

Supporting Information for

Copper-Catalyzed Synthesis of Arylcarboxamides from Aldehyde and Isocyanides: Isocyano Group as an N1 Synthon

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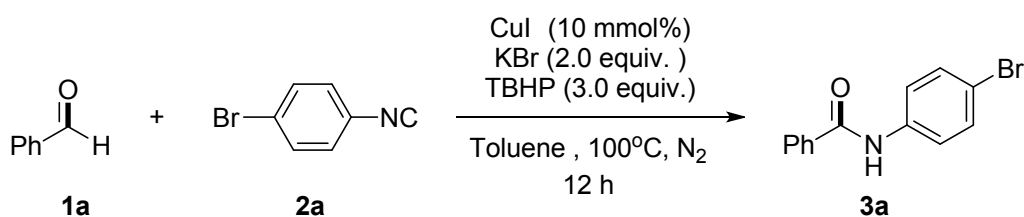
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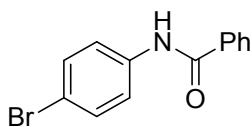
I. General information

All reagents were purchased from commercial sources and used without treatment, unless otherwise indicated. The products were purified by column chromatography over silica gel. $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectra were recorded at 25 °C on a Varian 400 MHz and 100 MHz, respectively, and TMS was used as internal standard. Mass spectra were recorded on BRUKER AutoflexIII Smartbeam MS-spectrometer. High resolution mass spectra (HRMS) were recorded on Bruker microTof by using ESI method.

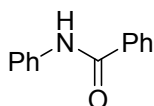
II. Synthesis and analytical data of compounds 3 and 4.



Typical synthetic procedure (with **3a** as an example): A mixture of **1a** (100 μL , 1.0 mmol) and **2a** (90 mg, 0.5 mmol) in toluene (2.0 mL) stirred at 100 °C, until the substrate **2a** was consumed as indicated by TLC about 12 h. The resulting mixture was concentrated and the residue was taken up in DCM. The organic layer was washed with brine, dried over MgSO_4 and concentrated. Purification of the crude product by column chromatography (silica gel; petroleum ether: ethyl acetate = 2: 1) afforded **3a** in 81% yield as a white solid.

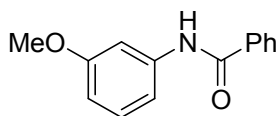


N-(4-bromophenyl)benzamide (3a): Yield 81% (111 mg). White solid, m.p. 205-206 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ_{H} 7.48~7.52 (m, 4H), 7.55~7.59 (m, 3H), 7.81 (s, 1H), 7.86 (d, $J = 7.6$ Hz, 2H); $^{13}\text{C-NMR}$ ($\text{DMSO-}d_6$, 100 MHz) δ_{C} 115.8, 122.7, 128.2, 128.9, 131.9, 132.2, 135.2, 139.1, 166.1; **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{13}\text{H}_{10}\text{BrNONa}$ $[\text{M}+\text{Na}]^+$: 297.9843, found: 297.9840.

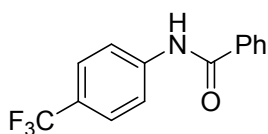


N-phenylbenzamide (3b): Yield 84% (83 mg). White solid, m.p. 163-164 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ_{H} 7.15 (t, $J = 7.6$ Hz, 1H), 7.36 (t, $J = 8.0$ Hz, 2H), 7.45~7.49 (m, 2H), 7.52~7.56 (m, 1H), 7.64 (d, $J = 8.0$ Hz, 2H), 7.86 (d, $J = 7.6$ Hz, 2H), 7.89 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ_{C} 120.2, 124.5, 127.0, 128.8, 129.1, 131.8, 135.0, 137.9, 165.7; **HRMS** (ESI-TOF) m/z

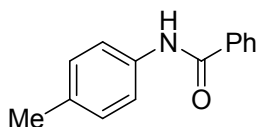
calculated for $C_{13}H_{11}NONa$ $[M+Na]^+$: 220.0738, found: 220.0739. -----



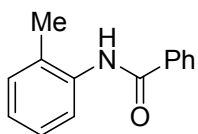
N-(3-methoxyphenyl)benzamide (3c): Yield 87% (99 mg). White solid, m.p. 109-110 °C; 1H -NMR (400 MHz, $CDCl_3$) δ_H 3.83 (s, 3H), 6.73 (dd, $J = 2.4, 8.4$ Hz, 1H), 7.14 (d, $J = 8.0$ Hz, 1H), 7.27 (t, $J = 7.6$ Hz, 1H), 7.46~7.50 (m, 3H), 7.54~7.58 (m, 1H), 7.88 (d, $J = 7.6$ Hz, 2H), 8.00 (s, 1H); ^{13}C -NMR ($CDCl_3$, 100 MHz) δ_C 55.2, 105.8, 110.4, 112.4, 127.0, 128.6, 129.6, 131.7, 134.8, 139.1, 160.1, 165.9; **HRMS** (ESI-TOF) m/z calculated for $C_{14}H_{13}NO_2Na$ $[M+Na]^+$: 250.0844, found: 250.0846. -----



N-(4-(trifluoromethyl)phenyl)benzamide (3d): Yield 46% (61 mg). White solid, m.p. 205-206 °C; 1H -NMR (400 MHz, $DMSO-d_6$) δ_H 7.54~7.58 (m, 2H), 7.61~7.65 (m, 1H), 7.74 (d, $J = 8.4$ Hz, 2H), 7.98 (d, $J = 7.6$ Hz, 2H), 8.03 (d, $J = 8.4$ Hz, 2H), 10.60 (s, 1H); ^{13}C -NMR (100 MHz, $DMSO-d_6$) δ_C 120.6, 123.5, 123.9, 124.2, 126.2, 126.3, 126.39, 126.43, 128.3, 129.0, 132.4, 135.0, 143.3, 166.5; **HRMS** (ESI-TOF) m/z calculated for $C_{14}H_{10}F_3NONa$ $[M+Na]^+$: 288.0612, found: 288.0605. -----

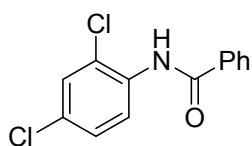


N-(p-tolyl)benzamide (3e): Yield 72% (76 mg). White solid, m.p. 159-160 °C; 1H -NMR (400 MHz, $CDCl_3$) δ_H 2.34 (s, 3H), 7.16 (d, $J = 8.4$ Hz, 2H), 7.44~7.48 (m, 2H), 7.51~7.55 (m, 3H), 7.85 (d, $J = 7.2$ Hz, 3H); ^{13}C -NMR (100 MHz, $CDCl_3$) δ_C 20.9, 120.3, 127.0, 128.7, 129.5, 131.7, 134.2, 135.0, 135.3, 165.6; **HRMS** (ESI-TOF) m/z calculated for $C_{14}H_{13}NONa$ $[M+Na]^+$: 234.0895, found: 234.0899. -----

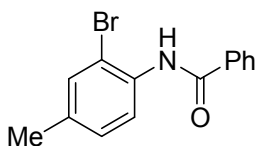


N-(o-tolyl)benzamide (3f): Yield 63% (66 mg). White solid, m.p. 146-147 °C; 1H -NMR (400 MHz, $CDCl_3$) δ_H 2.36 (s, 3H), 7.13~7.17 (m, 1H), 7.25~7.29 (m, 2H), 7.50~7.54 (m, 2H), 7.57~7.61 (m, 1H), 7.73 (s, 1H), 7.92 (d, $J = 7.6$ Hz, 2H), 7.97 (d, $J =$

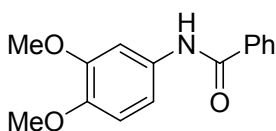
8.0 Hz, 1H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ_{C} 17.9, 123.1, 125.4, 126.9, 127.1, 128.8, 129.3, 130.6, 131.9, 135.0, 135.8, 165.7; **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{14}\text{H}_{13}\text{NONa}$ $[\text{M}+\text{Na}]^+$: 234.0895, found: 234.0897. -----



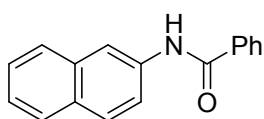
N-(2,4-dichlorophenyl)benzamide (3g): Yield 42% (56 mg). White solid, m.p. 117-118 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ_{H} 7.32 (dd, $J = 2.4, 8.8$ Hz, 1H), 7.44 (d, $J = 2.4$ Hz, 1H), 7.52~7.63 (m, 3H), 7.93 (d, $J = 7.6$ Hz, 2H), 8.41 (s, 1H), 8.55 (d, $J = 9.2$ Hz, 1H); $^{13}\text{C-NMR}$ (100 MHz, CDCl_3) δ_{C} 122.1, 123.5, 127.0, 128.0, 128.7, 128.9, 129.1, 132.3, 133.4, 134.2, 165.2; **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{13}\text{H}_9\text{Cl}_2\text{NONa}$ $[\text{M}+\text{Na}]^+$: 287.9959, found: 287.9958. -----



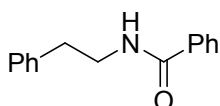
N-(2-bromo-4-methylphenyl)benzamide (3h): Yield 59% (85 mg). White solid, m.p. 147-148 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ_{H} 2.35 (s, 3H), 7.20 (d, $J = 8.4$ Hz, 1H), 7.43 (s, 1H), 7.52~7.56 (m, 2H), 7.58~7.62 (m, 1H), 7.96 (d, $J = 7.2$ Hz, 2H), 8.41~8.43 (m, 2H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ_{C} 20.1, 113.6, 121.6, 127.0, 128.9, 129.1, 132.0, 132.5, 133.2, 134.6, 135.3, 165.1; **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{14}\text{H}_{12}\text{BrNONa}$ $[\text{M}+\text{Na}]^+$: 311.9994, found: 312.0010. -----



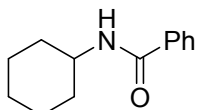
N-(3,4-dimethoxyphenyl)benzamide (3i): Yield 76% (98 mg). White solid, m.p. 173-175 °C; $^1\text{H-NMR}$ (400 MHz, CDCl_3) δ_{H} 3.83 (s, 3H), 3.86 (s, 3H), 6.81 (d, $J = 8.4$ Hz, 1H), 7.02 (d, $J = 8.0$ Hz, 1H), 7.42~7.45 (m, 3H), 7.50~7.53 (m, 1H), 7.86 (d, $J = 7.6$ Hz, 2H), 8.07 (s, 1H); $^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz) δ_{C} 55.8, 56.0, 105.1, 111.1, 112.2, 126.9, 128.7, 131.5, 131.7, 134.8, 145.9, 148.9, 165.7; **HRMS** (ESI-TOF) m/z calculated for $\text{C}_{15}\text{H}_{15}\text{NO}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 280.0950, found: 280.0945. -----



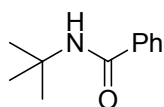
***N*-(naphthalen-2-yl)benzamide (3j)**: Yield 73% (90 mg). White solid, m.p. 165-166 °C; **¹H-NMR** (400 MHz, CDCl₃) δ_H 7.45 (d, *J* = 8.4 Hz 1H), 7.48~7.52 (m, 3H), 7.56~7.59 (m, 1H), 7.62 (dd, *J* = 1.6, 8.8 Hz, 1H), 7.80~7.84 (m, 3H), 7.93 (d, *J* = 8.0 Hz, 2H), 8.18 (s, 1H), 8.36 (s, 1H); **¹³C-NMR** (CDCl₃, 100 MHz) δ_C 117.0, 120.1, 125.1, 126.5, 127.0, 127.5, 127.7, 128.76, 128.78, 130.7, 131.9, 133.8, 134.9, 135.3, 165.9; **HRMS** (ESI-TOF) *m/z* calculated for C₁₇H₁₃NONa [M+Na]⁺ : 270.0895, found: 270.0907. -----



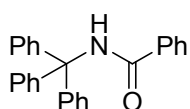
***N*-phenethylbenzamide (3k)**: Yield 61% (69 mg). White solid, m.p. 117-118 °C; **¹H-NMR** (400 MHz, CDCl₃) δ_H 2.93 (t, *J* = 6.8 Hz, 2H), 3.68~3.73 (m, 2H), 6.28 (s, 1H), 7.22~7.25 (m, 3H), 7.30~7.32 (m, 2H), 7.37~7.39 (m, 2H), 7.45~7.48 (m, 1H), 7.69 (d, *J* = 7.6 Hz, 2H); **¹³C-NMR** (100 MHz, CDCl₃) δ_C 35.6, 41.1, 126.5, 126.8, 128.5, 128.6, 128.7, 131.3, 134.6, 138.9, 167.4; **HRMS** (ESI-TOF) *m/z* calculated for C₁₅H₁₅NONa [M+Na]⁺ : 248.1051, found: 248.1028. -----



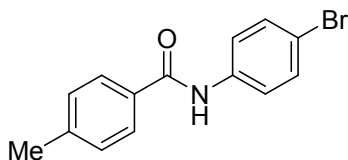
***N*-cyclohexylbenzamide (3l)**: Yield 76% (77 mg). White solid, m.p. 146-147 °C; **¹H-NMR** (400 MHz, CDCl₃) δ_H 1.18~1.29 (m, 3H), 1.37~1.46 (m, 2H), 1.63~1.66 (m, 1H), 1.73~1.76 (m, 2H), 2.02 (d, *J* = 11.6 Hz, 2H), 3.94~4.01 (m, 1H), 6.10 (s, 1H), 7.38~7.42 (m, 2H), 7.45~7.49 (m, 1H), 7.75 (d, *J* = 7.2 Hz, 2H); **¹³C-NMR** (CDCl₃, 100 MHz) δ_C 24.9, 25.5, 33.2, 48.6, 126.8, 128.4, 131.1, 135.0, 166.6; **HRMS** (ESI-TOF) *m/z* calculated for C₁₃H₁₇NONa [M+Na]⁺ : 226.1208, found: 226.1215. -----



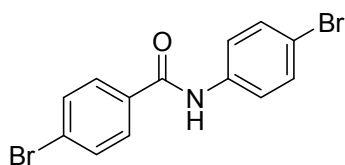
***N*-(*tert*-butyl)benzamide (3m)**: Yield 78% (69 mg). White solid, m.p. 134-135 °C; **¹H-NMR** (400 MHz, CDCl₃) δ_H 1.47 (s, 9H), 5.98 (s, 1H), 7.38~7.42 (m, 2H), 7.45~7.48 (m, 1H), 7.72 (d, *J* = 7.6 Hz, 2H); **¹³C-NMR** (100 MHz, CDCl₃) δ_C 28.8, 51.5, 126.6, 128.4, 131.0, 135.8, 166.9; **HRMS** (ESI-TOF) *m/z* calculated for C₁₁H₁₅NONa [M+Na]⁺ : 200.1051, found: 200.1050. -----



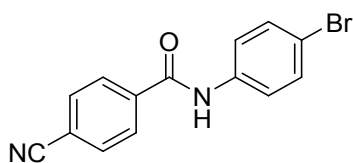
***N*-tritylbenzamide (3n)**: Yield 32% (58 mg). White solid, m.p. 160-162 °C; ¹H-NMR (400 MHz, CDCl₃) δ_H 7.25~7.30 (m, 16H), 7.39~7.43 (m, 2H), 7.46~7.50 (m, 1H), 7.79 (d, *J* = 7.6 Hz, 2H); ¹³C-NMR (100 MHz, CDCl₃) δ_C 70.7, 126.9, 127.1, 128.0, 128.6, 128.63, 131.5, 135.2, 144.6, 166.3; **HRMS** (ESI-TOF) *m/z* calculated for C₂₆H₂₁NONa [M+Na]⁺ : 386.1521, found: 386.1526. -----



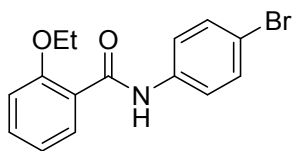
***N*-(4-bromophenyl)-4-methylbenzamide (4a)**: Yield 85% (123 mg). White solid, m.p. 185-186 °C; ¹H-NMR (400 MHz, DMSO-*d*₆) δ_H 2.38 (s, 3H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.53 (d, *J* = 8.8 Hz, 2H), 7.76~7.78 (m, 2H), 7.87 (d, *J* = 8.0 Hz, 2H), 10.29 (s, 1H); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ_C 21.5, 115.7, 122.7, 128.2, 129.4, 131.9, 132.3, 139.2, 142.3, 165.9; **HRMS** (ESI-TOF) *m/z* calculated for C₁₄H₁₂BrNONa [M+Na]⁺ : 312.0000, found: 312.0002. -----



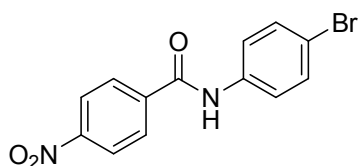
4-Bromo-*N*-(4-bromophenyl)benzamide (4b): Yield 66% (116 mg). White solid, m.p. 234-235 °C; ¹H-NMR (400 MHz, DMSO-*d*₆) δ_H 7.54 (d, *J* = 8.4 Hz, 2H), 7.74~7.78 (m, 4H), 7.91 (d, *J* = 8.4 Hz, 2H), 10.45 (s, 1H); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ_C 116.0, 122.7, 126.0, 130.3, 131.9, 131.93, 134.2, 138.9, 165.1; **HRMS** (ESI-TOF) *m/z* calculated for C₁₃H₁₀Br₂NO [M+H]⁺ : 353.9129, found: 353.9136. -----



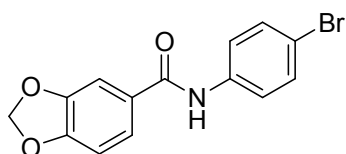
***N*-(4-bromophenyl)-4-cyanobenzamide (4c)**: Yield 57% (85 mg). White solid, m.p. 205-206 °C; ¹H-NMR (400 MHz, DMSO-*d*₆) δ_H 7.54~7.55 (m, 2H), 7.77 (d, *J* = 8.0 Hz, 2H), 8.01~8.04 (m, 2H), 8.11 (d, *J* = 8.0 Hz, 2H), 10.62 (s, 1H); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ_C 114.5, 116.3, 118.8, 122.8, 129.1, 132.0, 132.9, 138.6, 139.1, 164.7; **HRMS** (ESI-TOF) *m/z* calculated for C₁₄H₁₀BrN₂O [M+H]⁺ : 300.9977, found: 300.9973. -----



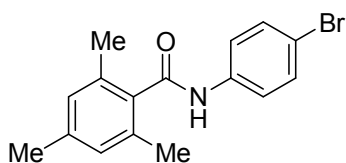
***N*-(4-bromophenyl)-2-ethoxybenzamide (4d)**: Yield 78% (124 mg). White solid, m.p. 191-192 °C; ¹H-NMR (400 MHz, DMSO-*d*₆) δ_H 1.39 (t, *J* = 6.8 Hz, 3H), 4.16 (q, *J* = 6.8 Hz, 2H), 7.07 (t, *J* = 7.6 Hz, 1H), 7.16 (d, *J* = 8.0 Hz, 1H), 7.48~7.55 (m, 3H), 7.68~7.74 (m, 3H), 10.26 (s, 1H); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ_C 15.0, 64.7, 113.4, 115.5, 121.0, 121.8, 124.7, 130.5, 132.1, 132.9, 138.9, 156.4, 164.9; **HRMS** (ESI-TOF) *m/z* calculated for C₁₅H₁₄BrNO₂Na [M+Na]⁺ : 342.0106, found: 342.0113. -



***N*-(4-bromophenyl)-4-nitrobenzamide (4e)**: Yield 37% (59 mg). Yellow solid, m.p. 247-248 °C; ¹H-NMR (400 MHz, DMSO-*d*₆) δ_H 7.55 (d, *J* = 8.8 Hz, 2H), 7.76 (d, *J* = 8.8 Hz, 2H), 8.21 (d, *J* = 8.8 Hz, 2H), 8.41 (d, *J* = 8.8 Hz, 2H), 10.71 (s, 1H); ¹³C-NMR (100 MHz, DMSO-*d*₆) δ_C 117.4, 122.1, 126.7, 129.6, 134.3, 137.4, 140.1, 152.1, 165.1; **HRMS** (ESI-TOF) *m/z* calculated for C₁₃H₉BrN₂O₃Na [M+Na]⁺ : 342.9694, found: 342.9698. -----

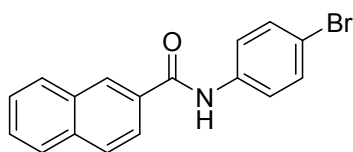


***N*-(4-bromophenyl)benzo[*d*][1,3]dioxole-5-carboxamide (4f)**: Yield 89% (142 mg). White solid, m.p. 222-223 °C; ¹H-NMR (400 MHz, CDCl₃) δ_H 6.11 (s, 2H), 7.16 (d, *J* = 8.8 Hz, 1H), 7.43 (d, *J* = 8.8 Hz, 1H), 7.56 (s, 1H), 7.66 (d, *J* = 8.0 Hz, 2H), 7.81 (d, *J* = 8.0 Hz, 2H), 8.83 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ_C 102.2, 105.8, 107.4, 115.4, 120.6, 121.4, 126.2, 131.7, 139.4, 149.1, 151.1, 165.9; **HRMS** (ESI-TOF) *m/z* calculated for C₁₄H₁₀BrNO₃Na [M+Na]⁺ : 341.9742, found: 341.9747. -----

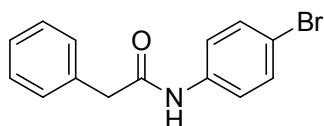


***N*-(4-bromophenyl)-2,4,6-trimethylbenzamide (4g)**: Yield 63% (100 mg). White solid, m.p. 217-218 °C; ¹H-NMR (400 MHz, CDCl₃) δ_H 2.18 (s, 3H), 2.22(s, 3H), 2.26 (s, 3H), 6.96 (s, 2H), 7.49 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 8.8 Hz, 2H), 8.23 (s, 1H); ¹³C-NMR (100 MHz, CDCl₃) δ_C 18.2, 21.1, 120.2, 124.5, 127.0, 128.8, 129.1, 131.8, 135.0, 141.9, 168.7; **HRMS** (ESI-TOF) *m/z*

calculated for $C_{16}H_{16}BrNONa$ $[M+Na]^+$: 340.0313, found: 340.0319. -----

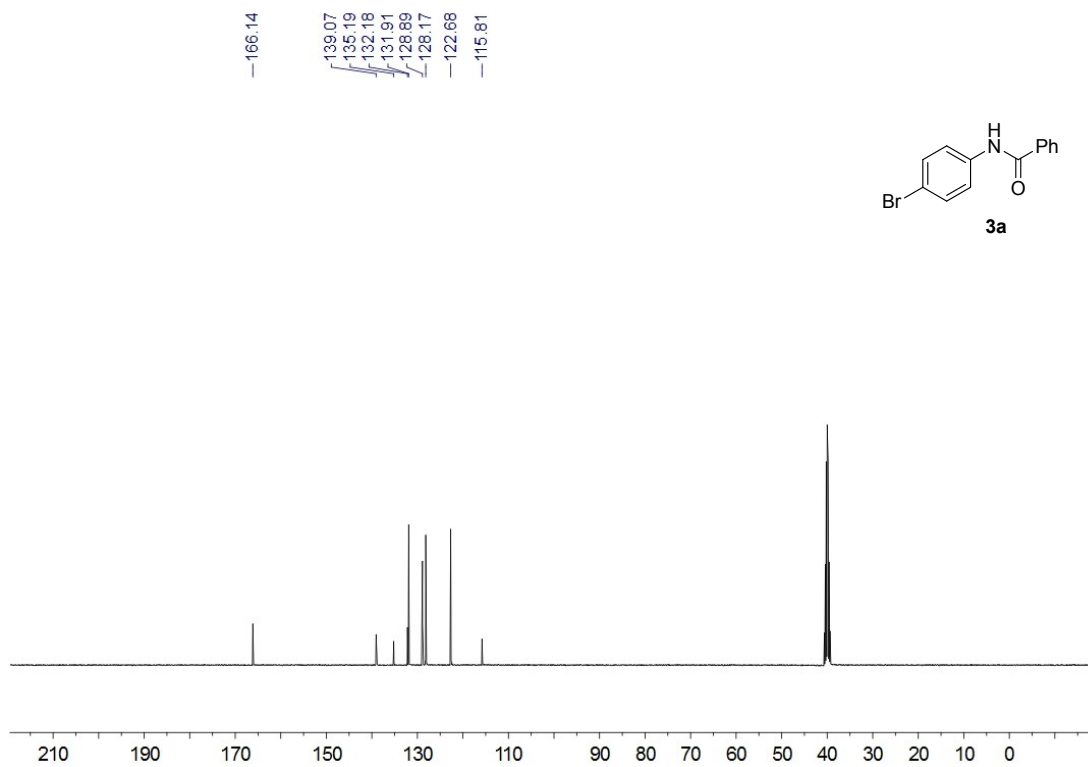
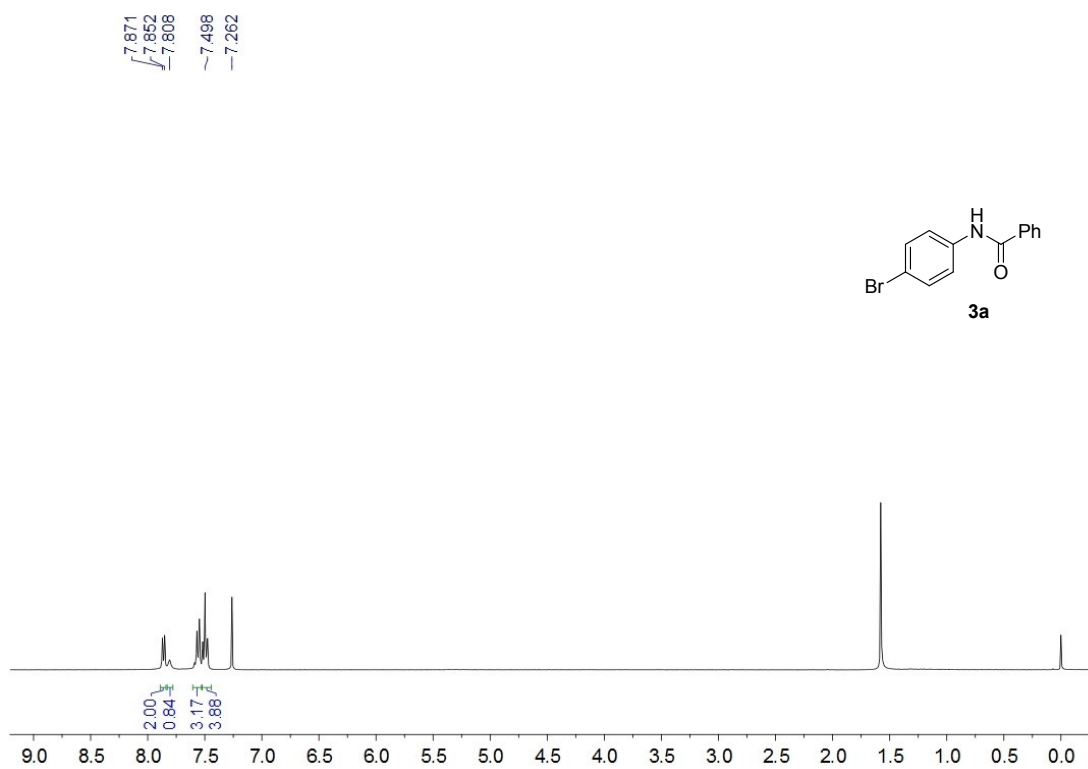


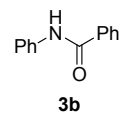
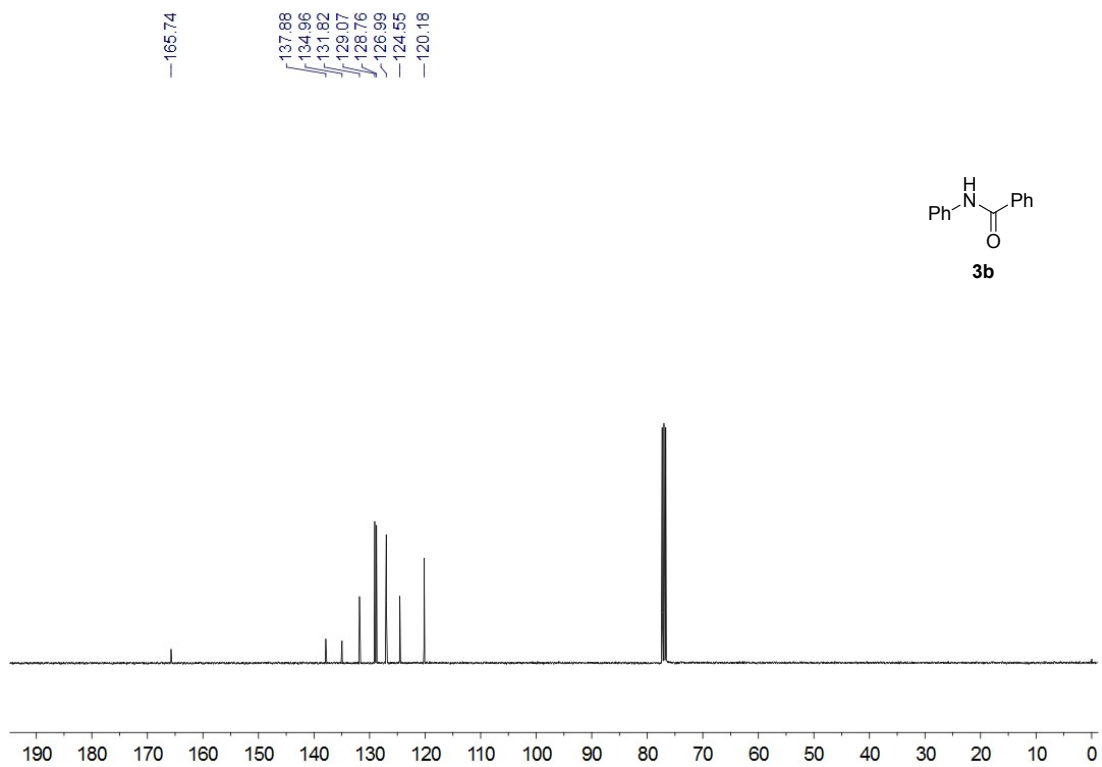
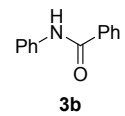
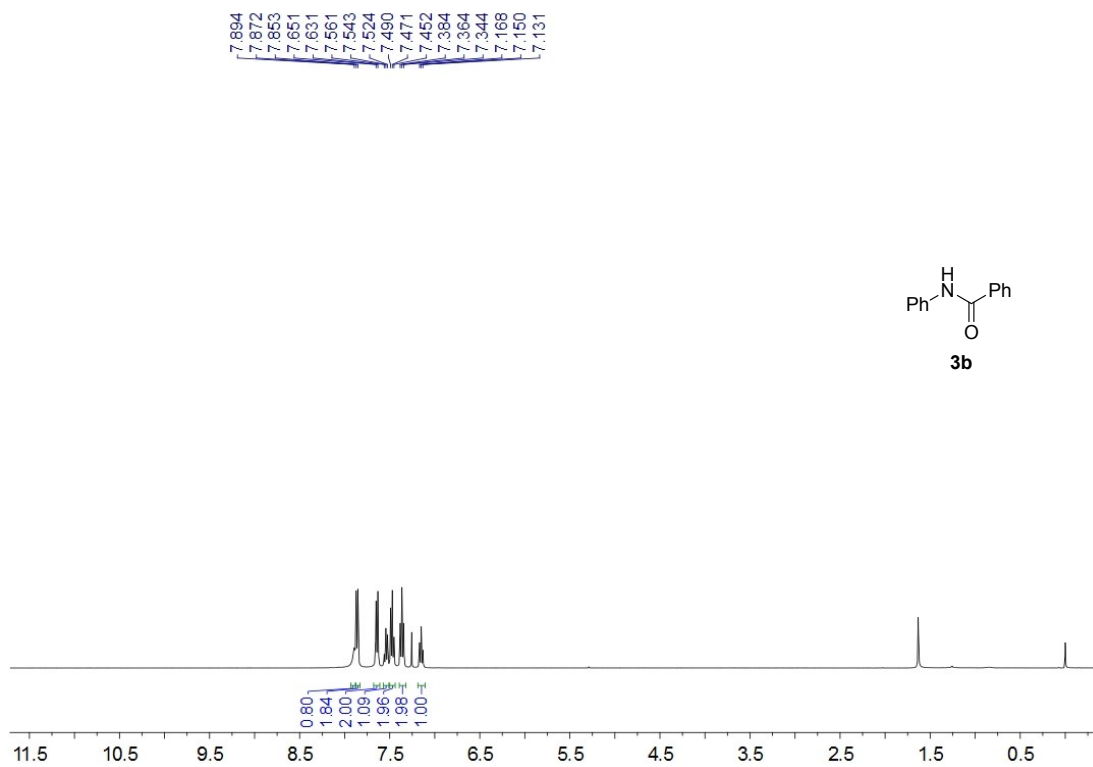
***N*-(4-bromophenyl)-2-naphthamide (4h)**: Yield 67 % (109 mg). White solid, m.p. 247-248 °C; **¹H-NMR** (400 MHz, DMSO-*d*₆) δ_H 7.57 (d, *J* = 8.8 Hz, 2H), 7.60~7.66 (m, 2H), 7.85 (d, *J* = 8.8 Hz, 2H), 8.00~8.10 (m, 4H), 8.60 (s, 1H), 10.59 (s, 1H); **¹³C-NMR** (100 MHz, DMSO-*d*₆) δ_C 115.9, 122.7, 124.9, 127.4, 128.2, 128.4, 128.54, 128.57, 129.45, 132.0, 132.5, 132.54, 134.8, 139.1, 166.2; **HRMS** (ESI-TOF) *m/z* calculated for $C_{17}H_{12}BrNONa$ $[M+Na]^+$: 348.0000, found: 348.0002. -----

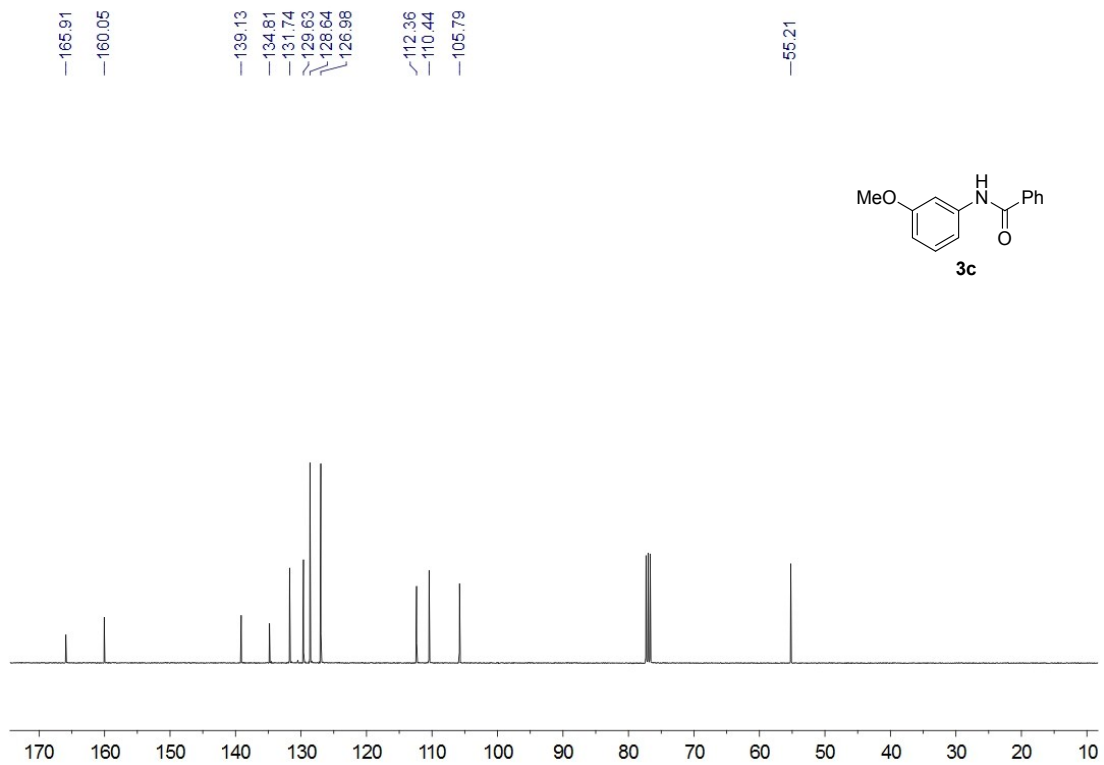
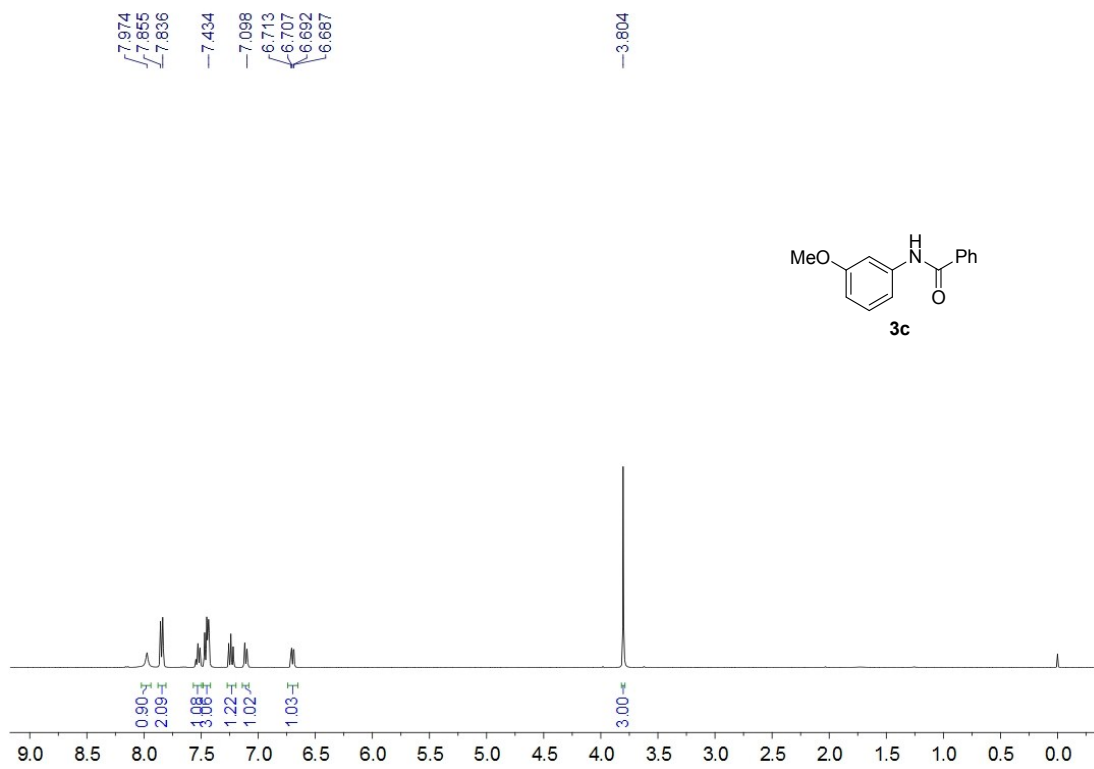


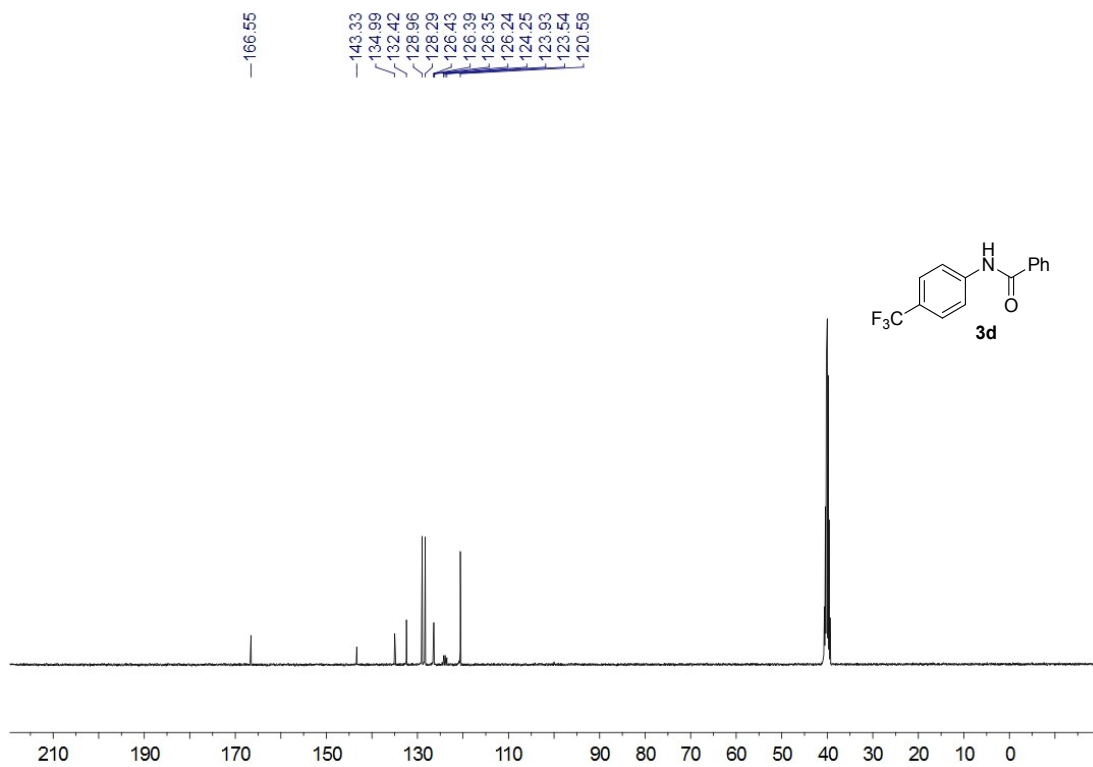
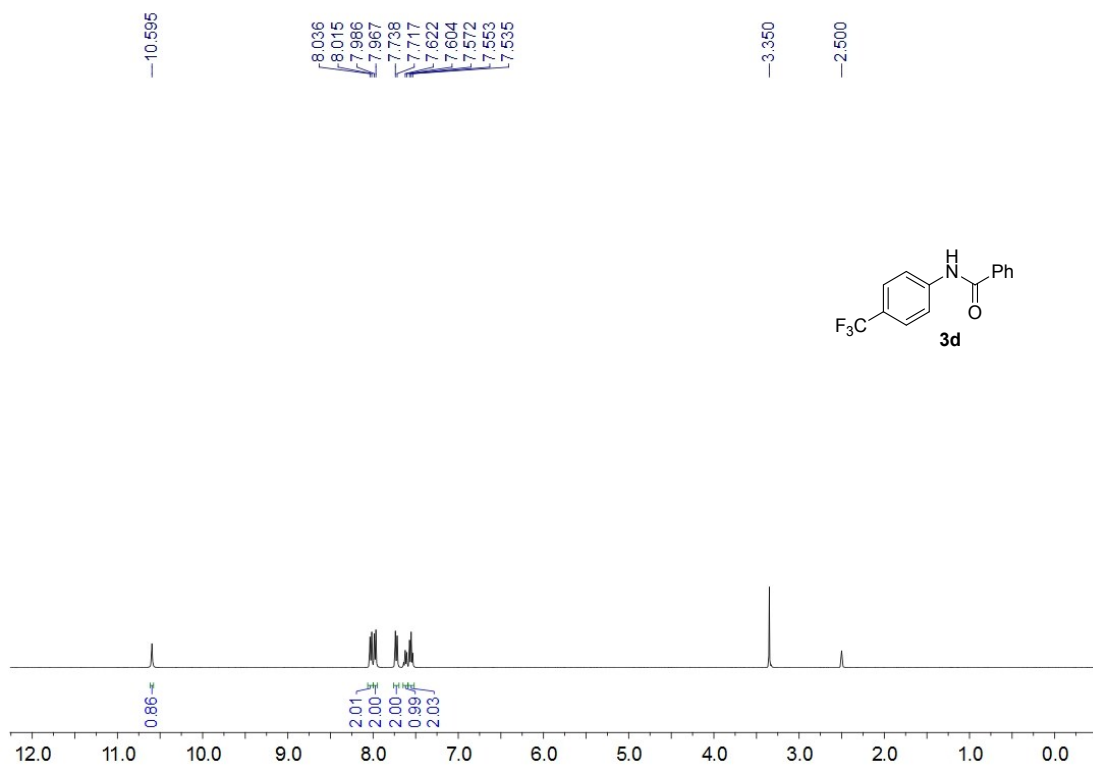
***N*-(4-bromophenyl)-2-phenylacetamide (3a')**: Yield 21 % (30 mg). White solid, m.p. 178-179 °C; **¹H-NMR** (400 MHz, CDCl₃) δ_H 3.71 (s, 2H), 7.23 (s, 1H), 7.30~7.41 (m, 9H); **¹³C-NMR** (100 MHz, CDCl₃) δ_C 44.7, 117.0, 121.4, 127.7, 129.3, 129.5, 131.9, 134.1, 136.7, 169.1; **HRMS** (ESI-TOF) *m/z* calculated for $C_{14}H_{12}BrNONa$ $[M+Na]^+$: 311.9994, found: 311.9998.

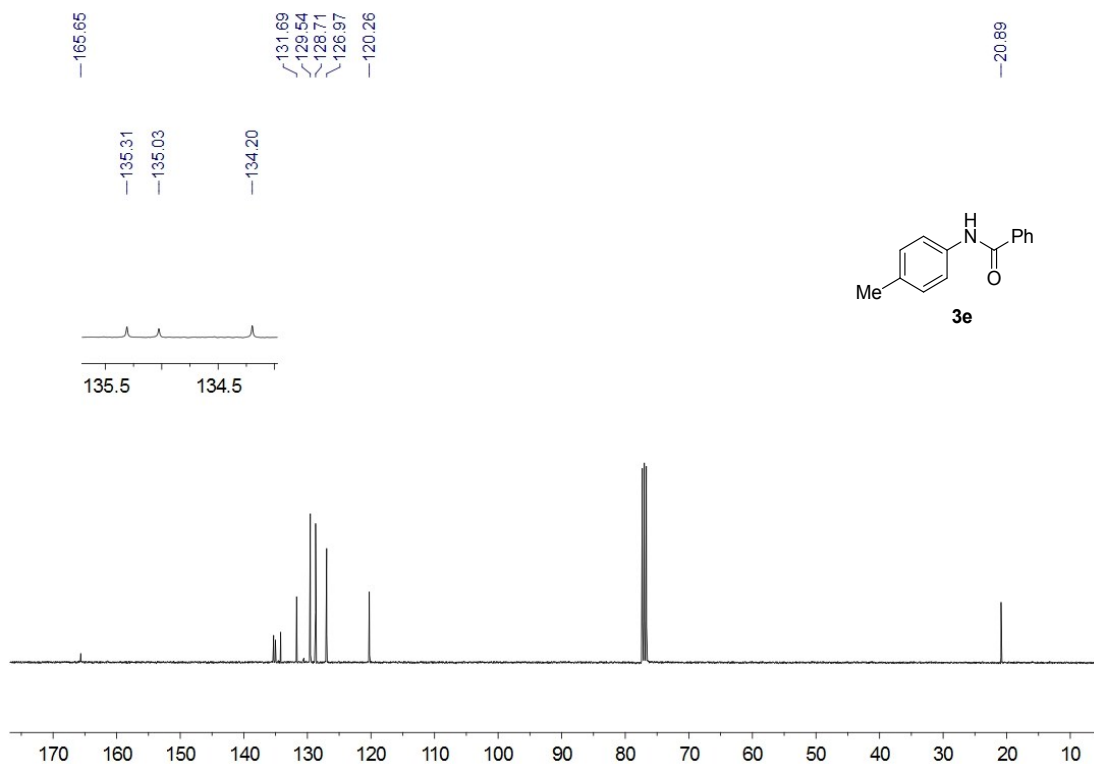
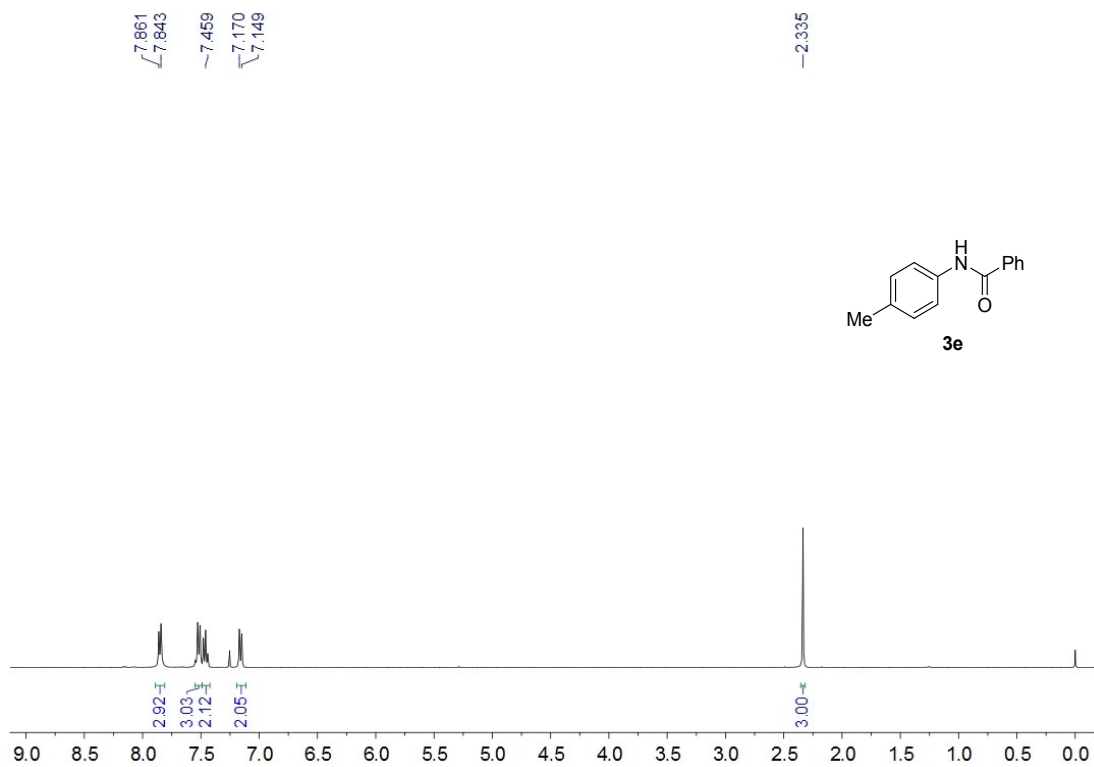
III. NMR spectra copies

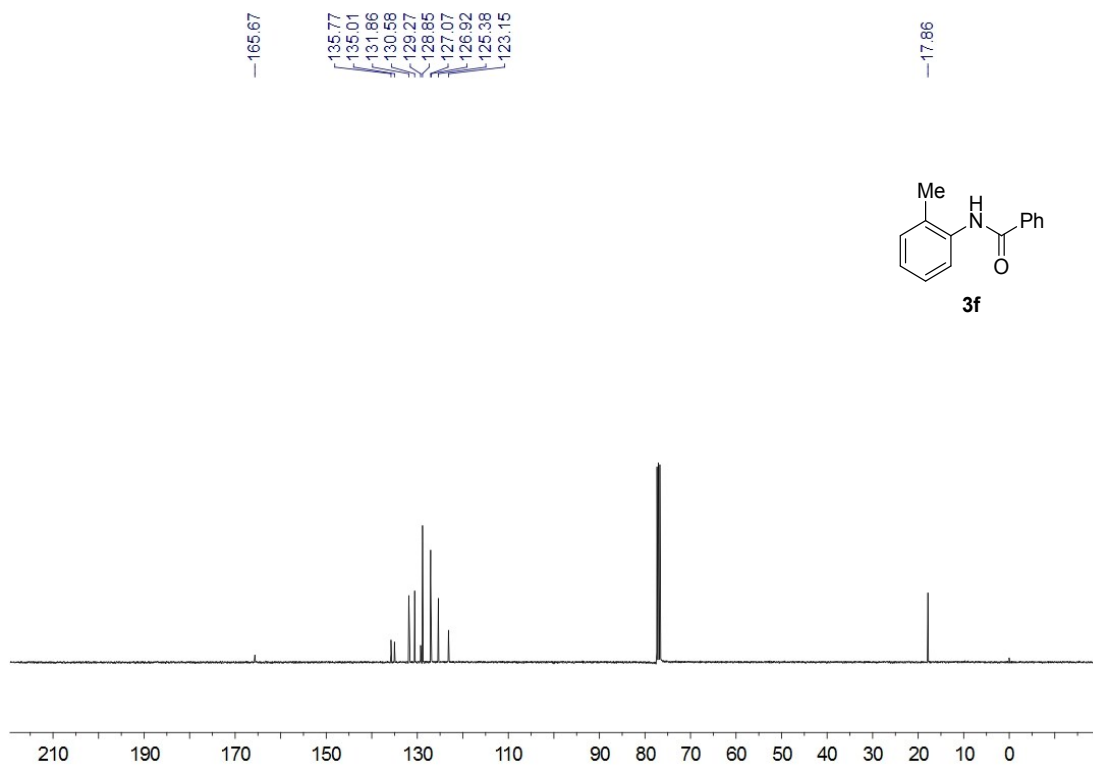
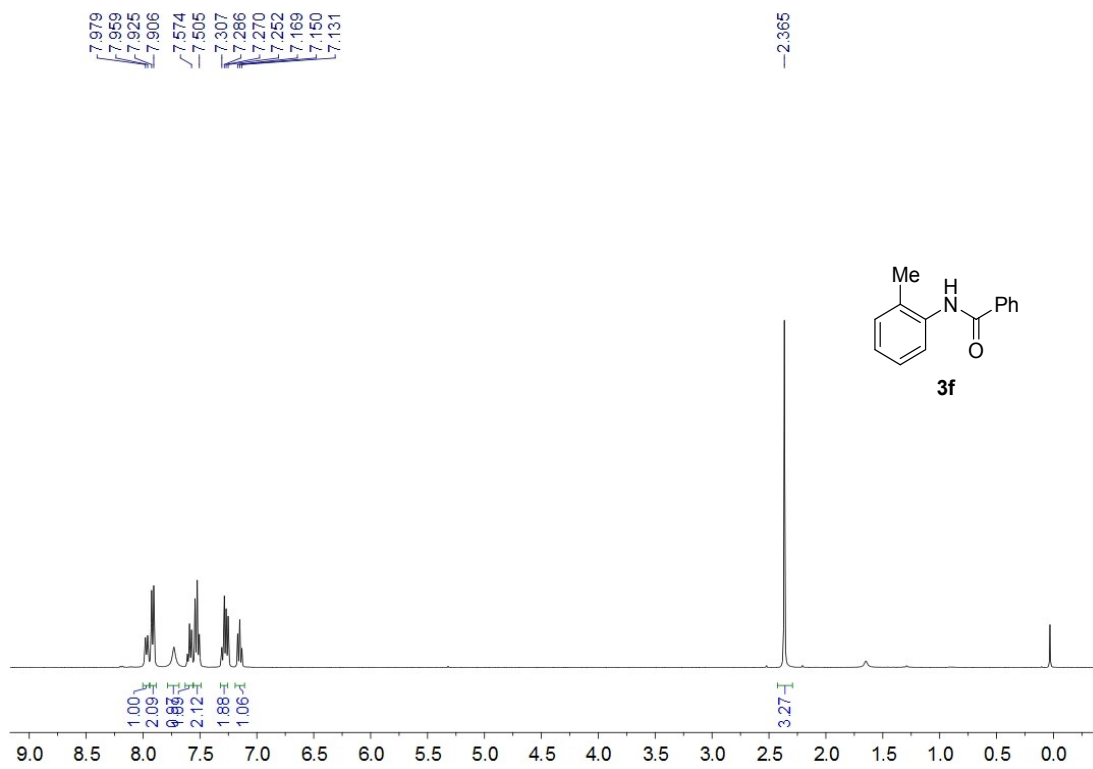




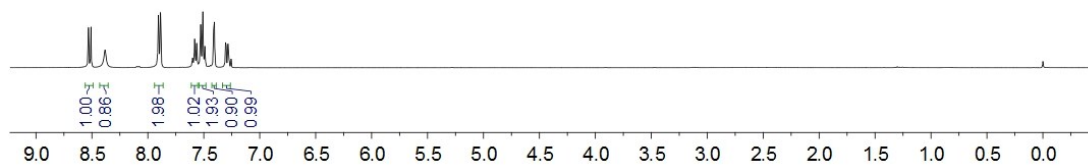
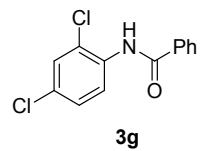




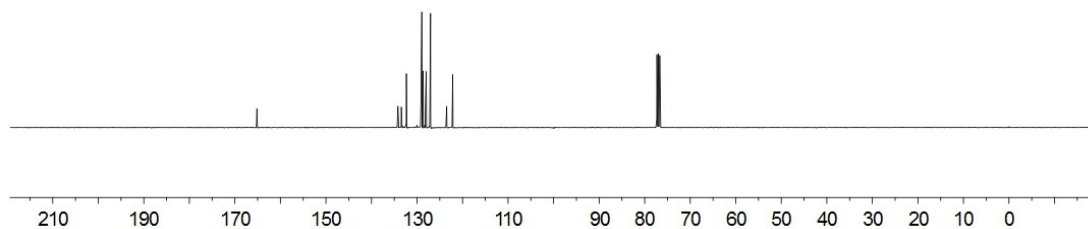
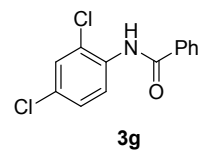


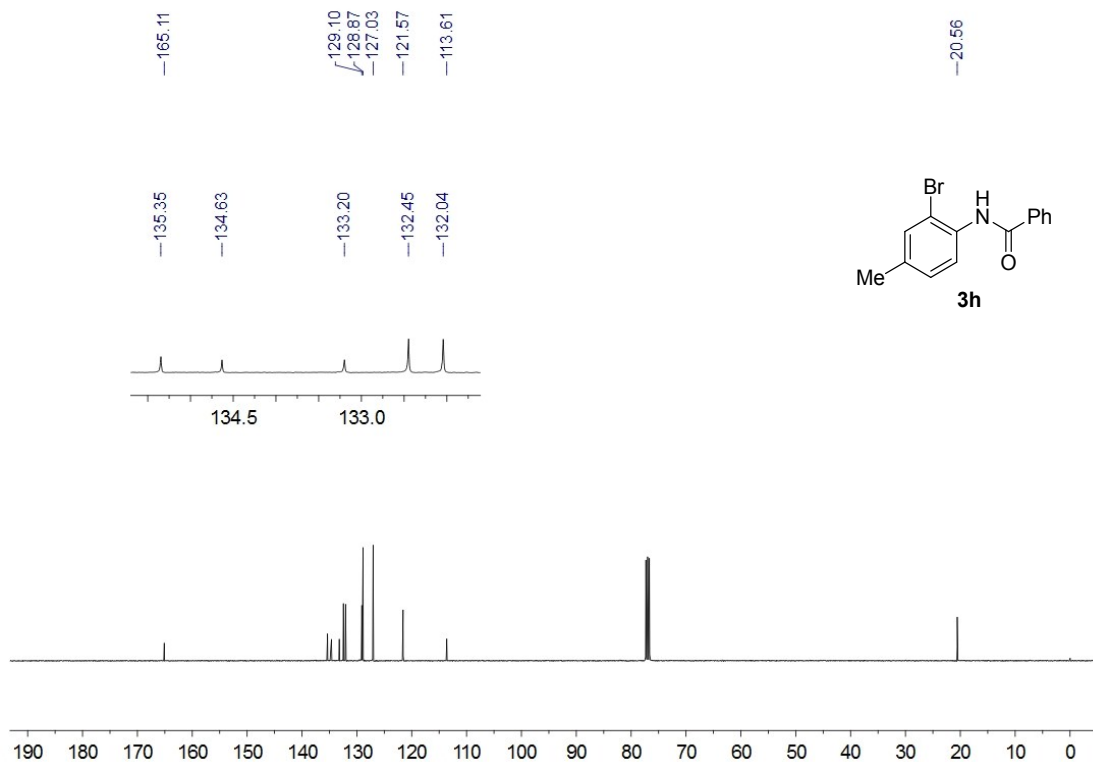
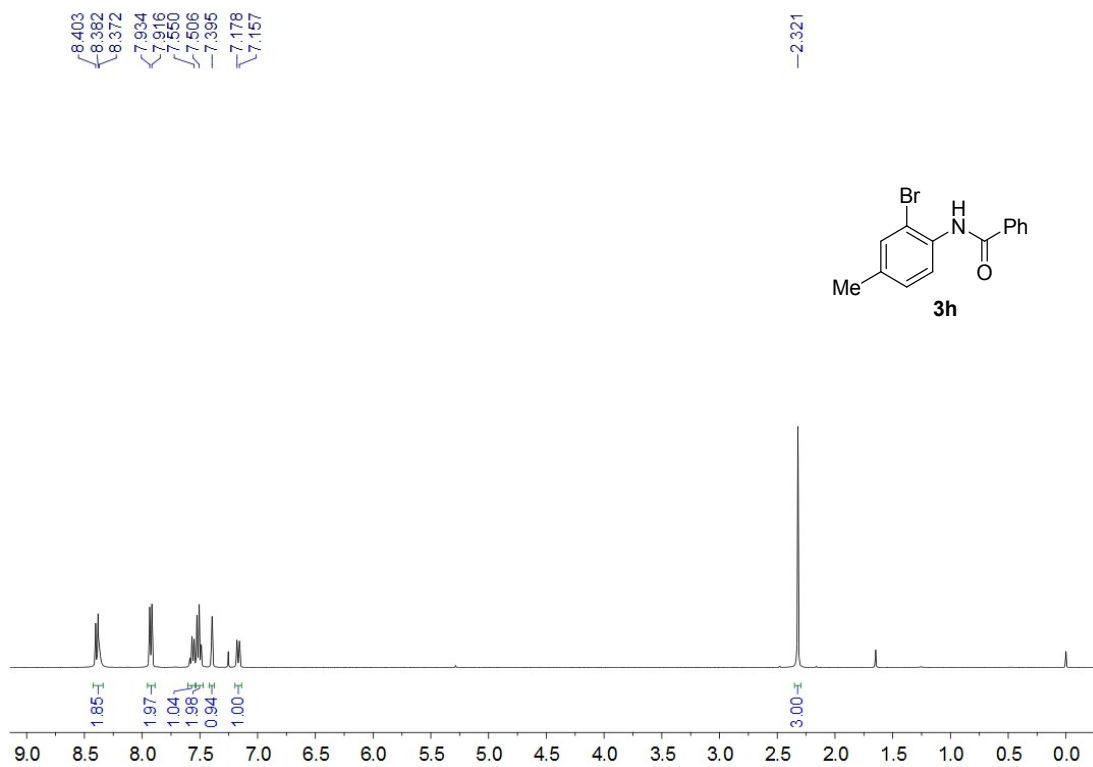


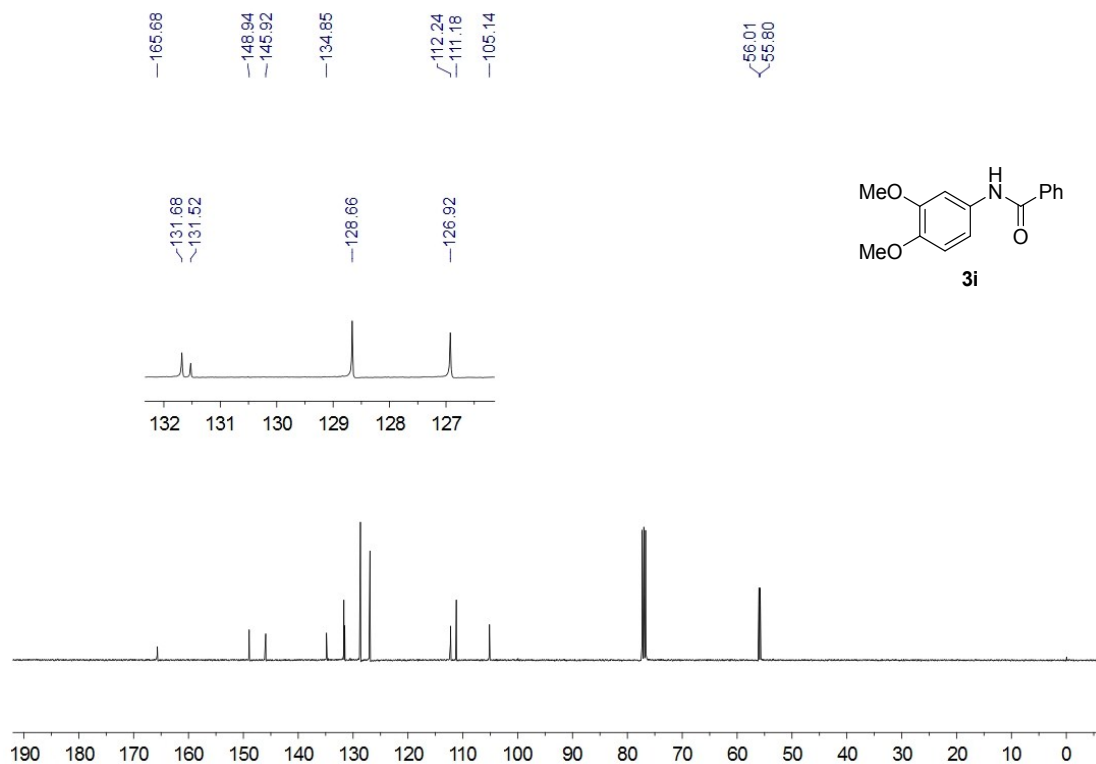
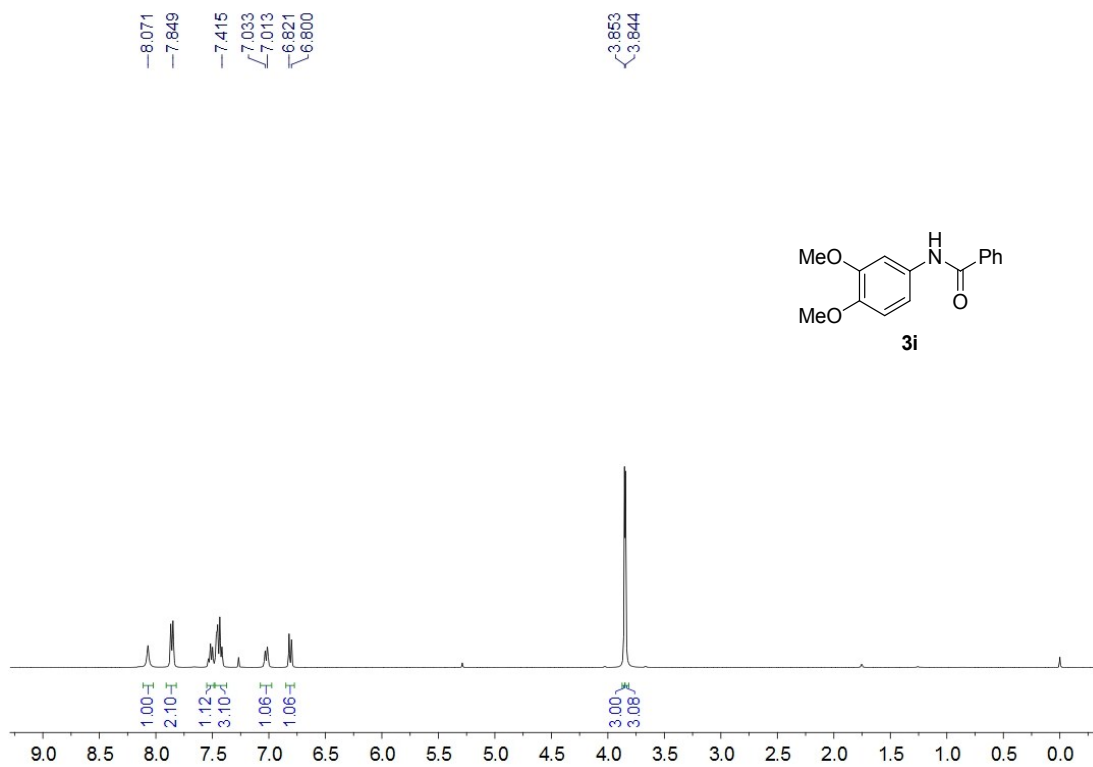
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7.278



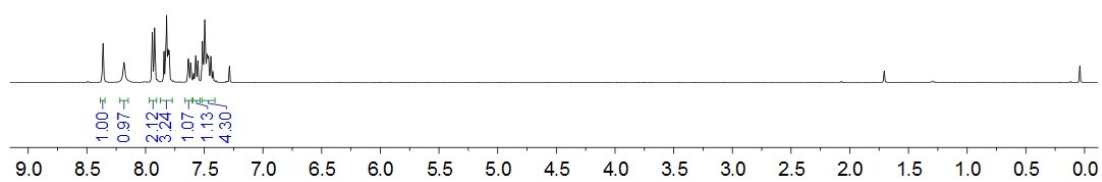
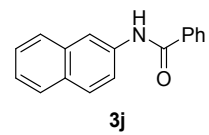
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117.05

