

Supporting Information

Organocatalytic C-H/C-H' Cross-Biaryl-Coupling: C-Selective Arylation of Sulfonanilides with Aromatic Hydrocarbons

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1. General Information Melting point (mp) was measured by Stuart[®] melting point apparatus SMP3 AC input 100 V. ¹H and ¹³C NMR spectra were collected on a JEOL JMN-400 (400 MHz) spectrometers using CDCl₃ or DMSO *d*-6 as a solvent. Chemical shifts of ¹H NMR were recorded in parts per million (ppm, δ) relative to tetramethylsilane (δ = 0.00 ppm) with the solvent resonance as an internal standard (CDCl₃, δ = 7.24 ppm, DMSO, δ = 2.54 ppm). Data are reported as follows: chemical shift in ppm (δ), integration, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, brs = broad singlet, m = multiplet), and coupling constant (Hz). Chemical shifts of ¹³C NMR were reported in ppm with the solvent as the internal standard (CDCl₃, δ = 77.0 ppm, DMSO, δ = 40.5 ppm). Infrared spectra (IR) were recorded on a JASCO FT/IR-4200 spectrometer; absorptions are reported in reciprocal centimeters. High resolution mass measurements were performed by the Elemental Analysis Section of Osaka University. Column chromatography was carried out on Merk Silica Gel 60 (230-400 mesh) eluting with ethyl acetate and hexane. Thin-layer chromatography (TLC) was performed on Merk Silica Gel F₂₅₄ plates (0.25 mm). The spots and bands were detected by UV light of irradiation (254, 365 nm).

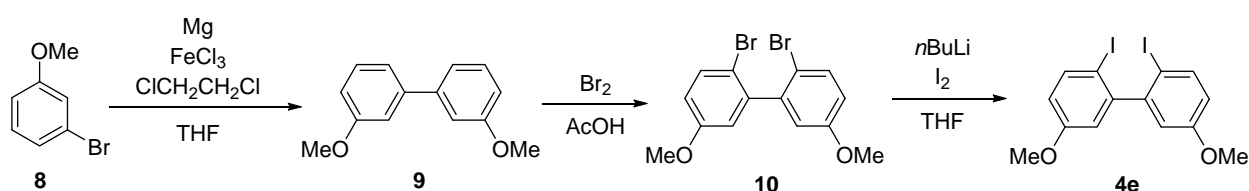
2. Materials PhI(OAc)₂ (PIDA) is commercially available. Regarding the bis(iodoarene)s, **4a** is commercially available and used without purification. The alkylated bis(iodoarene)s **4b** and **4c** were readily prepared in single step from corresponding iodoarenes by our oxidative biaryl coupling method.^{1,2)} Compound **4d** was prepared according to the literatures.^{3,4)} Sulfonanilides **1a-d**, **1i** and **1j** were prepared from commercially available amines and sulfonyl chloride. Sulfonanilides **1e-h** were synthesized by Ullman coupling of corresponding aryl bromides and methanesulfonamide.⁵⁾ Compounds **2k** and **2l** were prepared from *p*-cresol by protecting with benzyl chlorides and *tert*-butyldiphenylsilyl chloride, respectively. *m*-Chloroperbenzoic acid (*m*CPBA) was dried under vacuum for 3 hours prior to use. Solvents and all other starting materials were commercially available and used without further purification.

3. General Procedure for PIDA Mediated Stoichiometric Cross-Coupling Reaction of Anilides with Aromatic Hydrocarbons (Scheme 2)

To a stirred solution of **1b** (60 mg, 0.20 mmol) and *p*-xylene **2a** (212 mg, 2.0 mmol) in (CF₃)₂CHOH (HFIP) (2 mL), PIDA (64 mg, 0.20 mmol) was added in one portion at room temperature, and it was stirred for 1 hour. Solvent was removed under reduced pressure and the crude residue was purified by column chromatography on silica-gel (hexane/ethyl acetate = 6:1) to give pure cross-coupling biaryl **3ba** (71 mg, 0.176 mmol).

4. Catalytic Cross-Coupling

4.1. Synthesis of catalyst **4e** ⁶⁻⁸⁾



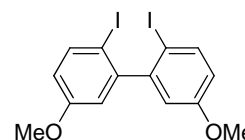
A dried three-necked flask equipped with a magnetic stirrer was charged under nitrogen, FeCl₃ (244 mg, 1.5 mmol) and 1,2-dichloroethane (2.37 mL, 30 mmol) were dissolved in THF (100 mL). A solution of Grignard reagent prepared from **8** (9.35 g, 50 mmol) in THF (*c.a.* 1.0 M) was added at once *via* a cannula to the resulting yellow-green solution. The resulting mixture was stirred at room temperature for 10 min., then hydrolyzed with a 1M aqueous HCl solution. After extraction with methylene chloride three times, the combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. The residue was purified by chromatography on silica-gel to give desired 3,3'-dimethoxybiphenyl **9** (4.87 g, 91%) as colorless oil.

To a solution of **9** (800 mg, 3.7 mmol) in acetic acid (6.67 mL), bromine (0.42 mL, 8.2 mmol) was added at room temperature. After stirring for 2 hours, saturated aqueous Na₂SO₃ was added and the mixture was stirred for 30 minutes. The crude product was extracted with chloroform three times, and the combined organic layer was dried over anhydrous Na₂SO₄ and concentrated under reduced pressure. Purification by washing with ethanol gave pure 2,2'-dibromo-5,5'-dimethoxybiphenyl **10** (930 mg, 67%) as a white powder.

To a solution of compound **10** (930 mg, 2.5 mmol) in THF (25 mL) at -78 °C, *n*-BuLi (3.26 mL, 1.6 M in hexane, 5.3 mmol) was added dropwise. The solution was stirred at the same temperature for 1 hour and then treated with a solution of I₂ (1.34 g, 5.3 mmol) in THF (10 mL). The reaction mixture was warmed to room temperature and stirred for 1 hour. After adding a saturated aqueous solution of NH₄Cl, the aqueous phase was extracted with AcOEt. The combined organic layer was washed with Na₂S₂O₃ aq. and dried over anhydrous Na₂SO₄. The solvents of the filtrate were removed under reduced pressure. Purification of the residue by column chromatography on SiO₂ (hexane/ethyl acetate = 10:1) gave the catalyst **4e** (990 mg, 85%) as colorless solid.

1-Iodo-2-(2-iodo-5-methoxyphenyl)-4-methoxybenzene (**4e**)

¹H NMR (400 MHz, CDCl₃) 3.79 (s, 6H), 6.68 (dd, *J* = 3.2, 8.0 Hz, 2H), 6.74 (d, *J* = 3.2 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 56.4, 85.4, 109.7, 121.2, 139.7, 142.4, 158.4 ppm.



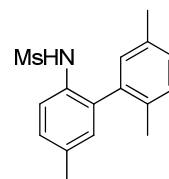
4.2 General Procedure for Cross-Coupling Reaction using Bis(iodoarene) Catalyst 4e

To a stirred solution of **1b** (60 mg, 0.20 mmol), *p*-xylene **2a** (212 mg, 2.0 mmol) and bis(iodoarene) **4e** (5 mg, 0.01 mmol) in CF₃CH₂OH (TFE)-CH₂Cl₂ (2:1, 3 mL), dry *m*CPBA (52 mg, 0.3 mmol) was added in one portion at room temperature under air, and it was stirred for 3 hours. After the reaction completion was checked by TLC, few drops of Na₂S₂O₃ aq. and saturated NaHCO₃ aq. were added to the reaction mixture, and the aqueous phase was extracted with CH₂Cl₂ three times. The combined extract was dried over anhydrous Na₂SO₄ and then evaporated to dryness. The crude residue was purified by column chromatography on silica-gel (hexane/ethyl acetate = 6:1) to give the pure cross-coupling product **3ba** (80 mg, 1.98 mmol).

4.3 Chemical Data of the Cross-Coupling Products 3

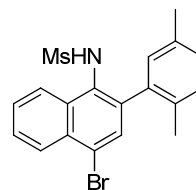
N-{2',5,5'-Trimethyl-(1,1'-biphenyl)-2-yl}methanesulfonamide (**3aa**)

Light yellow oil; ¹H NMR (400 MHz, CDCl₃) 2.04 (s, 3H), 2.33 (s, 6H), 2.84 (s, 3H), 6.02 (s, 1H), 6.91 (s, 1H), 6.96 (s, 1H), 7.11-7.19 (m, 3H), 7.53 (d, *J* = 8.0 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 19.2, 20.7, 20.9, 39.4, 119.2, 129.3, 129.6, 130.1, 130.8, 130.9, 131.8, 132.4, 133.1, 134.2, 136.2, 136.2 ppm; IR (KBr): 3287, 3018, 2292, 2862, 2735, 1611, 1495, 1385, 1333, 1274, 1214, 1159, 1044, 970, 888, 818, 763, 645, 607 cm⁻¹.



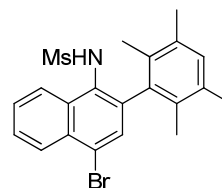
N-{4-Bromo-2-(2,5-dimethylphenyl)naphthalen-1-yl}methanesulfonamide (**3ba**)

Colorless solid; mp: 156-160 °C (hexane-ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 2.13 (s, 3H), 2.31 (s, 3H), 2.35 (s, 3H), 6.24 (s, 1H), 7.09 (s, 1H), 7.14 (d, *J* = 8.0 Hz, 1H), 7.22 (d, *J* = 7.6 Hz, 1H), 7.65-7.67 (m, 2H), 7.71 (s, 1H), 8.27 (dd, *J* = 2.0, 7.6 Hz, 1H), 8.34 (dd, *J* = 2.4, 7.6 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 20.2, 21.6, 42.1, 123.7, 125.2, 128.2, 128.6, 128.8, 129.7, 130.0, 131.3, 131.4, 132.4, 132.8, 133.6, 133.9, 136.4, 138.2, 138.9 ppm; IR (KBr): 3262, 3066, 3033, 2922, 2860, 1592, 1495, 1455, 1391, 1314, 1267, 1204, 1151, 1054, 912, 739, 697, 622 cm⁻¹; HRMS (FAB) Calcd for C₁₉H₁₈BrNO₂S [M]⁺ 403.0242, found 403.0239.



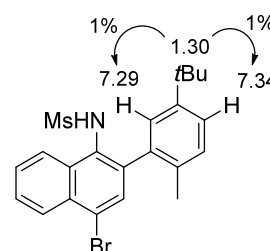
N-{4-Bromo-2-(2,3,5,6-tetramethylphenyl)naphthalen-1-yl}methanesulfonamide (**3bb**)

Colorless solid; mp: 214-216 °C (hexane-ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 1.93 (s, 6H), 2.26 (s, 6H), 2.28 (s, 3H), 5.98 (s, 1H), 7.04 (s, 1H), 7.62 (s, 1H), 7.65-7.68 (m, 2H), 8.28-8.31 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 17.1, 20.1, 41.6, 123.0, 124.3, 127.6, 127.8, 128.1, 129.5, 131.6, 132.0, 132.1, 132.2, 133.3, 134.3, 137.4, 138.4 ppm; IR (KBr): 3259, 2925, 1590, 1389, 1315, 1258, 1216, 1148, 1095, 1042, 974, 874, 760 cm⁻¹; HRMS (FAB) Calcd for C₂₁H₂₂BrNO₂S [M]⁺ 431.0555, found 431.0551.



N-[4-Bromo-2-{5-(*tert*-butyl)-2-methylphenyl}naphthalen-1-yl]methanesulfonamide (**3bc**, including small amount of regioisomer)

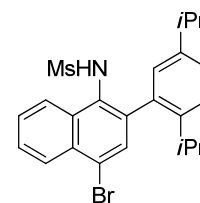
Colorless oil; ¹H NMR (400 MHz, CDCl₃) δ 1.30 (s, 9H), 2.11 (s, 3H), 2.20 (s, 3H), 6.37 (s, 1H), 7.23 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 2.1 Hz, 1H), 7.34 (dd, *J* = 2.1, 8.2 Hz, 1H), 7.60-7.65 (m, 2H), 7.73 (s, 1H), 8.24-8.30 (m, 2H) ppm. ¹³C NMR (100 MHz, CDCl₃) δ 14.1, 19.3, 20.2, 29.6, 31.3, 34.3, 34.4, 34.5, 41.2, 41.5, 60.4, 77.2, 123.0, 123.1, 124.3,



124.5, 125.4, 127.4, 127.47, 127.52, 127.8, 128.0, 128.1, 129.1, 129.2, 130.0, 130.2, 131.8, 131.9, 132.1, 133.1, 133.2, 134.8, 135.6, 137.3, 138.2, 138.7, 149.1, 151.8 ppm; IR (KBr): 3260, 2962, 2868, 2362, 2340, 1590, 1503, 1394, 1314, 1262, 1233, 1204, 1148, 1055, 974, 881, 826, 800, 759, 703, 651 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{23}\text{H}_{26}\text{BrNNaO}_2\text{S}$ $[\text{M} + \text{Na}]^+$ 468.0609, found 468.0603.

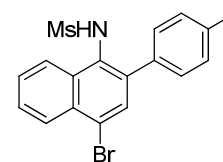
***N*-{4-Bromo-2-(2,5-diisopropylphenyl)naphthalen-1-yl}methanesulfonamide (3bd)**

Colorless solid; mp: 155-158 °C (hexane-ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 1.01 (d, $J = 6.8$ Hz, 3H), 1.19 (d, $J = 6.8$ Hz, 9H), 2.20 (s, 3H), 2.62 (heptet, $J = 6.8$ Hz, 1H), 2.86 (heptet, $J = 6.8$ Hz, 1H), 6.07 (s, 1H), 7.07 (d, $J = 1.6$ Hz, 1H), 7.23 (dd, $J = 1.6, 8.0$ Hz, 1H), 7.31 (d, $J = 8.0$ Hz, 1H), 7.60-7.65 (m, 2H), 7.71 (s, 1H), 8.23-8.28 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 23.9, 24.8, 24.9, 26.3, 30.7, 34.5, 42.6, 123.7, 125.1, 126.7, 128.0, 128.5, 128.7, 129.1, 129.5, 130.1, 132.8, 132.9, 133.9, 137.2, 139.3, 145.0, 147.3 ppm; IR (KBr): 3259, 2960, 1591, 1496, 1391, 1313, 1204, 1148, 1052, 974, 911, 734, 648, 601 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{23}\text{H}_{26}\text{BrNO}_2\text{S}$ $[\text{M}]^+$ 459.0868, found 459.0870.



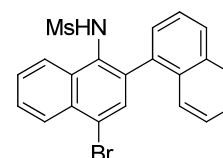
***N*-{4-Bromo-2-(*p*-tolyl)naphthalen-1-yl}methanesulfonamide (3be)**

Colorless solid; mp: 190-193 °C (hexane-ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 2.31 (s, 3H), 2.42 (s, 3H), 6.45 (s, 1H), 7.30-7.36 (m, 4H), 7.63-7.69 (m, 2H), 7.81 (s, 1H), 8.25 (dd, $J = 2.0, 7.6$ Hz, 1H), 8.39 (dd, $J = 2.0, 7.6$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 21.3, 41.0, 123.6, 125.1, 127.4, 127.9, 128.0, 128.1, 129.4, 129.8, 131.7, 132.1, 133.6, 135.3, 138.4, 138.5 ppm; IR (KBr): 3266, 1590, 1514, 1392, 1316, 1148, 1055, 975, 912, 823, 793, 740 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{18}\text{H}_{16}\text{BrNO}_2\text{S}$ $[\text{M}]^+$ 389.0085, found 389.0083.



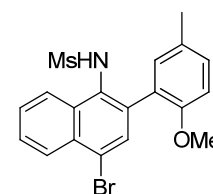
***N*-{4'-Bromo-(1,2'-binaphthalen)-1'-yl}methanesulfonamide (3bf)**

Colorless solid; mp: 158-160 °C (hexane-ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 2.04 (s, 3H), 6.11 (s, 1H), 7.47-7.50 (m, 2H), 7.53-7.56 (m, 2H), 7.60 (t, $J = 6.8$ Hz, 1H), 7.70-7.72 (m, 2H), 7.88 (s, 1H), 7.95 (m, 2H), 8.32 (dd, $J = 2.0, 7.6$ Hz, 1H), 8.45 (dd, $J = 2.0, 7.6$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 41.1, 123.5, 124.6, 125.4, 125.5, 126.6, 127.4, 127.7, 128.1, 128.1, 128.2, 129.0, 129.2, 129.6, 131.1, 132.2, 132.6, 133.4, 133.6, 135.6, 136.6 ppm; IR (KBr): 3263, 3057, 2930, 1588, 1494, 1313, 1205, 1149, 973, 910, 733, 647 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{21}\text{H}_{16}\text{BrNO}_2\text{S}$ $[\text{M}]^+$ 425.0085, found 425.0078.



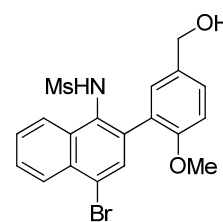
***N*-{4-Bromo-2-(2-methoxy-5-methylphenyl)naphthalen-1-yl}methanesulfonamide (3bg)**

Colorless solid; mp: 167-169 °C (hexane-ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 2.23 (s, 3H), 2.37 (s, 3H), 3.85 (s, 3H), 7.01 (d, $J = 8.4$ Hz, 1H), 7.20 (s, 1H), 7.23-7.27 (m, 2H), 7.64-7.67 (m, 2H), 7.80 (s, 1H), 8.22 (dd, $J = 2.4, 7.2$ Hz, 1H), 8.60 (dd, $J = 2.4, 7.2$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 20.5, 39.8, 56.8, 112.4, 123.2, 126.5, 126.8, 127.1, 127.6, 128.1, 129.7, 130.9, 131.9, 132.0, 132.3, 132.5, 133.4, 134.1, 153.1 ppm; IR (KBr): 3280, 3021, 2928, 1588, 1503, 1363, 1320, 1240, 1155, 1057, 1023, 973, 880, 811, 768 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{19}\text{H}_{18}\text{BrNO}_3\text{S}$ $[\text{M}]^+$ 419.0191, found 419.0177.

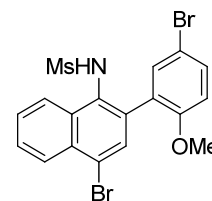


***N*-[4-Bromo-2-{5-(hydroxymethyl)-2-methoxyphenyl}naphthalen-1-yl]methanesulfonamide (3bh)**

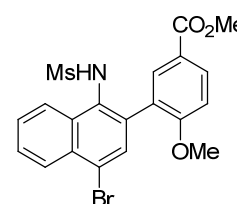
Colorless solid; mp: 177-180 °C (hexane-ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 2.26 (s, 3H), 3.88 (s, 3H), 4.72 (s, 2H), 7.09-7.11 (m, 2H), 7.44-7.47 (m, 2H), 7.63-7.69 (m, 2H), 7.80 (s, 1H), 8.23 (dd, *J* = 2.2, 5.4 Hz, 1H), 8.58 (dd, *J* = 2.2, 5.4 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 39.6, 56.1, 63.7, 111.7, 122.7, 125.7, 126.4, 126.7, 127.1, 127.6, 128.6, 129.1, 130.3, 131.5, 131.8, 132.9, 133.8, 134.4, 154.2 ppm; IR (KBr): 3274, 2933, 1589, 1503, 1362, 1316, 1250, 1151, 1057, 1022, 974, 883, 813, 770 cm⁻¹; HRMS (FAB) Calcd for C₁₉H₁₈BrNO₄S [M]⁺ 435.0140, found 435.0143.

***N*-{4-Bromo-2-(5-bromo-2-methoxyphenyl)naphthalen-1-yl}methanesulfonamide (3bi)**

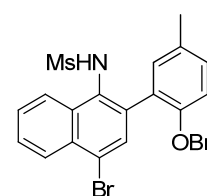
Colorless solid; mp: 143-145 °C (hexane-ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 2.33 (s, 3H), 3.84 (s, 3H), 6.97-7.00 (m, 2H), 7.55-7.56 (m, 2H), 7.64-7.66 (m, 2H), 7.76 (s, 1H), 8.23 (dd, *J* = 2.0, 7.6 Hz, 1H), 8.54 (dd, *J* = 2.0, 7.6 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 40.2, 56.7, 113.8, 114.0, 123.3, 126.2, 126.9, 127.7, 128.2, 129.2, 129.8, 131.5, 132.4, 132.8, 132.9, 133.3, 134.3, 154.4 ppm; IR (KBr): 3285, 3019, 2938, 2842, 1585, 1488, 1329, 1248, 1154, 1114, 1054, 1020, 973, 878, 809, 766, 623, 562 cm⁻¹; HRMS (FAB) Calcd for C₁₈H₁₅Br₂NO₃S [M]⁺ 482.9139, found 482.9138.

**Methyl 3-(4-bromo-1-methylsulfonamidonaphthalen-2-yl)-4-methoxybenzoate (3bj)**

Colorless solid; mp: 167-170 °C (hexane-ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 2.28 (s, 3H), 3.91 (s, 3H), 3.94 (s, 3H), 6.86 (s, 1H), 7.14 (d, *J* = 8.8 Hz, 1H), 7.65-7.67 (m, 2H), 7.79 (s, 1H), 8.12 (d, *J* = 2.0 Hz, 1H), 8.16 (d, *J* = 8.8 Hz, 1H), 8.24 (dd, *J* = 3.2, 7.2 Hz, 1H), 8.54 (dd, *J* = 3.2, 7.2 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 40.6, 52.6, 57.0, 111.9, 123.8, 124.2, 126.4, 127.3, 127.6, 128.1, 128.5, 130.0, 132.1, 132.5, 132.8, 133.6, 133.7, 133.8, 159.2, 166.4 ppm; IR (KBr): 3278, 3020, 2950, 1715, 1606, 1503, 1436, 1364, 1319, 1259, 1224, 1151, 1122, 1055, 1019, 974, 879, 766 cm⁻¹; HRMS (FAB) Calcd for C₂₀H₁₈BrNO₅S [M]⁺ 463.0089, found 463.0076.

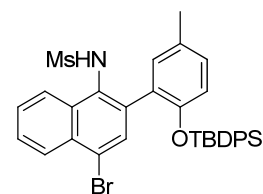
***N*-[2-{2-(Benzyloxy)-5-methylphenyl}-4-bromonaphthalen-1-yl]methanesulfonamide (3bk)**

Colorless solid; mp: 193-195 °C (hexane-ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 2.24 (s, 3H), 2.39 (s, 3H), 4.94 (d, *J* = 12.0 Hz, 1H), 5.15 (d, *J* = 12.0 Hz, 1H), 7.05 (d, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 1H), 7.15-7.26 (m, 5H), 7.40 (s, 1H), 7.66-7.68 (m, 2H), 7.73 (s, 1H), 8.24 (dd, *J* = 2.4, 7.2 Hz, 1H), 8.58 (dd, *J* = 2.4, 7.2 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 20.6, 39.8, 72.9, 115.9, 123.1, 126.5, 126.7, 127.4, 127.5, 128.0, 128.3, 128.5, 128.6, 129.6, 130.8, 131.9, 132.2, 132.4, 132.8, 133.5, 134.2, 135.4, 152.2 ppm; IR (KBr): 3268, 3066, 3032, 2925, 1587, 1502, 1363, 1321, 1225, 1153, 1110, 970, 911, 883, 808, 736, 697 cm⁻¹; HRMS (FAB) Calcd for C₂₅H₂₂BrNO₃S [M]⁺ 495.0504, found 495.0508.



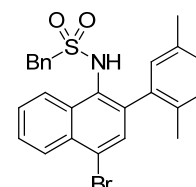
***N*-[[4-Bromo-2-[2-{{tert-butyl}diphenylsilyloxy}-5-methylphenyl]naphthalen-1-yl]]methanesulfonamide (3bl)**

Colorless solid; mp: 190-192 °C (hexane-ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 0.69 (s, 9H), 2.18 (s, 3H), 2.21 (s, 3H), 6.64 (d, *J* = 8.4 Hz, 1H), 6.83 (d, *J* = 7.2 Hz, 1H), 7.09 (s, 1H), 7.14-7.18 (m, 2H), 7.24-7.33 (m, 5H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.43 (s, 1H), 7.50-7.51 (d, *J* = 7.2 Hz, 2H), 7.56 (s, 1H), 7.61-7.63 (m, 2H), 8.19 (dd, *J* = 4.4, 5.2 Hz, 1H), 8.55 (dd, *J* = 4.4, 5.2 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 19.1, 20.5, 26.4, 39.7, 120.8, 123.1, 126.4, 126.8, 127.6, 127.7, 127.9, 128.1, 129.4, 129.7, 130.1, 130.2, 130.5, 130.8, 131.6, 132.0, 132.2, 132.3, 132.5, 133.4, 134.5, 135.4, 135.5, 149.3 ppm; IR (KBr): 3279, 3072, 2931, 1858, 1588, 1499, 1428, 1363, 1320, 1229, 1155, 1112, 971, 924, 885, 821, 761, 701, 669, 614 cm⁻¹; HRMS (FAB) Calcd for C₃₄H₃₅BrNO₃SSi [M+H]⁺ 644.1285, found 644.1292.



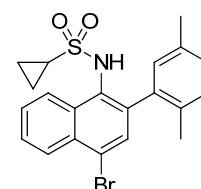
***N*-(4-Bromo-2-(2,5-dimethylphenyl)naphthalen-1-yl)-1-phenylmethanesulfonamide (3ca)**

Colorless solid; mp: 169-171 °C (hexane-ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 2.16 (s, 3H), 2.40 (s, 3H), 3.51 (s, 2H), 5.95 (s, 1H), 7.03-7.05 (m, 2H), 7.18-7.19 (m, 2H), 7.28-7.29 (m, 4H), 7.63-7.66 (m, 2H), 7.71 (s, 1H), 8.22-8.29 (m, 2H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 19.6, 20.9, 60.2, 122.9, 124.1, 127.6, 127.7, 127.8, 128.3, 128.5, 128.6, 128.7, 129.3, 130.4, 130.8, 130.9, 131.8, 132.0, 133.3, 133.5, 135.6, 138.3, 138.8 ppm; IR (KBr): 3262, 3033, 2922, 2860, 1592, 1495, 1455, 1391, 1314, 1204, 1151, 1054, 912, 739, 622 cm⁻¹; HRMS (FAB) Calcd for C₂₅H₂₂BrNO₂S [M]⁺ 479.0555, found 479.0556.



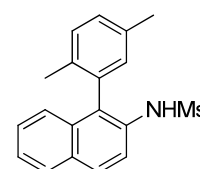
***N*-(4-Bromo-2-(2,5-dimethylphenyl)naphthalen-1-yl)cyclopropanesulfonamide (3da)**

Colorless solid; mp: 150-152 °C (hexane-ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 0.56-0.65 (m, 2H), 0.83-0.96 (m, 2H), 1.59-1.65 (m, 1H), 2.14 (s, 3H), 2.34 (s, 3H), 6.15 (s, 1H), 7.10-7.13 (m, 2H), 7.19 (d, *J* = 7.6 Hz, 1H), 7.64-7.66 (m, 2H), 7.71 (s, 1H), 8.26 (dd, *J* = 2.4, 8.0 Hz, 1H), 8.41 (dd, *J* = 2.4, 8.0 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 6.0, 19.5, 20.9, 31.2, 122.6, 125.1, 127.4, 127.7, 127.8, 129.1, 129.2, 130.6, 130.7, 131.8, 132.1, 133.0, 133.1, 135.6, 137.5, 137.9 ppm; IR (KBr): 3268, 3017, 2923, 2856, 1590, 1496, 1453, 1361, 1321, 1144, 1039, 910, 890, 813, 763, 734, 707, 565, 512 cm⁻¹; HRMS (FAB) Calcd for C₂₁H₂₀BrNO₂S [M]⁺ 429.0398, found 429.0399.



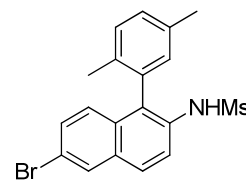
***N*-(1-(2,5-Dimethylphenyl)naphthalen-2-yl)methanesulfonamide (3ea)**

Colorless solid; mp: 143-145 °C (hexane-ethyl acetate); ¹H NMR (400 MHz, CDCl₃) δ 1.94 (s, 3H), 2.40 (s, 3H), 2.96 (s, 3H), 6.28 (s, 1H), 7.00 (s, 1H), 7.23 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 7.2 Hz, 1H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.39 (td, *J* = 8.0, 1.2 Hz, 1H), 7.45 (td, *J* = 8.0, 1.2 Hz, 1H), 7.88-7.98 (m, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 19.8, 21.8, 40.9, 119.3, 126.1, 126.4, 127.8, 128.1, 128.9, 130.0, 130.9, 131.6, 131.7, 132.0, 132.7, 133.4, 134.5, 135.3, 137.5 ppm; IR (KBr): 3335, 3016, 2923, 1620, 1594, 1497, 1469, 1401, 1365, 1323, 1254, 1229, 1160, 982, 912, 88, 816, 744, 649, 620 cm⁻¹; HRMS (FAB) Calcd for C₁₉H₁₉NO₂S [M]⁺ 325.1136, found 325.1136.



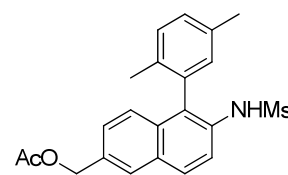
***N*-(6-Bromo-1-(2,5-dimethylphenyl)naphthalen-2-yl)methanesulfonamide (3fa)**

Colorless amorphous; ^1H NMR (400 MHz, CDCl_3) δ 1.88 (s, 3H), 2.37 (s, 3H), 2.94 (s, 3H), 6.22 (s, 1H), 6.93 (s, 1H), 7.05 (d, $J = 9.2$ Hz, 1H), 7.25 (s, 1H), 7.31 (d, $J = 7.6$ Hz, 1H), 7.41 (d, $J = 7.6$ Hz, 1H), 7.80 (d, $J = 8.8$ Hz, 1H), 7.94 (d, $J = 8.8$ Hz, 1H) 8.01 (s, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 18.9, 21.0, 40.2, 119.2, 119.3, 127.2, 127.4, 128.2, 130.0, 130.2, 130.3, 130.6, 131.1, 131.3, 131.8, 132.2, 133.0, 134.3, 136.9 ppm; IR (KBr): 3336, 3015, 2923, 2855, 1587, 1497, 1465, 1423, 1362, 1323, 1261, 1160, 1069, 983, 912, 857, 824, 739, 648, 514 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{19}\text{H}_{18}\text{BrNO}_2\text{S}$ $[\text{M}]^+$ 403.0242, found 403.0244.



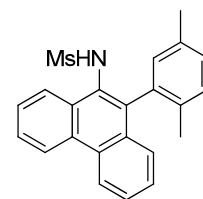
***N*-(5-(2,5-Dimethylphenyl)-6-(methylsulfonamido)naphthalen-2-yl)methyl acetate (3ga)**

Light yellow amorphous; ^1H NMR (400 MHz, CDCl_3) δ 1.89 (s, 3H), 2.10 (s, 3H), 2.35 (s, 3H), 2.92 (s, 3H), 5.22 (s, 2H), 6.23 (s, 1H), 6.93 (s, 1H), 7.18 (d, $J = 8.8$ Hz, 1H), 7.22 (d, $J = 7.2$ Hz, 1H), 7.29-7.34 (m, 2H), 7.83 (s, 1H), 7.88 (d, $J = 9.2$ Hz, 1H), 7.93 (d, $J = 9.2$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 19.7, 21.7, 21.8, 40.9, 66.9, 119.5, 126.9, 127.8, 127.9, 128.3, 130.0, 130.9, 131.3, 131.5, 131.9, 133.0, 133.1, 133.6, 134.2, 135.2, 137.5, 171.6 ppm; IR (KBr): 3335, 3015, 2926, 1737, 1599, 1479, 1429, 1366, 1323, 1230, 1159, 1027, 983, 889, 826, 735, 698, 618, 517 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{22}\text{H}_{23}\text{NO}_4\text{S}$ $[\text{M}]^+$ 397.1348, found 397.1349.



***N*-(10-(2,5-Dimethylphenyl)phenanthren-9-yl)methanesulfonamide (3ha)**

Colorless solid; mp: 199-201 $^\circ\text{C}$ (hexane-ethyl acetate); ^1H NMR (400 MHz, CDCl_3) δ 1.97 (s, 3H), 2.38 (s, 3H), 2.43 (s, 3H), 6.09 (s, 1H), 7.13 (s, 1H), 7.21 (d, $J = 8.0$ Hz, 1H), 7.28 (d, $J = 8.0$ Hz, 1H), 7.40 (d, $J = 8.0$ Hz, 1H), 7.48 (t, $J = 8.0$ Hz, 1H), 7.66 (t, $J = 8.0$ Hz, 1H), 7.70-7.72 (m, 2H), 8.41-8.43 (m, 1H), 8.73-8.76 (m, 2H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 19.9, 21.4, 42.4, 123.2, 123.3, 125.4, 127.5, 127.7, 127.8, 127.9, 128.0, 128.8, 129.7, 130.6, 131.0, 131.1, 131.5, 131.6, 132.0, 134.8, 136.1, 136.9, 137.0 ppm; IR (KBr): 3261, 3022, 1490, 1448, 1320, 1217, 1150, 1071, 1043, 973, 889, 769 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{23}\text{H}_{21}\text{NO}_2\text{S}$ $[\text{M}]^+$ 375.1293, found 375.1294.

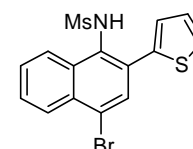


4.4 Chemical Data of the Cross-Coupling products 6

To a stirred solution of anilide **1i** (40 mg, 0.20 mmol), *p*-xylene **5a** (168 mg, 2.0 mmol) and bis(iodoarene) **4e** (5 mg, 0.01 mmol) in $\text{CF}_3\text{CH}_2\text{OH}$ (TFE)- CH_2Cl_2 (2:1, 3 mL), dry *m*CPBA (52 mg, 0.3 mmol) was added in one portion at room temperature and it was then stirred for 3 h. After the reaction completion was checked by TLC, few drops of $\text{Na}_2\text{S}_2\text{O}_3$ aq. and saturated NaHCO_3 aq. were added to the reaction mixture, and the aqueous phase was extracted with CH_2Cl_2 three times. The combined extract was dried over anhydrous Na_2SO_4 and then evaporated to dryness. The crude residue was purified by column chromatography on silica-gel (hexane/ethyl acetate = 10:1) to give pure cross-coupling biaryl **6b** (41 mg, 0.15 mmol).

***N*-(4-Bromo-2-(thiophen-2-yl)naphthalen-1-yl)methanesulfonamide (6a)**

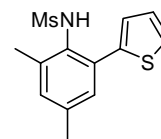
Colorless solid; mp: 204-208 $^\circ\text{C}$ (hexane-ethyl acetate) ^1H NMR (400 MHz, CDCl_3) δ 2.55 (s, 3H), 6.54 (s, 1H), 7.17 (t, $J = 4.0$ Hz, 1H), 7.31 (d, $J = 2.8$ Hz, 1H), 7.49 (d, $J = 5.2$ Hz, 1H), 7.63-7.70 (m, 2H), 7.94 (s, 1H), 8.23 (d, $J = 7.2$ Hz, 1H), 8.28 (d, $J = 7.2$ Hz, 1H) ppm; ^{13}C



NMR (100 MHz, CDCl₃) δ 40.9, 100.5, 124.0, 125.3, 127.4, 127.6, 127.8, 128.1, 128.3, 128.3, 131.6, 131.6, 132.4, 133.8, 139.0 ppm; IR (KBr): 3268, 2929, 1588, 1494, 1379, 1315, 1148, 975, 878, 787, 761 cm⁻¹.

N-{2,4-Dimethyl-6-(thiophen-2-yl)phenyl}methanesulfonamide (**6b**)⁹⁾

Yellow amorphous; ¹H NMR (400 MHz, CDCl₃) δ 2.32 (s, 3H), 2.41 (s, 3H), 2.46 (s, 3H), 6.41 (s, 1H), 7.06-7.09 (m, 2H), 7.12 (d, *J* = 1.6 Hz, 1H), 7.16 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.36 (s, *J* = 5.2, 1.2 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 19.6, 20.8, 40.6, 126.2, 127.2, 127.4, 128.7, 129.6, 131.9, 133.4, 138.2, 139.6, 140.7 ppm; IR (KBr): 3550, 3270, 2925, 2290, 1602, 1386, 1312, 1220, 1146, 976, 909, 856, 763, 702, 607 cm⁻¹.



5. Stoichiometric Reaction Using Prepared Hypervalent Iodine **4e'** (Eq. 1)

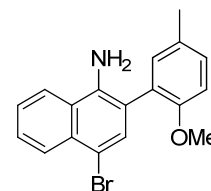
To a stirred solution of **1b** (60 mg, 0.2 mmol), *p*-xylene **2a** (212 mg, 2.0 mmol) in TFE-CH₂Cl₂ (2:1, 3 mL), prepared hypervalent iodoarene **4e'** (90 mg, 0.15 mmol) was added in one portion at room temperature and it was then stirred for 1 hour. Solvent was removed under vacuum and the crude residue was purified by column chromatography on silica-gel (hexane/ethyl acetate = 6:1) to give pure cross-coupling biaryl **6a** (55 mg, 0.137 mmol) in 68 % yield.

6. Deprotection of the Ms Group

To a stirred solution of **3ea** (60 mg, 0.30 mmol) and Boc₂O (79 mg, 0.36 mmol) in CH₂Cl₂ (3 mL), DMAP (5 mg) was added at room temperature under air, and it was stirred for 30 min. Solvent was removed under reduced pressure. The crude residue was dissolved in THF (5 mL) under nitrogen atmosphere and *n*-BuLi (1.6 M in hexane, 0.56 mL, 0.9 mmol) (or LDA prepared from *n*BuLi and *i*Pr₂NH for **3bg**) was added dropwise at 0 °C. After stirring 15 min., N₂ balloon was replaced by dry O₂ balloon and then stirred for an hour at room temperature. Water was added to the reaction mixture and the aqueous phase was extracted with AcOEt three times. The combined extract was dried over anhydrous Na₂SO₄ and then evaporated to dryness. The crude residue was dissolved to CH₂Cl₂ (1 mL) and then CF₃CO₂H (0.3 mL) was added at room temperature. After reaction completion was confirmed by TLC, solvent was removed under vacuum and crude product was purified by column chromatography on SiO₂ (hexane/ethyl acetate = 8:1) to give pure amine **7ea** (67 mg, 0.27 mmol).

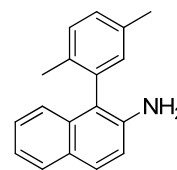
4-Bromo-2-(2-methoxy-5-methylphenyl)naphthalen-1-amine (**7bg**)

Colorless amorphous; ¹H NMR (400 MHz, CDCl₃) δ 2.34 (s, 3H), 3.76 (s, 3H), 4.18 (brs, 2H), 6.93 (d, *J* = 8.4 Hz, 1H), 7.11 (d, *J* = 2.0 Hz, 1H), 7.18 (dd, *J* = 2.0, 8.4 Hz, 1H), 7.48-7.59 (m, 3H), 7.86 (d, *J* = 8.0 Hz, 1H), 8.21 (dd, *J* = 1.0, 8.4 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 20.8, 56.2, 111.2, 111.8, 120.4, 121.9, 125.2, 126.0, 127.1, 127.3, 128.0, 130.1, 130.9, 132.0, 132.9, 133.0, 139.8, 155.0 ppm.



1-(2,5-Bimethylphenyl)naphthalen-2-amine (7ea)

Colorless oil; ^1H NMR (400 MHz, CDCl_3) δ 1.94 (s, 3H), 2.32 (s, 3H), 3.57 (brs, 2H), 6.99-7.01 (m, 2H), 7.08-7.26 (m, 5H), 7.66 (d, $J = 8.4$ Hz, 1H), 7.70 (d, $J = 8.4$ Hz, 1H) ppm; ^{13}C NMR (100 MHz, CDCl_3) δ 18.8, 20.8, 117.8, 119.2, 121.9, 123.9, 126.1, 127.7, 127.8, 128.3, 128.5, 130.3, 131.4, 133.3, 134.7, 135.8, 135.9, 140.6 ppm; IR (KBr): 3479, 3384, 2920, 2352, 2330, 2245, 1895, 1731, 1622, 1507, 1382, 1282, 1145, 1024, 905, 811, 748 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{18}\text{H}_{17}\text{N}$ $[\text{M}]^+$ 247.1361, found 247.1359.

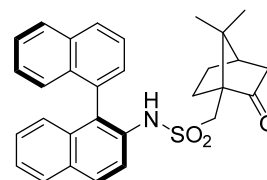


7. Synthesis of Optically Active Binaphthyl Amine 7jf

3jf was obtained according to our general procedure under the condition using **4e** as the catalyst and $(\text{CF}_3)_2\text{CHOH}-\text{CH}_2\text{Cl}_2$ (2:1) as the solvent. Diastereomers, **3jf** and **3jf'**, were isolated by silica-gel chromatography (benzene/chloroform/ethyl acetate = 20 : 2 : 1) as eluent.

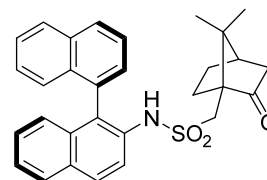
(*R*_a)-*N*-{(1,1'-Binaphthalen)-2-yl}-1-{(1*R*,4*R*)-7,7-dimethyl-3-oxobicyclo[2.2.1]heptan-1-yl}methanesulfonamide (less polar, 3jf)

Colorless amorphous; ^1H NMR (400 MHz, CDCl_3) δ 0.64 (s, 3H), 0.90 (s, 3H), 1.23-1.29 (m, 1H), 1.48-1.55 (m, 1H), 1.75 (d, $J = 18.4$ Hz, 1H), 1.86-2.02 (m, 2H), 2.19-2.24 (m, 2H), 2.61 (d, $J = 14.8$ Hz, 1H), 3.38 (d, $J = 14.8$ Hz, 1H), 6.51 (s, 1H), 7.04 (d, $J = 8.4$ Hz, 1H), 7.20-7.31 (m, 3H), 7.39 (t, $J = 8.0$ Hz, 1H), 7.44-7.50 (m, 2H), 7.64 (t, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.95-8.02 (m, 3H), 8.09 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 19.6, 19.7, 25.2, 26.8, 42.4, 42.6, 47.9, 49.9, 58.4, 119.3, 125.1, 125.4, 125.7, 125.9, 126.0, 126.6, 126.8, 127.0, 128.0, 128.7, 129.0, 129.4, 129.6, 130.8, 132.3, 132.4, 133.2, 133.5, 134.1, 214.5 ppm; IR (KBr): 2958, 1742, 1619, 1594, 1507, 1471, 1405, 1367, 1325, 1263, 1213, 1149, 1048, 981, 943, 867, 806, 751, 608, 567 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{30}\text{H}_{29}\text{NO}_3\text{S}$ $[\text{M} + \text{Na}]^+$ 506.1766, found 506.1760.



(*S*_a)-*N*-{(1,1'-Binaphthalen)-2-yl}-1-{(1*R*,4*R*)-7,7-dimethyl-3-oxobicyclo[2.2.1]heptan-1-yl}methanesulfonamide (more polar, 3jf')

Colorless amorphous; ^1H NMR (400 MHz, CDCl_3) δ 0.55 (s, 3H), 0.92 (s, 3H), 1.26-1.30 (m, 1H), 1.50-1.57 (m, 1H), 1.75 (d, $J = 18.4$ Hz, 1H), 1.91-1.98 (m, 2H), 2.11-2.18 (m, 2H), 2.76 (d, $J = 14.8$ Hz, 1H), 3.15 (d, $J = 14.8$ Hz, 1H), 6.71 (s, 1H), 7.03 (d, $J = 8.4$ Hz, 1H), 7.21-7.24 (m, 2H), 7.29 (t, $J = 7.6$ Hz, 1H), 7.39 (t, $J = 7.6$ Hz, 1H), 7.47-7.50 (m, 2H), 7.65 (t, $J = 8.0$ Hz, 1H), 7.89 (d, $J = 8.0$ Hz, 1H), 7.95-8.02 (m, 3H), 8.06 (d, $J = 9.2$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3) δ 19.6, 19.7, 25.5, 26.8, 42.3, 42.7, 47.9, 50.4, 58.6, 120.0, 125.2, 125.4, 125.9, 126.0, 126.1, 126.5, 126.7, 127.0, 127.9, 128.7, 128.9, 129.3, 129.5, 130.9, 132.4, 132.5, 133.2, 133.5, 134.1, 214.6 ppm; IR (KBr): 2958, 1742, 1619, 1594, 1506, 1471, 1404, 1367, 1325, 1264, 1213, 1149, 1047,

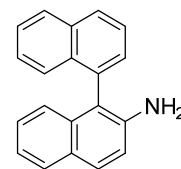


981, 867, 805, 781, 609, 567 cm^{-1} ; HRMS (FAB) Calcd for $\text{C}_{30}\text{H}_{29}\text{NO}_3\text{S}$ $[\text{M} + \text{Na}]^+$ 506.1766, found 506.1760.

Deprotection of **3jf** and **3jf'** was carried out according to the procedure for the deprotection of the Ms group (3 steps, 80% yield for *R*- and *S*-isomers, respectively).

1-(Naphthalene-8-yl)naphthalen-2-amine (7jf)¹⁰⁾

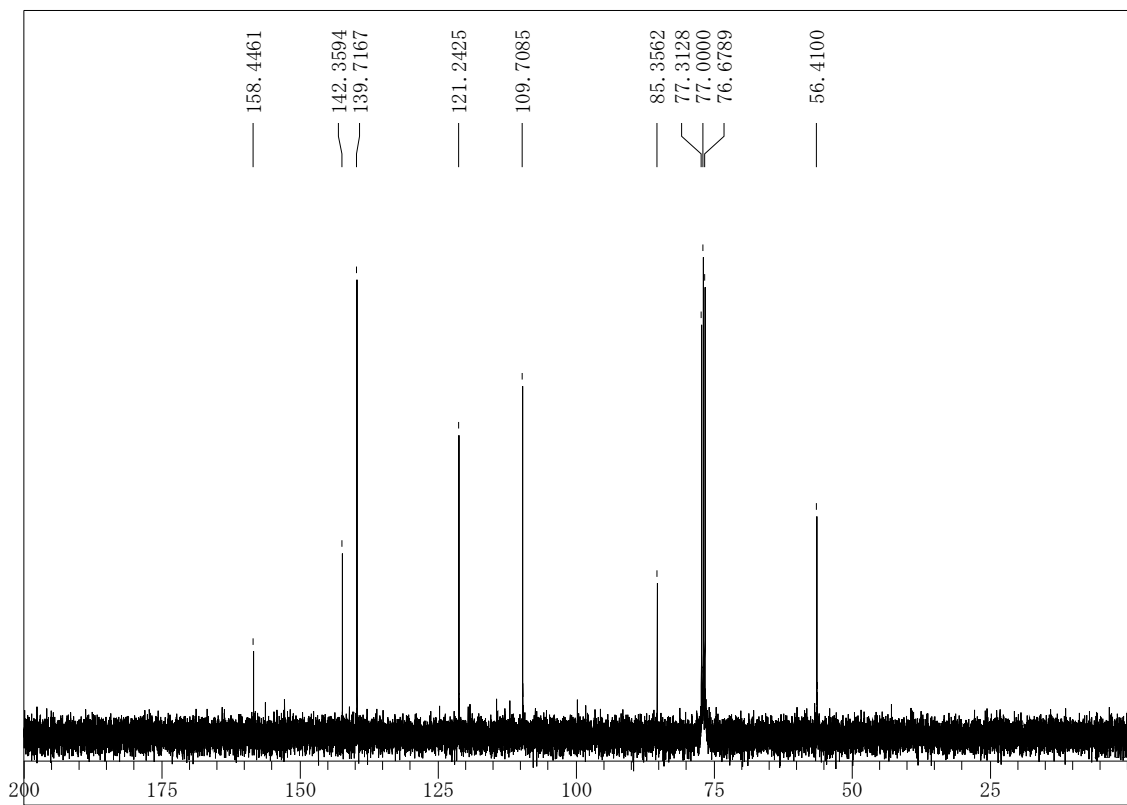
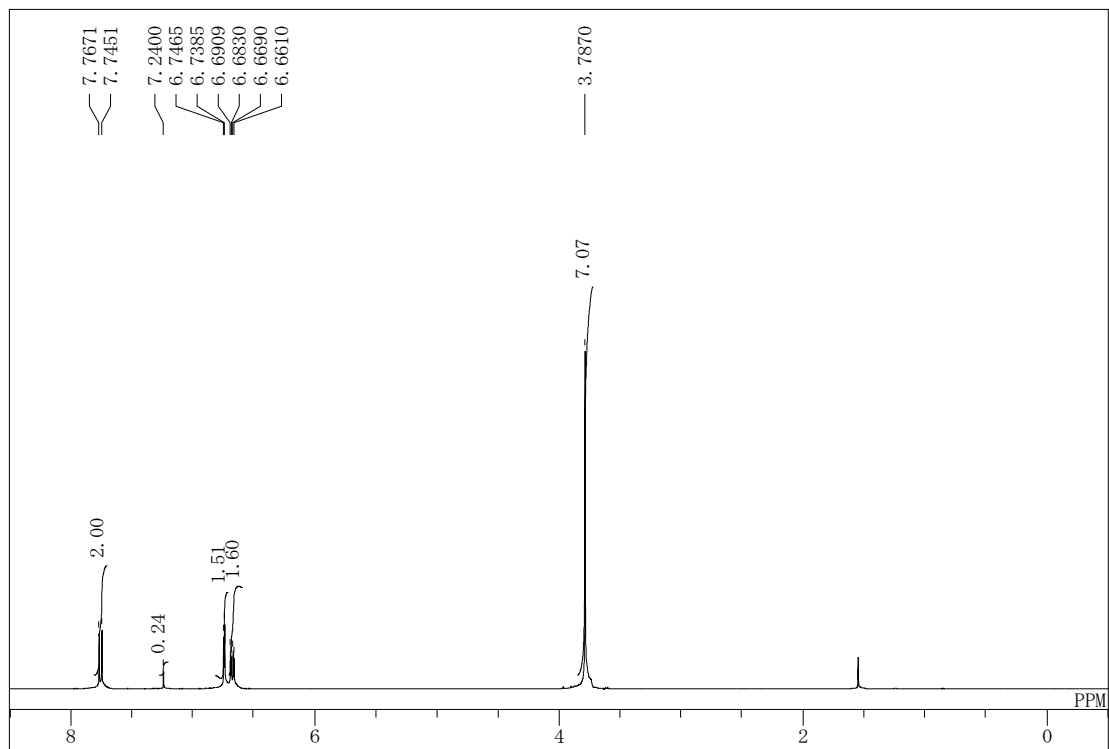
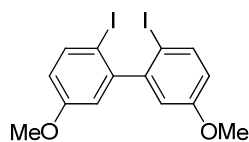
Colorless solid; ¹H NMR (400 MHz, CDCl₃) δ 3.56 (bs, 2H), 7.00 (dd, *J* = 0.8, 8.0 Hz, 1H), 7.10 (d, *J* = 8.0 Hz, 1H), 7.13-7.23 (m, 2H), 7.28-7.32 (m, 1H), 7.40 (d, *J* = 8.4 Hz, 1H), 7.48 (td, *J* = 8.4, 1.2 Hz, 2H), 7.62 (dd, *J* = 6.8, 8.0 Hz, 1H), 7.78 (dd, *J* = 6.8, 8.0 Hz, 2H), 7.95 (d, *J* = 8.0 Hz, 1H), 7.96 (d, *J* = 8.0 Hz, 1H) ppm.



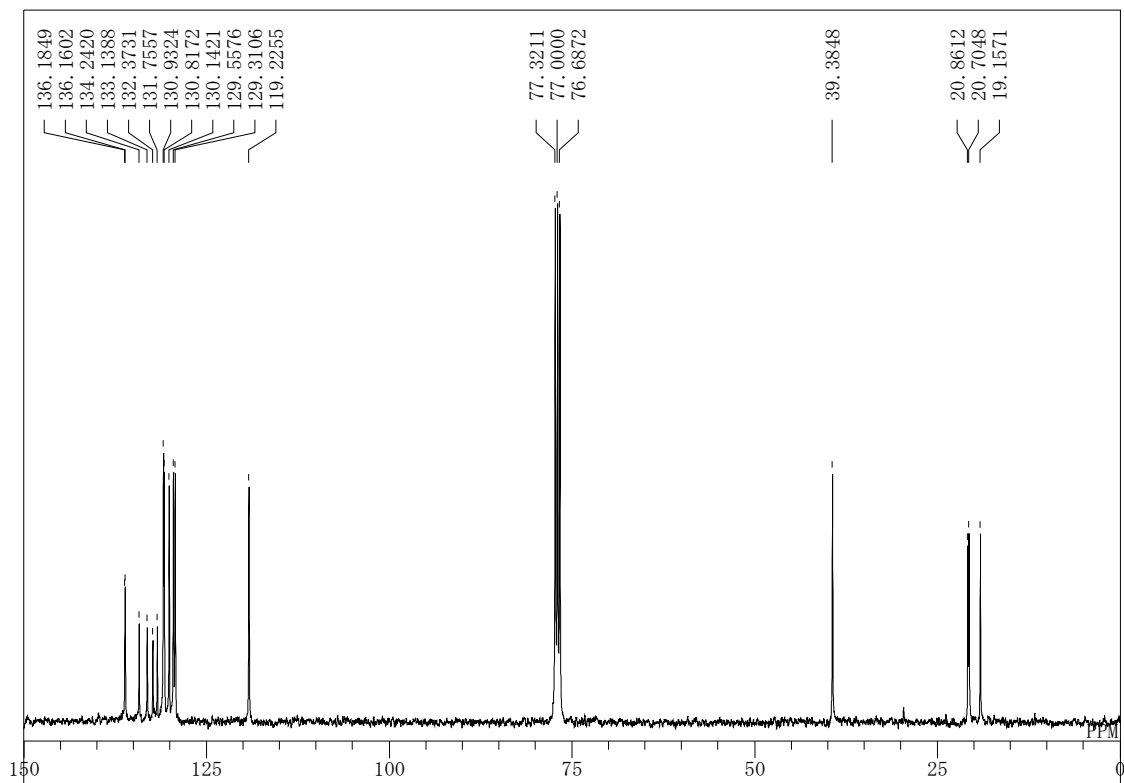
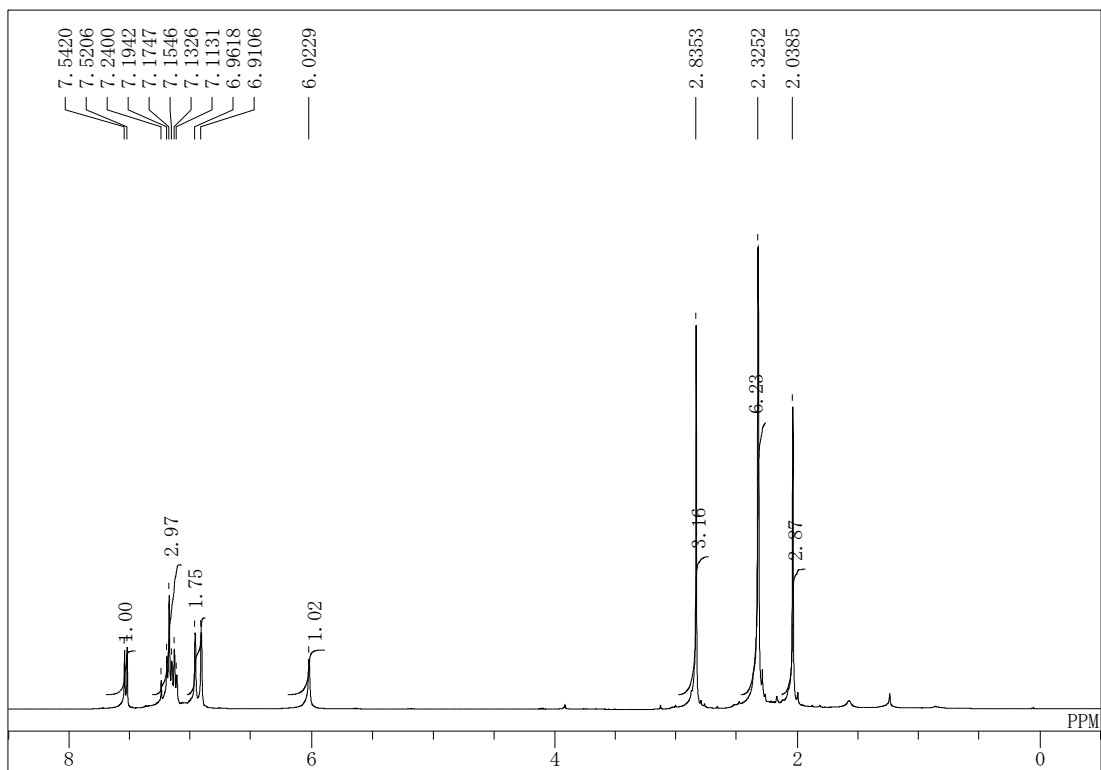
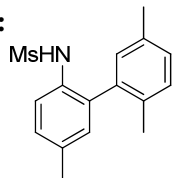
The enantiomeric excesses of (*R*)- and (*S*)-**7jf** were determined as >96% by HPLC with a Daicel Chiralpac OD-H (hexane/*i*-propanol = 90 : 1, 0.8 mL/min), respectively: *t*_R = 9.8 min for *S* isomer and *t*_R = 12.1 min for *R* isomer.

8. Spectrum Chart of the Catalyst and Products

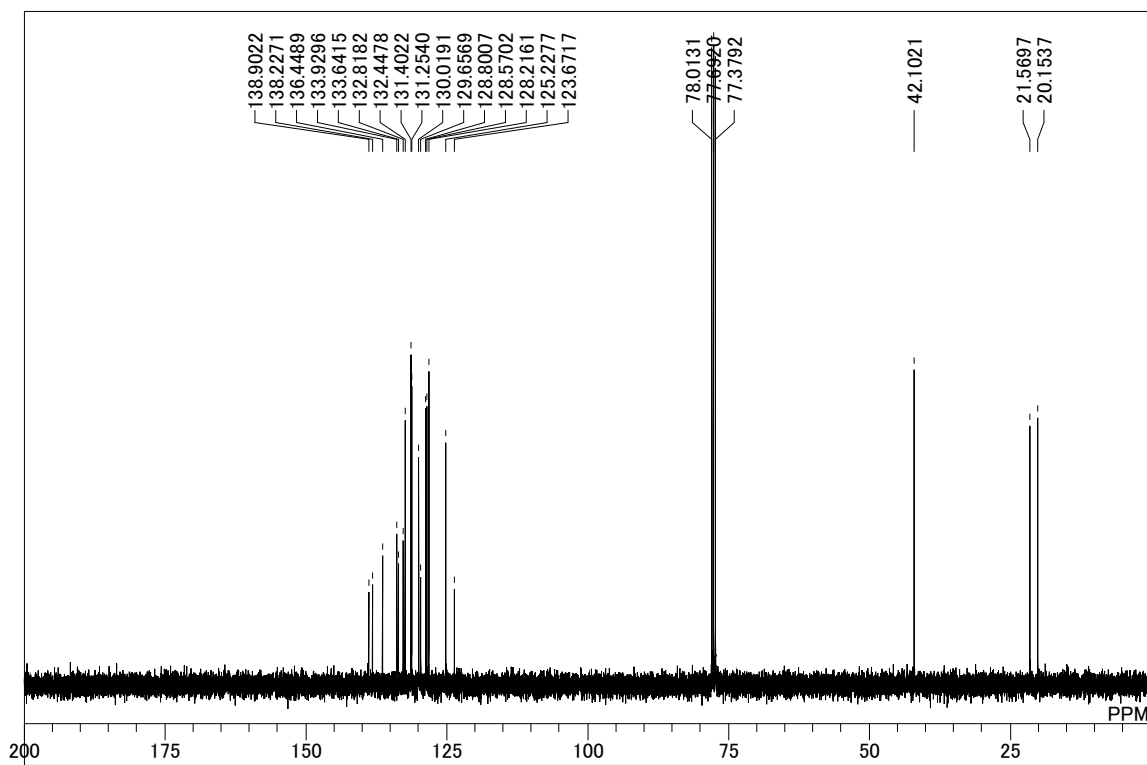
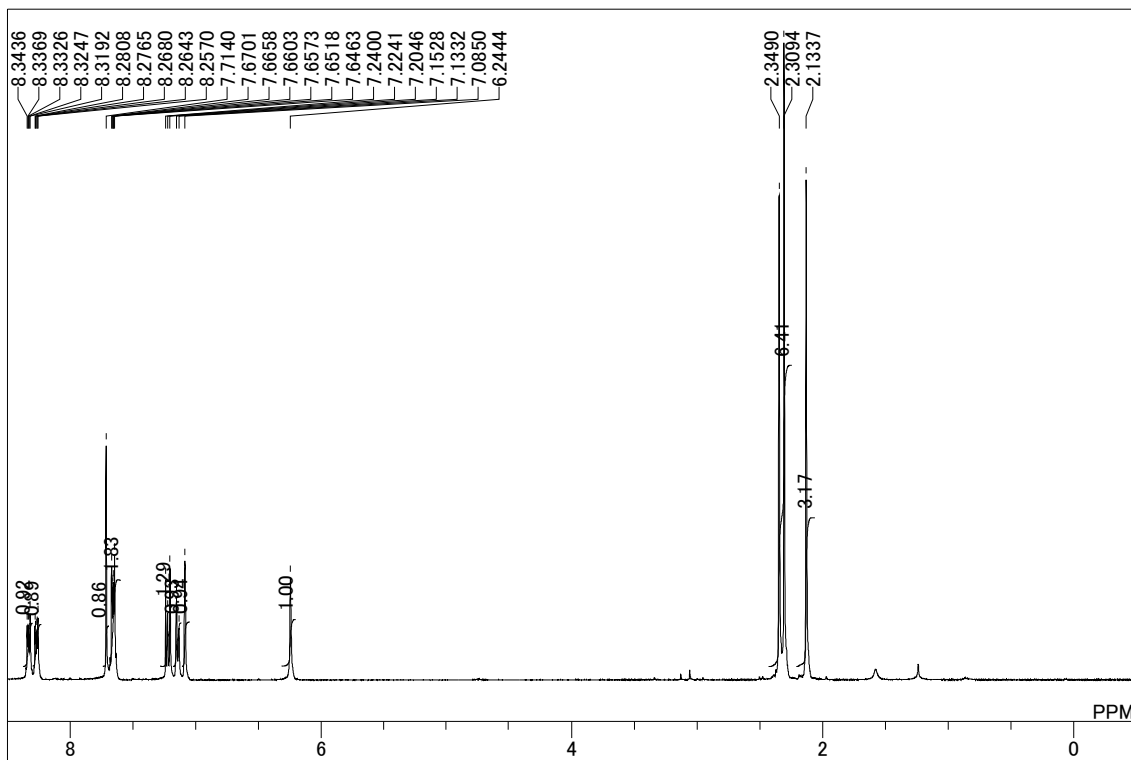
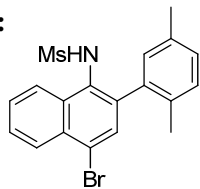
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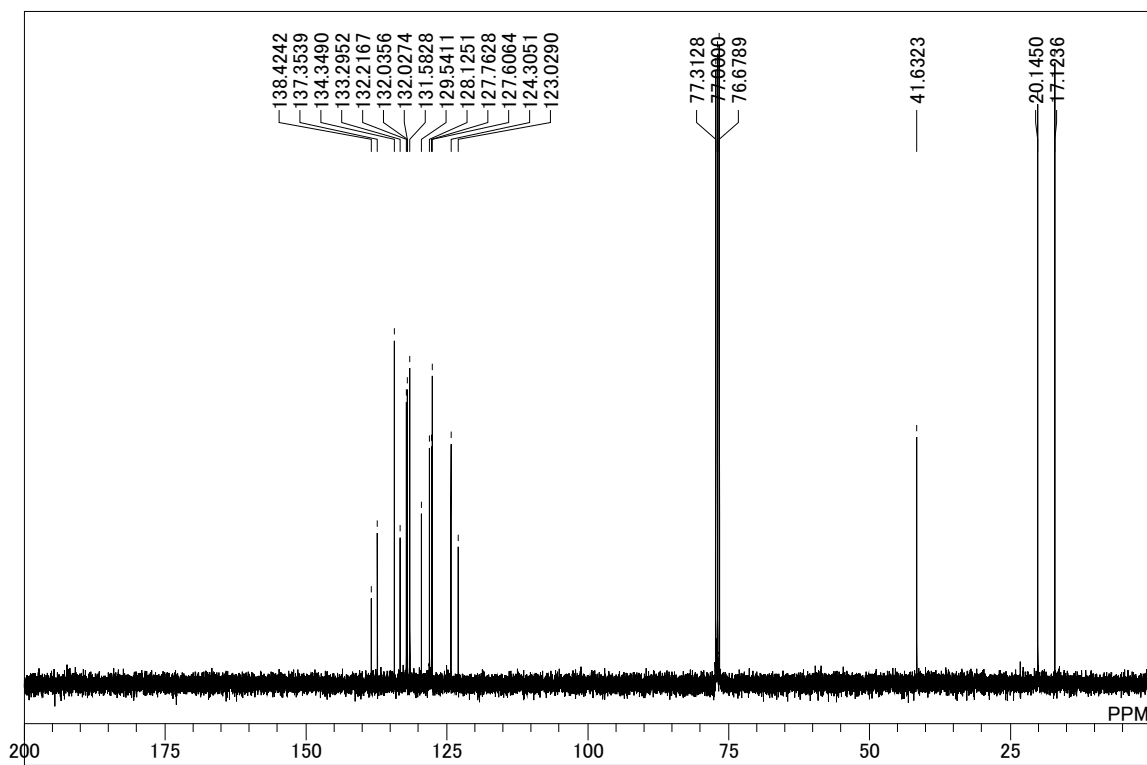
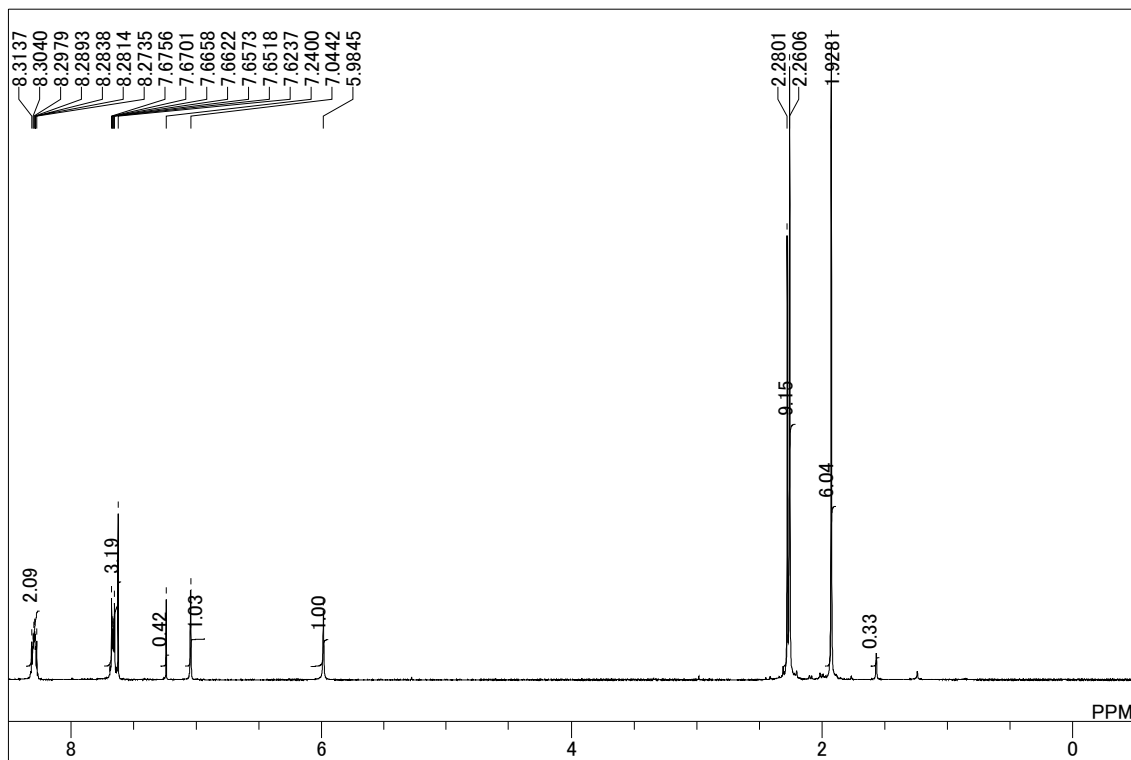
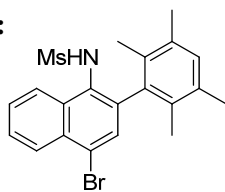
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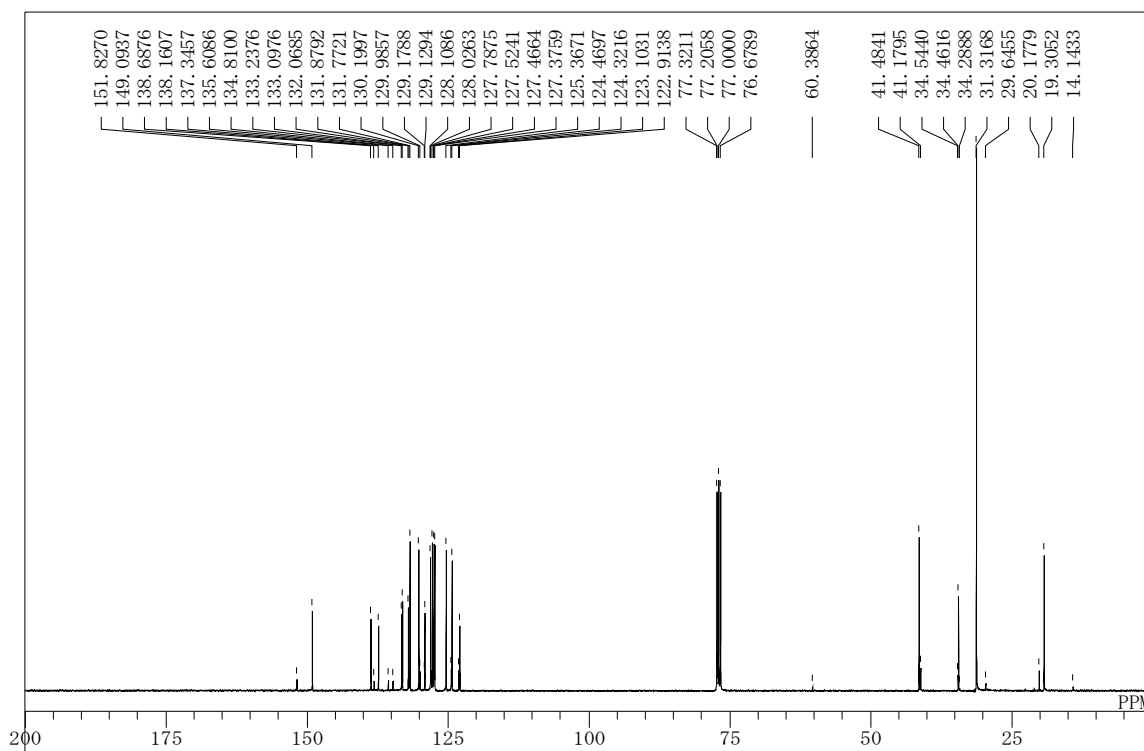
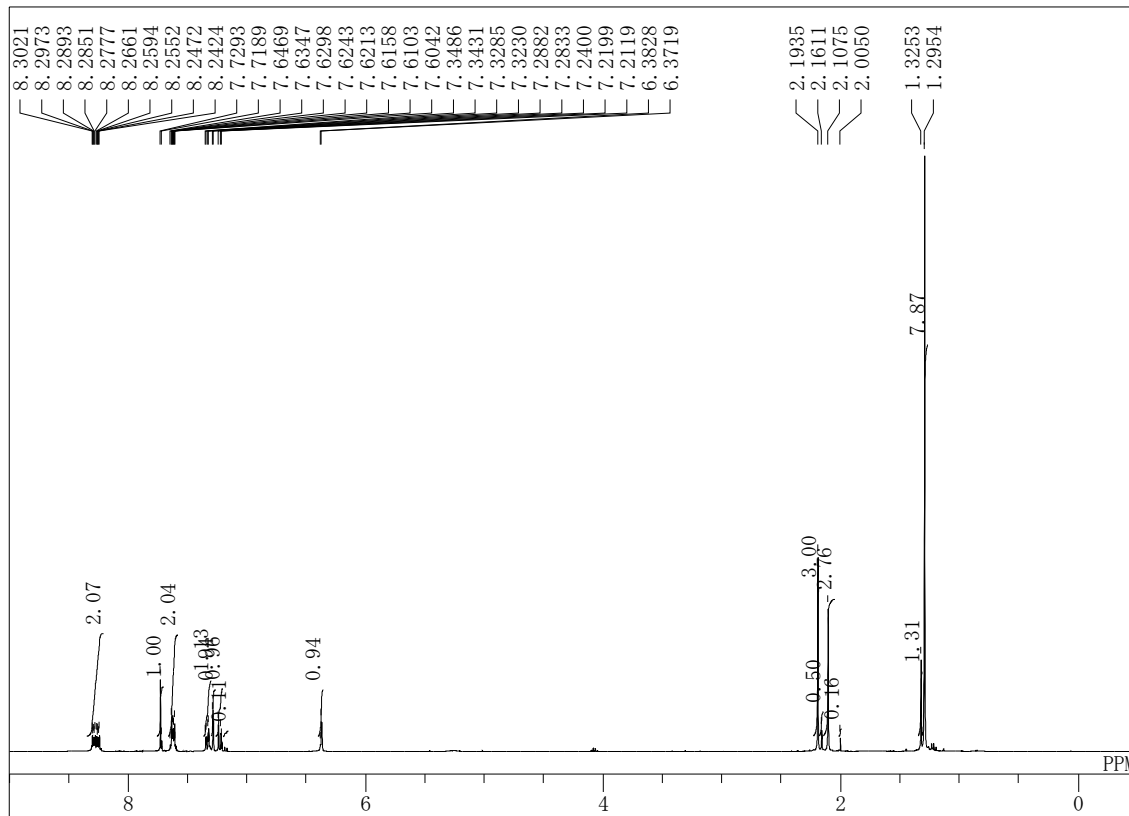
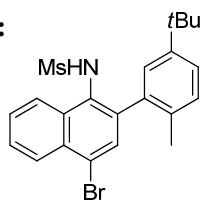
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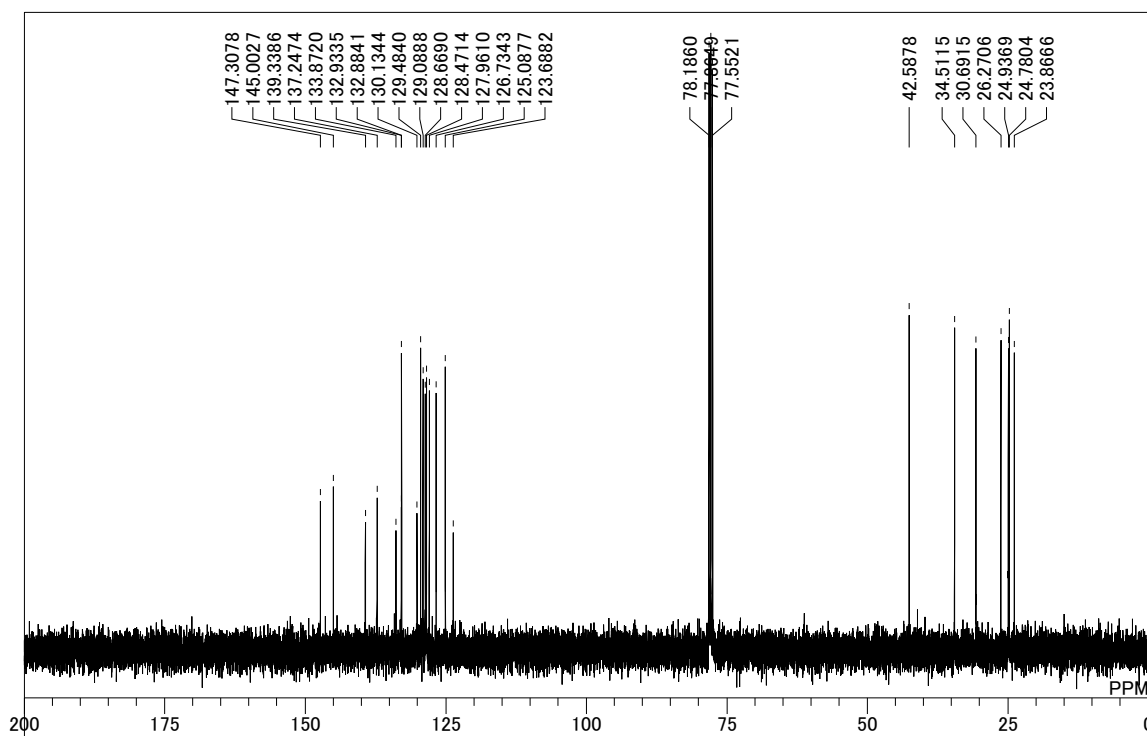
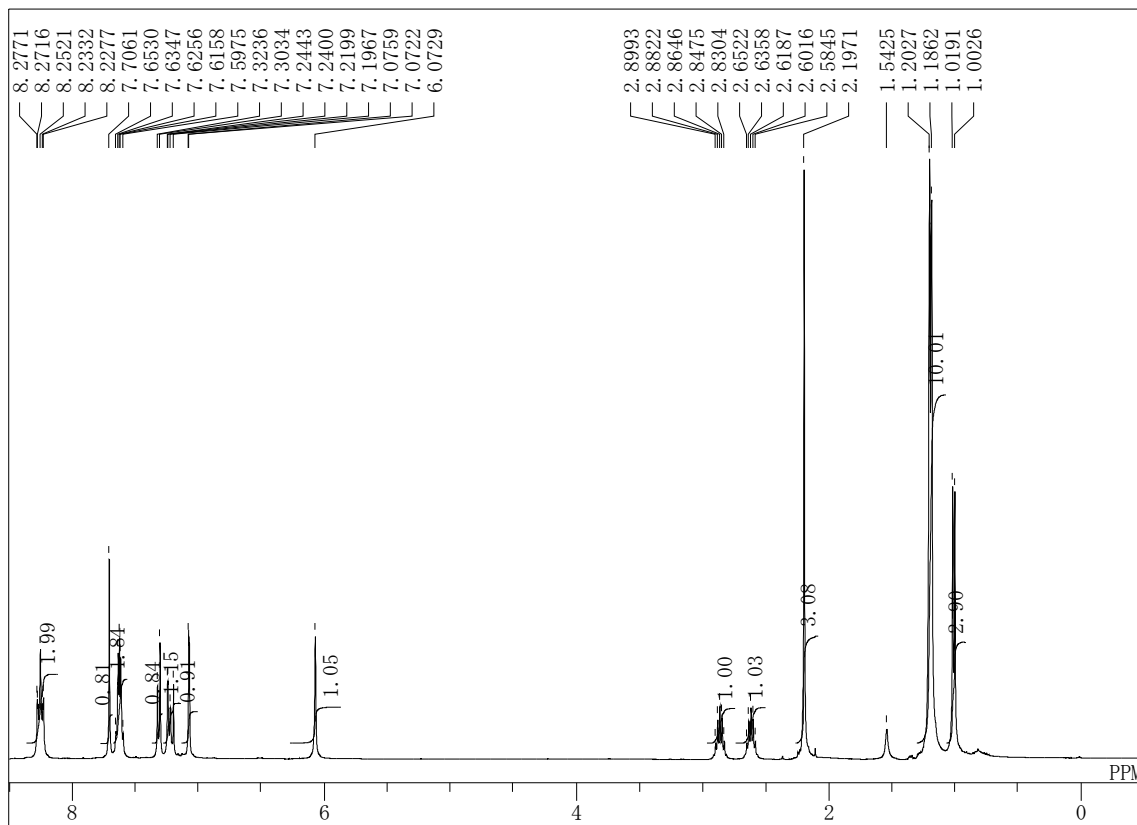
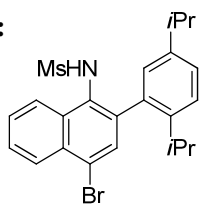
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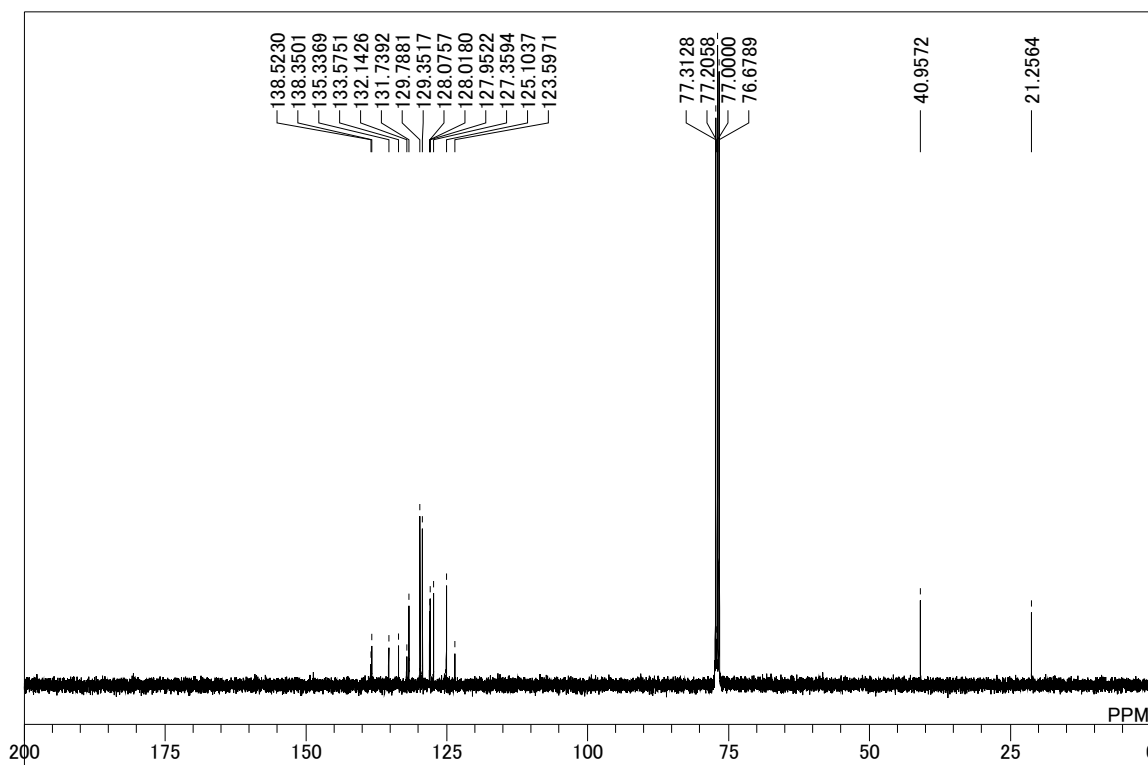
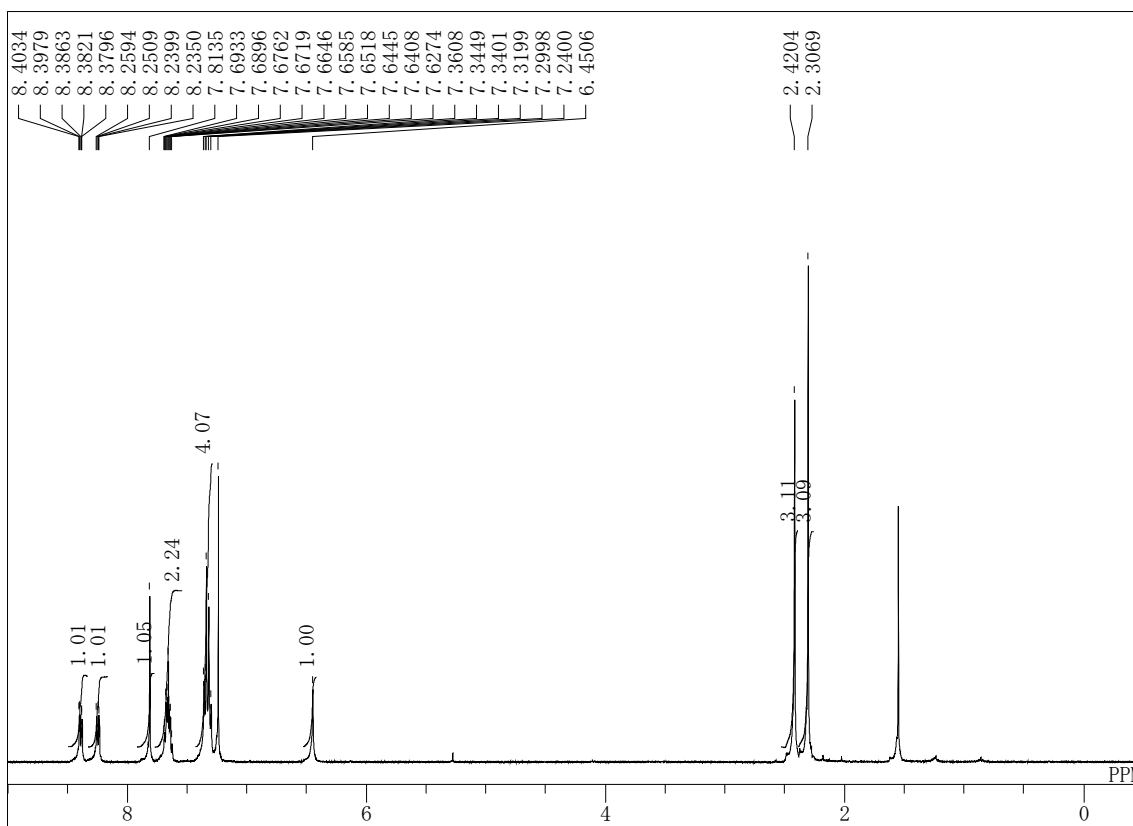
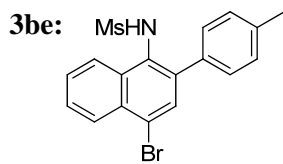


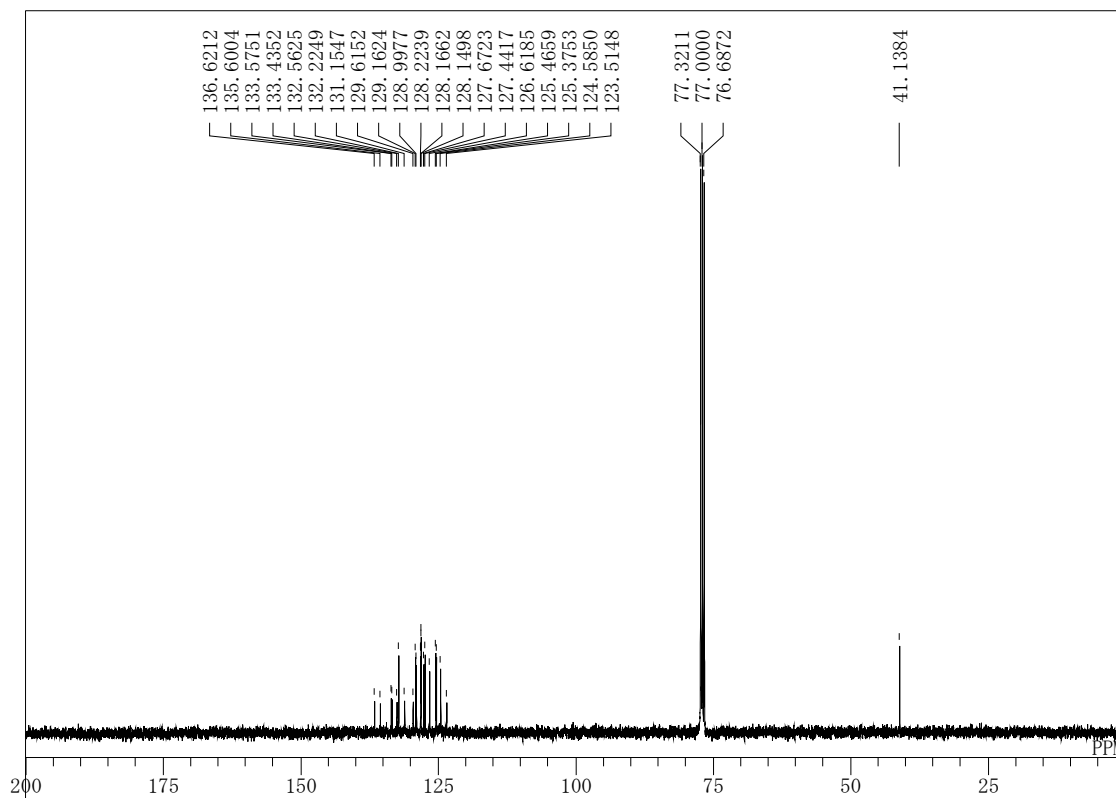
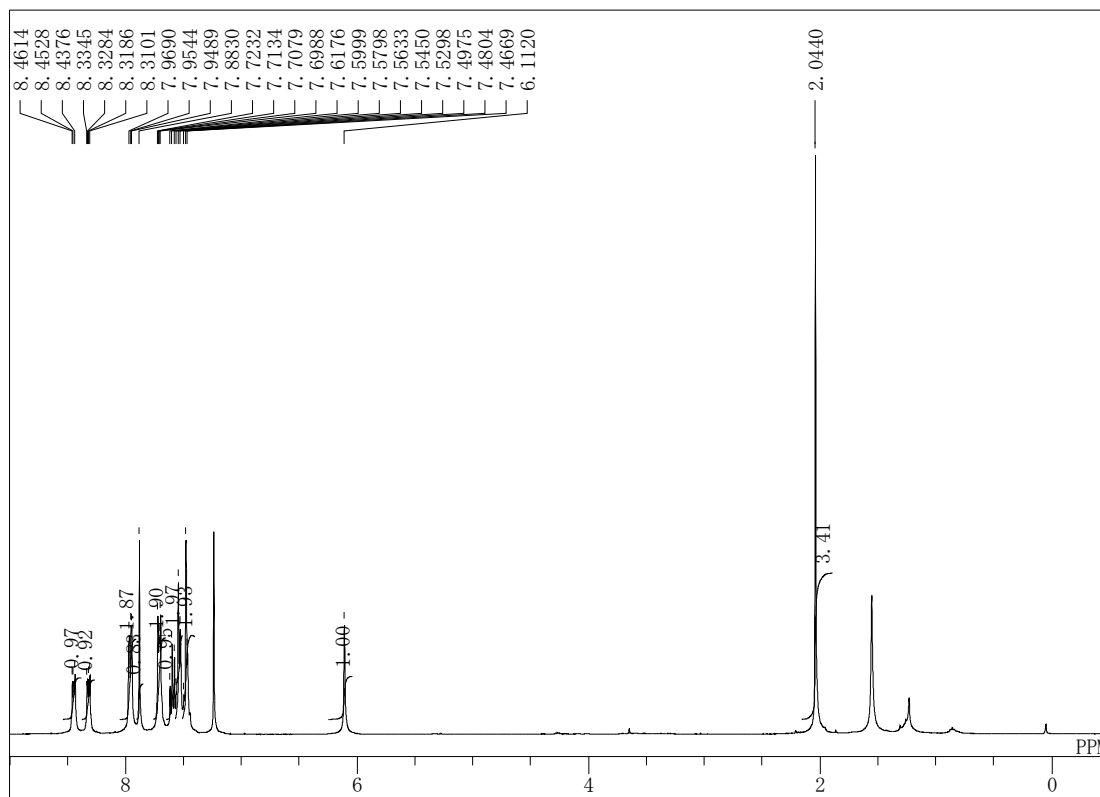
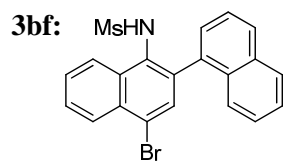
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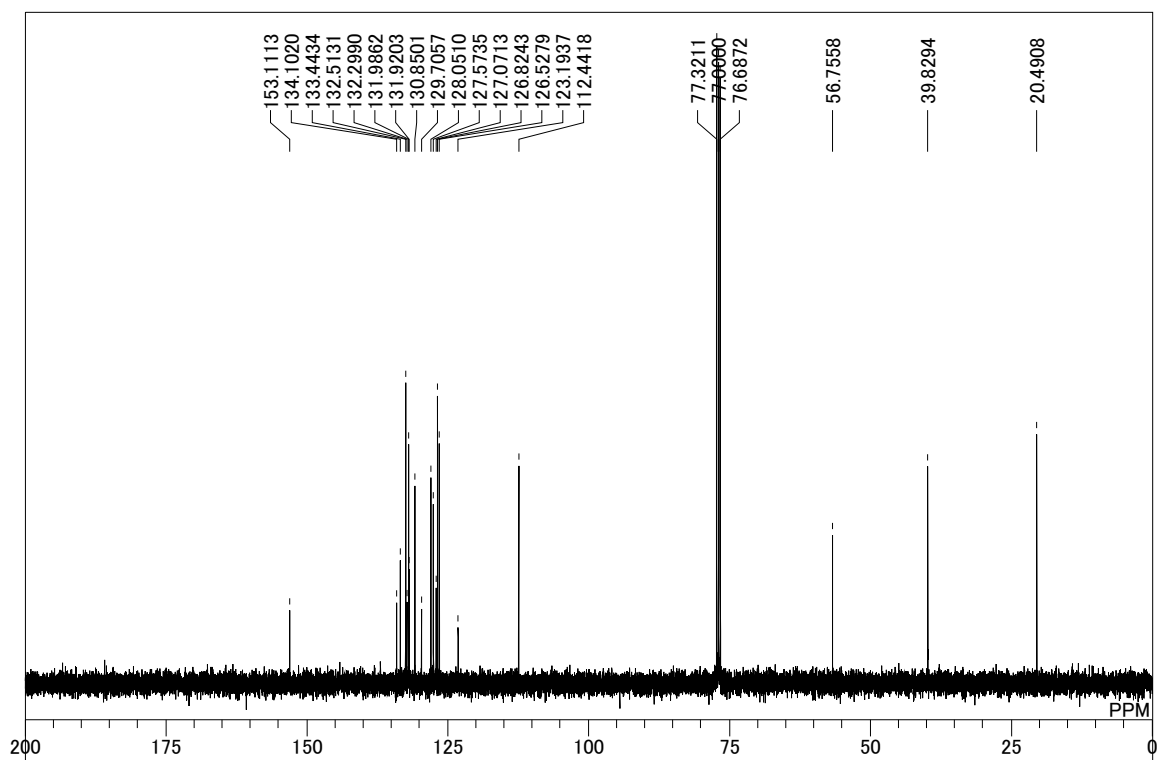
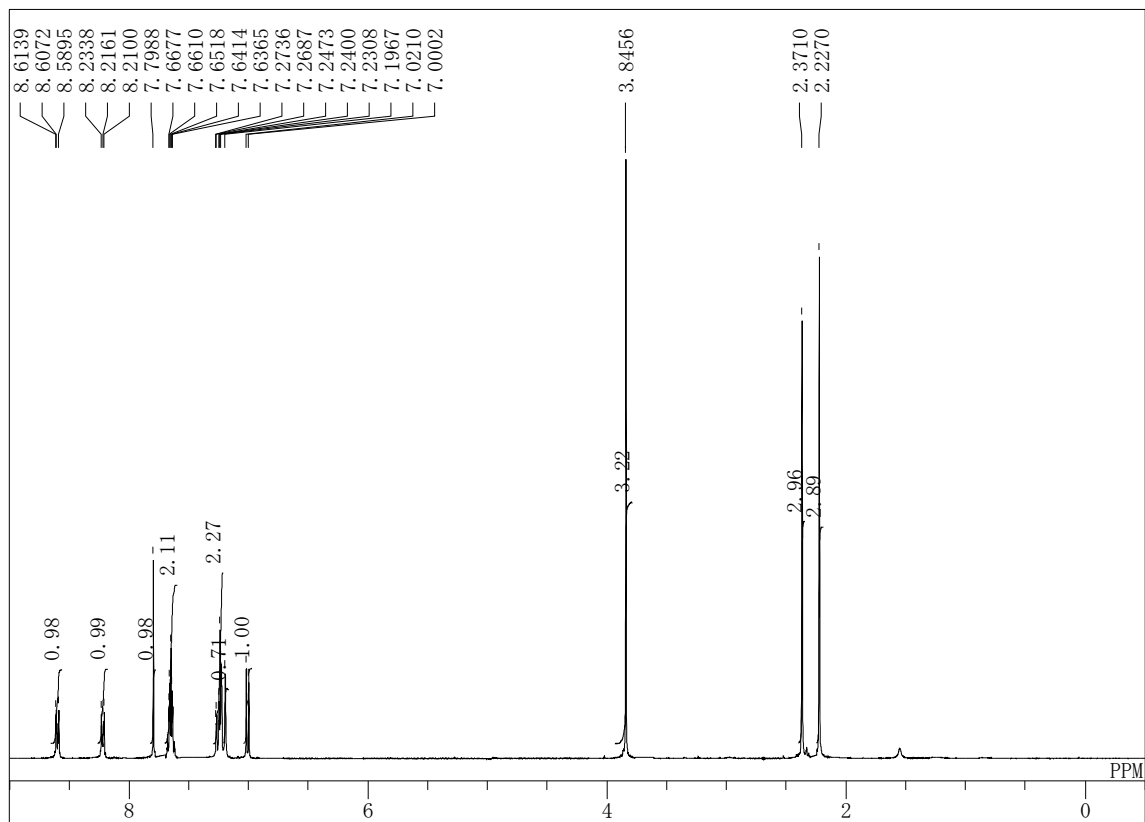
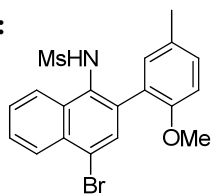
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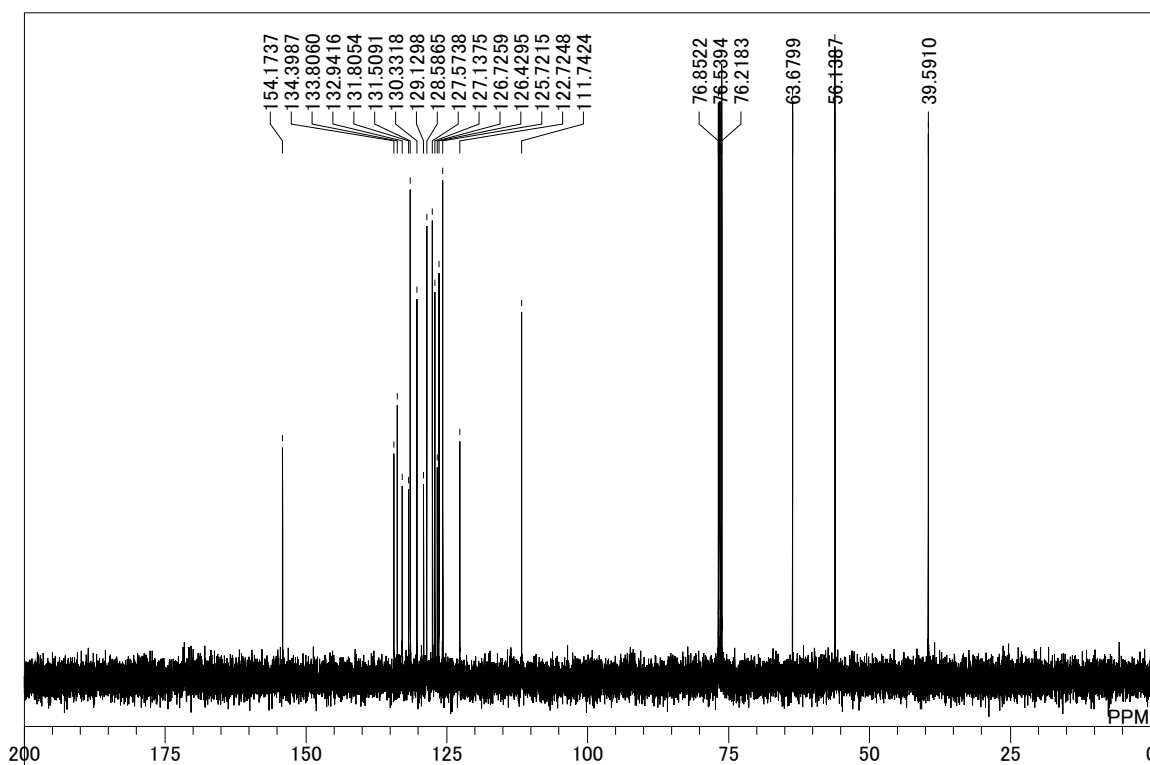
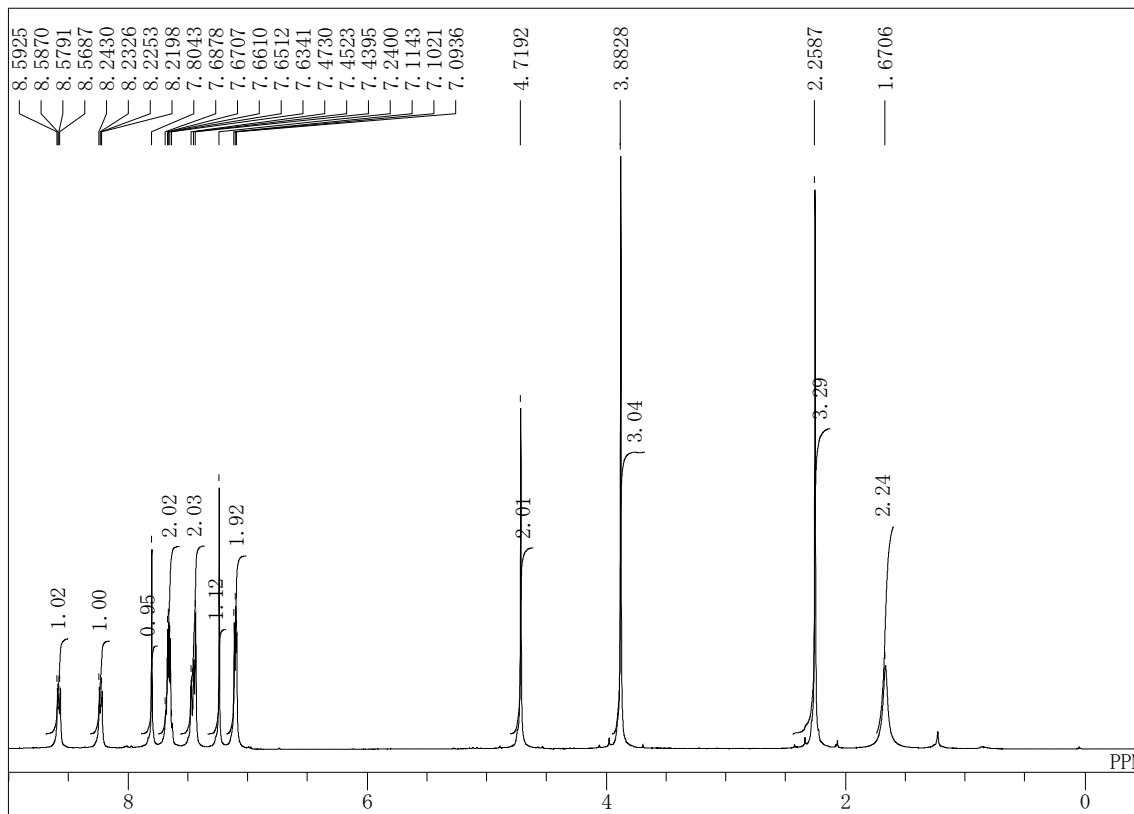
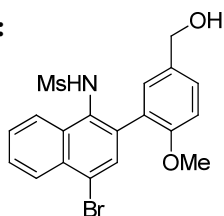




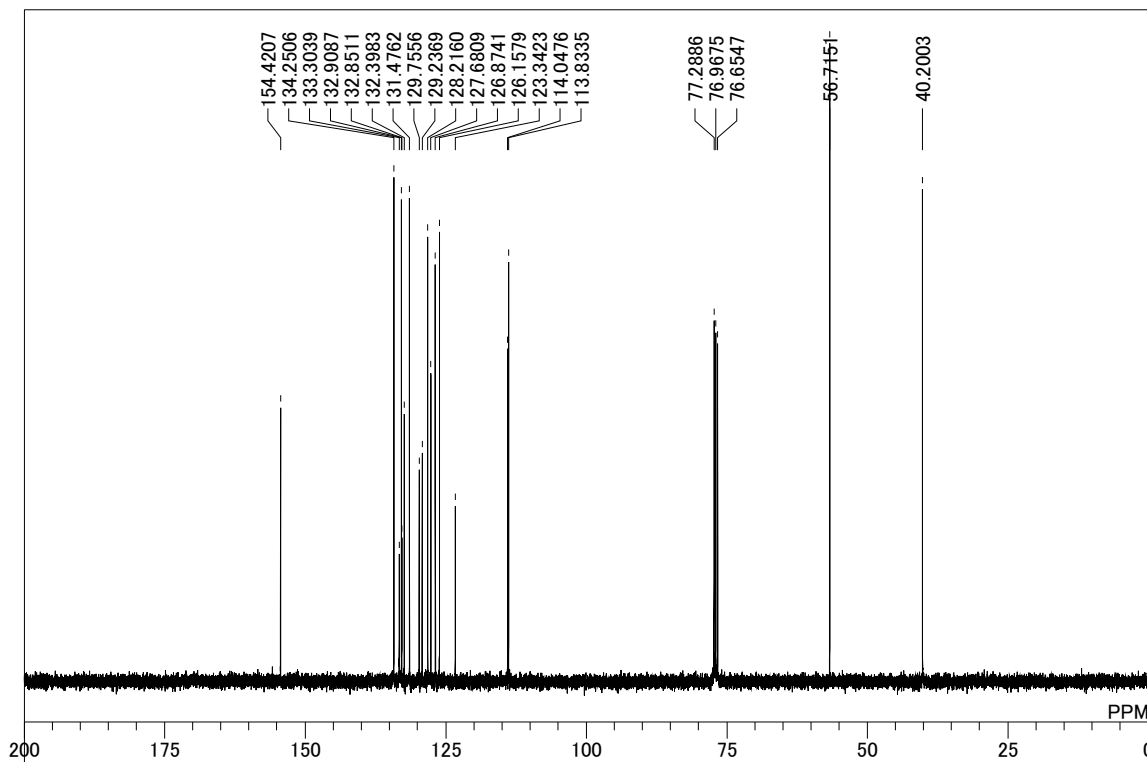
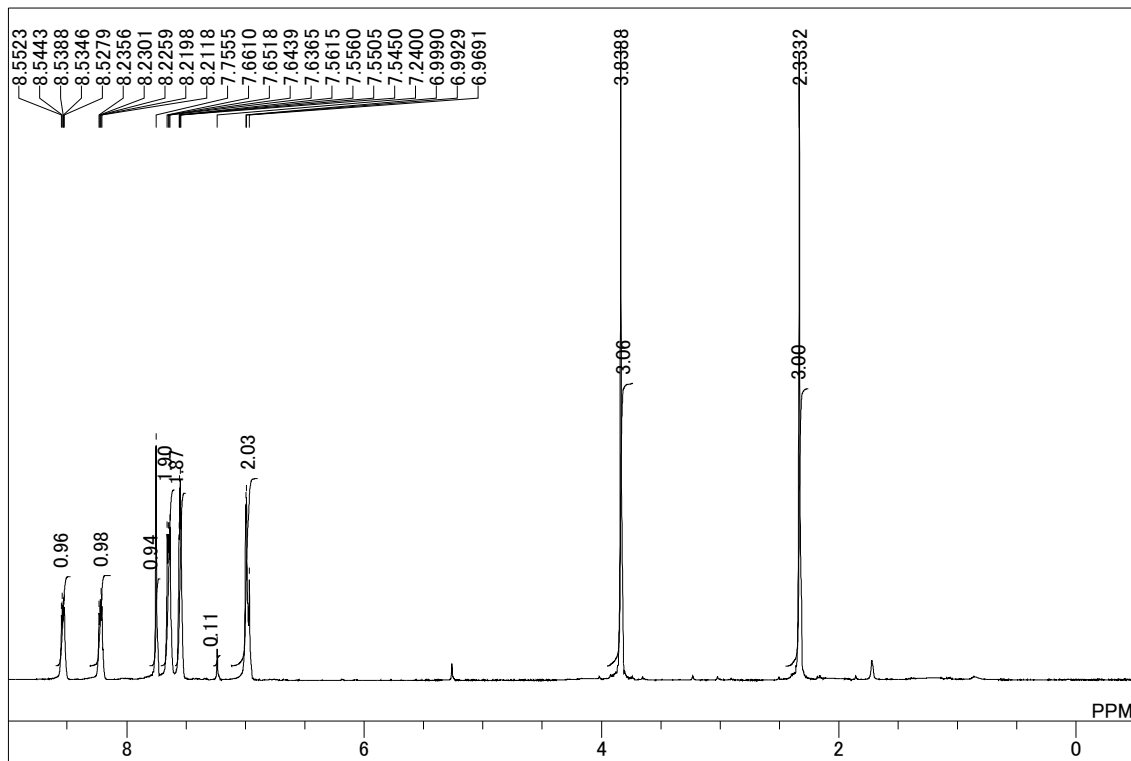
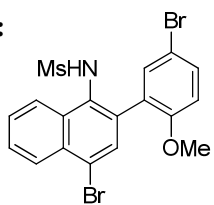
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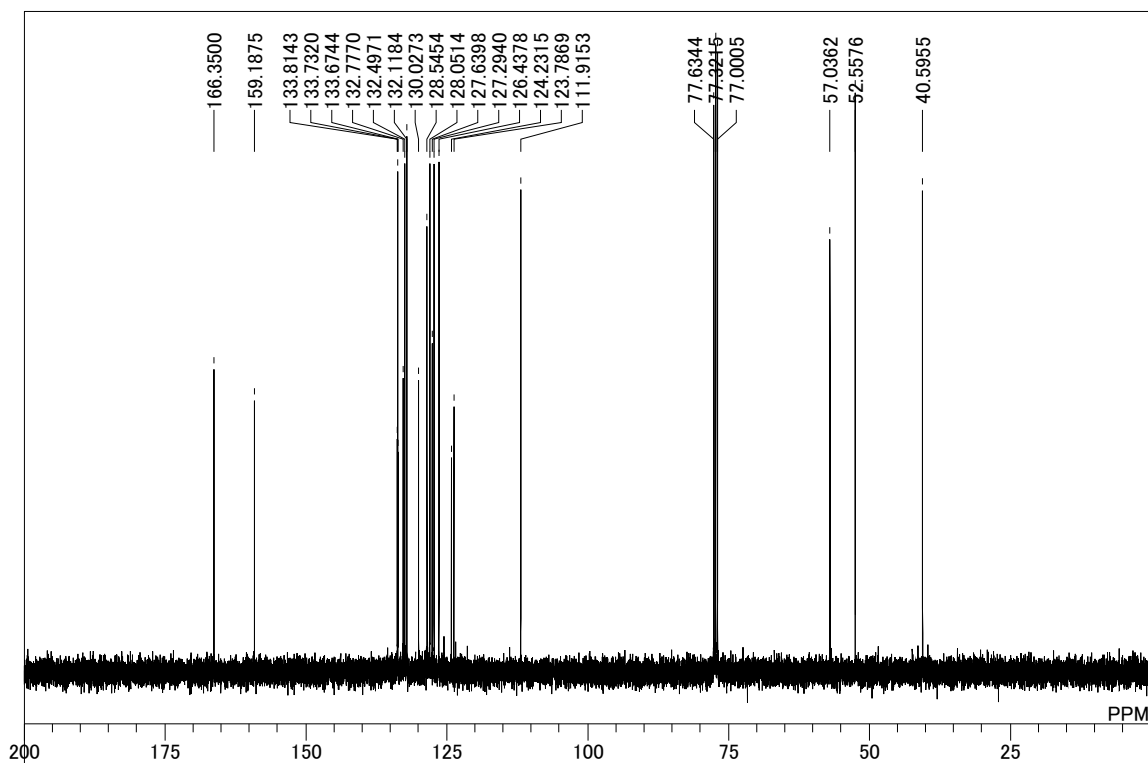
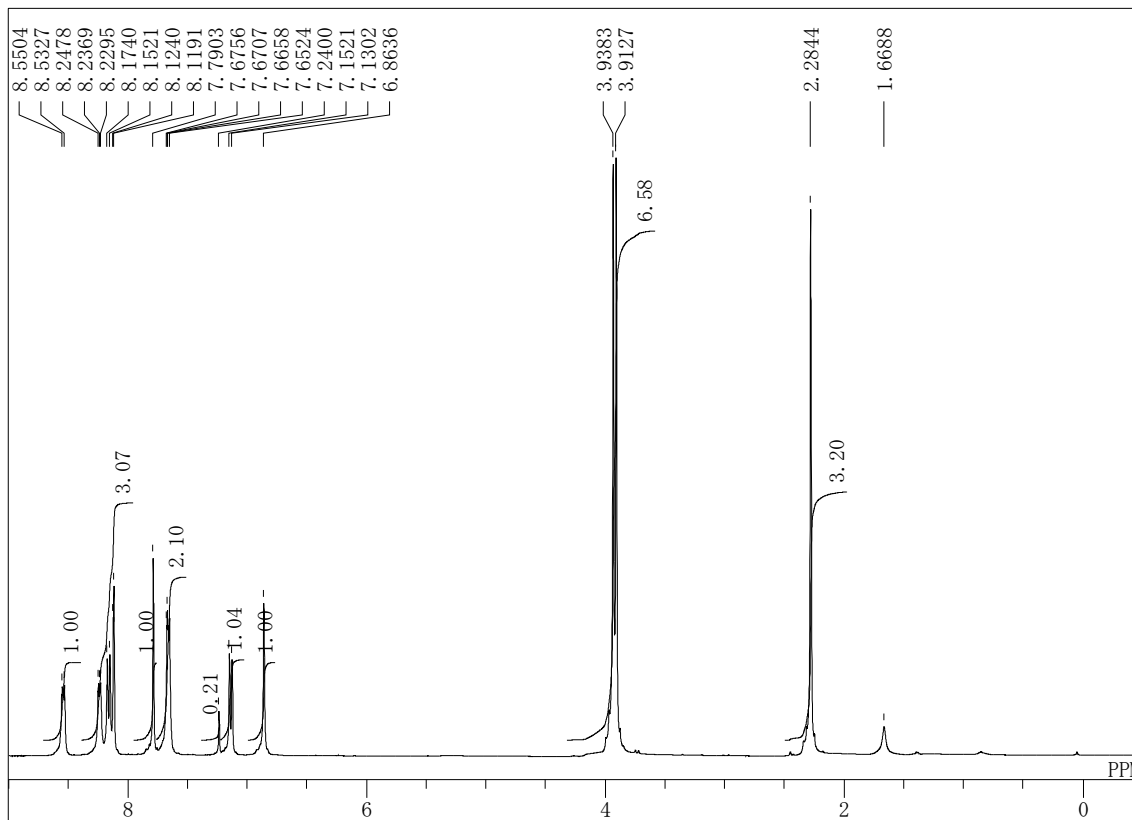
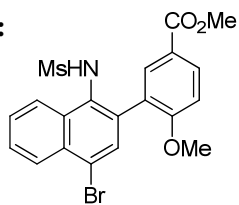
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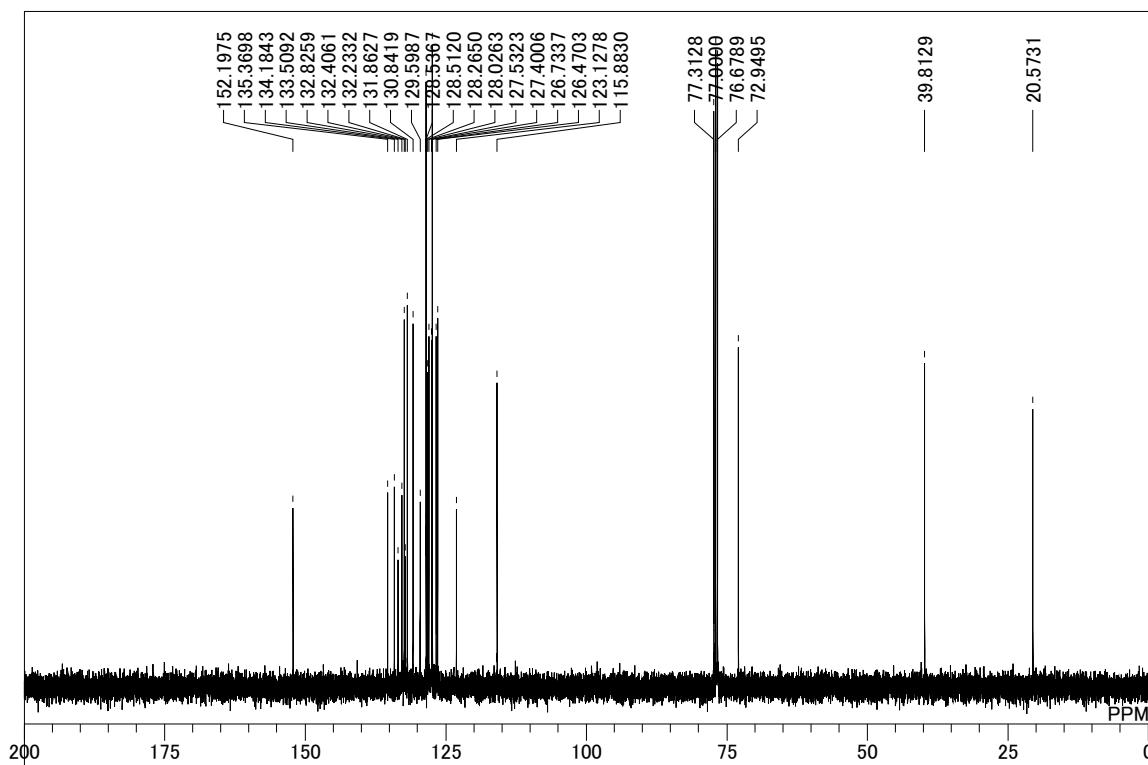
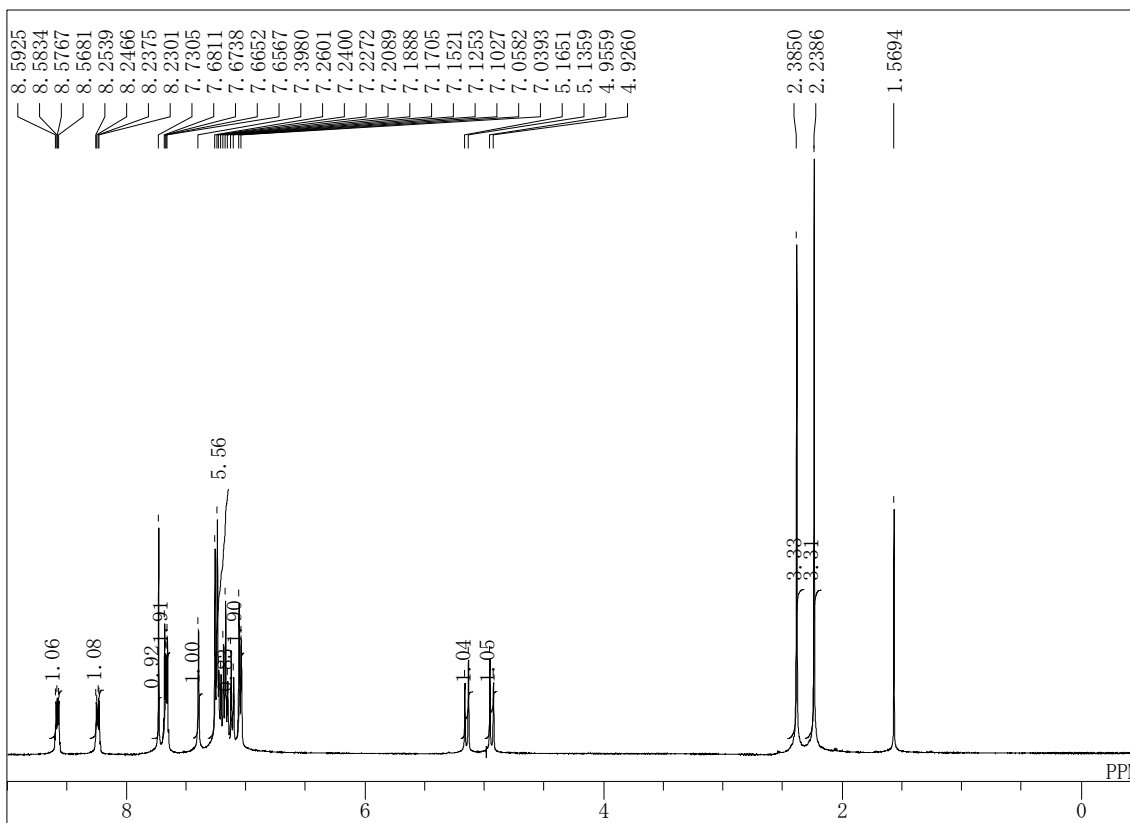
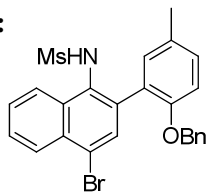
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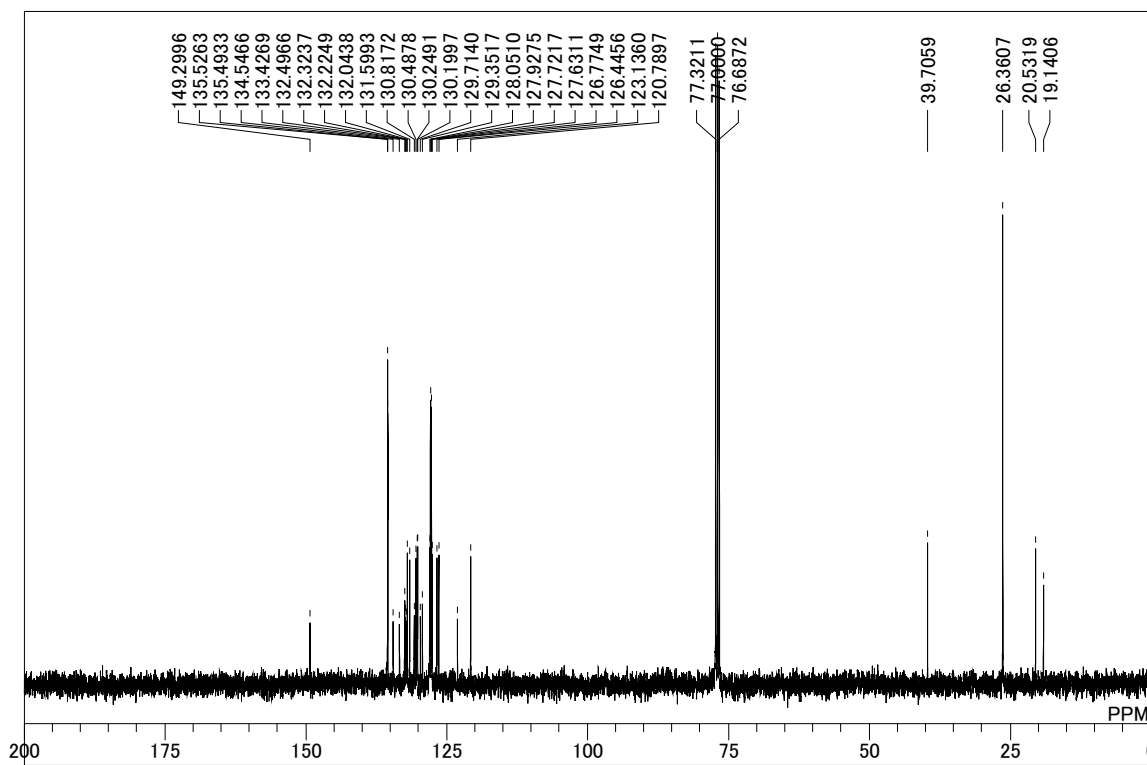
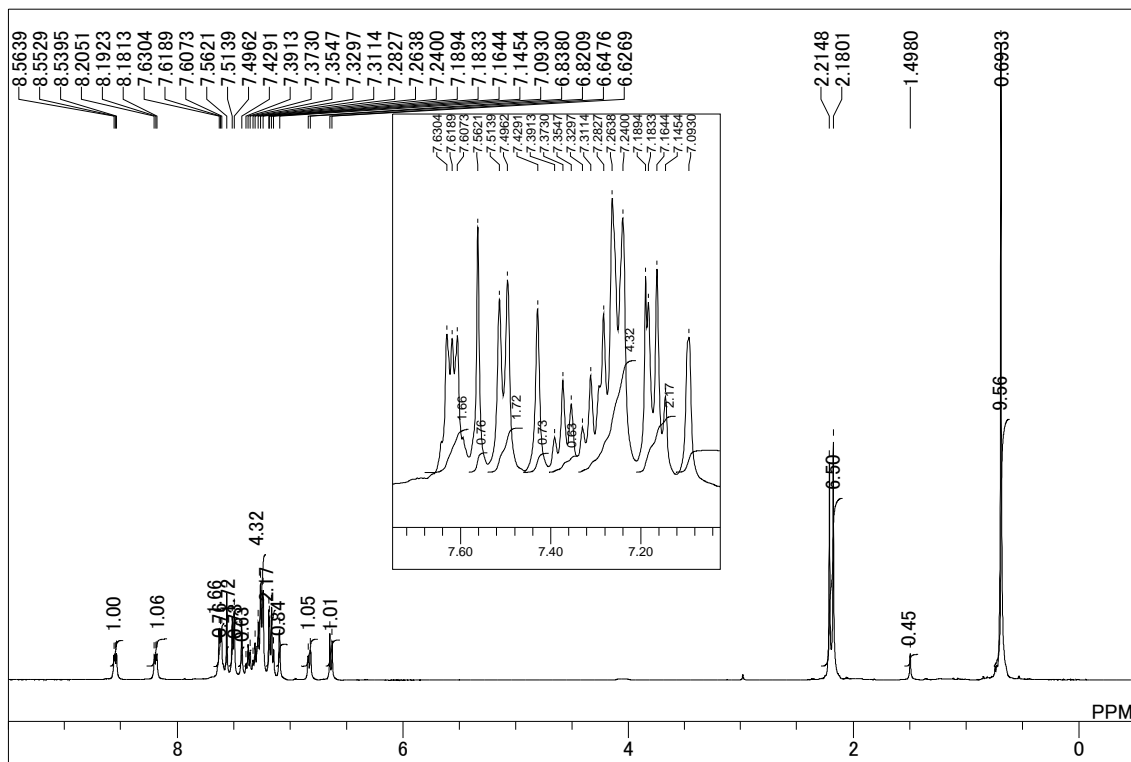
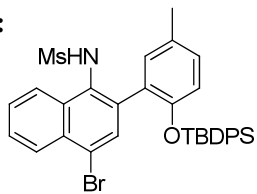
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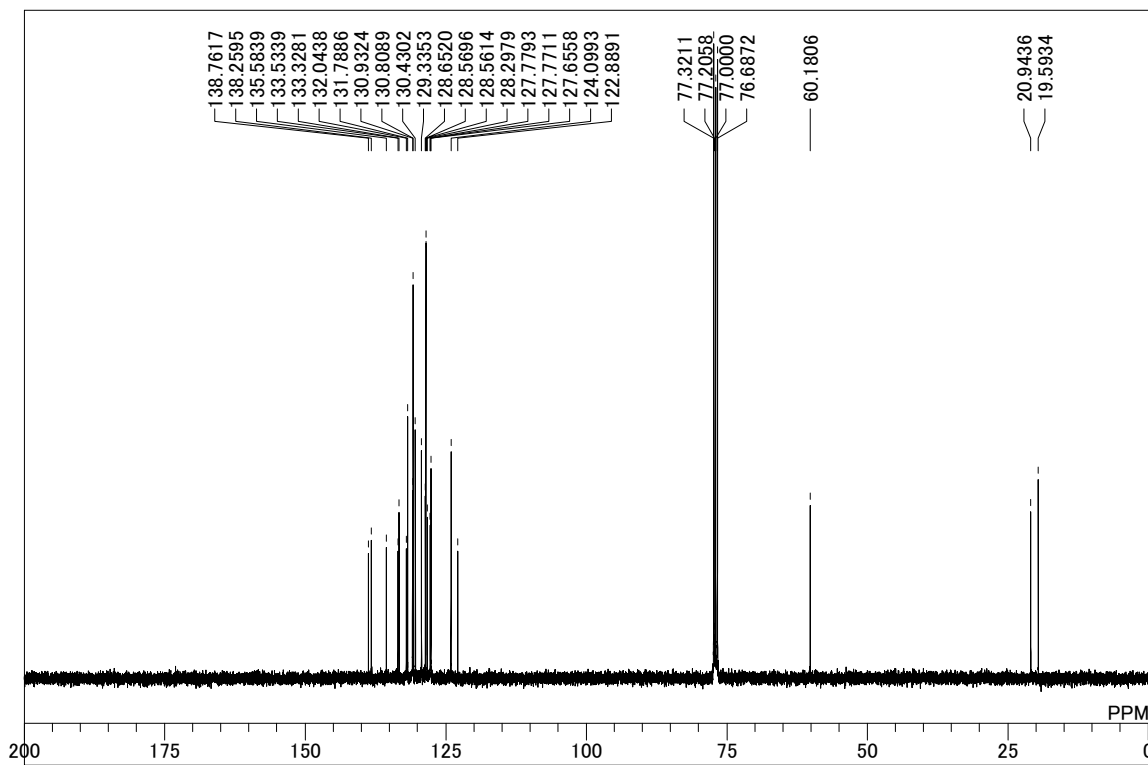
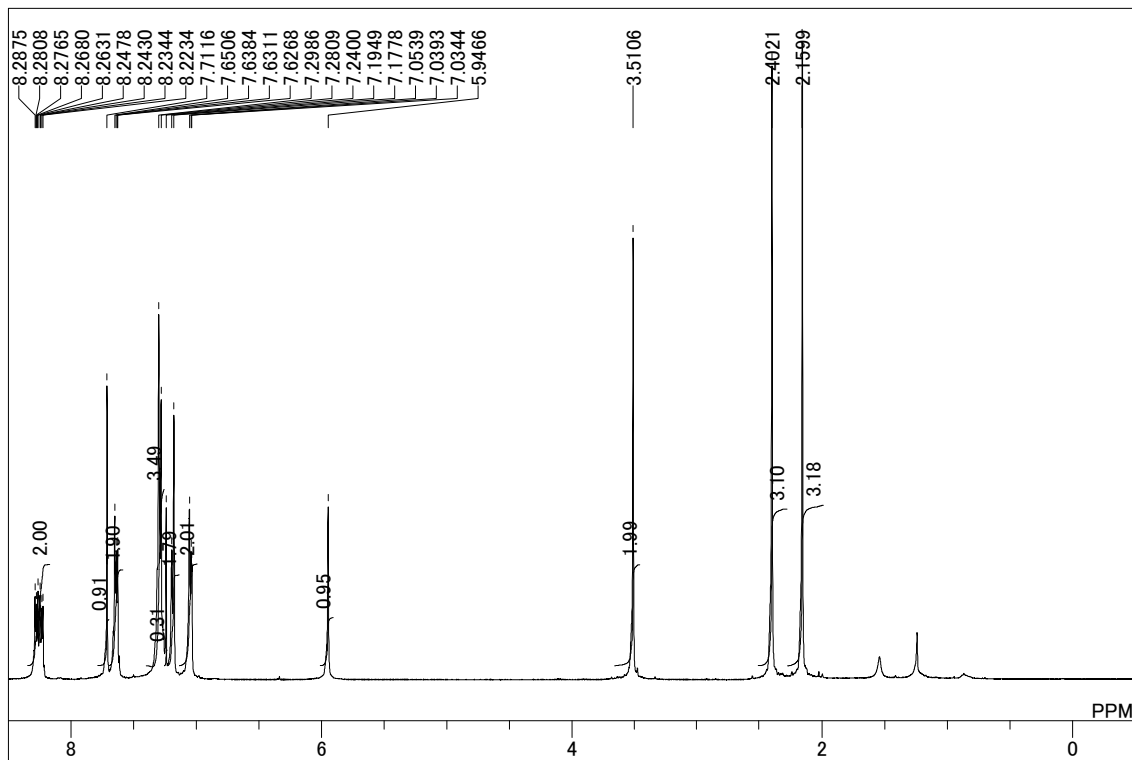
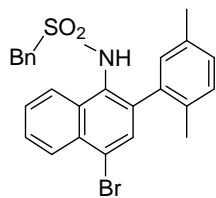
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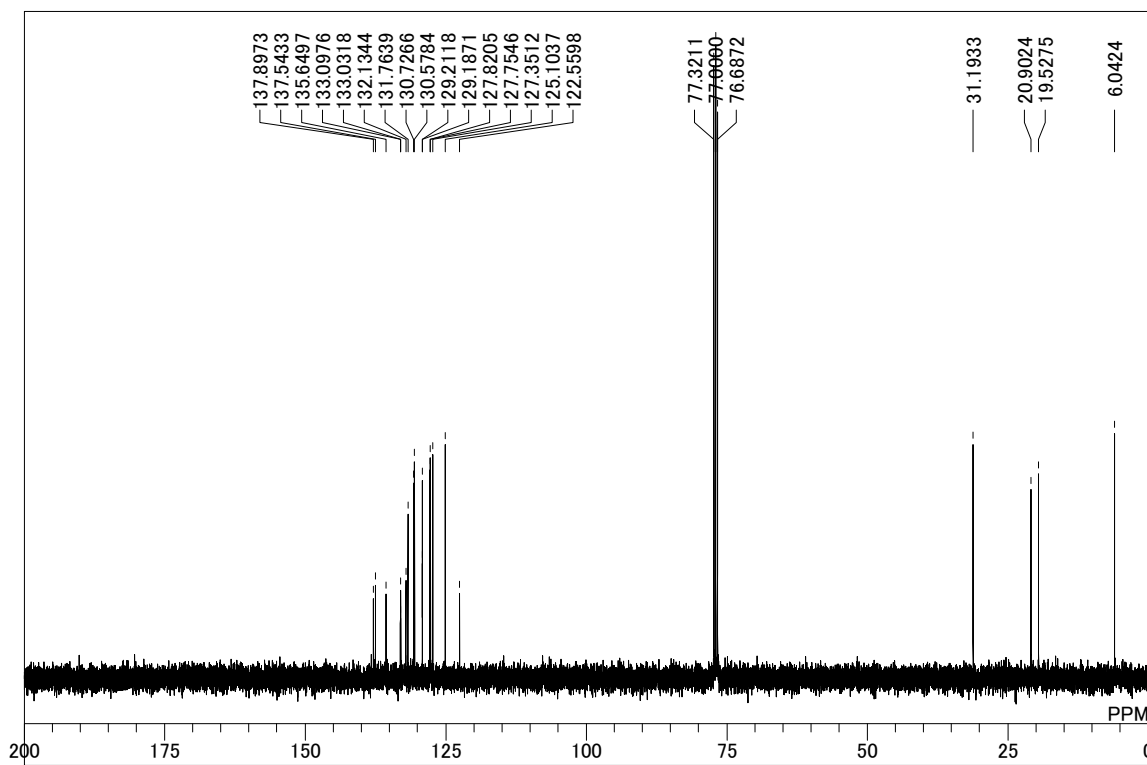
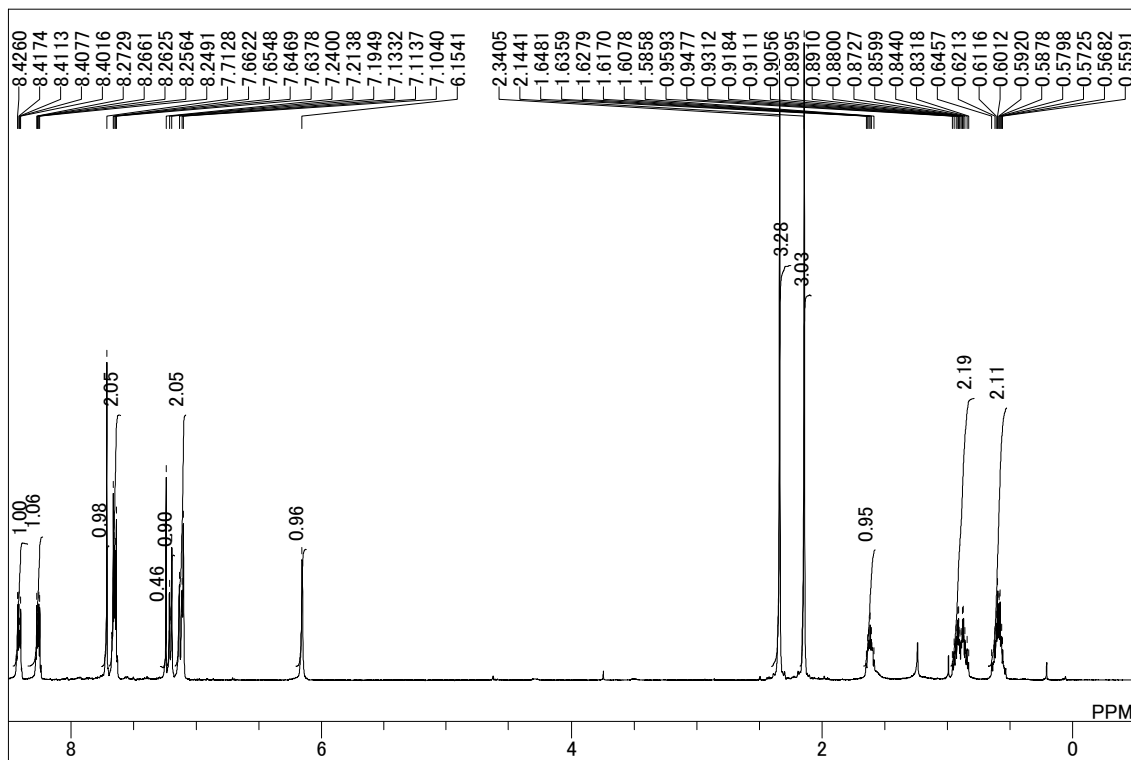
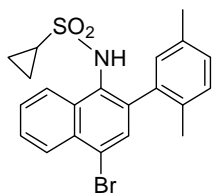
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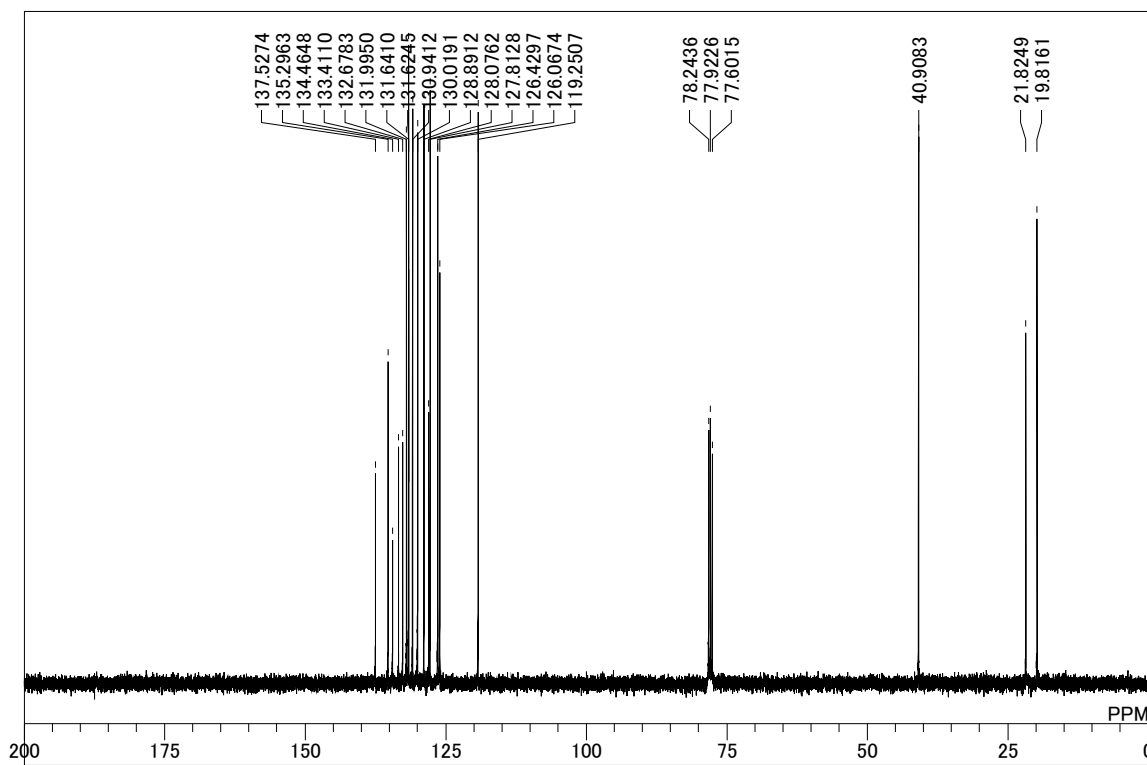
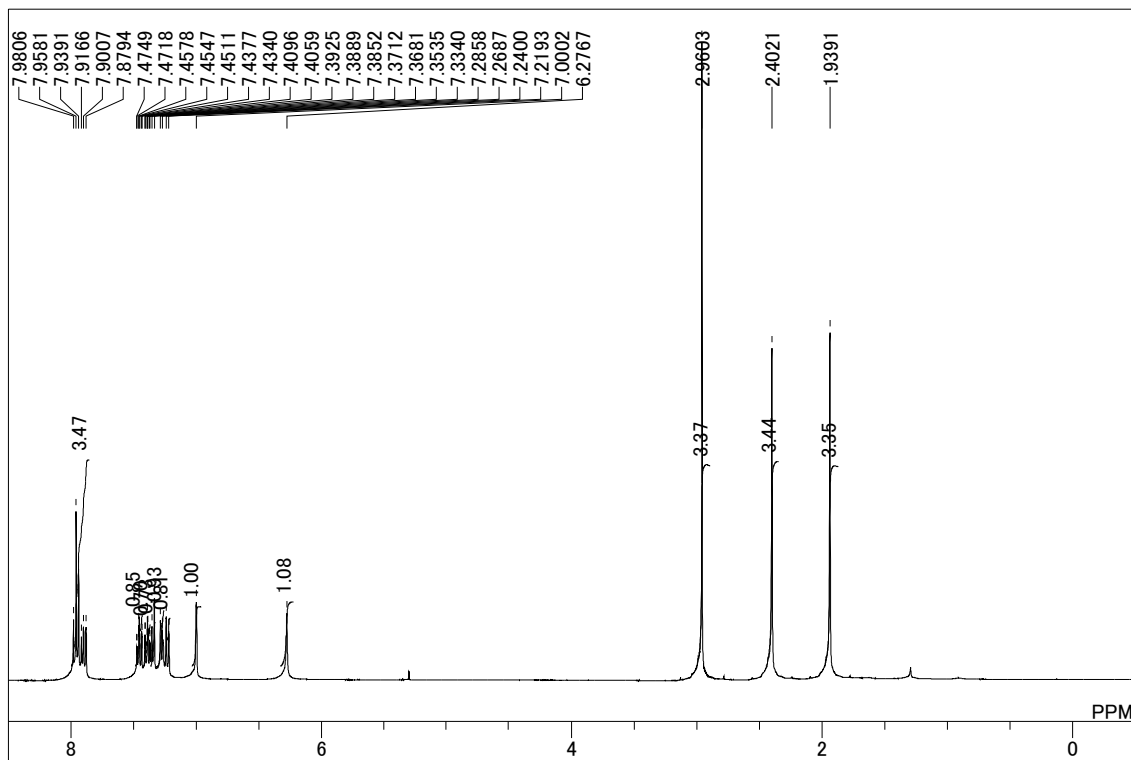
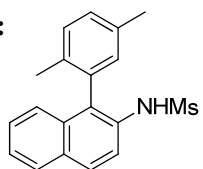
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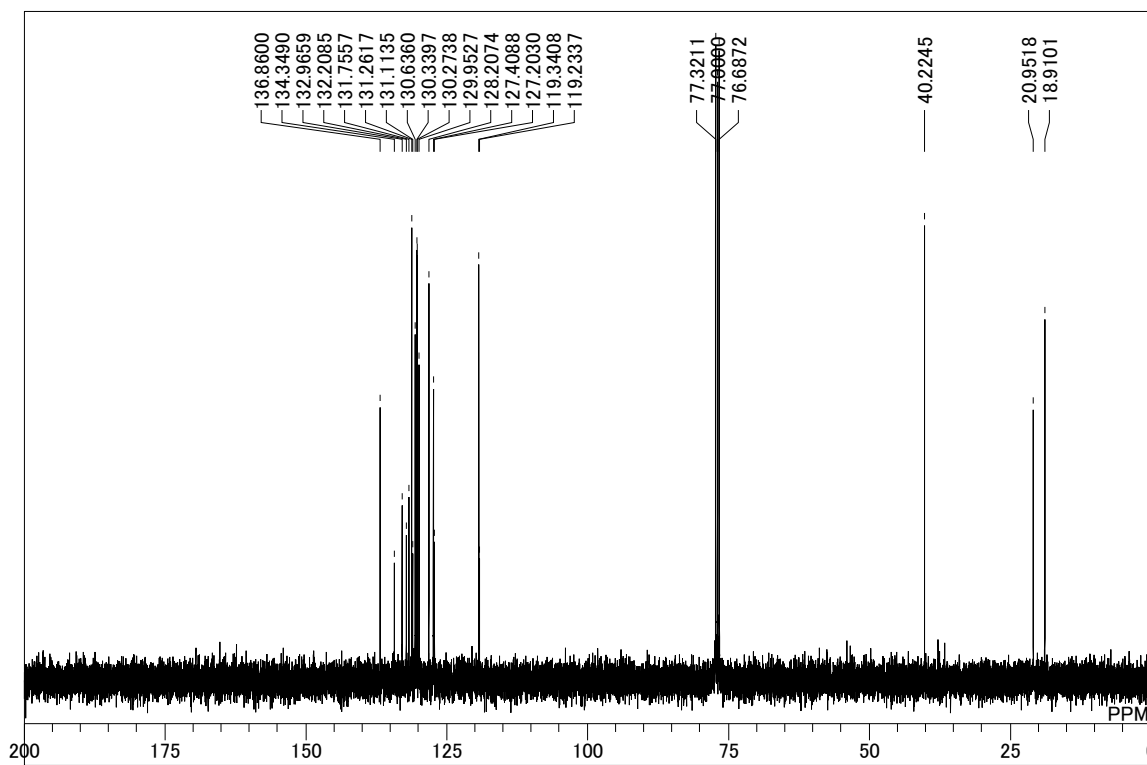
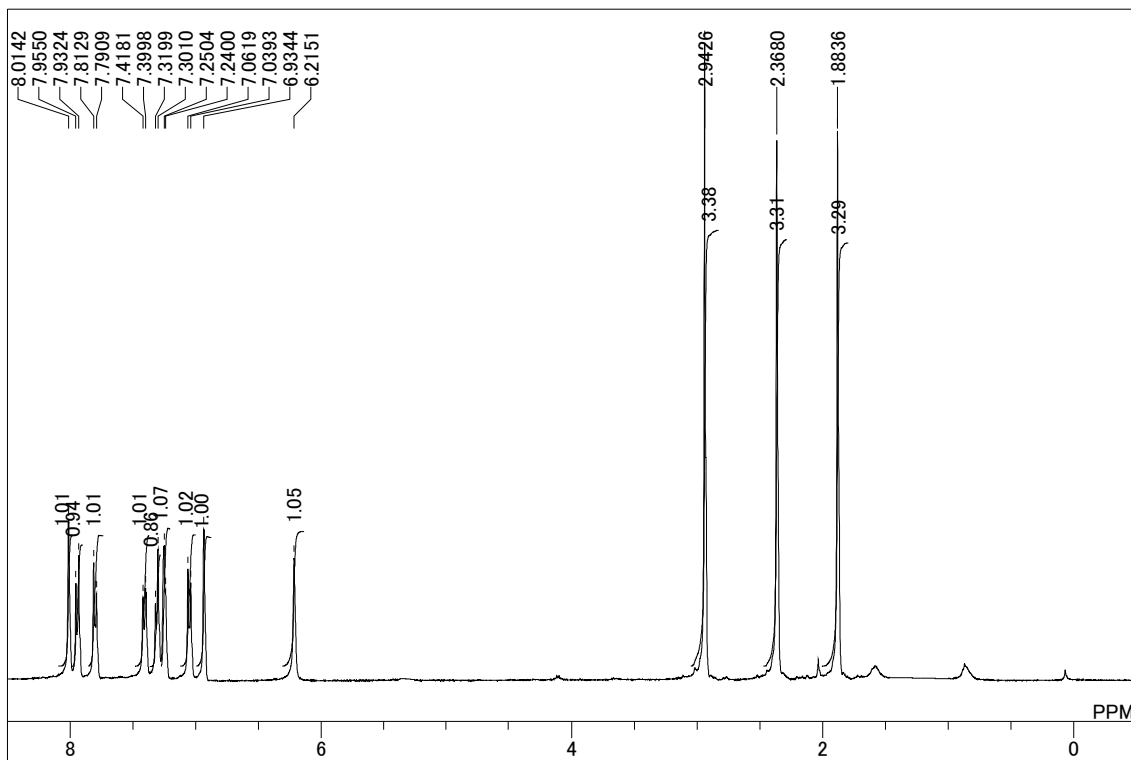
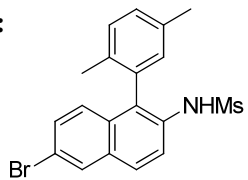
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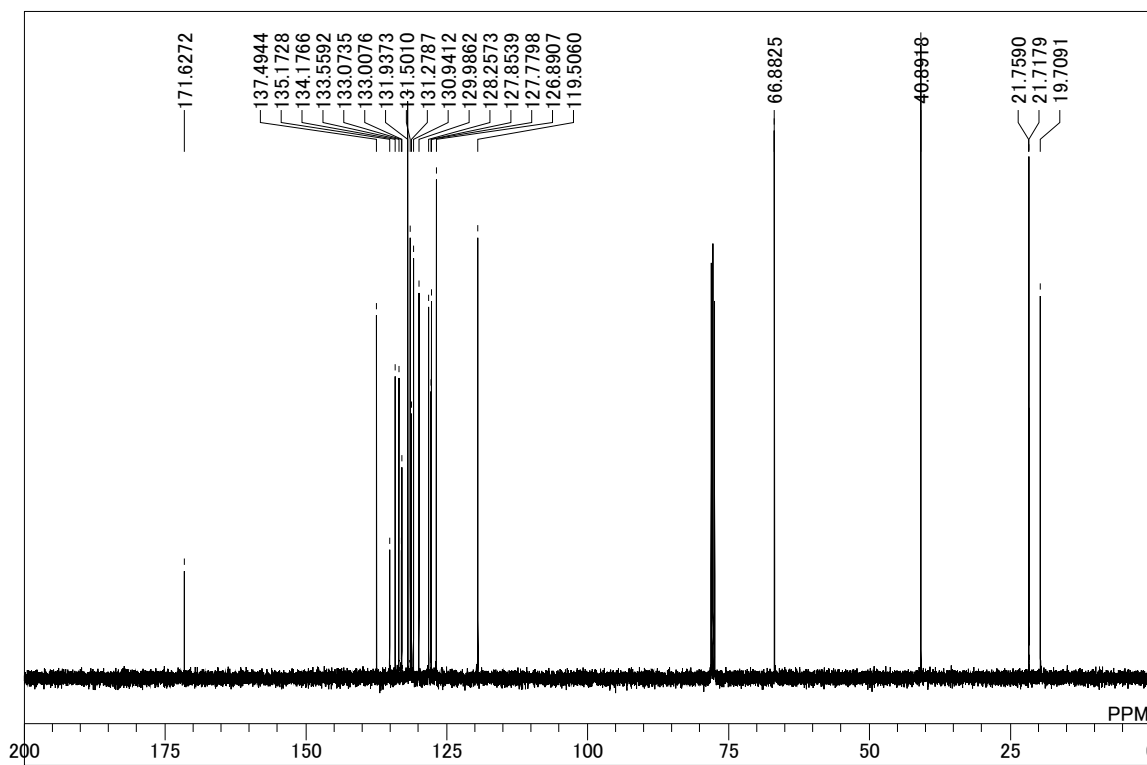
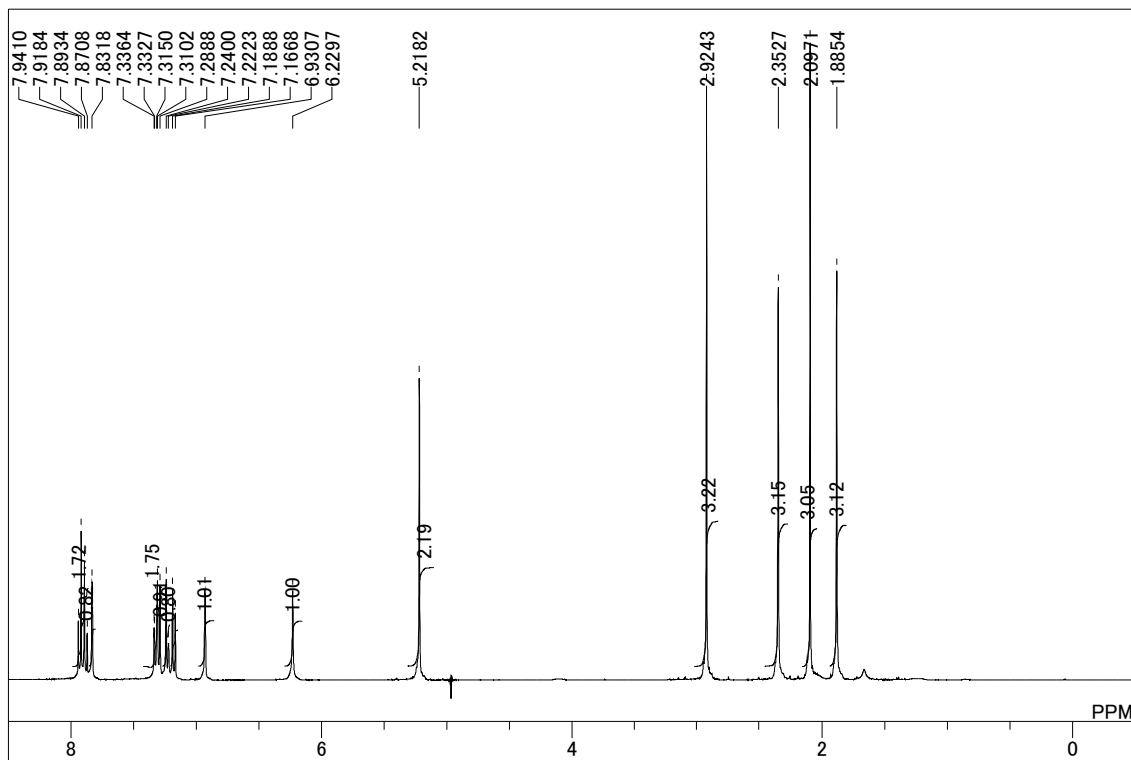
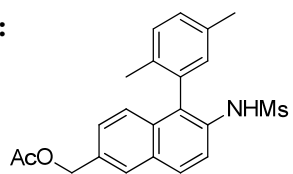
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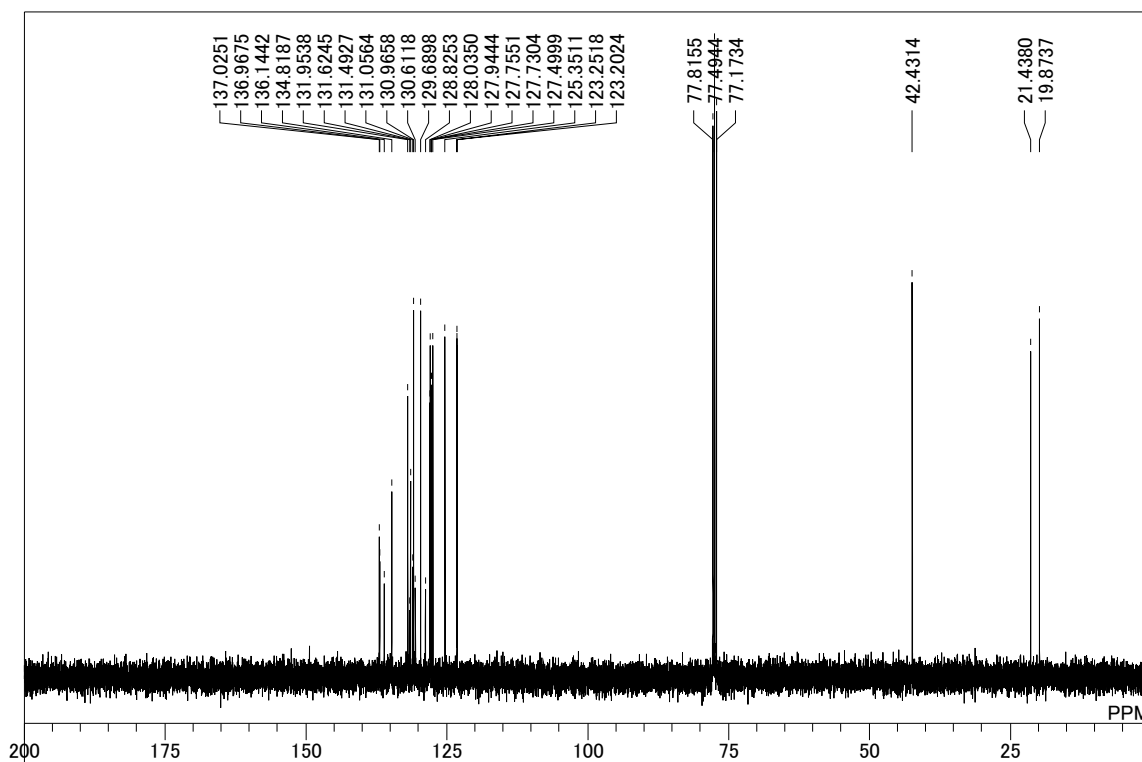
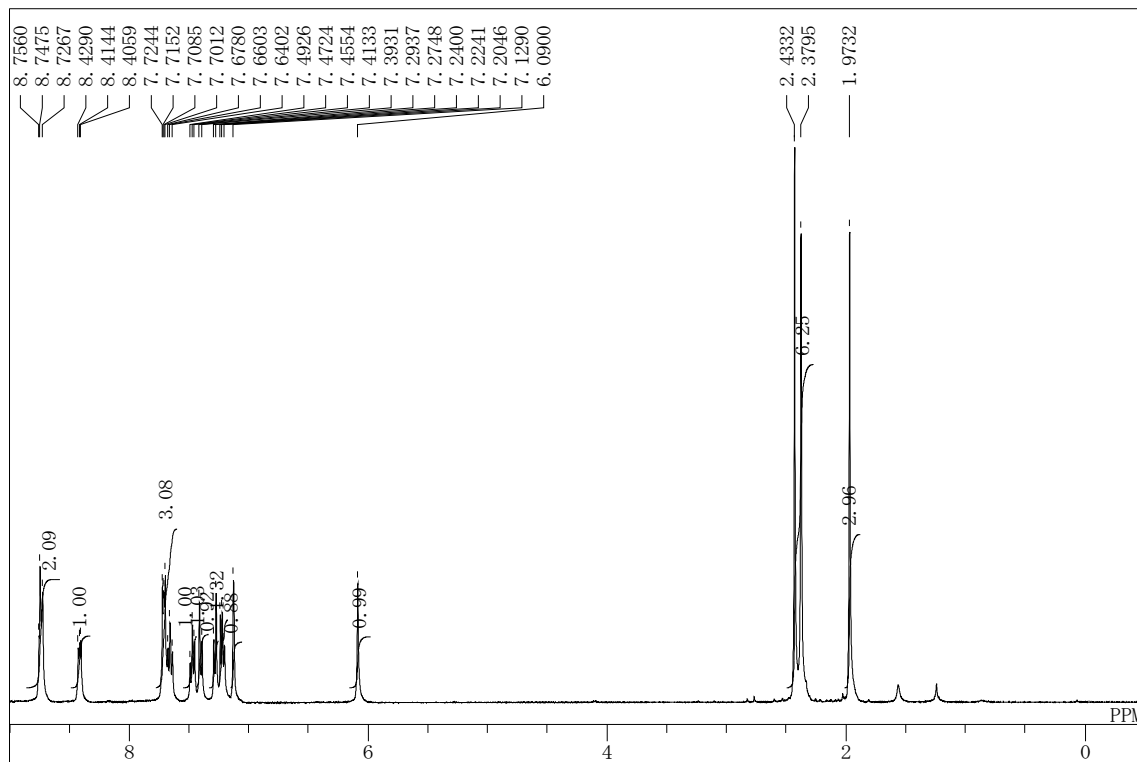
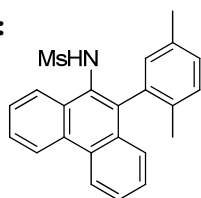
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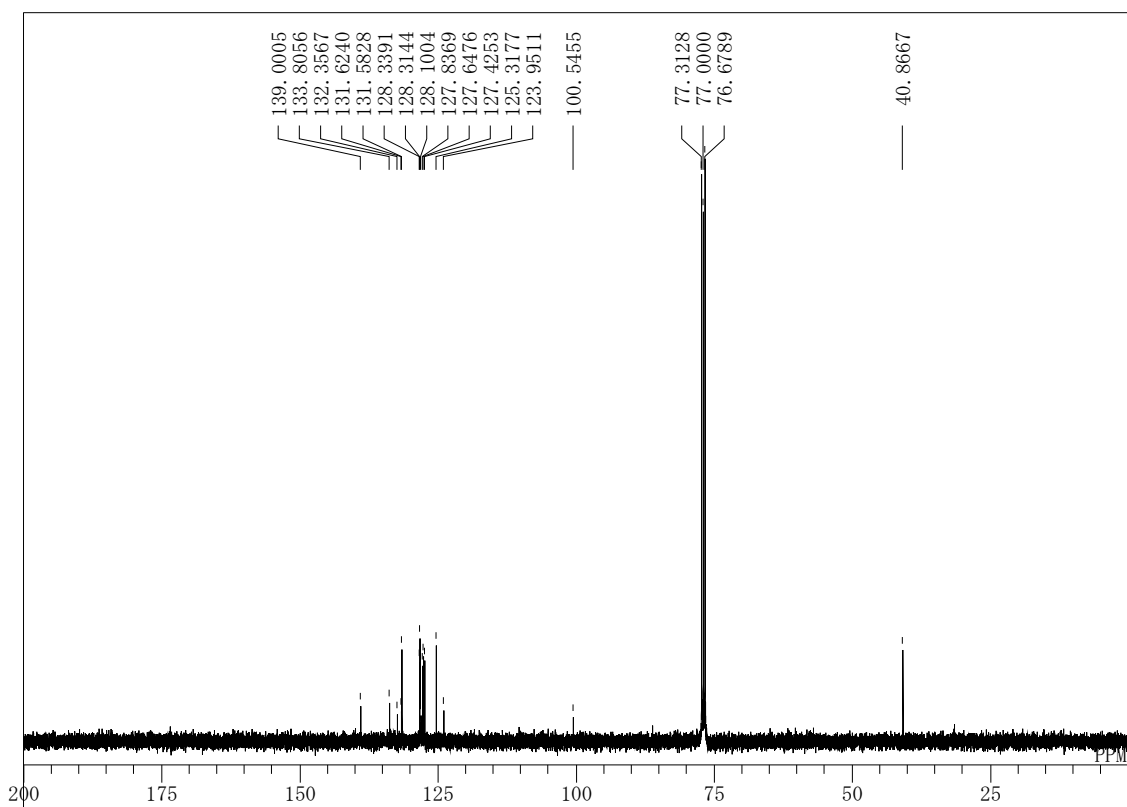
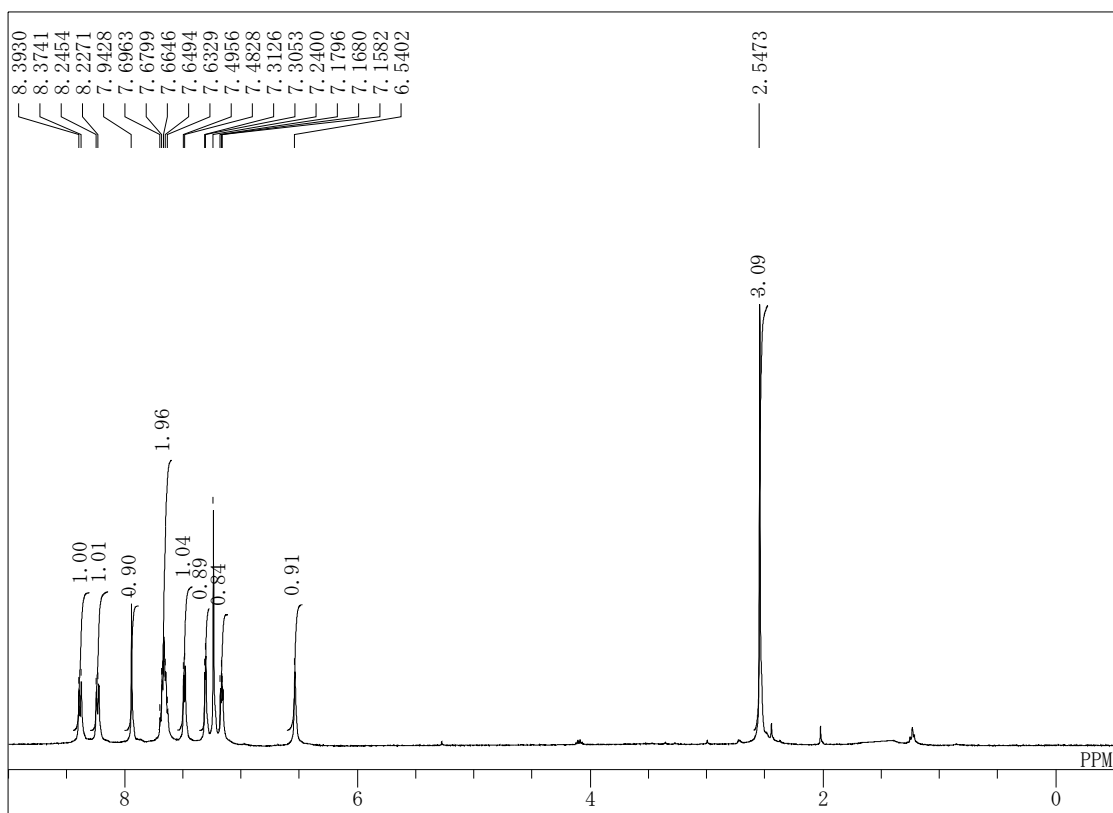
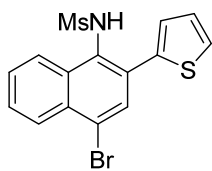
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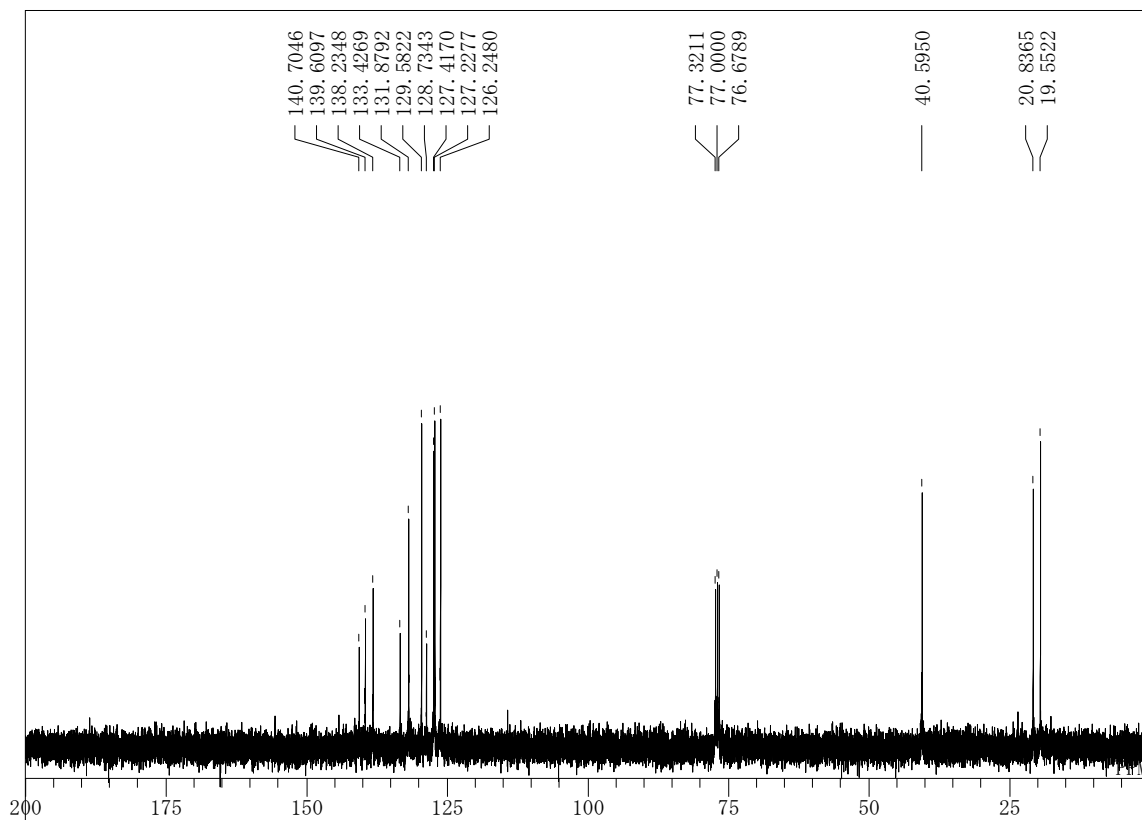
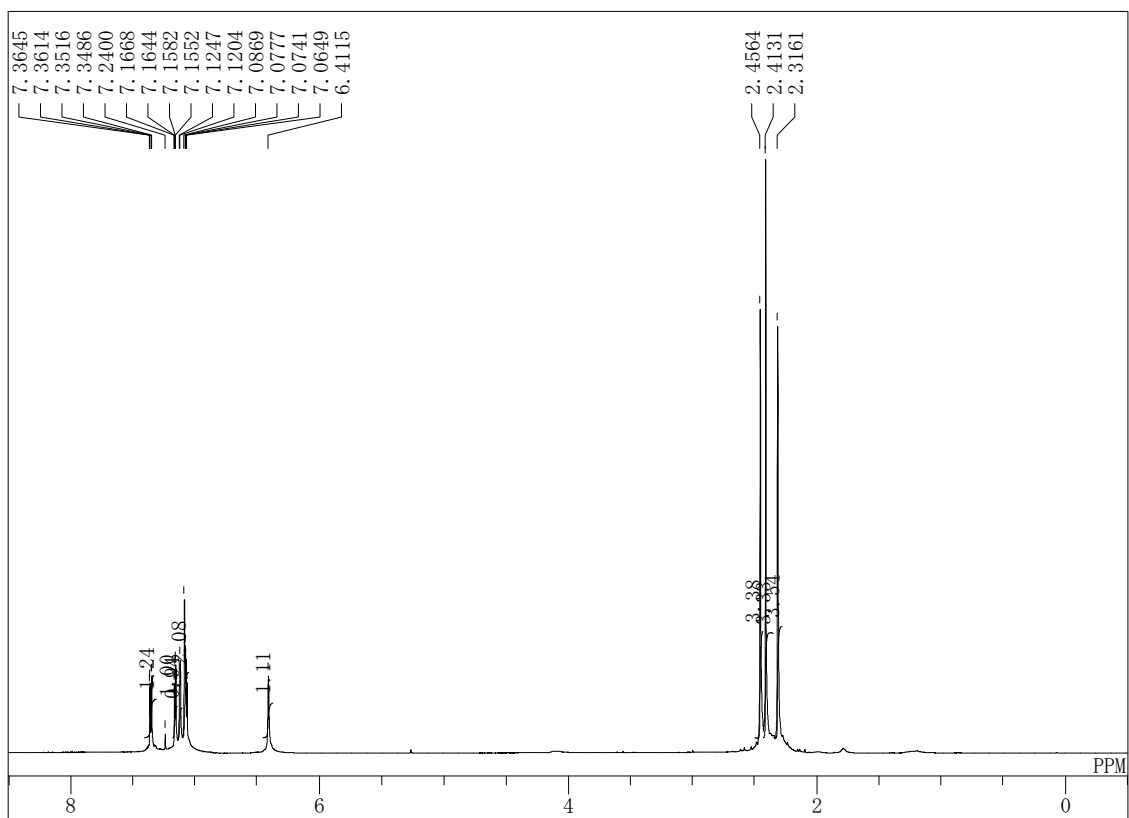
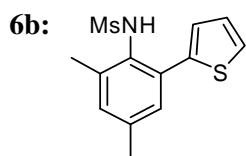


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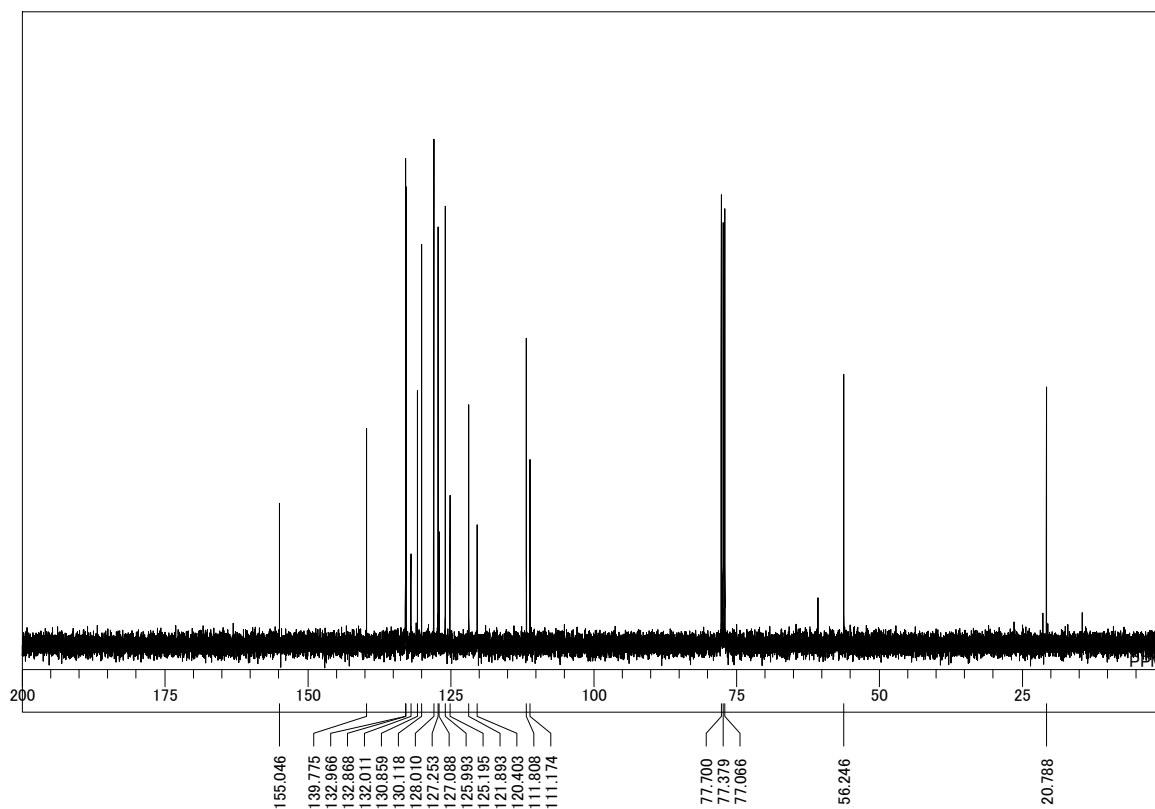
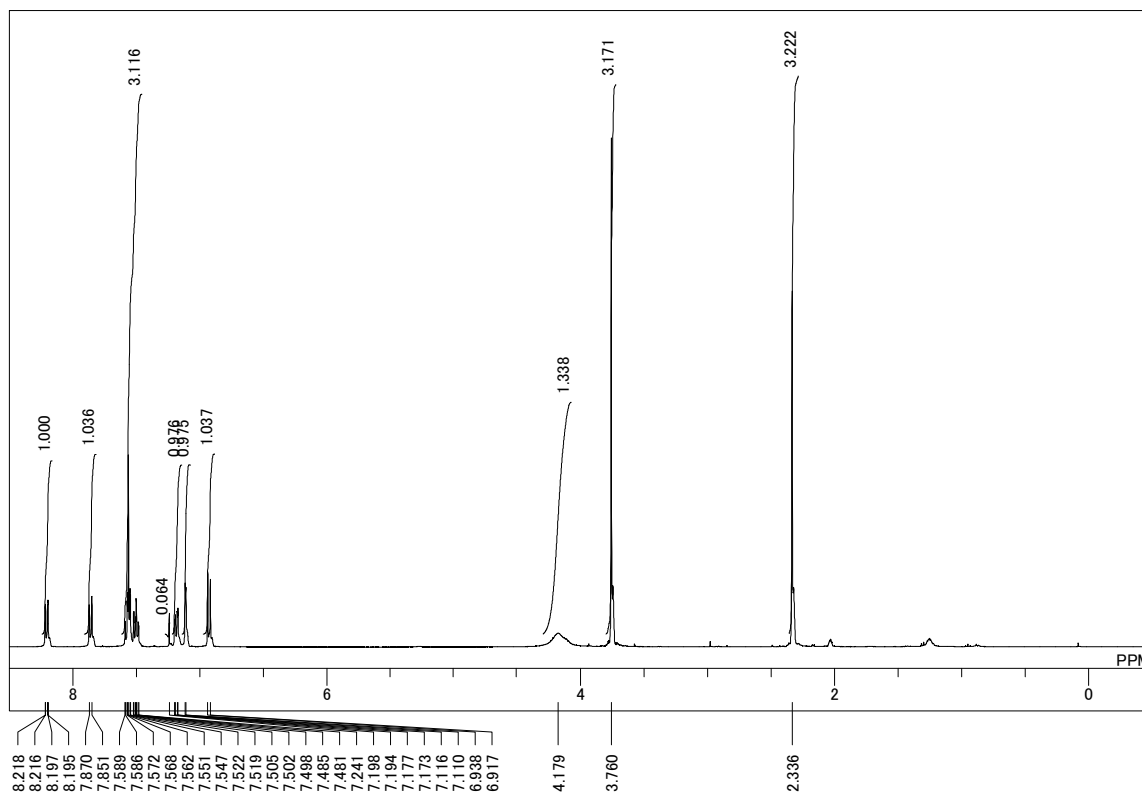
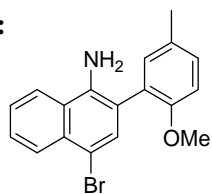


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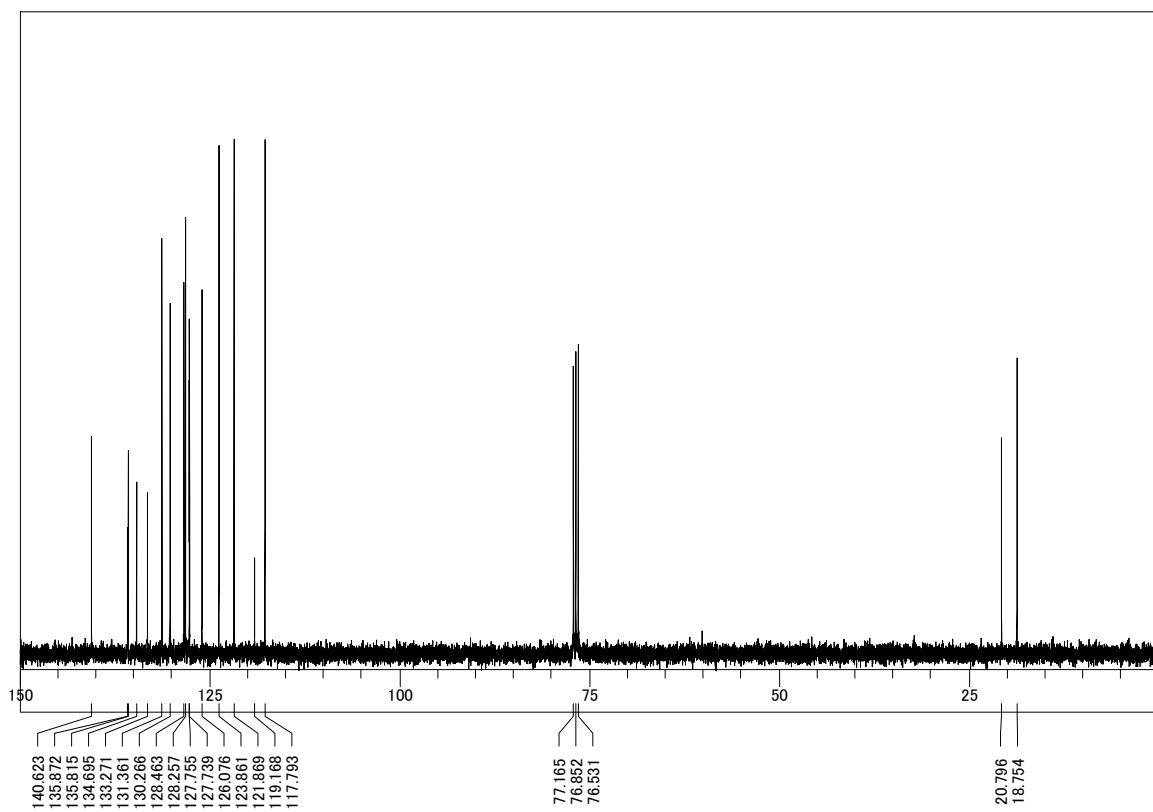
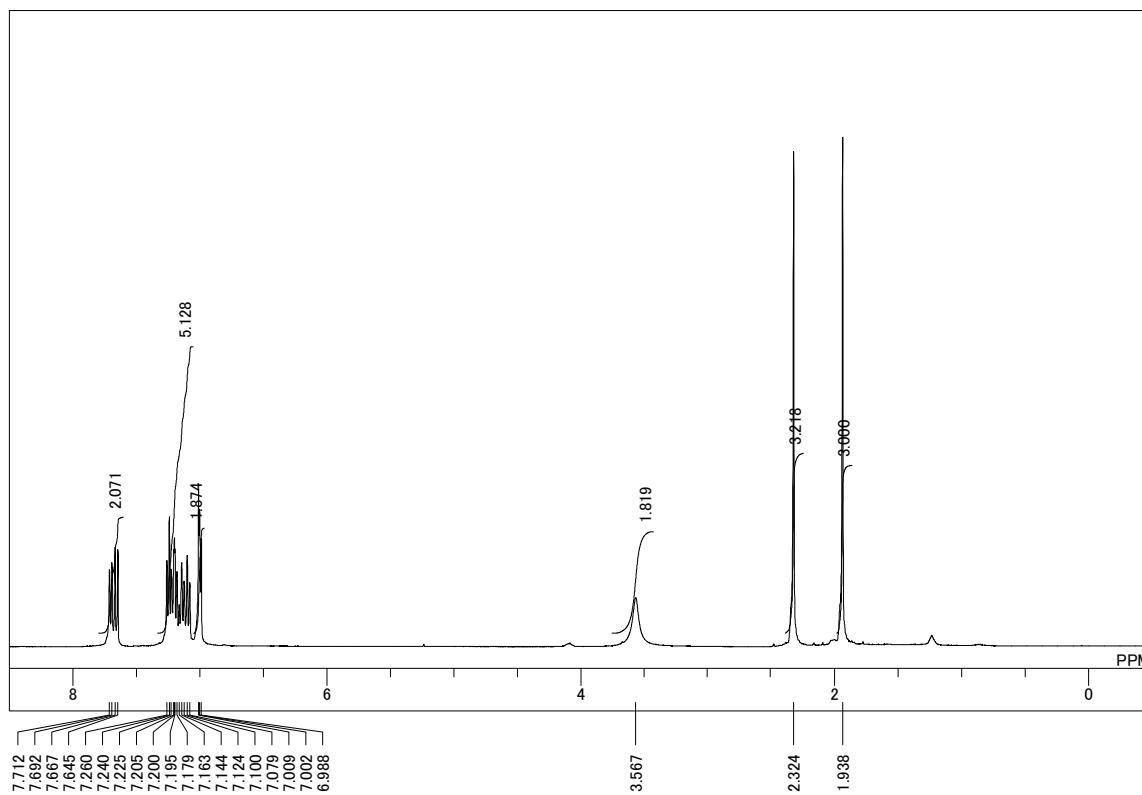
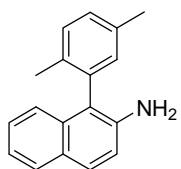




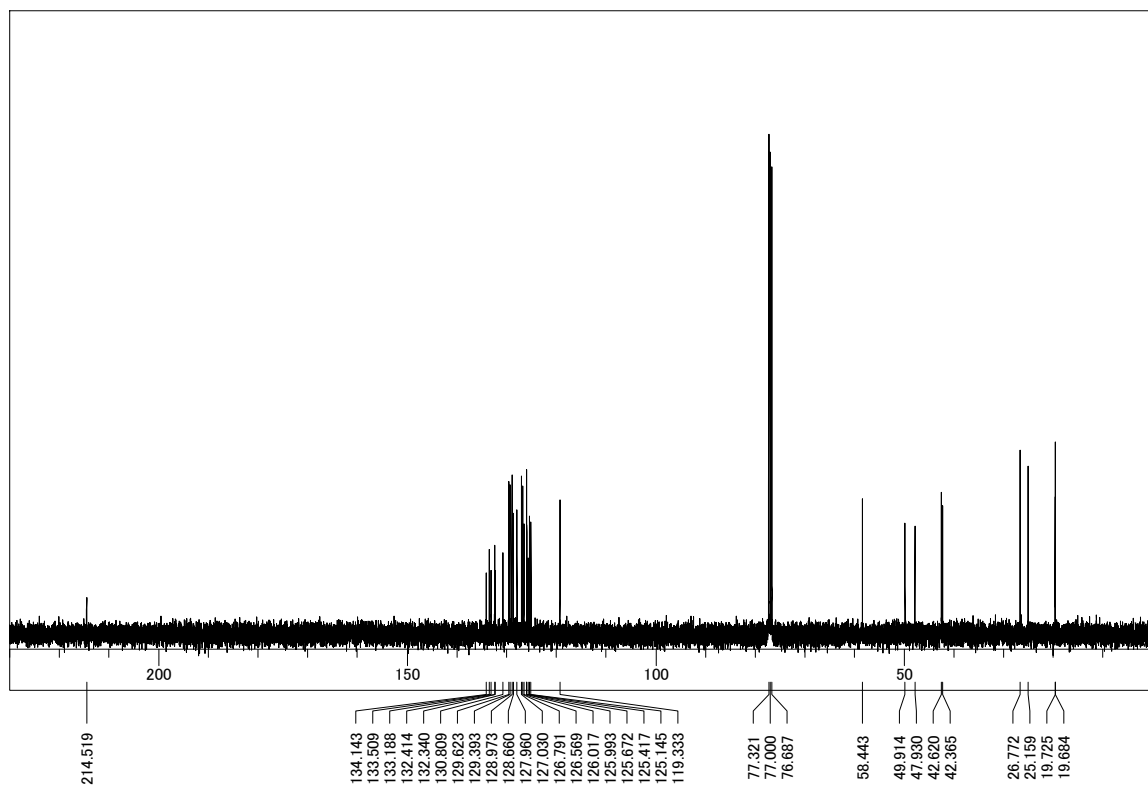
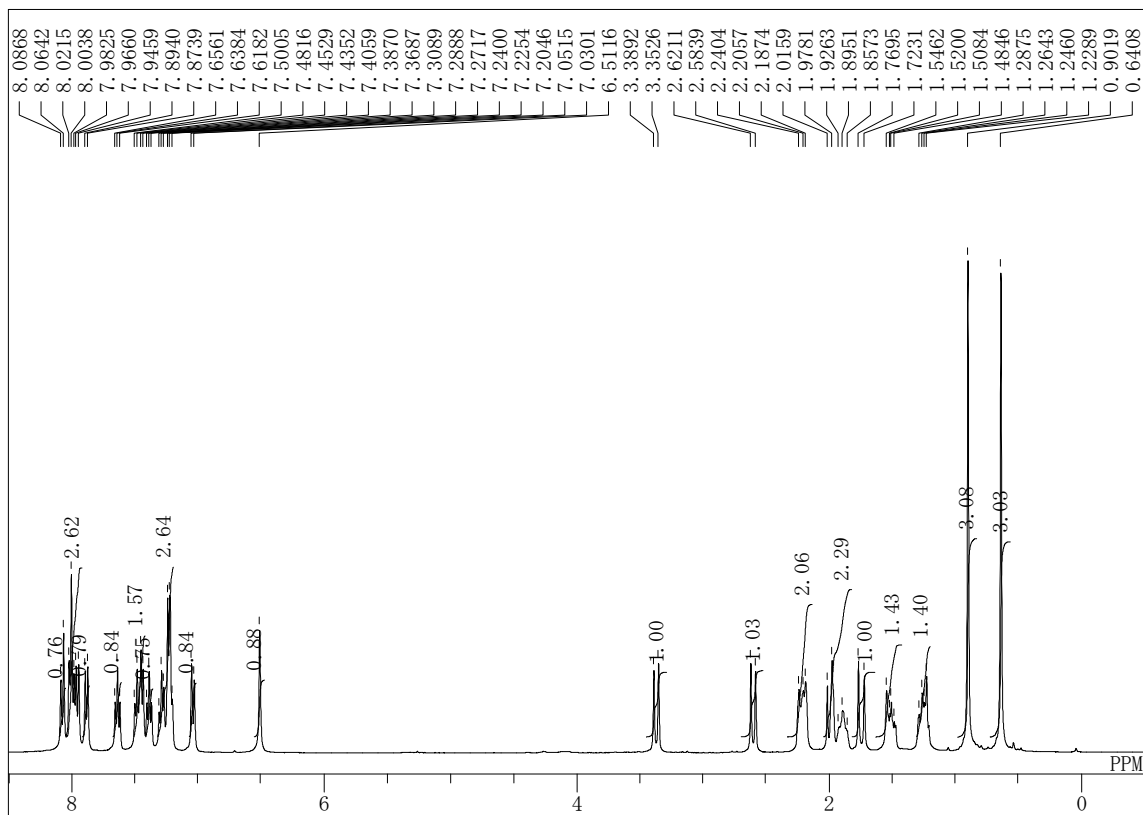
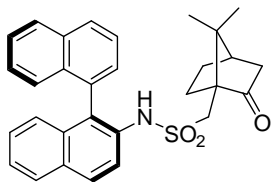
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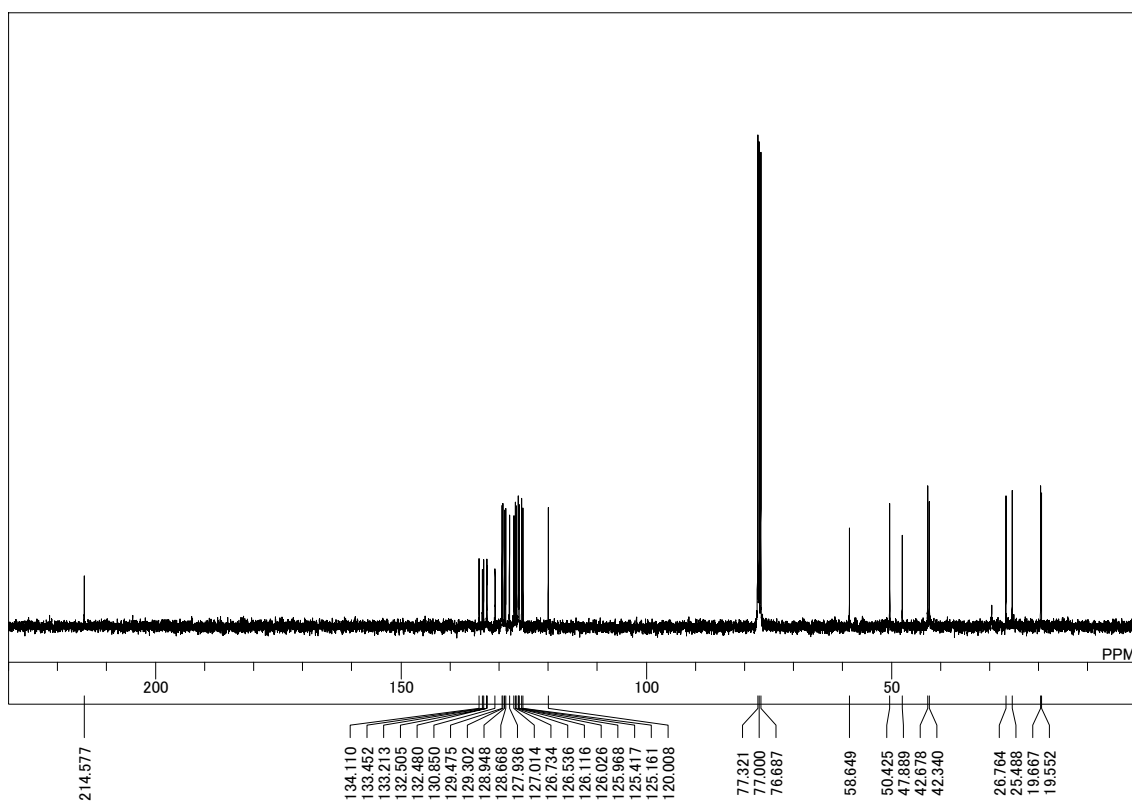
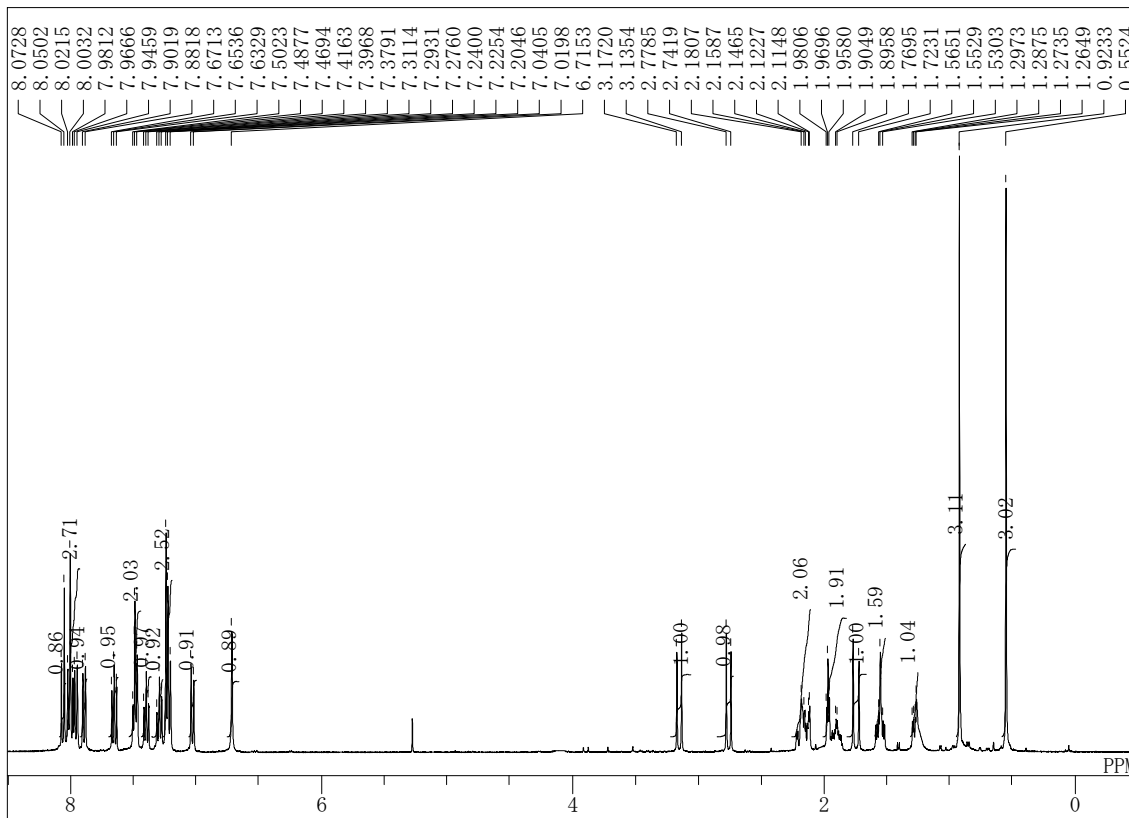
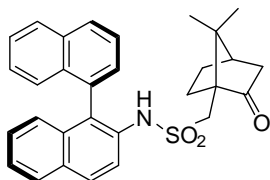
7ea:



3jf:



3jf' (other isomer) :



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