Supporting Information

Nickel-Catalyzed Thiocarbonylation of Arylboronic Acids with Sulfonyl Chlorides for the Synthesis of Thioesters

Xinxin Qi,[†] Zhi-Peng Bao,[†] Xin-Tong Yao,[†] Xiao-Feng Wu*[,†,‡]

[†]Department of Chemistry, Zhejiang Sci-Tech University, Hangzhou, Zhejiang 310018, People's Republic of China

[‡]Leibniz-Institut für Katalyse e.V. an der Universität Rostock, Albert-Einstein-Straße 29a, Rostock 18059, Germany

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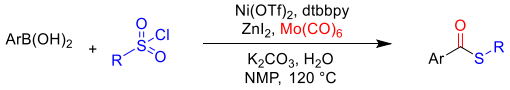
1. General Information

Unless otherwise noted, all reactions were carried out under a nitrogen atmosphere. All reagents were from commercial sources, all solvents are extra dry solvents and used as received without further purification. Column chromatography was performed on silica gel (200-300 meshes) using petroleum ether (b.p. 60-90 ºC) and ethyl acetate as the eluents. ^{1}H and ^{13}C NMR spectra were taken on 400 MHz instruments and spectral data were reported in ppm relative to tetramethylsilane (TMS) as the internal standard and $CDCl_3$ (^{1}H NMR δ 7.26, ^{13}C 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.

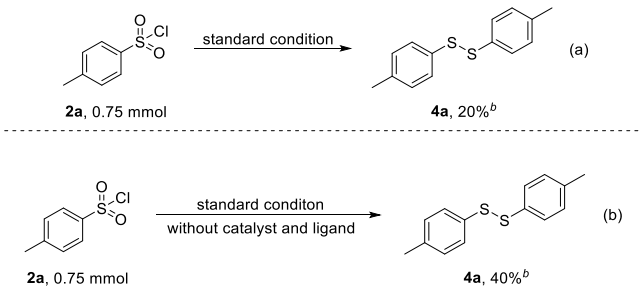
2. General Procedure

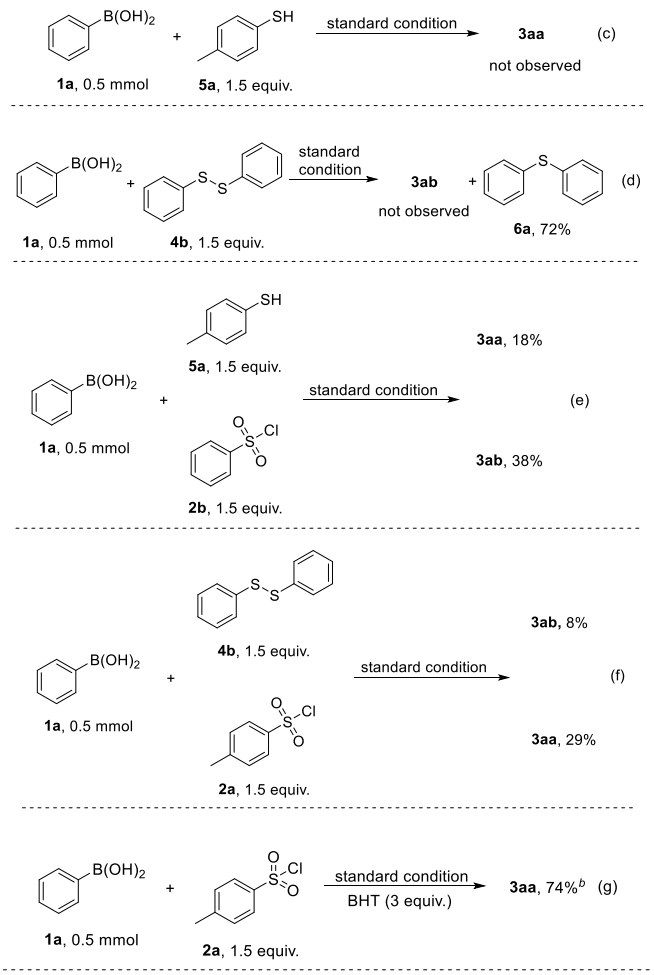


$Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acids (0.5 mmol), sulfonyl chlorides (0.75 mmol), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. The tube was sealed, and the mixture was stirred at 120 ℃ (oil bath) for 16 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.

1 mmol scale: $Ni(OTf)_2$ (20 mol%), dtbbpy (20 mol%), ZnI_2 (40 mol%), $Mo(CO)_6$ (1 mmol), K_2CO_3 (1.5 mmol) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acids (1 mmol), sulfonyl chlorides (1.5 mmol), H_2O (50 mol%), and NMP (4 mL) were added into the tube via syringe. The tube was sealed, and the mixture was stirred at 120 ℃ for 16 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 product **3aa** in 70% yield (159.6 mg).

3. Mechanistic Studies





(a) $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. 4-methylbenzenesulfonyl chloride **2a** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. The tube was sealed and the mixture was stirred at 120 ℃ (oil bath) for 16 h. After the reaction was completed, the crude mixture was filtered and concentrated under vacuum. The crude product was purified by column chromatography (PE, volume ratio) to afford the desired **4a** as a **colorless viscous liquid** (18.5 mg, 20%).

(b) ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. 4-methylbenzenesulfonyl chloride **2a** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. The tube was sealed and the mixture was stirred at 120 ℃ (oil bath) for 16 h. After the reaction was completed, the crude mixture was filtered and concentrated under vacuum. The crude product was purified by column chromatography (PE, volume ratio) to afford the desired **4a** as a **colorless viscous liquid** (36.9 mg, 40%).

(c) $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), 4-methylbenzenethiol **5a** (0.75 mmol, 93.0 mg), H_2O (50 mol%, 4.5 mg),

and NMP (2 mL) were added into the tube via syringe. The tube was sealed and the mixture was stirred at 120 °C (oil bath) for 16 h.

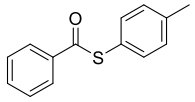
(d) $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), 1,2-diphenyldisulfane **4b** (0.75 mmol, 163.5 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. The tube was sealed and the mixture was stirred at 120 °C (oil bath) for 16 h. After the reaction was completed, the product **6a** was observed in 72% yield. (Yields determined by GC analysis using dodecane as an internal standard).

(e) $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), 4-methylbenzenethiol **5a** (0.75 mmol, 93.0 mg), benzenesulfonyl chloride **2b** (0.75 mmol, 132.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. The tube was sealed and the mixture was stirred at 120 °C (oil bath) for 16 h. After the reaction was completed, the product **3aa** was observed in 18% yield, the product **3ab** was observed in 38% yield. (Yields determined by GC analysis using dodecane as an internal standard).

(f) $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), 1,2-diphenyldisulfane **4b** (0.75 mmol, 163.5 mg), 4-methylbenzenesulfonyl chloride **2a** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. The tube was sealed and the mixture was stirred at 120 °C (oil bath) for 16 h. After the reaction was completed, the product **3ab** was observed in 8% yield, the product **3aa** was observed in 29% yield. (Yields determined by GC analysis using dodecane as an internal standard).

(g) BHT (1.5 mmol, 330.5 mg), $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), 4-methylbenzenesulfonyl chloride **2a** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. The tube was sealed and the mixture was stirred at 120 °C (oil bath) for 16 h. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1, volume ratio) to give the product **3aa** as a **light yellow solid** (84.4 mg, 74%).

4. Characterization of Products



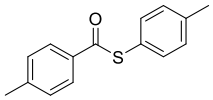
S-(*p*-tolyl) benzothioate (**3aa**)[7]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), 4-methylbenzenesulfonyl chloride **2a** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3aa** as a **light yellow solid** (82.1 mg, 72%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, *J* = 0.6 Hz, 1H), 8.00 (d, *J* = 1.3 Hz, 1H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.25 (d, *J* = 7.9 Hz, 2H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 139.7, 136.7, 134.9, 133.5, 130.0, 128.6, 127.4, 123.7, 21.3.

M.p. 65.0 - 67.8 °C



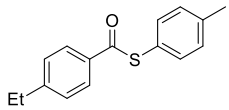
S-(*p*-tolyl) 4-methylbenzothioate (**3ba**)[7]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. *p*-tolylboronic acid **1b** (0.5 mmol, 68.0 mg), 4-methylbenzenesulfonyl chloride **2a** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3ba** as a **white soild** (62.9 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.30 - 7.24 (m, 4H), 2.43 (s, 3H), 2.40 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 144.4, 139.7, 135.0, 134.2, 130.0, 129.4, 127.5, 124.0, 21.7, 21.3.

M.p. 117.3 - 119.5 °C



S-(*p*-tolyl) 4-ethylbenzothioate (**3ca**)[7]

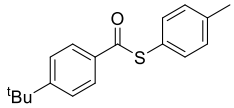
General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. (4-ethylphenyl)boronic acid **1c** (0.5 mmol, 75.0 mg), 4-methylbenzenesulfonyl chloride **2a** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe.

Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3ca** as a **white soild** (112.7 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J* = 8.3 Hz, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.30 (d, *J* = 8.4 Hz, 2H), 7.26 (d, *J* = 8.0 Hz, 2H), 2.72 (q, *J* = 7.6 Hz, 2H), 2.40 (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.

M.p. 82.4 - 84.5 °C



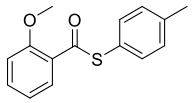
S-(*p*-tolyl) 4-(*tert*-butyl)benzothioate (**3da**)[7]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. (4-(tert-butyl)phenyl)boronic acid **1d** (0.5 mmol, 89.1 mg), 4-methylbenzenesulfonyl chloride **2a** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate =100:1，volume ratio) to give the titled product **3da** as a **white soild** (99.4 mg, 70%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 - 7.94 (m, 2H), 7.54 - 7.46 (m, 2H), 7.39 (d, *J* = 8.1 Hz, 2H), 7.30 - 7.24 (m, 2H), 2.40 (s, 3H), 1.35 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 157.4, 139.7, 135.0, 134.1, 130.0, 127.4, 125.6, 124.0, 35.2, 31.1, 21.4.

M.p. 74.6 - 77.8 °C



S-(*p*-tolyl) 2-methoxybenzothioate (**3ea**)

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. (2-methoxyphenyl)boronic acid **1e** (0.5 mmol, 76.0 mg), 4-methylbenzenesulfonyl chloride **2a** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1 to 50:1，volume ratio) to give the titled product **3ea** as a **light yellow viscous liquid** (76.1 mg, 59%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, *J* = 7.7 Hz, 1H), 7.47 (t, *J* = 7.0 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 2H), 7.24 (d, *J* = 7.7 Hz, 2H), 7.03 - 6.97 (m, 2H), 3.93 (s, 3H), 2.38 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5, 158.1, 139.4, 134.8, 133.8, 129.9, 126.4, 125.2, 120.4, 112.1, 55.8, 21.3.

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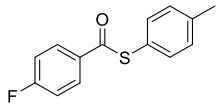


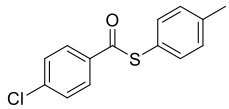
S-(*p*-tolyl) 4-fluorobenzothioate (**3fa**)[7]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. (4-fluorophenyl)boronic acid **1f** (0.5 mmol, 70.0 mg), 4-methylbenzenesulfonyl chloride **2a** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3fa** as a **white soild** (93.5 mg, 76%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 - 8.05 (m, 2H), 7.42 (d, *J* = 8.1 Hz, 2H), 7.29 (d, *J* = 8.0 Hz, 2H), 7.21 - 7.13 (m, 2H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 188.9, 165.9 (d, *J* = 255.2 Hz), 139.8, 134.9, 132.9, 130.0, 129.9 (d, *J* = 9.3 Hz), 123.4, 115.8 (d, *J* = 22.0 Hz), 21.3.

M.p. 64.2 - 66.8 °C



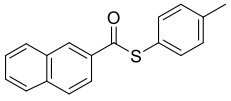
S-(*p*-tolyl) 4-chlorobenzothioate (**3ga**)[7]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. (4-chlorophenyl)boronic acid **1g** (0.5 mmol, 78.0 mg), 4-methylbenzenesulfonyl chloride **2a** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3ga** as a **white soild** (78.6 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) 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).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.5, 140.0, 140.0, 135.0, 134.9, 130.2, 129.0, 128.8, 123.3, 21.4.

M.p. 107.5 - 109.3 °C



S-(*p*-tolyl) naphthalene-2-carbothioate (**3ha**)[7]

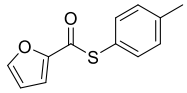
General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. naphthalen-2-ylboronic acid **1h** (0.5 mmol, 86.0 mg), 4-methylbenzenesulfonyl chloride **2a** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography

(petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3ha** as a **white soild** (116.8 mg, 84%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.63 (s, 1H), 8.07 - 7.97 (m, 2H), 7.91 (t, *J* = 8.3 Hz, 2H), 7.67 - 7.55 (m, 2H), 7.51 - 7.44 (m, 2H), 7.30 (d, *J* = 7.8 Hz, 2H), 2.43 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 139.8, 135.8, 135.0, 134.0, 132.5, 130.1, 129.6, 128.9, 128.6, 127.8, 126.9, 123.9, 123.3, 21.3.

M.p.117.2 - 119.5 °C



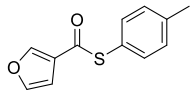
S-(*p*-tolyl) furan-2-carbothioate (**3ia**)[1]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. furan-2-ylboronic acid **1i** (0.5 mmol, 56.0 mg), 4-methylbenzenesulfonyl chloride **2a** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3ia** as a **white soild** (60.0 mg, 55%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 0.6 Hz, 1H), 7.38 (d, *J* = 8.0 Hz, 2H), 7.27 - 7.24 (m, 3H), 6.58 - 6.53 (m, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 179.0, 150.4, 146.4, 146.3, 139.9, 135.0, 130.1, 122.6, 116.1, 112.3, 112.3, 21.3.

M.p. 72.5 - 74.8 °C



S-(*p*-tolyl) furan-3-carbothioate (**3ja**)

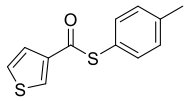
General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. furan-3-ylboronic acid **1j** (0.5 mmol, 56.0 mg), 4-methylbenzenesulfonyl chloride **2a** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3ja** as a **white soild** (65.4 mg, 60%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (s, 1H), 7.51 - 7.42 (m, 1H), 7.39 - 7.32 (m, 2H), 7.25 (d, *J* = 3.6 Hz, 2H), 6.81 - 6.76 (m, 1H), 2.39 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 183.5, 146.1, 146.0, 144.1, 144.1, 139.8, 134.8, 130.0, 126.4, 123.1, 108.4, 21.3.

M.p. 65.8 - 68.2 °C

HRMS (ESI-TOF): $[M+Na]^+$ calcd. for $C_{12}H_{10}NaO_2S^+$, 241.0294; found, 241.0301.



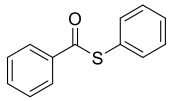
S-(*p*-tolyl) thiophene-3-carbothioate (**3ka**)[7]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. thiophen-3-ylboronic acid **1k** (0.5 mmol, 64.0 mg), 4-methylbenzenesulfonyl chloride **2a** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3ka** as a **white soild** (105.3 mg, 90%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 - 8.22 (m, 1H), 7.65 - 7.60 (m, 1H), 7.47 - 7.38 (m, 3H), 7.31 (d, *J* = 7.9 Hz, 2H), 2.45 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 184.0, 140.3, 139.8, 134.9, 130.9, 130.0, 126.5, 126.1, 123.6, 21.3.

M.p. 67.8 - 70.2 °C

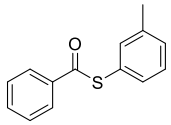


S-phenyl benzothioate (**3ab**)[8]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), benzenesulfonyl chloride **2b** (0.75 mmol, 132.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3ab** as a **light yellow viscous liquid** (70.7 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.4 Hz, 2H), 7.62 (t, *J* = 7.4 Hz, 1H), 7.55 - 7.49 (m, 4H), 7.48 - 7.45 (m, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.1, 136.7, 135.1, 133.6, 129.5, 129.2, 128.7, 127.5, 127.4.



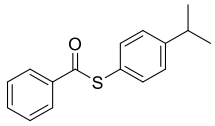
S-(*m*-tolyl) benzothioate (**3ac**)

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), 3-methylbenzenesulfonyl chloride **2c** (0.75 mmol, 143.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3ac** as a **light yellow viscous liquid** (70.7 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 - 7.96 (m, 2H),7.61 - 7.55 (m, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.36 - 7.27 (m, 3H), 7.26 - 7.21 (m, 1H), 2.37 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.3, 139.1, 136.7, 135.6, 133.5, 132.1, 130.4, 129.0, 128.7, 127.4, 126.9, 21.3.

HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{14}H_{13}OS^+$, 229.0682; found, 229.0689.



S-(4-isopropylphenyl) benzothioate (**3ad**)

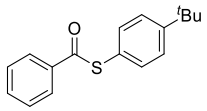
General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), 4-isopropylbenzenesulfonyl chloride **2d** (0.75 mmol, 163.5 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3ad** as a **white soild** (82.0 mg, 64%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 - 7.97 (m, 2H), 7.61 (t, *J* = 7.4 Hz, 1H), 7.55 - 7.42 (m, 4H), 7.33 (d, *J* = 8.1 Hz, 2H), 3.02 - 2.91 (m, 1H), 1.29 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.6, 150.5, 136.7, 135.0, 133.5, 128.7, 127.5, 127.4, 124.1, 34.0, 23.8.

M.p. 66.5 - 68.7 °C

HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{16}H_{17}OS^+$, 257.0995; found, 257.0991.



S-(4-(*tert*-butyl)phenyl) benzothioate (**3ae**)

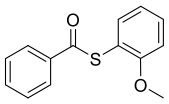
General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), 4-(tert-butyl)benzenesulfonyl chloride **2e** (0.75 mmol, 174.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3ae** as a **white solid** (110.7 mg, 82%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04 (d, *J* = 7.7 Hz, 2H), 7.61 (t, *J* = 7.4 Hz, 1H),7.53 - 7.42 (m, 6H) 1.36 (s, 9H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.5, 152.7, 136.7, 134.7, 133.5, 128.7, 127.4, 126.4, 123.8, 34.8, 31.2.

M.p. 69.1 - 71.5 °C

HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{17}H_{19}OS^+$, 271.1151; found, 271.1148.



S-(2-methoxyphenyl) benzothioate (**3af**)

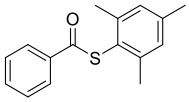
General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), 2-methoxybenzenesulfonyl chloride **2f** (0.75 mmol, 154.5 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1 to 50:1，volume ratio) to give the titled product **3af** as a **white soild** (94.0 mg, 77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 - 8.02 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.52 - 7.44 (m, 4H), 7.09 - 7.00 (m, 2H), 3.86 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.2, 159.7, 137.2, 136.7, 133.4, 131.7, 128.6, 127.5, 121.1, 115.4, 111.6, 56.0.

M.p. 97.6 - 100.8 °C

HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{14}H_{13}O_2S^+$, 245.0631; found, 245.0624.



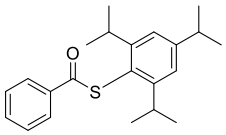
S-mesityl benzothioate (**3ag**)

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), 2,4,6-trimethylbenzenesulfonyl chloride **2g** (0.75 mmol, 163.5 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3ag** as a **light yellow viscous liquid** (84.5 mg, 66%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.12 (d, *J* = 7.5 Hz, 2H), 7.63 (t, *J* = 7.4 Hz, 1H), 7.52 (t, *J* = 7.7 Hz, 2H), 7.07 (s, 2H), 2.40 (s, 6H), 2.36 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.4, 142.9, 139.9, 137.0, 133.3, 129.2, 128.6, 127.5, 123.1, 21.6, 21.1.

HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{16}H_{17}OS^+$, 257.0995; found, 257.1002.



S-(2,4,6-triisopropylphenyl) benzothioate (**3ah**)

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an

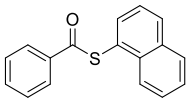
oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), 2,4,6-triisopropylbenzenesulfonyl chloride **2h** (0.75 mmol, 226.6 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3ah** as a **white soild** (149.7 mg, 88%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26 - 8.06 (m, 2H), 7.65 (t, *J* = 7.4 Hz, 1H), 7.54 (t, *J* = 7.6 Hz, 2H), 7.24 - 7.17 (m, 2H), 3.64 - 3.49 (m, 2H), 3.05 - 2.95 (m, 1H), 1.40 - 1.34 (m, 6H), 1.34 - 1.24 (m, 12H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.4, 152.8, 151.1, 137.0, 133.3, 128.6, 127.5, 122.1, 121.2, 34.4, 32.0, 24.4, 23.9, 23.5.

M.p.69.4 - 72.8 °C

HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{22}H_{29}OS^+$, 341.1934; found, 341.1944.



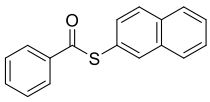
S-(naphthalen-1-yl) benzothioate (**3ai**)[8]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), naphthalene-1-sulfonyl chloride **2i** (0.75 mmol, 169.5 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3ai** as a **white soild** (68.7 mg, 52%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.35 - 8.31 (m, 1H), 8.20 (d, *J* = 7.4 Hz, 2H), 8.07 (d, *J* = 8.3 Hz, 1H), 8.02-7.96 (m, 1H), 7.88 (d, *J* = 7.1 Hz, 1H), 7.70 (t, *J* = 7.4 Hz, 1H), 7.66 - 7.56 (m, 5H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 189.6, 136.6, 135.5, 134.6, 134.2, 133.7, 131.0, 128.7, 128.6, 127.6, 127.2, 126.4, 125.6, 125.4, 124.8.

M.p. 113.2 - 115.6 °C



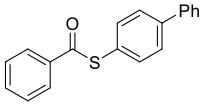
S-(naphthalen-2-yl) benzothioate (**3aj**)[8]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), naphthalene-2-sulfonyl chloride **2j** (0.75 mmol, 169.5 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3aj** as a **white soild** (85.8 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 - 8.10 (m, 3H), 7.97 - 7.86 (m, 3H), 7.66 - 7.49 (m, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 136.6, 134.9, 133.6, 133.5, 133.3, 131.3, 128.7, 128.7, 127.9, 127.7, 127.4, 127.1, 126.5, 124.6.

M.p. 100.8 - 103.5 °C



S-([1,1'-biphenyl]-4-yl) benzothioate (**3ak**)

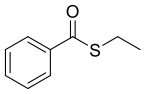
General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), [1,1'-biphenyl]-4-sulfonyl chloride **2k** (0.75 mmol, 189.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1，volume ratio) to give the titled product **3ak** as a **white soild** (98.6 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.09 - 8.06 (m, 2H), 7.69 (d, *J* = 8.3 Hz, 2H), 7.66 - 7.58 (m, 5H), 7.56 - 7.44 (m, 4H), 7.40 (t, *J* = 7.3 Hz, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.2, 142.5, 140.2, 136.6, 135.4, 133.7, 128.8, 128.8, 128.0, 127.8, 127.5, 127.2, 126.2.

M.p. 140.6 - 142.8 °C

HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{19}H_{15}OS^+$, 291.0838; found, 291.0848.

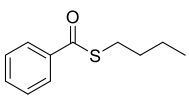


S-ethyl benzothioate (**3al**)[2]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), ethanesulfonyl chloride **2l** (0.75 mmol, 96.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether, volume ratio) to give the titled product **3al** as a **Light yellow liquid** (46.5 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 - 7.92 (m, 2H), 7.60 - 7.53 (m, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 3.08 (q, *J* = 7.4 Hz, 2H), 1.35 (t, *J* = 7.4 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 137.2, 133.2, 128.5, 127.1, 23.4, 14.7.



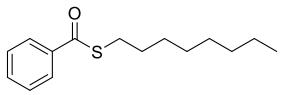
S-butyl benzothioate (**3am**)[4]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), butane-1-sulfonyl chloride **2m** (0.75 mmol, 117.0

mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether , volume ratio) to give the titled product **3am** as a **Colorless liquid** (70.8 mg, 73%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00 - 7.95 (m, 2H), 7.55 (t, *J* = 7.4 Hz, 1H), 7.44 (t, *J* = 7.7 Hz, 2H), 3.08 (t, *J* = 7.3 Hz, 2H), 1.79 - 1.58 (m, 2H), 1.57 - 1.36 (m, 2H), 0.95 (t, *J* = 7.3 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 137.3, 133.2, 128.5, 127.1, 31.6, 28.7, 22.0, 13.6.

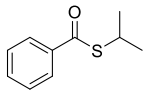


S-octyl benzothioate (**3an**)[3]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), octane-1-sulfonyl chloride **2n** (0.75 mmol, 159.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether , volume ratio) to give the titled product **3an** as a **Colorless liquid** (70.0 mg, 56%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 - 7.97 (m, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.49 (t, *J* = 7.7 Hz, 2H), 3.12 (t, *J* = 7.4 Hz, 2H), 1.76 - 1.68 (m, 2H), 1.52 - 1.43 (m, 2H), 1.38 - 1.31 (m, 8H), 0.93 (t, *J* = 6.8 Hz, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.1, 137.3, 133.1, 128.5, 127.1, 31.8, 29.5, 29.1, 29.1, 29.0, 28.9, 22.6, 14.1.

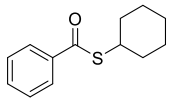


S-isopropyl benzothioate (**3ao**)[3]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), propane-2-sulfonyl chloride **2o** (0.75 mmol, 106.5 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether , volume ratio) to give the titled product **3ao** as a **Light yellow liquid** (61.2 mg, 68%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 - 7.93 (m, 2H), 7.58 - 7.52 (m, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 3.92 - 3.80 (m, 1H), 1.41 (d, *J* = 6.9 Hz, 6H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 192.0, 137.4, 133.1, 128.5 127.1, 34.9, 23.1.



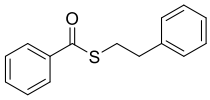
S-cyclohexyl benzothioate (**3ap**)[5]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three

times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), cyclohexanesulfonyl chloride **2p** (0.75 mmol, 136.5 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether, volume ratio) to give the titled product **3ap** as a **colorless liquid** (71.5 mg, 65%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 - 7.93 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 3.79 - 3.64 (m, 1H), 2.06 - 1.97 (m, 2H), 1.81 - 1.72 (m, 2H), 1.68 - 1.60 (m, 1H), 1.58 - 1.46 (m, 4H), 1.37 - 1.27 (m, 1H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.7, 137.4, 133.0, 128.4, 127.1, 42.5, 33.1, 26.0, 25.6.

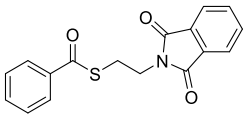


S-phenethyl benzothioate (**3aq**)[6]

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), 2-phenylethane-1-sulfonyl chloride **2q** (0.75 mmol, 153.0 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1, volume ratio) to give the titled product **3aq** as a **colorless liquid** (75.0 mg, 62%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.7 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 7.36 - 7.20 (m, 5H), 3.35 - 3.28 (m, 2H), 3.01 - 2.92 (m, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 191.8, 140.0, 137.1, 133.3, 128.6, 128.6, 128.5, 127.2, 126.5, 35.9, 30.4.



S-(2-(1,3-dioxoisoindolin-2-yl)ethyl) benzothioate (**3ar**)

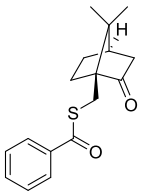
General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), 2-(1,3-dioxoisoindolin-2-yl)ethane-1-sulfonyl chloride **2r** (0.75 mmol, 204.7 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 30:1 to 20:1, volume ratio) to give the titled product **3ar** as a **white solid** (77.8 mg, 50%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 - 7.90 (m, 2H), 7.88 - 7.83 (m, 2H), 7.74 - 7.69 (m, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.7 Hz, 2H), 4.02 (t, *J* = 6.6 Hz, 2H), 3.41 (t, *J* = 6.6 Hz, 2H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 190.9, 168.0, 136.7, 134.0, 133.5, 132.0, 128.6, 127.3, 123.4, 37.2, 27.5.

M.p. 113.3 - 115.5 °C

HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{17}H_{14}NO_3S^+$, 312.0689; found, 312.0692.



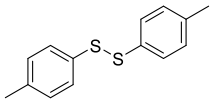
S-(((1S,4R)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methyl) benzothioate (**3as**)

General Procedure was followed with $Ni(OTf)_2$ (20 mol%, 35.7 mg), dtbbpy (20 mol%, 26.8 mg), ZnI_2 (40 mol%, 63.8 mg), $Mo(CO)_6$ (0.5 mmol, 132.0 mg), K_2CO_3 (0.75 mmol, 103.7 mg) were added to an oven-dried tube (15 mL), which was then placed under vacuum and refilled with nitrogen for three times. Phenylboronic acid **1a** (0.5 mmol, 61.0 mg), ((1S,4R)-7,7-dimethyl-2-oxobicyclo[2.2.1]heptan-1-yl)methanesulfonyl chloride **2s** (0.75 mmol, 187.5 mg), H_2O (50 mol%, 4.5 mg), and NMP (2 mL) were added into the tube via syringe. Upon completion the mixture was concentrated and purified via flash column chromatography (petroleum ether / ethyl acetate = 100:1, volume ratio) to give the titled product **3as** as a **colorless viscous liquid** (108.0 mg, 75%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 - 7.95 (m, 2H), 7.58 - 7.51 (m, 1H), 7.43 (t, *J* = 7.7 Hz, 2H), 3.38 (d, *J* = 13.8 Hz, 1H), 3.13 (d, *J* = 13.8 Hz, 1H), 2.45 - 2.36 (m, 1H), 2.11 (t, *J* = 4.4 Hz, 1H), 2.04 - 1.94 (m, 1H), 1.93 - 1.85 (m, 2H), 1.61 - 1.52 (m, 1H), 1.41 - 1.31 (m, 1H), 1.11 (s, 3H), 0.95 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 217.2, 192.2, 137.0, 133.2, 128.5, 127.2, 60.7, 47.9, 43.7, 43.0, 26.7, 26.6, 24.9, 20.1, 19.7.

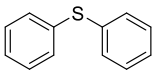
HRMS (ESI-TOF): $[M+H]^+$ calcd. for $C_{17}H_{21}O_2S^+$, 289.1257; found, 289.1269.



1,2-di-*p*-tolyldisulfane(**4a**)[9]

General Procedure was followed with **3 (a)** and **3 (b)**.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 (d, *J* = 8.2 Hz, 2H), 7.11 (d, *J* = 8.1 Hz, 2H), 2.32 (s, 6H).



Diphenyl sulfide(**6a**)[10]

General Procedure was followed with **3 (d)**.

GC-MS (EI, 70eV): m/z(%)= 186 (M+,100), 185 (80), 184 (40), 171 (10), 152 (10), 77 (10), 65 (10), 51 (15).

5. References

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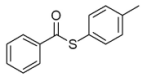
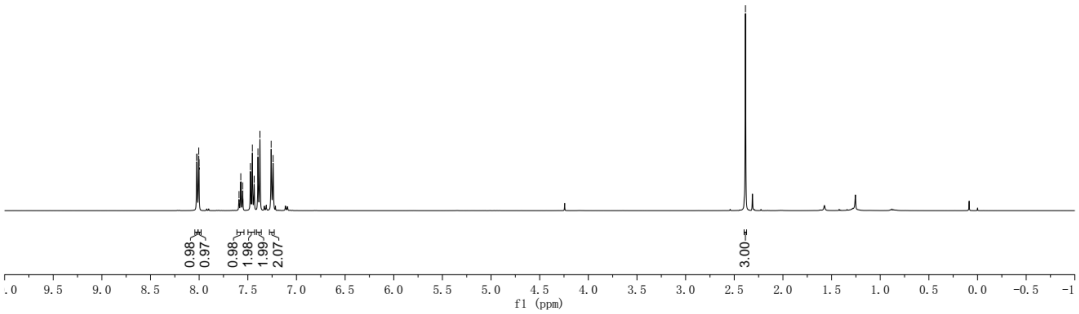
6. Copy of ^{1}H and ^{13}C NMR Spectra of product

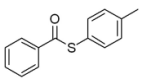
^{1}H NMR 400 MHz, $CDCl_3$



3aa



^{13}C NMR 101 MHz, $CDCl_3$



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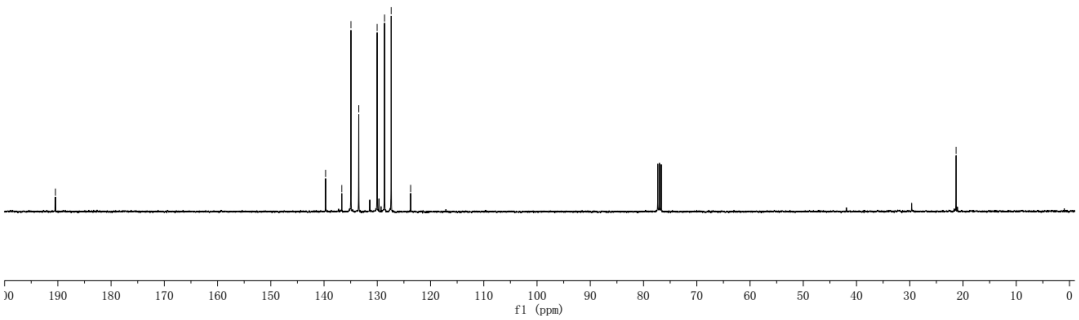
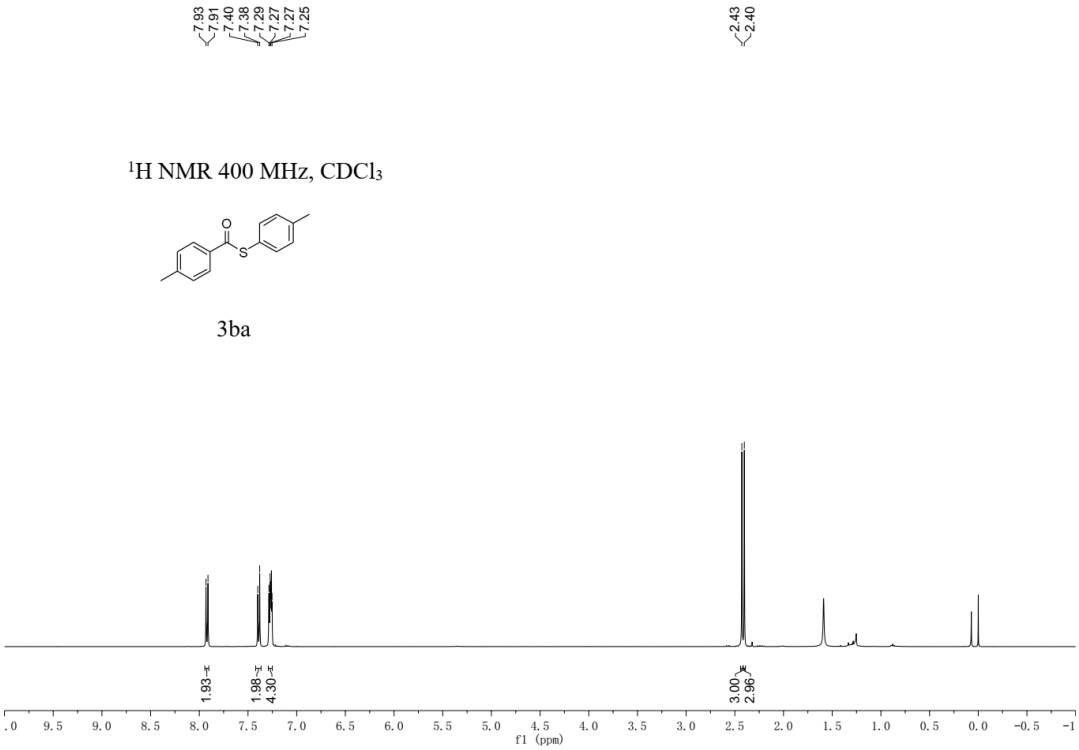
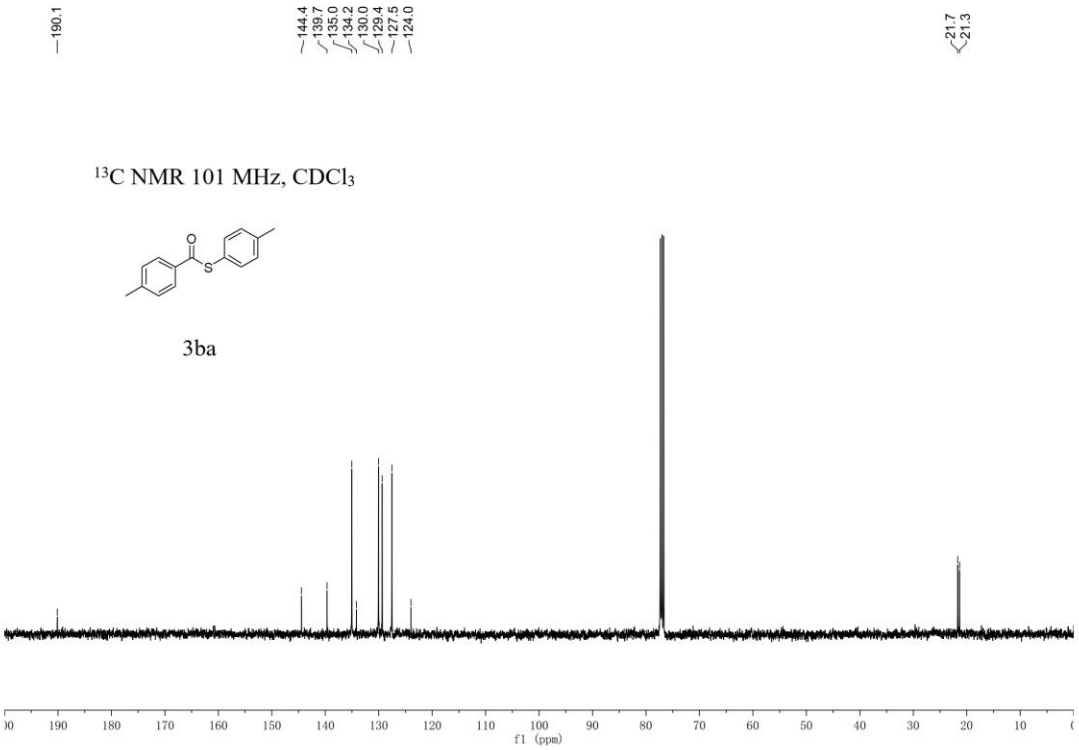
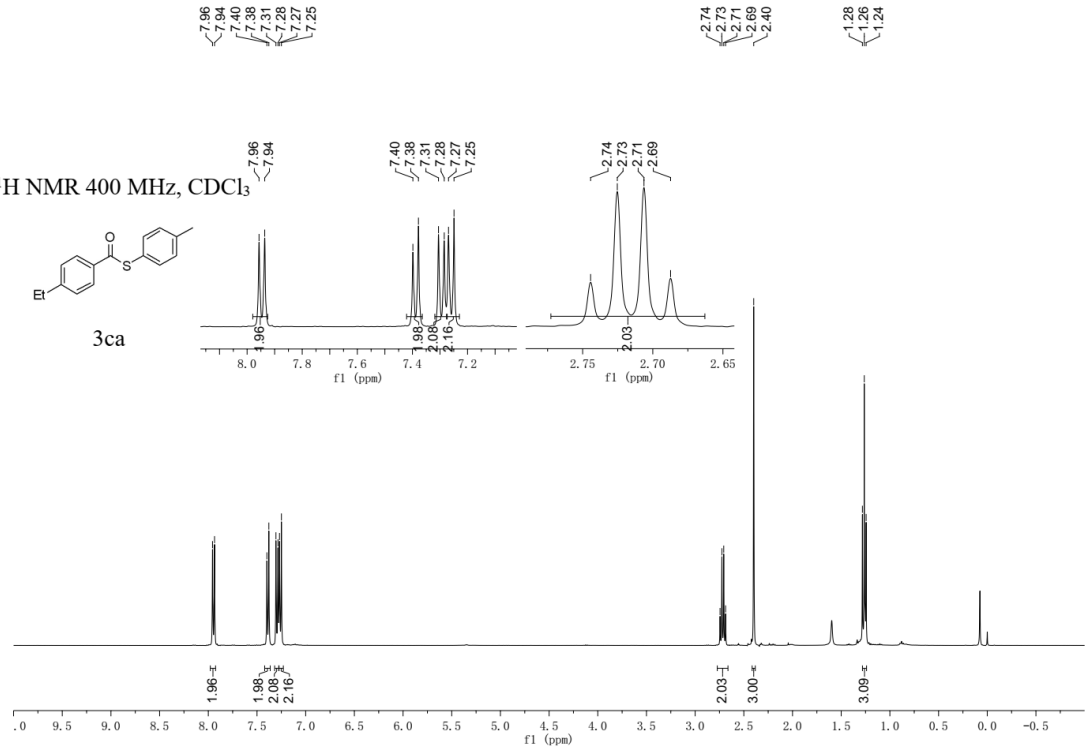


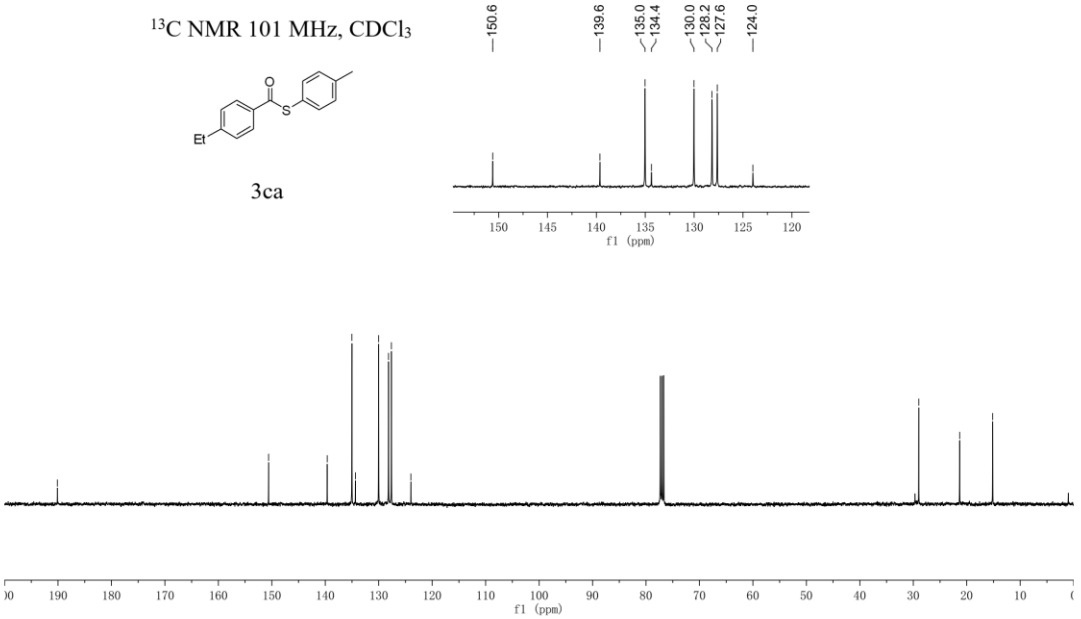

7.93
7.91
7.40
7.38
7.29
7.27
7.27
7.25
2.43
2.40
1H NMR 400 MHz, CDCl3
3ba
1.93
1.98
4.30
3.00
2.96
f1 (ppm)


190.1
144.4
139.7
135.0
134.2
130.0
129.4
127.5
124.0
21.7
21.3
13C NMR 101 MHz, CDCl3
3ba
f1 (ppm)

^{1}H NMR 400 MHz, $CDCl_3$



^{13}C NMR 101 MHz, $CDCl_3$



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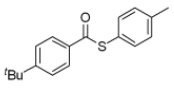
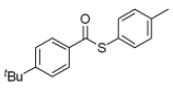
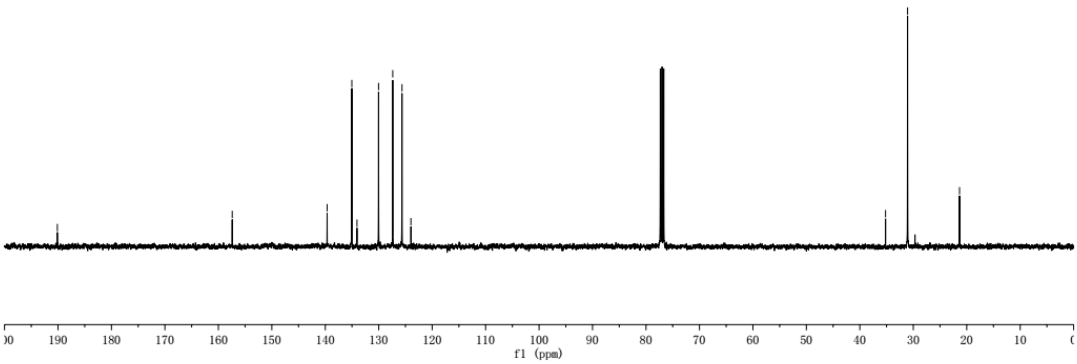


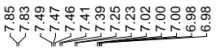
3da

^{13}C NMR 101 MHz, $CDCl_3$

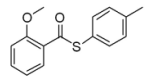


3da

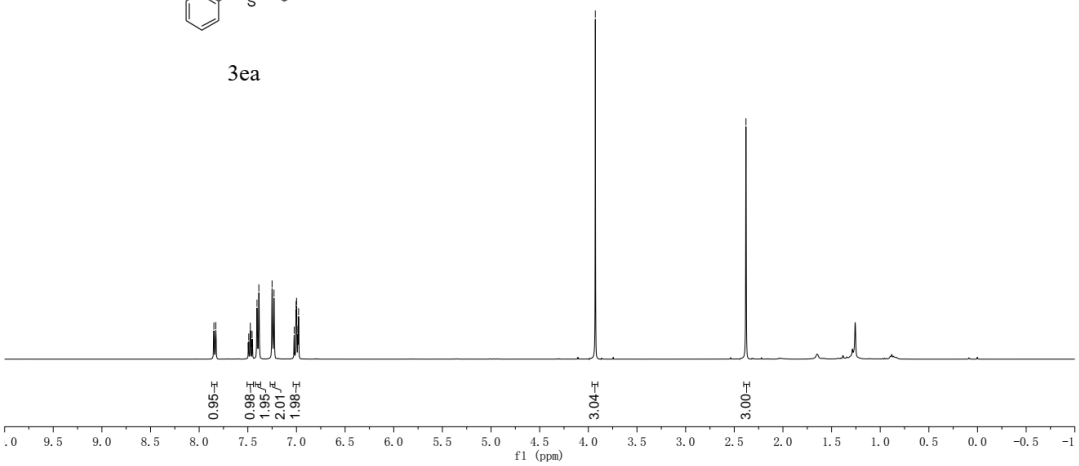


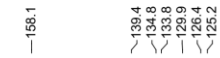


^{1}H NMR 400 MHz, $CDCl_3$

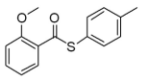


3ea

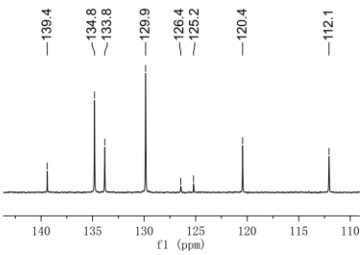


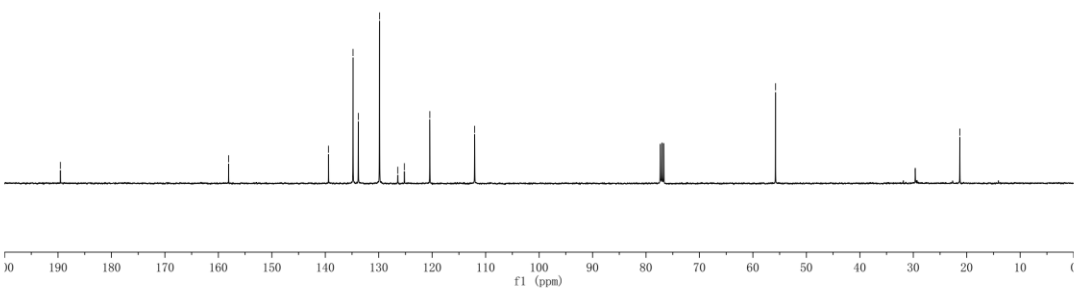


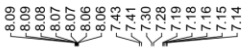
^{13}C NMR 101 MHz, $CDCl_3$



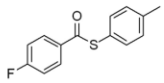
3ea







^{1}H NMR 400 MHz, $CDCl_3$



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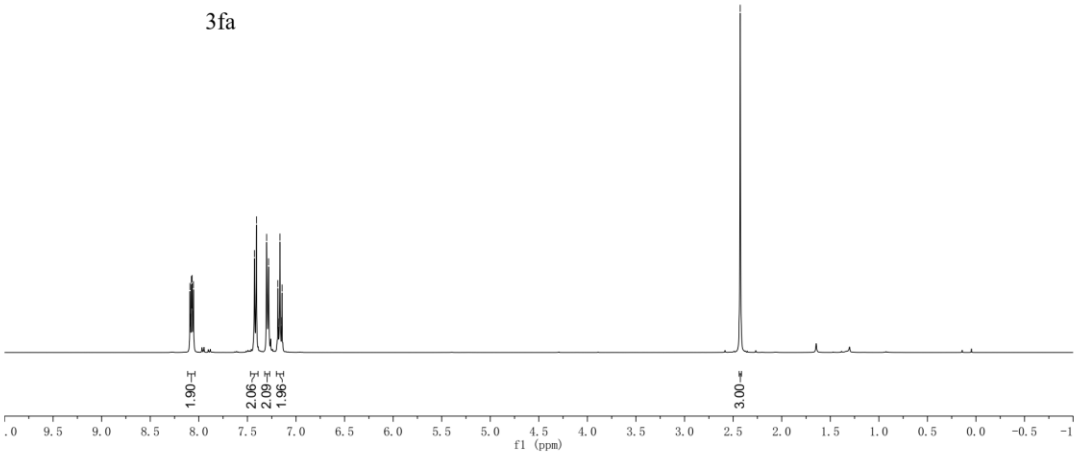
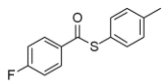


^{13}C NMR 101 MHz, $CDCl_3$



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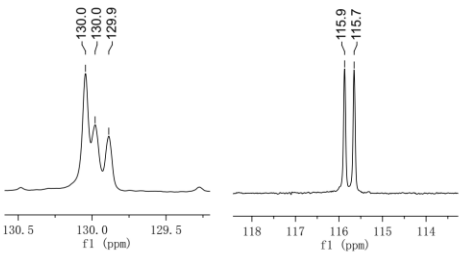
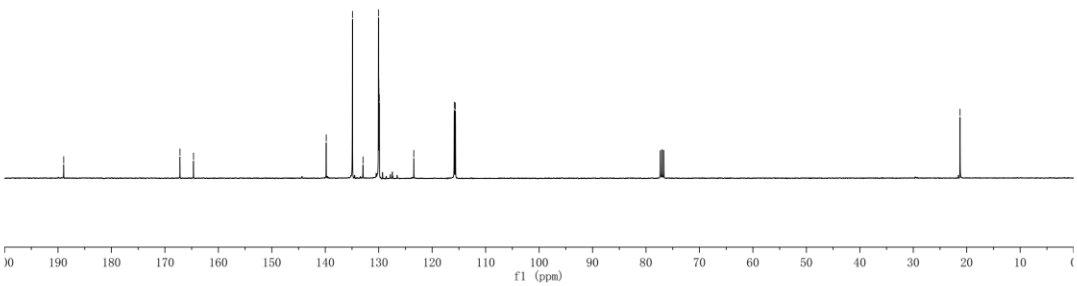
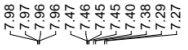
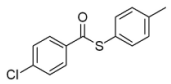






^{1}H NMR 400 MHz, $CDCl_3$



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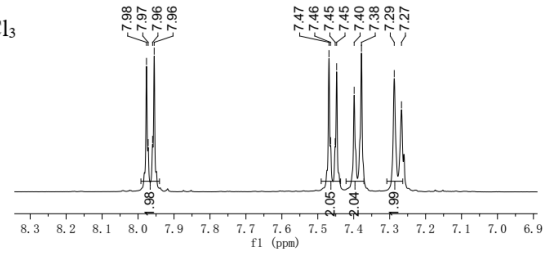
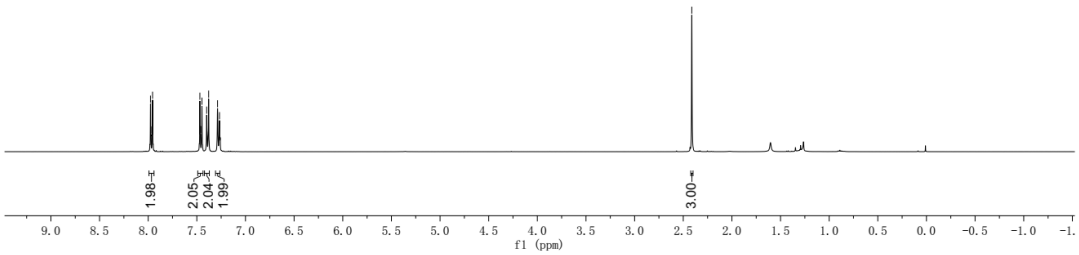
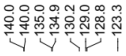
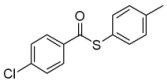






^{13}C NMR 101 MHz, $CDCl_3$



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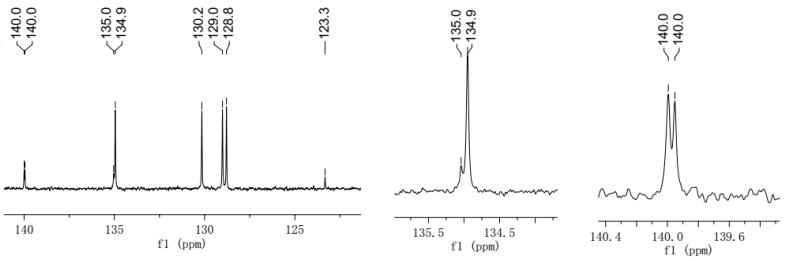
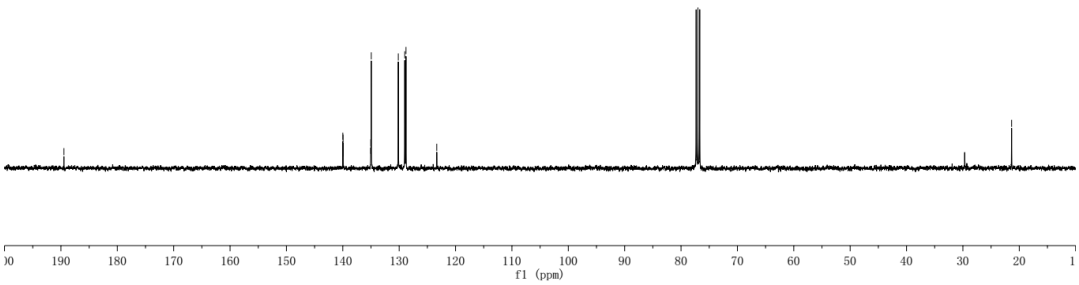
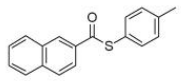


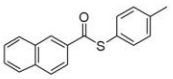


^{1}H NMR 400 MHz, $CDCl_3$



3ha

^{13}C NMR 101 MHz, $CDCl_3$



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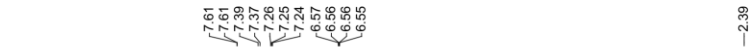
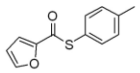
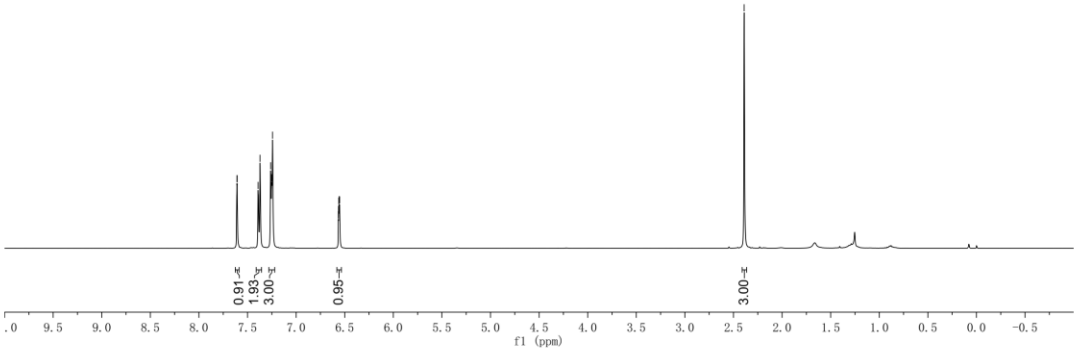
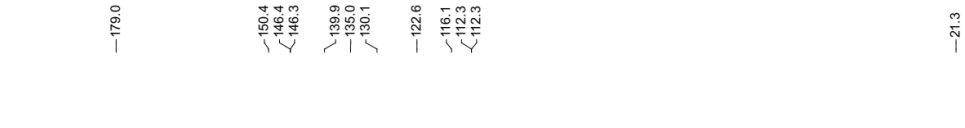


^{1}H NMR 400 MHz, $CDCl_3$

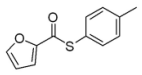


3ia





^{13}C NMR 101 MHz, $CDCl_3$



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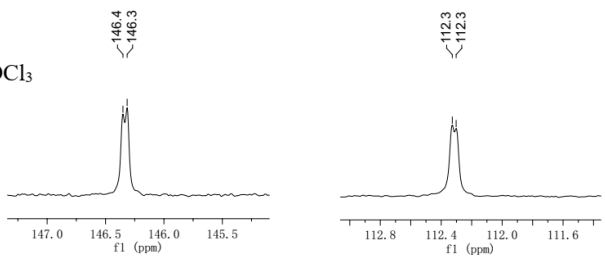
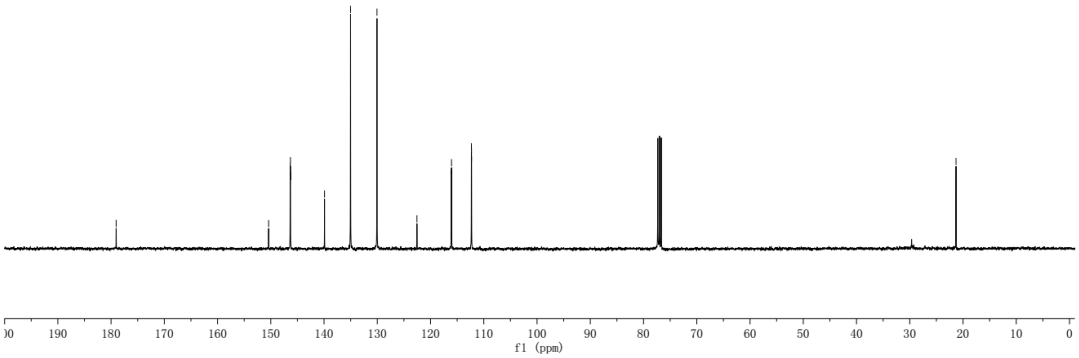
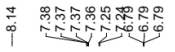
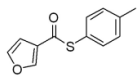






^{1}H NMR 400 MHz, $CDCl_3$



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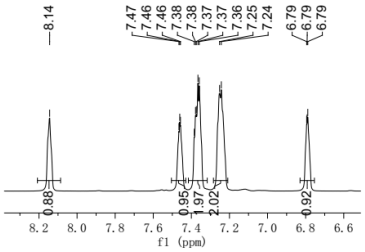
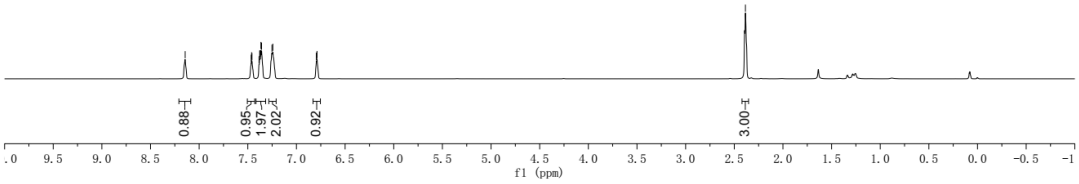
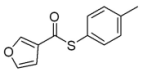




^{13}C NMR 101 MHz, $CDCl_3$



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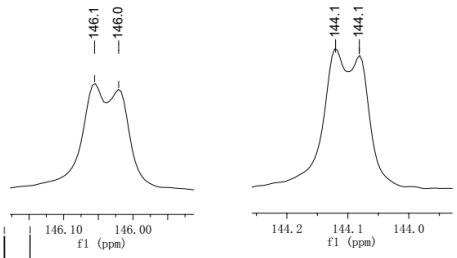
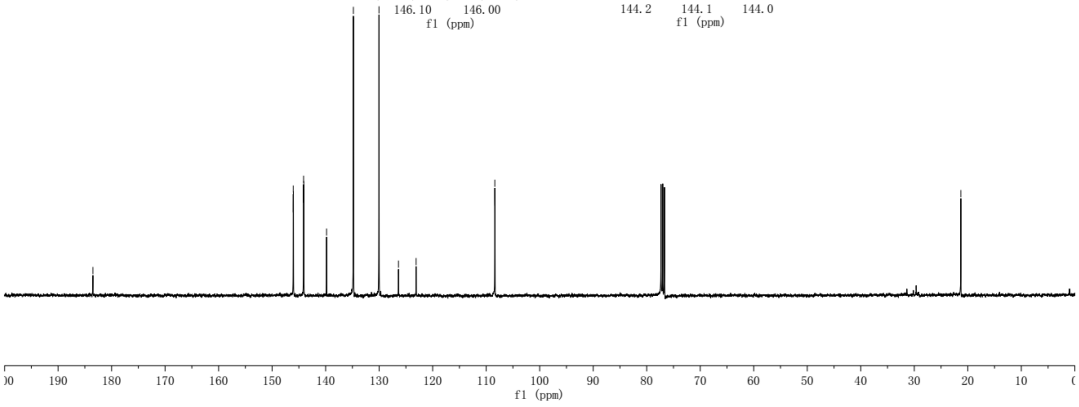
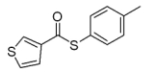




^{1}H NMR 400 MHz, $CDCl_3$



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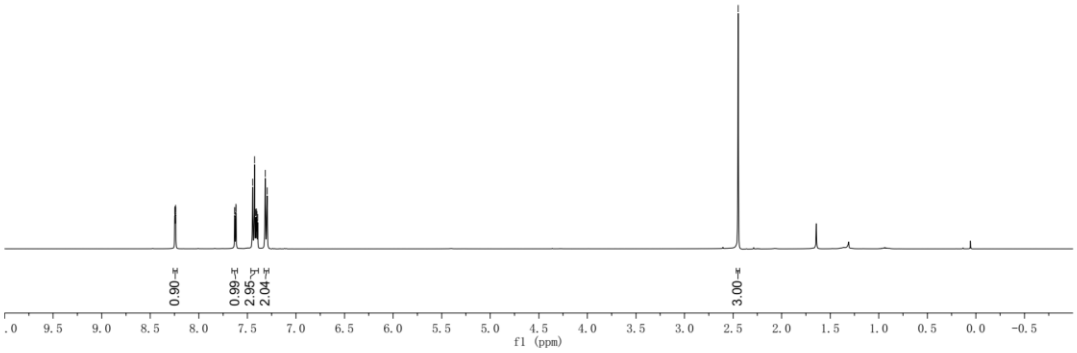
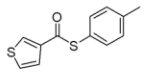


^{13}C NMR 101 MHz, $CDCl_3$



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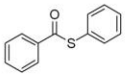
^{1}H NMR 400 MHz, $CDCl_3$



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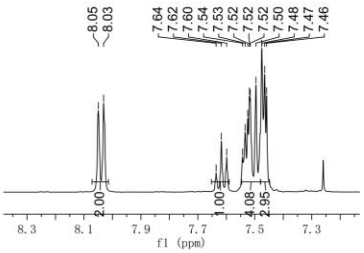
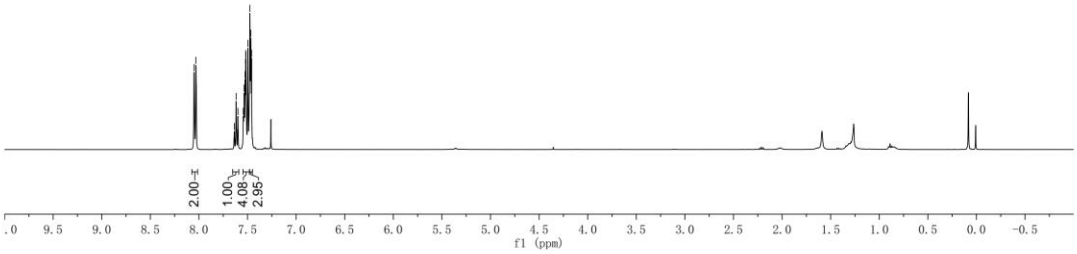
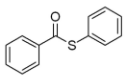




^{13}C NMR 101 MHz, $CDCl_3$



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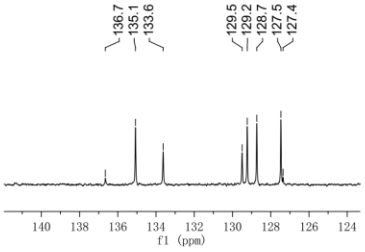

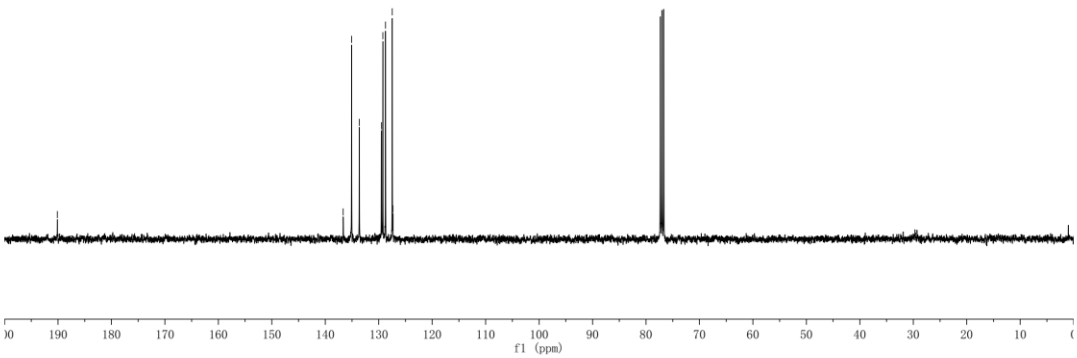

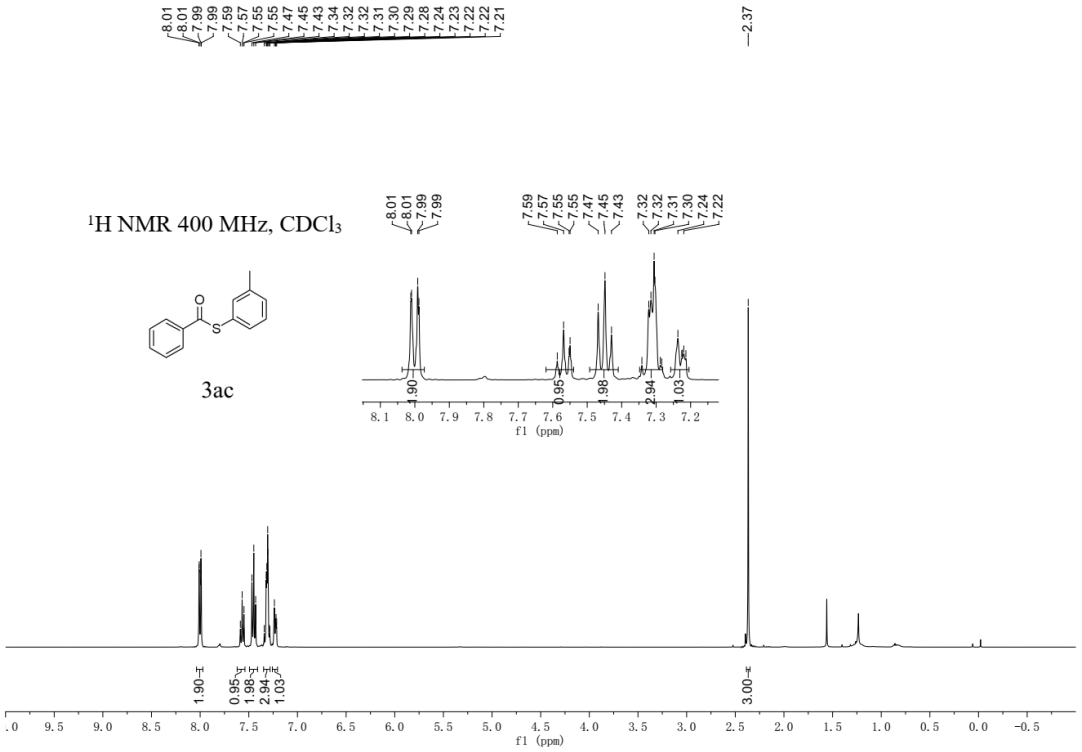
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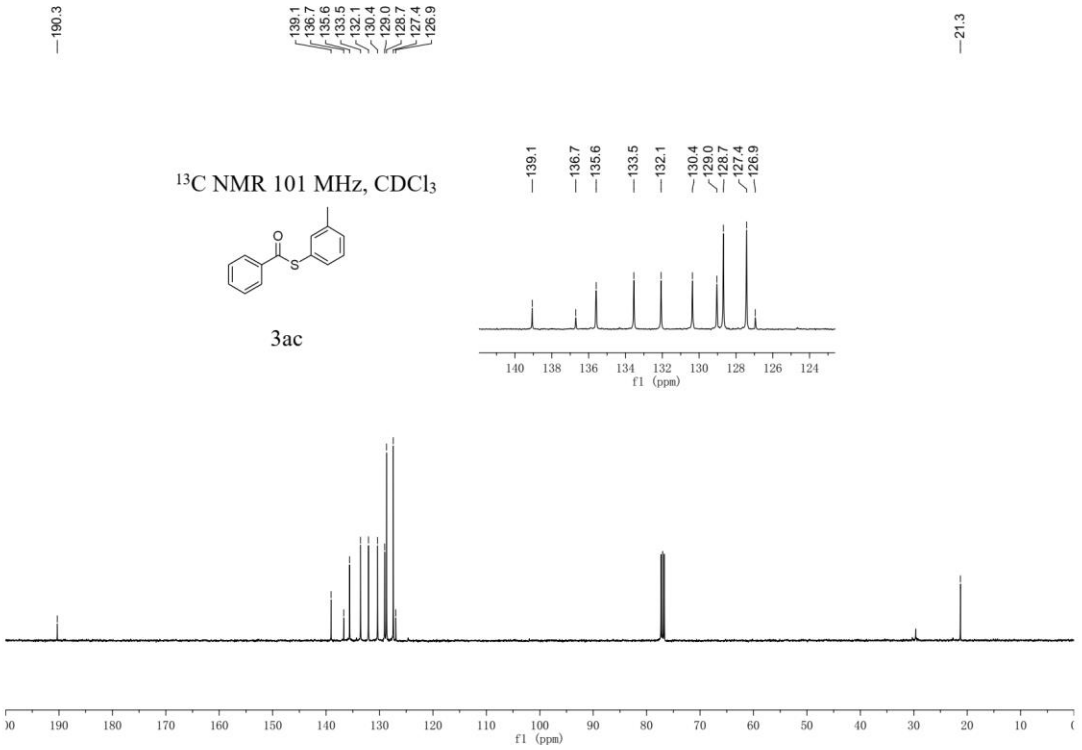
8.01
7.99
7.99
7.59
7.57
7.55
7.55
7.47
7.45
7.43
7.34
7.32
7.31
7.30
7.29
7.28
7.24
7.23
7.22
7.22
7.21
2.37
1H NMR 400 MHz, CDCl3
3ac
1.90
0.95
1.98
2.94
1.03
3.00
f1 (ppm)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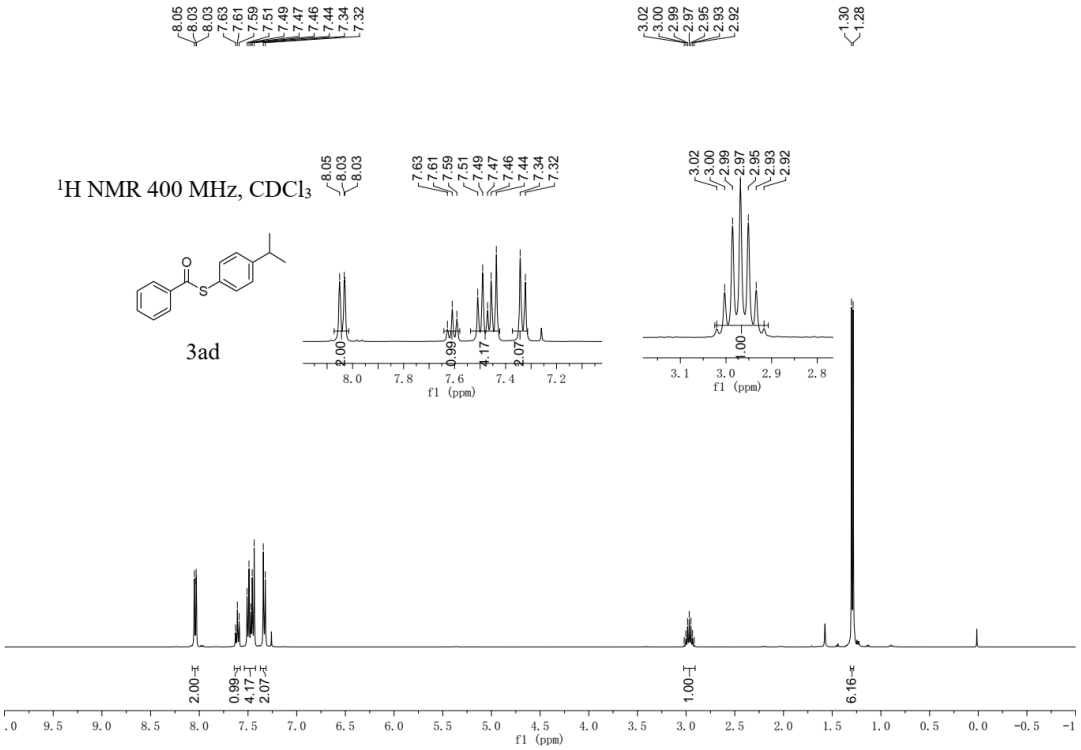
139.1
136.7
135.6
133.5
132.1
130.4
129.0
128.7
127.4
126.9
21.3
13C NMR 101 MHz, CDCl3
3ac
f1 (ppm)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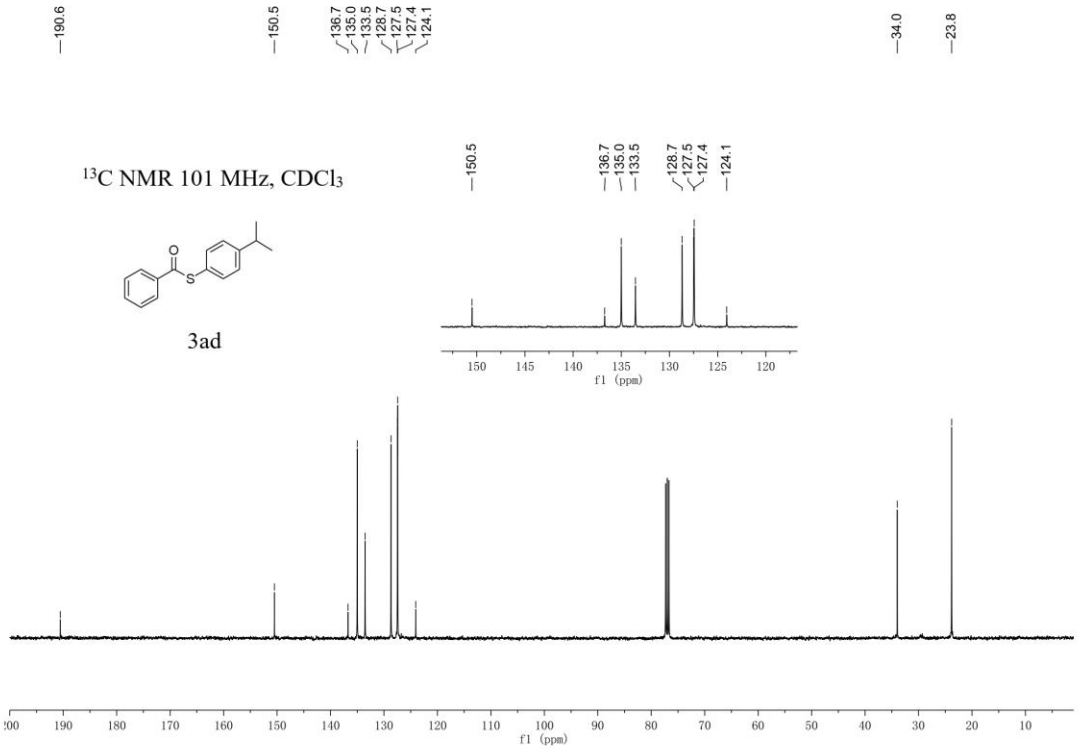
8.03
8.03
7.63
7.61
7.59
7.51
7.49
7.47
7.46
7.44
7.34
7.32
3.02
3.00
2.99
2.97
2.95
2.93
2.92
1.30
1.28
1H NMR 400 MHz, CDCl3
3ad
2.00
0.99
4.17
2.07
1.00
6.16
f1 (ppm)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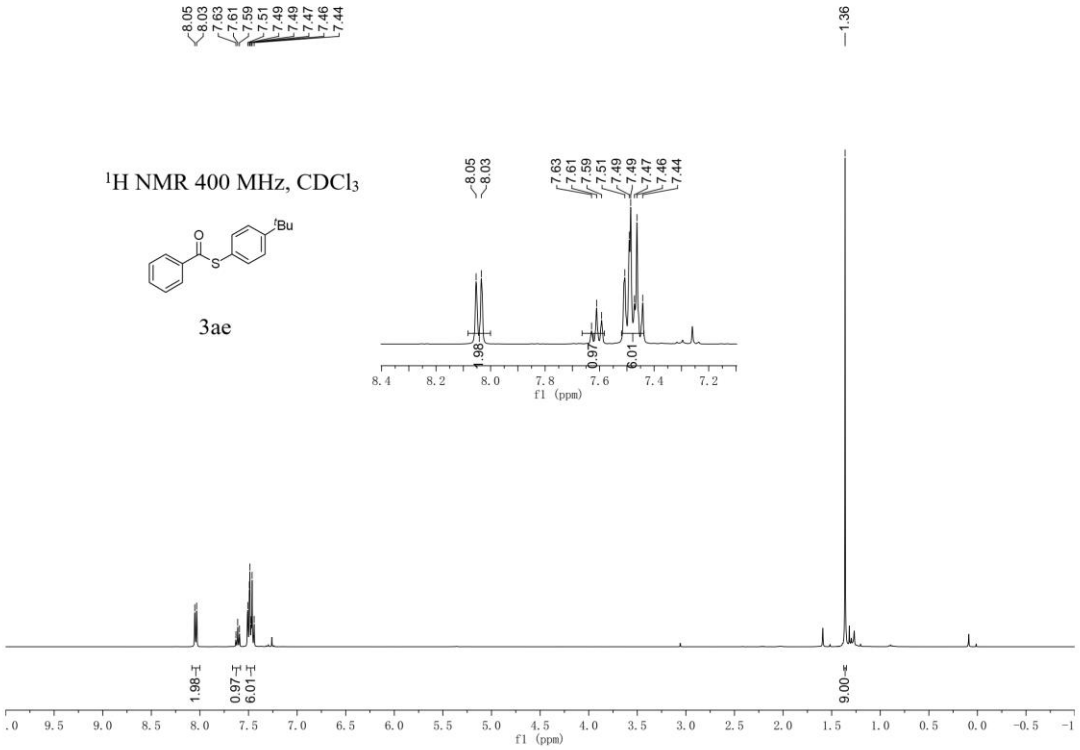
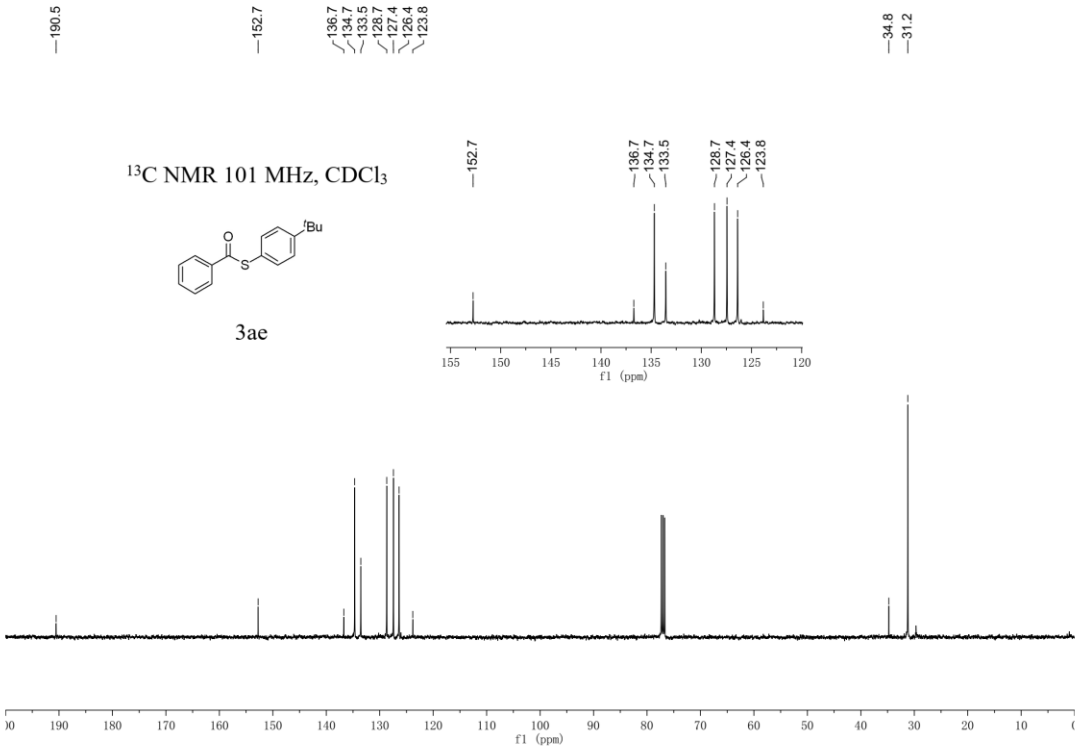
150.5
136.7
135.0
133.5
128.7
127.5
127.4
124.1
34.0
23.8
13C NMR 101 MHz, CDCl3
3ad
f1 (ppm)


8.05
8.03
7.63
7.61
7.59
7.51
7.49
7.49
7.47
7.46
7.44
1.36
^{1}H NMR 400 MHz, CDCl$_3$
tBu
O
S
3ae
1.98
0.97
6.01
9.00
f1 (ppm)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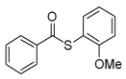
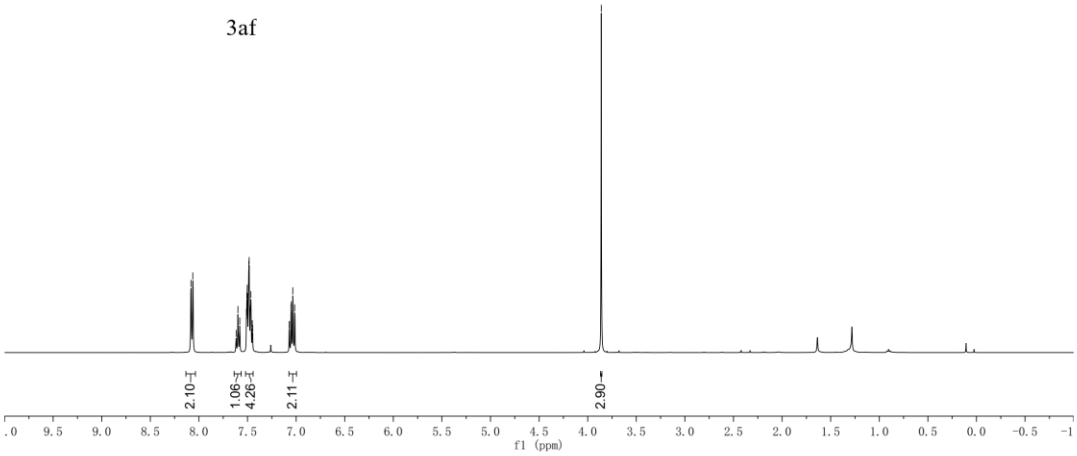
152.7
136.7
134.7
133.5
128.7
127.4
126.4
123.8
34.8
31.2
^{13}C NMR 101 MHz, CDCl$_3$
tBu
O
S
3ae
f1 (ppm)

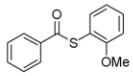
^{1}H NMR 400 MHz, $CDCl_3$



3af



^{13}C NMR 101 MHz, $CDCl_3$



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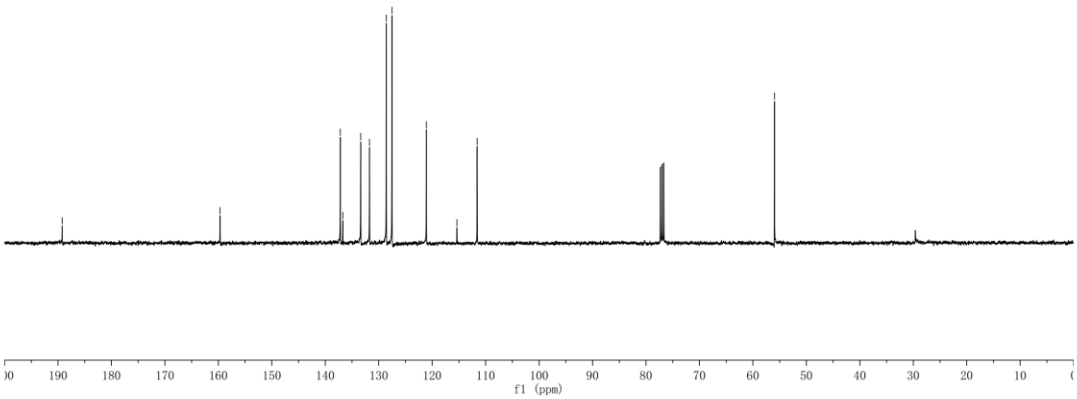
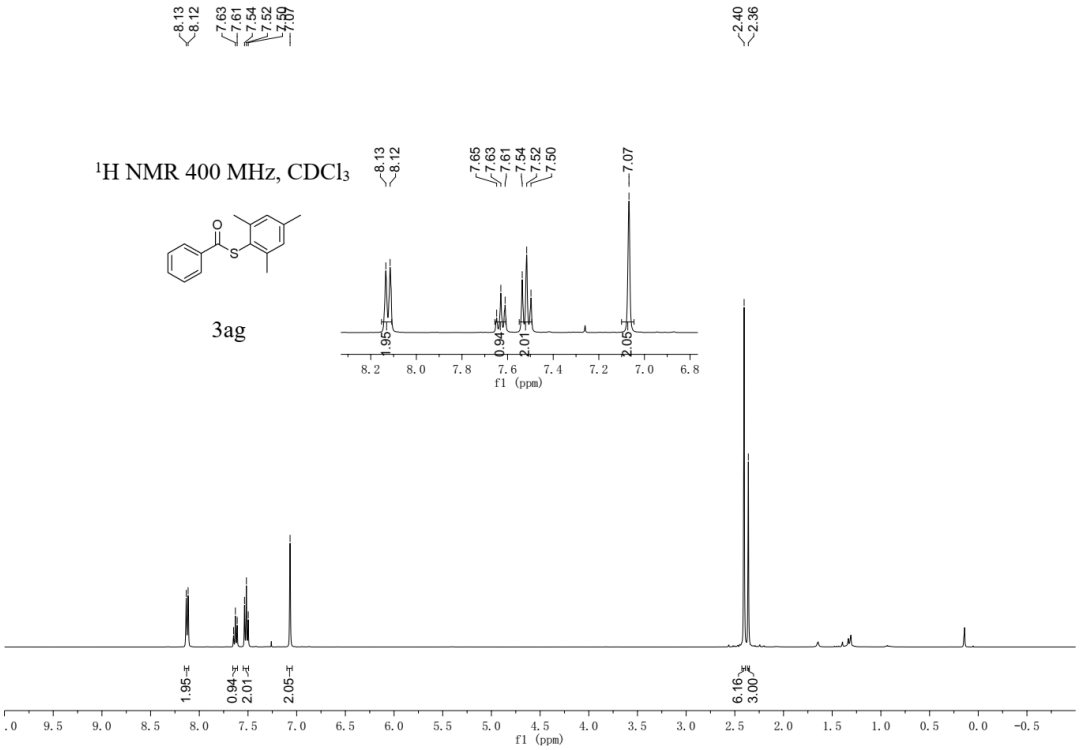
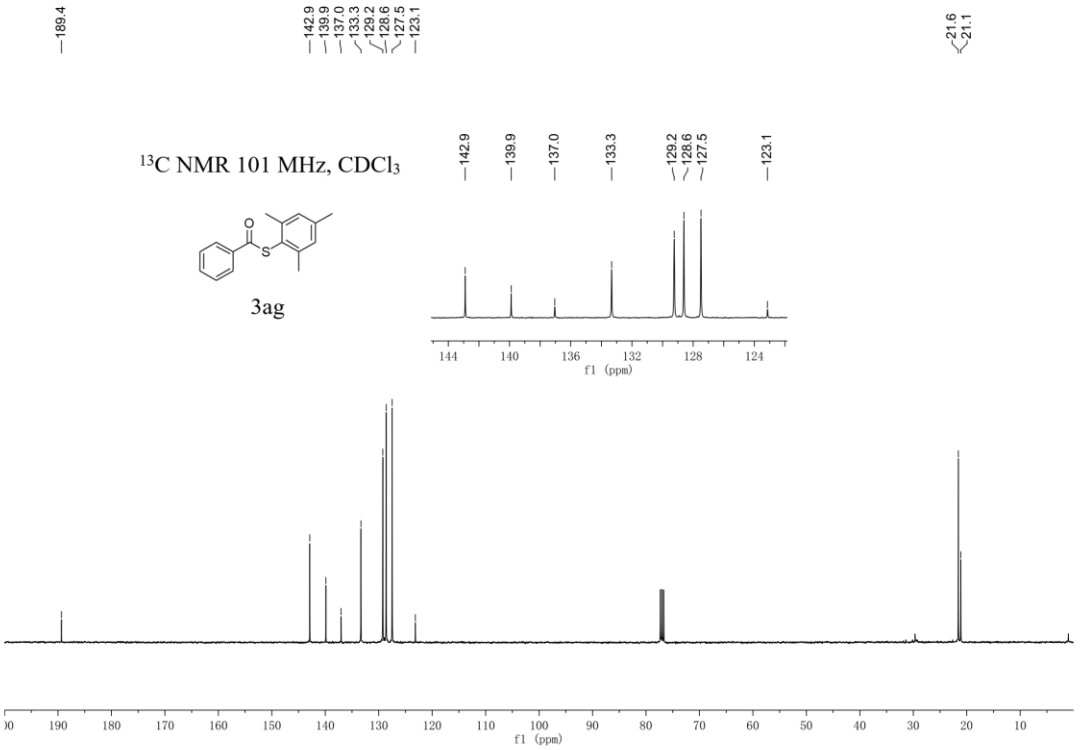
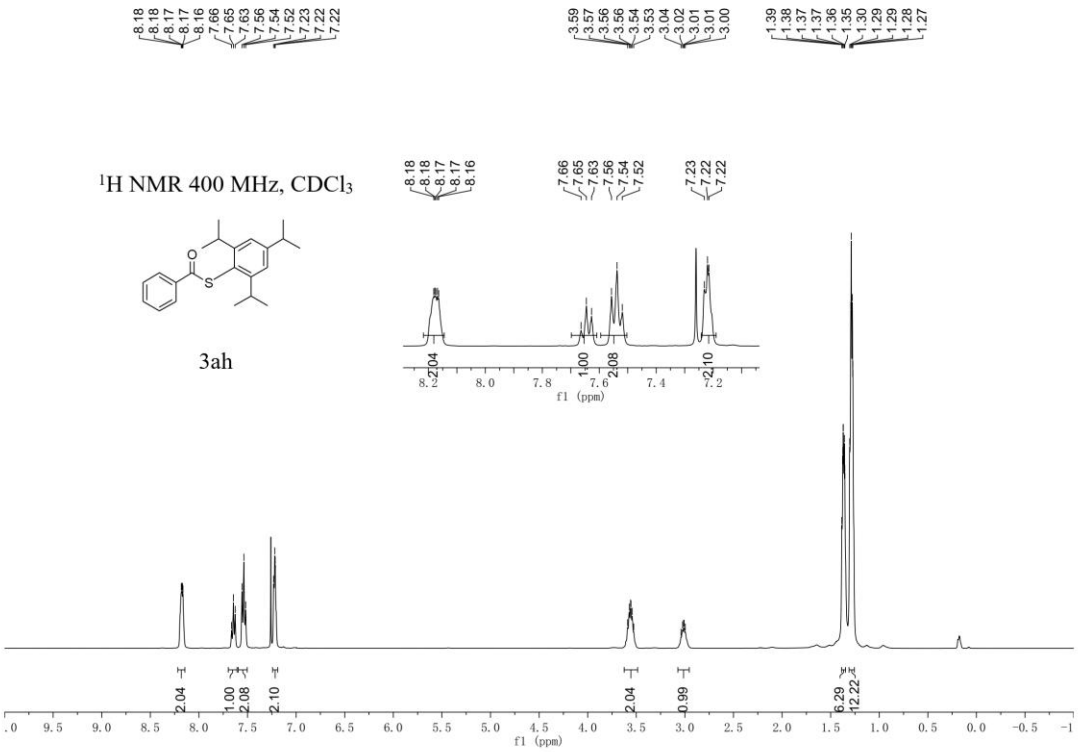



8.13
8.12
7.63
7.61
7.54
7.52
7.50
7.07
2.40
2.36
1H NMR 400 MHz, CDCl3
3ag
1.95
0.94
2.01
2.05
6.16
3.00
f1 (ppm)


189.4
142.9
139.9
137.0
133.3
129.2
128.6
127.5
123.1
21.6
21.1
13C NMR 101 MHz, CDCl3
3ag
f1 (ppm)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7.22
3.59
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3.56
3.54
3.53
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3.02
3.01
3.01
3.00
1.39
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1.36
1.35
1.30
1.29
1.29
1.28
1.27
1H NMR 400 MHz, CDCl3
3ah
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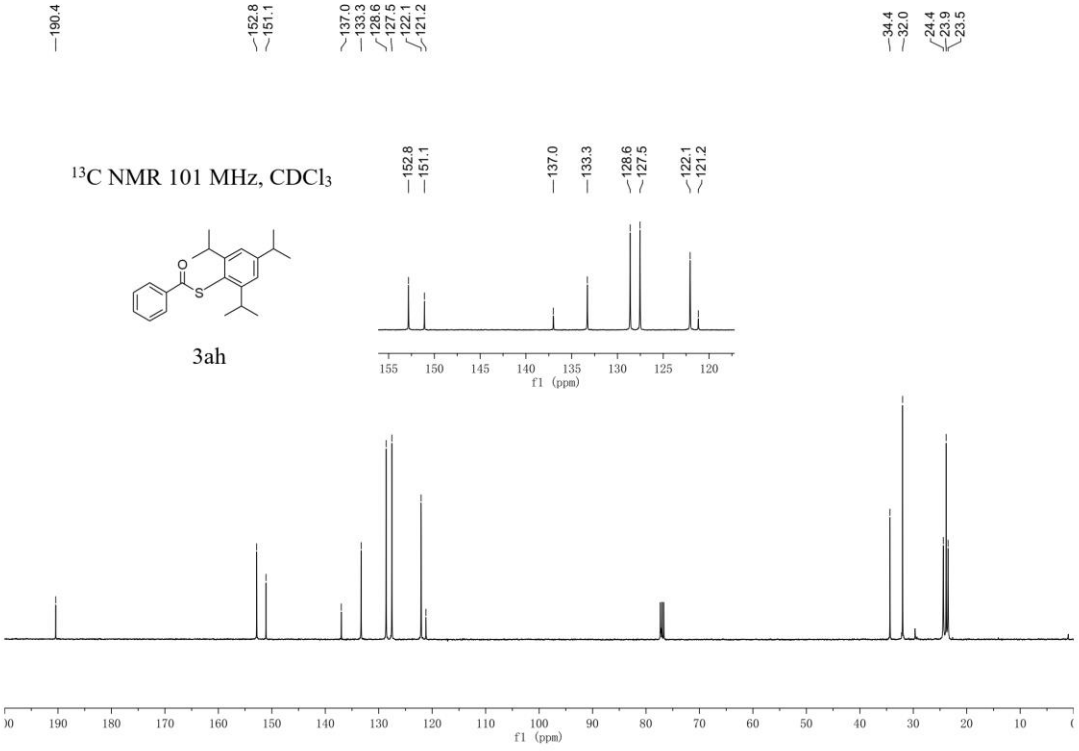
1.00
2.08
2.10
2.04
0.99
6.29
12.22
f1 (ppm)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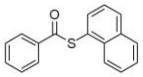
151.1
137.0
133.3
128.6
127.5
122.1
121.2
34.4
32.0
24.4
23.9
23.5
13C NMR 101 MHz, CDCl3
3ah
f1 (ppm)

^{1}H NMR 400 MHz, $CDCl_3$



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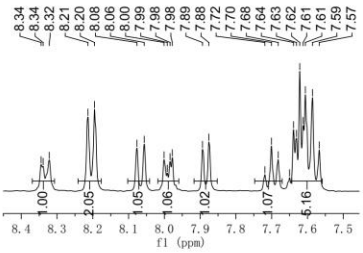
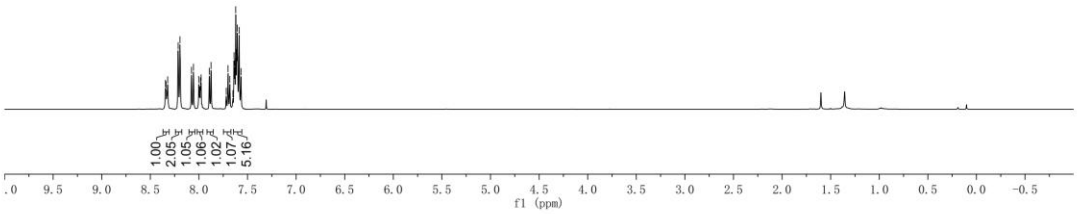
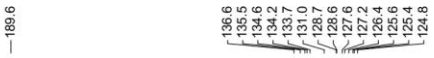
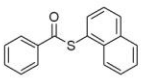






^{13}C NMR 101 MHz, $CDCl_3$



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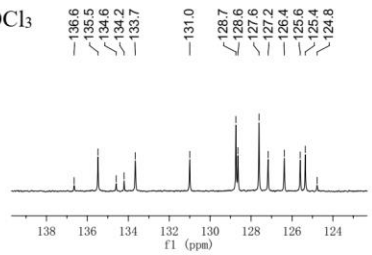
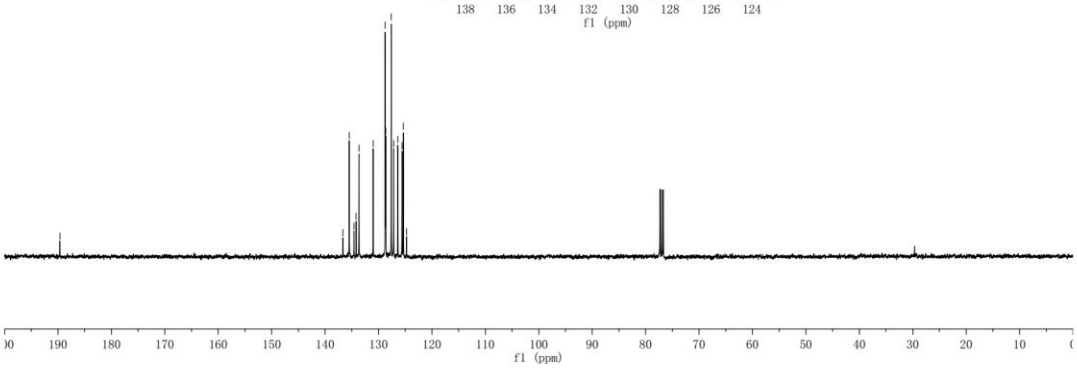
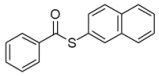




^{1}H NMR 400 MHz, $CDCl_3$



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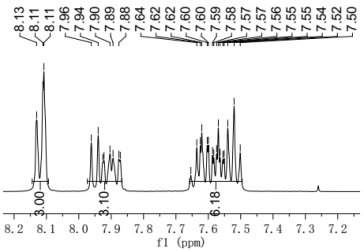
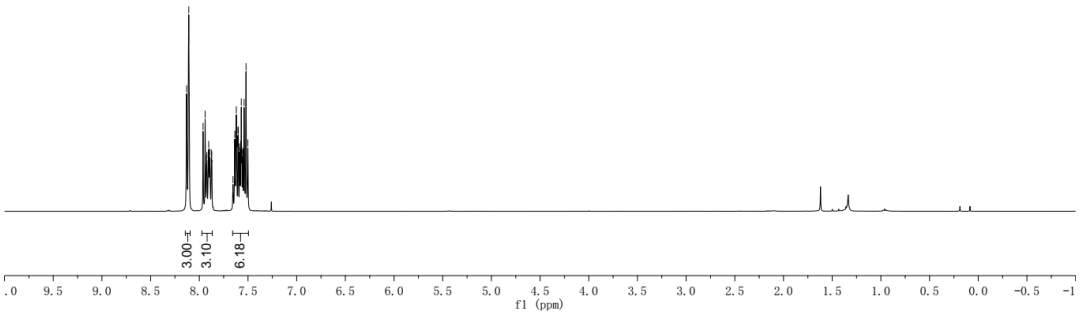
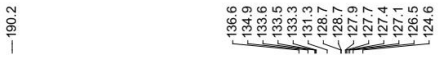
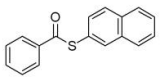






^{13}C NMR 101 MHz, $CDCl_3$



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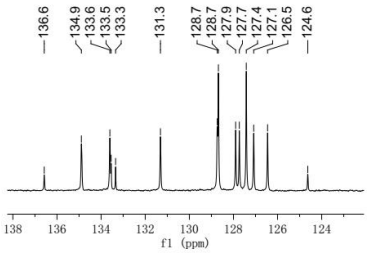
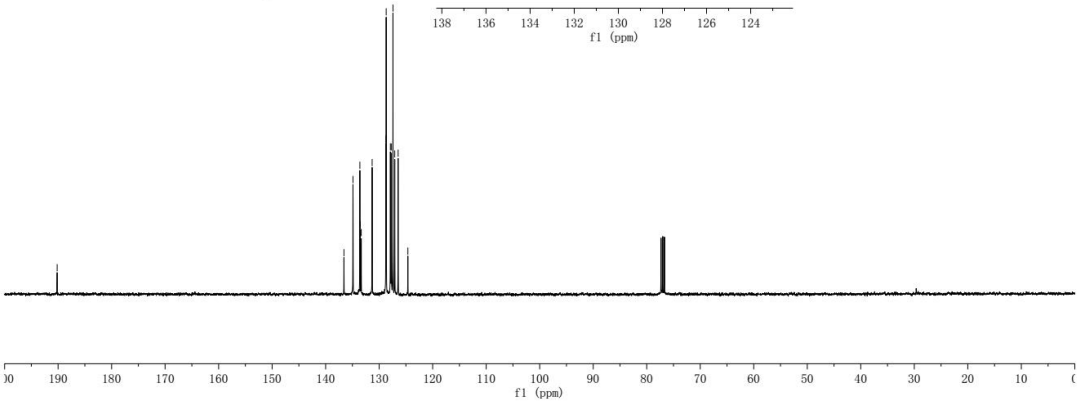
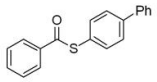




^{1}H NMR 400 MHz, $CDCl_3$



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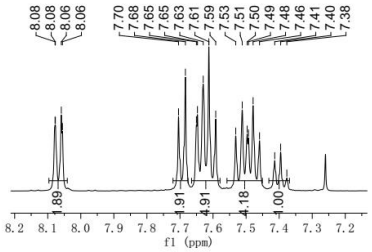
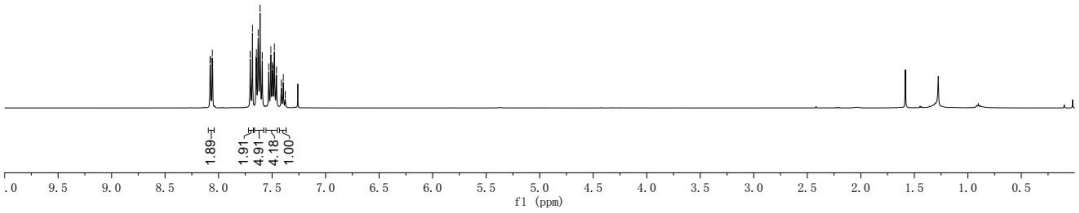
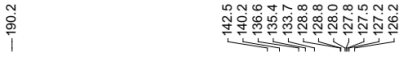
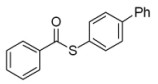






^{13}C NMR 101 MHz, $CDCl_3$



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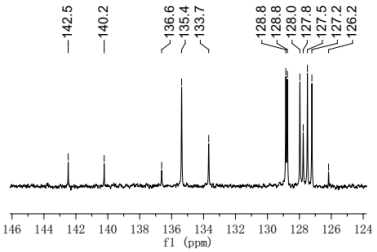
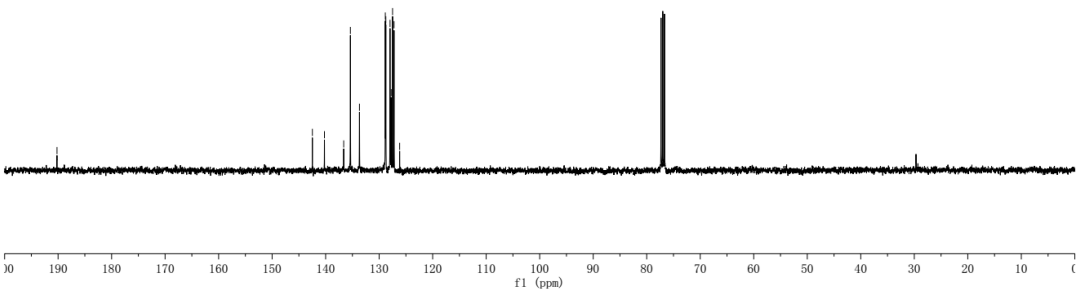
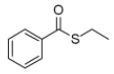




^{1}H NMR 400 MHz, $CDCl_3$



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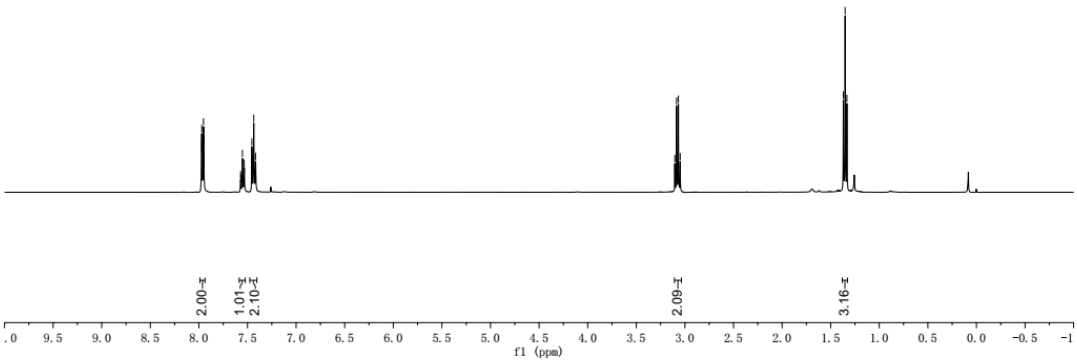
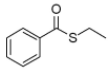


^{13}C NMR 101 MHz, $CDCl_3$



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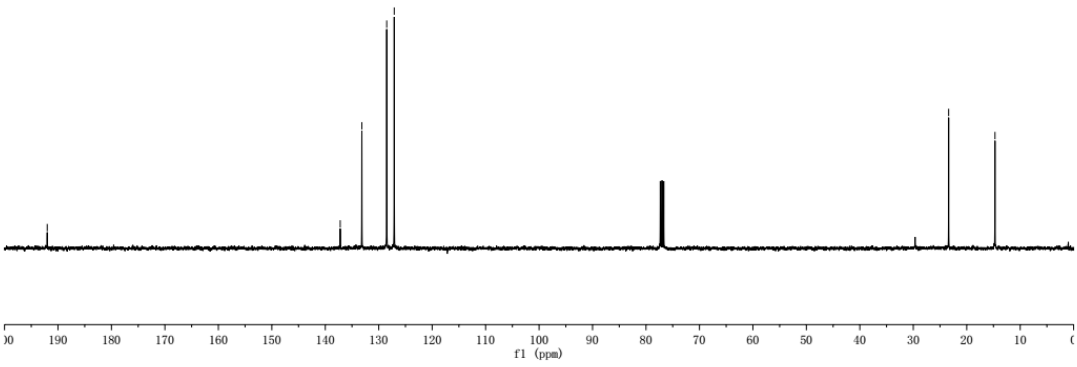

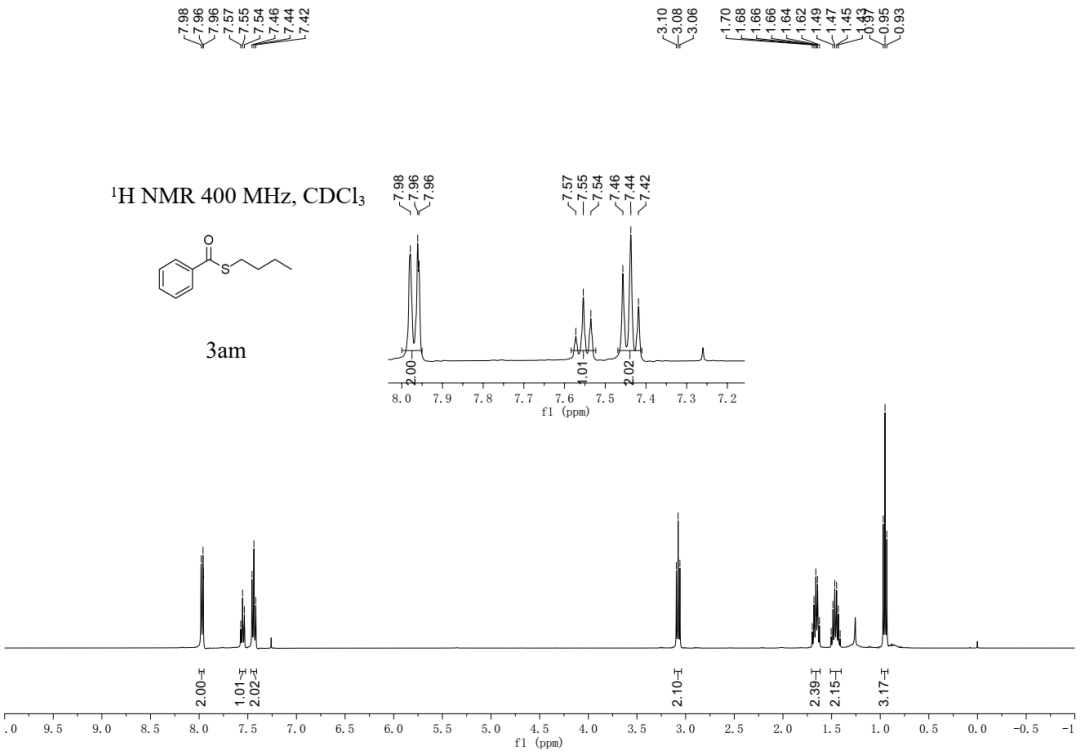
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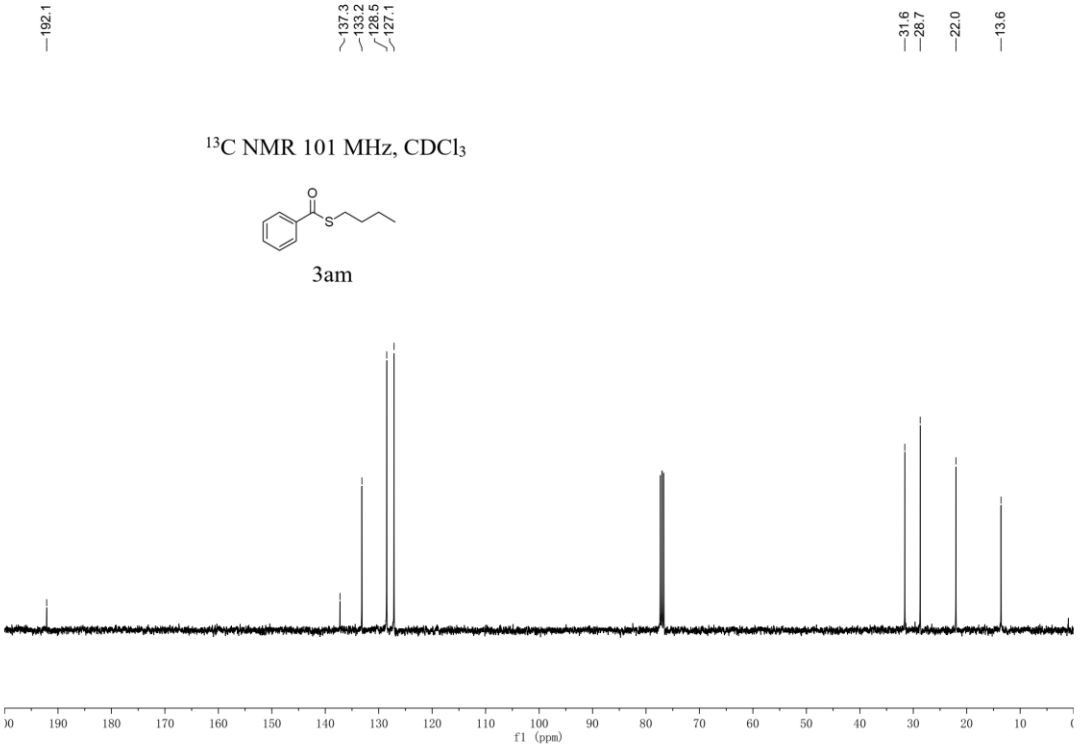
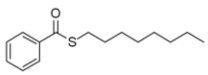
1.70
1.68
1.66
1.66
1.64
1.62
1.49
1.47
1.45
0.97
0.95
0.93
1H NMR 400 MHz, CDCl3
3am
2.00
1.01
2.02
2.10
2.39
2.15
3.17
f1 (ppm)


192.1
137.3
133.2
128.5
127.1
31.6
28.7
22.0
13.6
13C NMR 101 MHz, CDCl3
3am
f1 (ppm)

^{1}H NMR 400 MHz, $CDCl_3$



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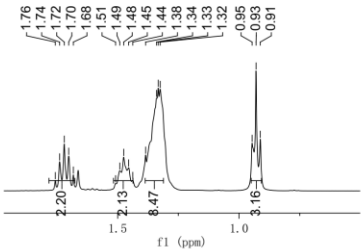
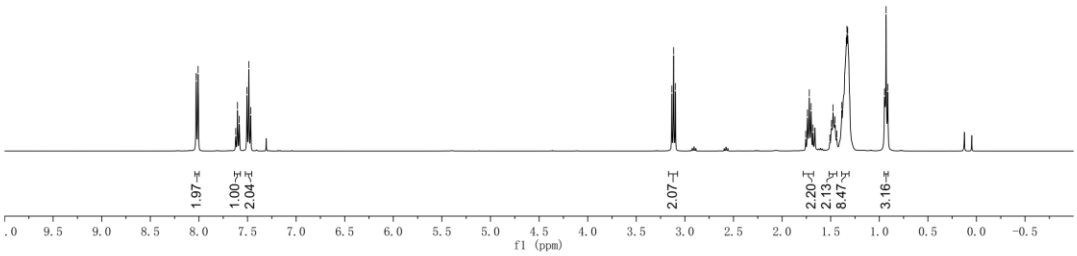
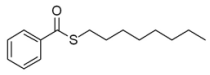




^{13}C NMR 101 MHz, $CDCl_3$



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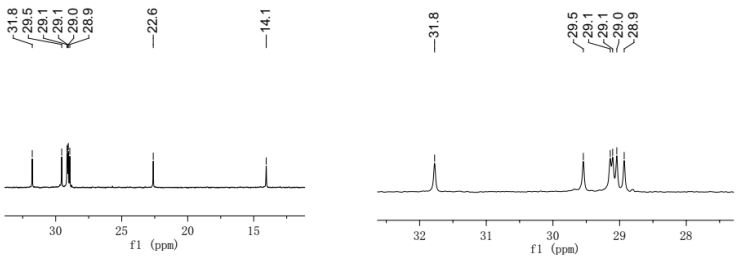

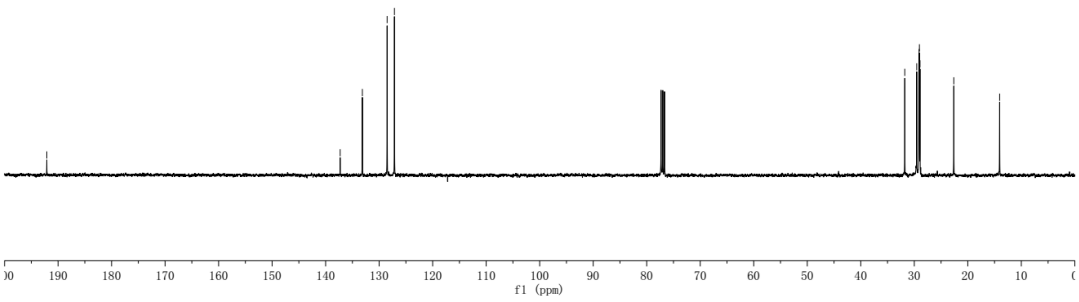

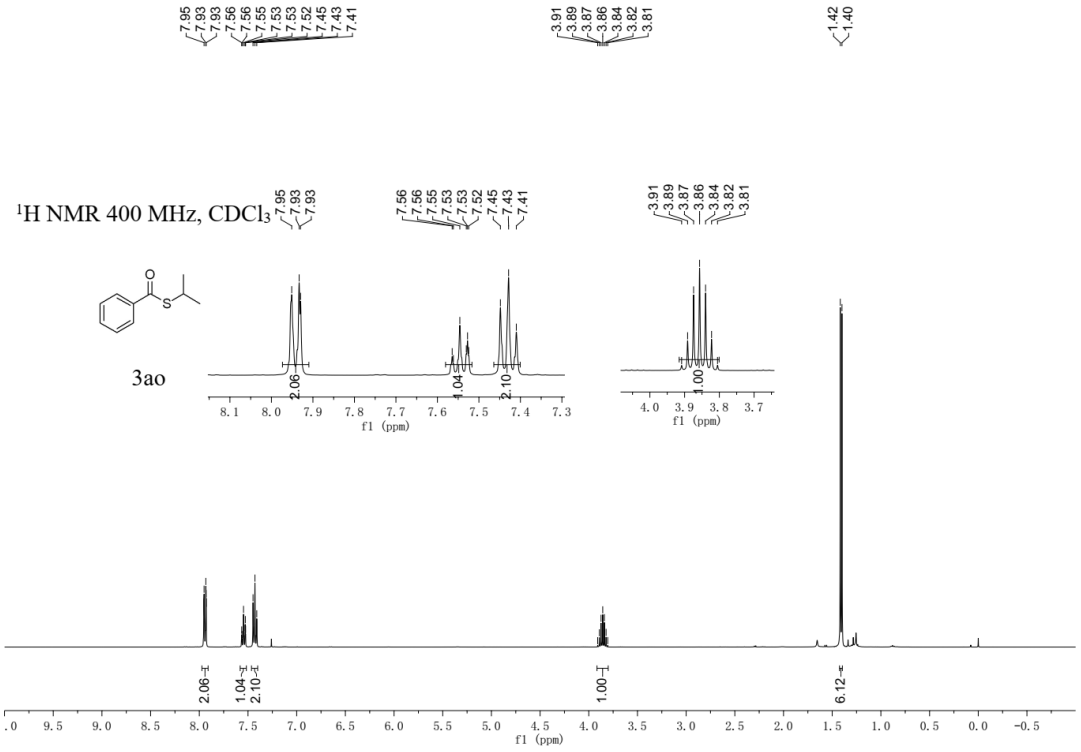
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3.86
3.84
3.82
3.81
1.42
1.40
1H NMR 400 MHz, CDCl3
3ao
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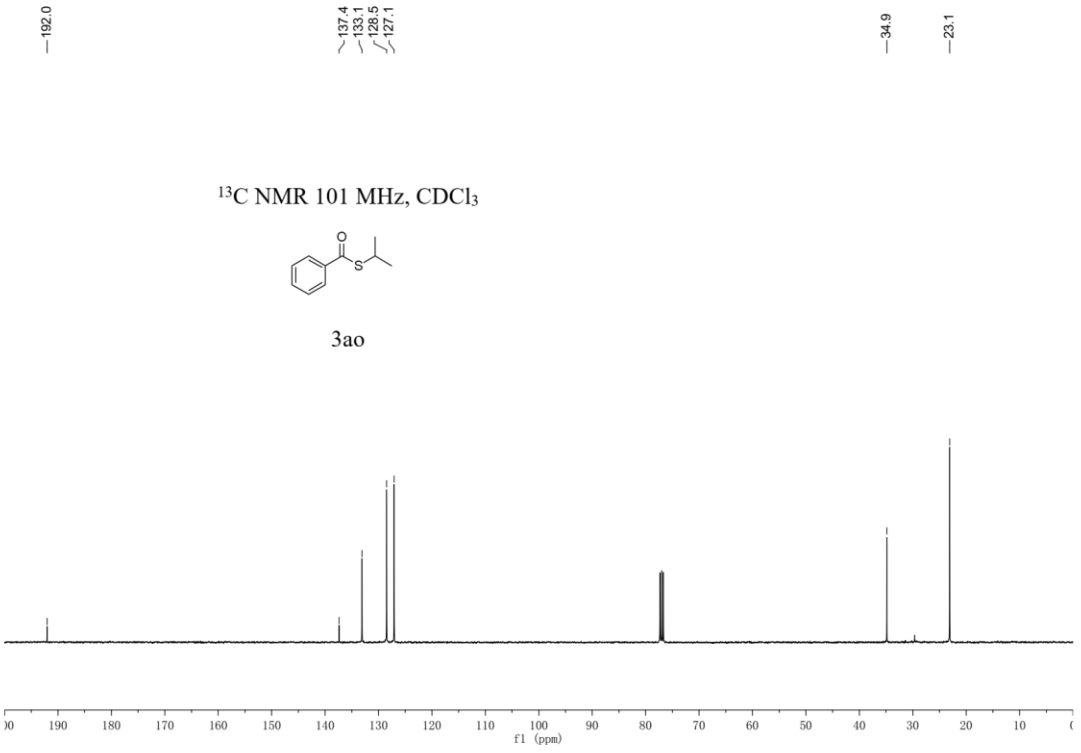
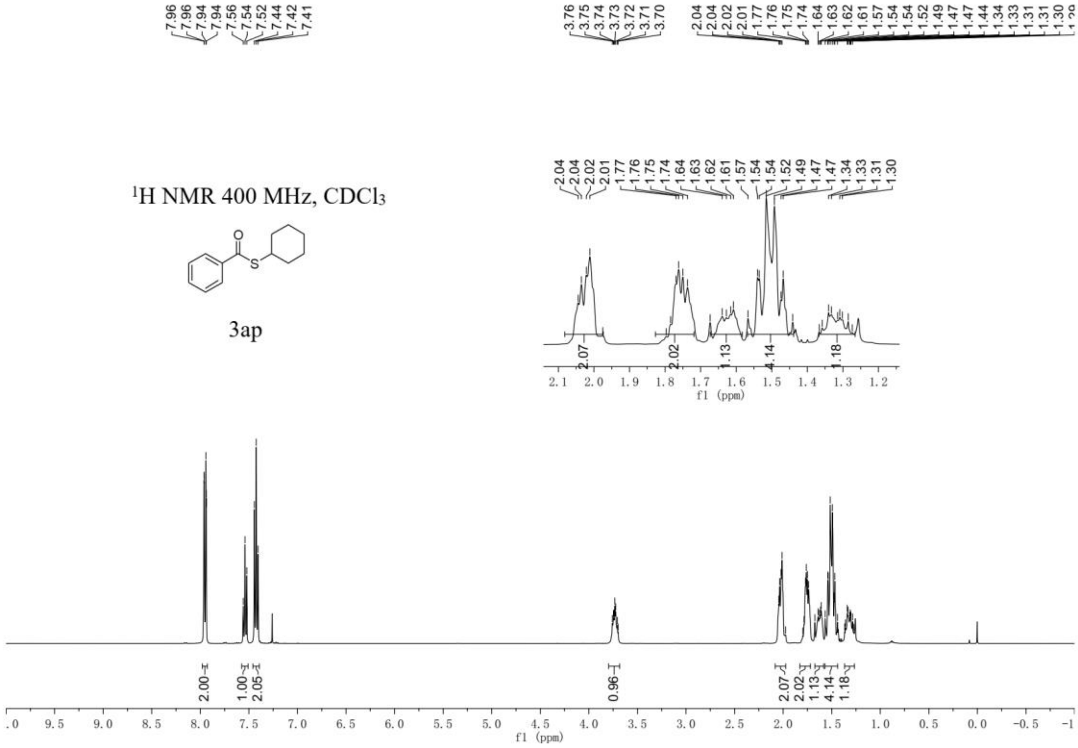
4.04
2.10
1.00
f1 (ppm)
2.06
1.04
2.10
1.00
6.12
f1 (ppm)


192.0
137.4
133.1
128.5
127.1
34.9
23.1
13C NMR 101 MHz, CDCl3
3ao
f1 (ppm)

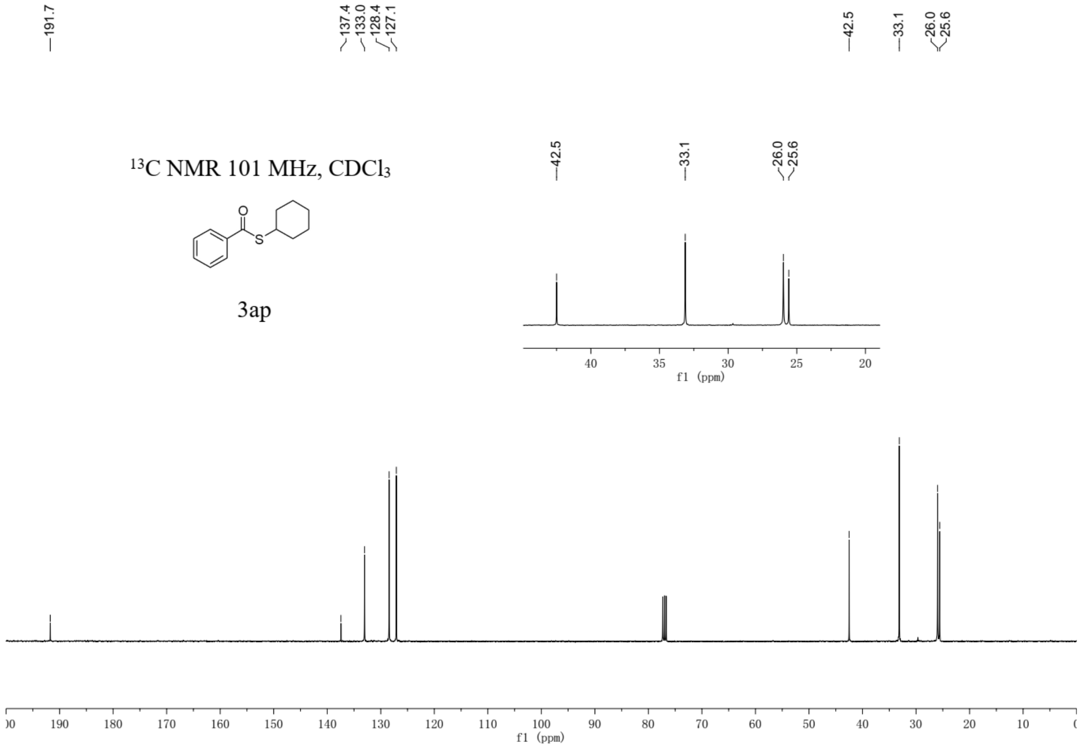
^{1}H NMR 400 MHz, $CDCl_3$

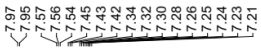
3ap



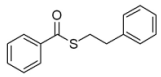
^{13}C NMR 101 MHz, $CDCl_3$

3ap





^{1}H NMR 400 MHz, $CDCl_3$



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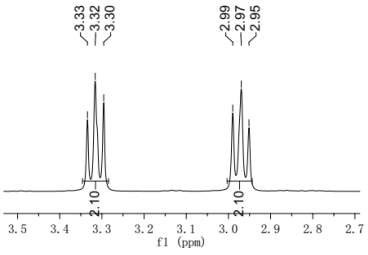
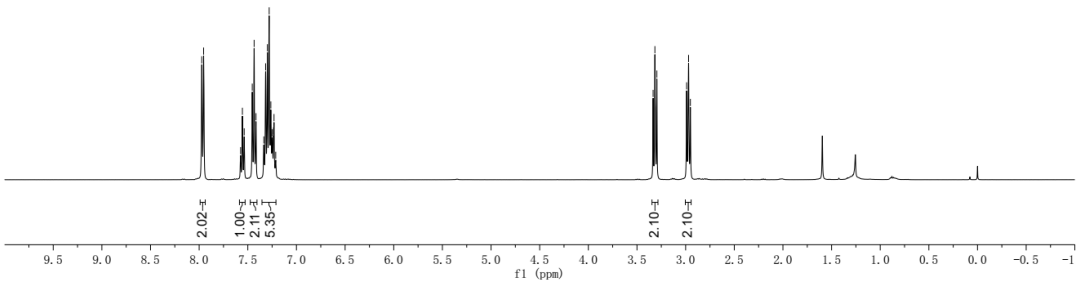
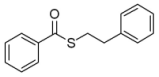




^{13}C NMR 101 MHz, $CDCl_3$



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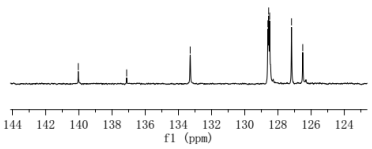
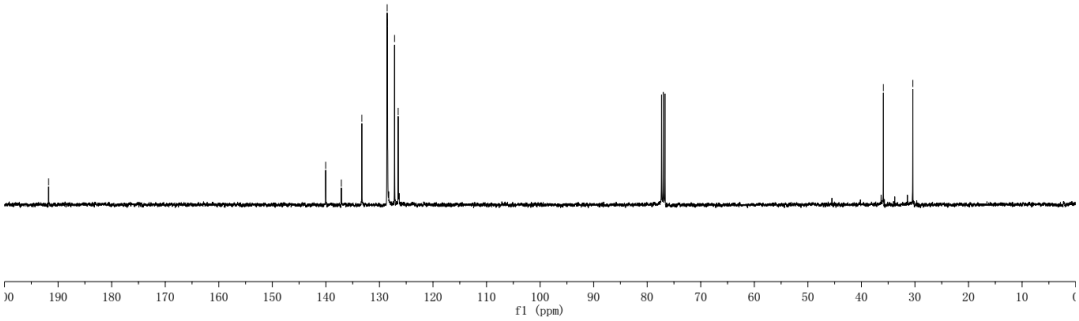
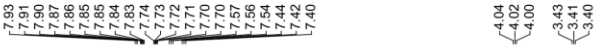
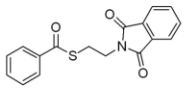






^{1}H NMR 400 MHz, $CDCl_3$



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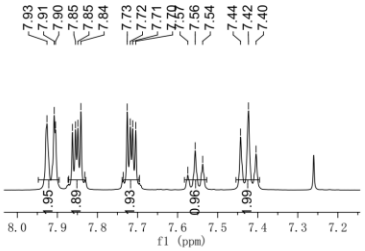
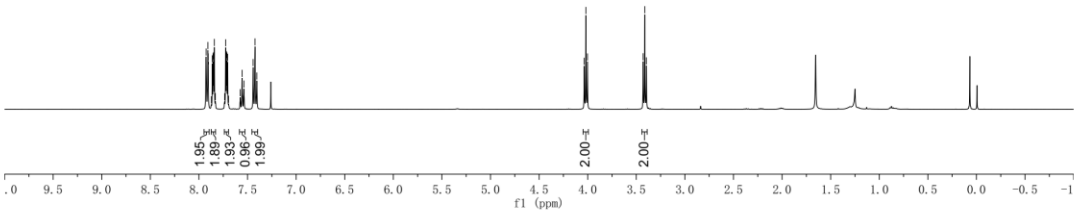
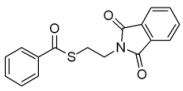




^{13}C NMR 101 MHz, $CDCl_3$



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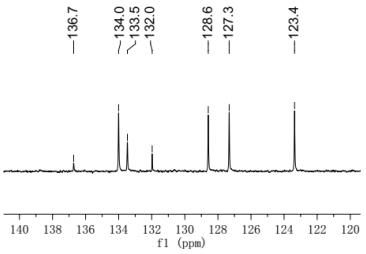
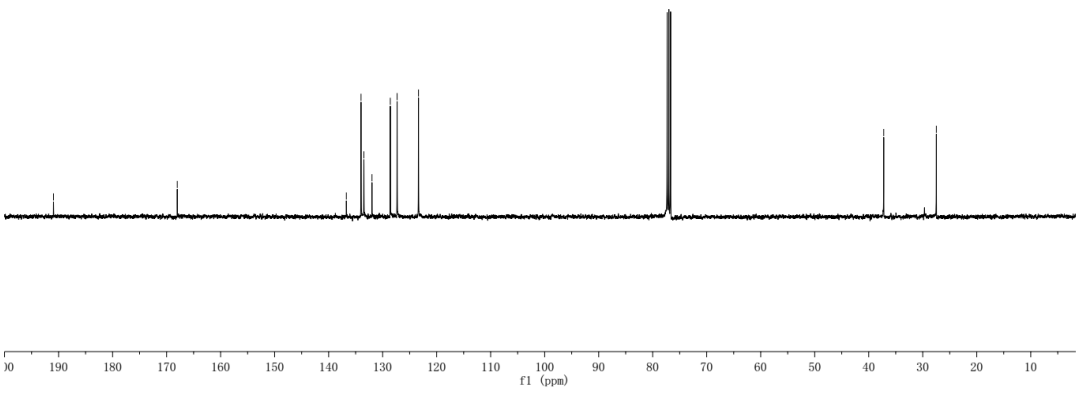
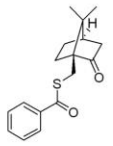


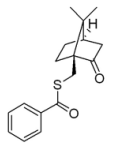


^{1}H NMR 400 MHz, $CDCl_3$

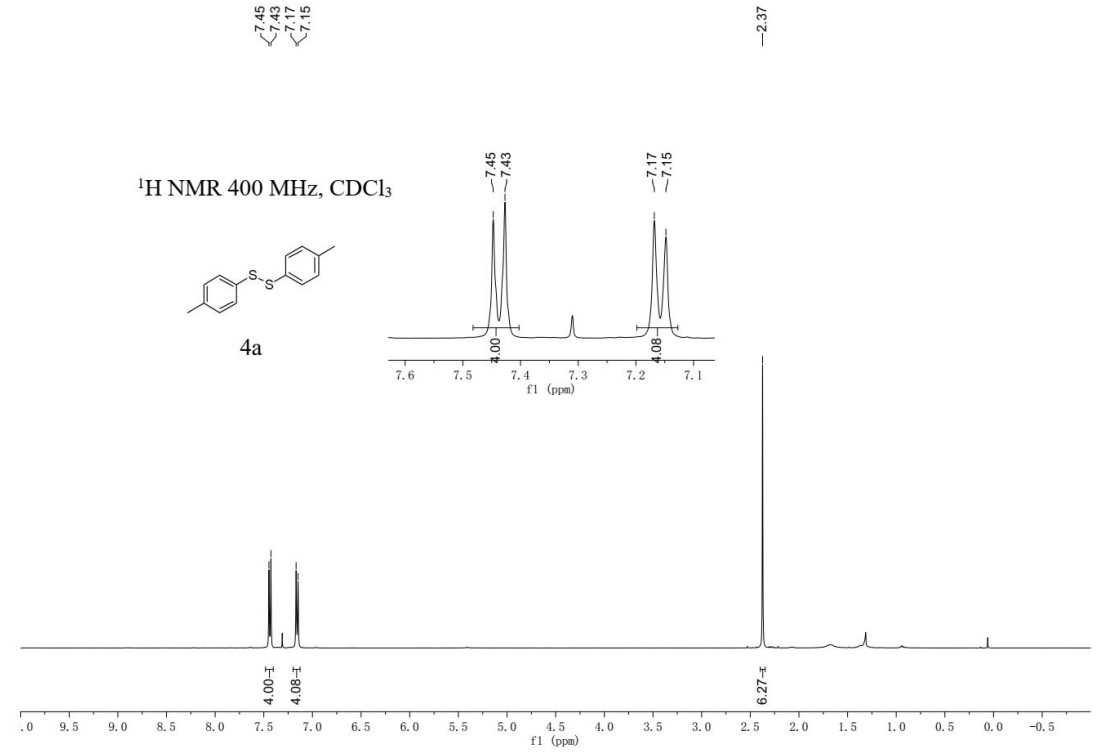


3as

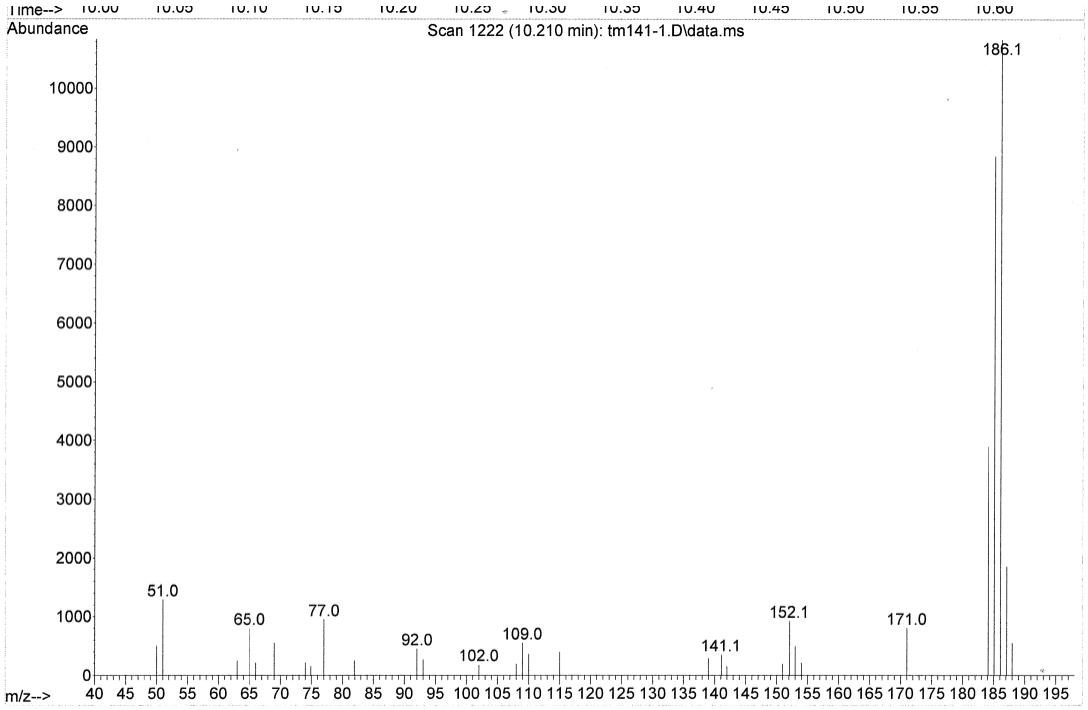
^{13}C NMR 101 MHz, $CDCl_3$



3as


7.45
7.43
7.17
7.15
2.37
^{1}H NMR 400 MHz, CDCl$_3$
4a
4.00
4.08
6.27
f1 (ppm)

6a,


Abundance
Scan 1222 (10.210 min): tm141-1.D\data.ms
186.1
51.0
65.0
77.0
92.0
102.0
109.0
141.1
152.1
171.0
m/z-->