Supporting Information

Continuous flow synthesis of substituted benzimidazoles by enzyme-electrochemical cascade method

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1. General Material Information for Continuous-flow Reactor

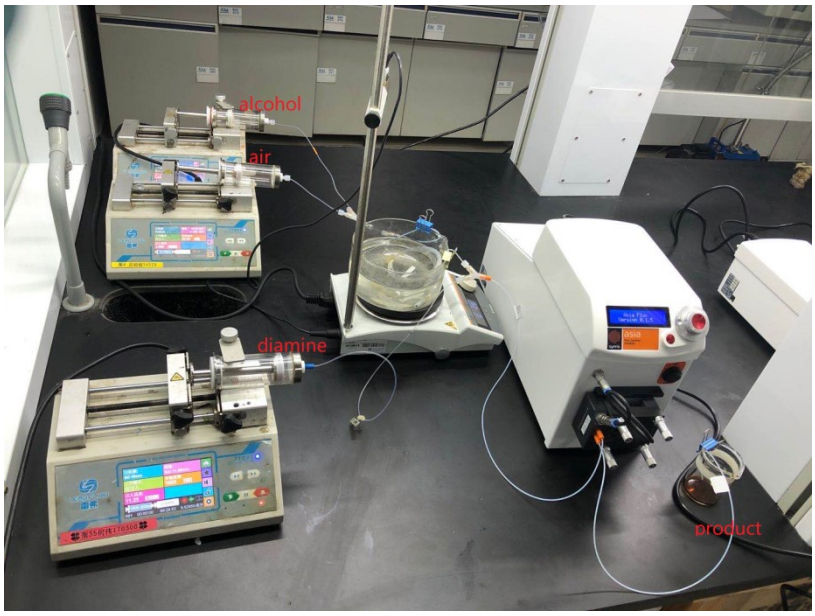


Fig. S1. the two-step continuous flow reactor

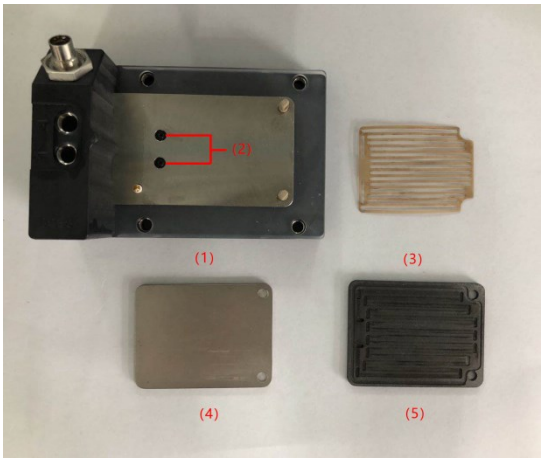
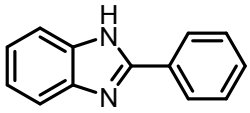


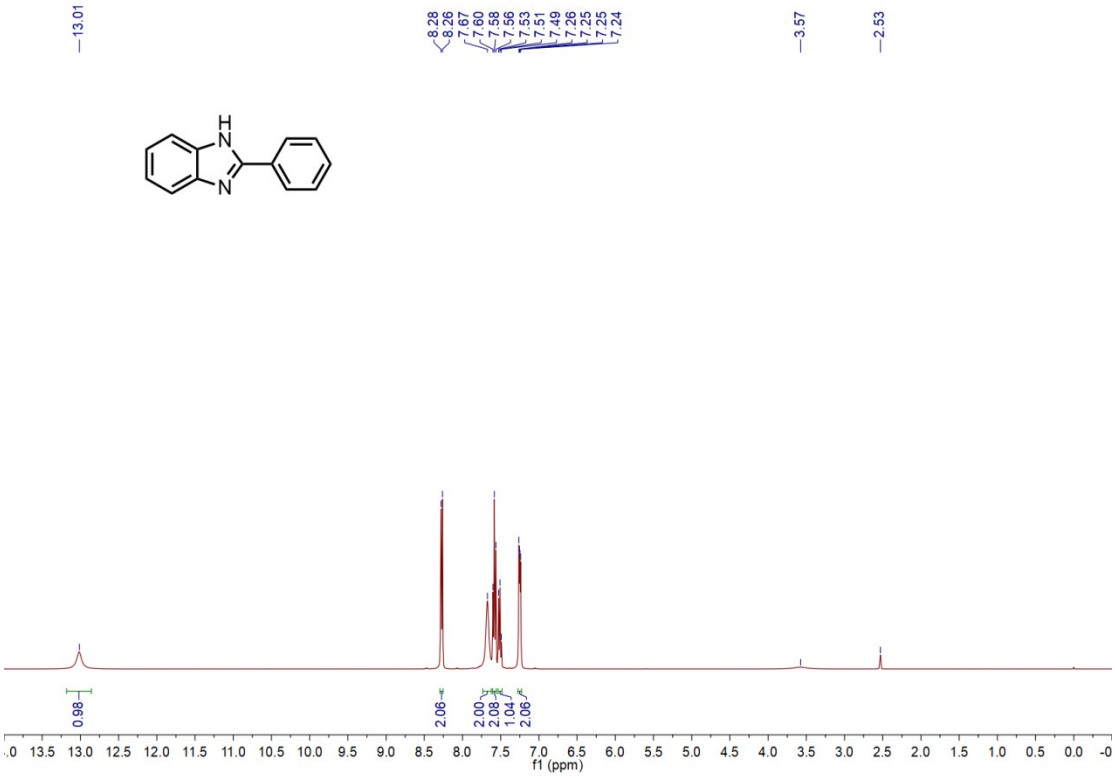
Fig. S2 the diagram of continuous-flow electrochemical reactor

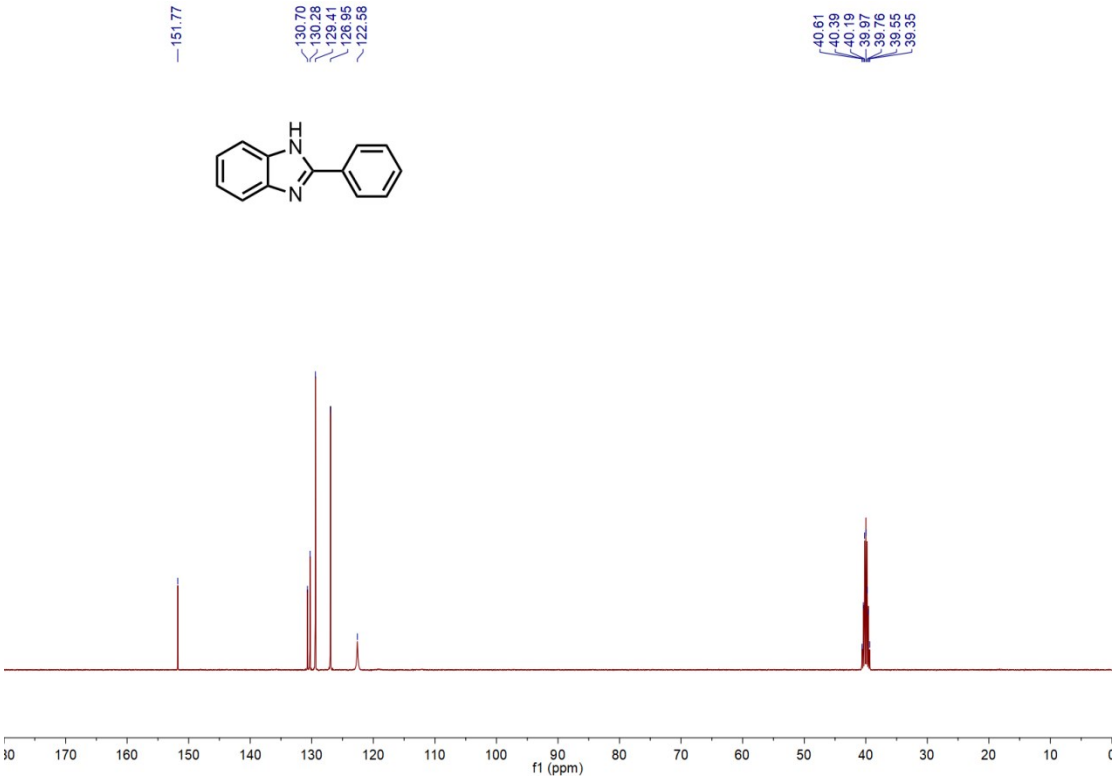
(1): electrode holder; (2): inlet and outlet; (3): channel reactor; (4): cathode; (5): Anode.

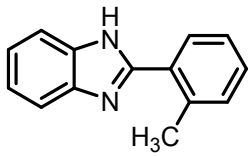
2. NMR Spectra



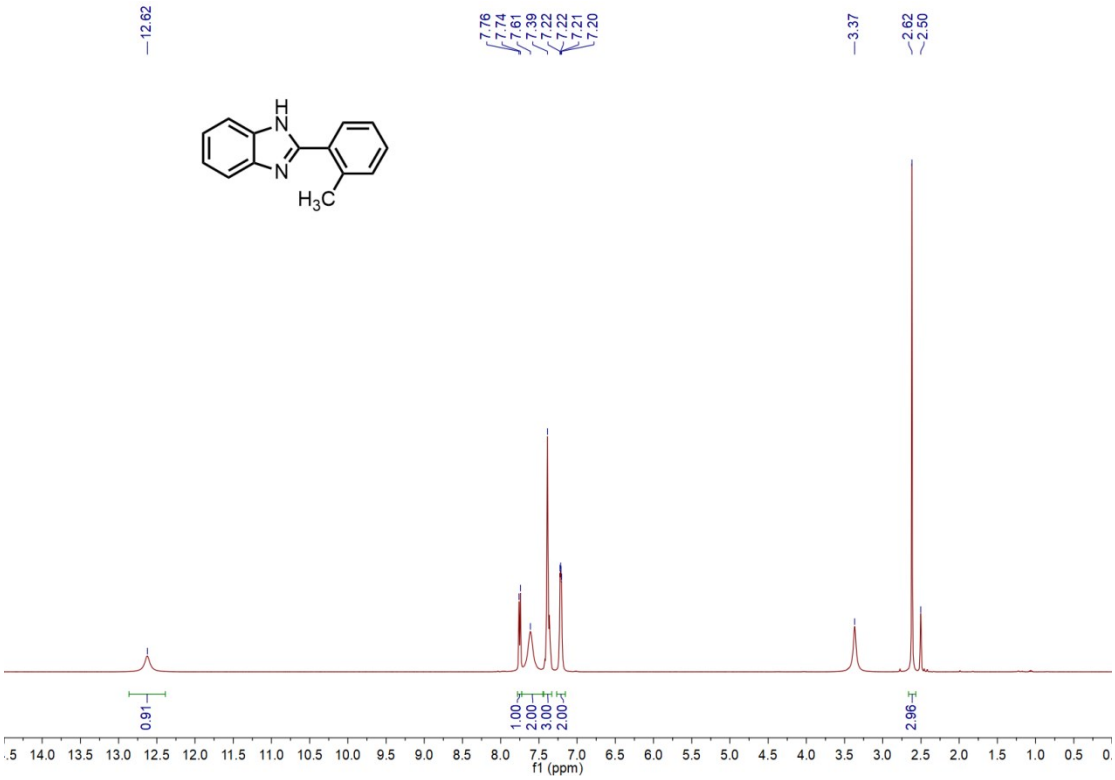
2-phenyl-1H-benzo[d]imidazole (4aa) Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 58.5 mg, yield 75%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.01 (s, 1H), 8.27 (d, J = 8.0 Hz, 2H), 7.67 (s, 2H), 7.58 (t, J = 7.6 Hz, 2H), 7.51 (t, J = 6.9 Hz, 1H), 7.25 (dd, J = 5.8, 3.1 Hz, 2H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.77 , 130.70 , 130.28 , 129.41 , 126.95 , 122.58; HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_{10}N_2H$ 195.0922, found 195.0926.

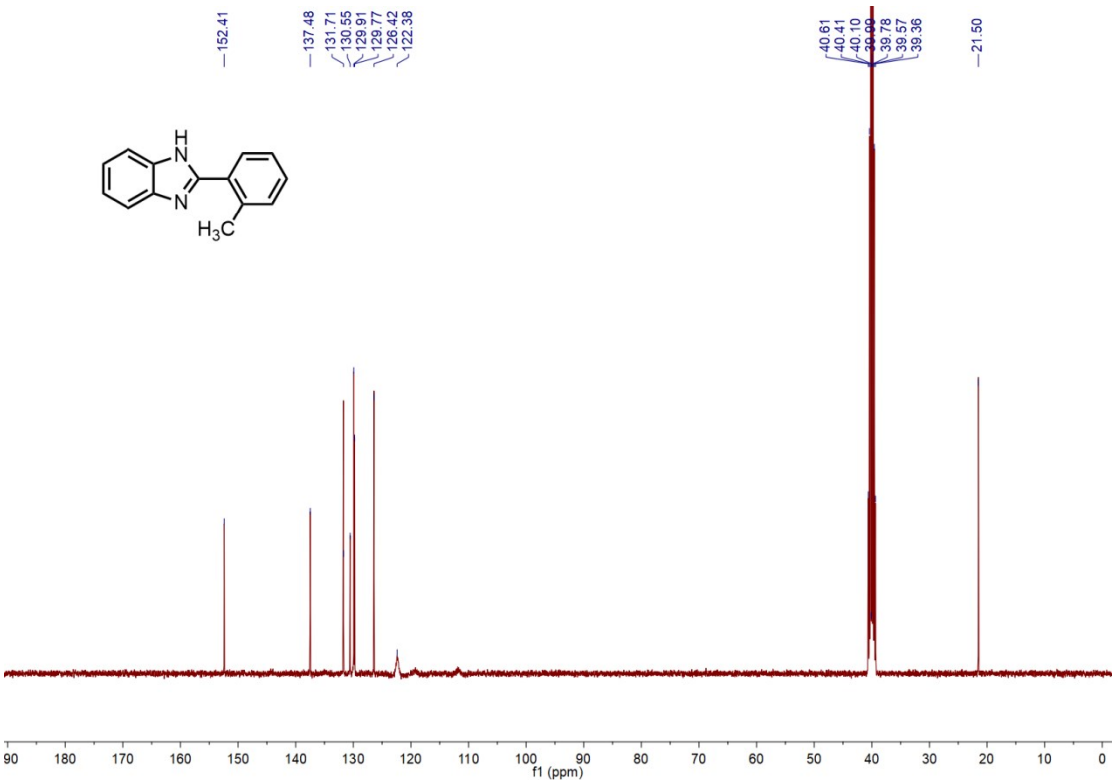


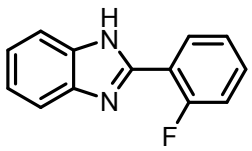




2-(o-tolyl)-1H-benzo[d]imidazole (4ab) Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 49.1 mg, yield 59%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.62 (s, 1H), 7.75 (d, J = 7.0 Hz, 2H), 7.61 (s, 2H), 7.39 (m, 3H), 7.21 (dd, J = 5.2, 2.9 Hz, 2H), 2.62 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.41, 137.48, 130.55, 129.91, 129.77, 126.42, 122.38, 21.50. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{12}N_2H$ 209.1073, found 209.1113.

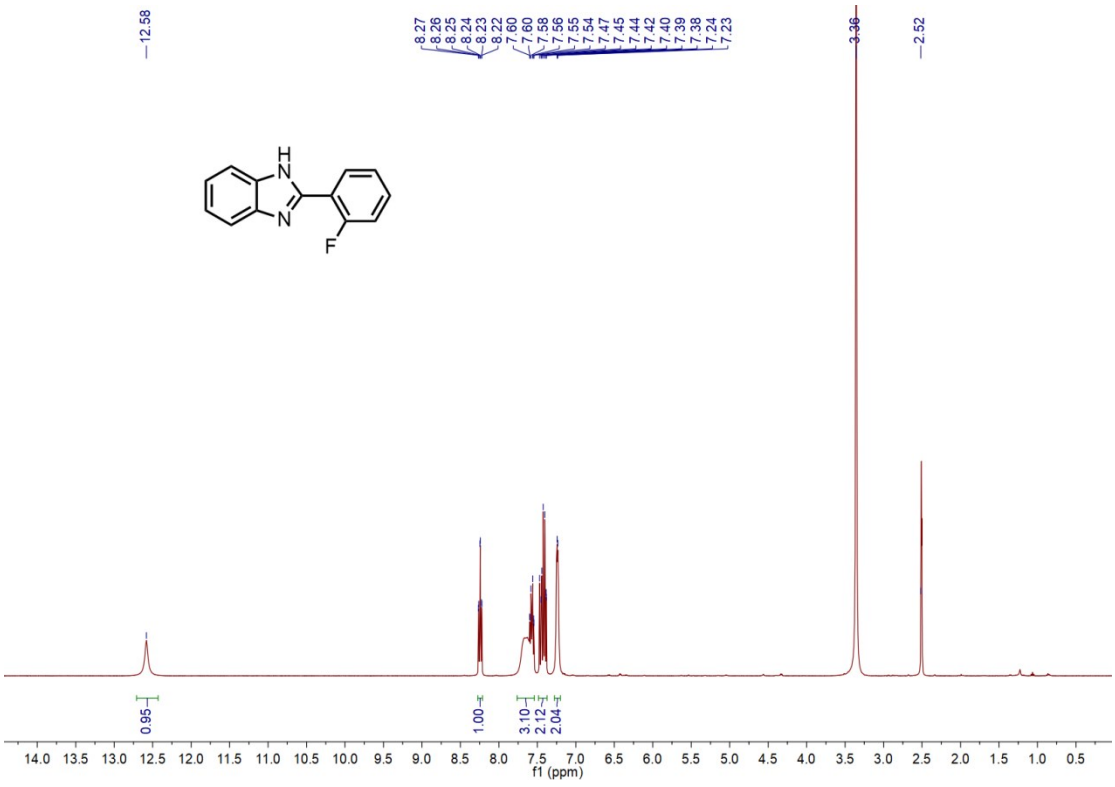


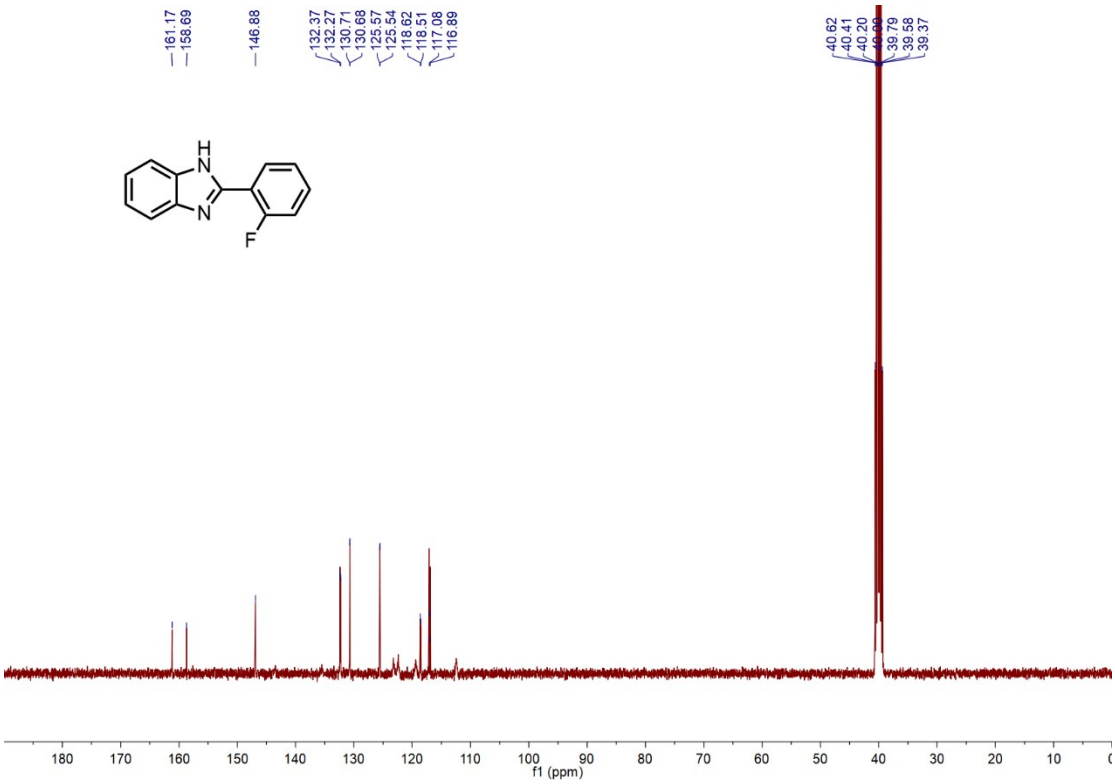




2-(2-Fluorophenyl)-1H-benzo[d]imidazole (4ac) Purification by column

chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 35.6 mg, yield 42%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.58 (s, 1H), 8.24 (td, J = 7.8, 1.8 Hz, 3H), 7.76 – 7.54 (m, 3H), 7.49 – 7.37 (m, 2H), 7.24 (d, J = 3.5 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.93 (d, $J_{C\text{-}F}$ = 250.1 Hz), 146.88, 132.32 (d, $J_{C\text{-}F}$ = 9.4 Hz), 130.70 (d, $J_{C\text{-}F}$ = 2.6 Hz), 125.55 (d, $J_{C\text{-}F}$ = 3.2 Hz), 118.56 (d, $J_{C\text{-}F}$ = 11.5 Hz), 117.08. ^{19}F NMR (376 MHz, DMSO-d_6) δ -114.66. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9FN_2H$ 213.0823, found 213.0848 .

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40.62
40.41
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39.58
39.37
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N
N
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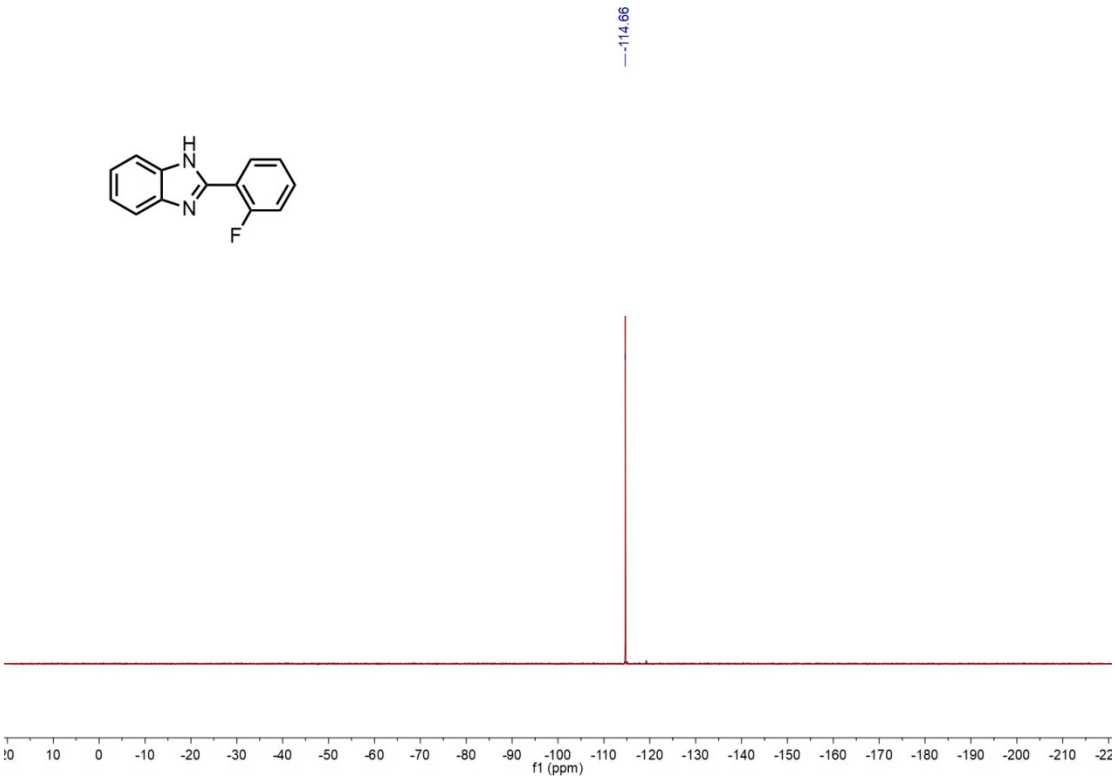
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N
F
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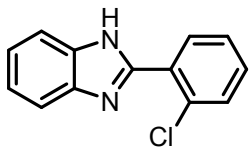
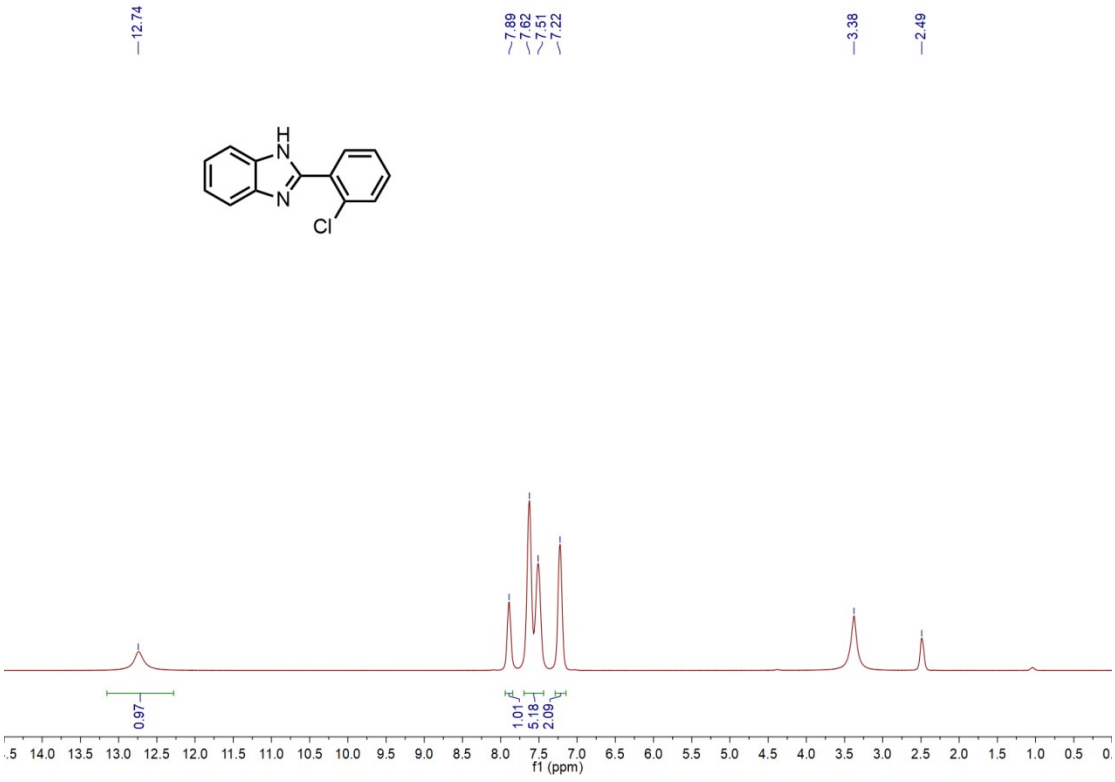
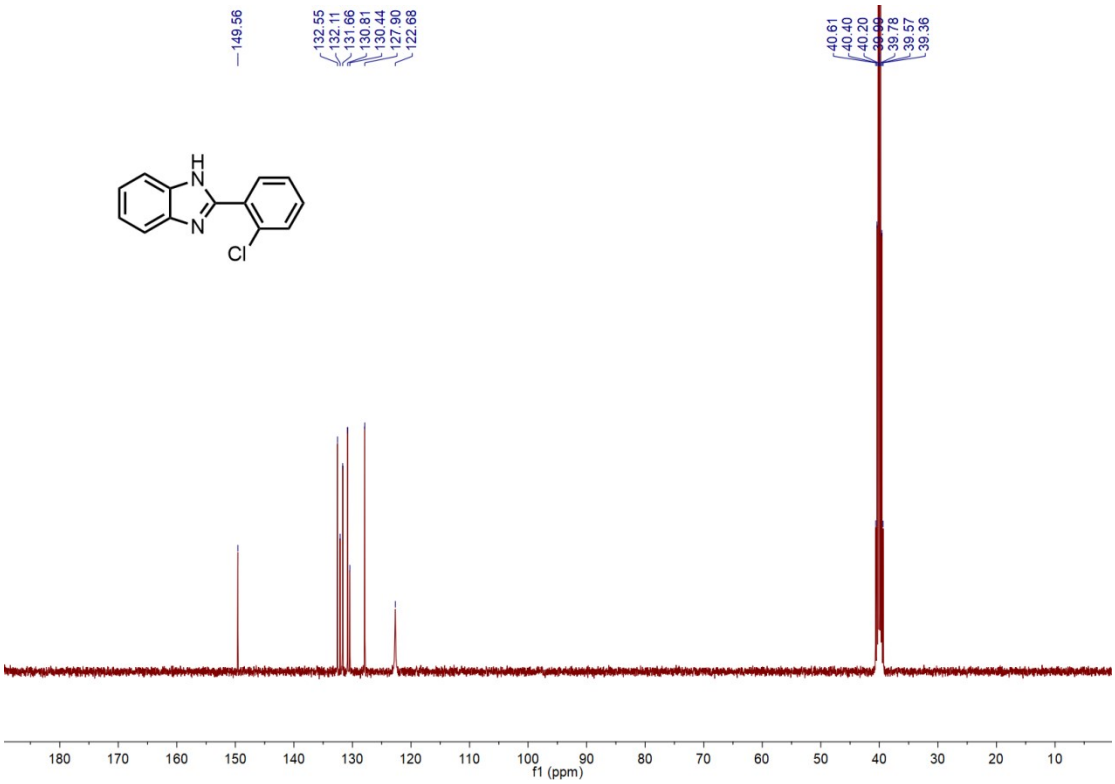
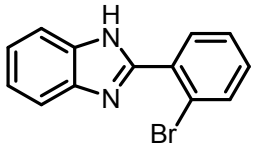
f1 (ppm)


H
N
N
Cl

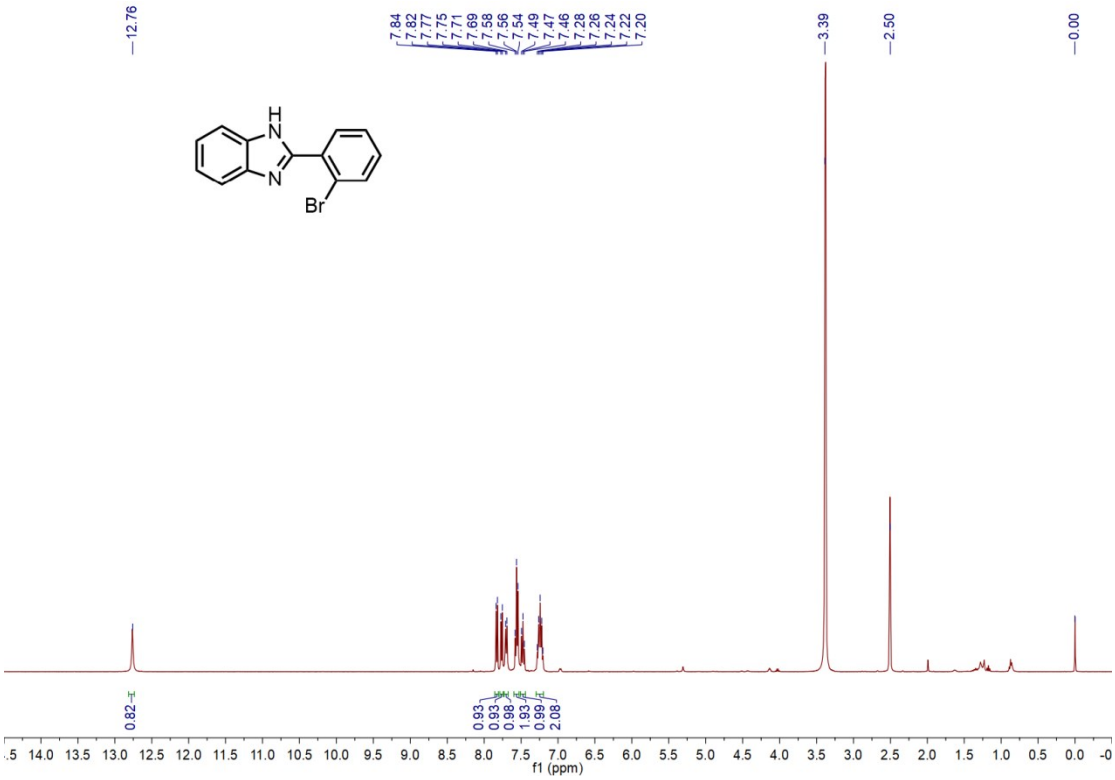
2-(2-chlorophenyl)-1H-benzo[d]imidazole (4ad) Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 79 mg, yield 79%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.74 (s, 1H), 7.89 (s, 1H), 7.57 (d, J = 45.9 Hz, 5H), 7.22 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 149.56, 132.55, 132.11, 131.66, 130.81, 130.44, 127.9, 122.68. HRMS (ESI) m/z: $[M+Na]^+$ calcd for $C_{13}H_9ClN_2Na$ 251.0346, found 251.0324.

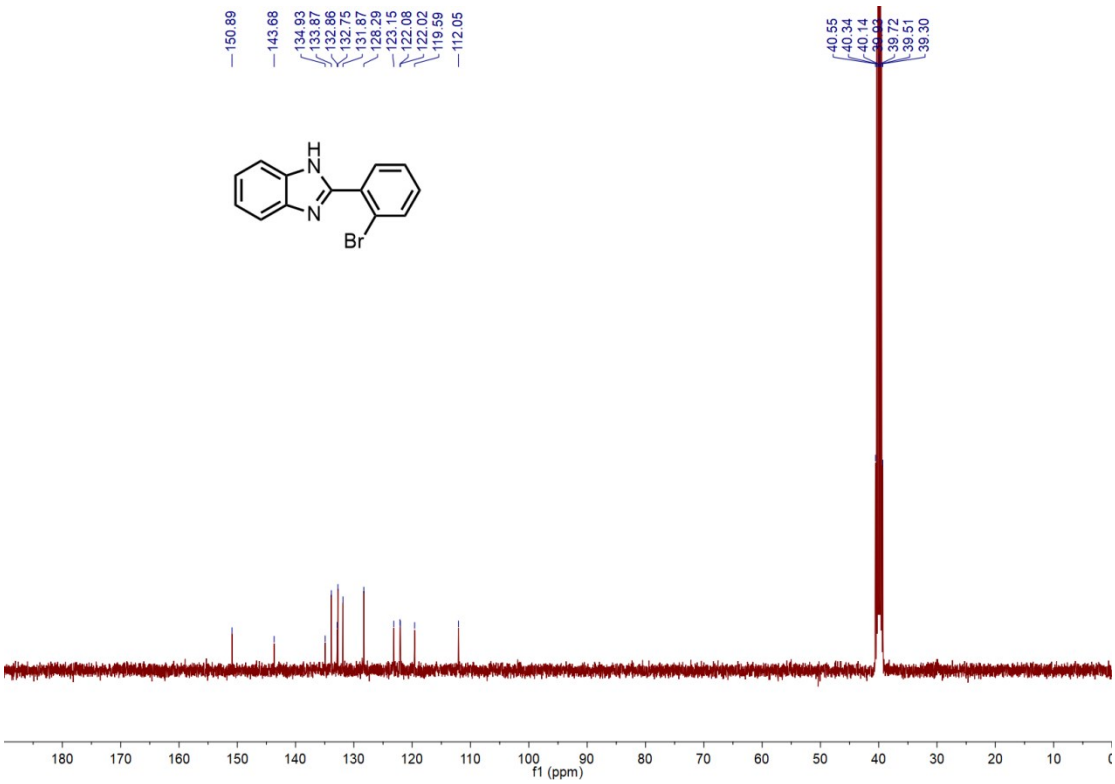


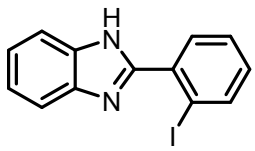




2-(2-Bromophenyl)-1H-benzo[d]imidazole (4ae) Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 53.3 mg, yield 49%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.76 (s, 1H), 7.83 (d, J = 8.0 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.70 (d, J = 7.7 Hz, 1H), 7.56 (t, J = 7.5 Hz, 2H), 7.47 (t, J = 7.6 Hz, 1H), 7.30 – 7.20 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.89, 143.68, 134.93, 133.87, 132.86, 132.75, 131.87, 128.29, 123.15, 122.08, 122.02, 119.59, 112.05. HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9BrN_2H$ 273.0022, found 273.0019.

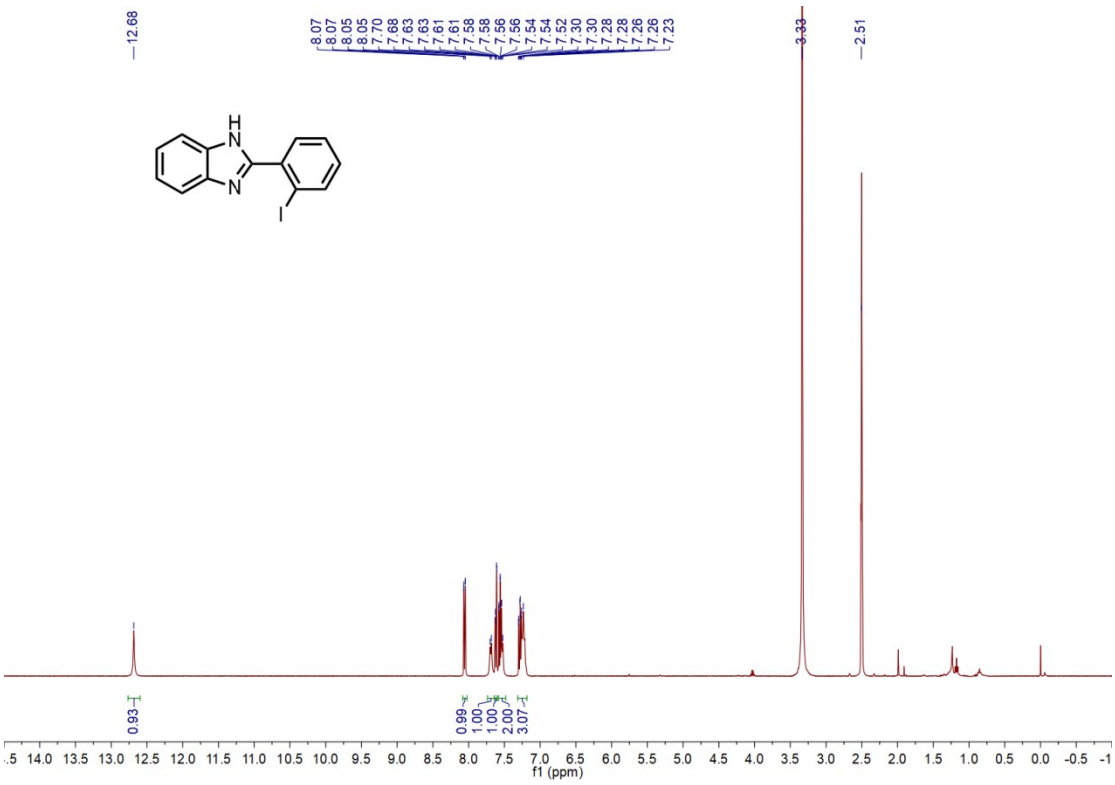


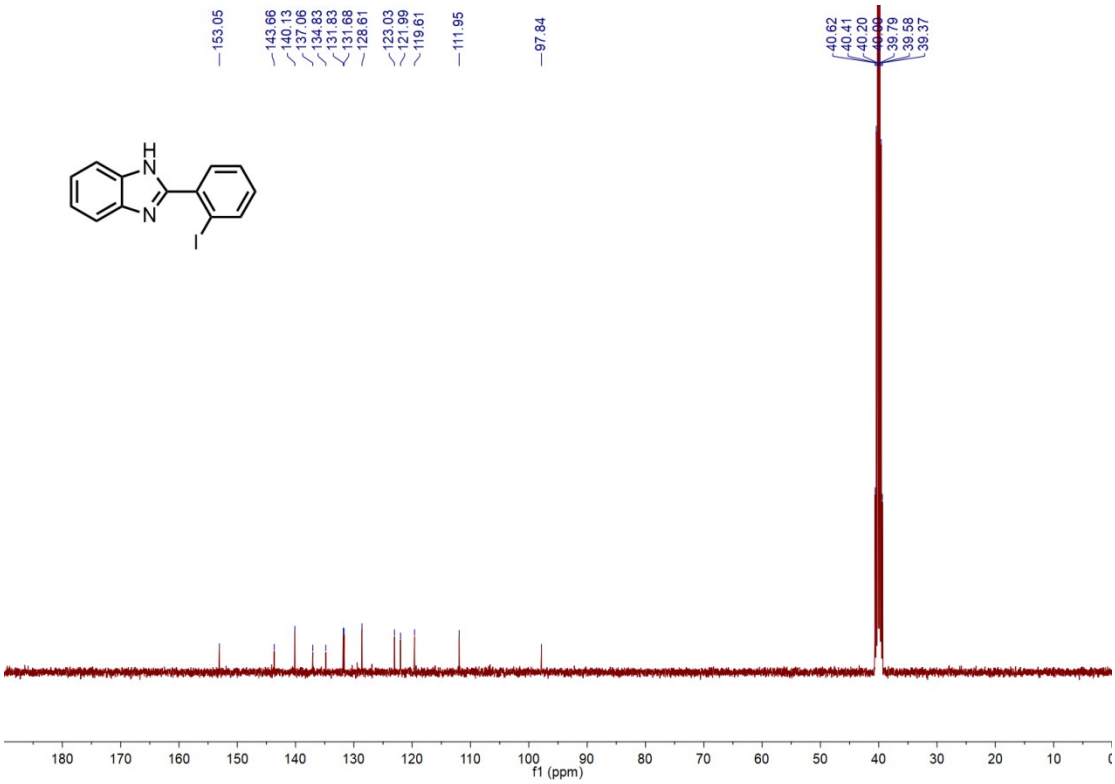


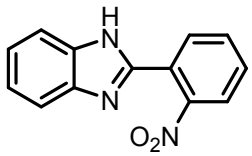


2-(2-Iodophenyl)-1H-benzo[d]imidazole (4af). Purification by column

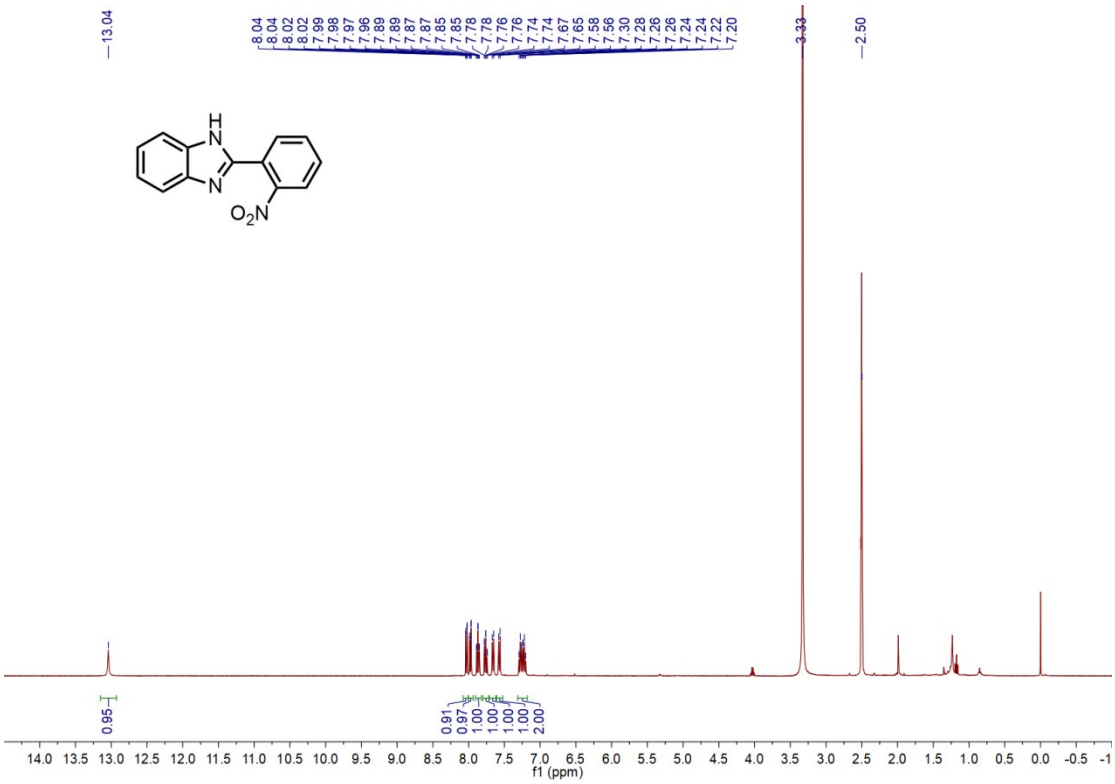
chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 70.4 mg, yield 55%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.68 (s, 1H), 8.06 (dd, J = 7.9, 0.9 Hz, 1H), 7.69 (d, J = 7.4 Hz, 1H), 7.62 (dd, J = 7.6, 1.7 Hz, 1H), 7.58 – 7.48 (m, 2H), 7.31 – 7.18 (m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.05, 143.66, 140.13, 137.06, 134.83, 131.83, 131.68, 128.61, 123.03, 121.99, 119.61, 111.95, 97.84. HRMS (ESI) m/z: [M+H] $^{+}$ calcd for $C_{13}H_9IN_2H$ 320.9883, found 320.9856.







2-(2-Nitrophenyl)-1H-benzo[d]imidazole (4aj). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 10/1); white solid; 56.4 mg, yield 59%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.04 (s, 1H), 8.03 (dd, J = 8.0, 1.1 Hz, 1H), 7.98 (dd, J = 7.7, 1.3 Hz, 1H), 7.87(td, J = 7.6, 1.2 Hz, 1H), 7.76 (td, J = 7.8, 1.4 Hz, 1H), 7.66 (d, J = 7.9 Hz, 1H), 7.57 (d, J = 7.8 Hz, 1H), 7.31 – 7.18 (m, 2H).^{13}C NMR (100 MHz, DMSO-d_6) δ 149.44 , 147.77 , 144.08 , 135.09 , 133.11 , 131.39 , 131.36 , 124.76 , 124.72 , 123.54 , 122.35 , 119.71 , 112.13 . HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9N_3O_2H$ 240.0768, found 240.0760.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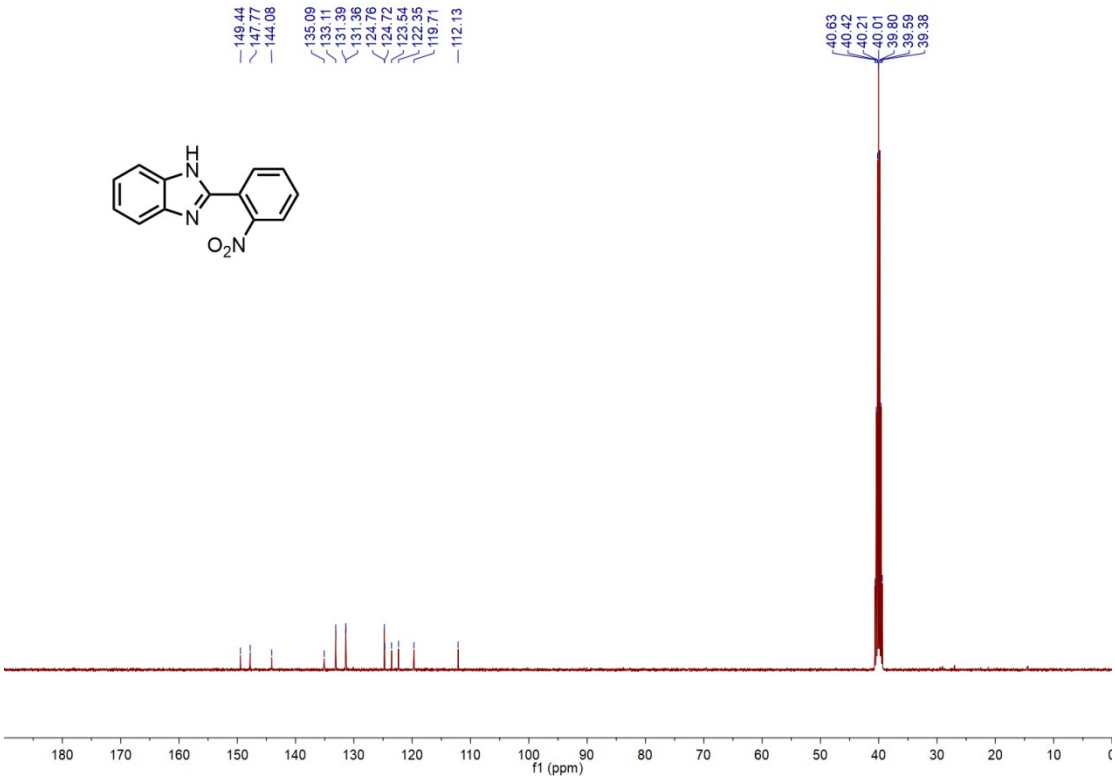
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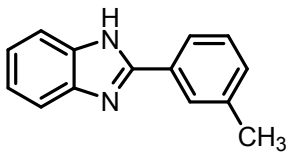
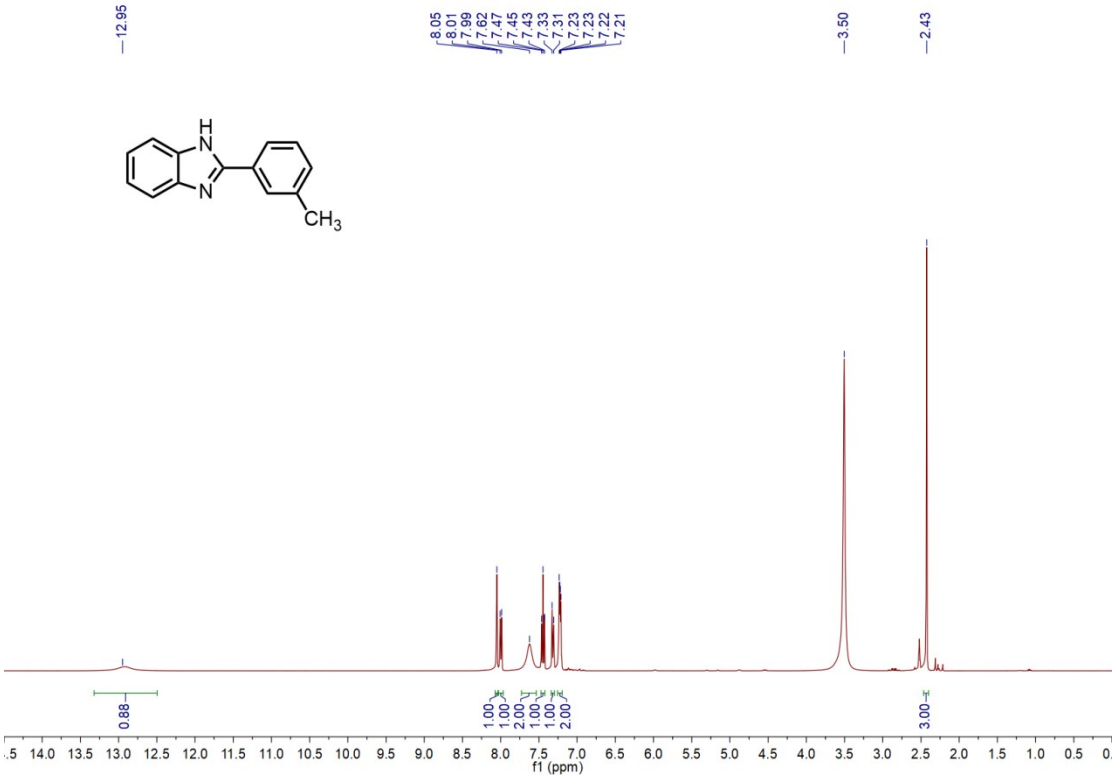
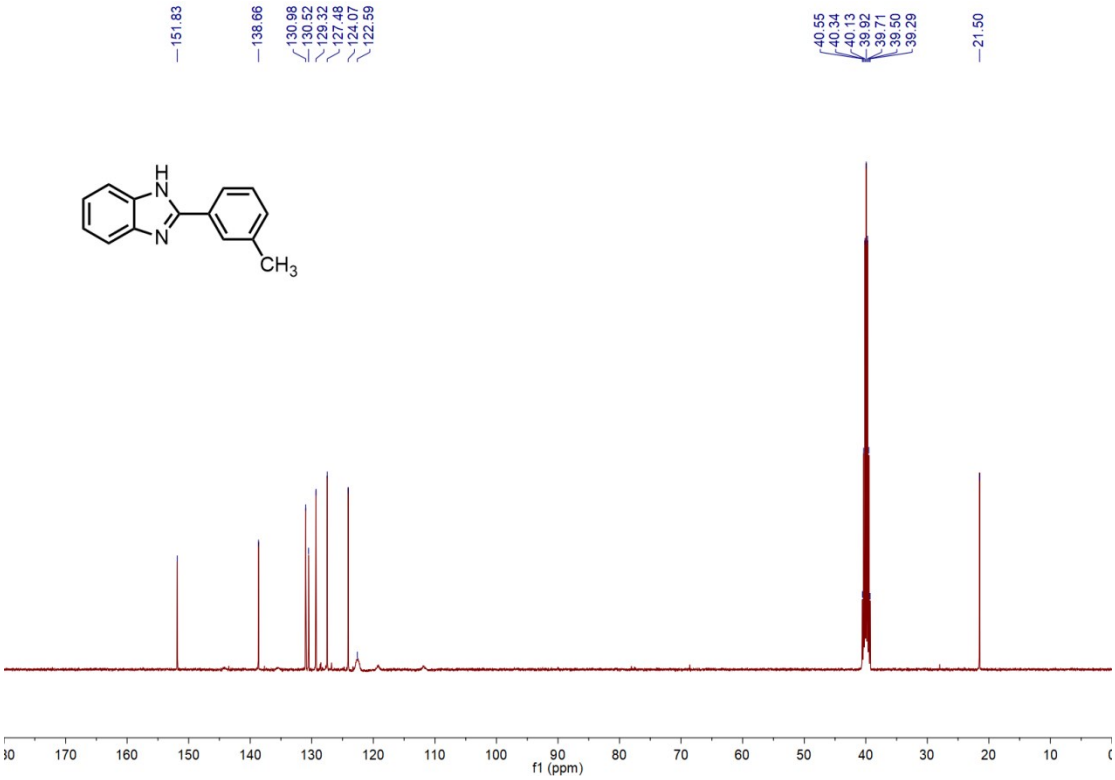
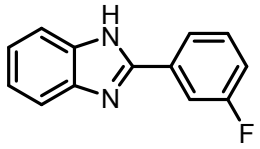


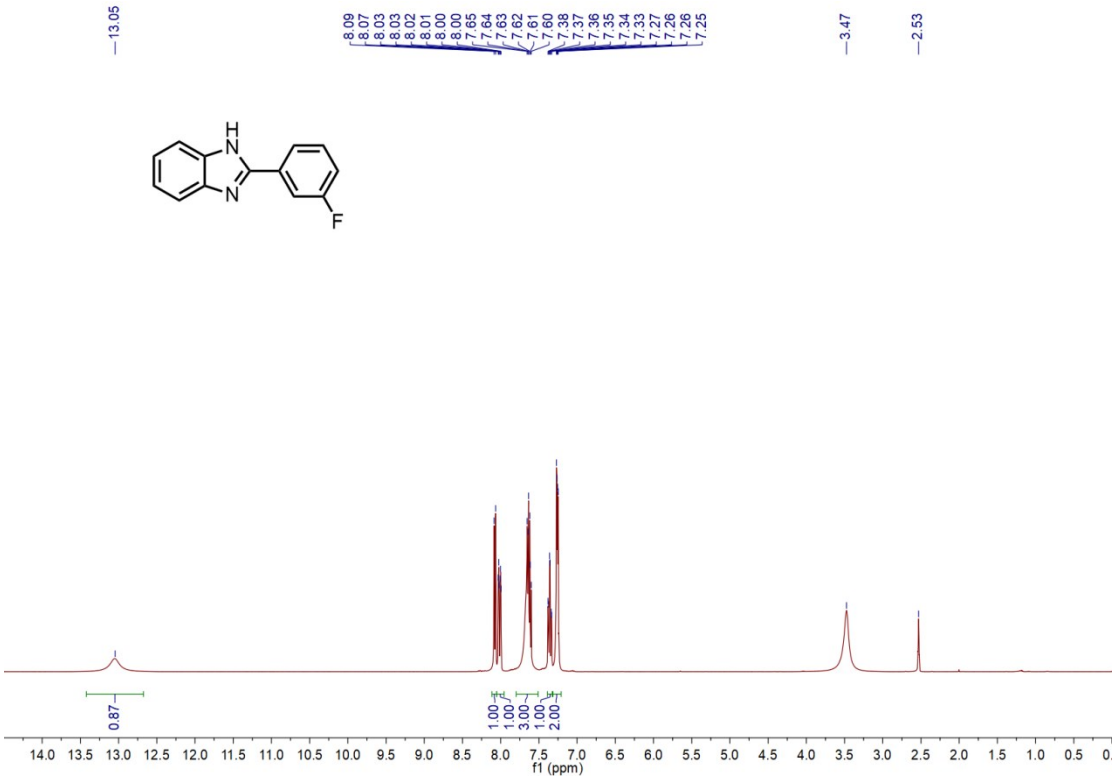
2-(m-Tolyl)-1H-benzo[d]imidazole (4ah). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 48.3 mg, yield 58%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.95 (s, 1H), 8.05 (s, 1H), 8.00 (d, J = 8.0 Hz, 1H), 7.62 (s, 2H), 7.46 (t, J = 7.6 Hz, 1H), 7.32 (d, J = 8.0 Hz, 1H), 7.22 (dd, J = 6.0, 3.1 Hz, 2H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.83, 138.66, 130.98, 130.52, 129.32, 127.48, 124.07, 21.50. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{12}N_2H$ 209.1073, found 209.1078.







2-(3-Fluorophenyl)-1H-benzo[d]imidazole (4ai) Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 37.3 mg, yield 44%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.05 (s, 1H), 8.08 (d, J = 7.9 Hz, 1H), 8.01 (dt, J = 10.3, 2.4 Hz, 1H), 7.80 – 7.51 (m, 3H), 7.36 (td, J = 8.3, 2.6 Hz, 1H), 7.26 (dd, J = 6.0, 3.1 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.93 (d, $J_{C\text{-}F}$ = 250.1 Hz), 146.88, 132.32 (d, $J_{C\text{-}F}$ = 9.4 Hz), 130.70 (d, $J_{C\text{-}F}$ = 2.6 Hz), 125.55 (d, $J_{C\text{-}F}$ = 3.2 Hz), 118.56 (d, $J_{C\text{-}F}$ = 11.5 Hz), 117.08. ^{19}F NMR (376 MHz, DMSO-d_6) δ -112.38. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9FN_2H$ 213.0823, found 213.0826.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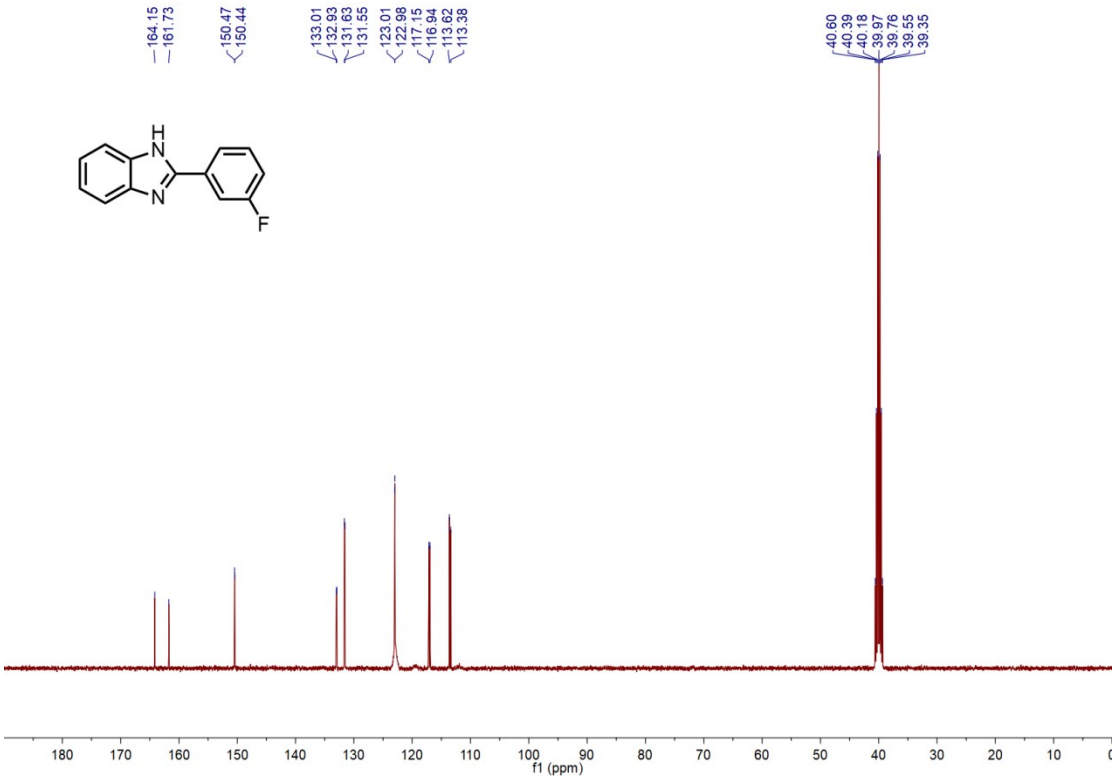
f1 (ppm)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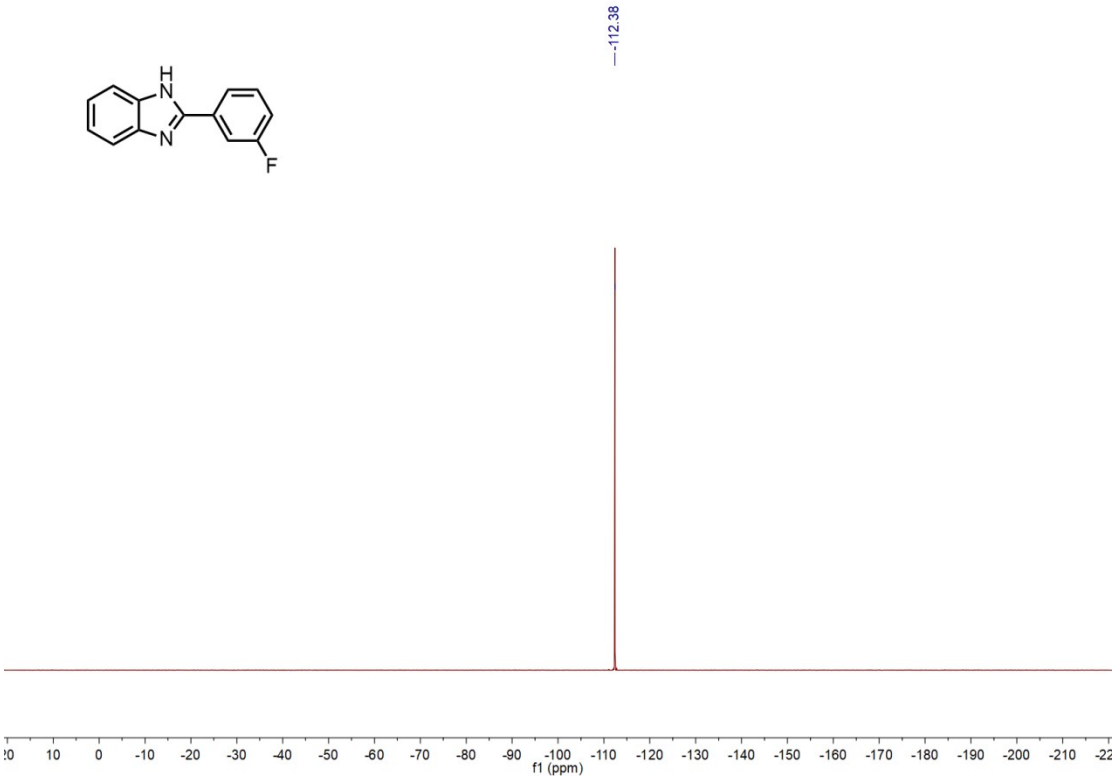
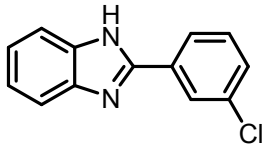
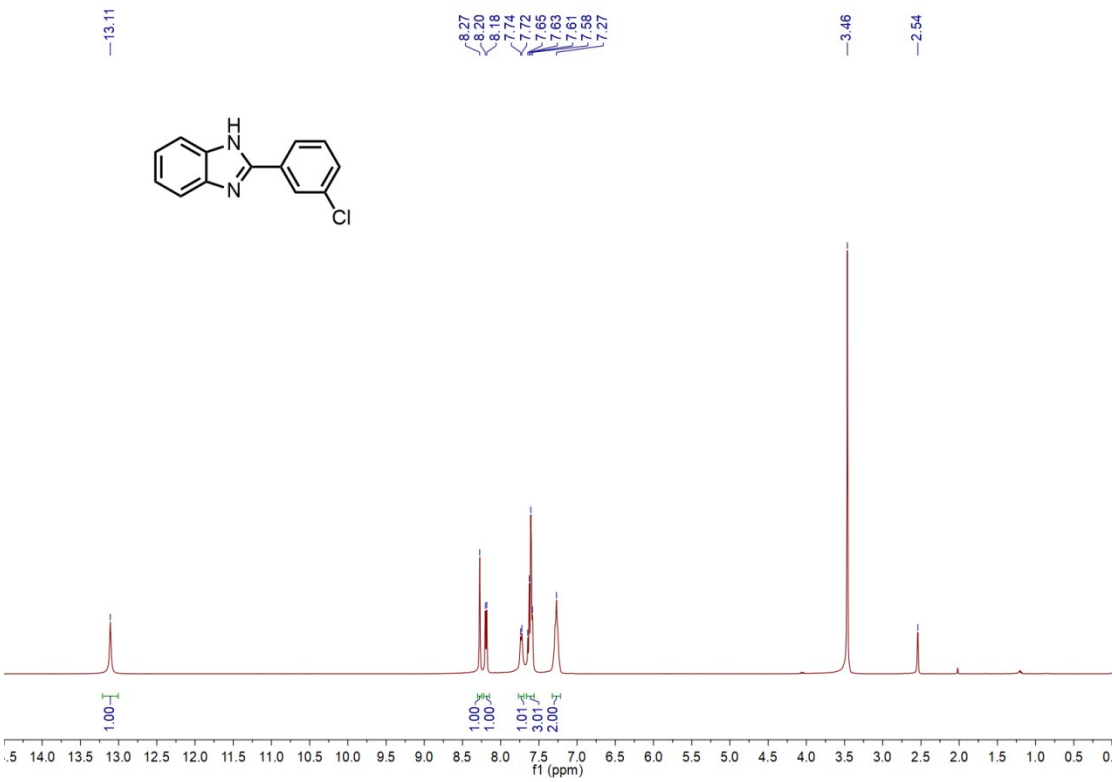
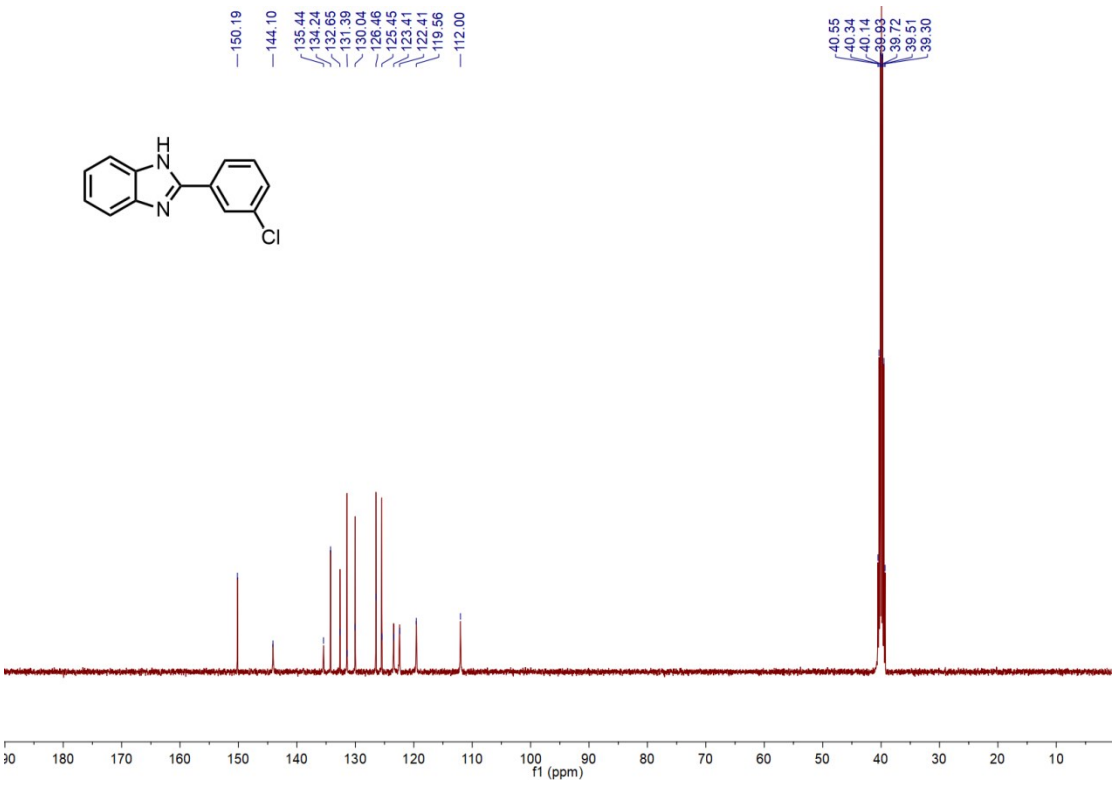




2-(2-chlorophenyl)-1H-benzo[d]imidazole (4aj) Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 67.4 mg, yield 74%;^{1}H NMR (400 MHz, DMSO-d_6) δ 13.11 (s, 1H), 8.27 (s, 1H), 8.19 (d, J = 7.2 Hz, 1H), 7.73 (d, J = 6.9 Hz, 1H), 7.62 (q, J = 8.1 Hz, 3H), 7.27 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.19, 144.10, 135.44, 134.24, 132.65, 131.39, 130.04, 126.46, 125.45, 123.41, 122.41, 119.56, 112.00. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9ClN_2H$ 229.0527, found 229.0523.


13.11
8.27
8.20
8.18
7.74
7.72
7.65
7.63
7.61
7.58
7.27
3.46
2.54
1.00
1.00
1.00
1.01
3.01
2.00
f1 (ppm)


150.19
144.10
135.44
134.24
132.65
131.39
130.04
126.46
125.45
123.41
122.41
119.56
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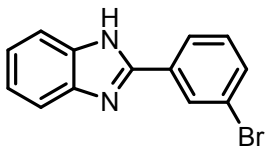
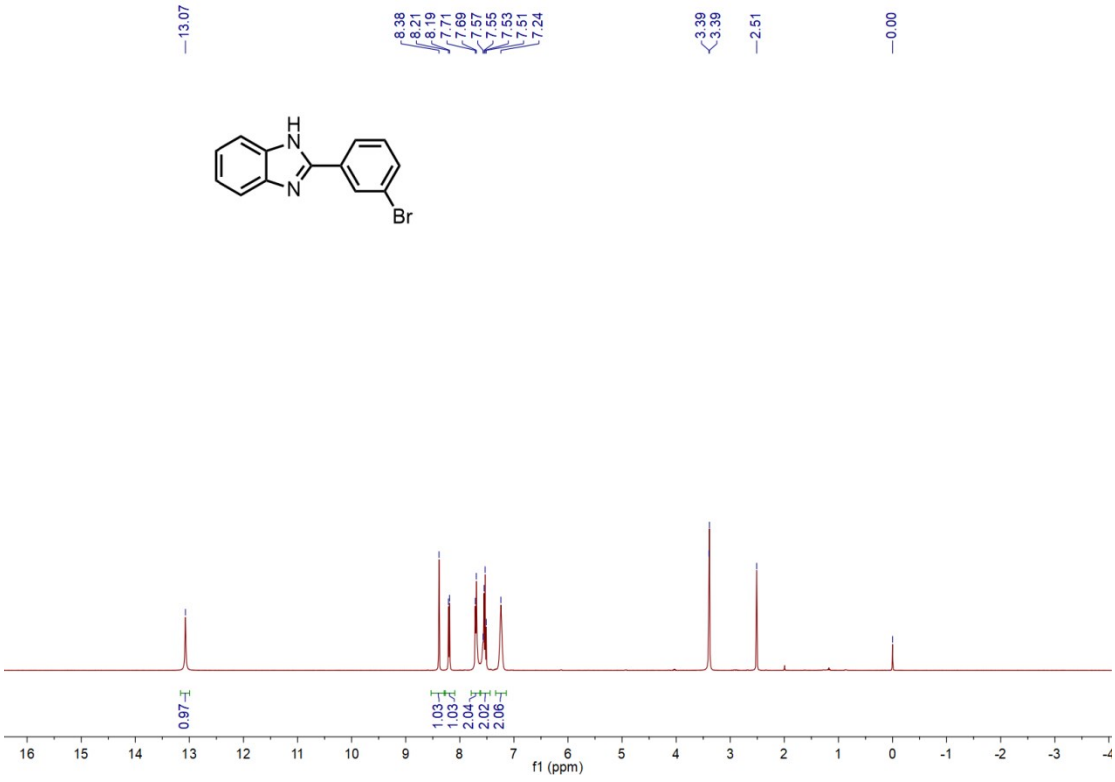
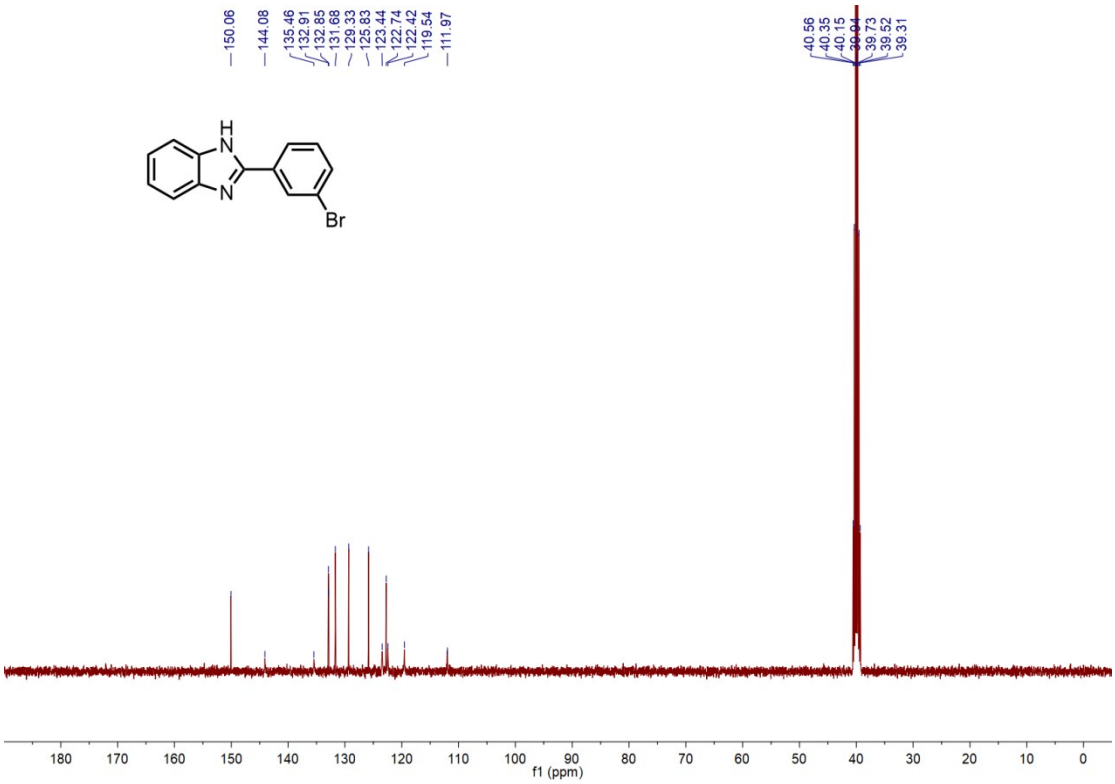
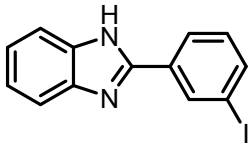
39.51
39.30
f1 (ppm)



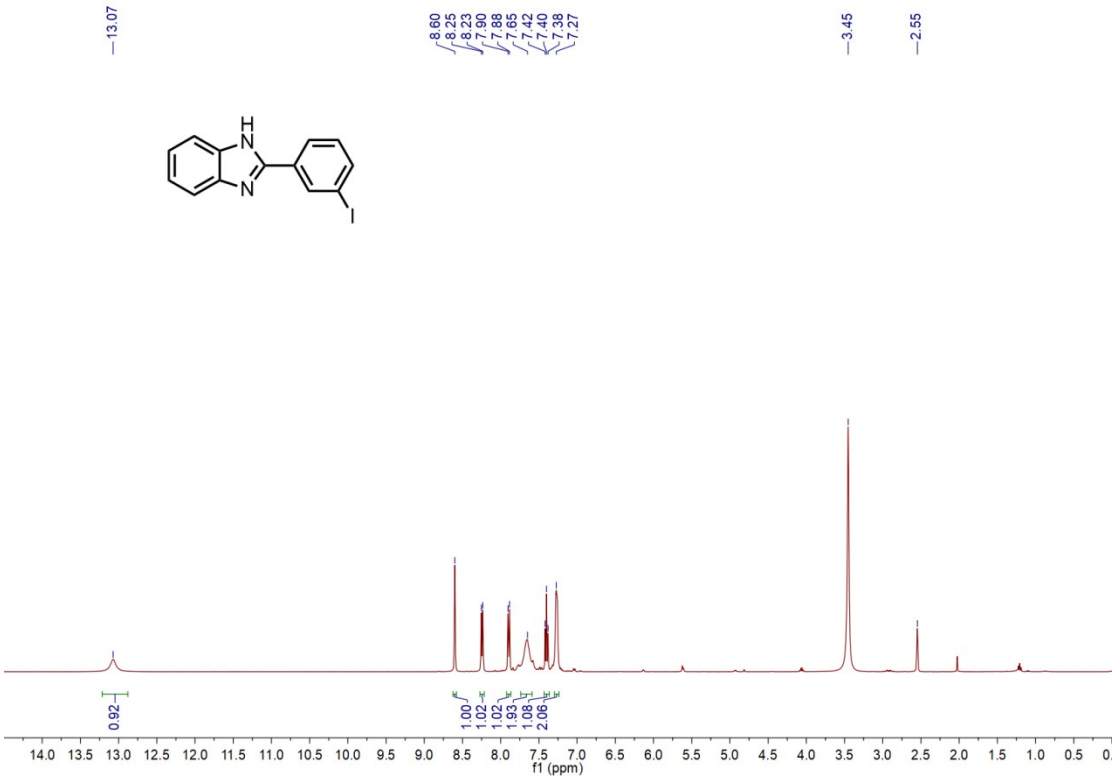
2-(3-Bromophenyl)-1H-benzo[d]imidazole (4ak) Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); yellow solid; 78.3 mg, yield 72%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.07 (s, 1H), 8.38 (s, 1H), 8.20 (d, J = 7.8 Hz, 1H), 7.70 (d, J = 7.8 Hz, 2H), 7.61 – 7.48 (m, 2H), 7.24 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.06, 144.08, 135.46, 132.91, 132.85, 131.68, 129.33, 125.83, 123.44, 122.74, 122.42, 119.54, 111.97. HRMS(ESI) m/z: [M+H] $^{+}$ calcd for $C_{13}H_9BrN_2H$ 273.0022, found 273.0021.

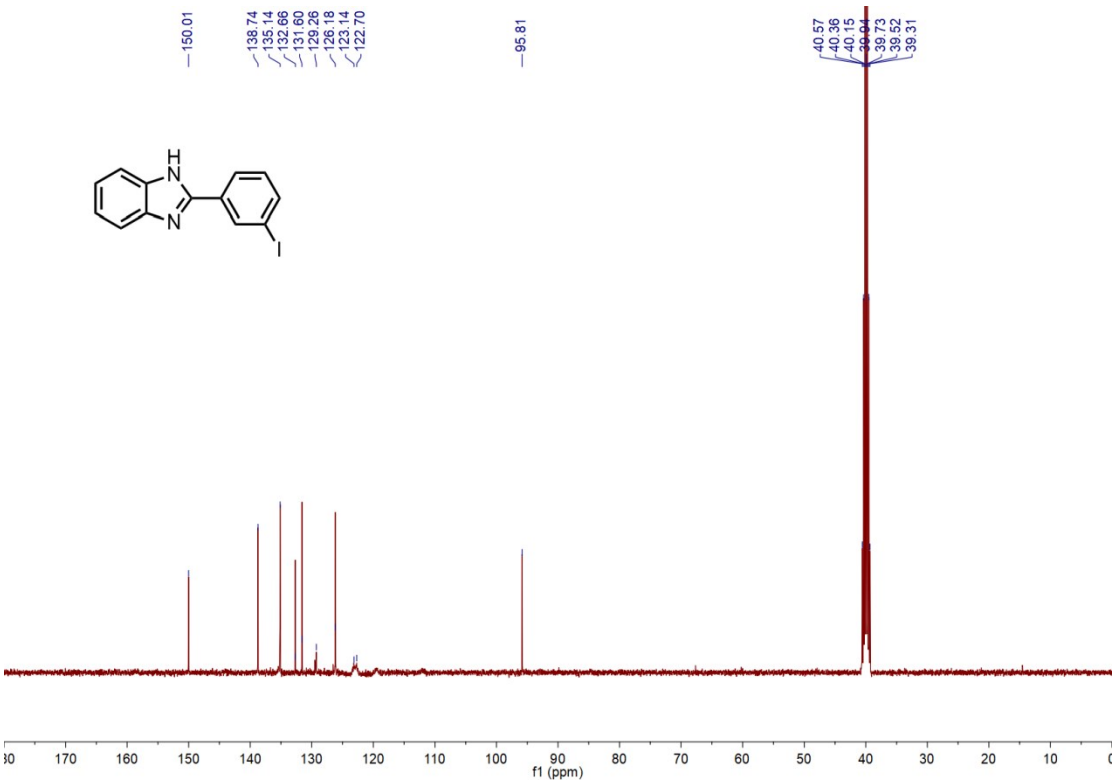


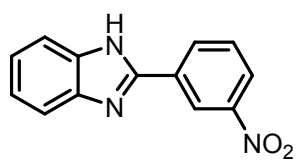




2-(3-Iodophenyl)-1H-benzo[d]imidazole (4al). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 80.6 mg, yield 63%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.07 (s, 1H), 8.60 (s, 1H), 8.24 (d, J = 7.8 Hz, 1H), 7.89 (d, J = 7.7 Hz, 1H), 7.65 (s, 2H), 7.40 (t, J = 7.8 Hz, 1H), 7.27 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.01, 138.74, 135.14, 132.66, 131.60, 129.26, 126.18, 123.14, 122.70, 95.81. HRMS (ESI) m/z: [M+H] $^{+}$ calcd for $C_{13}H_9IN_2H$ 320.9883, found 320.9856.

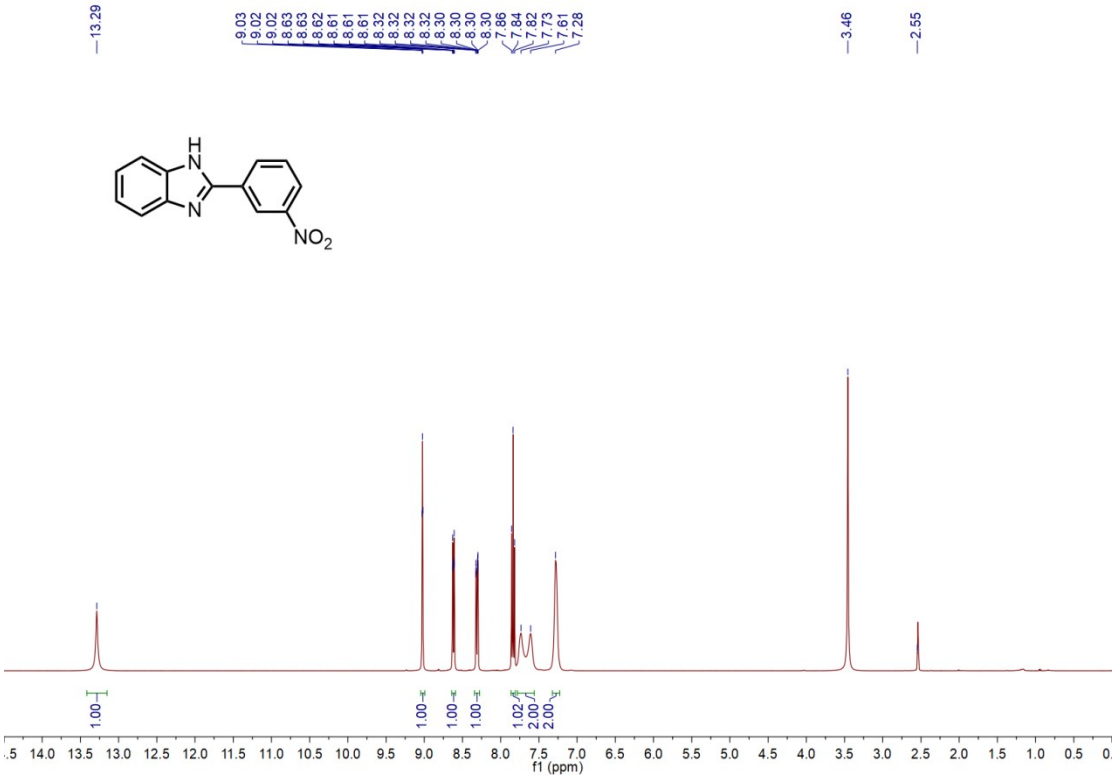


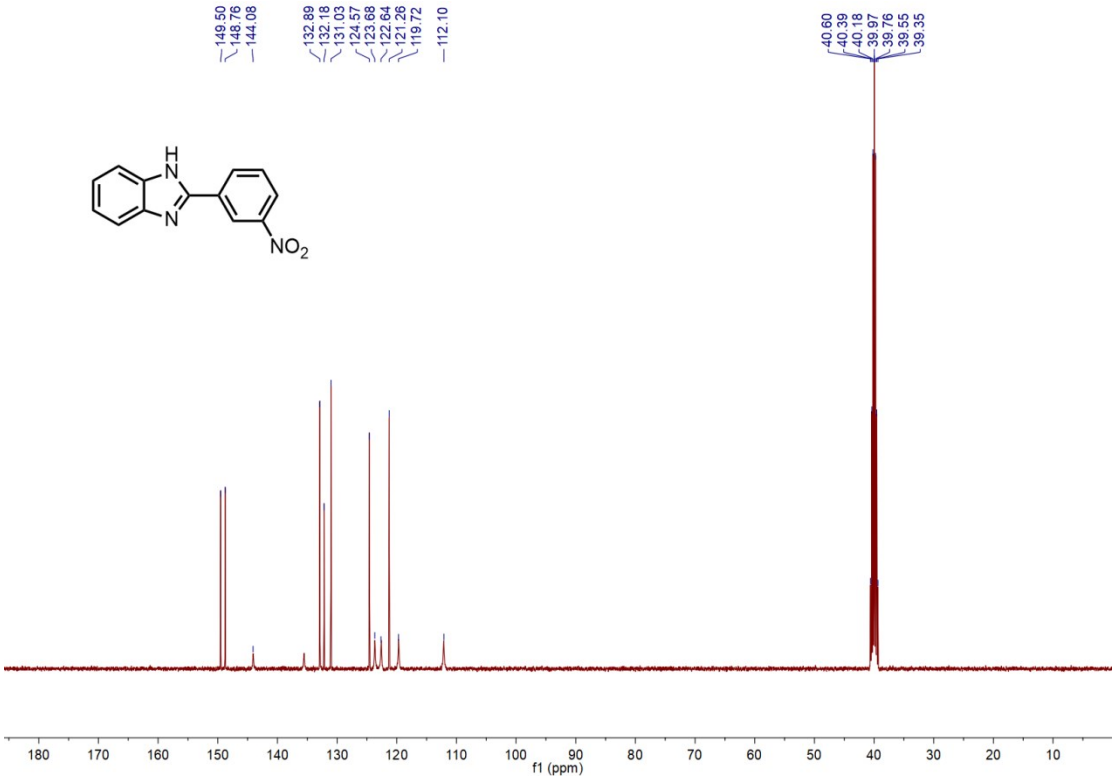


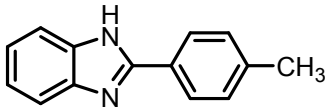


2-(3-Nitrophenyl)-1H-benzo[d]imidazole (4am). Purification by column

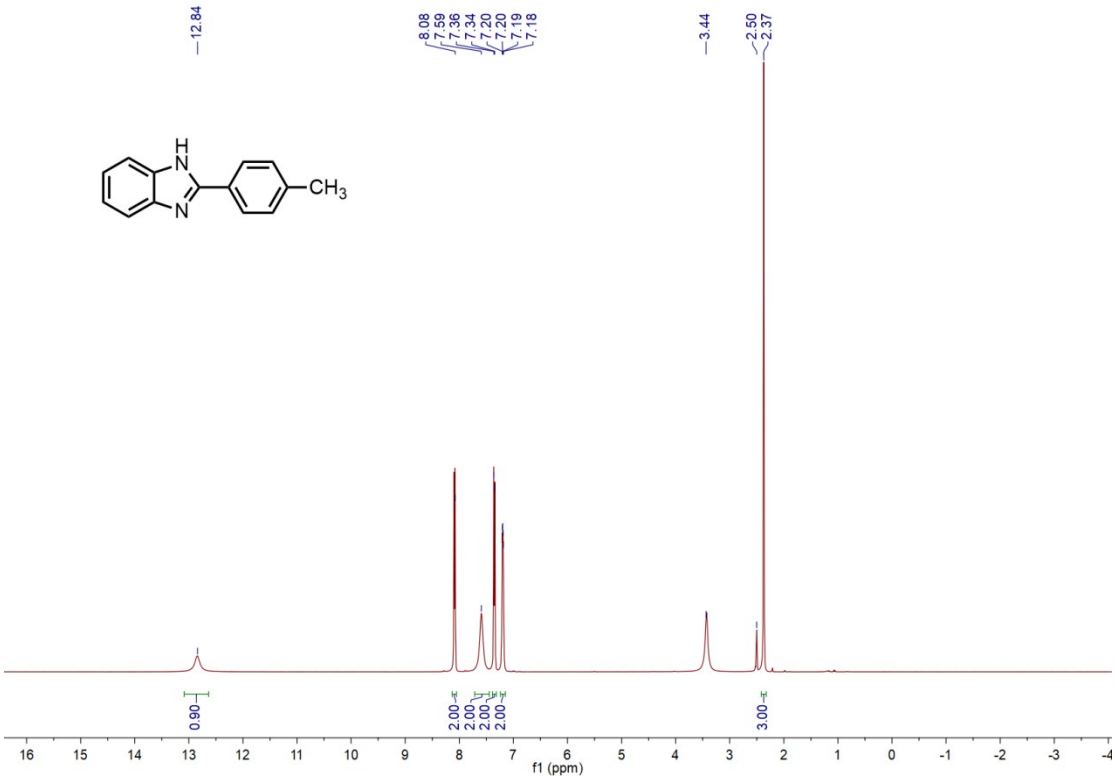
chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 59.3 mg, yield 62%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 1H), 9.05 – 8.99 (m, 1H), 8.62 (dd, J = 7.8, 2.4 Hz, 1H), 8.31 (ddd, J = 8.2, 2.3, 0.9 Hz, 1H), 7.84 (t, J = 8.0 Hz, 1H), 7.67 (d, J = 50.6 Hz, 2H), 7.28 (s, 2H). ^{113}C NMR (100 MHz, DMSO-d_6) δ 149.50, 148.76, 144.08, 135.55, 132.89, 132.18, 131.03, 124.57, 123.68, 122.64, 121.26, 119.72, 112.10. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9N_3O_2H$ 240.0768, found 240.0765.

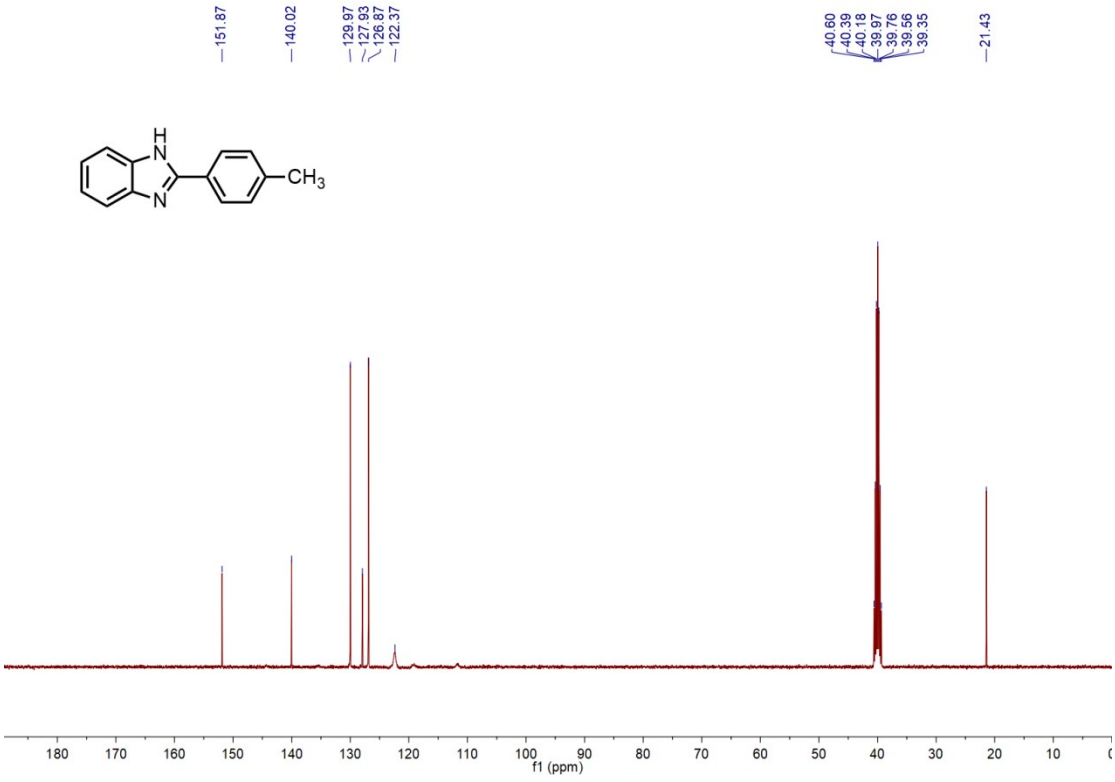






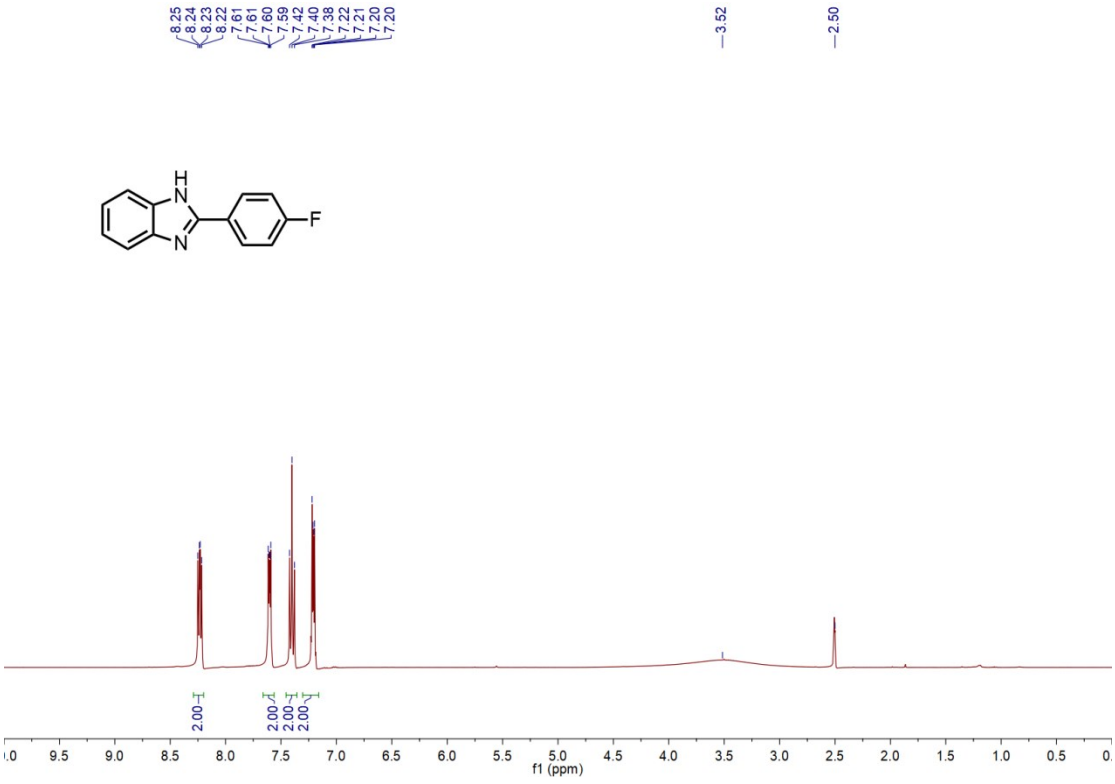
2-(p-Tolyl)-1H-benzo[d]imidazole (4an). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 54.9 mg, yield 66%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.84 (s, 1H), 8.08 (d, 2H), 7.59 (s, 2H), 7.35 (d, J = 6.6 Hz, 2H), 7.19 (dd, J = 5.5, 2.9 Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.87, 140.02, 129.97, 127.93, 126.87, 122.37, 21.43. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{12}N_2H$ 209.1073, found 209.1076.

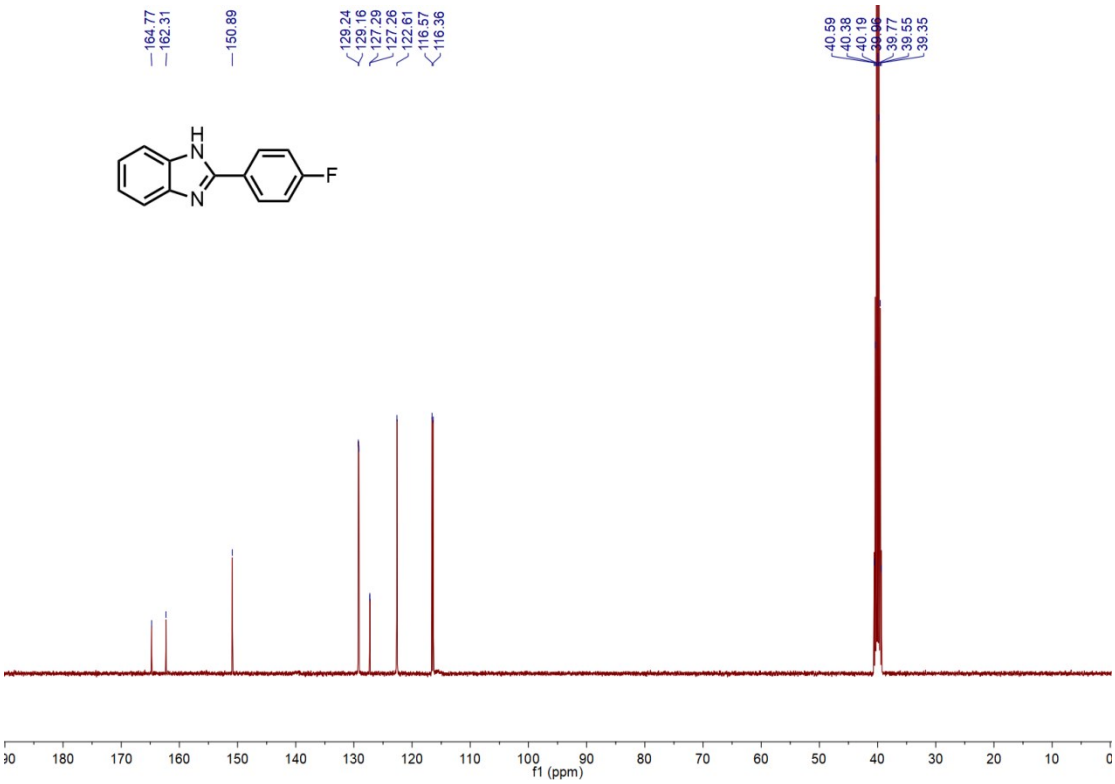


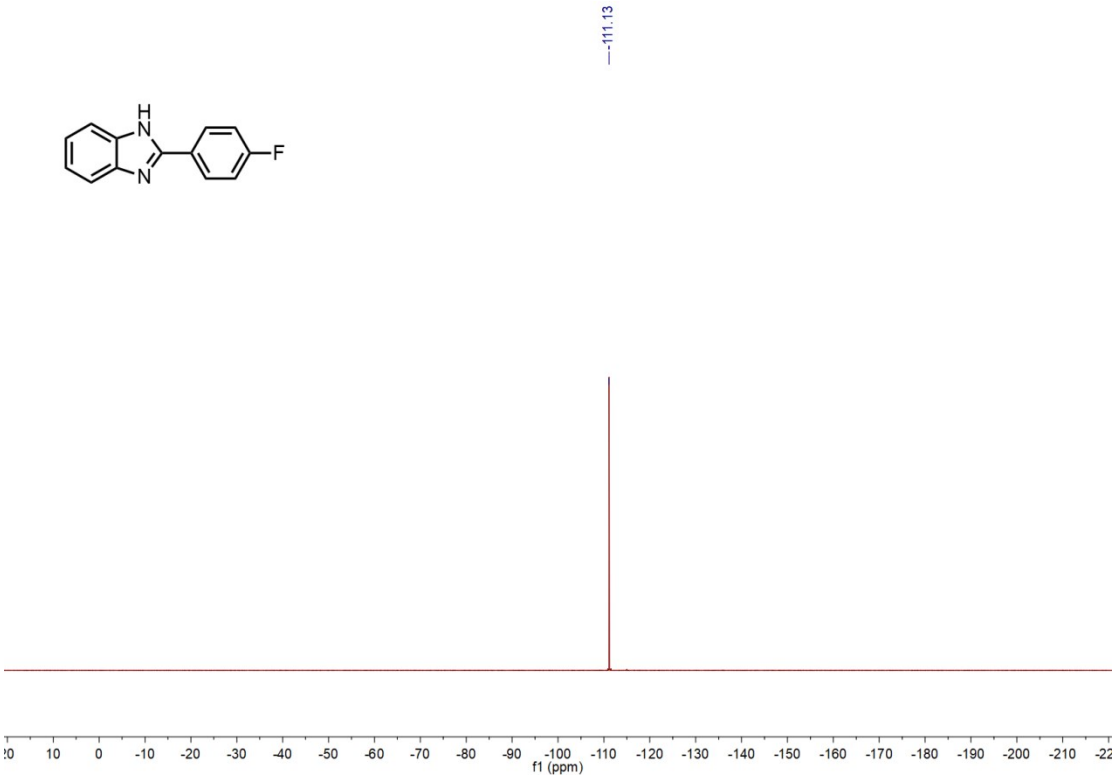


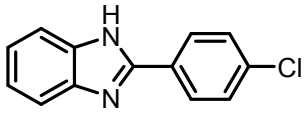
2-(4-Fluorophenyl)-1H-benzo[d]imidazole (4ao). Purification by column

chromatography on silica gel (petroleum ether/ethyl acetate 20/1); yellow solid; 53.6 mg, yield 63%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 (dd, J = 8.8, 5.5 Hz, 2H), 7.60 (dd, J = 5.9, 3.2 Hz, 2H), 7.40 (t, J = 8.8 Hz, 2H), 7.21 (dd, J = 6.0, 3.2 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 163.54 (d, $J_{C\text{-}F}$ = 247.3 Hz), 150.89, 129.20 (d, $J_{C\text{-}F}$ = 8.6 Hz), 127.28 (d, $J_{C\text{-}F}$ = 2.9 Hz), 122.61, 116.47 (d, $J_{C\text{-}F}$ = 21.9 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -111.13. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9FN_2H$ 213.0823, found 213.0818.



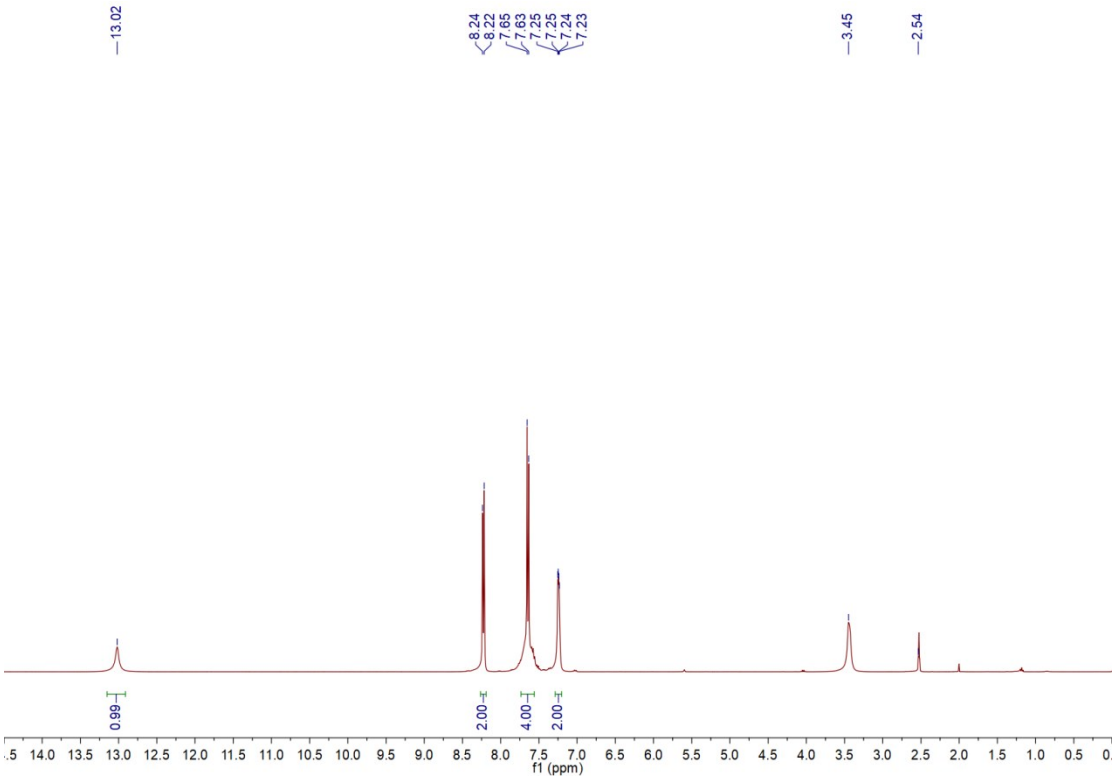


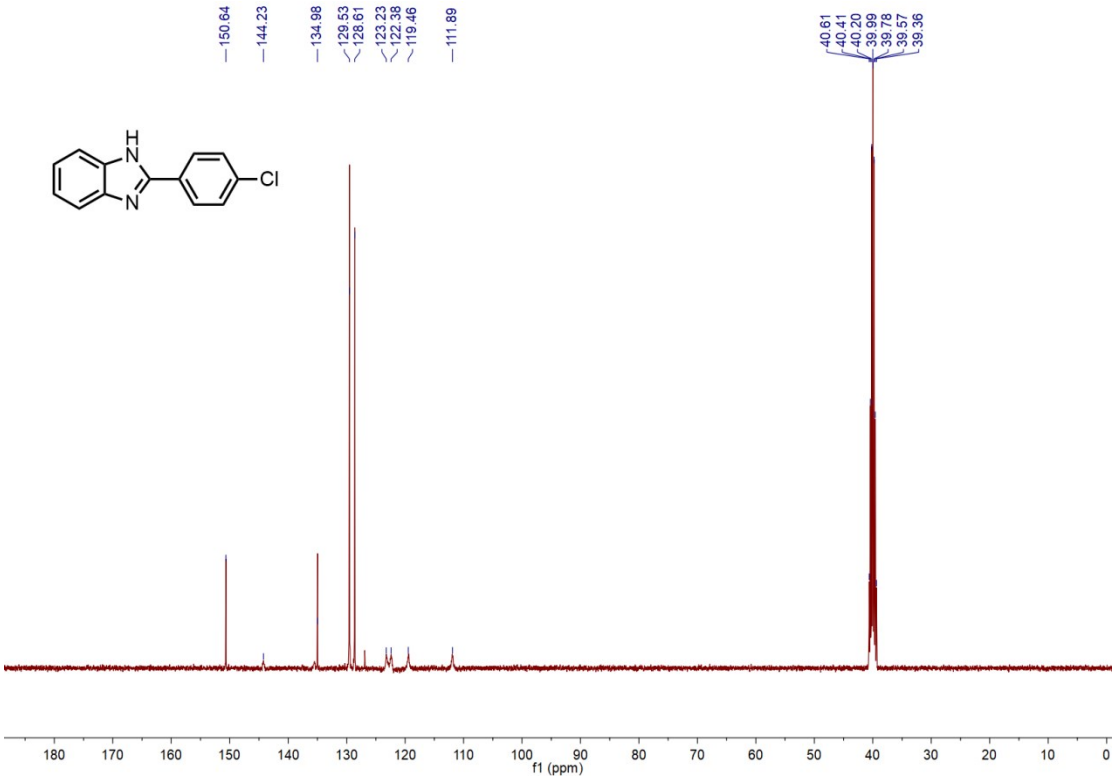


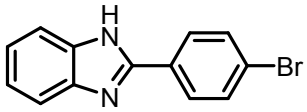


2-(4-Chlorophenyl)-1H-benzo[d]imidazole (4ap). Purification by column

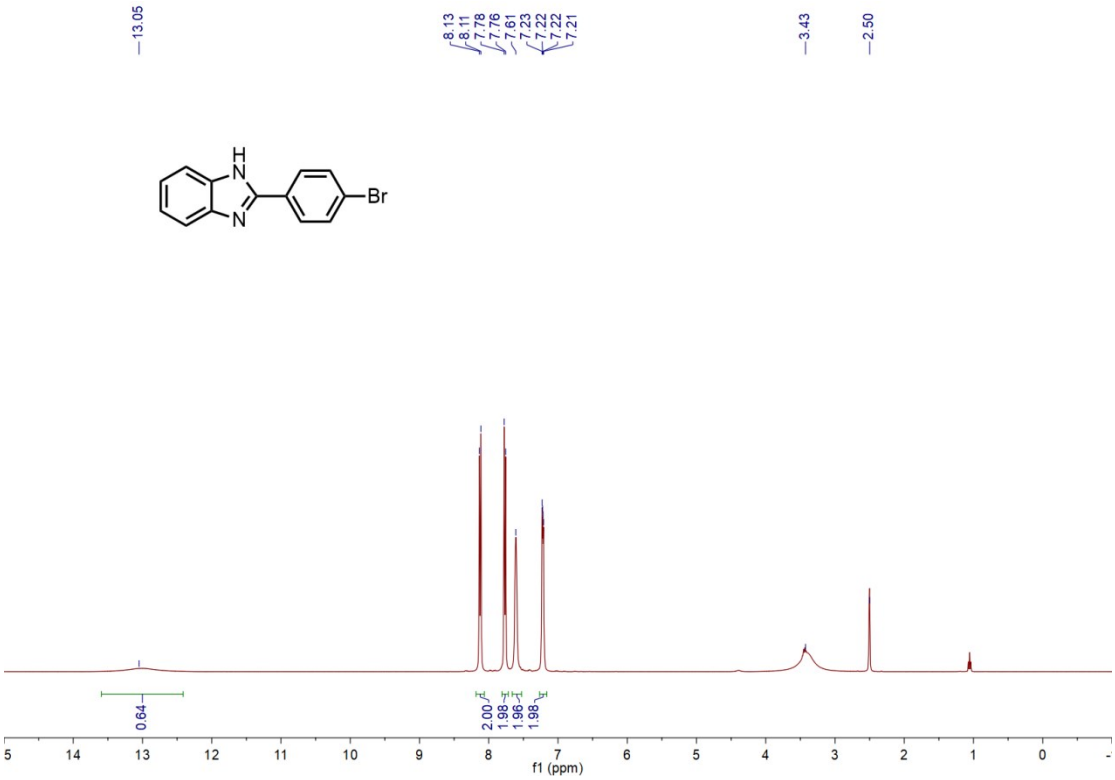
chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 68.4 mg, yield 75%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.02 (s, 1H), 8.23 (d, J = 8.5 Hz, 2H), 7.64 (d, J = 8.5 Hz, 4H), 7.24 (dd, J = 5.8, 2.6 Hz, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.64, 144.23, 134.98, 129.53, 128.61, 123.23, 122.38, 119.46, 111.89. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9ClN_2H$ 229.0527, found 229.0525.

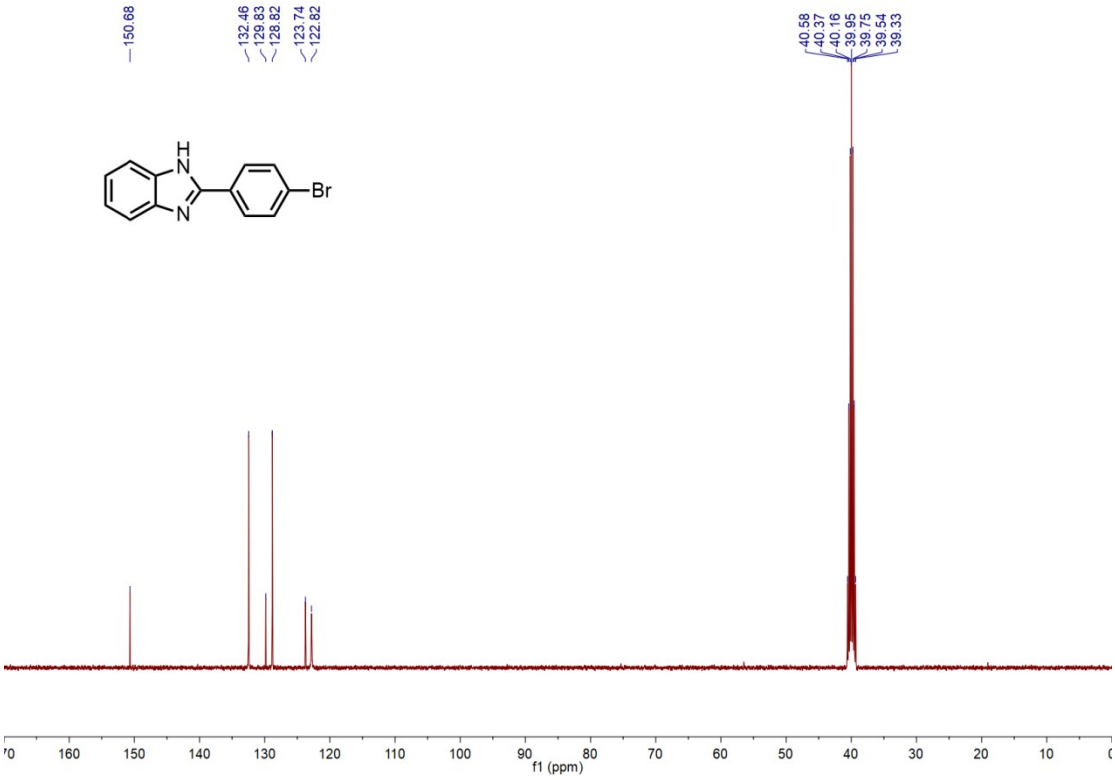


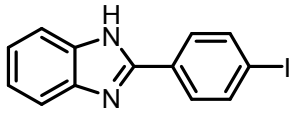




2-(4-Bromophenyl)-1H-benzo[d]imidazole (4aq) Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 77.2 mg, yield 71%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.05 (s, 1H), 8.12 (d, J = 8.3 Hz, 2H), 7.77 (d, J = 8.4 Hz, 2H), 7.61 (s, 2H), 7.22 (dd, J = 5.8, 3.1 Hz,2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.68, 132.46, 129.83, 128.82, 123.74, 122.82. HRMS(ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9BrN_2H$ 273.0022, found 273.0018.

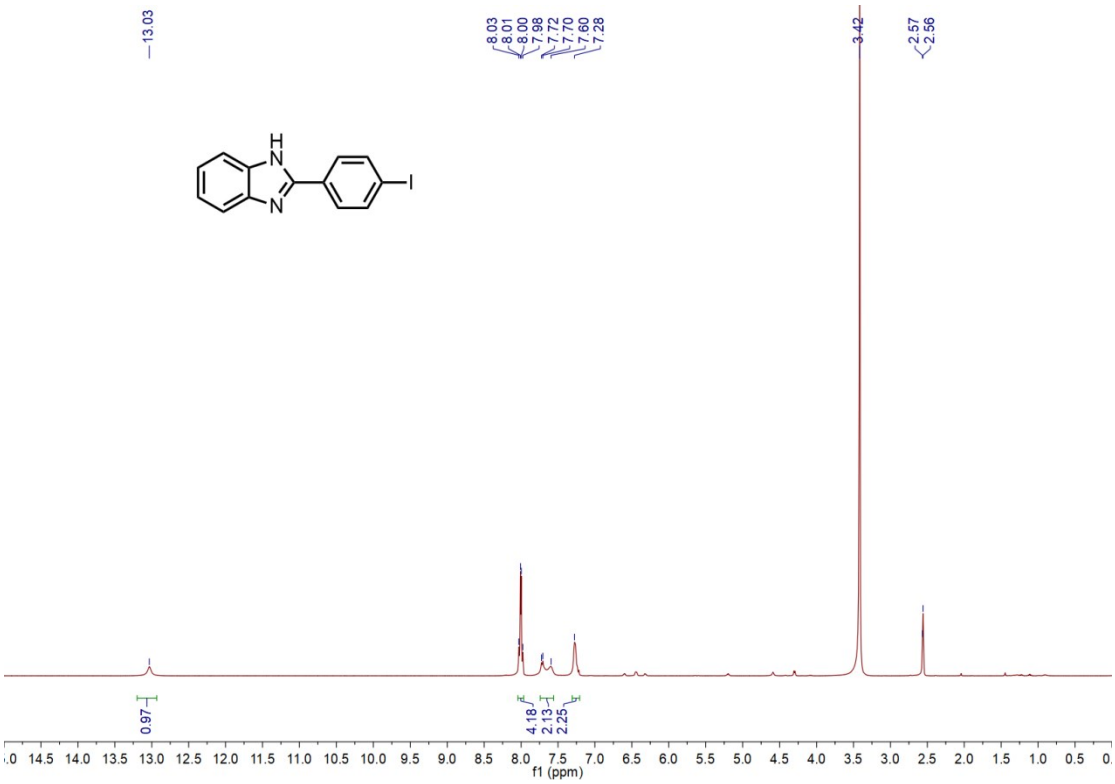


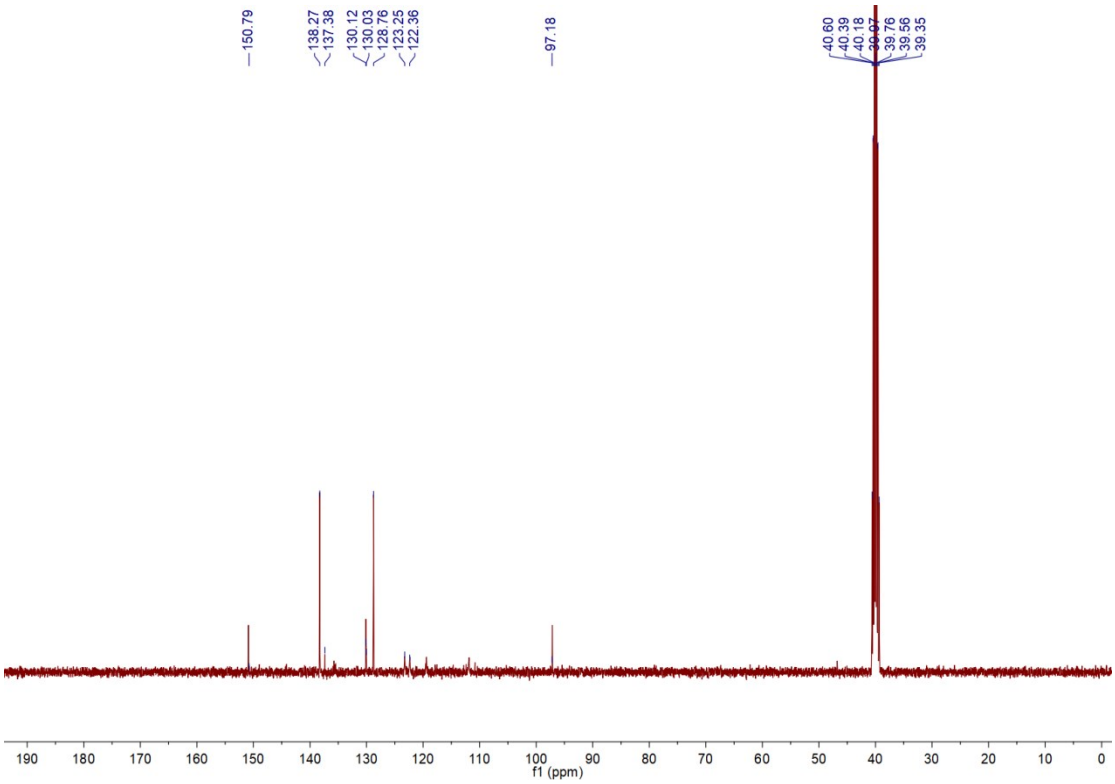


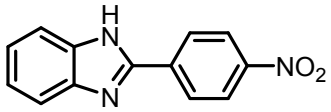


2-(4-Iodophenyl)-1H-benzo[d]imidazole (4ar). Purification by column

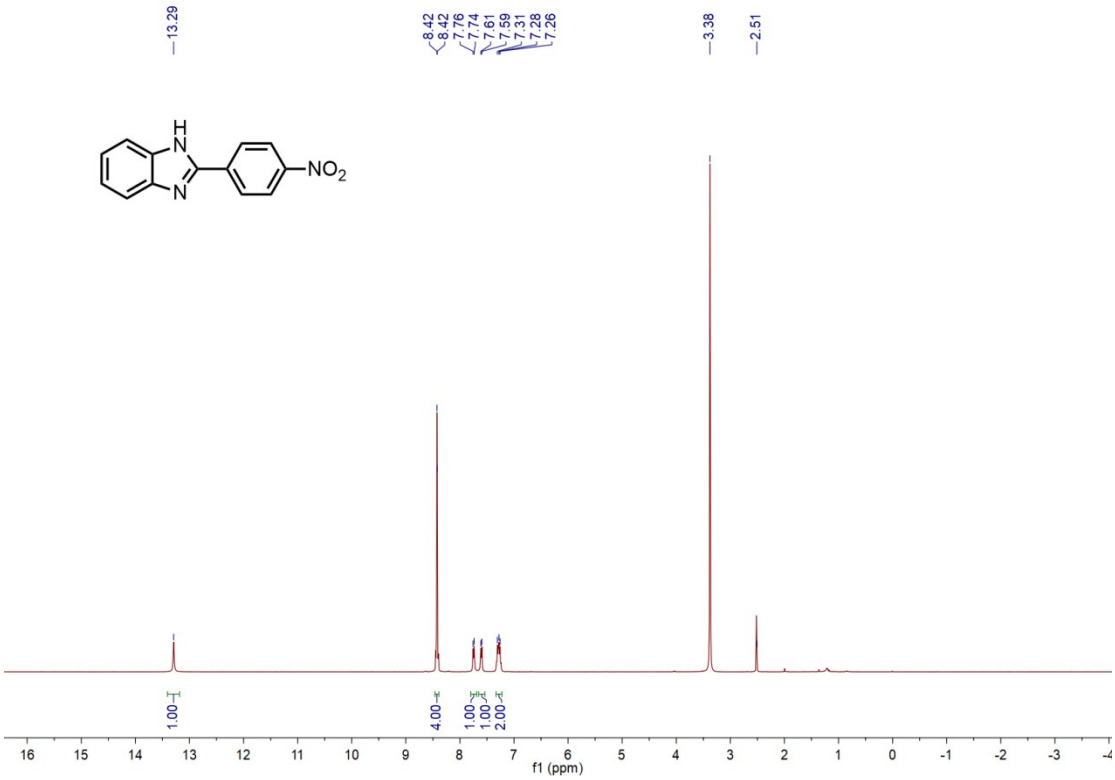
chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 71.7 mg, yield 56%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.03 (s, 1H), 8.04 – 7.96 (m, 4H), 7.74 – 7.56 (m, 2H), 7.28 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 150.88, 138.27, 137.38, 130.12, 128.76, 123.25, 122.36, 97.18. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9IN_2H$ 320.9883, found 320.9856.







2-(4-Nitrophenyl)-1H-benzo[d]imidazole (4as). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 52.6 mg, yield 55%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.29 (s, 1H), 8.42 (d, J = 2.0 Hz, 4H), 7.75 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 7.6 Hz, 1H), 7.33 – 7.22 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-d) δ 154.22, 153.03, 149.05, 141.25, 140.45, 132.61, 129.51, 128.82, 127.55, 124.67, 117.03. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9N_3O_2H$ 240.0768, found 240.0765.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8.42
8.42
7.76
7.74
7.61
7.59
7.31
7.28
7.26
3.38
2.51
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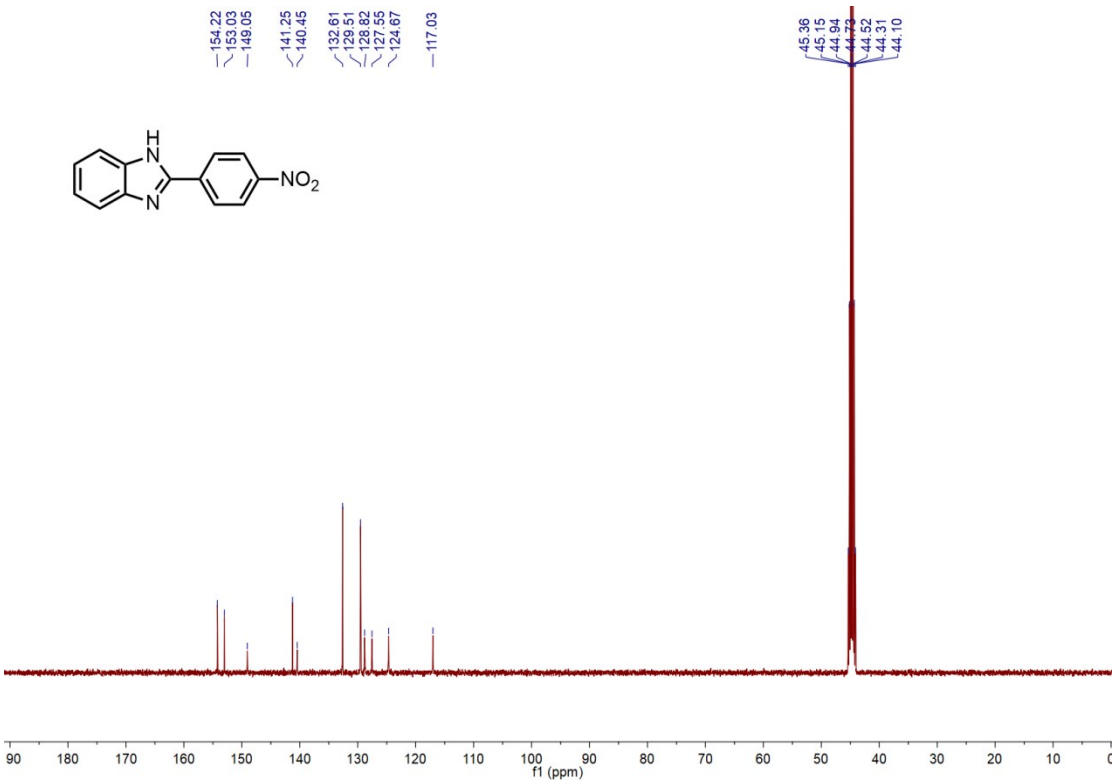
1.00
1.00
2.00
f1 (ppm)


154.22
153.03
149.05
141.25
140.45
132.61
129.51
128.82
127.55
124.67
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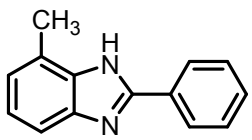
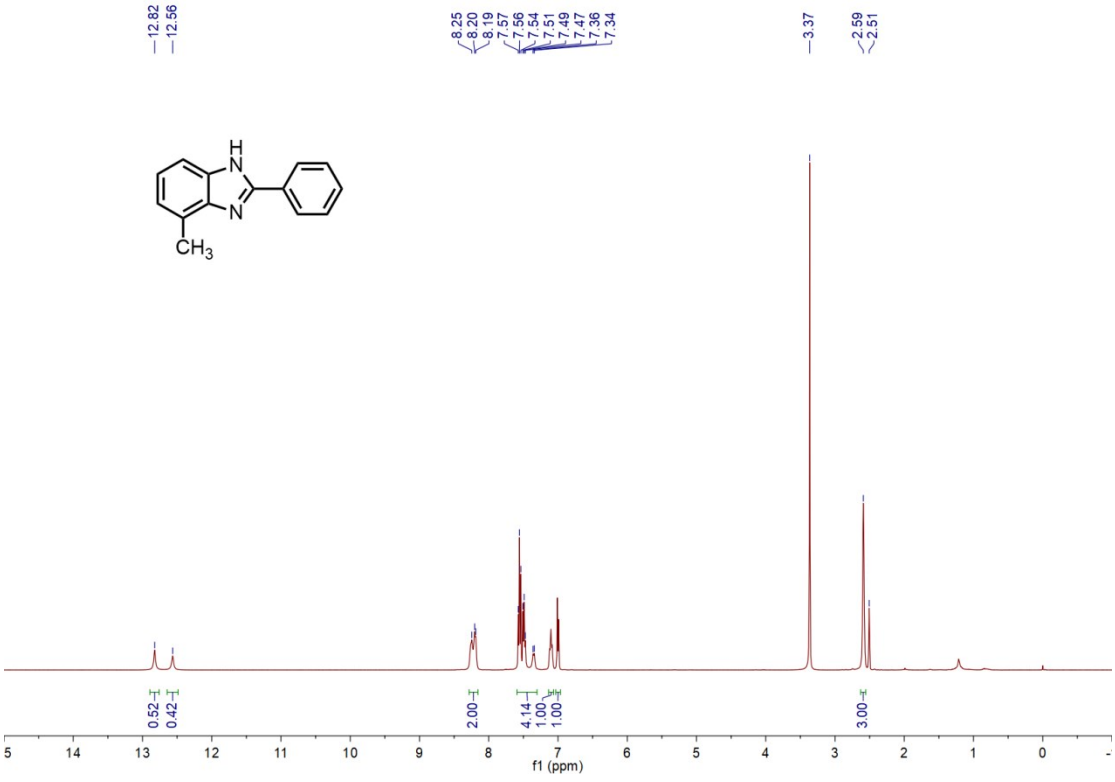
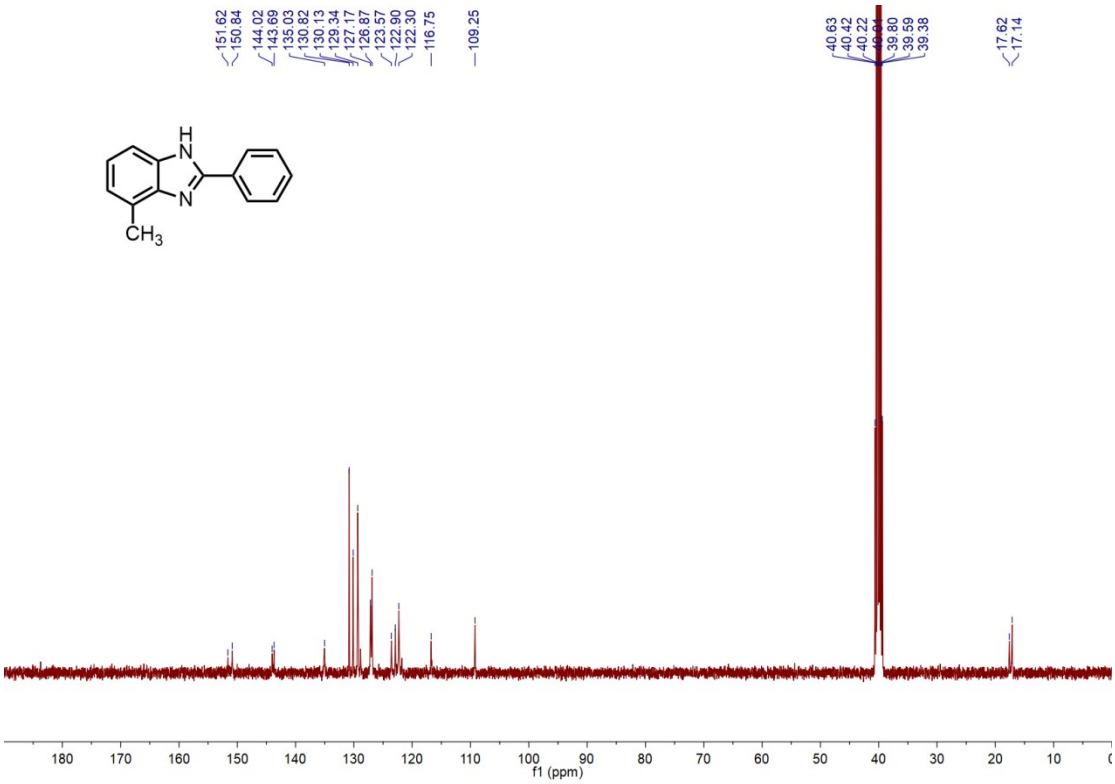
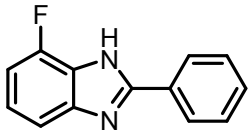
45.36
45.15
44.94
44.73
44.52
44.31
44.10
NO2
f1 (ppm)


CH3

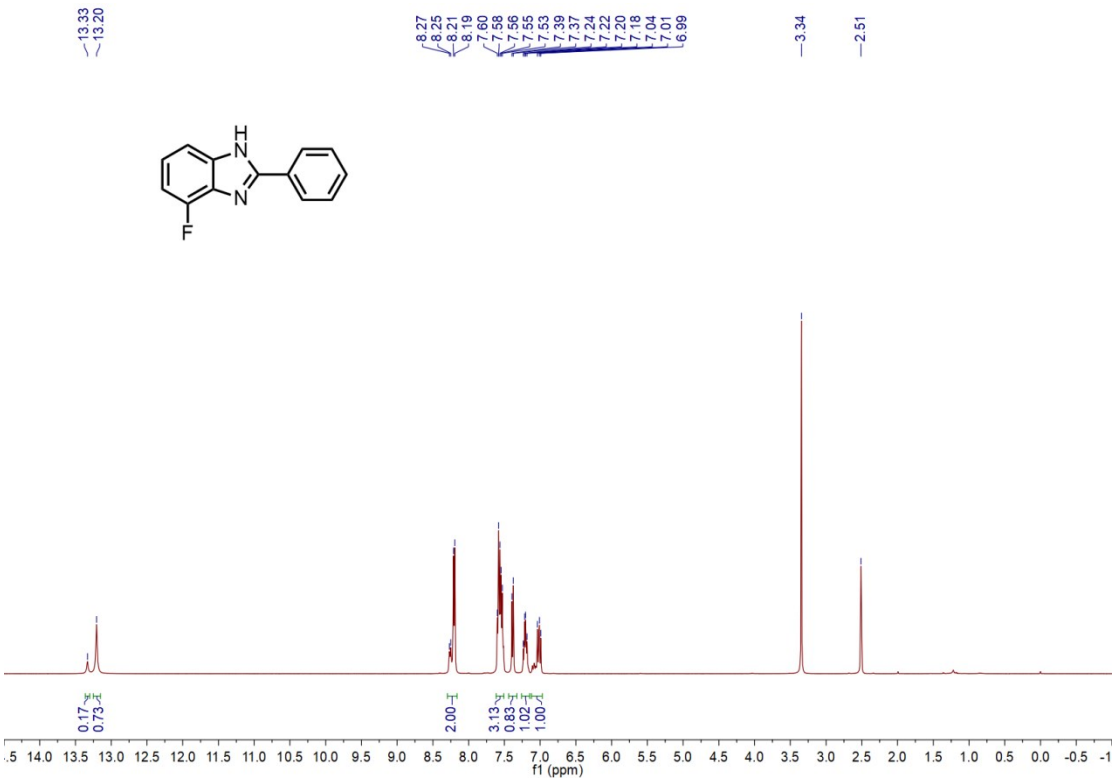
4-methyl-2-phenyl-1H-benzo[d]imidazole (4ba). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 44.9 mg, yield 54%; mixture of tautomers (1.2:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.82 (s, 1H), 12.56 (s, 1H), 8.28 – 8.16 (m, 2H), 7.52 (td, J = 26.1, 7.1 Hz, 4H), 7.10 (t, J = 7.7 Hz, 1H), 7.00 (d, J = 7.2 Hz, 1H), 2.59 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.62, 150.84, 144.02, 143.69, 135.03, 130.82, 130.13, 129.34, 127.17, 126.87, 123.57, 122.90, 122.30, 116.75, 109.25, 17.62, 17.14. HRMS (ESI) m/z: [M+H] $^{+}$ calcd for $C_{14}H_{12}N_2H$ 209.1073, found 209.1068.







4-Fluorophenyl-2-phenyl-1H-benzo[d]imidazole (4bb). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 43.2 mg, yield 51%; mixture of tautomers (0.4:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.33 (s, 1H), 13.20 (s, 1H), 8.23 (dd, J = 23.0, 7.4 Hz, 2H), 7.56 (dt, J = 13.4, 6.8 Hz, 3H), 7.38 (d, J = 8.0 Hz, 1H), 7.26 – 7.15 (m, 1H), 7.12 – 6.97 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 154.87, 152.39, 152.23, 138.56 (d, $J_{C\text{-}F}$ = 9.1 Hz), 132.70 (d, $J_{C\text{-}F}$ = 16.6 Hz), 130.67, 130.10, 129.48, 127.33, 127.09, 123.50 (d, $J_{C\text{-}F}$ = 7.2 Hz), 122.43, 108.34 (d, $J_{C\text{-}F}$ = 3.5 Hz), 107.46 (d, $J_{C\text{-}F}$ = 16.6Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -128.76 – -129.02 (m), -129.45 – -129.60 (m). HRMS (ESI) m/z: [M+H] $^{+}$ calcd for $C_{13}H_9FN_2H$ 213.0823, found 213.0818.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7.22
7.20
7.18
7.04
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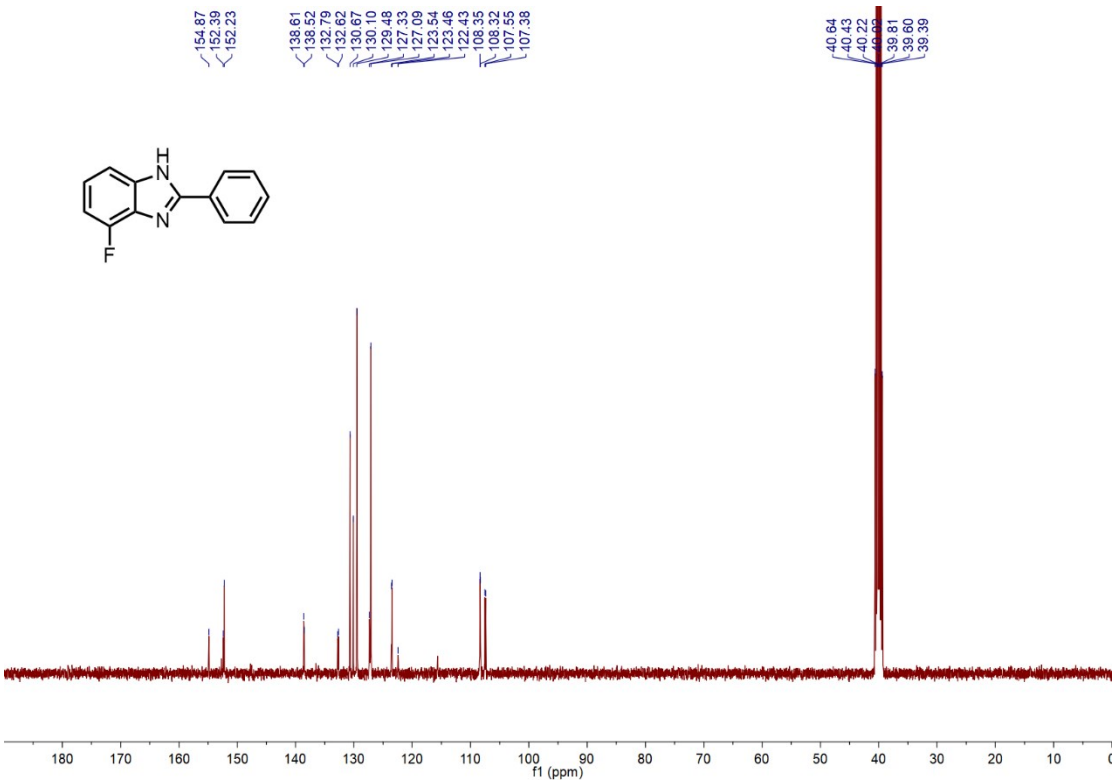
f1 (ppm)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127.09
123.54
123.46
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40.43
40.22
39.81
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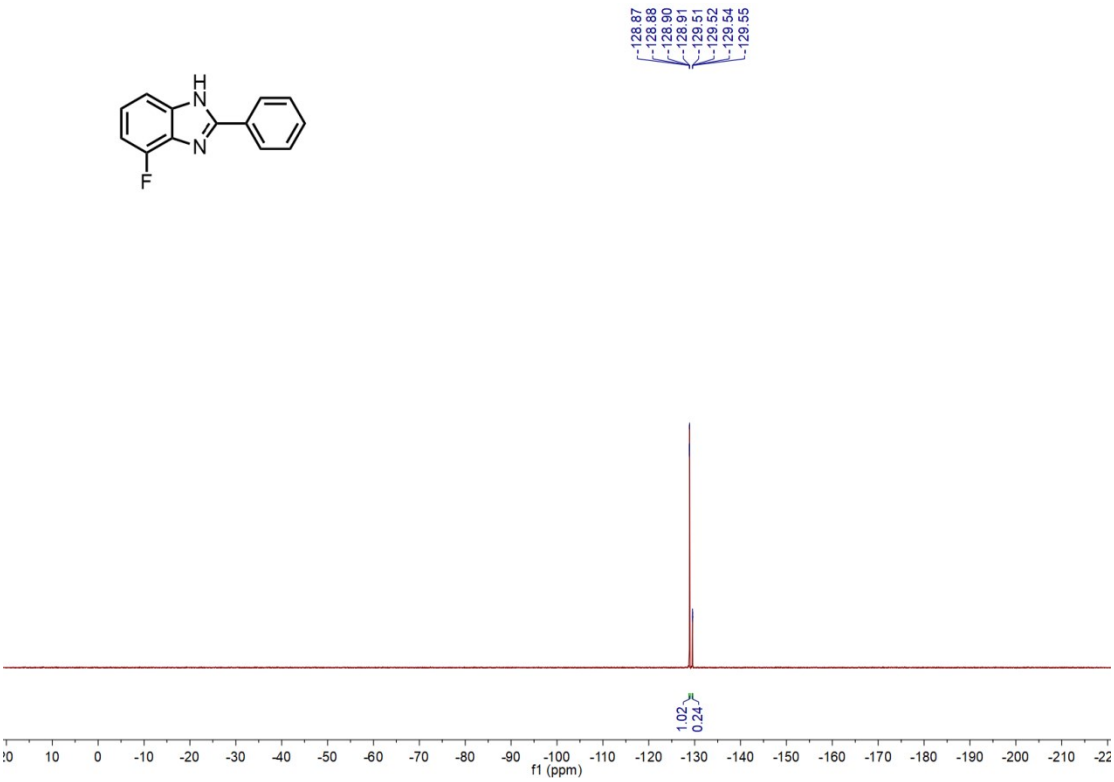
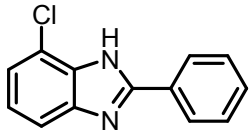
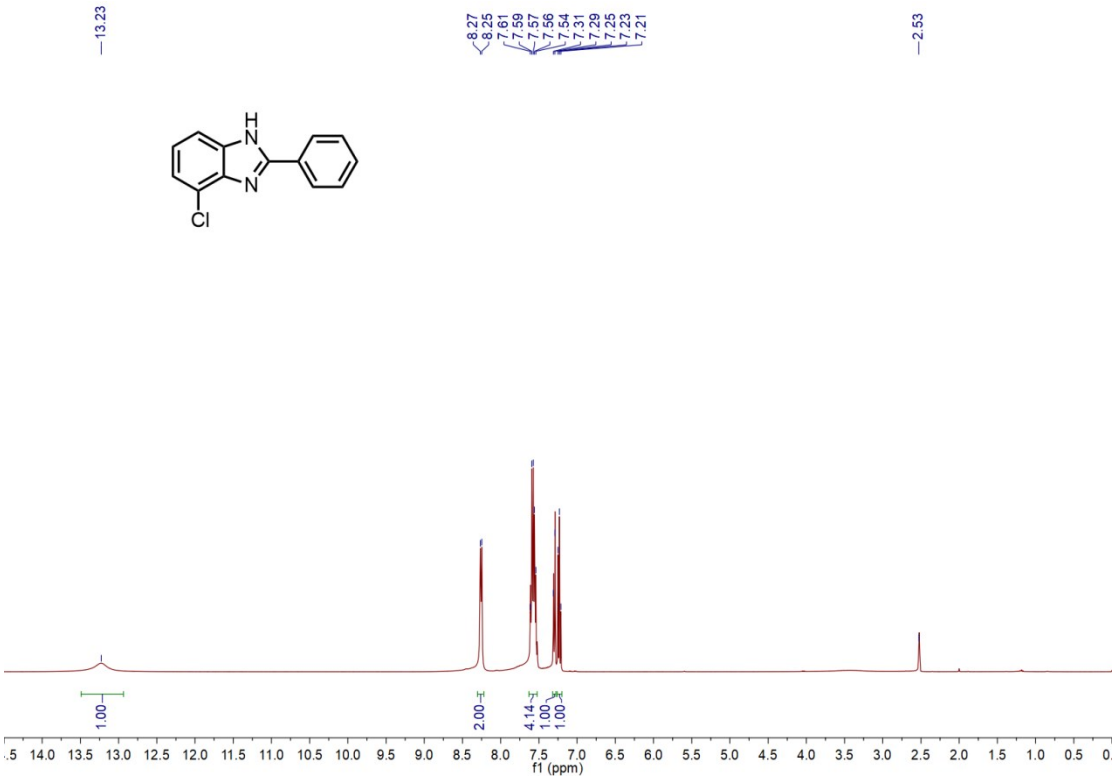
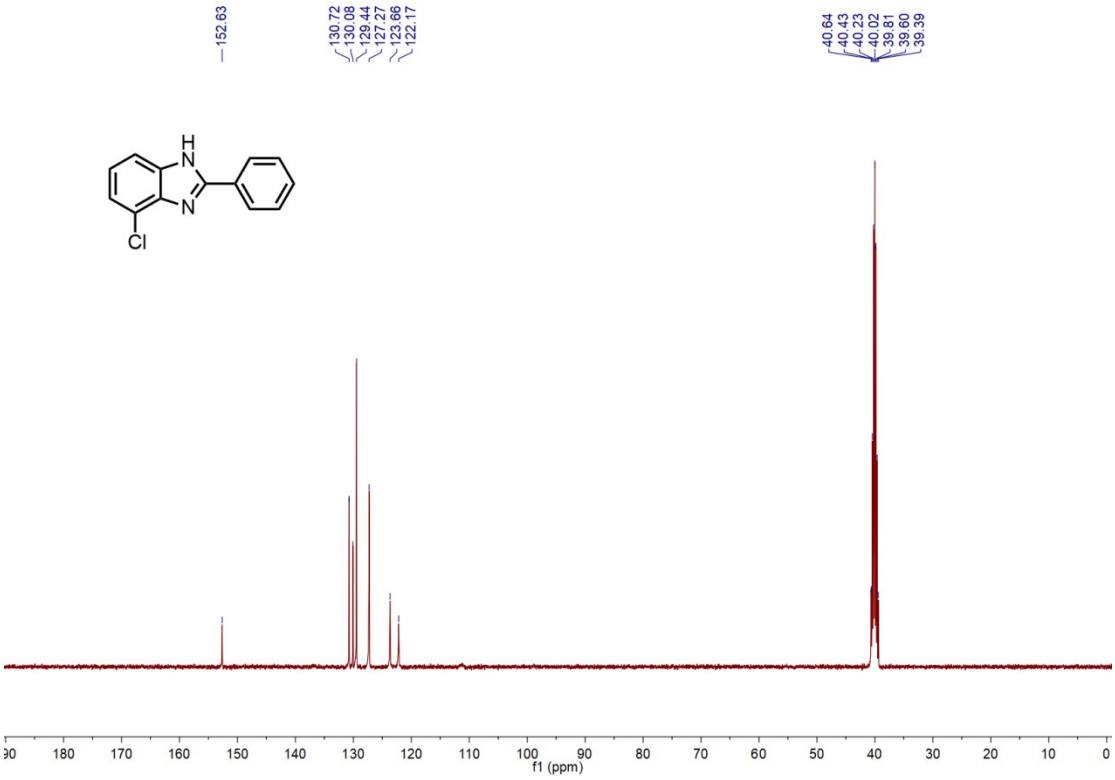
39.39
f1 (ppm)

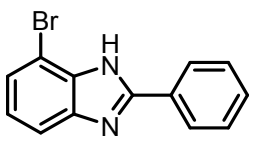




4-Chlorophenyl-2-phenyl-1H-benzo[d]imidazole (4bc). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 67 mg, yield 67%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.23 (s, 1H), 8.26 (d, J = 7.3 Hz, 2H), 7.63 – 7.52 (m, 4H), 7.30 (d, J = 7.7, 0.9 Hz, 1H), 7.23 (t, J = 7.8 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.63, 130.72, 130.08, 129.44, 127.27, 123.66, 122.17. HRMS (ESI) m/z: [M+Na] $^{+}$ calcd for $C_{13}H_{9}ClN_2Na$ 251.0346, found 251.0339.

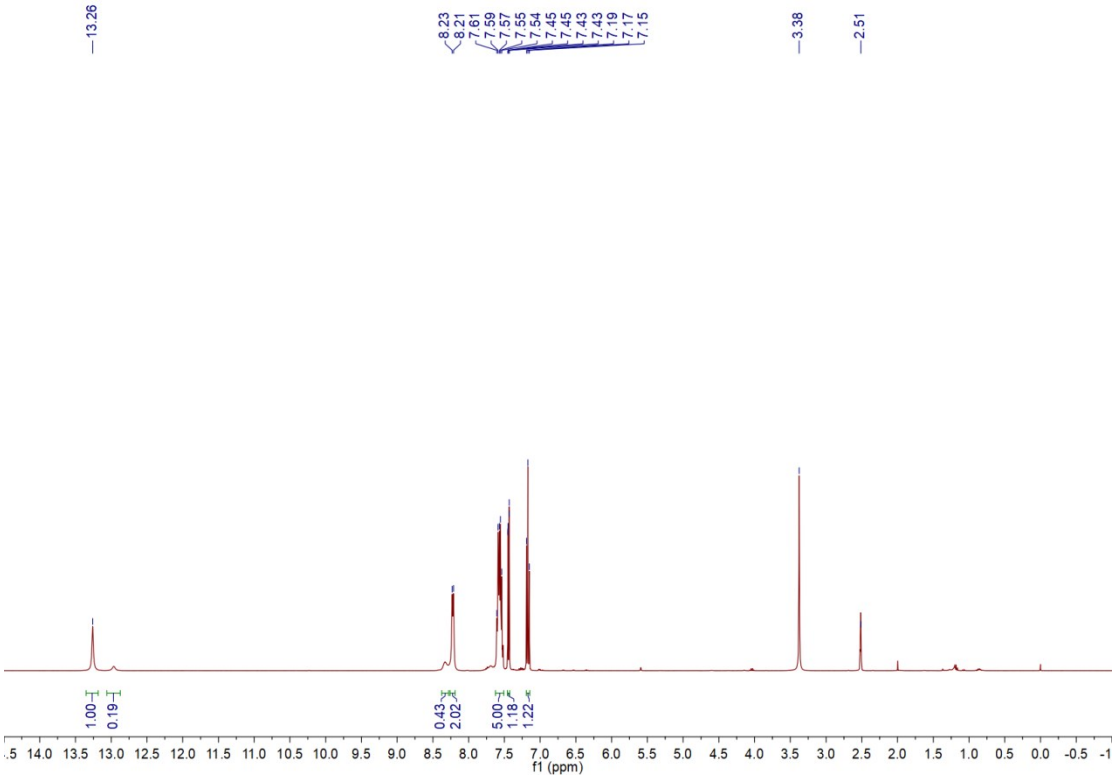


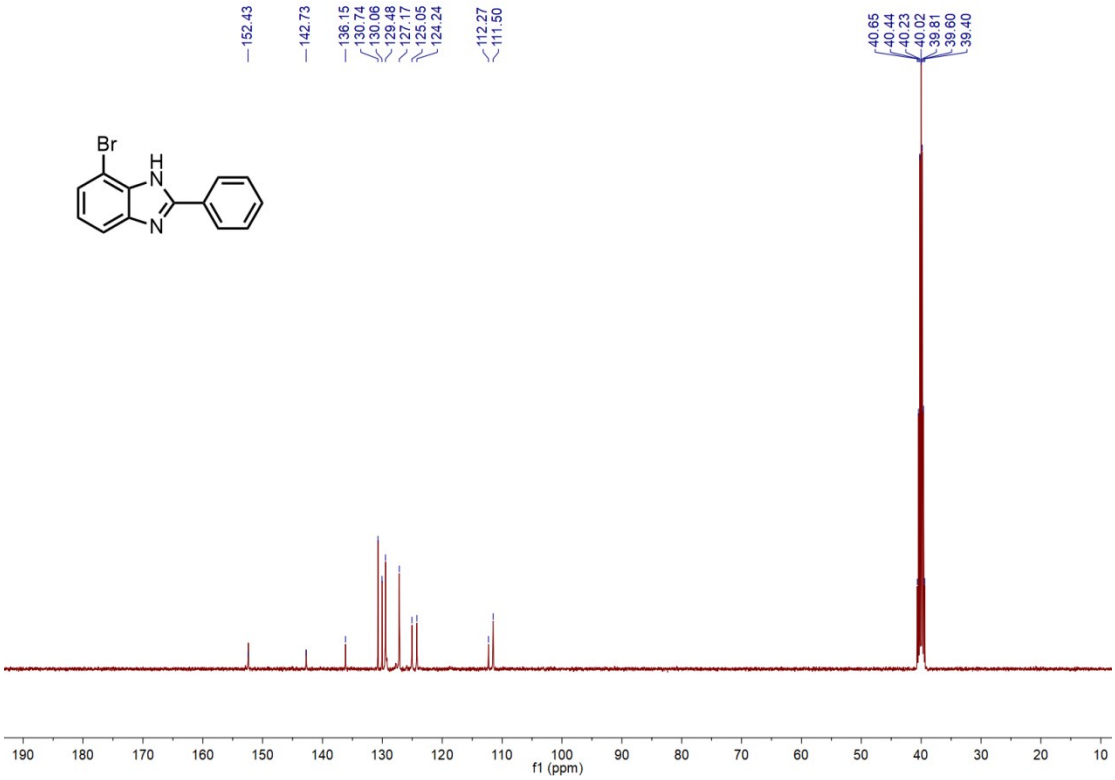


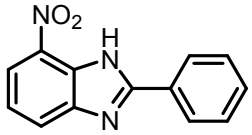


4- Bromophenyl -2-phenyl-1H-benzo[d]imidazole (4bd). Purification by column

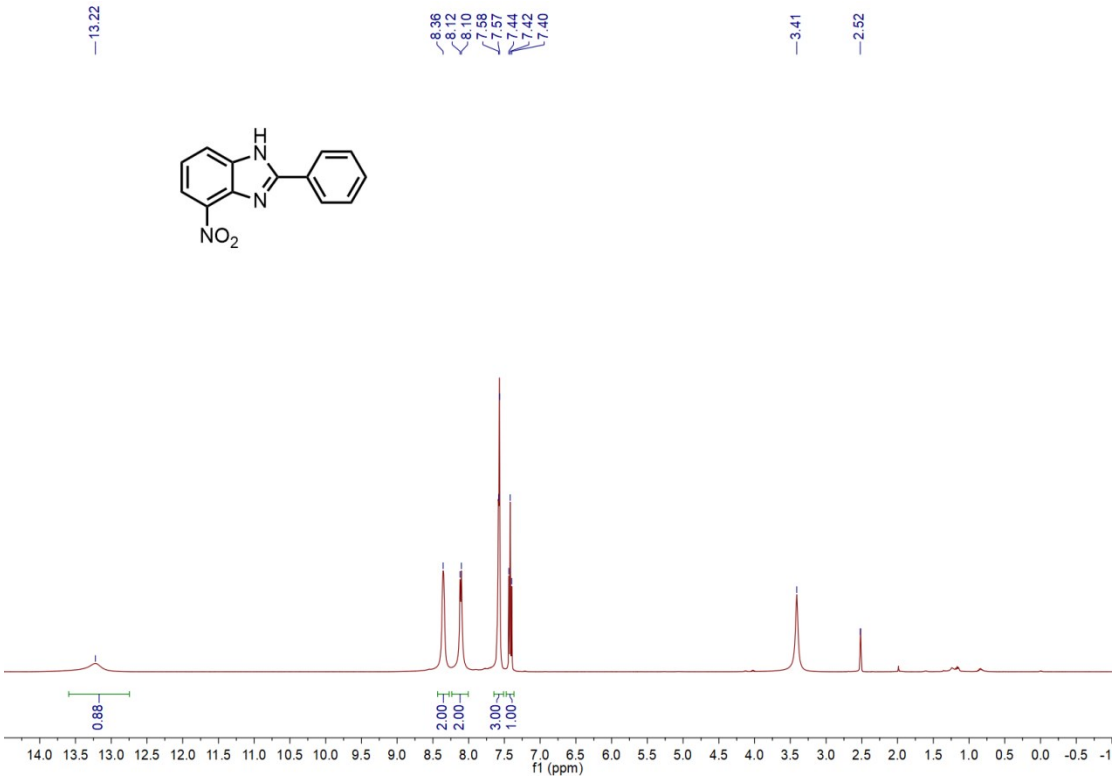
chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 70.7 mg, yield 65%; mixture of tautomers (5.3:1). ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.26 (s, 1H), 12.96 (s, 0H), 8.33 (s, 2H), 8.22 (d, J = 7.1 Hz, 2H), 7.57 (dt, J = 13.1, 6.9 Hz, 5H), 7.44 (dd, J = 7.7, 0.8 Hz, 1H), 7.17 (t, J = 7.9 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.43, 142.73, 136.15, 130.74, 130.06, 129.48, 127.17, 125.05, 124.24, 112.27, 111.50. HRMS(ESI) m/z: [M+H] $^{+}$ calcd for $C_{13}H_9BrN_2H$ 273.0022, found 273.0016.

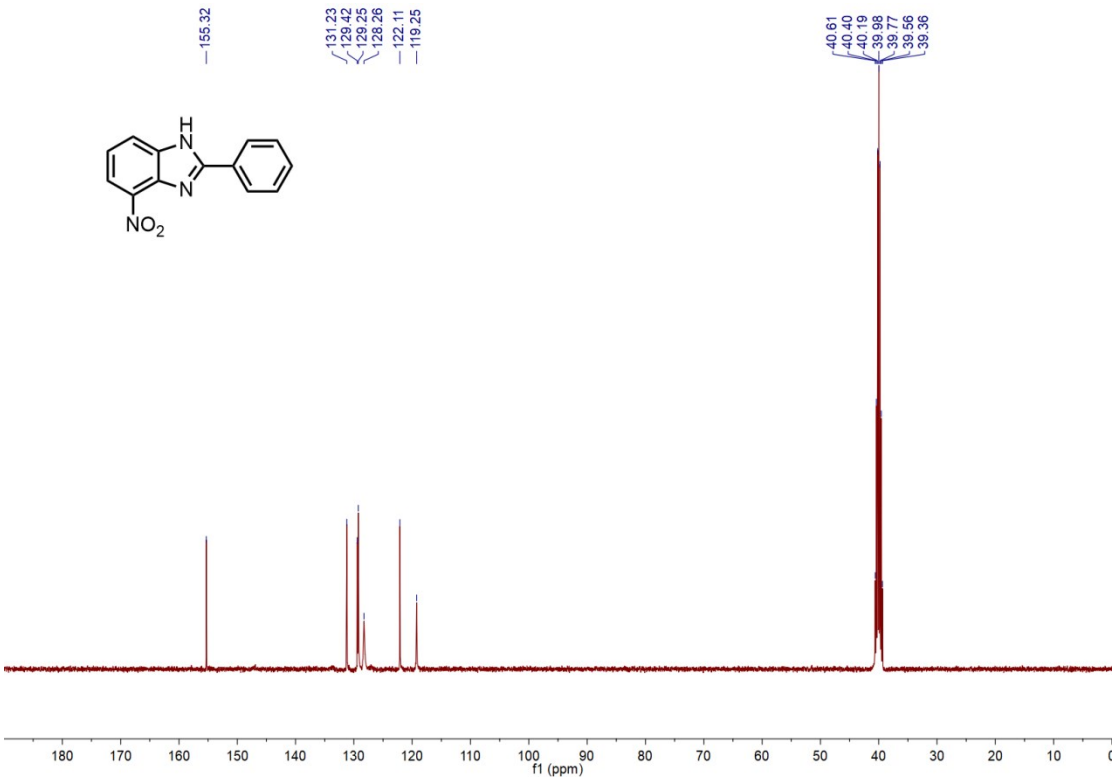


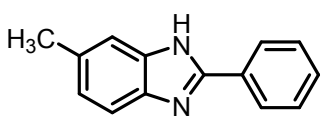




4- Nitrophenyl-2-phenyl-1H-benzo[d]imidazole (4be). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 66 mg, yield 69%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.22 (s, 1H), 8.36 (s, 2H), 8.11 (d, J = 7.8 Hz, 2H), 7.57 (d, J = 5.2 Hz, 3H), 7.42 (t, J = 8.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 155.32, 131.23, 129.42, 129.25, 128.26, 122.11, 119.25. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9N_3O_2H$ 240.0768, found 240.0766.

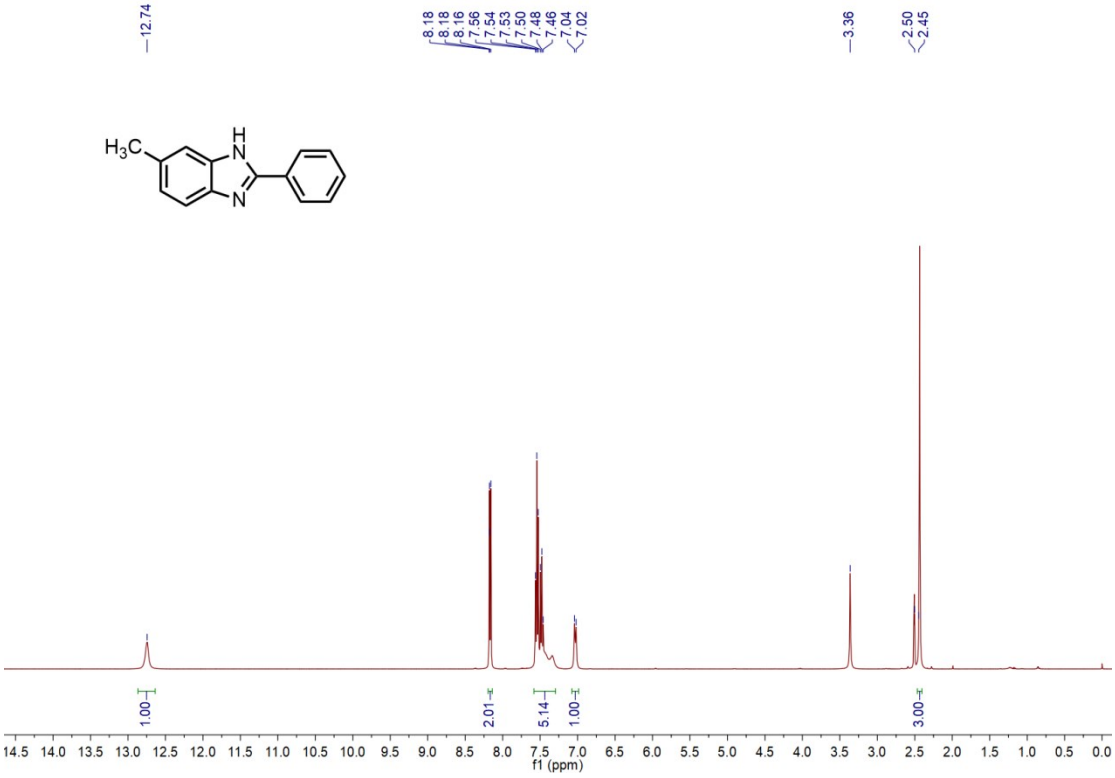


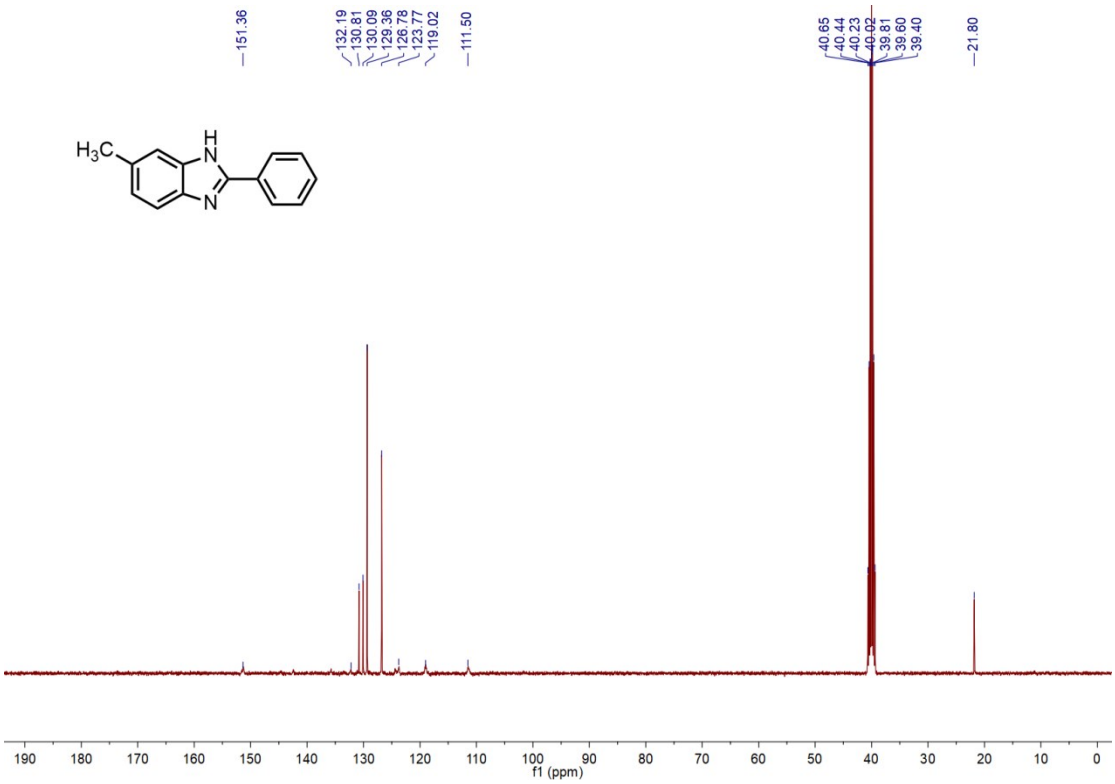


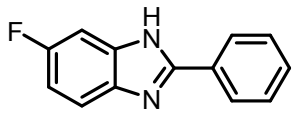


6-methyl-2-phenyl-1H-benzo[d]imidazole (4bf). Purification by column

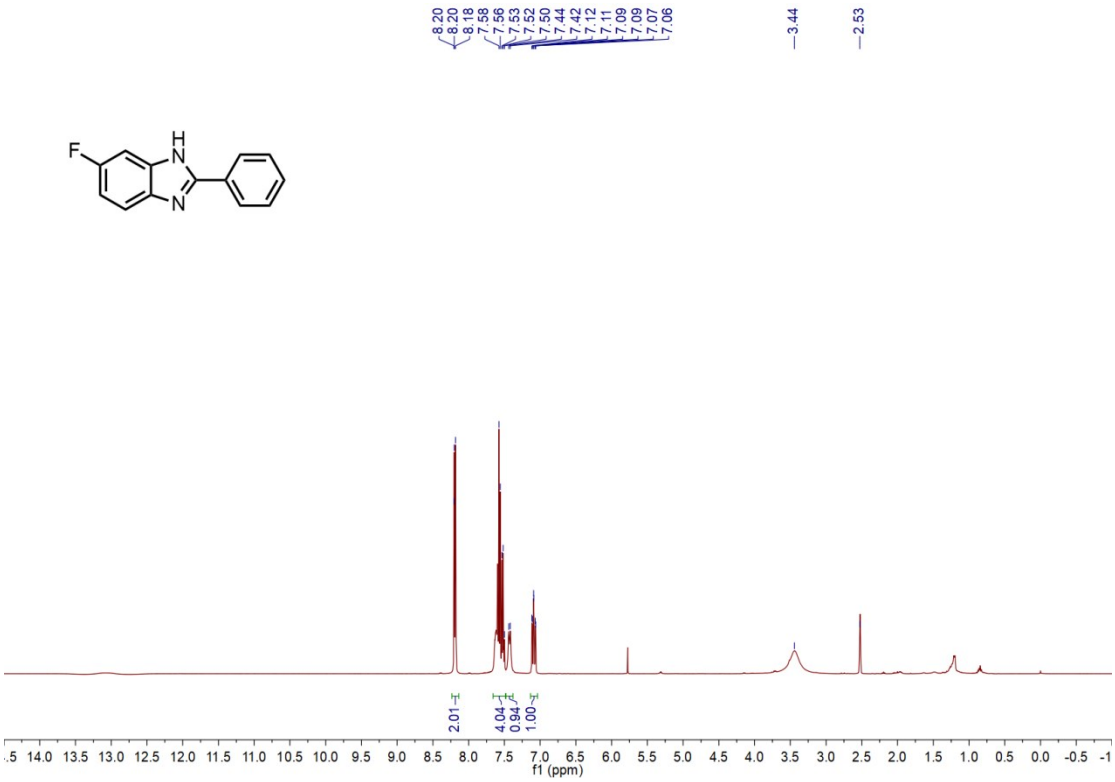
chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 43.2 mg, yield 52%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.74 (s, 1H), 8.19 – 8.14 (m, 2H), 7.51 (dt, J = 26.6, 7.2 Hz, 5H), 7.03 (d, J = 7.9 Hz, 1H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 151.36, 132.19, 130.81, 130.09, 129.36, 126.78, 123.77, 119.02, 111.50, 21.80. HRMS (ESI) m/z: [M+H] $^{+}$ calcd for $C_{14}H_{12}N_2H$ 209.1073, found 209.1070.







6-Fluorophenyl-2-phenyl-1H-benzo[d]imidazole (4bg). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 48.3 mg, yield 57%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 – 8.14 (m, 2H), 7.55 (dd, J = 16.2, 7.4 Hz, 4H), 7.43 (d, J = 8.8 Hz, 1H), 7.09 (td, J = 9.9, 2.5 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 159.14 (d, $J_{C\text{-}F}$ = 235.0 Hz), 153.08, 130.48, 130.34, 129.45, 126.90, 110.67 (d, $J_{C\text{-}F}$ = 25.0 Hz). ^{19}F NMR (376 MHz, DMSO-d_6) δ -120.65 (d, J = 667.1 Hz). HRMS (ESI) m/z: [M+H] $^{+}$ calcd for $C_{13}H_9FN_2H$ 213.0823, found 213.0810.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7.09
7.09
7.07
7.06
3.44
2.53
F
H
N
N
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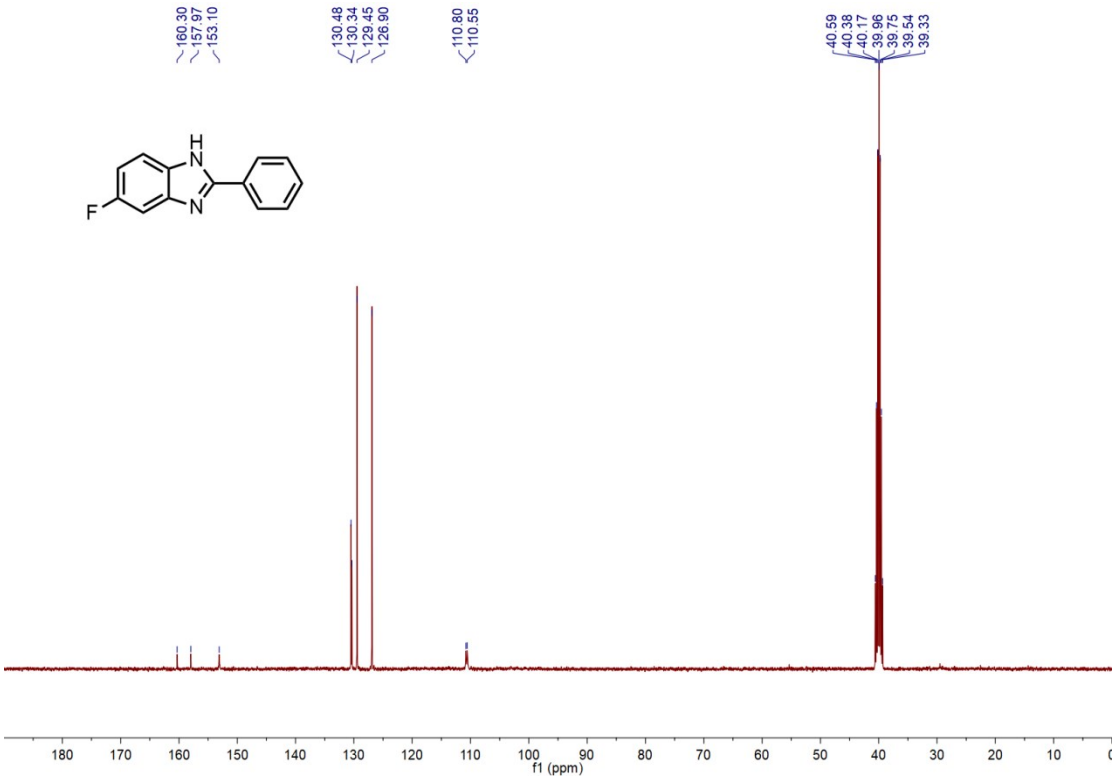
1.00
f1 (ppm)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130.34
129.45
126.90
110.80
110.55
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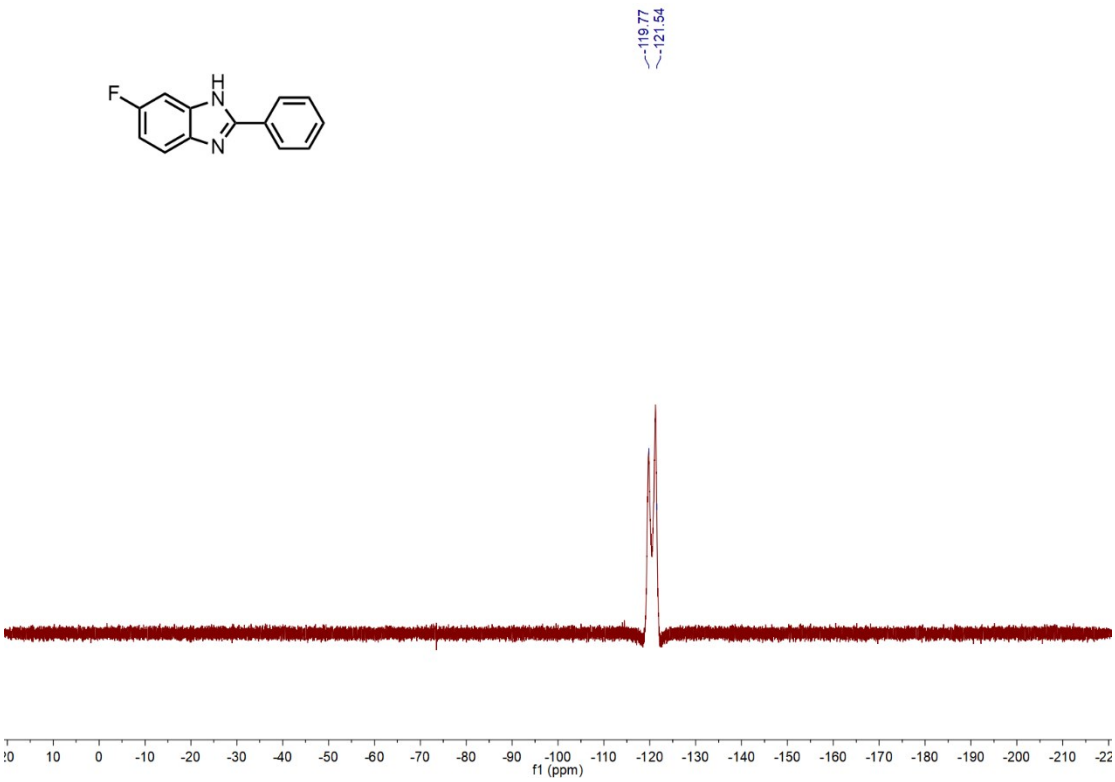
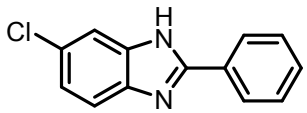
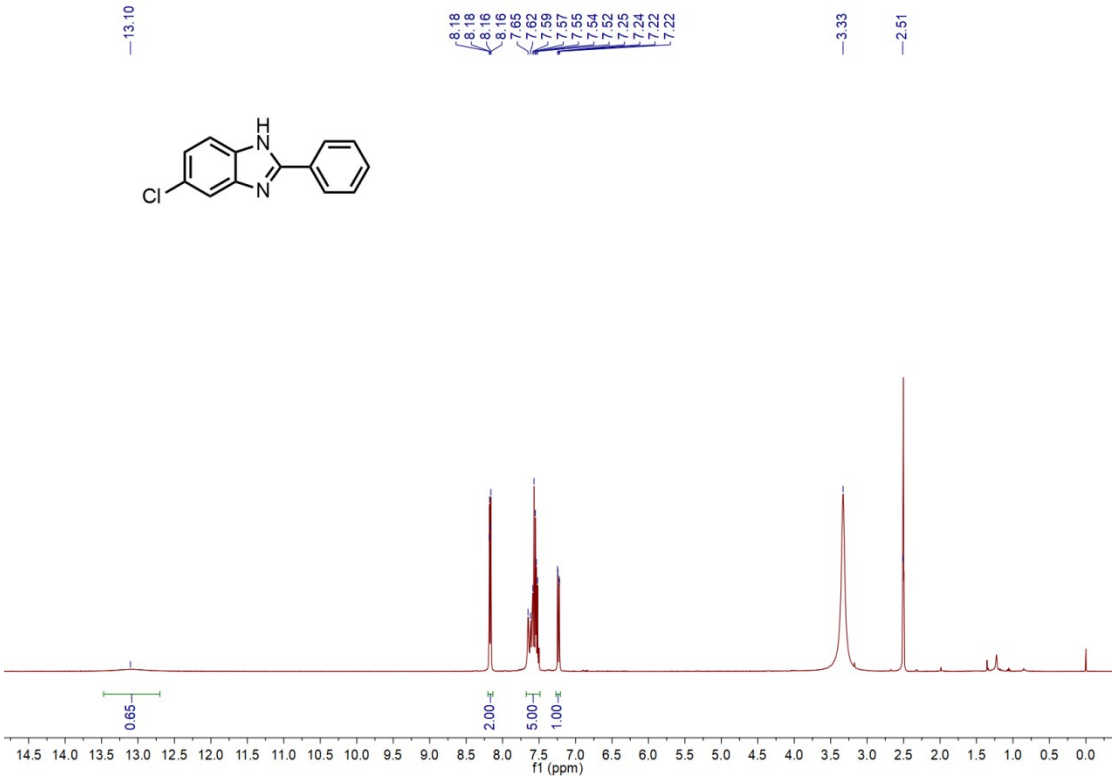
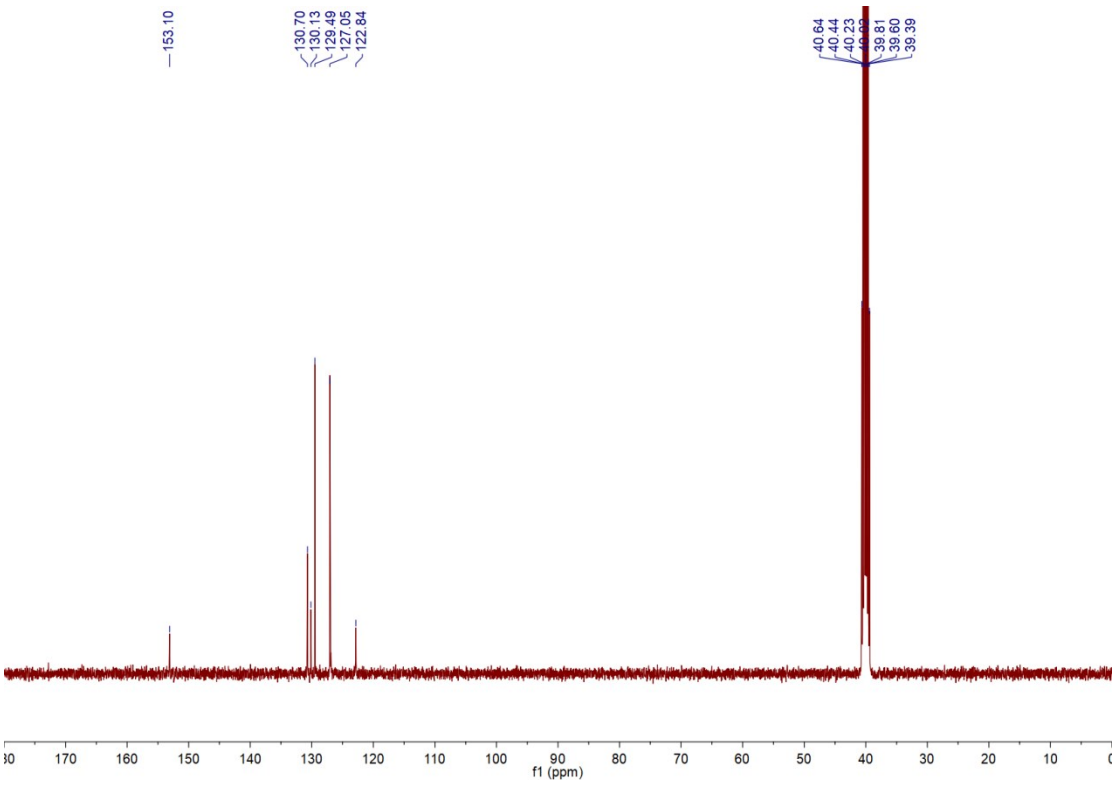
40.38
40.17
39.96
39.75
39.54
39.33
F
H
N
N
f1 (ppm)

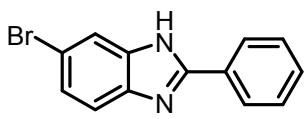




6-Chlorophenyl-2-phenyl-1H-benzo[d]imidazole (4bh). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1) ; white solid; 68 mg, yield 76%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.10 (s, 1H), 8.17 (dd, J = 8.2, 1.4 Hz, 2H), 7.68 – 7.48 (m, 7H), 7.23 (dd, J = 8.5, 2.0 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.63, 130.72, 130.08, 129.44, 127.27, 123.66, 122.17. HRMS (ESI) m/z: [M+H] $^{+}$ calcd for $C_{13}H_{9}ClN_2H$ 229.0527, found 225.0523

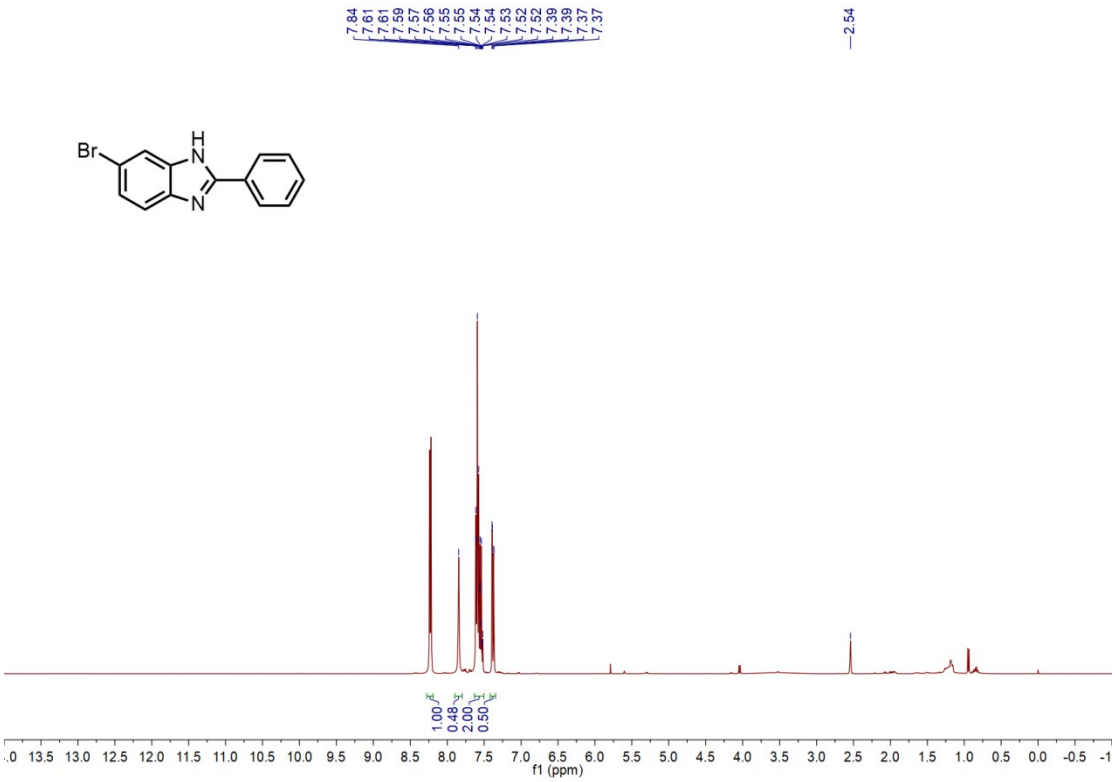


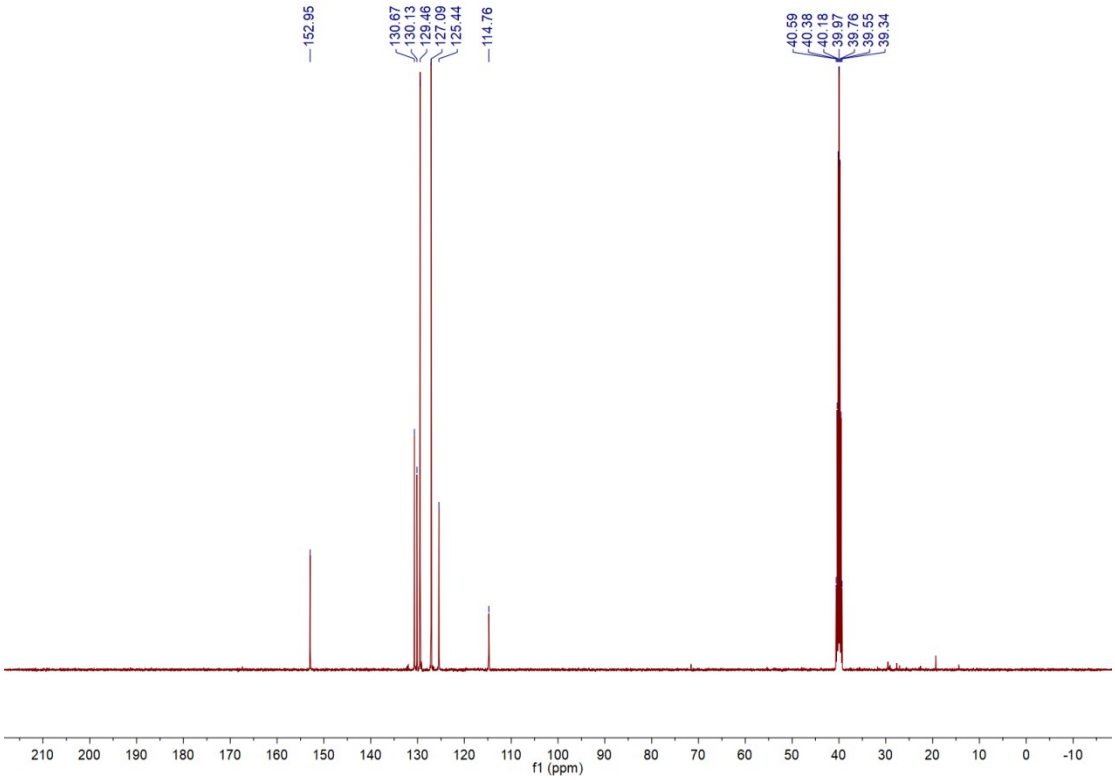


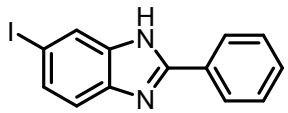


6-Bromophenyl-2-phenyl-1H-benzo[d]imidazole (4bi). Purification by column

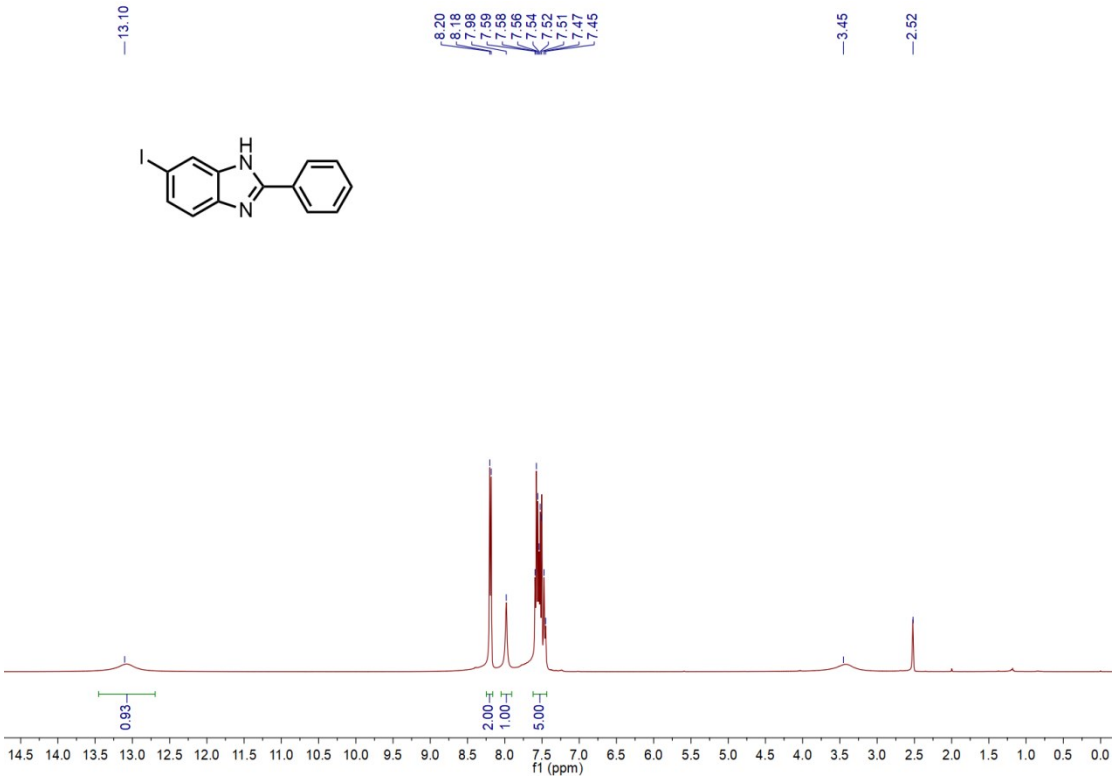
chromatography on silica gel (petroleum ether/ethyl acetate 20/1) ; white solid; 76 mg, yield 70%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.28 – 8.19 (m, 2H), 7.84 (s, 1H), 7.63 – 7.50 (m, 4H), 7.38(dd, J = 8.5, 1.9 Hz, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.95, 130.67, 130.13, 129.46, 127.09, 125.44, 114.76. HRMS(ESI) m/z: [M+H] $^{+}$ calcd for $C_{13}H_9BrN_2H$ 273.0022, found 273.0015.

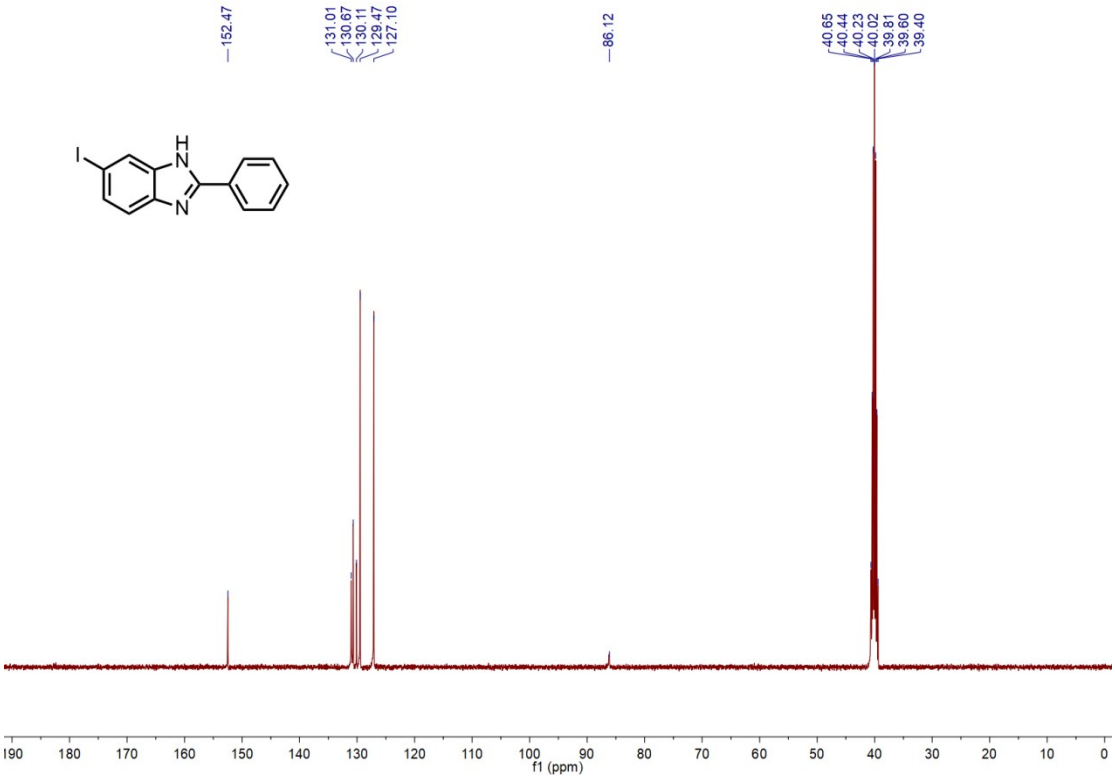


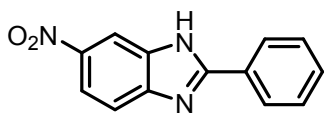




6-Iodophenyl-2-phenyl-1H-benzo[d]imidazole (4bj). Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 87 mg, yield 68%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.10 (s, 1H), 8.19 (d, J = 7.9 Hz, 2H), 7.98 (s, 1H), 7.62 – 7.44 (m, 5H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 152.47, 131.01, 130.67, 130.11, 129.47, 127.10, 86.12. HRMS (ESI) m/z: [M+H] $^{+}$ calcd for $C_{13}H_9IN_2H$ 320.9883, found 320.9875.

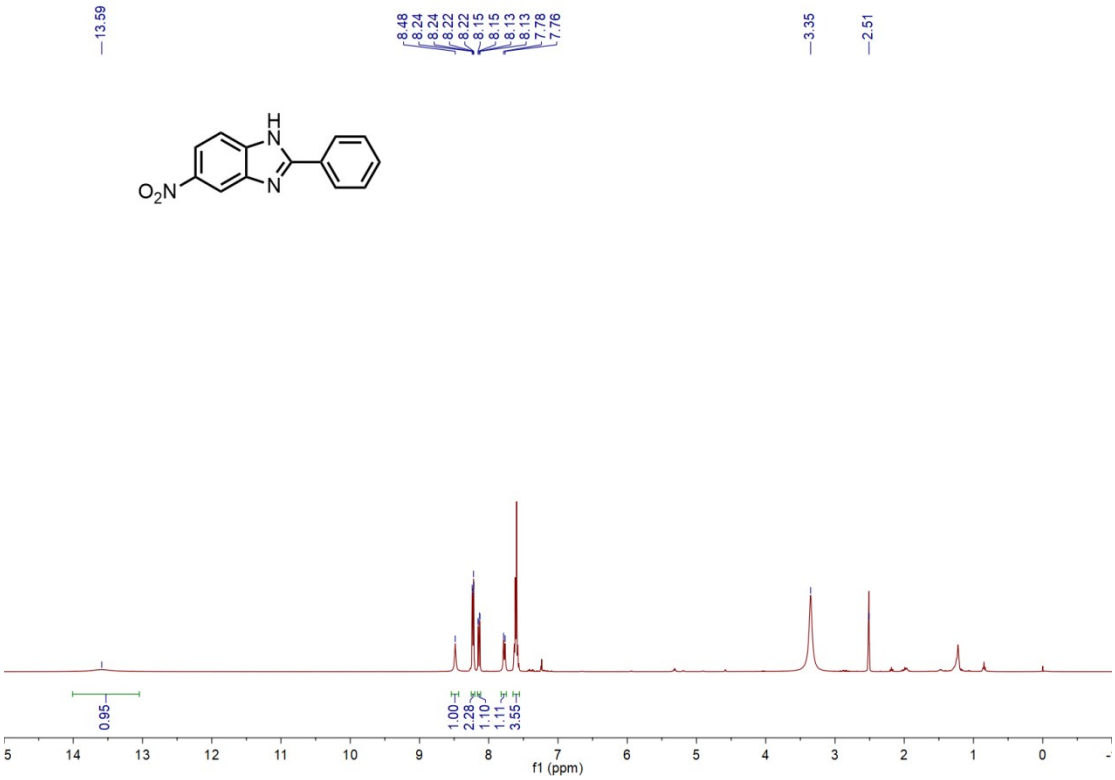


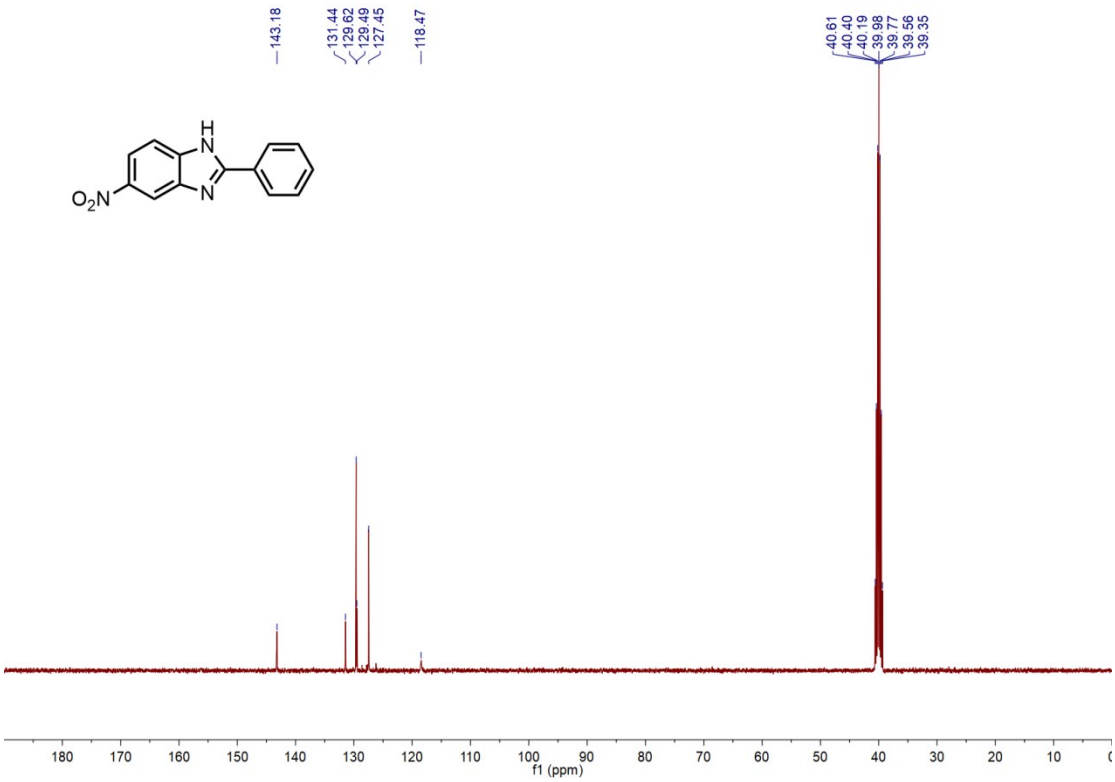


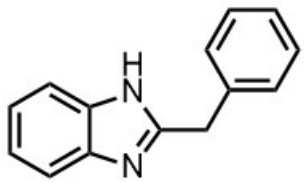


6-Nitrophenyl-2-phenyl-1H-benzo[d]imidazole (4bk). Purification by column

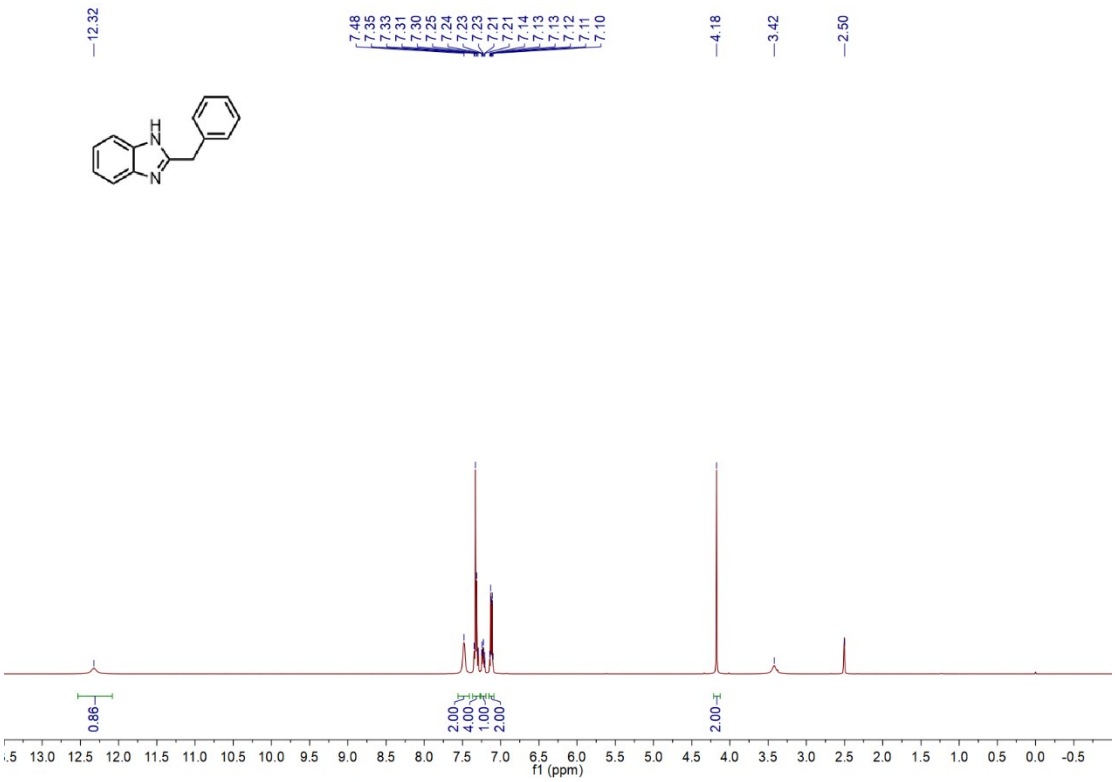
chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 61 mg, yield 64%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 13.59 (s, 1H), 8.48 (s, 1H), 8.23 (dd, J = 7.8, 1.7 Hz, 2H), 8.14 (dd, J = 8.9, 2.2 Hz, 1H), 7.77 (d, J = 8.1 Hz, 1H), 7.65 – 7.56 (m, 4H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 143.18, 131.44, 129.62, 129.49, 127.45, 118.47. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{13}H_9N_3O_2H$ 240.0768, found 240.0767.







2-Benzyl-1H-benzoimidazole **(**4at**).** Purification by column chromatography on silica gel (petroleum ether/ethyl acetate 20/1); white solid; 1.26 g, yield 58%; ^{1}H NMR (400 MHz, DMSO-d_6) δ 12.32 (s, 1H), 7.48 (s, 2H), 7.32 (d, J = 6.9 Hz, 4H), 7.26 – 7.19 (m, 1H), 7.15 – 7.08 (m, 2H), 4.18 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 153.99, 138.14, 129.23, 128.95, 126.99, 121.76, 35.42. HRMS (ESI) m/z: $[M+H]^+$ calcd for $C_{14}H_{12}N_2H$ 209.1073, found 209.1113.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7.13
7.12
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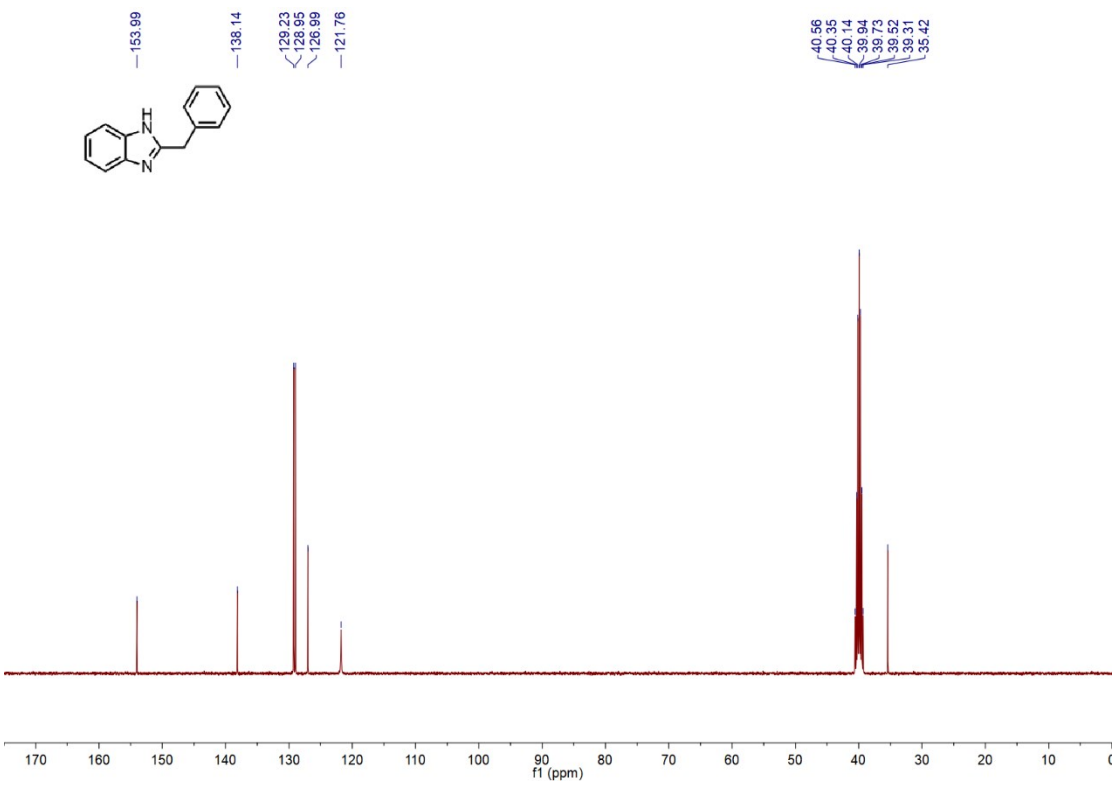
4.00
1.00
2.00
2.00
f1 (ppm)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126.99
121.76
40.56
40.35
40.14
39.94
39.73
39.52
39.31
35.42
f1 (ppm)