

Electronic Supplementary Information

Copper-Catalyzed C-C Direct Cross-Coupling: An Efficient Approach to Phenyl-2-(phenylthiophenyl)-methanones

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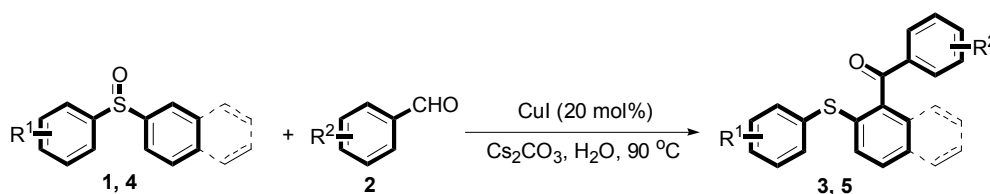
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Experimental Details

General Information

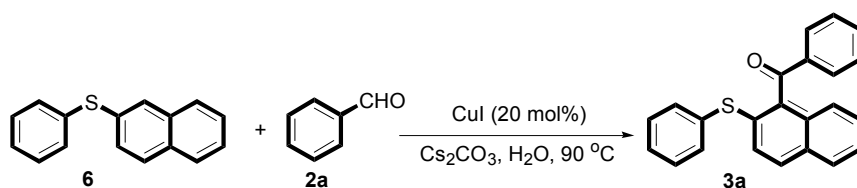
All reagents used in the experiment were obtained from commercial sources and used without further purification. Unless otherwise noted, all reactions were carried out at N₂ atmosphere. Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. All NMR spectra were recorded on Bruker AVANCE III-400 spectrometer at 400 MHz and 100 MHz for ¹H and ¹³C NMR in CDCl₃, respectively. The NMR chemical shift was reported in ppm relative to 7.26 and 77 ppm of CDCl₃ as the standards of ¹H and ¹³C NMR, respectively. The ¹H NMR spectra were reported in delta (δ) units, parts per million (ppm) downfield from the internal standard. Coupling constants are reported in Hertz (Hz). Mass spectras were performed on a Bruker Esquire 3000plus mass spectrometer equipped with ESI interface and ion trap analyzer. The ESI-HRMS were tested on Bruker 7-tesla FT-ICR MS equipped with an electrospray source.

General procedure for preparation of 3 and 5



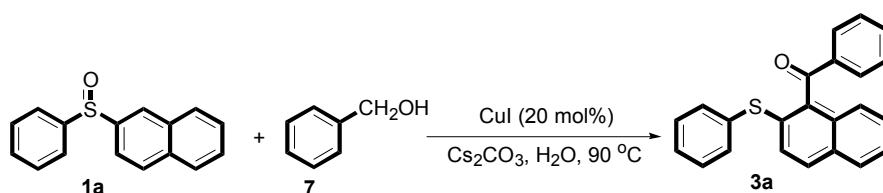
A mixture of 2-benzenesulfinylnaphthalene **1a** (90.7 mg, 0.36 mmol), benzaldehyde **2a** (69 mg, 0.3 mmol), CuI (38.0 mg, 20 mol%) and Cs₂CO₃ (326.5 mg, 2 equiv) in H₂O (4 mL) was stirred in N₂ at 90 °C for 10 h. After completion of the reaction, the mixture was quenched with saturated salt water (10 mL), and then the solution was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and dried by sodium sulfate. The pure product phenyl-(2-phenylsulfanylnaphthalen-1-yl)-methanone **3a** (83.7 mg, 82% yield) was obtained by flash column chromatography on silica gel, washed by cyclohexane/ethyl acetate = 4:1.

General reaction procedure for 6 and 2a



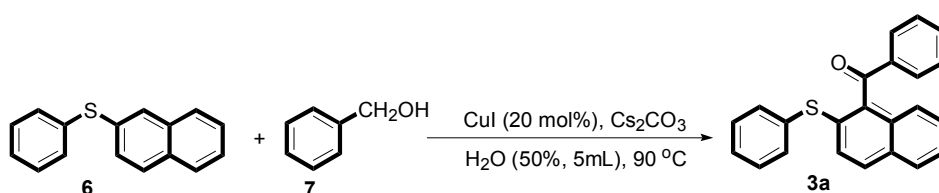
A mixture of 2-phenylsulfanylnaphthalene **6** (85.1 mg, 0.36 mmol), benzaldehyde **2a** (69 mg, 0.3 mmol), CuI (38.0 mg, 20 mol%) and Cs₂CO₃ (326.5 mg, 2 equiv) in H₂O (4 mL) was stirred in N₂ at 90 °C for 10 h. After completion of the reaction, the mixture was quenched with saturated salt water (10 mL), and then the solution was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and dried by sodium sulfate. No product phenyl-(2-phenylsulfanylnaphthalen-1-yl)-methanone **3a** was obtained by flash column chromatography on silica gel, washed by cyclohexane/ethyl acetate = 4:1.

General reaction procedure for 1a and 7



A mixture of 2-benzenesulfinylnaphthalene **1a** (90.7 mg, 0.36 mmol), phenyl-methanol **7** (32.4 mg, 0.3 mmol), CuI (38.0 mg, 20 mol%) and Cs₂CO₃ (326.5 mg, 2 equiv) in H₂O (4 mL) was stirred in N₂ at 90 °C for 10 h. After completion of the reaction, the mixture was quenched with saturated salt water (10 mL), and then the solution was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and dried by sodium sulfate. No product phenyl-(2-phenylsulfanylnaphthalen-1-yl)-methanone **3a** was obtained by flash column chromatography on silica gel, washed by cyclohexane/ethyl acetate = 4:1.

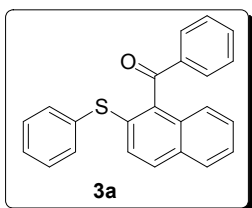
General reaction procedure for 6 and 7



A mixture of 2-phenylsulfanylnaphthalene **6** (85.1 mg, 0.36 mmol), phenyl-methanol **7**, CuI (38.0

mg, 20 mol%) and Cs₂CO₃ (326.5 mg, 2 equiv) in H₂O₂ (50%, 5 mL) was stirred in N₂ at 90 °C for 10 h. After completion of the reaction, the mixture was quenched with saturated sodium sulfite water (10 mL), and then the solution was extracted with ethyl acetate (3 × 10 mL). The organic layers were combined and dried by sodium sulfate. The pure product phenyl-(2-phenylsulfanylnaphthalen-1-yl)-methanone **3a** (68.4 mg, 67% yield) was obtained by flash column chromatography on silica gel, washed by cyclohexane/ethyl acetate = 4:1.

Analytical Datas

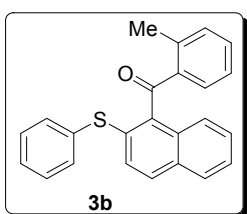


Phenyl-(2-phenylsulfanylnaphthalen-1-yl)-methanone (3a): (83.7 mg 82%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 127.6-129.6 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.56-8.45 (m, 1 H), 8.06 (d, *J* = 8.0 Hz, 1 H), 8.01-7.92 (m, 1 H), 7.79 (d, *J* = 7.5 Hz, 2 H), 7.64-7.55 (m, 2 H), 7.55-7.48 (m, 2 H), 7.37 (m, 2 H), 7.13-7.06 (m, 2 H), 7.06-6.95 (m, 3 H);

¹³C NMR (100 MHz, CDCl₃): δ 196.8, 144.8, 137.3, 137.2, 134.4, 134.3, 133.3, 130.6, 129.7, 128.71, 128.66, 128.4, 128.1, 127.3, 127.1, 126.4, 126.3, 125.5, 124.2;

ESI-HRMS *m/z*: Calcd for C₂₃H₁₆ONaS [M+Na]⁺ 363.0820, found 363.0817.

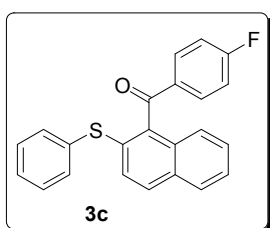


(2-Phenylsulfanylnaphthalen-1-yl)-o-tolylmethanone (3b): (84.0 mg 79%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 114.3.4-115.2 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.45 (d, *J* = 8.5 Hz, 1 H), 8.06 (d, *J* = 8.4 Hz, 1 H), 7.95 (d, *J* = 8.5 Hz, 1 H), 7.65-7.51 (m, 3 H), 7.34-7.15 (m, 3 H), 7.11-6.95 (m, 4 H), 6.90 (d, *J* = 7.6 Hz, 2 H), 2.66 (s, 3 H);

¹³C NMR (100 MHz, CDCl₃): δ 199.2, 146.1, 139.7, 137.3, 137.2, 134.6, 134.4, 131.74, 131.66, 131.64, 130.6, 128.63, 128.61, 128.0, 127.3, 126.8, 126.5, 126.3, 125.3, 125.1, 124.8, 21.5;

ESI-HRMS *m/z*: Calcd for C₂₄H₁₈ONaS [M+Na]⁺ 377.0976, found 377.0975.



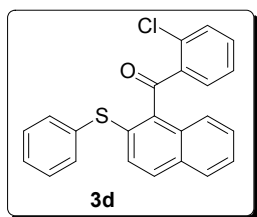
(4-Fluorophenyl)-(2-phenylsulfanylnaphthalen-1-yl)-methanone (3c): (92.5 mg 86%,

cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 87.5-89.2 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.54-8.44 (m, 1 H), 8.06 (d, *J* = 8.4 Hz, 1 H), 8.00-7.92 (m, 1 H), 7.80-7.72 (m, 2 H), 7.64-7.55 (m, 2 H), 7.49 (d, *J* = 8.4 Hz, 1 H), 7.12-6.97 (m, 5 H), 6.97-6.91 (m, 2 H);

¹³C NMR (100 MHz, CDCl₃): δ 195.3, 165.8, 144.4, 137.2, 134.5, 133.7, 132.4, 130.8, 128.8, 128.7, 128.2, 127.4, 127.2, 126.5, 126.3, 125.6, 124.1, 115.5;

ESI-HRMS *m/z*: Calcd for C₂₃H₁₅ONaSF [M+Na]⁺ 381.0725, found 381.0724.

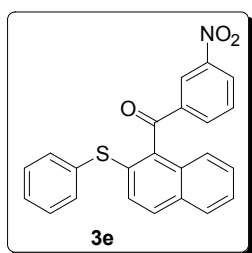


(2-Chlorophenyl)-(2-phenylsulfanylnaphthalen-1-yl)-methanone (3d): (91.1 mg 83, 81%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 101.3-103.5 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.46 (d, *J* = 8.4 Hz, 1 H), 8.06 (d, *J* = 8.4 Hz, 1 H), 7.95 (d, *J* = 8.4 Hz, 1 H), 7.68 (d, *J* = 8.4 Hz, 1 H), 7.64-7.52 (m, 2 H), 7.40 (dd, *J* = 7.6, 0.8 Hz, 1 H), 7.29-7.20 (m, 2 H), 7.14-7.07 (m, 1 H), 7.07-6.98 (m, 3 H), 6.85-6.77 (m, 2 H);

¹³C NMR (100 MHz, CDCl₃): δ 196.5, 144.8, 138.1, 137.2, 134.8, 134.7, 132.6, 132.0, 131.3, 130.8, 130.6, 128.6, 128.5, 128.1, 127.7, 126.9, 126.8, 126.5, 126.2, 125.6, 125.2;

ESI-HRMS *m/z*: Calcd for C₂₃H₁₅ONaSCl [M+Na]⁺ 397.0430, found 397.0427.



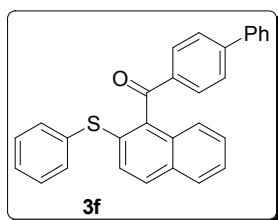
(3-Nitrophenyl)-(2-phenylsulfanylnaphthalen-1-yl)-methanone (3e): (105.2 mg 91%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 99.5-101.5 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.51-8.44 (m, 1 H), 8.35-8.30 (m, 1 H), 8.30-8.23 (m, 1 H), 8.17-8.08 (m, 2 H), 8.05-7.97 (m, 1 H), 7.70-7.59 (m, 2 H), 7.58-7.47 (m, 2 H), 7.09-6.94 (m, 3 H), 6.86-6.76 (m, 2 H);

¹³C NMR (100 MHz, CDCl₃): δ 194.9, 147.9, 143.1, 138.9, 136.7, 134.8, 134.7, 134.5, 131.4, 129.5,

128.8, 128.6, 127.9, 127.2, 126.7, 126.5, 126.4, 125.7, 124.2;

ESI-HRMS m/z : Calcd for $C_{23}H_{15}NO_3SNa$ $[M+Na]^+$ 408.0670, found 408.0667.

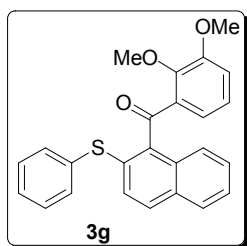


(2-phenylsulfonylnaphthalen-1-yl)-4-phenylmethanone (3f): (100.0 mg 80%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 125.5-126.5 °C;

1H NMR (400 MHz, $CDCl_3$): δ 8.57-8.47 (m, 1 H), 8.08 (d, J = 8.4 Hz, 1 H), 8.03-7.93 (m, 1 H), 7.84 (d, J = 8.4 Hz, 2 H), 7.69-7.52 (m, 7 H), 7.52-7.35 (m, 3 H), 7.15-6.94 (m, 5 H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 196.4, 145.9, 144.9, 139.9, 137.4, 136.0, 134.6, 134.4, 130.7, 130.3, 128.9, 128.8, 128.7, 128.2, 128.1, 127.3, 127.2, 127.0, 126.5, 126.3, 125.5, 124.3;

ESI-HRMS m/z : Calcd for $C_{29}H_{20}ONaS$ $[M+Na]^+$ 439.1133, found 439.1129.

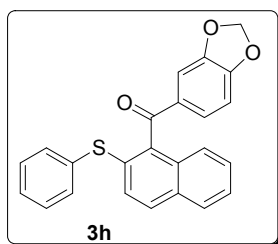


(2-phenylsulfonylnaphthalen-1-yl)-3,4-dimethoxybenzoyl methanone (3g): (92.5 mg 77%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 144.5-145.5 °C;

1H NMR (400 MHz, $CDCl_3$): δ 8.45 (d, J = 8.4 Hz, 1 H), 7.96 (d, J = 8.8 Hz, 1 H), 7.89 (d, J = 7.6 Hz, 1 H), 7.75 (d, J = 8.8 Hz, 1 H), 7.58-7.43 (m, 2 H), 7.13 (t, J = 8.4 Hz, 1 H), 7.05-6.90 (m, 3 H), 6.81-6.72 (m, 2 H), 6.37 (d, J = 8.4 Hz, 2 H), 3.60 (s, 6 H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 196.7, 158.0, 146.3, 138.5, 134.8, 134.5, 131.5, 130.0, 128.4, 128.3, 127.6, 127.4, 127.3, 126.4, 126.3, 126.2, 124.5, 119.9, 103.9, 55.7;

ESI-HRMS m/z : Calcd for $C_{25}H_{20}O_3NaS$ $[M+Na]^+$ 423.1031, found 423.1030.

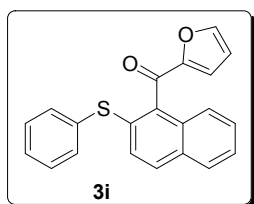


Benzo[1,3]dioxol-5-yl-(2-phenylsulfanyl-naphthalen-1-yl)-methanone (3h): (89.9 mg 78%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 120.9-123.0 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.51-8.41 (m, 1 H), 8.03 (d, *J* = 8.4 Hz, 1 H), 7.98-7.91 (m, 1 H), 7.63-7.52 (m, 2 H), 7.48 (d, *J* = 8.0 Hz, 1 H), 7.37 (d, *J* = 1.6 Hz, 1 H), 7.23-7.16 (m, 1 H), 7.14-7.06 (m, 2 H), 7.06-6.94 (m, 3 H), 6.69 (dd, *J* = 8.0, 2.4 Hz, 1 H), 6.02 (s, 2 H);

¹³C NMR (100 MHz, CDCl₃): δ 195.0, 152.1, 148.1, 145.0, 137.4, 134.4, 134.3, 132.2, 130.6, 128.73, 128.67, 128.1, 127.3, 127.19, 127.16, 126.5, 126.1, 125.5, 124.1, 108.7, 107.7, 101.9;

ESI-HRMS *m/z*: Calcd for C₂₄H₁₆O₃NaS [M+Na]⁺ 407.0718, found 407.0715.

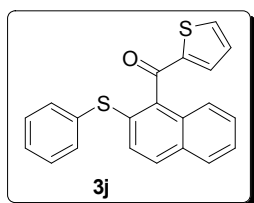


Furan-2-yl(2-phenylsulfanylnaphthalen-1-yl)methanone (3i): (84.3 mg 85%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 115.5-116.5 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.52-8.42 (m, 1 H), 8.03 (d, *J* = 8.4 Hz, 1 H), 7.99-7.90 (m, 1 H), 7.65-7.50 (m, 4 H), 7.15-7.06 (m, 2 H), 7.06-6.97 (m, 3 H), 6.94 (d, *J* = 3.6 Hz, 1 H), 6.50-6.43 (m, 1 H);

¹³C NMR (100 MHz, CDCl₃): δ 184.2, 152.8, 147.5, 143.5, 137.4, 134.6, 134.3, 130.5, 128.74, 128.67, 128.1, 127.4, 127.3, 127.2, 126.7, 125.6, 124.2, 120.4, 112.5;

ESI-HRMS *m/z*: Calcd for C₂₁H₁₄O₂NaS [M+Na]⁺ 353.0612, found 353.0613.

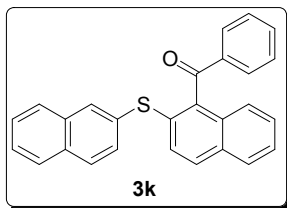


(2-Phenylsulfanylnaphthalen-1-yl)thiophen-2-yl-methanone (3j): (87.3 mg 84%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 116.0-116.5 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.54-8.44 (m, 1 H), 8.03 (d, *J* = 8.4 Hz, 1 H), 7.98-7.90 (m, 1 H), 7.69 (d, *J* = 5.2 Hz, 1 H), 7.62-7.51 (m, 3 H), 7.26 (s, 1 H), 7.13-7.06 (m, 2 H), 7.06-6.96 (m, 4 H);

¹³C NMR (100 MHz, CDCl₃): δ 188.9, 144.7, 144.6, 137.5, 135.3, 135.1, 134.5, 134.4, 130.5, 128.8, 128.7, 128.11, 128.08, 127.41, 127.35, 126.7, 125.6, 124.0;

ESI-HRMS *m/z*: Calcd for C₂₁H₁₄ONaS₂ [M+Na]⁺ 369.0384, found 369.0385.

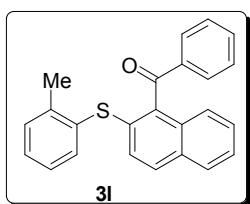


[2-(Naphthalen-2-ylsulfanyl)naphthalen-1-yl]phenyl-methanone (3k): (97.2 mg 83%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 145.5-147.5 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.55-8.45 (m, 1 H), 8.09 (d, *J* = 8.0 Hz, 1 H), 8.05-7.96 (m, 3 H), 7.85 (d, *J* = 8.0 Hz, 2 H), 7.70 (d, *J* = 8.4 Hz, 1 H), 7.66-7.53 (m, 4 H), 7.46 (m, 1 H), 7.07-6.98 (m, 2 H), 6.98-6.90 (m, 3 H);

¹³C NMR (100 MHz, CDCl₃): δ 196.9, 145.0, 137.3, 135.6, 134.7, 134.6, 134.4, 132.7, 132.2, 130.8, 129.6, 128.73, 128.67, 128.6, 128.5, 128.2, 127.7, 127.3, 127.1, 126.6, 126.5, 126.4, 125.6, 124.41, 124.39;

ESI-HRMS *m/z*: Calcd for C₂₇H₁₈ONaS [M+Na]⁺ 413.0976, found 413.0974.

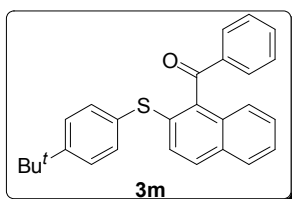


Phenyl-(2-o-tolylsulfanyl)naphthalen-1-yl)-methanone (3l): (92.5 mg 87%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 100.5-102.5 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.38 (d, *J* = 8.0 Hz, 1 H), 8.06 (d, *J* = 8.4 Hz, 1 H), 7.97 (d, *J* = 9.2 Hz, 1 H), 7.79-7.67 (m, 2 H), 7.64-7.54 (m, 2 H), 7.54-7.44 (m, 2 H), 7.33 (m, 2 H), 7.02 (d, *J* = 7.2 Hz, 1 H), 6.93 (m, 1 H), 6.83 (d, *J* = 7.6 Hz, 1 H), 6.53 (d, *J* = 7.6 Hz, 1 H), 2.26 (s, 3 H);

¹³C NMR (100 MHz, CDCl₃): δ 196.8, 144.8, 137.1, 136.6, 135.0, 134.6, 134.4, 133.2, 130.5, 129.8, 129.7, 128.7, 128.2, 128.1, 127.3, 126.9, 126.6, 126.5, 126.3, 125.2, 124.5, 20.0;

ESI-HRMS *m/z*: Calcd for C₂₄H₁₈ONaS [M+Na]⁺ 377.0976, found 377.0973.

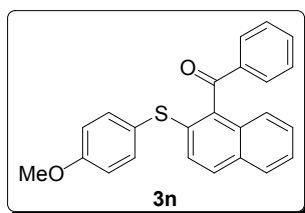


Phenyl-(2-p-tolylsulfanyl)naphthalen-1-yl)-methanone (3m): (87.6 mg 86%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 106.8-107.6 °C;

^1H NMR (400 MHz, CDCl_3): δ 8.60-8.49 (m, 1 H), 8.03 (d, $J = 8.4$ Hz, 1 H), 7.99-7.90 (m, 1 H), 7.73 (d, $J = 8.4$ Hz, 2 H), 7.65-7.55 (m, 2 H), 7.54-7.43 (m, 2 H), 7.33 (m, 2 H), 7.09 (d, $J = 8.4$ Hz, 2 H), 6.90 (d, $J = 8.4$ Hz, 2 H), 1.20 (s, 9 H);

^{13}C NMR (100 MHz, CDCl_3): δ 196.9, 148.7, 144.7, 137.2, 134.7, 134.4, 133.7, 133.2, 130.5, 129.8, 128.6, 128.3, 128.0, 127.23, 127.20, 126.9, 126.6, 125.8, 124.2, 34.3, 31.2;

ESI-HRMS m/z : Calcd for $\text{C}_{27}\text{H}_{24}\text{ONaS}$ $[\text{M}+\text{Na}]^+$ 419.1446, found 419.1447.

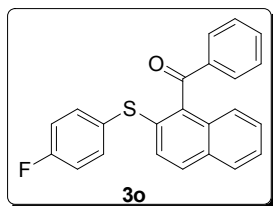


[2-(4-Methoxyphenylsulfanyl)-naphthalen-1-yl]-phenylmethanone (3n): (97.8 mg 88%, cyclohexane/ethyl acetate = 2:1). Pale yellow solid, Pale yellow oil;

^1H NMR (400 MHz, CDCl_3): δ 8.58-8.52 (m, 1 H), 8.00 (d, $J = 8.4$ Hz, 1 H), 7.96-7.90 (m, 1 H), 7.80-7.73 (m, 2 H), 7.62-7.56 (m, 2 H), 7.56-7.50 (m, 1 H), 7.46 (d, $J = 8.4$ Hz, 1 H), 7.41-7.35 (m, 2 H), 7.02 (d, $J = 9.2$ Hz, 2 H), 6.65 (d, $J = 8.8$ Hz, 1 H), 3.68 (s, 3 H);

^{13}C NMR (100 MHz, CDCl_3): δ 197.0, 158.2, 144.2, 137.3, 134.4, 134.3, 133.3, 130.2, 130.1, 129.9, 128.6, 128.4, 128.1, 127.9, 127.7, 127.2, 126.5, 124.2, 114.5, 55.2;

ESI-HRMS m/z : Calcd for $\text{C}_{24}\text{H}_{19}\text{O}_2\text{S}$ $[\text{M}+\text{H}]^+$ 371.1100, found 371.1107.

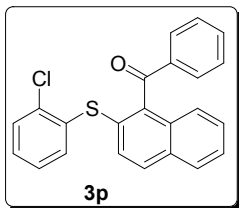


[2-(4-Fluorophenylsulfanyl)-naphthalen-1-yl]-phenylmethanone (3o): (80.6 mg 75%, cyclohexane/ethyl acetate = 2:1). Pale yellow solid, Mp: 106.8-109.5 $^\circ\text{C}$;

^1H NMR (400 MHz, CDCl_3): δ 8.52-8.45 (m, 1 H), 8.04 (d, $J = 8.4$ Hz, 1 H), 7.99-7.93 (m, 1 H), 7.76 (d, $J = 8.4$ Hz, 2 H), 7.64-7.57 (m, 2 H), 7.57-7.51 (m, 1 H), 7.49 (d, $J = 8.4$ Hz, 1 H), 7.38 (m, 2 H), 7.02-6.95 (m, 2 H), 6.83-6.75 (m, 2 H);

^{13}C NMR (100 MHz, CDCl_3): δ 196.8, 161.2, 144.7, 137.1, 134.4, 133.4, 132.2, 130.7, 129.8, 129.5, 128.8, 128.4, 128.2, 127.3, 126.8, 126.3, 124.2, 116.0, 115.8;

ESI-HRMS m/z : Calcd for $\text{C}_{23}\text{H}_{16}\text{OF}$ $[\text{M}+\text{H}]^+$ 359.0900, found 359.0905.

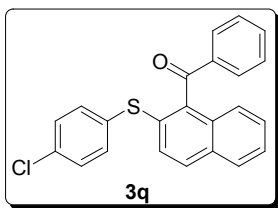


[2-(2-Chlorophenylsulfanyl)-naphthalen-1-yl]-phenylmethanone (3p): (88.9 mg 79%, cyclohexane/ethyl acetate = 2:1). Pale yellow solid, Mp: 119.5-120.8 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.36 (d, *J* = 8.4 Hz, 1 H), 8.07 (d, *J* = 8.4 Hz, 1 H), 7.95 (d, *J* = 7.2 Hz, 1 H), 7.75 (d, *J* = 8.0 Hz, 2 H), 7.62-7.43 (m, 4 H), 7.33 (m, 2 H), 7.21 (dd, *J* = 8.0, 1.2 Hz, 1 H), 6.93 (dd, *J* = 7.6, 1.6 Hz, 1 H), 6.85 (dd, *J* = 8.0, 1.6 Hz, 1 H), 6.50 (d, *J* = 8.0 Hz, 2 H);

¹³C NMR (100 MHz, CDCl₃): δ 196.5, 145.4, 136.9, 136.6, 134.3, 133.4, 131.1, 130.8, 129.7, 129.2, 128.7, 128.38, 128.37, 127.8, 127.4, 126.9, 126.13, 126.10, 125.0, 124.3;

ESI-HRMS *m/z*: Calcd for C₂₃H₁₆OClS [M+H]⁺ 375.0605, found 375.0611.

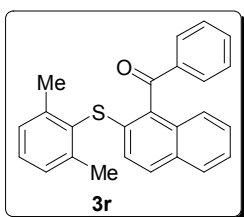


[2-(4-Chlorophenylsulfanyl)-naphthalen-1-yl]-phenylmethanone (3q): (78.7 mg 70%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 115.5-116.2 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.48-8.39 (m, 1 H), 8.06 (d, *J* = 8.4 Hz, 1 H), 8.01-7.92 (m, 1 H), 7.76 (d, *J* = 7.2 Hz, 2 H), 7.65-7.57 (m, 2 H), 7.57-7.47 (m, 2 H), 7.38 (m, 2 H), 7.09-7.00 (m, 2 H), 6.95-6.85 (m, 2 H);

¹³C NMR (100 MHz, CDCl₃): δ 196.7, 144.9, 137.0, 135.8, 134.4, 134.3, 133.5, 131.5, 130.9, 129.8, 128.9, 128.8, 128.5, 128.3, 127.4, 126.2, 125.8, 124.2;

ESI-HRMS *m/z*: Calcd for C₂₃H₁₅ONaSCl [M+Na]⁺ 397.0430, found 397.0432.

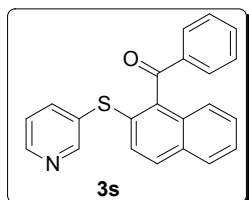


[2-(2,6-Dimethylphenylsulfanyl)-naphthalen-1-yl]-phenylmethanone (3r): (89.5 mg 81%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 153.9-156.5 °C;

^1H NMR (400 MHz, CDCl_3): δ 8.66-8.58 (m, 1 H), 7.92-7.86 (m, 1 H), 7.80 (d, $J = 8.0$ Hz, 1 H), 7.63-7.53 (m, 4 H), 7.50-7.43 (m, 1 H), 7.35-7.23 (m, 3 H), 6.84-6.72 (m, 3 H), 2.01 (s, 6 H);

^{13}C NMR (100 MHz, CDCl_3): δ 195.8, 141.5, 138.6, 135.9, 134.0, 133.1, 133.0, 132.7, 129.8, 128.6, 128.2, 128.0, 127.22, 127.16, 127.13, 125.5, 125.4, 21.7;

ESI-HRMS m/z : Calcd for $\text{C}_{25}\text{H}_{21}\text{OS}$ $[\text{M}+\text{H}]^+$ 369.1308, found 369.1314.

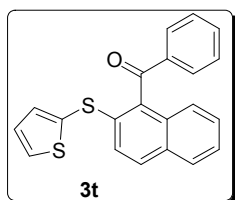


Phenyl-[2-(pyridin-3-ylsulfanyl)-naphthalen-1-yl]-methanone (3s): (81.9 mg 80%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 119.8-123.0 $^\circ\text{C}$;

^1H NMR (400 MHz, CDCl_3): δ 8.33 (dd, $J = 8.0, 1.2$ Hz, 1 H), 8.32-8.15 (br, 2 H), 8.14 (d, $J = 8.0$ Hz, 1 H), 8.01 (dd, $J = 7.6, 1.6$ Hz, 1 H), 7.74 (dd, $J = 8.0, 1.2$ Hz, 2 H), 7.69-7.58 (m, 2 H), 7.58-7.50 (m, 2 H), 7.37 (m, 2 H), 6.83-6.67 (m, 2 H);

^{13}C NMR (100 MHz, CDCl_3) δ : 196.2, 149.0, 148.6, 145.5, 136.8, 134.3, 134.2, 133.6, 131.6, 129.7, 128.9, 128.7, 128.5, 127.6, 125.8, 124.3, 122.7, 120.89;

ESI-HRMS m/z : Calcd for $\text{C}_{22}\text{H}_{16}\text{ONS}$ $[\text{M}+\text{H}]^+$ 342.0947, found 342.0950.

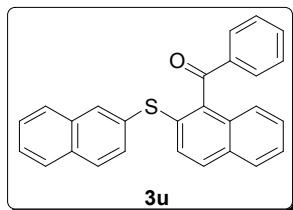


Phenyl-[2-(thiophen-2-ylsulfanyl)-naphthalen-1-yl]-methanone (3t): (86.3 mg 83%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 96.5-97.5 $^\circ\text{C}$;

^1H NMR (400 MHz, CDCl_3): δ 8.78 (d, $J = 8.4$ Hz, 1 H), 7.98 (d, $J = 8.4$ Hz, 1 H), 7.92 (d, $J = 8.0$ Hz, 1 H), 7.82 (d, $J = 8.0$ Hz, 2 H), 7.71-7.64 (m, 1 H), 7.64-7.53 (m, 2 H), 7.46-7.38 (m, 3 H), 7.10 (dd, $J = 5.2, 1.2$ Hz, 1 H), 6.94 (d, $J = 7.6$ Hz, 1 H), 6.79-6.71 (m, 1 H);

^{13}C NMR (100 MHz, CDCl_3): δ 196.8, 143.4, 137.2, 134.7, 134.4, 133.9, 133.4, 131.7, 130.3, 130.0, 129.1, 128.7, 128.4, 128.1, 127.9, 127.2, 126.9, 126.3, 124.1;

ESI-HRMS m/z : Calcd for $\text{C}_{21}\text{H}_{15}\text{OS}_2$ $[\text{M}+\text{H}]^+$ 347.0559, found 347.0563.

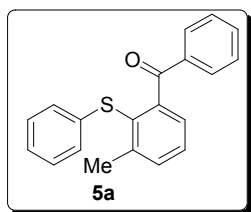


[2-(Naphthalen-2-ylsulfanyl)-naphthalen-1-yl]-phenylmethanone (3u): (90.2 mg 77%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 136.4-138.0 °C;

¹H NMR (400 MHz, CDCl₃): δ 8.51(d, *J* = 8.4 Hz, 1 H), 8.08 (d, *J* = 8.4 Hz, 1 H), 7.97(d, *J* = 8.8 Hz, 1 H), 7.78 (d, *J* = 8.4 Hz, 2 H), 7.72-7.64 (m, 1 H), 7.63-7.50 (m, 5 H), 7.47 (t, *J* = 7.4 Hz, 1 H), 7.43-7.28 (m, 5 H), 7.10 (dd, *J* = 8.4, 1.6 Hz, 1 H);

¹³C NMR (100 MHz, CDCl₃): δ 196.8, 144.8, 137.2, 134.7, 134.5, 134.4, 133.5, 133.3, 131.5, 130.7, 129.8, 128.7, 128.4, 128.3, 128.2, 127.6, 127.3, 127.1, 126.5, 126.3, 125.6, 125.5, 125.4, 124.3;

ESI-HRMS *m/z*: Calcd for C₂₇H₁₈ONaS [M+Na]⁺ 413.0976, found 413.0975.

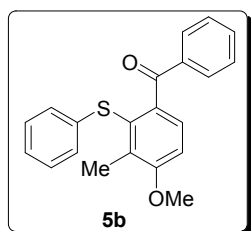


(3-Methyl-2-phenylsulfanylphenyl)-phenylmethanone (5a): (72.1 mg, 79%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 50.0-52.5 °C;

¹H NMR (400 MHz, CDCl₃): δ 7.85 (d, *J* = 7.2 Hz, 2 H), 7.65-7.58 (m, 1 H), 7.54 (d, *J* = 4.8 Hz, 2 H), 7.48 (d, *J* = 7.6 Hz, 2 H), 7.40-7.33 (m, 1 H), 7.28-7.20 (m, 2 H), 7.19-7.13 (m, 1 H), 7.10-7.04 (m, 2 H), 2.50 (s, 3 H);

¹³C NMR (100 MHz, CDCl₃) δ 196.8, 146.5, 144.2, 137.3, 136.9, 133.1, 132.0, 129.8, 129.3, 128.8, 128.6, 128.3, 127.2, 125.49, 125.45, 20.8;

ESI-HRMS *m/z*: Calcd for C₂₀H₁₆ONaS [M+Na]⁺ 327.0820, found 327.0823.



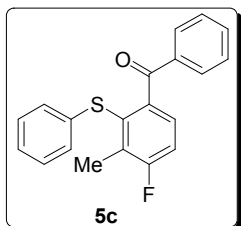
(4-Methoxy-3-methyl-2-phenylsulfanylphenyl)-phenylmethanone (5b): (78.2 mg, 78%,

cyclohexane/ethyl acetate = 4:1). Pale yellow oil;

^1H NMR (400 MHz, CDCl_3): δ 7.74-7.66 (m, 2 H), 7.63-7.46 (m, 1 H), 7.37-7.29 (m, 3 H), 7.15-7.00 (m, 6 H), 3.78 (s, 3 H), 2.38 (s, 3 H);

^{13}C NMR (100 MHz, CDCl_3): δ 196.1, 160.1, 144.2, 137.2, 137.0, 134.3, 133.1, 132.2, 129.8, 128.6, 128.2, 125.9, 124.6, 123.6, 60.5, 16.7;

ESI-HRMS m/z : Calcd for $\text{C}_{21}\text{H}_{18}\text{O}_2\text{NaS}$ $[\text{M}+\text{Na}]^+$ 357.0925, found 357.0927.

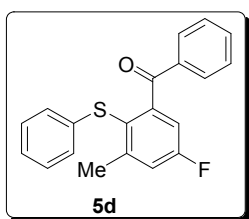


(4-Fluoro-3-methyl-2-phenylsulfanylphenyl)-phenylmethanone (5c): (79.8 mg, 80%, cyclohexane/ethyl acetate = 4:1). Pale yellow oil;

^1H NMR (400 MHz, CDCl_3): δ 7.72 (d, $J = 8.4$ Hz, 2 H), 7.52 (d, $J = 7.4$ Hz, 1 H), 7.38 (dd, $J = 7.6$ Hz, 2 H), 7.30-7.19 (m, 2 H), 7.19-7.11 (m, 2 H), 7.11-7.05 (m, 1 H), 6.97 (d, $J = 8.4$ Hz, 2 H), 2.30 (d, $J = 2.8$ Hz, 3 H);

^{13}C NMR (100 MHz, CDCl_3): δ 196.1, 161.9, 142.0, 137.3, 136.2, 133.3, 131.9, 131.1, 129.8, 128.9, 128.4, 127.5, 126.4, 125.9, 116.2, 12.6;

ESI-HRMS m/z : Calcd for $\text{C}_{20}\text{H}_{15}\text{ONaSF}$ $[\text{M}+\text{Na}]^+$ 345.0725, found 345.0724.

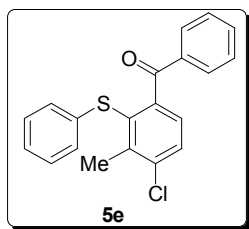


(5-Fluoro-3-methyl-2-phenylsulfanylphenyl)-phenylmethanone (5d): (79.3 mg, 82%, cyclohexane/ethyl acetate = 4:1). Pale yellow oil;

^1H NMR (400 MHz, CDCl_3): δ 7.73 (d, $J = 8.4$ Hz, 2 H), 7.53 (dd, $J = 7.4$ Hz, 1 H), 7.38 (dd, $J = 7.6$ Hz, 2 H), 7.20-7.10 (m, 3 H), 7.10-7.03 (m, 1 H), 6.99 (dd, $J = 8.0, 2.8$ Hz, 1 H), 6.94-6.92 (m, 2 H), 2.39 (s, 3 H);

^{13}C NMR (100 MHz, CDCl_3): δ 195.3, 162.8, 148.4, 147.3, 136.64, 136.58, 133.5, 129.8, 128.8, 128.6, 128.4, 126.9, 125.6, 123.8, 118.8, 112.6, 21.1;

ESI-HRMS m/z : Calcd for $C_{20}H_{15}FOS$ $[M+Na]^+$ 345.0725, found 345.0721.

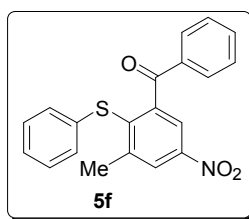


(4-Chloro-3-methyl-2-phenylsulfanylphenyl)-phenylmethanone (5e): (84.4 mg, 83%, cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 66.0-68.9 °C;

1H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, $J = 8.4$ Hz, 2 H), 7.58-7.48 (m, 2 H), 7.38 (t, $J = 7.8$ Hz, 2 H), 7.23-7.11 (m, 3 H), 7.11-7.03 (m, 1 H), 7.00-6.93 (m, 2 H), 2.49 (s, 3 H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 195.8, 145.0, 142.0, 137.0, 136.8, 136.2, 133.4, 130.9, 130.3, 129.7, 128.9, 128.4, 127.4, 125.9, 125.8, 18.3;

ESI-HRMS m/z : Calcd for $C_{20}H_{15}ONaSCl$ $[M+Na]^+$ 361.0430, found 361.0433.

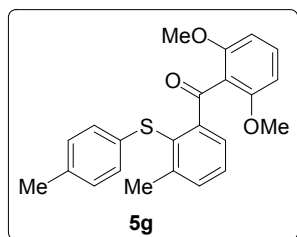


(3-Methyl-5-nitro-2-phenylsulfanylphenyl)-phenylmethanone (5f): (89.1 mg, 85%, cyclohexane/ethyl acetate = 4:1). Pale yellow oil;

1H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, $J = 2.4$ Hz, 1 H), 8.08 (d, $J = 2.0$ Hz, 1 H), 7.72 (d, $J = 8.4$ Hz, 2 H), 7.62-7.54 (m, 1 H), 7.42 (t, $J = 7.8$ Hz, 2 H), 7.21-7.08 (m, 3 H), 7.06-6.98 (m, 2 H), 2.44 (s, 3 H);

^{13}C NMR (100 MHz, $CDCl_3$): δ 194.3, 147.3, 146.3, 145.4, 138.6, 136.1, 134.5, 134.0, 129.8, 129.2, 129.0, 128.6, 126.9, 125.9, 120.3, 21.5;

ESI-HRMS m/z : Calcd for $C_{20}H_{16}NO_3S$ $[M+H]^+$ 350.0851, found 350.0849.



(2,6-Dimethoxyphenyl)-(3-methyl-2-p-tolylsulfanylphenyl)-methanone (5g): (90.8 mg, 80%,

cyclohexane/ethyl acetate = 4:1). Pale yellow solid, Mp: 132.1-132.6 °C;

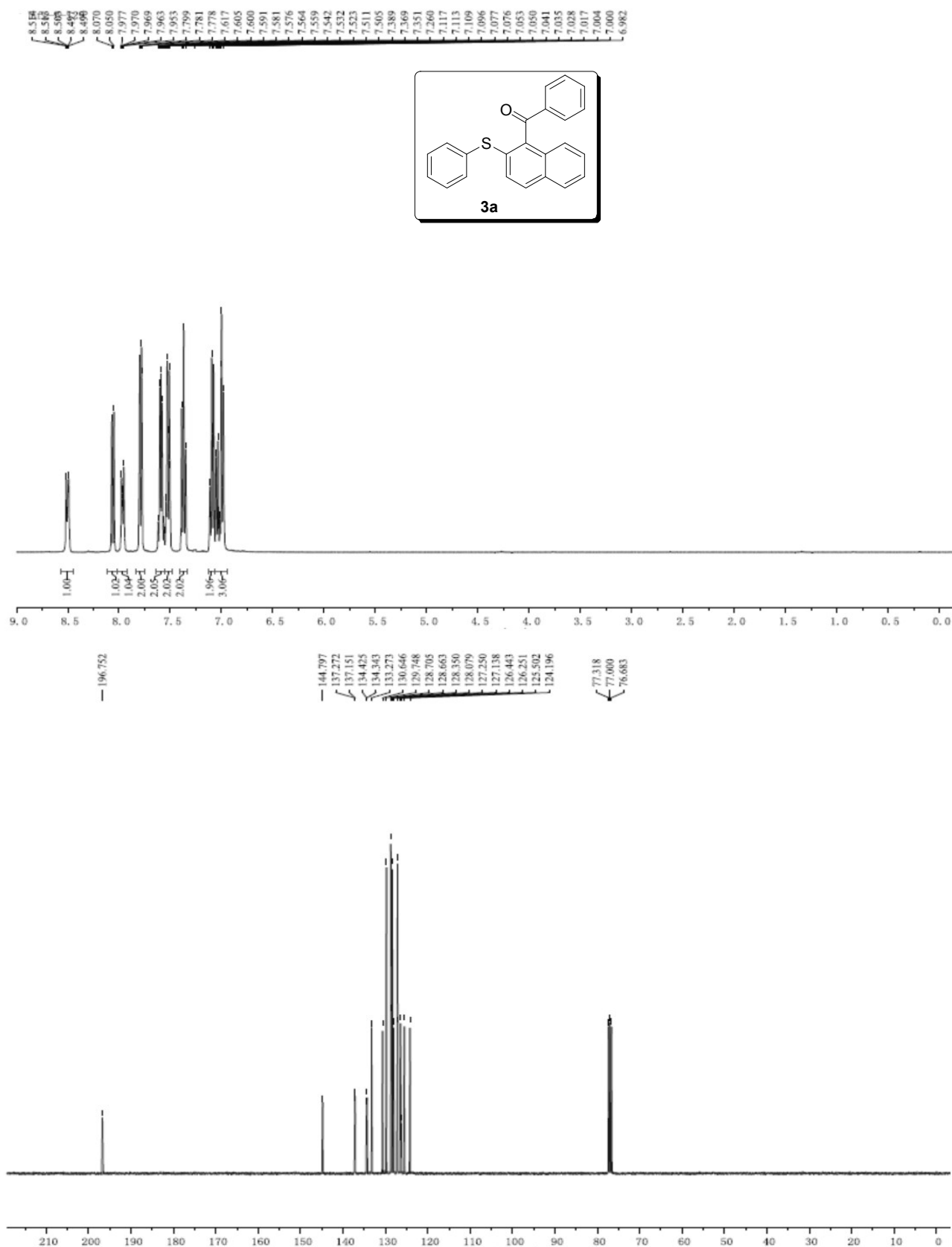
¹H NMR (400 MHz, CDCl₃): δ 7.44 (dd, *J* = 7.6, 1.6 Hz, 1 H), 7.36-7.25 (m, 2 H), 7.21 (dd, *J* = 8.4 Hz, 1 H), 6.93 (d, *J* = 8.4 Hz, 2 H), 6.85 (d, *J* = 8.0 Hz, 2 H), 6.47 (d, *J* = 8.4 Hz, 2 H), 3.64 (s, 6 H), 2.28 (s, 3 H), 2.25 (s, 3 H);

¹³C NMR (100 MHz, CDCl₃): δ 196.0, 158.0, 147.0, 143.9, 134.7, 134.5, 133.1, 131.2, 130.4, 129.2, 128.2, 127.5, 127.1, 119.9, 104.0, 55.8, 21.3, 20.9;

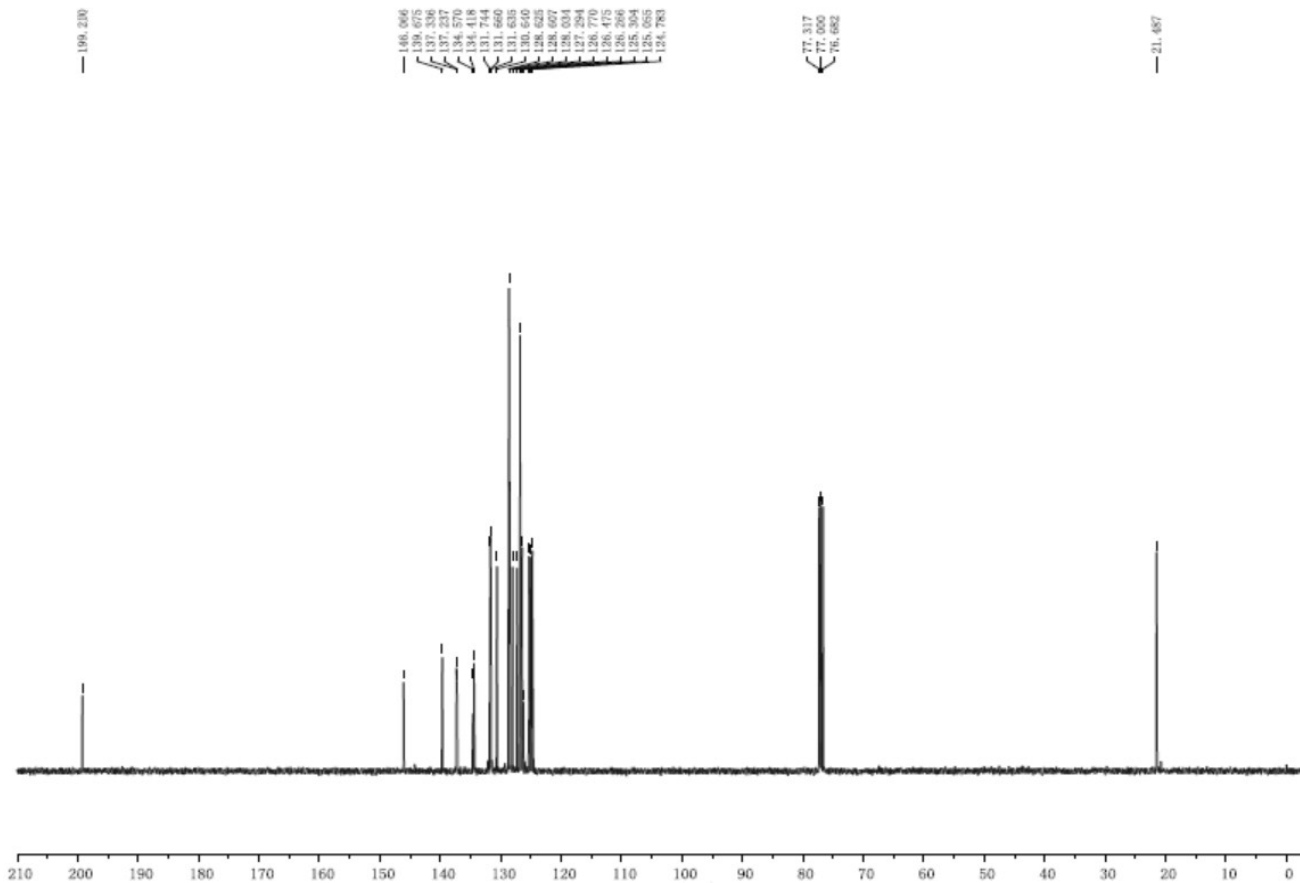
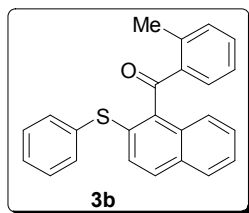
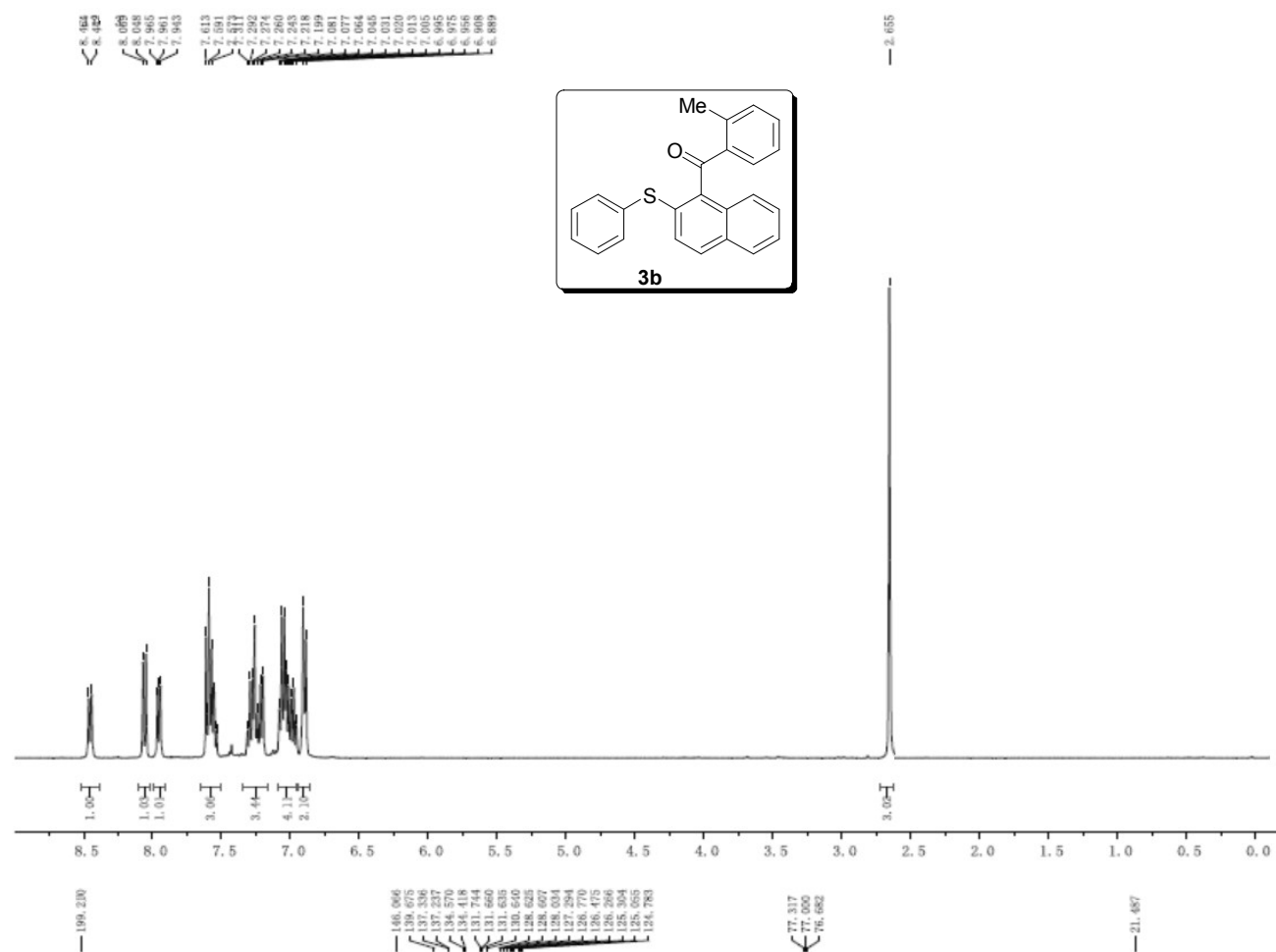
ESI-HRMS *m/z*: Calcd for C₂₃H₂₂O₃NaS [M+Na]⁺ 401.1187, found 401.1188.

Spectrums

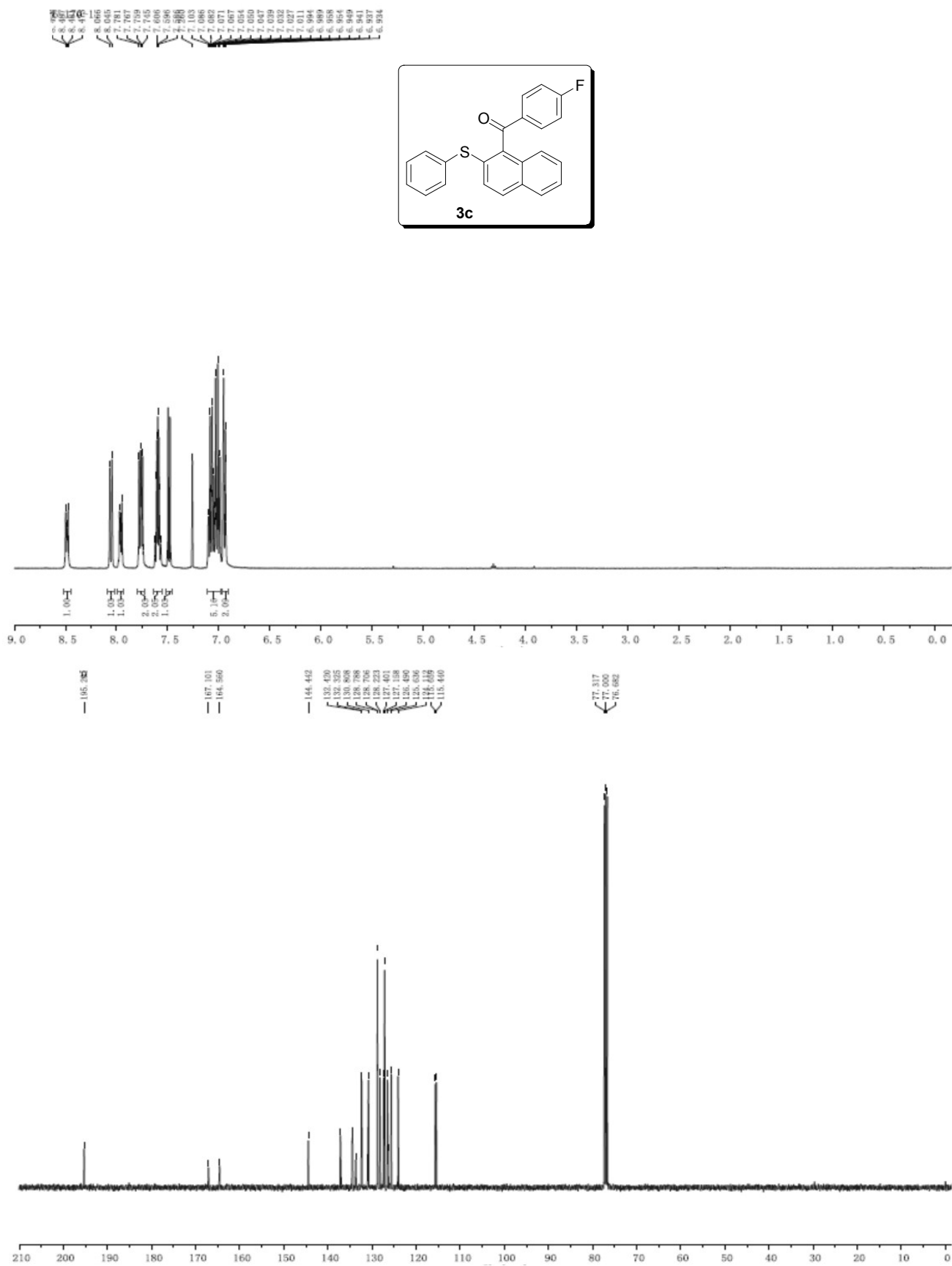
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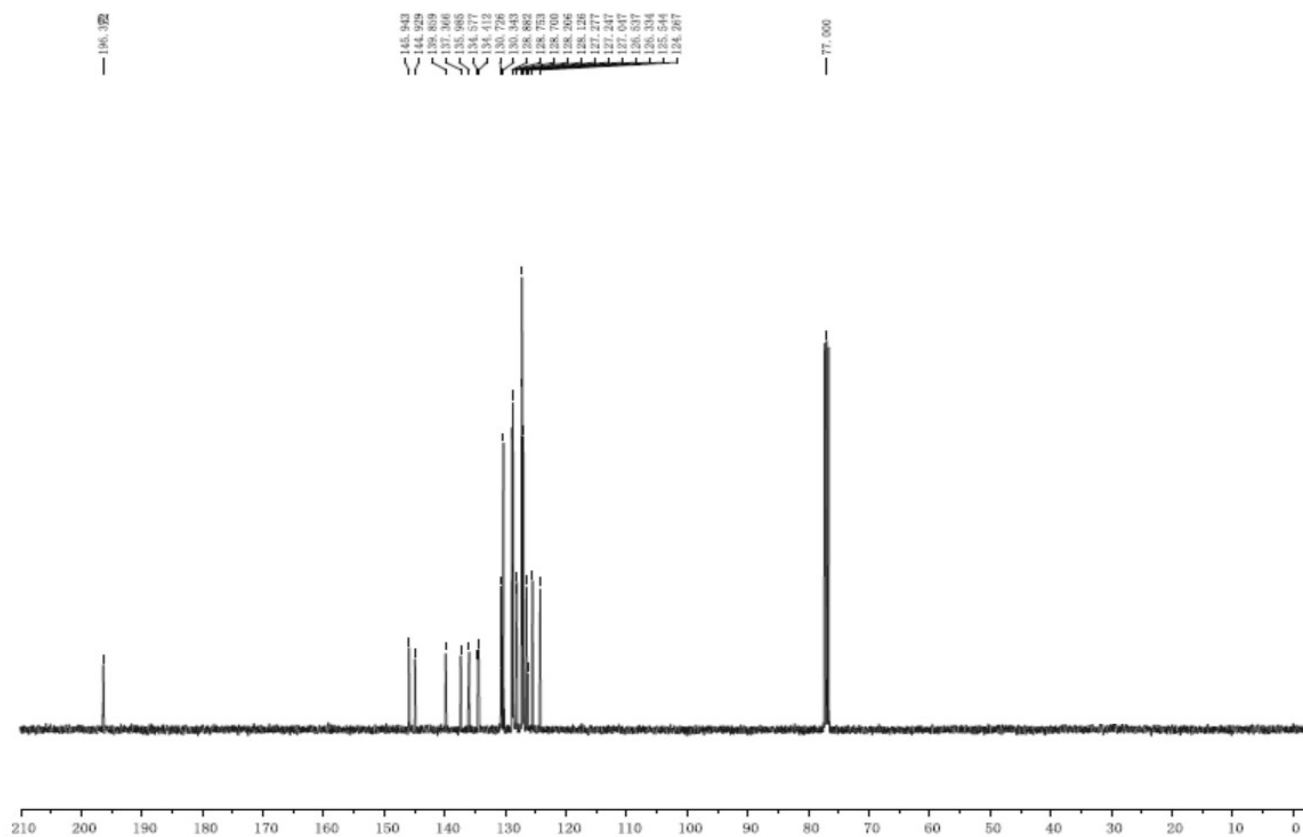
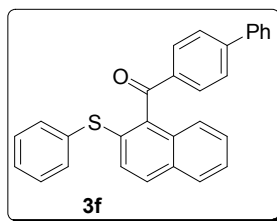
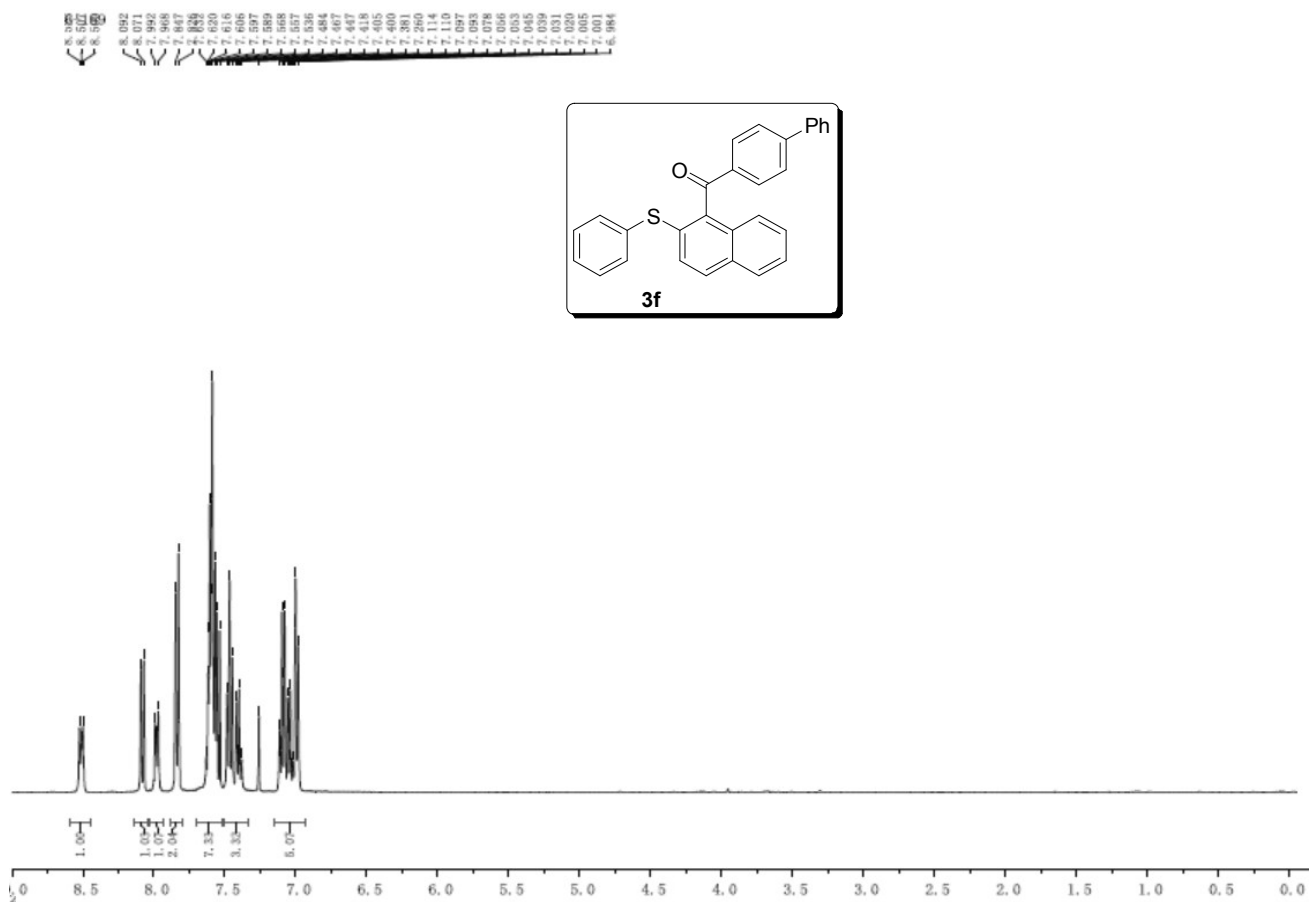
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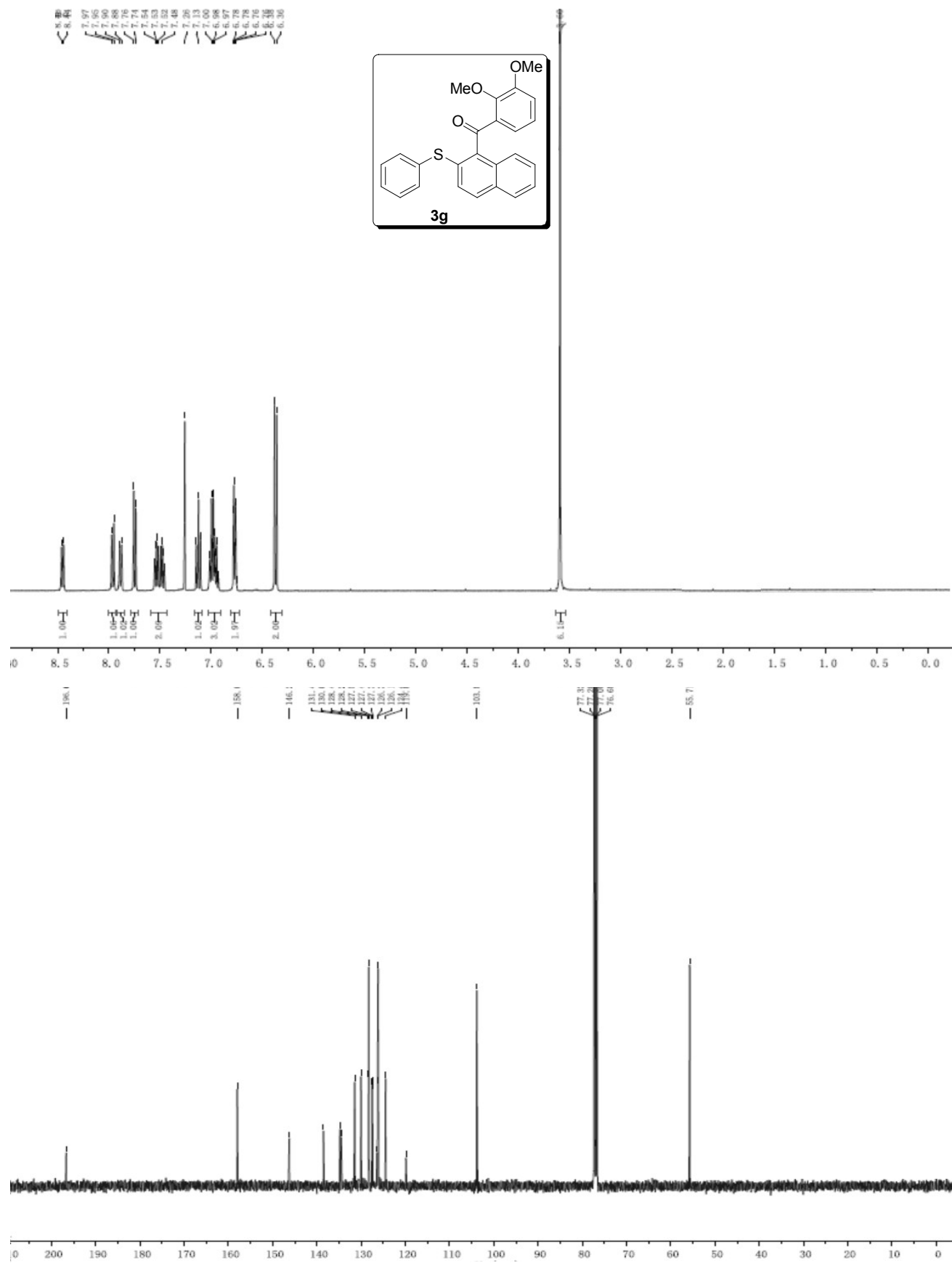
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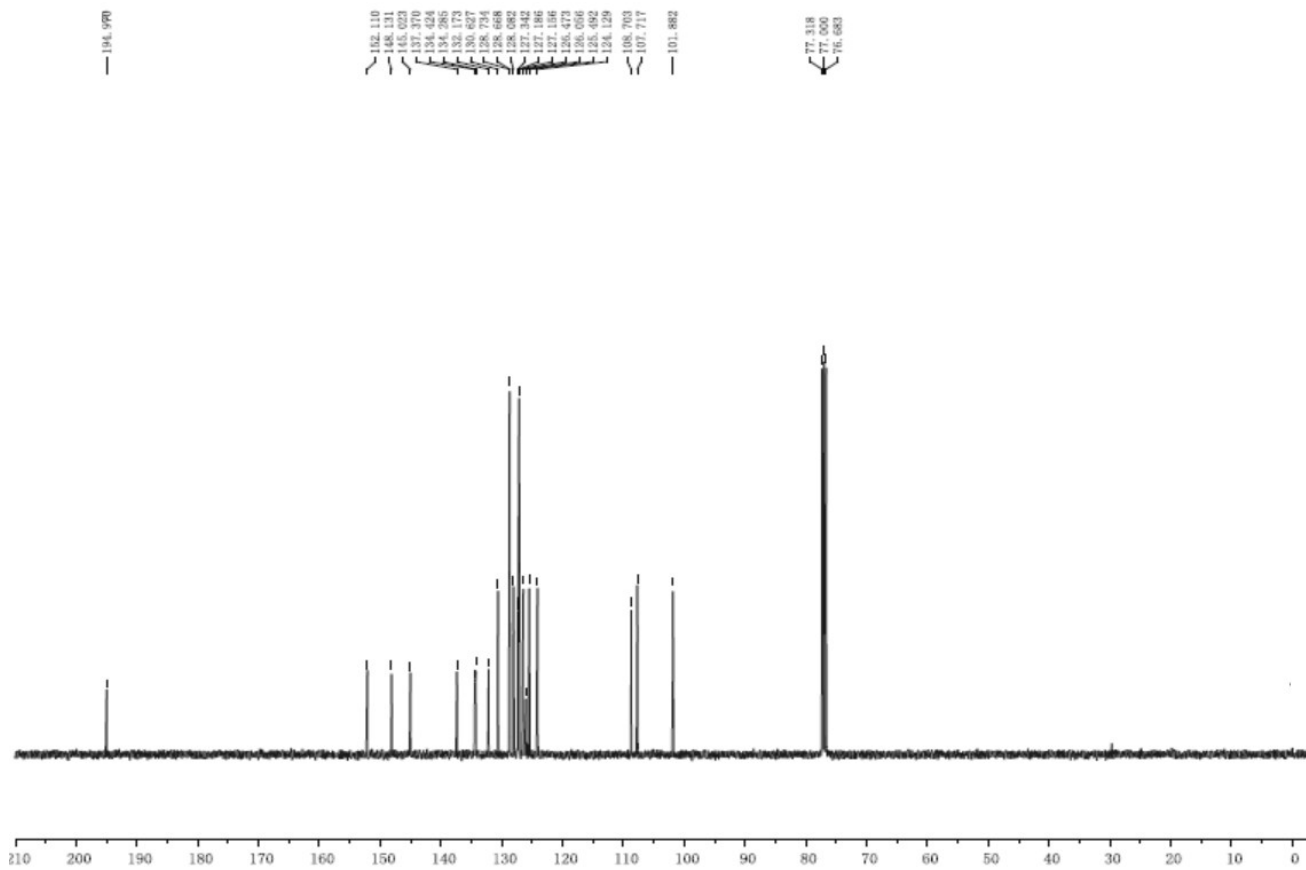
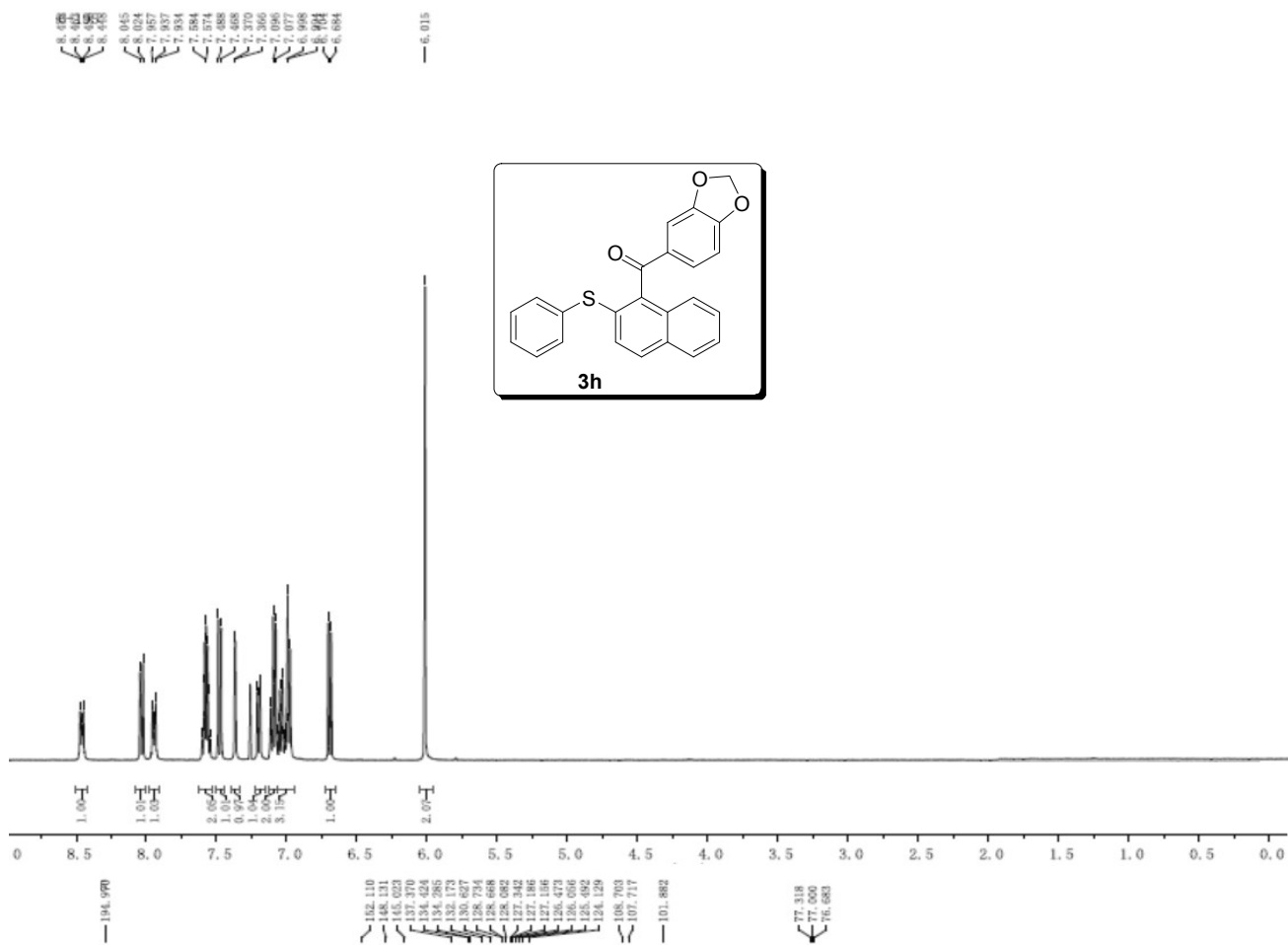
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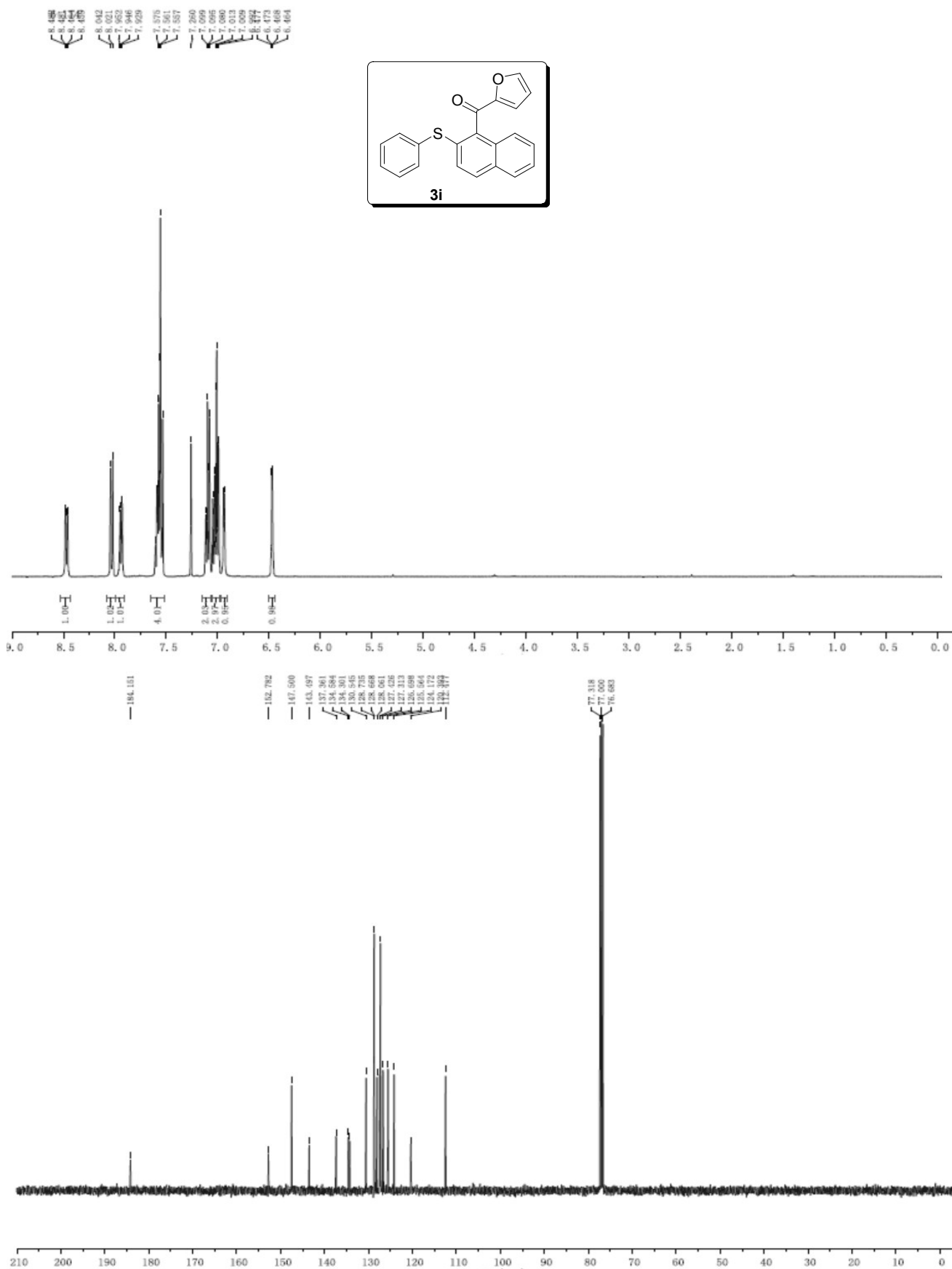
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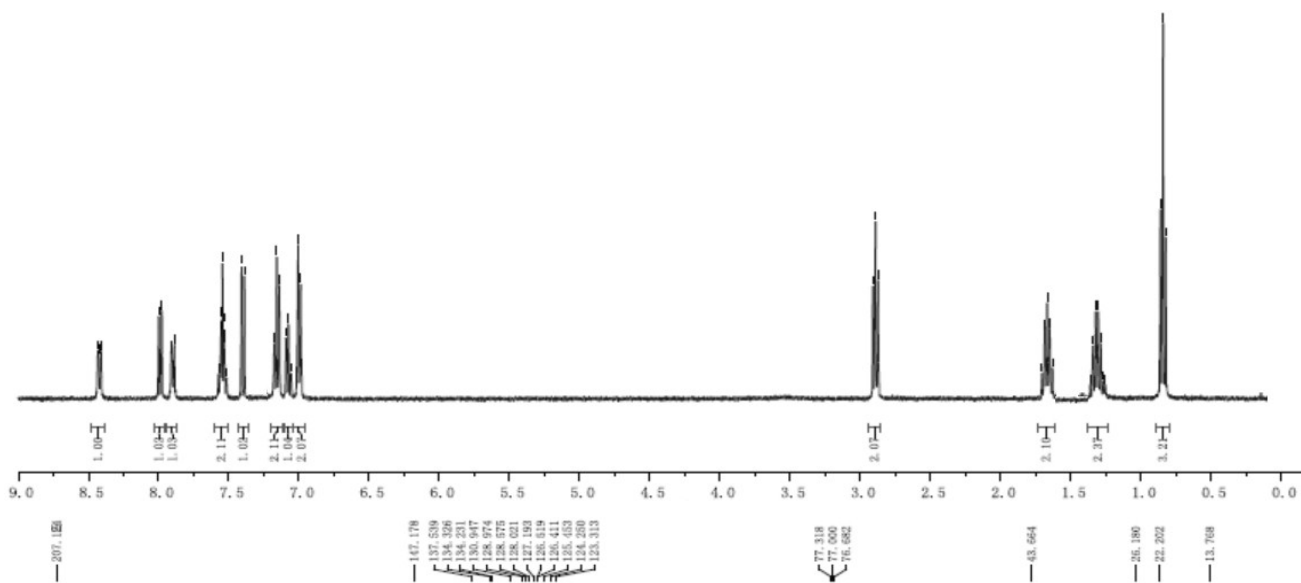
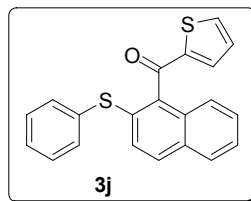
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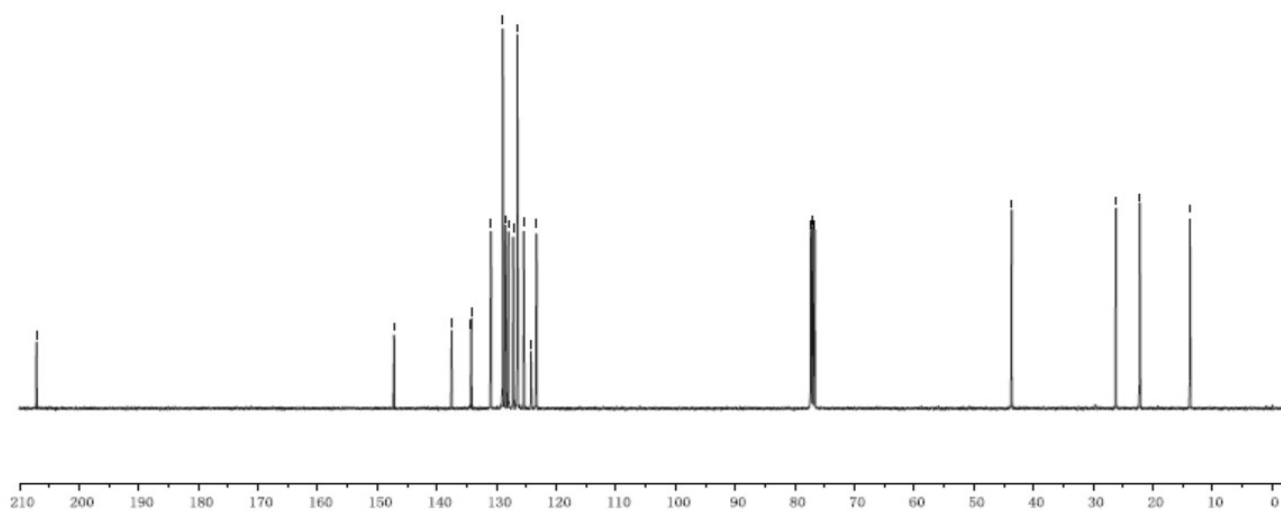
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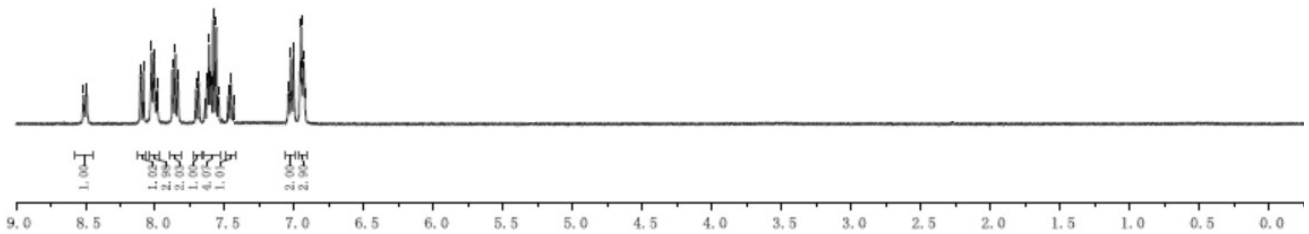
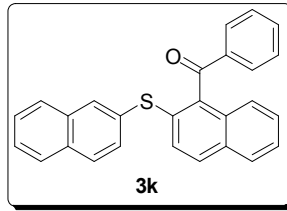
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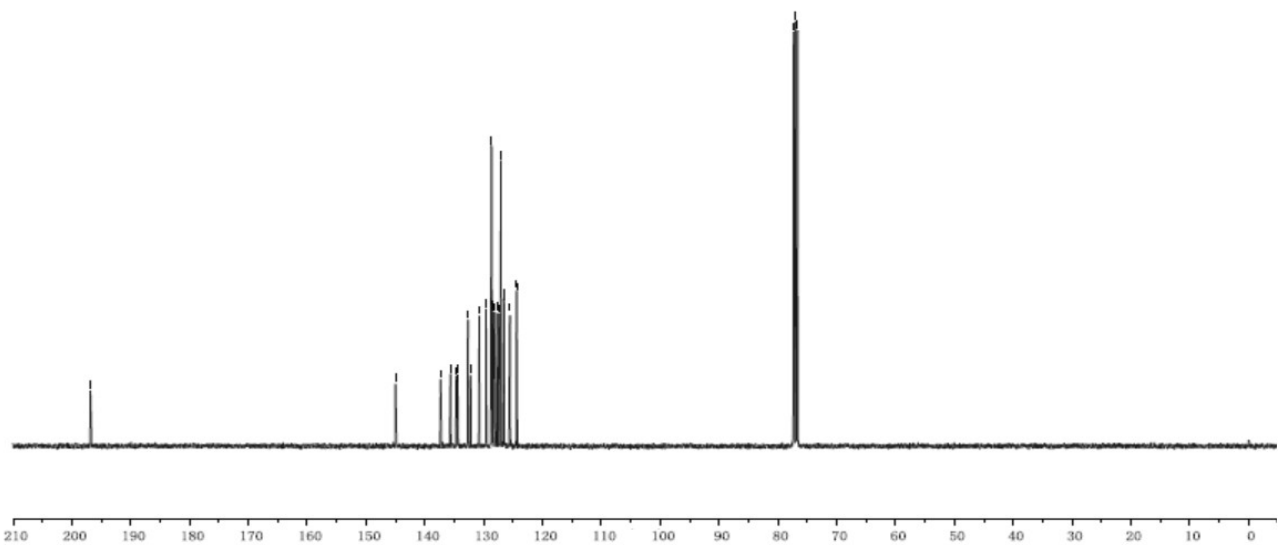
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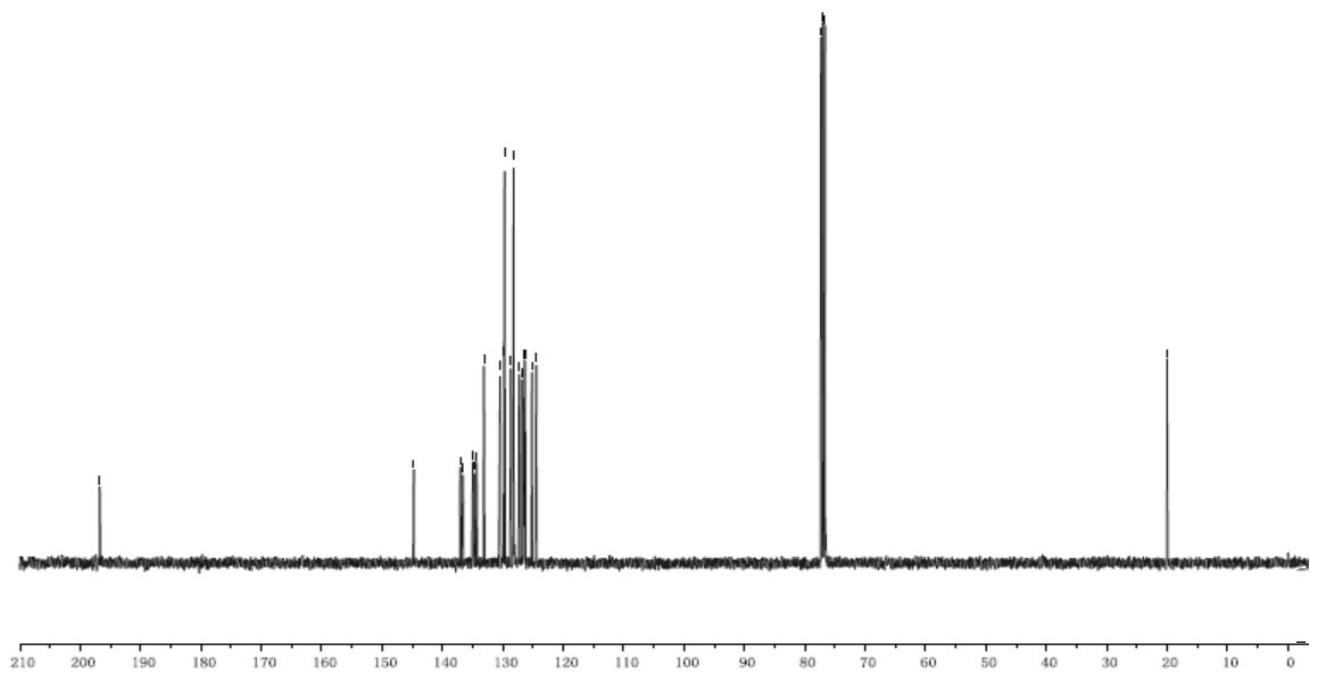
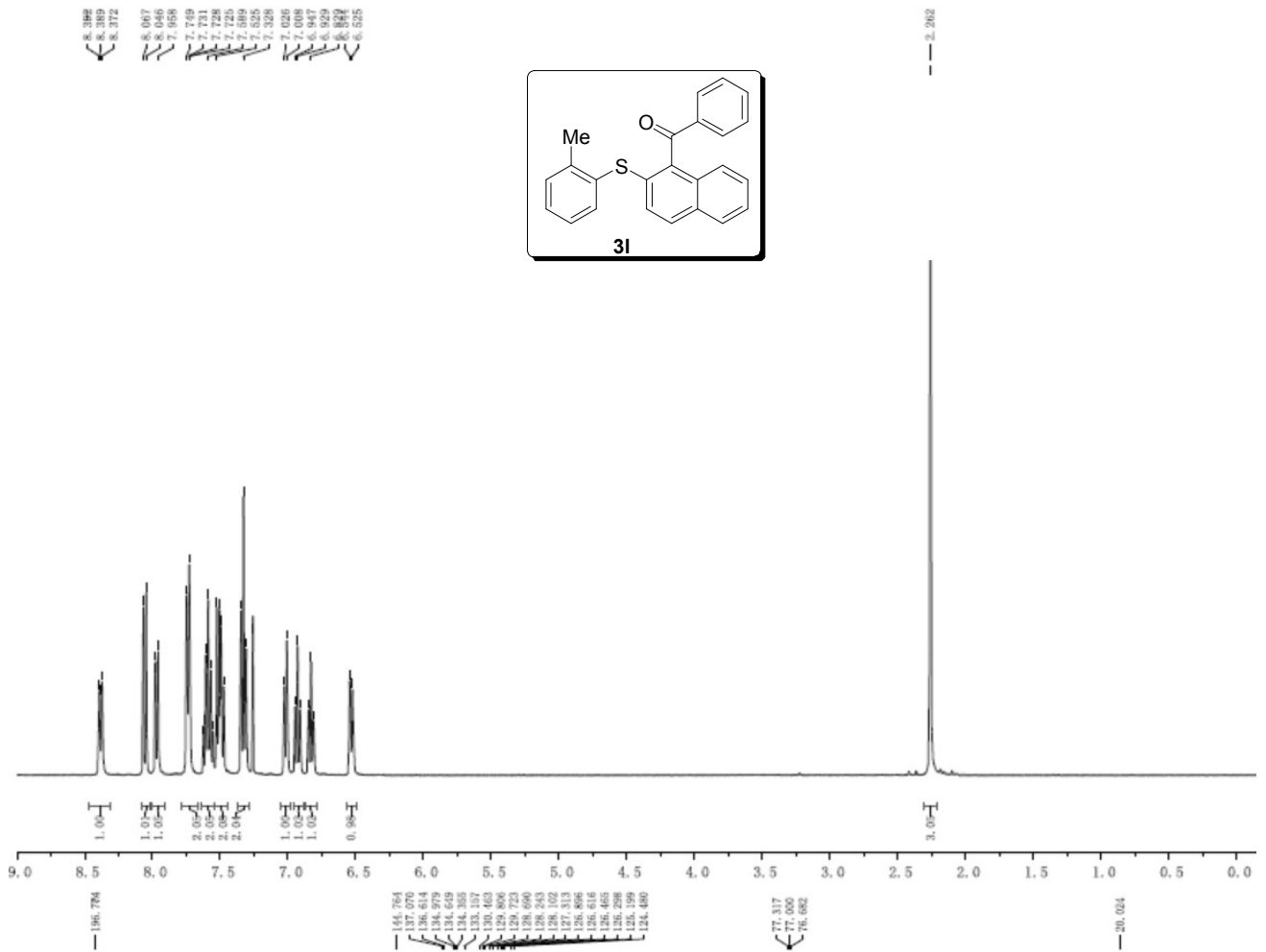


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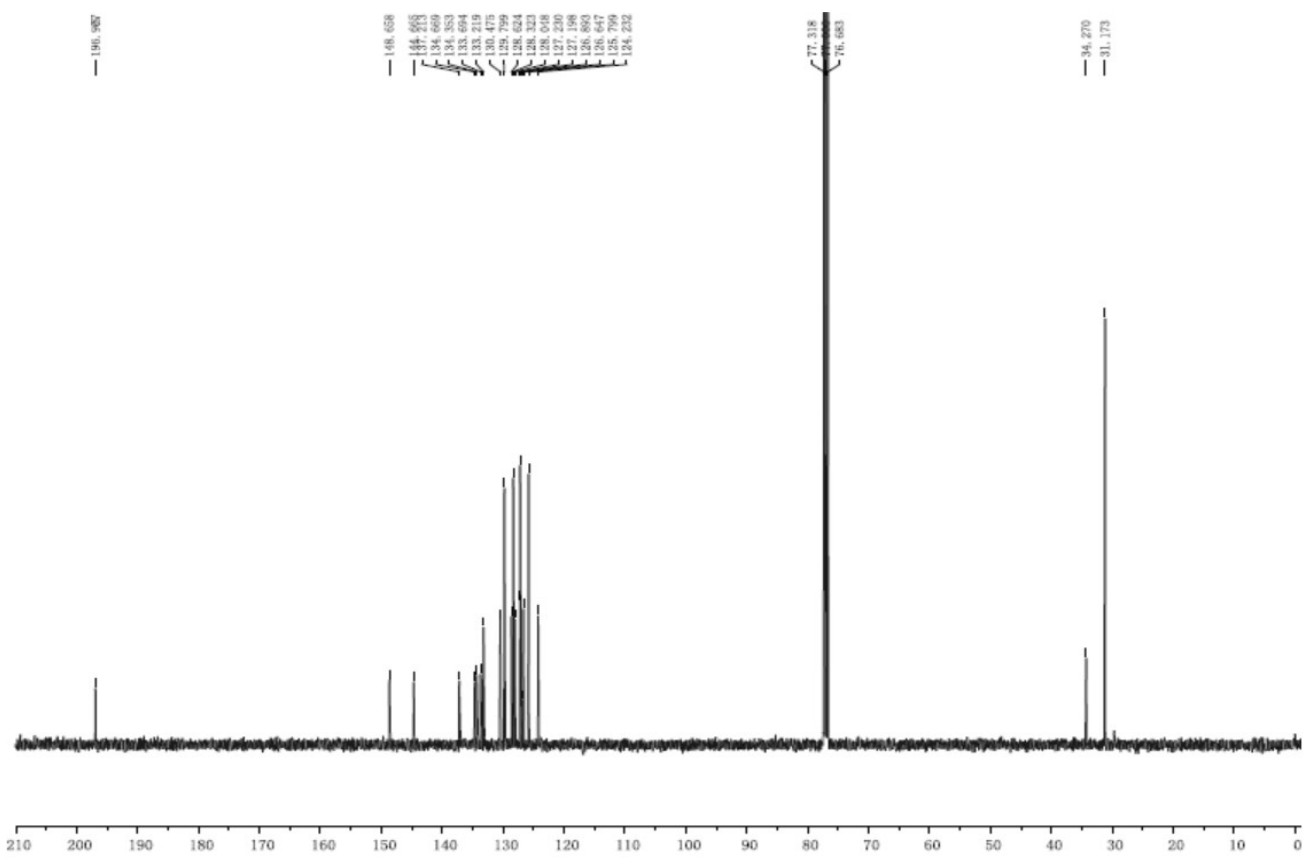
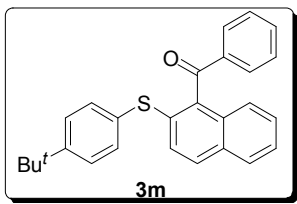
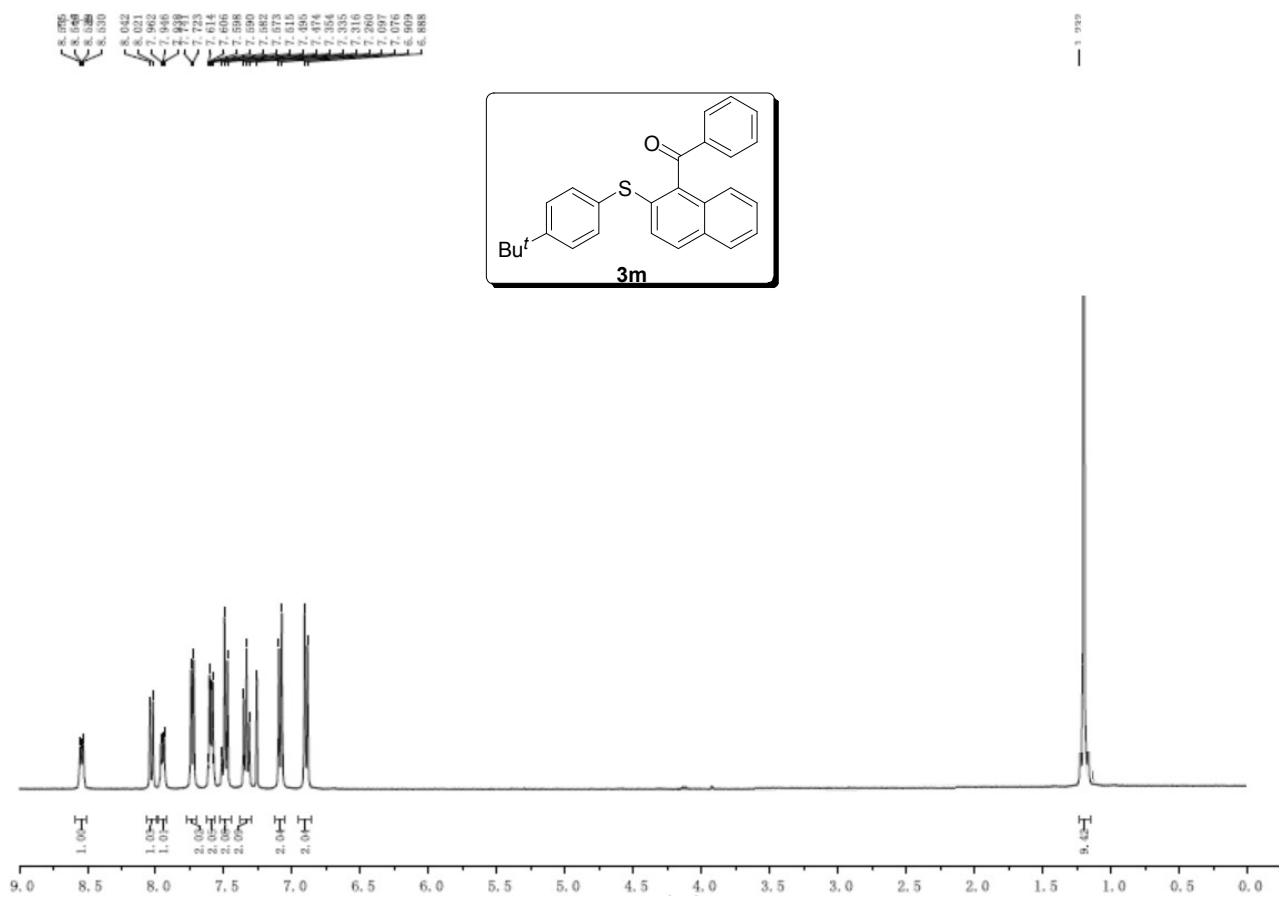


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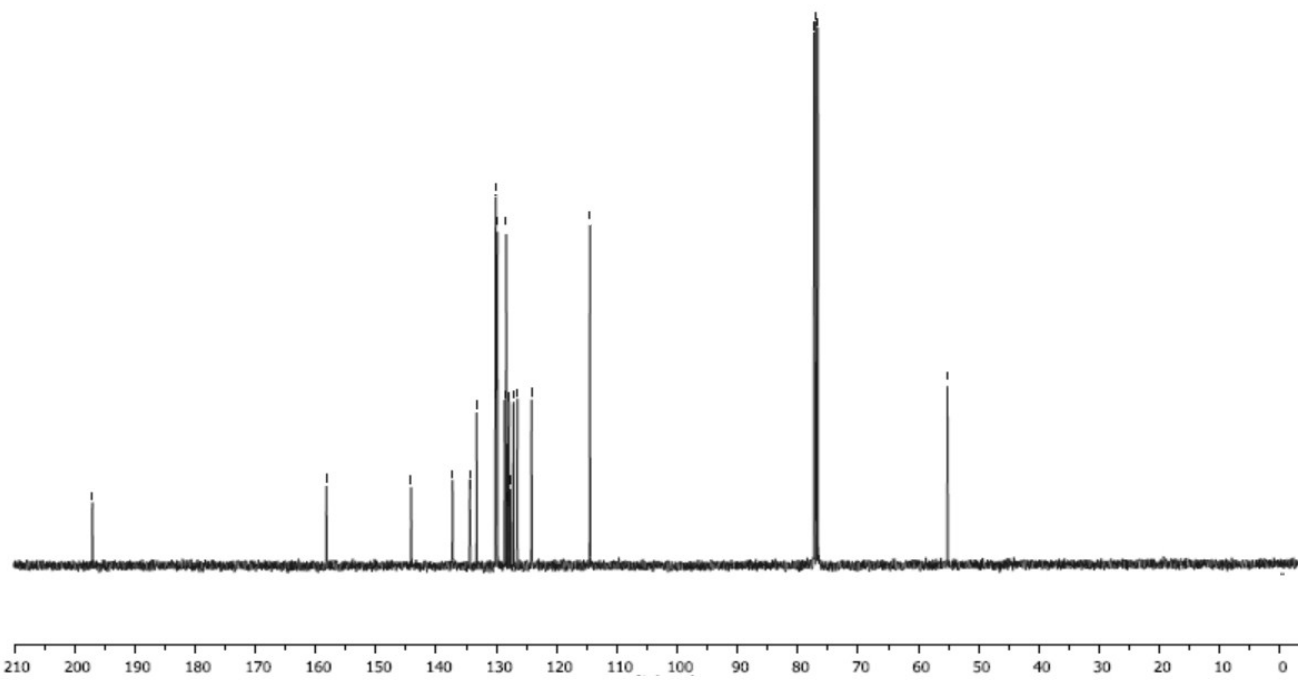
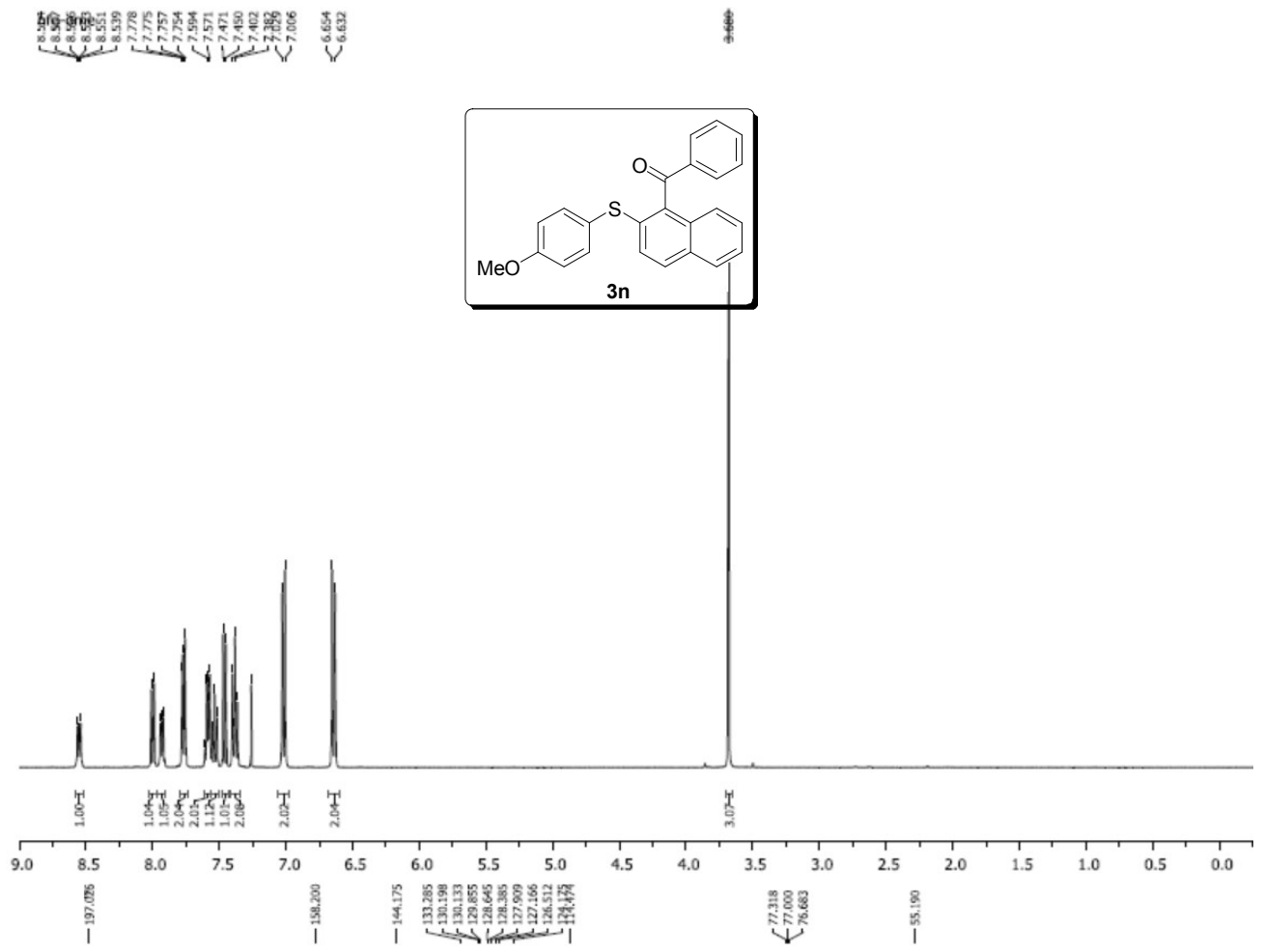




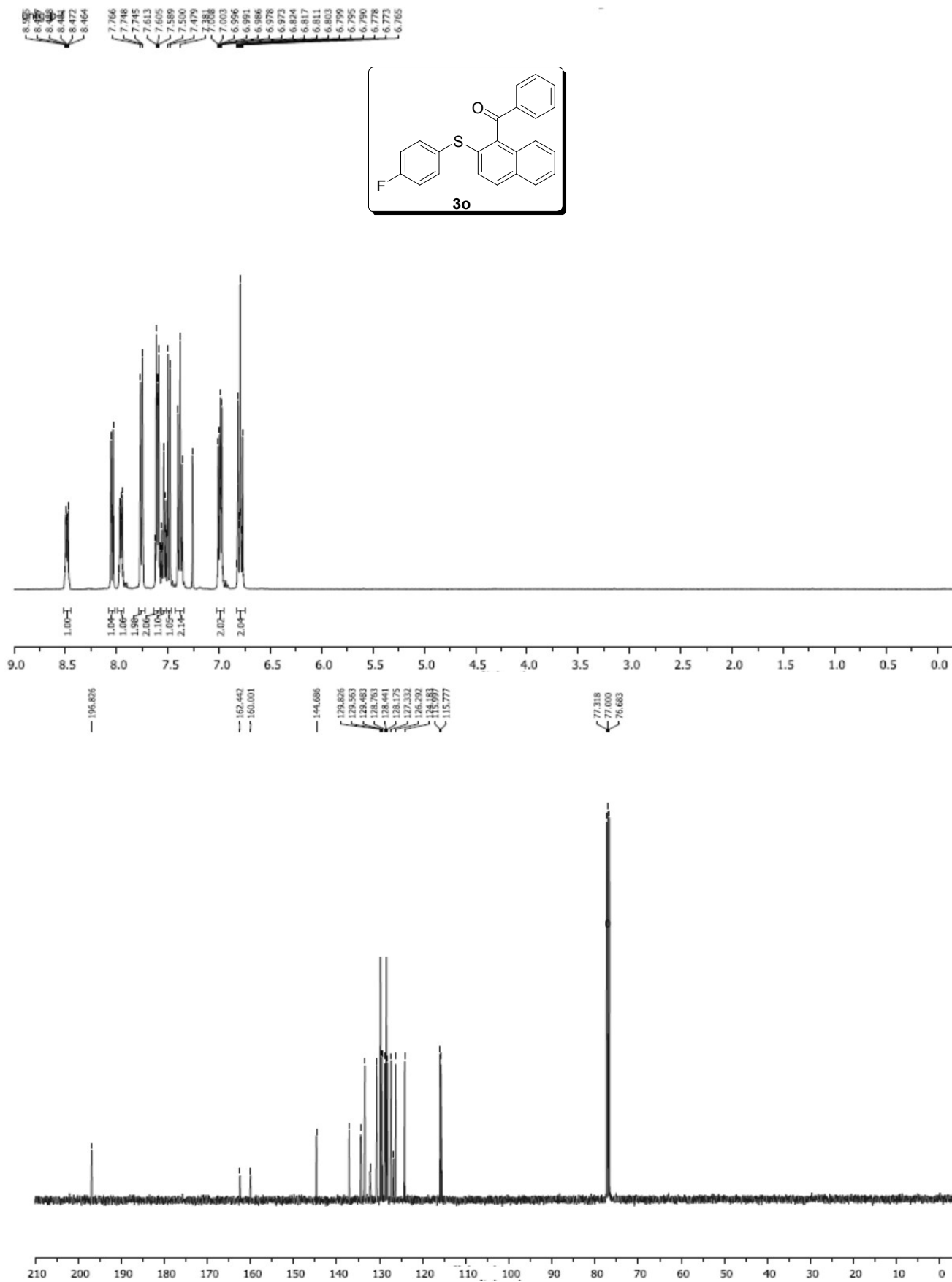
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3n

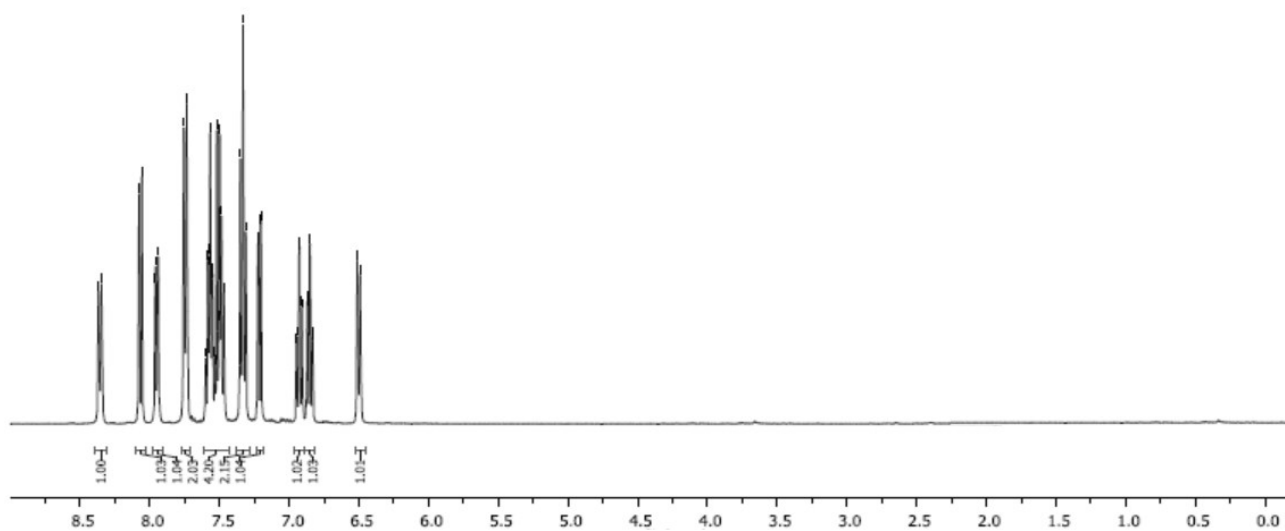
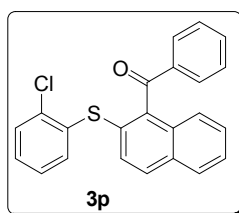


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3p

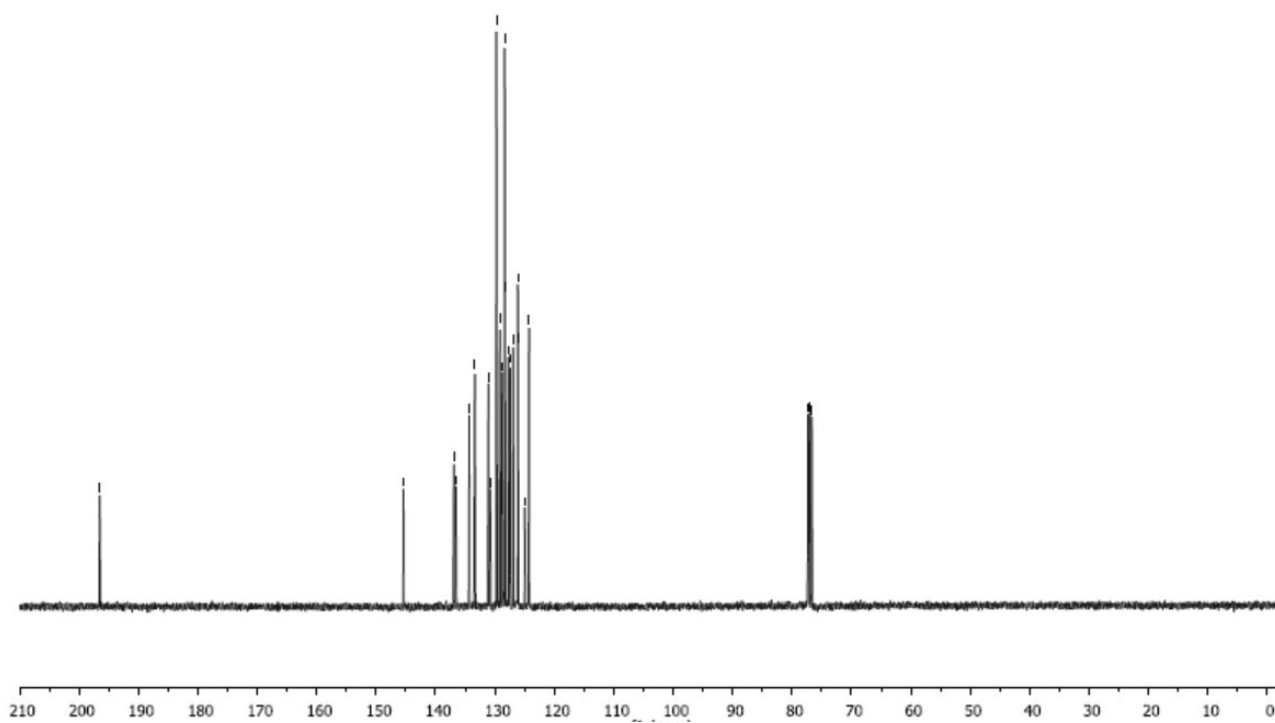
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6.851
6.482



196.519

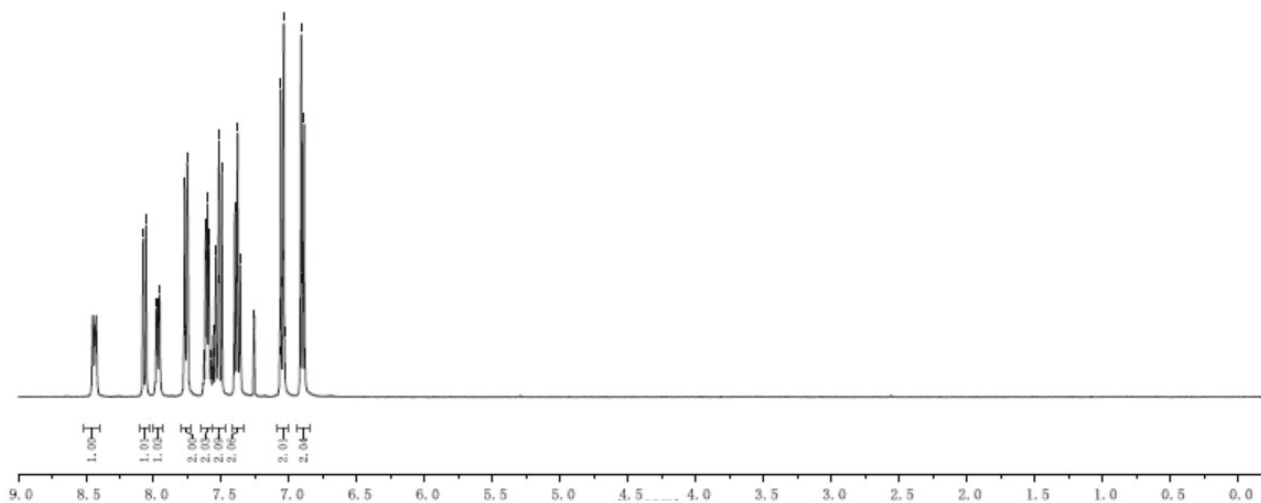
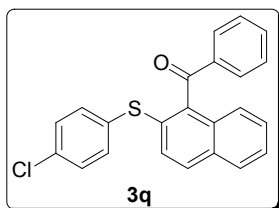
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124.989
124.252

77.318
77.000
76.682



3q

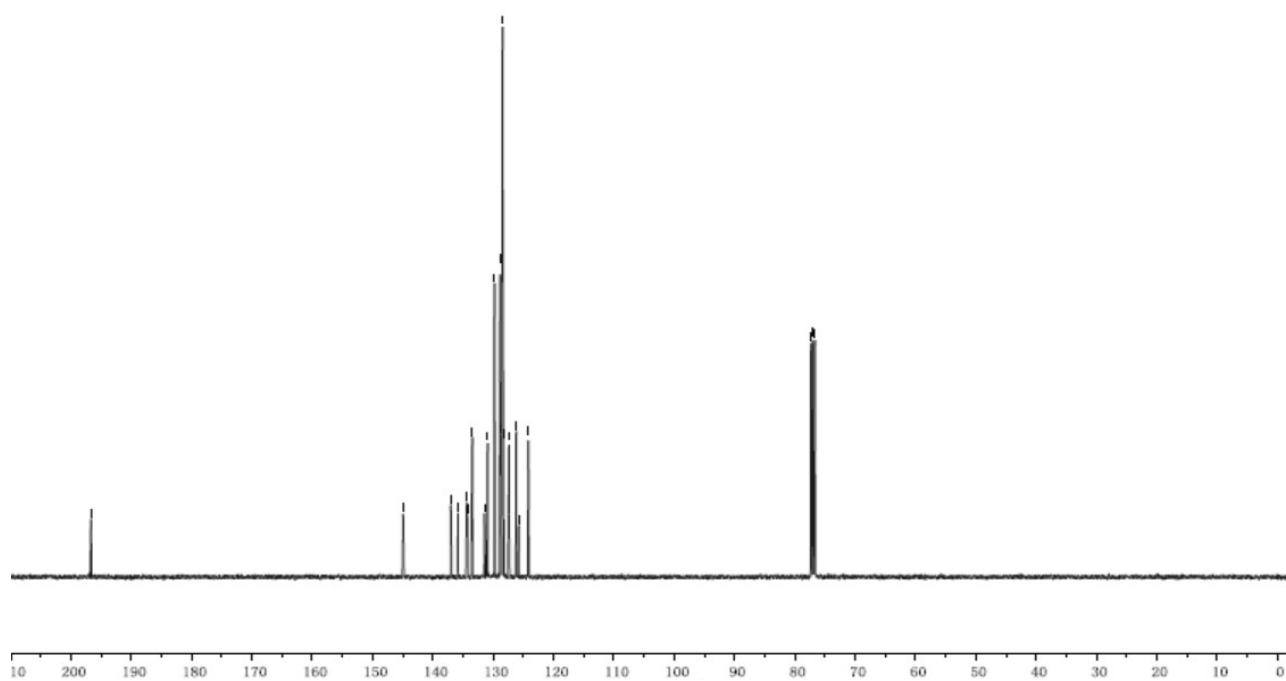
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7.5903
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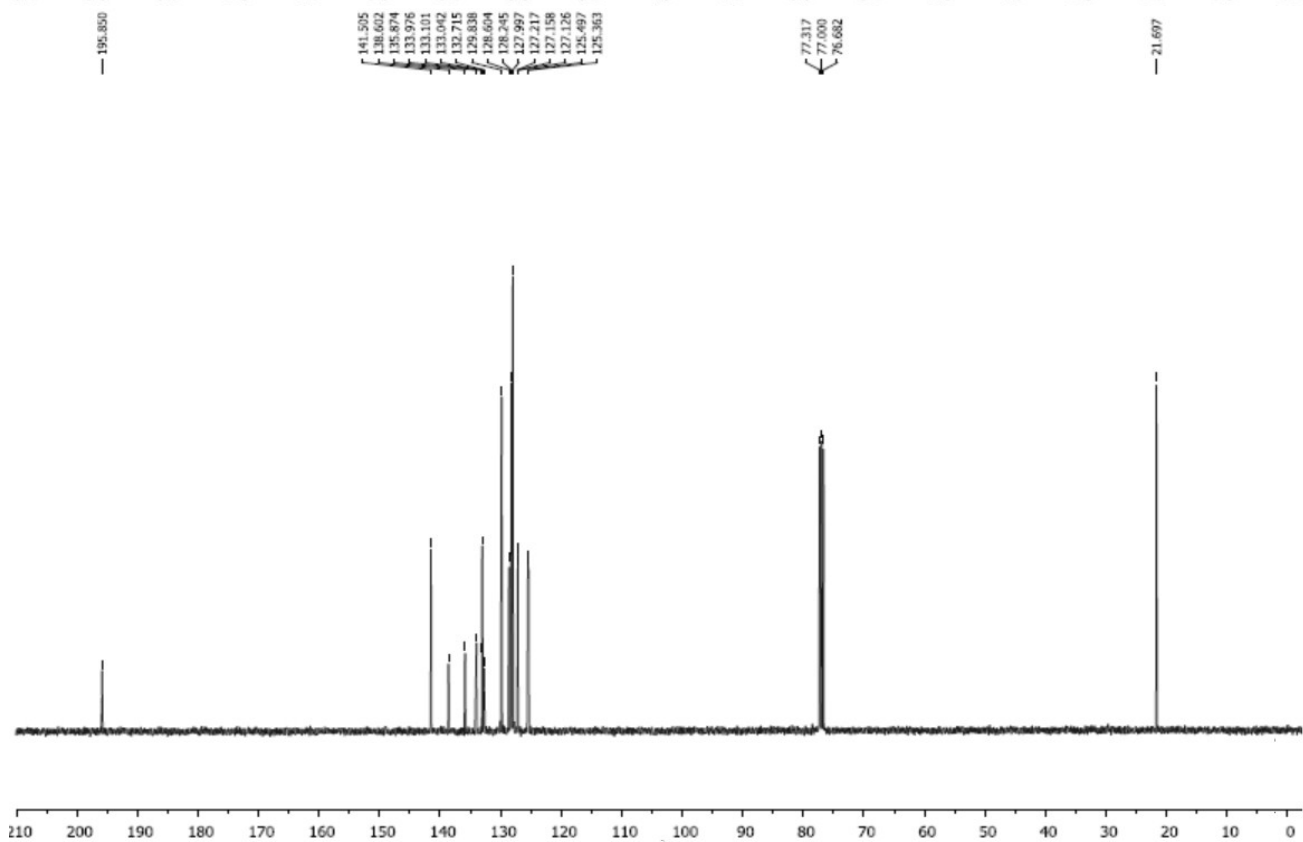
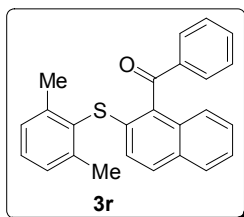
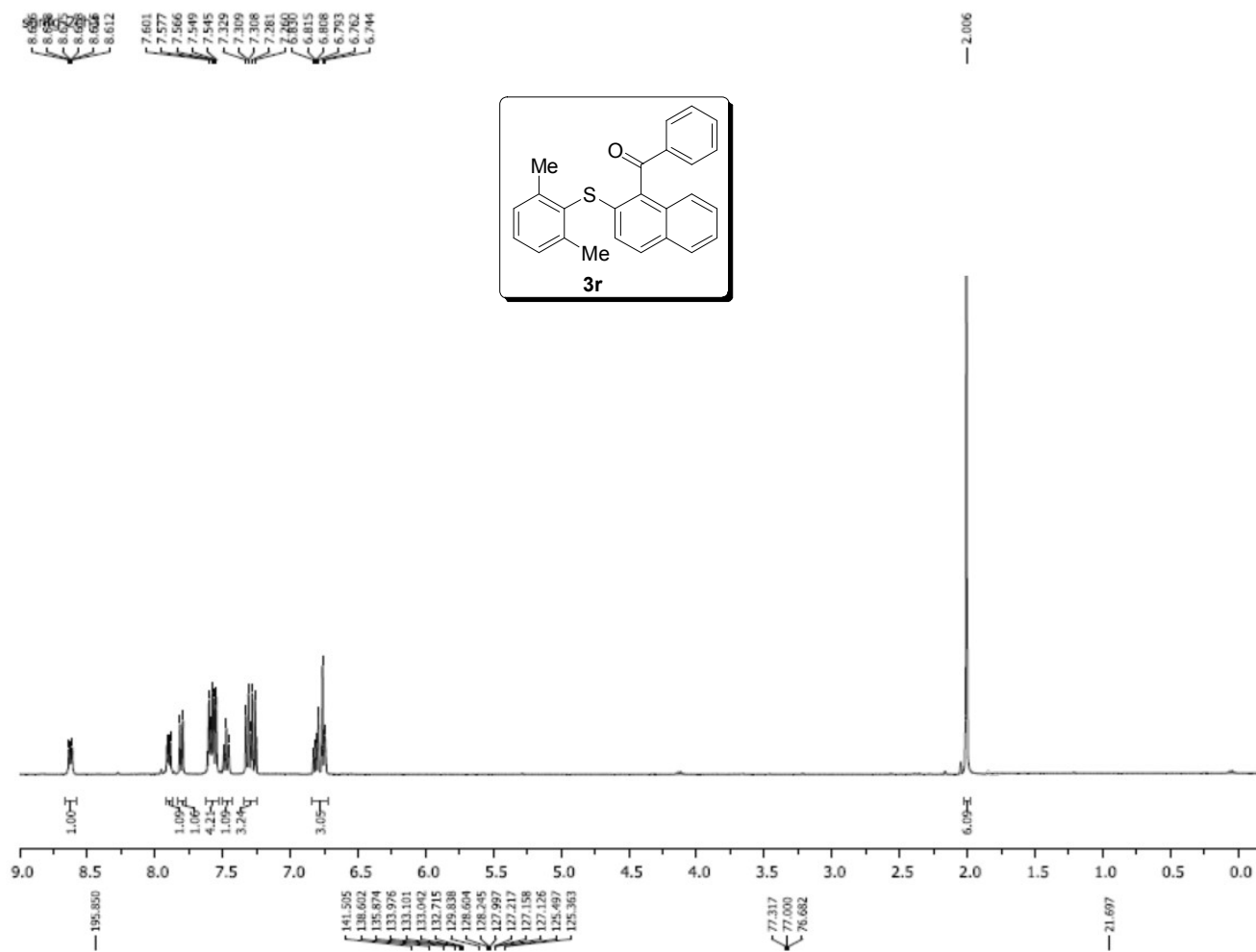
— 130k, 6002

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134.385
134.255
133.463
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131.594
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77.317
77.000
76.682

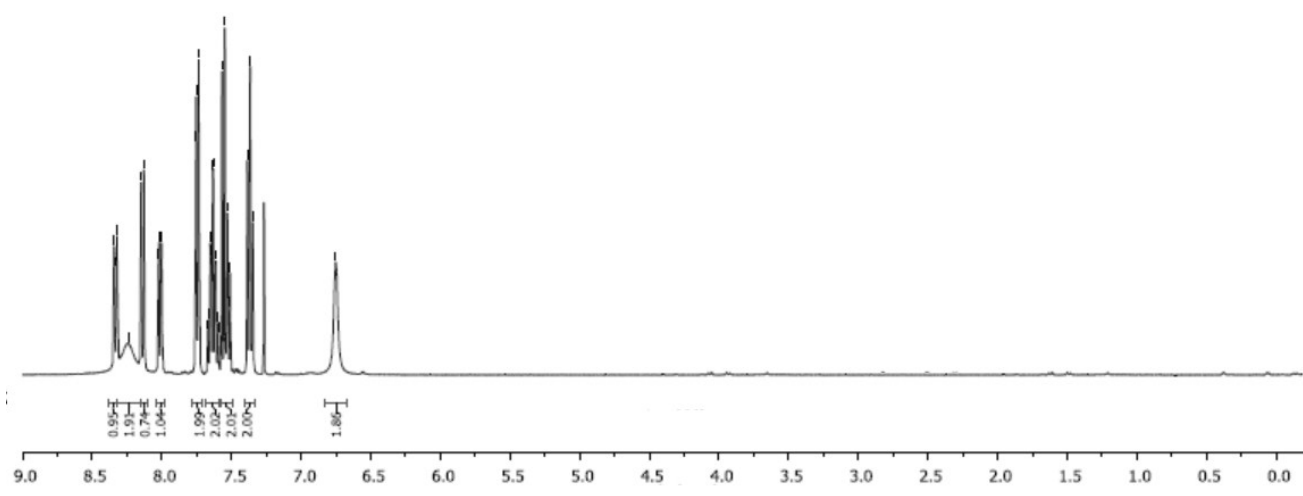
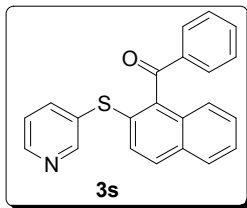


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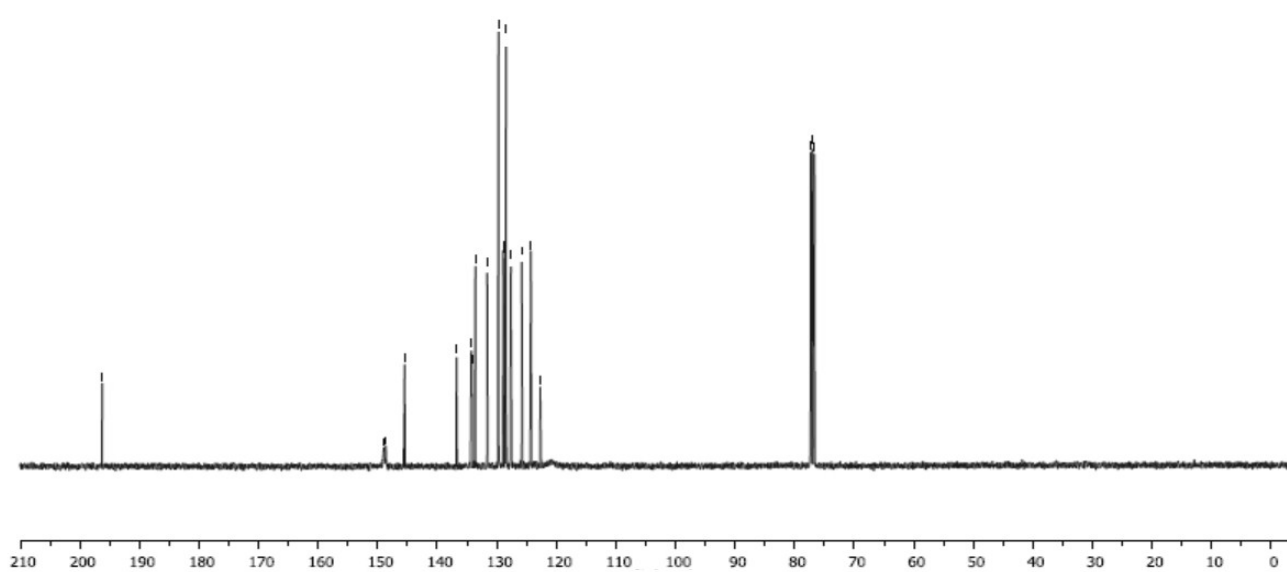


3s

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8.000
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6.751

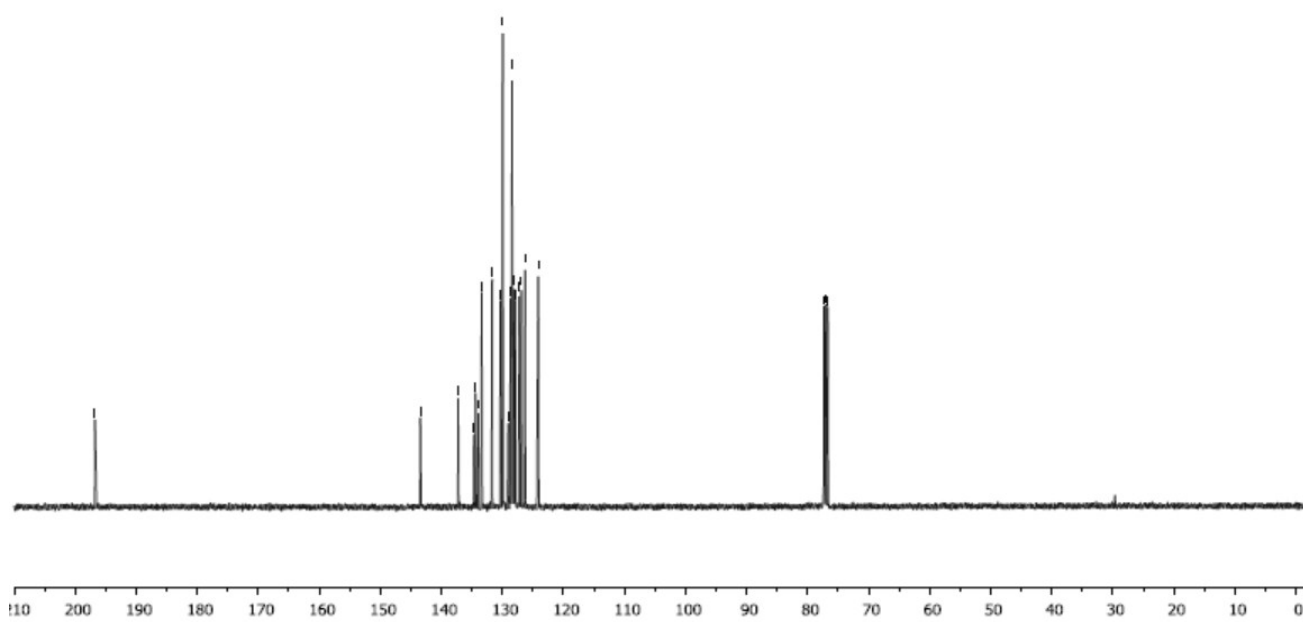
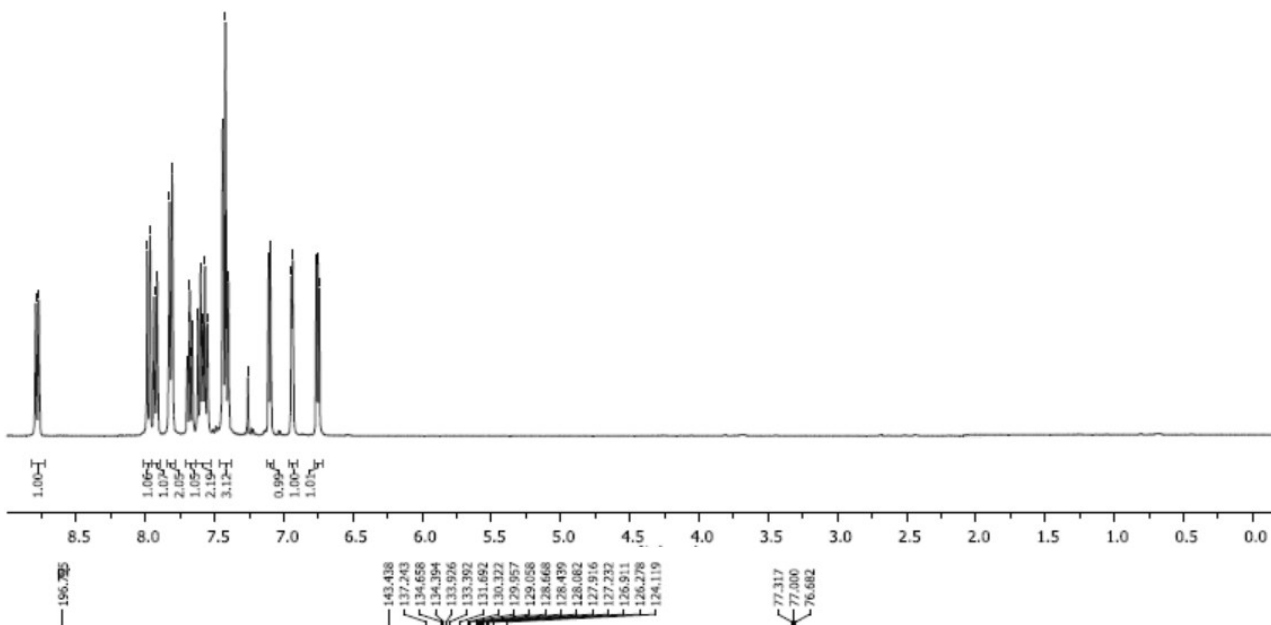
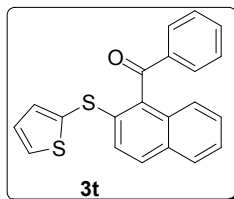


196.250
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148.639
145.470
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134.289
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133.594
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124.286
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77.000
76.682



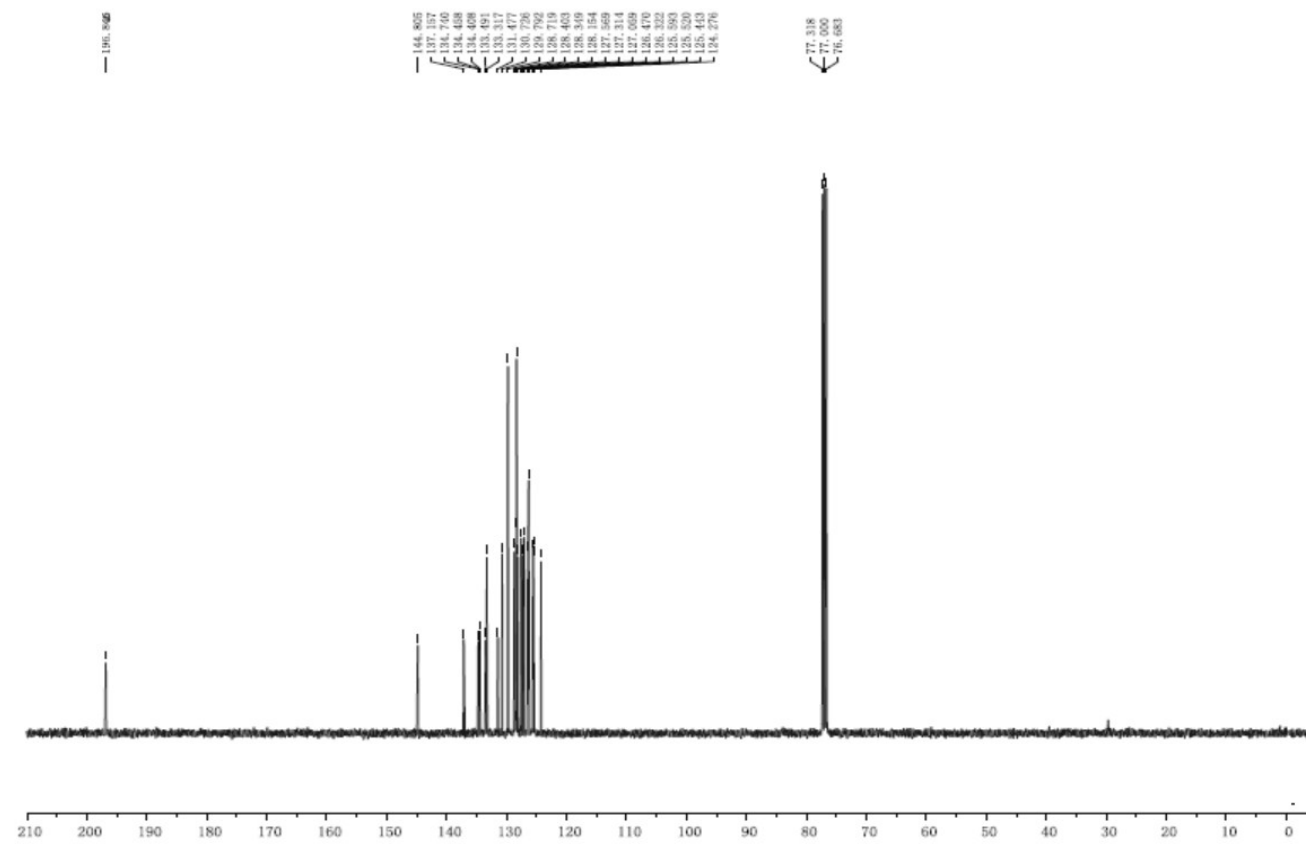
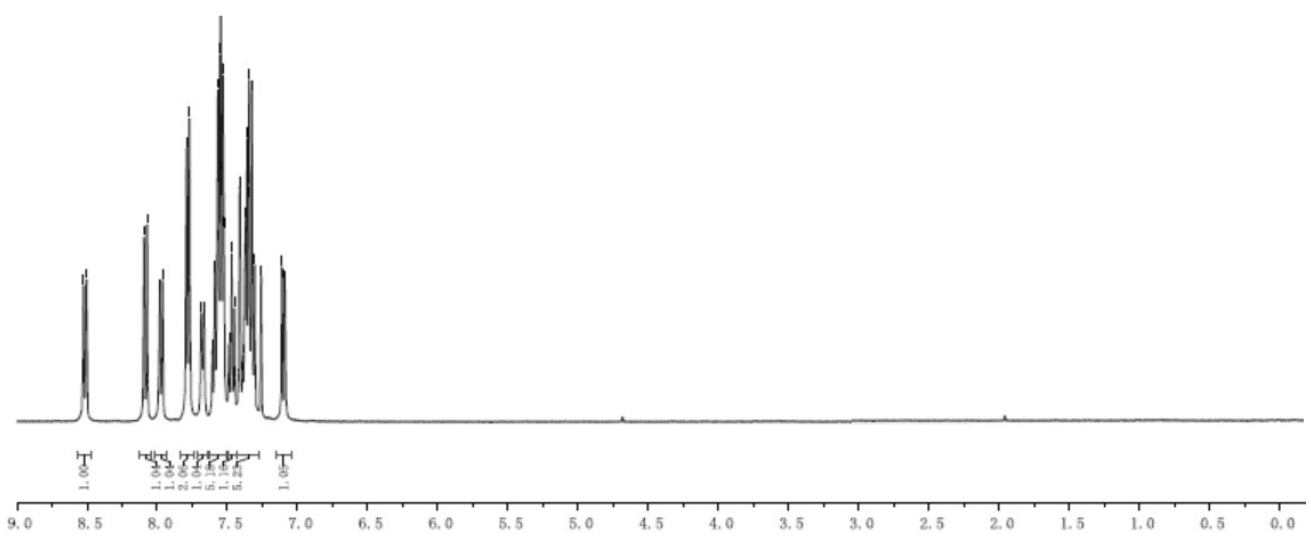
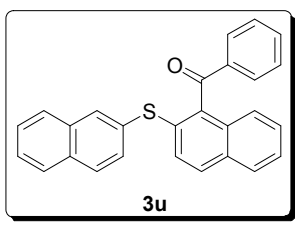
3t

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7.682
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7.675
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7.422
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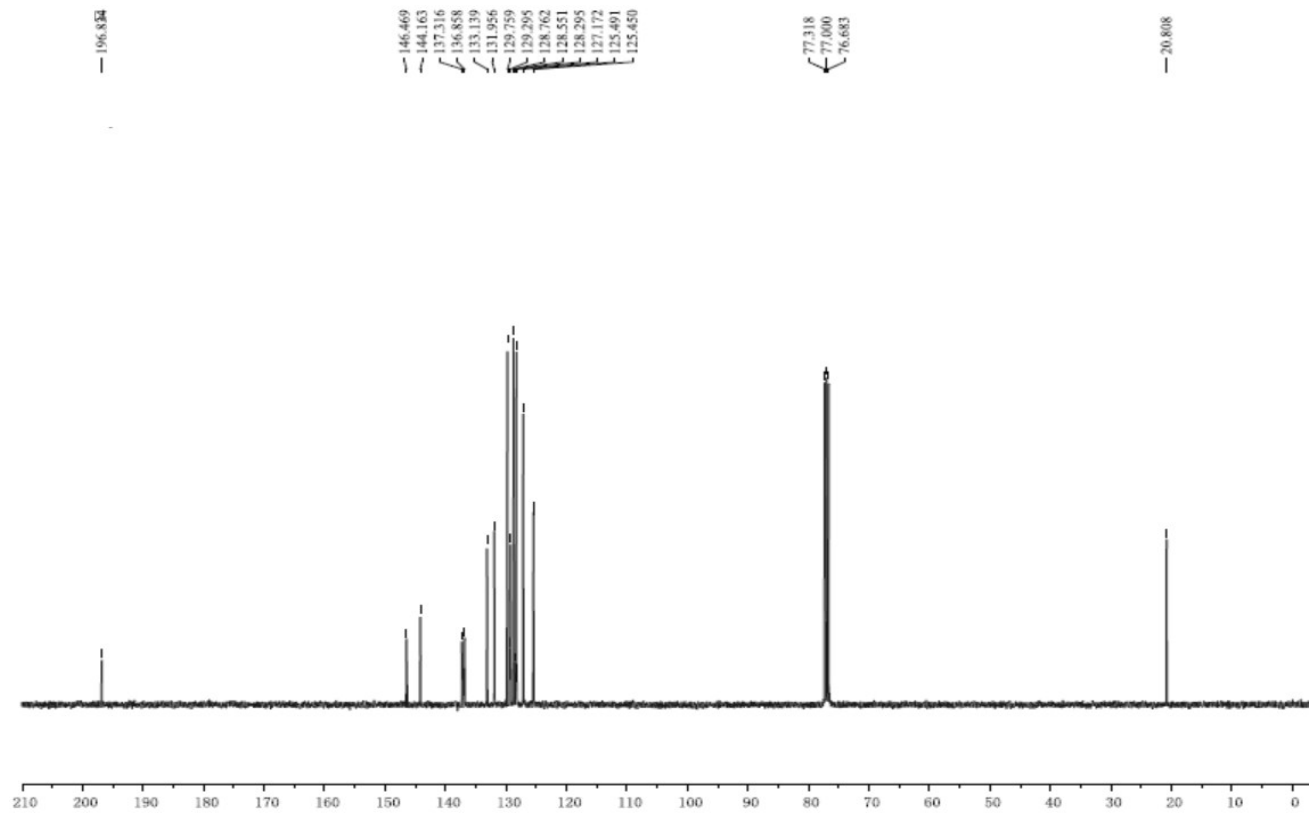
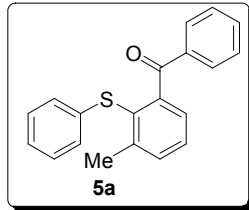
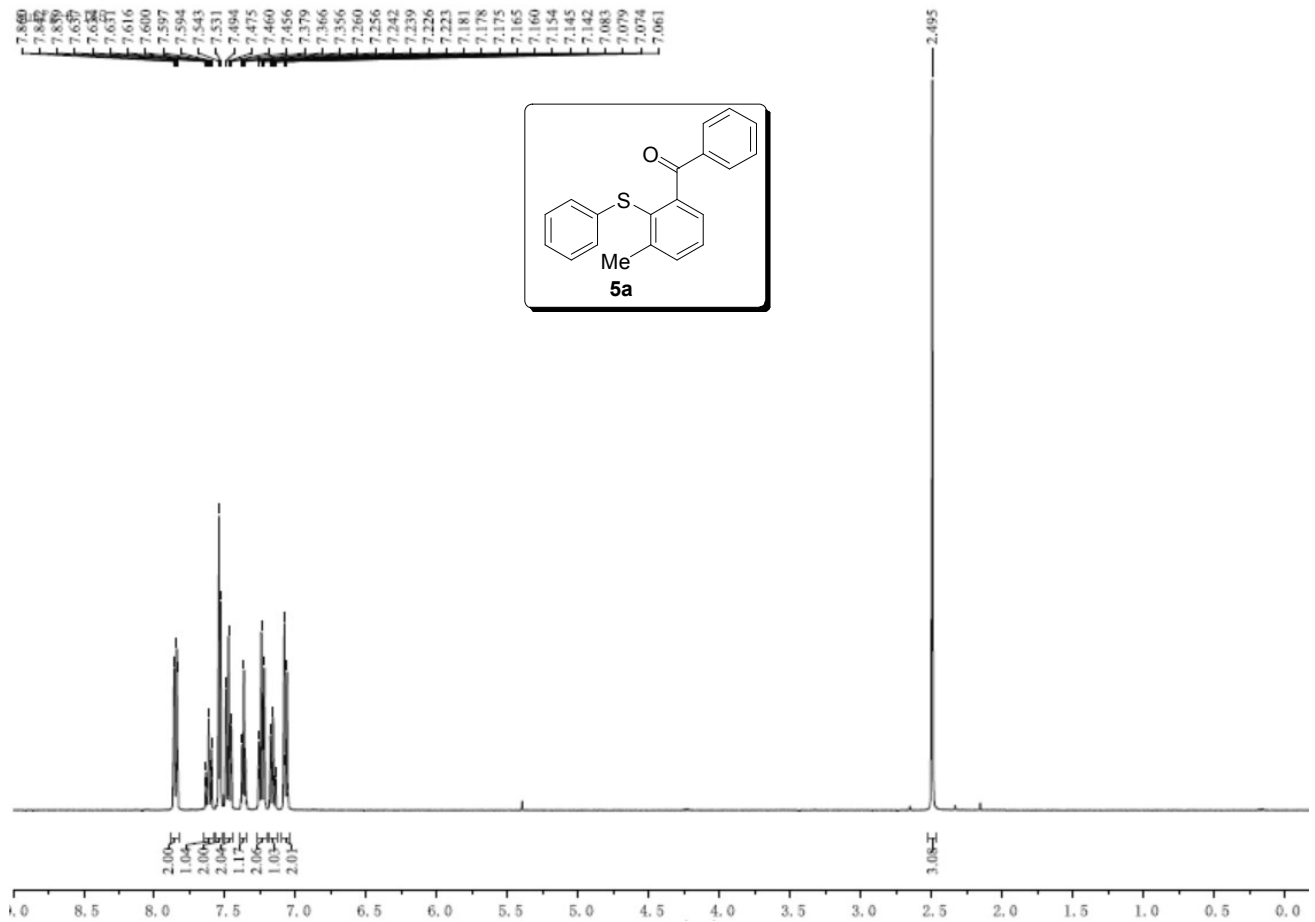


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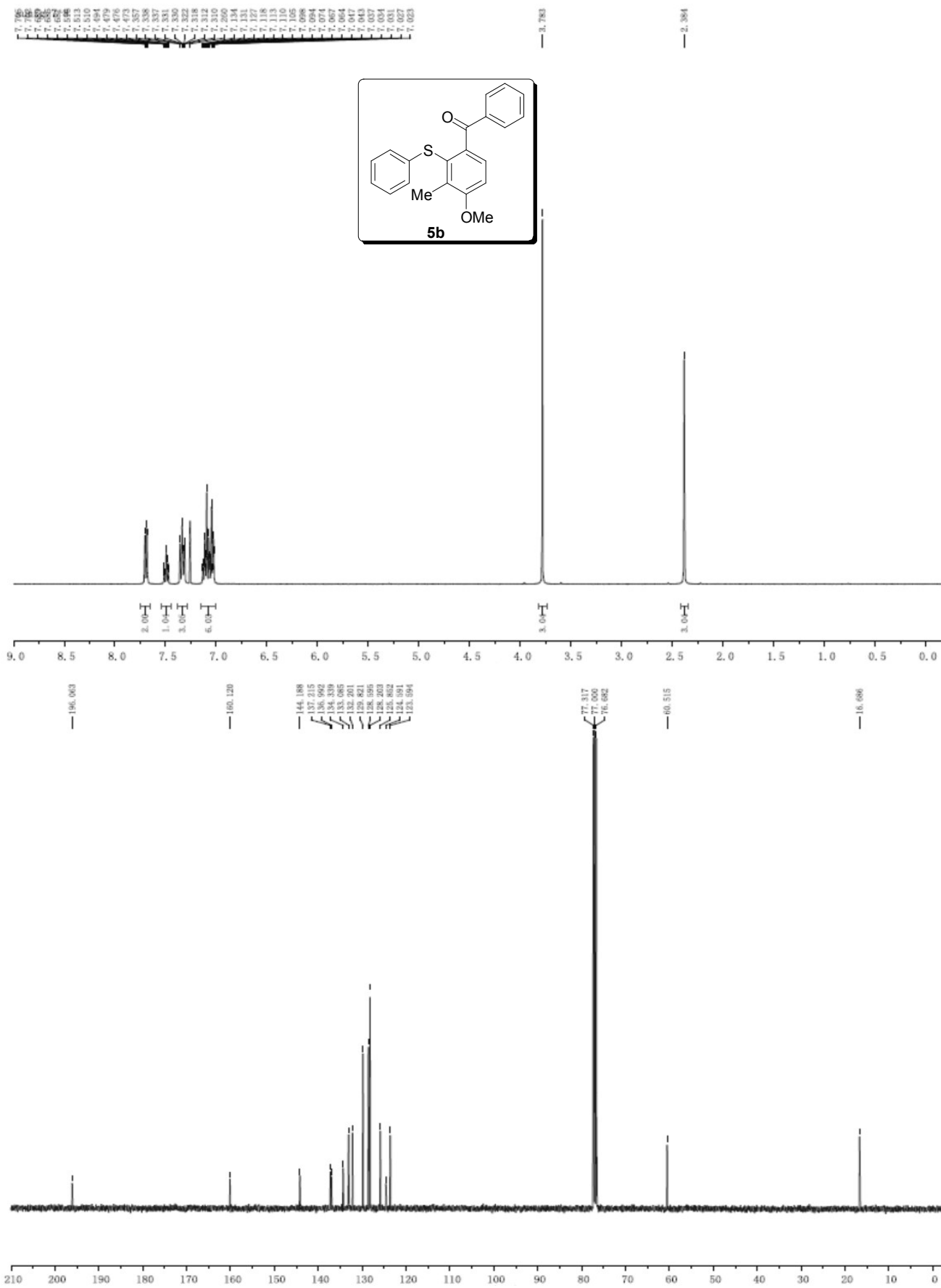
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7.7688
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7.6770
7.6664
7.6654
7.6505
7.6591
7.6588
7.6668
7.6661
7.6523
7.6522
7.6541
7.6532
7.6526
7.6524
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7.4819
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7.4019
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7.3690
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7.2600
7.1111
7.1107
7.0590
7.0885



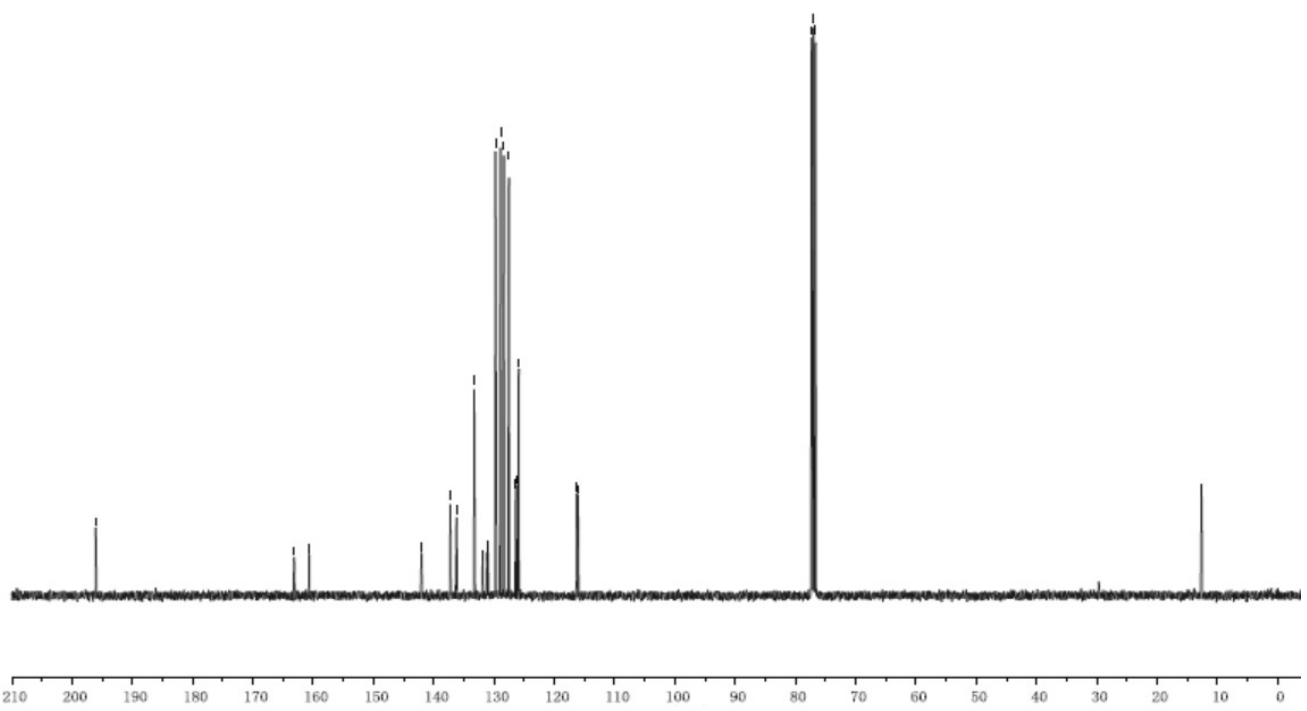
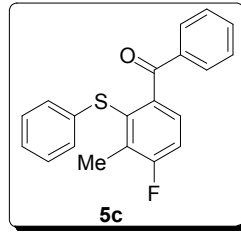
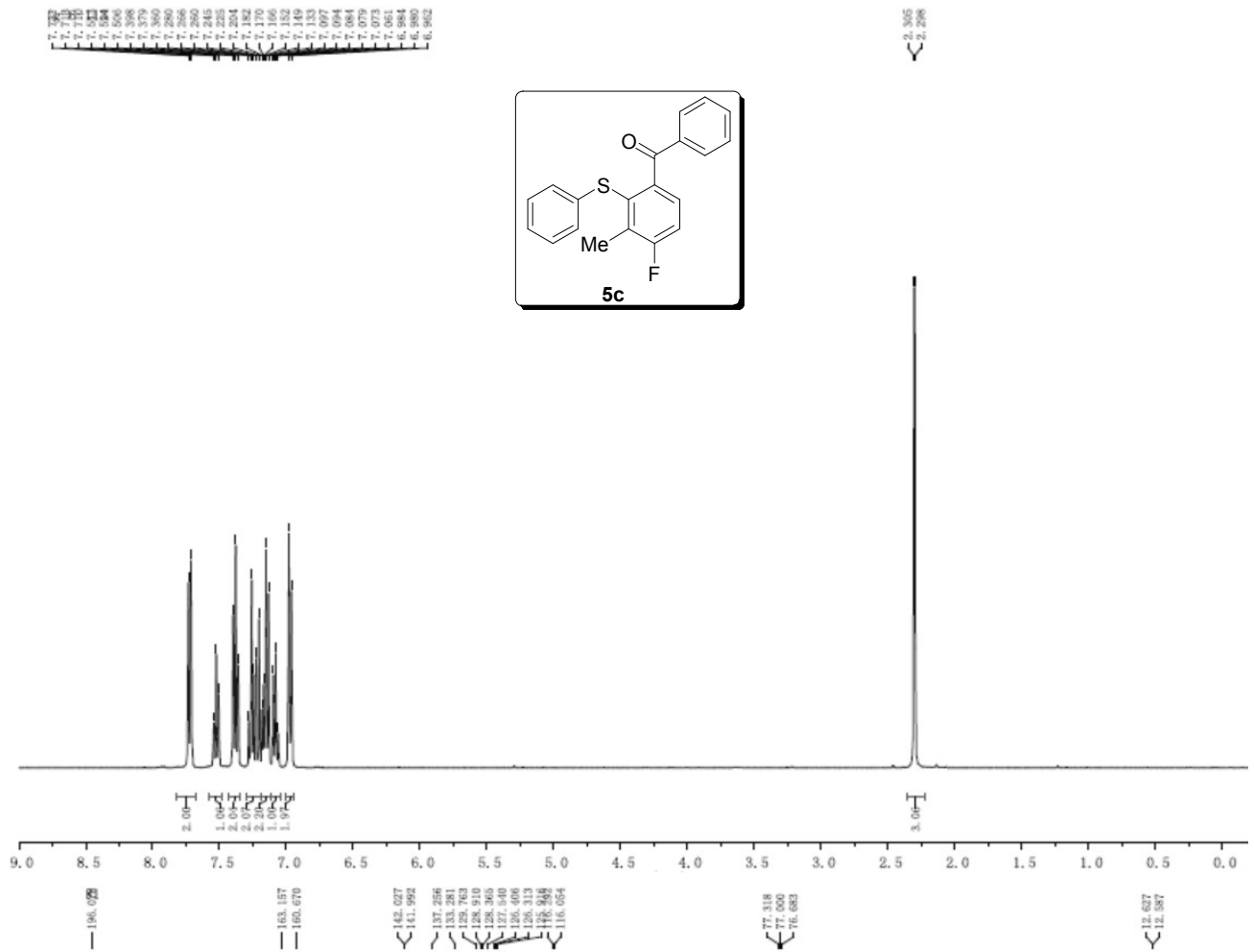
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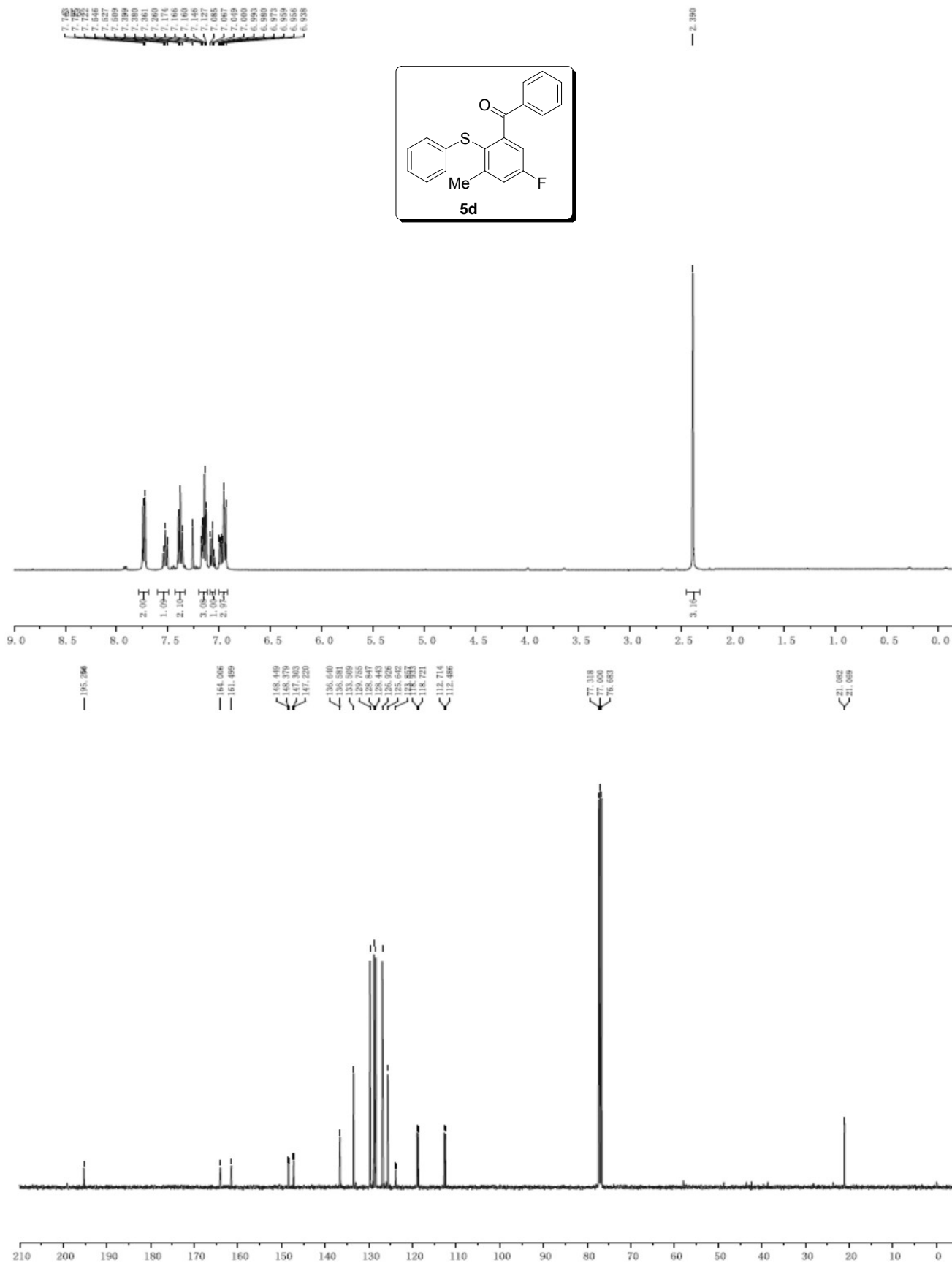
5b



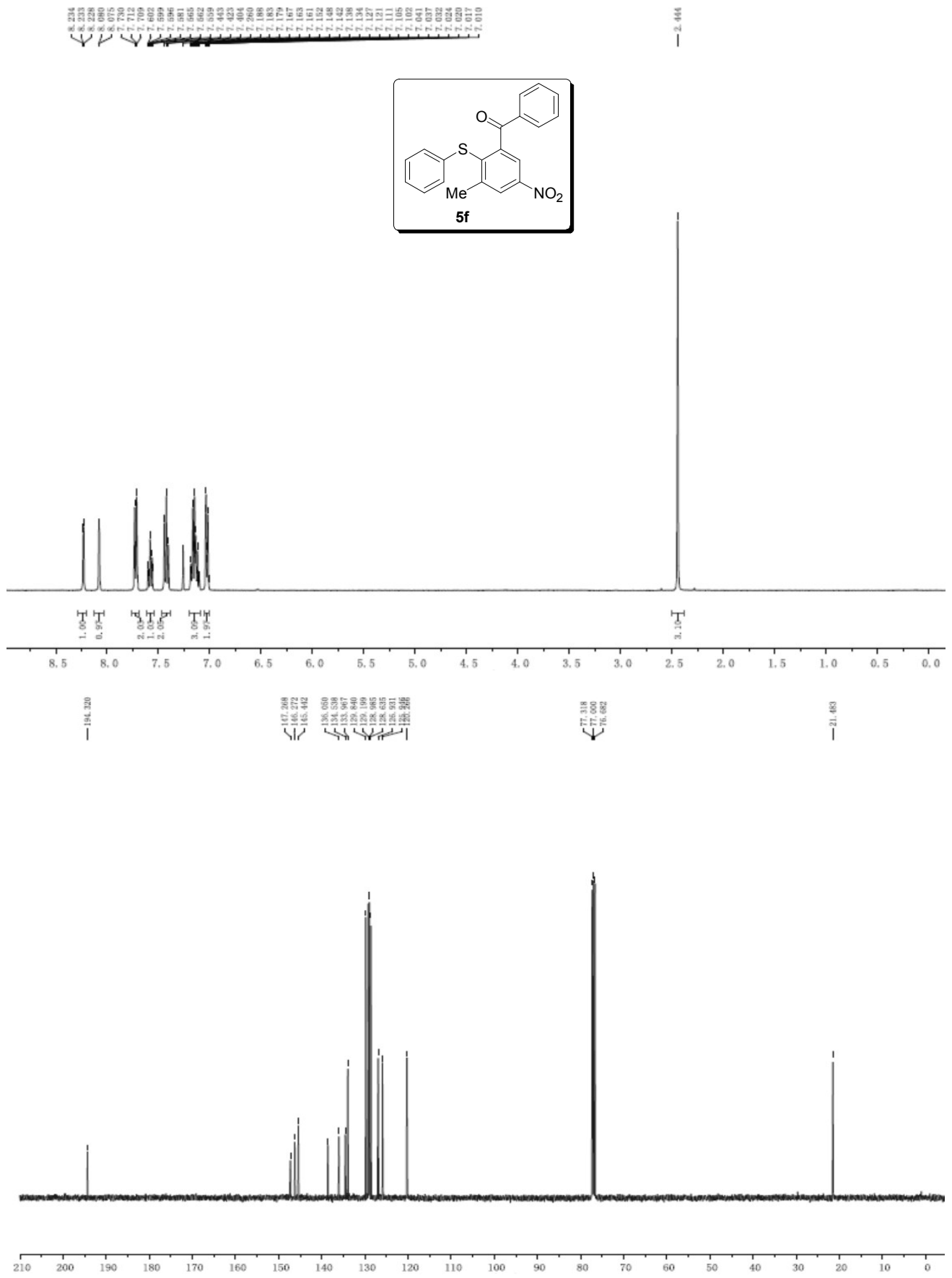
5c



5d



5e



5g

