Supporting Information

Copper-Catalyzed Intermolecular Amidation and Imidation of Unactivated Alkanes

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General Experimentals

Tetrahydrofuran, hexanes, benzene, acetonitrile, and cyclohexane were used as purchased unless otherwise noted. All other reagents were purchased from Sigma-Aldrich, Alfa Aesar, and VWR and used as received unless otherwise noted. All reactions were conducted under a nitrogen atmosphere unless otherwise noted. GCMS data are obtained on an Agilent 6890-N GC system containing an Alltech EC-1 capillary column and an Agilent 5973 mass selective detector. NMR spectra were acquired on a 400 MHz NMR spectrometer at University of California, Berkeley NMR facility. Chemical shifts are reported in ppm relative to a residual solvent peak $CDCl_3$ = 7.26 ppm for ^{1}H NMR spectroscopy and 77.23 ppm for ^{13}C NMR spectroscopy. UV-vis spectroscopy was performed on a Cary 100 under PC control. Low-temperature EPR spectroscopy was performed on the Varian E109 EPR spectrometer equipped with a Model 102 Microwave Bridge at 20K using an Air Products LTR liquid He cryostat at Lawrence Berkeley National Laboratory. Measurement of conductivity was determined on a VWR Digital Conductivity Meter. Elemental analyses were conducted at the Technical University of Berlin and University of California, Berkeley. $[(phen)CuCl]_2(\mu\text{-}Cl)_2$ was synthesized according to the reported procedure (Hossain, M. M.; Shyu, S.-G. *Adv. Synth. Catal.* **2010**, *352*, 3061). $[Cu(Mes)]_n$ was synthesized according to the reported procedure (Tsuda, T.; Yazawa, T.; Watanabe, K.; Fujii, T.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 192).

Synthesis of [(phen)Cu(phth)$_2$] (1-phth$_2$)

Under an atmosphere of nitrogen, a 100 mL round-bottom flask was charged with $[(phen)CuCl]_2(\mu\text{-}Cl)_2$ (267 mg, 0.420 mmol), a large magnetic stirring bar, and anhydrous THF (20 mL). Under a positive flow of nitrogen, to the green suspension, was slowly added potassium phthalimide (330 mg, 1.78 mmol) as a solid. After 12 h at room temperature, a greenish-blue precipitate was collected on a medium porosity frit and washed with THF (20 mL) and then Et_2O (20 mL). The crude product was dissolved in MeOH (25 mL) and filtered through a glass frit. Slow evaporation of the concentrated MeOH solution gave microcrystalline products. Yield = 72%. FT-IR (Nujol): δ 3290 (m), 3159 (m), 1682 (m), 1657 (s), 1640 (s), 1621 (m), 1601 (m), 1582 (m), 1552 (m), 1518 (m), 1426 (s), 1307 (m), 1177 (m), 1147 (w), 1122 (s), 1050 (w), 873 (w), 854 (s), 821 (w), 761 (m), 630 (m) cm^{-1}. Anal. Calcd for $C_{28}H_{16}N_4O_4Cu$: C, 62.74; H, 3.01; N, 10.45. Found: C, 63.02; H, 3.10; N, 10.21.

Synthesis of $[(phen)Cu(NHSO_2Ph)_2]$ (2)

Under an atmosphere of nitrogen, a 25 mL round-bottom flask was charged with H_2NSO_2Ph (159 mg, 1.00 mmol), NaO*t*Bu (96 mg, 1.0 mmol), a stirring bar, and anhydrous THF (10 mL). The mixture was stirred for 0.5 h. This mixture was transferred to a 100 mL round-bottom Schlenk flask containing a green suspension of $[(phen)CuCl]_2(\mu\text{-}Cl)_2$ (150 mg, 0.240 mmol), a large stirring bar, and anhydrous THF (20 mL) under an atmosphere of nitrogen. The reaction mixture produced a light blue suspension after 12 h. The blue solids were collected on a porous frit, washed with copious amounts of THF, MeOH, and Et_2O to remove NaCl. The blue solids were dried under dynamic vacuum to give product. Yield = 84%. FT-IR (Nujol): δ 3327 (s), 3273 (s), 3232 (s), 3061 (s), 1625 (m), 1605 (m), 1587 (s), 1518 (s), 1494 (w), 1478 (w), 1443 (s), 1428 (s), 1343 (w), 1276 (s), 1224 (s), 1130 (s), 1096 (s), 1070 (w), 1025 (w), 962 (s), 868 (m), 849 (s), 755 (s), 693 (s), 647 (w), 606 (s), 553 (s) cm^{-1}. Anal. Calcd for $C_{24}H_{20}N_4O_4S_2Cu$: C, 51.83; H, 3.62; N, 10.07. Found: C, 51.61; H, 3.95; N, 9.72.

Synthesis of $[(phen)Cu(NHCOPh)_2]$ (3)

Under an atmosphere of nitrogen, a 25 round-bottom flask was charged with NaO*t*Bu (96 mg, 1.0 mmol), H_2NCOPh (122 mg, 1.00 mmol), a stirring bar, and anhydrous THF (10 mL). The mixture was stirred for 0.5 h. The resulting mixture was transferred to a 100 mL round-bottom Schlenk flask containing $[(phen)CuCl]_2(\mu\text{-}Cl)_2$ (150 mg, 0.240 mmol), a large stirring bar, and

anhydrous THF (20 mL). The reaction mixture gradually produced a dark green suspension and eventually became a greenish-brown suspension. After 12 h at room temperature, the resulting greenish-brown solids were collected on a porous frit, washed with copious amounts of THF, MeOH (50 mL), and Et_2O (50 mL), and dried under dynamic vacuum to give product. Yield = 70%. FT-IR (Nujol): δ 3366 (NH, s), 3172 (s), 1660 (C=O, s), 1625 (s), 1578 (s), 1405 (s), 1299 (w), 1144 (w), 1123 (w), 1026 (w), 880 (w), 854 (w), 810 (w), 791 (w), 771 (w), 706 (w), 685 (w), 636 (w) cm^{-1}. Anal. Calcd for $C_{26}H_{20}N_4O_2Cu$: C, 64.52; H, 4.16; N, 11.58. Found: C, 64.38; H, 4.44; N, 11.15.

Synthesis of $[(phen)_2Cu][Cu(NHSO_2Ph)_2]$ (4)

A 20 mL scintillation vial was charged with [Cu(Mes)] (200 mg, 1.09 mmol), a stirring bar, and anhydrous THF (4 mL). An anhydrous THF (3 mL) solution of 1,0-phenanthroline (197 mg, 1.09 mmol) was added to the reaction mixture to give a deep red solution. After 15 minutes, to the deep red reaction mixture was added H_2NSO_2Ph (180 mg, 1.14 mmol) as a solid in small portions with a spatula. After 3 h, the orange precipitate was collected on a medium porous frit and washed with pentane (20 mL) and dried under vacuum to give an orange solids. Yield = 71%. ^{1}H NMR (DMSO-d_6, 400 MHz, 25 °C): δ 9.01 (br s, 2H), 8.78 (br s, 2H), 8.23 (br s, 2H), 7.97 (br s, 2H), 7.75 (br s, 2H), 7.33 (br s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, 25 °C): δ 149.9, 149.5, 143.7, 137.6, 129.6, 129.3, 128.4, 127.4, 125.8, 125.5. FT-IR (Nujol): δ 3350 (s, NH), 1621 (w), 1582 (w), 1506 (m), 1446 (s), 1292 (vs), 1280 (vs), 1186 (s), 1144 (vs), 1094 (vs), 954 (vs), 848 (vs), 762 (vs), 718 (s), 698 (vs), 636 (m), 588 (vs), 553 (vs). Anal. Calcd for $C_{36}H_{28}N_6O_4S_2Cu_2$: C, 54.06; H, 3.53; N, 10.51. Found: C, 53.63; H, 3.35; N, 10.13.

Synthesis of $[(phen)_2Cu][Cu(NHCOPh)_2]$ (5)

A 20 mL scintillation vial was charged with [Cu(Mes)] (200 mg, 1.09 mmol), anhydrous THF (4 mL), and a stirring bar. An anhydrous THF (3 mL) solution of 1,0-phenanthroline (197 mg, 1.09 mmol) was added to the reaction mixture to give a deep red solution. After 15 minutes, benzamide (138 mg, 1.14 mmol) was added to the reaction mixture as a solid in small portions with a spatula. After 3 h, the purple precipitate was collected on a porous frit, washed with pentane (20 mL), and dried under vacuum to give dark purple solids. Yield = 66%. ^{1}H NMR

(DMSO-d_6, 400 MHz, 25 °C): δ 9.00 (br s, 2H), 8.80 (d, J = 4.0 Hz, 2H), 8.26 (br s, 2H), 7.99 (br s, 3H), 7.71 (br s, 1H), 7.26 (br s, 3H). ^{13}C NMR (DMSO-d_6, 100 MHz, 25 °C: δ 173.0, 150.0, 143.6, 141.1, 137.7, 129.3, 128.9, 127.9, 127.5, 127.4, 126.0. FT-IR (Nujol): δ 3227 (m, NH), 3050 (m), 1622 (m), 1590 (vs), 1560 (vs), 1507 (w), 1492 (w), 1422 (s), 1400 (s), 1311 (w), 1300 (w), 1289 (vw), 1265 (m), 1224 (w), 1208 (w), 1068 (w), 1023 (w), 882 (w), 852 (s), 839 (s), 760 (s), 714 (s), 700 (s), 679 (m) cm^{-1}. Anal. Calcd for $C_{38}H_{28}N_6O_2Cu_2$: C, 62.71; H, 3.88; N, 11.55. Found: C, 61.78; H, 3.68; N, 11.48.

Synthesis of [(L1)CuCl]

In air and at room temperature, a 250 mL round-bottom flask was charged with $CuCl_2{\cdot}2H_2O$ (1.00 g, 5.87 mmol), a large stirring bar, and THF (20 mL). To this reaction mixture was slowly added a THF (5 mL) solution of **L1H** (1.00 g, 5.87 mmol) to give a dark forest green solution. After 15 minutes, triethylamine (900 μL, 6.46 mmol) was added to the reaction mixture. The reaction mixture was stirred for 3 h. The reaction mixture was filtered through a medium porosity frit containing Celite to remove $HClNEt_3$ and washed with THF (50 mL) to give a green filtrate. All volatile materials were evaporated under reduced pressure, and the resulting crude product was triturated with hexanes (25 mL) to give a green suspension. The green solids were collected via vacuum filtration and dried under vacuum to give product. Yield = 80%. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ 8.80 ($\Delta\nu_{1/2}$ = 63 Hz), 7.92 ($\Delta\nu_{1/2}$ = 50 Hz), 6.95 ($\Delta\nu_{1/2}$ = 25 Hz), 3.15 ($\Delta\nu_{1/2}$ = 62 Hz). 1.44 ($\Delta\nu_{1/2}$ = 38 Hz). FT-IR (KBr): δ 3081 (w), 3042 (m), 3028 (w), 3018 (w), 2978 (w), 2954 (w), 2884 (m), 2862 (m), 2834 (m), 1633 (s), 1597 (s), 1535 (s), 1471 (s), 1451 (s), 1395 (s), 1348 (s), 1325 (s), 1278 (w), 1241 (m), 1195 (s), 1183 (m), 1168 (w), 1146 (s), 1129 (m), 1103 (w), 1070 (m), 1038 (m), 1020 (s), 978 (m), 960 (m), 910 (s), 896 (m), 845 (m), 801 (w), 781 (m), 757 (s), 735 (s), 642 (m), 614 (s), 592 (m), 550 (m), 495 (w), 469 (s) cm^{-1}. UV-vis (CH_2Cl_2) nm (ε = M$^{-1}{\cdot}$cm^{-1}): 316 (13,919), 380 (13,360), 650 (609). Anal. Calcd for $C_{11}H_{15}N_2OCuCl$: C, 45.52; H, 5.21; N, 9.65. Found: C, 45.83; H, 5.11; N, 9.62.

Synthesis of [(L1)Cu(phth)] (6)

Under an atmosphere of nitrogen, a 100 mL round-bottom flask was charged with [(**L1**)CuCl] (1.00 g, 3.44 mmol), a medium-sized magnetic stirring bar, and anhydrous THF (50 mL). To this reaction mixture was added potassium phthalimide (670 mg, 3.62 mmol) under a positive flow of

nitrogen. The reaction mixture gradually became a blue-green suspension, and it was stirred for an additional 3 h. The suspension was filtered on a medium porosity frit by vacuum filtration in air. The collected green crystalline product was washed with THF (25 mL) and *n*-pentane (25 mL) and dried under vacuum to give product. Yield = 90%. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ 10.33 ($\Delta\nu_{1/2}$ = 150 Hz), 8.07 ($\Delta\nu_{1/2}$ = 200 Hz), 5.27 ($\Delta\nu_{1/2}$ = 5 Hz), 2.37 ($\Delta\nu_{1/2}$ = 6 Hz). FT-IR (KBr): δ 3052 (w), 3020 (w), 2984 (w), 2917 (w), 2847 (w), 2797 (w), 1725 (w), 1647 (s), 1623 (s), 1600 (s), 1526 (m), 1463 (m), 1443 (m), 1402 (w), 1371 (m), 1358 (m), 1350 (m), 1307 (s), 1247 (w), 1195 (m), 1181 (m), 1146 (m), 1127 (s), 1075 (w), 1027 (w), 983 (w), 956 (w), 907 (w), 852 (w), 796 (w), 774 (m), 724 (s), 678 (w), 643 (w), 620 (w), 592 (w), 536 (m) cm^{-1}. UV-vis (CH_2Cl_2), nm (ε = $M^{-1}\cdot cm^{-1}$): 380 (10,026), 593 (442). Anal. Calcd for $C_{19}H_{19}N_3O_3Cu$: C, 56.92; H, 4.78; N, 10.48. Found: C, 56.95; H, 4.71; N, 10.51.

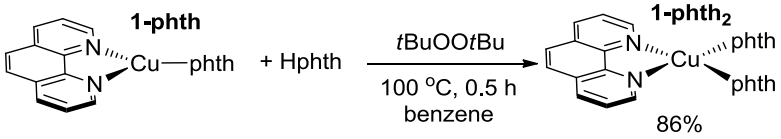
Synthesis of [(L1)Cu(NHSO$_2$Ph)] (7)

Under an atmosphere of nitrogen, a 100 mL round-bottom flask was charged with [(**L1**)CuCl] (1.00 g, 3.44 mmol), NaO^{t}Bu (352 mg, 3.66 mmol), a large magnetic stirring bar, and anhydrous THF (50 mL). The resulting yellow-brown solution was stirred at room temperature for 0.5 h. To this reaction mixture was added H_2NSO_2Ph (595 mg, 3.78 mmol) as a solid under a positive flow of nitrogen. The reaction mixture rapidly became a green suspension and was stirred for an additional 2.5 h. The green suspension was filtered on a medium porosity frit by vacuum filtration in air. The collected green crystalline product was washed with THF (25 mL) and *n*-pentane (25 mL) and dried under vacuum. Yield = 82%. ^{1}H NMR ($CDCl_3$, 200 MHz, 25 °C): δ 8.40 (v br, $\Delta\nu_{1/2}$ = 125 Hz), 7.53 ($\Delta\nu_{1/2}$ = 50 Hz), 7.02 ($\Delta\nu_{1/2}$ = 38 Hz). Line broadening into the baseline is possible to account for the reduction of expected proton resonances because from 2.0 – 5.0 ppm the baseline is broad. FT-IR (Nujol): δ 3290 (s), 3056 (w), 3015 (w), 2977 (w), 2887 (w), 2838 (w), 2795 (w), 1635 (s), 1601 (s), 1533 (s), 1453 (s), 1403 (s), 1353 (s), 1332 (s), 1241 (s), 1196 (s), 1162 (w), 1147 (s), 1130 (s), 1090 (s), 1025 (m), 1002 (w), 979 (s), 908 (s), 849 (w), 798 (w), 775 (s), 754 (s), 735 (s), 691 (s), 643 (w), 597 (s), 550 (s), 493 (w), 465 (w), 453 (w) cm^{-1}. UV-vis (CH_2Cl_2), nm (ε = $M^{-1}\cdot cm^{-1}$): 304 (9976), 380 (12,713), 622 (242). Anal. Calcd for $C_{17}H_{21}N_3O_3SCu$: C, 49.68; H, 5.15; N, 10.22; S, 7.80. Found: C, 49.50; H, 5.05; N, 10.03; S, 7.72.

Synthesis of [(L1)Cu(NHCOPh)] (8)

Under an atmosphere of nitrogen, a 100 mL round-bottom flask was charged with [(**L1**)CuCl] (1.00 g, 3.44 mmol), NaO^{t}Bu (352 mg, 3.66 mmol), a magnetic stirring bar, and anhydrous THF (25 mL) and Et_2O (25 mL). The resulting yellow-brown solution was stirred at room temperature for 0.5 h. To this reaction mixture was added H_2NCOPh (595 mg, 3.78 mmol) as a solid under a positive flow of nitrogen. The reaction mixture rapidly became a green suspension. The reaction mixture was stirred for an additional 2.5 h. The resulting light green crystalline material was collected on a medium porosity frit via vacuum filtration in air and dried under vacuum. Yield = 38%. ^{1}H NMR ($CDCl_3$, 400 MHz, 25 °C): δ 7.88 ($\Delta\nu_{1/2}$ = 20 Hz), 7.53-7.57 (m, $\Delta\nu_{1/2}$ = 50 Hz), 7.48 (m, $\Delta\nu_{1/2}$ = 20 Hz), 6.24 ($\Delta\nu_{1/2}$ = 150 Hz). 1.96 ($\Delta\nu_{1/2}$ = 200 Hz). FT-IR (KBr): δ 3368 (s), 3350 (s), 3175 (s), 3058 (w), 3024 (w), 2976 (w), 2858 (w), 2781 (w), 1678 (m), 1660 (m), 1634 (s), 1625 (s), 1599 (s), 1575 (m), 1552 (m), 1536 (m), 1468 (s), 1450 (w), 1403 (m), 1345 (m), 1321 (m), 1274 (w), 1250 (w), 1240 (w), 1215 (w), 1198 (m), 1151 (m), 1125 (w), 1105 (w), 1076 (w), 1033 (m), 1024 (m), 999 (w), 973 (w), 953 (w), 907 (m), 849 (w), 844 (w), 832 (w), 809 (w), 796 (w), 774 (w), 758 (s), 735 (w), 708 (s), 669 (w), 642 (w), 626 (w), 616 (w), 598 (w) cm^{-1}. UV-vis (CH_2Cl_2), nm (ε = M^{-1}·cm^{-1}): 382 (4,325), 651 (135). Anal. Calcd for $C_{19}H_{24}N_3O_2Cu$: C, 58.52; H, 6.20; N, 10.78. Found: C, 58.75; H, 6.15; N, 10.85.

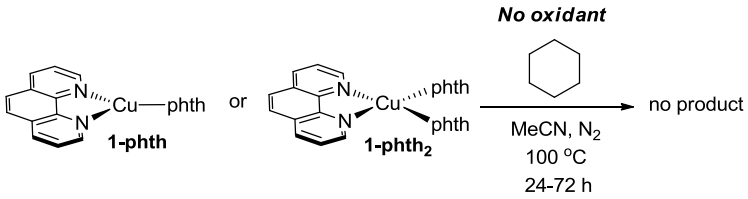
Isolation of 1-phth$_2$ from 1-phth



Inside a nitrogen-filled glovebox, an oven-dried 4 mL vial was charged with **1-phth** (20 mg, 0.060 mmol), phthalimide (11 mg, 0.080 mmol), a small stirring bar, and anhydrous benzene (2 mL). The vial was removed from the glovebox and to this reaction mixture was added ^{t}BuOO^{t}Bu (18.4 μL, 0.100 mmol) under a positive flow of dinitrogen. The orange reaction mixture was heated at 100 °C for 0.5 h and produced a light blue suspension. The blue solids were collected on a medium porosity frit and washed with THF (5 mL) and Et_2O (5 mL) and dried under vacuum. Yield = 86%. The identity of **1-phth$_2$** was confirmed by comparing the FT-IR spectrum

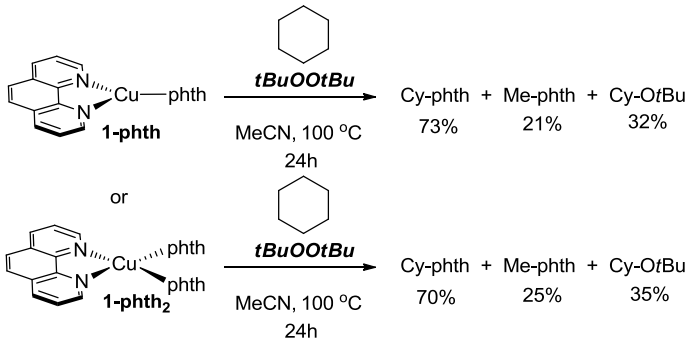
to that of an authentic sample of **1-phth$_2$** and elemental analysis. The aunthetic sample of **1-phth$_2$** was prepared from the reaction of [(phen)CuCl]$_2$(μ-Cl)$_2$ and Kphth (see above).

Stoichiometric reaction of 1-phth$_2$ or 1-phth with cyclohexane in the absence of *t*BuOO*t*Bu



In a nitrogen-filled glovebox, an oven-dried 4 mL scintillation vial was charged with **1-phth$_2$** (32 mg, 0.060 mmol) or **1-phth** (23 mg, 0.060 mmol), cyclohexane (500 μL, 5.00 mmol), MeCN (2 mL), and a small stirring bar. The vial was tightly sealed with a Teflon-lined cap, removed from the glovebox, and placed in a preheated aluminum block at 100 °C for 24–72 h. Analysis of the reaction mixture by gas chromatography [IS = dodecane (13.5 μL, 0.0600 mmol)] revealed no detectable Cy-phth product. The stoichiometric reactions were performed 3 times from independently synthesized batches of **1-phth** and **1-phth$_2$**.

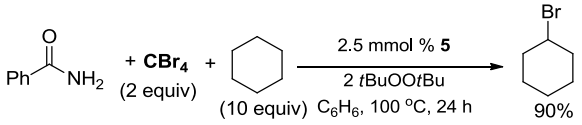
Stoichiometric reaction of 1-phth$_2$ or 1-phth with cyclohexane in the presence of *t*BuOO*t*Bu



In a nitrogen-filled glovebox, an oven-dried 4 mL scintillation vial was charged **1-phth$_2$** (32 mg, 0.060 mmol) or **1-phth** (23 mg, 0.060 mmol), cyclohexane (500 μL, 5.00 mmol), MeCN (2 mL), and a small stirring bar. The vial was tightly sealed with a Teflon-lined cap and removed from the glovebox. Under a positive pressure of nitrogen, *t*BuOO*t*Bu (200 μL, 1.00 mmol) was added to the reaction mixture. The vial was subsequently placed in a preheated aluminum block at 100 °C for 24 h. The yield of Cy-phth, Me-phth, and Cy-O*t*Bu from the reaction mixture was

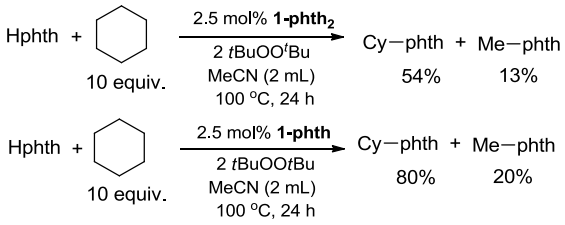
quantified by gas chromatography with dodecane (13.5 μL, 0.0600 mmol) as internal standard. The stoichiometric reactions were performed 3 times from independently synthesized batches of **1-phth** and **1-phth$_2$**.

Catalytic amidation of cyclohexane in the presence of CBr_4



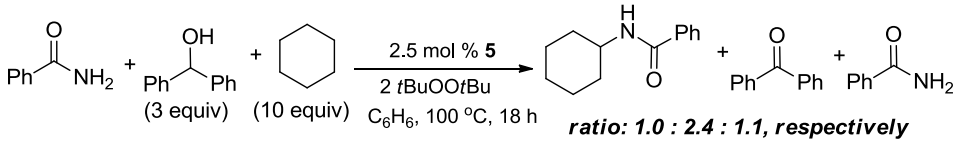
In a nitrogen-filled glovebox, an oven-dried 4 mL scintillation vial was charged with 2.5 mmol% of complex **5** (4.5 mg, 0.0012 mmol), benzamide (60 mg, 0.50 mmol), CBr_4 (332 mg, 1.00 mmol), cyclohexane (500 μL, 5.00 mmol), benzene (1.5 mL), and a small stirring bar. The vial was tightly sealed with a Teflon-lined cap and removed from the glovebox. The vial was placed in a preheated aluminum block at 100 °C for 24 h. Analysis of the reaction mixture was performed by gas chromatography with dodecane (113 μL, 0.500 mmol) as an internal standard. Bromocyclohexane was the only new product and was obtained in 90% based on benzamide.

Catalytic amidation of cyclohexane by 1-phth$_2$ and 1-phth in MeCN



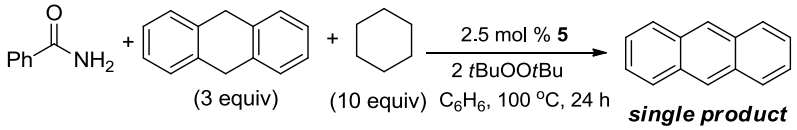
In a nitrogen-filled glovebox, an oven-dried 4 mL scintillation vial was charged with **1-phth$_2$** (6.9 mg, 0.012 mmol) or **1-phth** (5.1 mg, 0.012 mmol), cyclohexane (500 μL, 5.00 mmol), MeCN (2 mL), and a small stirring bar. The vial was removed from the glovebox. Under a positive pressure of nitrogen, *t*BuOO*t*Bu (200 μL, 1.00 mmol) was added to the reaction mixture. The vial was subsequently placed in a preheated aluminum block at 100 °C for 24 h. The yield of Cy-phth and Cy-O*t*Bu from the reaction mixture was quantified by gas chromatography with dodecane (113 μL, 0.500 mmol) as an internal standard. The reaction catalyzed by **1-phth** yielded Cy-phth (80%) and Cy-O*t*Bu (20%). The reaction catalyzed by **1-phth$_2$** yielded Cy-phth (54%) and Me-phth (13%) based on Hphth.

Catalytic amidation of cyclohexane in the presence of diphenylmethanol



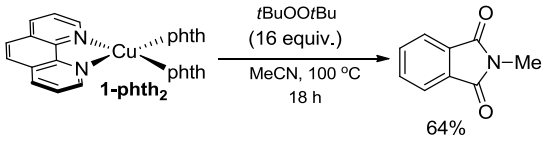
In a nitrogen-filled glovebox, an oven-dried 4 mL scintillation vial was charged with 2.5 mol% of **5** (4.5 mg, 0.012 mmol), benzamide (60.0 mg, 0.500 mmol), diphenylmethanol (184 mg, 1.50 mmol), and a small stirring bar. The vial was removed from the glovebox. Under a positive flow of dinitrogen, to the vial was added a mixture of cyclohexane (500 μL, 5.00 mmol), (154 μL, 1.50 mmol), *t*BuOO*t*Bu (200 μL, 1.00 mmol), and benzene (1.5 mL). The vial was placed in a preheated aluminum block at 100 °C for 24 h. The reaction mixture was analyzed by gas chromatography and the products were quantified against an internal standard of dodecane (113 μL, 0.500 mmol). The reaction produced *N*-cyclohexylbenzamide (47%, based on benzamide) and benzophenone in a ratio of 1.0:2.4, respectively.

Catalytic amidation of cyclohexane in the presence of 9,10-dihydroanthracene



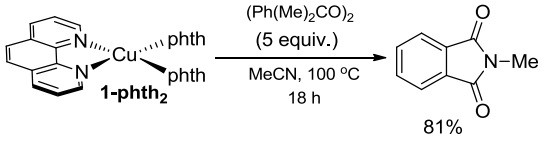
In a nitrogen-filled glovebox, an oven-dried 4 mL scintillation vial was charged with 2.5 mol% of **5** (4.5 mg, 0.012 mmol), benzamide (60 mg, 0.50 mmol), 9,10-dihydroanthracene (270 mg, 1.50 mmol), and a small stirring bar. The vial was then removed from the glovebox. Under a positive flow of dinitrogen, to the vial was added a mixture of cyclohexane (500 μL, 5.00 mmol), (154 μL, 1.50 mmol), *t*BuOO*t*Bu (200 μL, 1.00 mmol), and benzene (1.5 mL). The vial was placed in a preheated aluminum block at 100 °C for 24 h. The reaction mixture was analyzed by gas chromatography. The reaction produced only anthracene.

Alkyl-radical trapping experiment: stoichiometric reaction of 1-phth$_2$ with *t*BuOO*t*Bu



In a nitrogen-filled glovebox, an oven-dried 4 mL scintillation vial was charged with **1-phth$_2$** (32 mg, 0.060 mmol), MeCN (2 mL), and a small stirring bar. The vial was tightly sealed with a Teflon-lined cap and removed from the glovebox. Under a positive pressure of nitrogen, *t*BuOO*t*Bu (200 μL, 1.00 mmol) was added to the reaction mixture. The vial was subsequently placed in a preheated aluminum block at 100 °C for 18 h. The yield of *N*-methylphthalimide (64%, based on copper) was quantified by gas chromatography with dodecane (13.5 μL, 0.0600 mmol) as an internal standard.

Alkyl-radical trapping experiment: stoichiometric reaction of 1-phth$_2$ with (PhC(Me)$_2$O)$_2$



In a nitrogen-filled glovebox, an oven-dried 4 mL scintillation vial was charged with **1-phth$_2$** (32 mg, 0.060 mmol), MeCN (2 mL), and a small stirring bar. The vial was tightly sealed with a Teflon-lined cap and removed from the glovebox. Under a positive pressure of dinitrogen, solid (PhC(Me)$_2$O)$_2$ (81 mg, 0.30 mmol) was added to the reaction mixture. The vial was subsequently placed in a preheated aluminum block at 100 °C for 18 h. The yield of *N*-methylphthalimide (81%, based on copper) was quantified by gas chromatography with dodecane (13.5 μL, 0.0600 mmol) as an internal standard.

Measurement of the kinetic isotope effect (KIE) of the catalytic amidation from separate reactions of CyH and CyH-*d*$_{12}$.

In a nitrogen-filled dry-box, an oven-dried 4 mL scintilliation vial was charged with 10 mol% of **5** (18 mg, 0.50 mmol), benzamide (60 mg, 0.50 mmol), and a small stirring bar. The vial was removed from the glovebox. Under an atmosphere of nitrogen, this vial was added cyclohexane

(500 μL, 5.00 mmol), *t*BuOO*t*Bu (200 μL, 1.00 mmol), and benzene (1.5 mL). All the vials were loaded onto a preheated aluminum block at 100 °C. At each designated time interval, the vial was cooled to room temperature, and dodecane (113 μL, 0.500 mmol) was added to the reaction mixture as an internal standard. The quantification of the products was determined by gas chromatography. The rate of the reaction for cyclohexane-d_{12} (500 μL, 5.00 mmol) was performed under the same conditions for 5 h.

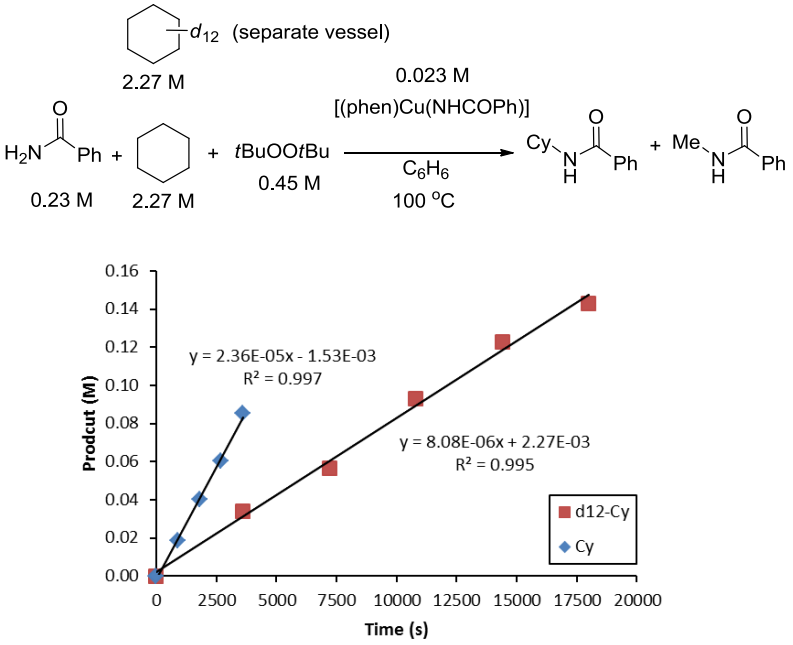


Figure S1. Rates of the amidation of CyH and CyH-d_{12}.

General procedure for measurement of the KIE from the reaction of a mixture of CyH and CyH-d_{12} in the same vessel.

Inside a nitrogen-filled glovebox, a 4 mL scintillation vial was charged with 2.5 mol % of [Cu] complex (1.25×10^{-2} mmol), benzamide (60 mg, 0.50 mmol), and a small stirring bar. The vial was removed from the glovebox. Under an atmosphere of nitrogen, this vial was charged with cyclohexane (250 μL, 2.50 mmol), cyclohexane-d_{12} (250 μL, 2.50 mmol), and *t*BuOO*t*Bu (200 μL, 1.00 mmol) in benzene (1.5 mL). After 20 h, the reaction mixture was cooled to room temperature, and dodecane (113 μL, 0.500 mmol) was added as an internal standard. The ratio of products from reaction of cyclohexane and cyclohexane-d_{12} was quantified by gas chromatography.

General set-up for kinetic studies on the catalytic amidation of cyclohexane by benzamide

In a nitrogen-filled glovebox, an oven-dried 4 mL scintillation vial was charged with 10 mol % of **5** (18 mg, 0.050 mmol), benzamide (60 mg, 0.50 mmol), and a small stirring bar. The vial was removed from the glovebox. Under an atmosphere of nitrogen, to this vial was charged cyclohexane (500 μL, 5.00 mmol), *t*BuOO*t*Bu (200 μL, 1.00 mmol), and benzene (1.5 mL). All the vials were loaded onto a preheated aluminum block at 100 °C. At each designated time interval, the vial was cooled to room temperature, and dodecane (113 μL, 0.500 mmol) was added to the reaction mixture as an internal standard. The quantification of products was determined by gas chromatography.

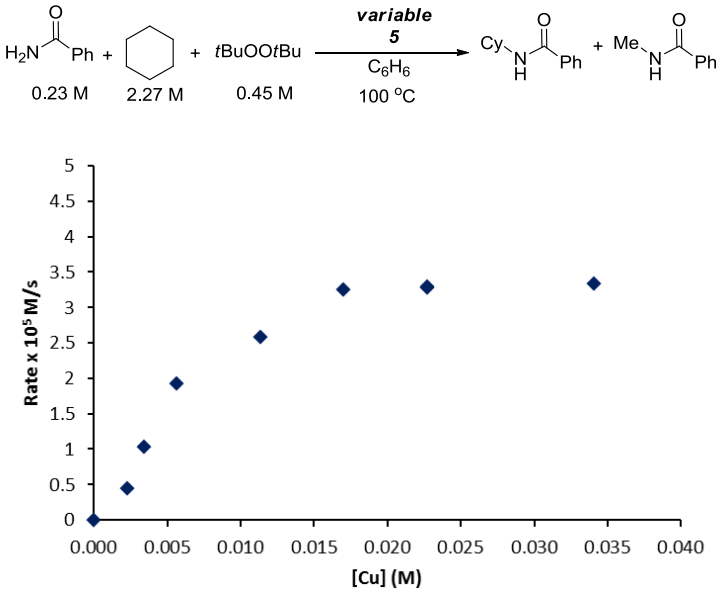


Figure S2. Effect of [Cu] on the rate of the catalytic amidation of cyclohexane.

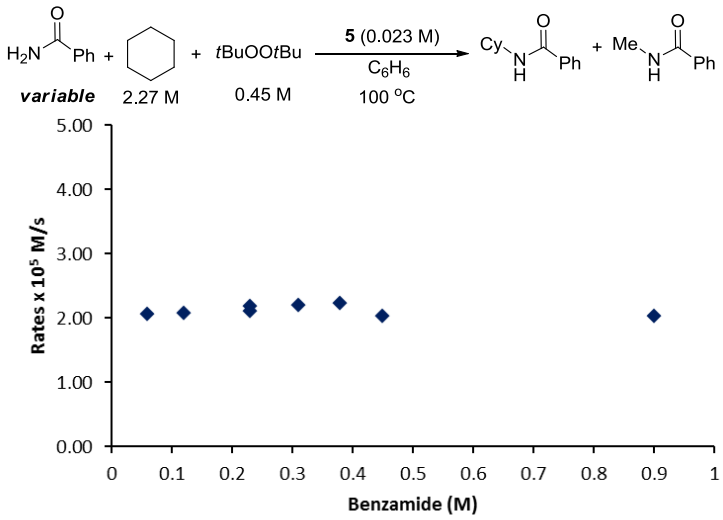


Figure S3. Effect of the concentration of benzamide on the rate of the catalytic amidation of cyclohexane.

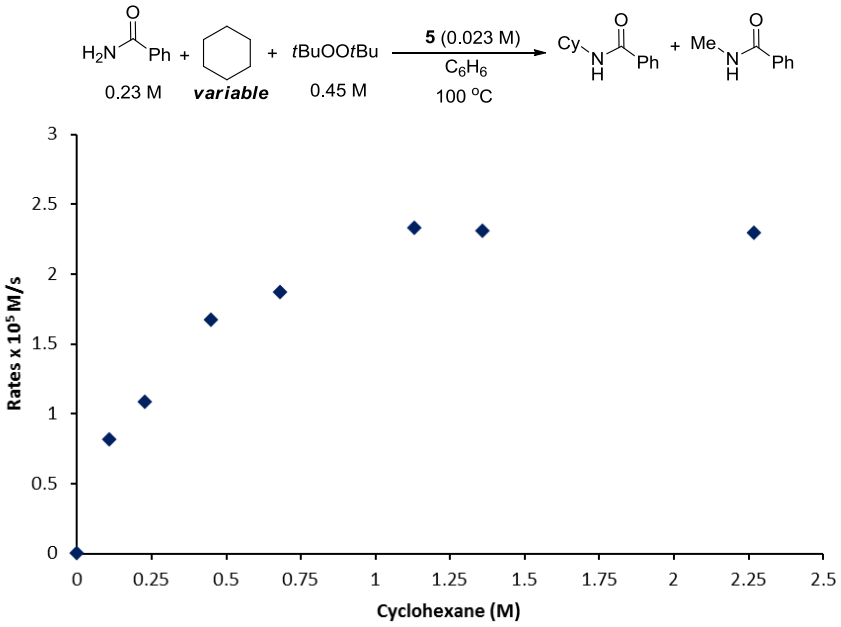


Figure S4. Effect of the concentration of cyclohexane on the rate of the catalytic amidation of cyclohexane.

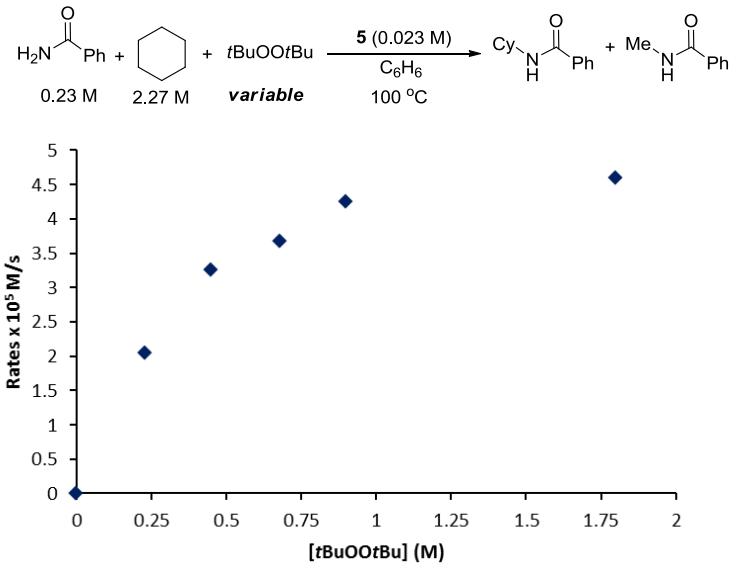
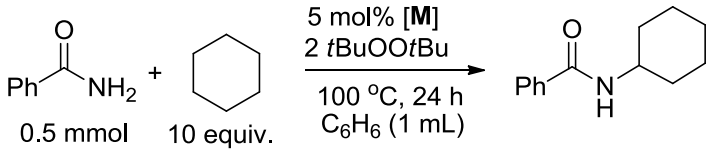


Figure S5. Effect of the concentration of *t*BuOO*t*Bu on the rate of the catalytic amidation of cyclohexane.

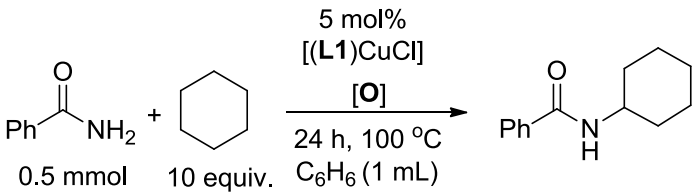
Table S1. Effect of the metal identity on the amidation of cyclohexane



Entry	[**M**]	% Yield[a]
1	(**L1**)CuCl	83
2	$(acac)_2Cu$	88
3	$(acac)_2Fe$	NP
4	$(acac)_2Co$	NP
5	$(acac)_2Ni$	NP
6	$(acac)_2Mn$	NP

[a]Yields of the C-N product were determined by GC analysis with dodecane as an internal standard. NP = no product.

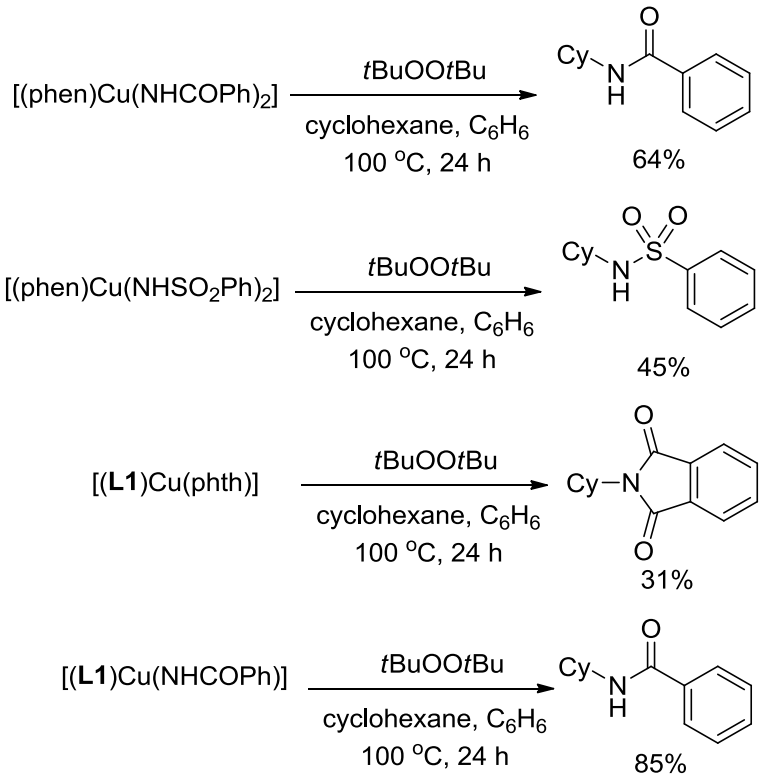
Table S2. Effect of the identity of the oxidant on the Cu-catalyzed amidation of cyclohexane with benzamide



Entry	[**O**]	Equiv.	% Yield[a]
1	*t*BuOO*t*Bu	2	83
2	$PhCMe_2OOH$	2	NP
3	*t*BuOOH	2	NP
4	*t*BuOOCOPh	2	NP
5	PhIO	2	NP
6	$PhI(OAc)_2$	2	NP

[a]Yields of the C-N product were determined by GC analysis with dodecane as an internal standard. NP = no product.

Scheme S1. Stoichiometric reactions of copper(II) amidate and imidate complexes



Important Note: In all of the above stoichiometric reactions, no *N*-alkyl product was observed in the absence of *t*BuOO*t*Bu.

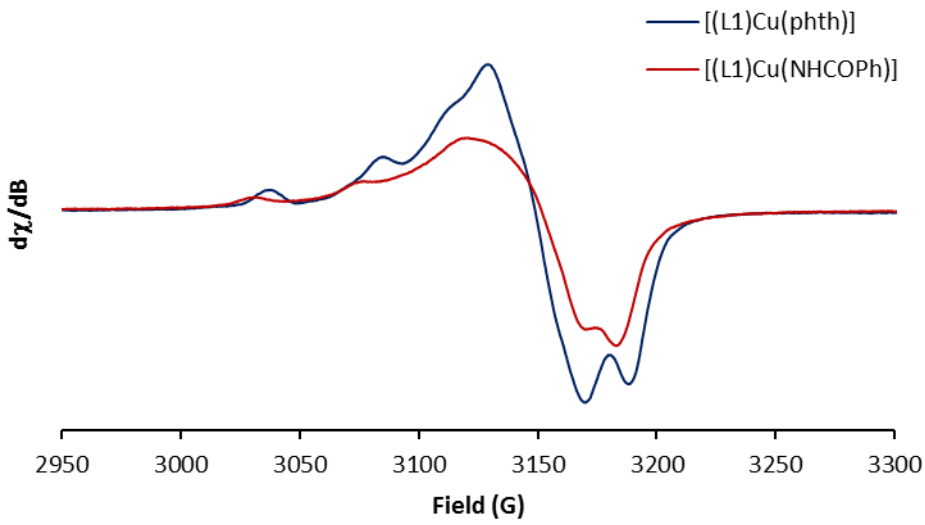


Figure S6. X-Band EPR of [(**L1**)Cu(phth)] (**6**) and [(**L1**)Cu(NHCOPh)] (**8**) in CH_2Cl_2 at 20 K.

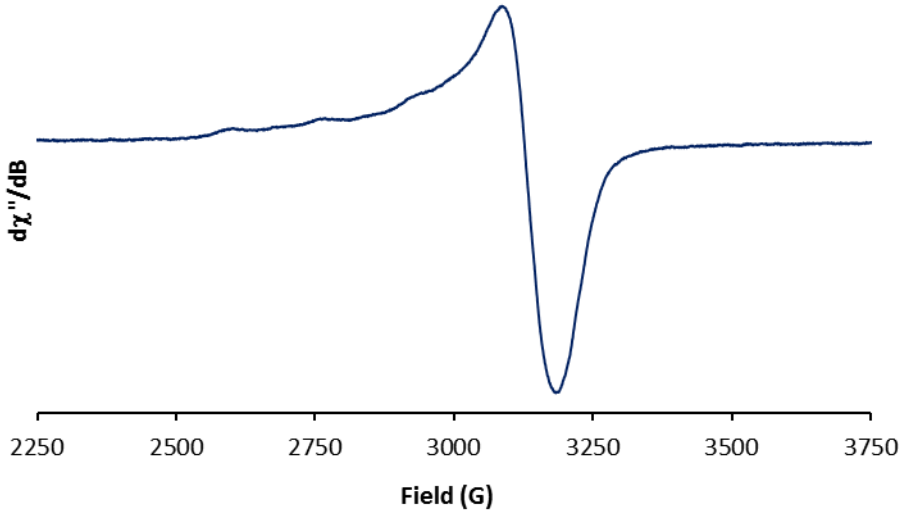


Figure S7. X-Band EPR of [(phen)Cu(phth)$_2$] (**1-phth$_2$)** in DMSO at 20 K.

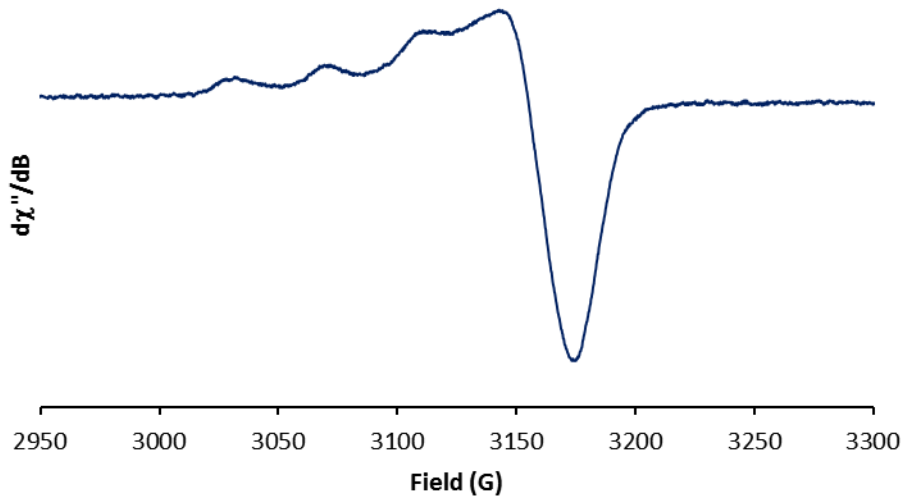
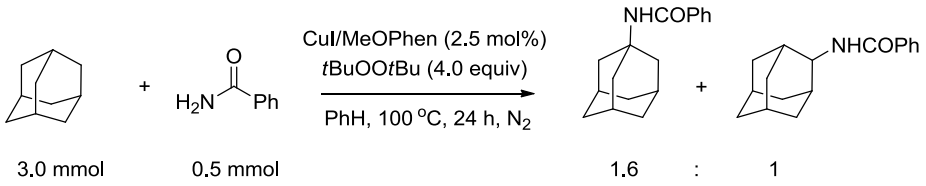


Figure S8. X-Band EPR of [(phen)Cu($NHSO_2Ph)_2$] (**2**) in DMSO at 20 K.

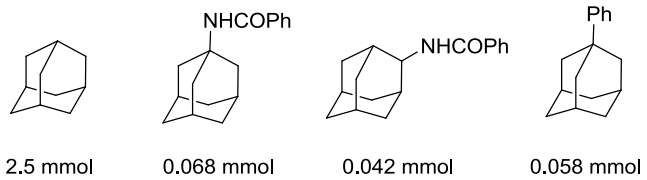
Mass balance experiment for the reaction of adamantane

In a nitrogen-filled glovebox, an oven-dried 4 mL scintillation vial was charged with CuI (2.4 mg, 0.013 mmol), 4,7-dimethoxy-1,10-phenanthroline (3.0 mg, 0.013 mmol), benzamide (60.5 mg, 0.500 mmol), adamantane (408 mg, 3.00 mmol), benzene (2.0 mL), and a small stirring bar. The vial was removed from the glovebox. Under a positive flow of dinitrogen, *t*BuOO*t*Bu (292 mg, 2.00 mmol) was added to the vial. The vial was tightly sealed with a Teflon-lined cap and stirred in a preheated aluminum block at 100 °C for 24 h. Analysis of the reaction mixture was performed by gas chromatography with dodecane (113 μL, 0.500 mmol) as an internal standard.

Scheme S2. Mass balance for adamantane.



Product distribution:



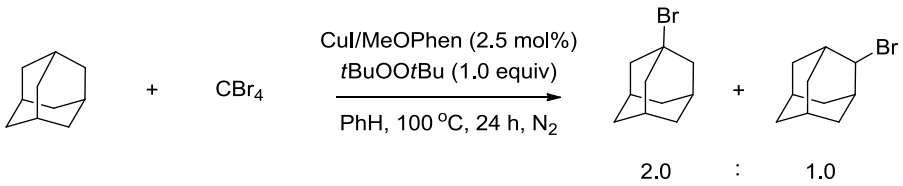
Mass balance: (2.5 + 0.11 + 0.058) / 3.0 = 90%

tertiary / secondary = (0.068 + 0.58) / 0.042 = 3.0 / 1

Catalytic amidation of adamantane in the presence of CBr_4

In a nitrogen-filled glovebox, an oven-dried 4 mL scintillation vial was charged with CuI (1.2 mg, 0.0063 mmol), 4,7-dimethoxy-1,10-phenanthroline (1.5 mg, 0.0063 mmol), benzamide (30.3 mg, 0.250 mmol), adamantane (680 mg, 5.00 mmol), CBr_4 (83.0 mg, 0.250 mmol), benzene (2.0 mL), and a small stirring bar. The vial was removed from the glovebox. Under a positive flow of dinitrogen, *t*BuOO*t*Bu (36.5 mg, 0.250 mmol) was added to the vial. The vial was tightly sealed with a Teflon-lined cap and stirred in a preheated aluminum block at 100 °C for 24 h. Analysis of the reaction mixture was performed by gas chromatography with dodecane (113 μL, 0.500 mmol) as an internal standard.

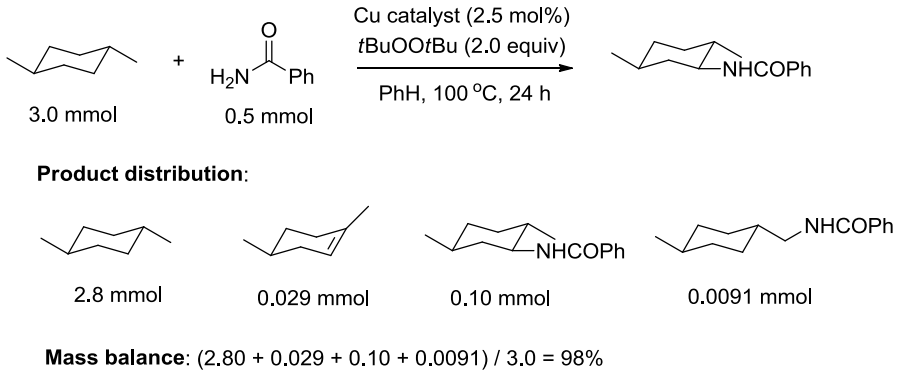
Scheme S3. Radical trapping experiment of adamantane.



Mass balance experiment for the reaction of *trans*-1,4-dimethylcyclohexane:

In a nitrogen-filled glovebox, an oven-dried 4 mL scintillation vial was charged with CuI (2.4 mg, 0.013 mmol), 4,7-dimethoxy-1,10-phenanthroline (3.0 mg, 0.013 mmol), benzamide (60.5 mg, 0.500 mmol), *trans*-1,4-dimethylcyclohexane (336 mg, 3.00 mmol), benzene (2.0 mL), and a small stirring bar. The vial was removed from the glovebox. Under a positive flow of dinitrogen, *t*BuOO*t*Bu (146 mg, 1.00 mmol) was added to the vial. The vial was tightly sealed with a Teflon-lined cap and stirred in a preheated aluminum block at 100 °C for 24 h. Analysis of the reaction mixture was performed by gas chromatography with dodecane (113 μL, 0.500 mmol) as an internal standard.

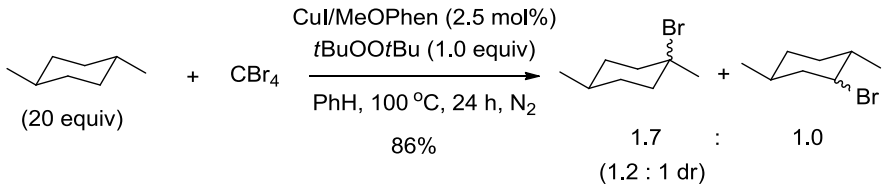
Scheme S4. Mass balance for trans-1,4-dimethylcyclohexane.



Catalytic amidation of *trans*-1,4-dimethylcyclohexane in the presence of CBr_4

In a nitrogen-filled glovebox, an oven-dried 4 mL scintillation vial was charged with CuI (1.2 mg, 0.0063 mmol), 4,7-dimethoxy-1,10-phenanthroline (1.5 mg, 0.0063 mmol), benzamide (30.3 mg, 0.250 mmol), *trans*-1,4-dimethylcyclohexane (560 mg, 5.00 mmol), CBr_4 (83.0 mg, 0.250 mmol), benzene (2.0 mL), and a small stirring bar. The vial was removed from the glovebox. Under a positive flow of dinitrogen, *t*BuOO*t*Bu (36.5 mg, 0.250 mmol) was added to the vial. The vial was tightly sealed with a Teflon-lined cap and stirred in a preheated aluminum block at 100 °C for 24 h. Analysis of the reaction mixture was performed by gas chromatography with dodecane (113 μL, 0.500 mmol) as an internal standard.

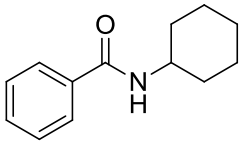
Scheme S5. Radical trapping experiment of trans-1,4-dimethylcyclohexane.



General Procedure for the Catalytic Amidation of Alkanes

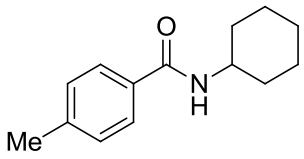
In air, a small 3 mL scintillation vial containing CuI (2.4 mg, 0.013 mmol), 4,7-dimethoxy-1,10-phenanthroline (3.0 mg, 0.013 mmol), and benzamide (60.5 mg, 0.500 mmol), was charged with benzene (1.0 mL), cyclohexane (420 mg, 5.00 mmol), and *t*BuOO*t*Bu (146 mg, 1.00 mmol) via syringe. The vial was capped with a Teflon lined cap and placed in a heating block at 100 °C for 24 h. After cooling to room temperature, the reaction mixture was directly purified by column chromatography on silica gel with ethyl acetate and hexanes as eluent.

***N*-cyclohexylbenzamide**



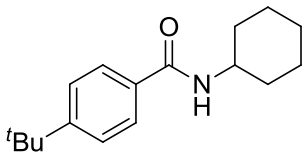
The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), benzamide (60.5 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (77.2 mg, 76% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.74 (m, 2H), 7.54–7.47 (m, 1H), 7.42 (dd, *J* = 11.4, 4.4 Hz, 2H), 6.19 (s, 1H), 4.07–3.91 (m, 1H), 2.04 (dd, *J* = 12.2, 2.9 Hz, 2H), 1.85–1.72 (m, 2H), 1.67 (dd, *J* = 9.2, 3.8 Hz, 1H), 1.52–1.34 (m, 2H), 1.34–1.18 (m, 3H). GC-MS: *m*/*z* 203 (35%, $[M^+]$), 160 (10%, $[M–C_3H_7]^+$), 105 (100%, [M-CyNH]$^+$). *N*-cyclohexylbenzamide was previously reported by Jiang, H.; Liu, B.; Li, Y.; Wang, A.; Huang, H. *Org. Lett.* **2011**, *13*, 1028.

***N*-cyclohexyl-4-methylbenzamide**



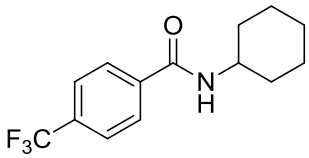
The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), 4-methylbenzamide (67.5 mg, 0.500 mmol), *t*BuO*Ot*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (77.2 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.1 Hz, 2H), 7.21 (d, *J* = 8.0 Hz, 2H), 6.22 (s, 1H), 3.97 (tdt, *J* = 11.8, 8.0, 3.8 Hz, 1H), 2.39 (s, 3H), 2.10–1.89 (m, 2H), 1.81–1.71 (m, 2H), 1.71–1.58 (m, 1H), 1.48–1.32 (m, 2H), 1.32–1.10 (m, 3H). GC-MS: *m*/*z* 217 (30%, $[M^+]$), 174 (4.0%, $[M–C_3H_7]^+$), 119 (100%, [M-CyNH]$^+$). *N*-cyclohexyl-4-methylbenzamide was previously reported by Jo, Y.; Ju, J.; Choe, J.; Song, K. H.; Lee, S. *J. Org. Chem.* **2009**, *74*, 6358.

4-(*tert*-butyl)-*N*-cyclohexylbenzamide



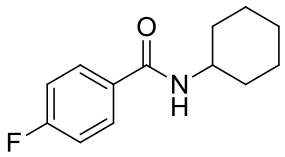
The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), 4-*tert*-butylbenzamide (88.5 mg, 0.500 mmol), *t*BuO*Ot*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (82.9 mg, 64% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74 (d, *J* = 8.3 Hz, 2H), 7.45 (d, *J* = 8.3 Hz, 2H), 6.21 (d, *J* = 6.1 Hz, 1H), 3.99 (tdt, *J* = 11.7, 8.1, 3.9 Hz, 1H), 2.08–1.96 (m, 2H), 1.82–1.71 (m, 2H), 1.71–1.60 (m, 1H), 1.47–1.38 (m, 2H), 1.35 (s, 9H), 1.32–1.14 (m, 3H). GC-MS: *m*/*z* 259 (50%, $[M^+]$), 176 (85%, $[M–Cy]^+$), 161 (100%, [M-CyNH]$^+$). 4-(*tert*-butyl)-*N*-cyclohexylbenzamide was previously reported by Jo, Y.; Ju, J.; Choe, J.; Song, K. H.; Lee, S. *J. Org. Chem.* **2009**, *74*, 6358.

***N*-cyclohexyl-4-(trifluoromethyl)benzamide**



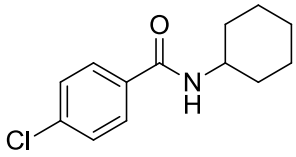
The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), 4-trifluoromethylbenzamide (94.5 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (98.6 mg, 73% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, *J* = 8.2 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 6.24 (d, *J* = 6.9 Hz, 1H), 4.00 (tdt, *J* = 11.6, 8.0, 3.9 Hz, 1H), 2.12–1.97 (m, 2H), 1.84–1.74 (m, 2H), 1.74–1.62 (m, 1H), 1.52–1.37 (m, 2H), 1.37–1.14 (m, 3H). GC-MS: *m*/*z* 271 (18%, $[M^+]$), 252 (8.0%, $[M–F]^+$), 173 (100%, $[M\text{-}CyNH]^+$). *N*-cyclohexyl-4-(trifluoromethyl)benzamide was previously reported by Prosser, A. R.; Banning, J. E.; Rubina, M.; Rubin, M. *Org. Lett.* **2010**, *12*, 3968.

_N_-cyclohexyl-4-fluorobenzamide



The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), *p*-fluorobenzamide (69.5 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (86.5 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 – 7.58 (m, 1H), 7.07 (t, *J* = 8.6 Hz, 2H), 6.01 (s, 1H), 3.94 (m, 1H), 2.00 (d, *J* = 12.1 Hz, 2H), 1.86 – 1.53 (m, 3H), 1.40 (td, *J* = 12.1, 3.2 Hz, 2H), 1.30–0.99 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.55, 164.52 (d, *J* = 249 Hz), 131.20 (d, *J* = 3 Hz), 129.10 (d, *J* = 8 Hz), 115.43 (d, *J* = 22 Hz), 48.77, 33.17, 25.49, 24.88. ESI-HR calc'd for $C_{13}H_{16}NOFNa$ ($[M+Na]^+$) 244.1108, found 244.1106.

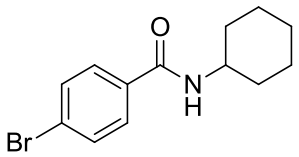
4-chloro-_N_-cyclohexylbenzamide



The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), 4-chlorobenzamide (77.8 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (97.4 mg, 82% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d,

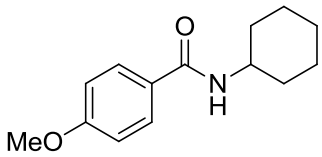
J = 8.5 Hz, 2H), 7.42–7.34 (m, 2H), 6.25 (d, *J* = 7.1 Hz, 1H), 3.95 (tdt, *J* = 11.6, 8.0, 3.9 Hz, 1H), 2.08–1.95 (m, 2H), 1.83–1.72 (m, 2H), 1.72–1.60 (m, 1H), 1.50–1.33 (m, 2H), 1.33–1.13 (m, 3H). GC-MS: *m*/*z* 237, 239 (25%, 8.0%, $[M^+]$), 156, 158 (75%, 25%, $[M–C_6H_9]^+$), 139, 141 (100%, 33%, $[M\text{-}CyNH]^+$). Ohshima, T.; Iwasaki, T.; Maegawa, Y.; Yoshiyama, A.; Mashima, K. *J. Am. Chem. Soc.* **2008**, *130*, 2944.

4-bromo-*N*-cyclohexylbenzamide



The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), 4-bromobenzamide (100 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (108 mg, 77% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.5 Hz, 2H), 7.56 (d, *J* = 8.5 Hz, 2H), 6.15 (d, *J* = 6.7 Hz, 1H), 3.97 (tdt, *J* = 11.6, 8.0, 3.9 Hz, 1H), 2.09–1.96 (m, 2H), 1.85–1.73 (m, 2H), 1.73–1.61 (m, 1H), 1.43 (tt, *J* = 15.5, 3.2 Hz, 2H), 1.35–1.13 (m, 3H). GC-MS: *m*/*z* 281, 283 (30%, $[M^+]$), 200, 202 (75%, $[M–C_6H_9]^+$), 183, 185 (100%, $[M\text{-}CyNH]^+$). 4-bromo-*N*-cyclohexylbenzamide was previously reported by Pelletier, G.; Bechara, W. B.; Charette, A. B. *J. Am. Chem. Soc.* **2010**, *132*, 12817.

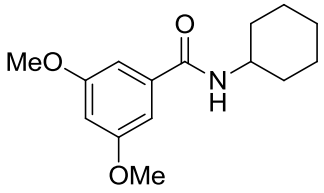
***N*-cyclohexyl-4-methoxybenzamide**



The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), 4-methoxybenzamide (75.5 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (91.3 mg, 78% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.69 (m, 2H), 6.97–6.85 (m, 2H), 6.08 (d, *J* = 7.0 Hz, 1H), 4.05–3.89 (m, 1H), 3.86 (s, 3H), 2.09–1.96 (m, 2H), 1.76 (ddd, *J* = 23.3, 13.6, 10.0 Hz, 2H), 1.71–1.60 (m, 1H), 1.50–1.34 (m, 2H), 1.34–1.14 (m, 3H). GC-MS: *m*/*z* 233 (20%, $[M^+]$), 151 (35%, $[M–C_6H_{10}]^+$), 135 (100%,

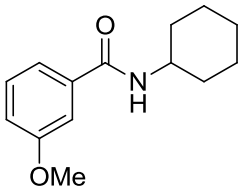
[M-CyNH]$^+$). *N*-cyclohexyl-4-methoxybenzamide was previously reported by Pelletier, G.; Bechara, W. B.; Charette, A. B. *J. Am. Chem. Soc.* **2010**, *132*, 12817.

_N_-cyclohexyl-3,5-dimethoxybenzamide



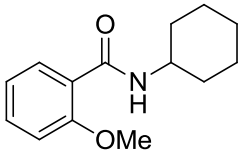
The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), 3,5-dimethoxybenzamide (90.5 mg, 0.500 mmol), *t*BuO*Ot*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (76.4 mg, 58% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.86 (d, *J* = 1.2 Hz, 2H), 6.52 (t, *J* = 2.2 Hz, 1H), 3.98–3.84 (m, 1H), 3.77 (s, 6H), 2.04–1.90 (m, 2H), 1.77–1.66 (m, 2H), 1.66–1.55 (m, 1H), 1.45–1.29 (m, 2H), 1.25–1.14 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.34, 160.70, 137.28, 104.76, 103.08, 55.42, 48.64, 33.01, 25.44, 24.82. ESI-HR calc'd for $C_{15}H_{21}NO_3Na$ ([M+Na]$^+$) 286.1414, found 286.1412.

_N_-cyclohexyl-3-methoxybenzamide



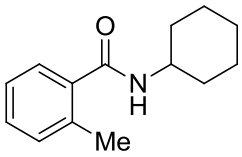
The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), 3-methoxybenzamide (75.5 mg, 0.500 mmol), *t*BuO*Ot*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (80.2 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.33 (m, 1H), 7.33–7.27 (m, 2H), 7.04–6.97 (m, 1H), 6.30 (d, *J* = 7.6 Hz, 1H), 4.03–3.87 (m, 1H), 3.82 (s, 3H), 2.07–1.96 (m, 2H), 1.79–1.69 (m, 2H), 1.69–1.58 (m, 1H), 1.47–1.32 (m, 2H), 1.32–1.14 (m, 3H). GC-MS: *m*/*z* 233 (15%, [M$^+$]), 151 (40%, [M–C_6H_{10}]$^+$), 135 (100%, [M-CyNH]$^+$). *N*-cyclohexyl-3-methoxybenzamide was previously reported by Jo, Y.; Ju, J.; Choe, J.; Song, K. H.; Lee, S. *J. Org. Chem.* **2009**, *74*, 6358.

***N*-cyclohexyl-2-methoxybenzamide**



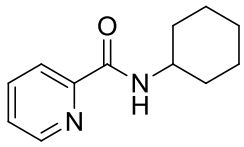
The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), 2-methoxybenzamide (75.5 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (81.2 mg, 70% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.22 (dd, *J* = 7.8, 1.8 Hz, 1H), 7.84 (d, *J* = 5.5 Hz, 1H), 7.48–7.38 (m, 1H), 7.08 (t, *J* = 7.5 Hz, 1H), 6.98 (d, *J* = 8.3 Hz, 1H), 4.11–3.99 (m, 1H), 3.97 (s, 3H), 2.09–1.95 (m, 2H), 1.81–1.69 (m, 2H), 1.69–1.57 (m, 1H), 1.46 (tt, *J* = 13.9, 3.1 Hz, 2H), 1.39–1.23 (m, 3H). GC-MS: *m*/*z* 233 (25%, $[M^+]$), 218 (2.0%, $[M–CH_3]^+$), 135 (100%, $[M\text{-}CyNH]^+$). *N*-cyclohexyl-2-methoxybenzamide was previously reported Jo, Y.; Ju, J.; Choe, J.; Song, K. H.; Lee, S. *J. Org. Chem.* **2009**, *74*, 6358.

***N*-cyclohexyl-2-methylbenzamide**



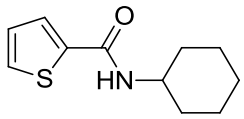
The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), 2-methylbenzamide (67.5 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (59.7 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37–7.27 (m, 2H), 7.25–7.17 (m, 2H), 5.75 (br, 1H), 4.07–3.86 (m, 1H), 2.45 (s, 3H), 2.11–1.98 (m, 2H), 1.82–1.72 (m, 2H), 1.72–1.60 (m, 1H), 1.50–1.35 (m, 2H), 1.33–1.12 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.20, 136.95, 135.62, 130.77, 129.51, 126.50, 125.59, 48.39, 33.09, 25.46, 24.80, 19.56. ESI-HR calc'd for $C_{14}H_{20}NO$ ($[M+H]^+$) 218.1539, found 218.1538.

***N*-cyclohexylpicolinamide**



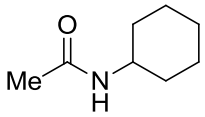
The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), picolinamide (61.0 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (85.6 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.53–8.46 (m, 1H), 8.17 (d, *J* = 7.8 Hz, 1H), 7.92 (t, *J* = 22.1 Hz, 1H), 7.80 (td, *J* = 7.7, 1.5 Hz, 1H), 7.43–7.33 (m, 1H), 4.01–3.84 (m, 1H), 1.98 (dd, *J* = 12.2, 2.9 Hz, 2H), 1.80–1.67 (m, 2H), 1.61 (dd, *J* = 9.1, 3.9 Hz, 1H), 1.43–1.20 (m, 5H). GC-MS: *m*/*z* 204 (20%, $[M^+]$), 161 (30%, $[M–C_3H_7]^+$), 98 (100%, $[M\text{-}PyCO]^+$). *N*-cyclohexylpicolinamide was previously reported by Auzeil, N.; Largeron, M.; Fleury, M. B. *J. Chem. Soc., Perkin Trans. 2*, **1999**, 1703.

***N*-cyclohexylthiophene-2-carboxamide**



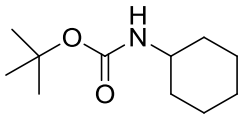
The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), thiophene-2-carboxamide (64.0 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (48.5 mg, 47% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 15.5, 14.8 Hz, 1H), 7.48–7.34 (m, 1H), 7.06 (dd, *J* = 4.8, 3.8 Hz, 1H), 6.22 (d, *J* = 6.4 Hz, 1H), 3.95 (tdt, *J* = 11.8, 8.0, 3.9 Hz, 1H), 2.02 (dd, *J* = 17.5, 8.3 Hz, 2H), 1.81–1.69 (m, 2H), 1.65 (dd, *J* = 9.3, 3.6 Hz, 1H), 1.45–1.32 (m, 2H), 1.32–1.15 (m, 3H). GC-MS: *m*/*z* 209 (15%, $[M^+]$), 166 (8.0%, $[M–C_3H_7]^+$), 111 (100%, $[M\text{-}CyNH]^+$). *N*-cyclohexylthiophene-2-carboxamide was previously reported by Pelletier, G.; Bechara, W. B.; Charette, A. B. *J. Am. Chem. Soc.* **2010**, *132*, 12817.

***N*-cyclohexylacetamide**



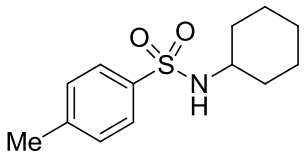
The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), acetamide (29.5 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (26.8 mg, 38% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.36 (s, 1H), 3.79 (tdt, *J* = 12.0, 8.1, 4.0 Hz, 1H), 1.99 (s, 3H), 1.98–1.91 (m, 2H), 1.79–1.70 (m, 2H), 1.70–1.60 (m, 1H), 1.47–1.33 (m, 2H), 1.25–1.07 (m, 3H). GC-MS: *m*/*z* 141 (30%, $[M^+]$), 112 (4.0%, $[M–C_2H_5]^+$), 60 (100%, $[M\text{-}Cy]^+$). *N*-cyclohexylacetamide was previously reported by Cazorla, C.; Métay, E.; Lemaire, M. *Tetrahedron* **2011**, *67*, 8615.

***tert*-butyl cyclohexylcarbamate**



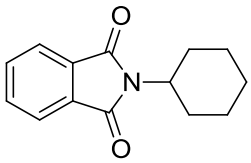
The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), *tert*-butyl carbamate (58.5 mg, 0.500 mmol), *t*BuOO*t*Bu (292 mg, 4.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of ,2-dichlorobenzene at 100 ºC to give the title compound as a white solid after column chromatography (76.3 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.47 (s, 1H), 3.44 (s, 1H), 1.92 (dd, *J* = 19.1, 16.5 Hz, 2H), 1.78–1.65 (m, 2H), 1.60 (ddd, *J* = 27.9, 15.6, 12.1 Hz, 1H), 1.46 (s, 9H), 1.32 (dd, *J* = 23.7, 11.3 Hz, 2H), 1.23–1.01 (m, 3H). GC-MS: *m*/*z* 199 (2.0%, $[M^+]$), 143 (35%, $[M–C_4H_9]^+$), 57 (100%, $[C_4H_9]^+$). *tert*-butyl cyclohexylcarbamate was previously reported by Guin, J.; Fröhlich, R.; Studer, A. *Angew. Chem. Int. Ed.* **2008**, *47*, 779.

***N*-cyclohexyl-4-methylbenzenesulfonamide**



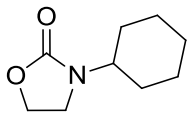
The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), 4-methylbenzenesulfonamide (85.6 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (69.7 mg, 55% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84–7.78 (m, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 4.99 (s, 1H), 3.14 (td, *J* = 13.5, 6.9 Hz, 1H), 2.45 (s, 3H), 1.76 (d, *J* = 10.5 Hz, 2H), 1.67–1.63 (m, 2H), 1.52 (d, *J* = 12.1 Hz, 1H), 1.33– 1.05 (m, 5H). GC-MS: *m*/*z* 253 (25%, $[M^+]$), 214 (100%, $[M–C_3H_7]^+$), 155 (60%, $[M\text{-}CyNMe]^+$). *N*-cyclohexyl-4-methylbenzenesulfonamide was previously reported by Zhang, J.; Yang, C.-G.; He, C. *J. Am. Chem. Soc.* **2006**, *128*, 1798.

2-cyclohexylisoindoline-1,3-dione



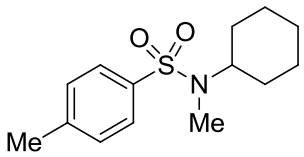
The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), phthalimide (73.5 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of 1,2-dichlorobenzene at 100 ºC to give the title compound as a white solid after column chromatography (85.7 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–7.79 (m, 2H), 7.76–7.66 (m, 2H), 4.13 (tt, *J* = 12.3, 3.9 Hz, 1H), 2.23 (qd, *J* = 12.5, 3.1 Hz, 2H), 1.85 (dd, *J* = 26.0, 14.2 Hz, 2H), 1.74 (dd, *J* = 20.0, 6.9 Hz, 3H), 1.47–1.20 (m, 3H). GC-MS: *m*/*z* 229 (25%, $[M^+]$), 186 (30%, $[M–C_3H_7]^+$), 148 (100%, $[M\text{-}Cy]^+$). 2-cyclohexylisoindoline-1,3-dione was previously reported by Worlikar, S. A.; Larock, R. C. *J. Org. Chem.* **2008**, *73*, 7175.

3-cyclohexyloxazolidin-2-one



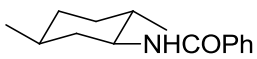
The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), oxazolidin-2-one (43.5 mg, 0.50 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a clear oil after column chromatography (38.8 mg, 46% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.35–4.17 (m, 2H), 3.73–3.57 (m, 1H), 3.48 (dd, *J* = 8.7, 7.3 Hz, 2H), 1.77–1.76 (m, 4H), 1.69–1.53 (m, 1H), 1.39–1.24 (m, 4H), 1.15–0.94 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 157.70, 61.88, 52.33, 40.41, 30.12, 25.20, 25.17. ESIHR calc'd for $C_9H_{15}NO_2Na$ ($[M+Na]^+$) 192.0995, found 192.0993.

_N_-cyclohexyl-_N_,4-dimethylbenzenesulfonamide



The reaction was performed according to the general procedure with cyclohexane (420 mg, 10.0 equiv), *N*,4-dimethylbenzenesulfonamide (92.6 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (39.2 mg, 30% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (d, *J* = 8.2 Hz, 2H), 7.31 (d, *J* = 7.8 Hz, 2H), 3.85–3.72 (m, 1H), 2.76 (s, 3H), 2.44 (s, 3H), 1.81–1.68 (m, 2H), 1.63 (d, *J* = 12.1 Hz, 1H), 1.51 (d, *J* = 6.2 Hz, 2H), 1.38–1.21 (m, 4H), 1.03 (ddd, *J* = 12.6, 8.2, 3.6 Hz, 1H). GC-MS: *m*/*z* 267 (35%, $[M^+]$), 224 (100%, $[M–C_3H_7]^+$), 155 (50%, [M-CyNMe]$^+$). *N*-cyclohexyl-*N*,4-dimethylbenzenesulfonamide was previously reported by Zhang, J.; Yang, C.-G.; He, C. *J. Am. Chem. Soc.* **2006**, *128*, 1798.

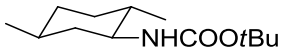
_N_-(2,5-dimethylcyclohexyl)benzamide



The reaction was performed according to the general procedure with *trans*-1,4-dimethylcyclohexane (1.00 mL, 13.6 equiv), benzamide (60.5 mg, 0.500 mmol), *t*BuOO*t*Bu (292 mg, 4.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of ,2-dichlorobenzene at 100 ºC. The selectivity of secondary and primary C-H amidation is 11:1, as determined by crude NMR. The major isomer was isolated by column chromatrography to give the title compound as

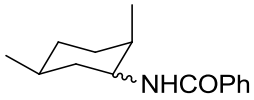
a white solid (79.3 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.75 (m, 2H), 7.54–7.48 (m, 1H), 7.48–7.41 (m, 2H), 6.02 (d, *J* = 8.3 Hz, 1H), 3.82–3.68 (m, 1H), 2.06 (ddd, *J* = 12.4, 5.6, 3.6 Hz, 1H), 1.81 (ddd, *J* = 13.2, 6.6, 3.3 Hz, 1H), 1.76–1.66 (m, 1H), 1.66–1.49 (m, 1H), 1.40– 1.27 (m, 1H), 1.27–1.13 (m, 1H), 1.07–0.98 (m, 3H), 0.98–0.91 (m, 4H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.99, 135.13, 131.15, 128.46, 126.78, 54.35, 42.31, 38.18, 34.50, 34.04, 31.96, 22.14, 18.88. ESI-HR calc'd for $C_{15}H_{21}NONa$ ($[M+Na]^+$) 254.1515, found 254.1514.

tert-butyl (2,5-dimethylcyclohexyl)carbamate



The reaction was performed according to the general procedure with *trans*-1,4-dimethylcyclohexane (1.00 mL, 13.6 equiv), *tert*-butyl carbamate (58.5 mg, 0.500 mmol), *t*BuOO*t*Bu (292 mg, 4.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of ,2-dichlorobenzene at 100 ºC. The selectivity of secondary and primary C-H amidation is 10.5:1, as determined by crude NMR. The major isomer was isolated by column chromatrography to give the title compound as a white solid (73.8 mg, 69% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.28 (s, 1H), 3.11 (m, 1H), 1.93 (d, *J* = 11.8 Hz, 1H), 1.75–1.64 (m, 1H), 1.60 (d, *J* = 13.0 Hz, 1H), 1.42 (s, 10H), 1.15–1.00 (m, 2H), 0.93 (d, *J* = 5.8 Hz, 3H), 0.87 (d, *J* = 6.5 Hz, 4H), 0.73 (q, *J* = 12.0 Hz, 1H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 155.66, 78.76, 55.27, 42.78, 38.37, 34.50, 34.11, 32.10, 28.40, 22.13, 18.73. ESI-HR calc'd for $C_{13}H_{25}NO_2Na$ ($[M+Na]^+$) 250.1778, found 250.1776.

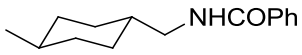
_N_-(2,5-dimethylcyclohexyl)benzamide



The reaction was performed according to the general procedure with *cis*-1,4-dimethylcyclohexane (1.00 mL, 14.0 equiv), benzamide (60.5 mg, 0.500 mmol), *t*BuOO*t*Bu (292 mg, 4.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of ,2-dichlorobenzene at 100 ºC. The selectivity of secondary and primary C-H amidation is 10.3:1, and diastereoselectivity for the secondary C-H amidation is 3.5:1, as determined by crude NMR. As the amidation products cannot be separated by column chromatrography, they were isolated as a mixture (64.2 mg, 56% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.79–7.71 (m, 3.2 H), 7.45–7.42 (m, 1.7H), 7.38–

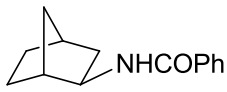
7.36 (m, 3.5H), 6.26 (s, 1.0H), 6.20 (s, 0.36H), 4.12 (ddt, *J* = 12.5, 8.4, 4.3 Hz, 0.28H), 3.96 (qt, *J* = 20.6, 10.3 Hz, 1H), 3.35 (t, *J* = 6.6 Hz, 0.25H). The aliphatic areas contain overlapping peaks. ^{13}C NMR (151 MHz, $CDCl_3$) δ 166.71, 135.08, 131.07, 131.01, 128.36, 128.32, 128.29, 126.83, 126.74, 51.06, 50.03, 37.27, 36.73, 35.13, 32.19, 31.89, 31.06, 30.40, 30.36, 30.21, 28.15, 27.99, 27.91, 26.40, 22.25, 19.28, 18.44, 11.61. ESI-HR calc'd for $C_{15}H_{21}NONa$ ($[M+Na]^+$) 254.1515, found 254.1513.

_N_-(4-methylcyclohexyl)methyl)benzamide



From the reaction of *trans*-1,4-dimethylcyclohexane with benzamide, the minor isomer was isolated by column chromatrography to give the title compound as a white solid (7.0 mg, 6% yield). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.78–7.72 (m, 2H), 7.49 (t, *J* = 7.3 Hz, 1H), 7.43 (t, *J* = 7.4 Hz, 2H), 6.18 (s, 1H), 3.31 (*J* = 10.0 Hz,, 2H), 1.79 (d, *J* = 11.8 Hz, 2H), 1.70 (d, *J* = 11.8 Hz, 2H), 1.56–1.48 (m, 1H), 1.34–1.29 (m, 1H), 1.07–0.97 (m, 2H), 0.93 (dd, *J* = 18.8, 8.6 Hz, 2H), 0.88 (d, *J* = 6.5 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.60, 134.93, 131.35, 128.59, 126.84, 46.24, 37.87, 34.66, 32.70, 30.90, 22.60. ESIHR calc'd for $C_{15}H_{21}NONa$ ($[M+Na]^+$) 254.1515, found 254.1514.

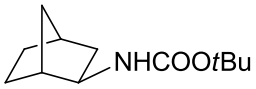
_N_-(bicyclo[2.2.1]heptan-2-yl)benzamide



The reaction was performed according to the general procedure with norbornane (800 mg, 16.6 equiv), benzamide (60.5 mg, 0.500 mmol), *t*BuOO*t*Bu (292 mg, 4.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of 1,2-dichlorobenzene at 100 ºC. The product was obtained as a single regioisomer with 13:1 dr, as determined by crude NMR. The major isomer was isolated by column chromatography as a white solid (86.8 mg, 81% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.75 (m, 2H), 7.50–7.42 (m, 1H), 7.40–7.36 (m, 2H), 6.35 (s, 1H), 3.92–3.88 (m, 1H), 2.30 (dd, *J* = 16.3, 10.8 Hz, 2H), 1.83 (dt, *J* = 28.7, 13.3 Hz, 1H), 1.61–1.40 (m, 3H), 1.38–1.13 (m, 4H). GC-MS: *m*/*z* 215 (20%, $[M^+]$), 186 (25%, $[M–C_2H_5]^+$), 105 (100%, [M-NorbornylNH]$^+$). *N*-

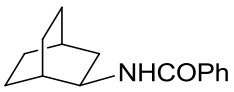
(bicyclo[2.2.1]heptan-2-yl)benzamide was previously reported by Guin, J.; Mück-Lichtenfeld, C.; Grimme, S.; Studer, A. *J. Am. Chem. Soc.* **2007**, *129*, 4498.

tert-butyl bicyclo[2.2.1]heptan-2-ylcarbamate



The reaction was performed according to the general procedure with norbornane (800 mg, 16.6 equiv), *tert*-butyl carbamate (58.5 mg, 0.500 mmol), *t*BuOO*t*Bu (292 mg, 4.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of 1,2-dichlorobenzene at 100 ºC. The product was obtained as a single regioisomer with 11:1 dr, as determined by crude NMR. The major isomer was isolated by column chromatography as a white solid (74.5 mg, 71% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.47 (s, 1H), 3.46 (s, 1H), 2.30–2.11 (m, 2H), 1.73 (dd, *J* = 29.7, 20.8 Hz, 1H), 1.56–1.36 (m, 11H), 1.30 (t, *J* = 12.4 Hz, 1H), 1.25–1.01 (m, 4H). GC-MS: *m*/*z* 211 (1.0%, $[M^+]$), 155 (25%, $[M–C_4H_9]^+$), 57 (100%, $[C_4H_9]^+$). *tert*-butyl bicyclo[2.2.1]heptan-2-ylcarbamate was previously reported by Guin, J.; Mück-Lichtenfeld, C.; Grimme, S.; Studer, A. *J. Am. Chem. Soc.* 2007, *129*, 4498.

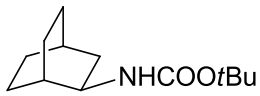
***N*-(-bicyclo[2.2.2]octan-2-yl)benzamide**



The reaction was performed according to the general procedure with bicyclo[2.2.2]octane (800 mg, 14.5 equiv), benzamide (60.5 mg, 0.500 mmol), *t*BuOO*t*Bu (292 mg, 4.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of ,2-dichlorobenzene at 100 ºC to give the title compound as a white solid after column chromatography (74.4 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83–7.75 (m, 2H), 7.55–7.47 (m, 1H), 7.44 (t, *J* = 7.4 Hz, 2H), 6.30 (br, 1H), 4.33–4.00 (m, 1H), 2.28–2.16 (m, 1H), 1.82 (dd, *J* = 5.5, 2.7 Hz, 1H), 1.79–1.46 (m, 9H), 1.35–1.25 (m, 1H).^{13}C NMR (101 MHz, $CDCl_3$) δ 167.00, 135.04, 131.13, 128.42, 126.77, 47.63,

35.20, 28.75, 25.53, 24.49, 24.42, 24.36, 19.85. ESI-HR calc'd for $C_{15}H_{20}NO$ ($[M+H]^+$) 230.1539, found 230.1538.

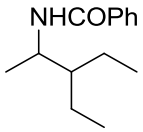
tert-butyl bicyclo[2.2.2]octan-2-ylcarbamate



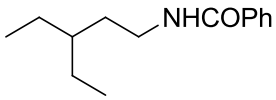
The reaction was performed according to the general procedure with bicyclo[2.2.2]octane (800 mg, 14.5 equiv), *tert*-butyl carbamate (58.5 mg, 0.500 mmol), *t*BuOO*t*Bu (292 mg, 4.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of ,2-dichlorobenzene at 100 ºC to give the title compound as a white solid after column chromatography (73.2 mg, 65% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 4.65 (s, 1H), 3.75 (s, 1H), 2.12 (t, *J* = 12.0 Hz, 1H), 1.76–1.54 (m, 5H), 1.48 (br, 15H), 1.19–1.05 (m, 1H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.42, 78.88, 48.21, 35.39, 29.04, 28.38, 25.51, 24.56, 24.44, 24.42, 19.55. ESI-HR calc'd for $C_{13}H_{23}NO_2Na$ ($[M+Na]^+$) 248.1621, found 248.1620.

_N_-(3-ethylpentan-2-yl)benzamide and _N_-(3-ethylpentyl)benzamide

The reaction was performed according to the general procedure with 3-ethylpentane (1.00 mL, 14.0 equiv), benzamide (60.5 mg, 0.500 mmol), *t*BuOO*t*Bu (292 mg, 4.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of 1,2-dichlorobenzene at 100 ºC. The two isomers were separated by column chromatography to give 39.4 mg of secondary C-H amidation product (36% yield) and 19.7 mg of primary C-H amidation product (18% yield) as white solids.



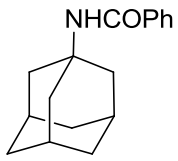
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.75 (m, 2H), 7.54–7.48 (m, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 6.08 (br, 1H), 4.42–4.28 (m, 1H), 1.51–1.35 (m, 5H), 1.21 (d, *J* = 6.8 Hz, 3H), 1.04–0.94 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.69, 135.10, 131.16, 128.46, 126.73, 46.82, 46.09, 22.18, 22.11, 17.75, 11.74, 11.55. ESI-HR calc'd for $C_{14}H_{22}NO$ ($[M+H]^+$) 220.1696, found 220.1694.



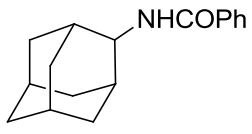
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.80–7.70 (m, 2H), 7.52–7.45 (m, 1H), 7.45–7.38 (m, 2H), 6.15 (s, 1H), 3.45 (ddd, *J* = 9.1, 7.6, 5.8 Hz, 2H), 1.61–1.51 (m, 2H), 1.41–1.27 (m, 5H), 0.93–0.81 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.44, 134.85, 131.25, 128.50, 126.78, 38.26, 38.14, 32.71, 25.28, 10.74. ESI-HR calc'd for $C_{14}H_{21}NONa$ ($[M+Na]^+$) 242.1515, found 242.1513.

_N_-((3s,5s,7s)-adamantan-1-yl)benzamide and _N_-((1r,3r,5r,7r)-adamantan-2-yl)benzamide

The reaction was performed according to the general procedure with adamantane (408 mg, 6.00 equiv), benzamide (60.5 mg, 0.500 mmol), *t*BuO*O*tBu (292 mg, 4.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of 1,2-dichlorobenzene at 100 ºC. The two isomers were separated by column chromatography to give 29.8 mg of tertiary C-H amidation product (23% yield) and 18.6 mg of secondary C-H amidation product (15% yield) as white solids.

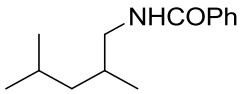


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76 (t, *J* = 7.7 Hz, 2H), 7.53–7.47 (m, 1H), 7.43 (dd, *J* = 14.2, 7.1 Hz, 2H), 5.86 (s, 1H), 2.16 (s, 9H), 1.80–1.70 (m, 6H). GC-MS: *m*/*z* 255 (55%, $[M^+]$), 212 (8.0%, $[M–C_3H_7]^+$), 198 (100%, $[M\text{-}C_4H_9]^+$). *N*-((3s,5s,7s)-adamantan-1-yl)benzamide was previously reported by Alsabeh, P. G.; Stradiotto, M.; Neumann, H.; Beller, M. *Adv. Synth. Catal.* **2012**, *354*, 3065.



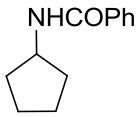
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79–7.76 (m, 2H), 7.53–7.47 (m, 1H), 7.47–7.39 (m, 2H), 6.43 (s, 1H), 4.30–4.21 (m, 1H), 2.05 (s, 2H), 1.90–1.84 (m, 8H), 1.81–1.66 (m, 5H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.64, 135.29, 131.24, 128.56, 126.80, 53.61, 37.50, 37.10, 32.09, 31.95, 27.23, 27.10. ESI-HR calc'd for $C_{17}H_{22}NONa$ ($[M+Na]^+$) 256.1696, found 256.1694.

***N*-(2,4-dimethylpentyl)benzamide**



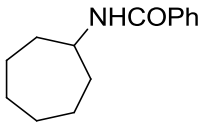
The reaction was performed according to the general procedure with 2,4-dimethylpentane (1.00 mL, 13.5 equiv), benzamide (60.5 mg, 0.500 mmol), *t*BuOO*t*Bu (292 mg, 4.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of ,2-dichlorobenzene at 100 ºC to give the title compound as a white solid after column chromatography (21.4 mg, 20% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87–7.74 (m, 2H), 7.54–7.50 (m, 1H), 7.49–7.42 (m, 2H), 6.35 (s, 1H), 3.42 (ddd, *J* = 13.2, 7.2, 5.8 Hz, 1H), 3.26 (ddd, *J* = 13.4, 7.3, 6.2 Hz, 1H), 1.91–1.83 (m, 1H), 1.79–1.66 (m, 1H), 1.27– 1.21 (m, 1H), 1.18–1.06 (m, 1H), 0.98 (d, *J* = 6.7 Hz, 3H), 0.95 (d, *J* = 6.6 Hz, 3H), 0.89 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.58, 134.91, 131.23, 128.49, 126.78, 46.21, 43.96, 31.07, 25.15, 23.40, 22.06, 17.79. ESI-HR calc'd for $C_{14}H_{21}NONa$ ($[M+Na]^+$) 242.1515, found 242.1513.

***N*-cyclopentylbenzamide**



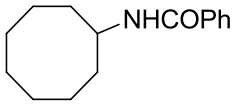
The reaction was performed according to the general procedure with cyclopentane (350 mg, 10.0 equiv), benzamide (60.5 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (64.7 mg, 69% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82–7.71 (m, 2H), 7.48 (t, *J* = 7.4 Hz, 1H), 7.40 (t, *J* = 7.4 Hz, 2H), 6.42 (d, *J* = 4.6 Hz, 1H), 4.46–4.32 (m, 1H), 2.15–1.99 (m, 2H), 1.79–1.68 (m, 2H), 1.68–1.58 (m, 2H), 1.58–1.44 (m, 2H). GC-MS: *m*/*z* 189 (35%, $[M^+]$), 122 (60%, $[M–C_5H_7]^+$), 105 (100%, $[M\text{-CypNH}]^+$). *N*-cyclopentylbenzamide was previously reported by Jiang, H.; Liu, B.; Li, Y.; Wang, A.; Huang, H. *Org. Lett.* **2011**, *13*, 1028.

***N*-cycloheptylbenzamide**



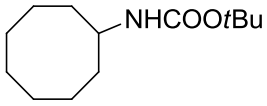
The reaction was performed according to the general procedure with cycloheptane (490 mg, 10.0 equiv), benzamide (60.5 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (81.6 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77–7.69 (m, 2H), 7.49–7.42 (m, 1H), 7.41–7.34 (m, 2H), 6.25 (s, 1H), 4.15–4.09 (m, 1H), 2.03–1.97 (m, 2H), 1.67–1.61 (m, 4H), 1.56–1.51 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.30, 135.03, 131.06, 128.36, 126.76, 50.82, 35.05, 27.93, 24.07. ESI-HR calc'd for $C_{14}H_{19}NONa$ ($[M+Na]^+$) 240.1359, found 240.1357.

_N_-cyclooctylbenzamide



The reaction was performed according to the general procedure with cyclooctane (560 mg, 10.0 equiv), benzamide (60.5 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (91.0 mg, 79% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81–7.74 (m, 2H), 7.52–7.45 (m, 1H), 7.45–7.38 (m, 2H), 6.28 (s, 1H), 4.29–4.15 (m, 1H), 2.00–1.87 (m, 2H), 1.77–1.50 (m, 12H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.25, 135.05, 131.05, 128.35, 126.76, 49.76, 32.25, 27.08, 25.36, 23.66. ESI-HR calc'd for $C_{15}H_{21}NONa$ ($[M+Na]^+$) 254.1515, found 254.1513.

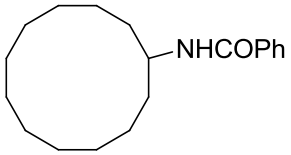
***tert*-butyl cyclooctylcarbamate**



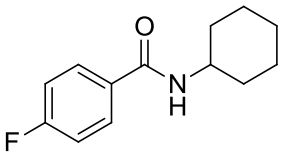
The reaction was performed according to the general procedure with cyclooctane (1.00 mL, 14.9 equiv), *tert*-butyl carbamate (58.5 mg, 0.500 mmol), *t*BuOO*t*Bu (292 mg, 4.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of 1,2-dichlorobenzene at 100 ºC to give the title

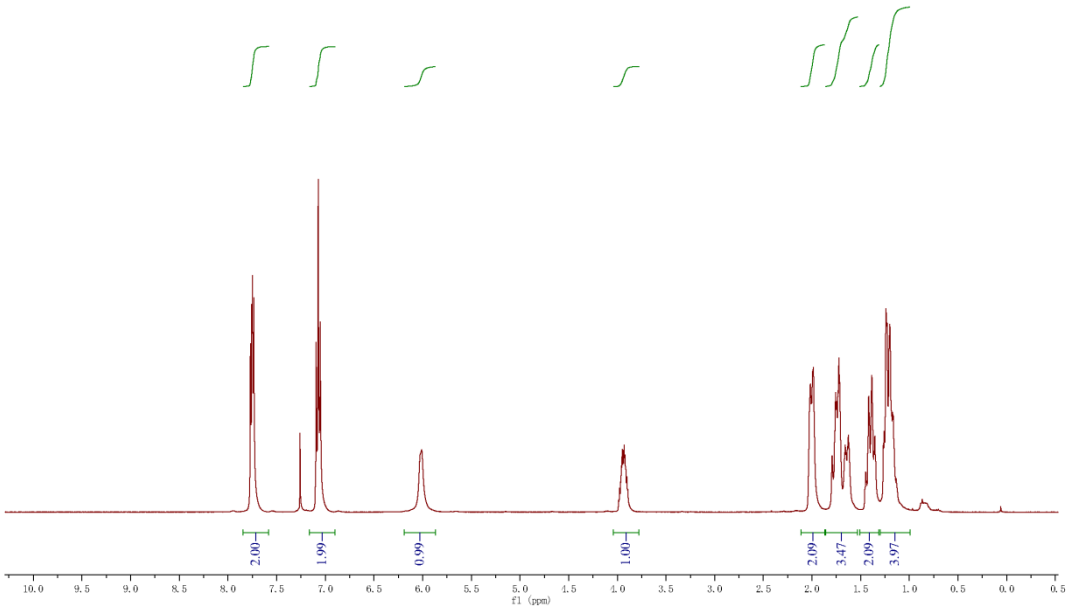
compound as a white solid after column chromatography (91.3 mg, 80% yield). ^{1}H NMR (600 MHz, $CDCl_3$) δ 4.50 (s, 1H), 3.63 (s, 1H), 1.79–1.77 (m, 2H), 1.67–1.43 (m, 12H), 1.40 (s, 9H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 154.99, 78.75, 50.43, 32.56, 28.38, 27.08, 25.46, 23.62. ESI-HR calc'd for $C_{13}H_{25}NO_2Na$ ($[M+Na]^+$) 250.1778, found 250.1776.

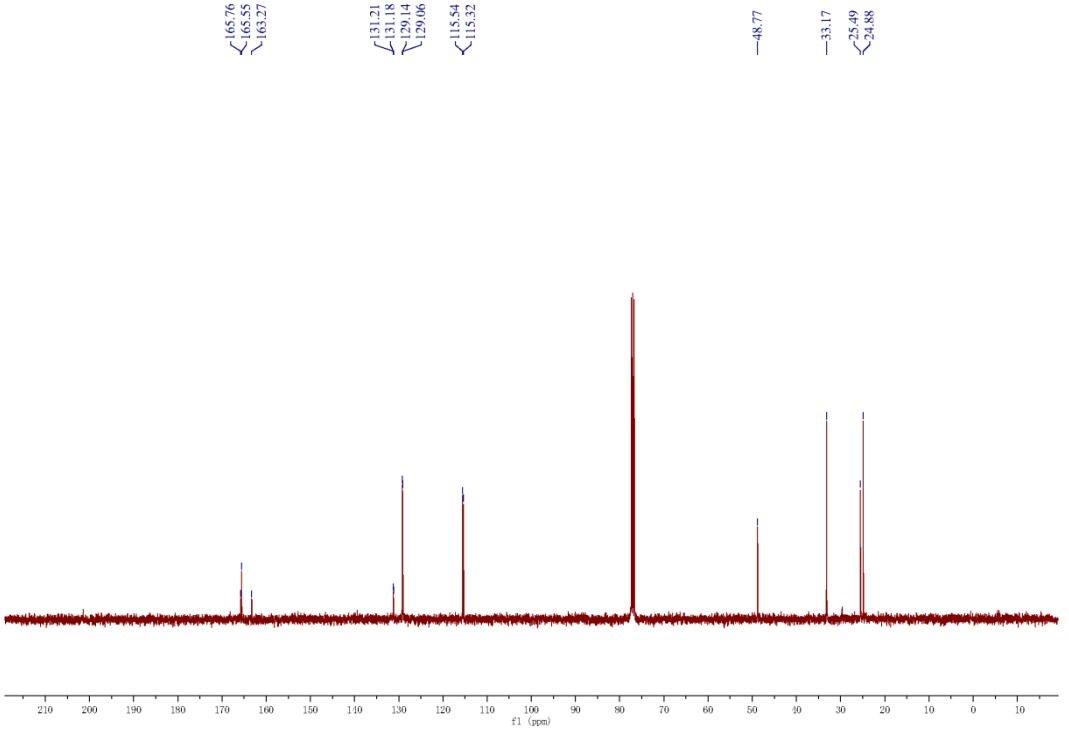
_N_-cyclododecylbenzamide

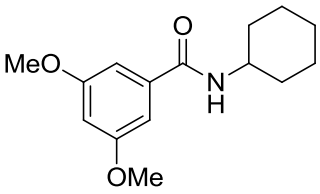


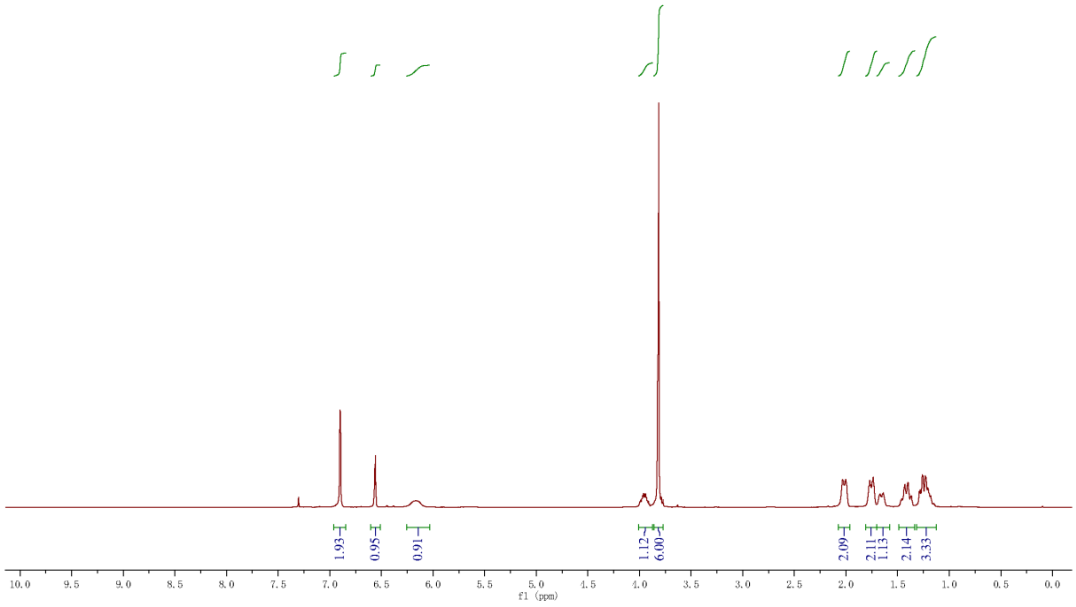
The reaction was performed according to the general procedure with cyclododecane (840 mg, 10.0 equiv), benzamide (60.5 mg, 0.500 mmol), *t*BuOO*t*Bu (146 mg, 2.00 equiv) and 2.5 mol % of CuI and $(MeO)_2$Phen in 1.0 mL of benzene at 100 ºC to give the title compound as a white solid after column chromatography (115 mg, 80% yield). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78–7.71 (m, 2H), 7.51–7.45 (m, 1H), 7.45–7.37 (m, 2H), 5.94 (br, 1H), 4.30–4.25 (m, 1H), 1.77–1.68 (m, 2H), 1.54–1.28 (m, 20H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 166.69, 135.01, 131.20, 128.49, 126.77, 46.52, 30.30, 23.95, 23.70, 23.46, 23.32, 21.44. ESIHR calc'd for $C_{19}H_{29}NONa$ ($[M+Na]^+$) 310.2141, found 310.2139.

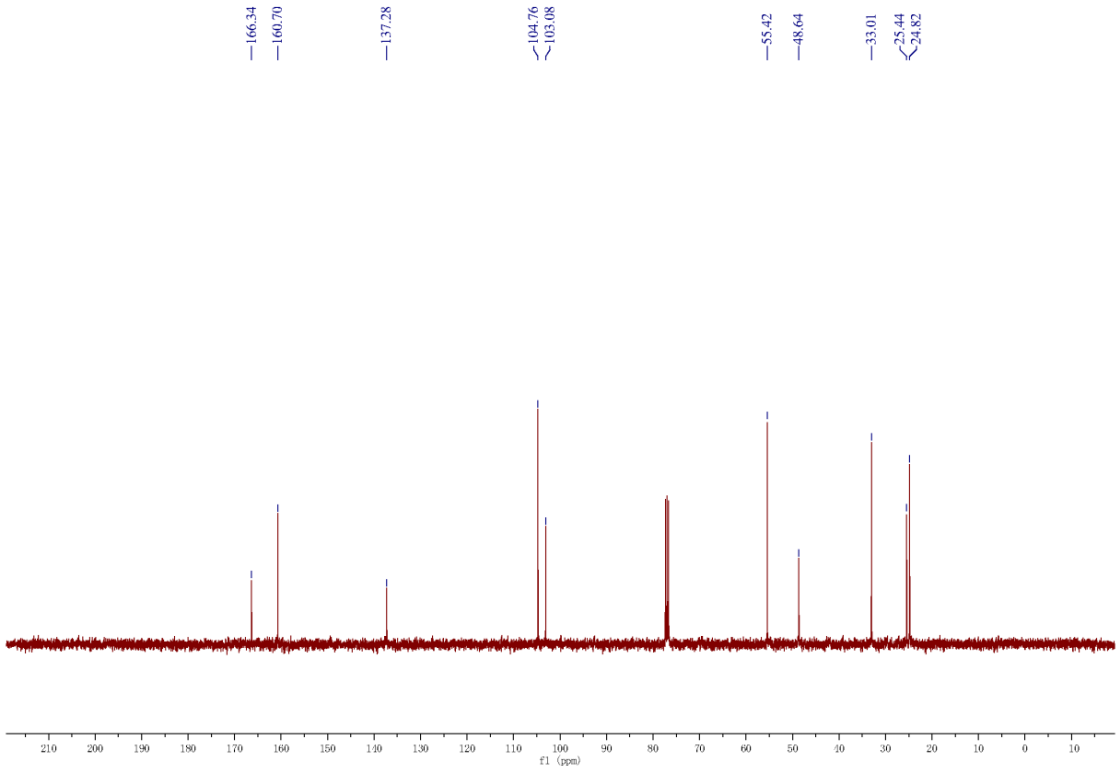

O
N
H
F

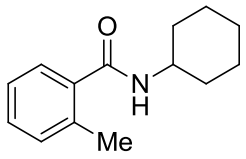

2.00
1.99
0.99
1.00
2.09
3.47
2.09
3.97
f1 (ppm)

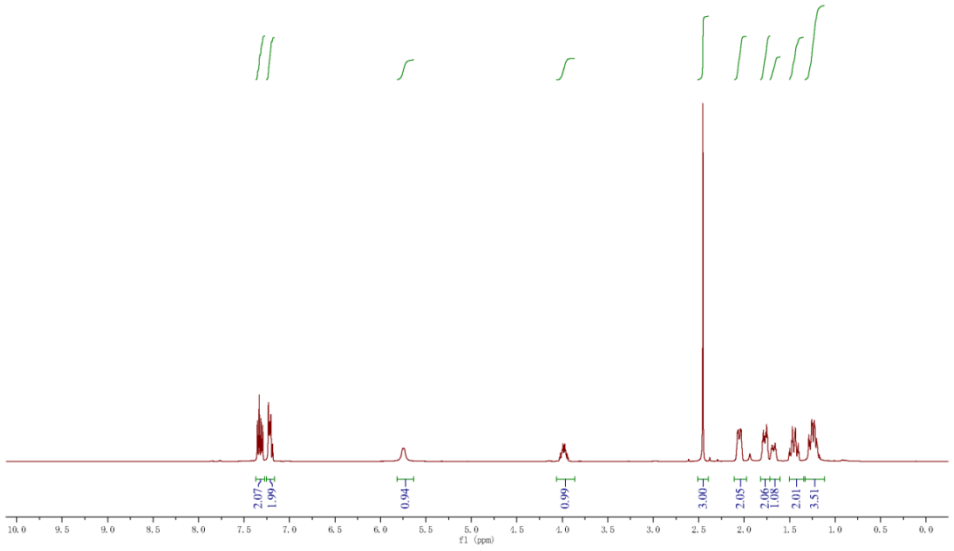

165.76
165.55
163.27
131.21
131.18
129.14
129.06
115.54
115.32
48.77
33.17
25.49
24.88
f1 (ppm)


MeO
O
N
H
OMe


1.93
0.95
0.91
1.12
6.00
2.09
2.11
1.13
2.14
3.33
f1 (ppm)


166.34
160.70
137.28
104.76
103.08
55.42
48.64
33.01
25.44
24.82
f1 (ppm)


O
N
H
Me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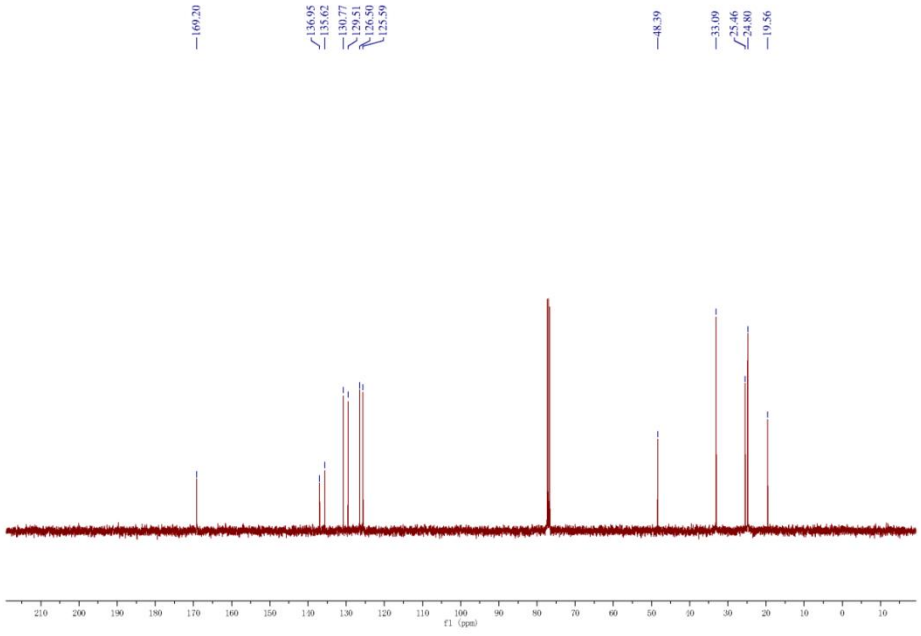
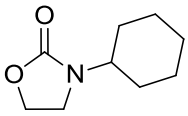
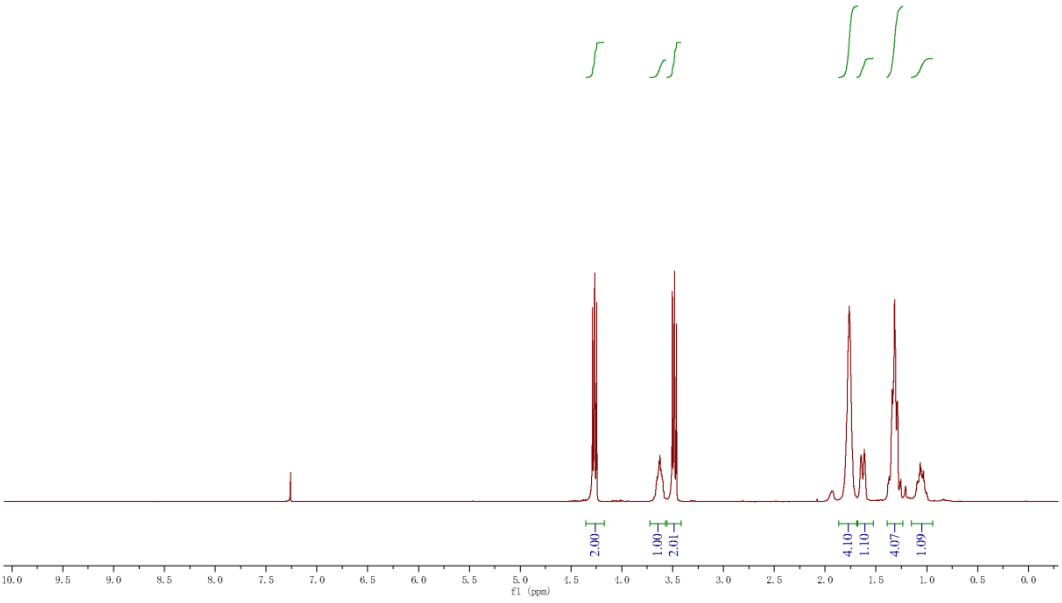
1.99
0.94
0.99
3.00
2.05
2.06
1.08
2.01
3.51
f1 (ppm)


169.20
136.95
135.62
130.77
129.51
126.50
125.59
48.39
33.09
25.46
24.80
19.56
f1 (ppm)

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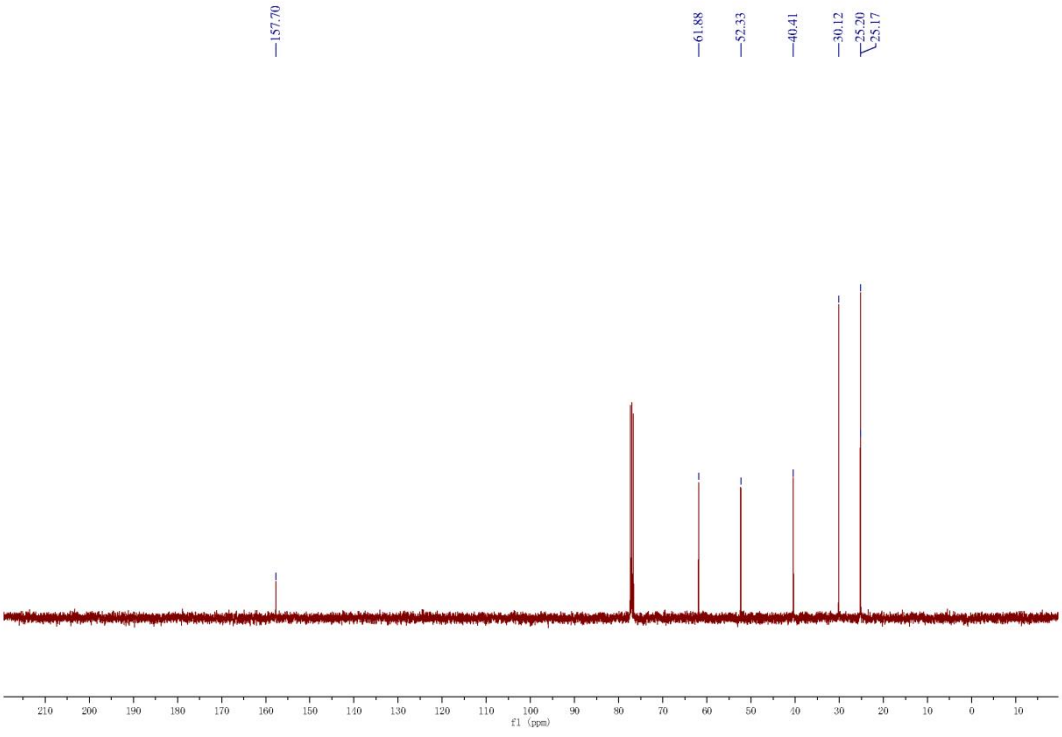
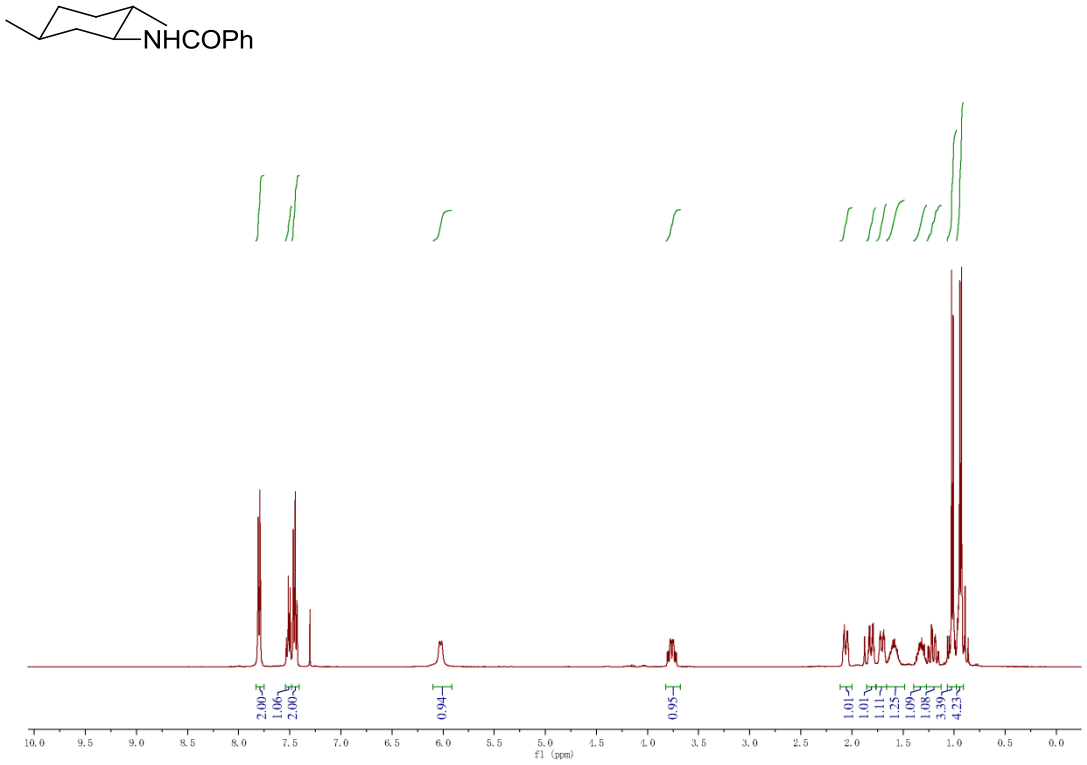
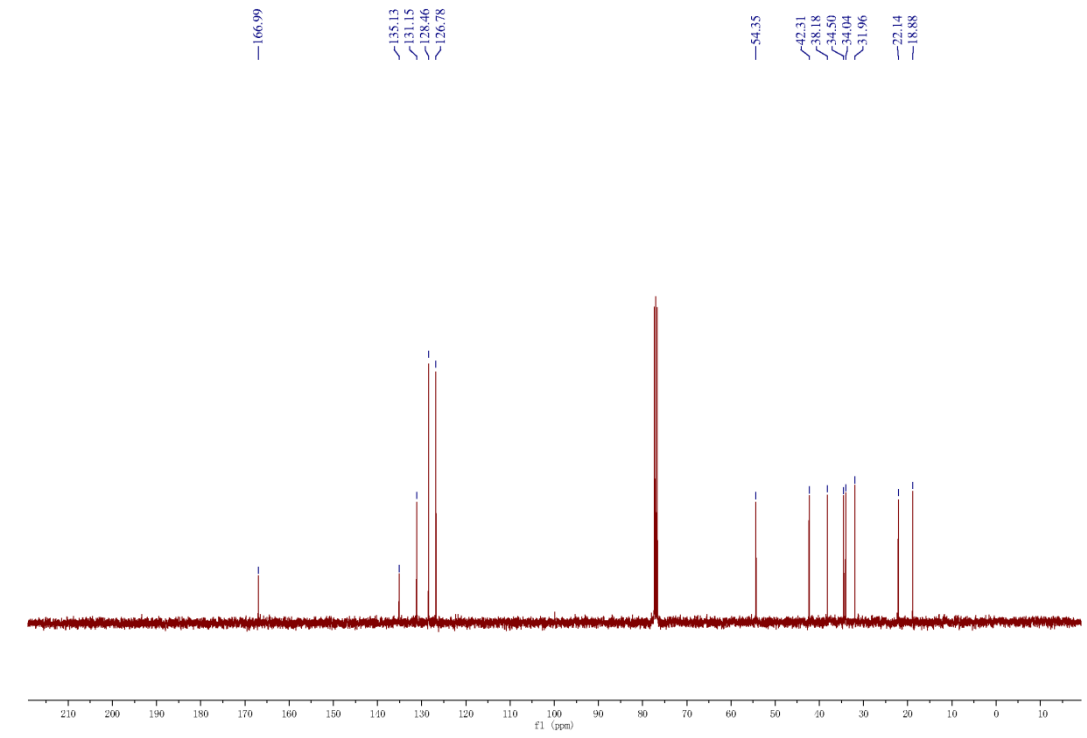
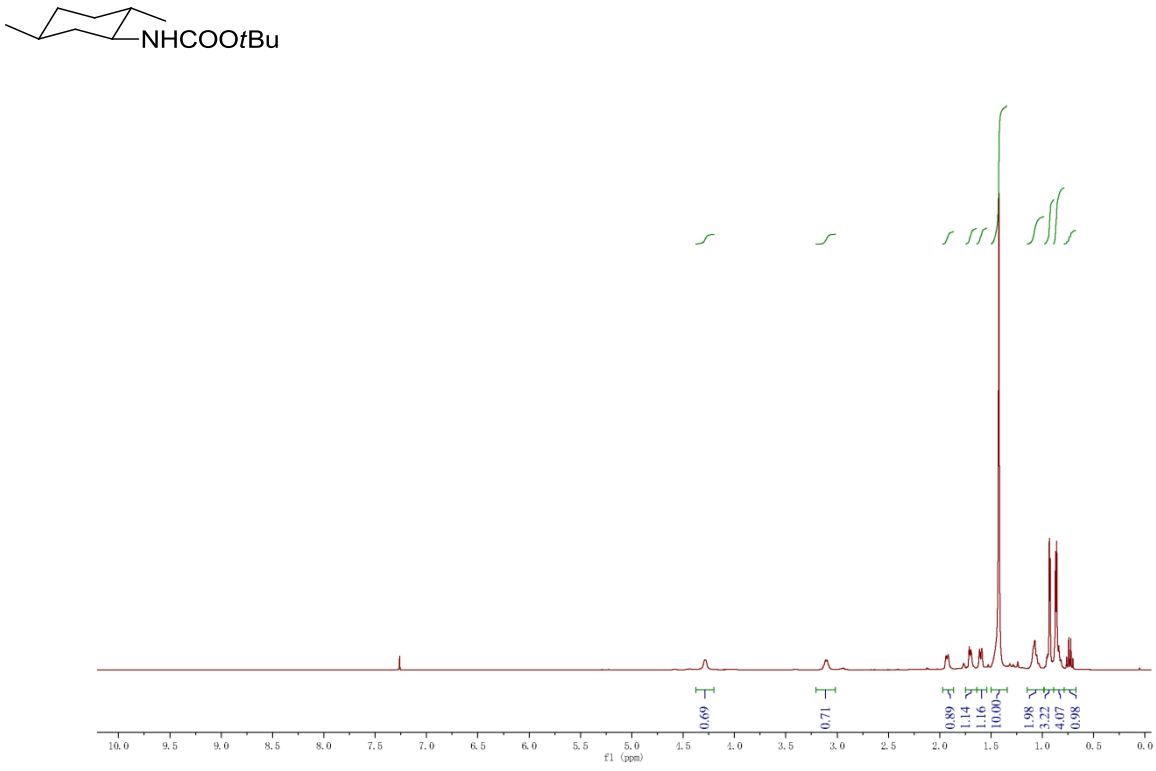
1.00
2.01
4.10
1.10
4.07
1.09
f1 (ppm)


157.70
61.88
52.33
40.41
30.12
25.20
25.17
f1 (ppm)


NHCOPh
2.00
1.06
2.00
0.94
0.95
1.01
1.01
1.11
1.25
1.09
1.08
3.39
4.23
f1 (ppm)


166.99
135.13
131.15
128.46
126.78
54.35
42.31
38.18
34.50
34.04
31.96
22.14
18.88
f1 (ppm)


NHCOOtBu
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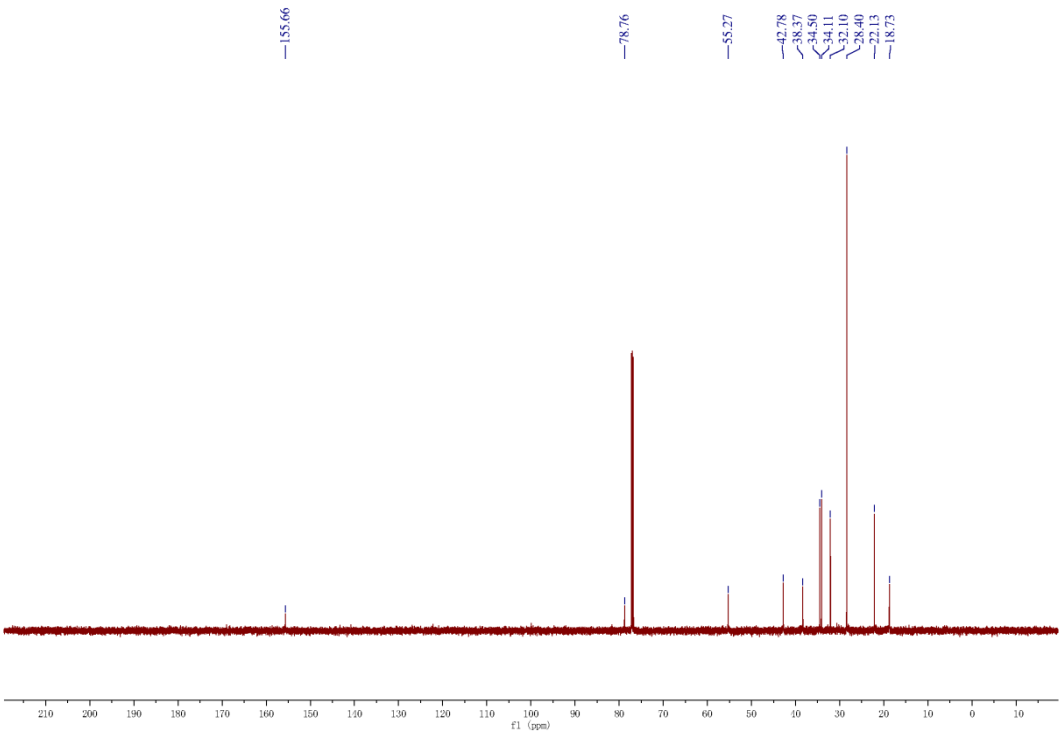
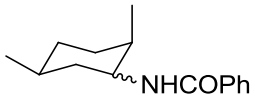
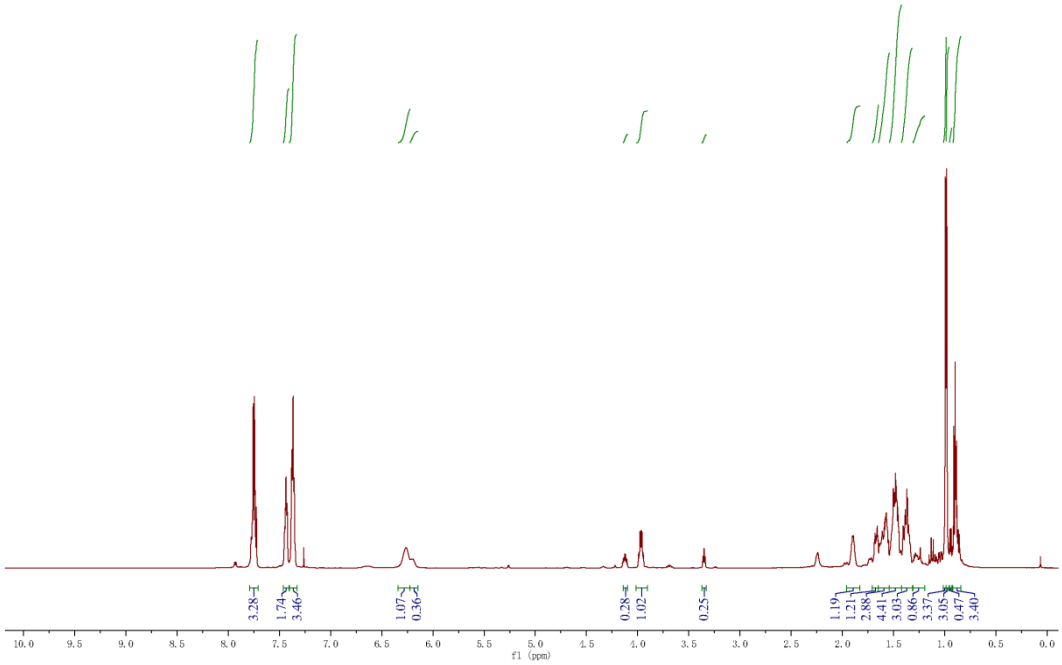
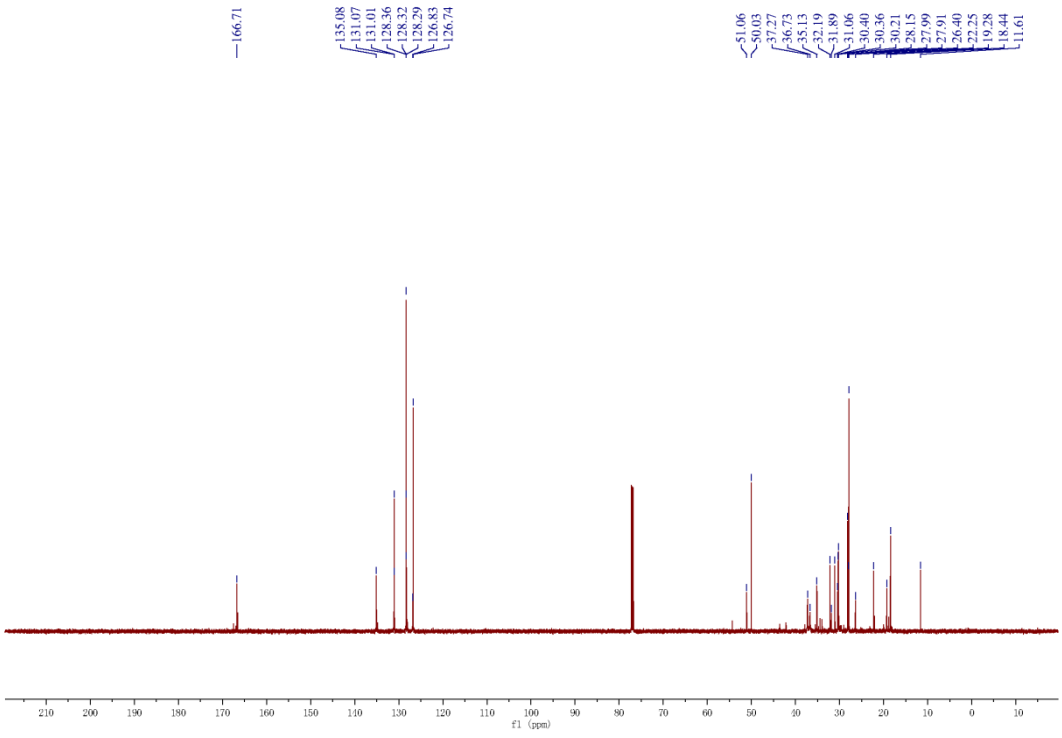
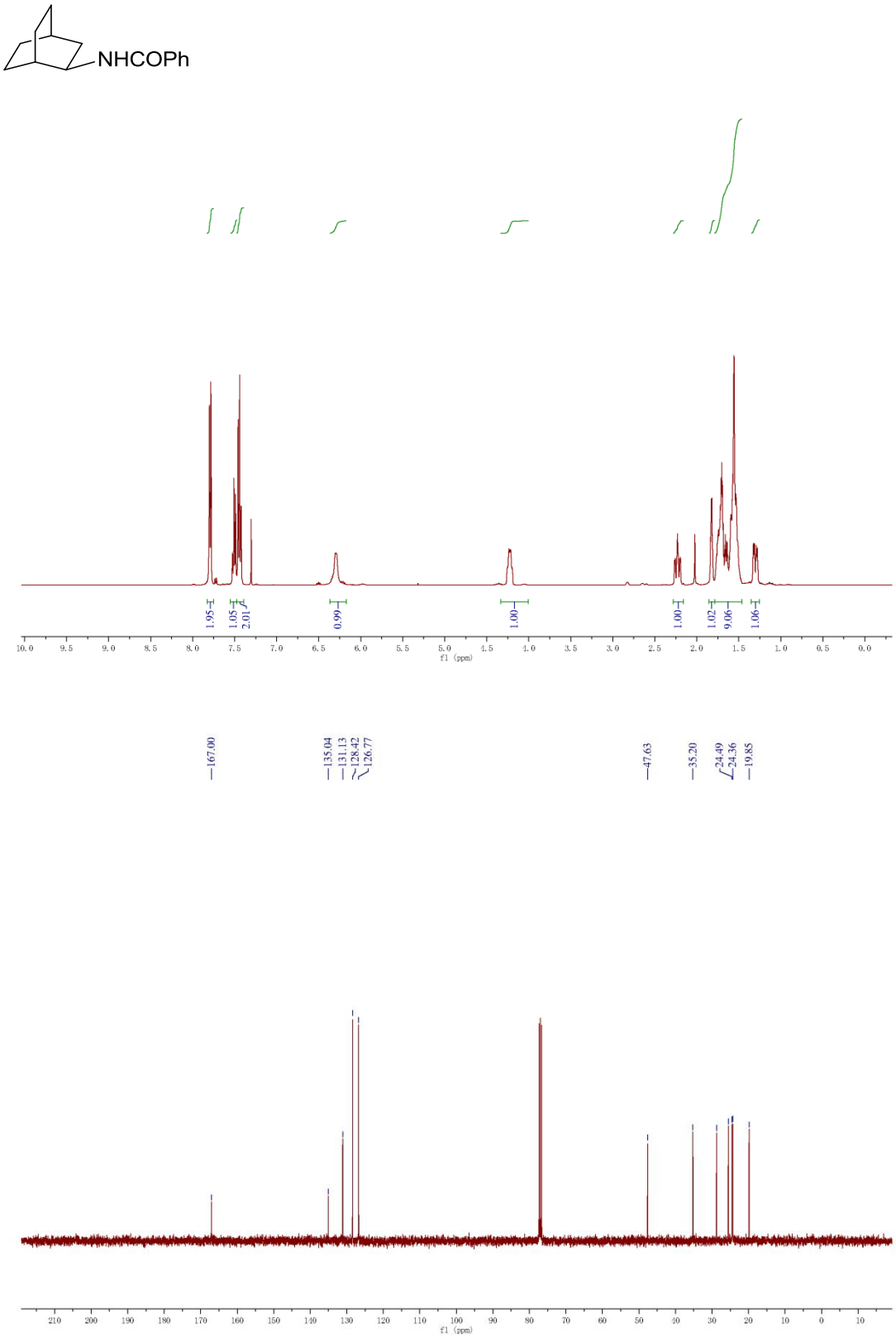
0.71
0.89
1.14
1.16
10.00
1.98
3.22
4.07
0.98
f1 (ppm)

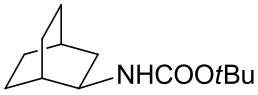

155.66
78.76
55.27
42.78
38.37
34.50
34.11
32.10
28.40
22.13
18.73
f1 (ppm)

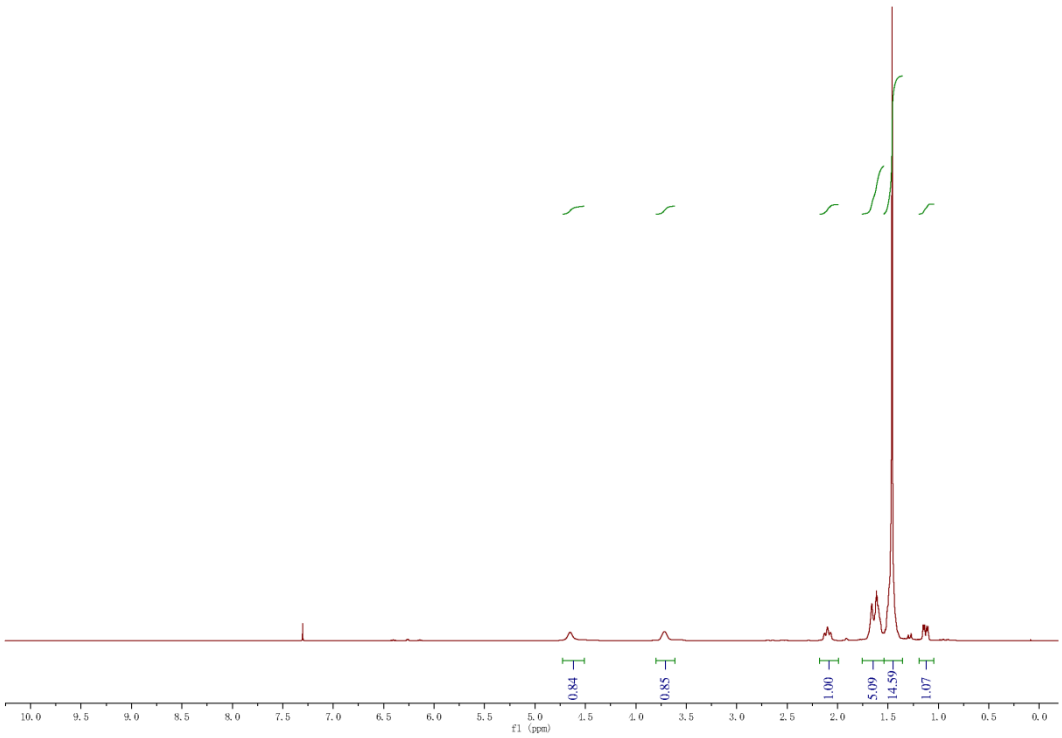

NHCOPh


3.28
1.74
3.46
1.07
0.36
0.28
1.02
0.25
1.19
1.21
2.88
4.41
3.03
0.86
3.37
3.05
0.47
3.40
f1 (ppm)


166.71
135.08
131.07
131.01
128.36
128.32
128.29
126.83
126.74
51.06
50.03
37.27
36.73
35.13
32.19
31.89
31.06
30.40
30.36
30.21
28.15
27.99
27.91
26.40
22.25
19.28
18.44
11.61
f1 (ppm)


NHCOPh
1.95
1.05
2.01
0.99
1.00
1.00
1.02
9.06
1.06
f1 (ppm)
167.00
135.04
131.13
128.42
126.77
47.63
35.20
24.49
24.36
19.85
f1 (ppm)


NHCOO*t*Bu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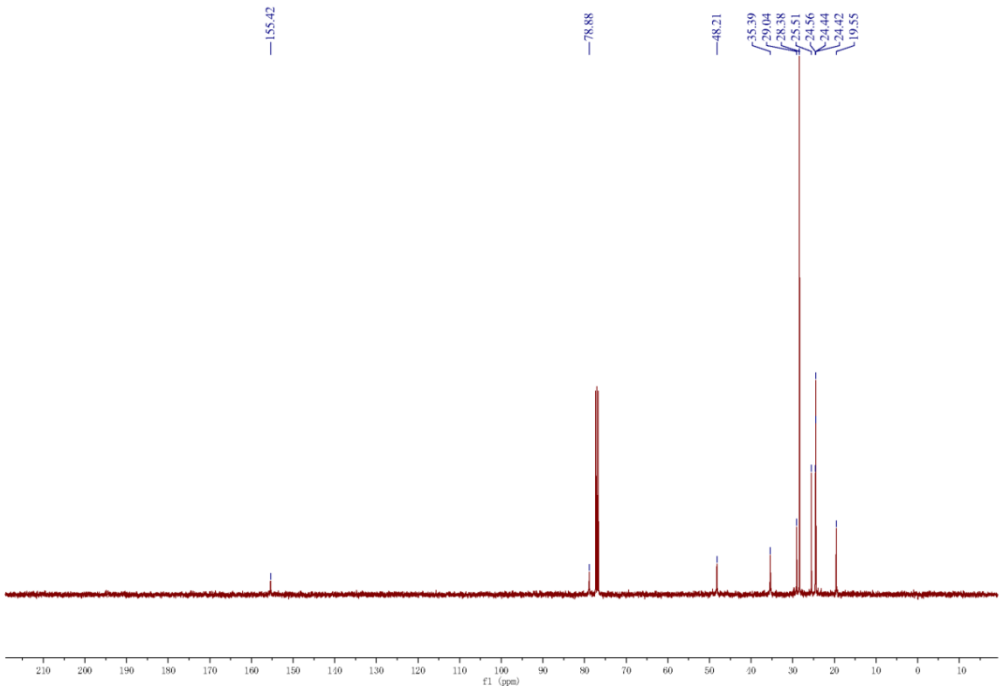
5.09
14.59
1.07
f1 (ppm)


155.42
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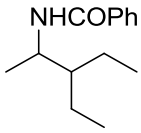
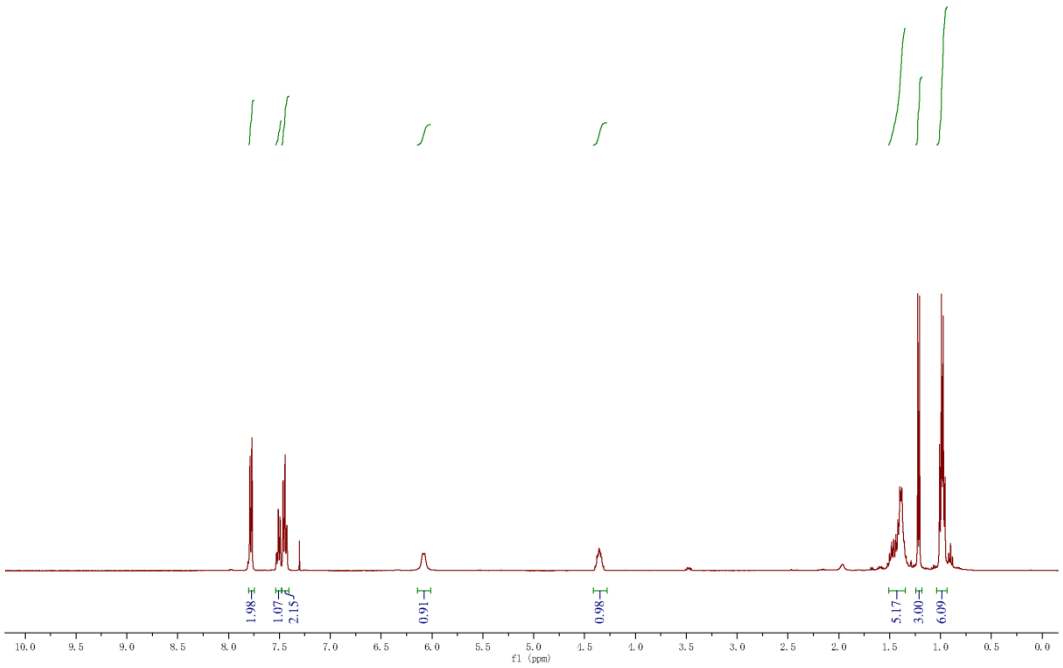
29.04
28.38
25.51
24.56
24.44
24.42
19.55
f1 (ppm)


NHCOPh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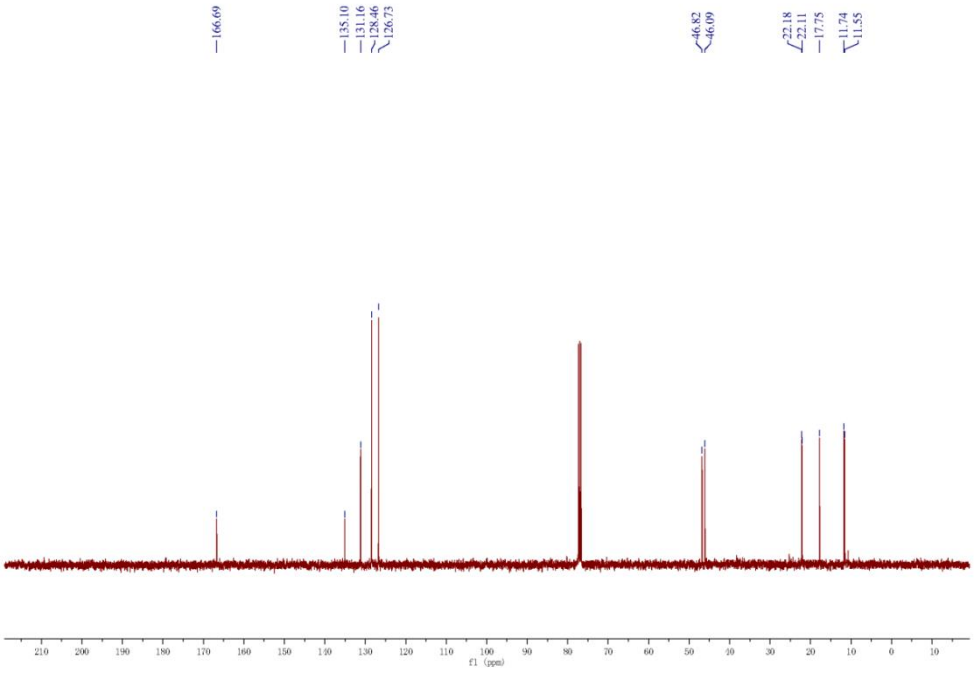
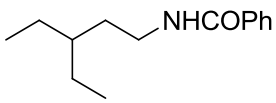
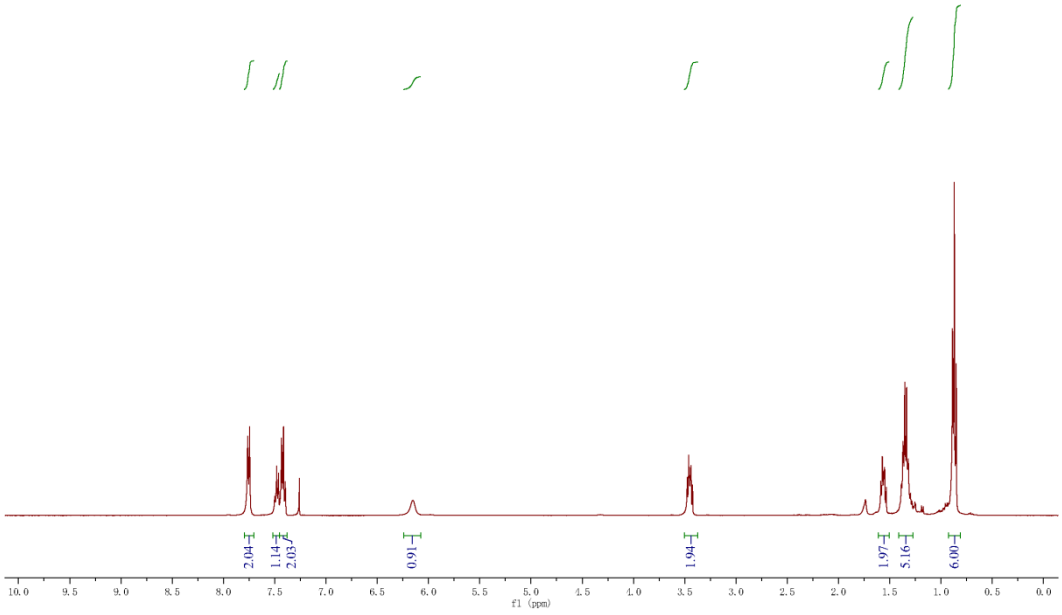
1.07
2.15
0.91
0.98
5.17
3.00
6.09
f1 (ppm)


166.69
135.10
131.16
128.46
126.73
46.82
46.09
22.18
22.11
17.75
11.74
11.55
f1 (ppm)


NHCOPh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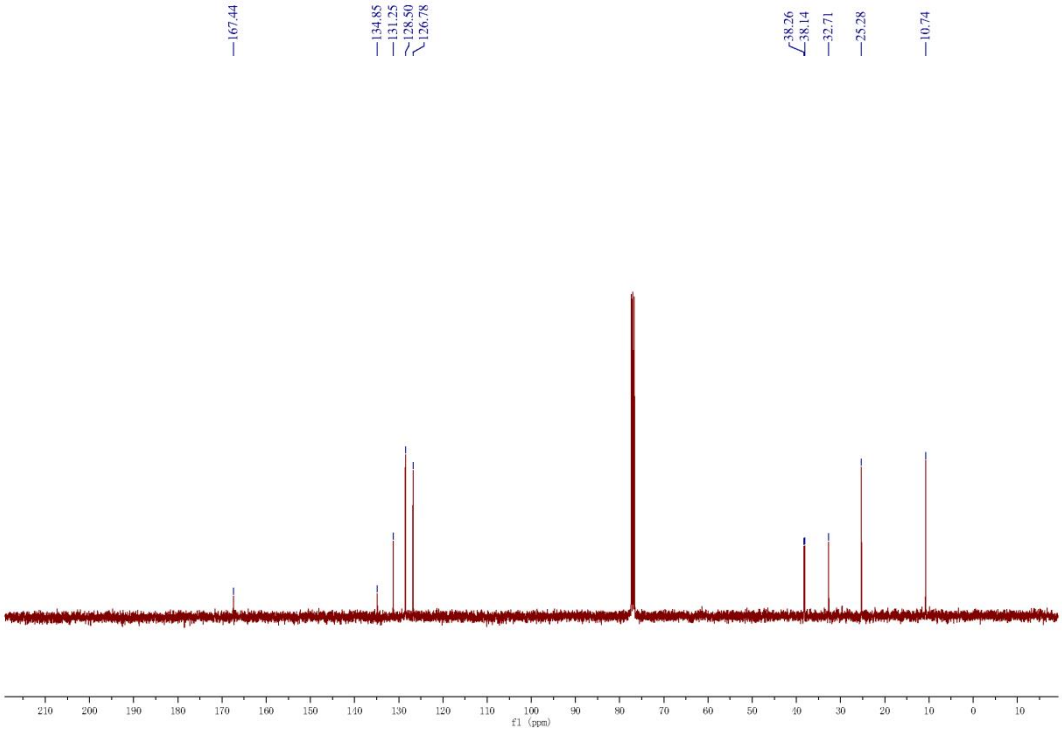
1.14
2.03
0.91
1.94
1.97
5.16
6.00
f1 (ppm)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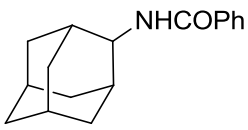
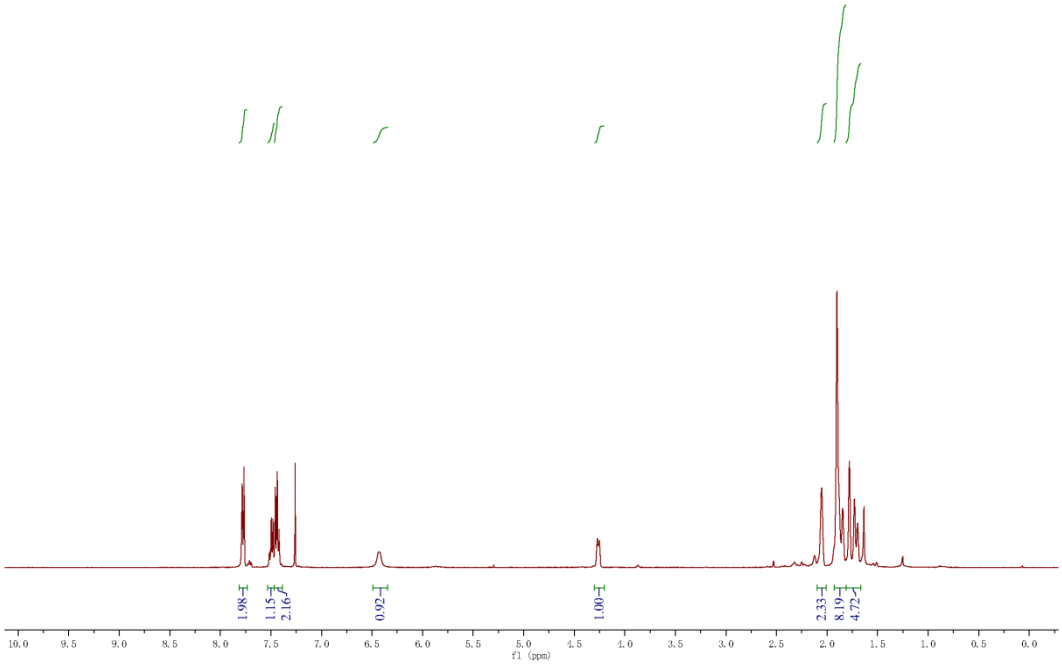
126.78
38.26
38.14
32.71
25.28
10.74
f1 (ppm)


NHCOPh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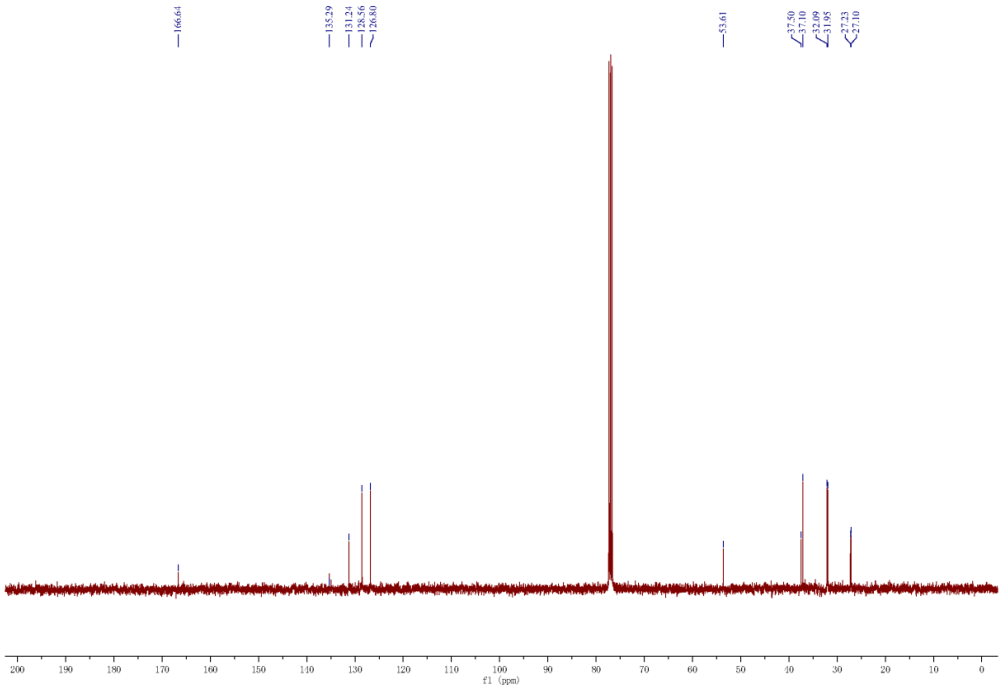
1.15
2.16
0.92
1.00
2.33
8.19
4.72
f1 (ppm)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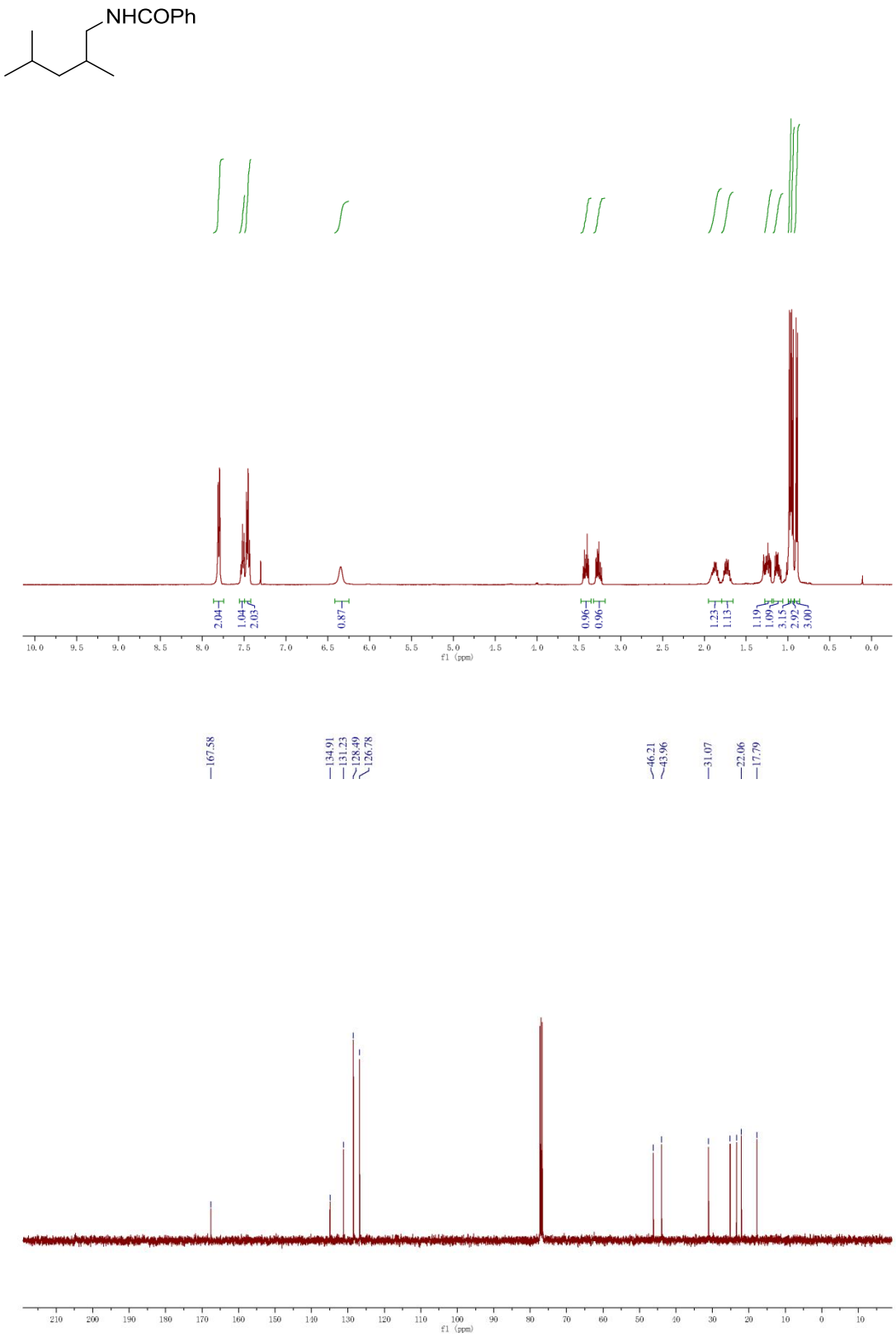
126.80
53.61
37.50
37.10
32.09
31.95
27.23
27.10
f1 (ppm)


NHCOPh
2.04
1.04
2.03
0.87
0.96
0.96
1.23
1.13
1.19
1.09
3.15
2.92
3.00
f1 (ppm)
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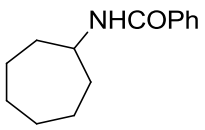
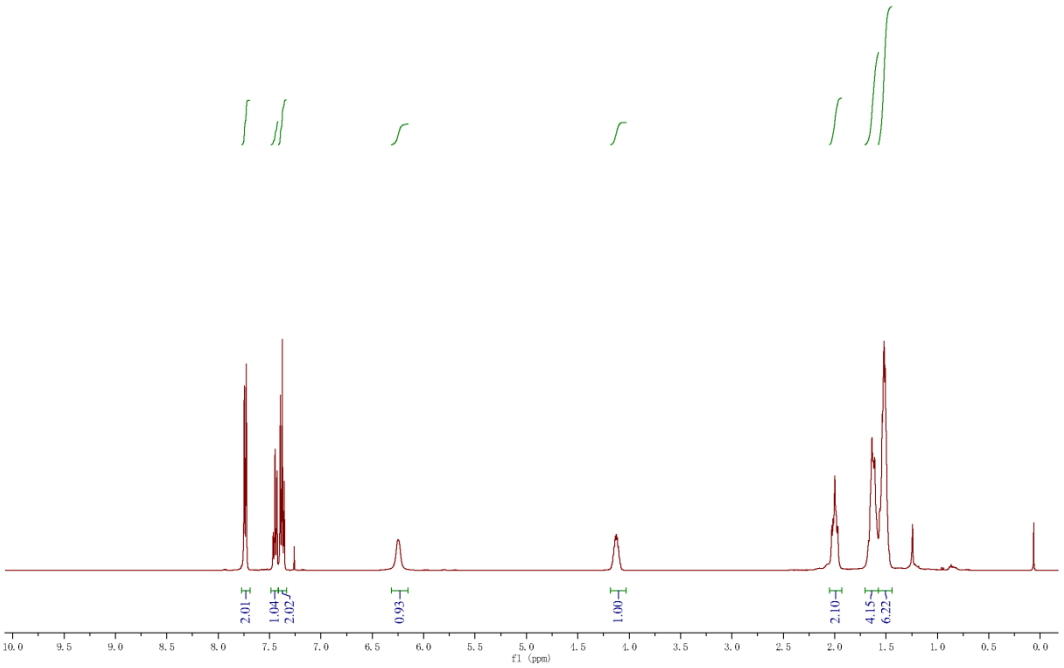
131.23
128.49
126.78
46.21
43.96
31.07
22.06
17.79
f1 (ppm)


NHCOPh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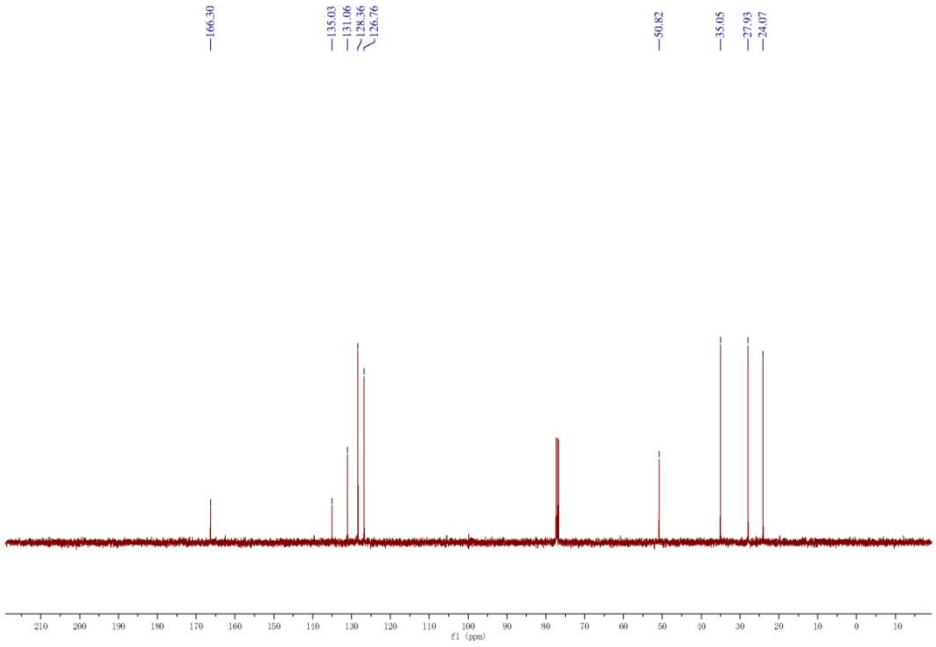
2.02
0.93
1.00
2.10
4.15
6.22
f1 (ppm)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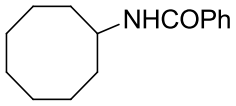
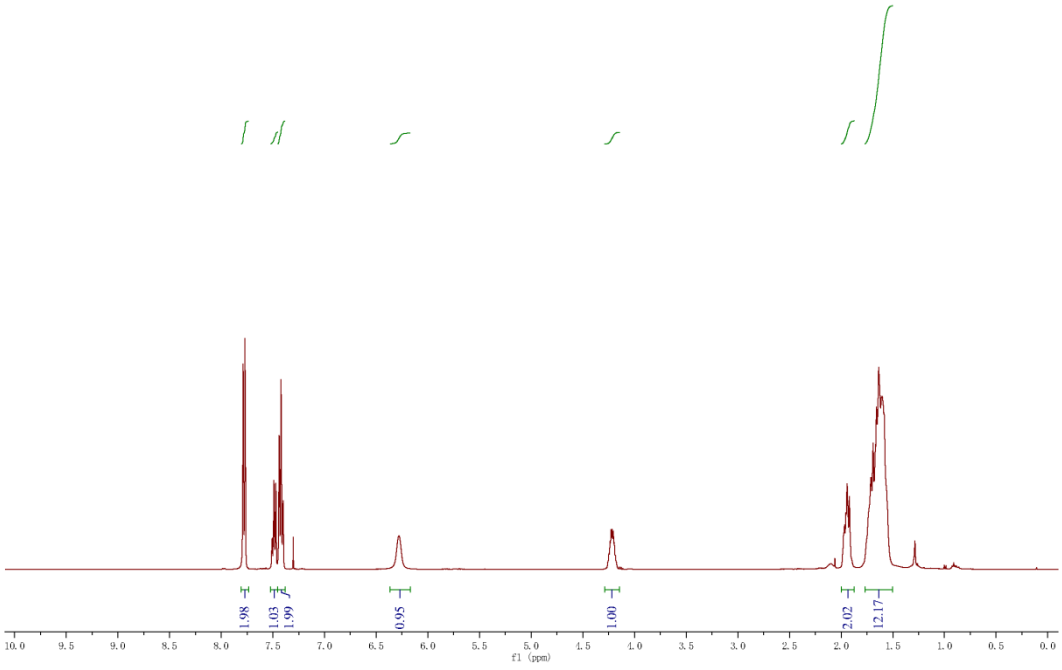
128.36
126.76
50.82
35.05
27.93
24.07
f1 (ppm)


NHCOPh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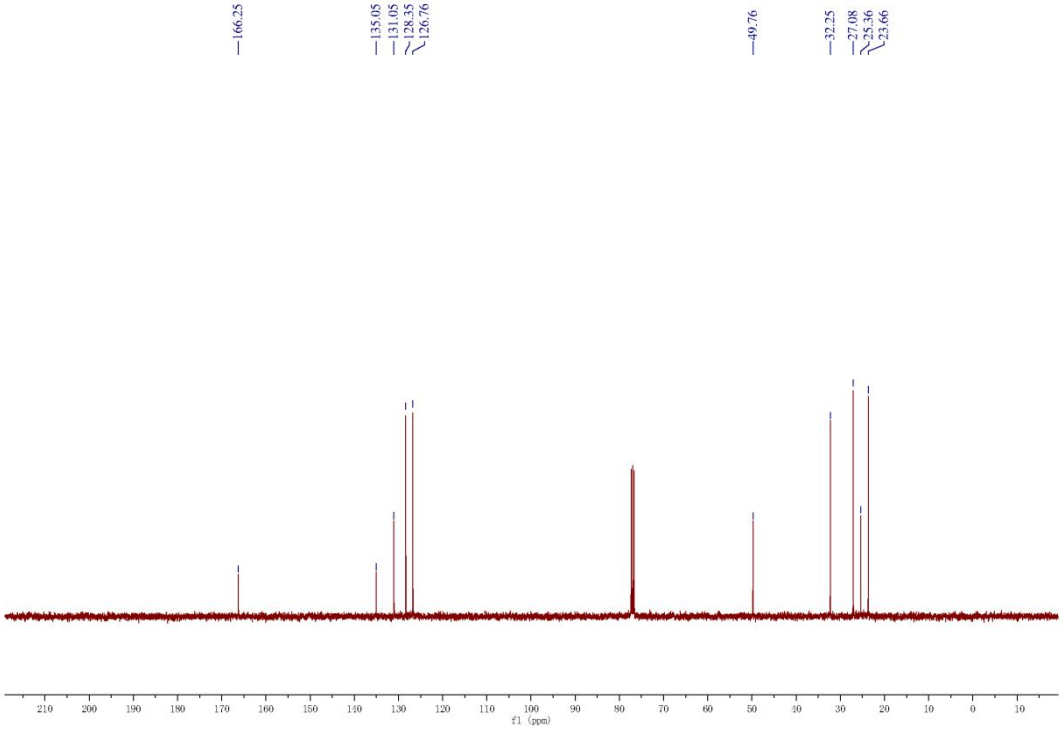
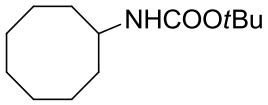
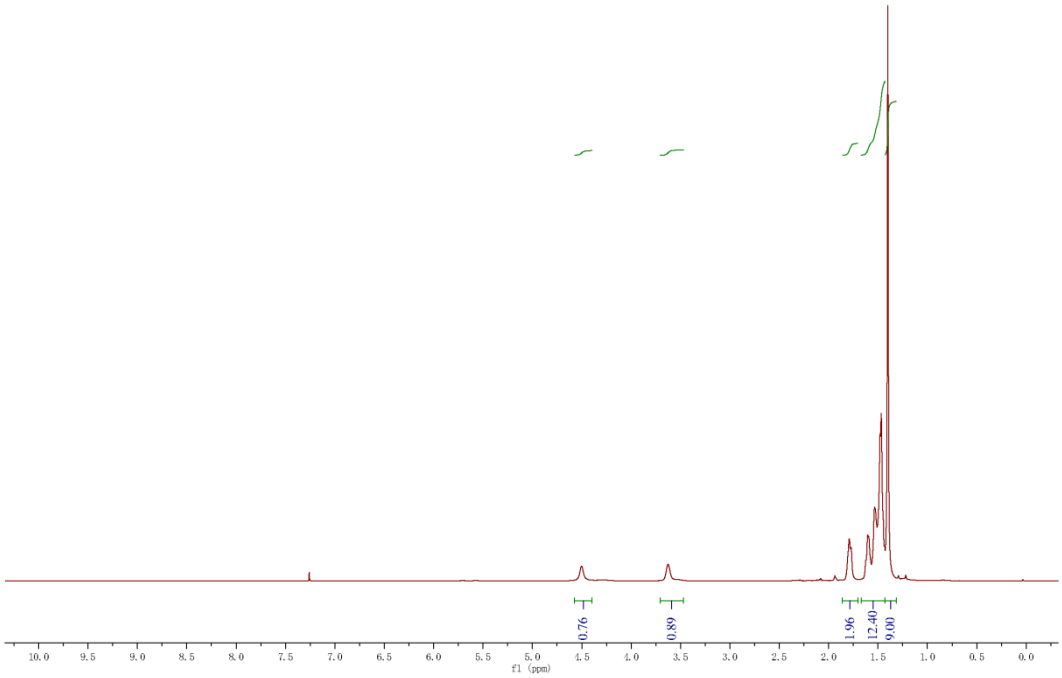
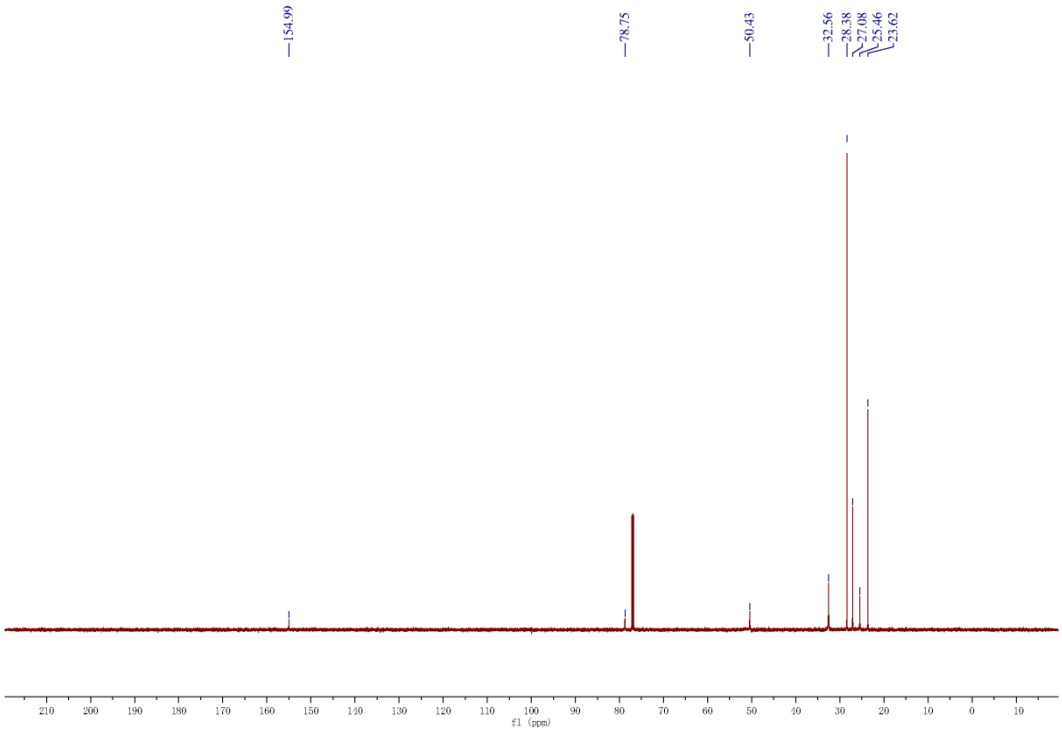
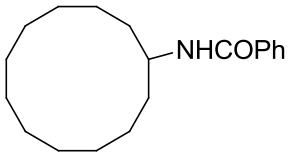
1.03
1.99
0.95
1.00
2.02
12.17
f1 (ppm)

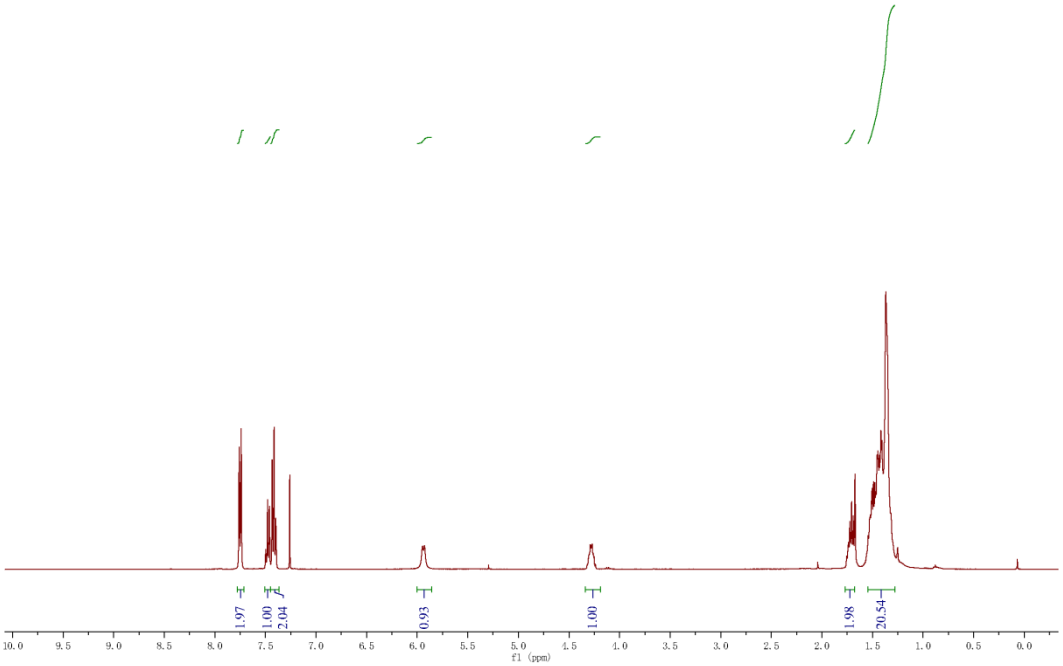

166.25
135.05
131.05
128.35
126.76
49.76
32.25
27.08
25.36
23.66
f1 (ppm)


NHCOO*t*Bu

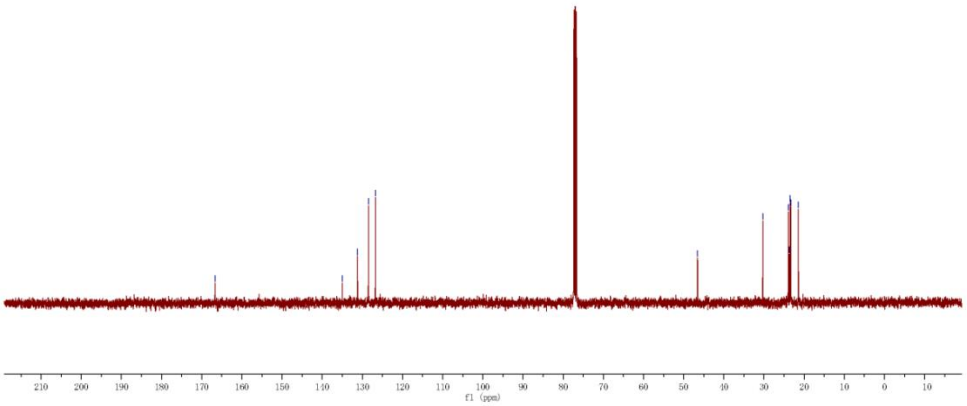

0.76
0.89
1.96
12.40
9.00
f1 (ppm)

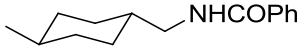

154.99
78.75
50.43
32.56
28.38
27.08
25.46
23.62
f1 (ppm)

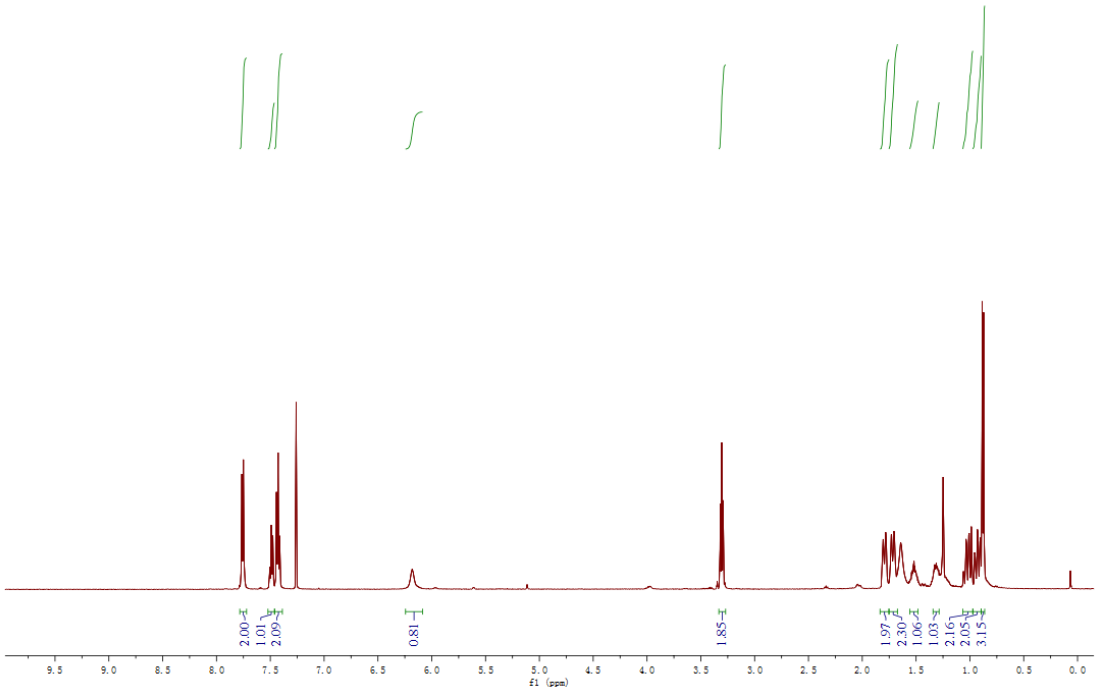

NHCOPh

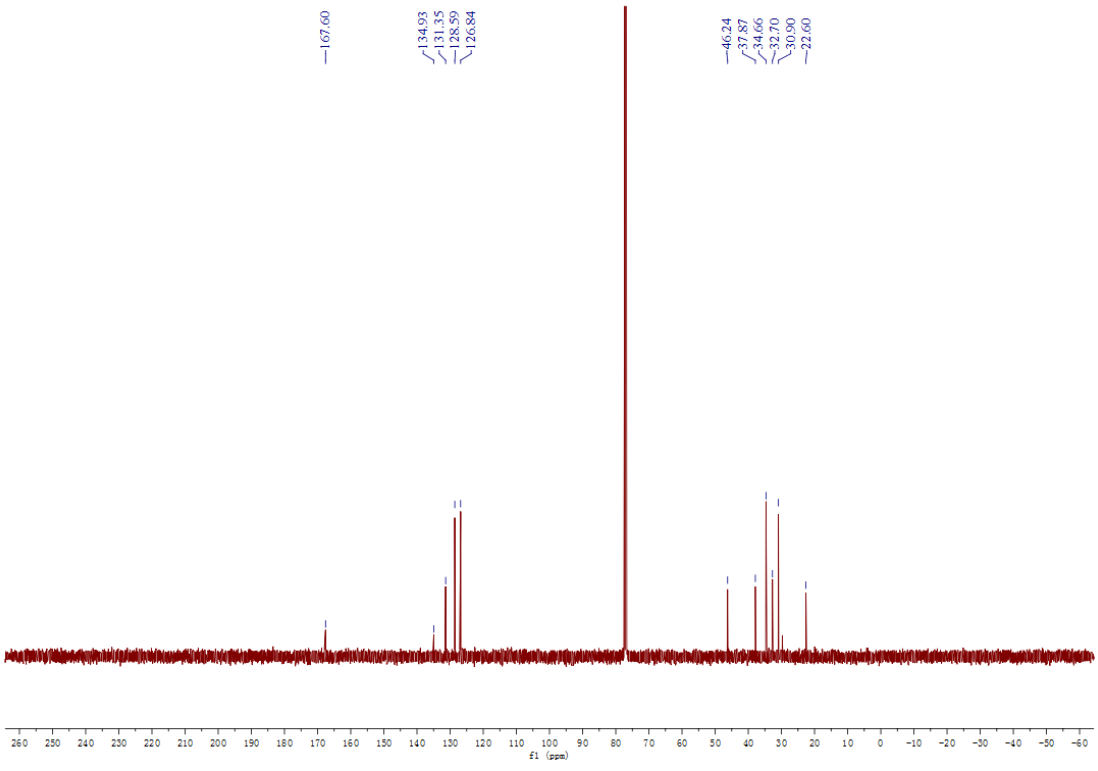

1.97
1.00
2.04
0.93
1.00
1.98
20.54
f1 (ppm)


166.69
135.01
131.20
128.49
126.77
46.52
30.30
23.95
23.70
23.46
23.32
21.44


f1 (ppm)


NHCOPh


2.00
1.01
2.09
0.81
1.85
1.97
2.30
1.06
1.03
2.16
2.05
3.15
f1 (ppm)


167.60
134.93
131.35
128.59
126.84
46.24
37.87
34.66
32.70
30.90
22.60
f1 (ppm)

Details of X-ray crystallography

Single crystals of **1-phth$_2$** for XRD measurement were obtained from slow evaporation of a concentrated MeOH solution. Single crystals of **6** and **7** were obtained from the slow diffusion of *n*-pentane into a saturated CH_2Cl_2 solution of the corresponding copper complexes. Complexes of **1-phth$_2$** and **4** were collected on Bruker Apex II under an Oxford Cryostream 700. Complexes of **6** and **7** were collected on an Oxford Diffraction Xcalibur S Sapphire at 150 K (Mo-Kα radiation, λ = 0.71073 Å). The structures were solved by direct methods and refined on *F*2 with the SHELX-97 or SIR-2011 package. The positions of the H atoms were calculated and considered isotropically according to a riding model.