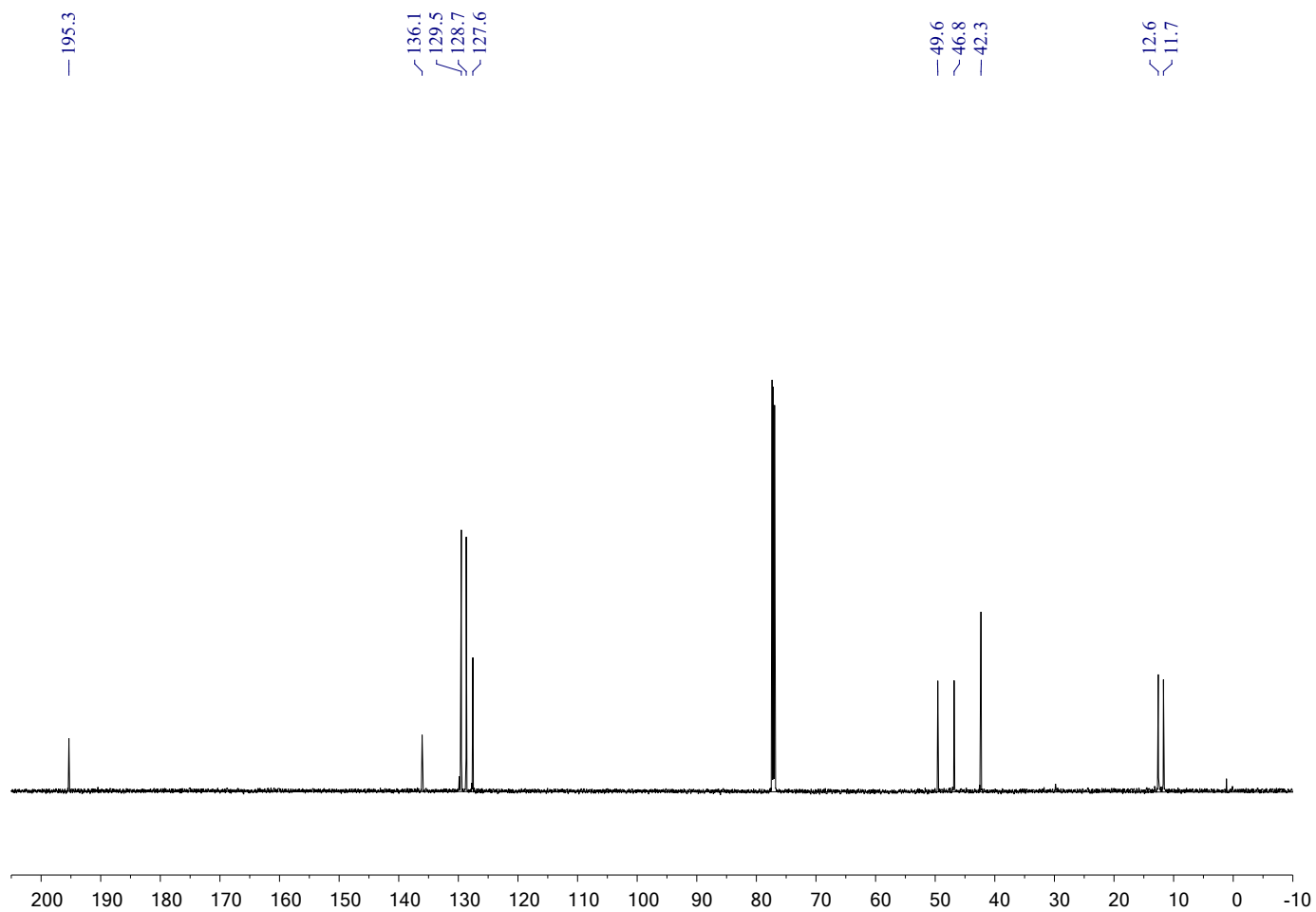


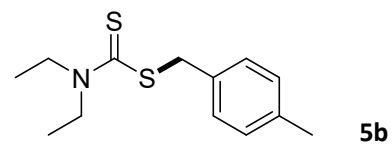


^1H NMR (600 MHz, CDCl_3)

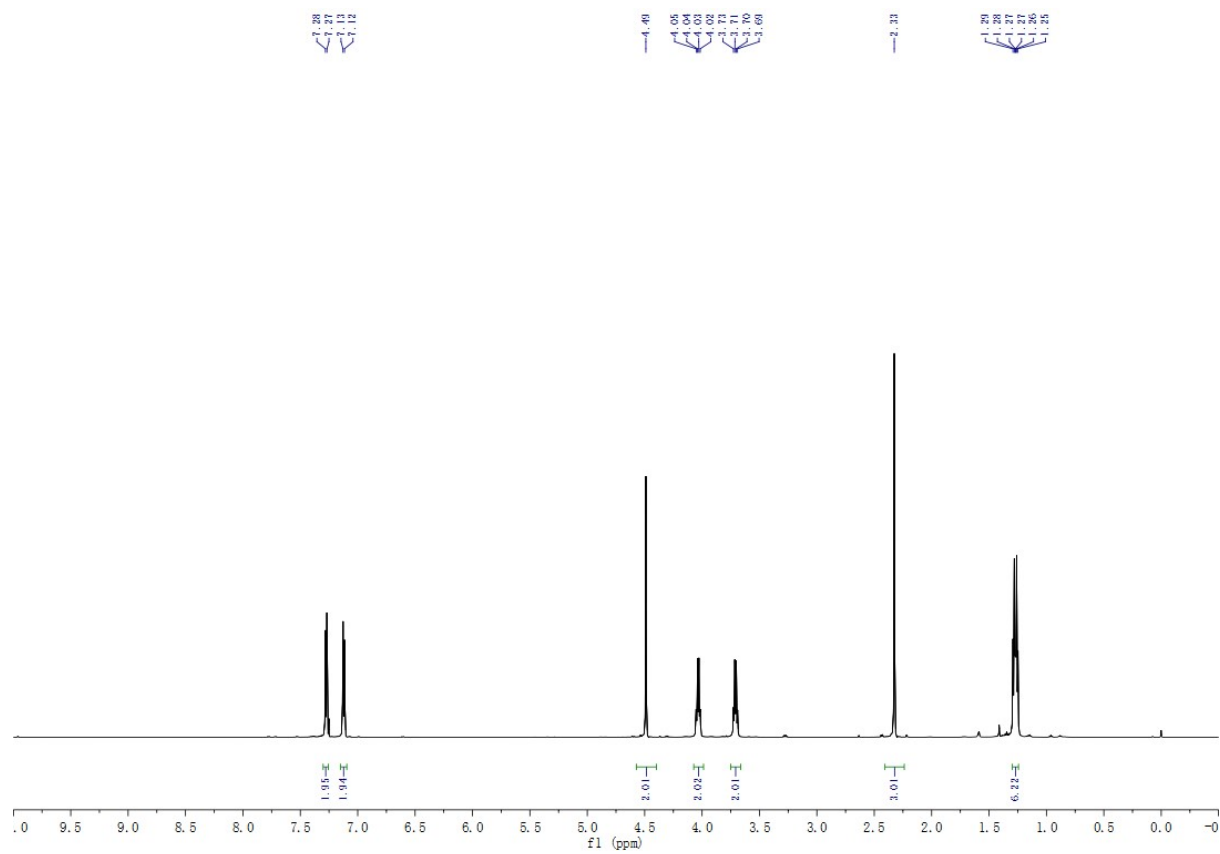


^{13}C NMR (150 MHz, CDCl_3)

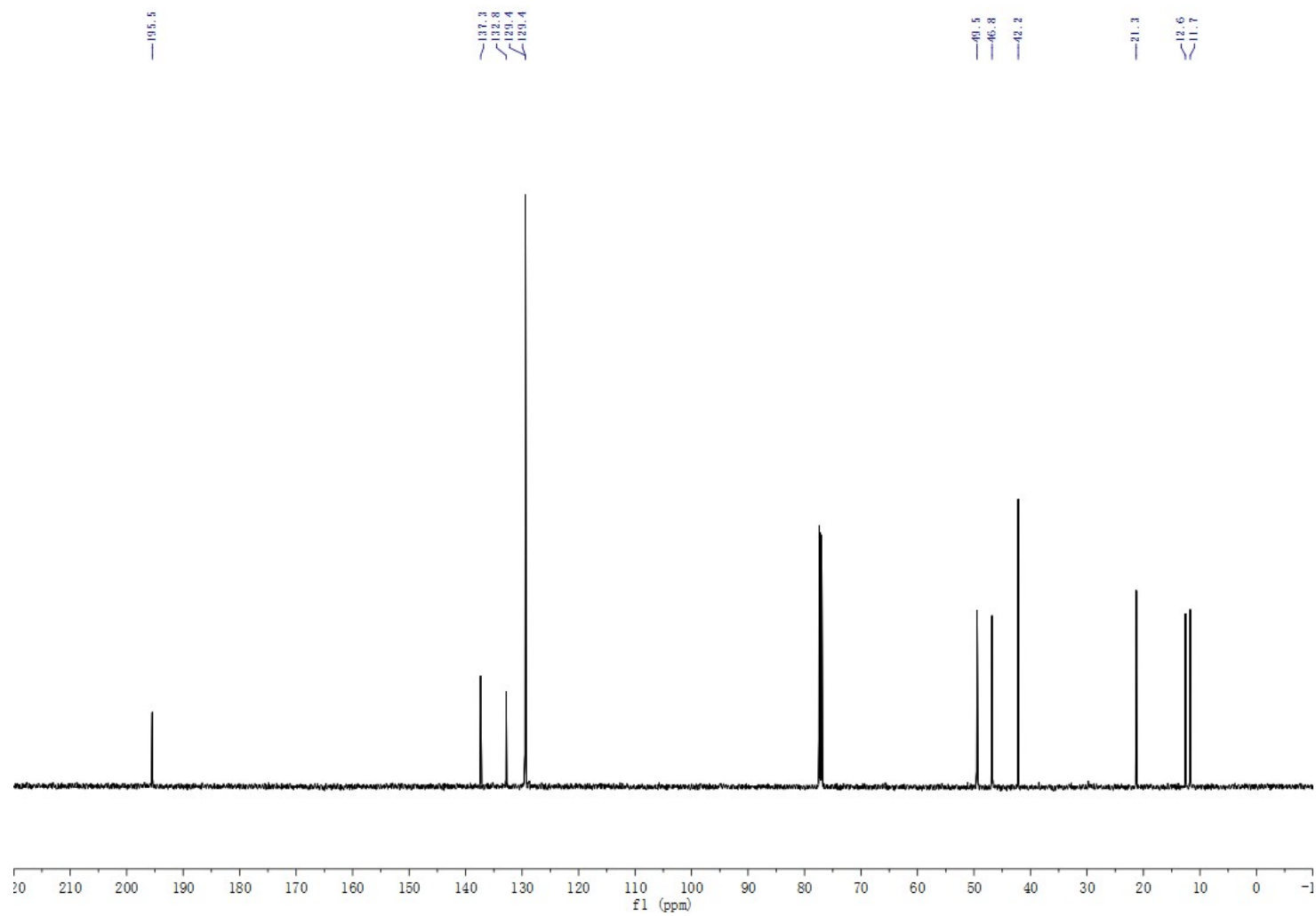


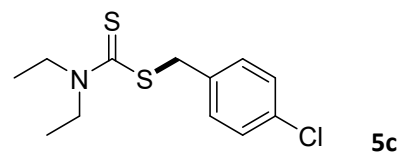


^1H NMR (600 MHz, CDCl_3)

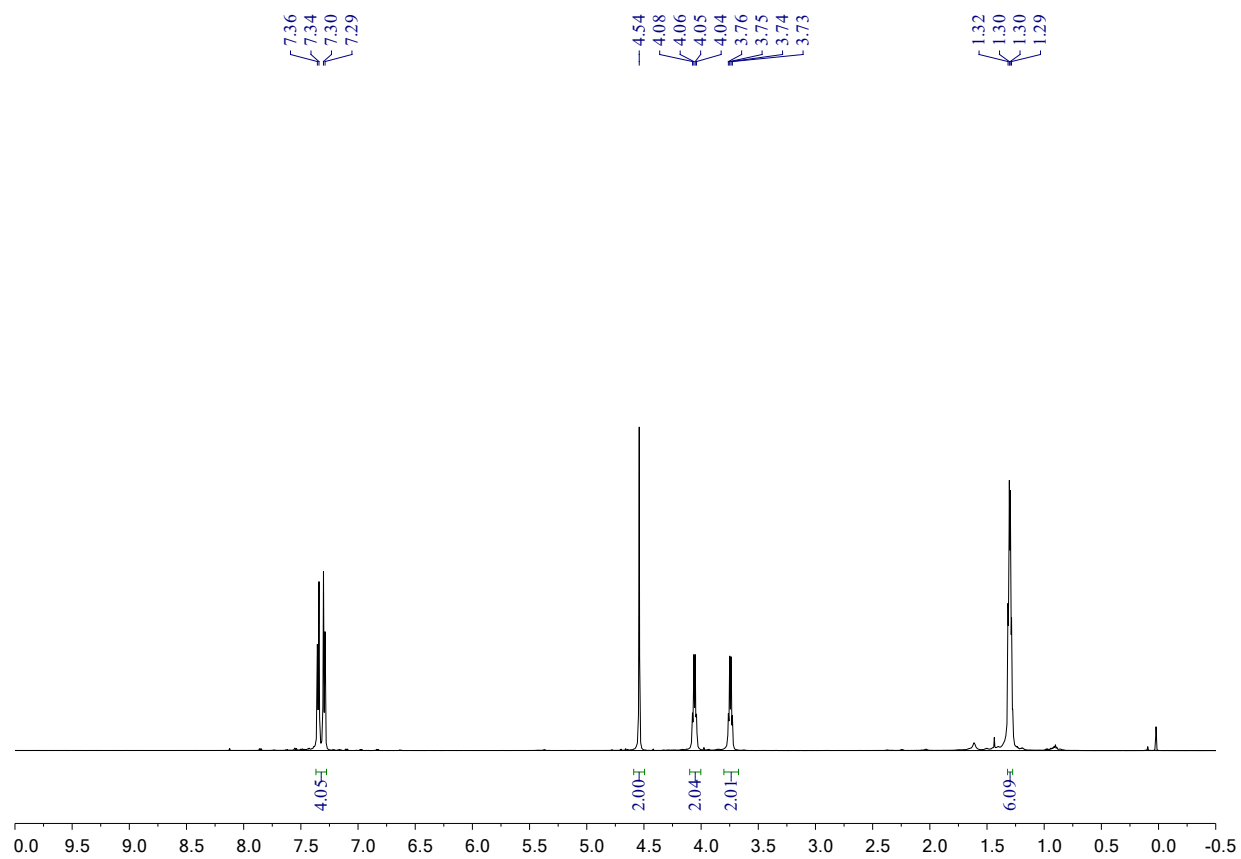


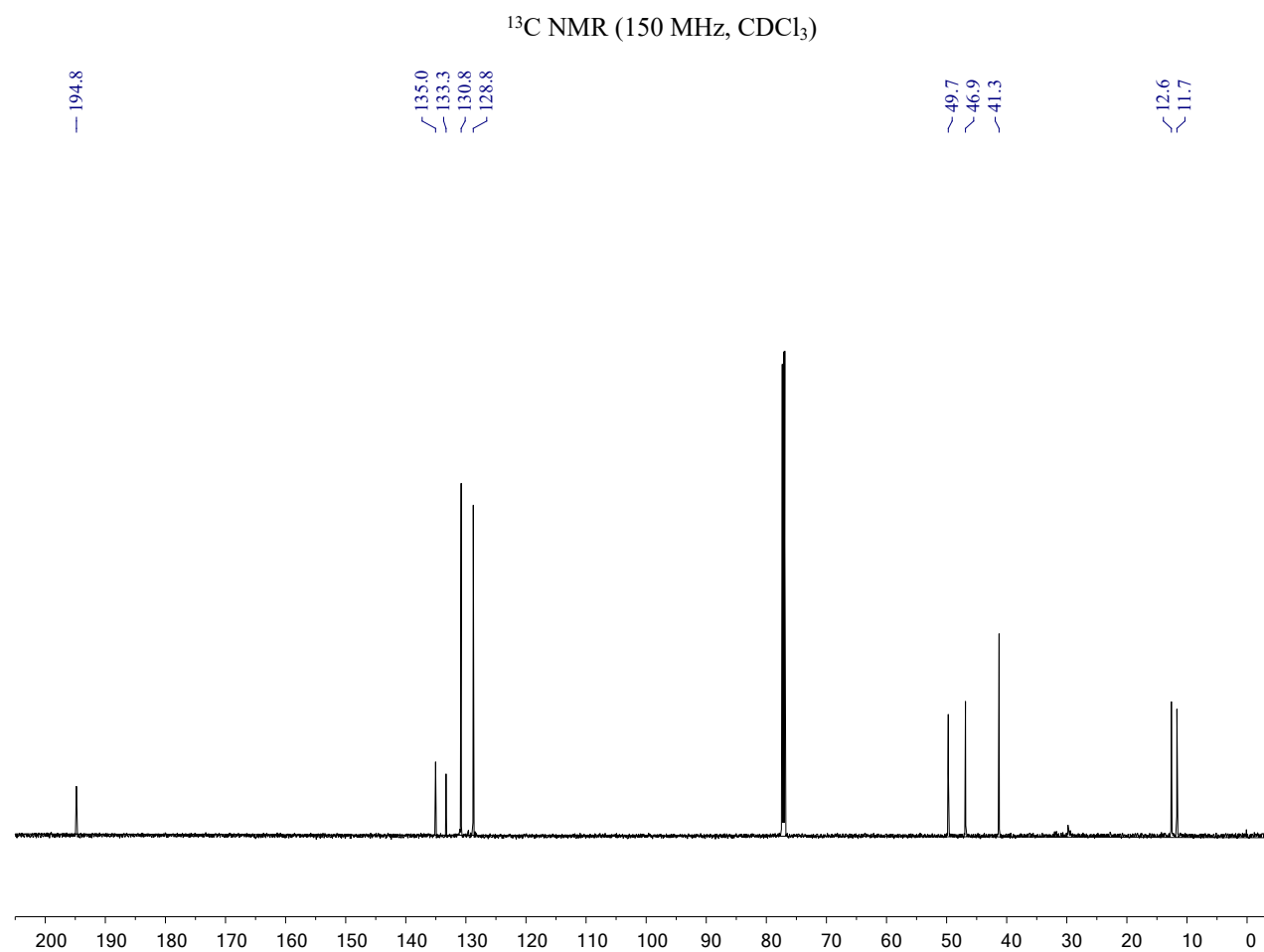
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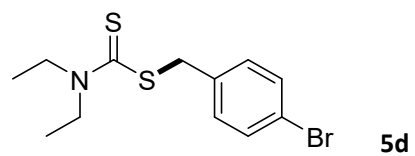




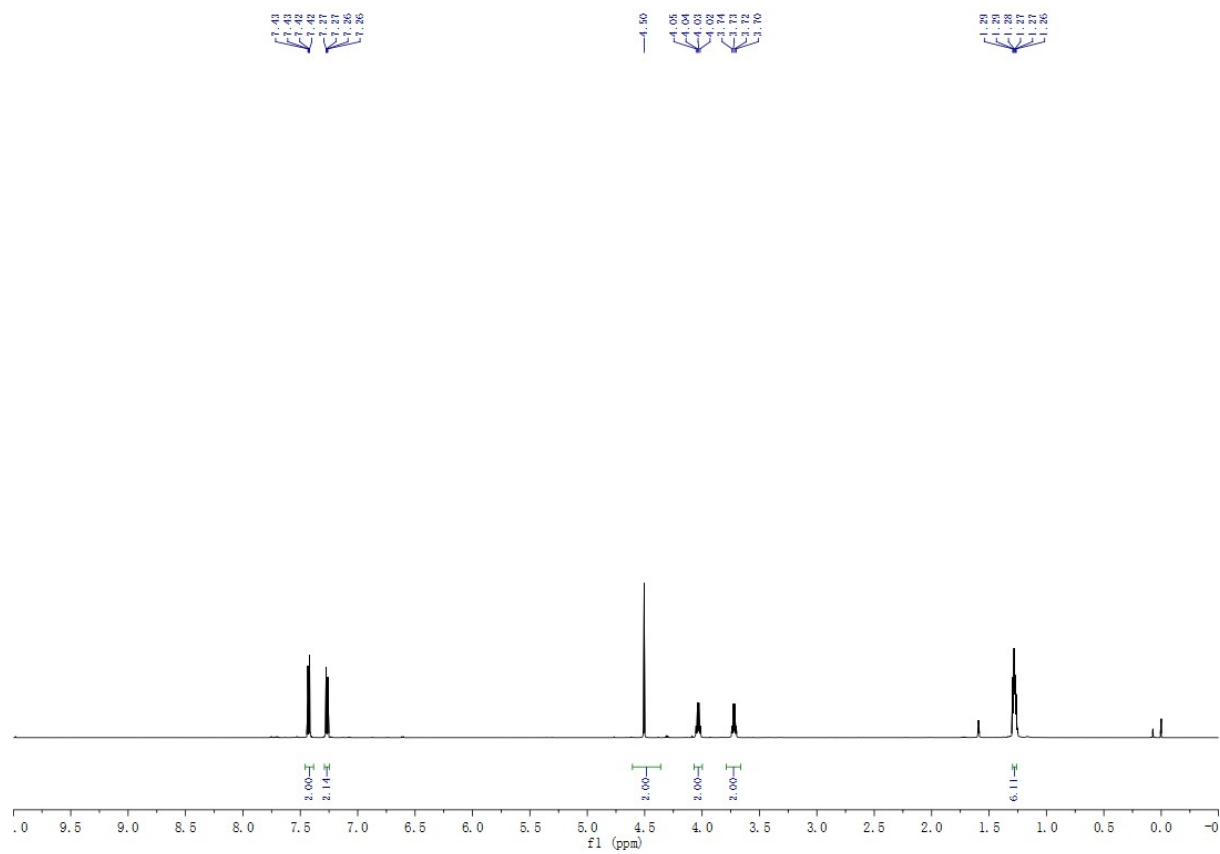
^1H NMR (600 MHz, CDCl_3)



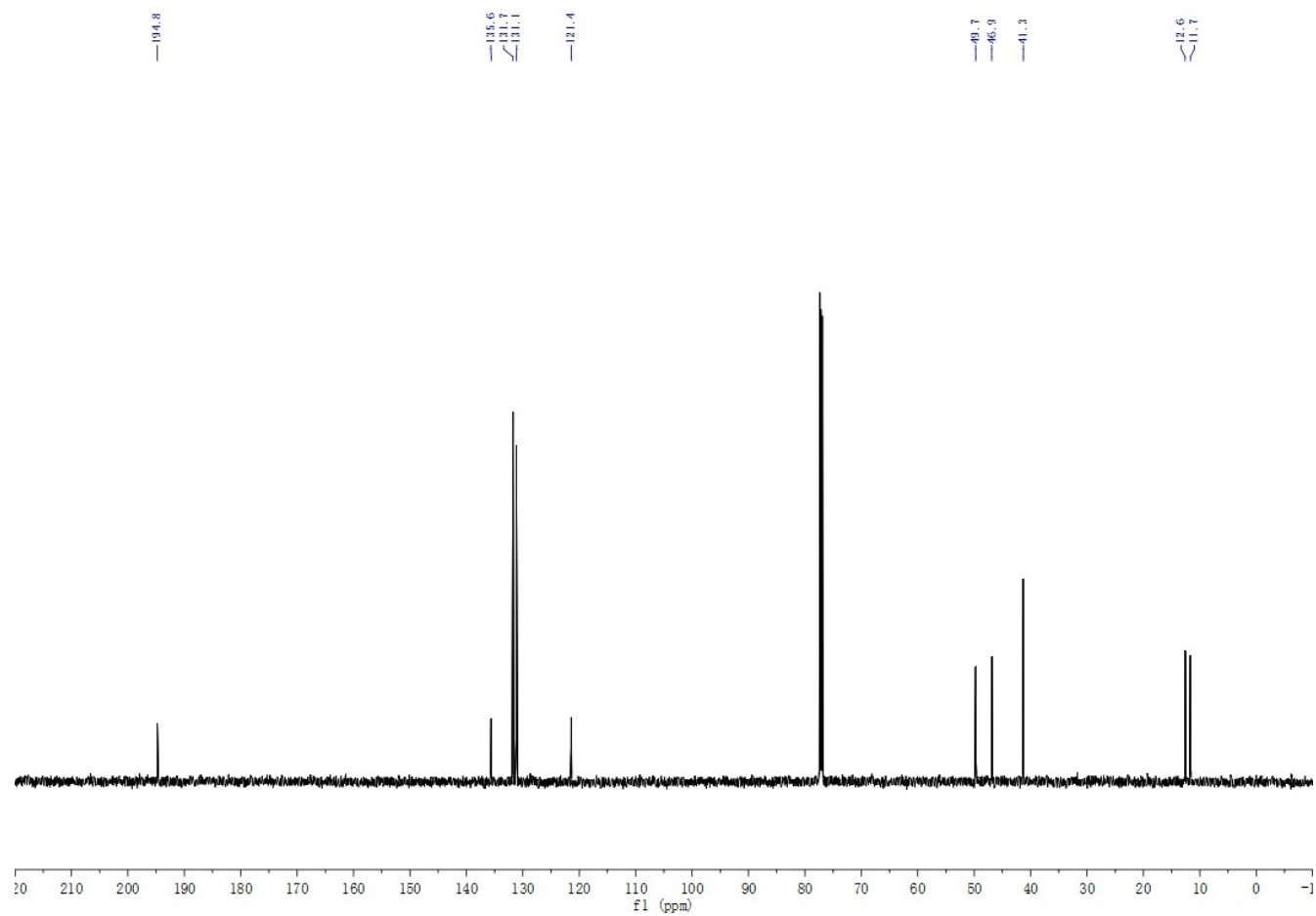


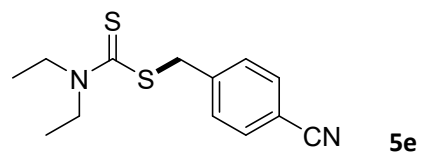


^1H NMR (600 MHz, CDCl_3)

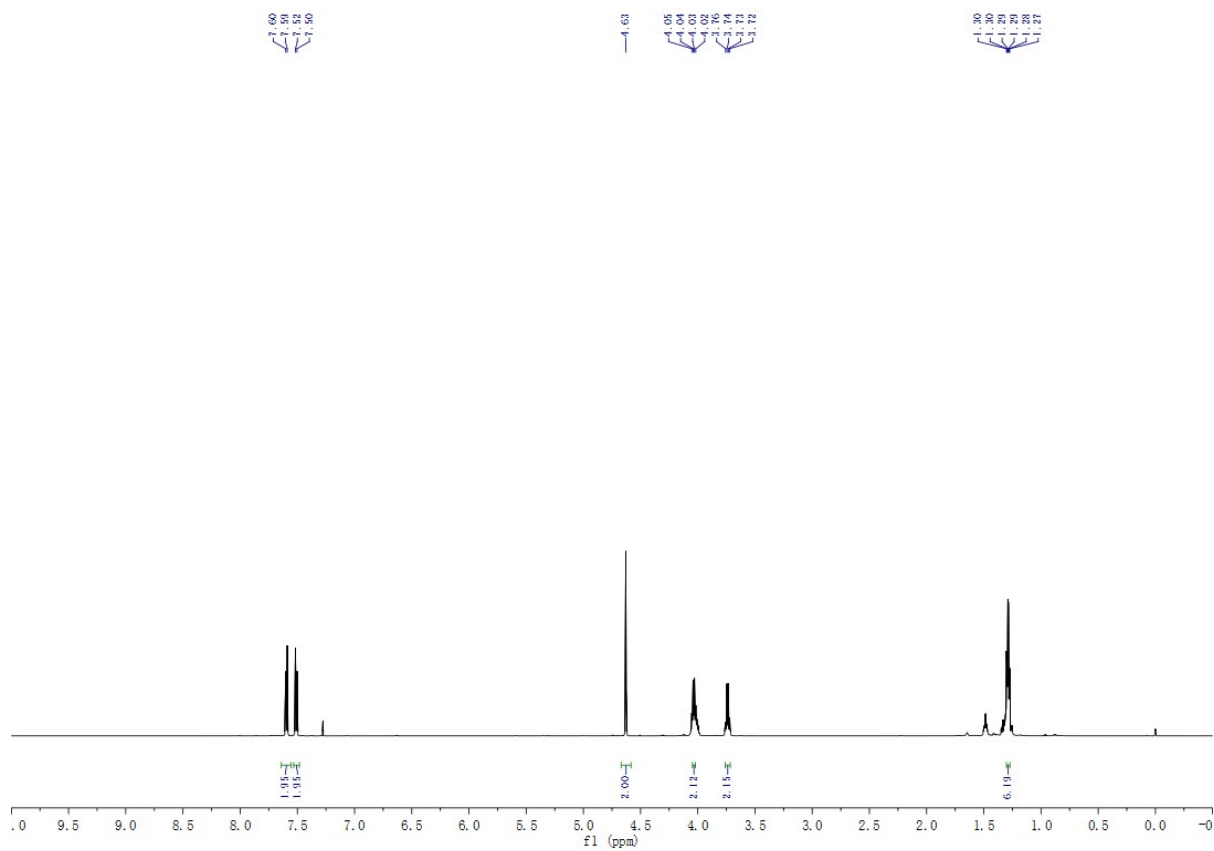


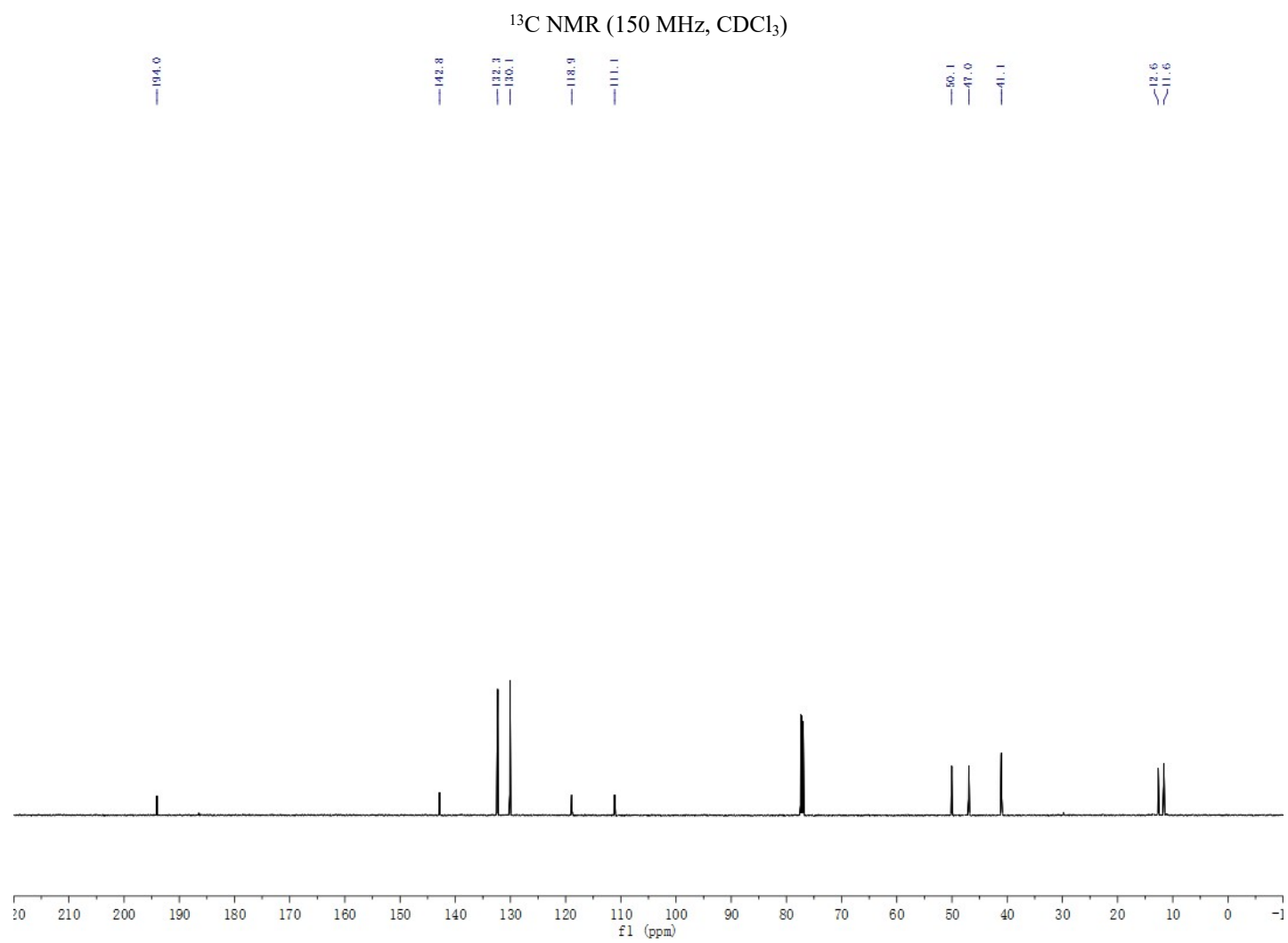
^{13}C NMR (150 MHz, CDCl_3)

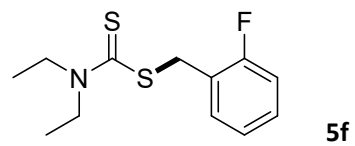




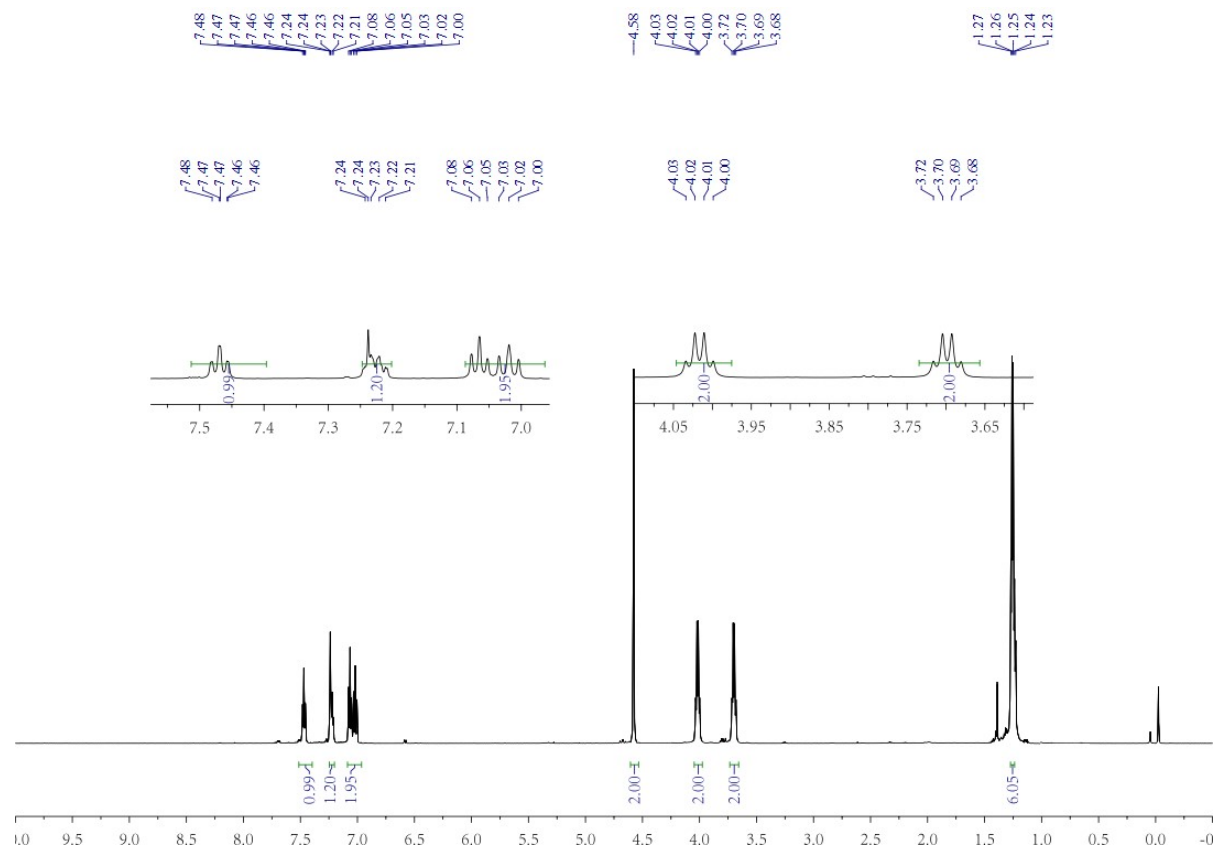
^1H NMR (600 MHz, CDCl_3)

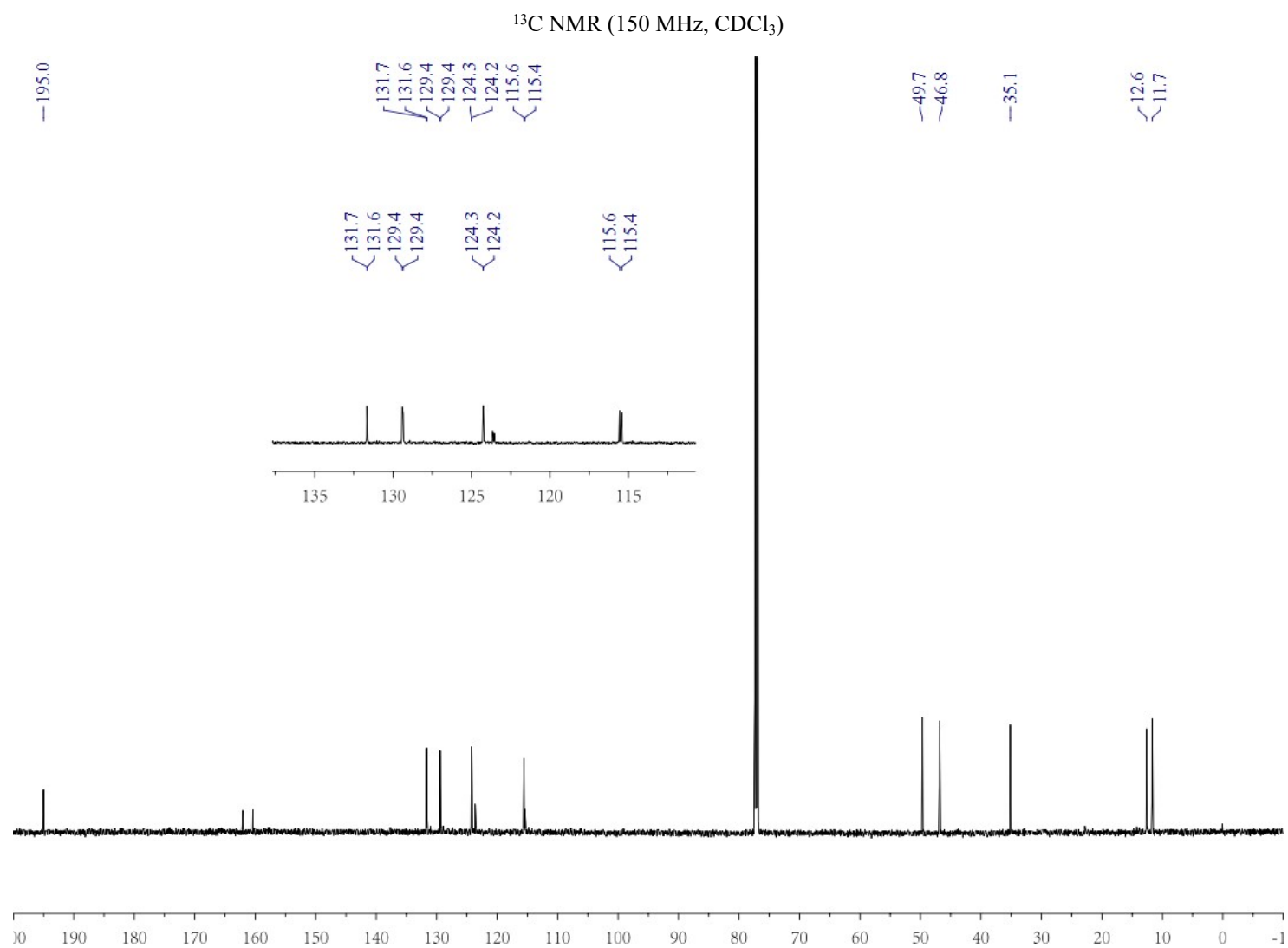


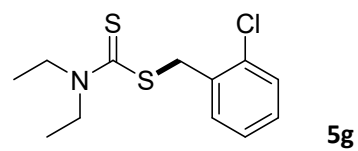




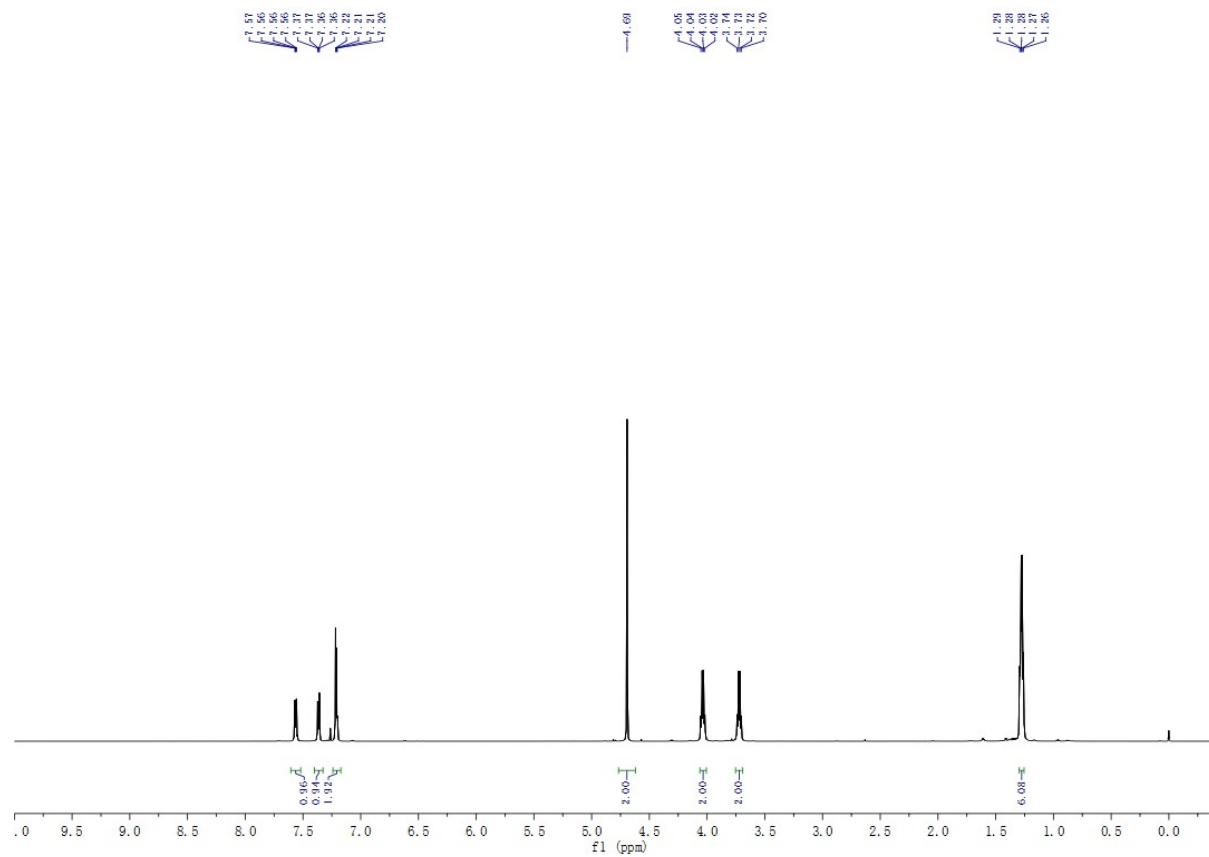
^1H NMR (600 MHz, CDCl_3)



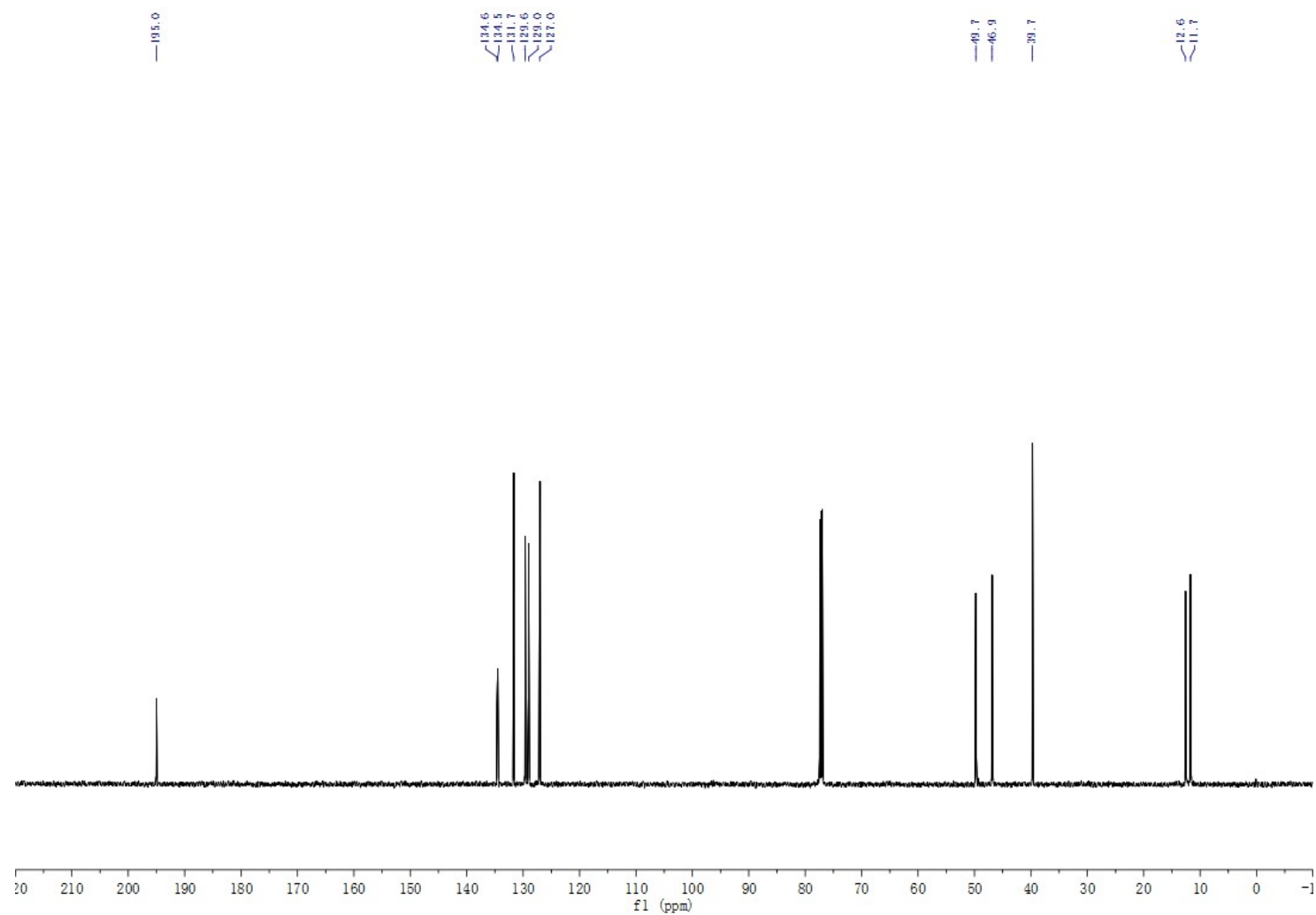


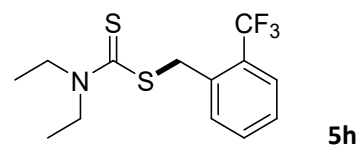


^1H NMR (600 MHz, CDCl_3)

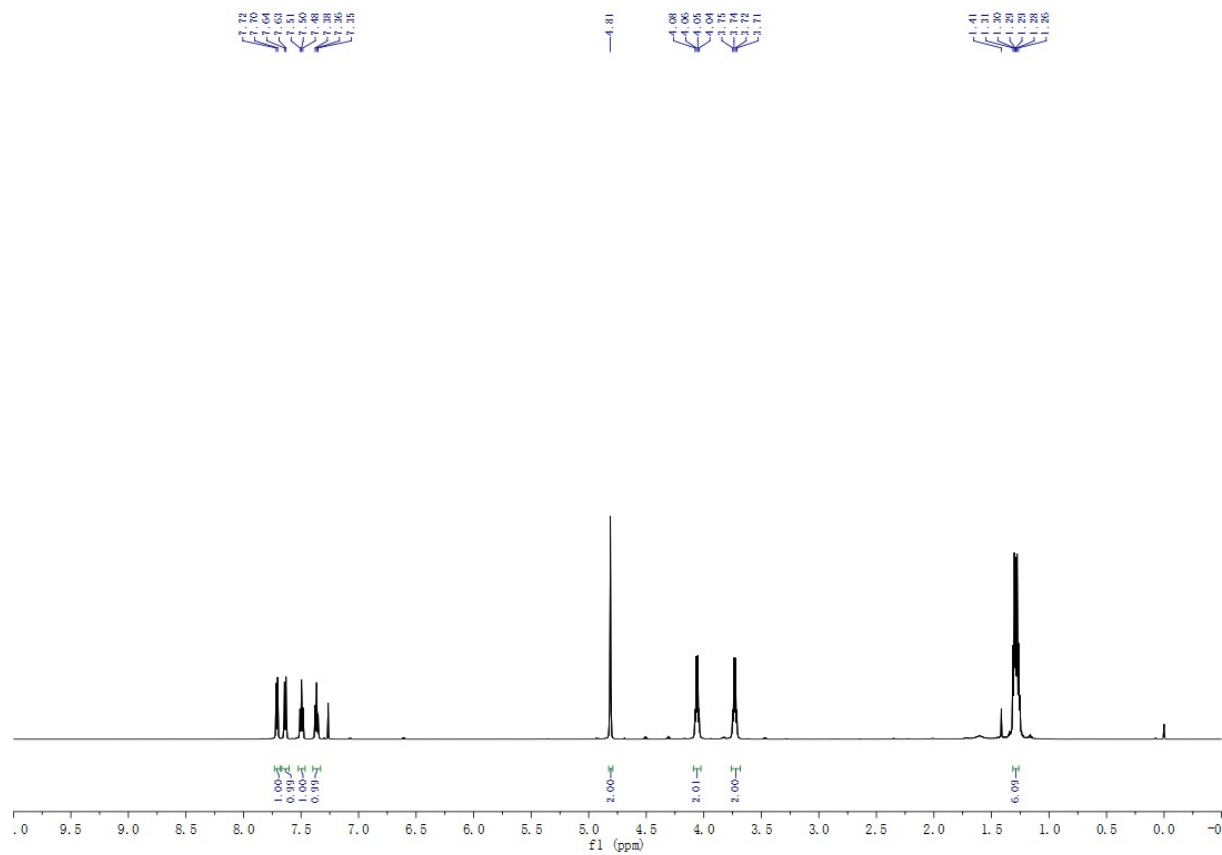


^{13}C NMR (150 MHz, CDCl_3)

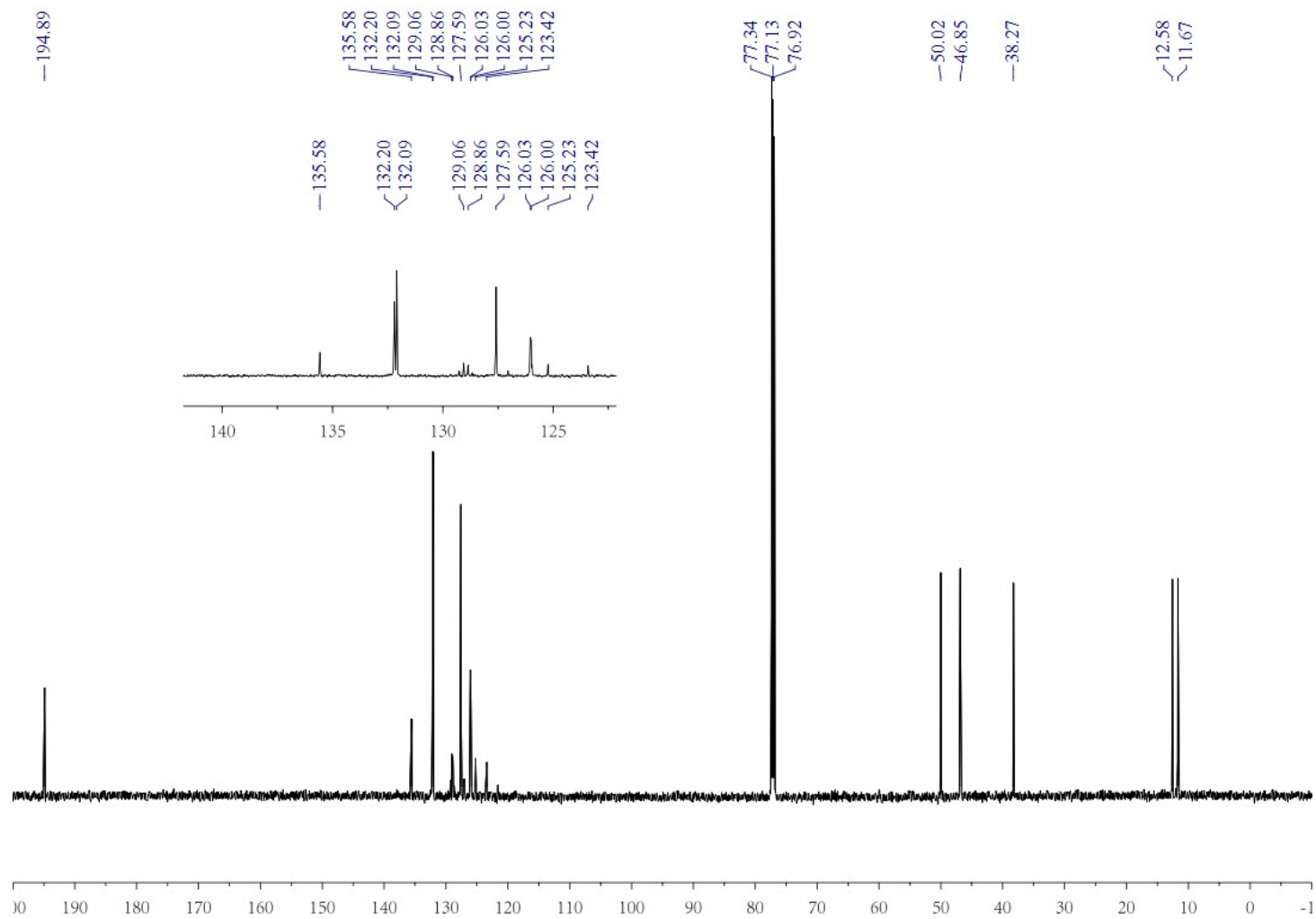




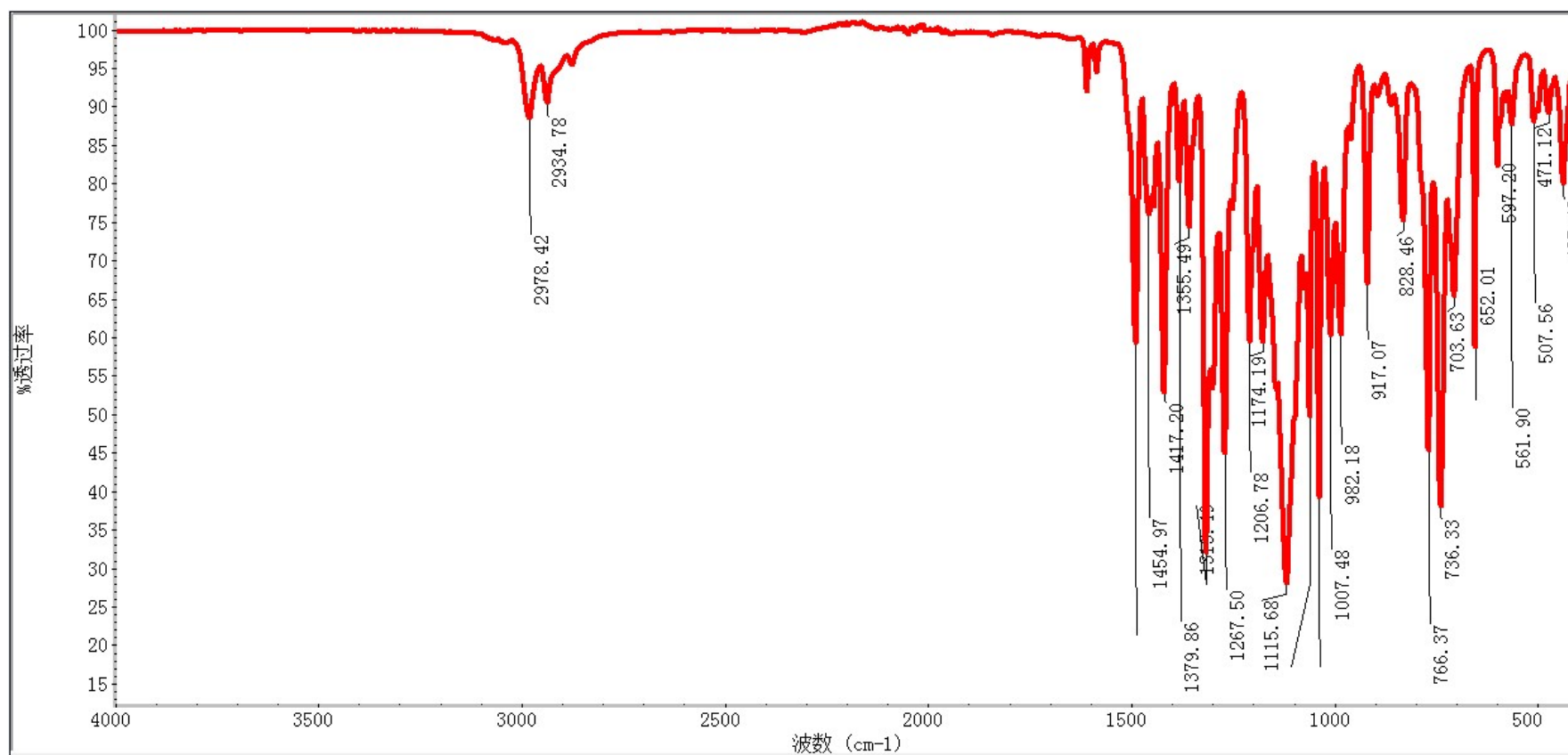
^1H NMR (600 MHz, CDCl_3)

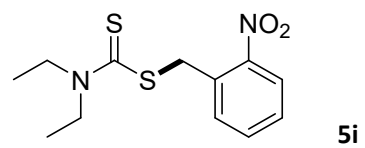


^{13}C NMR (150 MHz, CDCl_3)

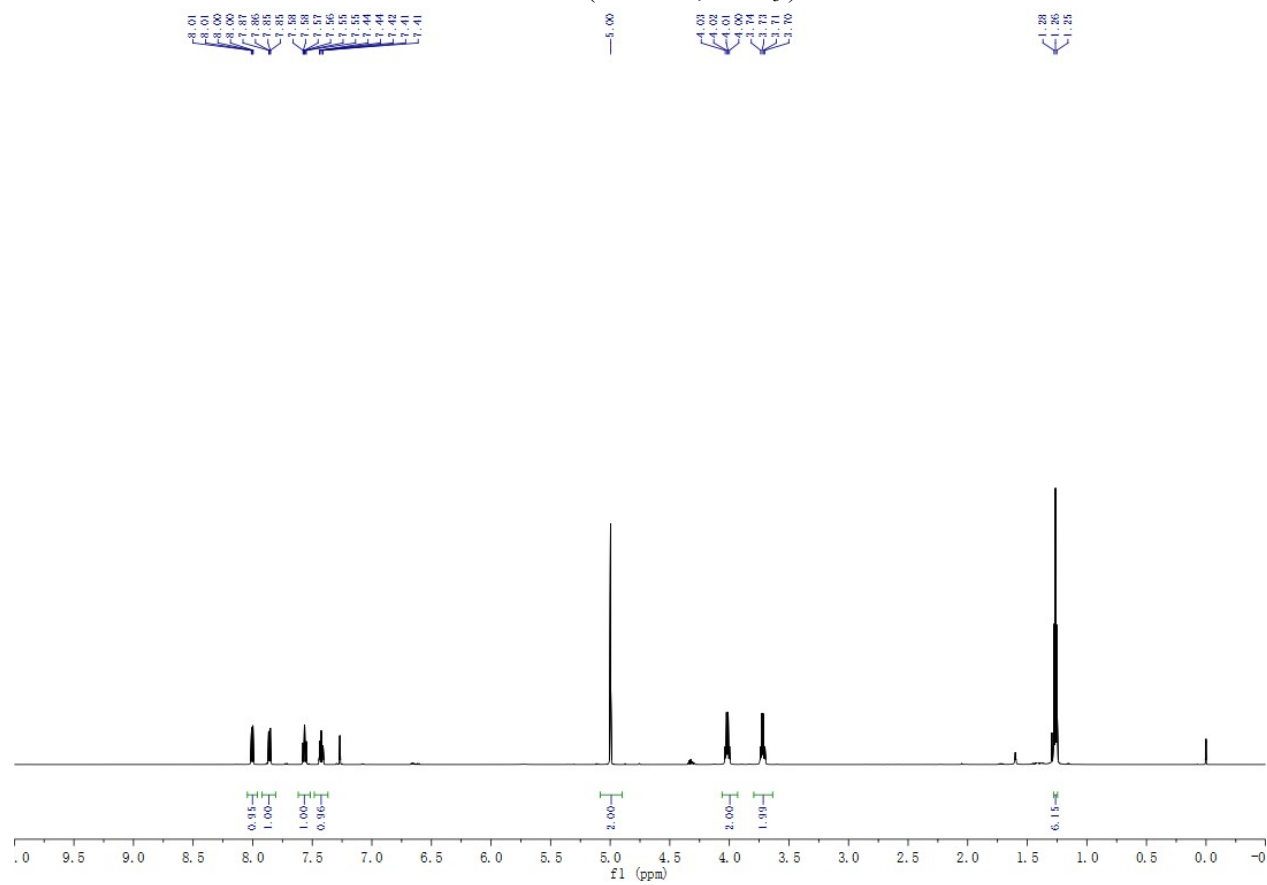


IR

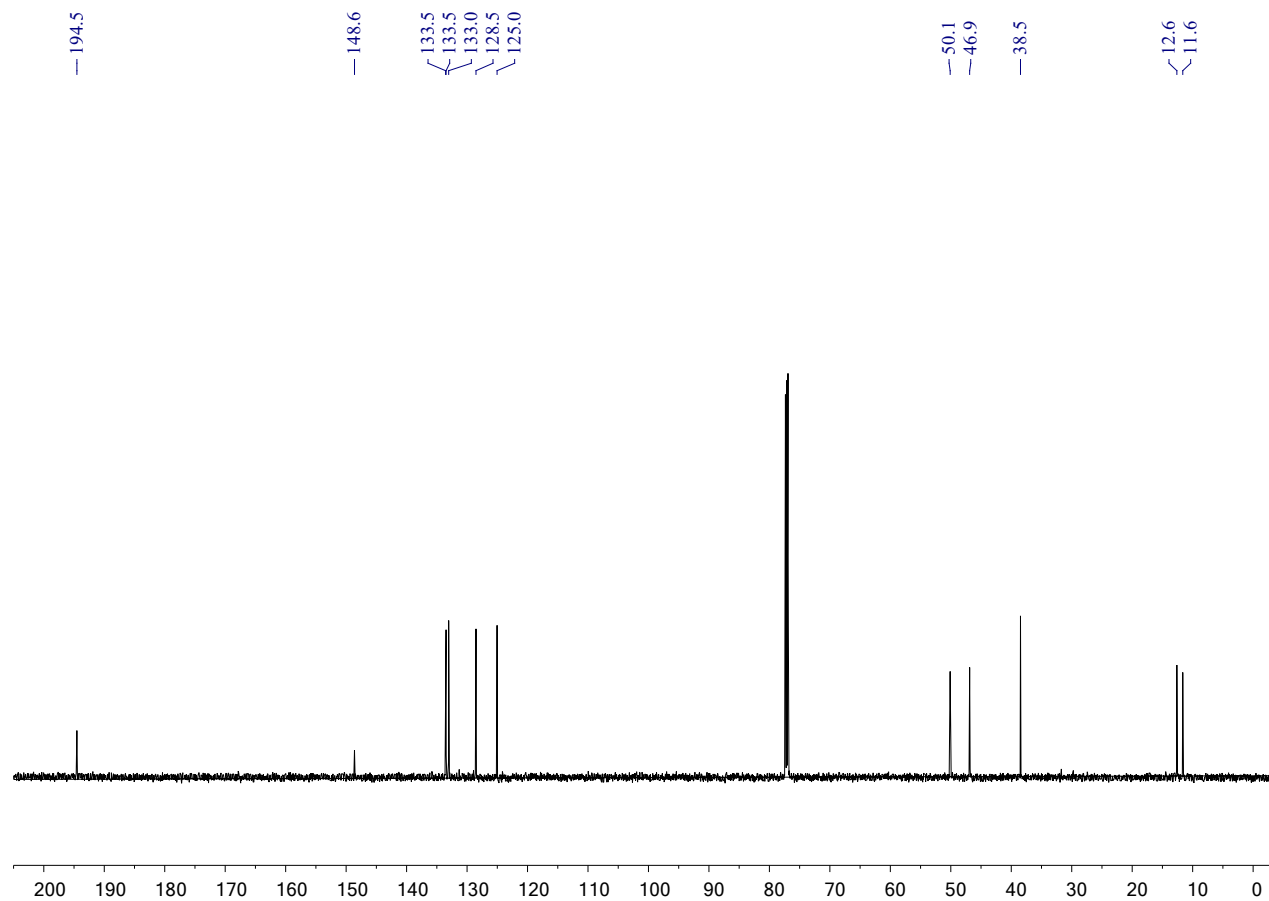


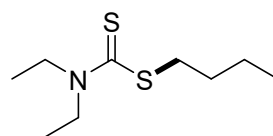


^1H NMR (600 MHz, CDCl_3)



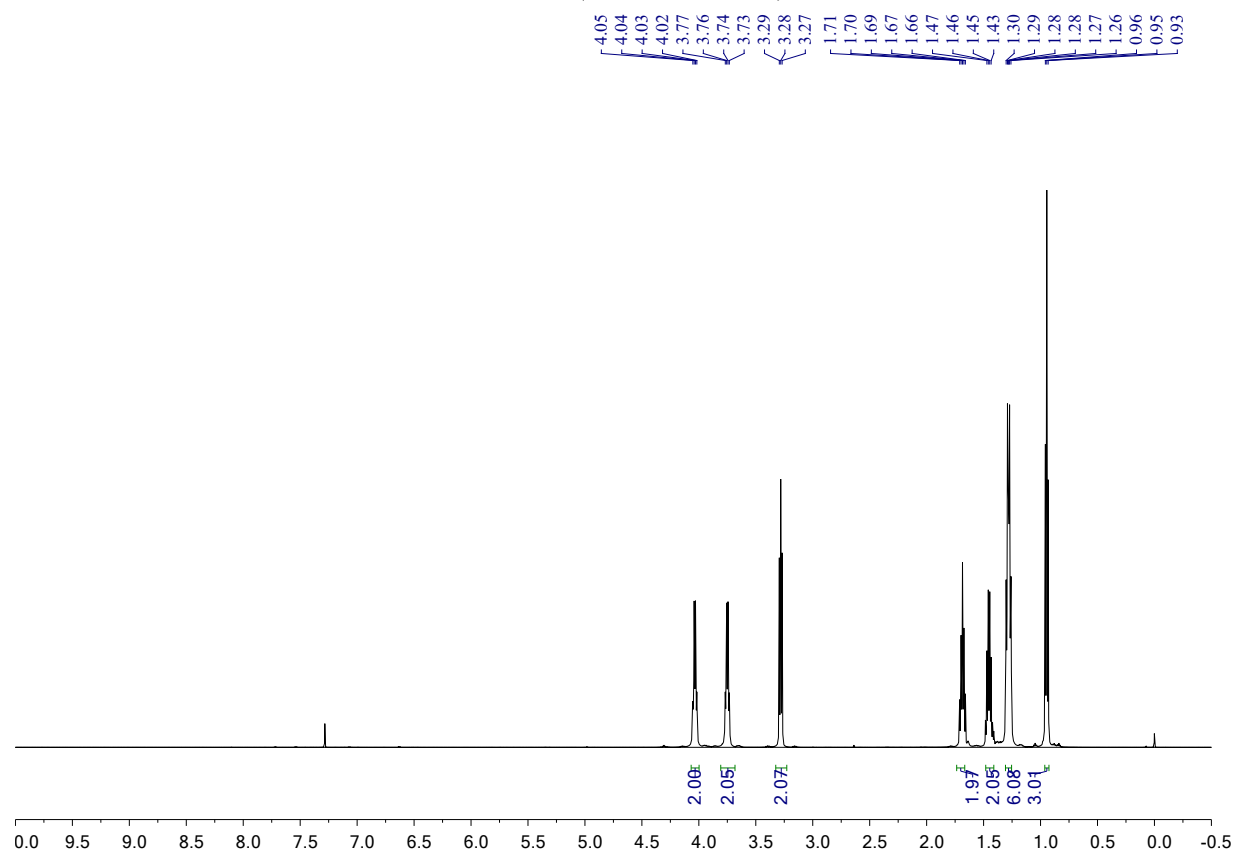
^{13}C NMR (150 MHz, CDCl_3)





5j

^1H NMR (600 MHz, CDCl_3)



^{13}C NMR (150 MHz, CDCl_3)

