

Concise synthesis of *N*-thiomethyl benzoimidazoles through a base-promoted sequential four-component assembly

Jingxin Tian,[†] Shanshan Yuan,[†] Fuhong Xiao,* Huawen, Huang, Guo-Jun Deng*

^a Key Laboratory of Environmentally Friendly Chemistry and Application of Ministry of Education, Hunan Province Key Laboratory of Green Organic Synthesis and Application, College of Chemistry, Xiangtan University, Xiangtan 411105, China. Fax: (+86)0731-58292251; Tel: (+86)0731-58298280; E-mail: fhxiao@xtu.edu.cn; gjdeng@xtu.edu.cn

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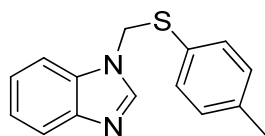
General information:

Thiolation reaction is conducted under an atmosphere of air. Flash column chromatography was performed over silica gel 48-75 μm . ^1H NMR and ^{13}C NMR spectra were recorded on Bruker-AV (400 and 100 MHz, respectively) instrument internally referenced to tetramethylsilane (TMS) or acetone signals. MS analyses were performed on an Agilent 5975 GC-MS instrument (EI). HRMS was conducted using electrospraying ionization (ESI) and was performed on a Thermo Scientific LTQ Orbitrap XL. The structures of known compounds were further corroborated by comparing their NMR data and MS data with those of literature. Reagents were used as received or prepared by our laboratory.

General procedure: (3aa):

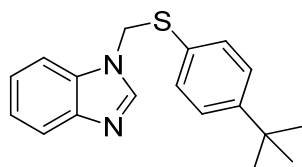
A 10 mL oven-dried reaction vessel was charged with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol), 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol), paraformaldehyde (24 mg, 0.8 mmol), 4-aminodiphenylamine (36.8 mg, 0.2 mmol), H_2O (0.2 mL) and 1,1,2,2-tetrachloroethane (0.7 mL) was added to the sealed reaction vessel by syringe. The resulting solution was stirred at 130 $^\circ\text{C}$ for 3 h. The volatiles were removed under vacuum and the residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3aa** as white solid; yield: 36.0 mg (71%), mp 72 - 74 $^\circ\text{C}$.

1-((*p*-Tolylthio)methyl)-1*H*-benzo[*d*]imidazole (3aa)



^1H NMR (400 MHz, CDCl_3) δ 7.82 - 7.76 (m, 1H), 7.45 (s, 1H), 7.43 - 7.38 (m, 2H), 7.10 - 7.03 (m, 4H), 5.34 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.9, 142.6, 139.5, 134.3, 132.7, 130.2, 128.1, 123.1, 122.5, 120.3, 110.3, 50.7, 21.1. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 255.0951, found 255.0953.

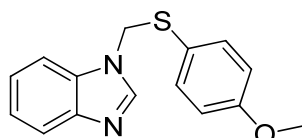
1-(((4-(*tert*-Butyl)phenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (3ab)



The reaction was conducted with 4-(*tert*-butyl)benzenethiol (**2b**, 86 μL , 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ab** as black solid; yield: 40.9 mg (69%), mp 62 - 64 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 7.78 (m, 1H), 7.52 (s, 1H), 7.32 (d, $J = 2.3$ Hz, 1H), 7.29 - 7.24 (m, 4H), 7.14 - 7.11 (m, 2H), 5.33 (s, 2H), 1.27 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 143.6, 142.6, 134.0, 132.8, 128.3, 126.4, 123.0, 122.5, 120.3, 110.3, 50.6, 34.6, 31.1. HRMS (ESI) calcd for $\text{C}_{18}\text{H}_{21}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 297.1420, found 297.1421.

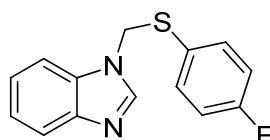
1-(((4-Methoxyphenyl)thio)methyl)-1H-benzo[d]imidazole (**3ac**)



The reaction was conducted with 4-methoxybenzenethiol (**2c**, 61.5 μL , 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 1:1) to give **3ac** as brown solid; yield: 29.1 mg (54%), mp 145 - 147 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 7.81 - 7.76 (m, 1H), 7.43 (s, 1H), 7.41 - 7.37 (m, 1H), 7.33 - 7.27 (m, 2H), 7.10 - 7.05 (m, 2H), 6.78 - 6.73 (m, 2H), 5.28 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.6, 143.9, 142.6, 136.5, 132.7, 123.1, 122.5, 122.0, 120.3, 114.9, 110.4, 55.3, 51.1. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{OS}^+$ ($\text{M}+\text{H}$) $^+$ 271.0899, found 271.0898.

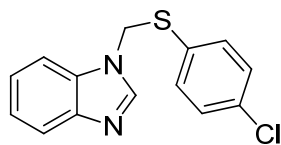
1-(((4-Fluorophenyl)thio)methyl)-1H-benzo[d]imidazole (**3ad**)



The reaction was conducted with 4-fluorobenzenethiol (**2d**, 53 μL , 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ad** as brown solid; yield: 32.5 mg (63%), mp 71 - 73 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 7.83 - 7.76 (m, 1H), 7.48 (s, 1H), 7.37 - 7.36 (m, 1H), 7.33 - 7.28 (m, 2H), 7.18 - 7.10 (m, 2H), 6.97 - 6.88 (m, 2H), 5.33 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.5 (d, $J = 249$ Hz), 143.9, 142.5, 136.8 (d, $J = 8.5$ Hz), 132.6, 126.7 (d, $J = 3.4$ Hz), 123.3, 122.7, 120.8, 116.6 (d, $J = 21.8$ Hz), 110.3, 50.8 (d, $J = 1.5$ Hz). HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{12}\text{FN}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 259.0700, found 259.0701.

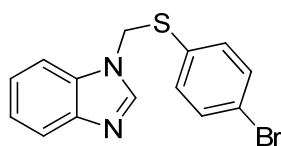
1-(((4-Chlorophenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (**3ae**)



The reaction was conducted with 4-chlorobenzenethiol (**2e**, 70 mg, 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ae** as white solid; yield: 32 mg (58%), mp 95 - 97 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.82 - 7.78 (m, 1H), 7.51 (s, 1H), 7.40 - 7.37 (m, 1H), 7.34 - 7.29 (m, 2H), 7.23 - 7.18 (m, 2H), 7.16 - 7.08 (m, 2H), 5.36 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 143.9, 142.5, 135.7, 135.6, 132.6, 130.1, 129.6, 123.3, 122.7, 120.5, 110.3, 50.4. HRMS (ESI) calcd for C₁₄H₁₂ClN₂S⁺ (M+H)⁺ 275.0404, found 275.0406.

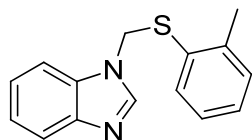
1-(((4-Bromophenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (**3af**)



The reaction was conducted with 4-bromobenzenethiol (**2f**, 97 mg, 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3af** as white solid; yield: 40.7 mg (64%), mp 108 - 110 °C.

¹H NMR (400 MHz, CDCl₃) δ 7.83 - 7.76 (m, 1H), 7.52 (s, 1H), 7.42 - 7.34 (m, 3H), 7.34 - 7.28 (m, 2H), 7.07 - 7.00 (m, 2H), 5.36 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 143.9, 142.5, 135.7, 132.6, 132.6, 130.7, 123.9, 123.3, 122.7, 120.5, 110.3, 50.3. HRMS (ESI) calcd for C₁₄H₁₂BrN₂S⁺ (M+H)⁺ 318.9899, found 318.9901.

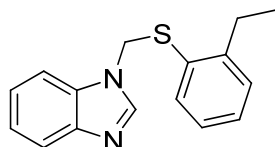
1-(((*o*-Tolylthio)methyl)-1*H*-benzo[*d*]imidazole (**3ag**)



The reaction was conducted with 2-methylbenzenethiol (**2g**, 61.5 μL, 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ag** as brown solid; yield: 28.4 mg (56%), mp 69 - 72 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.80 - 7.73 (m, 1H), 7.41 (s, 1H), 7.36 - 7.34 (m, 1H), 7.31 - 7.27 (m, 2H), 7.24 - 7.13 (m, 3H), 7.10 - 7.06 (m, 1H), 5.34 (s, 2H), 2.11 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.8, 142.4, 141.9, 135.2, 132.9, 131.1, 130.7, 129.4, 127.0, 123.1, 122.5, 120.4, 110.1, 50.0, 20.4. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 255.0951, found 255.0953.

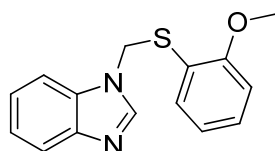
1-(((2-Ethylphenyl)thio)methyl)-1H-benzo[d]imidazole (3ah)



The reaction was conducted with 2-ethylbenzenethiol (**2h**, 66 μL , 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ah** as green solid; yield: 30 mg (56%), mp 33 - 35 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 7.80 - 7.74 (m, 1H), 7.42 (s, 1H), 7.35 - 7.32 (m, 1H), 7.31 - 7.24 (m, 3H), 7.20 - 7.15 (m, 2H), 7.10 - 7.06 (m, 1H), 5.35 (s, 2H), 2.51 (q, $J = 7.5$ Hz, 2H), 0.99 (t, $J = 7.5$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 147.8, 143.8, 142.5, 135.1, 132.8, 130.6, 129.6, 129.3, 126.9, 123.1, 122.5, 120.4, 110.1, 50.4, 26.9, 15.3. HRMS (ESI) calcd for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 269.1107, found 269.1106.

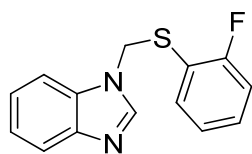
1-(((2-Methoxyphenyl)thio)methyl)-1H-benzo[d]imidazole (3ai)



The reaction was conducted with 2-methoxybenzenethiol (**2i**, 61 μL , 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ai** as white solid; yield: 25.5 mg (47%), mp 100 - 103 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 7.78 - 7.71 (m, 1H), 7.54 (s, 1H), 7.43 - 7.38 (m, 1H), 7.33 - 7.25 (m, 3H), 7.14 - 7.12 (m, 1H), 6.87 - 6.85 (m, 1H), 6.80 - 6.75 (m, 1H), 5.44 (s, 2H), 3.75 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.5, 143.7, 142.6, 136.5, 133.1, 131.2, 123.1, 122.4, 121.2, 120.2, 118.7, 111.1, 110.2, 55.7, 48.1. HRMS (ESI) calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{OS}^+$ ($\text{M}+\text{H}$) $^+$ 271.0899, found 271.0898.

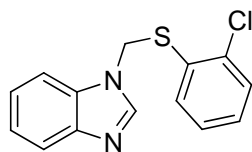
1-(((2-Fluorophenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (**3aj**)



The reaction was conducted with 2-fluorobenzenethiol (**2j**, 53 μ L, 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3aj** as black solid; yield: 33.5 mg (65%), mp 99 - 101 $^{\circ}$ C.

^1H NMR (400 MHz, CDCl_3) δ 7.77 - 7.75 (m, 1H), 7.55 (s, 1H), 7.42 - 7.40 (m, 1H), 7.35 - 7.26 (m, 3H), 7.11 (t, $J = 8.8$ Hz, 1H), 7.04 - 7.00 (m, 1H), 6.93 (t, $J = 7.5$ Hz, 1H), 5.43 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 162.6 (d, $J = 246$ Hz), 143.8, 142.5, 136.6, 132.8, 131.7 (d, $J = 8.1$ Hz), 124.9 (d, $J = 3.9$ Hz), 123.2, 122.6, 120.4, 118.1 (d, $J = 17.8$ Hz), 116.2 (d, $J = 22.6$ Hz), 110.1, 48.4, 48.4. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{12}\text{FN}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 259.0700, found 259.0701.

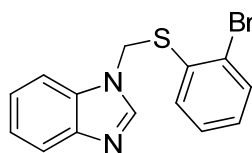
1-(((2-Chlorophenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (**3ak**)



The reaction was conducted with 2-chlorobenzenethiol (**2k**, 56.7 μ L, 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ak** as brown liquid; yield: 31.3 mg (57%).

^1H NMR (400 MHz, CDCl_3) δ 7.78 - 7.73 (m, 1H), 7.54 (s, 1H), 7.46 - 7.44 (m, 1H), 7.42 - 7.37 (m, 1H), 7.32 - 7.21 (m, 3H), 7.06 - 7.01 (m, 2H), 5.47 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 142.4, 138.3, 136.5, 132.9, 130.8, 130.3, 129.9, 127.5, 123.2, 122.6, 120.4, 110.1, 48.1. HRMS (ESI) calcd for $\text{C}_{14}\text{H}_{12}\text{ClN}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 275.0404, found 275.0405.

1-(((2-Bromophenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (**3al**)

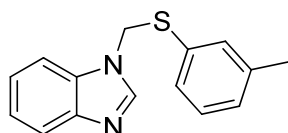


The reaction was conducted with 2-bromobenzenethiol (**2l**, 60 μ L, 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3al** as white solid; yield:

40.7 mg (64%), mp 90 - 92 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.80 - 7.72 (m, 1H), 7.67 - 7.59 (m, 1H), 7.54 (s, 1H), 7.44 - 7.35 (m, 1H), 7.31 - 7.25 (m, 2H), 7.16 - 7.13 (m, 1H), 7.08 - 6.98 (m, 2H), 5.47 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.8, 142.5, 136.4, 133.6, 132.9, 132.0, 130.8, 129.2, 128.2, 123.2, 122.6, 120.4, 110.1, 48.5. HRMS calcd for $\text{C}_{14}\text{H}_{12}\text{BrN}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 318.9899, found 318.9901.

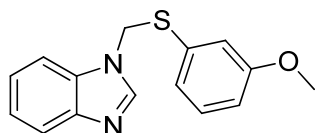
1-((*m*-Tolylthio)methyl)-1*H*-benzo[*d*]imidazole (3am)



The reaction was conducted with 3-methylbenzenethiol (**2m**, 61 μL , 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3am** as black liquid; yield: 30.9 mg (61%).

^1H NMR (400 MHz, CDCl_3) δ 7.82 - 7.76 (m, 1H), 7.51 (s, 1H), 7.38 - 7.36 (m, 1H), 7.32 - 7.27 (m, 2H), 7.16 - 7.12 (m, 2H), 7.03 - 6.98 (m, 2H), 5.37 (s, 2H), 2.22 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.9, 142.6, 139.3, 134.6, 132.8, 131.5, 130.9, 129.8, 129.2, 123.1, 122.5, 120.4, 110.3, 50.3, 21.0. HRMS calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 255.0951, found 255.0953.

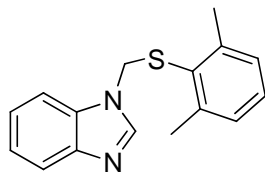
1-(((3-Methoxyphenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (3an)



The reaction was conducted with 3-methoxybenzenethiol (**2n**, 62 μL , 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3an** as brown liquid; yield: 33.6 mg (62%).

^1H NMR (400 MHz, CDCl_3) δ 7.82 - 7.75 (m, 1H), 7.56 (s, 1H), 7.41 - 7.36 (m, 1H), 7.33 - 7.27 (m, 2H), 7.20 - 7.14 (m, 1H), 6.87 - 6.79 (m, 2H), 6.63 - 6.64 (m, 1H), 5.39 (s, 2H), 3.61 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.9, 143.8, 142.6, 132.8, 130.2, 126.0, 123.2, 122.6, 120.4, 118.8, 115.4, 110.3, 55.2, 50.2. HRMS calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{OS}^+$ ($\text{M}+\text{H}$) $^+$ 271.0900, found 271.0898.

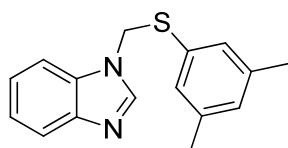
1-(((2,6-Dimethylphenyl)thio)methyl)-1*H*-benzo[*d*]imidazole (3ao)



The reaction was conducted with 2,6-dimethylbenzenethiol (**2o**, 68 μ L, 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ao** as white solid; yield: 21 mg (39%), mp 116 - 118 $^{\circ}$ C.

^1H NMR (400 MHz, CDCl_3) δ 7.79 - 7.73 (m, 1H), 7.29 - 7.26 (m, 4H), 7.17 - 7.13 (m, 1H), 7.04 (d, $J = 7.5$ Hz, 2H), 5.24 (s, 2H), 2.13 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.7, 143.6, 142.4, 133.0, 130.3, 129.6, 128.5, 123.2, 122.5, 120.3, 109.8, 49.1, 21.4. HRMS calcd for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 269.1107, found 269.1106.

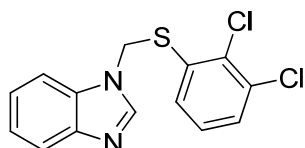
1-(((3,5-Dimethylphenyl)thio)methyl)-1H-benzo[d]imidazole (**3ap**)



The reaction was conducted with 3,5-dimethylbenzenethiol (**2p**, 68 μ L, 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ap** as green liquid; yield: 35.5 mg (66%).

^1H NMR (400 MHz, CDCl_3) δ 7.82 - 7.75 (m, 1H), 7.53 (s, 1H), 7.38 - 7.33 (m, 1H), 7.31 - 7.26 (m, 2H), 6.92 (s, 1H), 6.80 (s, 2H), 5.35 (s, 2H), 2.19 (s, 6H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.8, 142.6, 139.1, 132.8, 131.5, 131.2, 130.8, 123.0, 122.5, 120.3, 110.3, 50.3, 21.0. HRMS calcd for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 269.1107, found 269.1106.

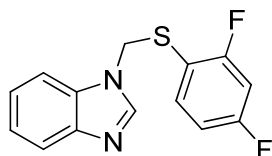
1-(((2,3-Dichlorophenyl)thio)methyl)-1H-benzo[d]imidazole (**3aq**)



The reaction was conducted with 2,3-dichlorobenzenethiol (**2q**, 89.6 mg, 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3aq** as white solid; yield: 37.8 mg (61%), mp 115 - 117 $^{\circ}$ C.

^1H NMR (400 MHz, CDCl_3) δ 7.78 - 7.71 (m, 1H), 7.61 (s, 1H), 7.41 - 7.38 (m, 2H), 7.33 - 7.27 (m, 2H), 6.95 - 6.90 (m, 2H), 5.49 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.8, 142.4, 136.1, 134.2, 133.9, 132.9, 132.5, 131.4, 127.6, 123.3, 122.7, 120.5, 110.0, 47.9. HRMS calcd for $\text{C}_{14}\text{H}_{11}\text{Cl}_2\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 309.0015, found 309.0011.

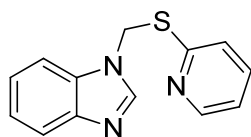
1-(((2,4-Difluorophenyl)thio)methyl)-1H-benzo[d]imidazole (3ar)



The reaction was conducted with 2,4-difluorobenzenethiol (**2r**, 57 μL , 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ar** as brown solid; yield: 9.3 mg (17%), mp 81 - 83 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 7.82 - 7.75 (m, 1H), 7.64 (s, 1H), 7.45 - 7.38 (m, 1H), 7.37 - 7.30 (m, 2H), 7.01 - 6.95 (m, 1H), 6.90 - 6.82 (m, 1H), 6.69 (t, $J = 8.0$ Hz, 1H), 5.41 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.9 (dd, $J = 102.9, 12.0$ Hz), 162.4 (dd, $J = 99.2, 12.1$ Hz), 143.7, 142.4, 138.1 (d, $J = 11.3$ Hz), 123.4, 122.8, 120.5, 113.5 (d, $J = 18.4$ Hz), 112.4 (dd, $J = 21.4, 3.9$ Hz), 110.1, 104.9, 104.9 (d, $J = 52.4$ Hz), 48.7. HRMS calcd for $\text{C}_{14}\text{H}_{11}\text{F}_2\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 277.0606, found 277.0604.

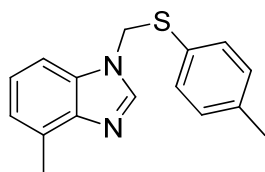
1-((Pyridin-2-ylthio)methyl)-1H-benzo[d]imidazole (3as)



The reaction was conducted with pyridine-2-thiol (**2s**, 55.5 mg, 0.5 mmol) and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3as** as yellow solid; yield: 18.9 mg (39%), mp 97 - 99 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 8.54 (d, $J = 4.8$ Hz, 1H), 8.21 (s, 1H), 7.77 (d, $J = 7.7$ Hz, 1H), 7.54 - 7.44 (m, 2H), 7.35 - 7.25 (m, 2H), 7.09 - 7.04 (m, 2H), 5.99 (s, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.9, 149.4, 143.9, 143.6, 136.7, 133.0, 123.1, 123.0, 122.4, 120.7, 120.3, 110.0, 43.1. HRMS calcd for $\text{C}_{13}\text{H}_{12}\text{N}_3\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 242.0746, found 242.0745.

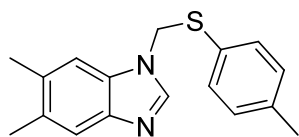
4-Methyl-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (3ba)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 3-methylbenzene-1,2-diamine (**1b**, 24.4 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ba** as brown liquid; yield: 32.1 mg (63%).

^1H NMR (400 MHz, CDCl_3) δ 7.42 (s, 1H), 7.26 - 7.20 (m, 2H), 7.12 - 7.04 (m, 5H), 5.31 (s, 2H), 2.66 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 143.2, 141.7, 139.4, 134.3, 132.3, 130.2, 130.2, 128.2, 123.0, 122.9, 107.8, 50.8, 21.1, 16.5. HRMS calcd for $\text{C}_{16}\text{H}_{17}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 269.1107, found 269.1106.

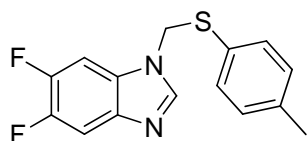
5,6-Dimethyl-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (3ca)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 4,5-dimethylbenzene-1,2-diamine (**1c**, 27.2 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ca** as brown solid; yield: 17.4 mg (31%), mp 115 - 117 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.53 (s, 1H), 7.32 (s, 1H), 7.13 (s, 1H), 7.10 - 7.03 (m, 4H), 5.29 (s, 2H), 2.38 (s, 6H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 142.6, 141.9, 139.4, 134.5, 132.3, 131.5, 131.2, 130.2, 128.4, 120.4, 110.6, 50.9, 21.1, 20.5, 20.2. HRMS calcd for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 283.1264, found 283.1267.

5,6-Difluoro-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (3da)

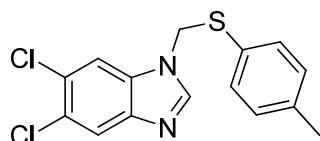


The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 4,5-difluorobenzene-1,2-diamine (**1d**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3da** as white solid; yield:

43.7 mg (75%), mp 133 - 135 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.56 - 7.52 (m, 1H), 7.46 (s, 1H), 7.15 - 7.11 (m, 1H), 7.08 - 7.04 (m, 4H), 5.28 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.3 (dd, $J = 30.6, 15.3$ Hz), 146.9 (dd, $J = 28.2, 15.3$ Hz), 144.0 (d, $J = 3.0$ Hz), 139.9, 139.1 (d, $J = 11.7$ Hz), 134.5, 130.3, 128.1 (d, $J = 11.0$ Hz), 127.6, 107.7 (d, $J = 19.8$ Hz), 98.6 (d, $J = 23.3$ Hz), 51.1, 21.1. HRMS calcd for $\text{C}_{15}\text{H}_{13}\text{F}_2\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 291.0762, found 291.0761.

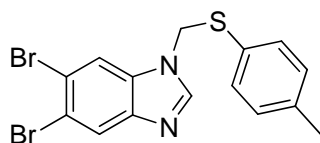
5,6-Dichloro-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (3ea)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 4,5-dichlorobenzene-1,2-diamine (**1e**, 35.4 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ea** as black solid; yield: 41.7 mg (65%), mp 155 - 157 °C.

^1H NMR (400 MHz, CDCl_3) δ 7.84 (s, 1H), 7.46 (s, 1H), 7.34 (s, 1H), 7.08 - 7.05 (m, 4H), 5.26 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.4, 143.2, 140.0, 134.6, 132.0, 130.3, 127.6, 127.2, 126.7, 121.5, 111.9, 51.1, 21.1. HRMS calcd for $\text{C}_{15}\text{H}_{13}\text{Cl}_2\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 323.0171, found 323.0175.

5,6-Dibromo-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (3fa)

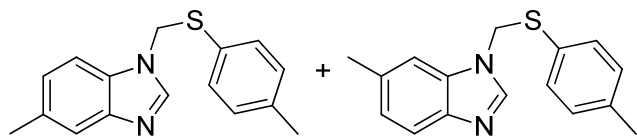


The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 4,5-dibromobenzene-1,2-diamine (**1f**, 53.2 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3fa** as white solid; yield: 48 mg (58%), mp 162 - 164 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.02 (s, 1H), 7.49 (s, 1H), 7.45 (s, 1H), 7.08 - 7.05 (m, 4H), 5.26 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 144.2, 144.1, 140.0, 134.6, 132.9, 130.3, 127.5, 124.7, 118.5, 117.9, 115.1, 51.2, 21.2. HRMS calcd for $\text{C}_{15}\text{H}_{13}\text{Br}_2\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 410.9161, found 410.9164.

5-Methyl-1-((p-tolylthio)methyl)-1H-benzo[d]imidazole (3ga) and

6-Methyl-1-((p-tolylthio)methyl)-1H-benzo[d]imidazole (3ga')

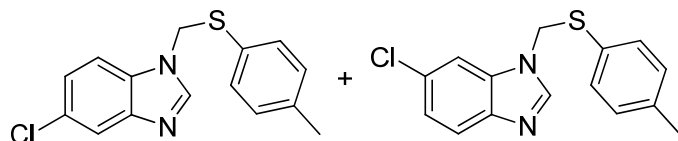


The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 4-methylbenzene-1,2-diamine (**1g**, 24.4 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ga** and **3ga'**; yield: 30 mg (59%).

¹H NMR (400 MHz, CDCl₃) δ 7.65 (d, J = 8.1 Hz, 1H), 7.57 (s, 1H), 7.37 (d, J = 2.5 Hz, 2H), 7.29 (d, J = 8.2 Hz, 1H), 7.14 - 7.09 (m, 4H), 7.06 (d, J = 6.6 Hz, 7H), 5.29 (d, J = 2.6 Hz, 4H), 2.48 (s, 6H), 2.30 (s, 6H).

5-Chloro-1-((p-tolylthio)methyl)-1H-benzo[d]imidazole (3ha) and

6-Chloro-1-((p-tolylthio)methyl)-1H-benzo[d]imidazole (3ha')

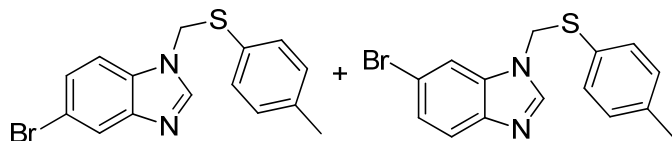


The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 4-chlorobenzene-1,2-diamine (**1h**, 28.5 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ha** and **3ha'**; yield: 41 mg (71%).

¹H NMR (400 MHz, CDCl₃) δ 7.75 (d, J = 1.5 Hz, 1H), 7.66 (d, J = 8.5 Hz, 1H), 7.44 (d, J = 7.5 Hz, 2H), 7.28 - 7.22 (m, 4H), 7.07 - 7.03 (m, 8H), 5.29 (s, 2H), 5.27 (s, 2H), 2.31 (d, J = 2.3 Hz, 6H).

5-Bromo-1-((p-tolylthio)methyl)-1H-benzo[d]imidazole (3ia) and

6-Bromo-1-((p-tolylthio)methyl)-1H-benzo[d]imidazole (3ia')



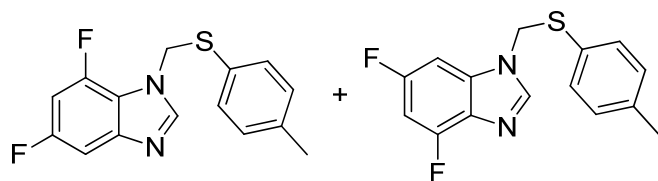
The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 4-bromobenzene-1,2-diamine (**1i**, 37.4 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ia** and **3ia'**; yield: 41 mg

(62%).

^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 1.6$ Hz, 1H), 7.62 (d, $J = 8.5$ Hz, 1H), 7.44 (s, 1H), 7.41 - 7.38 (m, 4H), 7.26 (s, 1H), 7.07 - 7.04 (m, 8H), 5.29 (s, 2H), 5.27 (s, 2H), 2.31 (d, $J = 4.3$ Hz, 6H).

5,7-Difluoro-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (3ja) and

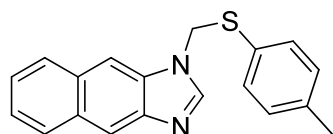
4,6-Difluoro-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (3ja')



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and 3,5-difluorobenzene-1,2-diamine (**1j**, 28.8 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ja** and **3ja'**; yield: 37.7 mg (65%).

^1H NMR (400 MHz, CDCl_3) δ 7.40 (s, 1H), 7.34 (s, 1H), 7.28 - 7.25 (m, 1H), 7.07 (d, $J = 1.9$ Hz, 8H), 6.88 - 6.76 (m, 3H), 5.42 (s, 2H), 5.27 (s, 2H), 2.32 (d, $J = 2.1$ Hz, 6H).

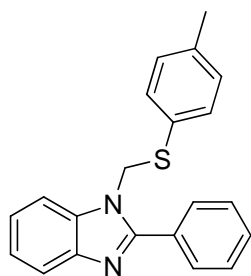
1-((*p*-Tolylthio)methyl)-1*H*-naphtho[2,3-*d*]imidazole (3ka)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol) and naphthalene-2,3-diamine (**1k**, 31.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 3:1) to give **3ka** as black solid; yield: 17.0 mg (28%), mp 134 - 136 °C.

^1H NMR (400 MHz, CDCl_3) δ 8.27 (s, 1H), 8.02 (d, $J = 7.7$ Hz, 1H), 7.94 (d, $J = 7.8$ Hz, 1H), 7.79 (s, 1H), 7.58 (s, 1H), 7.47 - 7.42 (m, 2H), 7.09 - 7.02 (m, 4H), 5.42 (s, 2H), 2.30 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.5, 143.9, 139.7, 134.7, 133.0, 130.5, 130.3, 130.3, 128.5, 128.2, 127.6, 124.7, 123.8, 117.6, 106.6, 51.1, 21.2. HRMS calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 305.1107, found 305.1111.

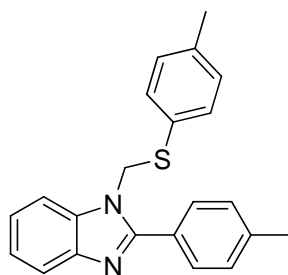
2-Phenyl-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (5aa)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol), benzaldehyde (**4a**, 41 μ L, 0.4 mmol), and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **5aa** as brown liquid; yield: 43.0 mg (65%).

^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, $J = 7.9$ Hz, 1H), 7.41 - 7.26 (m, 8H), 7.00 - 6.92 (m, 4H), 5.42 (s, 2H), 2.29 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.8, 142.9, 139.4, 134.7, 130.0, 129.7, 129.5, 129.4, 128.4, 127.9, 122.9, 122.9, 119.9, 111.3, 50.5, 21.1. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{19}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 331.1264, found 331.1267.

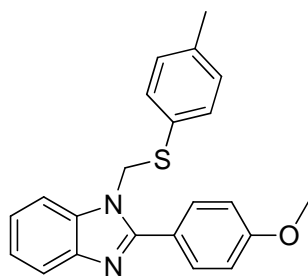
2-(*p*-Tolyl)-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (**5ab**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol), 4-methylbenzaldehyde (**4b**, 47 μ L, 0.4 mmol), and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **5ab** as brown solid; yield: 48.5 mg (70%), mp 115 - 117 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 7.8$ Hz, 1H), 7.33 - 7.25 (m, 5H), 7.19 (d, $J = 7.9$ Hz, 2H), 7.05 (d, $J = 8.1$ Hz, 2H), 6.98 (d, $J = 7.9$ Hz, 2H), 5.43 (s, 2H), 2.40 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.9, 142.9, 139.8, 139.3, 134.8, 134.6, 130.0, 129.3, 129.1, 128.1, 126.6, 122.7, 122.7, 119.8, 111.1, 50.4, 21.4, 21.1. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 345.1420, found 345.1418.

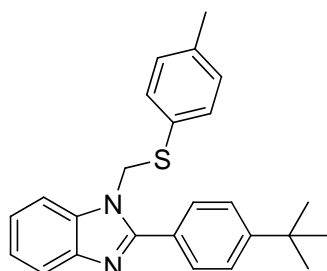
2-(4-Methoxyphenyl)-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (**5ac**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol), 4-methoxybenzaldehyde (**4c**, 49 μ L, 0.4 mmol), and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **5ac** as green liquid; yield: 32.4 mg (45%).

^1H NMR (400 MHz, CDCl_3) δ 7.78 (d, $J = 7.8$ Hz, 1H), 7.37 (d, $J = 8.7$ Hz, 2H), 7.30 - 7.24 (m, 3H), 7.07 (d, $J = 8.1$ Hz, 2H), 6.99 (d, $J = 7.9$ Hz, 2H), 6.90 (d, $J = 8.7$ Hz, 2H), 5.43 (s, 2H), 3.86 (s, 3H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.6, 153.8, 142.9, 139.2, 134.8, 134.6, 130.8, 130.0, 128.1, 122.7, 122.6, 121.9, 119.6, 113.8, 111.1, 55.3, 50.5, 21.1. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{OS}^+$ ($\text{M}+\text{H}$) $^+$ 361.1369, found 361.1367.

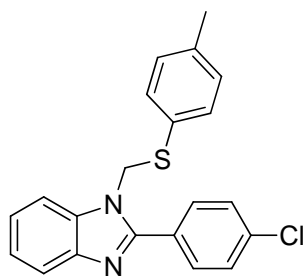
2-(4-(*tert*-Butyl)phenyl)-1-((*p*-tolylthio)methyl)-1H-benzo[*d*]imidazole (**5ad**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol), 4-(*tert*-butyl)benzaldehyde (**4d**, 67 μ L, 0.4 mmol), and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **5ad** as white solid; yield: 36.8 mg (48%), mp 129 - 131 $^{\circ}\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 7.79 (d, $J = 7.8$ Hz, 1H), 7.41 - 7.34 (m, 4H), 7.31 - 7.23 (m, 3H), 7.04 (d, $J = 8.1$ Hz, 2H), 6.95 (d, $J = 8.0$ Hz, 2H), 5.46 (s, 2H), 2.31 (s, 3H), 1.34 (d, $J = 6.5$ Hz, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.0, 152.9, 143.1, 139.2, 134.9, 134.7, 130.0, 129.1, 128.2, 126.6, 125.4, 122.8, 122.8, 119.9, 111.2, 50.6, 34.8, 31.3, 21.2. HRMS (ESI) m/z calcd for $\text{C}_{25}\text{H}_{27}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 387.1890, found 387.1886.

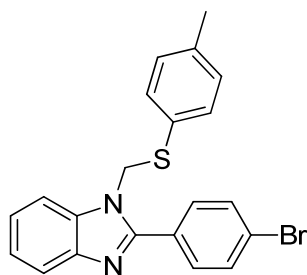
2-(4-Chlorophenyl)-1-((*p*-tolylthio)methyl)-1H-benzo[*d*]imidazole (**5ae**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol), 4-chlorobenzaldehyde (**4e**, 47 μ L, 0.4 mmol), and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **5ae** as brown solid; yield: 23.4 mg (32%), mp 121 - 123 $^{\circ}$ C.

^1H NMR (400 MHz, CDCl_3) δ 7.83 - 7.78 (m, 1H), 7.36 - 7.28 (m, 7H), 7.03 - 6.97 (m, 4H), 5.42 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 142.9, 139.6, 136.0, 134.8, 134.8, 130.7, 130.1, 128.7, 128.0, 127.8, 123.2, 123.1, 120.0, 111.3, 50.5, 21.2. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{18}\text{ClN}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 365.0874, found 365.0872.

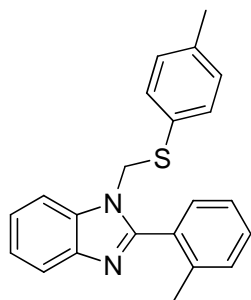
2-(4-Bromophenyl)-1-((p-tolylthio)methyl)-1H-benzo[d]imidazole (**5af**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol), 4-bromobenzaldehyde (**4f**, 74 mg, 0.4 mmol), and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **5af** as brown solid; yield: 36.4 mg (45%), mp 127 - 130 $^{\circ}$ C.

^1H NMR (400 MHz, CDCl_3) δ 7.82 - 7.78 (m, 1H), 7.50 (d, $J = 8.5$ Hz, 2H), 7.35 - 7.28 (m, 3H), 7.25 - 7.23 (m, 2H), 7.03 - 6.96 (m, 4H), 5.42 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.6, 142.9, 139.6, 134.8, 134.8, 131.7, 130.9, 130.1, 128.5, 127.7, 124.3, 123.2, 123.1, 120.0, 111.3, 50.5, 21.2. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{18}\text{BrN}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 409.0369, found 409.0370.

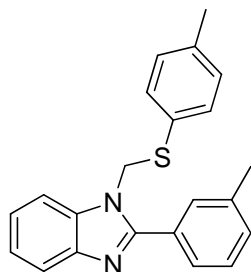
2-(o-Tolyl)-1-((p-tolylthio)methyl)-1H-benzo[d]imidazole (**5ag**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol), 2-methylbenzaldehyde (**4g**, 46 μ L, 0.4 mmol), and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **5ag** as green liquid; yield: 37.0 mg (54%).

^1H NMR (400 MHz, CDCl_3) δ 7.82 - 7.74 (m, 1H), 7.41 - 7.36 (m, 1H), 7.33 - 7.22 (m, 4H), 7.09 (t, $J = 7.5$ Hz, 1H), 6.94 (d, $J = 8.9$ Hz, 4H), 6.77 (d, $J = 7.2$ Hz, 1H), 5.23 (s, 2H), 2.32 (s, 3H), 2.08 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 153.2, 143.0, 139.1, 137.9, 134.4, 133.7, 130.2, 130.2, 130.0, 129.7, 128.9, 128.0, 125.4, 122.7, 122.6, 119.8, 111.3, 49.9, 21.1, 19.6. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 345.1420, found 345.1423.

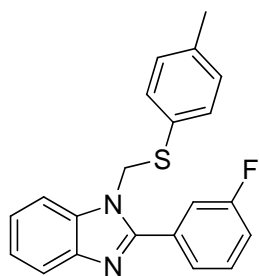
2-(*m*-Tolyl)-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (**5ah**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol), 3-methylbenzaldehyde (**4h**, 47 μ L, 0.4 mmol), and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **5ah** as brown liquid; yield: 40.1 mg (58%).

^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, $J = 7.7$ Hz, 1H), 7.37 - 7.24 (m, 5H), 7.18 (d, $J = 7.1$ Hz, 1H), 7.14 (s, 1H), 7.02 - 6.96 (m, 4H), 5.44 (s, 2H), 2.34 (s, 3H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 154.0, 143.0, 139.2, 138.3, 134.7, 134.7, 130.4, 130.1, 130.0, 129.4, 128.2, 127.9, 126.3, 122.8, 119.9, 111.3, 50.3, 21.2, 21.1. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 345.1420, found 345.1420.

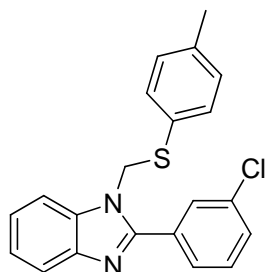
2-(3-Fluorophenyl)-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (**5ai**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol), 3-fluorobenzaldehyde (**4i**, 42 μ L, 0.4 mmol), and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **5ai** as brown liquid; yield: 24.9 mg (36%).

^1H NMR (400 MHz, CDCl_3) δ 7.82 - 7.79 (m, 1H), 7.40 - 7.28 (m, 4H), 7.17 - 7.08 (m, 2H), 7.01 - 6.93 (m, 5H), 5.43 (s, 2H), 2.32 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 161.2, 152.4 (d, J = 2.7 Hz), 143.0, 139.7, 134.9, 134.6, 131.6 (d, J = 8.3 Hz), 130.1, 129.9 (d, J = 8.2 Hz), 127.5, 124.9 (d, J = 3.1 Hz), 123.1 (d, J = 15.3 Hz), 120.1, 116.7 (d, J = 6.4 Hz), 116.5 (d, J = 4.2 Hz), 111.4, 50.4, 21.1. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{18}\text{FN}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 349.1169, found 349.1168.

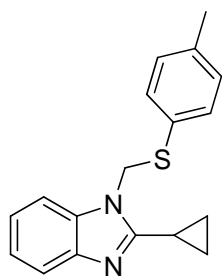
2-(3-Chlorophenyl)-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (**5aj**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol), 3-chlorobenzaldehyde (**4j**, 45 μ L, 0.4 mmol), and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **5aj** as brown solid; yield: 36.5 mg (50%), mp 82 - 85 $^\circ\text{C}$.

^1H NMR (400 MHz, CDCl_3) δ 7.82 - 7.79 (m, 1H), 7.42 - 7.20 (m, 7H), 6.97 - 6.92 (m, 4H), 5.41 (s, 2H), 2.33 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 152.3, 143.0, 139.8, 134.9, 134.6, 134.5, 131.2, 130.1, 129.6, 129.5, 129.5, 129.2, 127.2, 123.2, 123.1, 120.1, 111.5, 50.3, 21.2. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{18}\text{ClN}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 365.0874, found 365.0871.

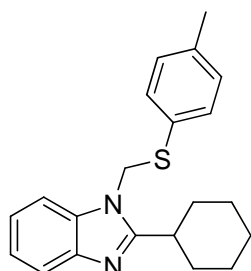
2-Cyclopropyl-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (**5ak**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol), cyclopropanecarbaldehyde (**4k**, 30 μ L, 0.4 mmol), and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **5ak** as brown liquid; yield: 18.7 mg (32%).

^1H NMR (400 MHz, CDCl_3) δ 7.65 (d, $J = 7.7$ Hz, 1H), 7.22 - 7.11 (m, 5H), 7.03 (d, $J = 7.9$ Hz, 2H), 5.43 (s, 2H), 2.30 (s, 3H), 1.46 - 1.39 (m, 1H), 1.04 - 0.99 (m, 2H), 0.86 - 0.81 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 156.4, 142.1, 139.6, 135.3, 134.4, 130.1, 128.1, 122.3, 122.0, 118.9, 109.8, 49.2, 21.1, 8.2, 7.2. HRMS (ESI) m/z calcd for $\text{C}_{18}\text{H}_{19}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 295.1264, found 295.1266.

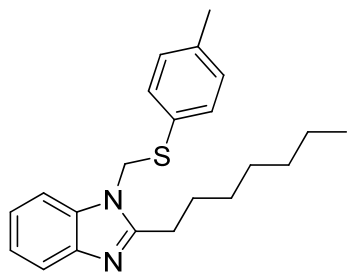
2-Cyclohexyl-1-((p-tolylthio)methyl)-1H-benzo[d]imidazole (**5al**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol), cyclohexanecarbaldehyde (**4l**, 48 μ L, 0.4 mmol), and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **5al** as brown liquid; yield: 17.3 mg (26%).

^1H NMR (400 MHz, CDCl_3) δ 7.72 (d, $J = 7.4$ Hz, 1H), 7.26 - 7.17 (m, 3H), 7.12 - 7.05 (m, 4H), 5.30 (s, 2H), 2.31 (s, 3H), 2.10 - 2.01 (m, 1H), 1.80 - 1.49 (m, 9H), 1.25 - 1.21 (m, 1H). ^{13}C NMR (100 MHz, CDCl_3) δ 159.1, 142.6, 139.7, 135.4, 133.8, 130.1, 128.2, 122.2, 122.1, 119.3, 110.1, 35.9, 31.6, 26.1, 25.7, 21.1. HRMS (ESI) m/z calcd for $\text{C}_{21}\text{H}_{25}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 337.1733, found 337.1734.

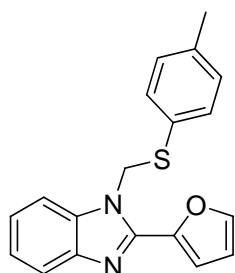
2-Heptyl-1-((p-tolylthio)methyl)-1H-benzo[d]imidazole (**5am**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol), octanal (**4m**, 64 μ L, 0.4 mmol), and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **5am** as brown liquid; yield: 17.4 mg (25%).

^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 7.7$ Hz, 1H), 7.25 - 7.18 (m, 3H), 7.09 - 7.01 (m, 4H), 5.29 (s, 2H), 2.31 (s, 3H), 1.67 (d, $J = 7.3$ Hz, 2H), 1.27 (d, $J = 16.2$ Hz, 10H), 0.88 (d, $J = 6.6$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 155.3, 142.5, 139.7, 135.3, 134.1, 130.1, 128.1, 122.2, 122.2, 119.2, 110.1, 49.3, 31.7, 29.5, 28.9, 27.2, 26.9, 22.6, 21.1, 14.1. HRMS (ESI) m/z calcd for $\text{C}_{22}\text{H}_{29}\text{N}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 353.2046, found 353.2044.

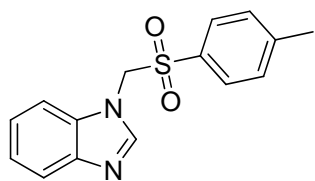
2-(Furan-2-yl)-1-((*p*-tolylthio)methyl)-1H-benzo[*d*]imidazole (**5an**)



The reaction was conducted with 4-methylbenzenethiol (**2a**, 62 mg, 0.5 mmol), furan-2-carbaldehyde (**4n**, 33 μ L, 0.4 mmol), and 1,2-diaminobenzene (**1a**, 21.6 mg, 0.2 mmol). The residue was purified by column chromatography (silica gel, petroleum ether/ethyl acetate = 5:1) to give **5an** as brown liquid; yield: 33.3 mg (52%).

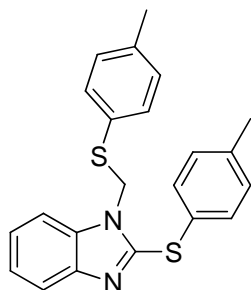
^1H NMR (400 MHz, CDCl_3) δ 7.71 (d, $J = 8.0$ Hz, 1H), 7.41 (d, $J = 1.1$ Hz, 1H), 7.25 - 7.20 (m, 1H), 7.17 - 7.12 (m, 1H), 7.06 - 7.00 (m, 3H), 6.95 (d, $J = 3.5$ Hz, 1H), 6.87 (d, $J = 7.9$ Hz, 2H), 6.46 - 6.43 (m, 1H), 5.69 (s, 2H), 2.21 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 145.1, 143.8, 143.6, 142.9, 139.2, 134.9, 134.6, 129.7, 128.1, 122.9, 122.9, 119.7, 112.7, 111.7, 110.3, 50.4, 21.0. HRMS (ESI) m/z calcd for $\text{C}_{19}\text{H}_{17}\text{N}_2\text{OS}^+$ ($\text{M}+\text{H}$) $^+$ 321.1056, found 321.1055.

1-(Tosylmethyl)-1H-benzo[*d*]imidazole (**6aa**)



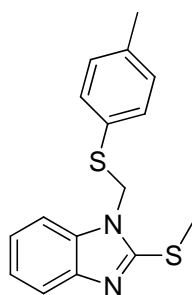
^1H NMR (400 MHz, CDCl_3) δ 7.77 (d, $J = 8.0$ Hz, 1H), 7.66 (s, 1H), 7.44 (d, $J = 8.2$ Hz, 2H), 7.26 (d, $J = 9.1$ Hz, 1H), 7.20 - 7.17 (m, 3H), 7.08 (d, $J = 8.1$ Hz, 1H), 5.38 (s, 2H), 2.38 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 146.4, 142.8, 142.7, 132.9, 132.1, 130.2, 128.8, 123.9, 123.1, 120.4, 109.5, 64.9, 21.6. calcd for $\text{C}_{15}\text{H}_{15}\text{N}_2\text{O}_2\text{S}^+$ ($\text{M}+\text{H}$) $^+$ 287.0849, found 287.0852.

2-(*p*-tolylthio)-1-((*p*-tolylthio)methyl)-1*H*-benzo[*d*]imidazole (7aa)



^1H NMR (400 MHz, CDCl_3) δ 7.70 (d, $J = 7.5$ Hz, 1H), 7.26 - 7.18 (m, 5H), 7.12 - 7.08 (m, 4H), 7.02 (d, $J = 8.0$ Hz, 2H), 5.45 (s, 2H), 2.31 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 149.1, 143.2, 139.5, 138.3, 135.1, 134.8, 131.6, 130.1, 130.0, 127.8, 127.4, 123.0, 122.6, 119.6, 110.5, 49.9, 21.2, 21.1. calcd for $\text{C}_{22}\text{H}_{21}\text{N}_2\text{S}_2^+$ ($\text{M}+\text{H}$) $^+$ 377.1141, found 377.1145.

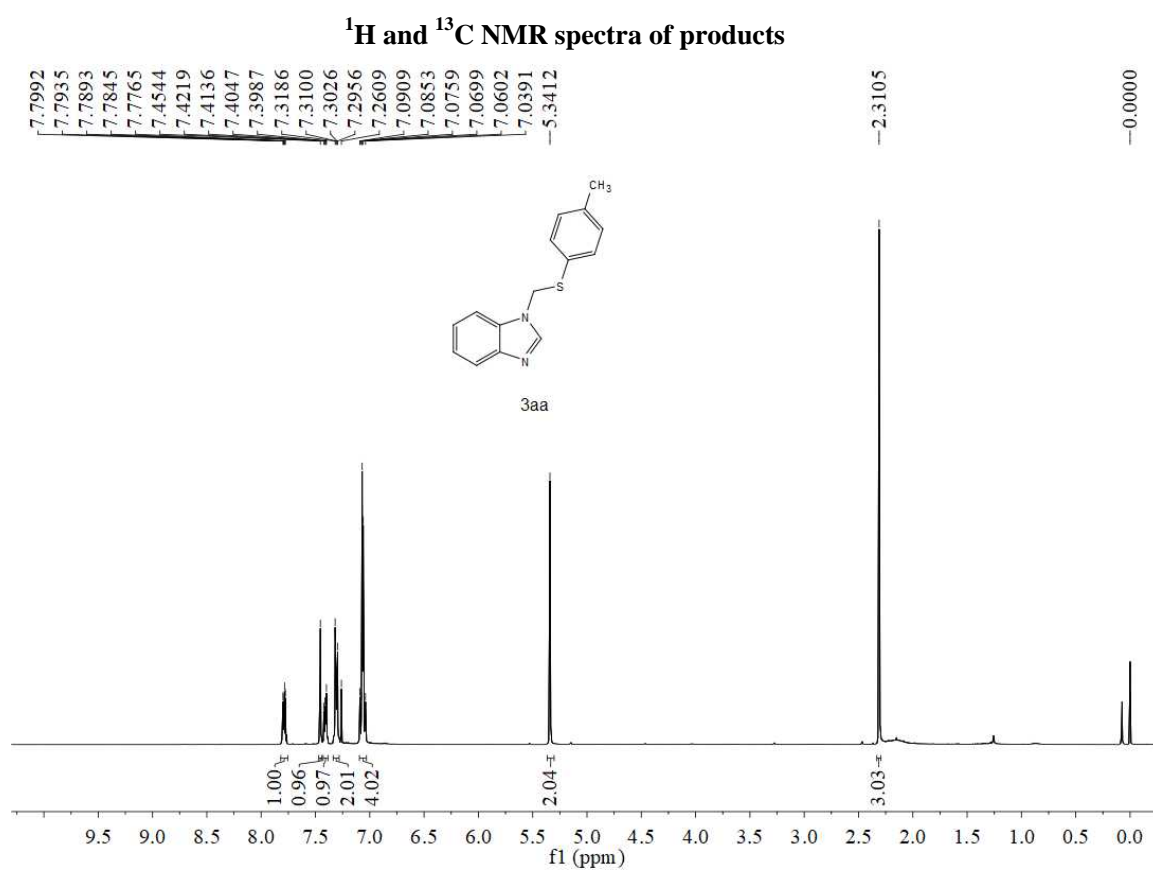
2-(Methylthio)-1-((phenylthio)methyl)-1*H*-benzo[*d*]imidazole (8aa)

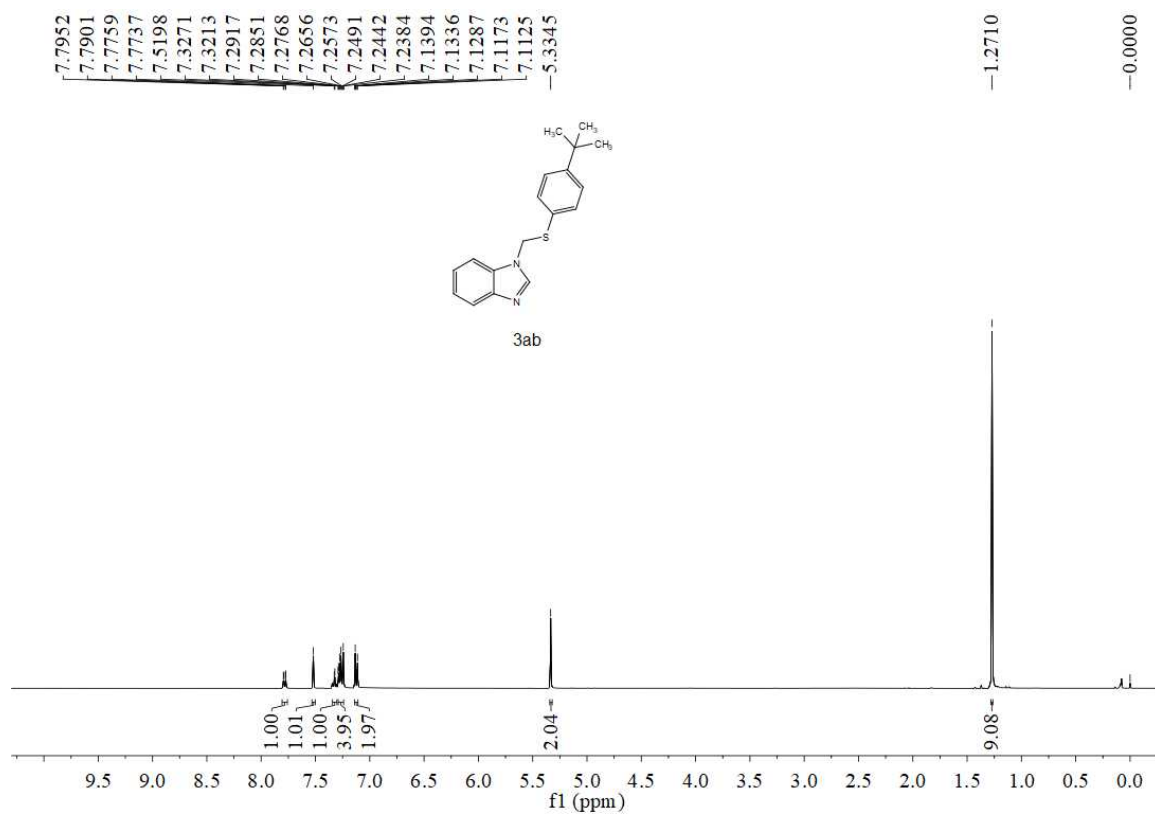
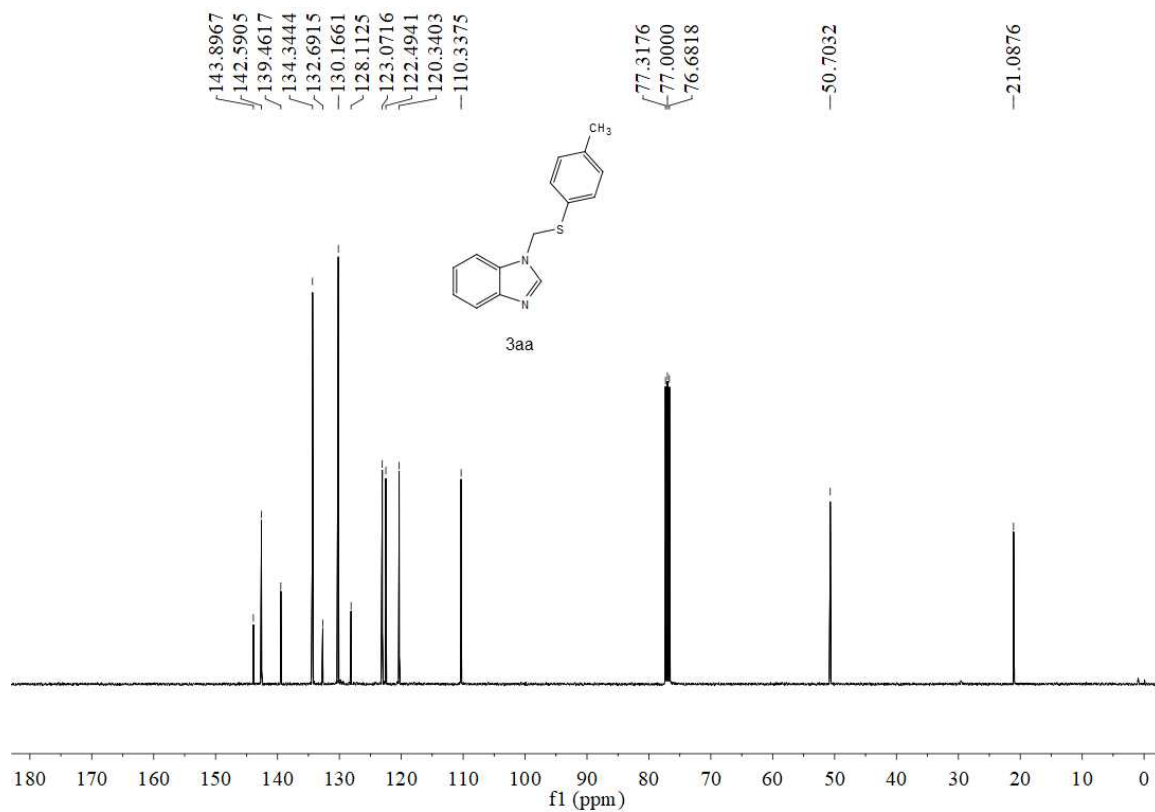


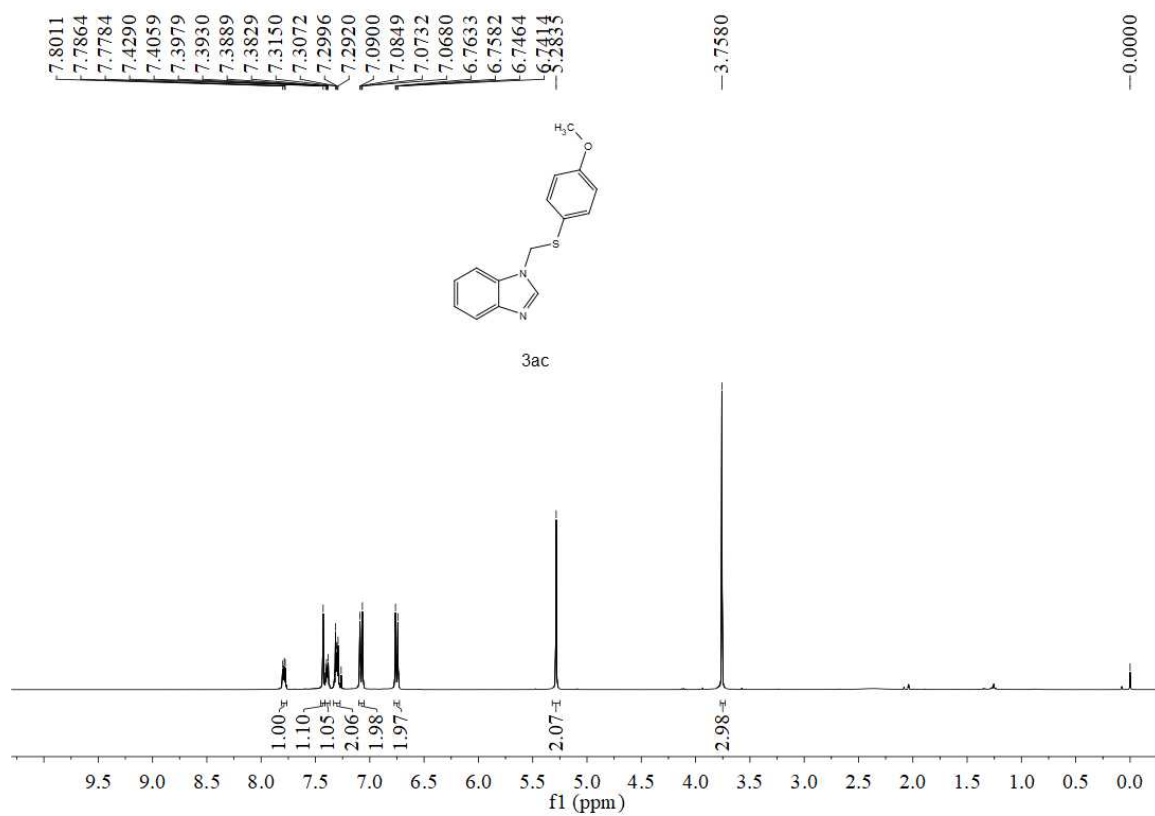
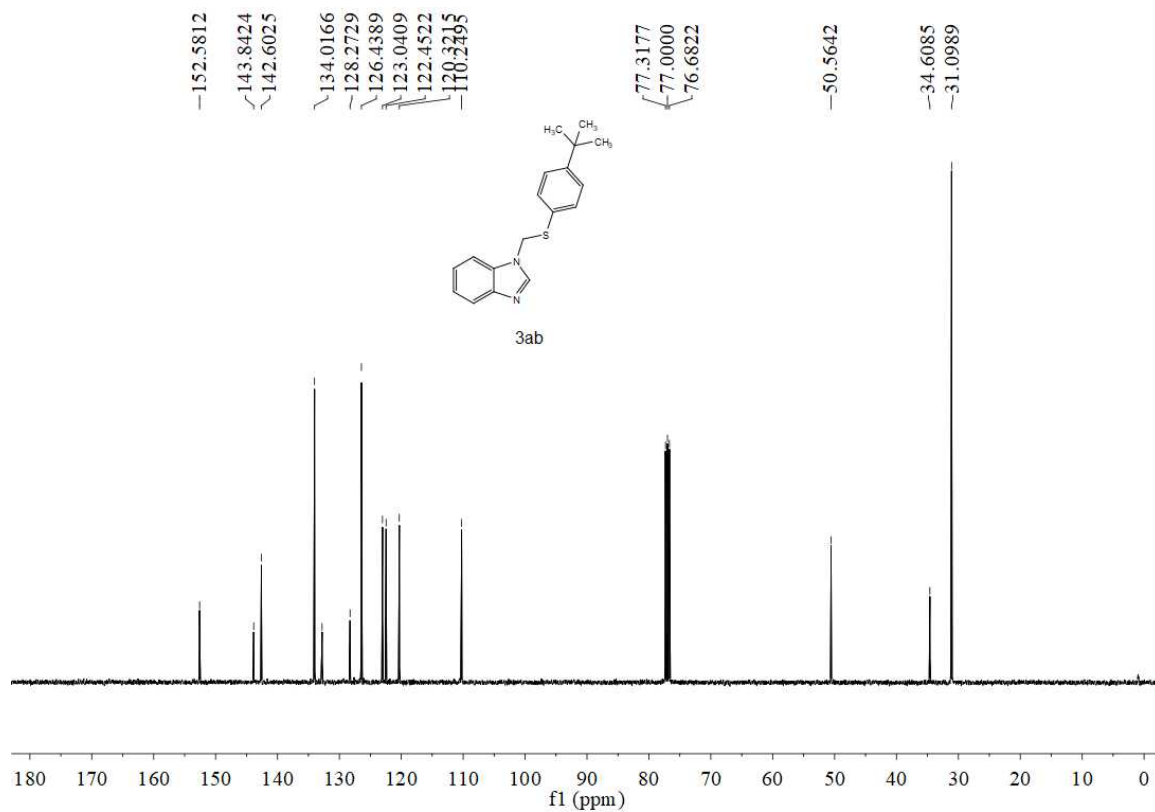
^1H NMR (400 MHz, CDCl_3) δ 7.68 (d, $J = 8.0$ Hz, 1H), 7.22 (t, $J = 7.6$ Hz, 1H), 7.13 (t, $J = 7.4$ Hz, 3H), 7.03 (t, $J = 8.8$ Hz, 3H), 5.31 (s, 2H), 2.68 (s, 3H), 2.31 (s, 3H). ^{13}C NMR (100 MHz,

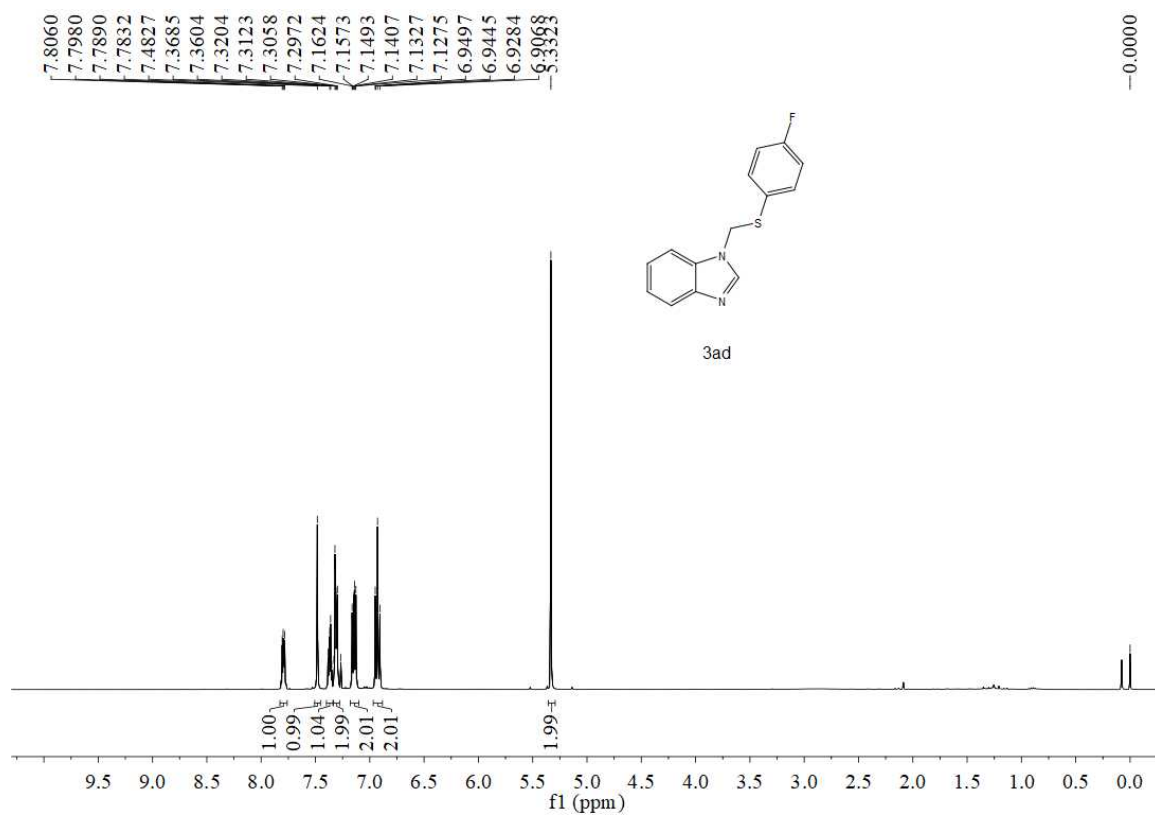
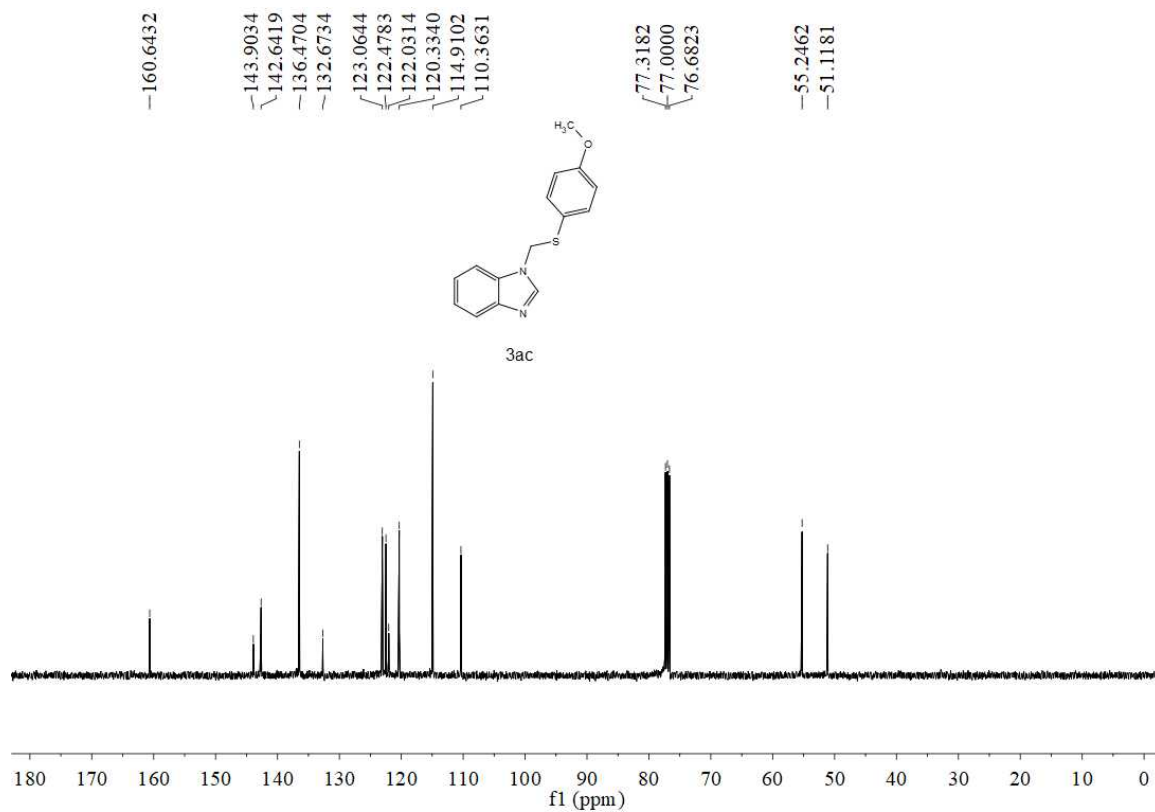
CDCl₃) δ 153.0, 143.2, 139.4, 135.3, 135.1, 129.9, 127.9, 122.2, 122.0, 118.1, 109.6, 49.8, 21.2,

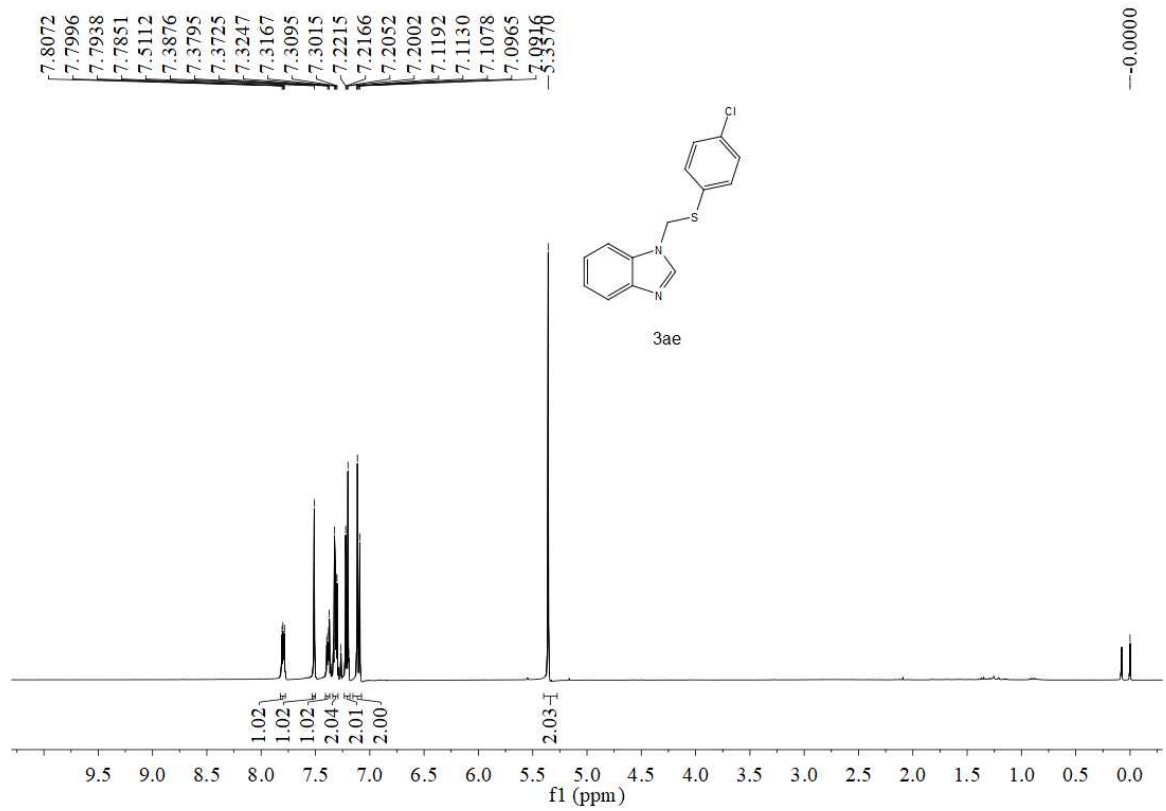
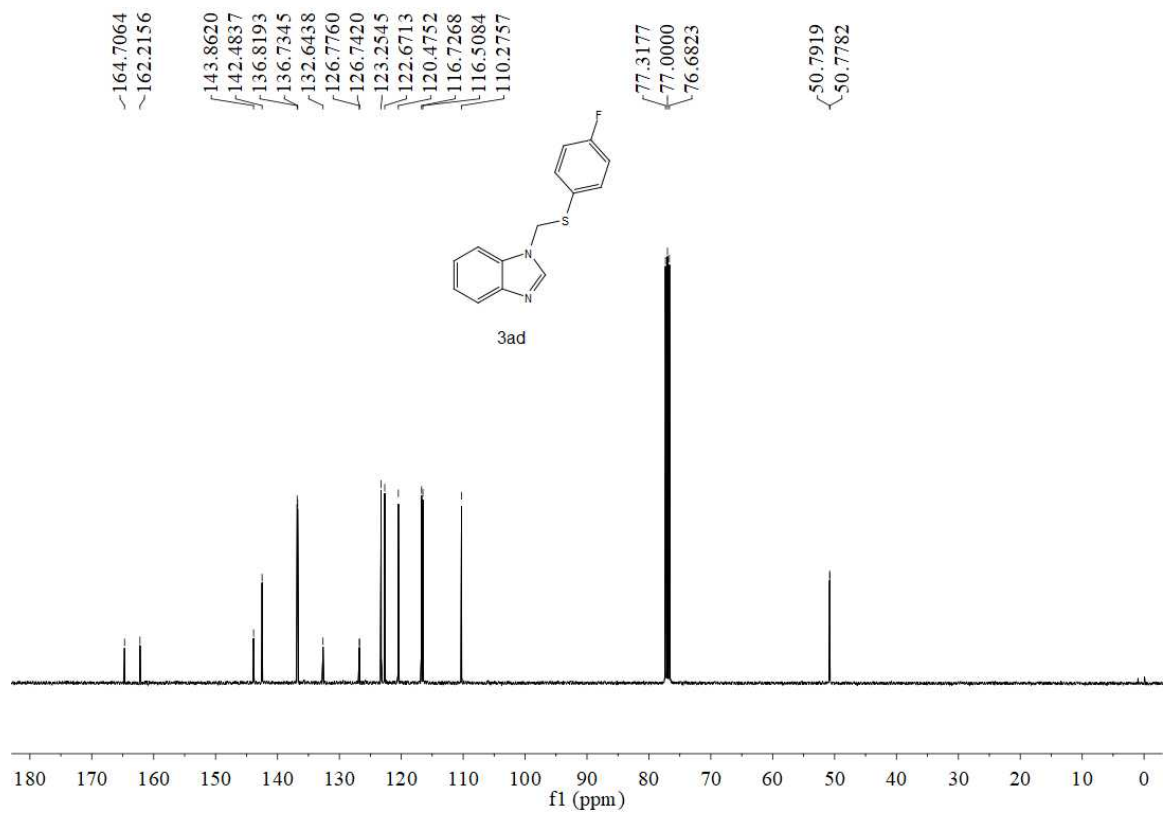
15.2. calcd for C₁₆H₁₇N₂S₂⁺ (M+H)⁺ 301.0828, found 301.0826.

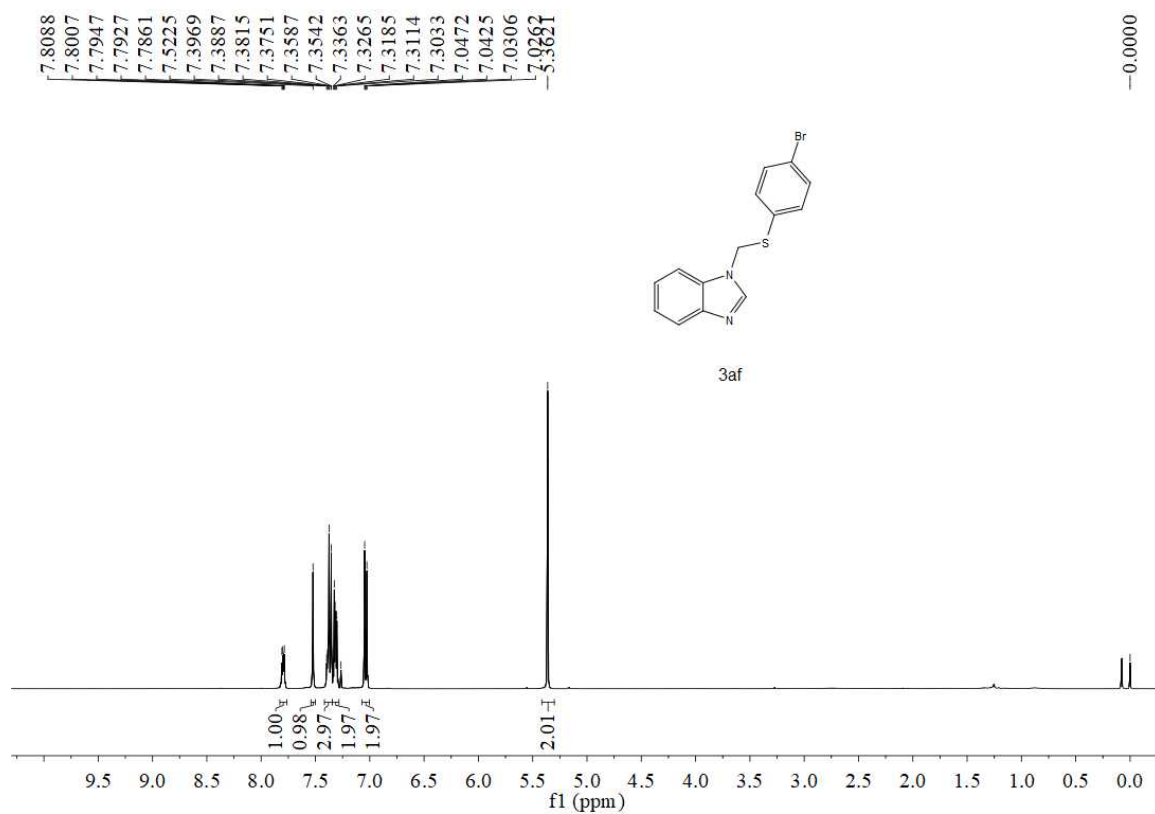
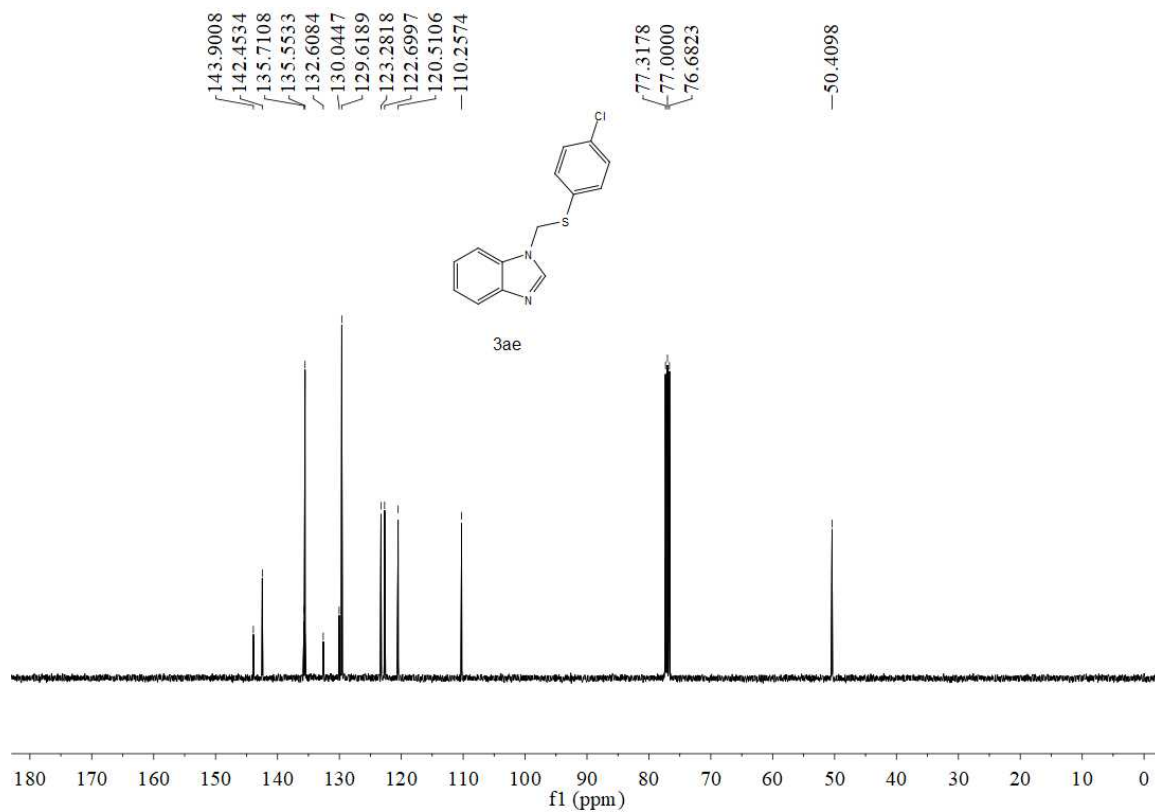


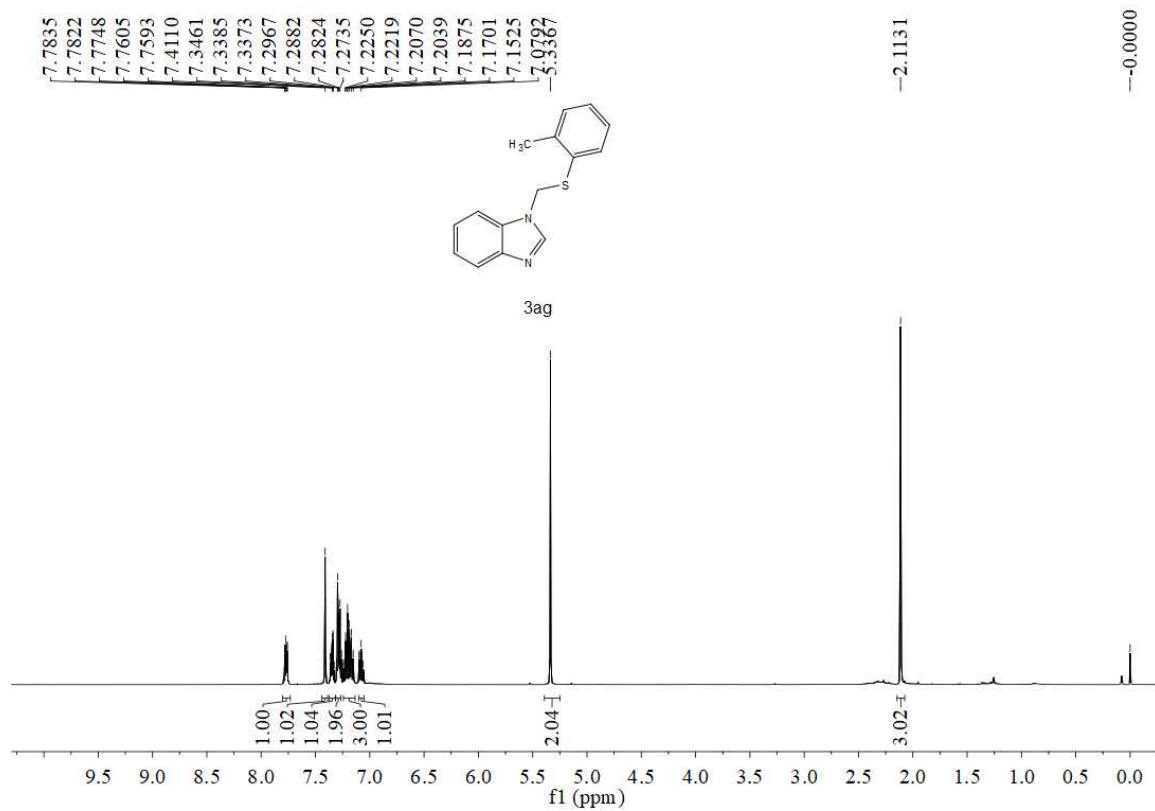
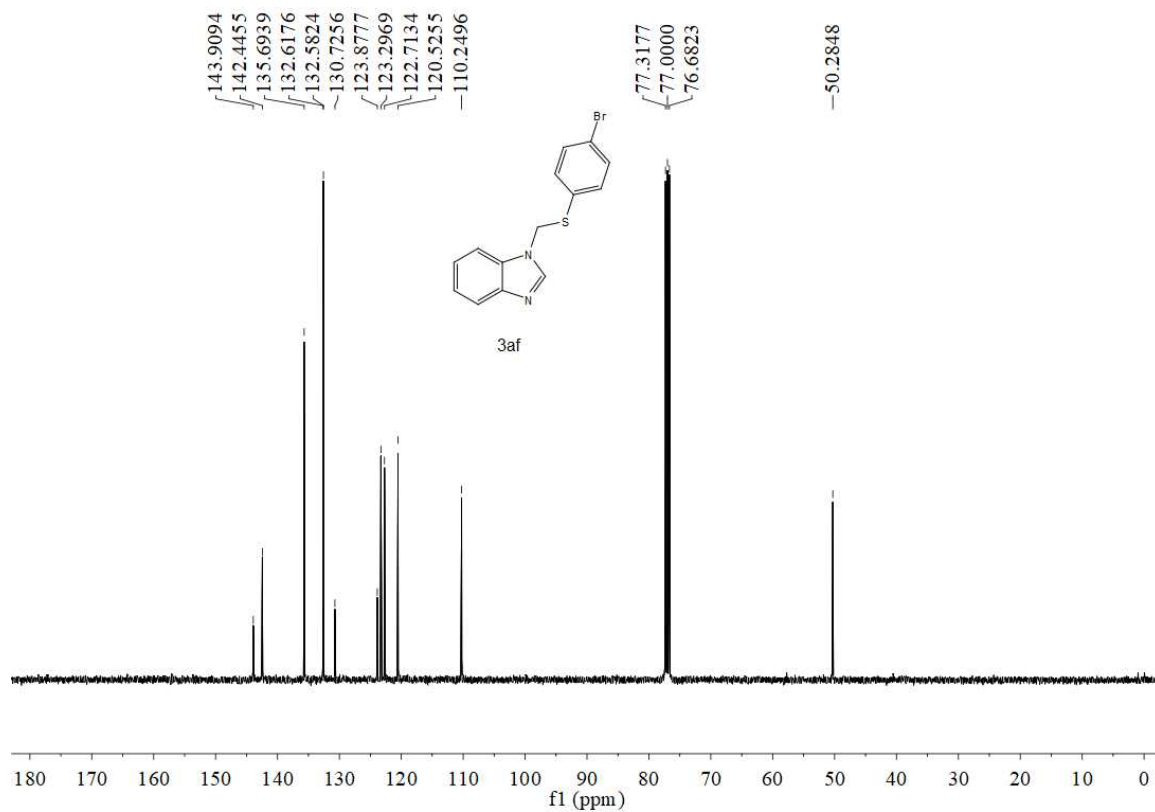


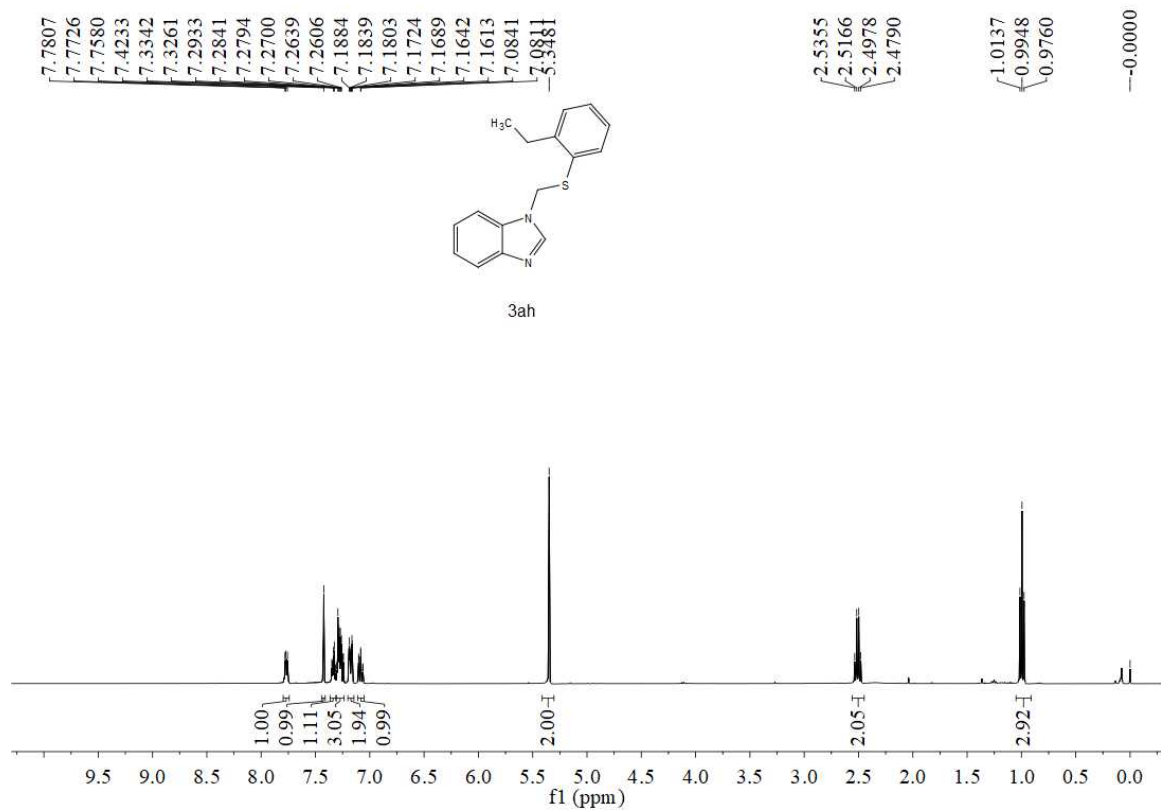
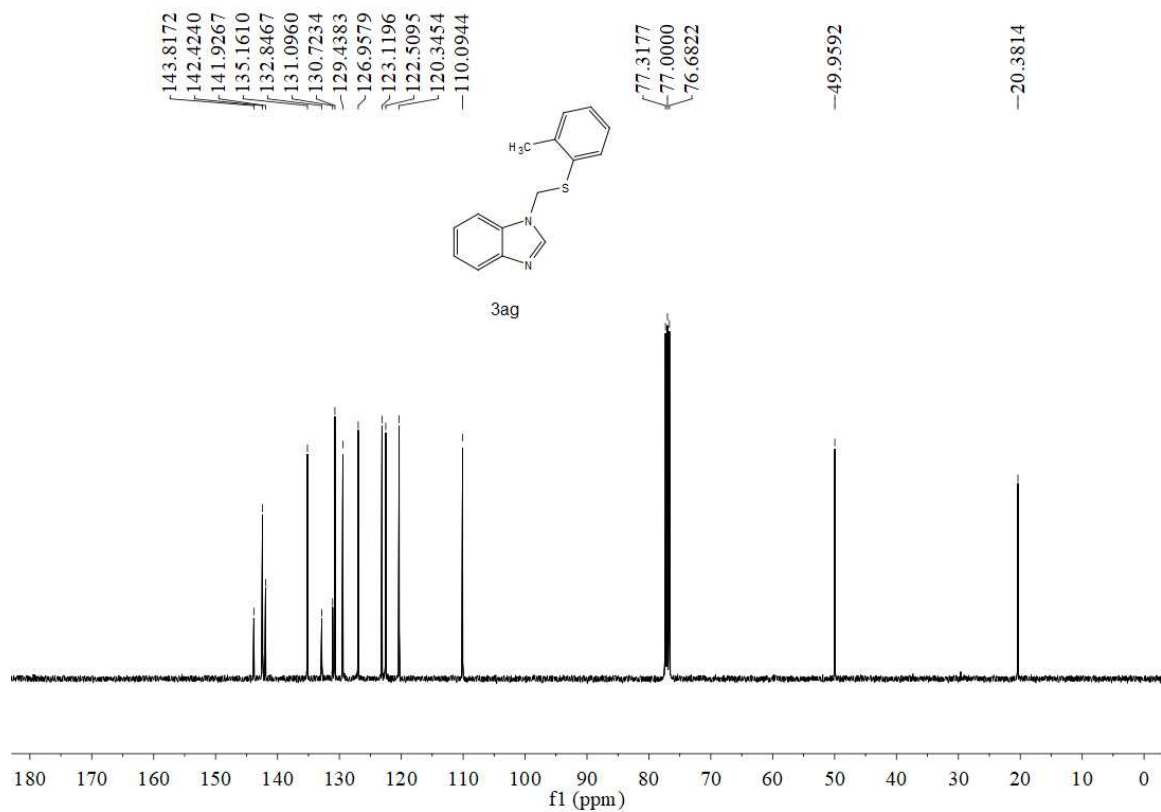


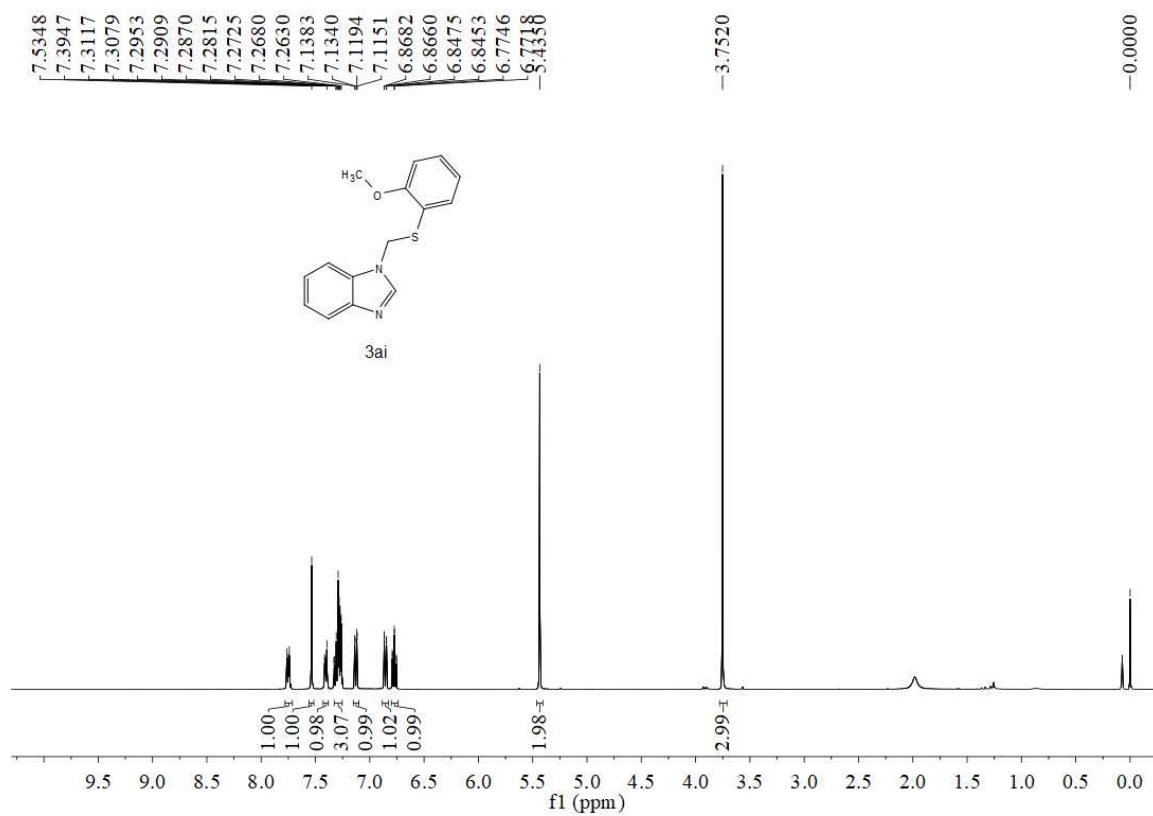
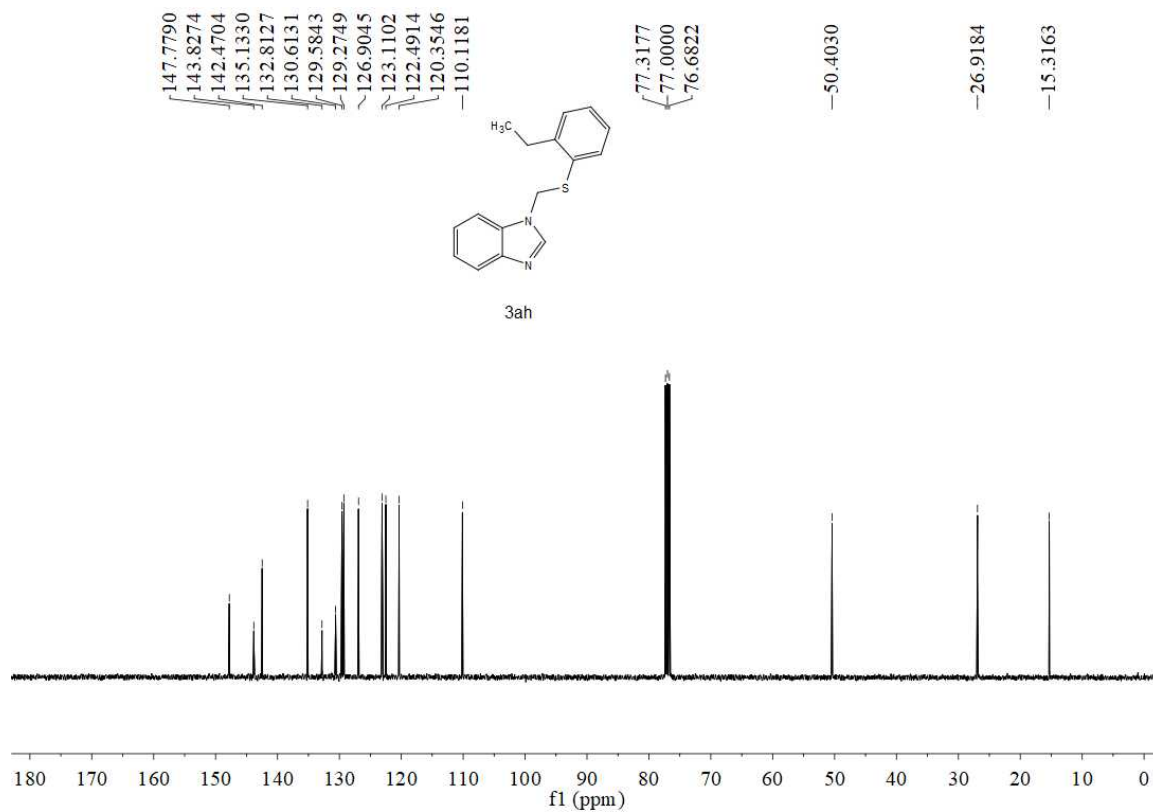


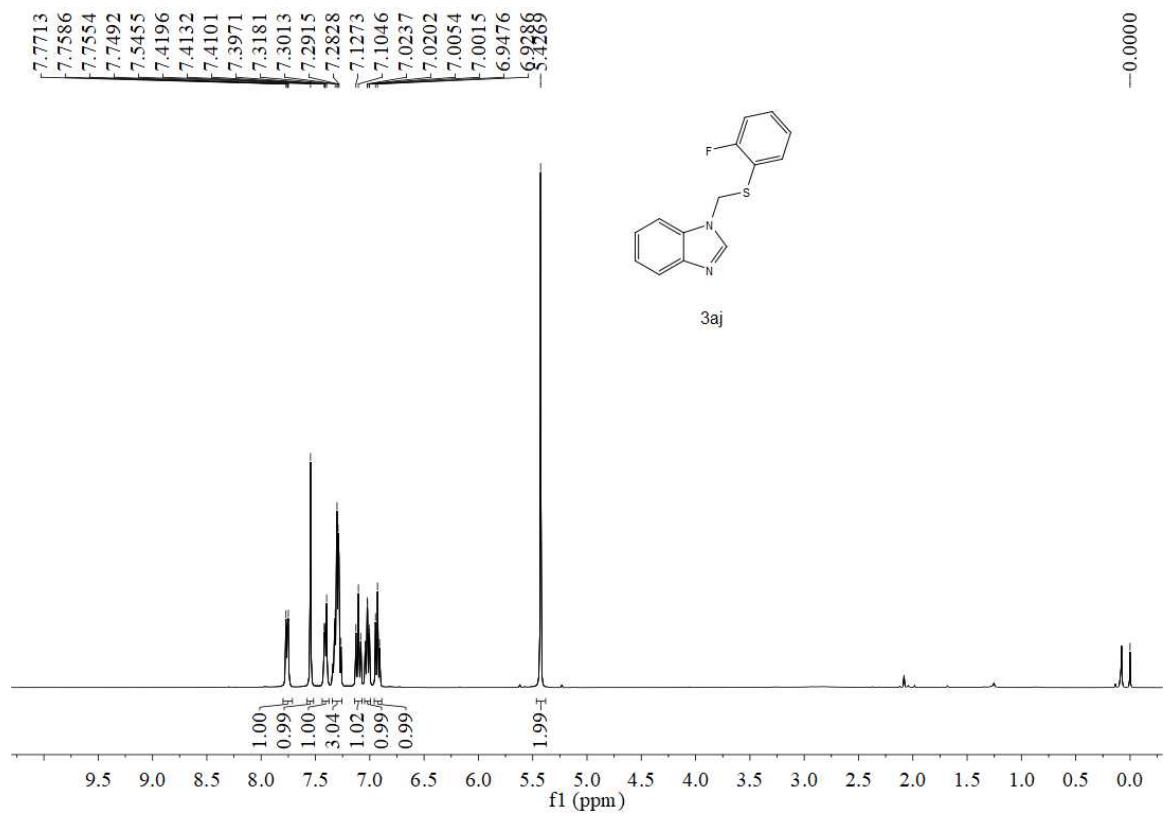
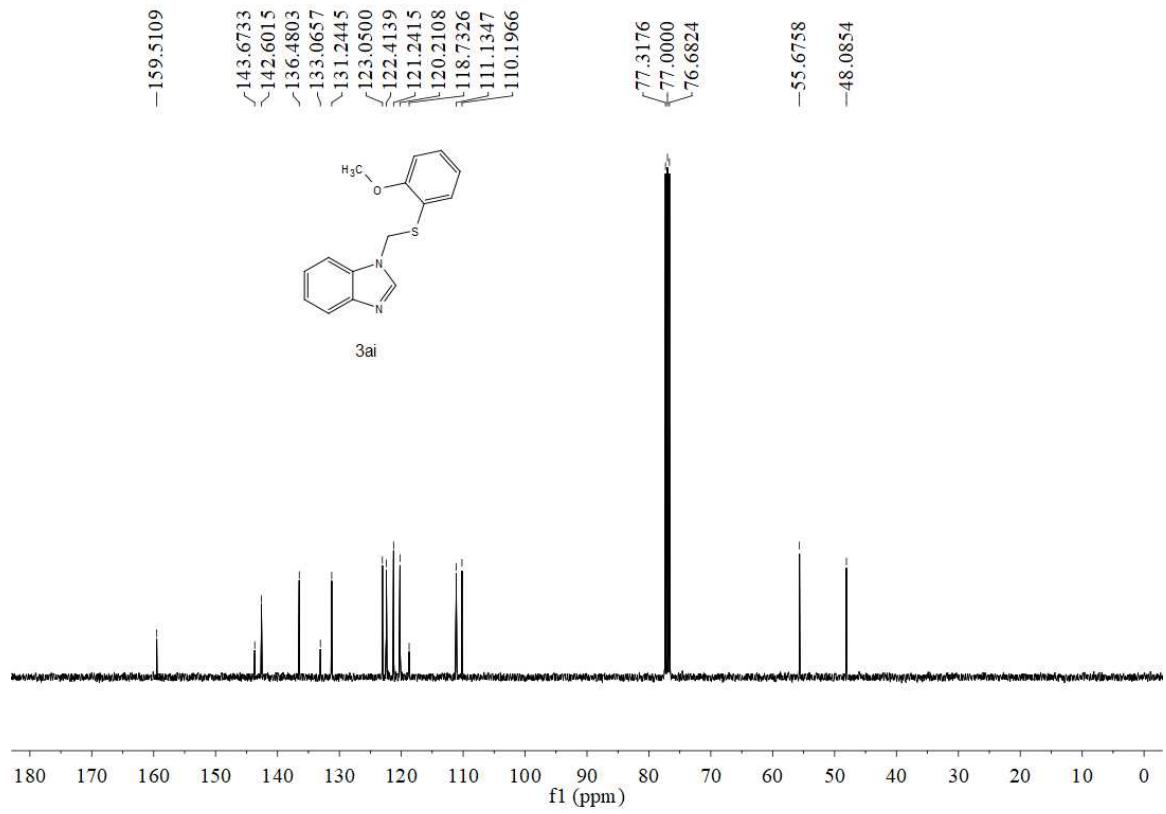


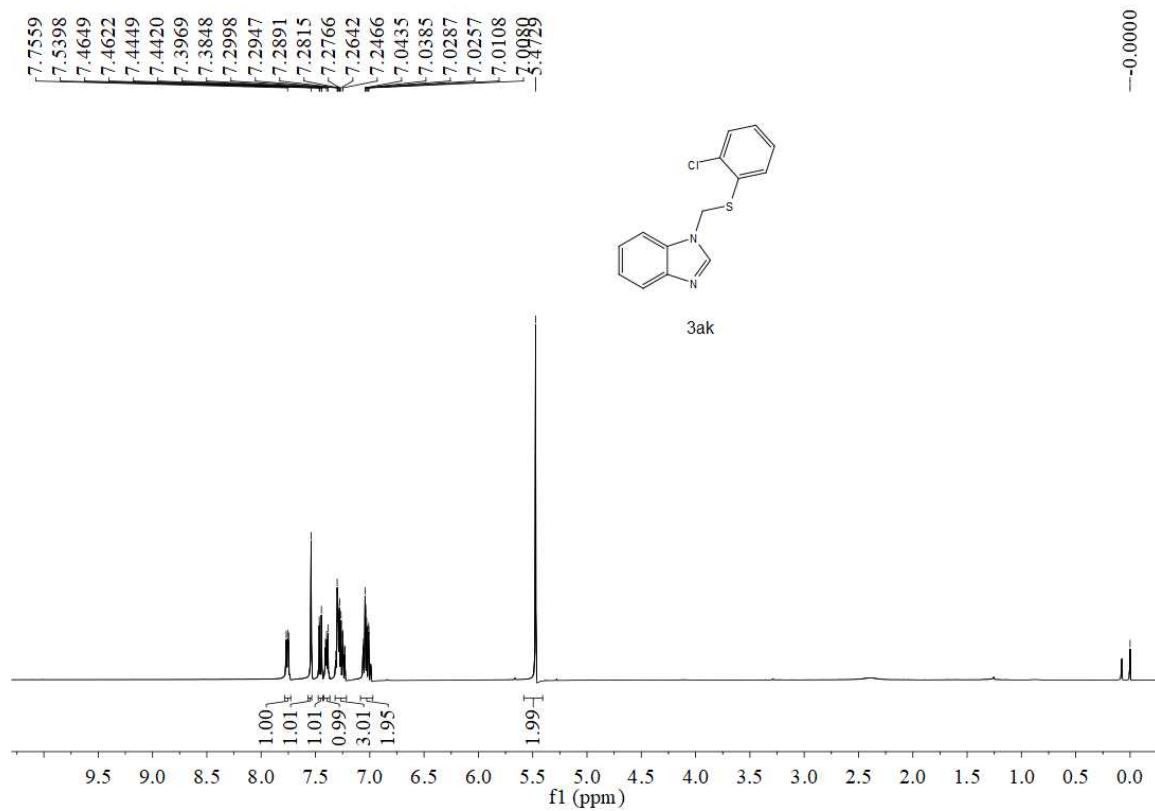
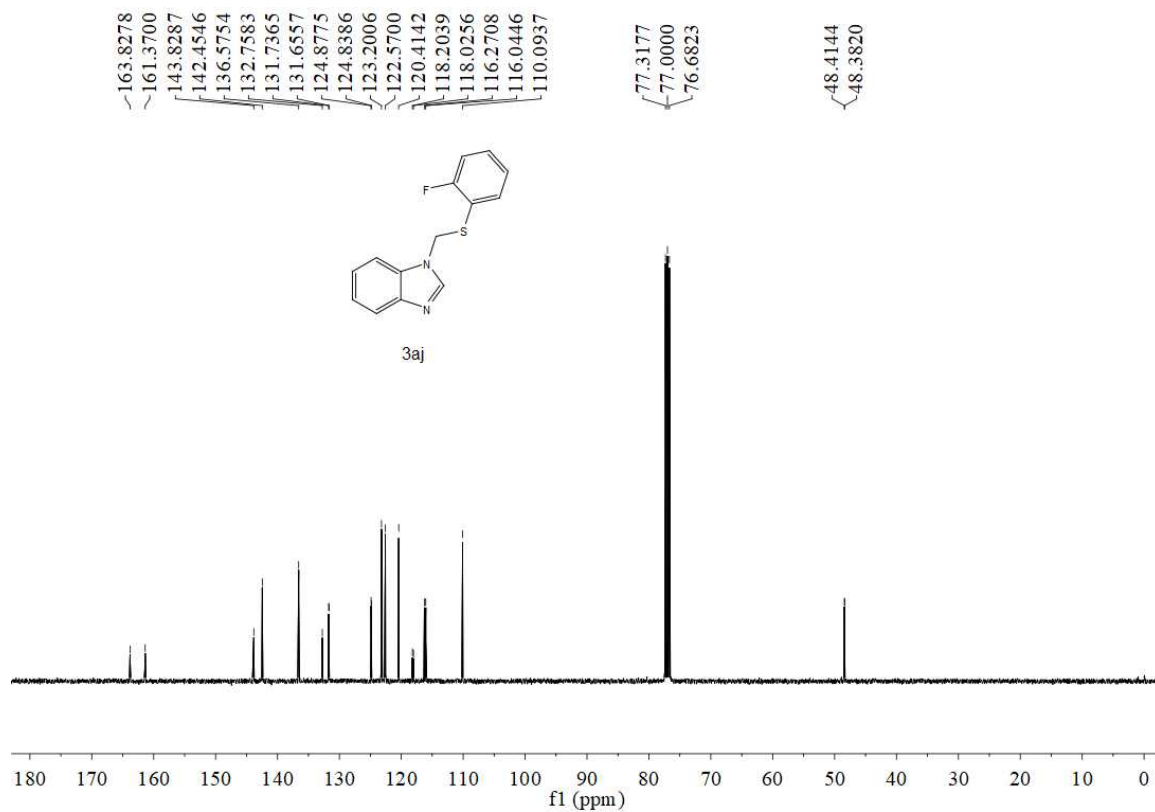


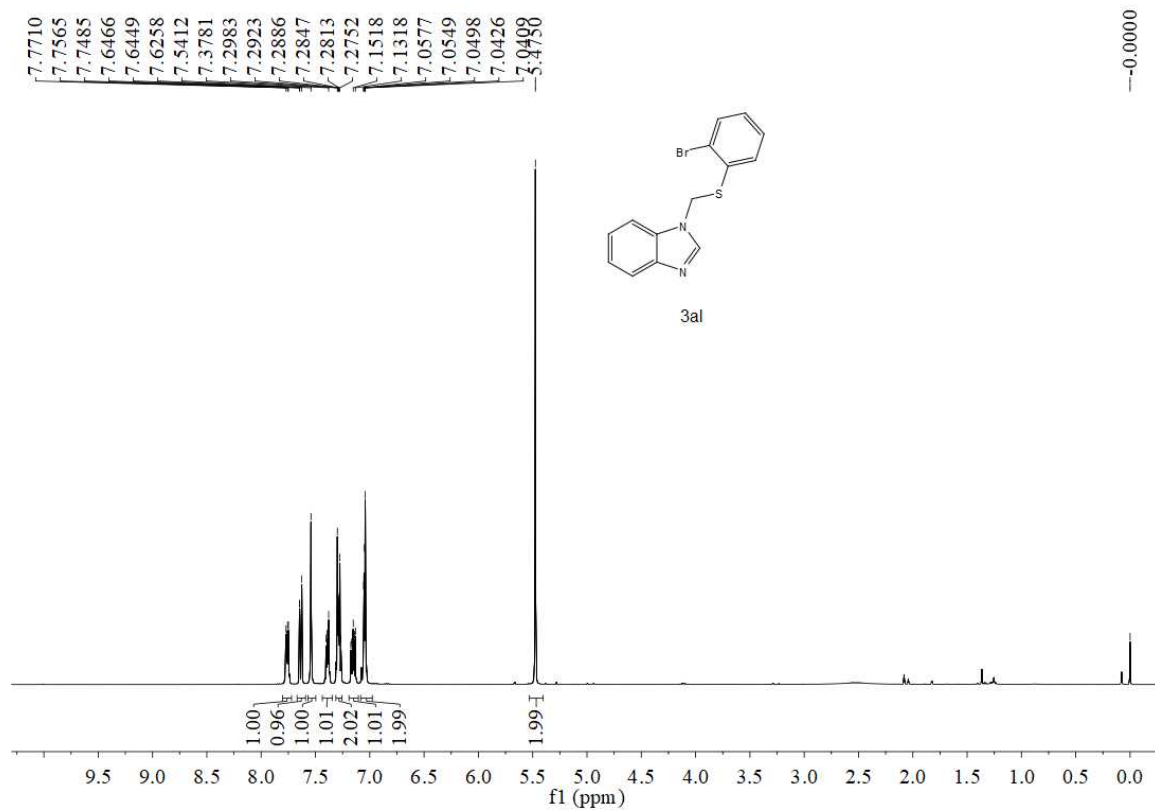
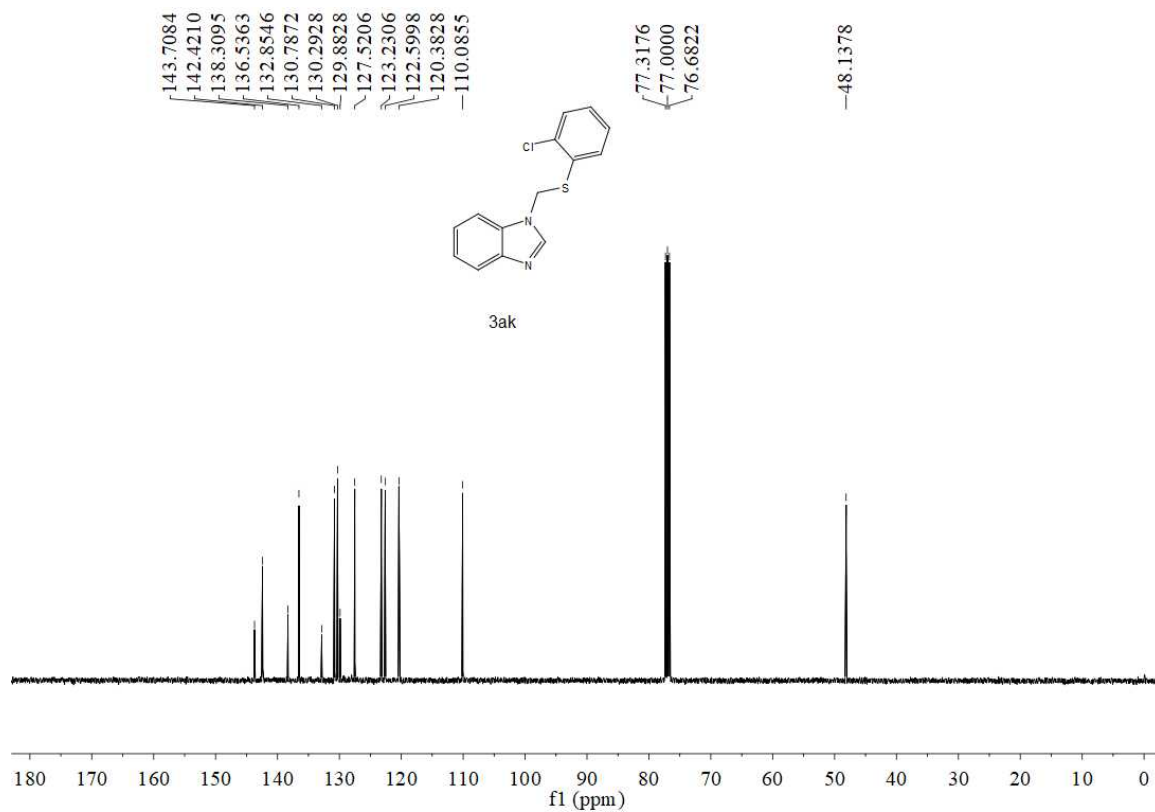


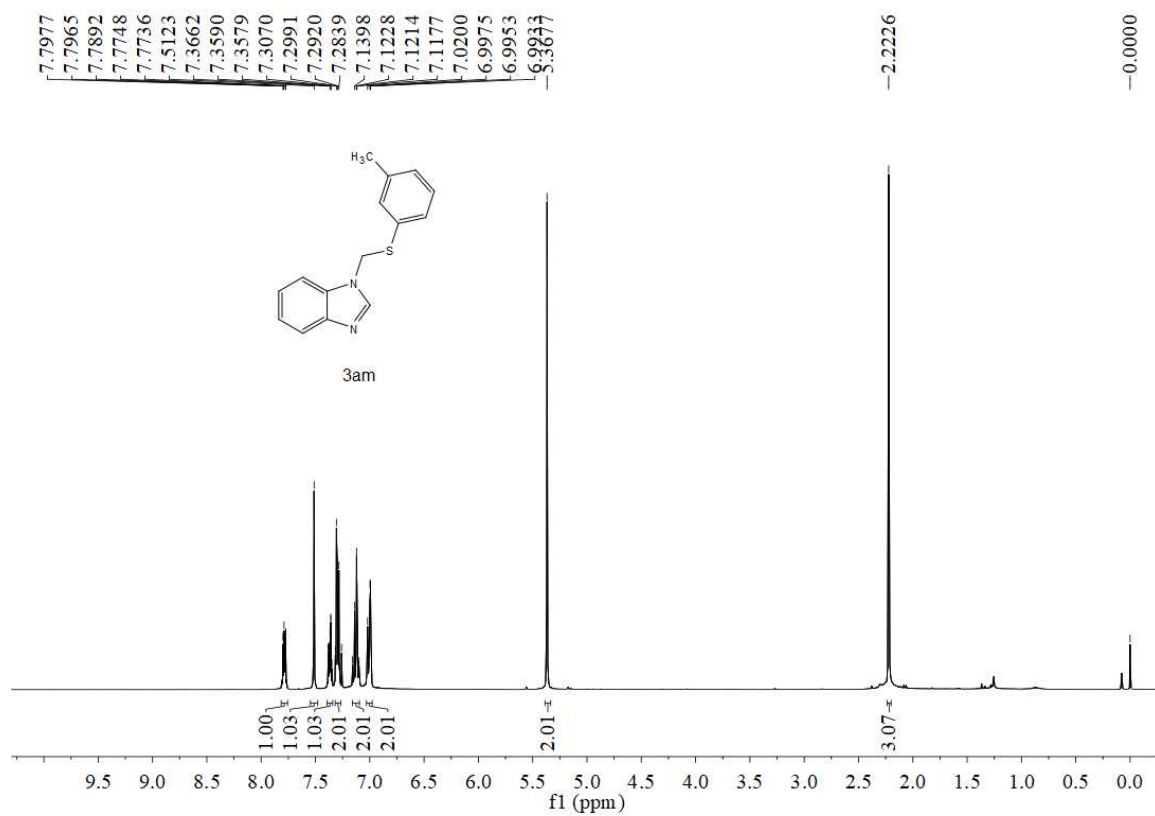
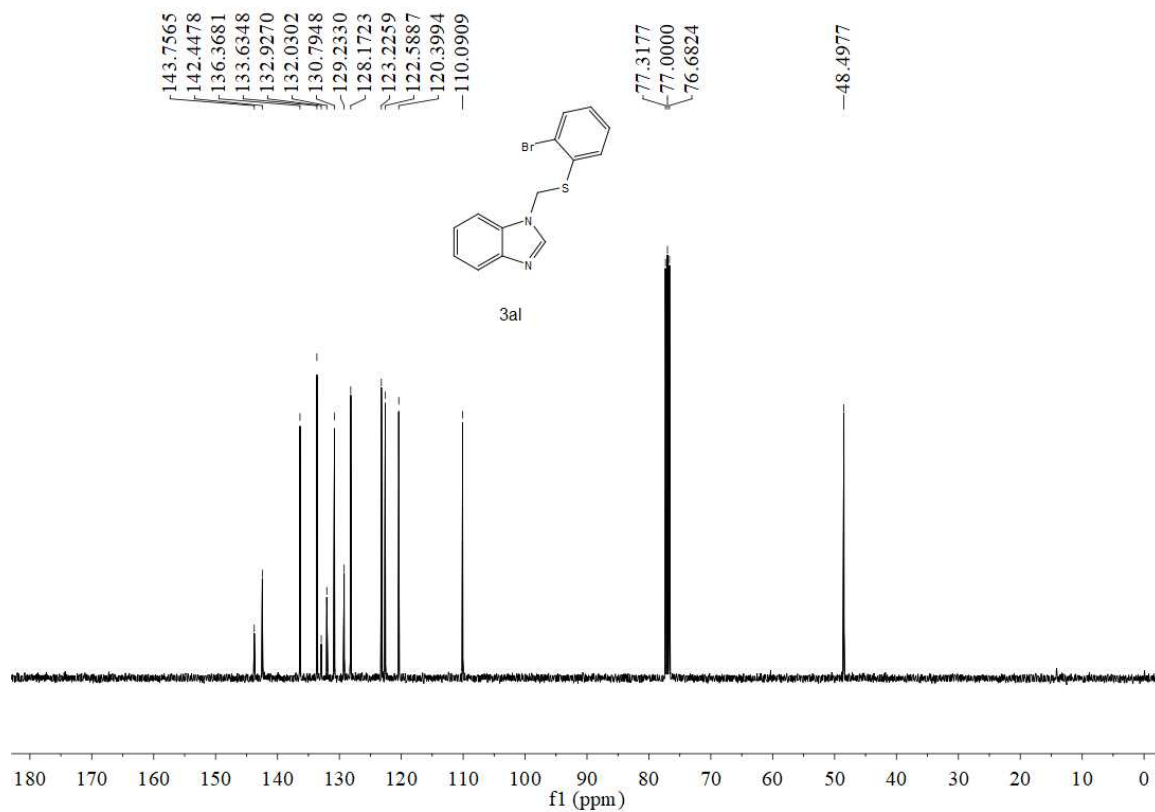


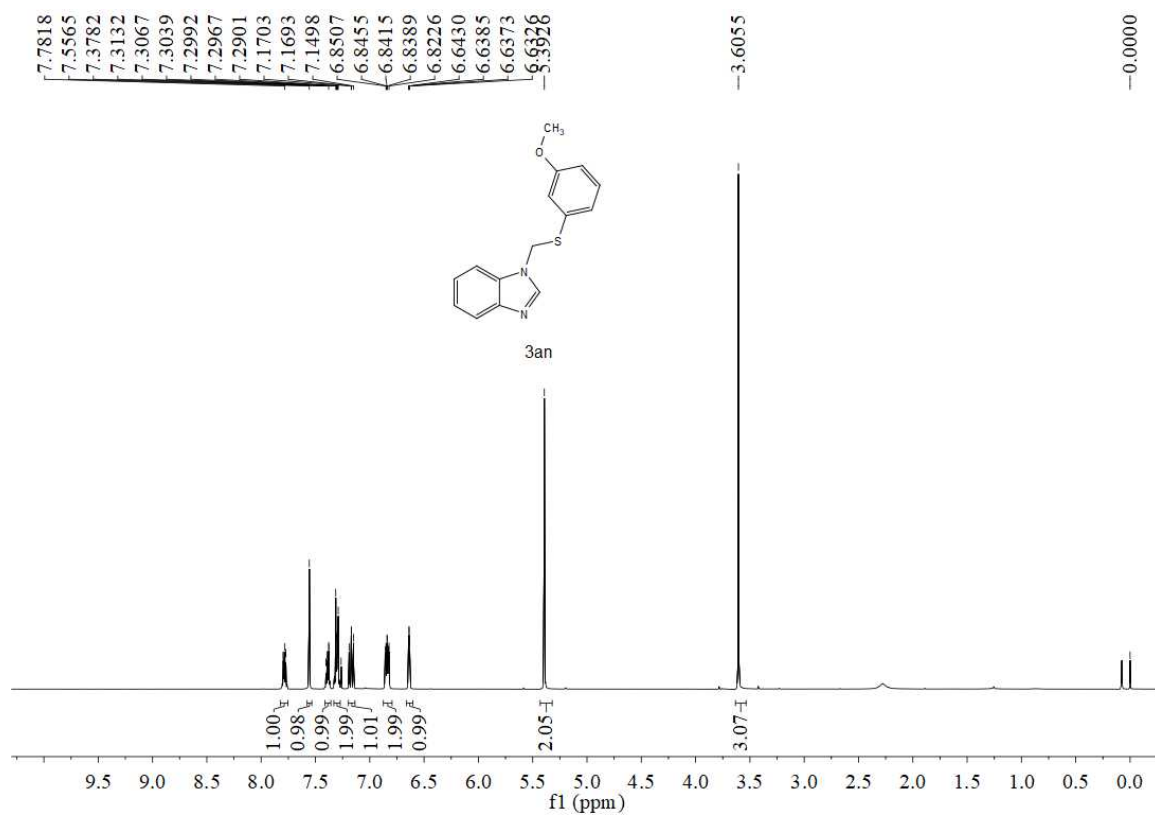
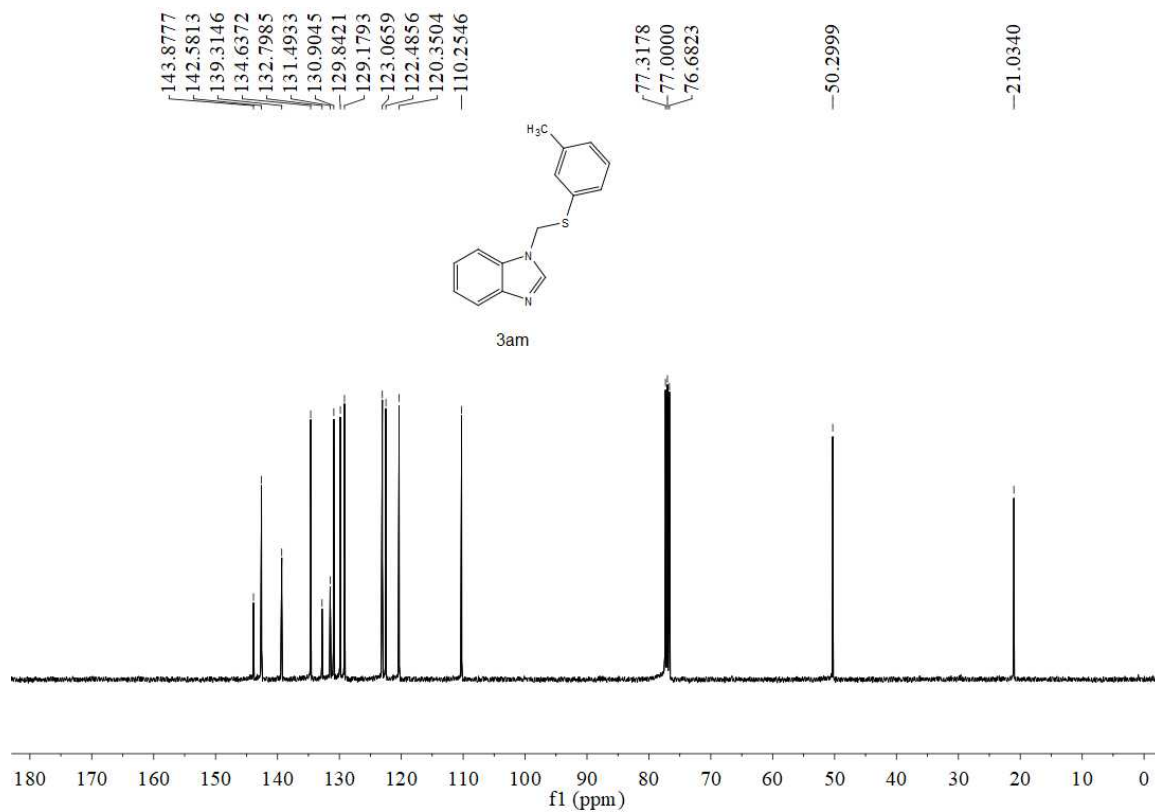


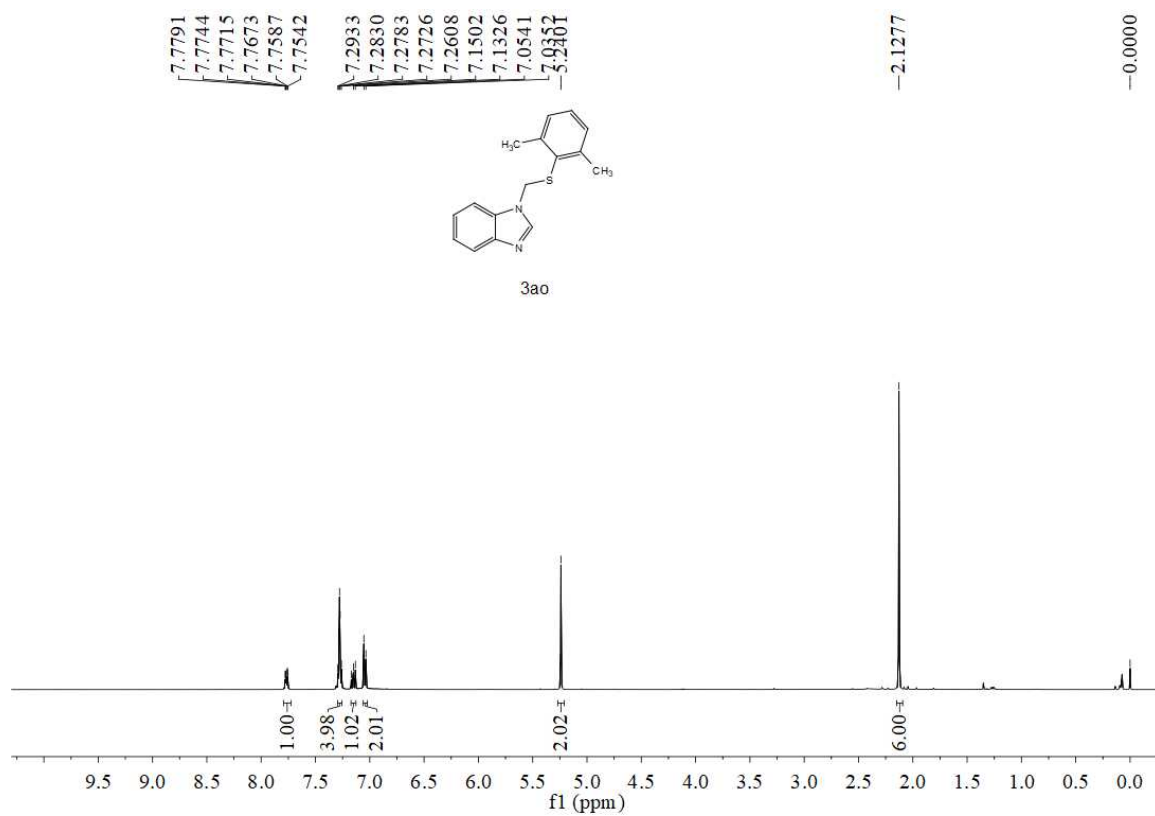
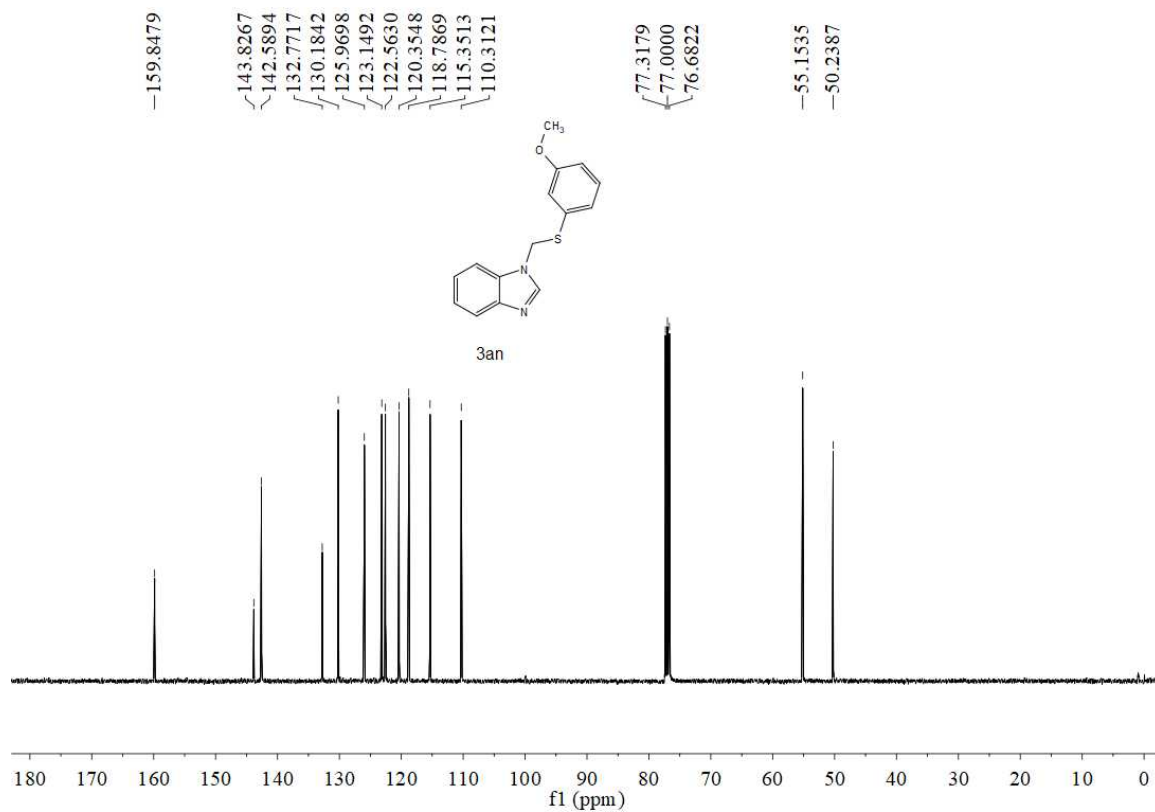


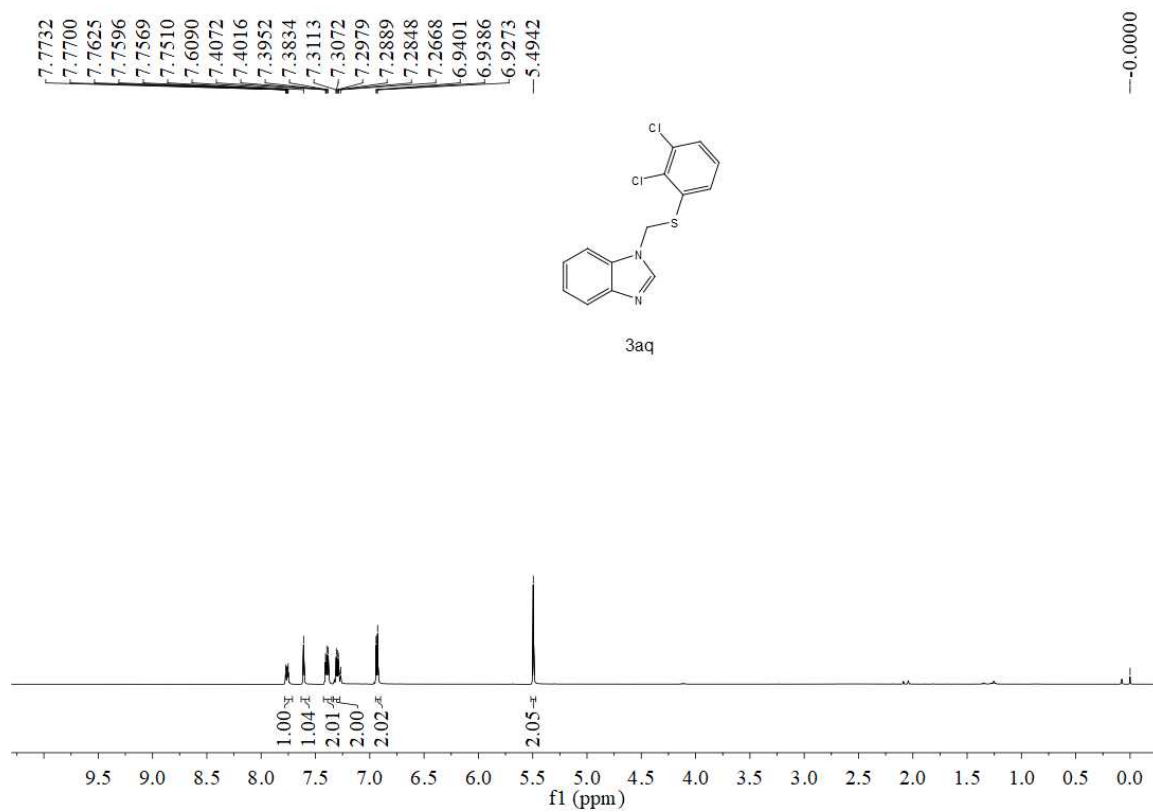
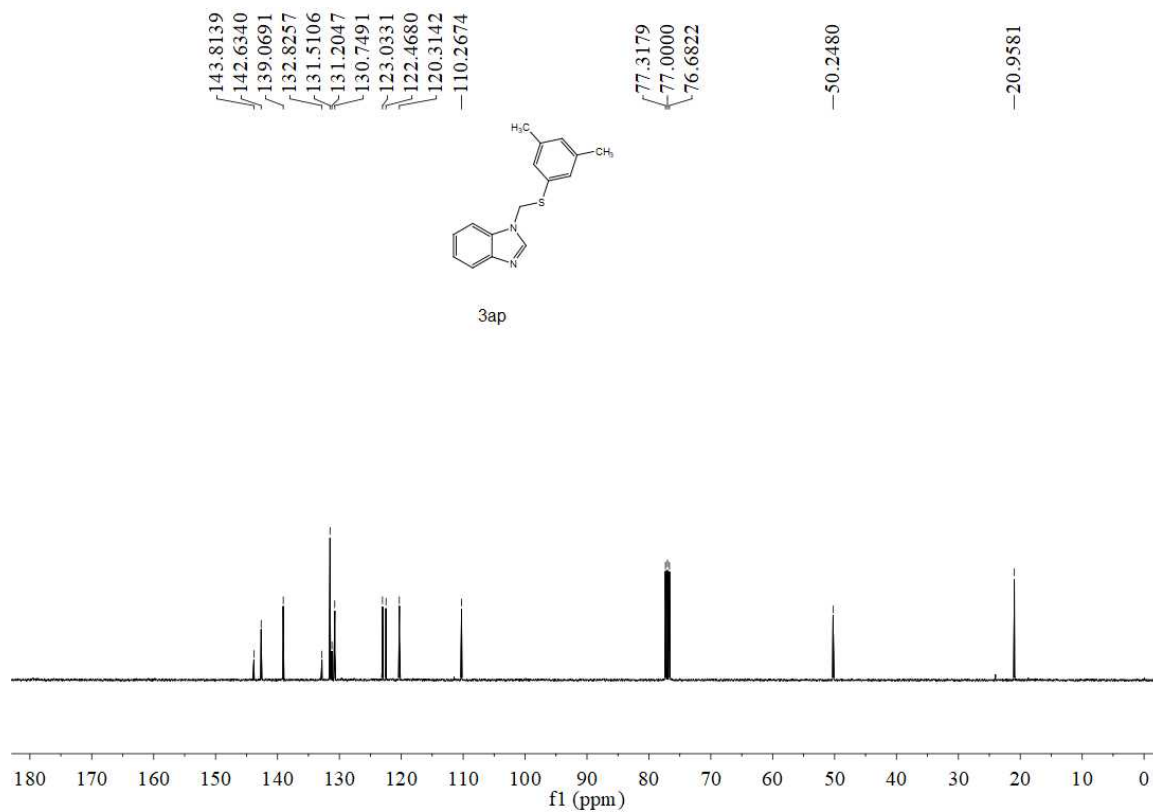


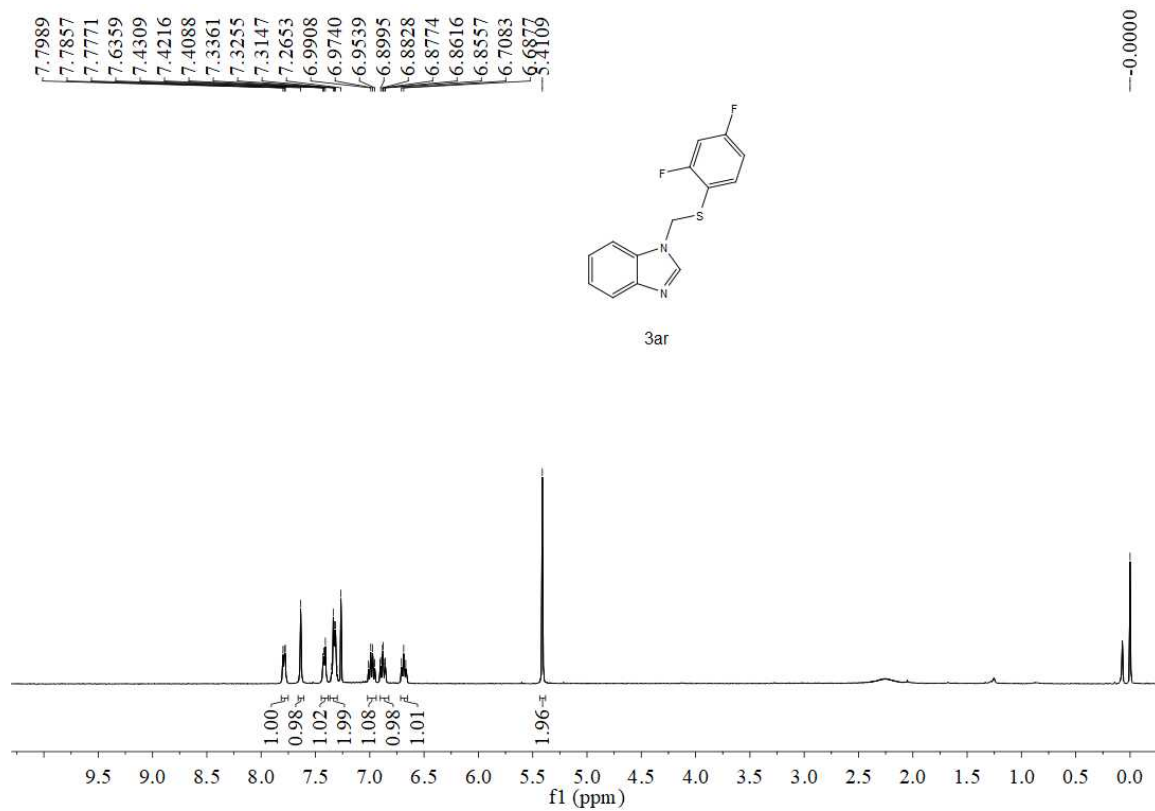
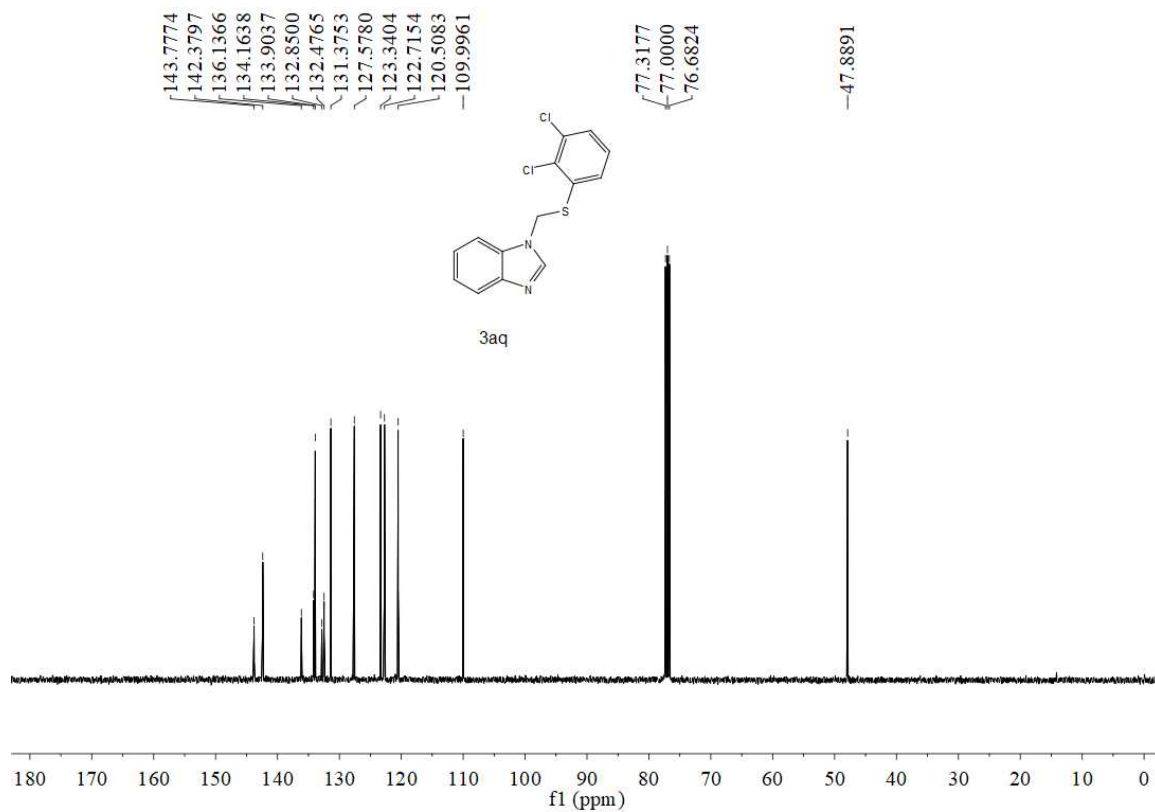


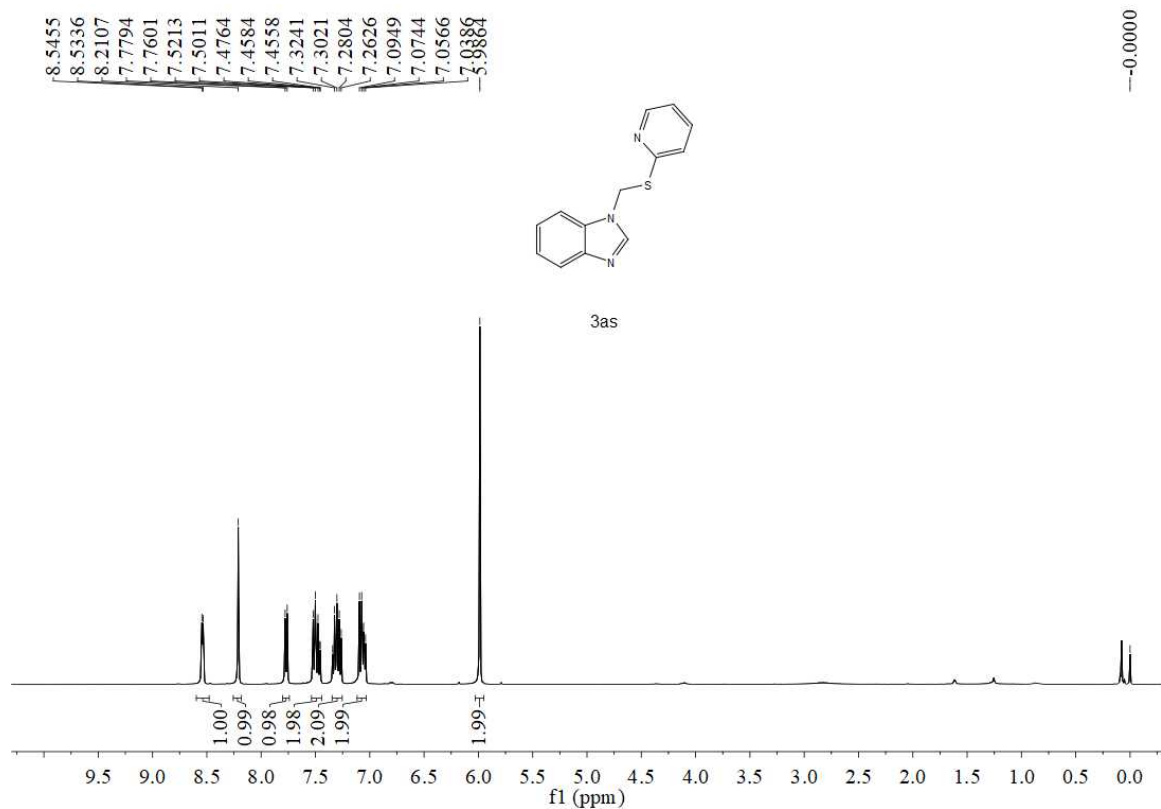
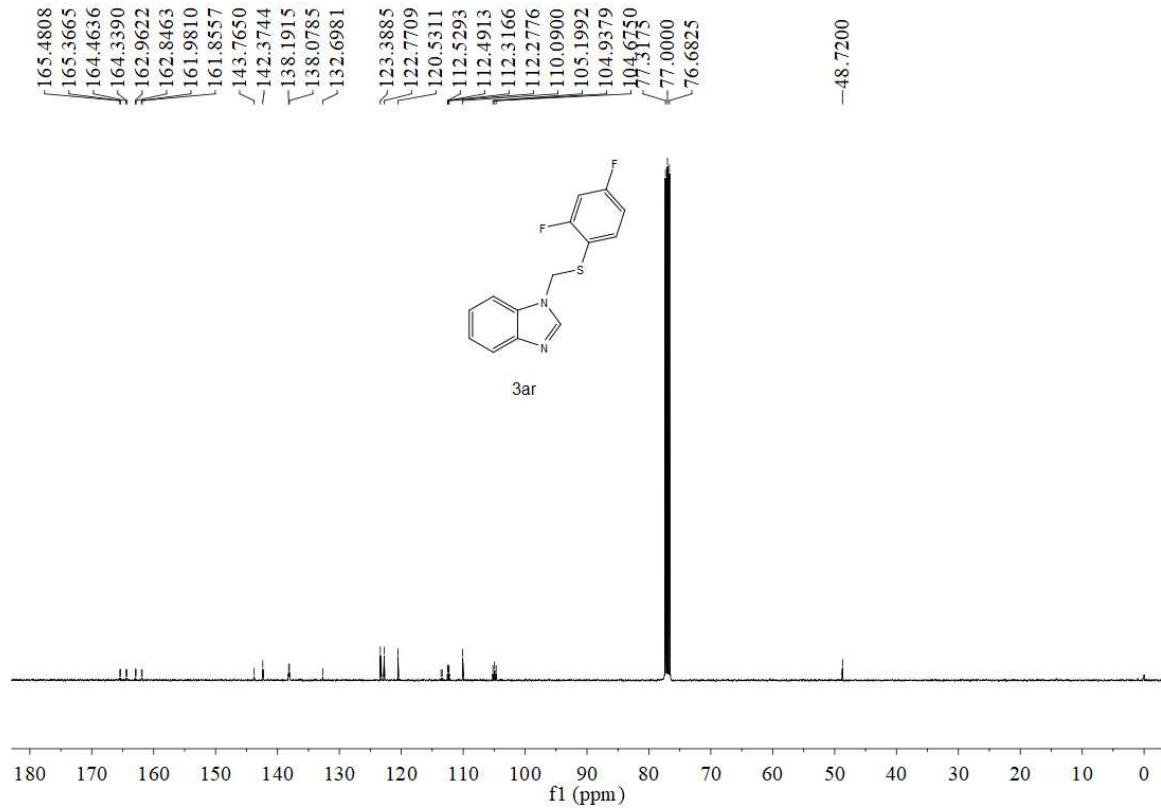


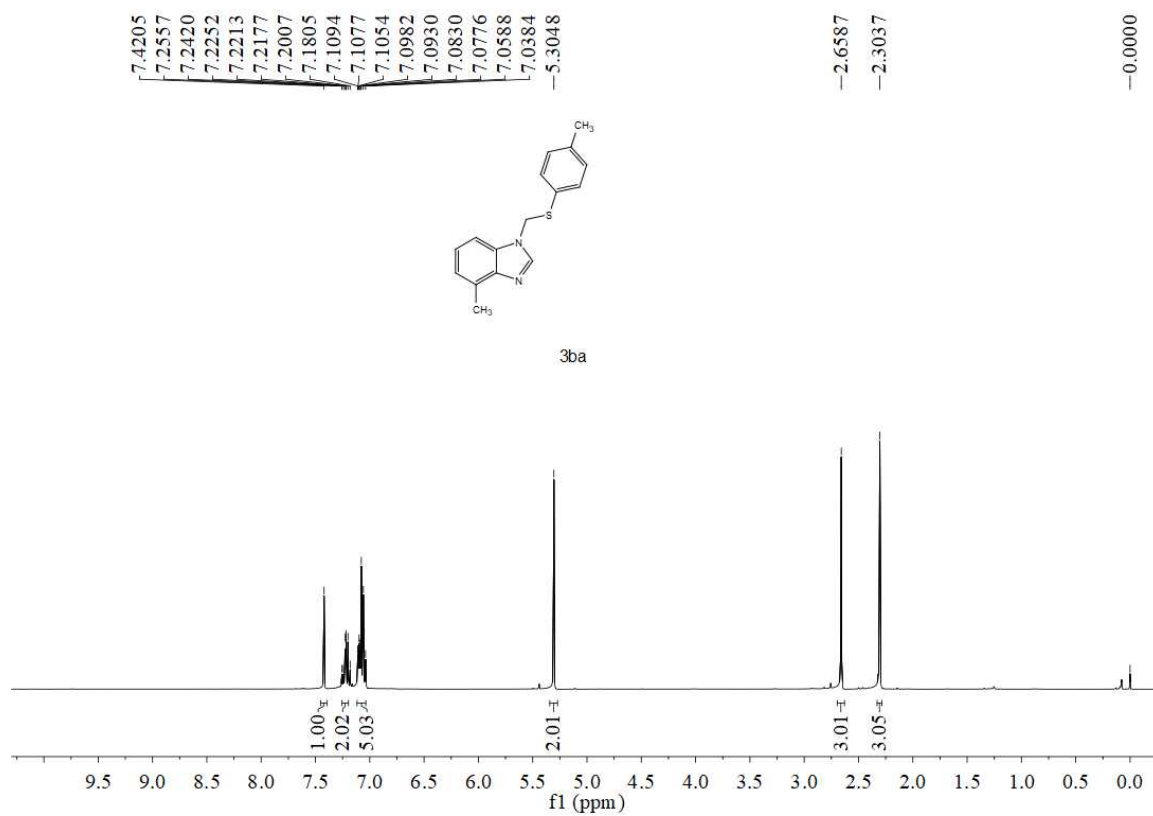
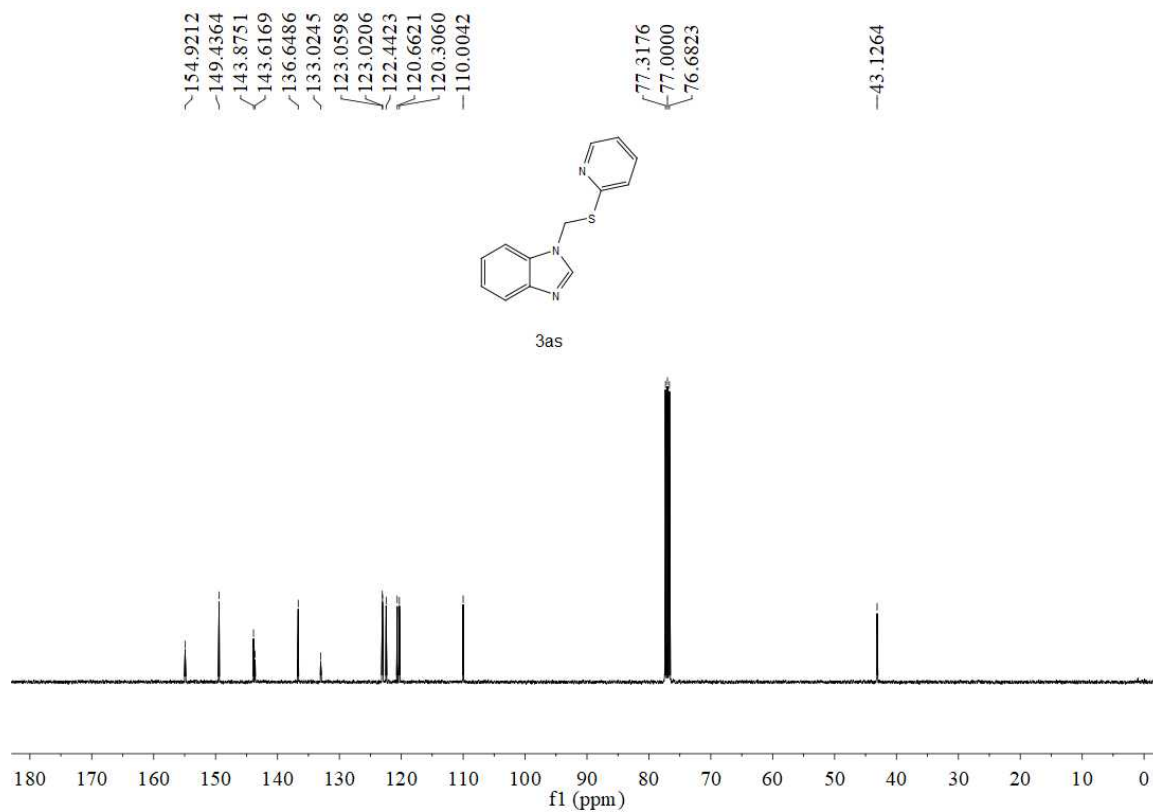


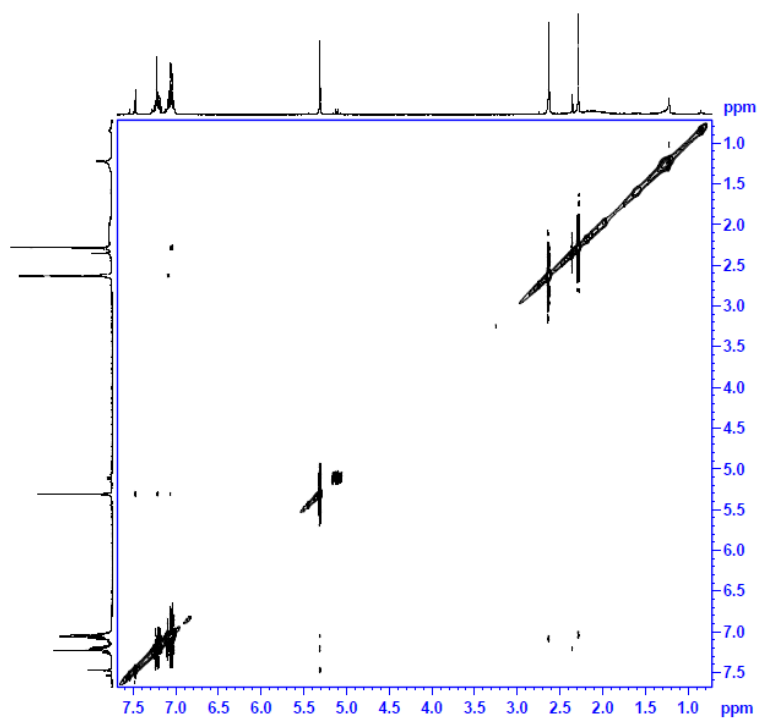




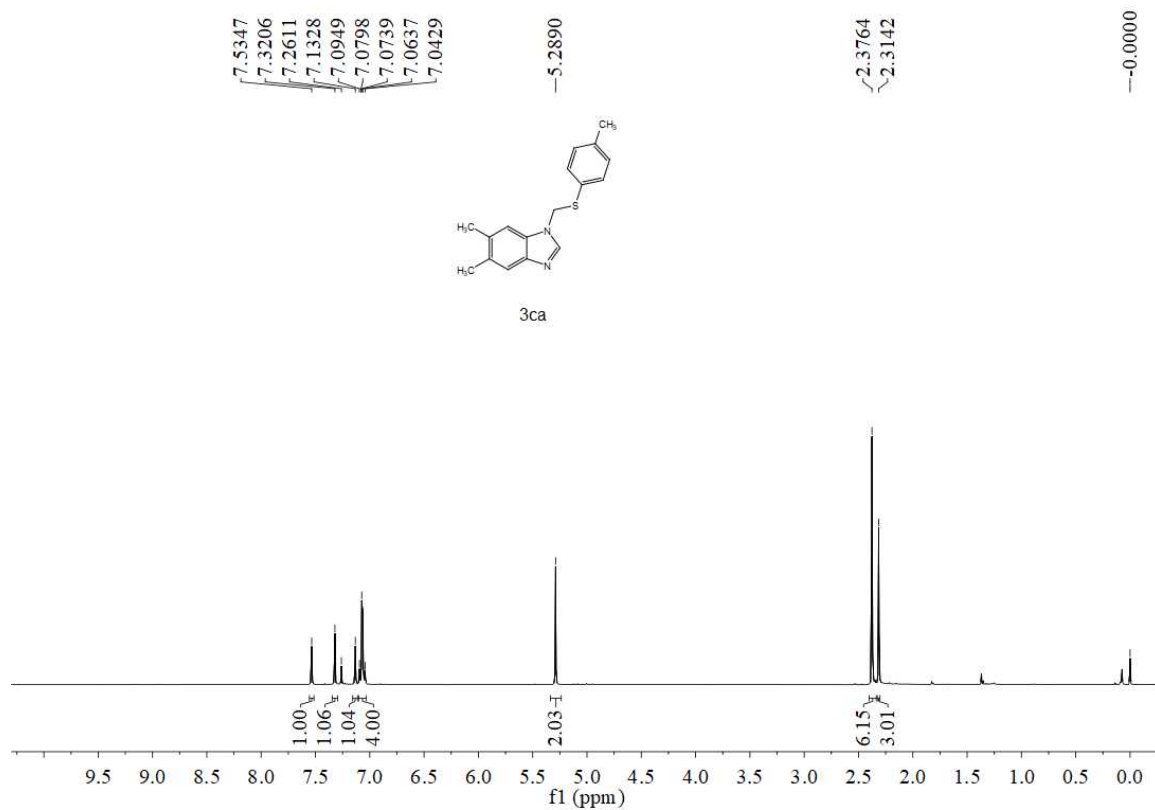
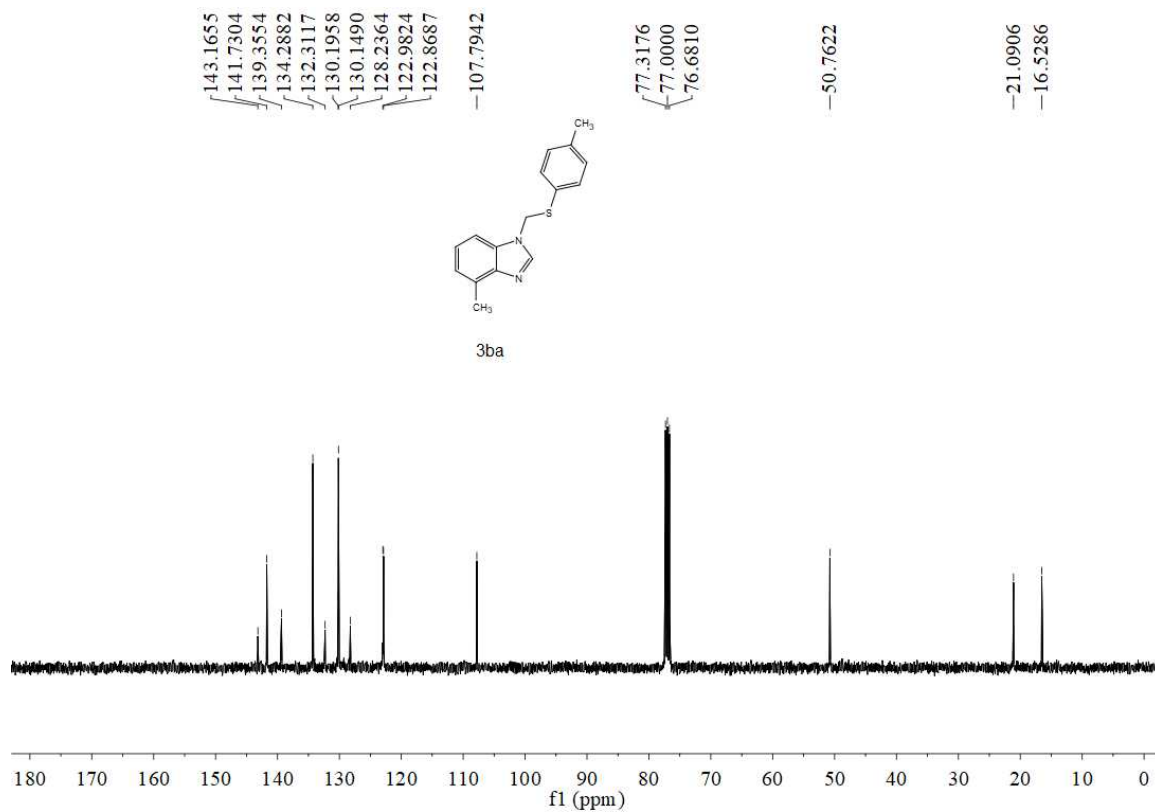


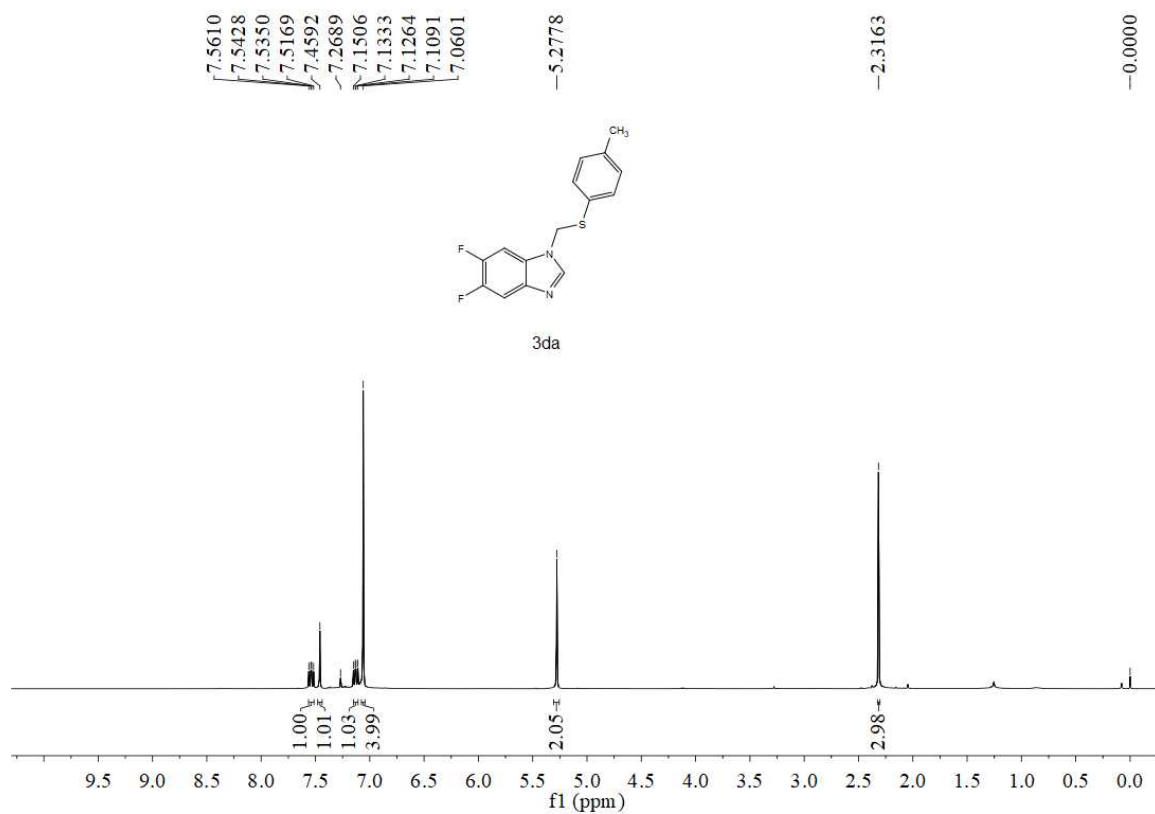
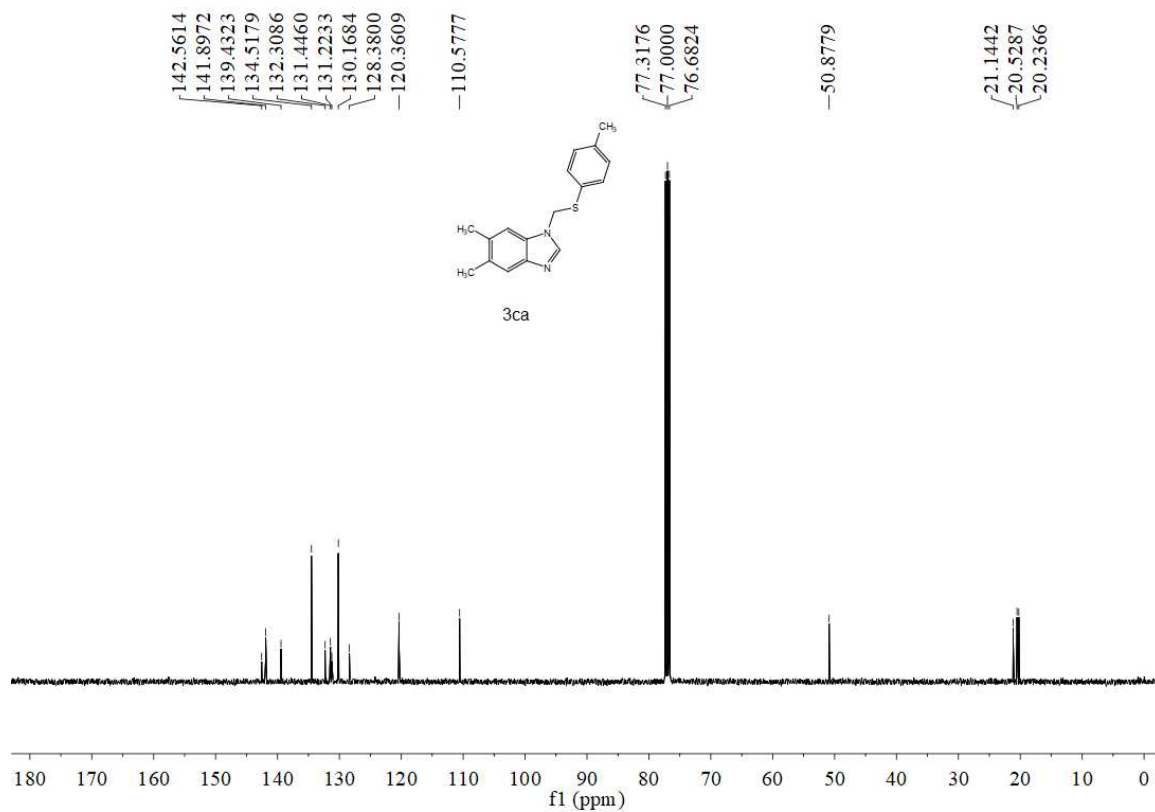


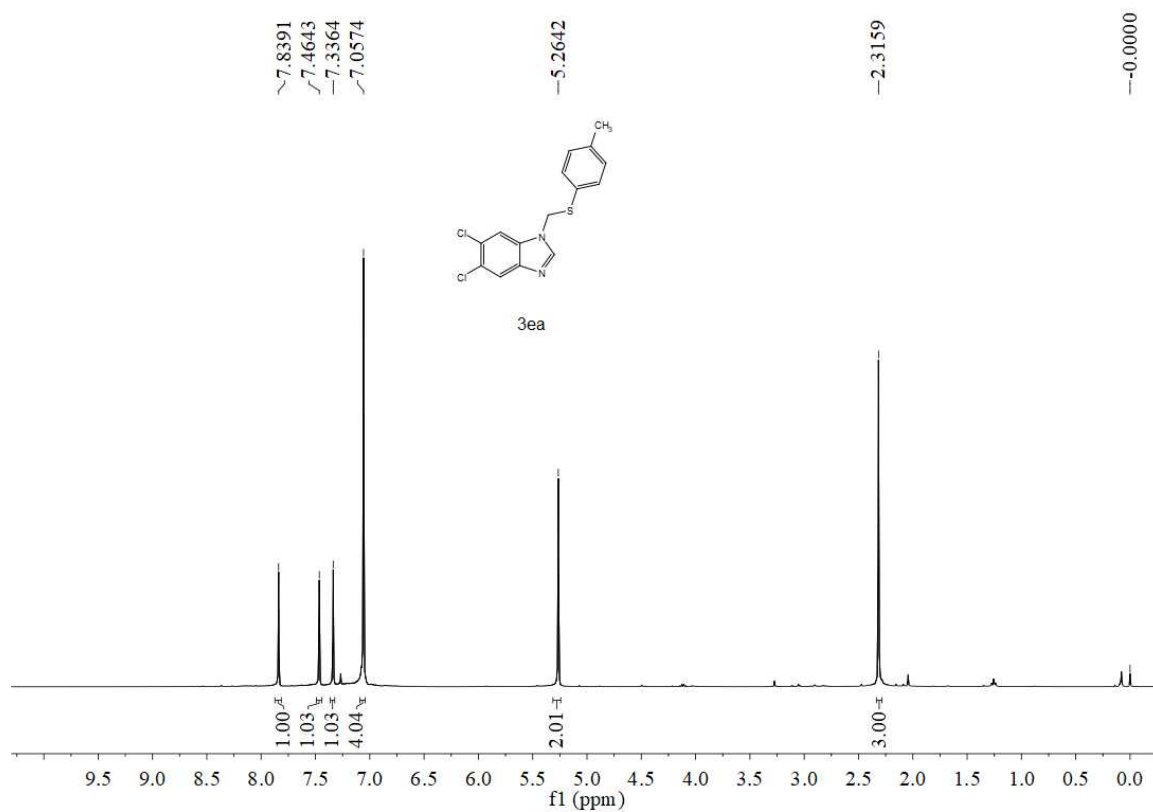
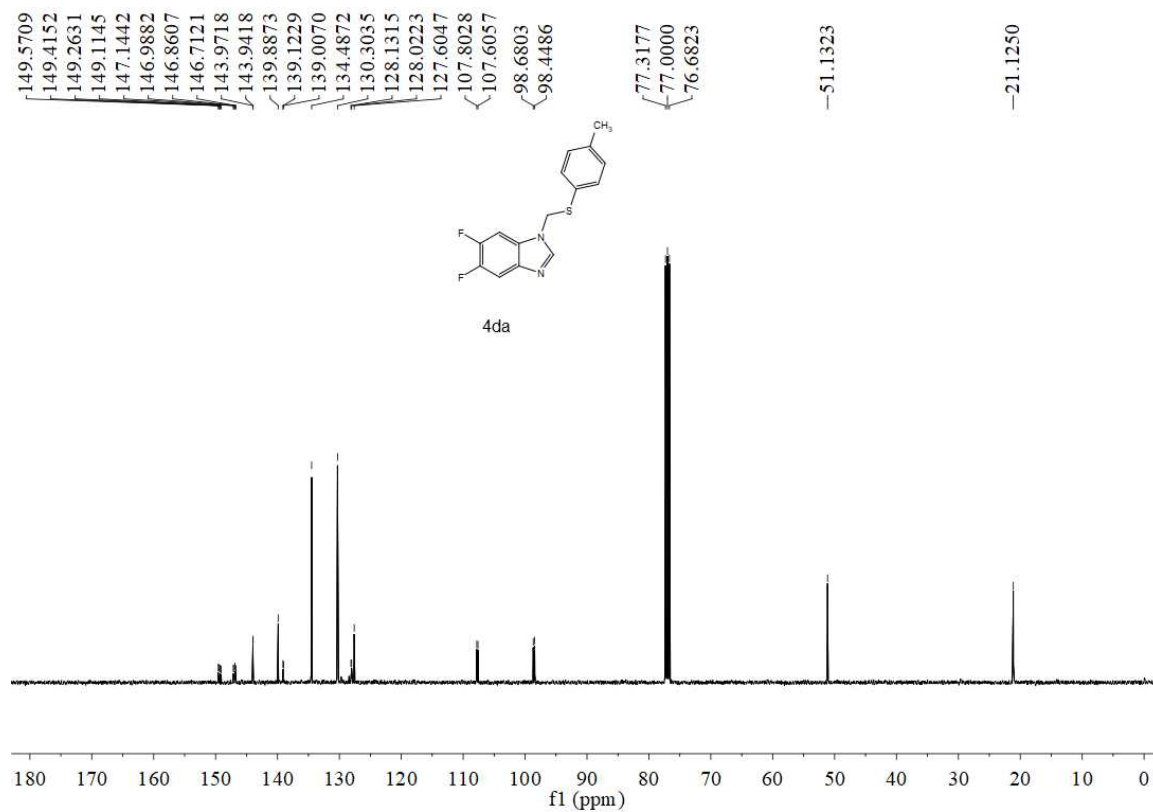


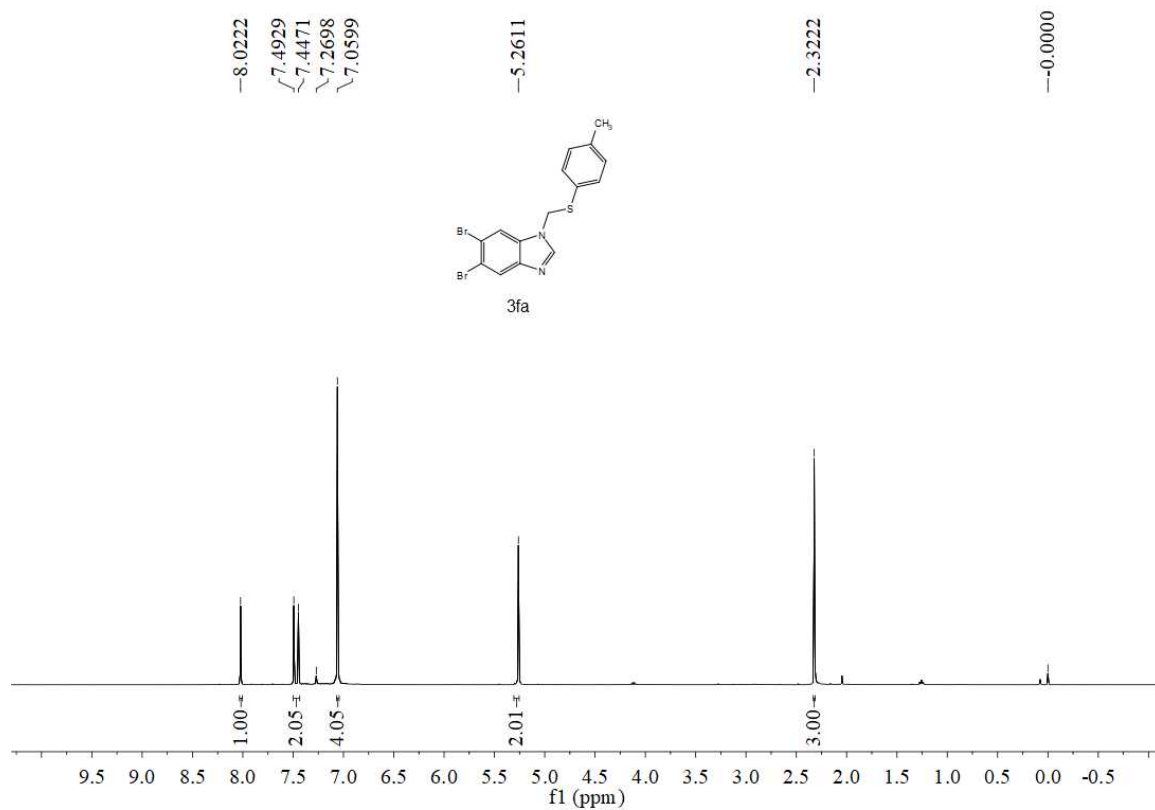
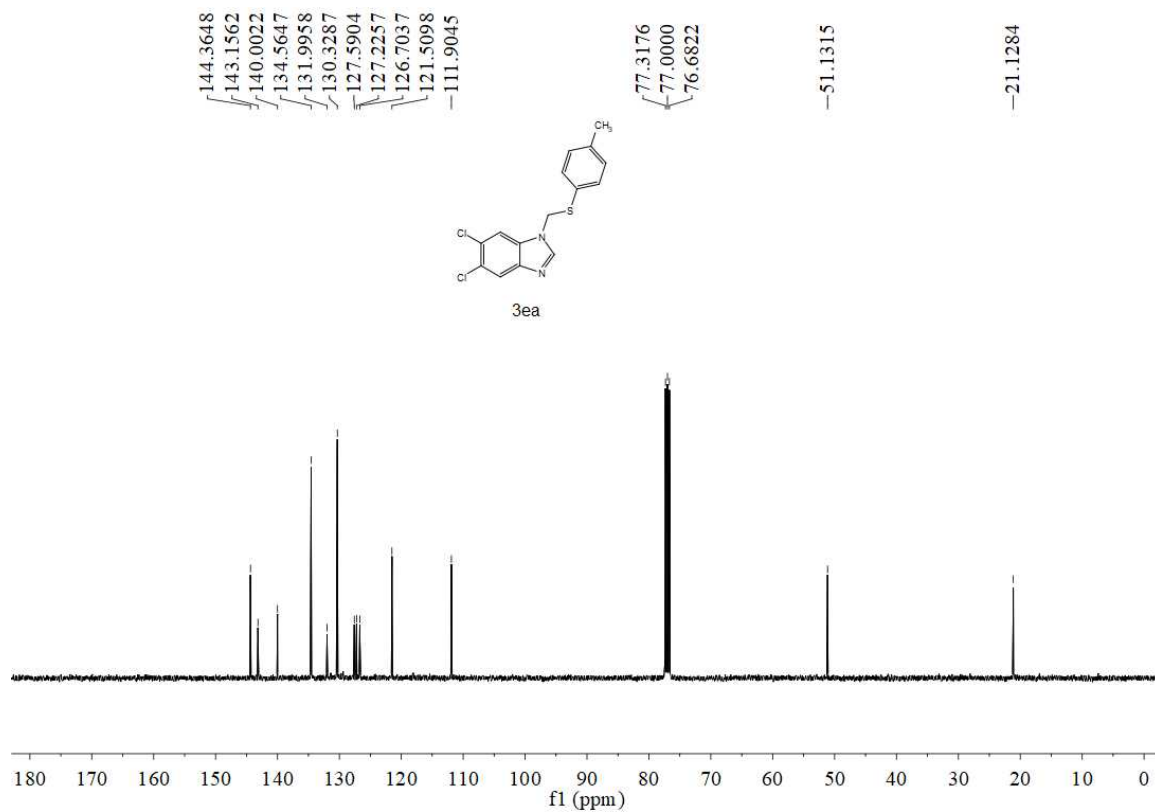


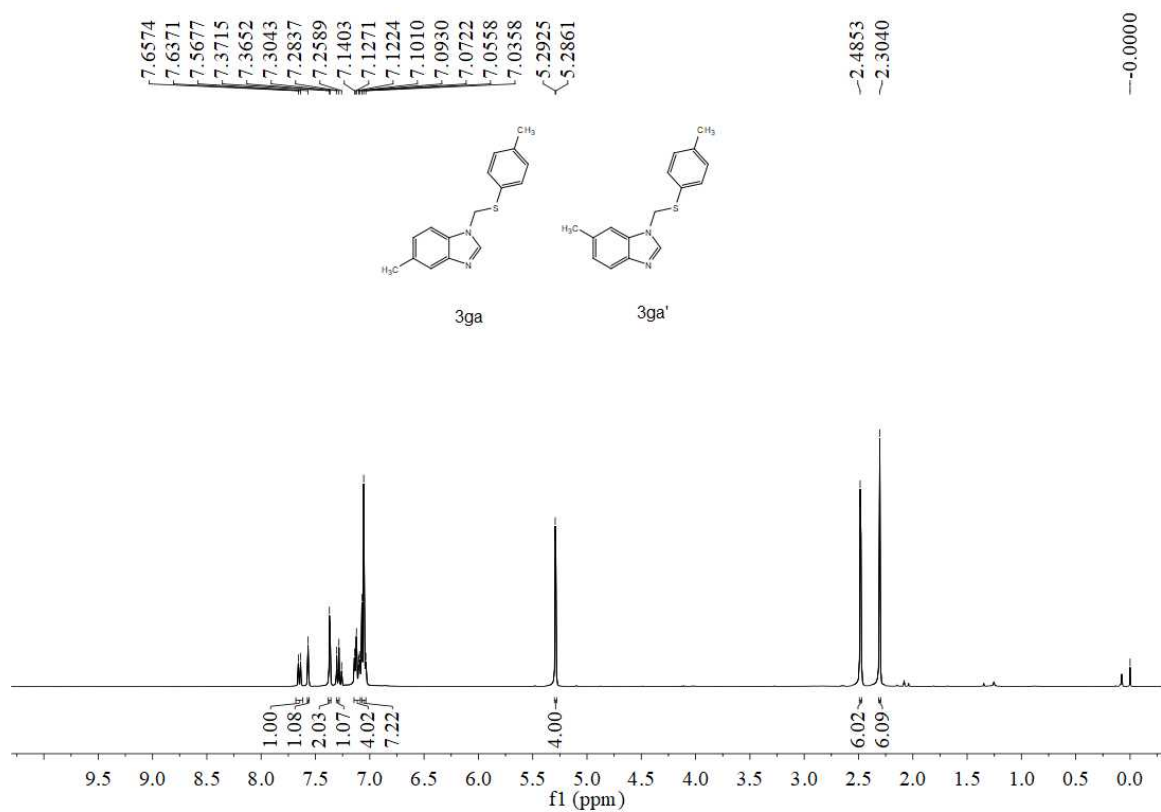
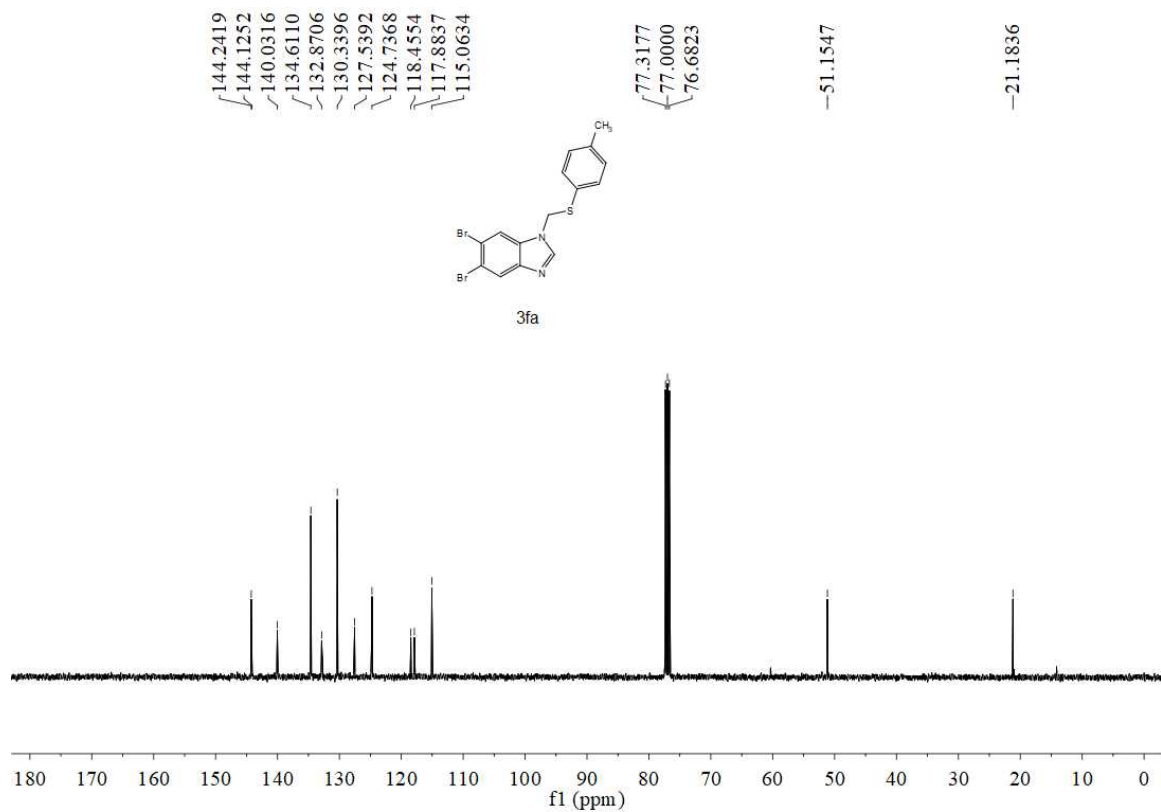
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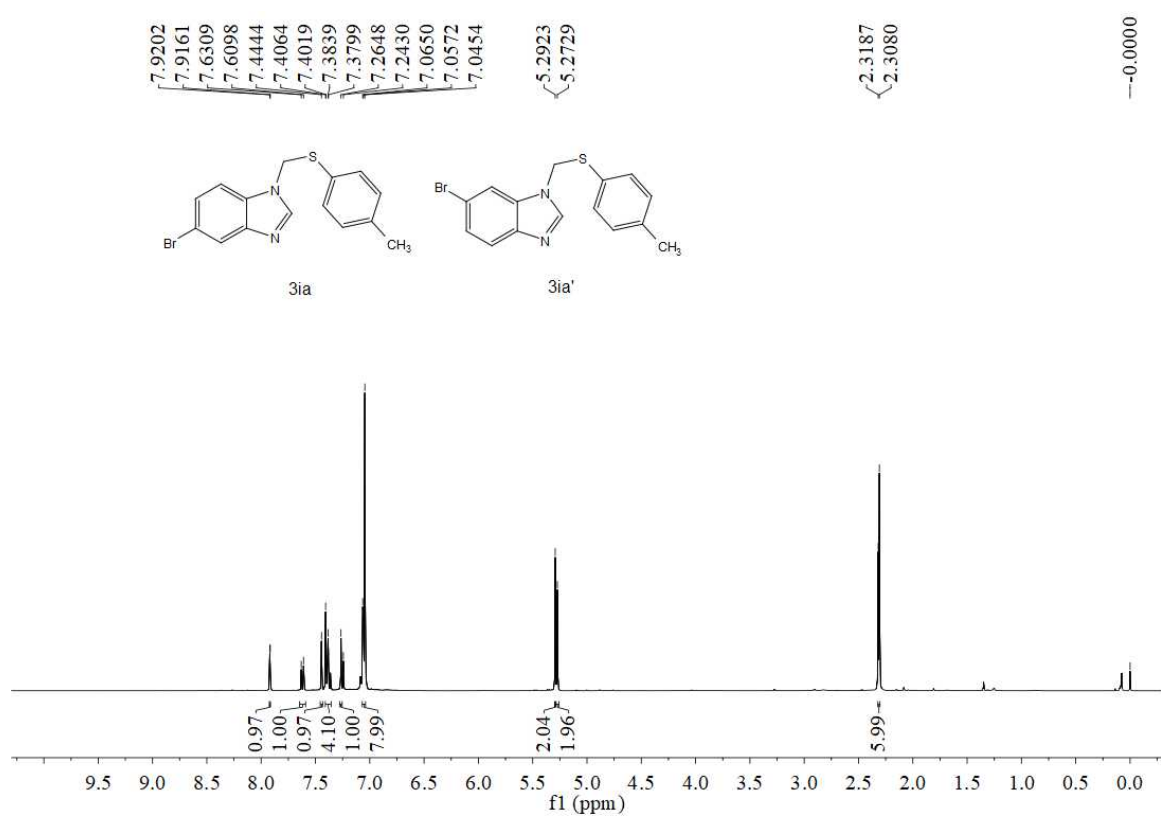
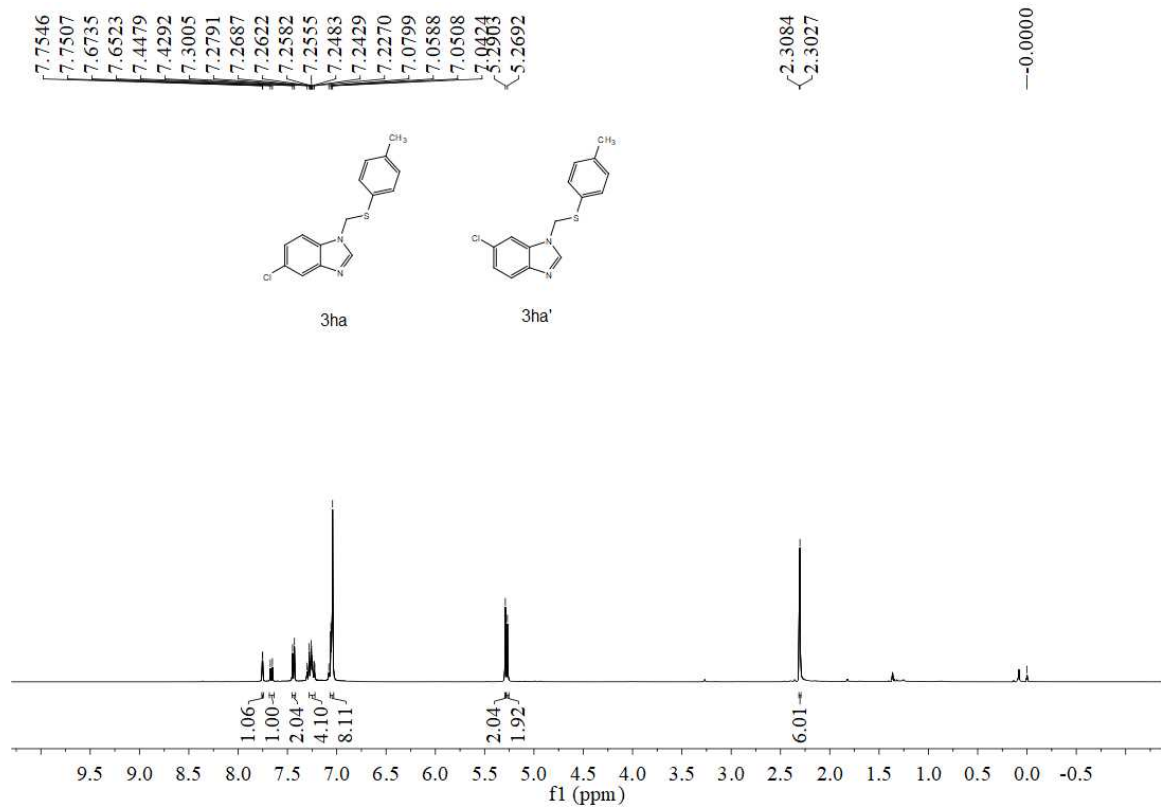


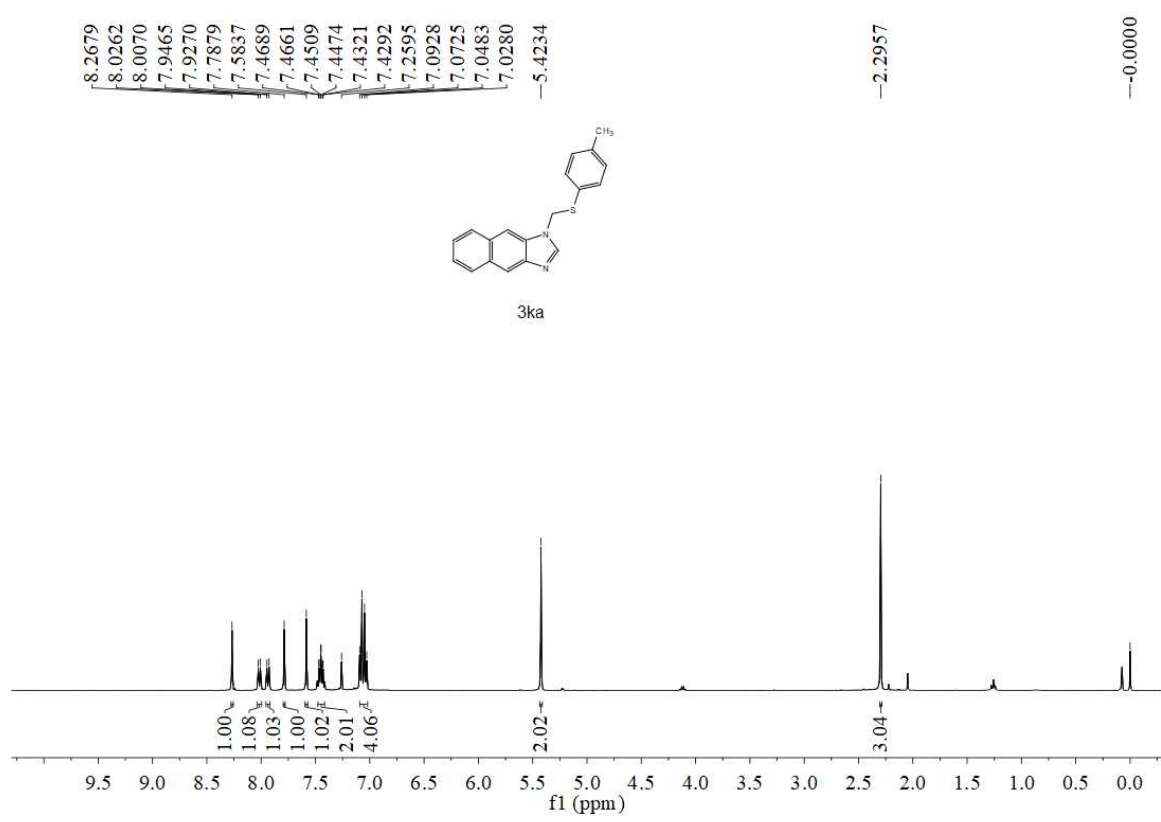
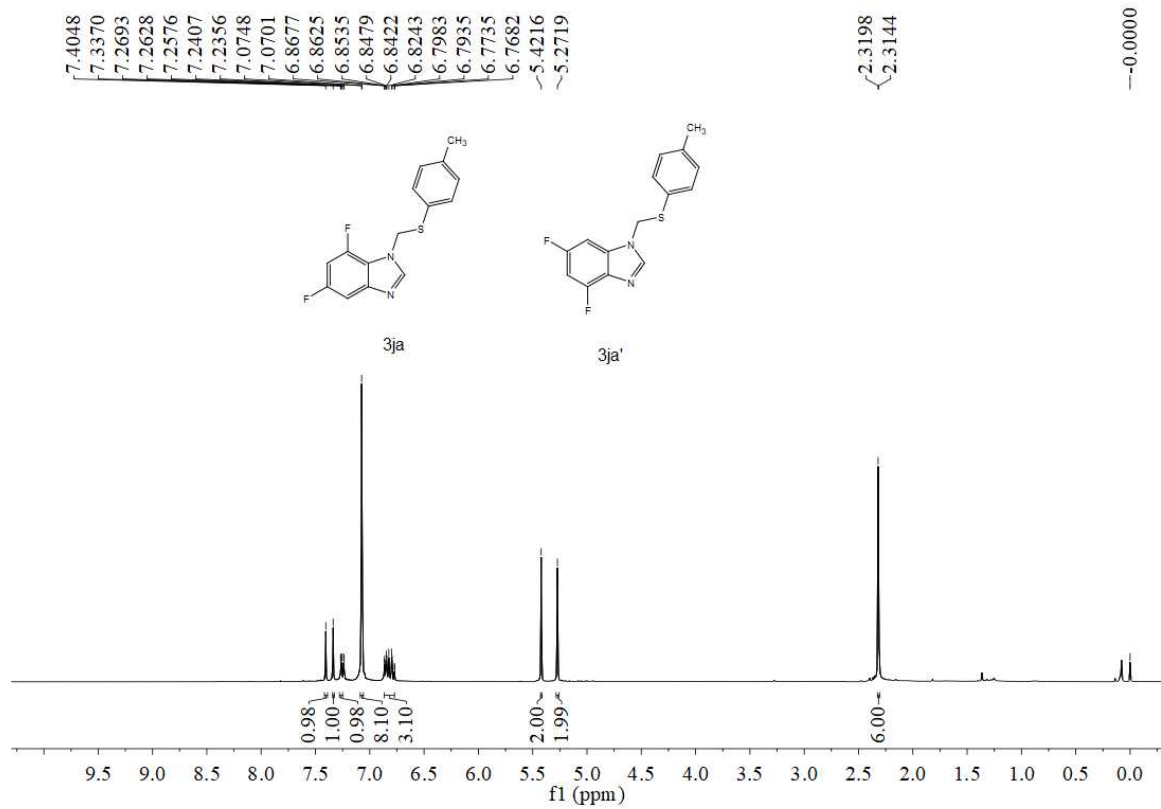


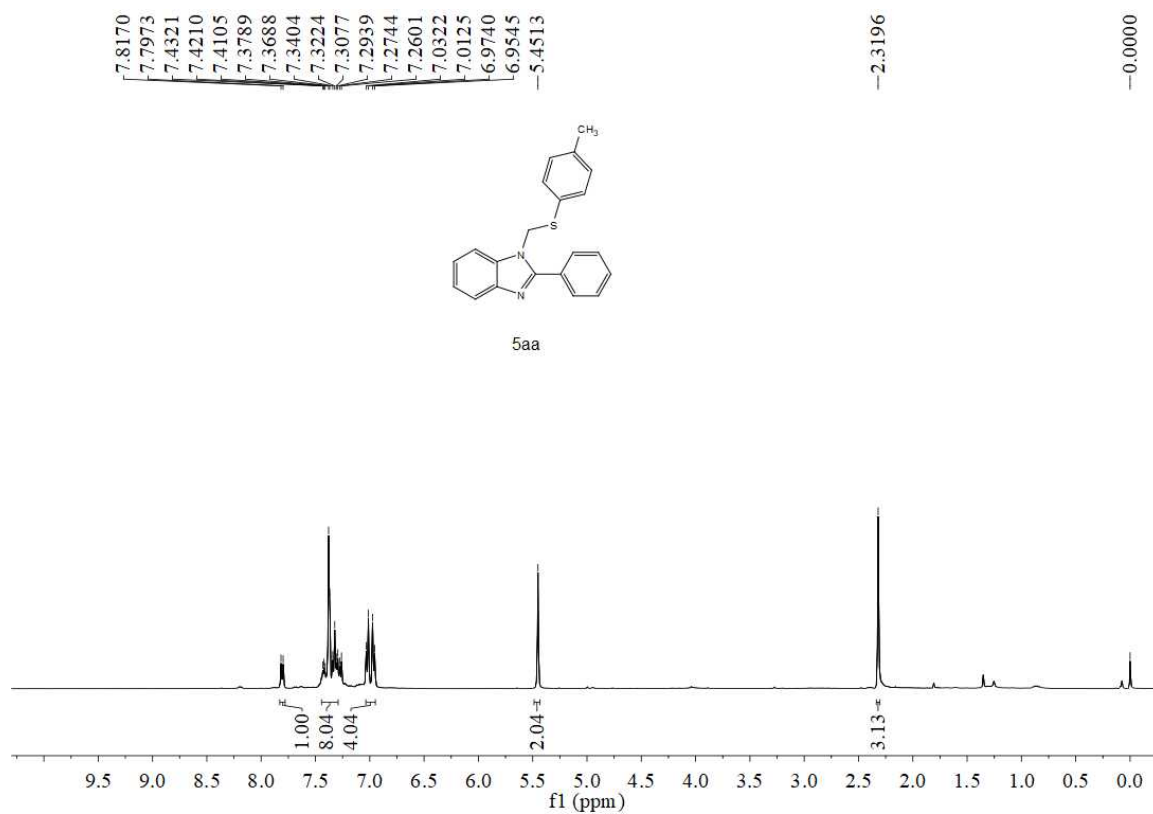
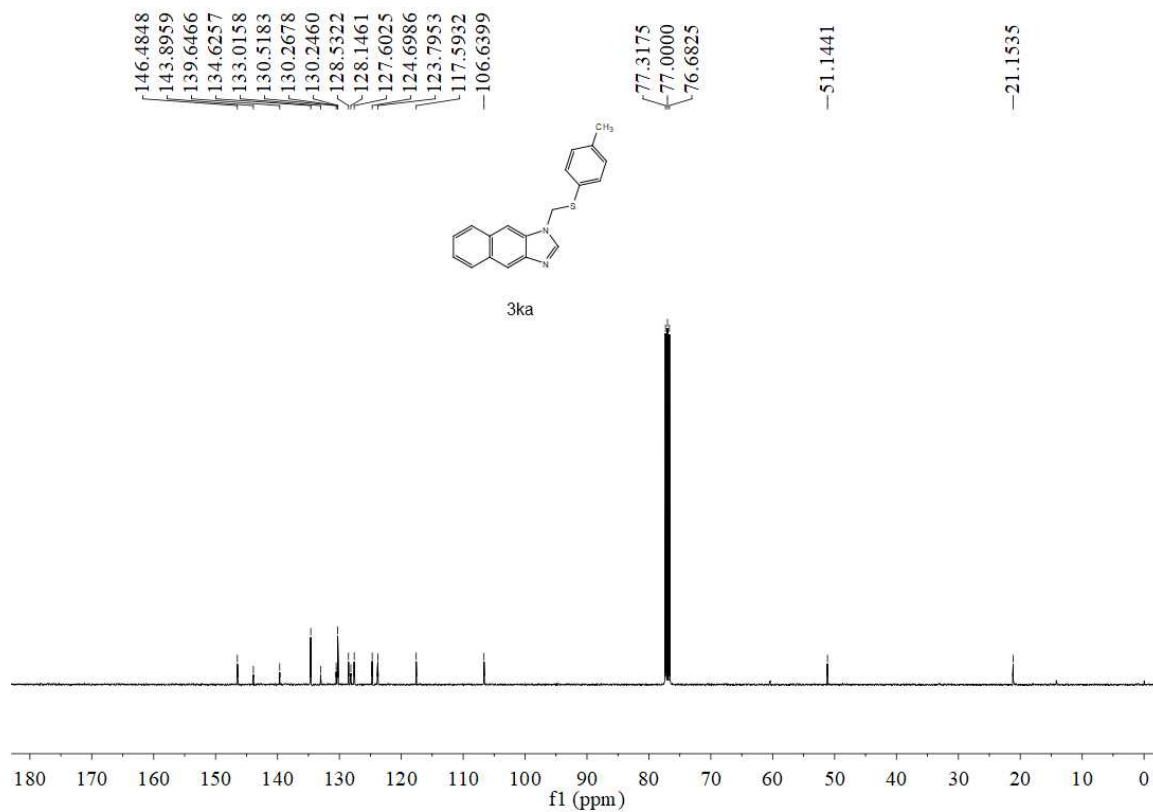


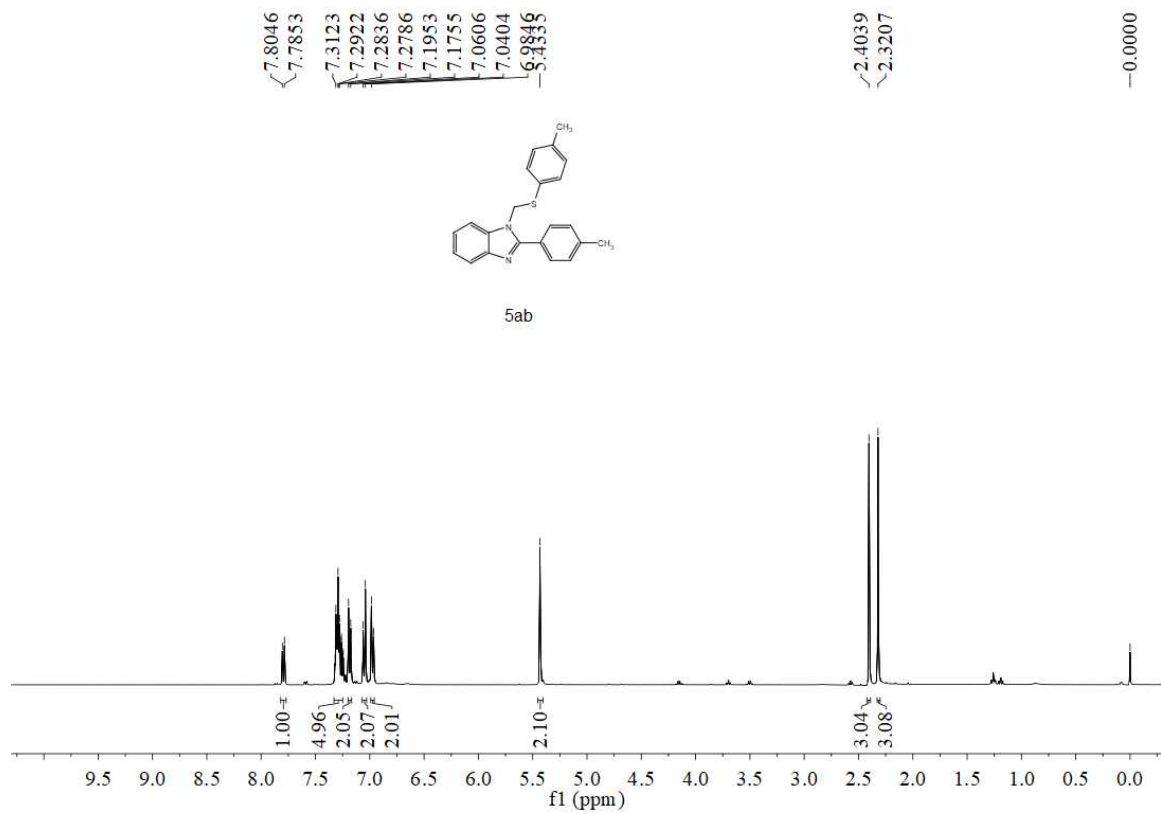
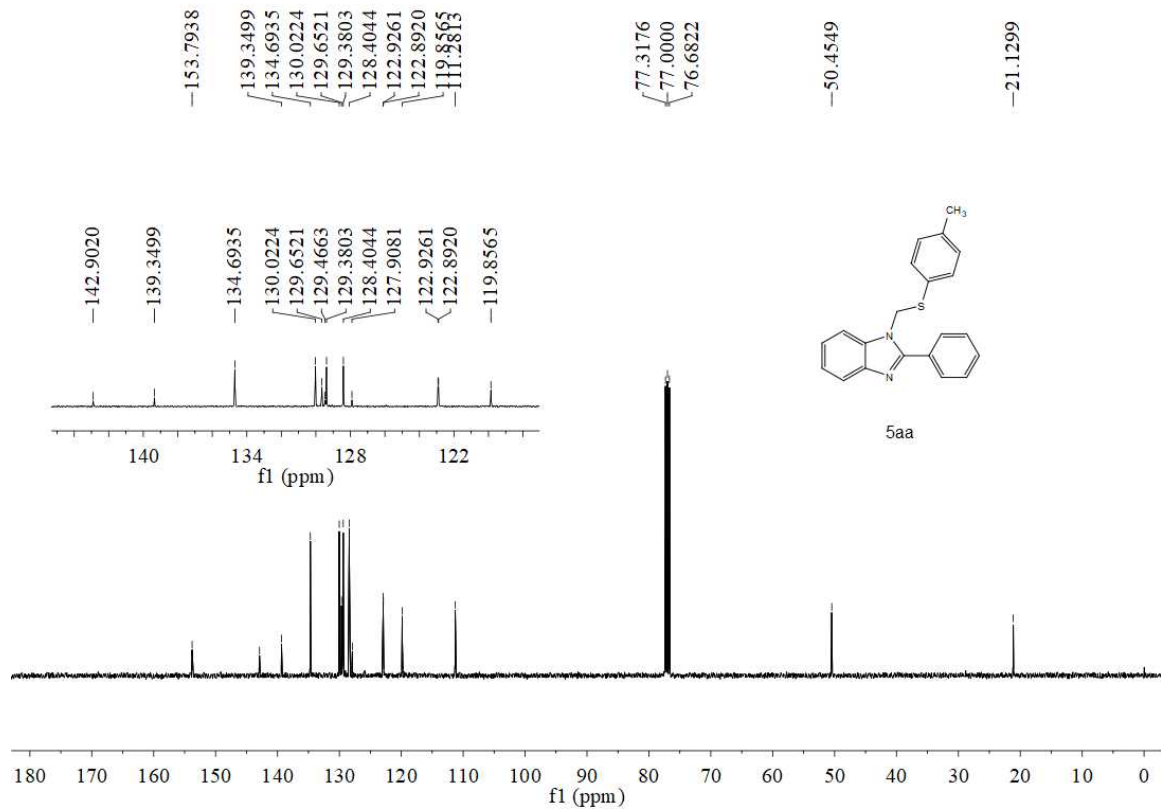


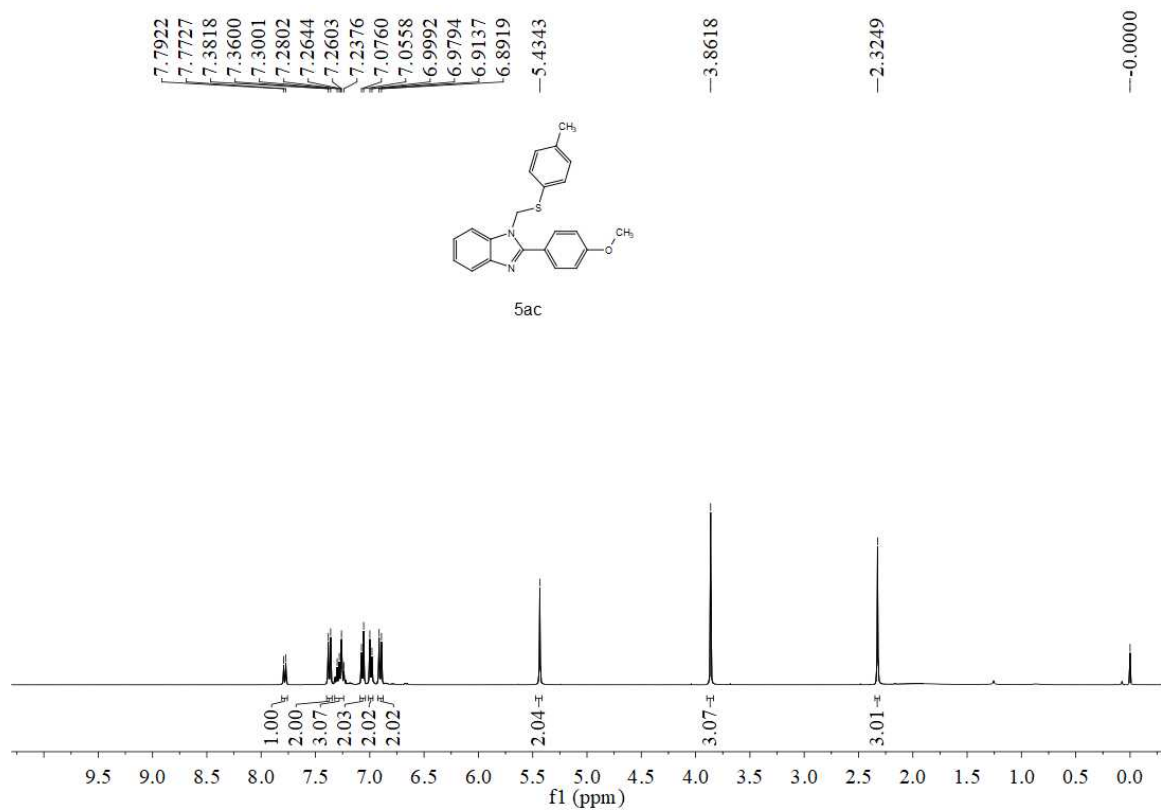
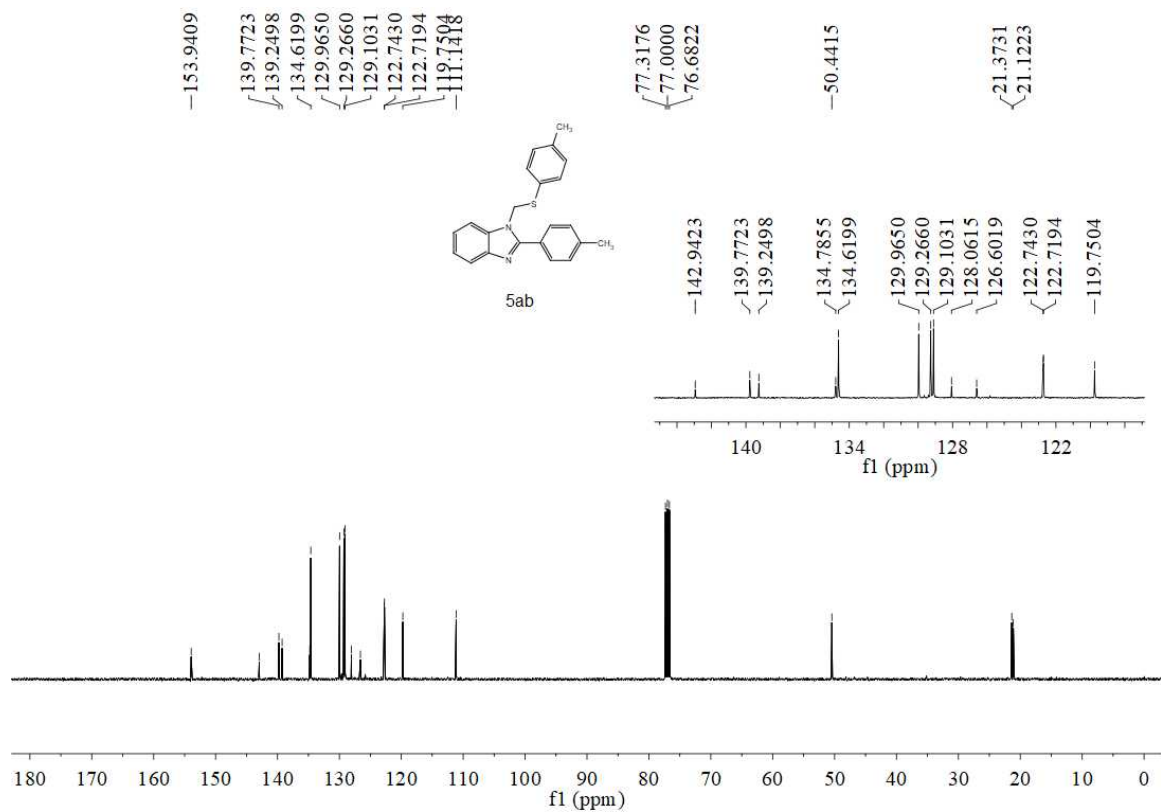


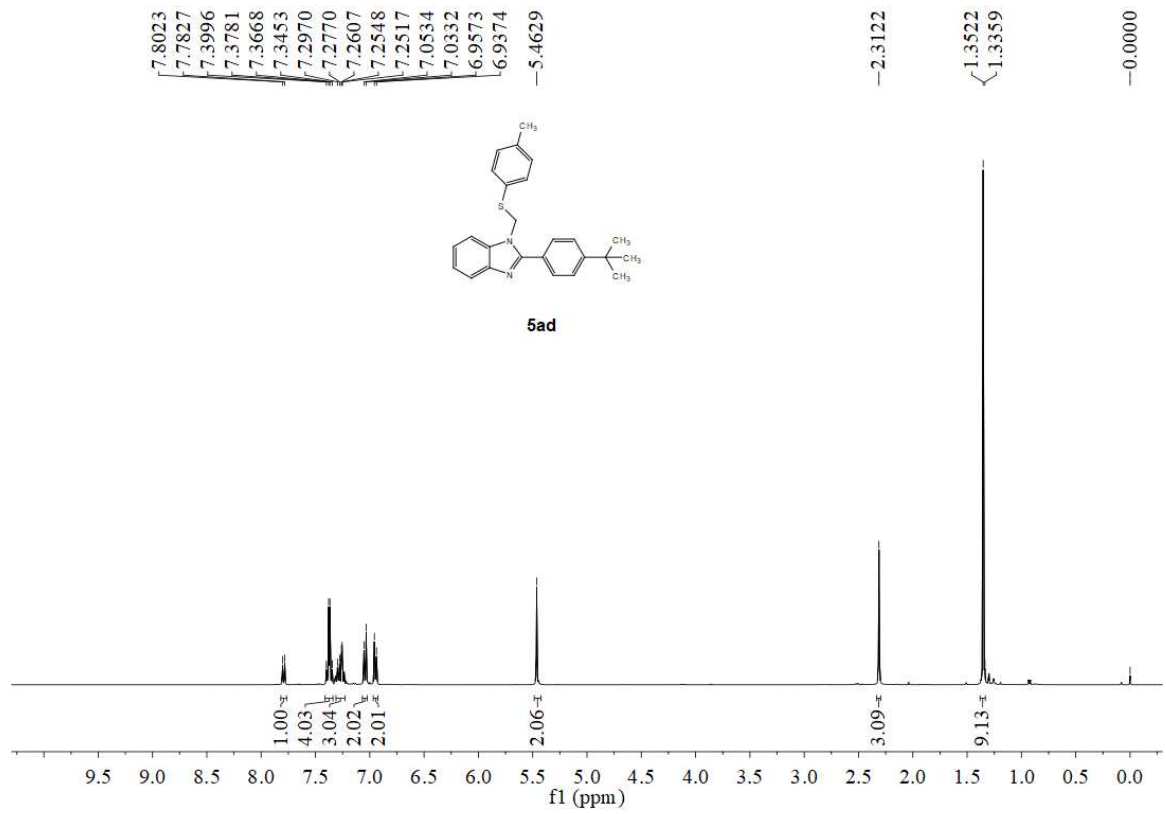
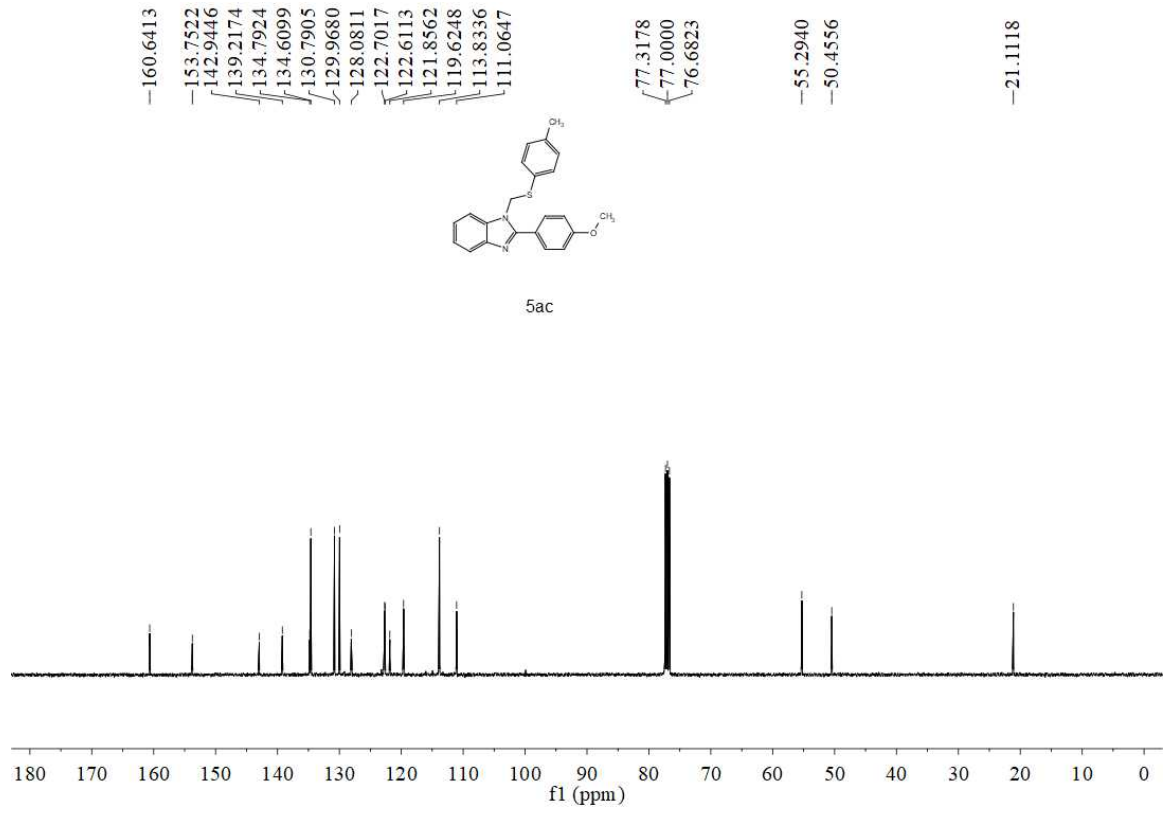


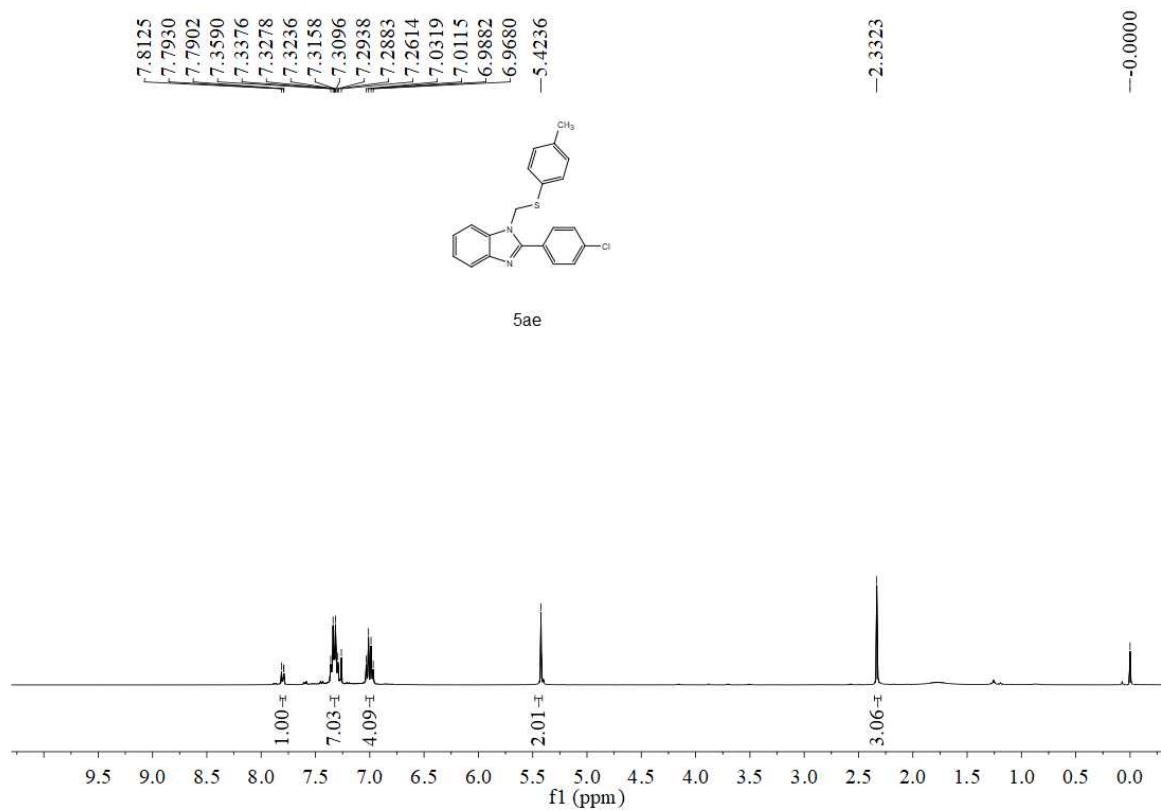
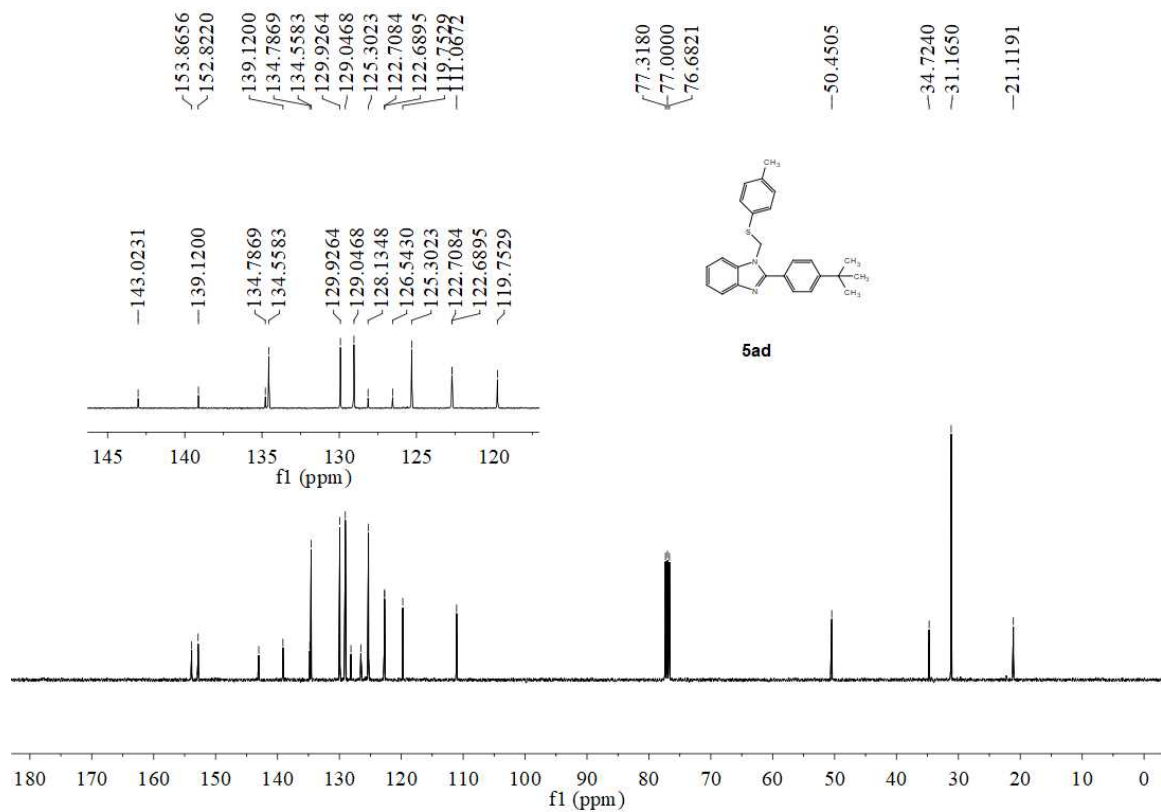


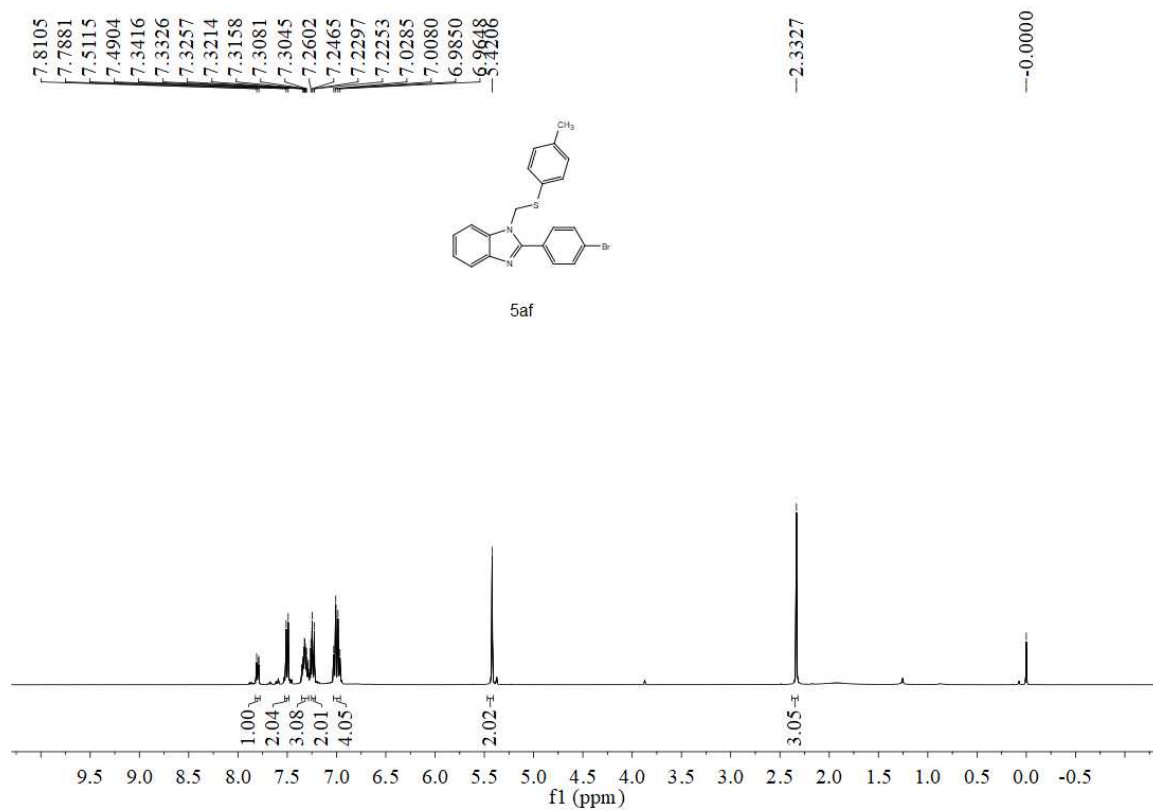
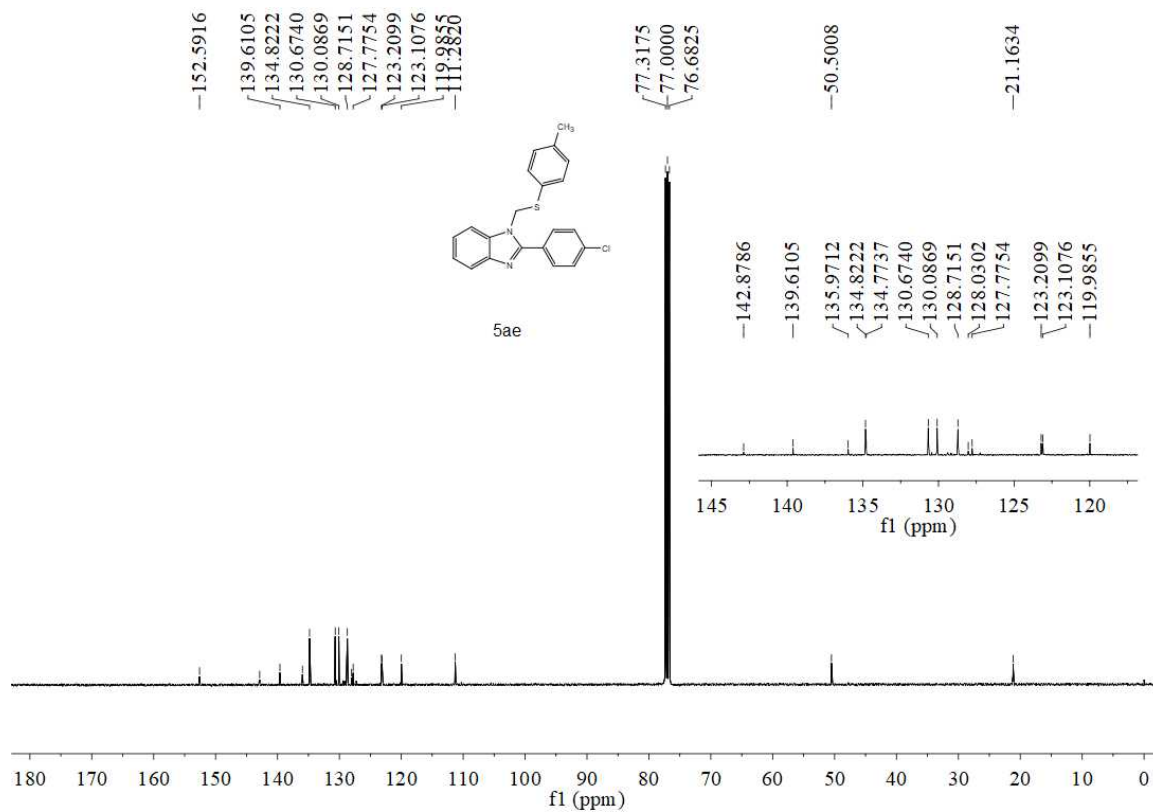


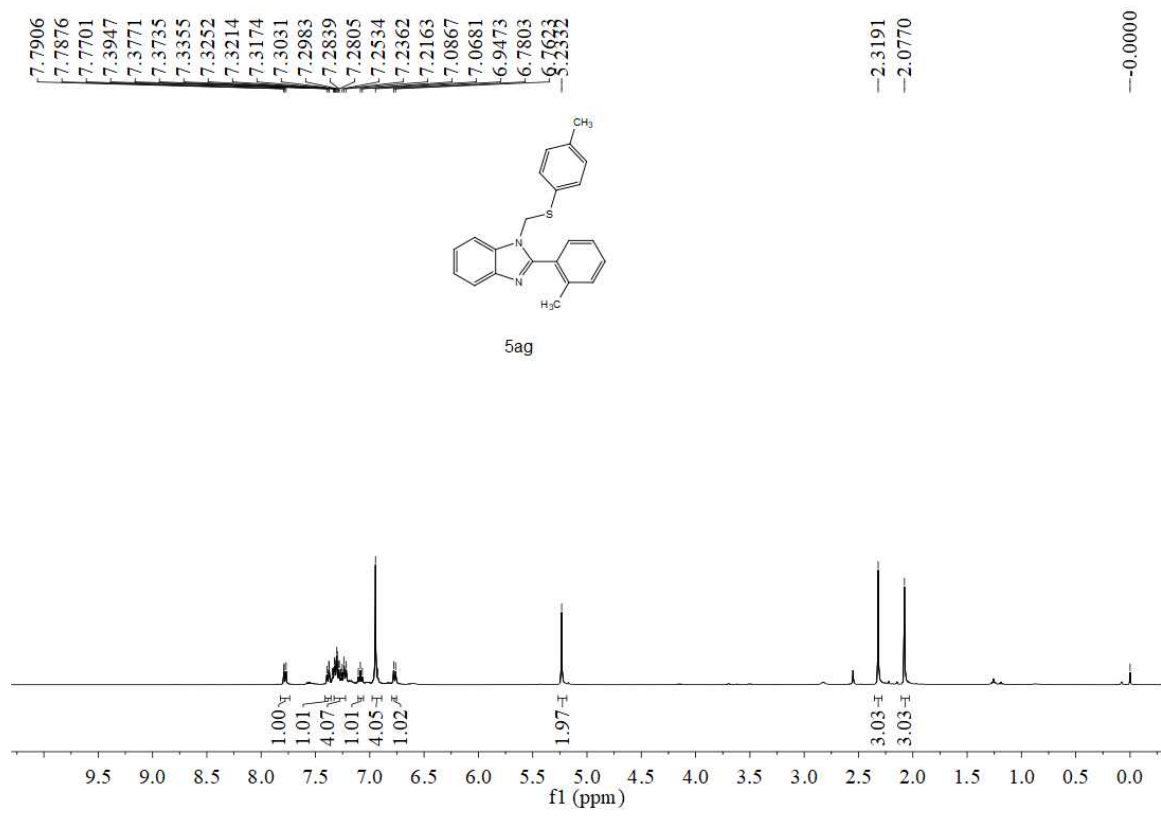
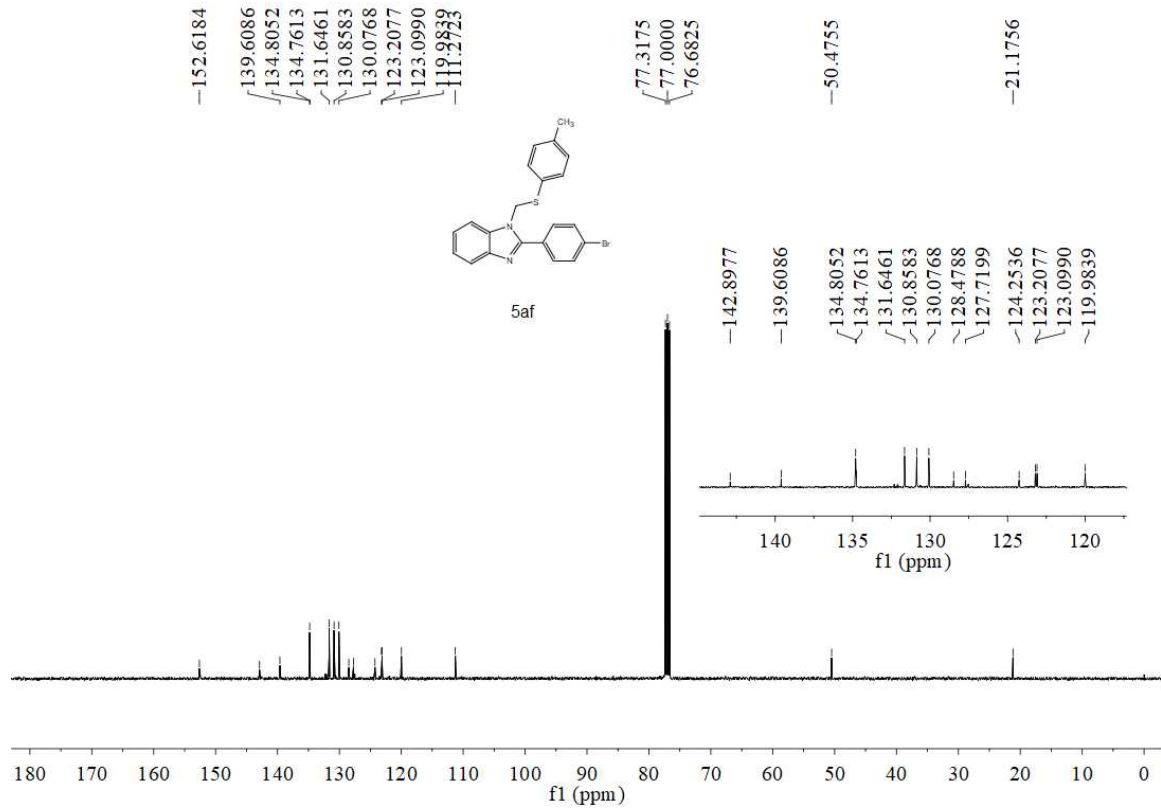


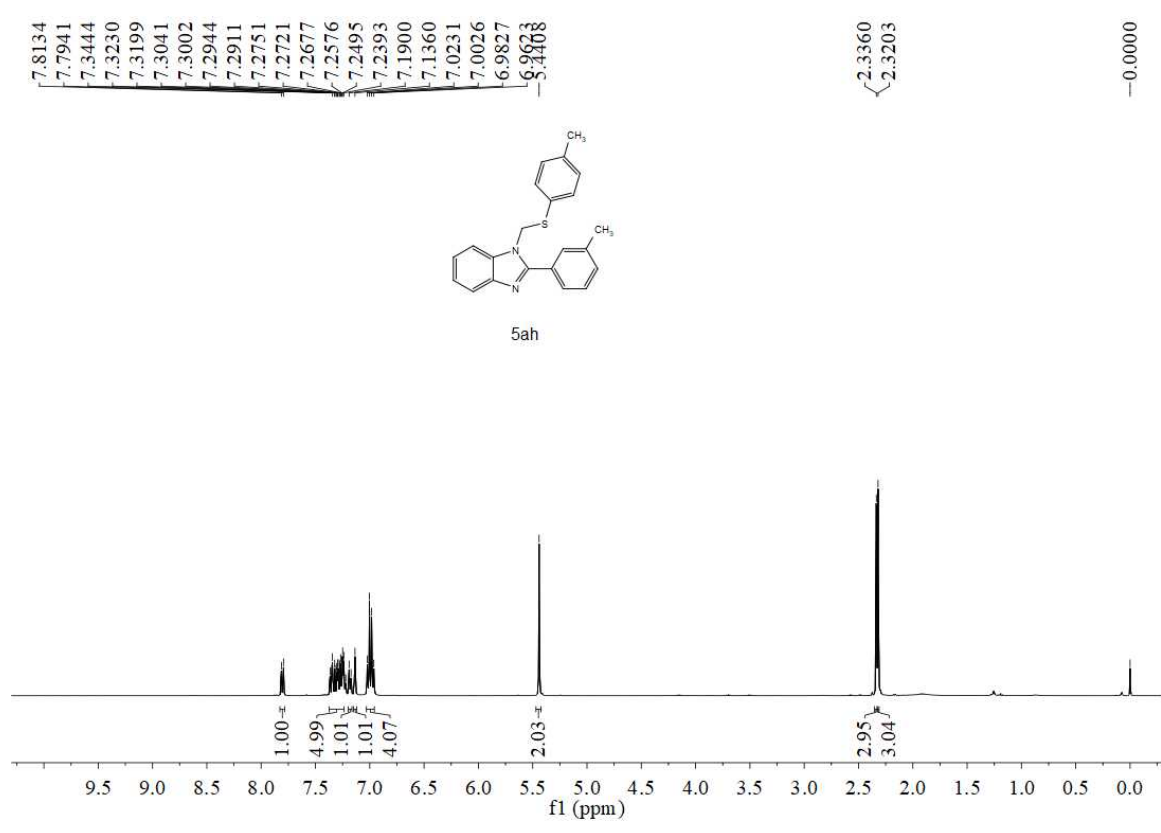
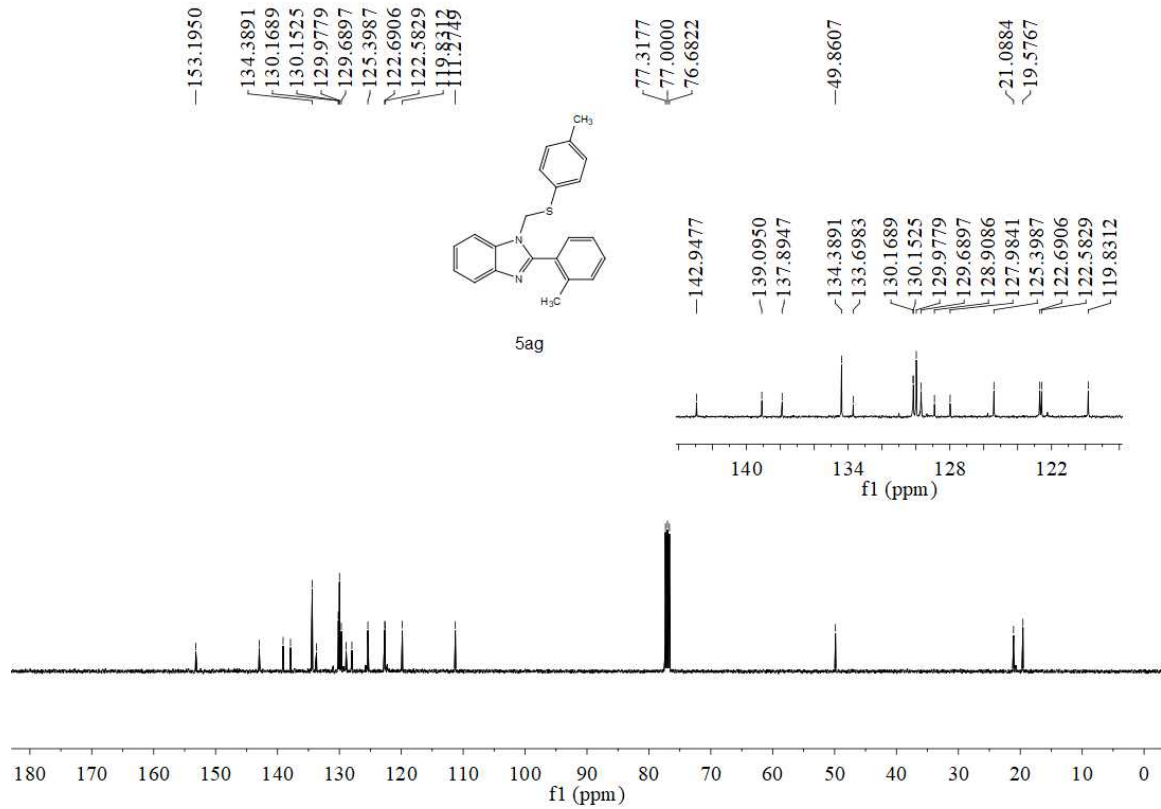


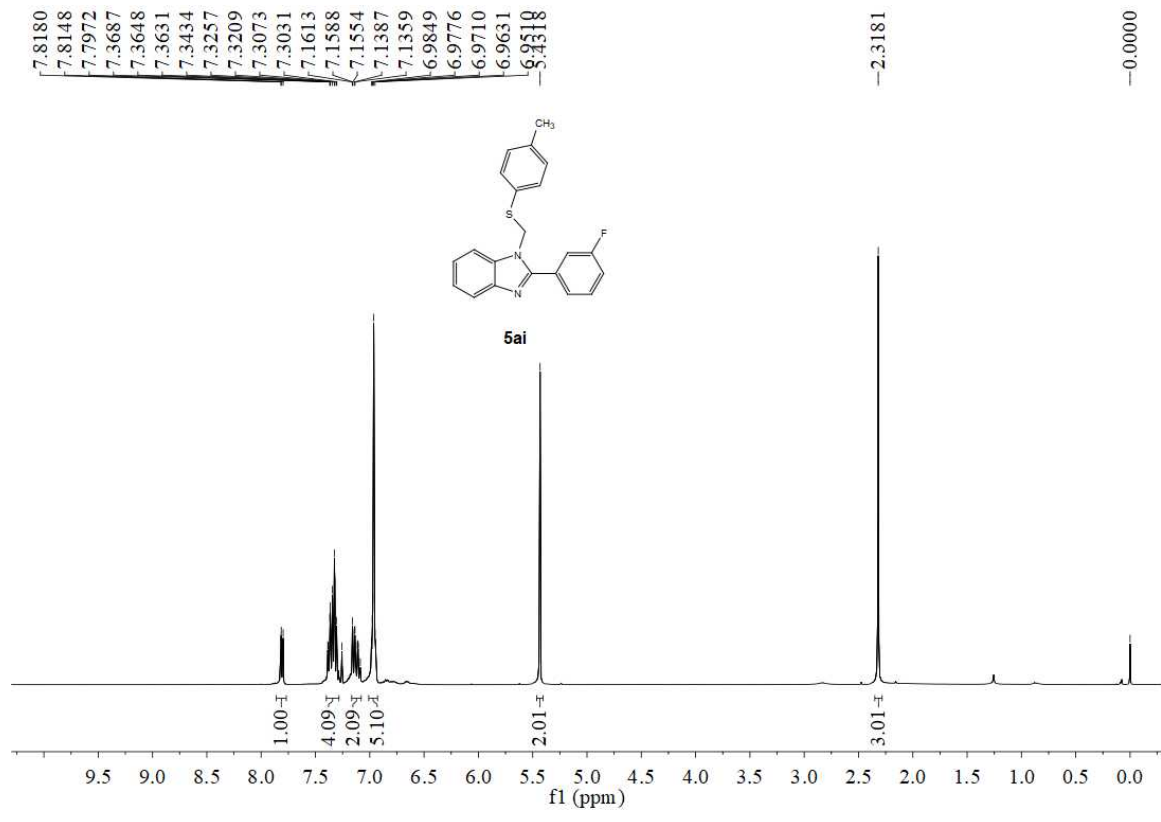
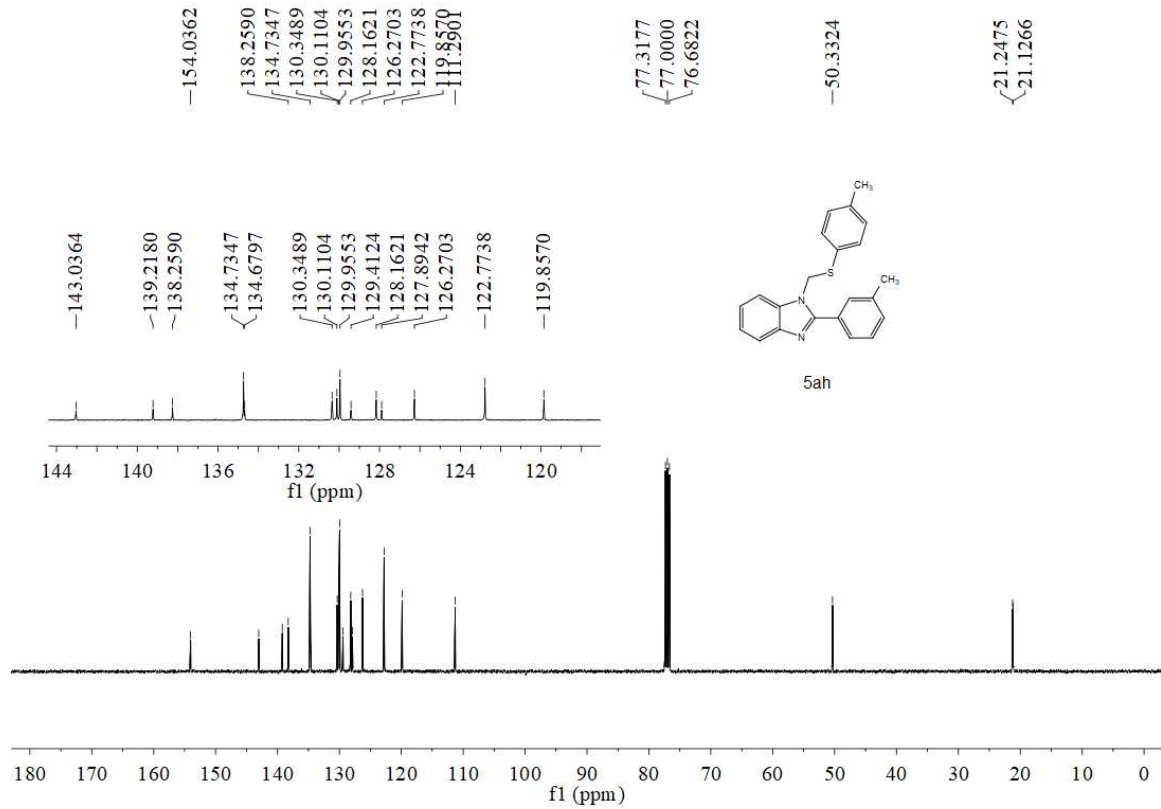


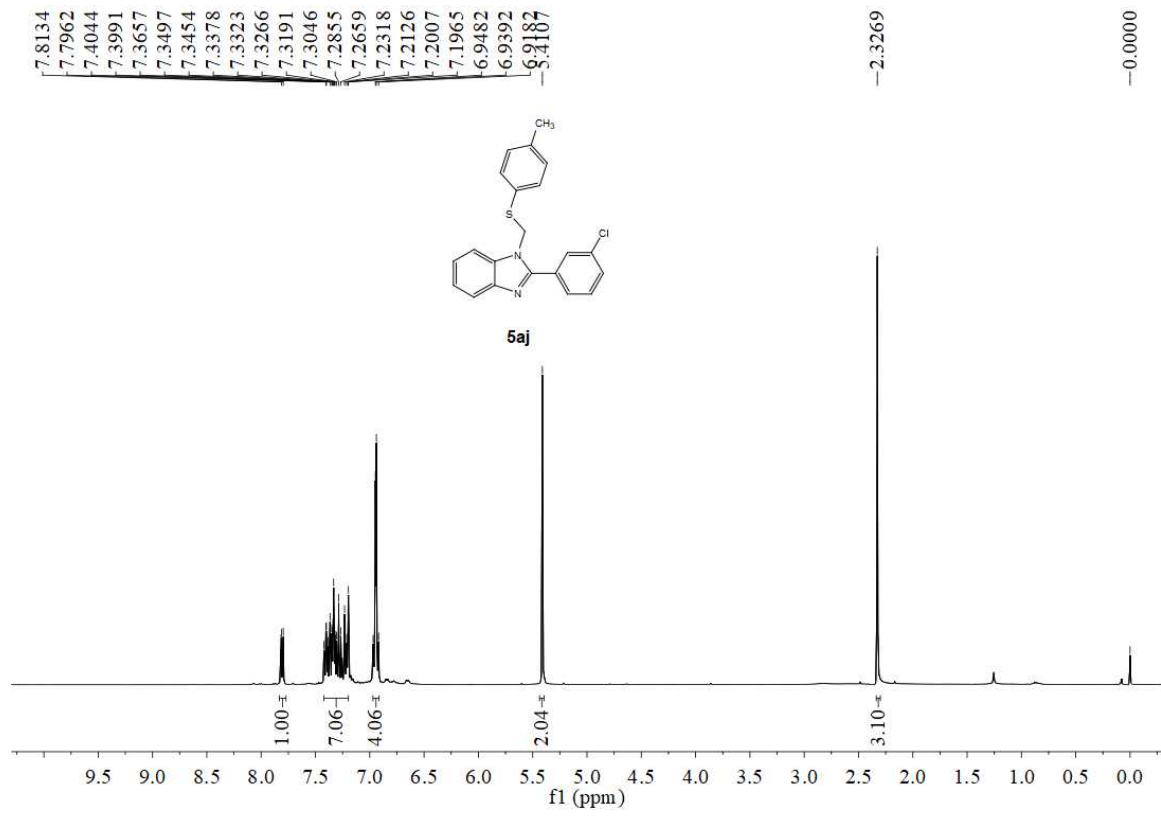
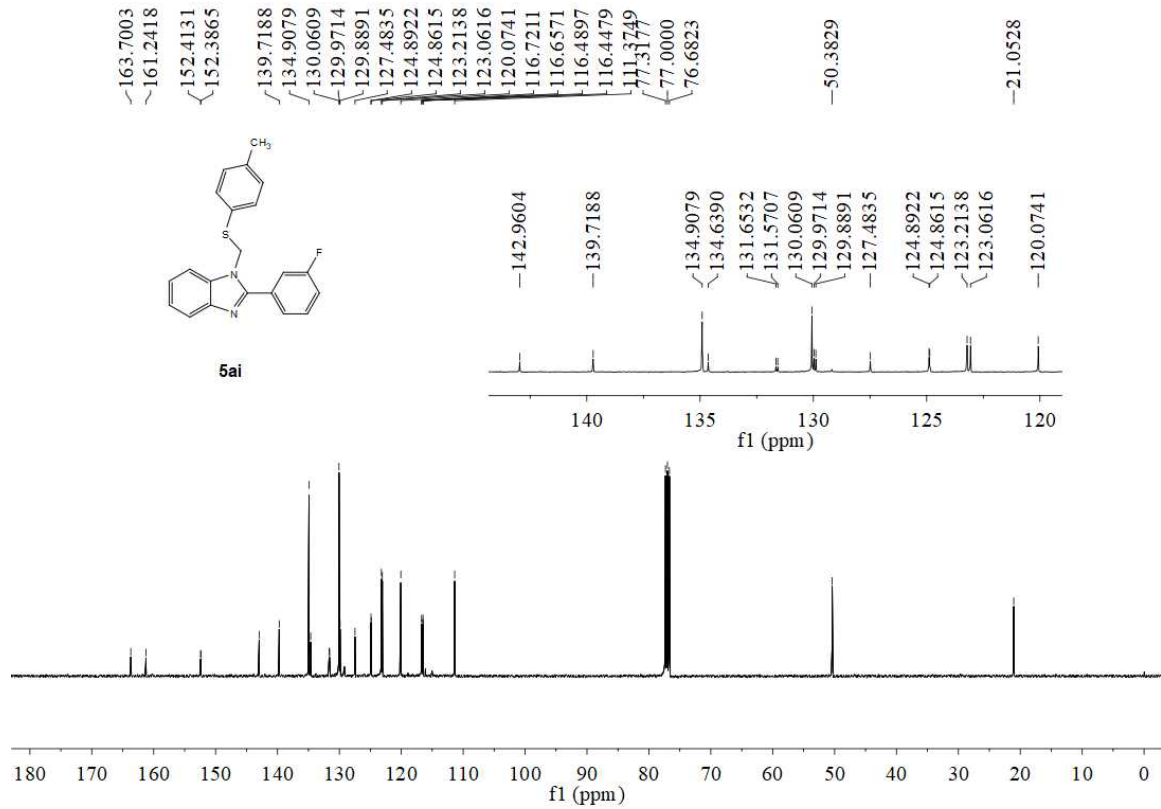


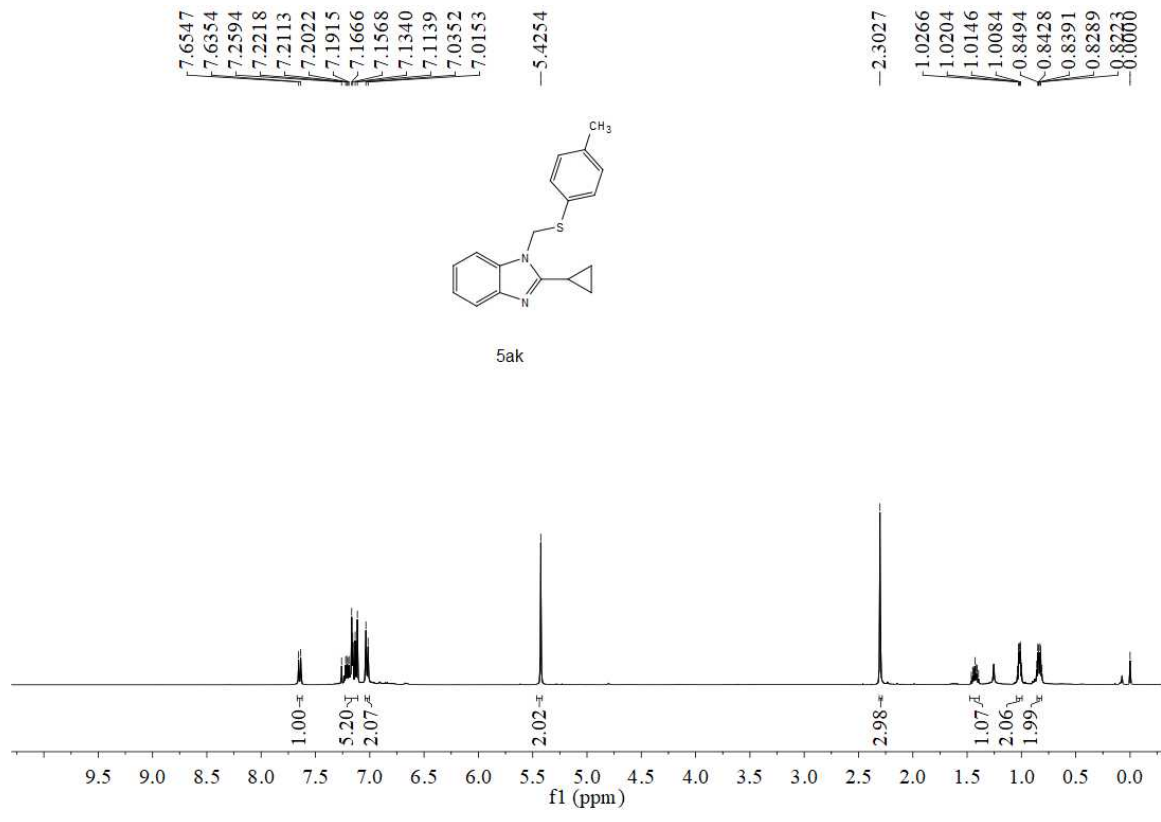
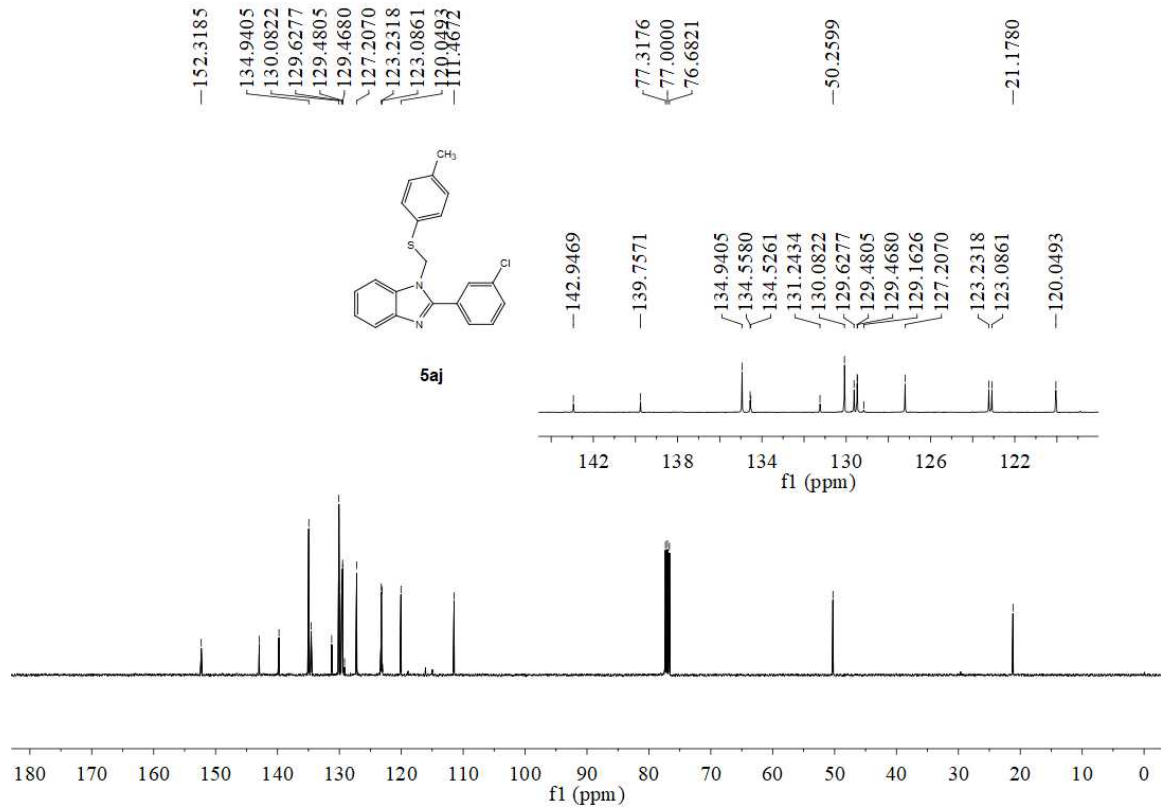












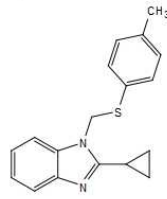
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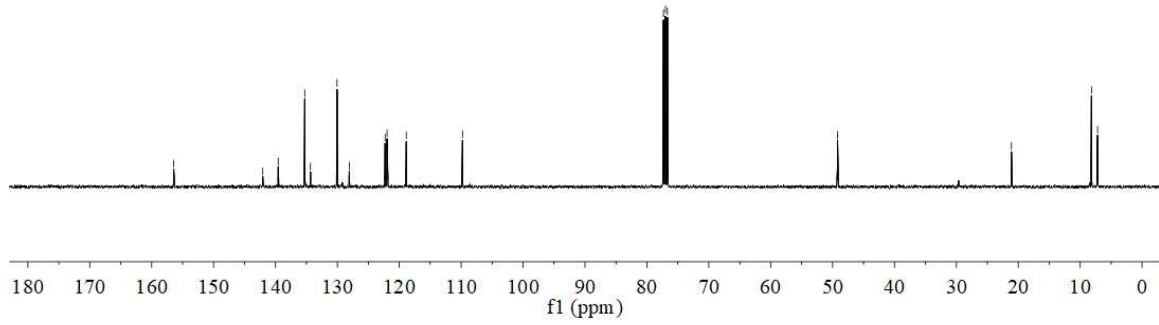
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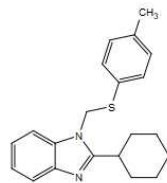


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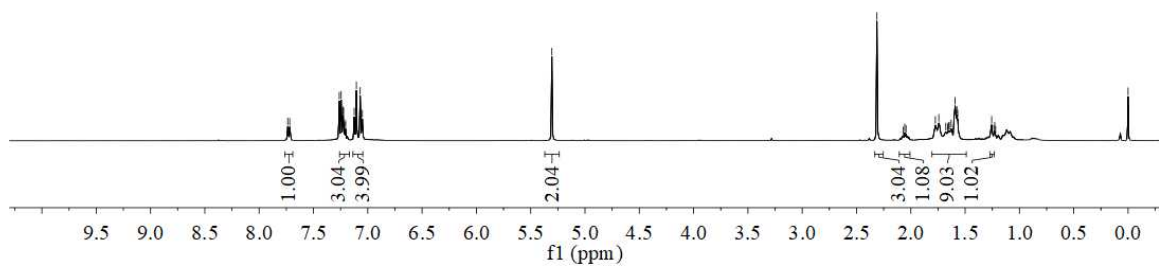


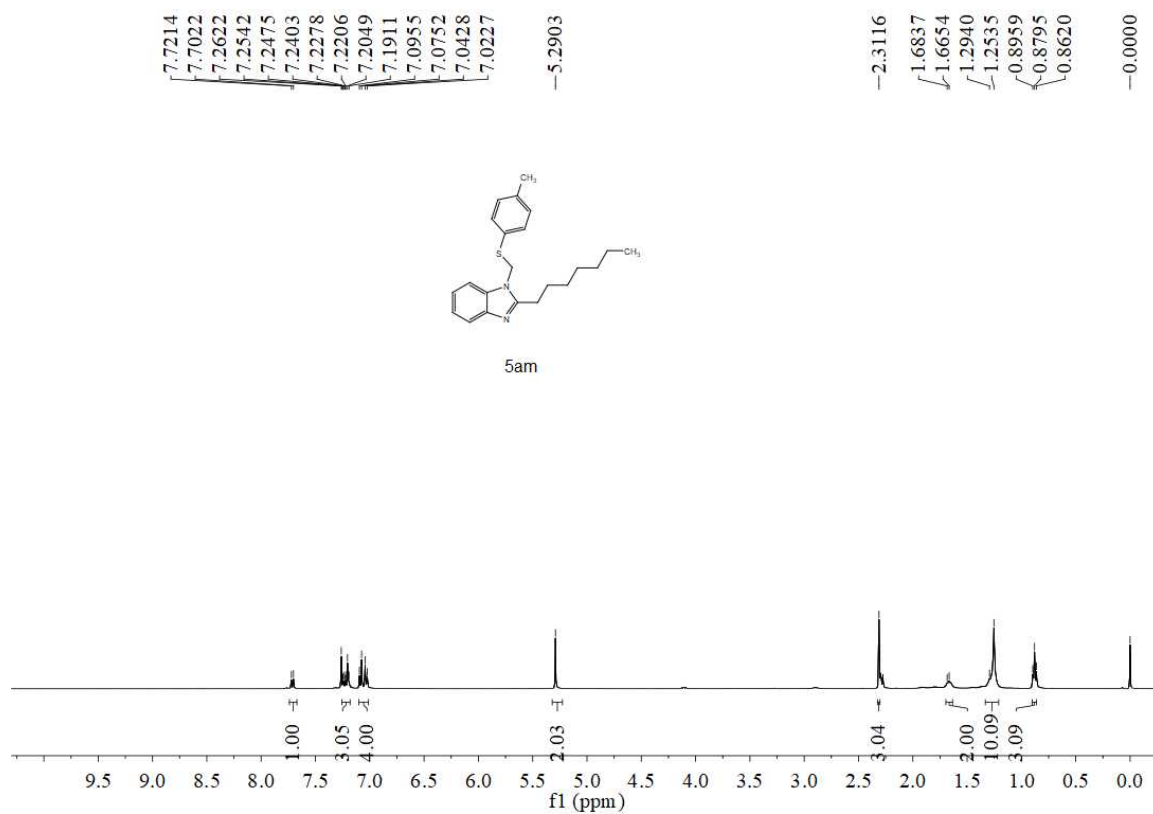
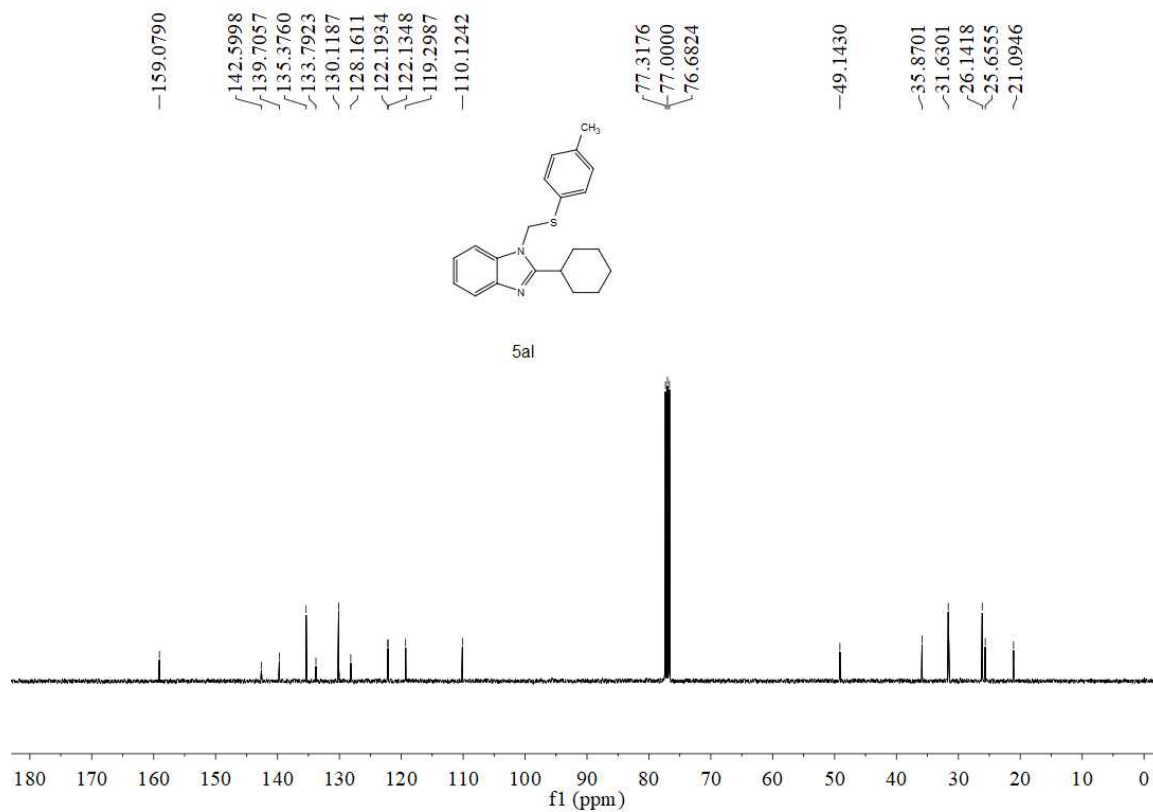
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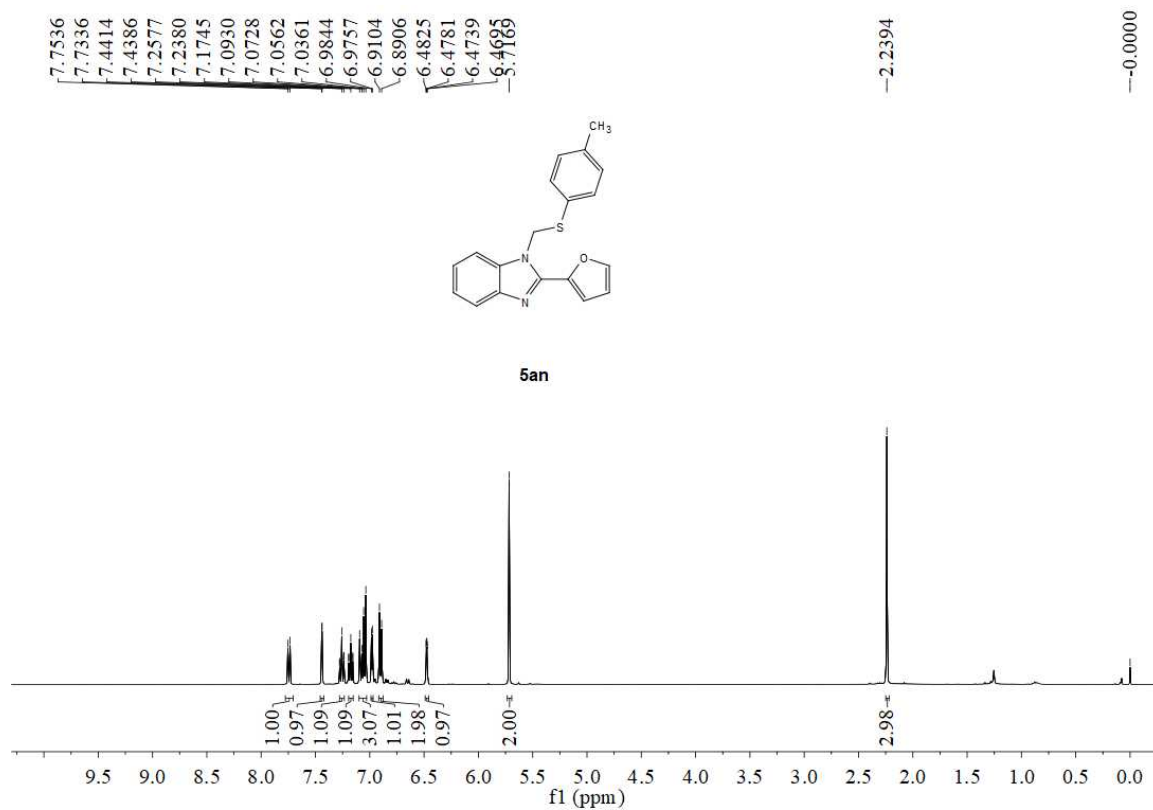
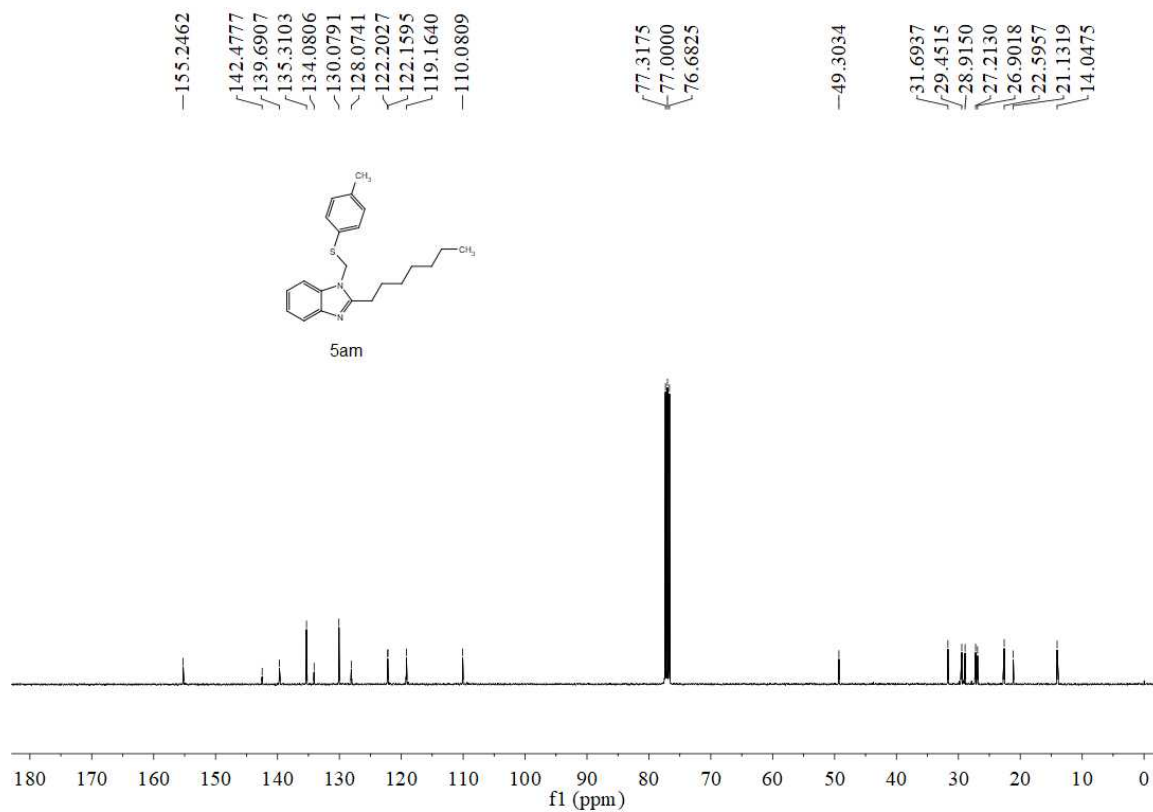
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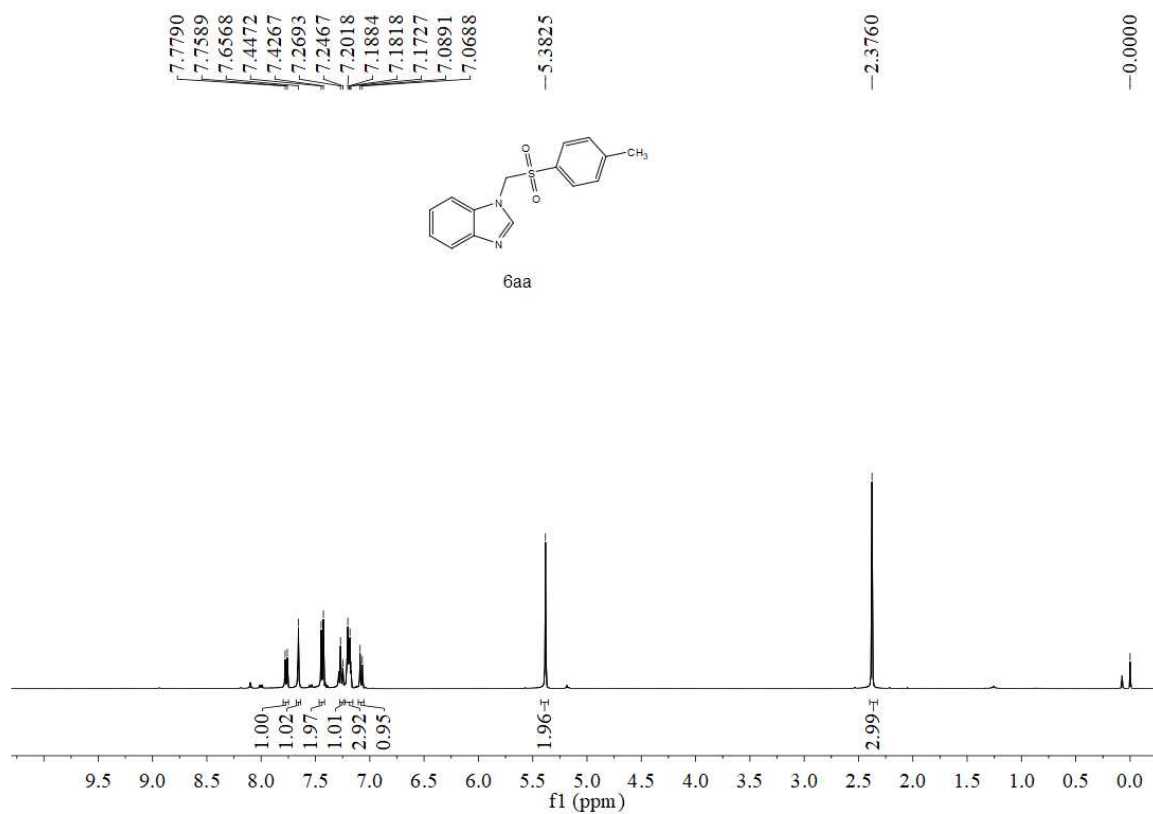
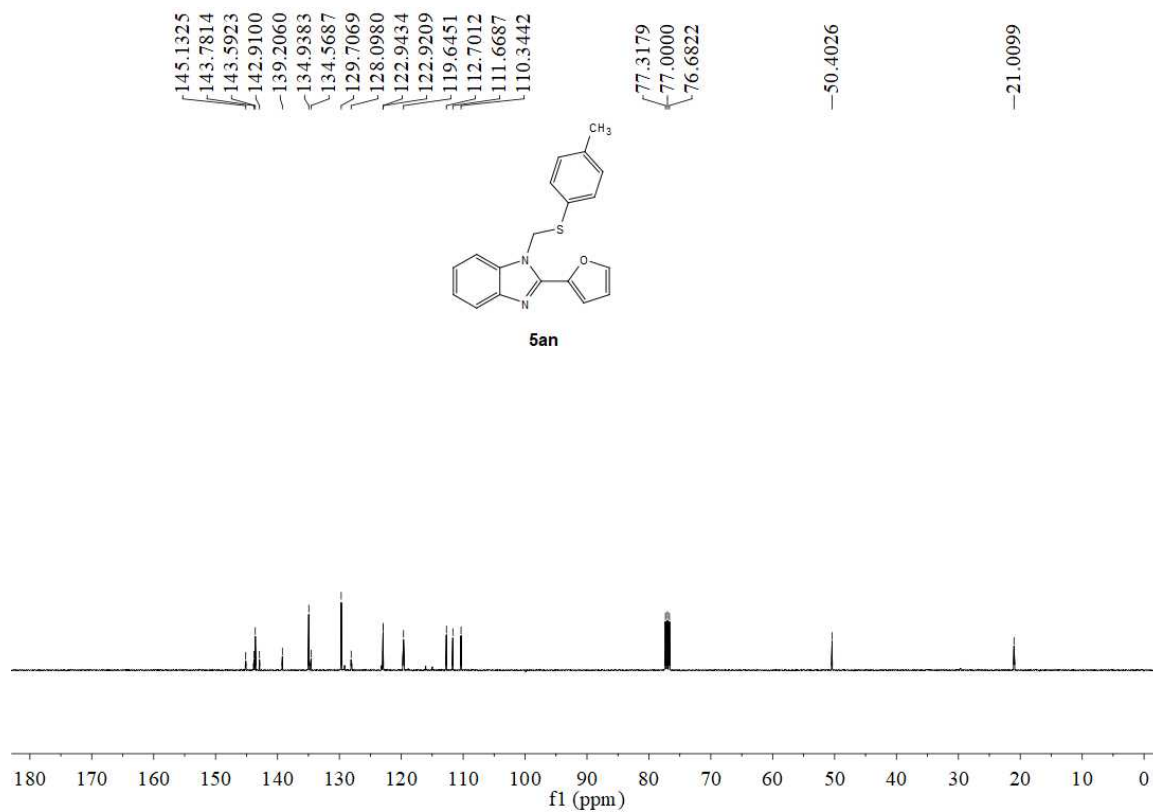


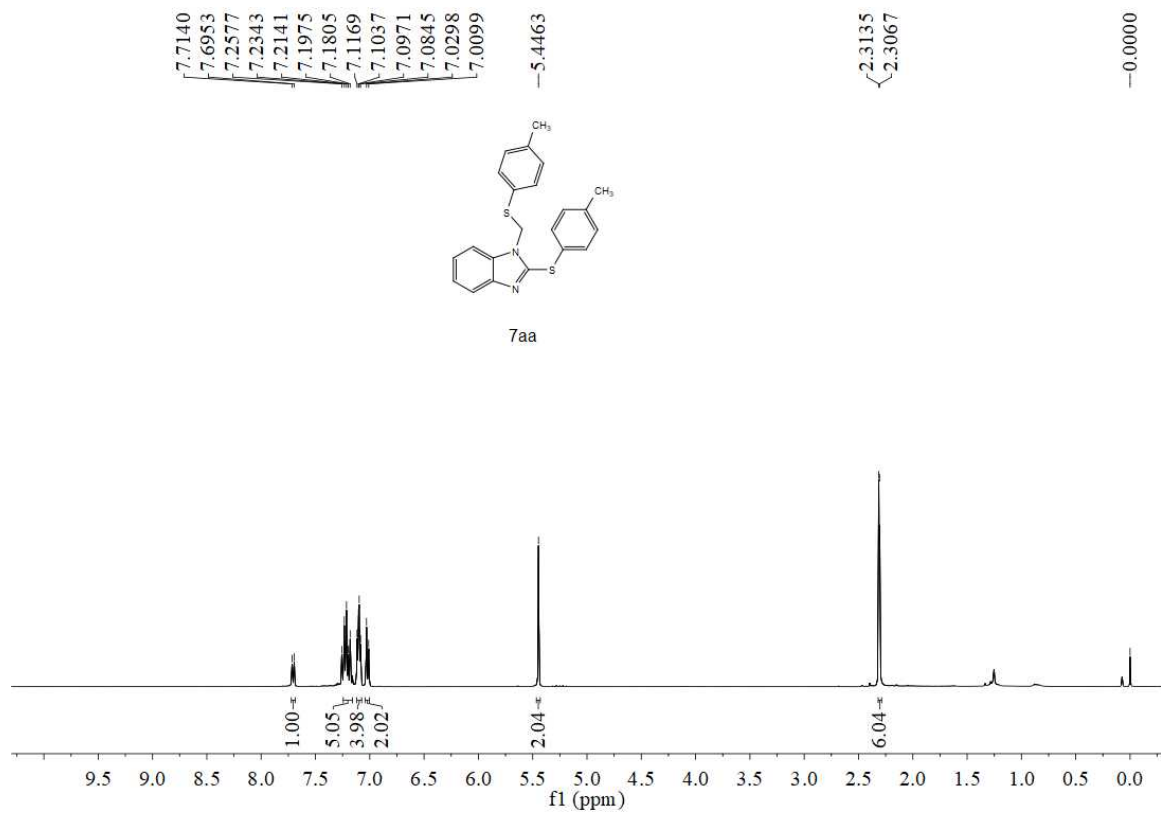
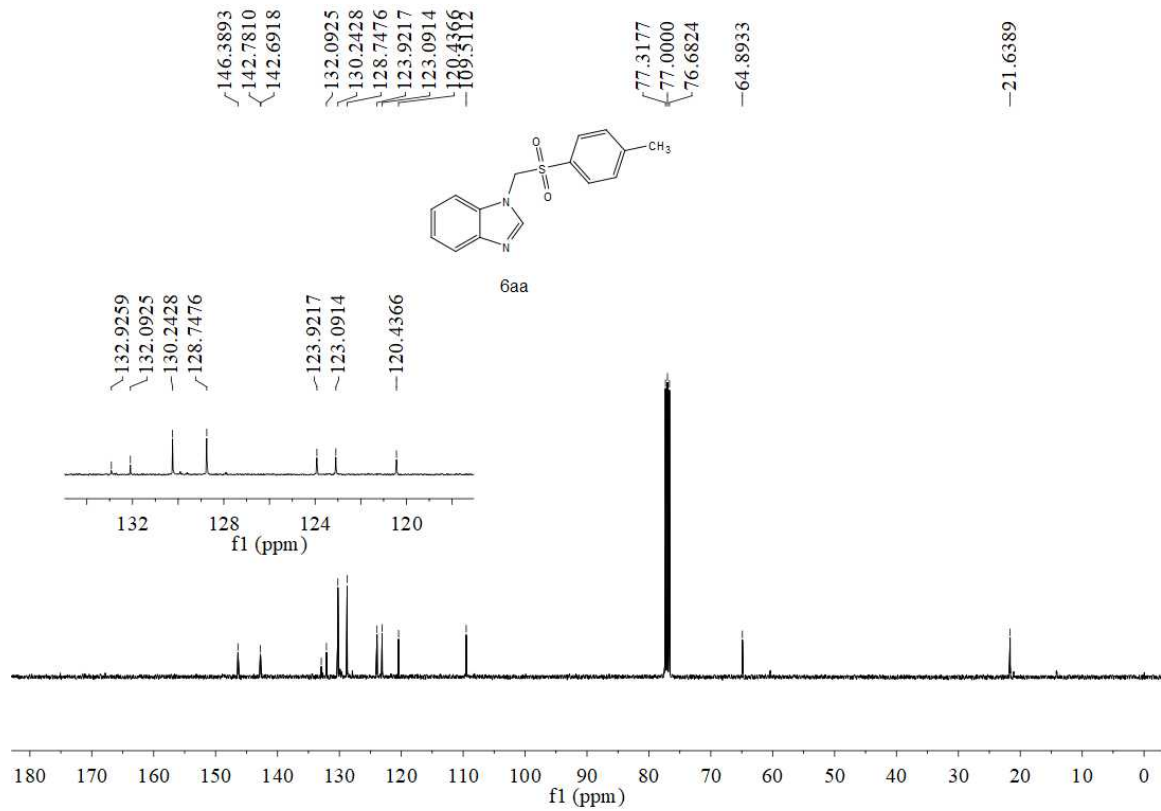
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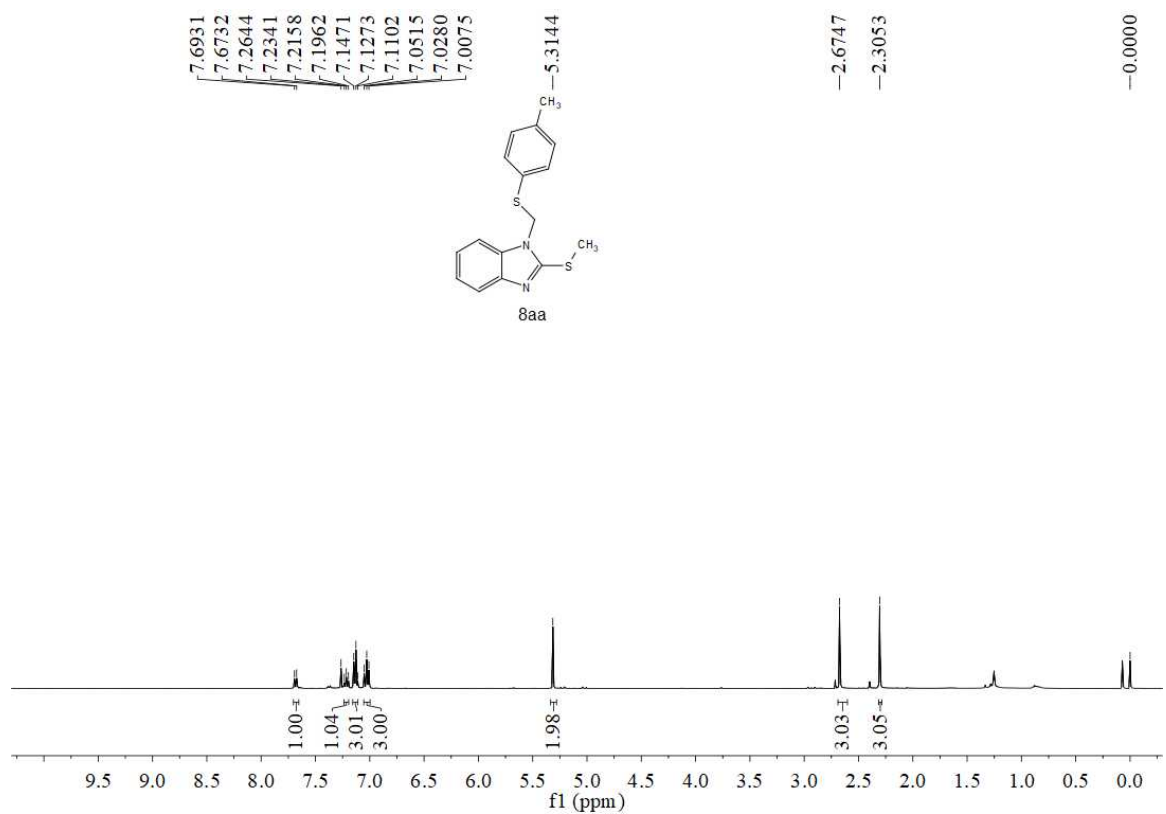
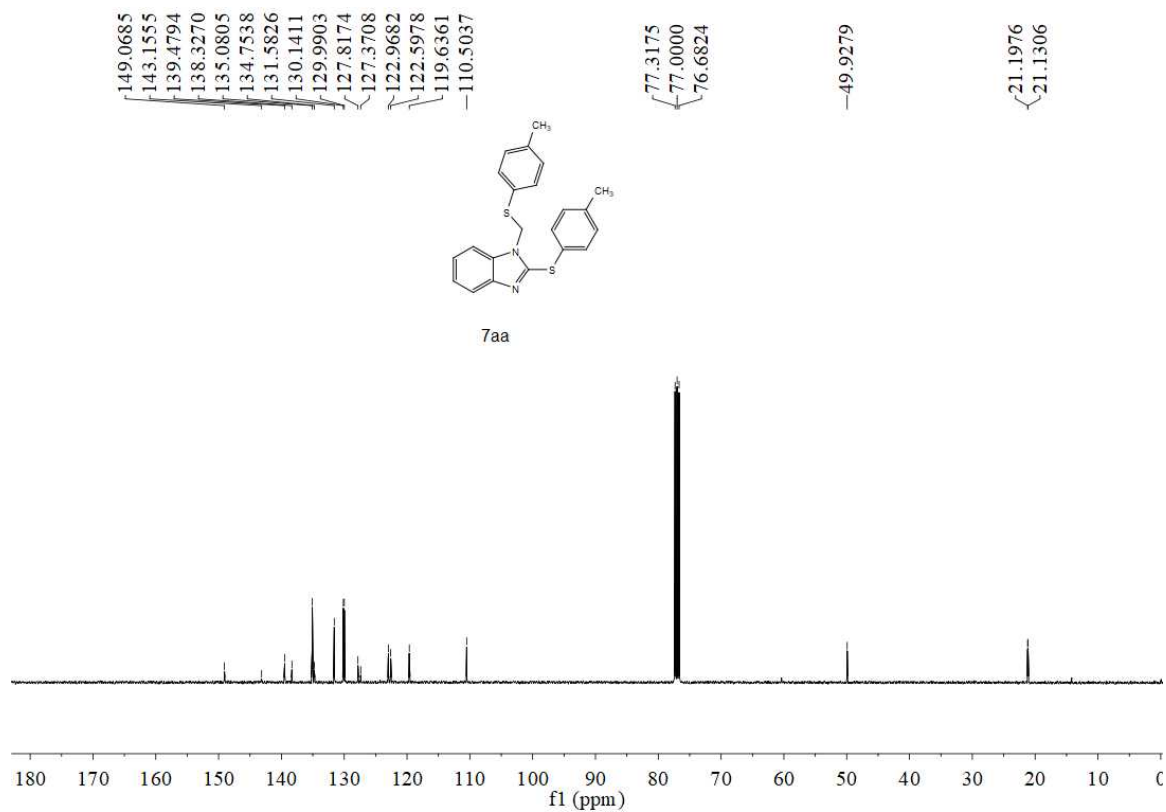










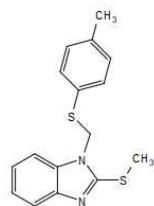


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