

Supporting Information

Palladium-Catalyzed Carbonylative Transformation of Aryl Iodides and Sulfonyl Chlorides: Convenient Access to Thioesters

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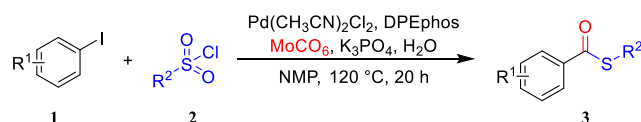
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1. General Information

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere. All reagents were from commercial sources and used as received without further purification. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (b.p. 60-90 °C) and ethyl acetate as the eluents. ¹H and ¹³C NMR spectra were taken on 400 MHz instruments and spectral data were reported in ppm relative to tetramethylsilane (TMS) as the internal standard and CDCl₃ (¹H NMR δ 7.26, ¹³C NMR δ 77.0) as solvent. All coupling constants (*J*) are reported in Hz with the following abbreviations: s = singlet, d = doublet, dd = double doublet, ddd = double doublet of doublets, t = triplet, dt = double triplet, q = quartet, m = multiplet, br = broad. Gas (GC) analyses were performed on a Shimadzu GC-2014C chromatograph equipped with FID detector. Mass spectra (MS) were measured on spectrometer by direct inlet at 70 eV.

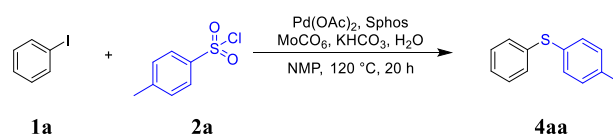
2. General Procedure

2.1 General Procedure of Thioesters 3



Pd(CH₃CN)₂Cl₂ (4 mol%), DPEphos (3.5 mol%), Mo(CO)₆ (0.7 mmol), K₃PO₄ (0.7 mmol) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Aryl iodides (0.5 mmol), sulfonyl chlorides (0.6 mmol), H₂O (0.5 mmol), and NMP (2 mL) were added into the tube via syringe. The tube was sealed and the mixture was stirred at 120 °C for 20 h. After the reaction was completed, the crude mixture was filtered and concentrated under vacuum. The crude product was purified by column chromatography on silica gel to afford the desired thioester products **3**.

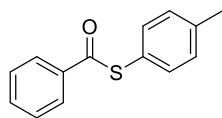
2.2 General Procedure of Thioether 4aa



Pd(OAc)₂ (4 mol%), Sphos (8 mol%), Mo(CO)₆ (0.75 mmol), KHCO₃ (0.7 mmol), 4-methylbenzenesulfonyl chloride (0.6 mmol), were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Iodobenzene (0.5 mmol), H₂O (0.5 mmol), and NMP (2 mL) were added into the tube via syringe. The tube was sealed and the mixture was stirred at 120 °C for 20 h. After the reaction was completed, the crude mixture was filtered and concentrated under vacuum. The crude product was purified by column chromatography on silica gel to afford the desired thioether product **4aa**.

3. Characterization of Products

3.1 Characterization of Thioesters

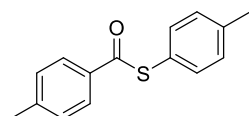


S-(*p*-tolyl) benzothioate (3aa)¹

Prepared from iodobenzene (102.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 100/1) the desired compound was isolated as a **light yellow solid** (91.2 mg, 80%). M.p. 65.0-68.0°C

¹H NMR (400 MHz, CDCl₃) δ 8.12 – 7.98 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.50 (t, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 190.5, 139.7, 136.7, 135.0, 133.5, 130.1, 128.7, 127.4, 123.7, 21.3.

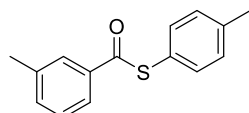


S-(*p*-tolyl) 4-methylbenzothioate (3ba)¹

Prepared from 1-iodo-4-methylbenzene (109.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 100/1) the desired compound was isolated as a **white solid** (102.0 mg, 84%). M.p. 117.3-119.5°C

¹H NMR (400 MHz, CDCl₃) δ 7.95 (d, *J* = 8.2 Hz, 2H), 7.41 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.27 (m, 4H), 2.44 (s, 3H), 2.42 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 190.0, 144.4, 139.6, 135.0, 134.1, 130.0, 129.3, 127.5, 123.9, 21.6, 21.3.



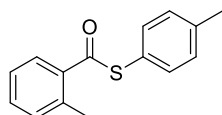
S-(*p*-tolyl) 3-methylbenzothioate (3ca)

Prepared from 1-iodo-3-methylbenzene (109.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 100/1) the desired compound was isolated as a **light yellow liquid** (97.0 mg, 80%).

¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 6.0 Hz, 2H), 7.45 – 7.35 (m, 4H), 7.29 (d, *J* = 8.0 Hz, 2H), 2.45 (s, 3H), 2.43 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 190.6, 139.6, 138.5, 136.7, 134.9, 134.3, 130.0, 128.5, 127.8, 124.6, 123.9, 21.3.

HRMS (ESI): [M+H]⁺ calcd for C₁₅H₁₅OS⁺, 243.0838; found, 243.0858.

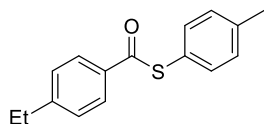


S-(*p*-tolyl) 2-methylbenzothioate (3da)¹

Prepared from 1-iodo-2-methylbenzene (109.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 100/1) the desired compound was isolated as a **white solid** (87.1 mg, 72%). M.p. 39.2-42.0°C

¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.42 (m, 3H), 7.33 – 7.27 (m, 4H), 2.51 (s, 3H), 2.42 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 192.6, 139.7, 137.3, 136.8, 134.8, 131.9, 131.7, 130.1, 128.5, 125.8, 124.7, 21.3, 20.7.



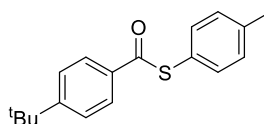
S-(p-tolyl) 4-ethylbenzothioate (3ea)

Prepared from 1-ethyl-4-iodobenzene (116.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 100/1) the desired compound was isolated as a **white solid** (100.0 mg, 78%). M.p. 82.4-84.5°C

^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 8.2$ Hz, 2H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.29 (d, $J = 8.2$ Hz, 2H), 7.25 (d, $J = 8.6$ Hz, 2H), 2.71 (q, $J = 7.6$ Hz, 2H), 2.39 (s, 3H), 1.26 (t, $J = 7.6$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 190.1, 150.6, 139.6, 135.0, 134.4, 130.0, 128.2, 127.6, 124.0, 29.0, 21.3, 15.1.

HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{16}\text{H}_{17}\text{OS}^+$, 257.0995; found, 257.1013.



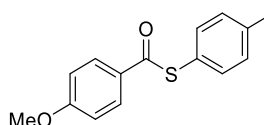
S-(p-tolyl) 4-(tert-butyl)benzothioate (3fa)

Prepared from 1-(tert-butyl)-4-iodobenzene (130.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 100/1) the desired compound was isolated as a **white solid** (105.1 mg, 74%). M.p. 74.6-77.8°C

^1H NMR (400 MHz, CDCl_3) δ 7.99 (d, $J = 8.5$ Hz, 2H), 7.51 (d, $J = 8.5$ Hz, 2H), 7.41 (d, $J = 8.1$ Hz, 2H), 7.28 (d, $J = 8.0$ Hz, 2H), 2.42 (s, 3H), 1.37 (s, 9H).

^{13}C NMR (101 MHz, CDCl_3) δ 190.0, 157.4, 139.6, 135.0, 134.1, 130.0, 127.4, 125.6, 124.0, 35.2, 31.0, 21.3.

HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{21}\text{OS}^+$, 285.1308; found, 285.1317.

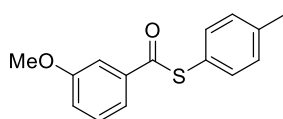


S-(p-tolyl) 4-methoxybenzothioate (3ga)¹

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the desired compound was isolated as a **light yellow solid** (98.0 mg, 76%). M.p. 63.2-65.6°C

^1H NMR (400 MHz, CDCl_3) δ 8.00 (d, $J = 8.9$ Hz, 2H), 7.38 (d, $J = 8.1$ Hz, 2H), 7.30 – 7.23 (m, 2H), 6.95 (d, $J = 8.9$ Hz, 2H), 3.87 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 189.0, 163.9, 139.6, 135.1, 130.0, 129.7, 129.5, 124.1, 113.9, 55.5, 21.3.



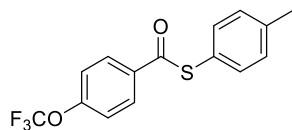
S-(p-tolyl) 3-methoxybenzothioate (3ha)

Prepared from 1-iodo-3-methoxybenzene (117.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the desired compound was isolated as a **light yellow liquid** (94.2 mg, 73%).

¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, *J* = 7.7 Hz, 1H), 7.51–7.50 (m, 1H), 7.42–7.35 (m, 3H), 7.27 (s, 1H), 7.25 (d, *J* = 2.1 Hz, 1H), 7.16–7.12 (m, 1H), 3.85 (s, 3H), 2.40 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 190.5, 159.8, 139.8, 138.0, 134.9, 130.1, 129.7, 123.8, 120.0, 119.9, 111.7, 55.4, 21.3.

HRMS (ESI): [M+Na]⁺ calcd for C₁₅H₁₄NaO₂S⁺, 281.0607; found, 281.0627.



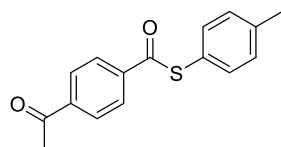
S-(p-tolyl) 4-(trifluoromethoxy)benzothioate (3ia)

Prepared from 1-iodo-4-(trifluoromethoxy)benzene (144.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the desired compound was isolated as a **light yellow solid** (98.3 mg, 63%). M.p. 39.5–41.6°C

¹H NMR (400 MHz, CDCl₃) δ 8.14–8.02 (m, 2H), 7.40 (d, *J* = 8.1 Hz, 2H), 7.35–7.26 (m, 4H), 2.42 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 189.2, 152.9, 140.1, 134.9, 130.2, 129.4, 127.5, 123.2, 120.5, 120.3 (q, *J* = 258.8 Hz), 21.4.

HRMS (ESI): [M+H]⁺ calcd for C₁₅H₁₂F₃O₂S⁺, 313.0505; found, 313.0522.



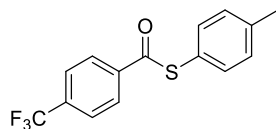
S-(p-tolyl) 4-acetylbenzothioate (3ja)

Prepared from 1-(4-iodophenyl)ethan-1-one (123.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 30/1) the desired compound was isolated as a **white solid** (109.3 mg, 81%). M.p. 104.8–107.0°C

¹H NMR (400 MHz, CDCl₃) δ 8.09 (d, *J* = 8.5 Hz, 2H), 8.04 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.65 (s, 3H), 2.41 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 197.2, 190.0, 140.5, 140.1, 140.0, 134.8, 130.2, 128.5, 127.6, 123.2, 26.8, 21.3.

HRMS (ESI): [M+H]⁺ calcd for C₁₆H₁₅O₂S⁺, 271.0787; found, 271.0802.

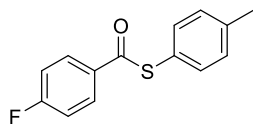


S-(p-tolyl) 4-(trifluoromethyl)benzothioate (3ka)¹

Prepared from 1-iodo-4-(trifluoromethyl)benzene (136.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the desired compound was isolated as a **white solid** (87.3 mg, 59%). M.p. 99.4–101.6°C

¹H NMR (400 MHz, CDCl₃) δ 8.13 (d, *J* = 8.2 Hz, 2H), 7.75 (d, *J* = 8.2 Hz, 2H), 7.40 (d, *J* = 8.0 Hz, 2H), 7.29 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 189.8, 140.2, 139.5, 134.9, 130.2, 127.8, 125.8 (d, *J* = 3.4 Hz), 123.5 (q, *J* = 272.7 Hz), 123.0, 21.3.

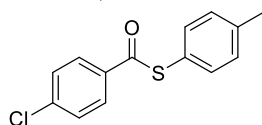


S-(p-tolyl) 4-fluorobenzothioate (3la)¹

Prepared from 1-fluoro-4-iodobenzene (111.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 100/1) the desired compound was isolated as a **white solid** (100.0 mg, 81%). M.p. 64.2-66.8°C

¹H NMR (400 MHz, CDCl₃) δ 8.08 – 8.01 (m, 2H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.30 – 7.23 (m, 2H), 7.19 – 7.12 (m, 2H), 2.40 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 189.1, 166.0 (d, *J* = 255.3 Hz), 140.0, 135.0, 133.0, 130.1, 130.0 (d, *J* = 9.4 Hz), 123.5, 115.9 (d, *J* = 22.1 Hz), 21.3.

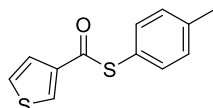


S-(p-tolyl) 4-chlorobenzothioate (3ma)¹

Prepared from 1-chloro-4-iodobenzene (119.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 100/1) the desired compound was isolated as a **white solid** (89.1 mg, 68%). M.p. 107.5-109.3°C

¹H NMR (400 MHz, CDCl₃) δ 7.97 (d, *J* = 8.6 Hz, 2H), 7.46 (d, *J* = 8.5 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.28 (d, *J* = 8.0 Hz, 2H), 2.41 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 189.4, 140.0, 139.9, 135.0, 134.9, 130.1, 129.0, 128.8, 123.3, 21.3.

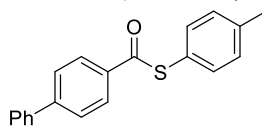


S-(p-tolyl) thiophene-3-carbothioate (3na)¹

Prepared from 3-iodothiophene (105.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the desired compound was isolated as a **white solid** (71.4 mg, 61%). M.p. 67.8-70.0°C

¹H NMR (400 MHz, CDCl₃) δ 8.19 – 8.17 (m, 1H), 7.58 – 7.55 (m, 1H), 7.38 (d, *J* = 8.1 Hz, 2H), 7.36 – 7.32 (m, 1H), 7.25 (d, *J* = 8.0 Hz, 1H), 2.39 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 183.9, 140.3, 139.8, 134.9, 130.9, 130.0, 126.5, 126.1, 123.5, 21.3.



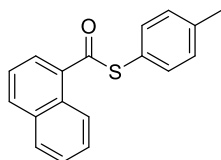
S-(p-tolyl) [1,1'-biphenyl]-4-carbothioate (3oa)

Prepared from 4-iodo-1,1'-biphenyl (140.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the desired compound was isolated as a **white solid** (114 mg, 75%). M.p. 121.2-123.4°C

¹H NMR (400 MHz, CDCl₃) δ 8.11 (d, *J* = 8.4 Hz, 2H), 7.71 (d, *J* = 8.4 Hz, 2H), 7.67 – 7.62 (m, 2H), 7.52 – 7.46 (m, 2H), 7.45 – 7.40 (m, 3H), 7.29 (d, *J* = 7.9 Hz, 2H), 2.42 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 190.1, 146.3, 139.8, 139.8, 135.4, 135.0, 130.1, 129.0, 128.3, 128.0, 127.3, 127.3, 123.8, 21.4.

HRMS (ESI): [M+H]⁺ calcd for C₂₀H₁₇OS⁺, 305.0995; found, 305.1012.



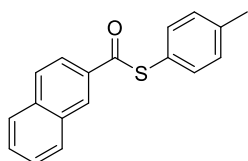
S-(*p*-tolyl)naphthalene-1-carbothioate (3pa)

Prepared from 1-iodonaphthalene (127.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 100/1) the desired compound was isolated as a **yellow solid** (96.0 mg, 69%). M.p. 60.8-62.5°C

¹H NMR (400 MHz, CDCl₃) δ 8.56 (d, *J* = 8.2 Hz, 1H), 8.25 – 8.21 (m, 1H), 8.05 (d, *J* = 8.2 Hz, 1H), 7.94 – 7.85 (m, 1H), 7.64 – 7.52 (m, 3H), 7.50 (d, *J* = 8.1 Hz, 2H), 7.33 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 192.7, 139.8, 134.8, 134.7, 133.8, 133.1, 130.1, 129.3, 128.3, 128.0, 127.9, 126.6, 125.3, 124.7, 124.4, 21.4.

HRMS (ESI): [M+Na]⁺ calcd for C₁₈H₁₄NaOS⁺, 301.0658; found, 301.0679.



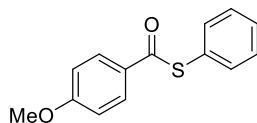
S-(*p*-tolyl)naphthalene-2-carbothioate (3qa)

Prepared from 2-iodonaphthalene (127.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the desired compound was isolated as a **white solid** (124 mg, 89%). M.p. 117.2-119.5°C

¹H NMR (400 MHz, CDCl₃) δ 8.63 (s, 1H), 8.07 – 7.98 (m, 2H), 7.91 (t, *J* = 8.2 Hz, 2H), 7.66 – 7.55 (m, 2H), 7.47 (d, *J* = 8.0 Hz, 2H), 7.31 (d, *J* = 7.9 Hz, 2H), 2.44 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 190.4, 139.8, 135.8, 135.0, 134.0, 132.4, 130.1, 129.5, 128.9, 128.6, 128.5, 127.8, 126.9, 123.8, 123.2, 21.3.

HRMS (ESI): [M+H]⁺ calcd for C₁₈H₁₅OS⁺, 279.0838; found, 279.0858.

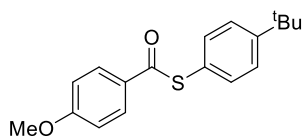


S-phenyl 4-methoxybenzothioate (3gb)¹

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and benzenesulfonyl chloride (106.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the desired compound was isolated as a **light yellow solid** (102.5 mg, 84%). M.p. 89.5-91.2°C

¹H NMR (400 MHz, CDCl₃) δ 8.11 – 7.95 (m, 2H), 7.57 – 7.51 (m, 2H), 7.49 – 7.44 (m, 3H), 6.97 (d, *J* = 8.9 Hz, 2H), 3.87 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 188.5, 163.9, 135.1, 129.6, 129.3, 129.1, 127.6, 113.8, 55.4.



S-(4-(*tert*-butyl)phenyl) 4-methoxybenzothioate (3gc)

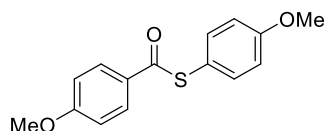
Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and 4-(*tert*-butyl)benzenesulfonyl chloride (139.2 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the

desired compound was isolated as a **light yellow solid** (83 mg, 55%). M.p. 84.6-85.8°C

¹H NMR (400 MHz, CDCl₃) δ 8.09 – 7.95 (m, 2H), 7.57 – 7.37 (m, 4H), 7.04 – 6.87 (m, 2H), 3.88 (s, 3H), 1.36 (s, 9H).

¹³C NMR (101 MHz, CDCl₃) δ 189.0, 163.9, 152.5, 134.8, 129.6, 129.5, 126.3, 124.1, 113.8, 55.5, 31.2.

HRMS (ESI): [M+Na]⁺ calcd for C₁₈H₂₀NaO₂S⁺, 323.1076; found, 323.1092.



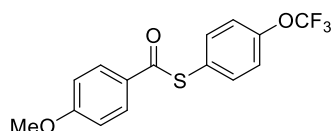
S-(4-methoxyphenyl) 4-methoxybenzothioate (3gd)

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and 4-methoxybenzenesulfonyl chloride (123.6 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 20/1) the desired compound was isolated as a **white solid** (110 mg, 80%). M.p. 126.9-129.5°C

¹H NMR (400 MHz, CDCl₃) δ 8.04 – 7.97 (m, 2H), 7.43 – 7.39 (m, 2H), 7.00 – 6.91 (m, 4H), 3.86 (s, 3H), 3.83 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 189.3, 163.8, 160.6, 136.6, 129.6, 129.3, 118.1, 114.8, 113.8, 55.4, 55.3.

HRMS (ESI): [M+Na]⁺ calcd for C₁₅H₁₄NaO₃S⁺, 297.0556; found, 297.0575.



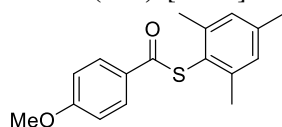
S-(4-(trifluoromethoxy)phenyl) 4-methoxybenzothioate (3ge)

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and 4-(trifluoromethoxy)benzenesulfonyl chloride (156.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 30/1) the desired compound was isolated as a **light yellow solid** (99 mg, 60%). M.p. 75.4-78.2°C

¹H NMR (400 MHz, CDCl₃) δ 8.04 – 7.94 (m, 2H), 7.58 – 7.51 (m, 2H), 7.29 (d, *J* = 8.1 Hz, 2H), 7.01 – 6.94 (m, 2H), 3.89 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 187.9, 164.2, 150.0, 136.7, 129.7, 129.0, 126.2, 121.4, 120.4 (q, *J* = 258 Hz), 114.0, 55.5.

HRMS (ESI): [M+H]⁺ calcd for C₁₅H₁₂F₃O₃S⁺, 329.0454; found, 329.0472.



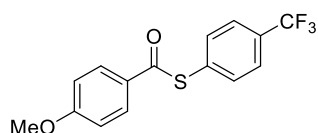
S-mesityl 4-methoxybenzothioate (3gf)

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and 2,4,6-trimethylbenzenesulfonyl chloride (130.8 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the desired compound was isolated as a **light yellow liquid** (112.0 mg, 78%).

¹H NMR (400 MHz, CDCl₃) δ 8.15 – 8.08 (m, 2H), 7.07 (s, 2H), 7.00 (d, *J* = 8.2 Hz, 2H), 3.89 (s, 3H), 2.42 (s, 3H), 2.42 (s, 3H), 2.37 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 187.8, 163.7, 142.9, 139.6, 129.8, 129.6, 129.1, 123.3, 113.7, 55.4, 21.6, 21.0.

HRMS (ESI): $[M+H]^+$ calcd for $C_{17}H_{19}O_2S^+$, 287.1100; found, 287.1120.



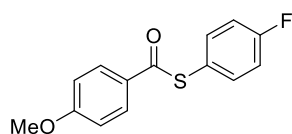
S-(4-(trifluoromethyl)phenyl) 4-methoxybenzothioate (3gg)

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and 4-(trifluoromethyl)benzenesulfonyl chloride (146.4 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 30/1) the desired compound was isolated as a **light yellow solid** (109.2 mg, 70%). M.p. 95.2-97.8°C

1H NMR (400 MHz, $CDCl_3$) δ 8.04 – 7.97 (m, 2H), 7.69 (d, $J = 8.3$ Hz, 2H), 7.64 (d, $J = 8.3$ Hz, 2H), 6.97 (d, $J = 8.9$ Hz, 2H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.2, 164.3, 135.2, 132.5, 131.2(d, $J = 32.9$ Hz), 129.8, 128.9, 125.9(d, $J = 3.0$ Hz), 123.9(q, $J = 272.3$ Hz), 114.0, 55.6.

HRMS (ESI): $[M+H]^+$ calcd for $C_{15}H_{12}F_3O_2S^+$, 313.0505; found, 313.0496.



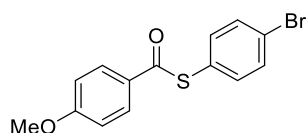
S-(4-fluorophenyl) 4-methoxybenzothioate (3gh)

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and 4-fluorobenzenesulfonyl chloride (116.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the desired compound was isolated as a **light yellow solid** (80.0 mg, 61%). M.p. 85.6-87.6°C

1H NMR (400 MHz, $CDCl_3$) δ 8.06 – 7.88 (m, 2H), 7.55 – 7.42 (m, 2H), 7.20 – 7.08 (m, 2H), 7.03 – 6.92 (m, 2H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.5, 164.1, 163.5 (d, $J = 249.8$ Hz), 137.2 (d, $J = 8.5$ Hz), 129.7, 129.1, 122.9, 116.4(d, $J = 22.1$ Hz), 113.9, 55.5.

HRMS (ESI): $[M+H]^+$ calcd for $C_{14}H_{12}FO_2S^+$, 263.0537; found, 263.0523.



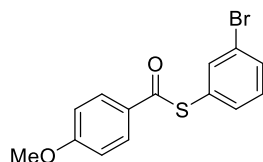
S-(4-bromophenyl) 4-methoxybenzothioate (3gi)

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and 4-bromobenzenesulfonyl chloride (152.3 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the desired compound was isolated as a **white solid** (114.3 mg, 71%). M.p. 100.2-102.3°C

1H NMR (400 MHz, $CDCl_3$) δ 8.05 – 7.94 (m, 2H), 7.65 – 7.53 (m, 2H), 7.45 – 7.34 (m, 2H), 7.02 – 6.89 (m, 2H), 3.88 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 187.8, 164.1 136.6, 132.3, 129.7, 129.0, 126.8, 124.0, 114.0, 55.5.

HRMS (ESI): $[M+H]^+$ calcd for $C_{14}H_{12}BrO_2S^+$, 322.9736; found, 322.9750.



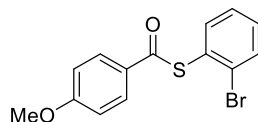
S-(3-bromophenyl) 4-methoxybenzothioate (3gj)

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and 3-bromobenzenesulfonyl chloride (152.3 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the desired compound was isolated as a **light yellow solid** (92.0 mg, 57%). M.p. 92.5-95.2°C

¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.7 Hz, 2H), 7.68 (s, 1H), 7.61 – 7.55 (m, 1H), 7.45 (d, *J* = 7.8 Hz, 1H), 7.32 (t, *J* = 7.9 Hz, 1H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 187.6, 164.1, 137.6, 133.7, 132.4, 130.4, 129.7, 129.0, 122.6, 114.0, 55.5.

HRMS (ESI): [M+H]⁺ calcd for C₁₄H₁₂BrO₂S⁺, 322.9736; found, 322.9753.



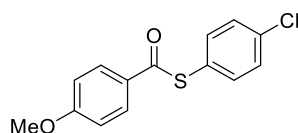
S-(2-bromophenyl) 4-methoxybenzothioate (3gk)

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and 2-bromobenzenesulfonyl chloride (152.3 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the desired compound was isolated as a **white solid** (102.0 mg, 63%). M.p. 147.2-150.0°C

¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 8.8 Hz, 2H), 7.78 – 7.71 (m, 1H), 7.65 – 7.58 (m, 1H), 7.43 – 7.36 (m, 1H), 7.33 – 7.27 (m, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 186.7, 164.1, 137.6, 133.5, 131.0, 130.0, 129.8, 129.4, 129.0, 127.9, 113.9, 55.5.

HRMS (ESI): [M+H]⁺ calcd for C₁₄H₁₂BrO₂S⁺, 322.9736; found, 322.9755.

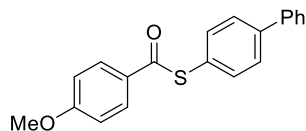


S-(4-chlorophenyl) 4-methoxybenzothioate (3gl)¹

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and 4-chlorobenzenesulfonyl chloride (126.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the desired compound was isolated as a **white solid** (97.3 mg, 70%). M.p. 146.2-158.0°C

¹H NMR (400 MHz, CDCl₃) δ 7.99 (d, *J* = 8.7 Hz, 2H), 7.50 – 7.38 (m, 4H), 6.96 (d, *J* = 8.8 Hz, 2H), 3.88 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 188.0, 164.1, 136.4, 135.8, 129.7, 129.4, 129.1, 126.1, 114.0, 55.5.



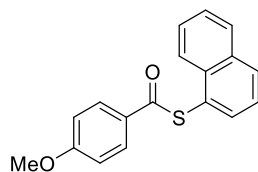
S-([1,1'-biphenyl]-4-yl) 4-methoxybenzothioate (3gm)

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and [1,1'-biphenyl]-4-sulfonyl chloride (151.2 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 50/1) the desired compound was isolated as a **white solid** (125.0 mg, 78%). M.p. 131.8-133.51°C

¹H NMR (400 MHz, CDCl₃) δ 8.04 (d, *J* = 8.8 Hz, 2H), 7.68 (d, *J* = 8.2 Hz, 2H), 7.63 (d, *J* = 7.7 Hz, 2H), 7.59 (d, *J* = 8.2 Hz, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.39 (t, *J* = 7.3 Hz, 1H), 6.98 (d, *J* = 8.8 Hz, 2H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 188.6, 164.0, 142.3, 140.3, 135.5, 129.7, 129.4, 128.8, 127.9, 127.7, 127.2, 126.5, 113.9, 55.5.

HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{20}\text{H}_{17}\text{O}_2\text{S}^+$, 321.0944; found, 321.0959.



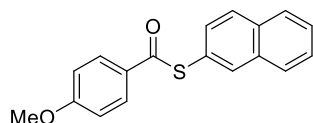
S-(naphthalen-1-yl) 4-methoxybenzothioate (3gn)

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and naphthalene-1-sulfonyl chloride (135.6 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 30/1) the desired compound was isolated as a **white solid** (112.0 mg, 76%). M.p. 122.8-125.2°C

^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, $J = 7.2$ Hz, 1H), 8.19 – 8.11 (m, 2H), 8.02 (d, $J = 8.2$ Hz, 1H), 7.97 – 7.92 (m, 1H), 7.88 – 7.83 (m, 1H), 7.62 – 7.52 (m, 3H), 7.01 (d, $J = 8.8$ Hz, 2H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 188.0, 163.9, 135.5, 134.6, 134.1, 130.8, 129.8, 129.3, 128.5, 127.0, 126.2, 125.5, 125.4, 125.0, 113.8, 55.4.

HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{15}\text{O}_2\text{S}^+$, 295.0787; found, 295.0804.



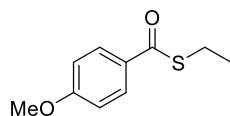
S-(naphthalen-2-yl) 4-methoxybenzothioate (3go)

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and naphthalene-2-sulfonyl chloride (135.6 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 40/1) the desired compound was isolated as a **white solid** (127.0 mg, 86%). M.p. 127.6-129.8°C

^1H NMR (400 MHz, CDCl_3) δ 8.10 – 8.00 (m, 3H), 7.95 – 7.81 (m, 3H), 7.62 – 7.51 (m, 3H), 6.98 (d, $J = 8.9$ Hz, 2H), 3.89 (s, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 188.8, 164.0, 135.0, 133.6, 133.4, 131.5, 129.7, 129.4, 128.7, 128.0, 127.8, 127.1, 126.5, 125.0, 113.9, 55.5.

HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{18}\text{H}_{15}\text{O}_2\text{S}^+$, 295.0787; found, 295.0805.



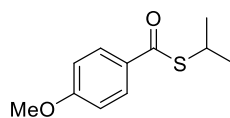
S-ethyl 4-methoxybenzothioate (3gp)

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and ethanesulfonyl chloride (76.8 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 30/1) the desired compound was isolated as a **colorless liquid** (78.4 mg, 80%).

^1H NMR (400 MHz, CDCl_3) δ 8.08 – 7.82 (m, 2H), 6.98 – 6.78 (m, 2H), 3.86 (s, 3H), 3.05 (q, $J = 7.4$ Hz, 2H), 1.34 (t, $J = 7.4$ Hz, 3H).

^{13}C NMR (101 MHz, CDCl_3) δ 190.6, 163.6, 130.1, 129.3, 113.7, 55.5, 23.3, 14.9.

HRMS (ESI): $[\text{M}+\text{H}]^+$ calcd for $\text{C}_{10}\text{H}_{13}\text{O}_2\text{S}^+$, 197.0631; found, 197.0649.



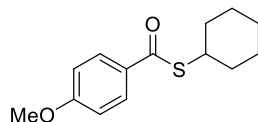
S-isopropyl 4-methoxybenzothioate (3gq)

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and propane-2-sulfonyl chloride (85.2 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 30/1) the desired compound was isolated as a **colorless liquid** (101.0 mg, 96%).

¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.83 (m, 2H), 6.97 – 6.77 (m, 2H), 3.88 – 3.77 (m, 1H), 3.84 (s, 3H), 1.39 (d, *J* = 6.9 Hz, 6H).

¹³C NMR (101 MHz, CDCl₃) δ 190.6, 163.5, 130.2, 129.2, 113.6, 55.4, 34.6, 23.2.

HRMS (ESI): [M+H]⁺ calcd for C₁₁H₁₅O₂S⁺, 211.0787; found, 211.0807.



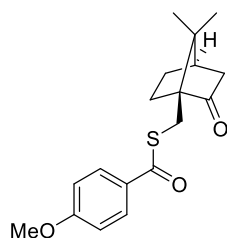
S-cyclohexyl 4-methoxybenzothioate (3gr)

Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and cyclohexanesulfonyl chloride (109.2 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 30/1) the desired compound was isolated as a **colorless liquid** (120.0 mg, 96%).

¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, *J* = 8.9 Hz, 2H), 6.88 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 3.71 – 3.63 (m, 1H), 2.02 – 1.98 (m, 2H), 1.75 – 1.71 (m, 2H), 1.61 – 1.58 (m, 1H), 1.55 – 1.39 (m, 4H), 1.35 – 1.18 (m, 1H).

¹³C NMR (101 MHz, CDCl₃) δ 190.2, 163.4, 130.2, 129.1, 113.5, 55.3, 42.2, 33.2, 26.0, 25.5.

HRMS (ESI): [M+H]⁺ calcd for C₁₄H₁₉O₂S⁺, 251.1100; found, 251.1116.



S-(((1S,4R)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methyl) 4-methoxybenzothioate (3gs)

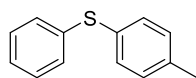
Prepared from 1-iodo-4-methoxybenzene (117.0 mg, 0.5 mmol) and ((1S,4R)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonyl chloride (150.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 20/1) the desired compound was isolated as a **colorless liquid** (96 mg, 60%).

¹H NMR (400 MHz, CDCl₃) δ 7.93 (d, *J* = 8.8 Hz, 2H), 6.87 (d, *J* = 8.9 Hz, 2H), 3.81 (s, 3H), 3.33 (d, *J* = 13.8 Hz, 1H), 3.06 (d, *J* = 13.8 Hz, 1H), 2.43 – 2.28 (m, 1H), 2.06 (t, *J* = 4.4 Hz, 1H), 1.99 – 1.81 (m, 3H), 1.55 – 1.48 (m, 1H), 1.36 – 1.27 (m, 1H), 1.07 (s, 3H), 0.91 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ 217.1, 190.4, 163.6, 129.7, 129.2, 113.6, 60.6, 55.3, 47.8, 43.6, 42.9, 26.6, 26.5, 24.5, 20.0, 19.6.

HRMS (ESI): [M+H]⁺ calcd for C₁₈H₂₃O₃S⁺, 319.1362; found, 319.1377.

3.2 Characterization of Thioether



phenyl(*p*-tolyl)sulfane (**4aa**)²

Prepared from iodobenzene (102.0 mg, 0.5 mmol) and 4-methylbenzenesulfonyl chloride (114.0 mg, 0.6 mmol). After purification by column chromatography (PE/EA = 200/1) the desired compound was isolated as a **colorless liquid** (70.0 mg, 70%).

¹H NMR (400 MHz, CDCl₃) δ 7.29 (d, *J* = 8.1 Hz, 2H), 7.27 – 7.22 (m, 4H), 7.21 – 7.15 (m, 1H), 7.13 (d, *J* = 7.9 Hz, 2H), 2.33 (s, 3H).

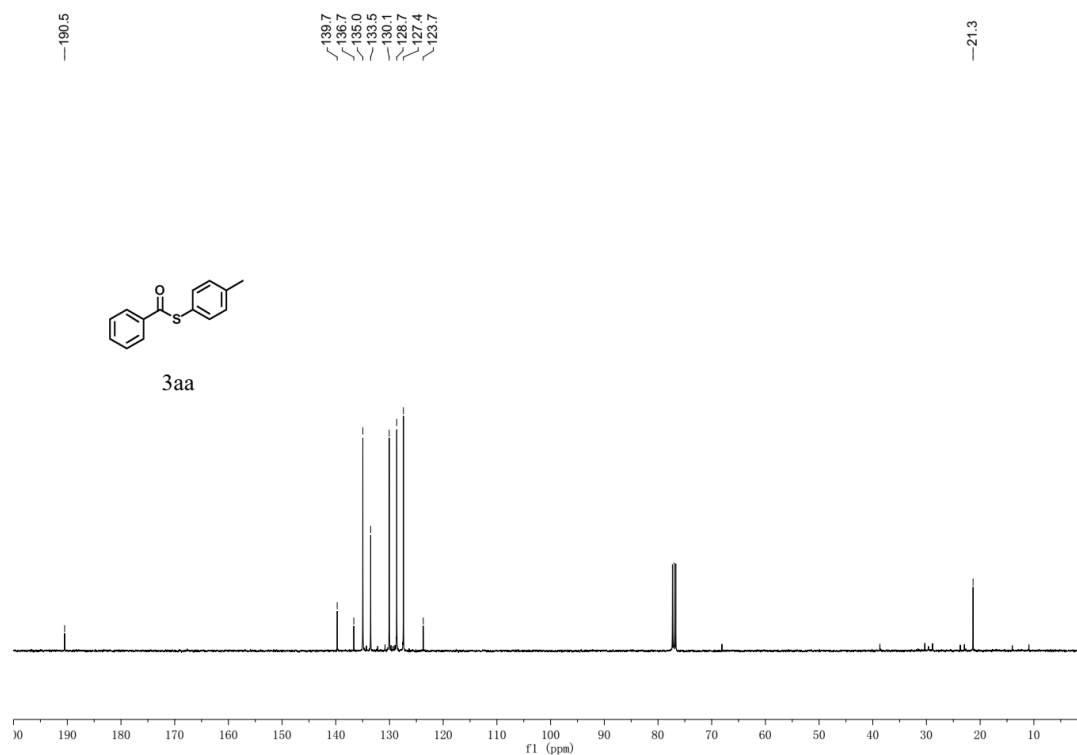
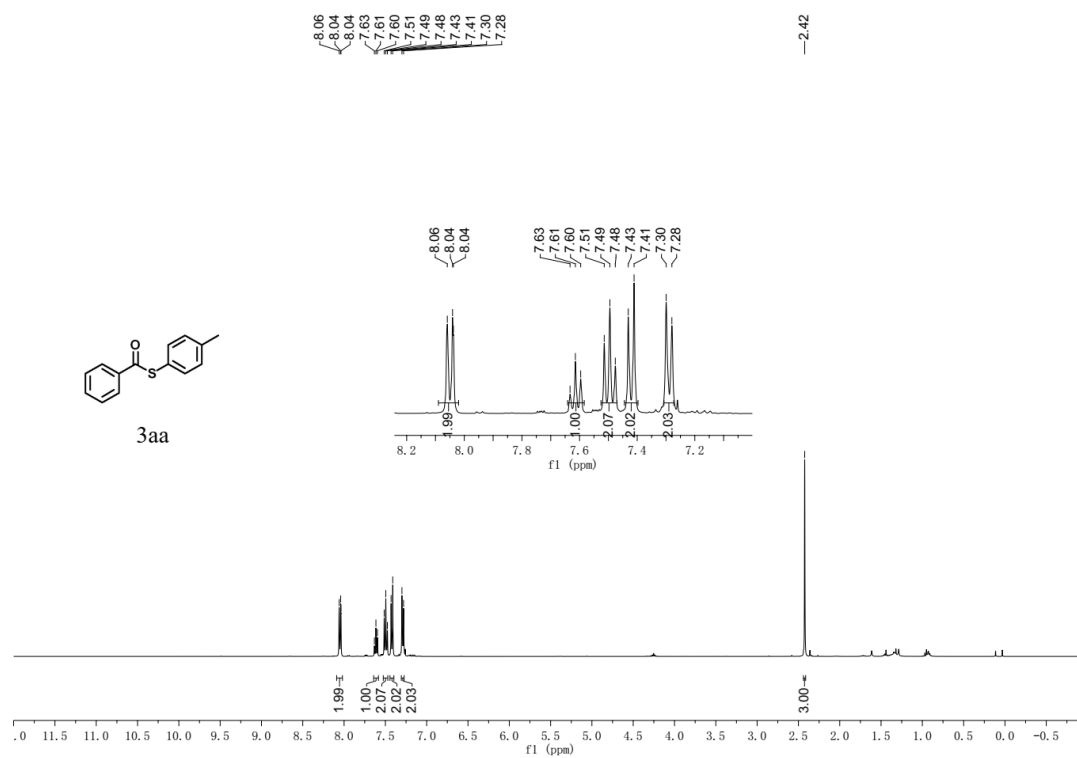
¹³C NMR (101 MHz, CDCl₃) δ 137.5, 137.1, 132.2, 131.2, 130.0, 129.7, 129.0, 126.4, 21.1.

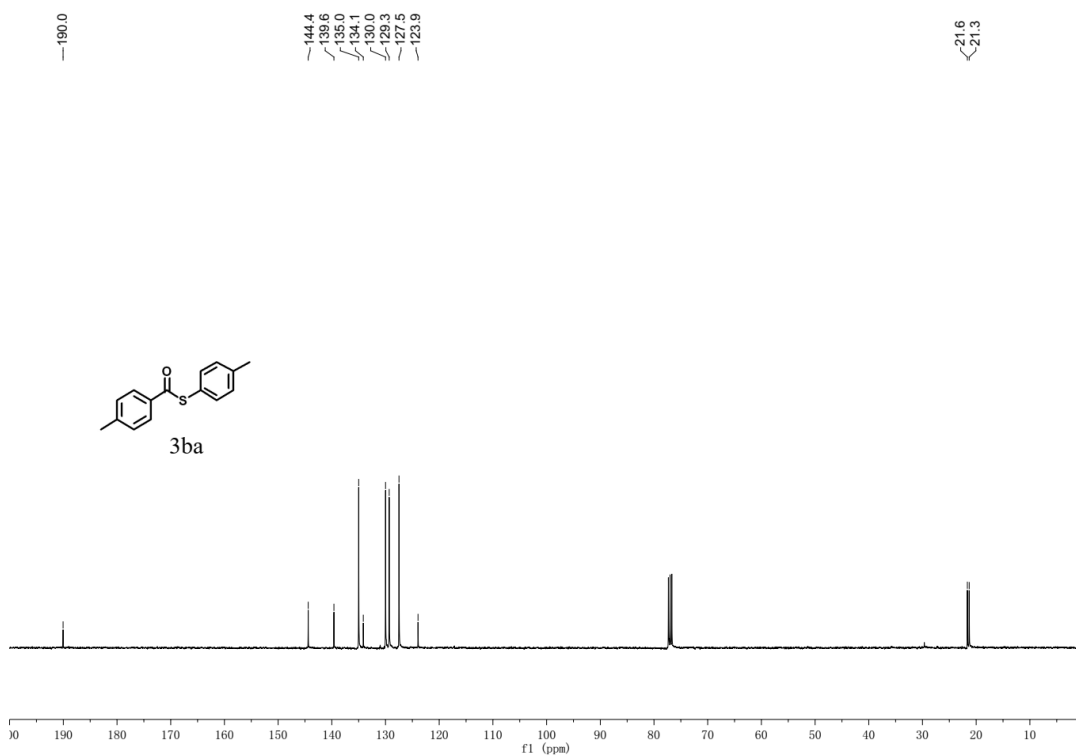
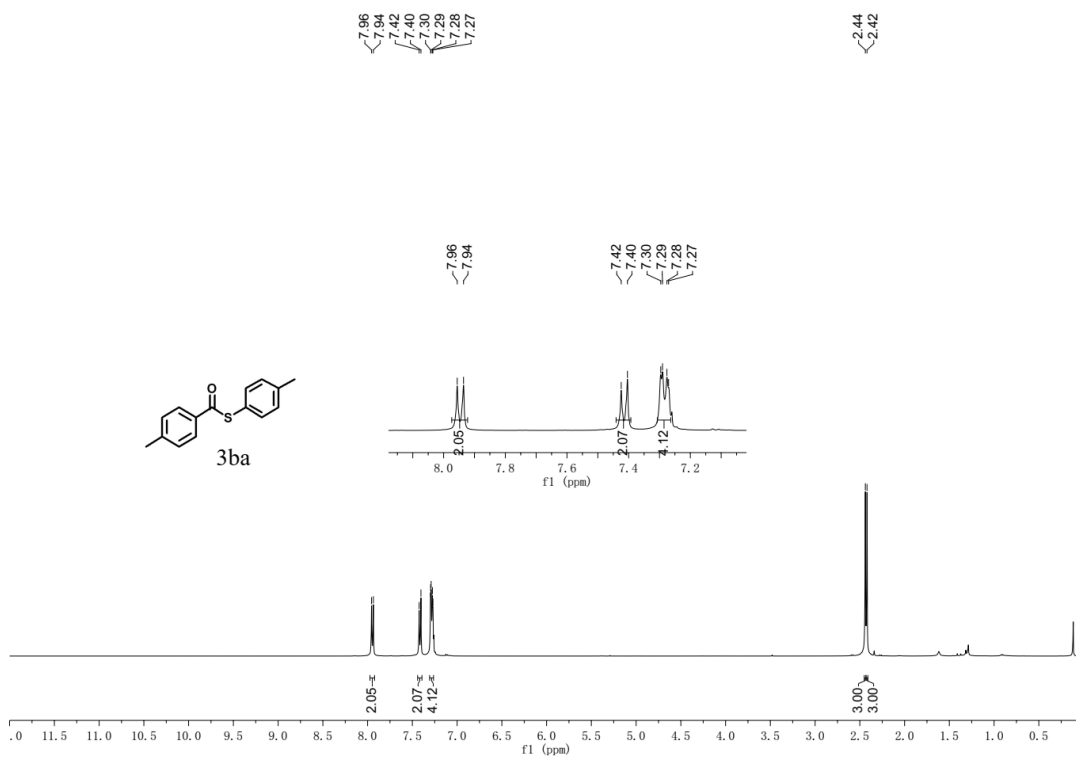
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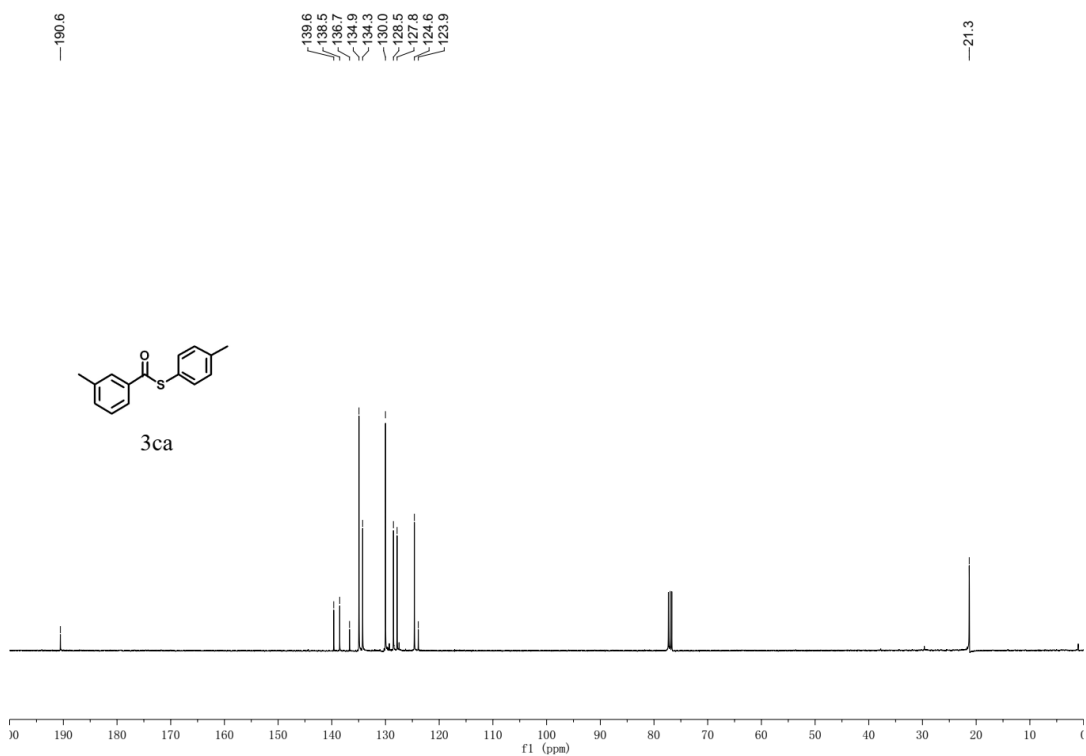
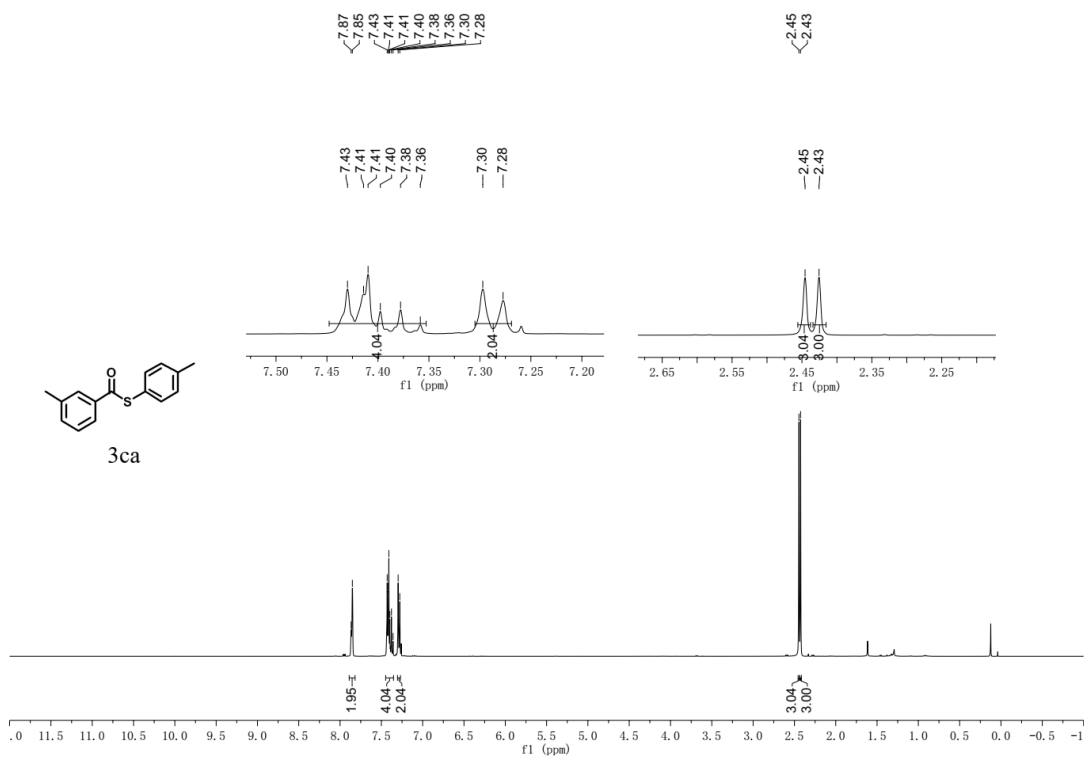
1. M. N. Burhardt, A. Ahlburg, T. Skrydstrup, Palladium-catalyzed thiocarbonylation of aryl, vinyl, and benzyl bromides. *J. Org. Chem.*, **2014**, *79*, 11830–11840.
2. Wang, X. Zhang, H. Liu, H. Chen, D. Huang, Nickel-catalyzed direct formation of the C–S bonds of aryl sulfides from arylsulfonyl chlorides and aryl iodides using Mn as a reducing agent. *Org. Chem. Front.* 2017, *4*, 31–36.

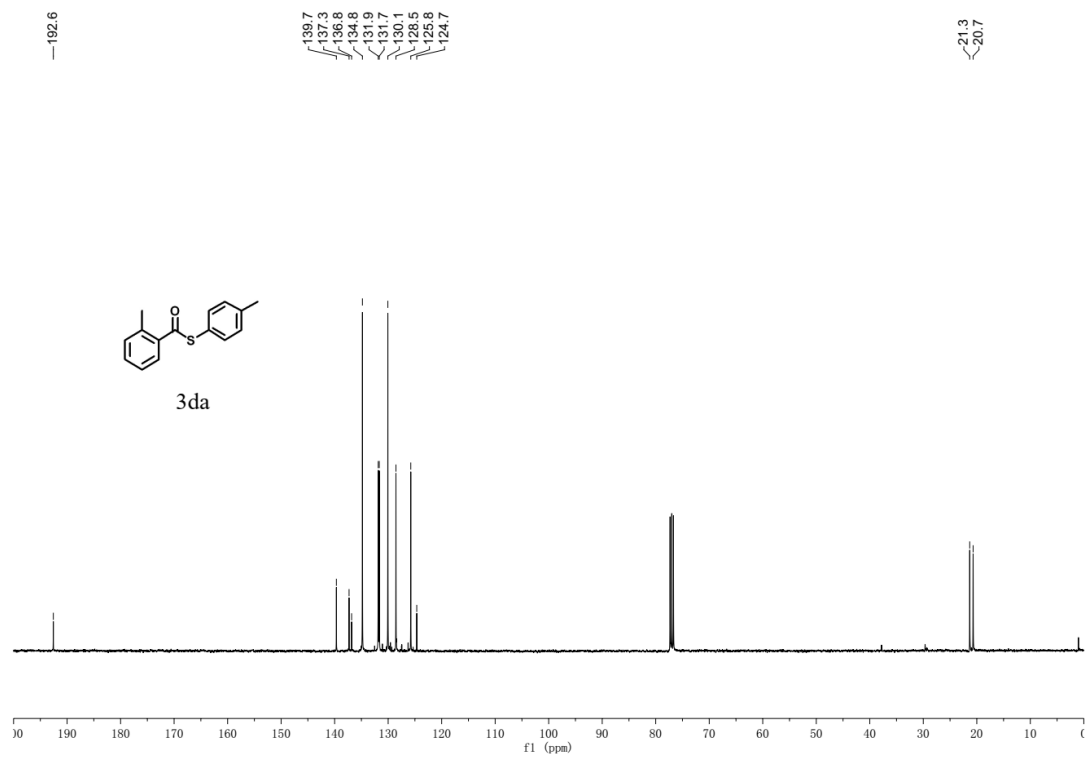
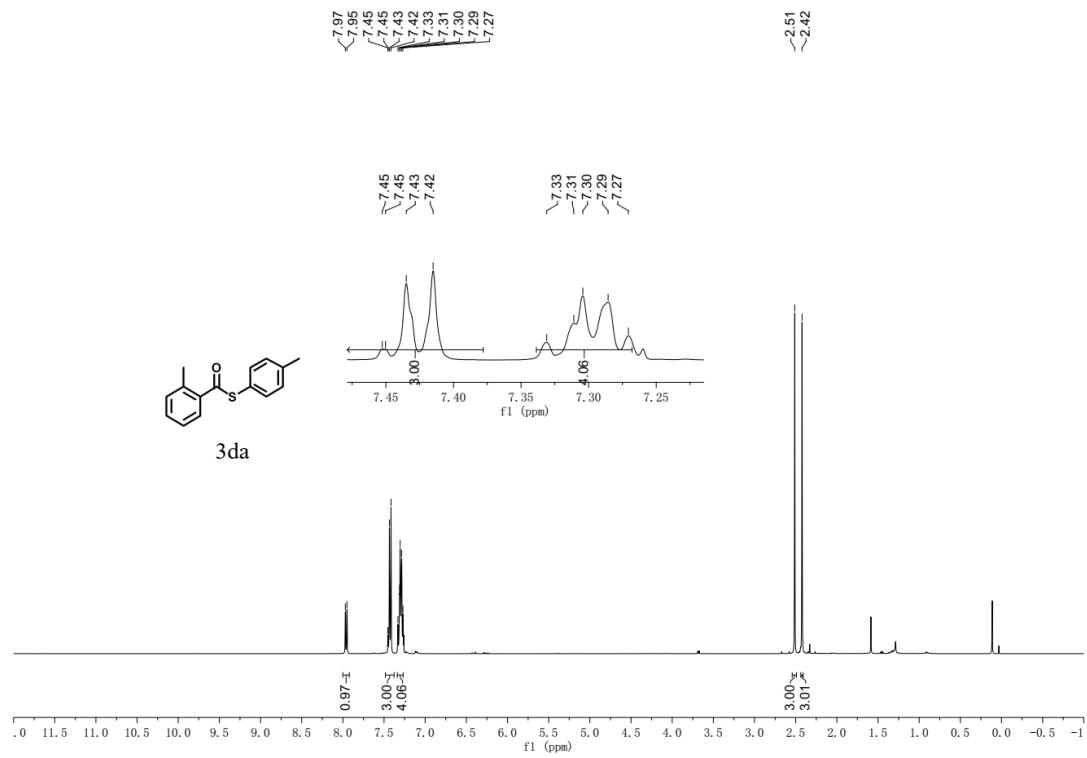
4. Copy of ^1H and ^{13}C NMR Spectra of Products

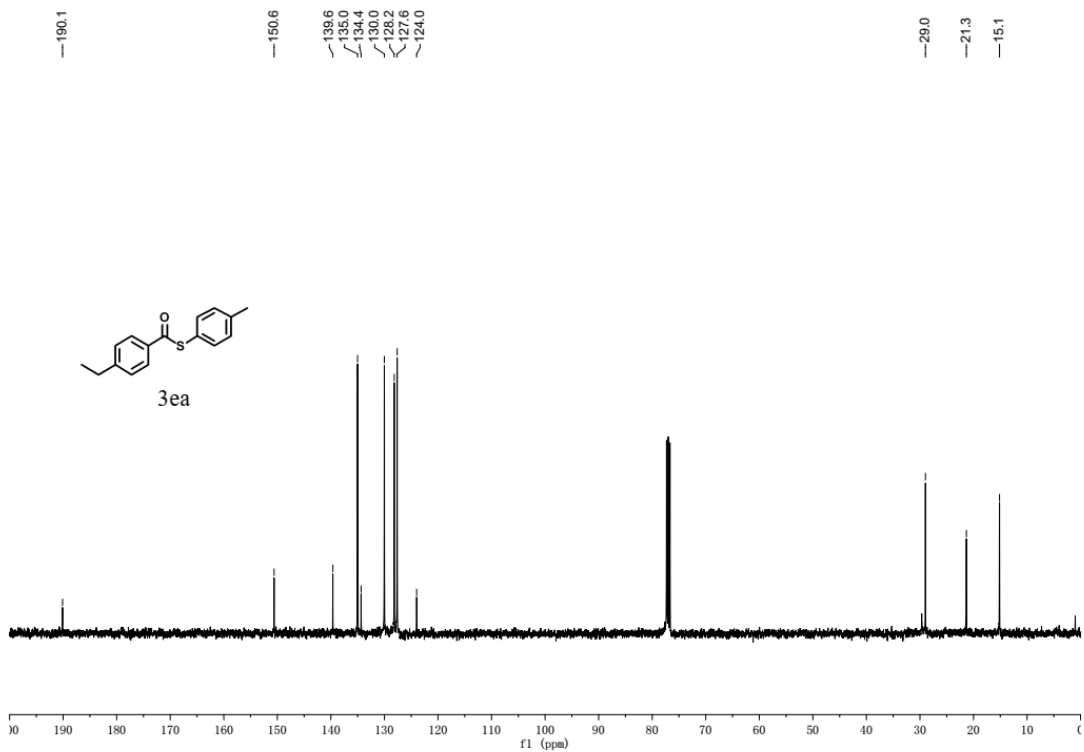
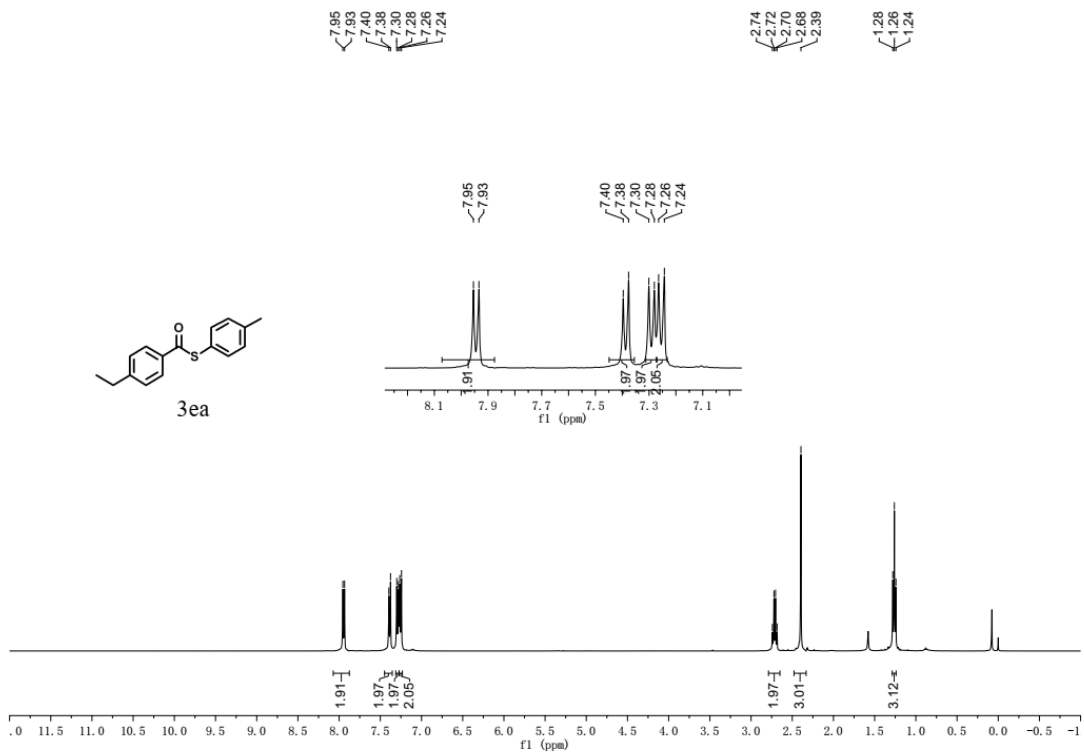
4.1 Copy of ^1H and ^{13}C NMR Spectra of Thioesters 3

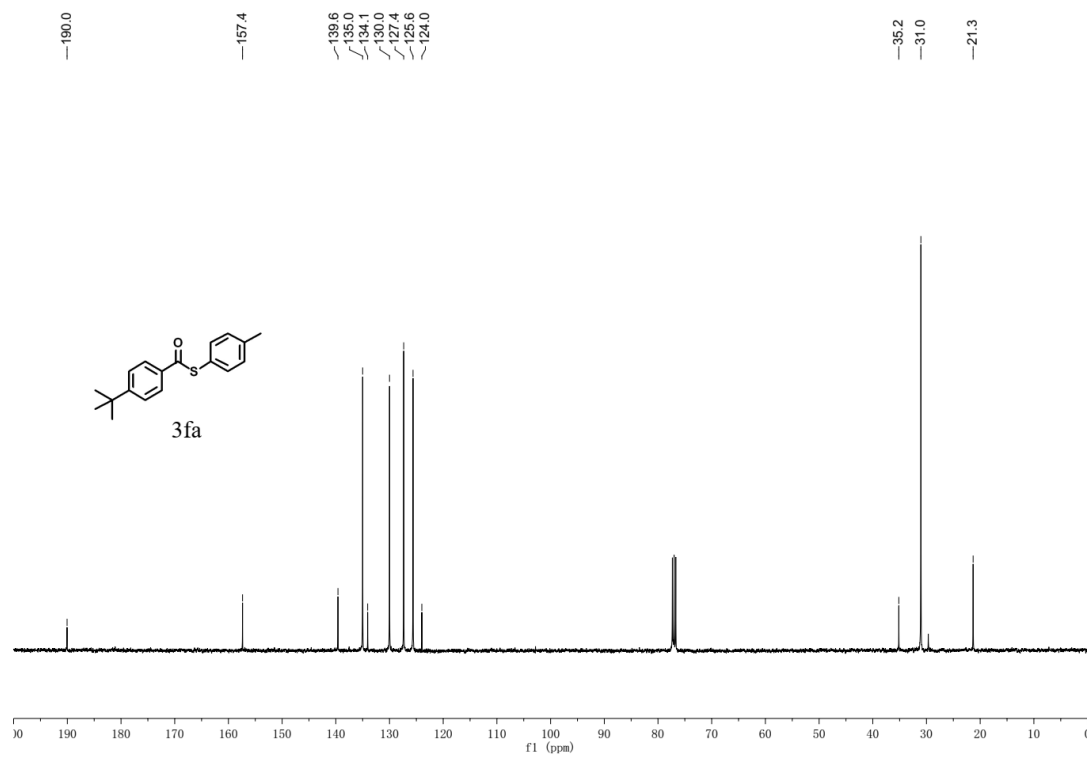
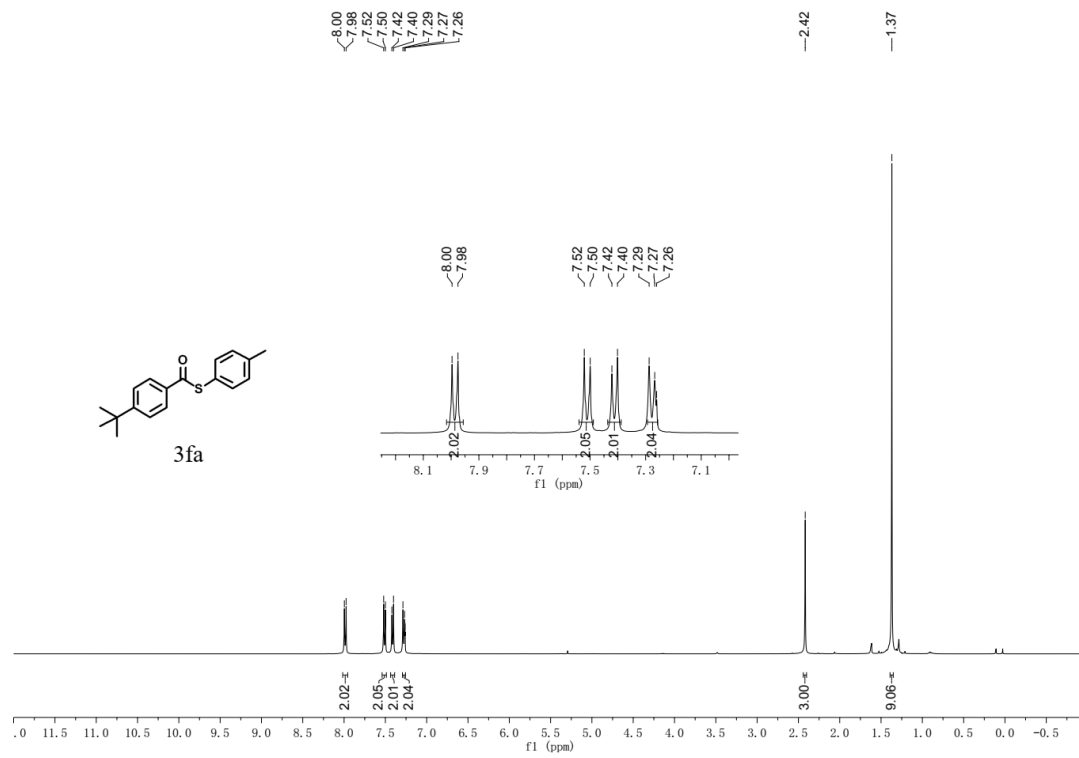


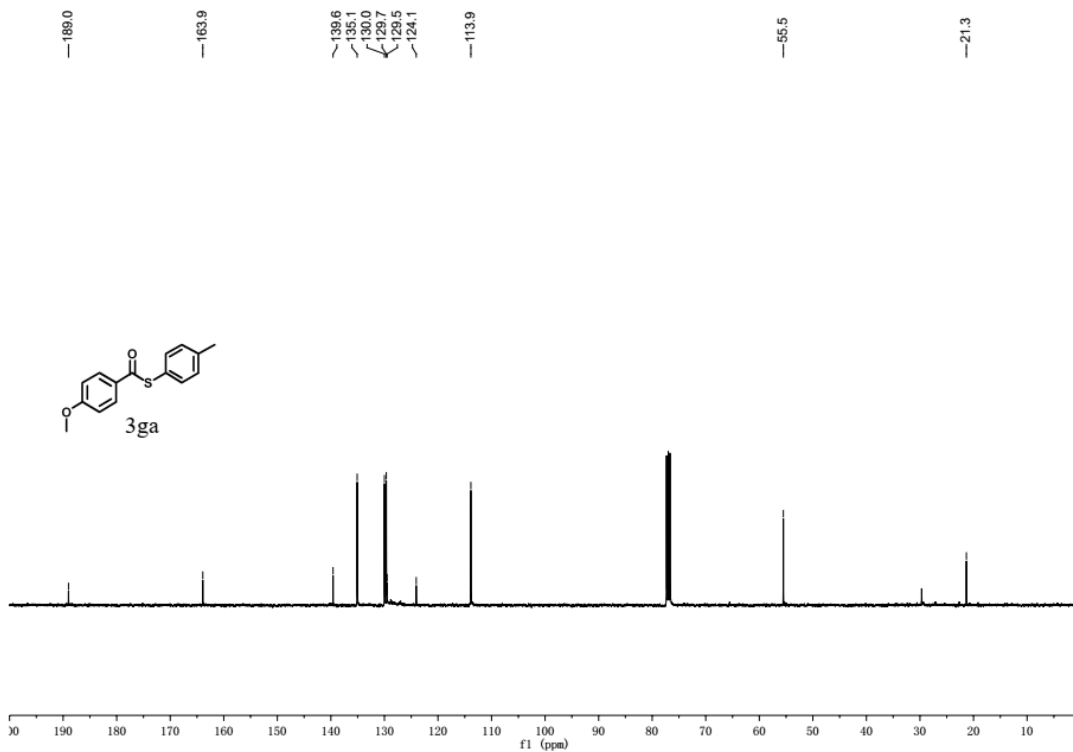
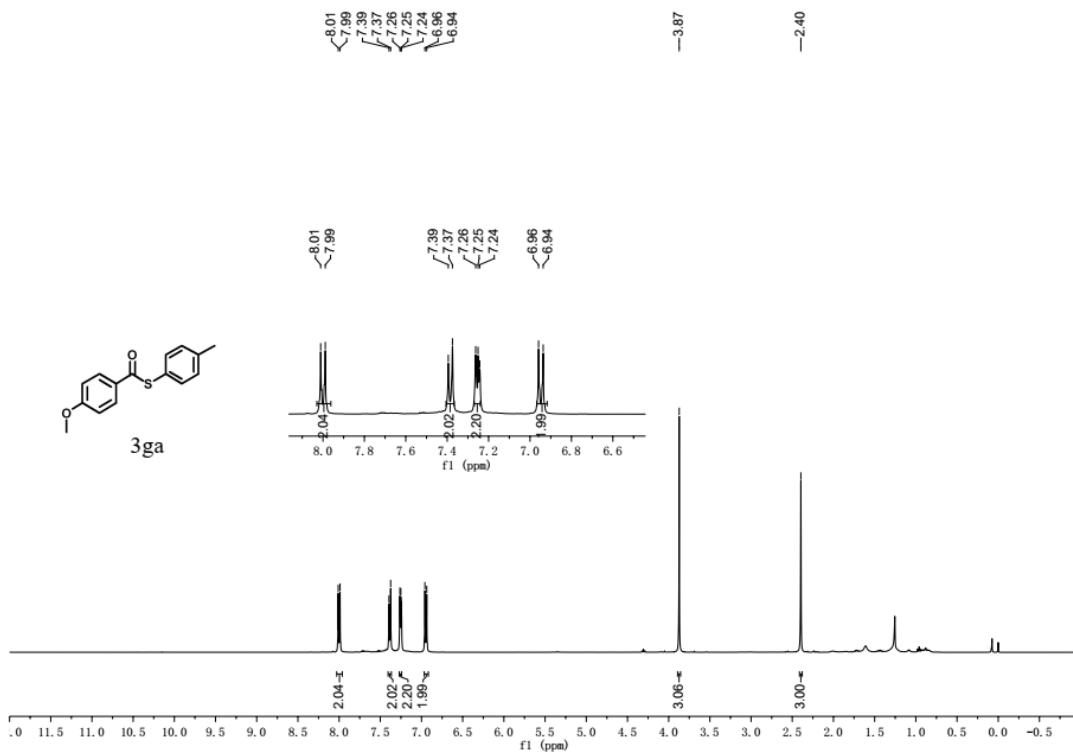


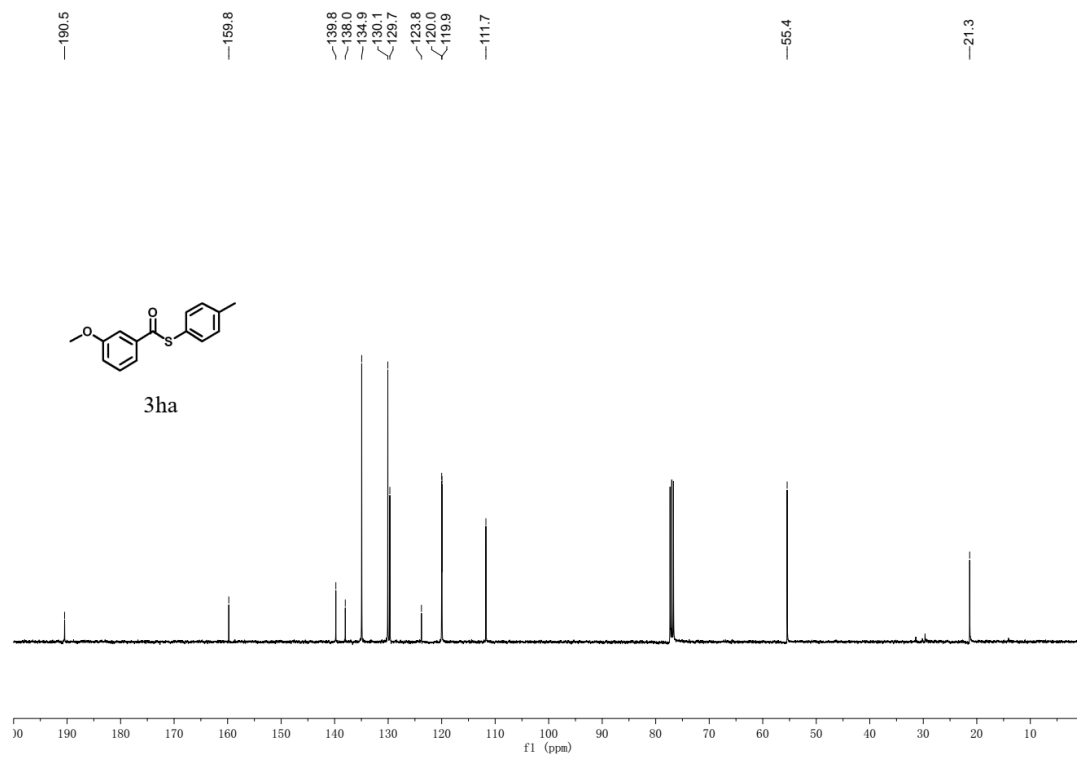
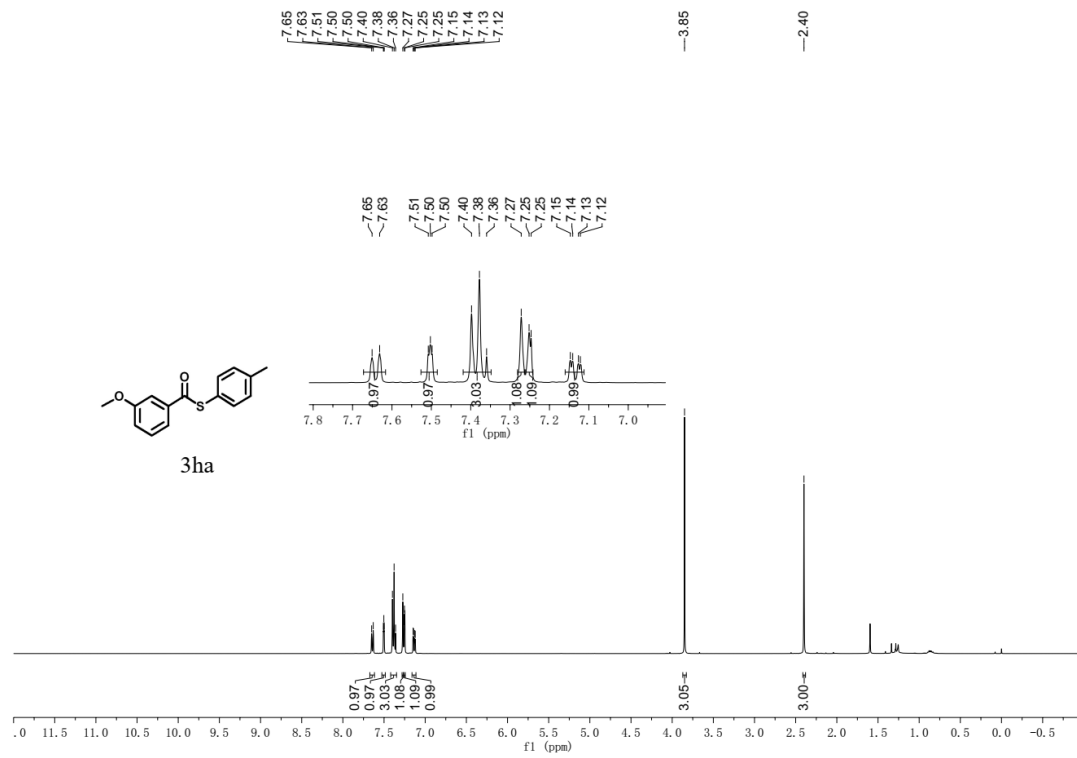


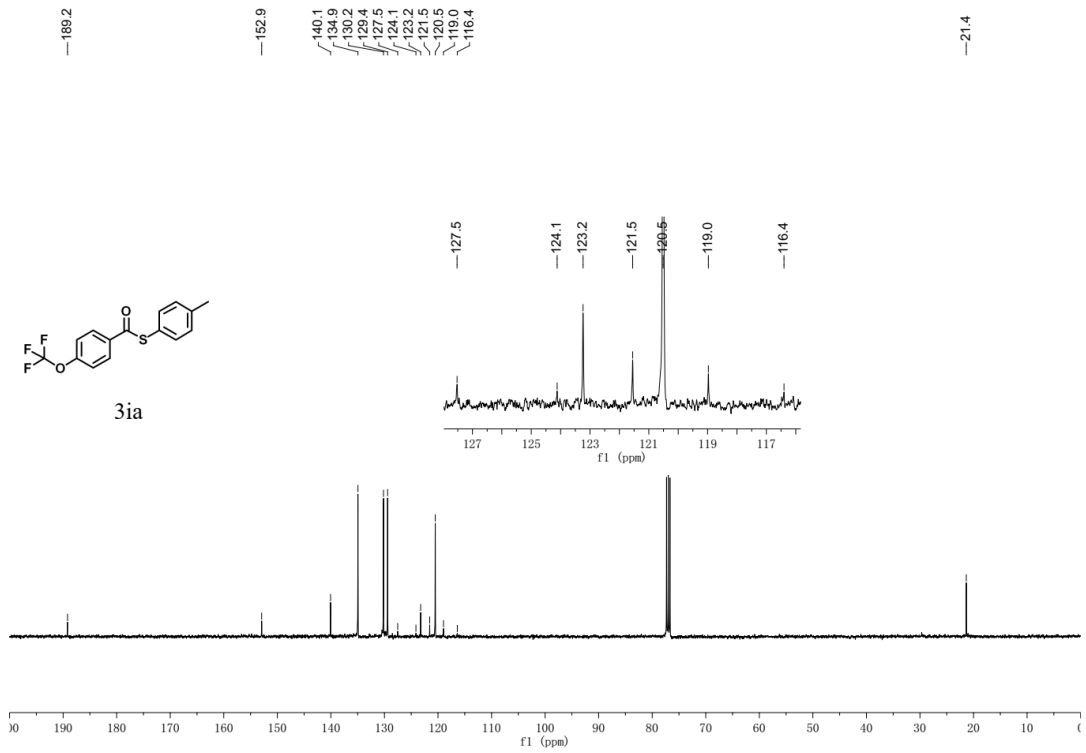
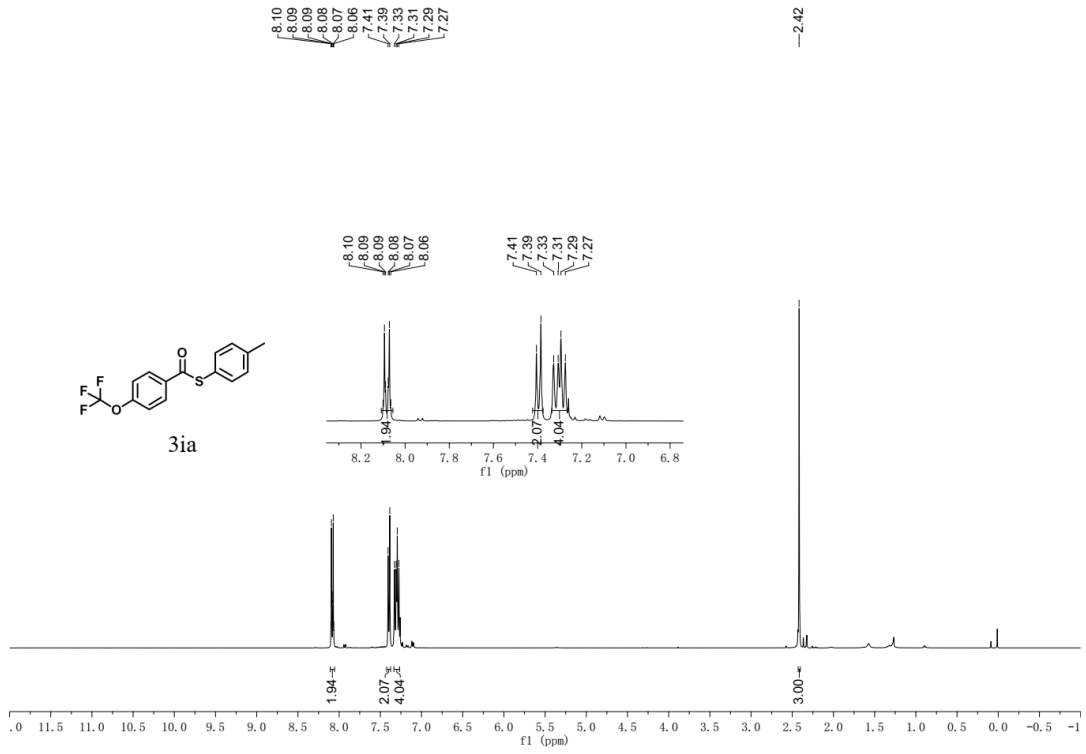


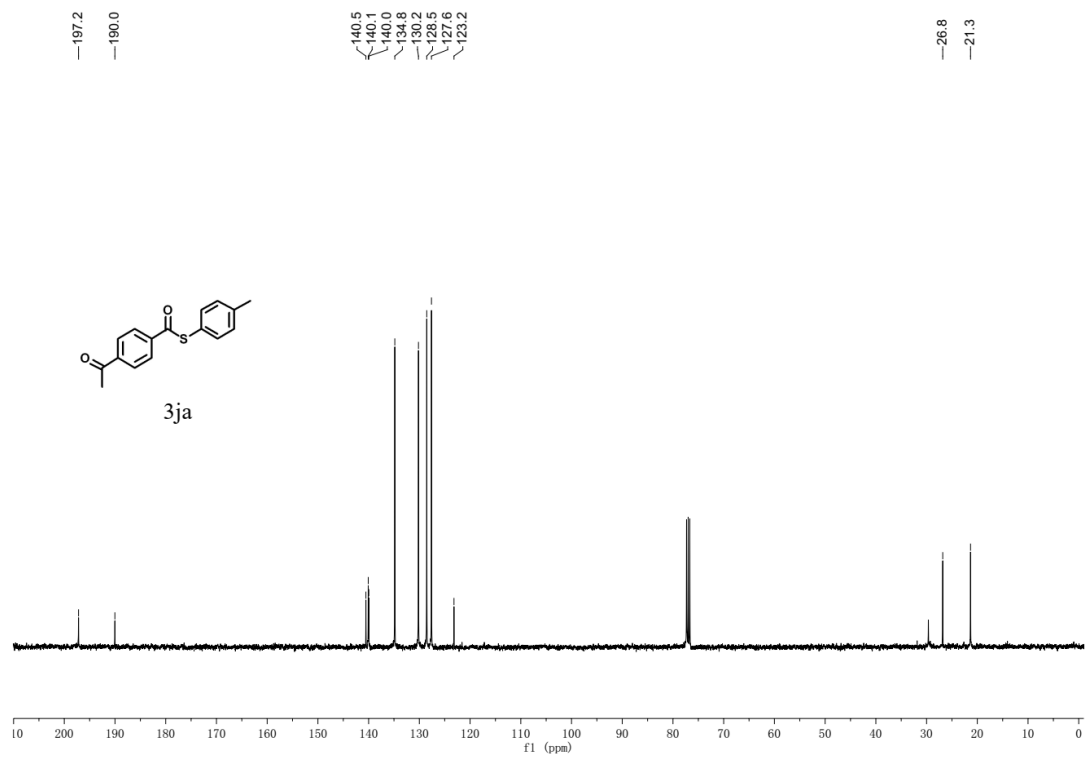
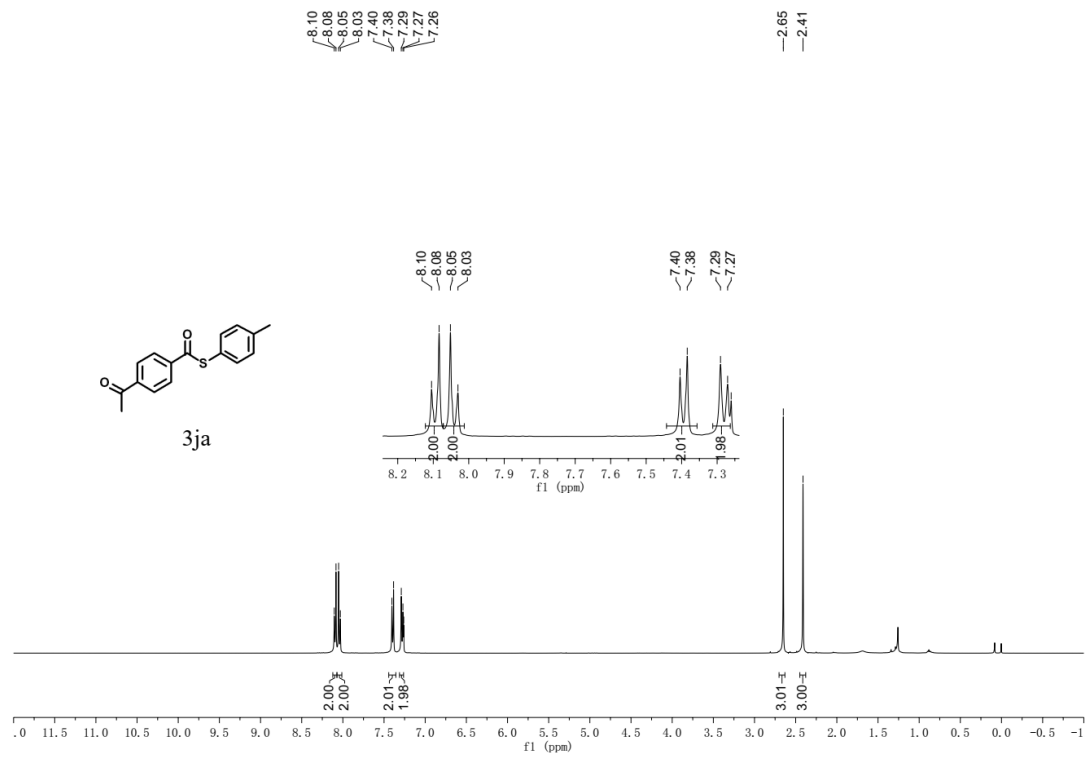


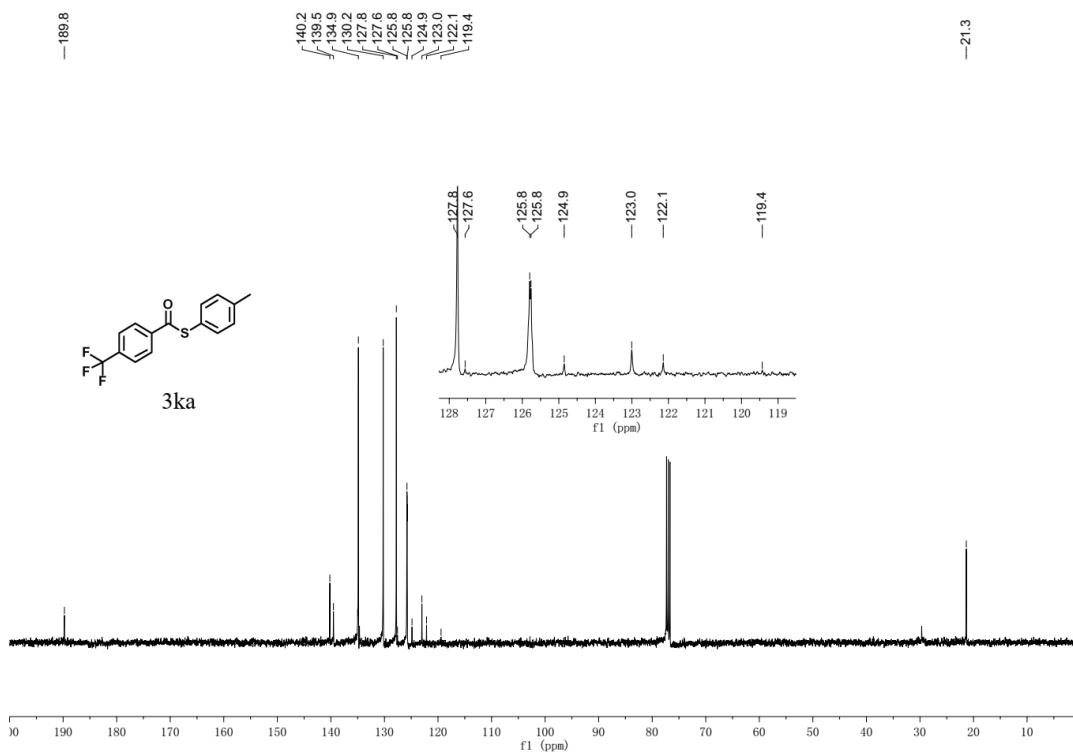
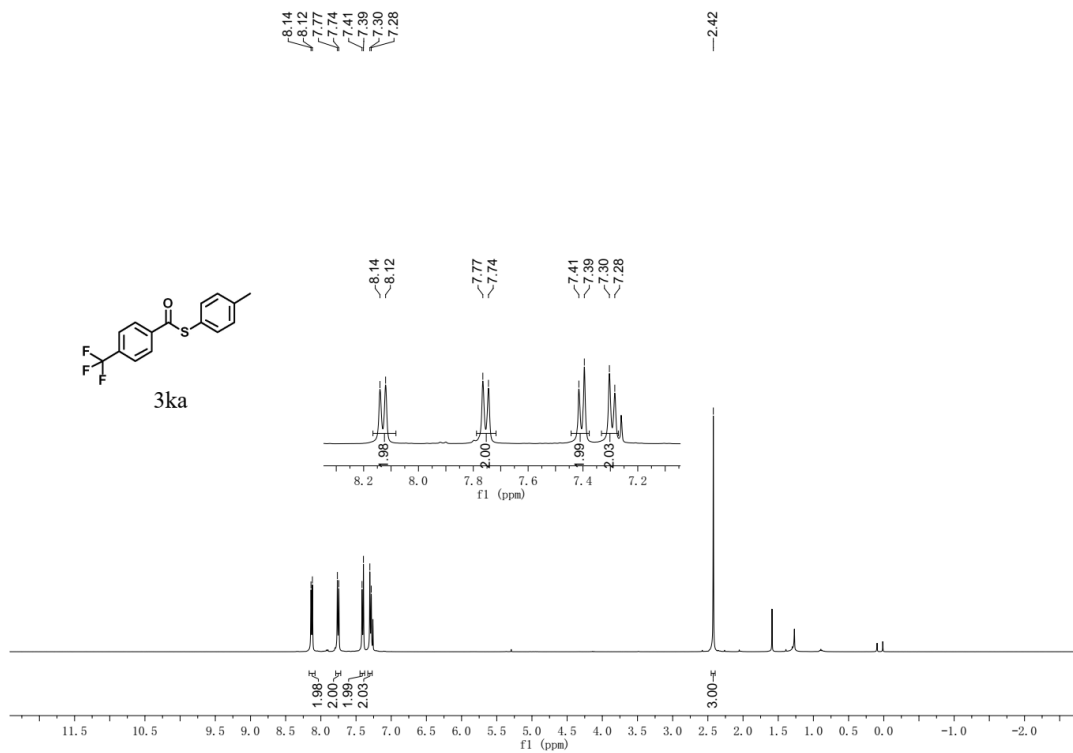


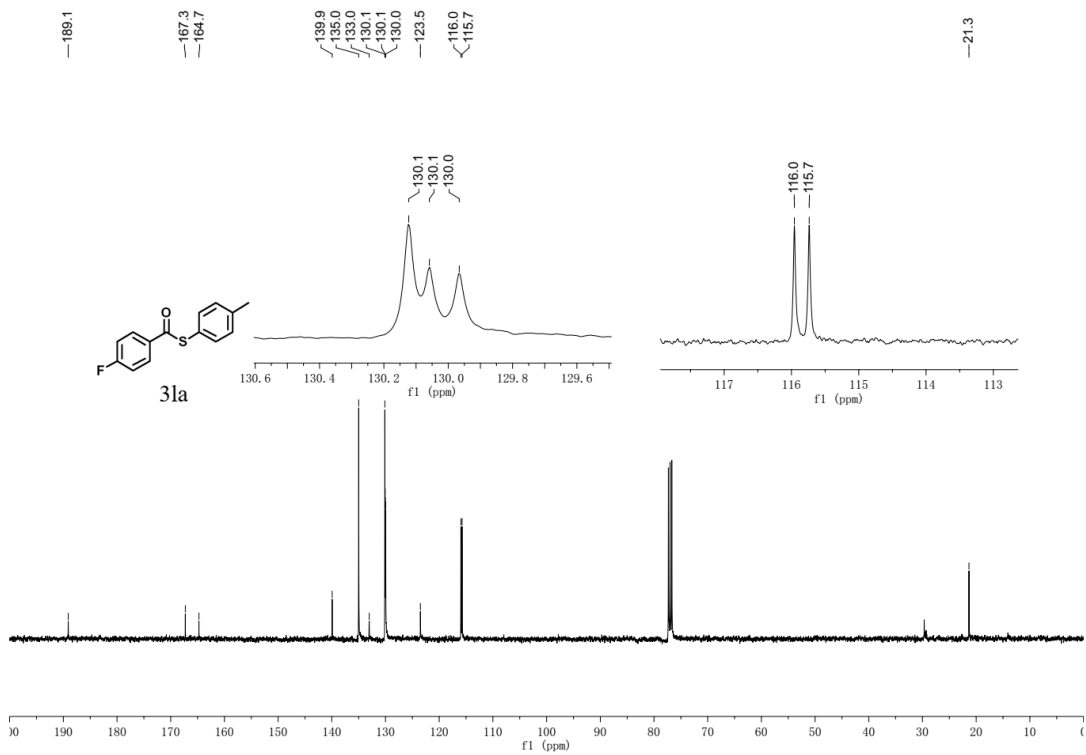
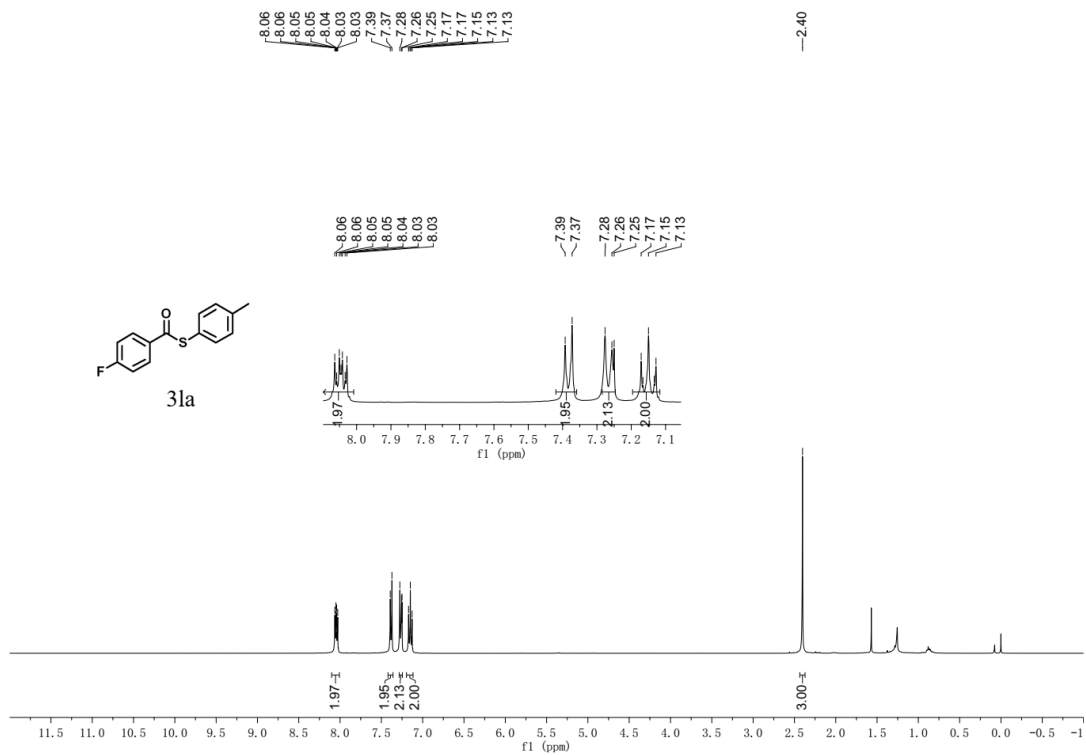


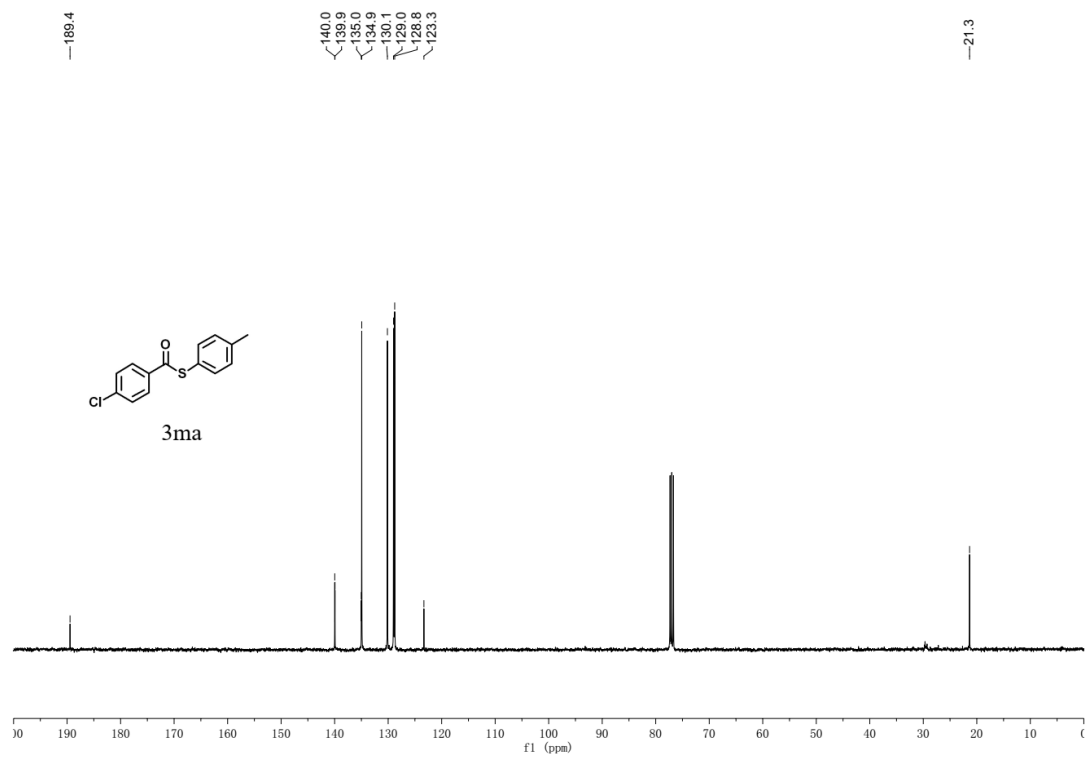
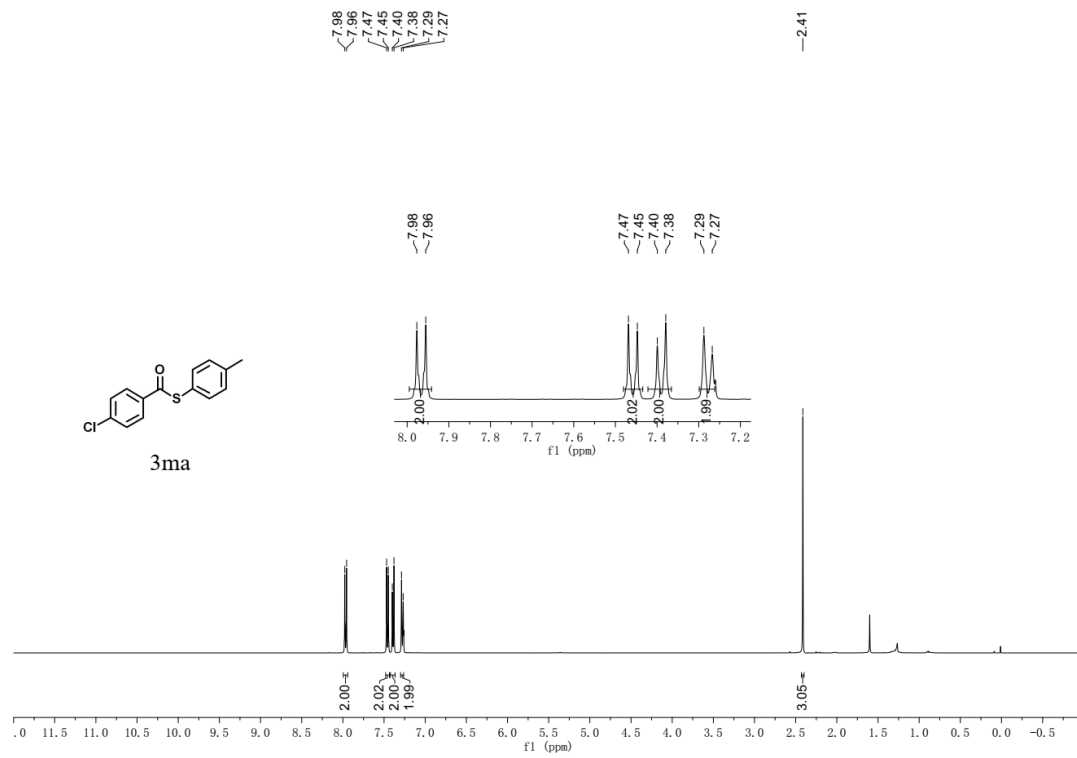


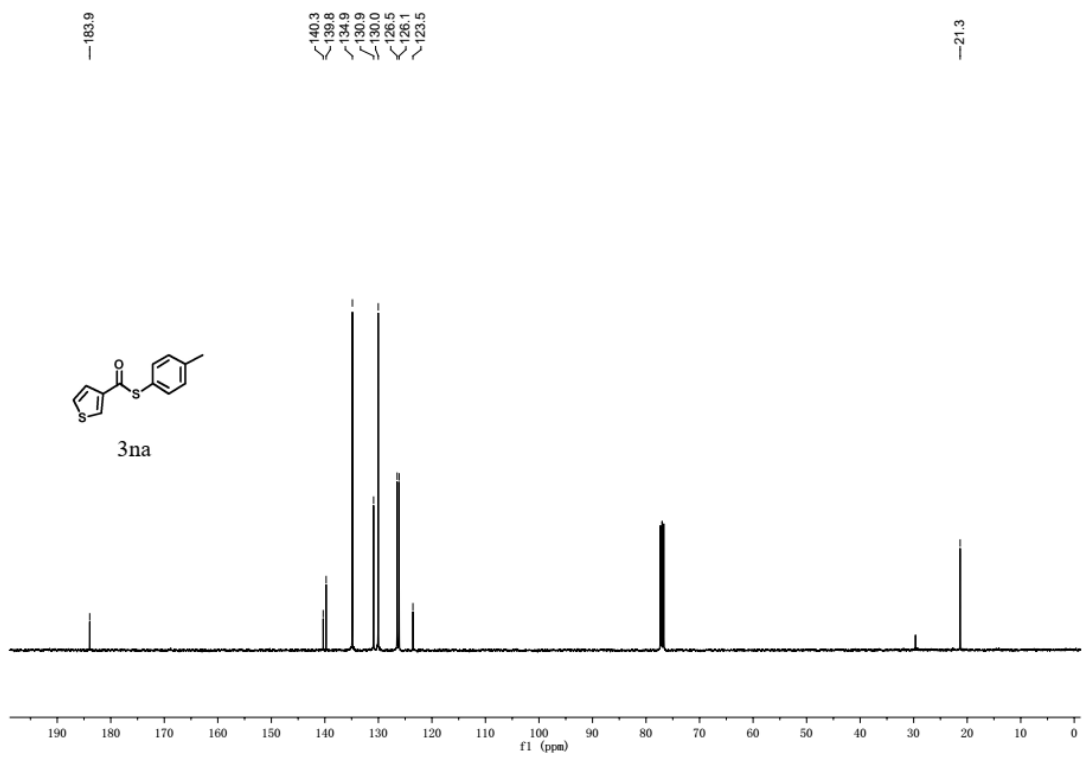
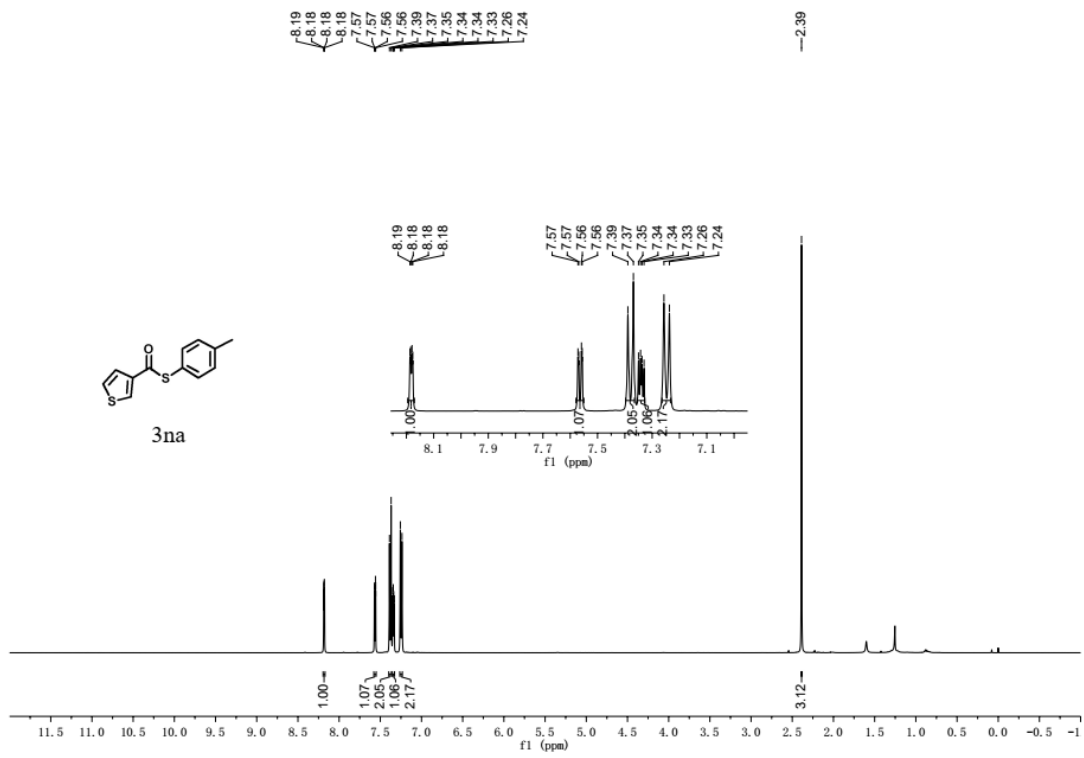


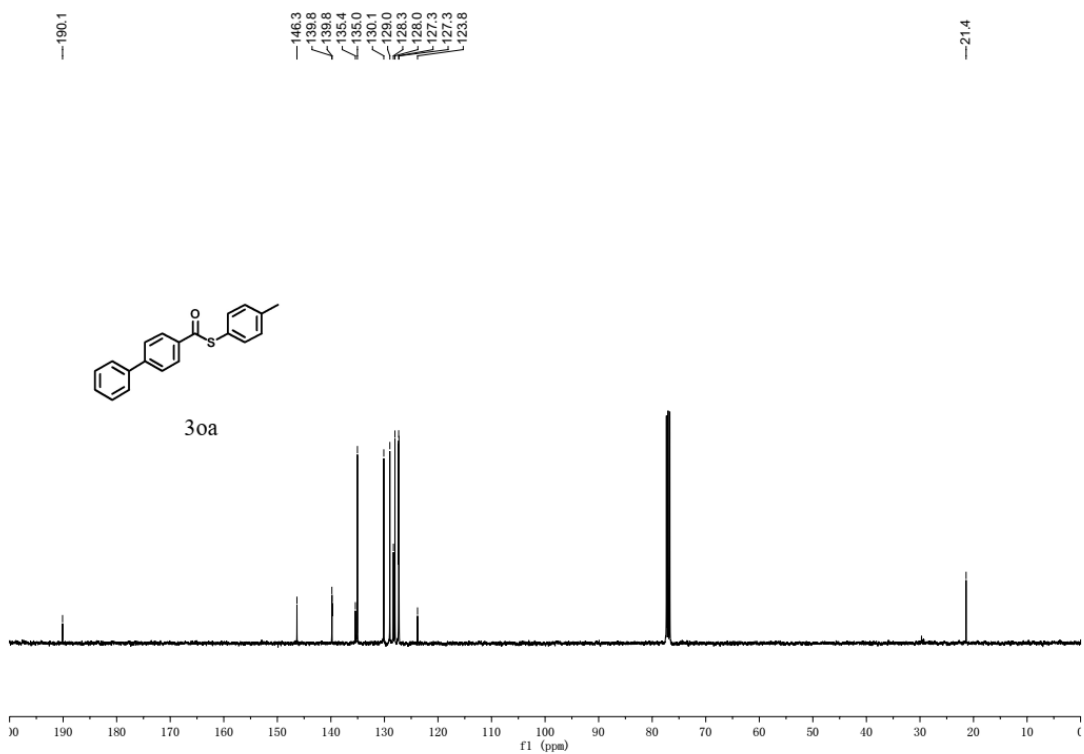
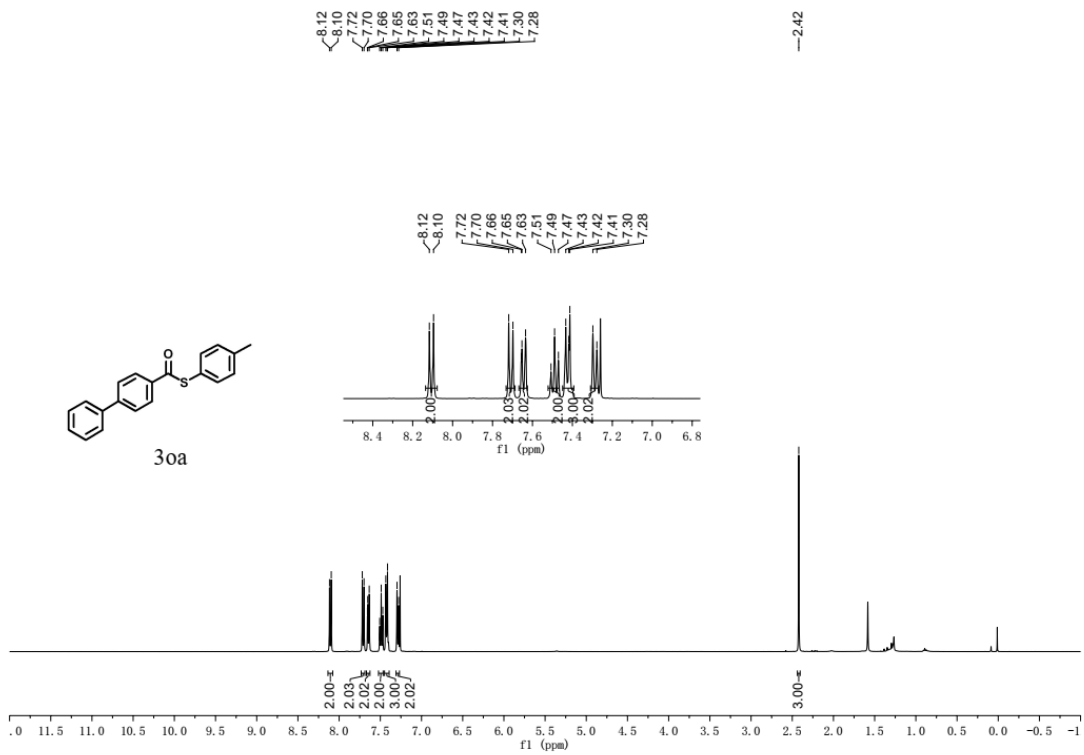


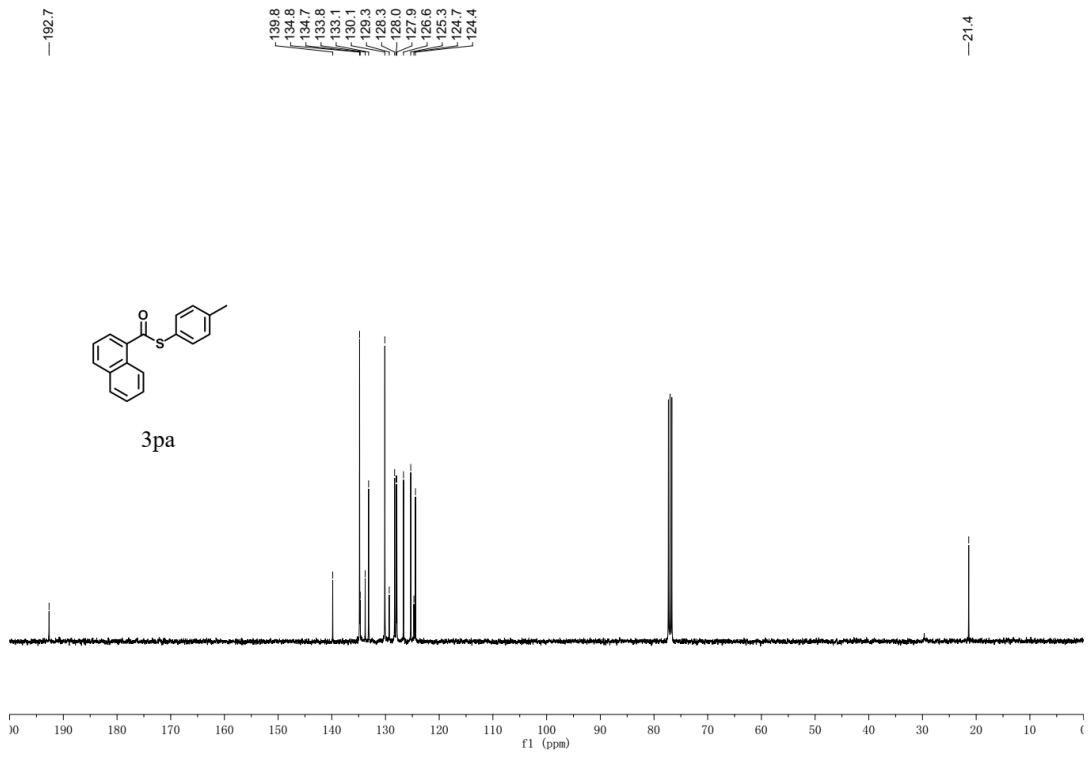
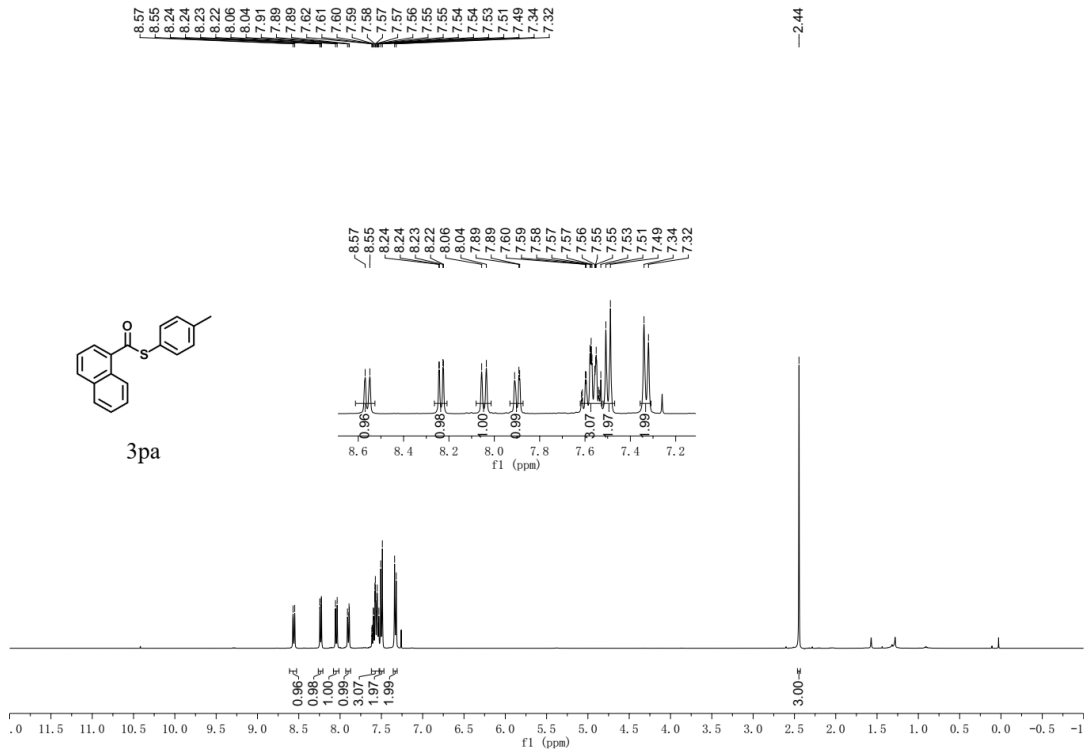


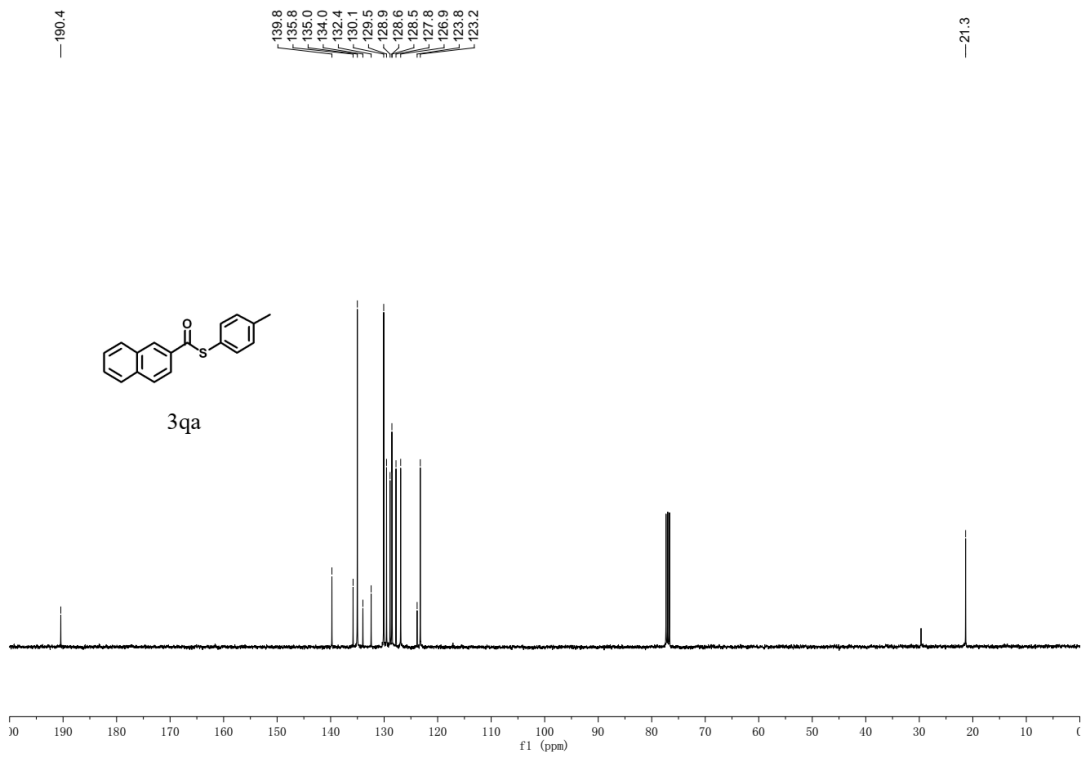
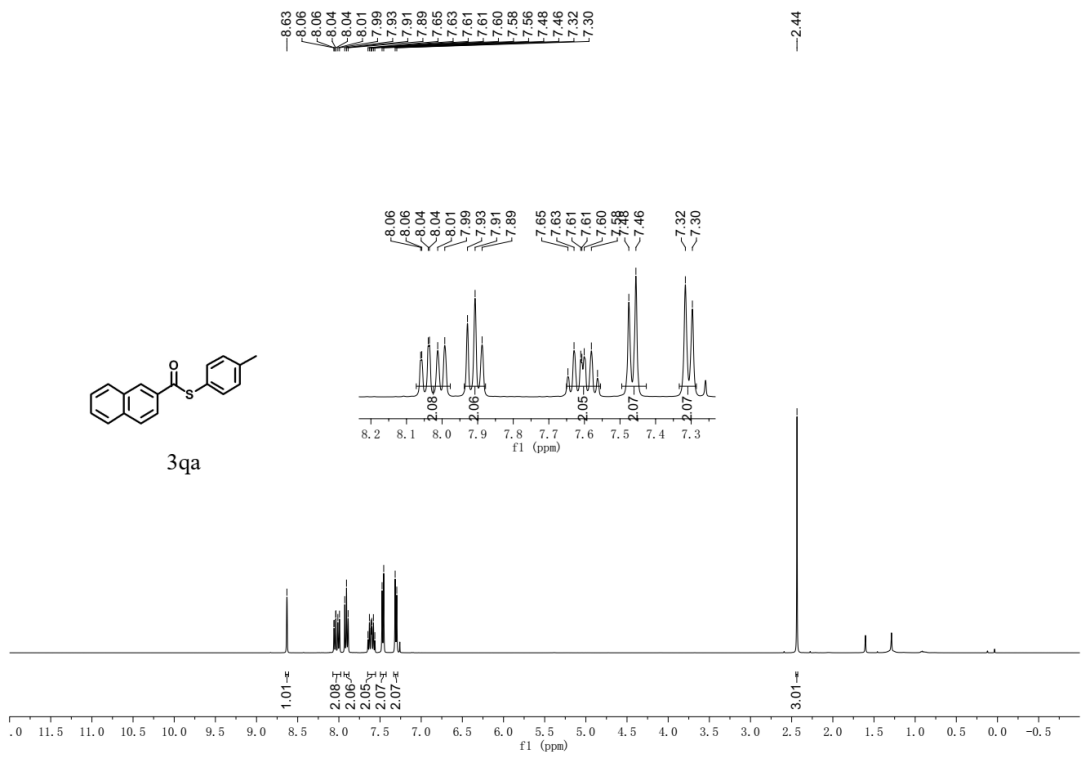


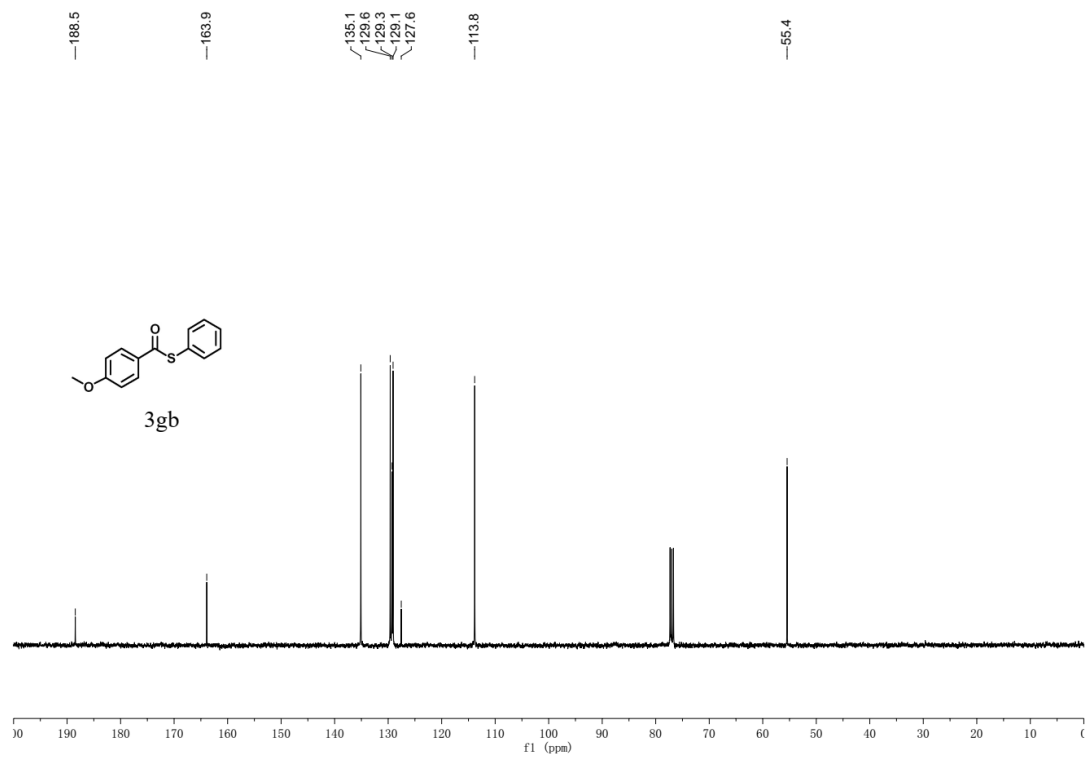
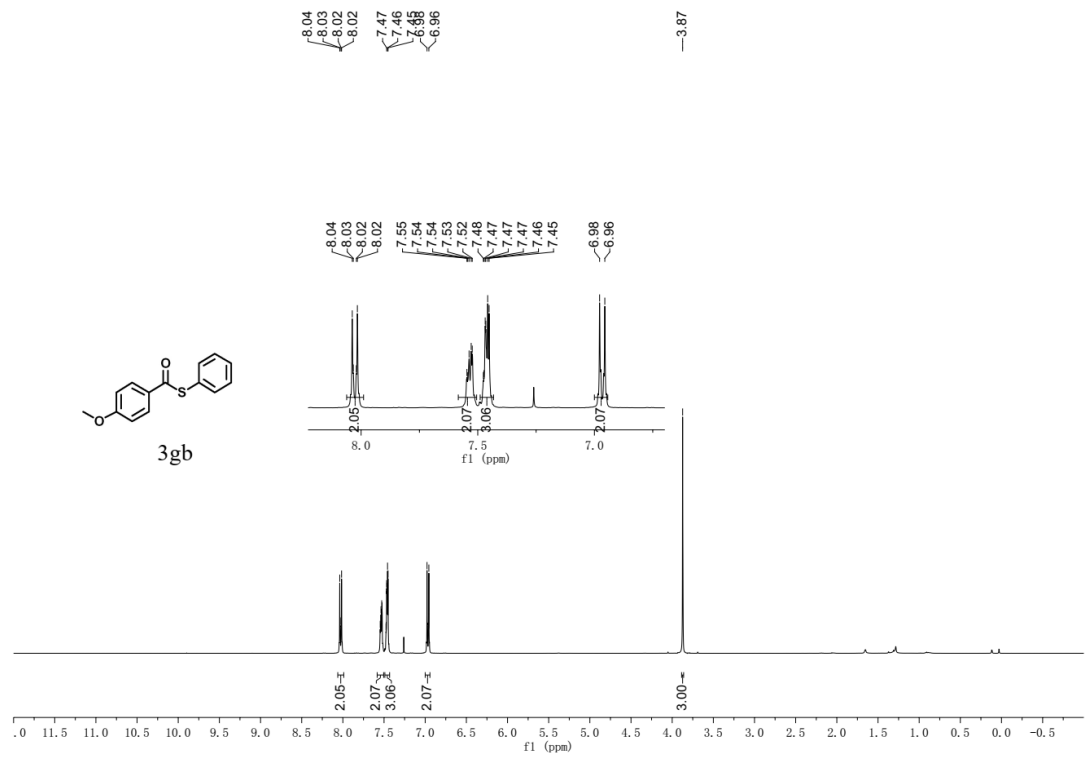


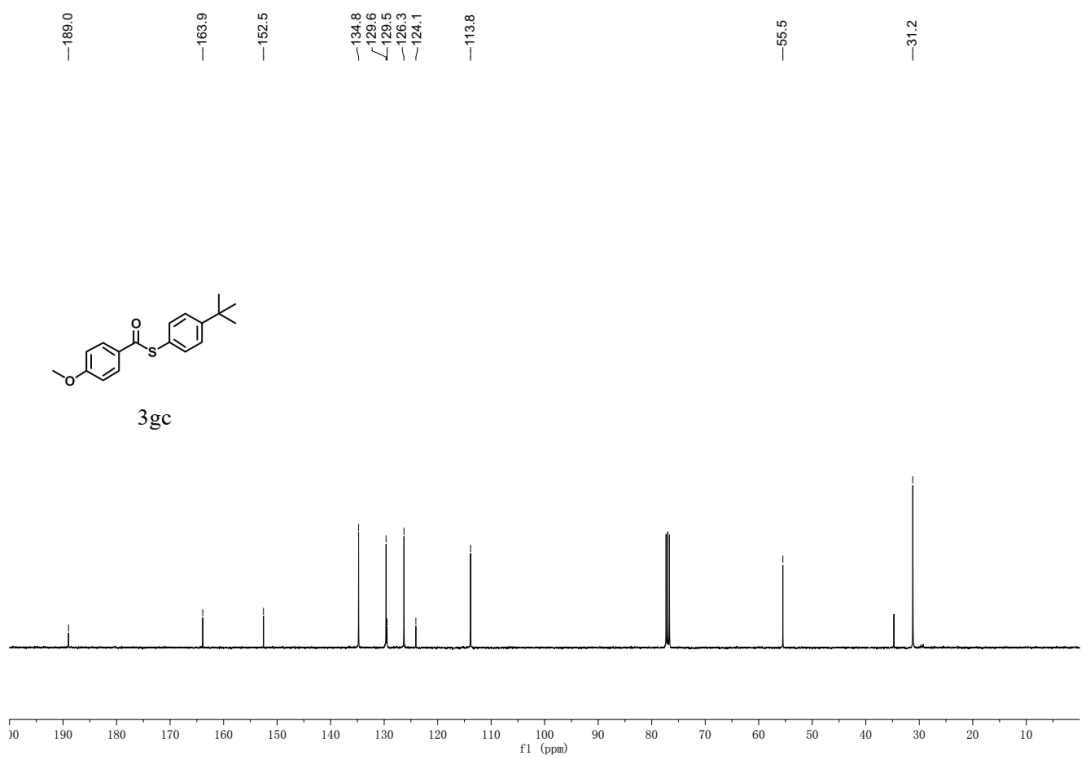
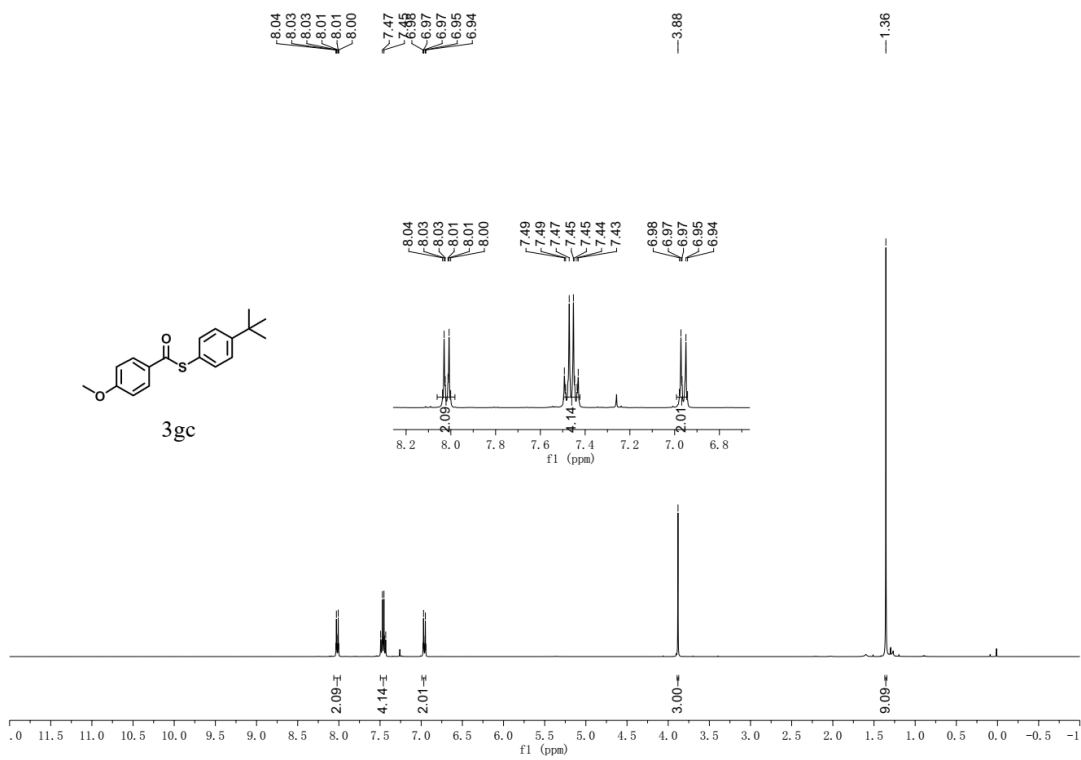


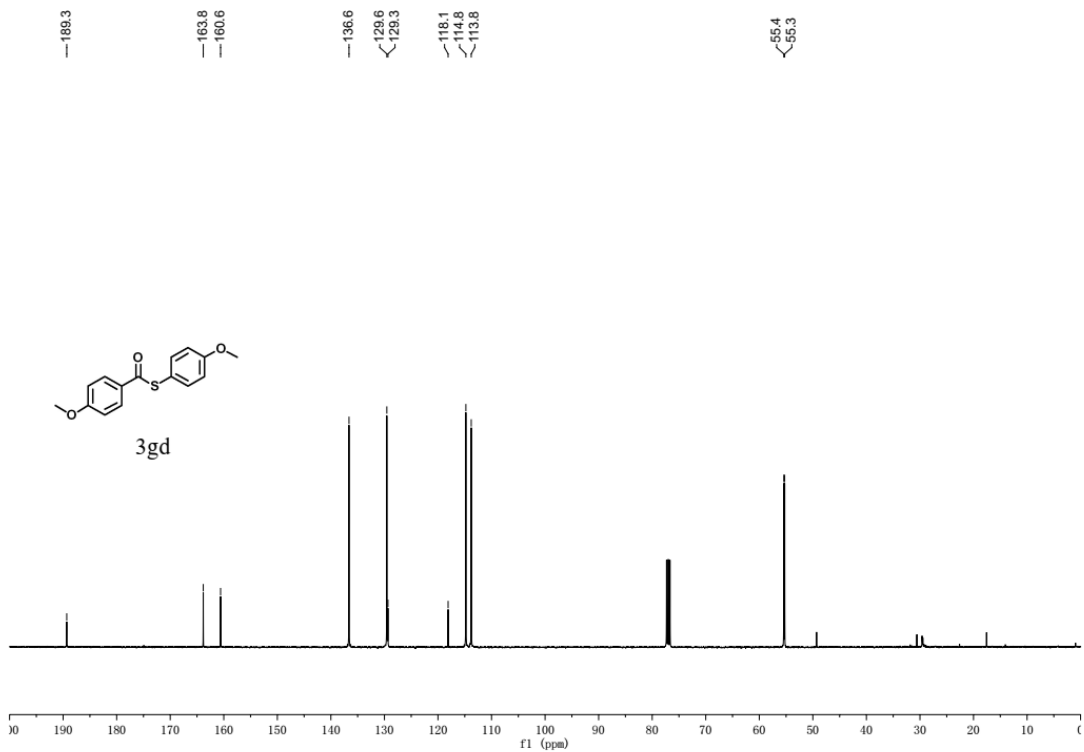
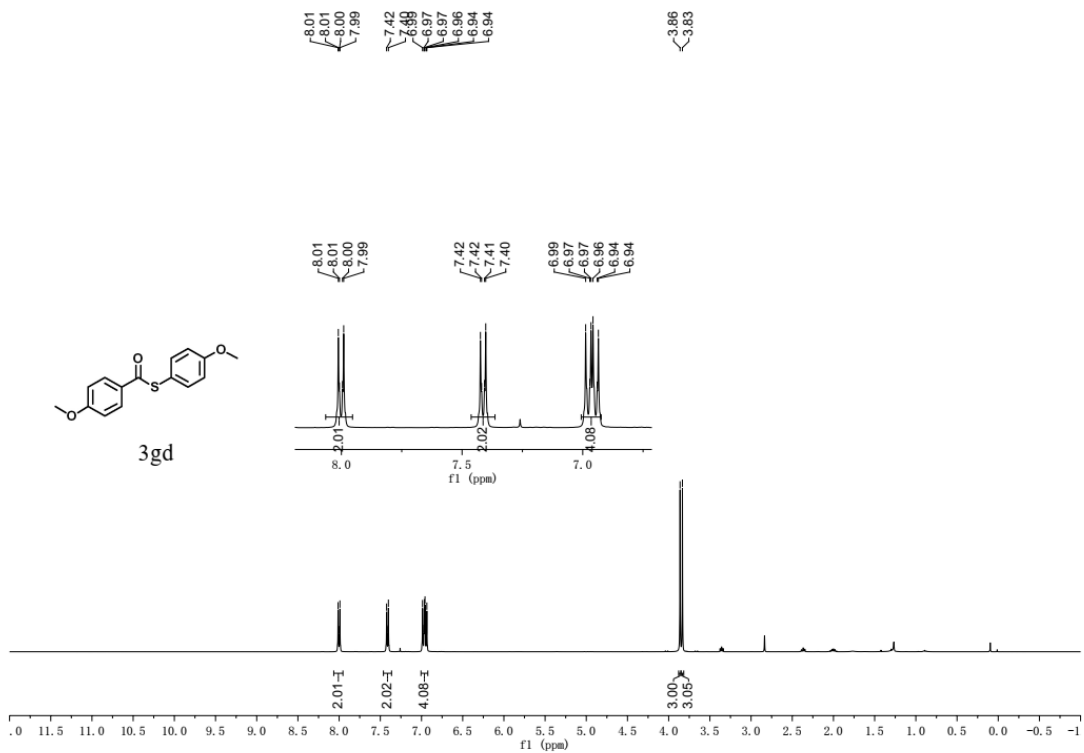


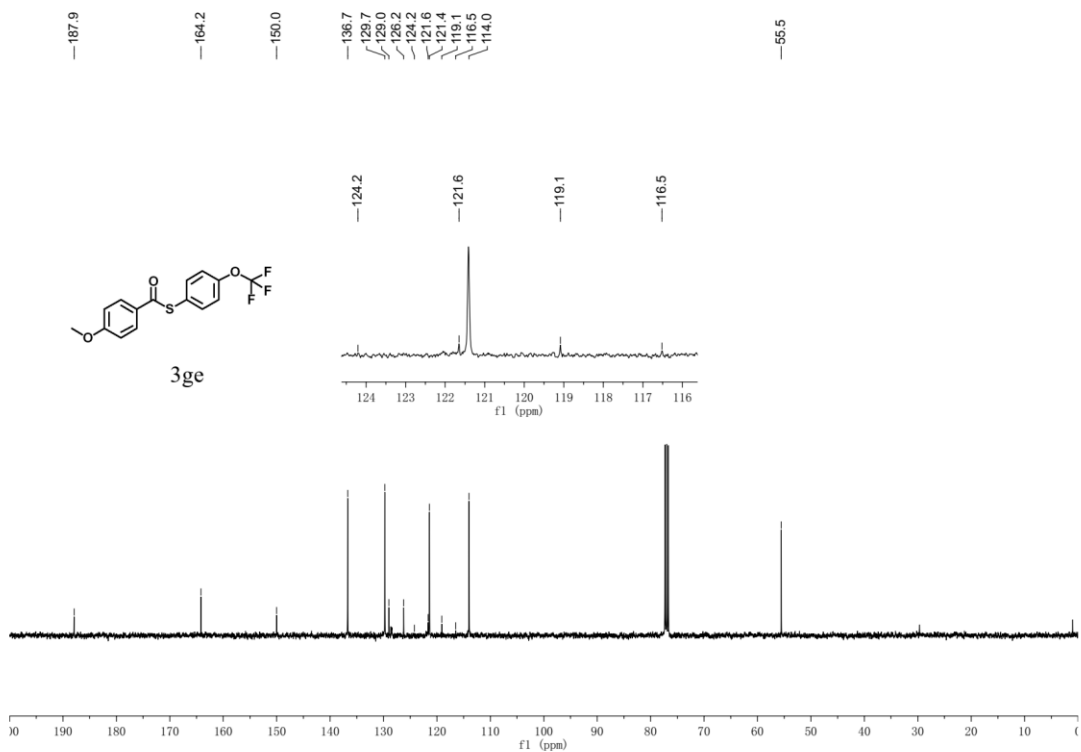
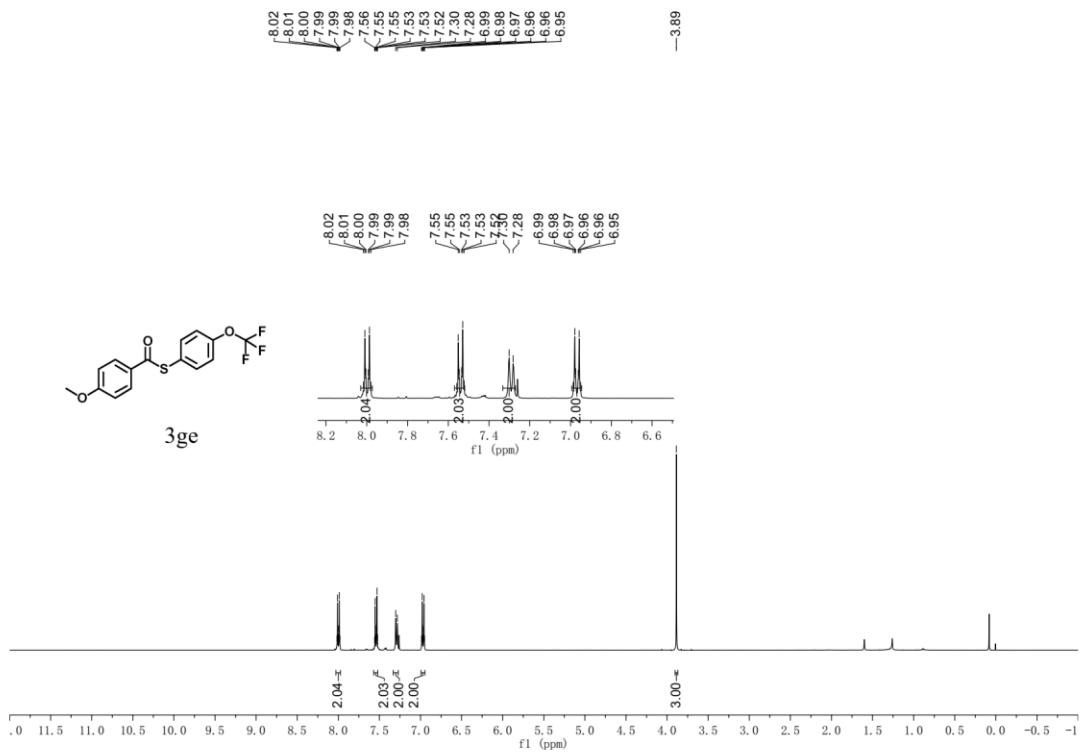


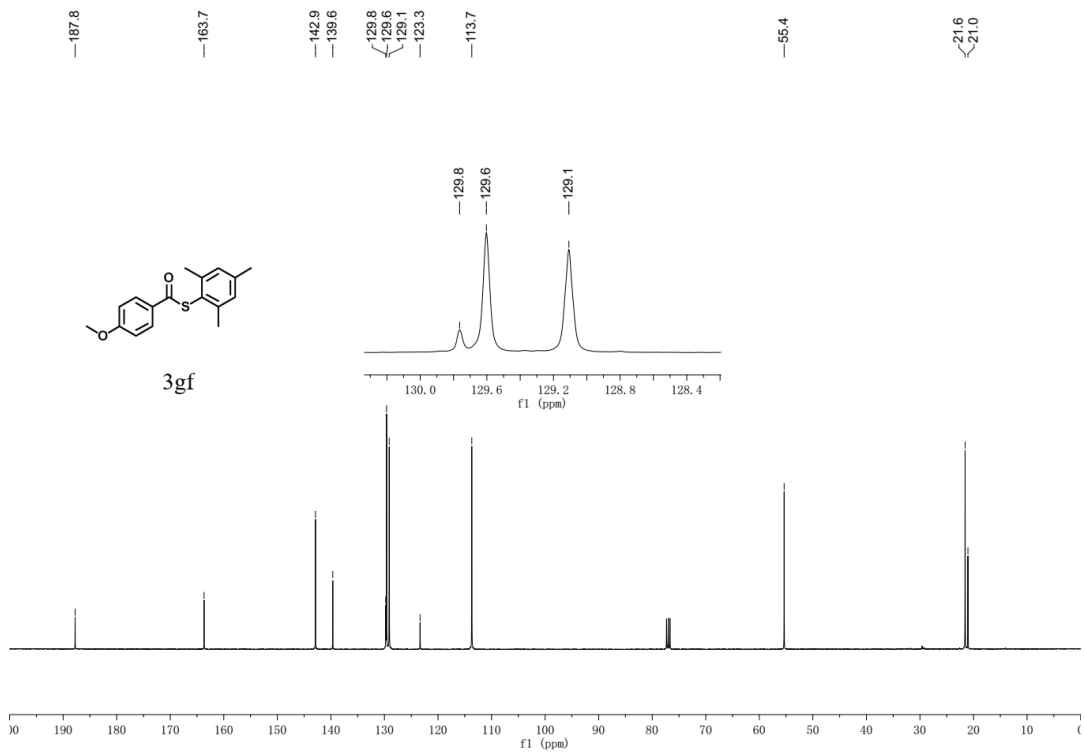
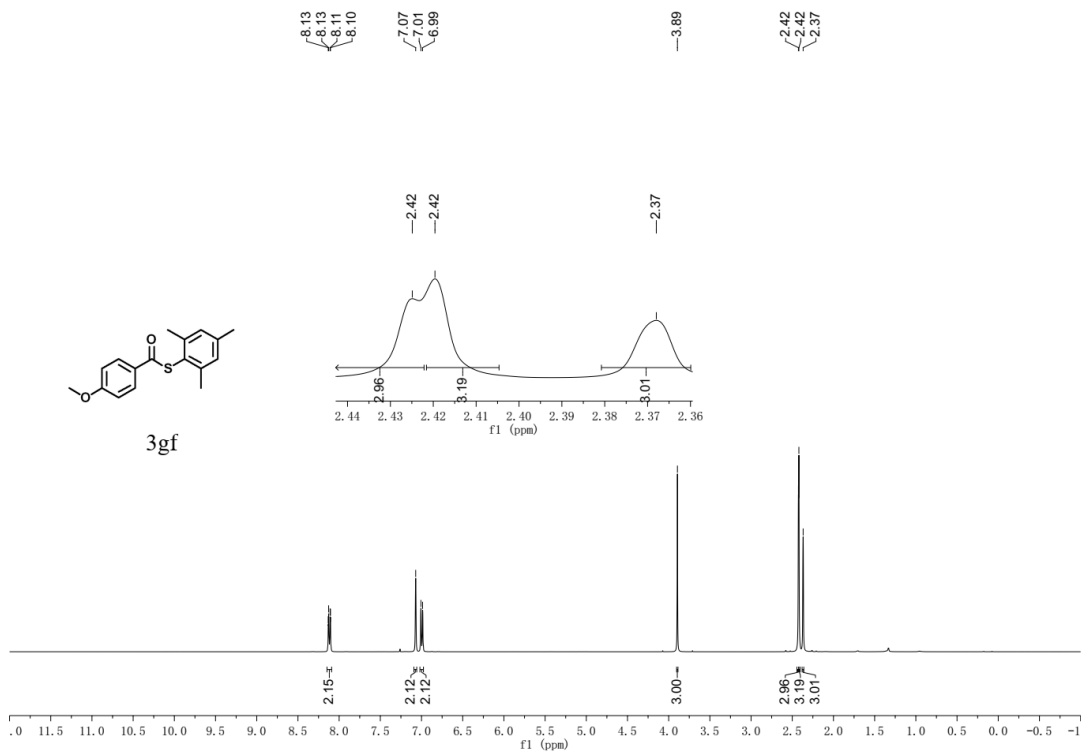


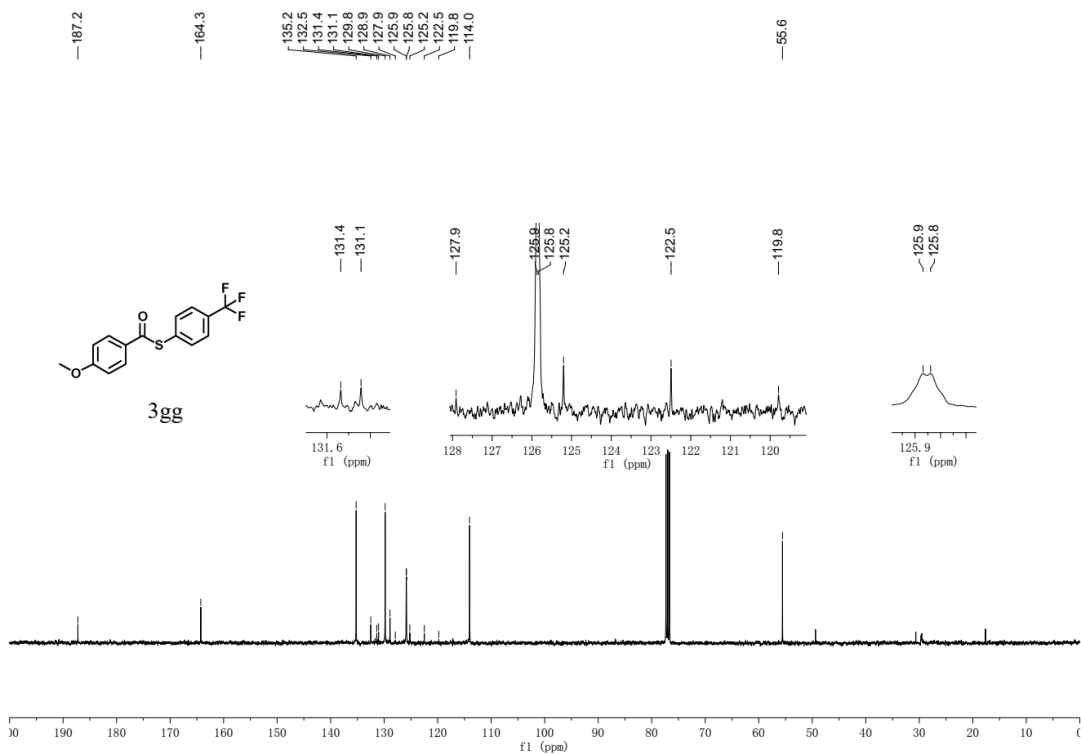
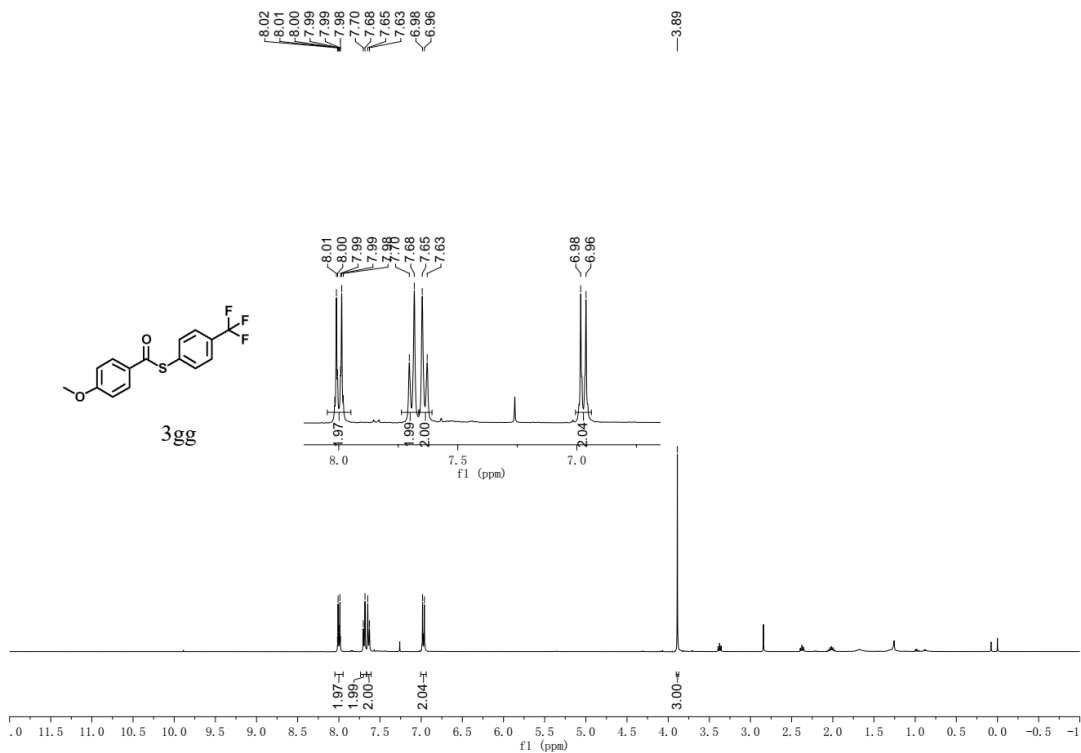


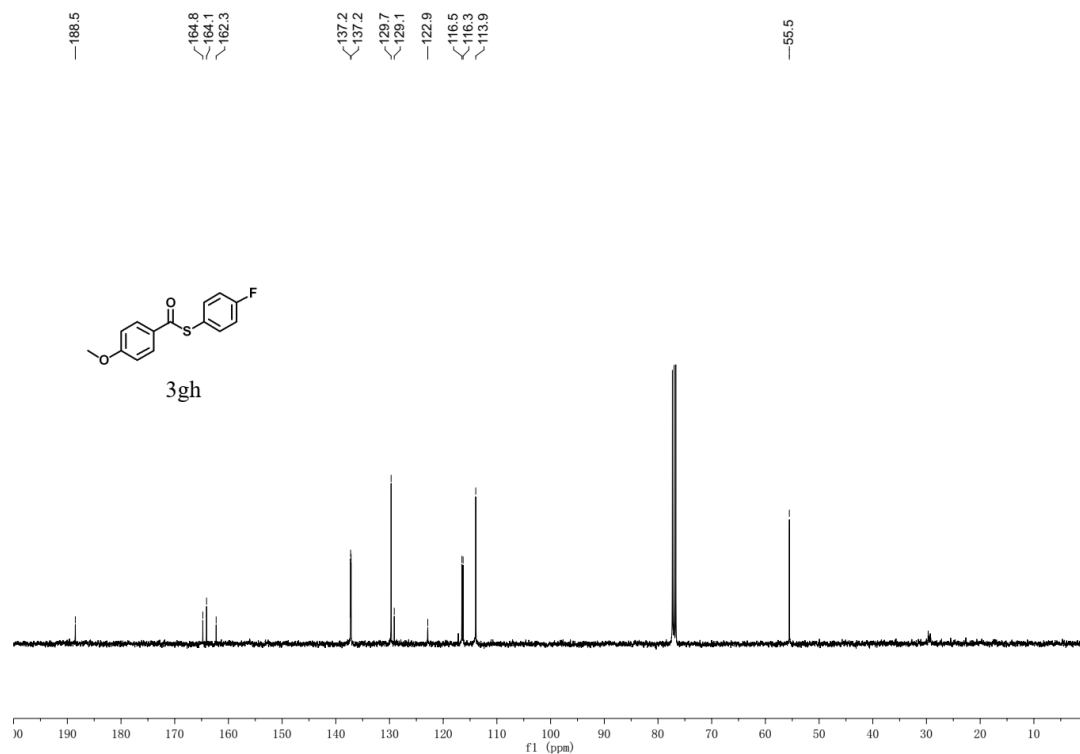
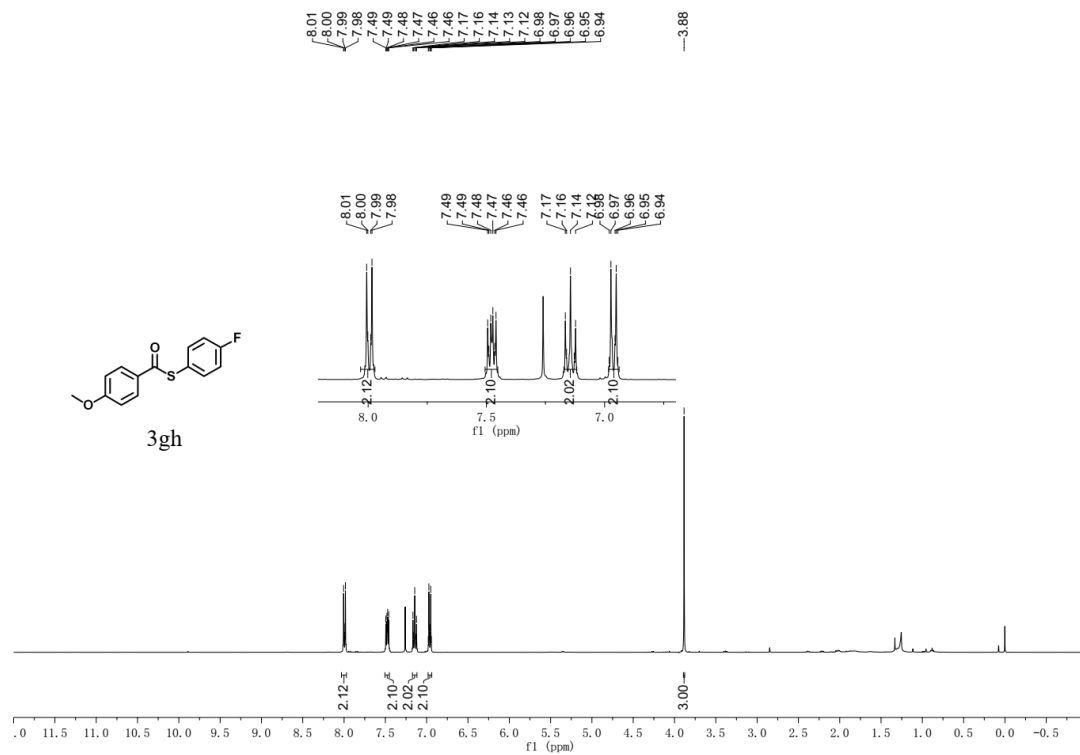


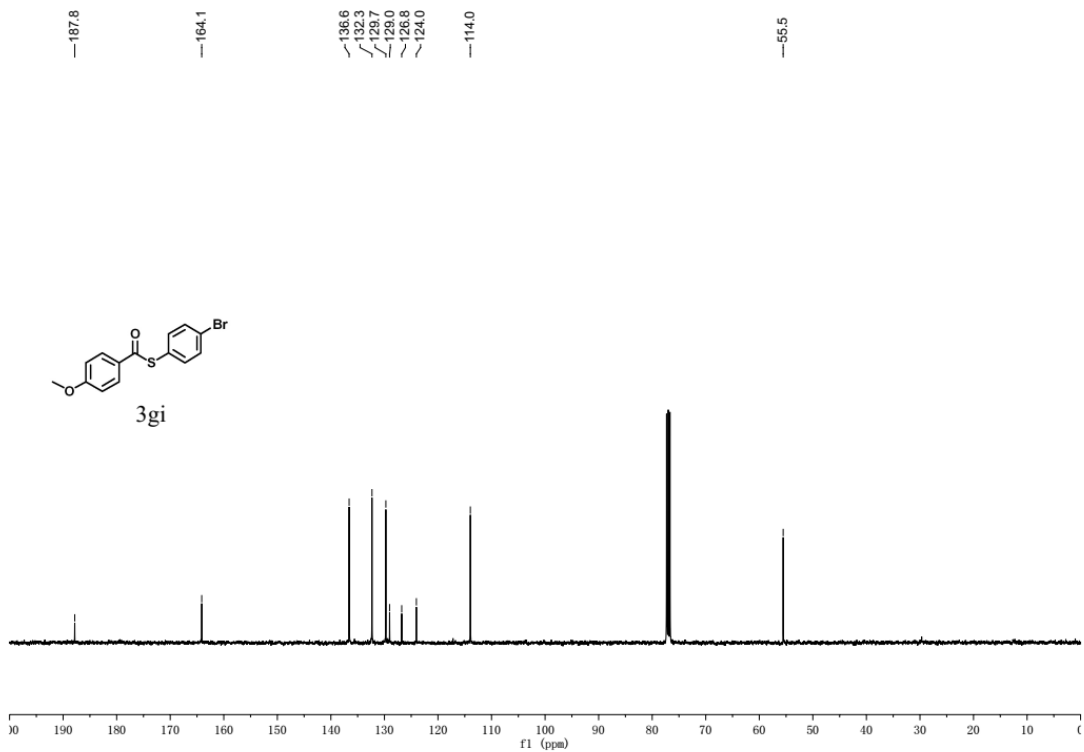
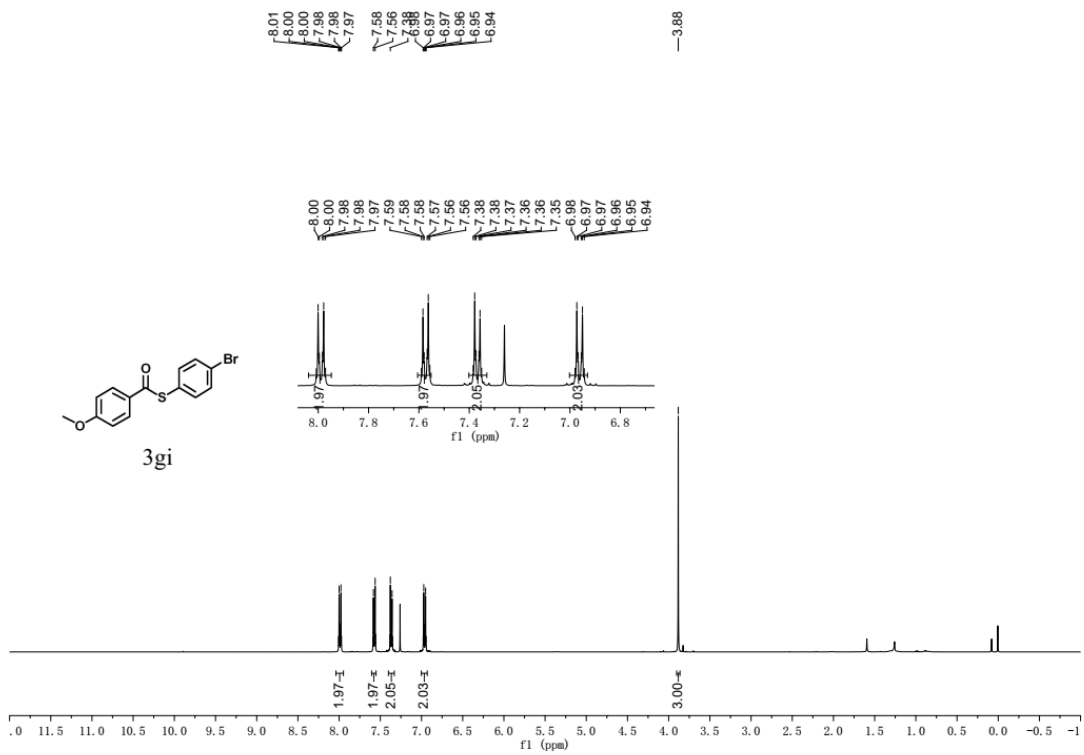


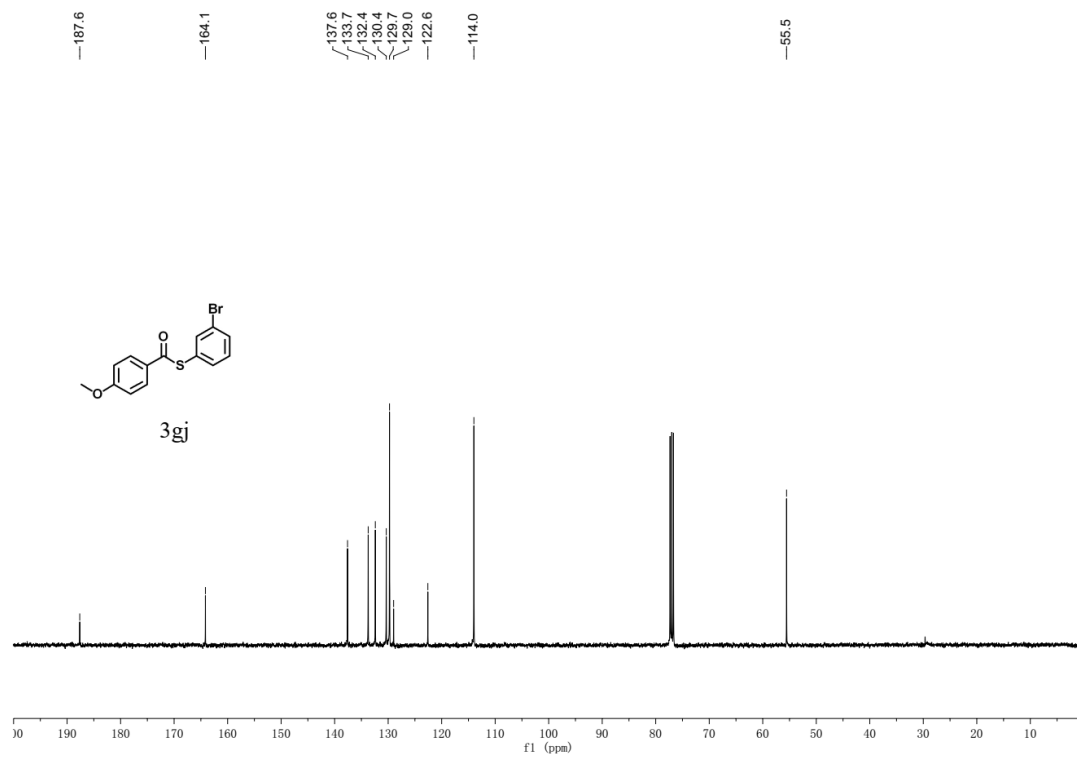
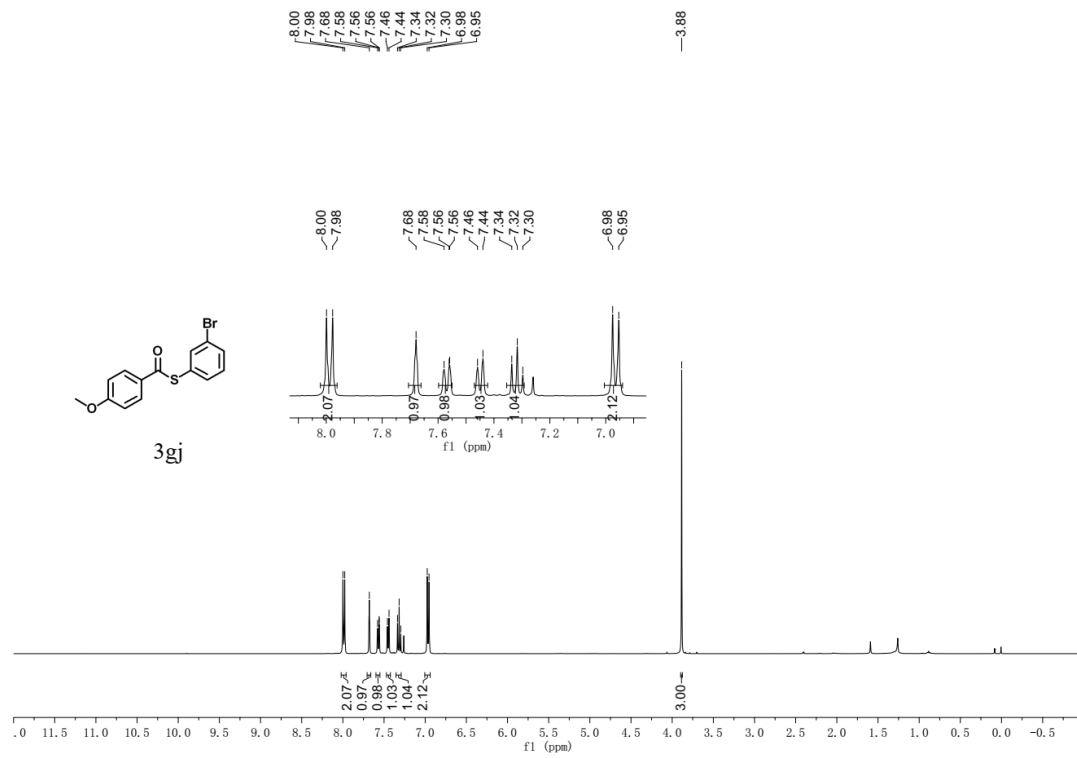


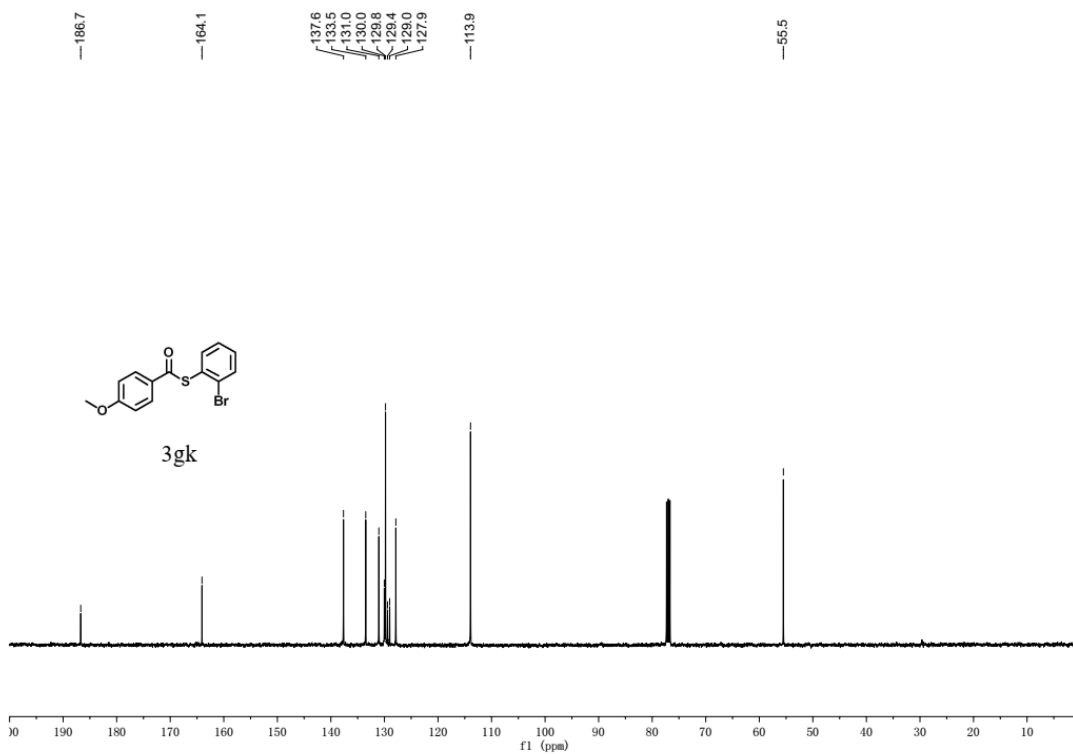
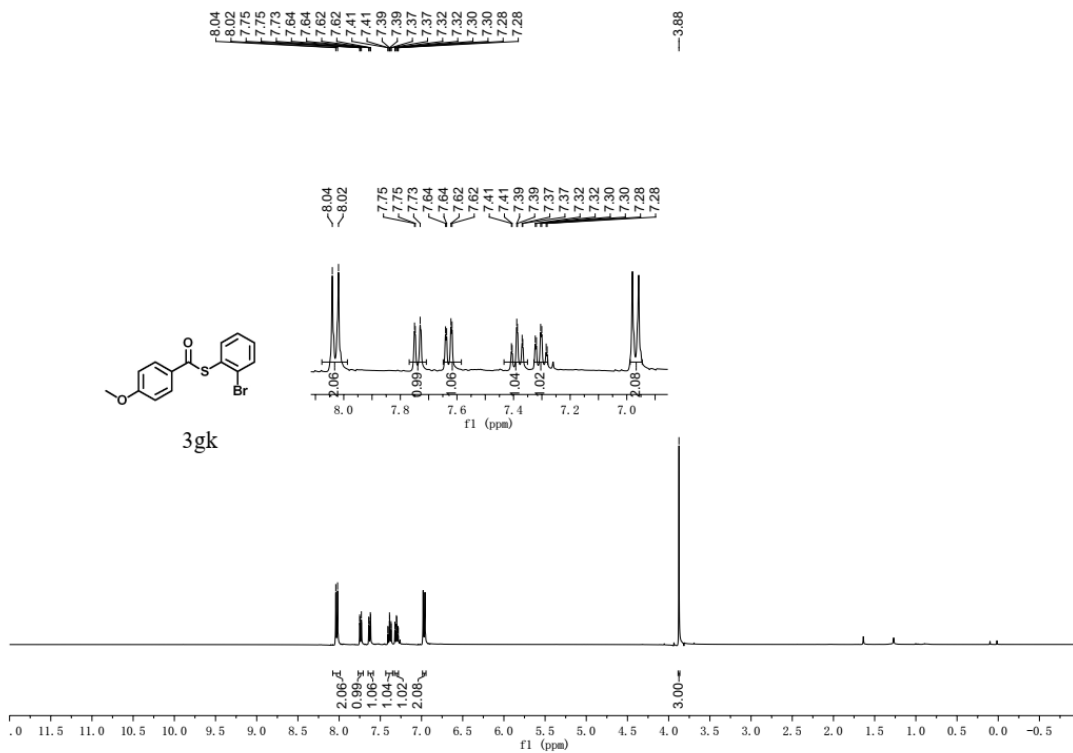


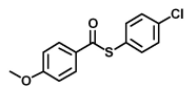




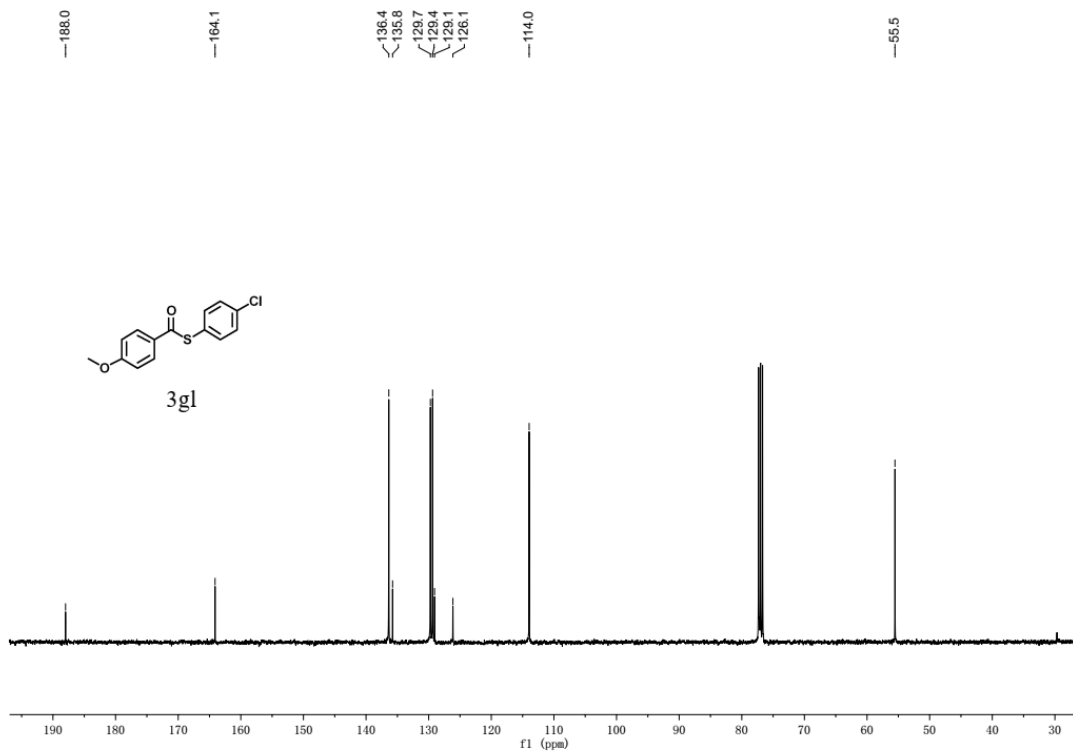
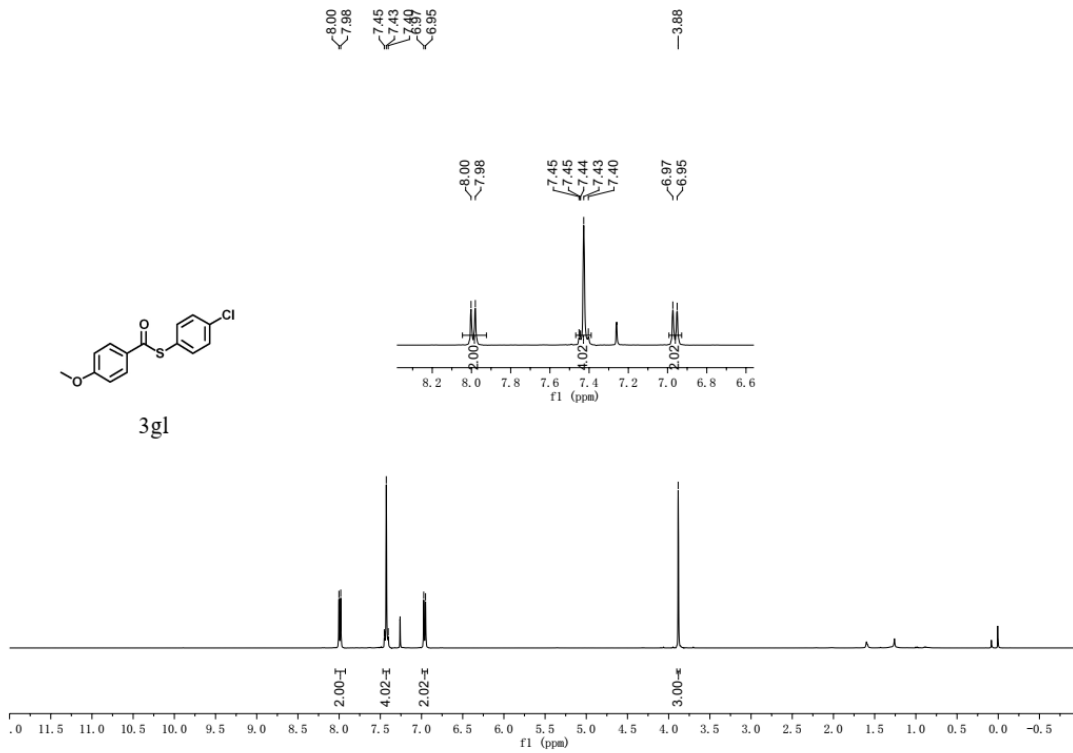


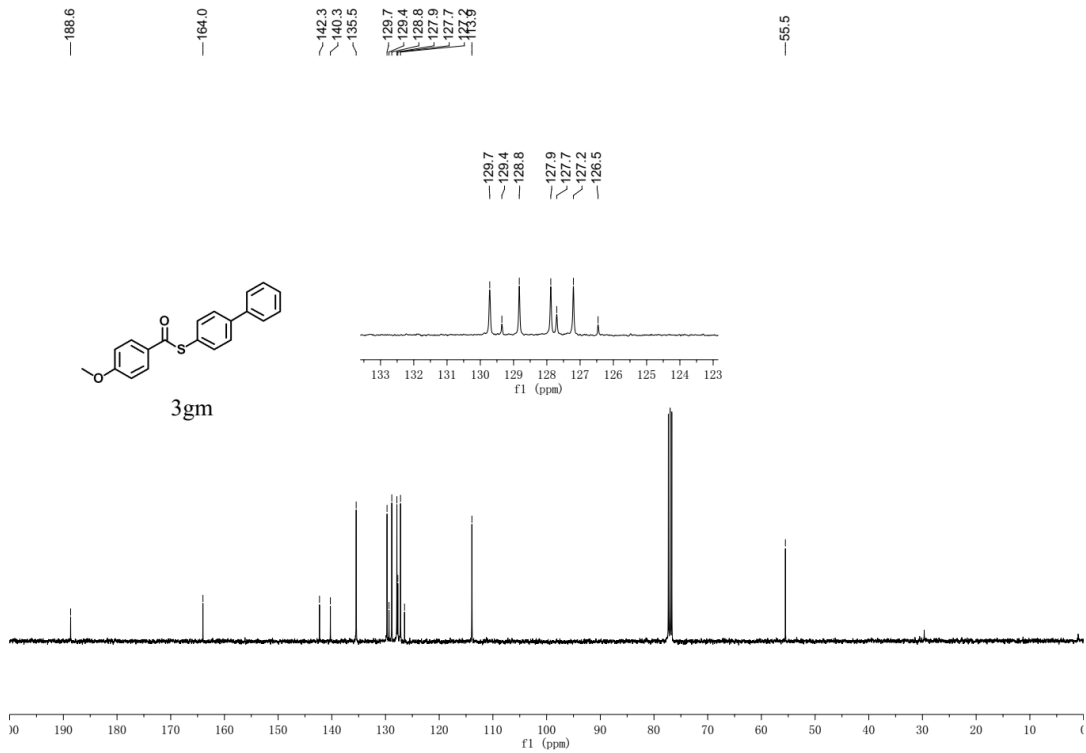
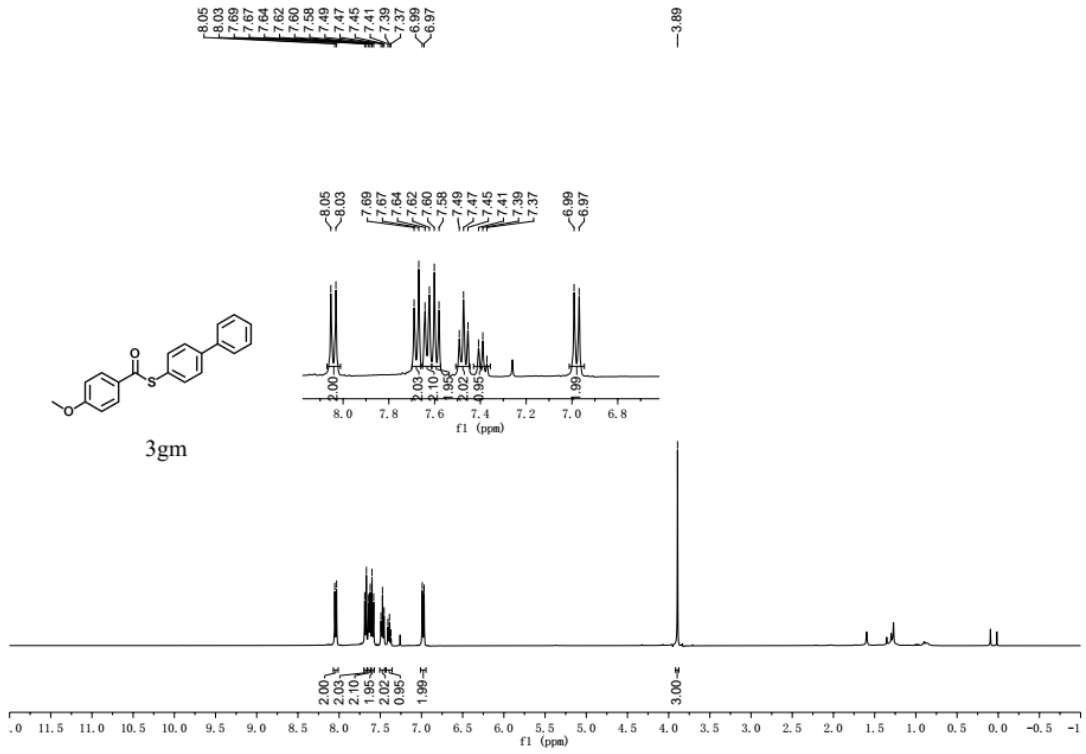


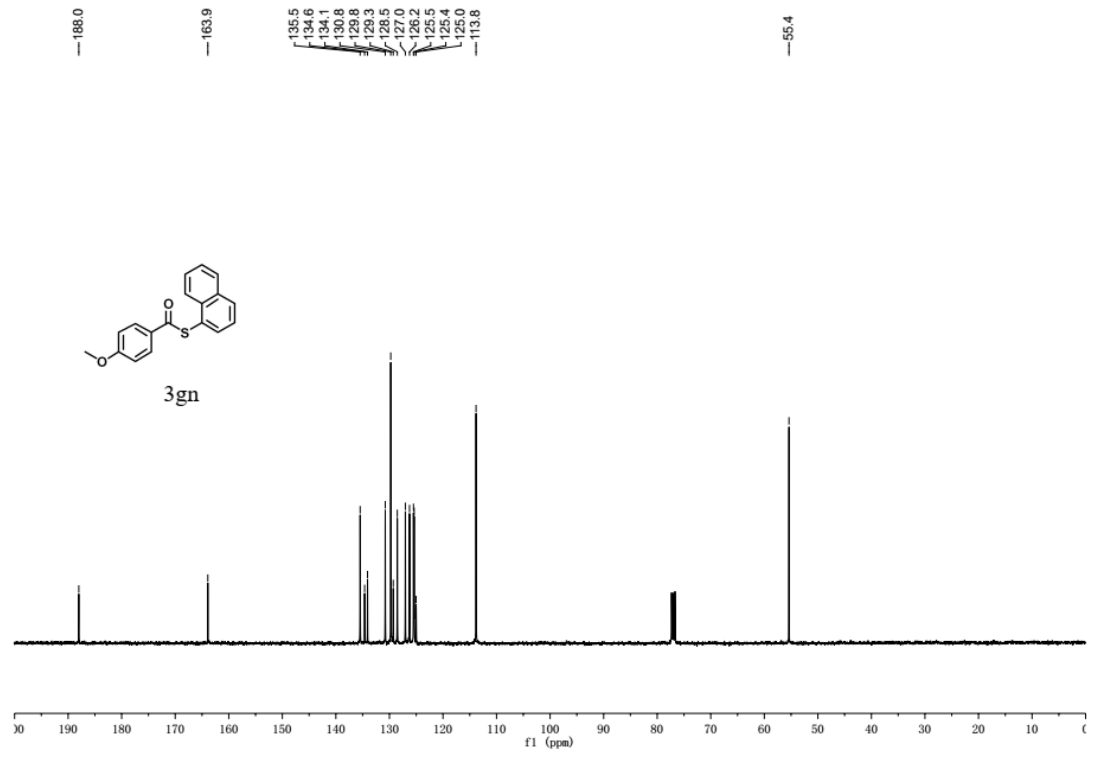
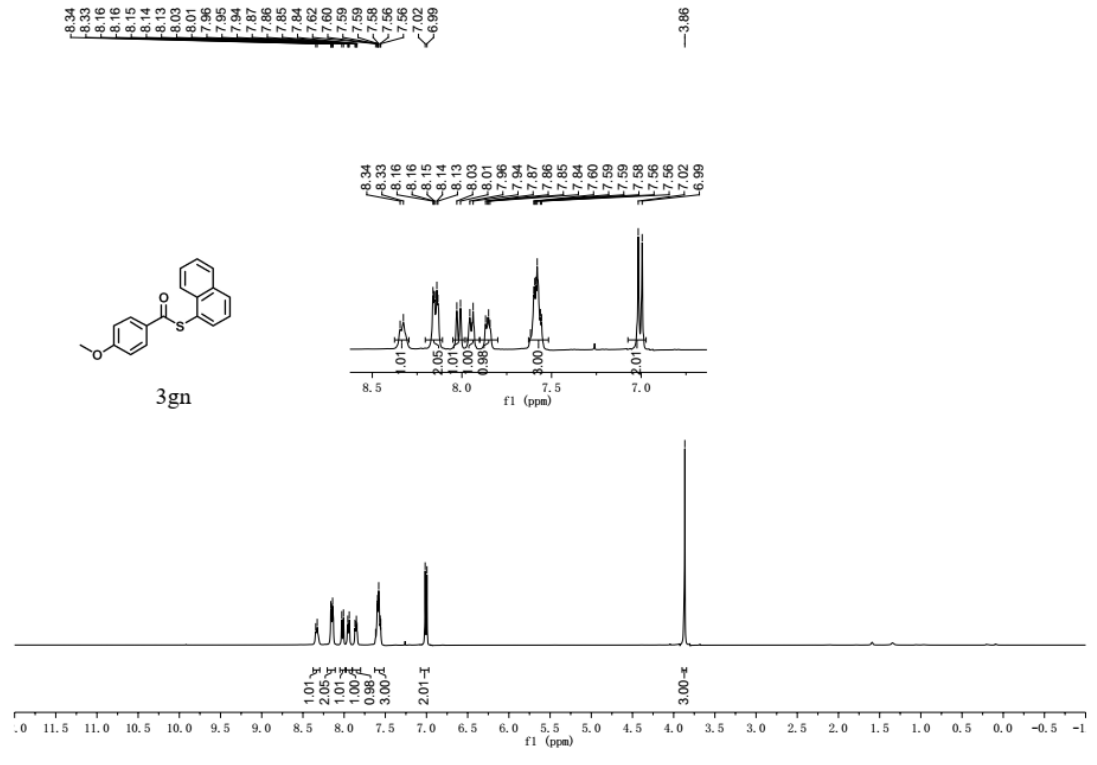


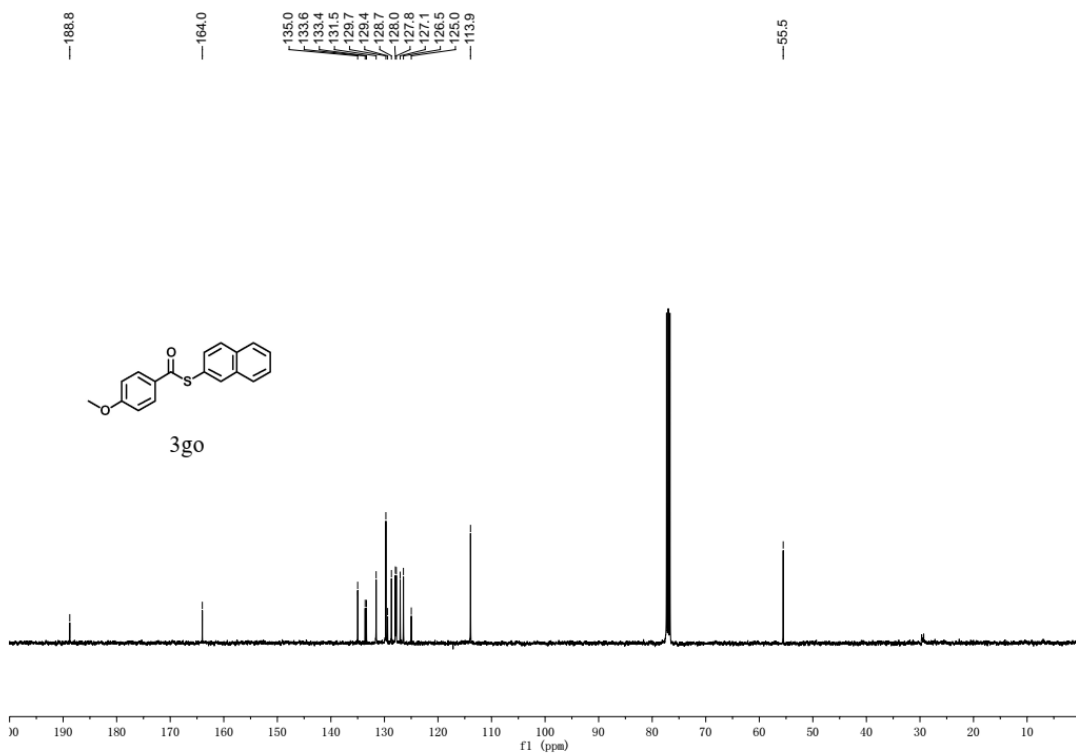
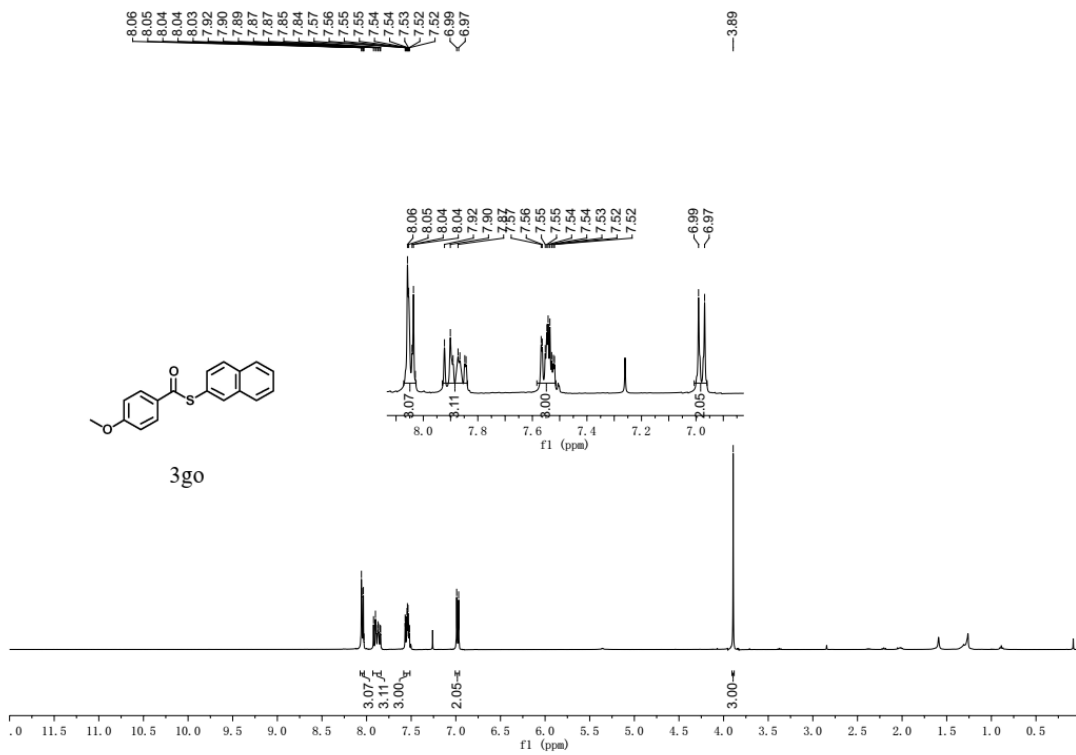


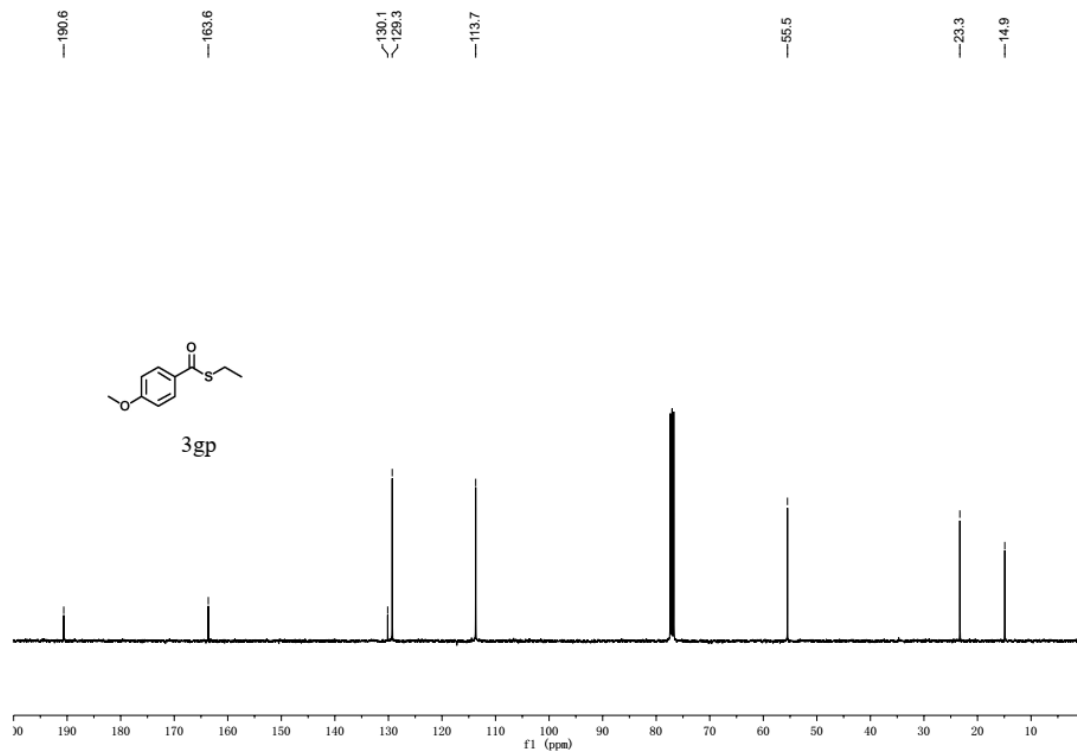
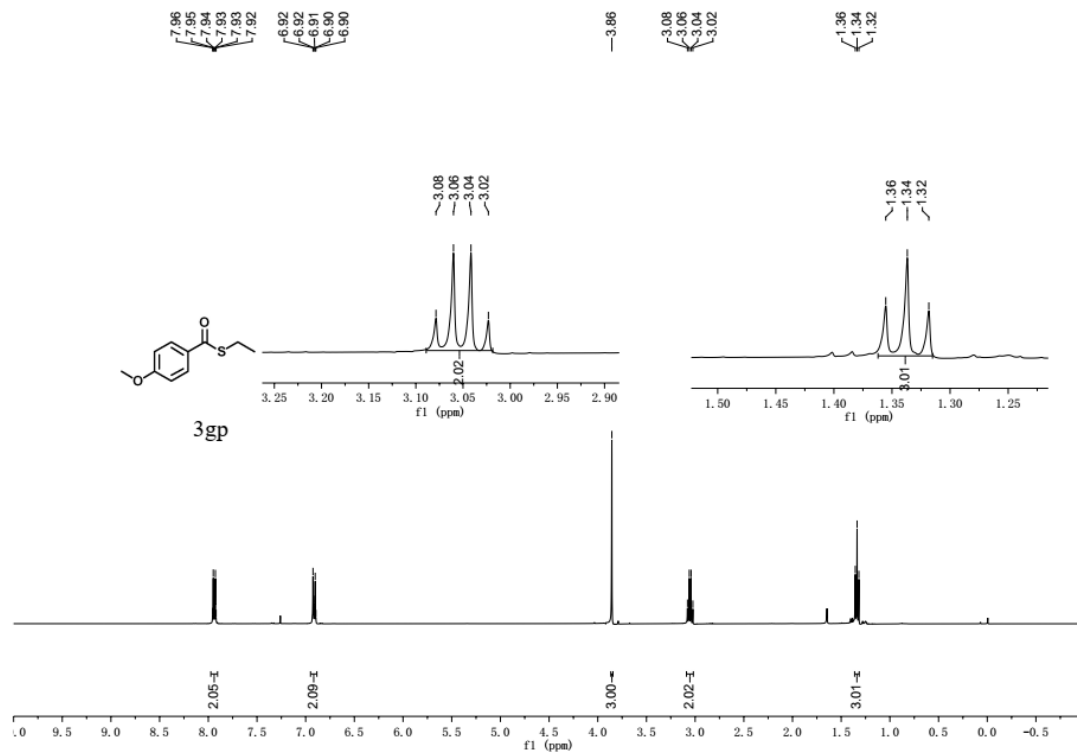
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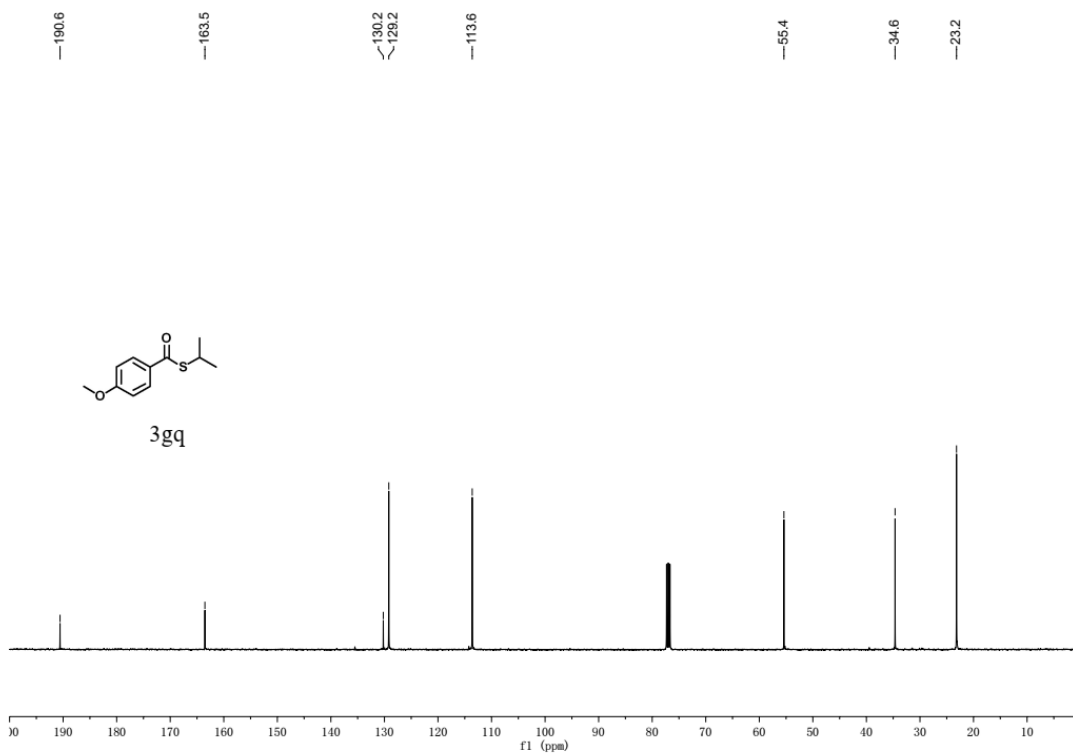
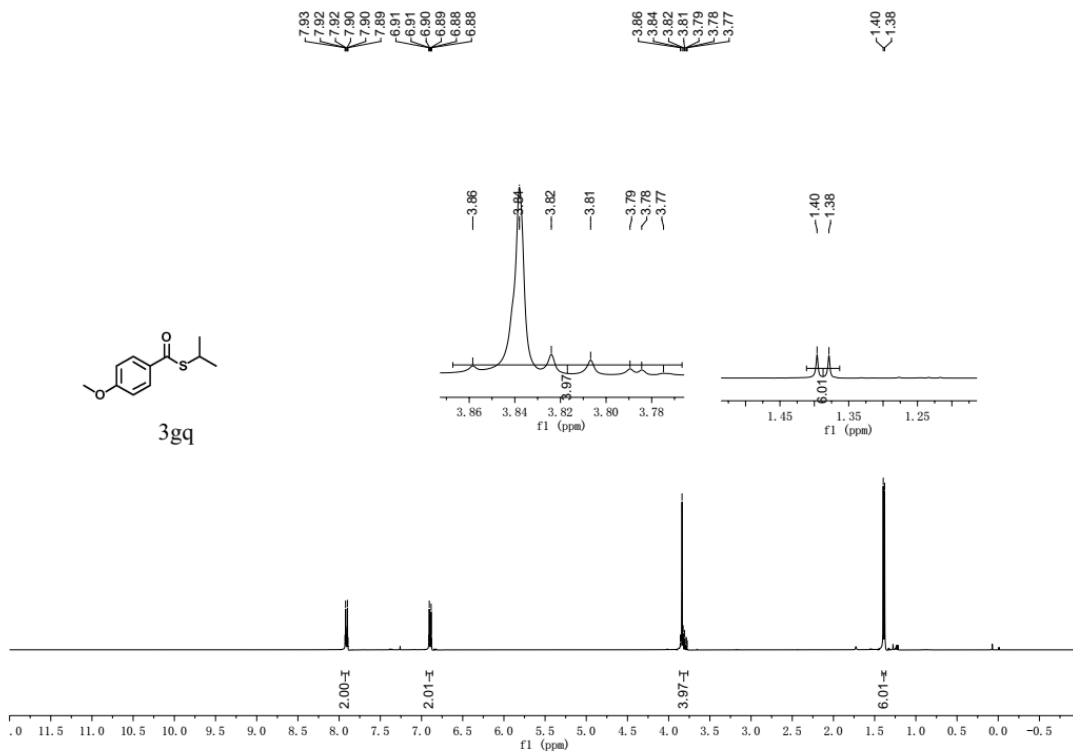


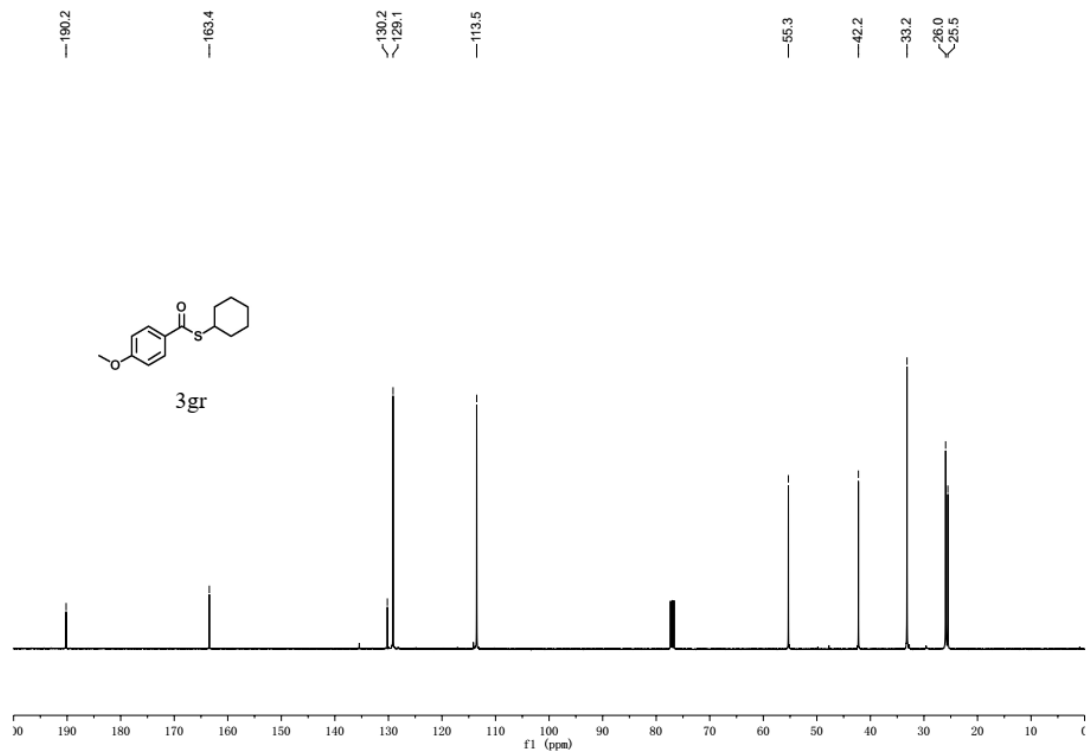
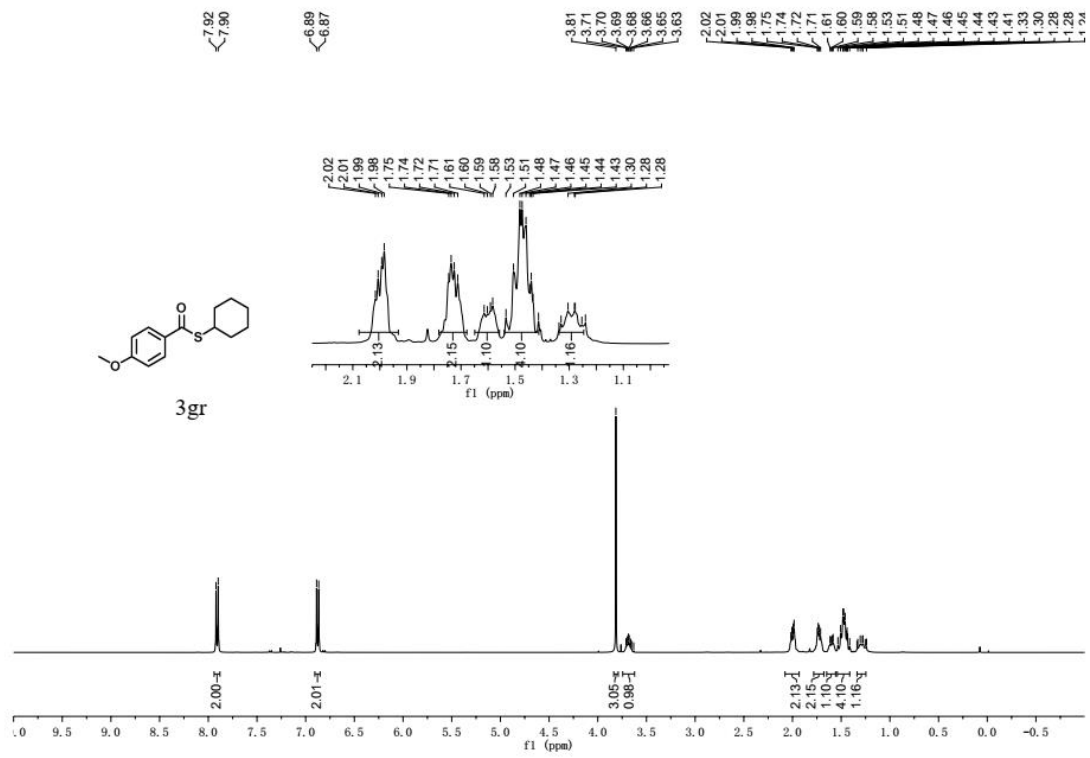


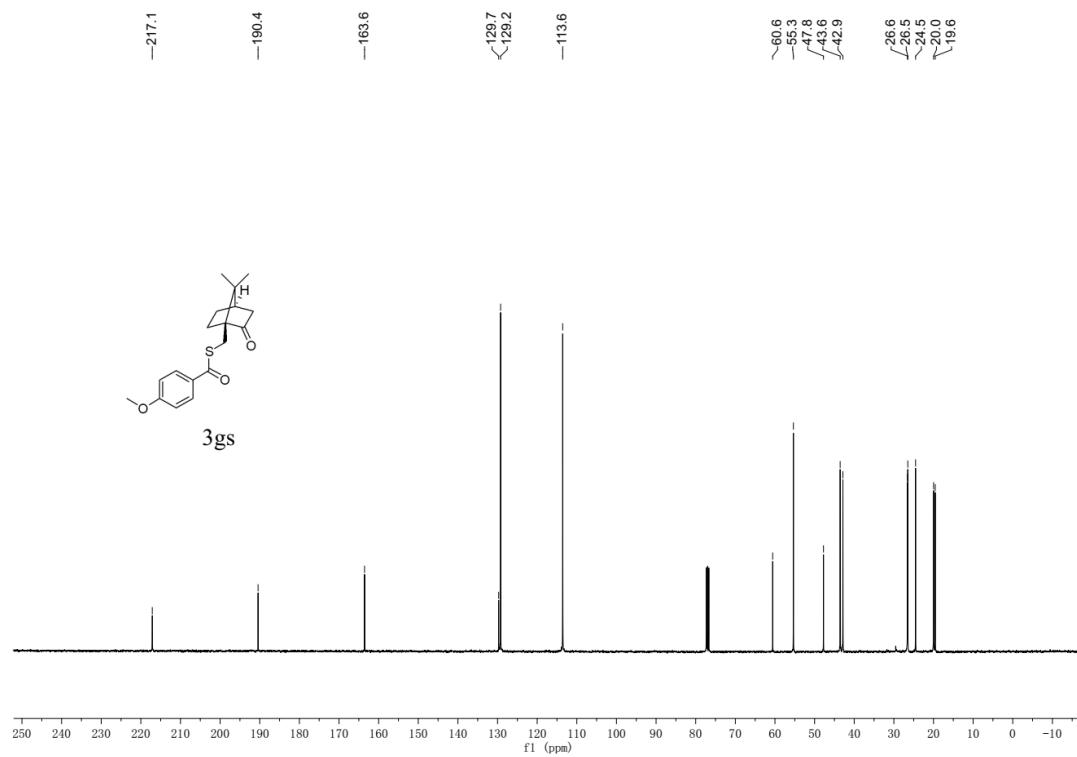
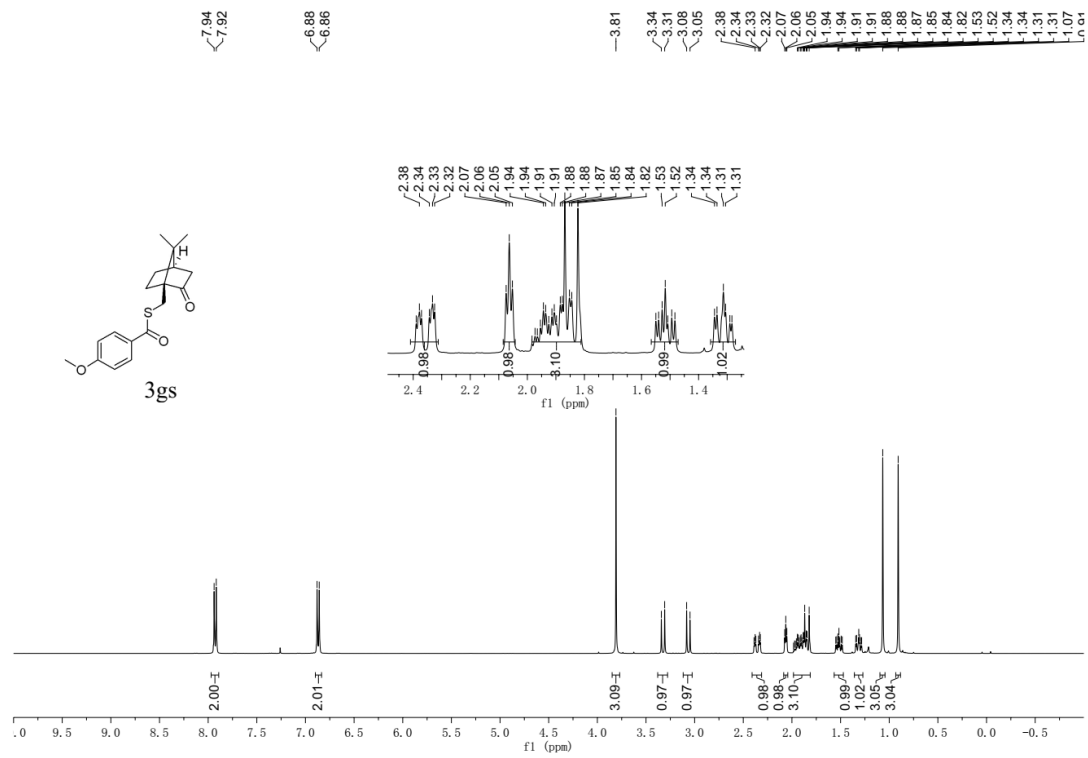












4.2 Copy of ^1H and ^{13}C NMR Spectra of Thioether 4aa

