Electronic Supplementary Information (ESI)

Synthesis of *N*-Aryl Amines Enabled by Photocatalytic Dehydrogenation

Jungwon Kim,[1,*] Siin Kim,[1,2,3] Geunho Choi,[1] Geun Seok Lee,[1] Donghyeok Kim,[1,2,3] Jungkweon Choi,[1,2,3] Hyotcherl Ihee[1,2,3,*] and Soon Hyeok Hong[1,*]

[1]Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea
[2]KI for the BioCentury, Korea Advanced Institute of Science and Technology (KAIST), Daejeon 34141, Republic of Korea
[3]Center for Nanomaterials and Chemical Reactions, Institute for Basic Science (IBS), Daejeon 34141, Republic of Korea

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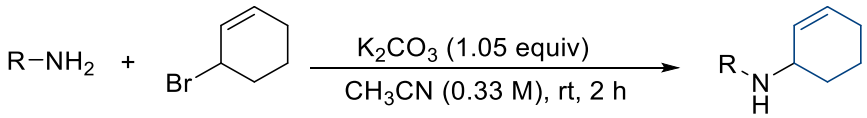
1. General Information

Unless otherwise noted, all reactions were performed under inert conditions. All reagents and solvents, unless otherwise noted, were purchased from commercial suppliers and used as received without further purification. All anhydrous solvents were purchased from commercial suppliers and degassed with dry argon before usage. All photocatalytic reactions were conducted under irradiation by 34 W blue LED lamps purchased from Kessil (Kessil H150 Blue), 2.5 cm away from the reaction vial with fan cooling. Reactions were monitored by thin-layer chromatography (TLC) on EMD Silica Gel 60 F254 plates and visualized using either UV light (254 nm) or by staining with potassium permanganate and heating. Gas chromatography (GC) was carried out using a 7980A GC system (Agilent Technologies) equipped with an HP-5 column and a flame ionization detector (FID). Nuclear magnetic resonance (NMR) spectra were recorded in $CDCl_3$ or DMSO-d_6 on a Bruker DPX-300 (300 MHz) spectrometer, Bruker AVANCE 300 (300 MHz), Bruker AVANCE 400 (400 MHz), Bruker AVANCE III HD (400 MHz), Varian 400 (400 MHz) and Varian 500 (500 MHz), and the residue solvent signal was used as a reference. Chemical shifts were reported in ppm and coupling constants in Hz. Multiplicity was indicated by one or more of the following: s (singlet); brs (broad singlet); d (doublet); t (triplet); q (quartet); quint (quintet); h (hexet); hept (heptet); m (multiplet). Stern-Volmer quenching experiment and quantum yield measurement were conducted via a Photon Technology International (PTI) QM-400 spectrofluorometer with FelixGX software and a Shimadzu UV-2600 spectrophotometer. Cyclic voltammetry was measured using an CHI 750E. We thank Organic Chemistry Research Center of Sogang University for HRMS-ESI analysis, KAIST Analysis Center for Research Advancement (KARA) for emission spectra measurement, and Professor Sungwoo Hong's laboratory for UV-Vis absorption spectroscopy measurement.

2. Substrate Preparation

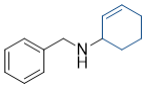
2.1. Synthesis of Secondary Allyl Amines with 3-Bromocyclohexene



(2.7 equiv) **A**

To a stirred solution of an amine (5.4 mmol, 2.7 equiv) and potassium carbonate (290 mg, 2.1 mmol, 1.05 equiv) in acetonitrile (6 mL) was added 3-bromocyclohexene (230 µL, 2.0 mmol, 1.0 equiv), and the mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with ethyl acetate (20 mL) and washed with saturated aqueous $NaHCO_3$ solution (50 mL) and brine (50 mL). The resulting organic layer was further dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude mixture was purified by silica gel flash column chromatography (acetone:hexane) to acquire the desired amine **A**.

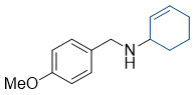
N-benzylcyclohex-2-en-1-amine (**A1**)



Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 4H), 7.23 (t, *J* = 7.1 Hz, 1H), 5.81 – 5.71 (m, 2H), 3.91 – 3.79 (m, 2H), 3.23 (s, 1H), 2.06 – 1.97 (m, 2H), 1.96 – 1.86 (m,

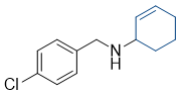
1H), 1.80 – 1.68 (m, 1H), 1.63 – 1.45 (m, 2H). Identity was confirmed by comparison with the literature.[1]

N-(4-methoxybenzyl)cyclohex-2-en-1-amine (**A2**)



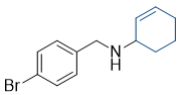
Yellow oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.27 (d, *J* = 9.0 Hz, 2H), 6.86 (d, *J* = 8.7 Hz, 2H), 5.80 – 5.70 (m, 2H), 3.79 (s, 3H), 3.78 (q, *J* = 12.7 Hz, 2H), 3.24 – 3.18 (m, 1H), 2.04 – 1.96 (m, 2H), 1.93 – 1.86 (m, 1H), 1.80 – 1.70 (m, 1H), 1.61 – 1.45 (m, 2H). Identity was confirmed by comparison with the literature.[1]

N-(4-chlorobenzyl)cyclohex-2-en-1-amine (**A3**)



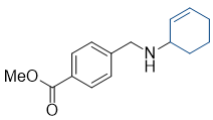
Red-brown oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.32 – 7.26 (m, 4H), 5.83 – 5.64 (m, 2H), 3.82 (q, *J* = 13.6 Hz, 2H), 3.22 – 3.16 (m, 1H), 2.07 – 1.92 (m, 2H), 1.92 – 1.82 (m, 1H), 1.79 – 1.69 (m, 1H), 1.61 – 1.42 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.3, 132.5, 129.8, 129.5, 129.2, 128.5, 52.4, 50.2, 29.5, 25.3, 20.2; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{13}H_{17}ClN$, 221.1044; found: 221.1046.

N-(4-bromobenzyl)cyclohex-2-en-1-amine (**A4**)



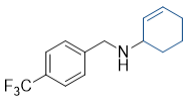
Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.28 – 7.22 (m, 2H), 7.22 – 7.13 (m, 2H), 6.76 (d, *J* = 7.4 Hz, 1H), 6.64 (d, J = 8.2 Hz, 2H), 4.30 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.7, 131.2, 129.7, 128.9, 120.4, 52.2, 50.1, 29.3, 25.2, 20.1; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{13}H_{17}BrN$, 266.0539; found: 221.0542.

Methyl 4-((cyclohex-2-en-1-ylamino)methyl)benzoate (**A5**)



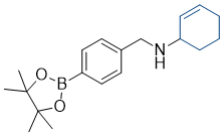
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 7.6 Hz, 2H), 7.39 (d, *J* = 7.7 Hz, 2H), 5.79 – 5.64 (m, 2H), 3.94 – 3.79 (m, 5H), 3.16 (s, 1H), 2.04 – 1.90 (m, 2H), 1.90 – 1.79 (m, 1H), 1.79 – 1.66 (m, 1H), 1.59 – 1.40 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 167.0, 146.2, 129.7, 129.7, 129.2, 128.7, 128.0, 52.5, 52.0, 50.6, 29.4, 25.3, 20.2; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{15}H_{20}NO_2$, 246.1489; found: 246.1491.

N-(4-(trifluoromethyl)benzyl)cyclohex-2-en-1-amine (**A6**)



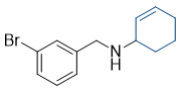
Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.1 Hz, 2H), 7.48 (d, *J* = 8.1 Hz, 2H), 5.84 – 5.67 (m, 2H), 3.91 (q, *J* = 14.2 Hz, 2H), 3.25 – 3.14 (m, 1H), 2.10 – 1.95 (m, 2H), 1.95 – 1.83 (m, 1H), 1.83 – 1.70 (m, 1H), 1.63 – 1.44 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.9, 129.6, 129.5, 129.3 (d, *J* = 32.6 Hz), 128.5, 125.4 (q, *J* = 3.7 Hz), 124.4 (q, *J* = 271.8 Hz), 52.6, 50.5, 29.5, 25.4, 20.2; ^{19}F NMR (376 MHz, $CDCl_3$) δ –62.5; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{14}H_{17}F_3N$, 256.1308; found: 256.1310.

N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)cyclohex-2-en-1-amine (**A7**)



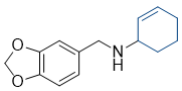
Yellow oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 2H), 7.38 (d, *J* = 7.7 Hz, 2H), 5.83 – 5.70 (m, 2H), 3.88 (q, *J* = 13.5 Hz, 2H), 3.22 (s, 1H), 2.04 – 1.93 (m, 2H), 1.93 – 1.85 (m, 1H), 1.80 – 1.70 (m, 1H), 1.58 – 1.48 (m, 2H), 1.33 (s, 12H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.9, 135.0, 129.8, 129.3, 127.7, 83.8, 75.1, 52.4, 51.0, 29.5, 25.4, 25.0, 20.3; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{19}H_{29}BNO_2$, 314.2289; found: 314.2288.

N-(3-bromobenzyl)cyclohex-2-en-1-amine (**A8**)



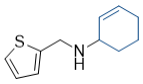
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.40 (d, *J* = 7.9 Hz, 1H), 7.31 (d, *J* = 7.5 Hz, 1H), 7.20 (t, *J* = 7.7 Hz, 1H), 5.87 – 5.72 (m, 2H), 3.85 (q, *J* = 13.0 Hz, 2H), 3.27 – 3.18 (m, 1H), 2.11 – 1.96 (m, 2H), 1.96 – 1.86 (m, 1H), 1.85 – 1.73 (m, 1H), 1.65 – 1.44 (m, 2H), 1.36 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 143.3, 131.1, 129.9, 129.7, 129.2, 126.7, 122.5, 52.4, 50.3, 29.4, 25.3, 20.2; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{13}H_{17}BrN$, 266.0539; found: 266.0539.

N-(benzo[*d*][1,3]dioxol-5-ylmethyl)cyclohex-2-en-1-amine (**A9**)



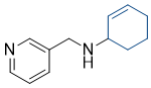
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.87 (s, 1H), 6.82 – 6.68 (m, 2H), 5.92 (s, 2H), 5.80 – 5.67 (m, 2H), 3.75 (q, *J* = 13.0 Hz, 2H), 3.23 – 3.14 (m, 1H), 2.07 – 1.92 (m, 2H), 1.93 – 1.82 (m, 1H), 1.81 – 1.68 (m, 1H), 1.62 – 1.41 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 146.5, 134.7, 129.8, 129.2, 121.3, 108.9, 108.1, 100.9, 52.3, 50.8, 29.5, 25.4, 20.3; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{14}H_{18}NO_2$, 232.1332; found: 232.1333.

N-(thiophen-2-ylmethyl)cyclohex-2-en-1-amine (**A10**)



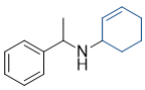
Light brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20 (dd, *J* = 4.3, 2.0 Hz, 1H), 6.99 – 6.91 (m, 2H), 5.82 – 5.69 (m, 2H), 4.06 (q, *J* = 13.6 Hz, 2H), 3.30 – 3.23 (m, 1H), 2.05 – 1.95 (m, 2H), 1.95 – 1.86 (m, 1H), 1.80 – 1.70 (m, 2H), 1.61 – 1.45 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 144.5, 129.5, 128.8, 126.3, 124.3, 124.0, 51.8, 45.3, 29.1, 25.1, 20.0; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{11}H_{16}NS$, 194.0998; found: 194.1000.

N-(pyridin-3-ylmethyl)cyclohex-2-en-1-amine (**A11**)



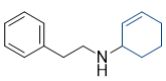
Brown oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H), 8.49 – 8.45 (m, 1H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.24 (dd, *J* = 7.8, 4.8 Hz, 1H), 5.82 – 5.76 (m, 1H), 5.73 – 5.67 (m, 1H), 3.85 (q, *J* = 13.1 Hz, 2H), 3.24 – 3.18 (m, 1H), 2.26 (s, 1H), 2.03 – 1.95 (m, 2H), 1.95 – 1.85 (m, 1H), 1.79 – 1.68 (m, 1H), 1.60 – 1.43 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 148.5, 136.2, 135.8, 129.9, 129.2, 123.5, 52.5, 48.1, 29.2, 25.3, 20.2; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{12}H_{17}N_2$, 189.1386; found: 189.1389.

N-(1-phenylethyl)cyclohex-2-en-1-amine (**A12**)



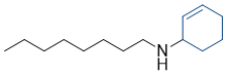
Yellow oil. Diastereomeric mixture (1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.36 – 7.24 (m, 8H), 7.24 – 7.16 (m, 2H), 5.85 – 5.69 (m, 2H), 5.69 – 5.51 (m, 2H), 3.98 (dq, *J* = 11.3, 6.6 Hz, 2H), 3.02 – 2.91 (m, 2H), 1.99 – 1.88 (m, 4H), 1.88 – 1.58 (m, 4H), 1.51 – 1.37 (m, 4H), 1.33 (d, *J* = 1.7 Hz, 3H), 1.30 (d, *J* = 1.6 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 146.1, 145.8, 130.8, 129.7, 128.5, 128.3, 128.3, 126.7, 126.6, 126.6, 55.0, 54.7, 50.2, 49.8, 30.6, 29.0, 25.3, 25.3, 25.1, 24.8, 20.5, 19.9; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{14}H_{20}N$, 202.1590; found: 202.1592.

N-phenethylcyclohex-2-en-1-amine (**A13**)



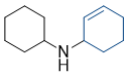
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 – 7.28 (m, 2H), 7.28 – 7.17 (m, 3H), 5.78 (d, *J* = 10.1 Hz, 1H), 5.70 (d, *J* = 10.4 Hz, 1H), 3.27 – 3.15 (m, 1H), 3.02 – 2.89 (m, 2H), 2.85 (t, *J* = 7.2 Hz, 2H), 2.07 – 1.95 (m, 2H), 1.95 – 1.83 (m, 1H), 1.80 – 1.64 (m, 1H), 1.64 – 1.49 (m, 1H), 1.49 – 1.36 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.1, 129.8, 128.9, 128.7, 128.4, 126.1, 52.9, 48.2, 36.7, 29.4, 25.3, 20.3; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{14}H_{20}N$, 202.1590; found: 202.1591.

N-octylcyclohex-2-en-1-amine (**A14**)



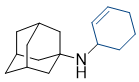
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.80 – 5.65 (m, 2H), 3.20 – 3.10 (m, 1H), 2.64 (td, *J* = 7.3, 2.9 Hz, 2H), 2.02 – 1.94 (m, 2H), 1.93 – 1.83 (m, 1H), 1.77 – 1.67 (m, 1H), 1.58 – 1.39 (m, 4H), 1.27 (d, *J* = 6.8 Hz, 10H), 0.87 (t, *J* = 6.7 Hz, 3H). Identity was confirmed by comparison with the literature.[1]

N-cyclohexylcyclohex-2-en-1-amine (**A15**)



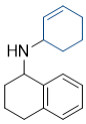
Colorless oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 5.77 – 5.66 (m, 2H), 3.29 (s, 1H), 2.64 – 2.56 (m, 1H), 2.05 – 1.92 (m, 2H), 1.89 – 1.81 (m, 3H), 1.76 – 1.67 (m, 3H), 1.65 – 1.58 (m, 1H), 1.58 – 1.50 (m, 1H), 1.45 – 1.36 (m, 1H), 1.30 – 1.21 (m, 2H), 1.17 – 1.02 (m, 3H). Identity was confirmed by comparison with the literature.[2]

N-(cyclohex-2-en-1-yl)adamantan-1-amine (**A16**)



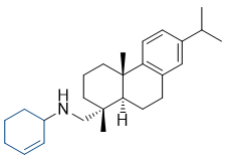
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 5.67 (d, *J* = 10.0 Hz, 1H), 5.59 (d, *J* = 9.9 Hz, 1H), 3.34 (s, 1H), 2.06 (s, 3H), 2.00 – 1.84 (m, 2H), 1.84 – 1.50 (m, 16H), 1.45 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 133.2, 127.5, 51.1, 44.8, 43.7, 36.7, 33.5, 29.7, 24.9, 20.5; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{16}H_{26}N$, 232.2060; found: 232.2063.

N-(cyclohex-2-en-1-yl)-1,2,3,4-tetrahydronaphthalen-1-amine (**A22**)



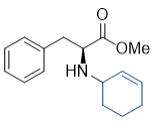
Yellow oil. Diastereomeric mixture (1:1). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.40 – 7.27 (m, 2H), 7.21 – 7.01 (m, 6H), 5.92 – 5.78 (m, 2H), 5.78 – 5.61 (m, 2H), 3.93 (dt, *J* = 10.1, 4.6 Hz, 2H), 3.43 – 3.31 (m, 2H), 2.84 – 2.62 (m, 4H), 2.04 – 1.46 (m, 20H), 1.22 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 139.9, 137.3, 137.3, 133.2, 130.9, 130.0, 129.0, 128.9, 128.7, 128.6, 128.3, 127.1, 126.5, 126.5, 126.4, 125.7, 52.6, 52.2, 50.7, 50.0, 39.1, 31.2, 29.6, 29.4, 29.3, 29.2, 28.6, 25.4, 20.5, 19.7, 18.8, 18.7; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{16}H_{22}N$, 228.1747; found: 228.1746.

N-(((*1R*,*4aS*,*10aR*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)cyclohex-2-en-1-amine (**A30**)



Colorless sticky oil. Diastereomeric mixture. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, *J* = 8.2 Hz, 1H), 7.01 (d, *J* = 7.9 Hz, 1H), 6.91 (s, 1H), 5.80 – 5.62 (m, 2H), 3.08 (s, 1H), 2.94 – 2.78 (m, 3H), 2.61 (dd, *J* = 11.8, 7.2 Hz, 1H), 2.38 – 2.23 (m, 2H), 2.04 – 1.93 (m, 2H), 1.88 – 1.64 (m, 7H), 1.64 – 1.50 (m, 2H), 1.50 – 1.35 (m, 4H), 1.25 (d, *J* = 6.9 Hz, 6H), 1.24 (s, 3H), 0.94 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.8, 145.5, 135.0, 130.7, 128.7, 126.9, 124.5, 123.9, 77.5, 77.2, 76.8, 58.7, 58.6, 54.0, 45.3, 45.0, 38.7, 37.6, 37.5, 37.1, 37.1, 36.2, 36.2, 33.6, 30.5, 29.8, 29.6, 25.5, 25.5, 24.1, 20.3, 20.3, 19.6, 19.4, 19.0, 19.0, 18.9; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{26}H_{40}N$, 366.3155; found: 366.3158.

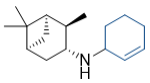
Methyl cyclohex-2-en-1-yl-*L*-phenylalaninate (**A31**)



Yellow green oil. Diastereomeric mixture (1:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.34 – 7.15 (m, 10H), 5.78 – 5.68 (m, 2H), 5.59 (d, *J* = 10.0 Hz, 1H), 5.52 (d, *J* = 9.8 Hz, 1H), 3.70 – 3.62 (m, 5H), 3.61 (s, 3H), 3.12 – 3.03 (m, 2H), 2.98 – 2.84 (m, 4H), 2.04 – 1.84 (m, 4H), 1.76 – 1.68 (m, 2H), 1.62 – 1.57 (m, 2H), 1.55 – 1.40 (m, 2H), 1.39 – 1.23 (m, 2H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 175.9, 175.8, 138.3, 138.2, 130.1, 129.7, 129.6, 129.6, 129.1, 128.6, 128.6,

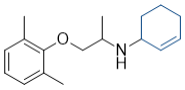
126.9, 126.9, 61.0, 60.8, 52.3, 51.8, 51.8, 51.8, 40.6, 40.6, 30.5, 29.4, 25.6, 25.6, 20.5, 19.9; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{16}H_{22}NO_2$, 260.1645; found: 260.1648.

(*1R*,*2R*,*3R*,*5S*)-*N*-(cyclohex-2-en-1-yl)-2,6,6-trimethylbicyclo[3.1.1]heptan-3-amine (**A32**)



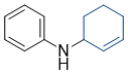
Brown oil. Diastereomeric mixture (1:1). ^{1}H NMR (400 MHz, CD_2Cl_2) δ 5.80 – 5.68 (m, 3H), 5.68 – 5.60 (m, 1H), 3.29 – 3.23 (m, 1H), 3.23 – 3.17 (m, 1H), 3.04 (tt, *J* = 10.4, 5.8 Hz, 2H), 2.41 – 2.26 (m, 4H), 2.07 – 1.90 (m, 6H), 1.90 – 1.81 (m, 2H), 1.81 – 1.76 (m, 2H), 1.76 – 1.66 (m, 4H), 1.61 – 1.50 (m, 4H), 1.46 – 1.37 (m, 2H), 1.21 (s, 6H), 1.08 (d, *J* = 7.3 Hz, 6H), 0.98 (s, 6H), 0.95 (dd, *J* = 9.4, 5.9 Hz, 2H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 131.6, 130.5, 128.7, 128.4, 53.7, 53.3, 50.9, 50.0, 48.5, 48.4, 46.1, 46.0, 42.5, 39.0, 39.0, 37.9, 37.4, 34.3, 34.1, 31.4, 29.3, 28.2, 28.1, 25.9, 25.9, 23.6, 23.6, 21.5, 21.4, 21.1, 20.3; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{16}H_{28}N$, 234.2216; found: 234.2219.

N-(1-(2,6-dimethylphenoxy)propan-2-yl)cyclohex-2-en-1-amine (**A34**)



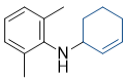
Yellow oil. Diastereomeric mixture (1:1). ^{1}H NMR (400 MHz, C_6D_6) δ 6.98 – 6.84 (m, 6H), 5.89 – 5.79 (m, 2H), 5.74 – 5.64 (m, 2H), 3.56 (ddd, *J* = 10.5, 8.8, 6.8 Hz, 2H), 3.47 (dd, *J* = 9.1, 4.9 Hz, 2H), 3.33 – 3.17 (m, 4H), 2.25 (s, 12H), 1.92 – 1.73 (m, 6H), 1.72 – 1.58 (m, 2H), 1.52 – 1.36 (m, 4H), 1.30 (s, 2H), 1.07 (d, *J* = 6.4 Hz, 3H), 1.03 (d, *J* = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 156.4, 131.8, 131.0, 131.0, 130.8, 129.3, 124.1, 77.1, 76.7, 50.7, 50.5, 50.3, 50.2, 31.3, 29.9, 25.7, 25.7, 20.5, 20.3, 18.6, 17.8, 16.5; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{17}H_{26}N$, 260.2009; found: 260.2013.

N-(cyclohex-2-en-1-yl)aniline (**A37**)



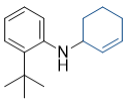
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.18 (t, *J* = 7.3 Hz, 2H), 6.78 – 6.62 (m, 3H), 5.91 – 5.81 (m, 1H), 5.76 (d, *J* = 10.2 Hz, 1H), 4.00 (s, 1H), 2.13 – 2.00 (m, 2H), 1.99 – 1.84 (m, 1H), 1.81 – 1.56 (m, 3H). Identity was confirmed by comparison with the literature.[3]

N-(cyclohex-2-en-1-yl)-2,6-dimethylaniline (**A38**)



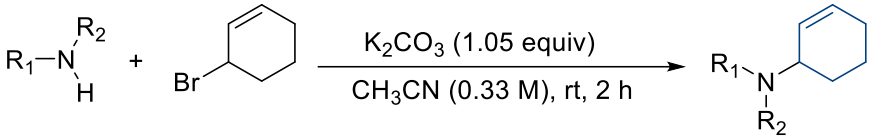
Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (d, *J* = 7.5 Hz, 2H), 6.81 (t, *J* = 7.5 Hz, 1H), 5.84 – 5.67 (m, 2H), 3.69 (s, 1H), 2.29 (s, 6H), 2.13 – 1.97 (m, 2H), 1.97 – 1.83 (m, 1H), 1.83 – 1.69 (m, 1H), 1.69 – 1.46 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 145.1, 130.4, 129.1, 128.9, 128.8, 121.4, 52.4, 30.6, 25.3, 20.4, 19.1; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{14}H_{20}N$, 202.1590; found: 202.1591.

2-(*tert*-Butyl)-*N*-(cyclohex-2-en-1-yl)aniline (**A39**)



Yellow oil. 1H NMR (400 MHz, $CDCl_3$) δ 7.26 (dd, *J* = 7.8, 1.6 Hz, 2H), 7.16 – 7.10 (m, 1H), 6.78 (d, *J* = 7.9 Hz, 1H), 6.70 (t, *J* = 7.4 Hz, 1H), 5.93 – 5.85 (m, 1H), 5.83 – 5.73 (m, 1H), 4.11 (s, 1H), 2.15 – 2.02 (m, 2H), 2.02 – 1.91 (m, 1H), 1.80 – 1.60 (m, 3H), 1.42 (s, 9H). Identity was confirmed by comparison with the literature.[3]

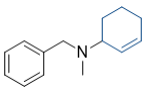
2.2. Synthesis of Tertiary Allyl Amines with 3-Bromocyclohexene



(1.2 equiv) **A**

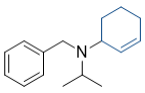
To a stirred solution of a amine (2.4 mmol, 1.2 equiv) and potassium carbonate (290 mg, 2.1 mmol, 1.05 equiv) in acetonitrile (6 mL) was added 3-bromocyclohexene (230 µL, 2.0 mmol, 1.0 equiv), and the mixture was stirred at room temperature for 2 h. The reaction mixture was diluted with ethyl acetate (20 mL) and washed with saturated aqueous $NaHCO_3$ solution (50 mL) and brine (50 mL). The resulting organic layer was further dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude mixture was purified by silica gel flash column chromatography (acetone:hexane) to aquire the desired amine **A**.

N-benzyl-*N*-methylcyclohex-2-en-1-amine (**A17**)



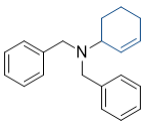
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 – 7.31 (m, 4H), 7.28 (t, *J* = 6.4 Hz, 1H), 5.93 – 5.84 (m, 1H), 5.80 (d, *J* = 10.2 Hz, 1H), 3.72 (d, J = 13.3 Hz, 1H), 3.53 (d, *J* = 13.3 Hz, 1H), 3.47 – 3.38 (m, 1H), 2.28 (s, 3H), 2.13 – 1.97 (m, 2H), 1.97 – 1.83 (m, 2H), 1.68 – 1.55 (m, 2H). Identity was confirmed by comparison with the literature.[4]

N-benzyl-*N*-isopropylcyclohex-2-en-1-amine (**A18**)



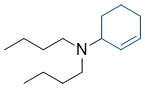
Yellow oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.5 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.19 (t, *J* = 7.3 Hz, 1H), 5.78 – 5.73 (m, 1H), 5.68 (d, *J* = 10.3 Hz, 1H), 3.70 (q, *J* = 15.2 Hz, 2H), 3.47 – 3.40 (m, 1H), 2.98 (hept, *J* = 6.5 Hz, 1H), 1.99 – 1.91 (m, 2H), 1.88 – 1.81 (m, 1H), 1.81 – 1.74 (m, 1H), 1.55 – 1.49 (m, 2H), 1.04 (t, *J* = 5.9 Hz, 6H). Identity was confirmed by comparison with the literature.[5]

N,*N*-dibenzylcyclohex-2-en-1-amine (**A19**)



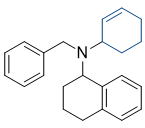
White solid. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.40 (d, *J* = 7.7 Hz, 4H), 7.29 (t, *J* = 7.5 Hz, 4H), 7.20 (t, *J* = 7.2 Hz, 2H), 5.85 – 5.79 (m, 1H), 5.74 (d, *J* = 10.3 Hz, 1H), 3.73 (d, *J* = 14.0 Hz, 2H), 3.54 (d, *J* = 14.0 Hz, 2H), 3.37 – 3.31 (m, 1H), 1.98 – 1.89 (m, 3H), 1.83 – 1.75 (m, 1H), 1.56 – 1.41 (m, 2H). Identity was confirmed by comparison with the literature.[6]

N,*N*-dibutylcyclohex-2-en-1-amine (**A20**)



Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.85 – 5.71 (m, 1H), 5.62 (d, *J* = 8.7 Hz, 1H), 3.46 – 3.27 (m, 1H), 2.56 – 2.28 (m, 4H), 2.08 – 1.91 (m, 2H), 1.88 – 1.71 (m, 2H), 1.55 – 1.23 (m, 11H), 0.90 (t, *J* = 7.2 Hz, 6H). Identity was confirmed by comparison with the literature.[2]

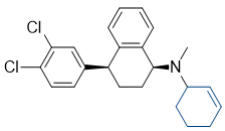
N-benzyl-*N*-(cyclohex-2-en-1-yl)-1,2,3,4-tetrahydronaphthalen-1-amine (**A23**)



Light yellow oil. Diastereomeric mixture (1.4:1). ^{1}H NMR (400 MHz, C_6D_6) δ 8.09 (d, *J* = 7.8 Hz, 1H), 8.06 (d, *J* = 7.8 Hz, 1.4H), 7.50 (d, *J* = 7.5 Hz, 2.8H), 7.46 (d, *J* = 7.5 Hz, 2H), 7.27 – 7.16 (m, 7H), 7.14 – 7.01 (m, 5H), 6.96 (s, 1H), 6.92 (d, *J* = 7.9 Hz, 1.4H), 5.90 (d, *J*

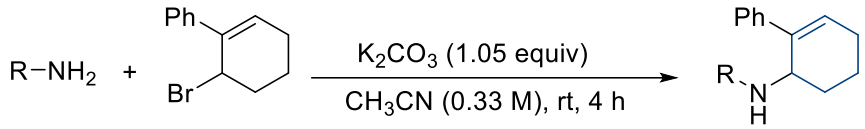
= 10.2 Hz, 1H), 5.86 (d, *J* = 10.3 Hz, 1.4H), 5.76 – 5.68 (m, 2.4H), 4.00 (dd, *J* = 10.3, 5.1 Hz, 1H), 3.93 – 3.64 (m, 6.2H), 3.54 – 3.46 (m, 1H), 3.45 – 3.37 (m, 1.4H), 2.66 – 2.55 (m, 2.4H), 2.51 – 2.39 (m, 2.4H), 2.09 – 2.00 (m, 1.4H), 1.98 – 1.89 (m, 2.4H), 1.86 – 1.66 (m, 8.2H), 1.63 – 1.46 (m, 7.2H), 1.36 – 1.18 (m, 4.8H); ^{13}C NMR (101 MHz, C_6D_6) δ 142.4, 141.7, 140.5, 140.2, 138.7, 138.7, 133.9, 131.7, 130.0, 129.8, 129.2, 129.1, 129.0, 128.8, 128.6, 128.5, 128.4, 127.1, 126.5, 126.2, 126.1, 58.5, 57.2, 54.1, 53.7, 50.7, 50.6, 30.5, 30.4, 30.3, 27.3, 27.3, 25.4, 25.4, 22.9, 22.8, 22.7, 22.3; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{23}H_{28}N$, 318.2216; found: 318.2217.

(*1S,4S*)-*N*-(cyclohex-2-en-1-yl)-4-(3,4-dichlorophenyl)-*N*-methyl-1,2,3,4-tetrahydronaphthalen-1-amine (**A33**)



Opaque sticky oil. Diastereomeric mixture (1:1). ^{1}H NMR (400 MHz, C_6D_6) δ 7.87 (dd, *J* = 12.2, 7.8 Hz, 2H), 7.20 – 7.15 (m, 2H), 7.10 (t, *J* = 2.5 Hz, 2H), 7.05 – 6.99 (m, 2H), 6.97 (dd, *J* = 8.3, 3.3 Hz, 2H), 6.75 (d, *J* = 7.5 Hz, 2H), 6.54 (ddd, *J* = 8.2, 4.4, 2.1 Hz, 2H), 5.82 – 5.70 (m, 4H), 3.84 (dt, *J* = 9.7, 5.1 Hz, 2H), 3.73 (q, *J* = 4.1 Hz, 2H), 3.40 – 3.34 (m, 1H), 3.34 – 3.27 (m, 1H), 2.20 (s, 3H), 2.17 (s, 3H), 1.89 – 1.61 (m, 15H), 1.56 – 1.37 (m, 5H); ^{13}C NMR (101 MHz, C_6D_6) δ 148.4, 140.6, 140.5, 138.6, 138.6, 132.6, 132.2, 131.6, 131.2, 131.2, 130.6, 130.5, 130.3, 130.2, 130.2, 129.8, 129.7, 129.3, 129.1, 128.6, 128.6, 127.2, 127.1, 127.1, 127.1, 60.9, 60.3, 57.7, 57.5, 44.0, 44.0, 33.0, 32.3, 30.2, 30.1, 27.2, 27.1, 25.6, 25.6, 22.0, 21.8, 21.0, 20.7; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{23}H_{26}Cl_2N$, 386.1437; found: 386.1439.

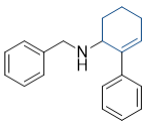
2.3. Synthesis of Allyl Amines with 6-Bromo-1-phenylcyclohexene



(2.7 equiv) **A**

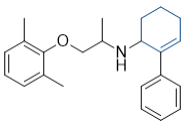
To a stirred solution of an amine (5.4 mmol, 2.7 equiv) and potassium carbonate (290 mg, 2.1 mmol, 1.05 equiv) in acetonitrile (6 mL) was added 6-bromo-1-phenylcyclohexene (474 mg, 2.0 mmol, 1.0 equiv), and the mixture was stirred at room temperature for 4 h. The reaction mixture was diluted with ethyl acetate (20 mL) and washed with saturated aqueous $NaHCO_3$ solution (50 mL) and brine (50 mL). The resulting organic layer was further dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude mixture was purified by silica gel flash column chromatography (acetone:hexane) to acquire the desired amine **A**.

N-benzyl-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-amine (**A25**)



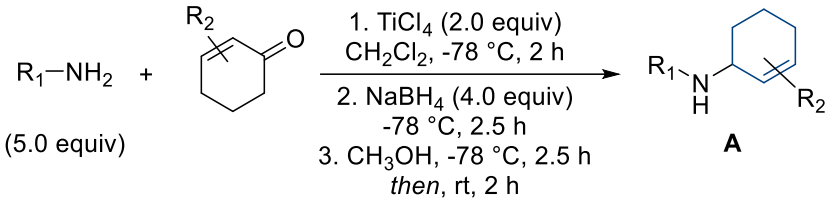
Yellow oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.31 – 7.28 (m, 5H), 7.27 – 7.20 (m, 3H), 7.20 – 7.16 (m, 2H), 6.10 (t, *J* = 3.8 Hz, 1H), 3.82 (d, *J* = 13.2 Hz, 1H), 3.79 (s, 1H), 3.72 (d, *J* = 13.2 Hz, 1H), 2.30 – 2.13 (m, 2H), 2.09 – 2.00 (m, 1H), 1.86 (d, *J* = 12.9 Hz, 1H), 1.79 (d, *J* = 11.6 Hz, 1H), 1.70 – 1.61 (m, 1H). Identity was confirmed by comparison with the literature.[7]

N-(1-(2,6-dimethylphenoxy)propan-2-yl)-2,3,4,5-tetrahydro-[1,1'-biphenyl]-2-amine (**A36**)



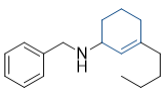
Brown oil. Diastereomeric mixture (1:1). ^{1}H NMR (300 MHz, CD_2Cl_2) δ 7.48 – 7.37 (m, 4H), 7.35 – 7.14 (m, 6H), 6.99 – 6.93 (m, 4H), 6.90 – 6.82 (m, 2H), 6.03 (t, *J* = 3.8 Hz, 1H), 5.99 (t, *J* = 4.0 Hz, 1H), 3.90 – 3.82 (m, 2H), 3.69 – 3.56 (m, 2H), 3.50 (dd, *J* = 8.7, 5.3 Hz, 1H), 3.38 (dd, *J* = 8.8, 6.2 Hz, 1H), 3.28 – 3.09 (m, 2H), 2.20 (s, 6H), 2.15 (s, 6H), 2.08 – 1.95 (m, 2H), 1.85 – 1.37 (m, 12H), 1.13 (d, *J* = 6.4 Hz, 3H), 1.09 (d, J = 6.3 Hz, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 156.3, 156.3, 142.5, 140.8, 140.6, 131.2, 131.2, 129.1, 128.6, 128.4, 128.3, 127.1, 127.0, 126.8, 126.7, 124.0, 124.0, 77.5, 76.7, 52.0, 51.8, 50.8, 50.3, 29.4, 27.7, 26.6, 19.8, 17.5, 17.3, 17.2, 16.5; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{23}H_{30}NO$, 336.2322; found: 336.2322.

2.4. Synthesis of Allyl Amines with Cyclohexenones



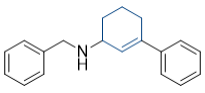
A modified procedure reported by K. Taniguchi and co-workers was applied.[8] To a stirred solution of the amine (10.0 mmol, 5.0 equiv) and the enone (2.0 mmol, 1.0 equiv) was added the 1.0 M solution of $TiCl_4$ (4 mL, 4.0 mmol, 2.0 equiv) dropwise at –78 ℃ for 30 min., and the resulting solution was further stirred for 2 h at the same temperature. Sodium borohydride (303 mg, 8.0 mmol, 4.0 equiv) was added, and the reaction mixture was further stirred for 2.5 h at –78 ℃. Methanol (9 mL) was added dropwise for 30 min., and the resulting mixture was further stirred for 2.5 h at –78 ℃ and 2 h at room temperature. After the reaction was complete, a mixture of ethyl acetate (10 mL) and a saturated aqueous $NaHCO_3$ (10 mL) was added and further stirred for 30 min. at rt. The generated solid was removed via filtration, and the resulting organic layer was further washed with brine (50 mL), dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude mixture was purified by silica gel flash column chromatography (acetone:hexane) to afford the desired amine **A**.

N-benzyl-3-butylcyclohex-2-en-1-amine (**A26**)



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.4 Hz, 2H), 7.23 (t, *J* = 7.2 Hz, 1H), 5.45 (s, 1H), 3.86 (q, *J* = 13.2 Hz, 2H), 3.25 (s, 1H), 1.99 – 1.90 (m, 4H), 1.89 – 1.83 (m, 1H), 1.82 – 1.74 (m, 1H), 1.58 – 1.42 (m, 2H), 1.42 – 1.33 (m, 2H), 1.32 – 1.23 (m, 2H), 0.89 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.8, 140.5, 128.4, 128.2, 126.8, 123.5, 52.8, 51.0, 37.5, 29.8, 29.4, 28.6, 22.5, 20.6, 14.0;HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{17}H_{26}N$, 244.2060; found: 244.2062.

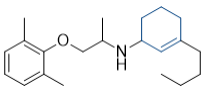
N-benzyl-3,4,5,6-tetrahydro-[1,1'-biphenyl]-3-amine (**A27**)



Dark blue oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.32 (m, 10H), 6.28 (s, 1H), 4.04 (dd, *J* = 2923.8, 12.7 Hz, 2H), 3.58 – 3.50 (m, 1H), 2.63 – 2.44 (m, 2H), 2.16 – 2.02 (m, 2H), 1.97 – 1.81 (m, 2H), 1.73 – 1.61 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.9,

140.6, 138.4, 128.3, 128.1, 128.1, 127.0, 126.8, 125.2, 53.1, 50.9, 29.1, 27.6, 20.7;HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{19}H_{22}N$, 264.1747; found: 264.1750.

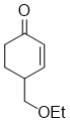
3-Butyl-*N*-(1-(2,6-dimethylphenoxy)propan-2-yl)cyclohex-2-en-1-amine (**A35**)



Yellow oil. ^{1}H NMR (300 MHz, C_6D_6) δ 6.97 – 6.85 (m, 3H), 5.68 – 5.60 (m, 1H), 3.64 – 3.55 (m, 1H), 3.55 – 3.46 (m, 1H), 3.39 – 3.22 (m, 2H), 2.26 (s, 6H), 1.94 (t, *J* = 7.4 Hz, 2H), 1.87 – 1.67 (m, 4H), 1.56 – 1.45 (m, 2H), 1.40 – 1.22 (m, 5H), 1.11 (d, *J* = 6.4 Hz, 3H), 0.88 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (101 MHz, C_6D_6) δ 156.5, 139.7, 131.0, 129.3, 124.7, 124.1, 76.8, 50.9, 50.4, 37.9, 31.4, 30.3, 29.0, 22.8, 20.8, 18.8, 16.6, 14.3; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{21}H_{34}NO$, 316.2635; found: 316.2636.

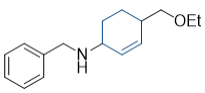
Following amines were synthesized from the newly synthesized enones, which were prepared by the previously reported methods.

4-(Ethoxymethyl)cyclohex-2-en-1-one[9]



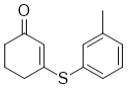
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 6.84 (ddd, *J* = 10.2, 2.6, 1.4 Hz, 1H), 5.91 (dd, *J* = 10.2, 2.5 Hz, 1H), 3.45 – 3.37 (m, 2H), 3.37 – 3.27 (m, 2H), 2.65 – 2.53 (m, 1H), 2.40 (dt, *J* = 16.7, 4.7 Hz, 1H), 2.34 – 2.19 (m, 1H), 2.05 – 1.95 (m, 1H), 1.74 – 1.59 (m, 1H), 1.14 – 1.03 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.5, 151.8, 129.7, 72.7, 66.5, 36.8, 36.6, 25.7, 15.0; HRMS-ESI (m/z) $[M+Na]^+$ calcd. for $C_9H_{14}NaO_2$, 177.0886; found: 177.0885.

N-benzyl-4-(ethoxymethyl)cyclohex-2-en-1-amine (**A28**)



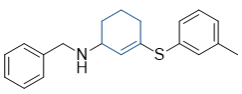
Yellow oil. Diastereomeric mixture. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.22 (m, 5H), 5.89 – 5.67 (m, 2H), 3.93 – 3.77 (m, 2H), 3.47 (q, *J* = 7.0 Hz, 2H), 3.38 – 3.18 (m, 3H), 2.49 – 2.29 (m, 1H), 2.14 – 2.02 (m, 1H), 1.97 – 1.84 (m, 1H), 1.77 – 1.24 (m, 3H), 1.19 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.4, 140.4, 130.9, 130.7, 130.0, 130.0, 128.2, 128.0, 128.0, 126.7, 74.7, 73.9, 66.2, 53.1, 51.7, 51.0, 50.6, 36.4, 35.8, 29.0, 26.3, 24.8, 24.6, 22.1, 15.1, 15.0; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{16}H_{24}NO$, 246.1852; found: 246.1855.

3-(*m*-Tolylthio)cyclohex-2-en-1-one[10]



Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (t, *J* = 5.3 Hz, 3H), 7.28 – 7.20 (m, 2H), 5.53 – 5.44 (m, 1H), 2.52 (t, *J* = 6.0 Hz, 2H), 2.36 (d, *J* = 6.3 Hz, 5H), 2.04 (p, *J* = 5.9 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.3, 167.4, 140.0, 136.1, 132.6, 131.1, 129.8, 127.7, 120.9, 37.4, 30.3, 23.1, 21.3; HRMS-ESI (m/z) $[M+Na]^+$ calcd. for $C_{13}H_{14}NaOS$, 241.0658; found: 241.0659

N-benzyl-3-(*m*-tolylthio)cyclohex-2-en-1-amine (**A29**)

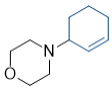


Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 7.21 – 7.15 (m, 3H), 7.07 (d, *J* = 7.1 Hz, 1H), 5.90 (s, 1H), 3.85 (s, 2H), 3.35 (s, 1H), 2.33 (s, 3H), 2.20 – 2.04 (m, 2H), 1.98 – 1.79 (m, 2H), 1.64 – 1.49 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 140.5, 138.8, 135.2, 133.5, 132.4, 131.3, 128.9, 128.8, 128.5, 128.2, 128.0, 127.0, 53.7, 51.0, 30.1, 29.0, 21.4, 21.2; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{20}H_{24}NS$, 310.1624; found: 310.1626.

2.5 Synthesis of Allyl Amines via Transition-Metal Catalysis

Amine **A21** was synthesized by the reaction between morpholine and 1,3-cyclohexadiene following the reported procedure.[2]

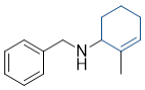
4-(Cyclohex-2-en-1-yl)morpholine (**A21**)



Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.89 – 5.78 (m, 1H), 5.65 (d, *J* = 10.2 Hz, 1H), 3.72 (t, *J* = 4.6 Hz, 4H), 3.17 (s, 1H), 2.68 – 2.49 (m, 4H), 1.99 (d, *J* = 13.0 Hz, 2H), 1.78 (dt, *J* = 8.9, 4.5 Hz, 2H), 1.63 – 1.46 (m, 2H). Identity was confirmed by comparison with the literature.[2]

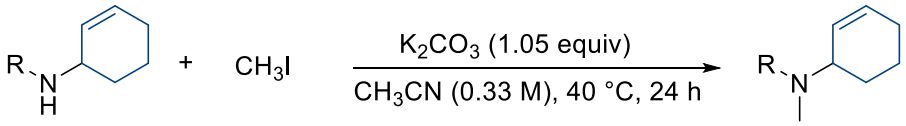
Amine **A24** was synthesized by the reaction between benzylamine and 2-methylcyclohex-2-en-1-yl acetate following the reported procedure.[11]

N-benzyl-2-methylcyclohex-2-en-1-amine (**A24**)



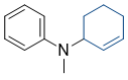
Light yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, *J* = 7.2 Hz, 2H), 7.32 (t, *J* = 7.5 Hz, 2H), 7.25 (t, *J* = 8.6 Hz, 1H), 5.51 (s, 1H), 3.90 (d, *J* = 13.2 Hz, 1H), 3.74 (d, *J* = 13.2 Hz, 1H), 3.03 (s, 1H), 2.06 – 1.86 (m, 3H), 1.84 – 1.77 (m, 1H), 1.74 (s, 3H), 1.65 (dt, *J* = 12.1, 5.3 Hz, 2H), 1.57 – 1.50 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 141.3, 135.6, 128.4, 128.3, 126.9, 124.8, 55.4, 51.4, 27.9, 25.6, 21.6, 18.7; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{14}H_{20}N$, 202.1590; found: 202.1590.

2.6. Synthesis of Tertiary Allyl Amines with Secondary Allyl Amines via Methylation



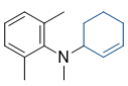
To a stirred solution of an amine (1.0 mmol, 1.0 equiv) and potassium carbonate (145 mg, 1.05 mmol, 1.05 equiv) in acetonitrile (3 mL) was added methyl iodide (311 µL, 5.0 mmol, 5.0 equiv), and the mixture was stirred at 40 ℃ for 24 h. The reaction mixture was diluted with ethyl acetate (20 mL) and washed with saturated aqueous $NaHCO_3$ solution (50 mL) and brine (50 mL). The resulting organic layer was further dried ($MgSO_4$), filtered, and concentrated in vacuo. The crude mixture was purified by silica gel flash column chromatography (CH_2Cl_2:hexane) to acquire the desired amine **A**.

N-(cyclohex-2-en-1-yl)-*N*-methylaniline (**A37-Me**)



Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.29 – 7.17 (m, 2H), 6.81 (d, *J* = 8.1 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 5.99 – 5.84 (m, 1H), 5.64 (d, *J* = 10.3 Hz, 1H), 4.52 – 4.39 (m, 1H), 2.80 (s, 3H), 2.13 – 1.97 (m, 2H), 1.95 – 1.78 (m, 2H), 1.78 – 1.53 (m, 2H). Identity was confirmed by comparison with the literature.[3]

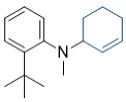
N-(cyclohex-2-en-1-yl)-*N*,2,6-trimethylaniline (**A38-Me**)



Colorless oil. 1H NMR (300 MHz, $CDCl_3$) δ 7.13 – 6.88 (m, 3H), 5.88 – 5.65 (m, 2H), 3.67 (s, 1H), 2.80 (s, 3H), 2.32 (s, 6H), 2.08 – 1.97 (m, 2H), 1.90 – 1.80 (m, 1H), 1.79 – 1.69 (m, 2H),

1.66 – 1.45 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.3, 137.7, 137.5, 130.4, 129.5, 129.0, 128.8, 124.6, 57.6, 36.4, 27.8, 25.3, 21.2, 20.1, 19.9; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{15}H_{22}N$, 216.1747; found: 216.1746.

2-(*tert*-Butyl)-*N*-(cyclohex-2-en-1-yl)-*N*-methylaniline (**A39-Me**)

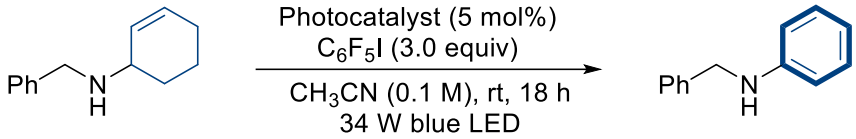


Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 7.9 Hz, 1H), 7.37 (d, *J* = 7.7 Hz, 1H), 7.26 – 7.20 (m, 1H), 7.16 (t, *J* = 7.3 Hz, 1H), 5.83 – 5.68 (m, 1H), 5.66 – 5.48 (m, 1H), 3.53 (s, 1H), 2.62 (s, 3H), 2.20 – 1.71 (m, 5H), 1.65 – 1.51 (m, 1H), 1.48 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 153.1, 148.1, 131.4, 129.3, 127.9, 127.3, 126.4, 125.5, 60.7, 40.1, 35.8, 31.5, 25.3, 25.2, 21.7; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{17}H_{26}N$, 244.2060; found: 244.2063.

3. Screening Experiments

An oven-dried 4 mL reaction vial equipped with a PTFE-coated stir bar was charged with photocatalyst, base, and solvent in a glovebox. The vial was closed with a Teflon-lined septum cap and taken out of the glovebox. Amine **A1** (18.8 mg, 0.1 mmol, 1.0 equiv) and perfluoroarene were added via a gas-tight syringe, and the solution was stirred for 24 h under 34 W blue LED irradiation with fan cooling. After the reaction was complete, dodecane (22.7 µL, 0.1 mmol, 1.0 equiv) was added, and the result was analyzed by GC.

Table S1 Screening of the photocatalyst

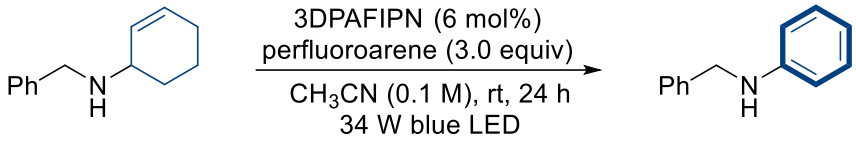


A1
0.1 mmol

B1

Photocatalyst	Yield **B1** (GC)
$Ir(ppy)_3$	18%
$[Ir(dFCF_3ppy)_2(dtbbpy)](PF_6)$	22%
3DPAFIPN (6 mol%)	**24%**
4CzTPN	18%
4CzPN	22%
$Ru(bpy)_3Cl_2$	22%

Table S2 Screening of the perfluoroarene

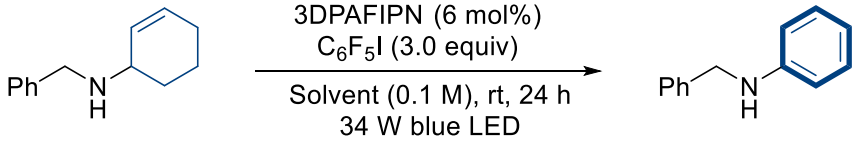


A1
0.1 mmol

B1

Perfluoroarene	Yield **B1** (GC)	Perfluoroarene	Yield **B1** (GC)
C_6F_5I	**19%**	$C_6F_5NO_2$	2%
C_6F_5Cl	0	C_6F_5N	2%
C_6F_5Br	0	$C_6F_5C(O)Cl$	0
C_6F_6	3%	$C_6F_5SO_2Cl$	0
C_6F_5H	2%	$C_6F_5B(OH)_2$	0
C_6F_5CN	0		

Table S3 Screening of the solvent

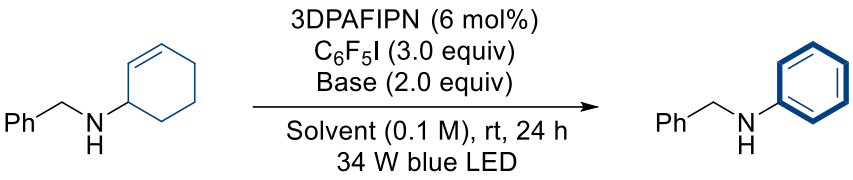


A1
0.1 mmol

B1

Solvent	Yield **B1** (GC)	Solvent	Yield **B1** (GC)
CH_3CN	22%	1,4-Dioxane	15%
CH_2Cl_2	**32%**	C_6F_6	12%
THF	19%	EtOAc	15%
DMA	9%	CH_3NO_2	6%
Benzene	18%	MTBE	15%
Ether	15%	H_2O	3%
1,2-DCE	29%	CH_3OH	4%
$CHCl_3$	15%	Acetone	16%
Chlorobenzene	16%	DMSO	6%

Table S4 Screening of the base

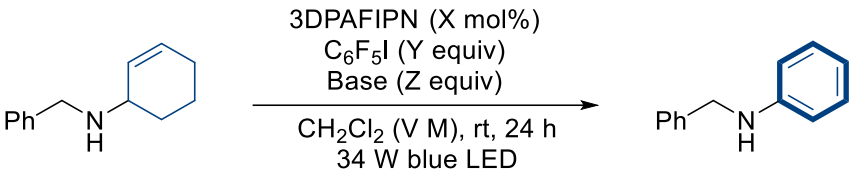


A1
0.1 mmol

B1

Base	Yield **B1** (GC)	Base	Yield **B1** (GC)
None	32%	2,6-Lutidine	51%
NaOAc	39%	2,2'-Bipyidyl	29%
NaOH	20%	4,4'-Bipyridyl	26%
K_2CO_3	**67%**	Na_2CO_3	56%
K_3PO_4	26%	**Cs_2CO_3**	**68%**
Pyridine	30%	Li_2CO_3	24%
3-Chloropyridine	29%	Rb_2CO_3	63%

Table S5 Screening of the concentration and the equivalence of the reagents

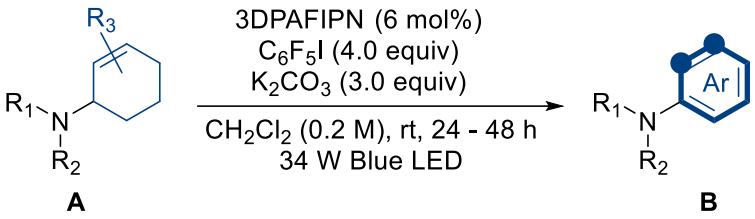


A1
0.2 mmol

B1

X	Y	Z	V	Yield **B1** (GC)
6.0	3.0	2.0	0.1	83%
6.0	3.0	2.0	0.2	82%
3.0	3.0	2.0	0.2	85%
6.0	3.0	3.0	0.2	85%
9.0	3.0	2.0	0.2	72%
6.0	4.0	2.0	0.2	85%
9.0	4.0	2.0	0.2	89%
6.0	**4.0**	**3.0**	**0.2**	**95%**
3.0	4.0	3.0	0.2	84%

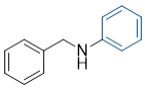
4. General Procedure for the Synthesis of *N*-Aryl Amines (B)



An oven-dried 4 mL reaction vial equipped with a PTFE-coated stir bar was charged with 3DPAFIPN (7.8 mg, 0.012 mmol, 6 mol%), potassium carbonate (82.9 mg, 0.6 mmol, 3.0 equiv), amine **A** (if solid, 0.2 mmol, 1.0 equiv), and CH_2Cl_2 (1 mL) in a glovebox. The vial was closed with a Teflon-lined septum cap and taken out of the glovebox. Amine **A** (if liquid, 0.2 mmol, 1.0 equiv) and iodopentafluorobenzene (107 µL, 0.8 mmol, 4.0 equiv) were added via a gas-tight syringe, and the solution was stirred for the indicated time under 34 W blue LED irradiation with fan cooling. After the reaction was complete, the mixture was directly loaded onto the silica gel and further purified by silica gel flash column chromatography (ether:hexane) to afford the corresponding *N*-aryl amine **B**.

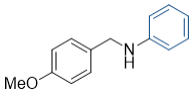
5. Characterization of *N*-Aryl Amines (B)

N-benzylaniline (**B1**)



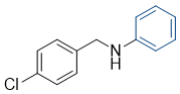
Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.43 – 7.26 (m, 5H), 7.21 (t, *J* = 7.9 Hz, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 8.5 Hz, 2H), 4.36 (s, 2H), 4.17 (s, 1H). Identity was confirmed by comparison with the literature.[12]

N-(4-methoxybenzyl)aniline (**B2**)



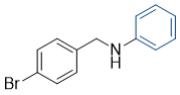
Yellow oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.32 (d, *J* = 8.4 Hz, 2H), 7.21 (t, *J* = 7.8 Hz, 2H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.75 (t, *J* = 7.2 Hz, 1H), 6.67 (d, *J* = 7.8 Hz, 2H), 4.28 (s, 2H), 4.01 (s, 1H), 3.83 (s, 3H). Identity was confirmed by comparison with the literature.[12]

N-(4-chlorobenzyl)aniline (**B3**)



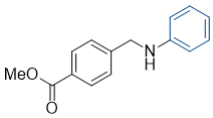
Yellow oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.35 – 7.28 (m, 4H), 7.24 – 7.15 (m, 2H), 6.76 (t, *J* = 7.1 Hz, 1H), 6.63 (d, *J* = 7.6 Hz, 2H), 4.32 (s, 2H), 4.08 (s, 1H). Identity was confirmed by comparison with the literature.[12]

N-(4-bromobenzyl)aniline (**B4**)



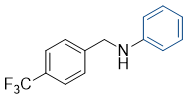
Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 (d, *J* = 8.4 Hz, 2H), 7.23 (d, *J* = 7.4 Hz, 2H), 7.22 – 7.13 (m, 2H), 6.76 (d, *J* = 14.5 Hz, 1H), 6.64 (d, *J* = 8.2 Hz, 2H), 4.30 (s, 2H). Identity was confirmed by comparison with the literature.[12]

Methyl 4-((phenylamino)methyl)benzoate (**B5**)



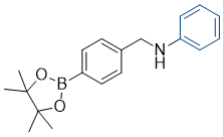
Colorless oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 8.01 (d, *J* = 8.3 Hz, 2H), 7.44 (d, *J* = 8.2 Hz, 2H), 7.17 (td, *J* = 7.4, 1.9 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 2H), 4.41 (s, 2H), 4.21 (s, 1H), 3.91 (s, 3H). Identity was confirmed by comparison with the literature.[13]

N-(4-(trifluoromethyl)benzyl)aniline (**B6**)



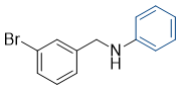
Colorless oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.62 (d, *J* = 7.7 Hz, 2H), 7.50 (d, *J* = 7.8 Hz, 2H), 7.20 (t, *J* = 7.8 Hz, 2H), 6.77 (t, *J* = 7.1 Hz, 1H), 6.63 (d, *J* = 7.7 Hz, 2H), 4.43 (s, 2H), 4.16 (s, 1H). Identity was confirmed by comparison with the literature.[13]

N-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzyl)aniline (**B7**)



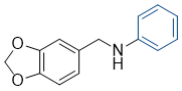
Yellow oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.0 Hz, 2H), 7.40 (d, *J* = 7.3 Hz, 2H), 7.18 (t, *J* = 7.1 Hz, 2H), 6.73 (t, *J* = 7.2 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 2H), 4.36 (s, 2H), 4.16 (s, 1H), 1.36 (s, 12H). Identity was confirmed by comparison with the literature.[12]

N-(3-bromobenzyl)aniline (**B8**)



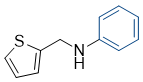
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (s, 1H), 7.41 (d, *J* = 8.1 Hz, 1H), 7.35 – 7.28 (m, 1H), 7.23 – 7.14 (m, 3H), 6.76 (tt, *J* = 7.3, 1.0 Hz, 1H), 6.67 – 6.58 (m, 2H), 4.33 (s, 2H). Identity was confirmed by comparison with the literature.[14]

N-(benzo[*d*][1,3]dioxol-5-ylmethyl)aniline (**B9**)



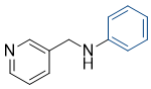
White solid. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.9 Hz, 2H), 6.87 (d, *J* = 1.3 Hz, 1H), 6.83 (d, *J* = 7.9 Hz, 1H), 6.79 – 6.74 (m, 2H), 6.68 (d, *J* = 8.0 Hz, 2H), 5.94 (s, 2H), 4.24 (s, 2H). Identity was confirmed by comparison with the literature.[15]

N-(thiophen-2-ylmethyl)aniline (**B10**)



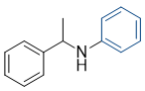
Yellow oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 3H), 7.05 – 7.01 (m, 1H), 7.01 – 6.95 (m, 1H), 6.77 (t, *J* = 7.2 Hz, 1H), 6.69 (d, *J* = 7.8 Hz, 2H), 4.52 (s, 2H), 4.12 (s, 1H). Identity was confirmed by comparison with the literature.[12]

N-(pyridin-3-ylmethyl)aniline (**B11**)



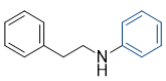
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (s, 1H), 8.53 (d, *J* = 4.3 Hz, 1H), 7.71 (d, *J* = 7.7 Hz, 1H), 7.28 (dd, *J* = 7.8, 4.7 Hz, 1H), 7.18 (t, *J* = 7.9 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.63 (d, *J* = 7.8 Hz, 2H), 4.37 (s, 2H). Identity was confirmed by comparison with the literature.[16]

N-(1-phenylethyl)aniline (**B12**)



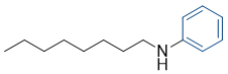
Yellow oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.2 Hz, 2H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.23 (t, *J* = 7.3 Hz, 1H), 7.10 (td, *J* = 7.4, 1.9 Hz, 2H), 6.68 (t, *J* = 7.1 Hz, 1H), 6.56 (d, *J* = 7.4 Hz, 2H), 4.49 (q, *J* = 6.7 Hz, 1H), 1.54 (d, *J* = 6.7 Hz, 3H). Identity was confirmed by comparison with the literature.[17]

N-phenethylaniline (**B13**)



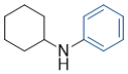
Colorless oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 2H), 7.31 – 7.24 (m, 3H), 7.24 – 7.17 (m, 2H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.5 Hz, 2H), 3.66 (s, 1H), 3.44 (t, *J* = 7.0 Hz, 2H), 2.95 (t, *J* = 7.0 Hz, 2H). Identity was confirmed by comparison with the literature.[13]

N-octylaniline (**B14**)



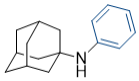
Yellow oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.6 Hz, 2H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.68 (d, *J* = 8.0 Hz, 2H), 3.11 (t, *J* = 7.2 Hz, 2H), 1.63 (p, *J* = 7.3 Hz, 2H), 1.41 – 1.36 (m, 2H), 1.32 – 1.27 (m, 8H), 0.88 (t, *J* = 6.9 Hz, 3H). Identity was confirmed by comparison with the literature.[16]

N-cyclohexylaniline (**B15**)



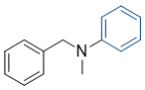
Colorless oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.17 (t, *J* = 7.9 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 1H), 6.60 (d, *J* = 7.8 Hz, 2H), 3.52 (s, 1H), 3.31 – 3.22 (m, 1H), 2.07 (d, *J* = 12.6 Hz, 2H), 1.81 – 1.73 (m, 2H), 1.69 – 1.61 (m, 1H), 1.39 (q, *J* = 11.9 Hz, 2H), 1.28 – 1.22 (m, 1H), 1.21 – 1.10 (m, 2H). Identity was confirmed by comparison the literature.[18]

N-phenyladamantan-1-amine (**B16**)



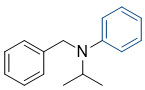
White solid. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.16 (t, *J* = 7.8 Hz, 2H), 6.90 – 6.76 (m, 3H), 2.10 (s, 3H), 1.88 (s, 6H), 1.70 – 1.64 (m, 6H). Identity was confirmed by comparison with the literature.[19]

N-benzyl-*N*-methylaniline (**B17**)



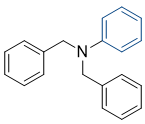
Yellow oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.41 – 7.34 (m, 2H), 7.34 – 7.22 (m, 5H), 6.88 – 6.75 (m, 3H), 4.60 (s, 2H), 3.08 (s, 3H). Identity was confirmed by comparison with the literature.[20]

N-benzyl-*N*-isopropylaniline (**B18**)



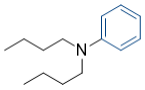
Yellow oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.38 – 7.29 (m, 4H), 7.29 – 7.21 (m, 1H), 7.19 (t, *J* = 7.9 Hz, 2H), 6.73 (d, *J* = 8.2 Hz, 2H), 6.69 (t, *J* = 7.2 Hz, 1H), 4.44 (s, 2H), 4.30 (p, J = 6.6 Hz, 1H), 1.23 (d, *J* = 6.6 Hz, 6H). Identity was confirmed by comparison with the literature.[20]

N,*N*-dibenzylaniline (**B19**)



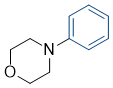
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.32 (m, 4H), 7.31 – 7.26 (m, 6H), 7.20 (dd, *J* = 8.8, 7.3 Hz, 2H), 6.78 (d, *J* = 8.2 Hz, 2H), 6.74 (t, *J* = 7.2 Hz, 1H), 4.69 (s, 4H). Identity was confirmed by comparison with the literature.[21]

N,*N*-dibutylaniline (**B20**)



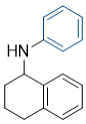
Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.20 (t, *J* = 7.9 Hz, 2H), 6.64 (d, *J* = 8.3 Hz, 2H), 6.62 (t, *J* = 7.5 Hz, 1H), 3.26 (d, *J* = 7.6 Hz, 4H), 1.64 – 1.51 (m, 4H), 1.40 – 1.30 (m, 4H), 0.95 (t, *J* = 7.3 Hz, 6H). Identity was confirmed by comparison with the literature.[20]

4-Phenylmorpholine (**B21**)



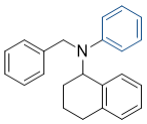
White solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.00 – 6.86 (m, 3H), 3.88 (t, *J* = 4.4 Hz, 4H), 3.17 (t, *J* = 4.5 Hz, 4H). Identity was confirmed by comparison with the literature.[20]

N-Phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (**B22**)



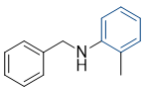
Light yellow oil. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.41 (d, *J* = 7.4 Hz, 1H), 7.24 – 7.11 (m, 5H), 6.77 – 6.66 (m, 3H), 4.65 (t, *J* = 4.4 Hz, 1H), 3.93 (s, 1H), 2.86 (dt, *J* = 16.2, 5.3 Hz, 1H), 2.78 (dt, *J* = 16.2, 6.9 Hz, 1H), 2.07 – 1.96 (m, 2H), 1.96 – 1.87 (m, 1H), 1.86 – 1.77 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.6, 138.3, 137.8, 129.5, 129.4, 129.2, 127.3, 126.2, 117.2, 112.9, 51.1, 29.5, 28.9, 19.5; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{16}H_{18}N$, 224.1434; found: 224.1434.

N-benzyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (**B23**)



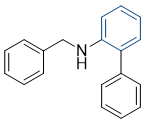
Beige solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30 – 7.05 (m, 11H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.71 (t, *J* = 7.2 Hz, 1H), 5.28 (t, *J* = 7.4 Hz, 1H), 4.34 (d, *J* = 18.1 Hz, 2H), 2.87 – 2.72 (m, 2H), 2.24 – 2.08 (m, 1H), 2.06 – 1.91 (m, 1H), 1.82 (d, *J* = 7.1 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 149.8, 140.1, 138.8, 137.5, 129.4, 129.3, 128.5, 127.5, 127.0, 126.6, 126.6, 126.2, 117.0, 113.7, 58.7, 51.5, 29.6, 29.2, 22.7; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{23}H_{24}N$, 314.1903; found: 314.1907.

N-benzyl-2-methylaniline (**B24**)



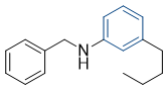
Colorless oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.45 – 7.18 (m, 5H), 7.17 – 7.06 (m, 2H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.65 (d, *J* = 7.9 Hz, 1H), 4.40 (s, 2H), 2.19 (s, 3H). Identity was confirmed by comparison with the literature.[22]

N-benzyl-[1,1'-biphenyl]-2-amine (**B25**)



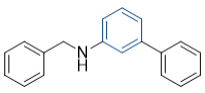
Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.53 – 7.42 (m, 4H), 7.40 – 7.29 (m, 5H), 7.29 – 7.24 (m, 1H), 7.24 – 7.17 (m, 1H), 7.14 (dd, *J* = 7.4, 1.5 Hz, 1H), 6.80 (dd, *J* = 7.3, 0.7 Hz, 1H), 6.69 (d, *J* = 8.1 Hz, 1H), 4.50 (s, 1H), 4.35 (s, 2H). Identity was confirmed by comparison with the literature.[22]

N-benzyl-3-butylaniline (**B26**)



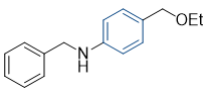
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 – 7.31 (m, 4H), 7.31 – 7.26 (m, 1H), 7.09 (dd, *J* = 8.7, 7.5 Hz, 1H), 6.60 (d, *J* = 7.4 Hz, 1H), 6.54 – 6.49 (m, 2H), 4.33 (s, 2H), 2.56 – 2.48 (m, 2H), 1.61 – 1.50 (m, 2H), 1.33 (t, *J* = 7.2 Hz, 2H), 0.91 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.2, 144.3, 138.9, 129.3, 128.8, 128.0, 127.5, 118.8, 113.9, 110.9, 49.1, 35.9, 33.7, 22.6, 14.1; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{17}H_{22}N$, 240.1747; found: 240.1749.

N-benzyl-[1,1'-biphenyl]-3-amine (**B27**)



Brown solid. ^{1}H NMR (600 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 2H), 7.44 – 7.39 (m, 4H), 7.36 (t, *J* = 7.6 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.29 (t, *J* = 7.3 Hz, 1H), 7.27 – 7.23 (m, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 6.89 (s, 1H), 6.69 – 6.64 (m, 1H), 4.40 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 148.1, 142.6, 141.7, 139.1, 129.8, 128.8, 128.8, 127.9, 127.5, 127.3, 127.3, 117.3, 112.4, 112.3, 48.9; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{19}H_{18}N$, 260.1434; found: 260.1437.

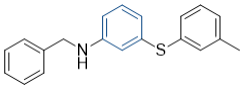
N-benzyl-4-(ethoxymethyl)aniline (**B28**)



Yellow oil. ^{1}H NMR (499 MHz, $CDCl_3$) δ 7.39 – 7.31 (m, 4H), 7.28 (d, *J* = 6.9 Hz, 1H), 7.16 (d, *J* = 8.5 Hz, 2H), 6.64 (dd, *J* = 8.4, 2.2 Hz, 2H), 4.39 (s, 2H), 4.34 (s, 2H), 3.50 (q, *J* = 7.0 Hz, 2H), 1.22 (t, *J* = 7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 147.7, 139.4,

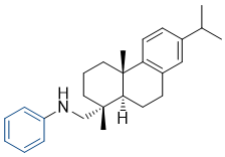
129.6, 128.7, 127.6, 127.3, 112.9, 72.8, 65.2, 48.4, 15.4; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{16}H_{20}NO$, 242.1539; found: 242.1544.

N-benzyl-3-(*m*-tolylthio)aniline(**B29**)



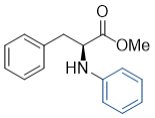
Brown oil. ^1H NMR (499 MHz, $CDCl_3$) δ 7.36 – 7.27 (m, 5H), 7.20 – 7.06 (m, 5H), 6.80 (d, *J* = 7.3 Hz, 1H), 6.77 (s, 1H), 6.74 – 6.67 (m, 1H), 4.27 (s, 2H), 2.32 (s, 3H); ^{13}C NMR (151 MHz, $CDCl_3$) δ 148.5, 139.0, 138.9, 137.0, 135.3, 132.1, 130.0, 129.1, 128.8, 128.5, 128.0, 127.7, 127.5, 120.1, 115.0, 111.8, 48.4, 21.4; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{20}H_{20}NS$, 306.1311; found: 306.1314.

N-(((*1R*,*4aS*,*10aR*)-7-isopropyl-1,4a-dimethyl-1,2,3,4,4a,9,10,10a-octahydrophenanthren-1-yl)methyl)aniline (**B30**)



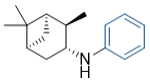
Sticky yellow oil. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.19 (d, *J* = 8.2 Hz, 1H), 7.17 – 7.09 (m, 2H), 6.99 (d, *J* = 8.2 Hz, 1H), 6.90 (s, 1H), 6.67 – 6.57 (m, 3H), 3.70 (s, 1H), 3.07 (d, *J* = 12.6 Hz, 1H), 2.95 – 2.75 (m, 4H), 2.32 (dt, *J* = 12.9, 3.3 Hz, 1H), 1.91 – 1.66 (m, 4H), 1.62 (dd, *J* = 12.0, 2.6 Hz, 1H), 1.53 – 1.34 (m, 3H), 1.25 (s, 3H), 1.23 (s, 3H), 1.21 (s, 3H), 1.03 (s, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 149.6, 147.9, 146.1, 135.3, 129.5, 127.2, 124.6, 124.2, 117.1, 112.9, 55.2, 45.8, 39.0, 37.9, 37.9, 36.6, 33.9, 30.5, 25.5, 24.2, 19.4, 19.3, 19.2; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{26}H_{36}N$, 362.2842; found: 362.2842.

Methyl phenyl-*L*-phenylalaninate (**B31**)



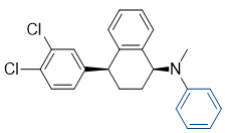
Yellow solid. ^1H NMR (499 MHz, $CDCl_3$) δ 7.32 – 7.27 (m, 2H), 7.27 – 7.24 (m, 1H), 7.20 – 7.15 (m, 4H), 6.75 (t, *J* = 7.3 Hz, 1H), 6.62 (d, *J* = 7.7 Hz, 2H), 4.37 (t, *J* = 6.3 Hz, 1H), 3.67 (s, 3H), 3.14 (qd, *J* = 13.6, 6.2 Hz, 2H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 173.9, 147.1, 137.0, 129.7, 129.7, 128.9, 127.3, 118.6, 113.8, 58.0, 52.3, 39.0; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{16}H_{18}NO_2$, 256.1332; found: 256.1334.

(*1R*,*2R*,*3R*,*5S*)-2,6,6-trimethyl-*N*-phenylbicyclo[3.1.1]heptan-3-amine (**B32**)



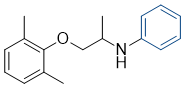
Brown oil. ^1H NMR (400 MHz, $CDCl_3$) δ 7.19 (t, *J* = 7.9 Hz, 2H), 6.76 – 6.60 (m, 3H), 3.69 (dt, *J* = 9.2, 5.9 Hz, 1H), 2.70 – 2.58 (m, 1H), 2.41 (dq, *J* = 10.1, 6.6, 5.7 Hz, 1H), 2.04 – 1.93 (m, 1H), 1.93 – 1.78 (m, 2H), 1.68 (ddd, *J* = 13.9, 5.2, 2.5 Hz, 1H), 1.27 (s, 1H), 1.26 (s, 3H), 1.17 (d, *J* = 7.1 Hz, 3H), 1.07 (s, 3H), 0.99 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 129.4, 117.5, 114.0, 52.7, 47.9, 47.0, 41.9, 38.6, 37.6, 34.5, 28.0, 23.6, 21.5; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{16}H_{24}N$, 230.1903; found: 230.1906.

(*1S*,*4S*)-4-(3,4-dichlorophenyl)-*N*-methyl-*N*-phenyl-1,2,3,4-tetrahydronaphthalen-1-amine (**B33**)



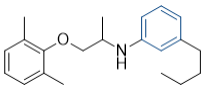
Off-white solid. ^1H NMR (400 MHz, CD_2Cl_2) δ 7.38 (d, *J* = 8.3 Hz, 2H), 7.25 (t, *J* = 7.8 Hz, 3H), 7.21 (d, *J* = 7.4 Hz, 2H), 7.18 (d, *J* = 1.8 Hz, 2H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.93 (dd, *J* = 8.1, 1.9 Hz, 1H), 6.90 (d, *J* = 8.6 Hz, 3H), 6.72 (t, *J* = 7.2 Hz, 1H), 5.15 (dd, *J* = 9.8, 6.2 Hz, 1H), 4.24 (t, *J* = 4.6 Hz, 1H), 2.71 (s, 3H), 2.38 – 2.25 (m, 1H), 2.09 – 1.95 (m, 1H), 1.91 – 1.72 (m, 2H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 150.8, 148.0, 138.7, 138.7, 132.4, 131.1, 131.0, 130.4, 130.1, 129.6, 128.7, 128.2, 127.6, 127.6, 116.9, 113.1, 58.4, 43.7, 33.4, 30.8, 21.4; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{23}H_{22}Cl_2N$, 382.1124; found: 382.1123.

N-(1-(2,6-dimethylphenoxy)propan-2-yl)aniline (**B34**)



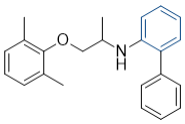
Dark blue oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.17 (m, 2H), 7.01 (d, *J* = 7.2 Hz, 2H), 6.96 – 6.91 (m, 1H), 6.78 – 6.69 (m, 3H), 3.93 – 3.85 (m, 1H), 3.85 – 3.79 (m, 2H), 2.27 (s, 6H), 1.48 (d, *J* = 6.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 155.3, 146.7, 131.0, 129.5, 129.1, 124.1, 118.0, 114.0, 74.2, 49.2, 18.1, 16.4; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{17}H_{22}NO$, 256.1696; found: 256.1699.

3-Butyl-*N*-(1-(2,6-dimethylphenoxy)propan-2-yl)aniline (**B35**)



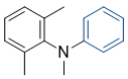
Colorless oil. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.05 (t, *J* = 7.7 Hz, 1H), 6.99 (d, *J* = 7.4 Hz, 2H), 6.90 (dd, *J* = 8.1, 6.8 Hz, 1H), 6.55 – 6.43 (m, 3H), 3.94 (s, 1H), 3.91 – 3.82 (m, 1H), 3.86 – 3.71 (m, 2H), 2.56 – 2.47 (m, 2H), 2.24 (s, 6H), 1.62 – 1.54 (m, 2H), 1.43 (d, *J* = 6.3 Hz, 3H), 1.40 – 1.30 (m, 2H), 0.92 (t, *J* = 7.3 Hz, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 155.8, 147.8, 144.6, 131.3, 129.4, 129.2, 124.2, 118.0, 113.9, 111.1, 74.7, 49.1, 36.2, 34.1, 22.8, 18.4, 16.4, 14.1; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{21}H_{30}NO$, 312.2322; found: 312.2323.

N-(1-(2,6-dimethylphenoxy)propan-2-yl)-[1,1'-biphenyl]-2-amine (**B36**)



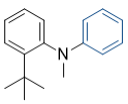
Yellow oil. ^{1}H NMR (400 MHz, CD_2Cl_2) δ 7.46 (d, *J* = 4.3 Hz, 4H), 7.37 (dd, *J* = 8.9, 4.6 Hz, 1H), 7.25 (t, *J* = 7.8 Hz, 1H), 7.11 (d, *J* = 7.4 Hz, 1H), 6.98 (d, *J* = 7.5 Hz, 2H), 6.94 – 6.86 (m, 1H), 6.81 (d, *J* = 8.3 Hz, 1H), 6.77 (dd, *J* = 7.3, 0.8 Hz, 2H), 4.39 (d, *J* = 6.0 Hz, 1H), 3.97 – 3.86 (m, 1H), 3.76 (d, *J* = 4.3 Hz, 2H), 2.14 (s, 6H), 1.39 (d, *J* = 6.5 Hz, 3H); ^{13}C NMR (101 MHz, CD_2Cl_2) δ 155.6, 144.6, 140.0, 131.3, 130.8, 129.8, 129.3, 129.2, 129.0, 128.4, 127.6, 124.3, 117.2, 111.2, 74.8, 49.0, 17.9, 16.2; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{23}H_{26}NO$, 332.2009; found: 332.2010.

N,2,6-trimethyl-*N*-phenylaniline (**B38-Me**)



Yellow oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 – 7.11 (m, 5H), 6.66 (t, *J* = 7.2 Hz, 1H), 6.40 (s, 2H), 3.18 (s, 3H), 2.09 (s, 6H). Identity was confirmed by comparison with the literature.[23]

2-(*tert*-Butyl)-*N*-methyl-*N*-phenylaniline (**B39-Me**)



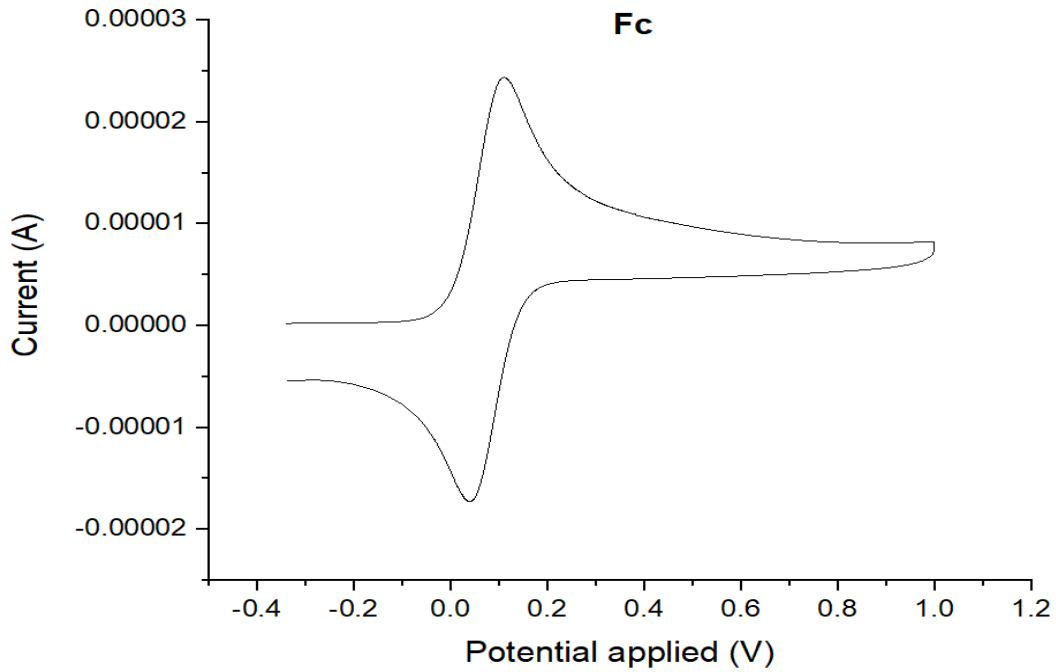
Yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.50 (m, 1H), 7.31 – 7.26 (m, 2H), 7.18 – 7.12 (m, 2H), 7.02 – 6.95 (m, 1H), 6.71 (t, *J* = 7.3 Hz, 1H), 6.49 (d, *J* = 8.0 Hz, 2H), 3.15 (s, 3H), 1.36 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ 151.4, 148.8, 148.6, 131.0, 128.6, 128.3, 128.2, 127.2, 117.0, 114.4, 42.2, 35.6, 31.6; HRMS-ESI (m/z) $[M+H]^+$ calcd. for $C_{17}H_{26}N$, 244.2060; found: 244.2057.

6. CV Experiments

6.1. Calibration of the Reference Electrode

<Electrode composition>
Working electrode: glassy carbon
Reference electrode: Ag wire in $AgNO_3$ (CH_3CN)
Counter electrode: carbon rod

<Procedure>
A solution of Ferrocene (Fc, 0.0010 M) and tetrabutylammonium perchlorate (0.10 M) in acetonitrile (10 mL) was transferred to an electrochemical cell equipped with the above three-electrode systems. The cyclic voltammogram was obtained using CHI 750E with a scan rate of 0.1 V/s and a scan range of −0.34 to 1.0 V.

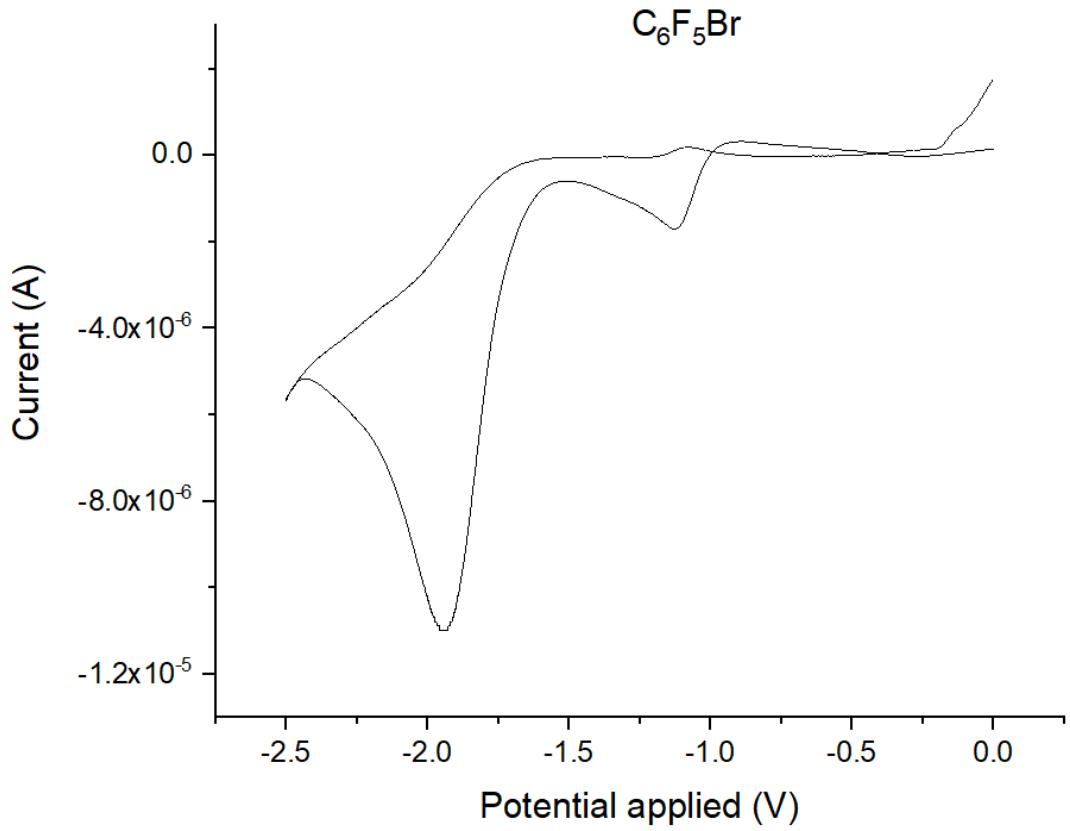


Measured: $E_{1/2}[Fc/Fc^+]$ = 0.076 V vs. Ag/Ag^+
Reference: $E_{1/2}[Fc/Fc^+]$ = 0.382 V vs. SCE (Saturated Calomel Electrode)[24]
Conversion constant: +0.306 V

6.2. C_6F_5Br

<Electrode composition>
Working electrode: glassy carbon
Reference electrode: Ag wire in $AgNO_3$ (CH_3CN)
Counter electrode: carbon rod

<Procedure>
A solution of C_6F_5Br (0.02 M) and tetrabutylammonium perchlorate (0.20 M) in acetonitrile (10 mL) was transferred to an electrochemical cell equipped with the above three-electrode systems. The cyclic voltammogram was obtained using CHI 750E with a scan rate of 0.2 V/s and a scan range of −2.5 to 0 V. Background subtraction was performed with the CV diagram without C_6F_5Br.

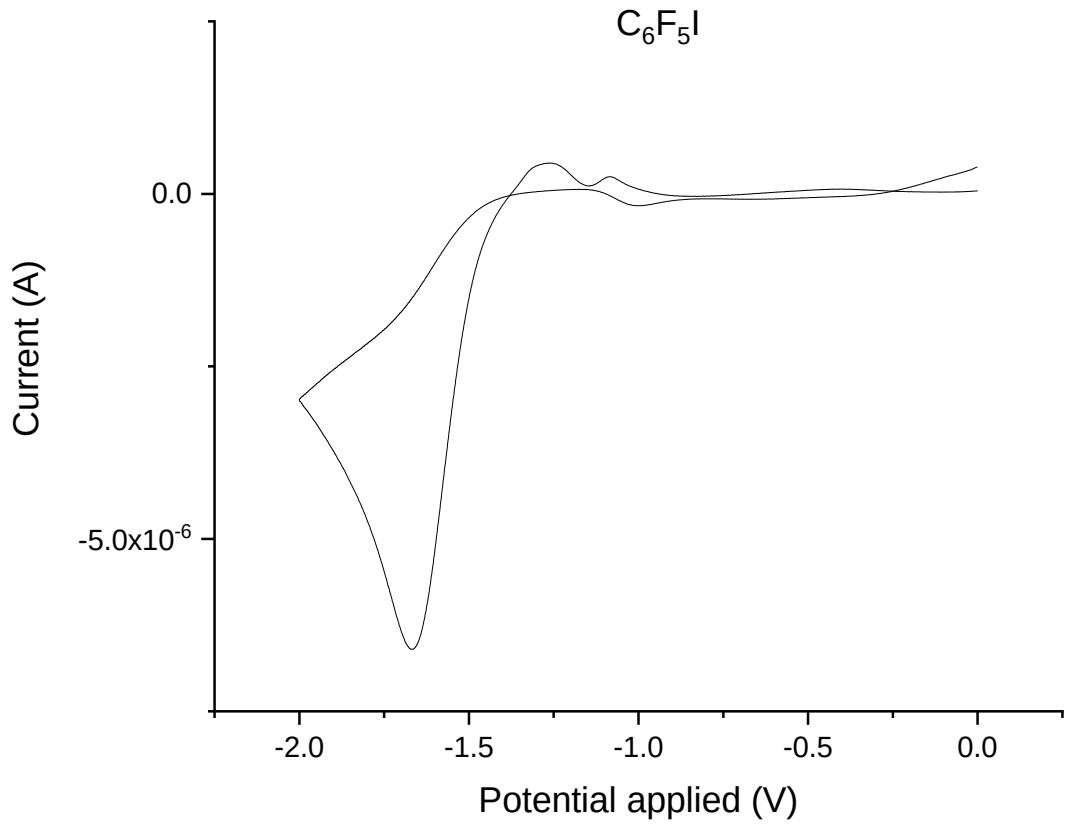


The cyclic voltammogram indicates that E_p^{red} = −1.942 V (−1.636 V vs. SCE in CH_3CN).

6.3. C_6F_5I

<Electrode composition>
Working electrode: glassy carbon
Reference electrode: Ag wire in $AgNO_3$ (CH_3CN)
Counter electrode: carbon rod

<Procedure>
A solution of C_6F_5I (0.02 M) and tetrabutylammonium perchlorate (0.20 M) in acetonitrile (10 mL) was transferred to an electrochemical cell equipped with the above three-electrode systems. The cyclic voltammogram was obtained using CHI 750E with a scan rate of 0.2 V/s and a scan range of −2.0 to 0 V. Background subtraction was performed with the CV diagram without C_6F_5I.

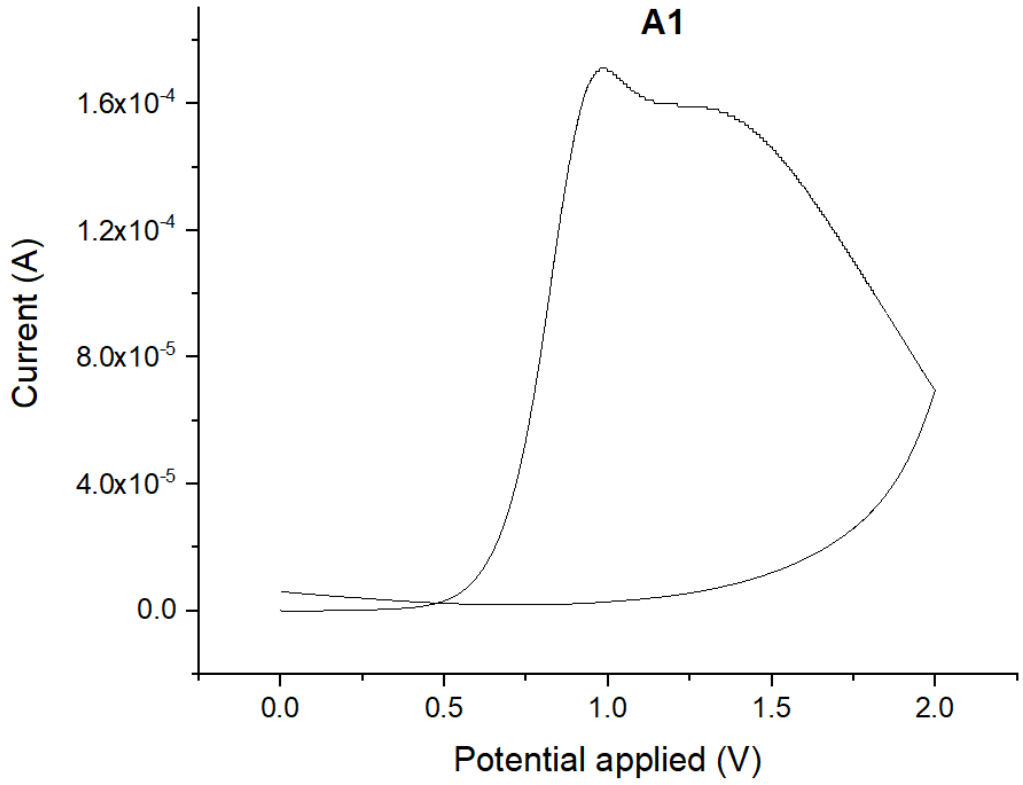


The cyclic voltammogram indicates that E_p^{red} = −1.665 V (−1.359 V vs. SCE in CH_3CN).

6.4. Amine A1

<Electrode composition>
Working electrode: glassy carbon
Reference electrode: Ag wire in $AgNO_3$ (CH_3CN)
Counter electrode: carbon rod

<Procedure>
A solution of **A1** (0.02 M) and tetrabutylammonium perchlorate (0.20 M) in acetonitrile (10 mL) was transferred to an electrochemical cell equipped with the above three-electrode systems. The cyclic voltammogram was obtained using CHI 750E with a scan rate of 0.2 V/s and a scan range of 0 to 2.0 V. Background subtraction was performed with the CV diagram without **A1**.

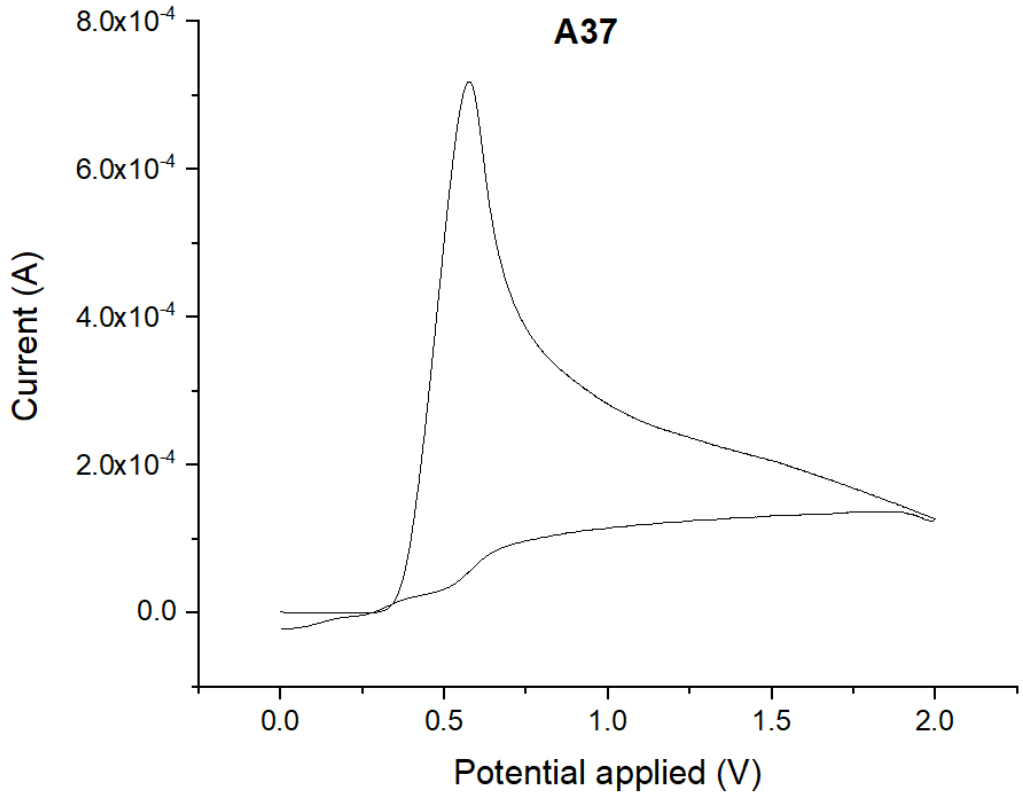


The cyclic voltammogram indicates that E_p^{ox} = 0.985 V (1.291 V vs. SCE in CH_3CN).

6.5. Amine A37

<Electrode composition>
Working electrode: glassy carbon
Reference electrode: Ag wire in $AgNO_3$ (CH_3CN)
Counter electrode: carbon rod

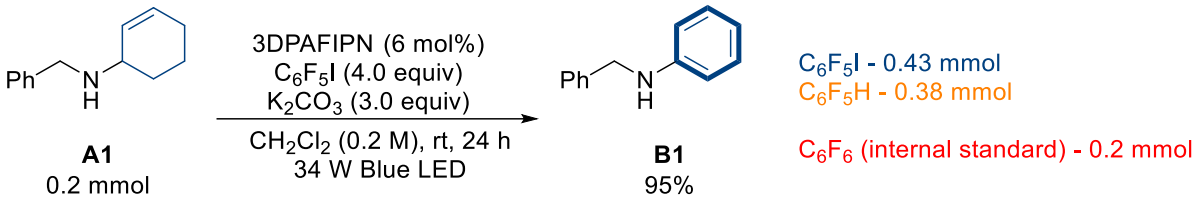
<Procedure>
A solution of **A37** (0.02 M) and tetrabutylammonium perchlorate (0.20 M) in acetonitrile (10 mL) was transferred to an electrochemical cell equipped with the above three-electrode systems. The cyclic voltammogram was obtained using CHI 750E with a scan rate of 0.2 V/s and a scan range of 0 to 2.0 V. Background subtraction was performed with the CV diagram without **A37**.



The cyclic voltammogram indicates that E_p^{ox} = 0.576 V (0.882 V vs. SCE in CH_3CN).

7. Observation of C_6F_5H in NMR Spectra

7.1. Table 4, entry 1



An oven-dried 4 mL reaction vial equipped with a PTFE-coated stir bar was charged with 3DPAFIPN (7.8 mg, 0.012 mmol, 6 mol%), potassium carbonate (82.9 mg, 0.6 mmol, 3.0 equiv), and CH_2Cl_2 (1 mL) in a glovebox. The vial was closed with a Teflon-lined septum cap and taken out of the glovebox. Amine **A1** (37.5 mg, 0.2 mmol, 1.0 equiv) and iodopentafluorobenzene (107 µL, 0.8 mmol, 4.0 equiv) were added via a gas-tight syringe, and the solution was stirred for the indicated time under 34 W blue LED irradiation with fan cooling. After the reaction was complete, dodecane (45.4 µL) and C_6F_6 (23 µL) were added and the reaction mixture was analyzed by GC and ^{19}F NMR spectroscopy. Full conversion of **A1** and the 95% yield of the **B1** were observed on GC. 93% conversion of C_6F_5I and the formation of C_6F_5H (95%) were observed on the ^{19}F NMR spectrum of the reaction mixture.

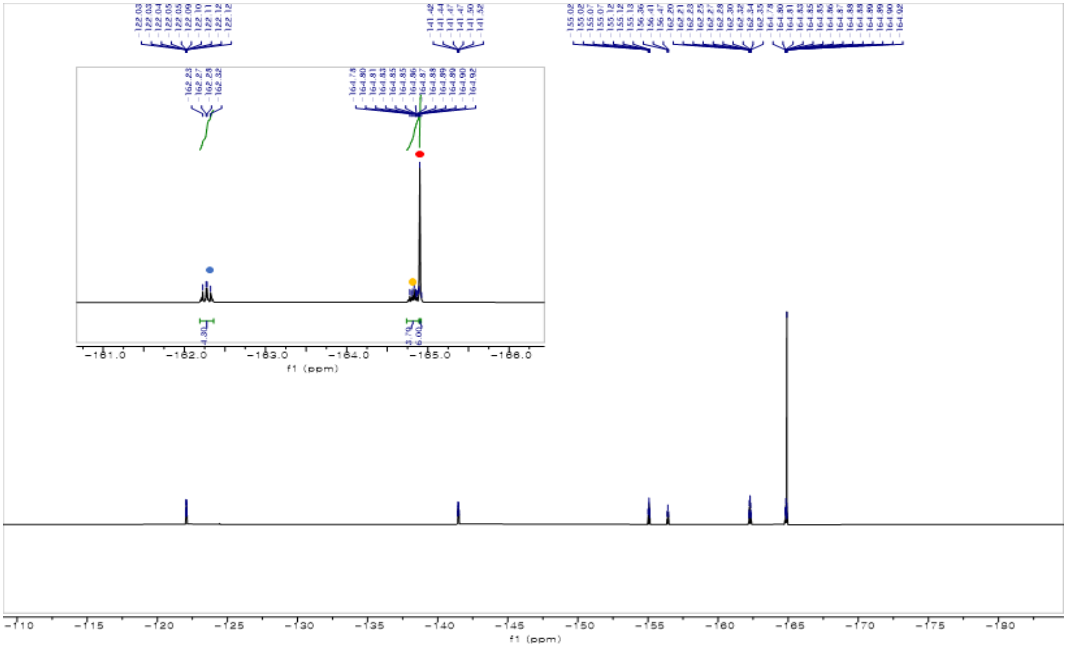
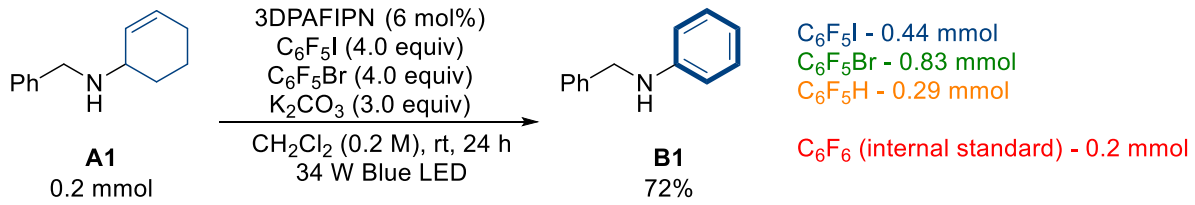


Fig. S1 ^{19}F NMR spectrum indicating the conversion of C_6F_5I and the formation of C_6F_5H.

The formation of C_6F_5H after the reaction clearly suggests the involvement of C_6F_5I in the reaction as an oxidant via the HAT process.

7.2. Table 4, entry 3



An oven-dried 4 mL reaction vial equipped with a PTFE-coated stir bar was charged with 3DPAFIPN (7.8 mg, 0.012 mmol, 6 mol%), potassium carbonate (82.9 mg, 0.6 mmol, 3.0 equiv), and CH_2Cl_2 (1 mL) in a glovebox. The vial was closed with a Teflon-lined septum cap and taken out of the glovebox. Amine **A1** (37.5 mg, 0.2 mmol, 1.0 equiv), iodopentafluorobenzene (107 µL, 0.8 mmol, 4.0 equiv), and bromopentafluorobenzene (99.7 µL, 0.8 mmol, 4.0 equiv) were added via a gas-tight syringe, and the solution was stirred for the indicated time under 34 W blue LED irradiation with fan cooling. After the reaction was complete, dodecane (45.4 µL) and C_6F_6 (23 µL) were added and the reaction mixture was analyzed by GC and ^{19}F NMR spectroscopy. Full conversion of **A1** and the 72% yield of the **B1** were observed on GC. 90% conversion of C_6F_5I and the formation of C_6F_5H (73%) were observed on the ^{19}F NMR spectrum of the reaction mixture. No conversion of C_6F_5Br was observed, indicating that the C_6F_5Br did not participate in the reaction at all.

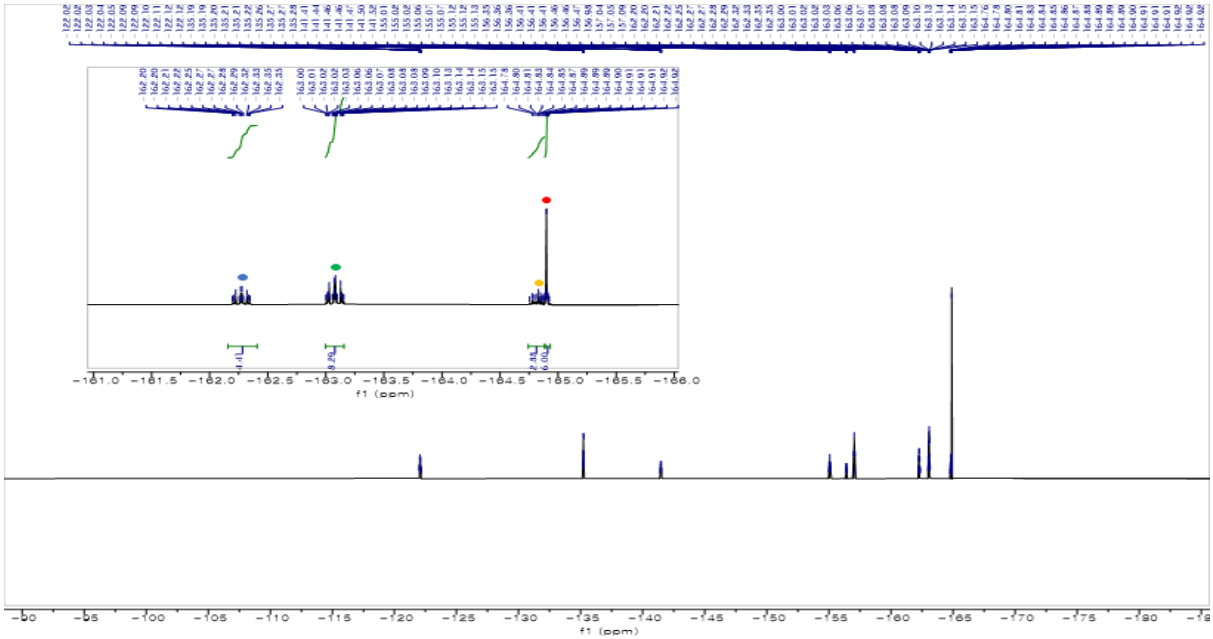
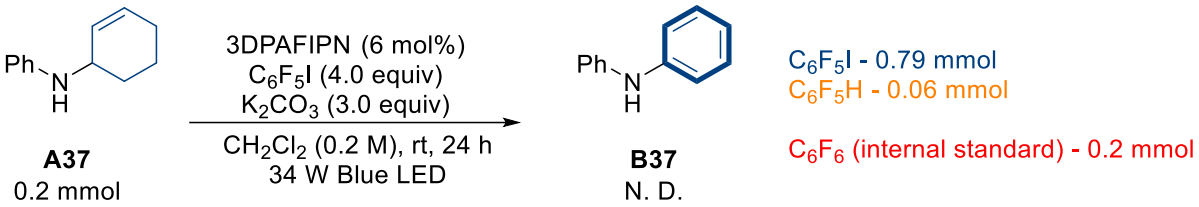


Fig. S2 ^{19}F NMR spectrum indicating the conversion of C_6F_5I, the formation of C_6F_5H, and the remaining C_6F_5Br.

7.3. Reaction with amine A37



An oven-dried 4 mL reaction vial equipped with a PTFE-coated stir bar was charged with 3DPAFIPN (7.8 mg, 0.012 mmol, 6 mol%), potassium carbonate (82.9 mg, 0.6 mmol, 3.0 equiv), and CH_2Cl_2 (1 mL) in a glovebox. The vial was closed with a Teflon-lined septum cap and taken out of the glovebox. Amine **A37** (34.7 mg, 0.2 mmol, 1.0 equiv) and iodopentafluorobenzene (107 µL, 0.8 mmol, 4.0 equiv) were added via a gas-tight syringe, and the solution was stirred for the indicated time under 34 W blue LED irradiation with fan cooling. After the reaction was complete, dodecane (45.4 µL) and C_6F_6 (23 µL) were added and the reaction mixture was analyzed by GC and ^{19}F NMR spectroscopy. No conversion of **A37** and no production of corresponding product **B37** were observed on GC. 2.5% conversion of C_6F_5I and the formation of C_6F_5H (15%) were observed on the ^{19}F NMR spectrum of the reaction mixture.

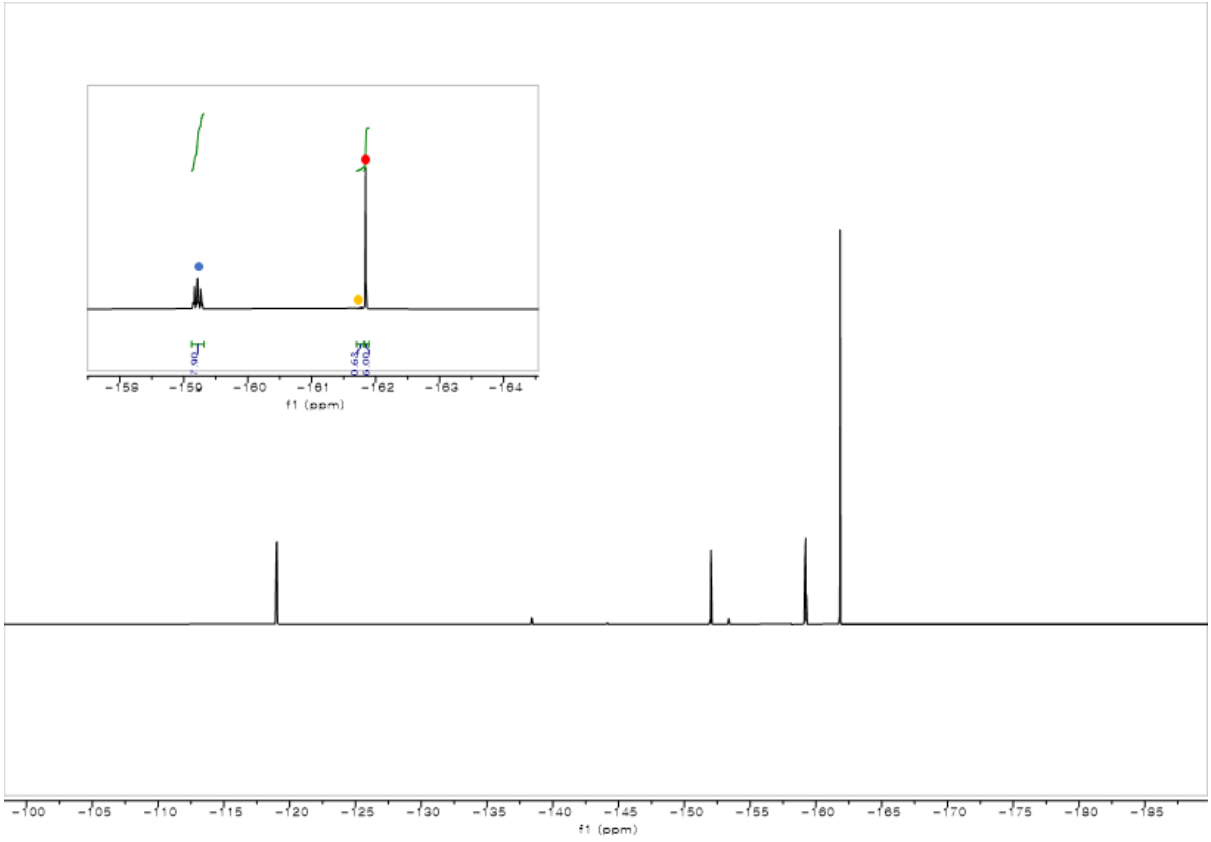


Fig. S3 ^{19}F NMR spectrum indicating the conversion of C_6F_5I and the formation of C_6F_5H.

8. Stern-Volmer Quenching Experiments

A solution of 3DPAFIPN in CH_2Cl_2 (5 μM) was prepared in a cuvette. Amine **A1**, C_6F_5I, and **B1** were used as quenchers. The prepared sample was excited at 375 nm and the emissions were measured between 390 - 725 nm. The absorbances of the 3DPAFIPN and quenchers were individually measured and used for the correction of the emission intensity.

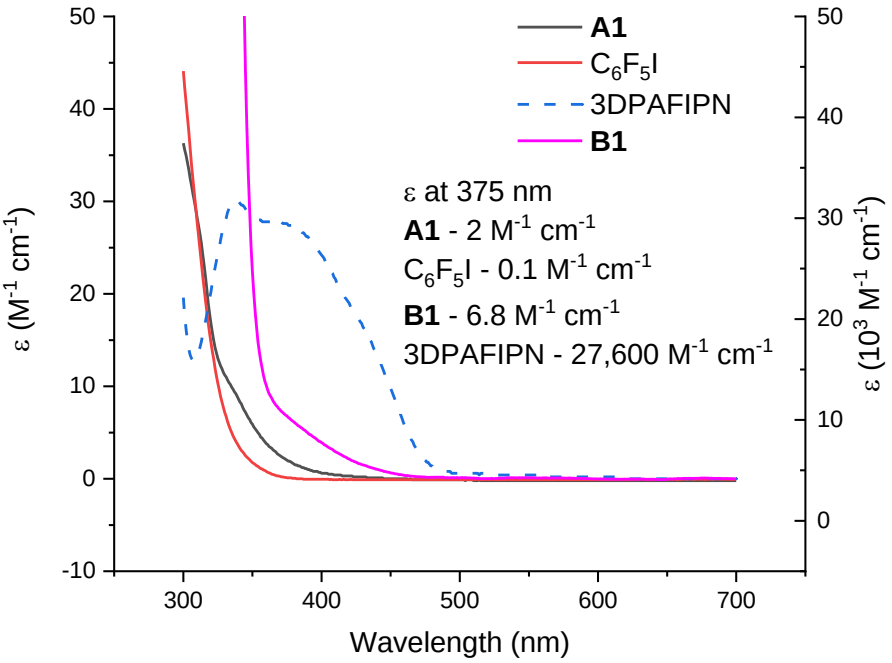


Fig. S4 UV-Vis spectra of **A1**, C_6F_5I, **B1**, and 3DPAFIPN in CH_2Cl_2.

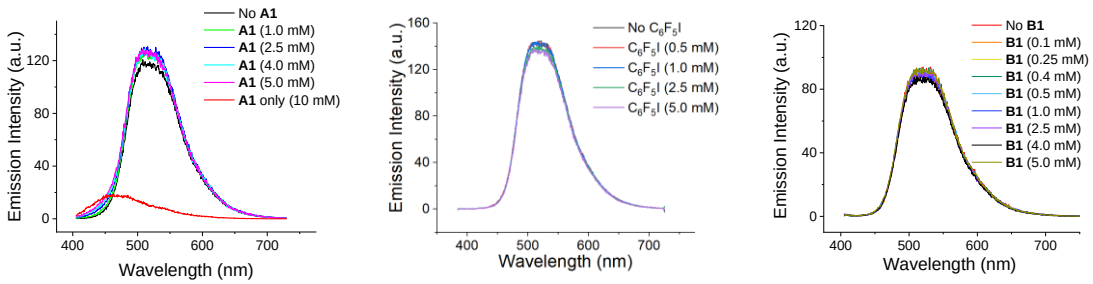


Fig. S5 Emission spectra with 3DPAFIPN and **A1** (left) / 3DPAFIPN and C_6F_5I (middle) / 3DPAFIPN and **B1** (right).

As depicted in Fig. S5, **A1** exhibits significant emission, which would contribute to the overall emission intensity in the mixture solution (Fig. S5, left). Therefore, a linear regression of the emission spectra was conducted to extract the contribution from 3DPAFIPN. The changes of the slope for the

quenching studies with **B1** (0.5 mM, 1:100 ratio) was observed; however, the linearity was maintained within the concentration ranges of the reaction conditions (~1:20 ratio).

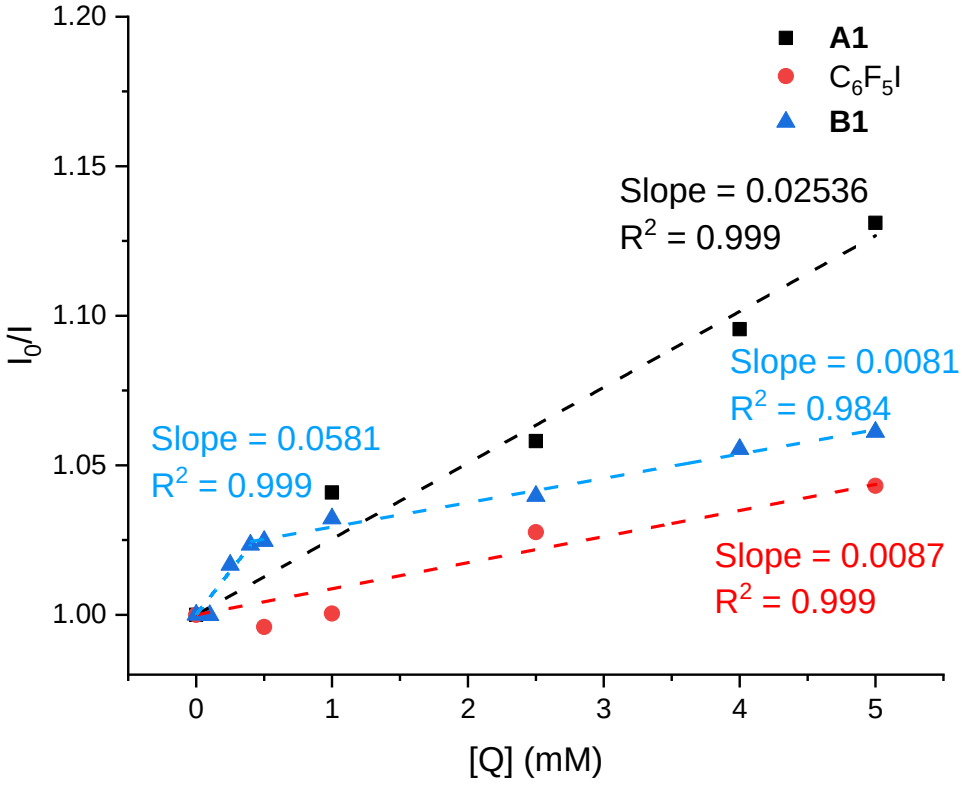
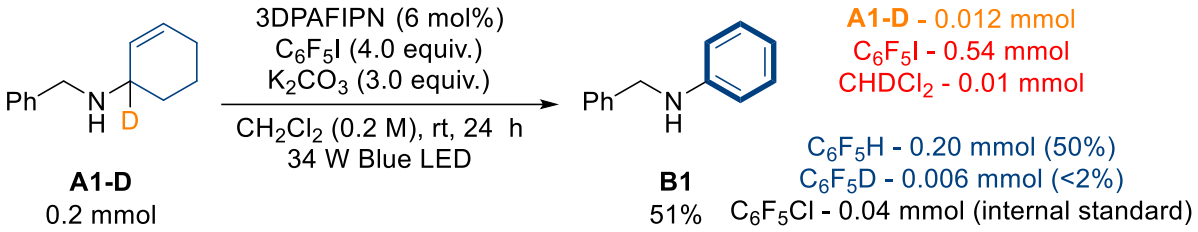


Fig. S6 Combined plot of Stern-Volmer quenching studies.

9. Control Experiments with Deuterated Species

9.1. Reaction with A1-D



An oven-dried 4 mL reaction vial equipped with a PTFE-coated stir bar was charged with 3DPAFIPN (7.8 mg, 0.012 mmol, 6 mol%), potassium carbonate (82.9 mg, 0.6 mmol, 3.0 equiv), and CH_2Cl_2 (1 mL) in a glovebox. The vial was closed with a Teflon-lined septum cap and taken out of the glovebox. Amine **A1-D** (37.7 mg, 0.2 mmol, 1.0 equiv) and iodopentafluorobenzene (107 µL, 0.8 mmol, 4.0 equiv) were added via a gas-tight syringe, and the solution was stirred for the indicated time under 34 W blue LED irradiation with fan cooling. After the reaction was complete, dodecane (45.4 µL) and C_6F_5Cl (5.2 µL) were added and the reaction mixture was analyzed by GC and $^1H/^2H/^{19}F$ NMR spectroscopy (CH_2Cl_2 or CD_2Cl_2). 6% of **A1-D** remained and the 51% yield of the **B1** was observed on GC. ^2H NMR spectroscopy suggested that only tiny amount of C_6F_5D and $CHDCl_2$ were produced. 65% conversion of C_6F_5I and the formation of C_6F_5H (50%) were observed in an ^{19}F NMR spectrum of the reaction mixture.

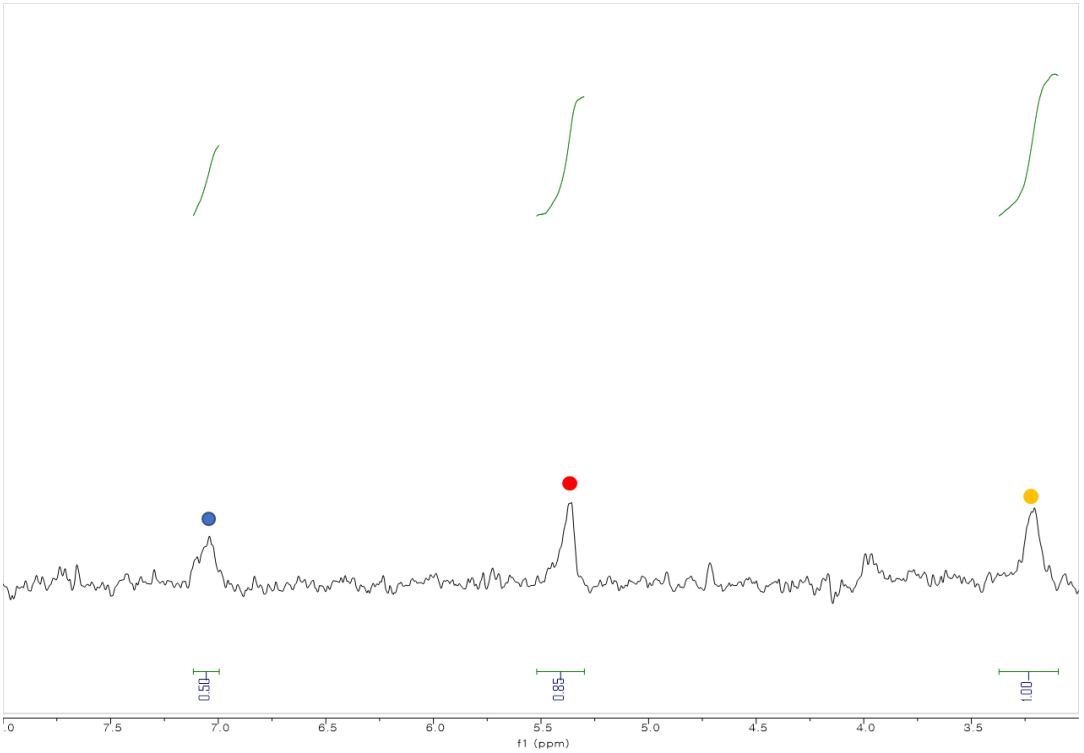


Fig. S7 ^2H NMR spectrum after the reaction with **A1-D** (CH_2Cl_2).

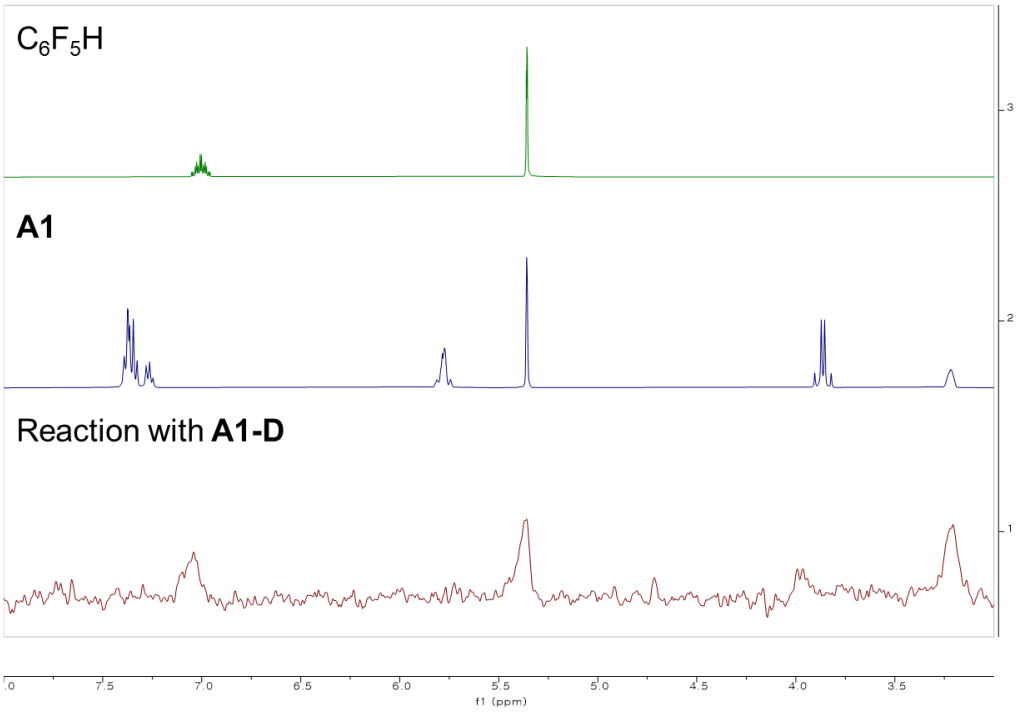


Fig. S8 Comparison of $^{1}H/^{2}H$ NMR spectra for the assignment of the observed peaks.

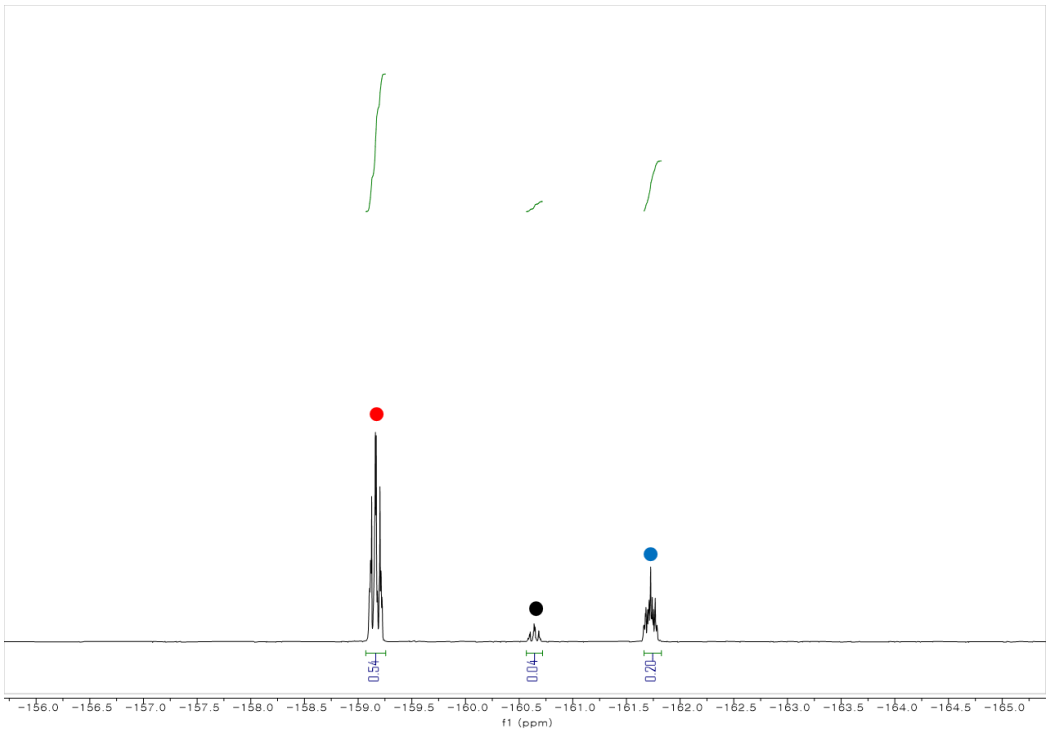
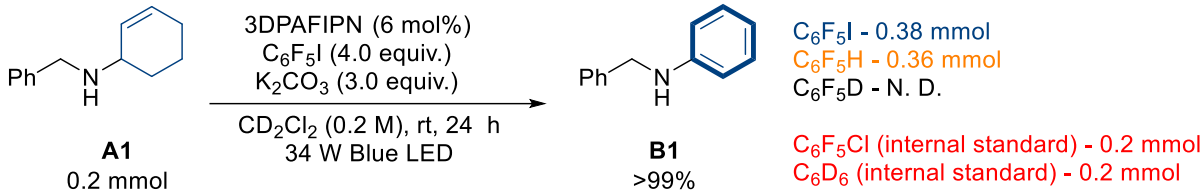


Fig. S9 ^{19}F NMR spectrum after the reaction with CD_2Cl_2.

9.2. Reaction with CD_2Cl_2



An oven-dried 4 mL reaction vial equipped with a PTFE-coated stir bar was charged with 3DPAFIPN (7.8 mg, 0.012 mmol, 6 mol%), potassium carbonate (82.9 mg, 0.6 mmol, 3.0 equiv), and CD_2Cl_2 (1 mL) in a glovebox. The vial was closed with a Teflon-lined septum cap and taken out of the glovebox. Amine **A1** (37.5 mg, 0.2 mmol, 1.0 equiv) and iodopentafluorobenzene (107 µL, 0.8 mmol, 4.0 equiv) were added via a gas-tight syringe, and the solution was stirred for the indicated time under 34 W blue LED irradiation with fan cooling. After the reaction was complete, dodecane (45.4 µL) and C_6F_5Cl (25.8 µL) were added and the reaction mixture was analyzed by GC and $^1H/^2H/^{19}F$ NMR spectroscopy. Full conversion of **A1** and the >99% yield of the **B1** were observed on GC. 105% conversion of C_6F_5I and the formation of C_6F_5H (90%) were observed on an ^{19}F NMR spectrum of the reaction mixture. No sign of the formation of C_6F_5D was detected on a ^2H NMR spectrum.

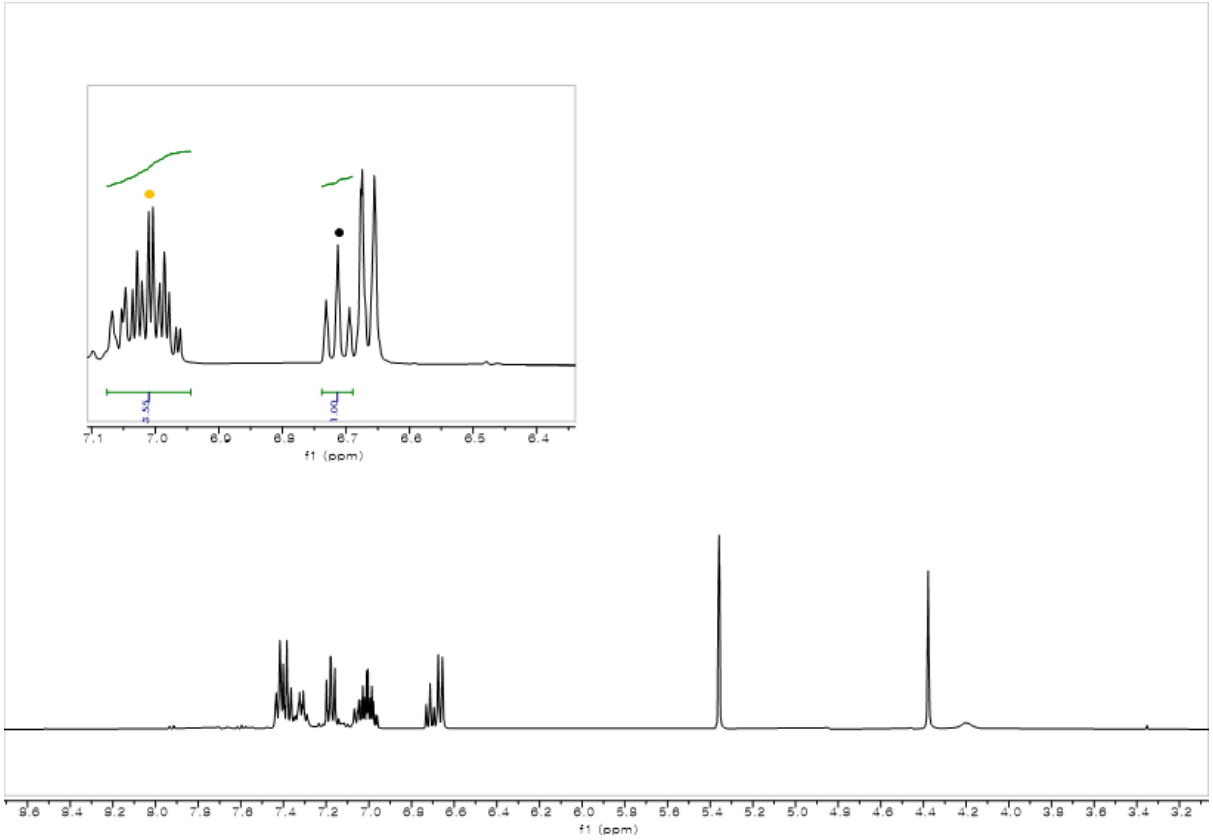


Fig. S10 ^1H NMR spectrum after the reaction with CD_2Cl_2.

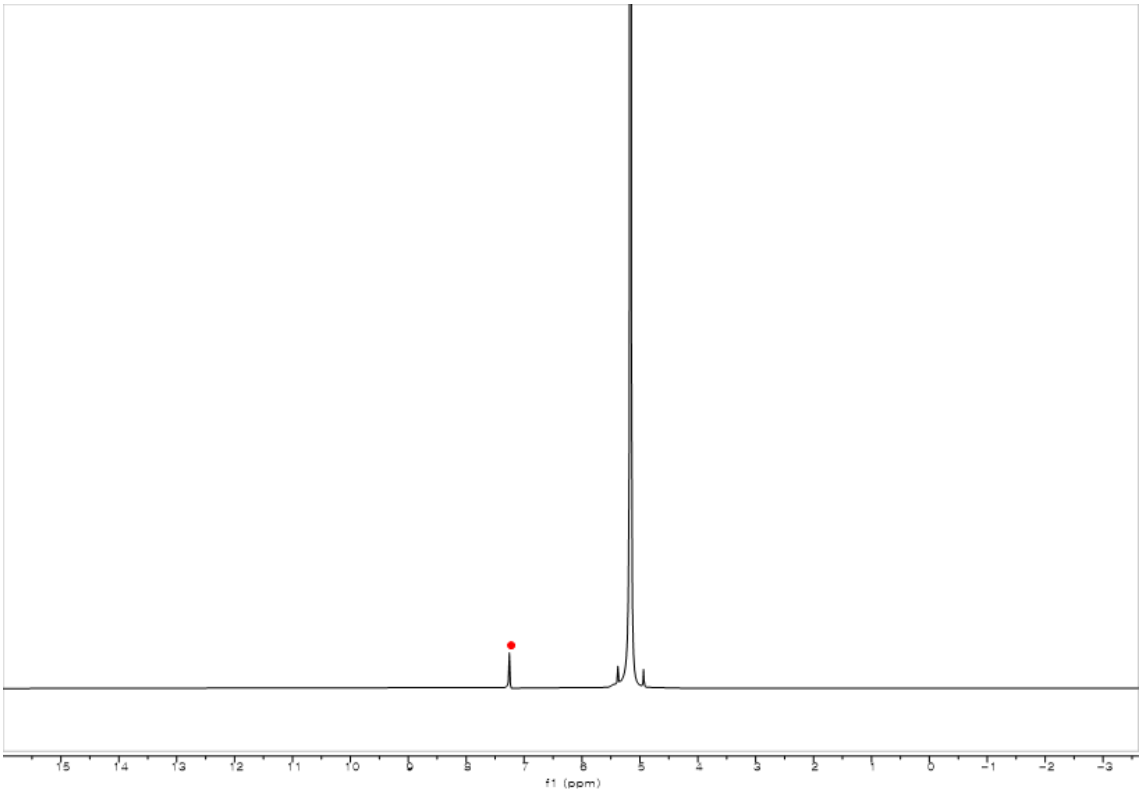


Fig. S11 ^{2}H NMR spectrum after the reaction with CD_2Cl_2.

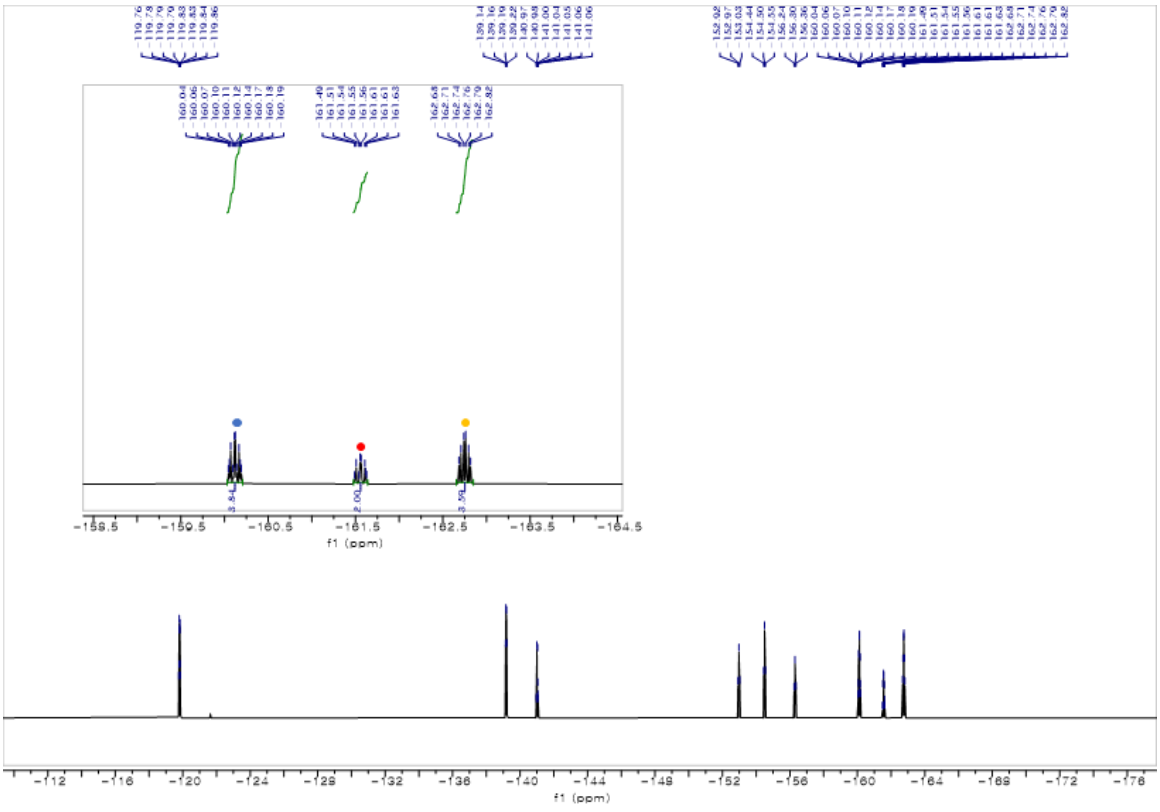
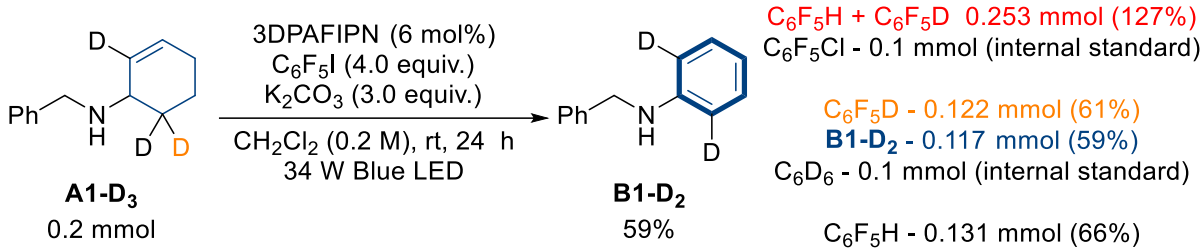


Fig. S12 ^{19}F NMR spectrum after the reaction with CD_2Cl_2.

9.3. Reaction with A1-D_3



An oven-dried 4 mL reaction vial equipped with a PTFE-coated stir bar was charged with 3DPAFIPN (7.8 mg, 0.012 mmol, 6 mol%), potassium carbonate (82.9 mg, 0.6 mmol, 3.0 equiv), and CH_2Cl_2 (1 mL) in a glovebox. The vial was closed with a Teflon-lined septum cap and taken out of the glovebox. Amine **A1-D_3** (38.1 mg, 0.2 mmol, 1.0 equiv) and iodopentafluorobenzene (107 µL, 0.8 mmol, 4.0 equiv) were added via a gas-tight syringe, and the solution was stirred for the indicated time under 34 W blue LED irradiation with fan cooling. After the reaction was complete, C_6D_6 (8.9 µL) and C_6F_5Cl (12.9 µL) were added and the reaction mixture was analysed with ^2H and ^{19}F NMR spectroscopies in CH_2Cl_2 and CD_2Cl_2, respectively. The formation of 127% of C_6F_5H and C_6F_5D was observed in ^{19}F NMR spectra of the reaction mixture. ^2H NMR spectroscopy suggested that 61% of C_6F_5D and 59% of the product (**B1-D_2**) exist in the reaction mixture, indicating that the formation of 61% of C_6F_5D and 66% of C_6F_5H during the reaction.

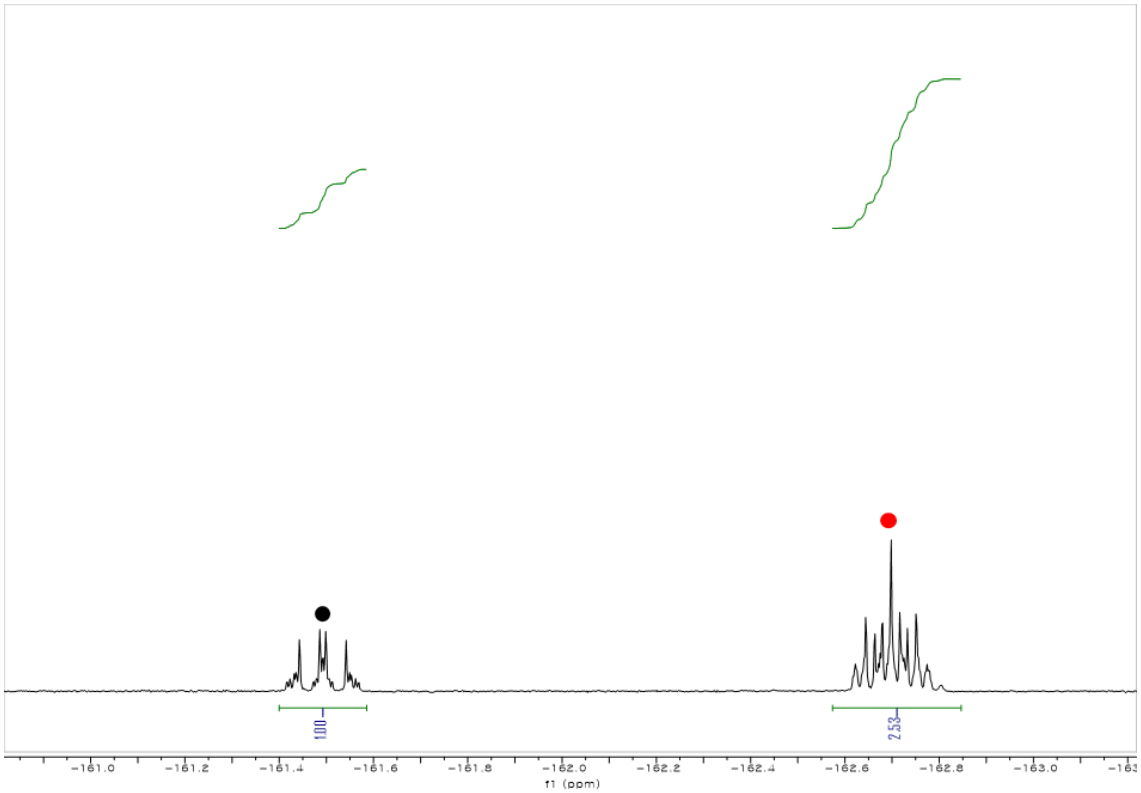


Fig. S13 ^{19}F NMR spectrum after the reaction with **A1-D$_3$**.

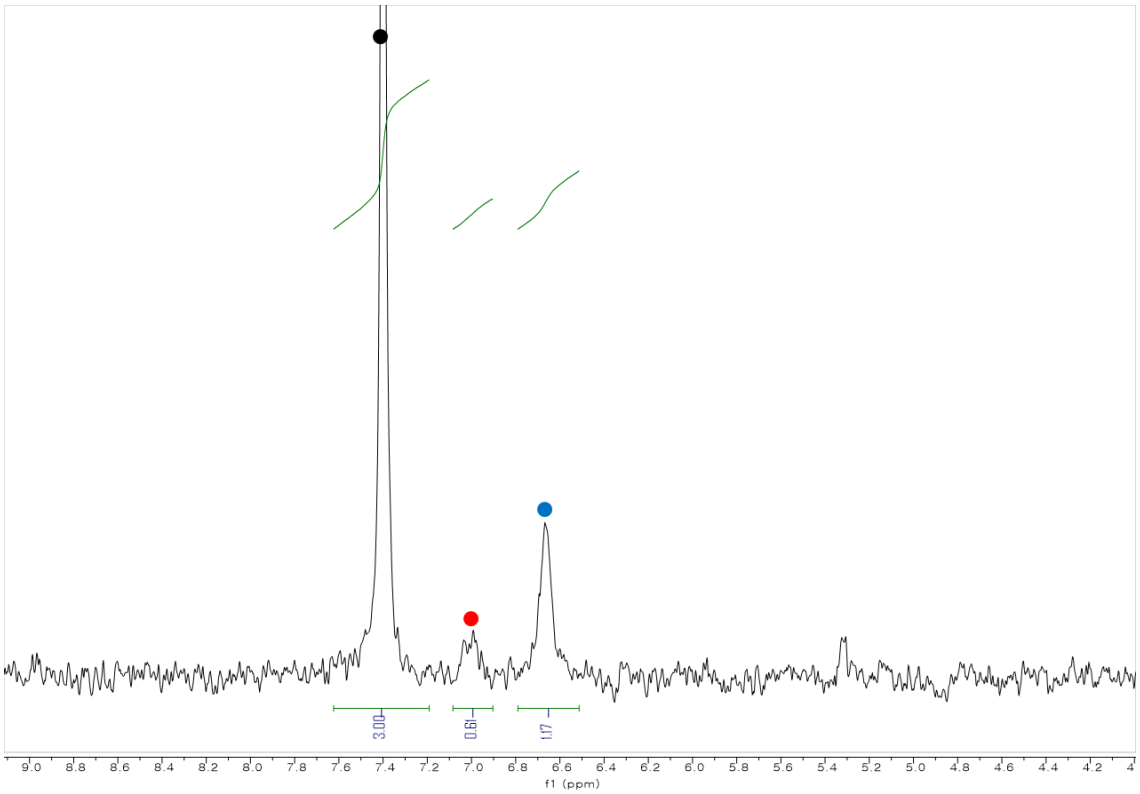
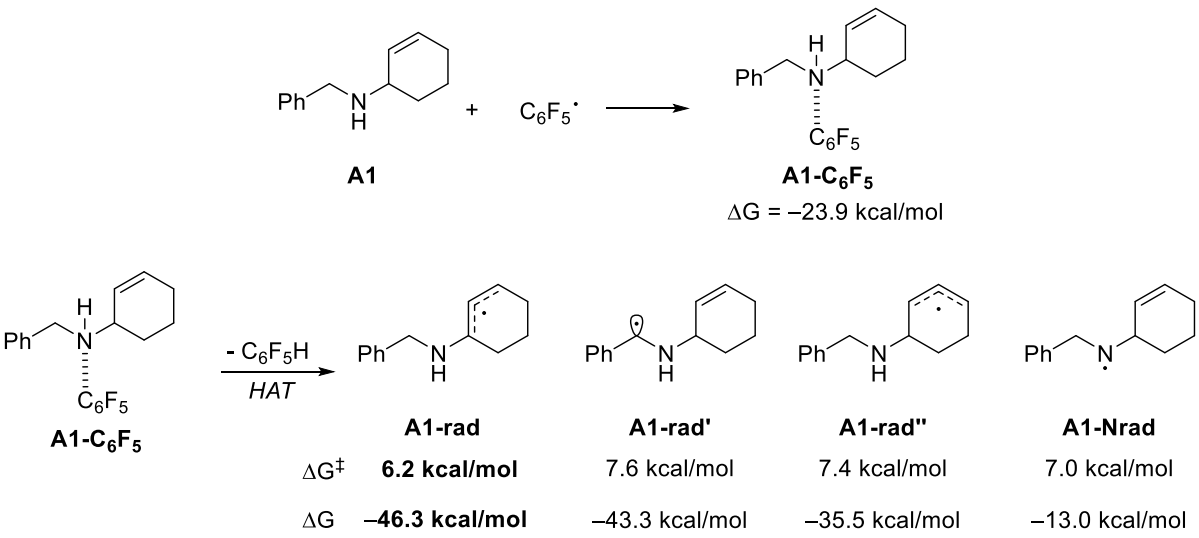


Fig. S14 ^{2}H NMR spectrum after the reaction with **A1-D$_3$**.

10. DFT Calculation

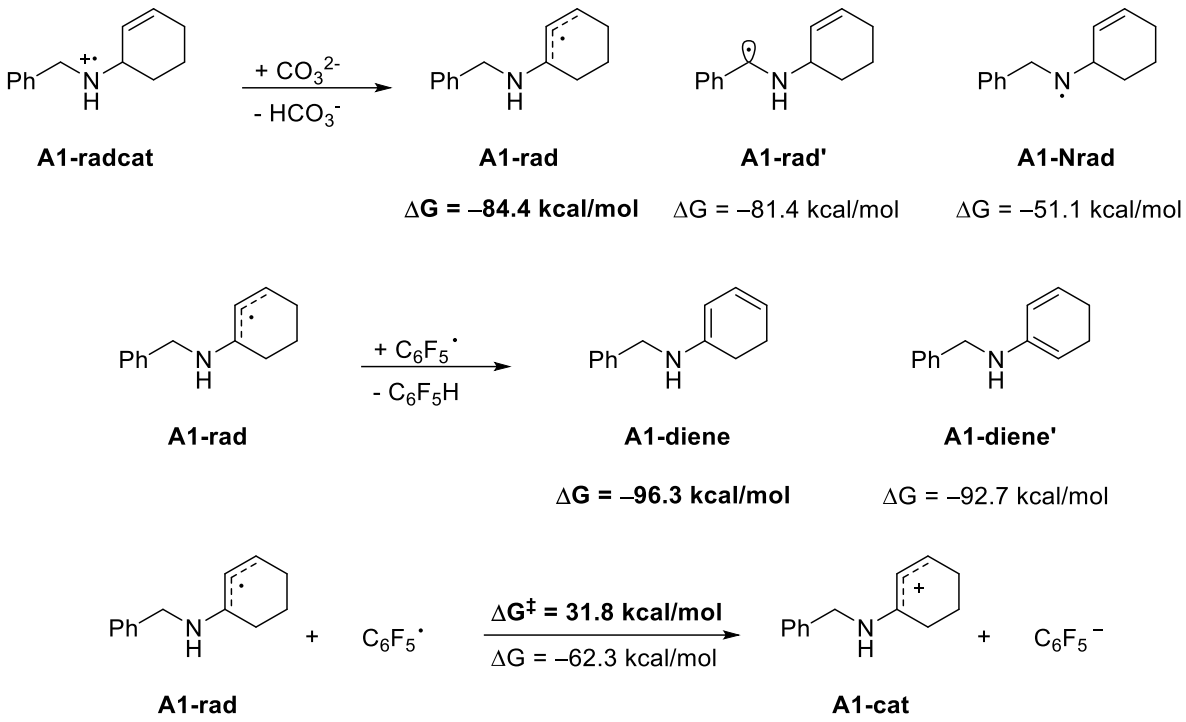
10.1. DFT Calculation of the Intermediates and the Reaction Pathways

All DFT calculations were carried out using Gaussian 09W.[25] Specifically, the (U)M06-2X functional and 6-31+G(d,p) basis set were used to conduct geometry optimization and frequency calculation in the gas phase. Single-point energy calculations were carried out on the optimized geometries using the (U)M06-2X functional and 6-311++G(3df,3pd) basis set. The solvation effect was considered using the SMD solvation model by Truhlar and coworkers for dichloromethane (ε = 8.93).[26] All structures were confirmed to be at local minima (ground state) by the absence of imaginary frequencies or at saddle point (transition state) by the existence of single imaginary frequency. The lowest-energy conformers were used in the final calculations. The energy barrier for single-electron transfer (SET) process was estimated by the Marcus theory of electron transfer, which can be calculated by the 4-point approaches developed by Nelson.[27]



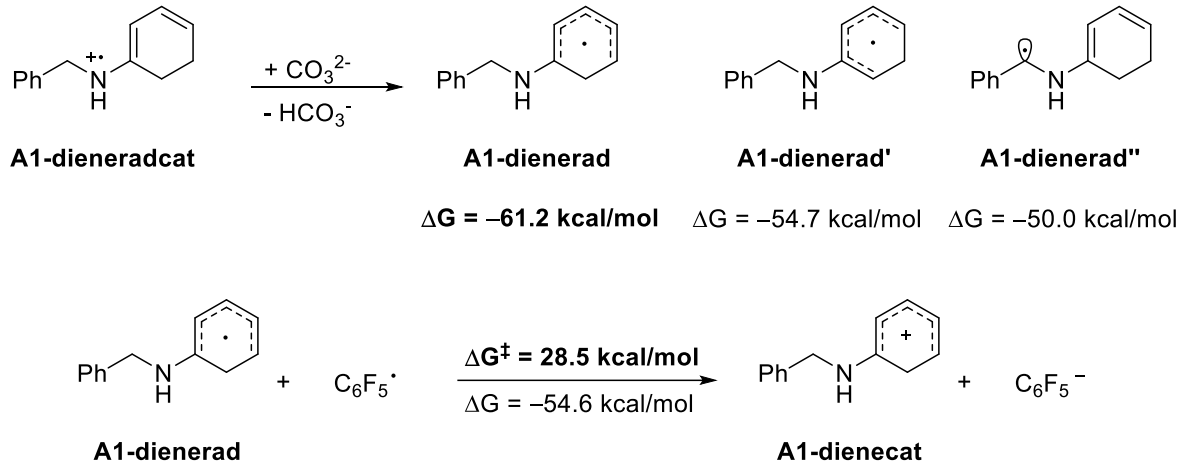
Scheme S1 HAT of **A1** by a C_6F_5 radical.

After the formation of the radical adduct between **A1** and a C_6F_5 radical (**A1-C_6F_5**), a HAT event can occur. Among four activated C-H bonds, the HAT on the C1 position would be the most probable pathway.



Scheme S2 Formation of diene intermediates.

The radical cation of the amine substrate (**A1-radcat**) prefers the deprotonation of the allylic α-nitrogen position, taking advantage of the stabilization by olefin and the nitrogen atom (**A1-rad**). A concurrent HAT event by a C_6F_5 radical provides more stable diene structure (**A1-diene**). The possibility of the SET event between **A1-rad** and a C_6F_5 radical would be very low, due to the high energy barrier for the SET process.



Scheme S3 Reactions with diene intermediates.

The diene radical cation species (**A1-dieneradcat**) still prefers the deprotonation from the C5 position rather than benzylic or C6 positions, taking advantage of the stabilized 7π-electron structure. The SET pathway from **A1-dienerad** is also not operative under the reaction conditions.

Table S6 Calculated energies

Species	G_{corr} (U)M06-2X/6-31+G(d,p)	E (U)M06-2X(CH_2Cl_2)/6-11++G(3df,3pd)	G(CH_2Cl_2)
CO_3^{2-}	-0.011737	-264.0052096	-264.0169466
HCO_3^-	0.001144	-264.5528875	-264.5517435
A1	0.234442	-560.304191	-560.069749
$C_6F_5^{\bullet}$	0.011793	-727.6874314	-727.6756384
C_6F_5H	0.027103	-728.4266511	-728.3995481
$C_6F_5^-$	0.013090	-727.9125690	-727.8994790
A1-C_6F_5	0.267591	-1288.051141	-1287.78355
A1-HATTS1	0.264307	-1288.037906	-1287.773599
A1-rad	0.220323	-559.6780441	-559.4577211
A1-HATTS2	0.266145	-1288.037552	-1287.771407
A1-rad'	0.220886	-559.6738614	-559.4529754
A1-HATTS3	0.261911	-1288.033665	-1287.771754
A1-rad''	0.219813	-559.6618137	-559.4405017
A1-HATTS4	0.263966	-1288.036291	-1287.772325
A1-Nrad	0.21878	-559.6235045	-559.4047245
A1-radcat	0.232438	-560.0904994	-559.8580614
A1-diene	0.211135	-559.0983939	-558.8872589
A1-diene'	0.211252	-559.0928504	-558.8815984
A1-cat	0.224355	-559.5575924	-559.3332374
A1-dieneradcat	0.210819	-558.9214035	-558.7105845
A1-dienerad	0.196721	-558.4700428	-558.2733218
A1-dienerad'	0.195745	-558.4587355	-558.2629905
A1-dienerad''	0.198019	-558.4406908	-41.97043746
A1-dienecat	0.199574	-558.3360056	-558.1364316

Table S7 Cartesian coordinates for the calculated intermediates

Species		Cartesian coordinates		
CO_3^{2-}	C	0.00000	0.00000	0.00088
	O	1.29577	-0.14831	-0.00020
	O	-0.77633	-1.04798	-0.00021
	O	-0.51944	1.19630	-0.00025
HCO_3^-	C	-0.15032	0.06923	-0.00007
	O	0.14708	1.28598	0.00004
	O	0.98689	-0.79608	0.00003
	H	1.72649	-0.17802	0.00005
	O	-1.23704	-0.51957	-0.00002
A1	C	2.57757	-0.46048	-1.22108
	C	4.05763	-0.60215	-0.86698
	C	4.51584	0.56616	0.00967
	C	3.50469	0.89054	1.07804
	C	2.26398	0.39869	1.09826
	C	1.71386	-0.52840	0.03704
	H	5.48438	0.34183	0.47142
	H	4.20630	-1.54401	-0.32314
	H	4.66637	-0.65780	-1.77474
	H	2.39943	0.50901	-1.70529
	H	2.26968	-1.24446	-1.92346
	H	3.81415	1.57812	1.86279
	H	1.59131	0.68404	1.90419
	H	1.75200	-1.56711	0.42458
	H	4.67660	1.46003	-0.60967
	N	0.33336	-0.16015	-0.28616
	H	0.09230	-0.53135	-1.20317
	C	-0.64639	-0.63689	0.68186
	H	-0.40761	-0.19108	1.65579
	H	-0.60238	-1.73176	0.82335
	C	-2.05240	-0.24102	0.29148
	C	-3.11592	-1.12756	0.47241
	C	-2.31144	1.02830	-0.23630
	C	-4.41877	-0.75416	0.14363
	H	-2.92268	-2.12012	0.87243
	C	-3.61151	1.40177	-0.56891
	H	-1.48051	1.71077	-0.38758
	C	-4.66976	0.51280	-0.37848
	H	-5.23480	-1.45532	0.28942
	H	-3.80008	2.38974	-0.97819
	H	-5.68221	0.80484	-0.63947
$C_6F_5^{\bullet}$	C	1.23108	0.37078	0.00000
	C	1.08234	-1.06622	0.00000
	C	-0.10999	-1.80871	-0.00001
	C	-1.20741	-0.99952	0.00000
	C	-1.16278	0.41182	0.00000
	C	0.09054	1.10676	0.00000
	F	0.08519	2.42854	0.00001
	F	-2.24572	1.14594	0.00001
	F	2.42674	0.93601	0.00000
	F	2.24114	-1.69315	-0.00001
	F	-2.45654	-1.49394	-0.00001
C_6F_5H	C	-1.19016	-0.96579	0.00001
	C	-1.20548	0.42345	0.00000

	C	0.00000	1.11548	-0.00001
	C	1.20548	0.42345	0.00000
	C	1.19016	-0.96579	0.00001
	C	0.00000	-1.67637	0.00002
	F	2.35746	-1.61323	0.00001
	F	2.35506	1.09319	-0.00001
	F	0.00000	2.44371	-0.00002
	F	-2.35506	1.09319	-0.00001
	F	-2.35746	-1.61323	0.00002
	H	0.00000	-2.75932	0.00003
$C_6F_5^-$	C	-1.14759	-1.01798	0.00001
	C	-1.19714	0.37309	0.00000
	C	0.00000	1.07599	-0.00001
	C	1.19714	0.37309	0.00000
	C	1.14759	-1.01798	0.00003
	C	0.00000	-1.77394	0.00003
	F	2.38678	-1.62237	0.00002
	F	2.35950	1.07136	-0.00002
	F	0.00000	2.42718	-0.00004
	F	-2.35950	1.07136	-0.00002
	F	-2.38678	-1.62237	0.00002
A1-C_6F_5	C	0.65271	-2.53479	-0.78699
	C	0.81430	-4.05209	-0.68949
	C	2.29399	-4.43005	-0.58738
	C	3.01976	-3.55923	0.40474
	C	2.50893	-2.42978	0.90087
	C	1.15963	-1.87153	0.49392
	H	2.40282	-5.48110	-0.29757
	H	0.28491	-4.41631	0.20026
	H	0.35633	-4.53828	-1.55572
	H	1.23445	-2.17155	-1.64373
	H	-0.39039	-2.25125	-0.95699
	H	4.00380	-3.88563	0.73545
	H	3.06816	-1.85882	1.64203
	H	0.43649	-2.06148	1.30016
	H	2.77757	-4.33604	-1.57001
	N	1.20382	-0.40941	0.36108
	H	1.36703	0.04656	1.25610
	C	2.04133	0.16471	-0.69880
	H	1.50087	0.08645	-1.64656
	C	2.34472	1.60882	-0.39169
	C	3.42122	1.93701	0.43717
	C	1.53392	2.62956	-0.89369
	C	3.68401	3.26575	0.76414
	H	4.06190	1.14509	0.82071
	C	1.79619	3.95929	-0.57006
	H	0.69605	2.37494	-1.53738
	C	2.86993	4.27906	0.25975
	H	4.52522	3.51008	1.40513
	H	1.16196	4.74603	-0.96617
	H	3.07406	5.31529	0.51012
	H	2.97508	-0.41019	-0.78788
	C	-0.90491	0.31667	0.09844
	C	-1.59011	0.16774	1.27810
	C	-1.60616	0.42300	-1.07673
	C	-2.98040	0.15882	1.31140
	F	-0.92617	0.02551	2.44799
	C	-2.99743	0.41885	-1.08790
	F	-0.96777	0.54580	-2.26281

	C	-3.68120	0.28324	0.11609
	F	-3.65276	0.02673	2.45787
	F	-3.68794	0.53539	-2.22578
	F	-5.01487	0.27122	0.12419
A1-HATTS1	C	-0.67471	3.02607	-0.76223
	C	0.70003	3.64262	-0.50476
	C	0.88286	3.95595	0.98228
	C	0.38143	2.83531	1.85478
	C	-0.36561	1.82273	1.40739
	C	-0.80153	1.69180	-0.03278
	H	1.93741	4.15489	1.20496
	H	1.47365	2.93251	-0.82547
	H	0.83241	4.54841	-1.10398
	H	-1.46429	3.69475	-0.39426
	H	-0.83684	2.87615	-1.83617
	H	0.63590	2.87565	2.91211
	H	-0.68753	1.04875	2.10013
	H	0.34123	4.87617	1.24346
	N	-2.15305	1.16851	-0.13348
	H	-2.52302	1.35363	-1.06379
	C	-2.26446	-0.25772	0.14726
	H	-1.98330	-0.42877	1.19307
	H	-1.55853	-0.85322	-0.46312
	C	-3.67223	-0.75680	-0.08025
	C	-3.90131	-1.97138	-0.7292
	C	-4.76706	-0.01324	0.37332
	C	-5.20003	-2.44422	-0.91612
	H	-3.05664	-2.55145	-1.09278
	C	-6.06473	-0.48177	0.18373
	H	-4.58775	0.93625	0.86922
	C	-6.28537	-1.69972	-0.46005
	H	-5.36235	-3.39045	-1.42299
	H	-6.90655	0.10420	0.53999
	H	-7.29731	-2.06365	-0.60779
	H	-0.09254	0.97284	-0.52957
	C	1.43544	-0.44117	-0.4258
	C	2.45126	-0.17020	-1.30734
	C	1.60978	-1.18330	0.71521
	C	3.71602	-0.69323	-1.04841
	F	2.26249	0.57608	-2.39854
	C	2.87190	-1.70965	0.97956
	F	0.61145	-1.42257	1.56852
	C	3.91794	-1.45829	0.09636
	F	4.73246	-0.46439	-1.87662
	F	3.09092	-2.44414	2.06745
	F	5.12376	-1.95932	0.34738
A1-rad	C	-2.51095	1.28643	0.46726
	C	-3.92121	0.86416	0.88903
	C	-4.58829	0.02371	-0.20576
	C	-3.70563	-1.12349	-0.60515
	C	-2.32530	-1.03733	-0.47036
	C	-1.69482	0.10330	0.02267
	H	-5.56130	-0.34196	0.14056
	H	-3.85350	0.26396	1.80414
	H	-4.52382	1.74851	1.11885
	H	-2.56928	2.01770	-0.35304
	H	-2.00487	1.79703	1.29804
	H	-4.15180	-2.02497	-1.00994
	H	-1.72170	-1.88964	-0.76974

	H	-4.79697	0.66861	-1.07526
	N	-0.32267	0.27160	0.05320
	H	0.01894	0.90627	0.76556
	C	0.57536	-0.83002	-0.24224
	H	0.37420	-1.16357	-1.26858
	H	0.39254	-1.69256	0.41838
	C	2.01355	-0.38732	-0.12131
	C	2.89579	-1.03931	0.74076
	C	2.47890	0.69288	-0.87960
	C	4.22492	-0.62653	0.84236
	H	2.54046	-1.87587	1.33701
	C	3.80318	1.10911	-0.77769
	H	1.79129	1.20355	-1.54886
	C	4.68057	0.44871	0.08402
	H	4.90075	-1.14313	1.51676
	H	4.15369	1.94679	-1.37272
	H	5.71368	0.77233	0.16259
A1-HATTS2	C	-0.23726	3.19825	0.12505
	C	1.10957	3.85880	-0.17439
	C	2.18411	2.79647	-0.42366
	C	1.68487	1.70944	-1.34048
	C	0.39465	1.54215	-1.64314
	C	-0.72113	2.41584	-1.09641
	H	3.08513	3.25205	-0.84958
	H	1.01394	4.49251	-1.06569
	H	1.40710	4.51065	0.65240
	H	-0.10517	2.51606	0.97442
	H	-0.99570	3.93503	0.40767
	H	2.42504	1.03438	-1.76994
	H	0.09730	0.74293	-2.32399
	H	-0.99461	3.14327	-1.87432
	H	2.49762	2.34937	0.53216
	N	-1.95603	1.67542	-0.81841
	H	-2.33439	1.28160	-1.67622
	C	-1.91021	0.66620	0.21065
	H	-1.73664	1.14352	1.18210
	C	-3.18180	-0.14590	0.24716
	C	-3.14753	-1.54095	0.21982
	C	-4.42011	0.50353	0.31284
	C	-4.32970	-2.28008	0.26877
	H	-2.19024	-2.05248	0.15391
	C	-5.60022	-0.23301	0.35952
	H	-4.44493	1.58952	0.32383
	C	-5.55797	-1.62787	0.33943
	H	-4.28855	-3.36456	0.24510
	H	-6.55511	0.28087	0.41327
	H	-6.47864	-2.20174	0.37527
	H	-1.04045	-0.05199	0.08898
	C	0.53168	-1.04510	0.43615
	C	1.03471	-1.84103	-0.56145
	C	1.33655	-0.38985	1.33363
	C	2.41298	-2.01494	-0.65520
	F	0.24044	-2.43729	-1.45698
	C	2.71568	-0.55307	1.24837
	F	0.83528	0.42932	2.26526
	C	3.24638	-1.36547	0.25062
	F	2.94413	-2.78602	-1.60248
	F	3.53345	0.07046	2.09580
	F	4.56437	-1.52640	0.16460

A1-rad'

C	2.73974	0.90924	-0.88547
C	4.17397	0.41408	-0.70075
C	4.43385	0.04406	0.76185
C	3.29724	-0.75672	1.34278
C	2.10926	-0.88796	0.74673
C	1.74528	-0.20147	-0.55297
H	5.36734	-0.52273	0.85409
H	4.33169	-0.47051	-1.33144
H	4.88708	1.17428	-1.03363
H	2.55936	1.75637	-0.20785
H	2.56183	1.26532	-1.90438
H	3.46805	-1.24629	2.29961
H	1.32450	-1.48939	1.20338
H	1.75119	-0.93872	-1.36881
H	4.57420	0.95480	1.36138
N	0.38697	0.33359	-0.51095
H	0.26761	1.08230	0.16272
C	-0.68296	-0.51356	-0.65821
H	-0.47352	-1.45024	-1.16513
C	-2.01063	-0.19700	-0.28276
C	-3.04527	-1.14743	-0.49934
C	-2.37741	1.03872	0.31389
C	-4.35131	-0.88332	-0.13058
H	-2.79314	-2.09920	-0.96024
C	-3.69279	1.28977	0.67956
H	-1.63451	1.81459	0.47532
C	-4.69236	0.33806	0.46715
H	-5.11793	-1.63201	-0.30728
H	-3.94440	2.24453	1.13230
H	-5.71772	0.54294	0.75520

A1-HATTS3

C	-0.37978	2.11076	1.22200
C	0.60055	3.25931	0.98854
C	1.24972	3.13112	-0.38565
C	0.28028	2.74479	-1.45712
C	-0.95510	2.30357	-1.19818
C	-1.51303	2.14365	0.19836
H	1.82583	4.02113	-0.66032
H	0.06152	4.21473	1.04153
H	1.36536	3.27734	1.77070
H	0.14196	1.14913	1.12023
H	-0.79263	2.15548	2.23642
H	0.62217	2.80556	-2.48774
H	-1.60694	2.03368	-2.02618
H	-2.15218	3.02329	0.41849
N	-2.29735	0.91082	0.28551
H	-2.36501	0.62195	1.25948
C	-3.64383	1.02571	-0.26245
H	-3.55832	1.27799	-1.32714
H	-4.22026	1.84376	0.20513
C	-4.41130	-0.26920	-0.12227
C	-5.75997	-0.26004	0.23888
C	-3.78519	-1.49479	-0.37250
C	-6.47822	-1.45125	0.33986
H	-6.25231	0.68730	0.44523
C	-4.49980	-2.68575	-0.26852
H	-2.73311	-1.49992	-0.64130
C	-5.84899	-2.66789	0.08635
H	-7.52611	-1.42778	0.62283
H	-4.00305	-3.63109	-0.46483
H	-6.40427	-3.59701	0.16848

	H	2.02950	2.30154	-0.32267
	C	2.78890	0.69545	-0.08432
	C	2.97783	-0.02057	-1.24073
	C	2.94632	0.14506	1.16340
	C	3.36658	-1.35463	-1.14799
	F	2.80846	0.52742	-2.44614
	C	3.33447	-1.18831	1.26605
	F	2.73645	0.85067	2.27922
	C	3.54044	-1.93051	0.10700
	F	3.57100	-2.08493	-2.24180
	F	3.50498	-1.76152	2.45543
	F	3.91135	-3.20407	0.19982
A1-rad’’	C	2.61751	-0.27407	-1.27614
	C	4.09602	-0.52850	-0.96506
	C	4.55940	0.30173	0.19625
	C	3.65233	0.78994	1.12432
	C	2.29740	0.49568	1.05995
	C	1.75772	-0.40686	-0.01636
	H	4.24541	-1.59662	-0.74116
	H	4.70738	-0.31855	-1.84940
	H	2.48967	0.74304	-1.66548
	H	2.26559	-0.97464	-2.04266
	H	4.01308	1.42391	1.93017
	H	1.60918	0.91413	1.78667
	H	1.84168	-1.45858	0.33580
	H	5.61734	0.51851	0.30087
	N	0.36560	-0.08163	-0.32243
	H	0.12039	-0.47206	-1.23017
	C	-0.58331	-0.57529	0.66841
	H	-0.34234	-0.10880	1.63209
	H	-0.50152	-1.66601	0.82372
	C	-2.00673	-0.22944	0.29450
	C	-3.03805	-1.14859	0.49743
	C	-2.31414	1.02573	-0.24113
	C	-4.35664	-0.82090	0.18278
	H	-2.80725	-2.13053	0.90364
	C	-3.62994	1.35355	-0.55955
	H	-1.50832	1.73373	-0.40999
	C	-4.65583	0.43223	-0.34715
	H	-5.14727	-1.54697	0.34554
	H	-3.85600	2.33097	-0.97504
	H	-5.68066	0.68860	-0.59700
A1-HATTS4	C	-4.28596	0.61510	0.87004
	C	-5.46805	-0.35284	0.92438
	C	-5.52881	-1.20170	-0.34803
	C	-4.16877	-1.72964	-0.72622
	C	-3.03051	-1.27763	-0.19490
	C	-2.96554	-0.16409	0.83332
	H	-6.22349	-2.03908	-0.21688
	H	-5.35380	-1.01247	1.79436
	H	-6.40467	0.19670	1.06032
	H	-4.37127	1.22855	-0.03628
	H	-4.27903	1.29454	1.72746
	H	-4.12789	-2.52536	-1.46768
	H	-2.07742	-1.71165	-0.49480
	H	-2.80968	-0.61464	1.82382
	H	-5.92868	-0.60577	-1.18082
	N	-1.83743	0.74798	0.64873
	H	-0.94118	0.31823	0.95353

	C	-1.68315	1.35568	-0.66874
	H	-2.45278	2.13289	-0.77088
	C	-0.31183	1.97449	-0.79707
	C	0.46337	1.75461	-1.93790
	C	0.22408	2.72471	0.25592
	C	1.76276	2.25325	-2.01836
	H	0.05750	1.16243	-2.75439
	C	1.52324	3.22013	0.17869
	H	-0.37538	2.89201	1.14661
	C	2.29870	2.98019	-0.95625
	H	2.36000	2.06307	-2.90488
	H	1.9338	3.78819	1.00779
	H	3.31416	3.35959	-1.01294
	H	-1.84314	0.63775	-1.48735
	C	0.63608	-0.58828	0.54250
	C	0.96796	-1.24973	-0.61424
	C	1.56963	-0.31340	1.51253
	C	2.27297	-1.69680	-0.79635
	F	0.07308	-1.46329	-1.58849
	C	2.87993	-0.75304	1.34356
	F	1.25335	0.36921	2.61826
	C	3.22400	-1.44443	0.18690
	F	2.62615	-2.34711	-1.90503
	F	3.80681	-0.51675	2.27102
	F	4.47442	-1.86875	0.01904
A1-Nrad	C	2.65941	0.87944	-0.93204
	C	4.11680	0.43766	-0.80651
	C	4.46778	0.16467	0.65765
	C	3.38990	-0.62914	1.34818
	C	2.17183	-0.82627	0.83988
	C	1.71653	-0.23926	-0.48678
	H	5.42158	-0.37000	0.73310
	H	4.27060	-0.47780	-1.39289
	H	4.78521	1.19808	-1.22175
	H	2.47061	1.74958	-0.29136
	H	2.41835	1.17192	-1.95897
	H	3.63065	-1.06254	2.31698
	H	1.44365	-1.41973	1.38905
	H	1.72331	-1.04809	-1.24236
	H	4.60923	1.11345	1.19425
	N	0.37376	0.28313	-0.31330
	C	-0.63310	-0.70417	-0.58232
	H	-0.39957	-1.65168	-0.06310
	H	-0.59026	-0.95510	-1.65862
	C	-2.03706	-0.26393	-0.22602
	C	-3.09691	-1.15676	-0.41158
	C	-2.30177	1.00953	0.27725
	C	-4.40198	-0.78527	-0.10169
	H	-2.89731	-2.15262	-0.80265
	C	-3.61013	1.38261	0.58879
	H	-1.47621	1.69782	0.42159
	C	-4.66249	0.49003	0.40105
	H	-5.21486	-1.48933	-0.25105
	H	-3.80531	2.37624	0.98086
	H	-5.67888	0.78309	0.64483
A1-radcat	C	-1.94788	1.13485	0.48453
	C	-3.44665	1.35086	0.27897
	C	-3.96969	0.47544	-0.85798
	C	-3.45859	-0.93210	-0.75767

	C	-2.45245	-1.31226	0.03835
	C	-1.72074	-0.35024	0.93627
	H	-5.06419	0.45992	-0.85790
	H	-3.98071	1.11918	1.20739
	H	-3.62243	2.40820	0.06207
	H	-1.41133	1.29385	-0.45864
	H	-1.53359	1.80726	1.23998
	H	-3.95476	-1.69068	-1.35839
	H	-2.15475	-2.35685	0.09001
	H	-2.05471	-0.43131	1.97983
	H	-3.67809	0.88880	-1.83306
	N	-0.31028	-0.61161	0.94363
	H	0.22720	-0.36986	1.77847
	C	0.45114	-1.05885	-0.20157
	H	-0.14196	-0.81996	-1.09565
	H	0.51827	-2.15846	-0.16181
	C	1.81779	-0.42882	-0.18880
	C	2.96574	-1.21453	-0.06769
	C	1.92961	0.96501	-0.28224
	C	4.22017	-0.61006	-0.04839
	H	2.88267	-2.29571	0.00236
	C	3.18452	1.56623	-0.25700
	H	1.03766	1.57768	-0.39513
	C	4.32907	0.77794	-0.14007
	H	5.11209	-1.22135	0.03667
	H	3.27030	2.64457	-0.33629
	H	5.30803	1.24517	-0.12563
A1-diene	C	-2.56810	1.30902	0.34000
	C	-3.93812	0.90360	0.88501
	C	-4.58758	-0.12429	-0.00714
	C	-3.81386	-1.02697	-0.63040
	C	-2.35606	-1.00809	-0.50606
	C	-1.73825	0.10164	-0.03242
	H	-5.66964	-0.16064	-0.08582
	H	-3.81100	0.47131	1.89053
	H	-4.57005	1.78897	0.99902
	H	-2.69092	1.91803	-0.56785
	H	-2.03396	1.92924	1.06904
	H	-4.26352	-1.81077	-1.23425
	H	-1.79013	-1.86931	-0.84279
	N	-0.37118	0.28494	0.00975
	H	-0.03705	0.93547	0.70894
	C	0.52475	-0.82146	-0.26873
	H	0.33524	-1.15589	-1.29750
	H	0.31981	-1.68011	0.39034
	C	1.96380	-0.38961	-0.12511
	C	2.82384	-1.03846	0.76146
	C	2.45215	0.67906	-0.88537
	C	4.15369	-0.63405	0.88504
	H	2.45064	-1.86603	1.35928
	C	3.77707	1.08711	-0.76143
	H	1.78214	1.18720	-1.57418
	C	4.63219	0.42977	0.12463
	H	4.81228	-1.14831	1.57801
	H	4.14546	1.91580	-1.35824
	H	5.66587	0.74682	0.22039
A1-diene'	C	2.34341	-0.92299	0.56506
	C	3.84846	-0.94298	0.69633
	C	4.51817	-0.18414	-0.45094

	C	3.85434	1.15264	-0.66512
	C	2.54702	1.30229	-0.42190
	C	1.73291	0.17069	0.06163
	H	5.58715	-0.05721	-0.25552
	H	4.14499	-0.48331	1.65271
	H	4.21273	-1.97422	0.71967
	H	1.77286	-1.76097	0.95046
	H	4.43791	1.98186	-1.05608
	H	2.04624	2.25354	-0.58677
	H	4.43095	-0.76805	-1.38064
	N	0.35201	0.36869	0.00555
	H	0.04987	0.90229	-0.80198
	C	-0.52306	-0.74623	0.31226
	H	-0.34094	-1.03357	1.35654
	H	-0.29296	-1.63032	-0.30553
	C	-1.97089	-0.35657	0.13547
	C	-2.82803	-1.12275	-0.65535
	C	-2.47381	0.78330	0.77281
	C	-4.16849	-0.76483	-0.80402
	H	-2.44359	-2.00567	-1.15968
	C	-3.80969	1.14486	0.62320
	H	-1.80511	1.38342	1.38410
	C	-4.66170	0.37002	-0.16549
	H	-4.82359	-1.37058	-1.42246
	H	-4.18887	2.03041	1.12398
	H	-5.70356	0.65176	-0.28139
A1-cat	C	2.43114	1.17804	0.74293
	C	3.74798	1.36110	-0.01585
	C	4.54973	0.06048	-0.01508
	C	3.70537	-1.12172	-0.36260
	C	2.35535	-1.13338	-0.31053
	C	1.64877	0.02757	0.17911
	H	5.39500	0.11543	-0.70753
	H	3.53563	1.65894	-1.04836
	H	4.32304	2.16789	0.44249
	H	2.63874	0.93329	1.79467
	H	1.82709	2.08971	0.73270
	H	4.21521	-2.03073	-0.67443
	H	1.79878	-2.01673	-0.60108
	H	4.99200	-0.12859	0.97547
	N	0.34906	0.07508	0.18761
	H	-0.09945	0.91169	0.55720
	C	-0.58839	-0.97436	-0.28710
	H	-0.43182	-1.86868	0.32393
	H	-0.33500	-1.20419	-1.32608
	C	-2.00068	-0.46844	-0.16625
	C	-2.57420	0.25935	-1.21258
	C	-2.72609	-0.68826	1.00764
	C	-3.86497	0.76644	-1.08383
	H	-2.01758	0.41863	-2.13313
	C	-4.01734	-0.18085	1.13483
	H	-2.28836	-1.26737	1.81728
	C	-4.58521	0.54674	0.08991
	H	-4.31083	1.32358	-1.90083
	H	-4.58149	-0.36067	2.04370
	H	-5.59316	0.93608	0.18705
A1-dieneradcat	C	-2.48549	1.21407	-0.69274
	C	-3.84462	1.35023	0.00279
	C	-4.52466	0.03269	0.16980

	C	-3.79909	-1.13645	0.27227
	C	-2.39763	-1.14050	0.19880
	C	-1.70111	0.03587	-0.18331
	H	-5.60367	0.00839	0.28177
	H	-3.71784	1.78817	1.00514
	H	-4.47847	2.04597	-0.55175
	H	-2.64653	1.03659	-1.76493
	H	-1.90485	2.13538	-0.59937
	H	-4.31293	-2.07227	0.46570
	H	-1.84870	-2.04901	0.41790
	N	-0.38863	0.09772	-0.18105
	H	0.05518	0.96021	-0.48825
	C	0.54245	-0.97912	0.22275
	H	0.38703	-1.83275	-0.44564
	H	0.28847	-1.27977	1.24425
	C	1.95770	-0.47299	0.13836
	C	2.53795	0.16870	1.23586
	C	2.67950	-0.60580	-1.05074
	C	3.83162	0.67662	1.14335
	H	1.98391	0.26020	2.16711
	C	3.97333	-0.09726	-1.14211
	H	2.23619	-1.11809	-1.90136
	C	4.54801	0.54425	-0.04574
	H	4.28262	1.16641	1.99976
	H	4.53424	-0.20947	-2.06381
	H	5.55804	0.93415	-0.11519
A1-dienerad	C	-2.55639	1.25856	0.60259
	C	-4.04400	1.08169	0.52069
	C	-4.61319	-0.03678	-0.00838
	C	-3.82142	-1.10309	-0.50617
	C	-2.41024	-1.02033	-0.46100
	C	-1.78055	0.08969	0.05295
	H	-5.69566	-0.11731	-0.04897
	H	-4.66239	1.88949	0.89954
	H	-2.24880	1.43495	1.64992
	H	-4.29336	-1.98811	-0.91614
	H	-1.82187	-1.84949	-0.83975
	N	-0.41395	0.25568	0.06751
	H	-0.05406	0.90934	0.75201
	C	0.48399	-0.83379	-0.27020
	H	0.28030	-1.13278	-1.30676
	H	0.29958	-1.71570	0.36293
	C	1.92122	-0.39267	-0.13813
	C	2.79192	-1.03476	0.74280
	C	2.39522	0.68021	-0.90141
	C	4.11893	-0.61880	0.85820
	H	2.42963	-1.86596	1.34225
	C	3.71731	1.09964	-0.78566
	H	1.71724	1.18259	-1.58681
	C	4.58326	0.44930	0.09505
	H	4.78640	-1.12774	1.54651
	H	4.07501	1.93128	-1.38479
	H	5.61483	0.77497	0.18419
	H	-2.24565	2.17151	0.06537
A1-dienerad'	C	-2.56078	1.15846	0.58982
	C	-4.05323	1.07993	0.62899
	C	-4.60721	-0.16141	0.00690
	C	-3.79382	-1.09823	-0.54891
	C	-2.38041	-0.95745	-0.56828

	C	-1.77365	0.19265	0.00573
	H	-5.68432	-0.29795	0.00783
	H	-4.41021	1.16302	1.67076
	H	-4.49093	1.96601	0.13423
	H	-2.08884	2.03564	1.02662
	H	-4.22791	-1.98965	-0.99318
	H	-1.77645	-1.73296	-1.02167
	N	-0.38348	0.36452	-0.05367
	H	-0.04089	1.01899	0.63946
	C	0.48877	-0.79185	-0.19895
	H	0.32116	-1.23233	-1.18943
	H	0.27261	-1.57536	0.54506
	C	1.93546	-0.37148	-0.08945
	C	2.79890	-0.99873	0.80934
	C	2.42921	0.65733	-0.89968
	C	4.13766	-0.61426	0.89480
	H	2.42148	-1.79352	1.44772
	C	3.76322	1.04518	-0.81370
	H	1.75487	1.15059	-1.59463
	C	4.62214	0.40870	0.08389
	H	4.79828	-1.11137	1.59836
	H	4.13551	1.84322	-1.44875
	H	5.66256	0.71097	0.15034
A1-dienerad''	C	-2.69030	-1.16305	0.59284
	C	-4.03514	-1.13203	-0.13543
	C	-4.59123	0.26899	-0.17951
	C	-3.74613	1.30781	-0.28356
	C	-2.29793	1.11757	-0.30010
	C	-1.77544	-0.06431	0.10755
	H	-5.66639	0.41766	-0.19346
	H	-3.89346	-1.48857	-1.16779
	H	-4.73371	-1.82255	0.34506
	H	-2.21334	-2.14229	0.46564
	H	-4.12848	2.32008	-0.38033
	H	-1.66061	1.93110	-0.62788
	N	-0.42027	-0.31885	0.22454
	H	-0.15582	-1.27986	0.39665
	C	0.58001	0.61279	0.19010
	H	0.28000	1.64300	0.33994
	C	1.94983	0.26759	0.05630
	C	2.94068	1.26641	0.24126
	C	2.39276	-1.04383	-0.25271
	C	4.28746	0.96616	0.13902
	H	2.62577	2.28012	0.47451
	C	3.74737	-1.33340	-0.34558
	H	1.67386	-1.83252	-0.45676
	C	4.70717	-0.33863	-0.14911
	H	5.02287	1.75116	0.28710
	H	4.05937	-2.34513	-0.58723
	H	5.76359	-0.57175	-0.22663
	H	-2.84641	-1.02074	1.67288
A1-dienecat	C	-2.50337	1.39578	-0.00073
	C	-3.99037	1.26199	-0.00048
	C	-4.59536	0.06265	0.00009
	C	-3.79381	-1.14140	0.00049
	C	-2.43034	-1.13972	0.00037
	C	-1.73262	0.10733	-0.00016
	H	-5.67542	-0.02294	0.00025
	H	-4.56378	2.18366	-0.00080

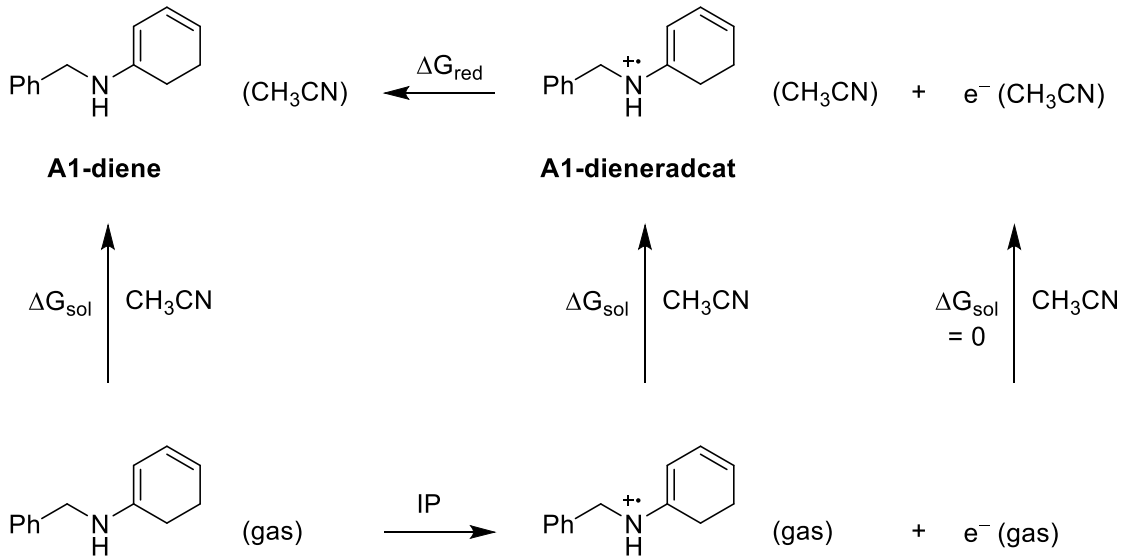
	H	-2.19876	1.99102	0.87256
	H	-4.30771	-2.09871	0.00091
	H	-1.87952	-2.07201	0.00071
	N	-0.42425	0.16388	-0.00019
	H	0.02829	1.07523	-0.00059
	C	0.50279	-0.99185	0.00029
	H	0.29598	-1.59419	-0.89010
	H	0.29587	-1.59353	0.89109
	C	1.92169	-0.48883	0.00019
	C	2.57435	-0.23378	1.20930
	C	2.57467	-0.23512	-1.20904
	C	3.87135	0.27473	1.20855
	H	2.07476	-0.44548	2.15172
	C	3.87167	0.27338	-1.20851
	H	2.07533	-0.44787	-2.15136
	C	4.51854	0.52904	-0.00004
	H	4.37847	0.46310	2.14880
	H	4.37904	0.46070	-2.14883
	H	5.53105	0.91874	-0.00012
	H	-2.19903	1.99002	-0.87480
A37-radcat	C	1.57767	0.84998	0.72698
	C	2.98801	1.34358	0.40497
	C	3.96461	0.16828	0.34160
	C	3.40270	-0.98271	-0.44526
	C	2.11933	-1.09149	-0.79875
	C	1.08286	-0.06757	-0.40581
	H	4.91235	0.48071	-0.10785
	H	2.98074	1.86832	-0.55813
	H	3.30584	2.06596	1.16090
	H	1.59259	0.27561	1.66193
	H	0.87722	1.68066	0.86243
	H	4.09394	-1.76105	-0.75947
	H	1.78331	-1.91907	-1.41979
	H	0.79951	0.52750	-1.28164
	H	4.21353	-0.18119	1.35270
	N	-0.12516	-0.78150	0.03386
	H	0.04816	-1.68504	0.47266
	C	-1.39261	-0.35658	-0.00122
	C	-1.74882	0.91816	-0.54577
	C	-2.41439	-1.21162	0.52836
	C	-3.06793	1.30331	-0.54723
	H	-0.98603	1.57534	-0.94545
	C	-3.72522	-0.80445	0.51172
	H	-2.13542	-2.17842	0.93764
	C	-4.06342	0.45299	-0.02483
	H	-3.34620	2.26873	-0.95476
	H	-4.49979	-1.44952	0.91063
	H	-5.10032	0.77068	-0.03736
A37-Me-radcat	C	-1.62873	-0.80198	0.91822
	C	-2.98559	-1.41933	0.57844
	C	-3.97511	-0.33944	0.13859
	C	-3.35654	0.61683	-0.84352
	C	-2.04321	0.71817	-1.06279
	C	-1.03327	-0.13722	-0.33437
	H	-4.86208	-0.79462	-0.31275
	H	-2.86110	-2.15252	-0.22767
	H	-3.36944	-1.96099	1.44658
	H	-1.75685	-0.04236	1.70021
	H	-0.92883	-1.55092	1.30326

	H	-4.02778	1.24706	-1.42214
	H	-1.65948	1.39441	-1.82358
	H	-0.67226	-0.89742	-1.03009
	H	-4.33875	0.22647	1.00712
	N	0.14307	0.67842	0.05379
	C	1.41344	0.21580	-0.01606
	C	1.69642	-1.15518	-0.31736
	C	2.51122	1.10164	0.22697
	C	2.99934	-1.59667	-0.36602
	H	0.89563	-1.86580	-0.47269
	C	3.80564	0.63873	0.15954
	H	2.33210	2.14850	0.43592
	C	4.06356	-0.70994	-0.13515
	H	3.20171	-2.64017	-0.57973
	H	4.62905	1.32319	0.32996
	H	5.08628	-1.06769	-0.18366
	C	-0.13701	2.01132	0.59785
	H	0.40514	2.15329	1.53357
	H	0.15196	2.78318	-0.12231
	H	-1.20778	2.09107	0.77542
A38-Me-radcat	C	1.38037	0.13166	1.28361
	C	2.84741	0.09480	1.71952
	C	3.69723	-0.68867	0.71654
	C	3.38621	-0.30829	-0.70600
	C	2.30033	0.37291	-1.07304
	C	1.28790	0.86340	-0.05558
	H	4.76182	-0.52627	0.91101
	H	3.22955	1.11967	1.80067
	H	2.92313	-0.35085	2.71444
	H	1.00007	-0.89050	1.20171
	H	0.76209	0.65152	2.02338
	H	4.09057	-0.61627	-1.47526
	H	2.14044	0.64113	-2.11494
	H	1.51903	1.92431	0.13517
	H	3.53476	-1.76934	0.83702
	N	-0.10133	0.95550	-0.57943
	C	-1.13403	0.09913	-0.24860
	C	-0.99826	-1.31473	-0.45544
	C	-2.34439	0.65479	0.29206
	C	-2.06588	-2.12656	-0.10414
	C	-3.36008	-0.22088	0.64295
	C	-3.23340	-1.59717	0.44768
	H	-1.99863	-3.19226	-0.29751
	H	-4.25904	0.17615	1.10340
	H	-4.04970	-2.25805	0.72026
	C	-2.49241	2.11371	0.64550
	H	-1.56961	2.52859	1.05992
	H	-2.78410	2.72184	-0.21563
	H	-3.27239	2.22664	1.39921
	C	0.16557	-1.91891	-1.19322
	H	0.43608	-1.32306	-2.06794
	H	1.06097	-2.00231	-0.57222
	H	-0.09909	-2.92105	-1.53279
	C	-0.35682	2.15044	-1.37787
	H	-1.33703	2.09099	-1.84526
	H	-0.26797	3.05822	-0.77289
	H	0.40978	2.18856	-2.15955
A39-Me-radcat	C	2.00315	-0.73290	-1.11684
	C	3.49506	-0.94949	-1.38131

C	4.33251	0.15383	-0.73080
C	3.88390	0.44986	0.67473
C	2.72858	0.02683	1.19209
C	1.75351	-0.81850	0.39161
H	5.39052	-0.12610	-0.71982
H	3.79812	-1.92428	-0.98017
H	3.67668	-0.98078	-2.45844
H	1.70321	0.24804	-1.50087
H	1.39732	-1.48759	-1.62770
H	4.54723	1.04249	1.30068
H	2.46577	0.25110	2.22414
H	1.88549	-1.86636	0.69544
H	4.27531	1.07857	-1.32172
N	0.33981	-0.54939	0.75562
C	-0.39204	0.50652	0.28160
C	0.30990	1.73881	0.09881
C	-1.81997	0.44259	0.06261
C	-0.37752	2.91834	-0.06382
C	-2.46089	1.67368	-0.04841
C	-1.77748	2.89178	-0.08099
H	0.16082	3.85673	-0.13362
H	-3.53529	1.69718	-0.18010
H	-2.33922	3.81596	-0.16814
C	-2.61629	-0.84234	-0.27740
C	-0.14937	-1.34542	1.87732
H	-1.08862	-0.94026	2.24209
H	-0.25489	-2.39851	1.60144
H	0.60031	-1.27417	2.67398
H	1.38629	1.74877	0.22182
C	-3.72096	-0.48321	-1.29987
H	-4.15114	-1.41077	-1.68556
H	-4.54182	0.07997	-0.84954
H	-3.32368	0.08522	-2.14581
C	-3.33703	-1.45386	0.94474
H	-4.09893	-2.15267	0.58753
H	-2.67550	-2.01769	1.60275
H	-3.84383	-0.68163	1.53175
C	-1.72988	-1.89185	-0.97401
H	-1.26654	-1.47170	-1.87324
H	-0.94121	-2.30143	-0.34235
H	-2.35611	-2.73242	-1.28414

10.2. DFT Calculation of the Redox Potential

The redox potentials (E^o) of the species were calculated using the protocol reported by Liu and Guo.[28] Computation was conducted to obtain values described in the thermodynamic cycles. All DFT calculations were carried out using Gaussian 09W.[25] Specifically, the (U)B3LYP functional and 6-31+G(d) basis set were used to conduct geometry optimization and frequency calculation in the gas phase. Single-point energy calculations were carried out on the optimized geometries using the 6-311++G(2df,2p) basis set. The solvation free energies in acetonitrile were calculated with 6-311++G(2df,2p) using D-PCM, including additional keywords (Icomp=4, TSNUM=60, TSARE=0.4, radii=bondi, alpha=1.20). All structures were confirmed to be at local minima by the absence of imaginary frequencies. The lowest-energy conformers were used in the final calculations.



Scheme S4 Thermodynamic cycle for the redox potential of **A1-diene**.

Table S8 Thermodynamic data for the calculation of the redox potential of **A1-diene**

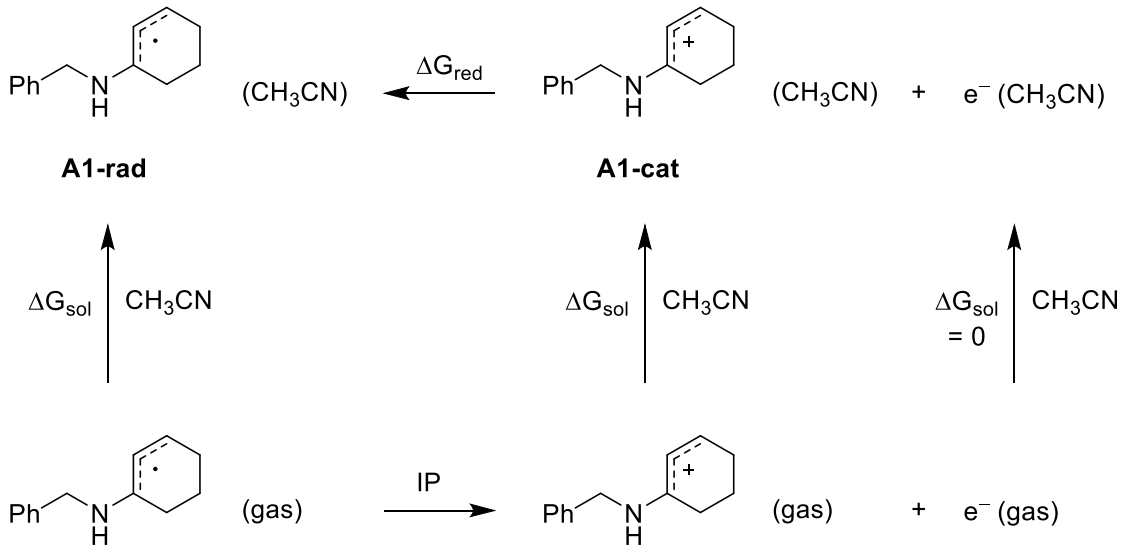
	A1-diene	**A1-dieneradcat**
H_{corr} [Hartree]	0.263184	0.263992
G_{corr} [Hartree]	0.210153	0.209409
E_{gas} [Hartree]	–559.3246798	–559.0901835
H_{gas} [kcal/mol]	–350816.1202	–350668.4646
G_{gas} [kcal/mol]	–350849.3976	–350702.7159
E (CH_3CN) [kcal/mol]	–559.3312702	–559.1610415
ΔG_{solv} [kcal/mol]	–4.135529038	–44.46403272

IP (ionization potential) = H_{gas} (**A1-dieneradcat**) – H_{gas} (**A1-diene**)
= (–350668.4646) – (–350816.1202) = 147.6556 kcal/mol = 6.40 eV

IP (corrected) = 6.40 eV + 0.28 eV = 6.68 eV
TΔS (ionization) = H_{gas} (**A1-dieneradcat**) – H_{gas} (**A1-diene**) – G_{gas} (**A1-dieneradcat**) + G_{gas} (**A1-diene**)
= (–350668.4646) – (–350816.1202) – (–350702.7159) + (–350849.3976) = 0.9739 kcal/mol

TΔS (ionization, corrected for the electron spin degeneracy)
= (0.9739) + 0.82 = 1.7939 kcal/mol

E^o (calc, **A1-dieneradcat**/**A1-diene**)
= IP (corrected) + (1/23.06)[–TΔS (ionization, corrected) + ΔG_{solv} (**A1-dieneradcat**) – ΔG_{solv} (**A1-diene**)] – 4.43[29]
= 6.68 + (1/23.06)[(–1.7939) + (–44.46403272) – (–4.135529038)] – 4.43 = 0.42 V



Scheme S5 Thermodynamic cycle for the redox potential of **A1-rad**.

Table S9 Thermodynamic data for the calculation of the redox potential of **A1-rad**

	A1-rad	**A1-cat**
H_{corr} [Hartree]	0.273959	0.277204
G_{corr} [Hartree]	0.219442	0.22304
E_{gas} [Hartree]	–559.9115427	–559.7250323
H_{gas} [kcal/mol]	–351177.6205	–351058.5473
G_{gas} [kcal/mol]	–351211.8304	–351092.5357
E (CH_3CN) [kcal/mol]	–559.9173762	–559.7956484
ΔG_{solv} [kcal/mol]	–3.660548651	–44.31224457

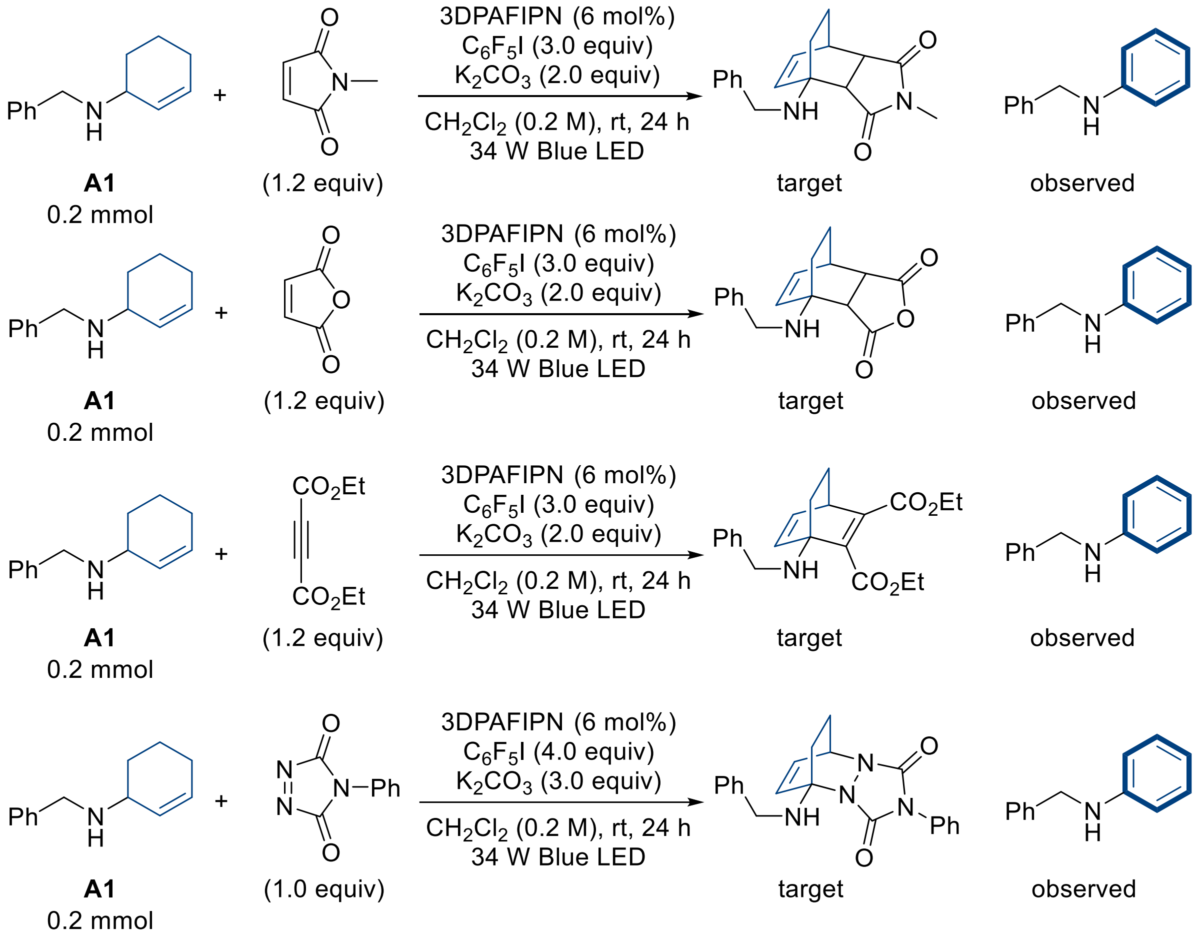
IP (ionization potential) = H_{gas} (**A1-cat**) – H_{gas} (**A1-rad**)
= (–351058.5473) – (–351177.6205) = 119.0732 kcal/mol = 5.16 eV

IP (corrected) = 5.16 eV + 0.28 eV = 5.44 eV
TΔS (ionization) = H_{gas} (**A1-cat**) – H_{gas} (**A1-rad**) – G_{gas} (**A1-cat**) + G_{gas} (**A1-rad**)
= (–351058.5473) – (–351177.6205) – (–351092.5357) + (–351211.8304) = –0.2215 kcal/mol

TΔS (ionization, corrected for the electron spin degeneracy)
= (–0.2215) + 0.82 = 0.5985 kcal/mol

E^o (calc, **A1-cat**/**A1-rad**)
= IP (corrected) + (1/23.06)[–TΔS (ionization, corrected) + ΔG_{solv} (**A1-cat**) – ΔG_{solv} (**A1-rad**)] – 4.43[29]
= 5.44 + (1/23.06)[(0.5985) + (–44.31224457) – (–3.660548651)] – 4.43 = –0.77 V

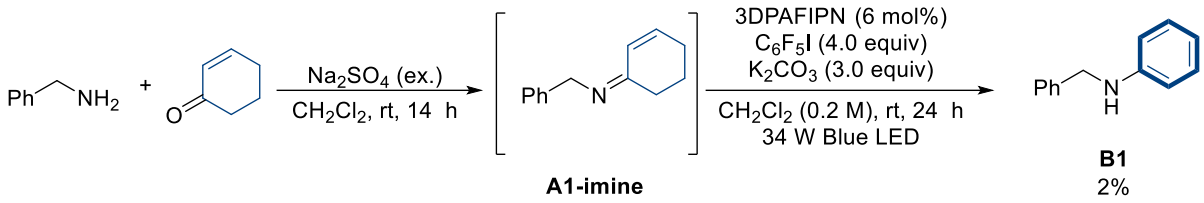
11. Trials to Trap the Diene Intermediate (A1-diene)



Scheme S6 Summary of the Diels-Alder trapping of **A1-diene** with the dienophiles.

The trapping of the proposed intermediate **A1-diene** was tried by adding a variety of dienophiles, such as *N*-methylsuccinimide, maleic anhydride, diethyl acetylenedicarboxylate, and 4-phenyl-1,2,4-triazoline-3,5-dione. In all cases, no desired Diels-Alder adduct was observable, and only the aromatized product **B1** was detected.

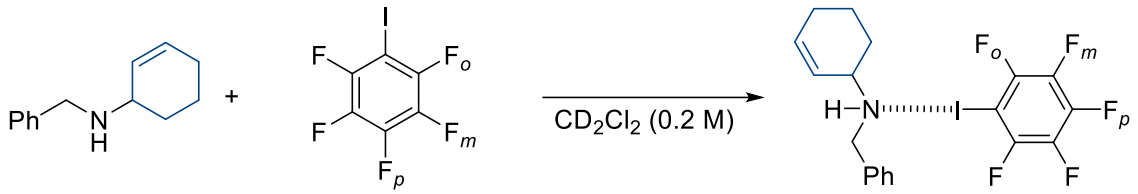
12. Reaction with in situ Generated Imine Intermediate (A1-imine)



An oven-dried 25 mL Schlenk tube equipped with a PTFE-coated stir bar was charged with benzylamine (341 µL, 2.0 mmol, 1.0 equiv), 2-cyclohexen-1-one (194 µL, 2.0 mmol, 1.0 equiv), sodium sulfate (700 mg), and CH_2Cl_2 (4 mL). The reaction mixture was degassed for 10 min. and stirred under inert atmosphere for 14 h at room temperatures. After the reaction was done, the reaction mixture was further filtered through a pad of sodium sulfate, and the organic layer was concentrated in vacuo and further utilized in the next step.

An oven-dried 4 mL reaction vial equipped with a PTFE-coated stir bar was charged with 3DPAFIPN (7.8 mg, 0.012 mmol, 6 mol%), potassium carbonate (82.9 mg, 0.6 mmol, 3.0 equiv), and CH_2Cl_2 (1 mL) in a glovebox. The vial was closed with a Teflon-lined septum cap and taken out of the glovebox. Imine **A1-imine** (37.1 mg, 0.2 mmol, 1.0 equiv) and iodopentafluorobenzene (107 µL, 0.8 mmol, 4.0 equiv) were added via a gas-tight syringe, and the solution was stirred for the indicated time under 34 W blue LED irradiation with fan cooling. After the reaction was complete, dodecane (45.4 µL) was added and the reaction mixture was analyzed by GC. Only 2% of the desired product **B1** was observed, indicating that the suggested **A1-imine** is not participating in the reaction as a key intermediate.

13. Experiments to Detect Halogen Bonding in the Reaction Conditions



A1
(0 / 1.5 equiv)

A solution of C_6F_5I (13.3 μL, 0.1 mmol) in CD_2Cl_2 (0.5 mL) was prepared in the NMR tube, ^{19}F NMR spectrum was obtained. Amine **A1** (28.1 mg, 0.15 mmol) was added to the solution, and ^{19}F NMR was obtained again to check the shifts in the NMR spectrum.

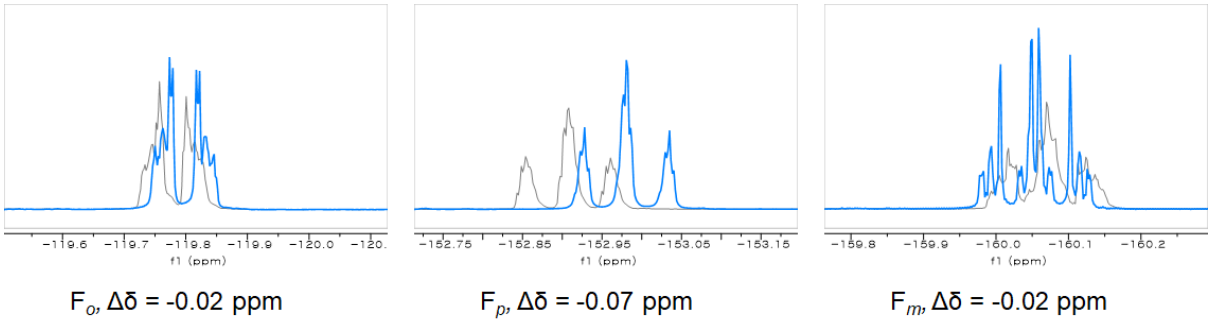
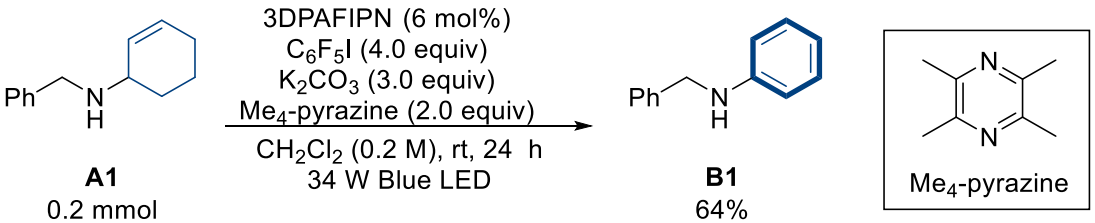


Fig. S15 Comparison of the ^{19}F NMR spectrum after the addition of **A1** to the solution of C_6F_5I.

Although slight changes in the chemical shifts were observed, this is not likely from the complexation mediated by halogen bonding. When comparing with previous examples of halogen bonding with C_6F_5I, the changed value is too small.[30]



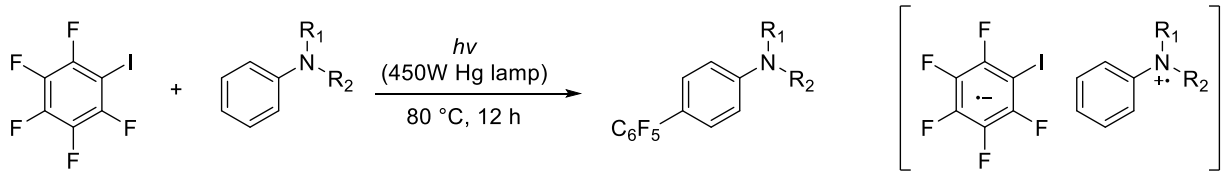
A1
0.2 mmol

B1
64%

In addition, 2,3,5,6-tetramethylpyrazine, which is known to form halogen bonding with iodine-containing molecules efficiently,[31] did not shut down the reactivity in the standard reaction conditions. This result suggested that the halogen bonding does not play a key role in the observed dehydrogenation reaction.

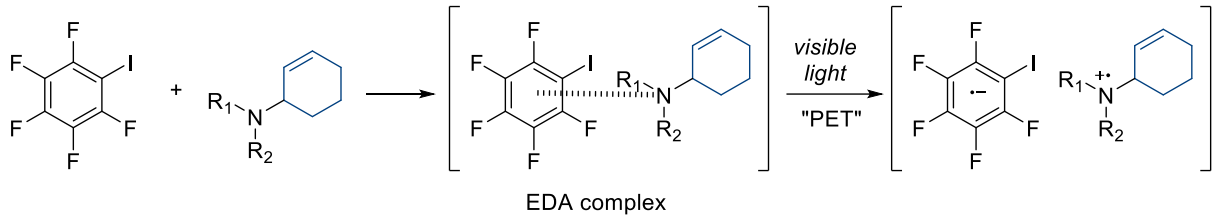
14. Experiments to Detect Electron Donor-Acceptor (EDA) Complexation

A. Photoinduce electron transfer (PET) between C_6F_5I and aniline via EDA complex



Q.-Y. Chen *J. Chem. Soc. Perkin. Trans. 1* **1993**, 1705.

B. PET between C_6F_5I and allylic amine via EDA complex



Scheme S7 Activation of C_6F_5I via photoinduced electron transfer.

Q.-Y. Chen and co-worker reported the reaction between C_6F_5I and aromatic compounds under UV irradiation, producing perfluoroarylated species.[32] The mechanism of the reaction was proposed as the photoinduced electron transfer (PET) between electron-deficient C_6F_5I and electron-rich aromatic species to generate radical species (Scheme S7A). A similar scenario was proposed to the developed CD process via the activation of C_6F_5I through the PET process of electron donor-acceptor (EDA) complex (Scheme S7B).

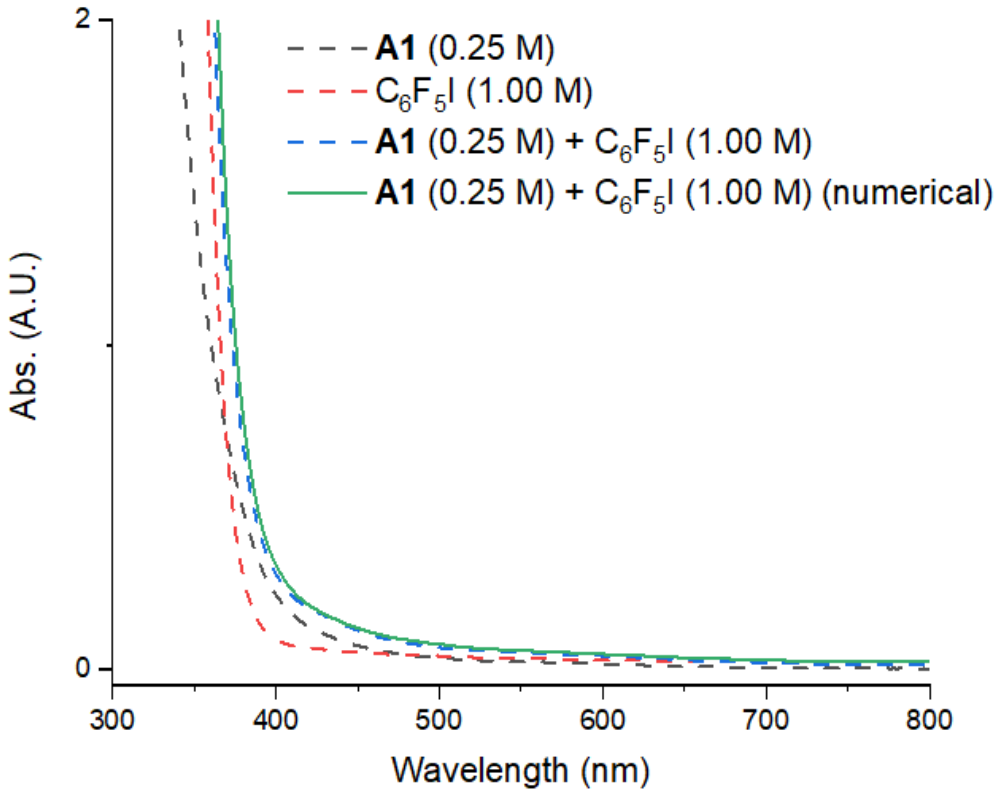


Fig. S16 UV-Vis absorption spectra for the **A1**, C_6F_5I, and their mixtures (CH_2Cl_2).

To check the possibility of the photoinduced electron transfer (PET) via the formation of electron donor-acceptor (EDA) complex, UV-Vis absorption spectra were checked (Fig. S16). It seemed that the absorption between 400 – 500 nm was enhanced significantly when the **A1** (0.25 M) and C_6F_5I (1.00 M) were mixed (Fig. S16, blue dashed line). However, this absorption spectrum is almost identical to the numerical sum of individual absorption spectra (Fig. S16, green solid line), indicating that no enhancement of the absorption of the blue light region via EDA complexation occurred in the reaction mixture.

15. Quantum Yield Measurement

The quantum yield was measured following a procedure reported by the Yoon group.[33]

15.1. Actinometry

The photon flux was measured following standard actinometry with potassium ferrioxalate. A potassium ferrioxlalate solution was prepared by dissolving 737 mg of potassium ferrioxalate in 10 mL of 0.05 M sulfuric acid. The solution was rigorously mixed for full solvation. Separately, 20 mg of 1,10-phenanthroline and 2.25 g of sodium acetate were dissolved in 10 mL of 0.5 M sulfuric acid. All solutions were handled in the dark at all times. 2.0 mL of the ferrioxalate solution was transferred to a cuvette and irradiated for 90.0 seconds at 436 nm with a slit size of 20.0 nm. After irradiation, 0.35 mL of the phenanthroline solution was added to the irradiated solution. Separately, 2.0 mL of the ferrioxalate solution was taken and mixed with 0.35 mL of the phenanthroline solution for comparison. After 1 h, the absorbance of the solutions was measured at 510 nm.

Conversion of the ferrioxalate solution could be calculated using the following equation:

$$\text{mol } Fe^{2+} = \frac{V\Delta A}{l \cdot \varepsilon}$$

Here, V is the volume of the solution, ΔA is the difference in absorbance at 510 nm, l is the cuvette dimension, and ε is the molar absorption coefficient.

The photon flux was calculated using the following equation:

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\emptyset \cdot t \cdot f}$$

Here, $\emptyset$ is the quantum yield of ferrioxalate, t is the irradiation time, and f is the fraction of light absorbed by the ferrioxalate solution at 436 nm.

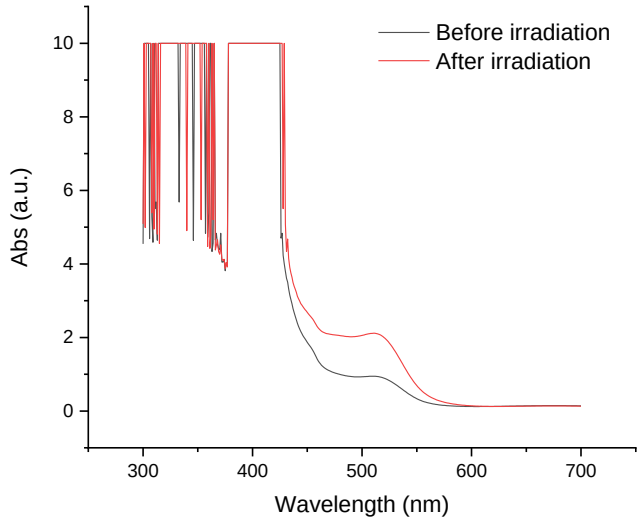


Fig. S17 Absorbance of the ferrioxalate solutions.

From the above absorption spectra, ΔA = 1.168.

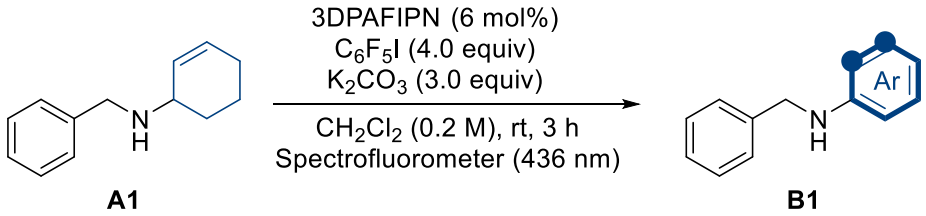
Therefore,

$$\text{mol } Fe^{2+} = \frac{V\Delta A}{l \cdot \varepsilon} = \frac{0.00235 \cdot 1.168}{1 \cdot 11000} \text{ mol} = 2.495 \times 10^{-7} \text{ mol}$$

Then,

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\emptyset \cdot t \cdot f} = \frac{2.495 \cdot 10^{-7}}{1.01 \cdot 90 \cdot 0.99833} \text{ einstein/s} = 2.75 \times 10^{-9} \text{ einstein/s}$$

15.2. Quantum Yield Measurement



An oven-dried 4 mL reaction vial equipped with a PTFE-coated stir bar was charged with 3DPAFIPN (15.6 mg, 0.024 mmol, 6 mol%), potassium carbonate (165.8 mg, 1.2 mmol, 3.0 equiv), and CH_2Cl_2 (2 mL) in a glovebox. The vial was closed with a Teflon-lined septum cap and taken out of the glovebox. **A1** (74.9 mg, 0.4 mmol, 1.0 equiv), and iodopentafluorobenzene (214 µL, 1.6 mmol, 4.0 equiv) were added via a gas-tight syringe, and the solution was irradiated for 10800 s (3 h) under the identical co nditions with the actinometry. The resulting mixture was analyzed by GC following the addition of do decane (90.8 µL, 0.4 mmol) as an internal standard to give 0.61% yield of the desired product.

$$\text{mol product} = 0.61\% \cdot 0.40 \text{ mmol} = 2.44 \cdot 10^{-6} \text{ mol}$$

$$\text{Quantum yield} = \frac{\text{mol product}}{\text{flux} \cdot t \cdot f} = \frac{2.44 \cdot 10^{-6}}{2.75 \cdot 10^{-9} \cdot 10800 \cdot 1} = 0.08$$

Here, flux is the photon flux, t is irradiation time, and f is the fraction of light absorbed at 436 nm. In this case, f was taken to be unity based on the absorption spectrum shown in Fig. S4.

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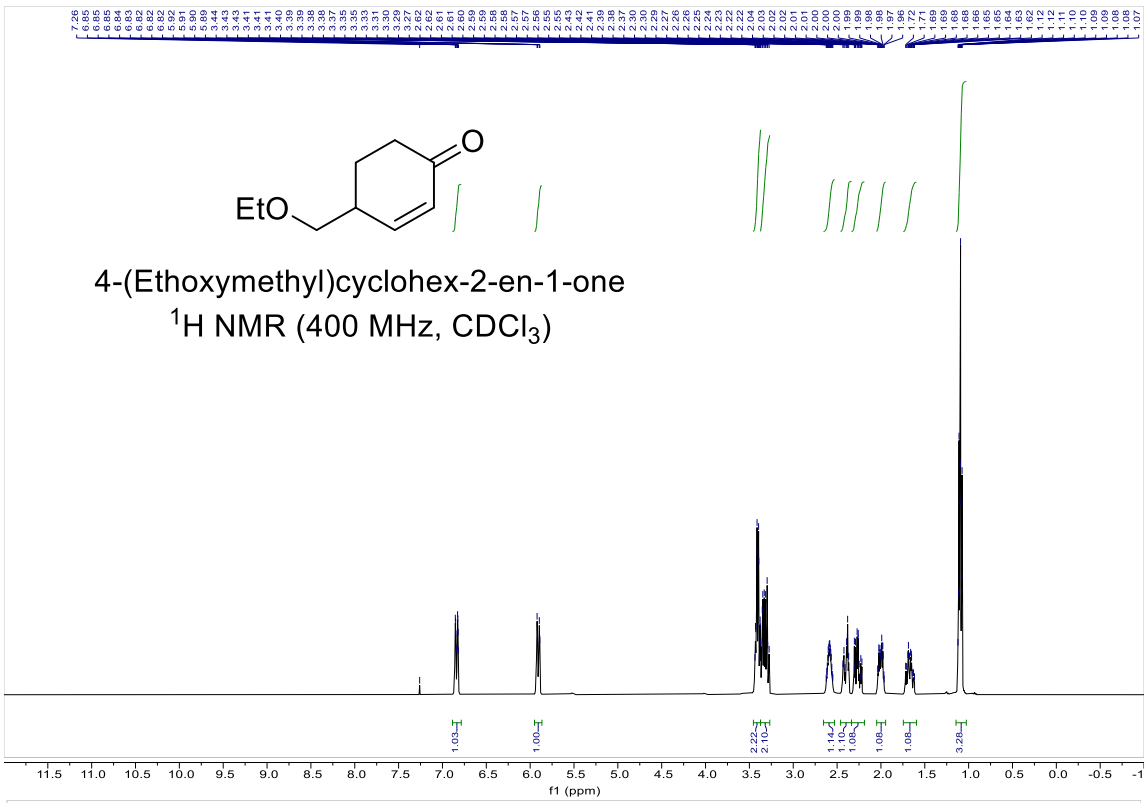
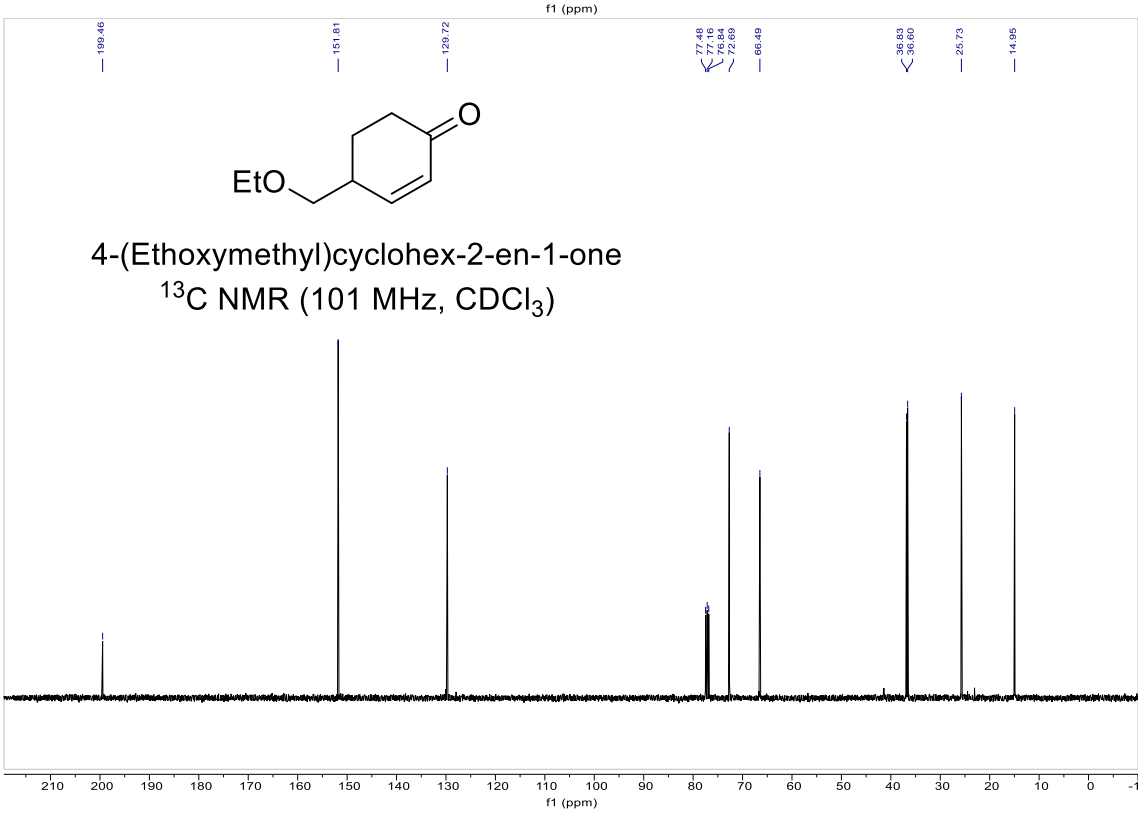
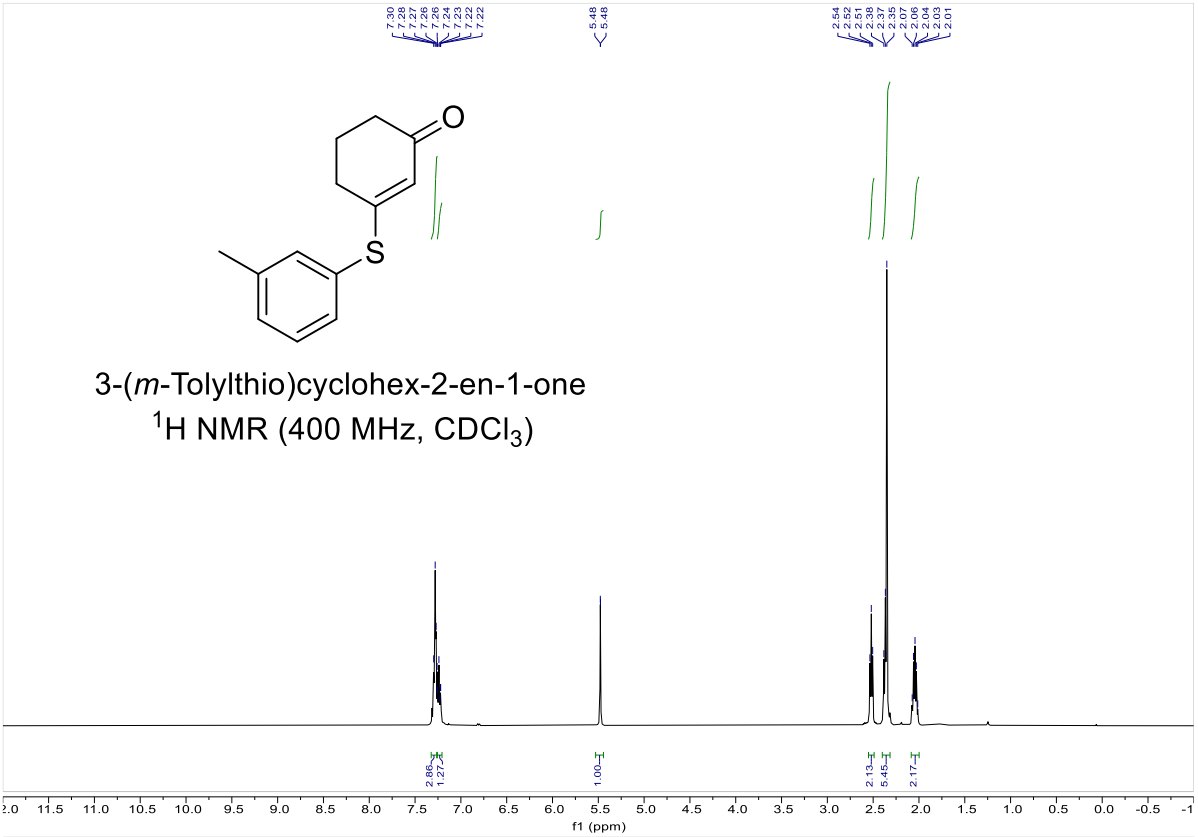
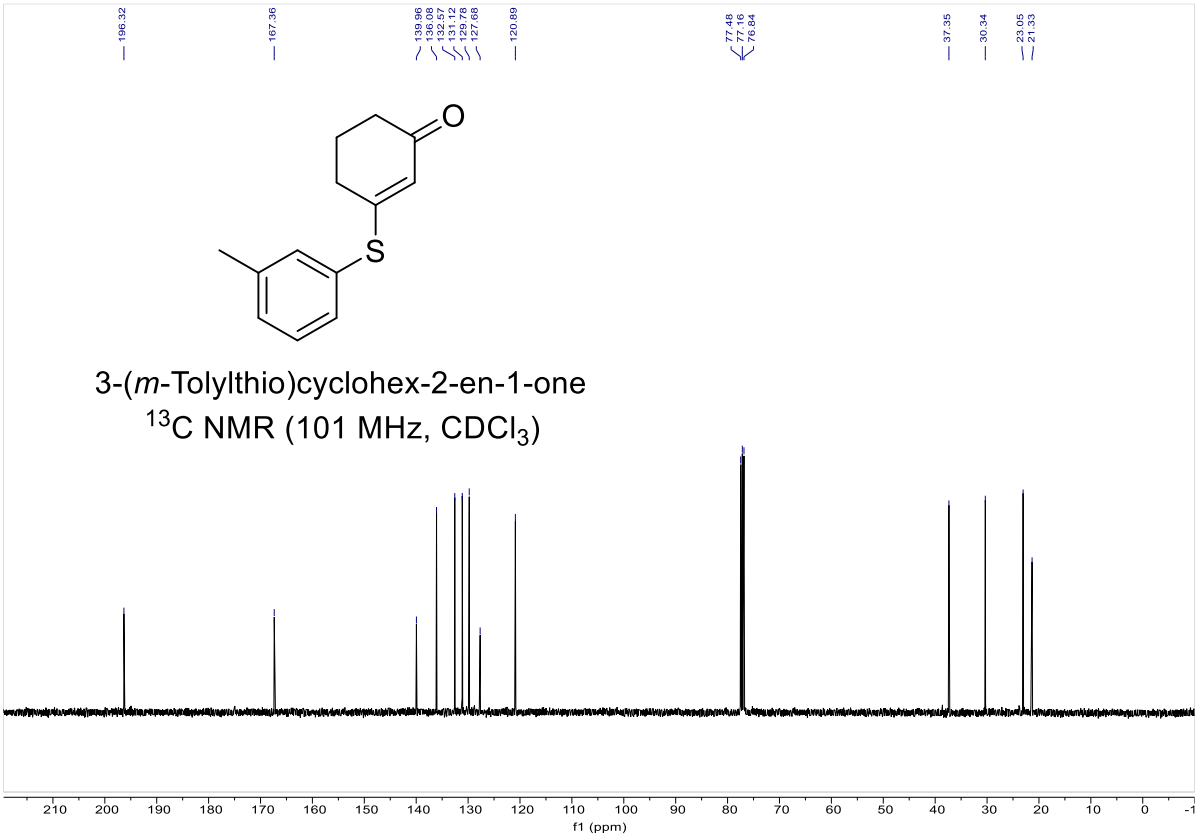
17. NMR Spectra






O
S
3-(m-Tolylthio)cyclohex-2-en-1-one
1H NMR (400 MHz, CDCl3)
f1 (ppm)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S
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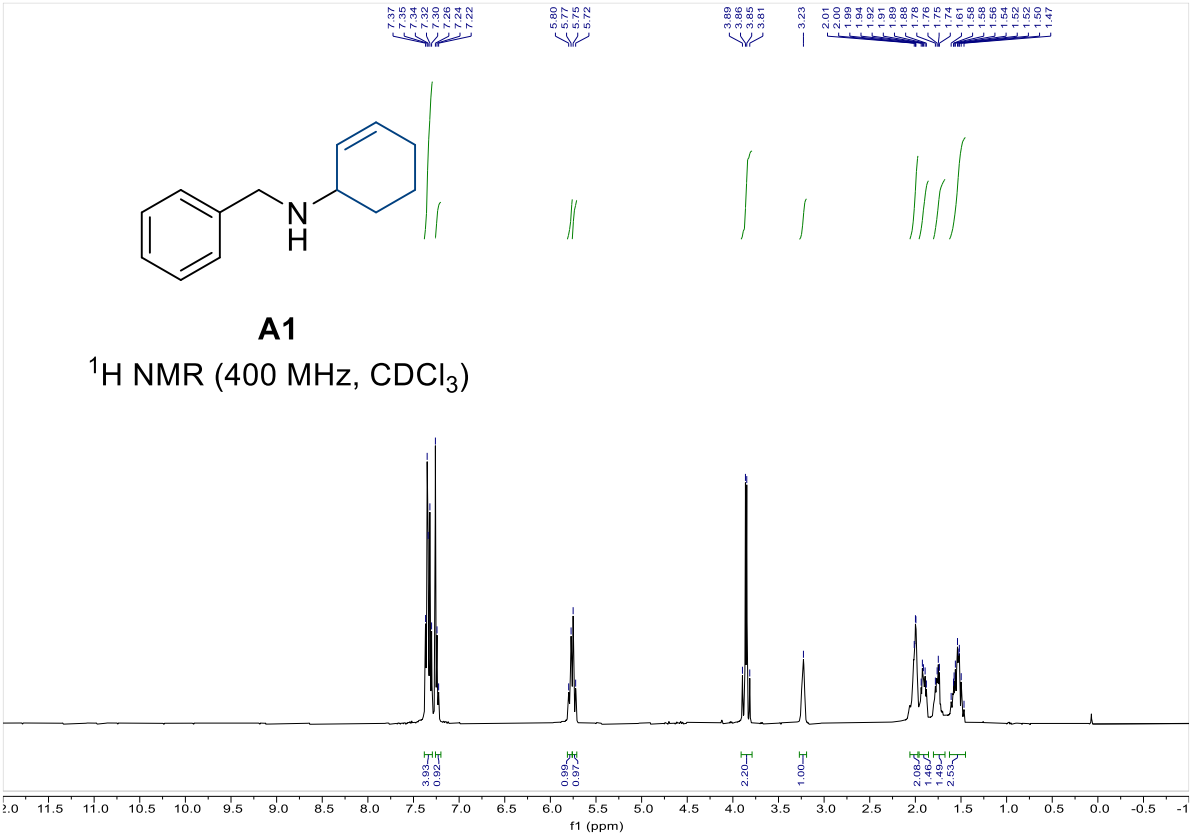
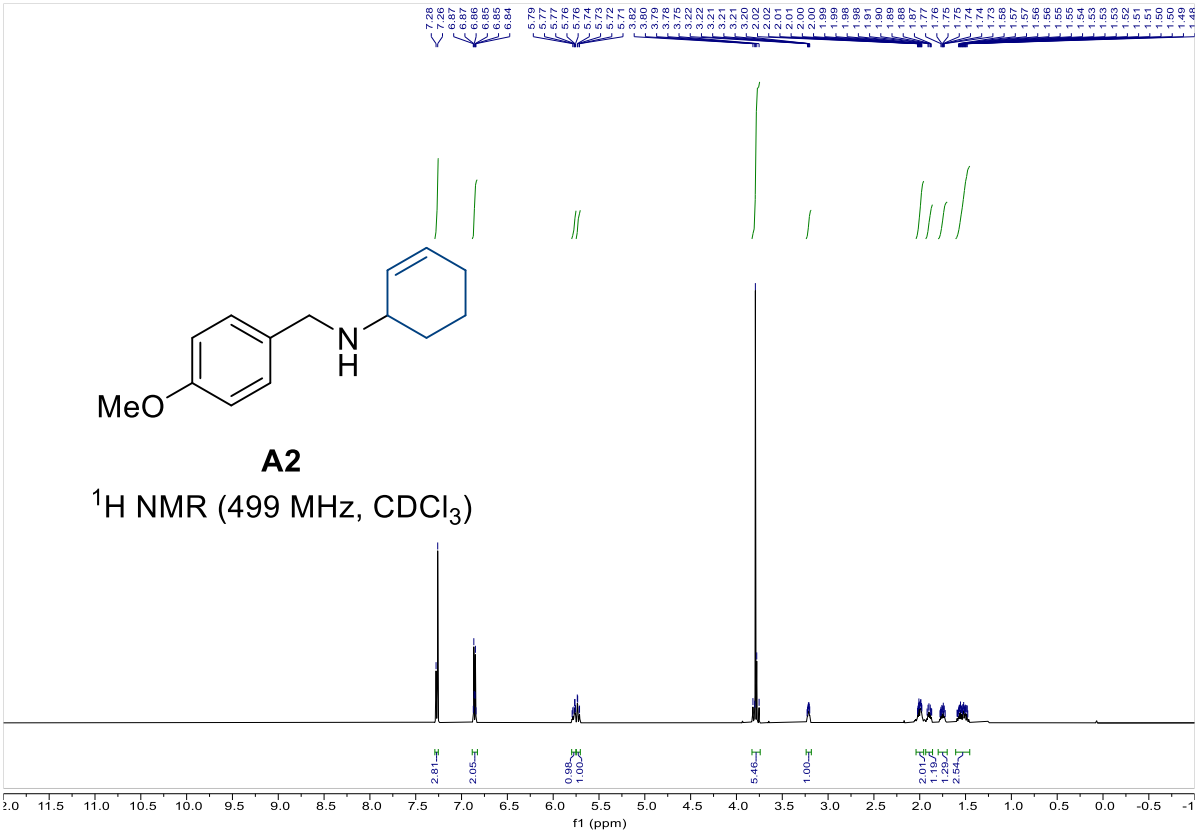
f1 (ppm)


A1
1H NMR (400 MHz, CDCl3)
f1 (ppm)


MeO
A2
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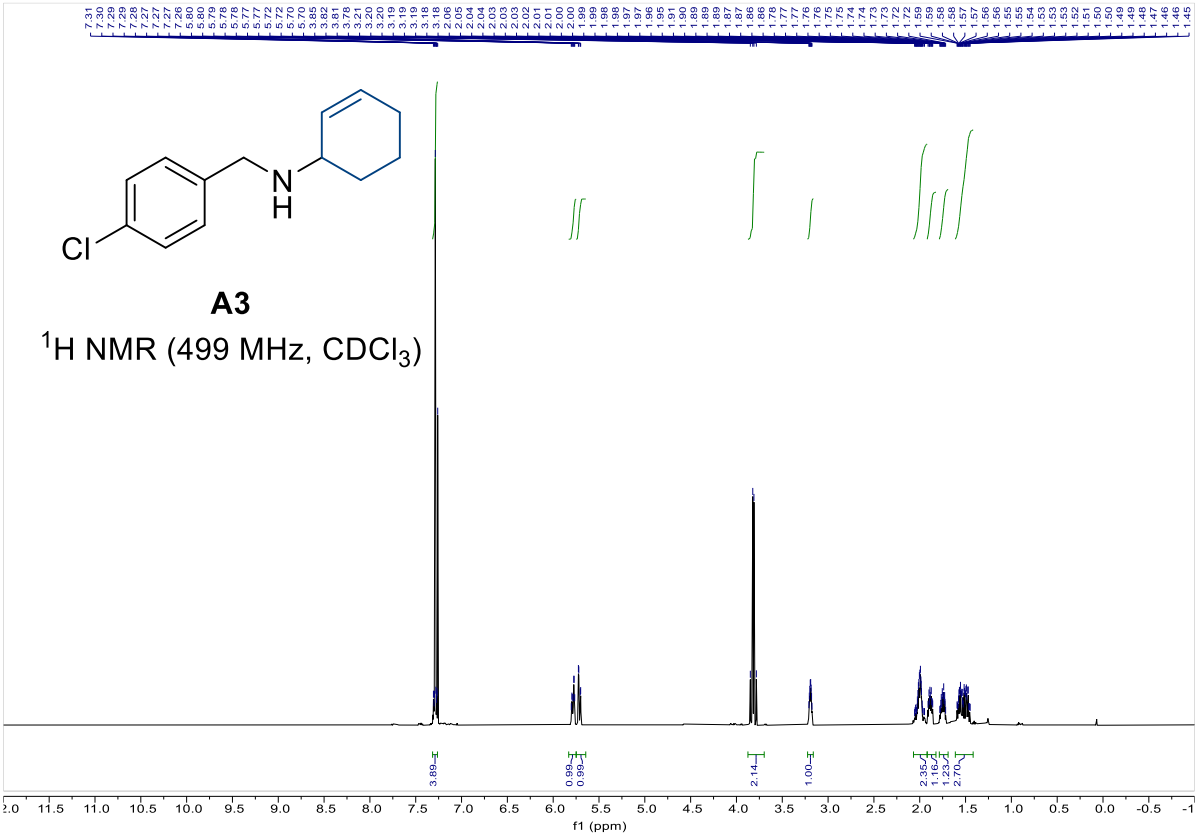
f1 (ppm)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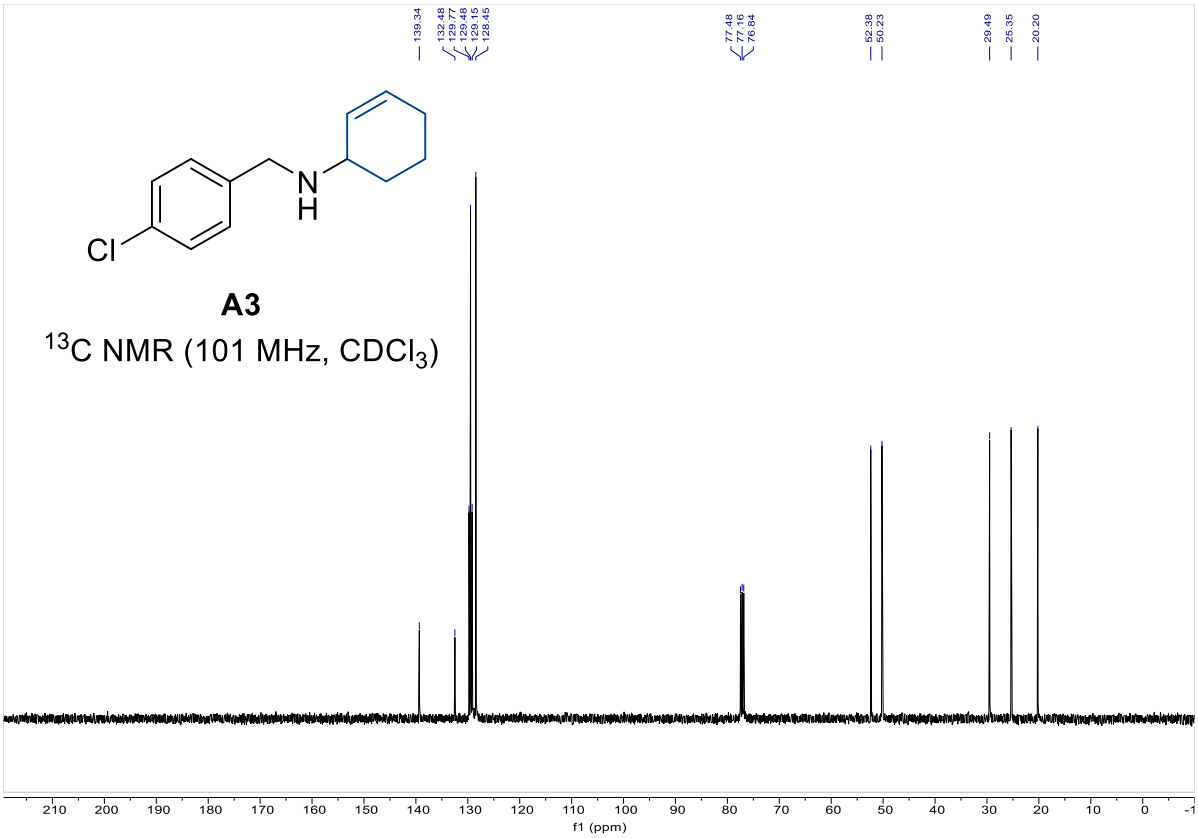
N
H
A3
1H NMR (499 MHz, CDCl3)
f1 (ppm)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H
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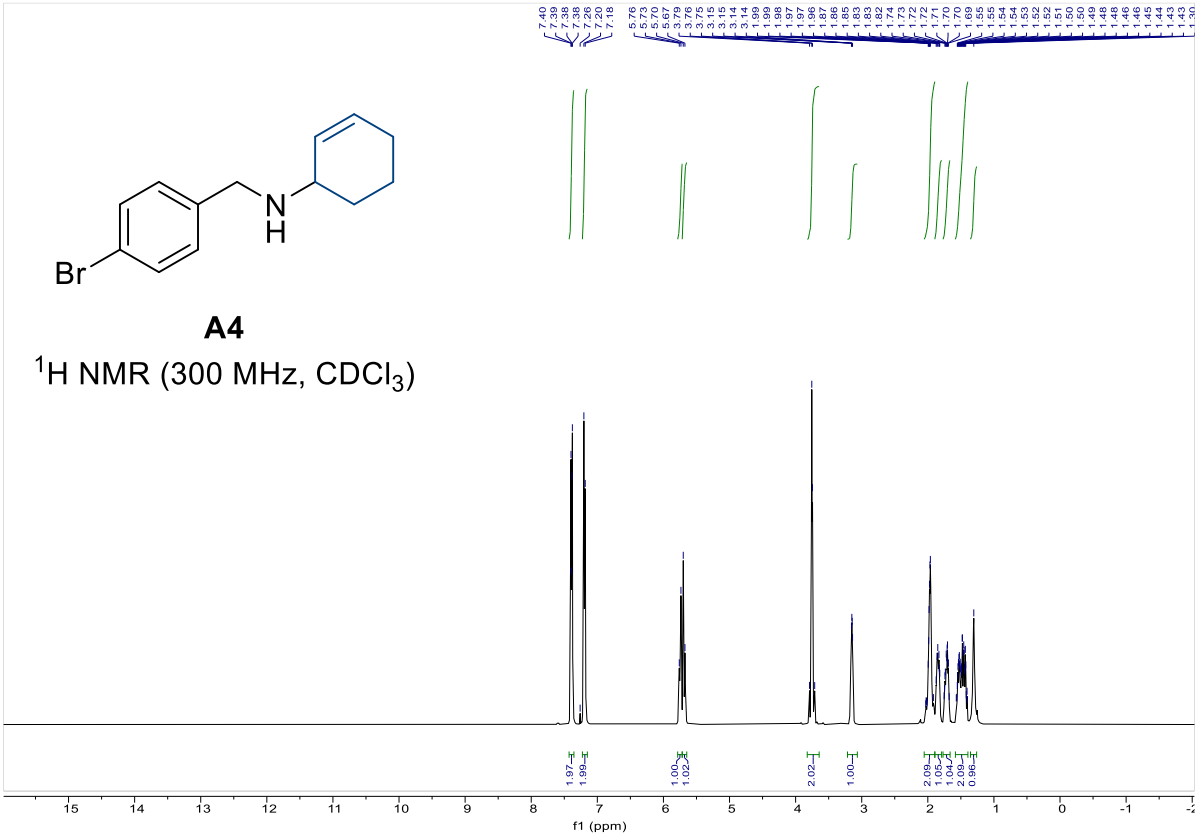
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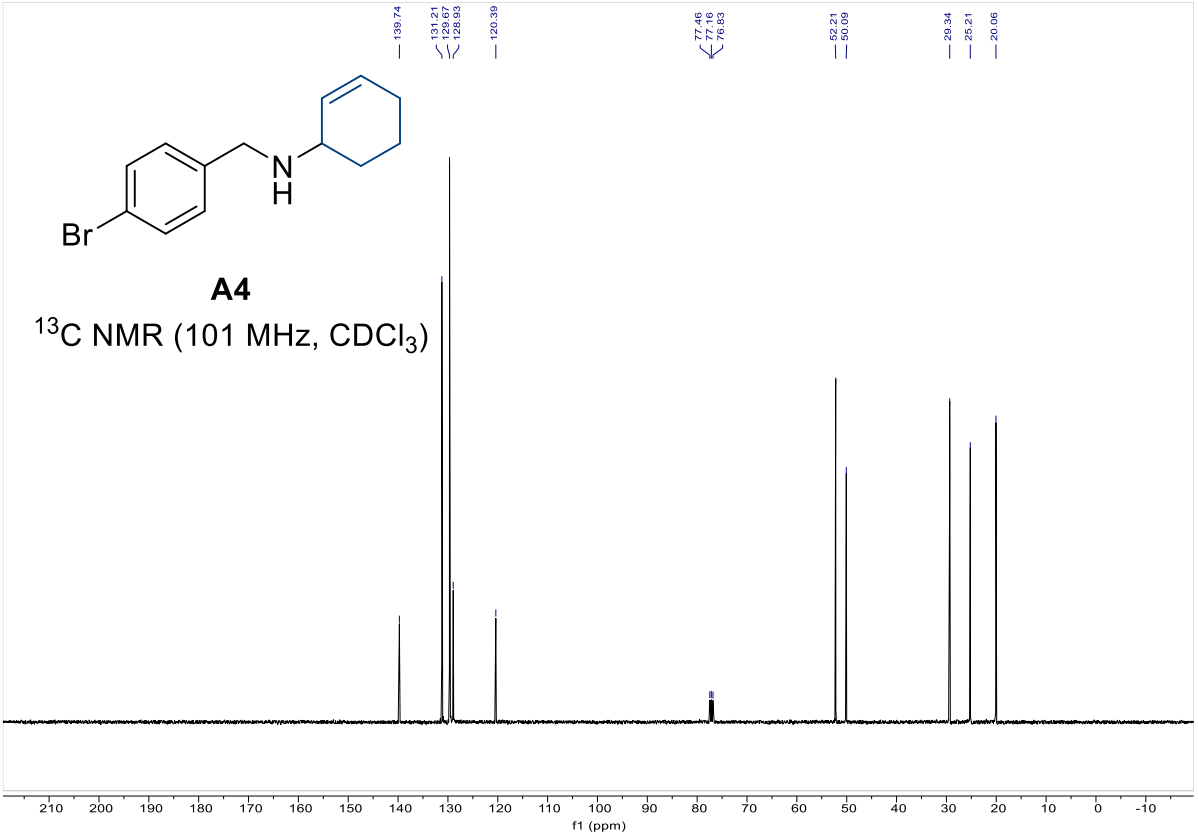
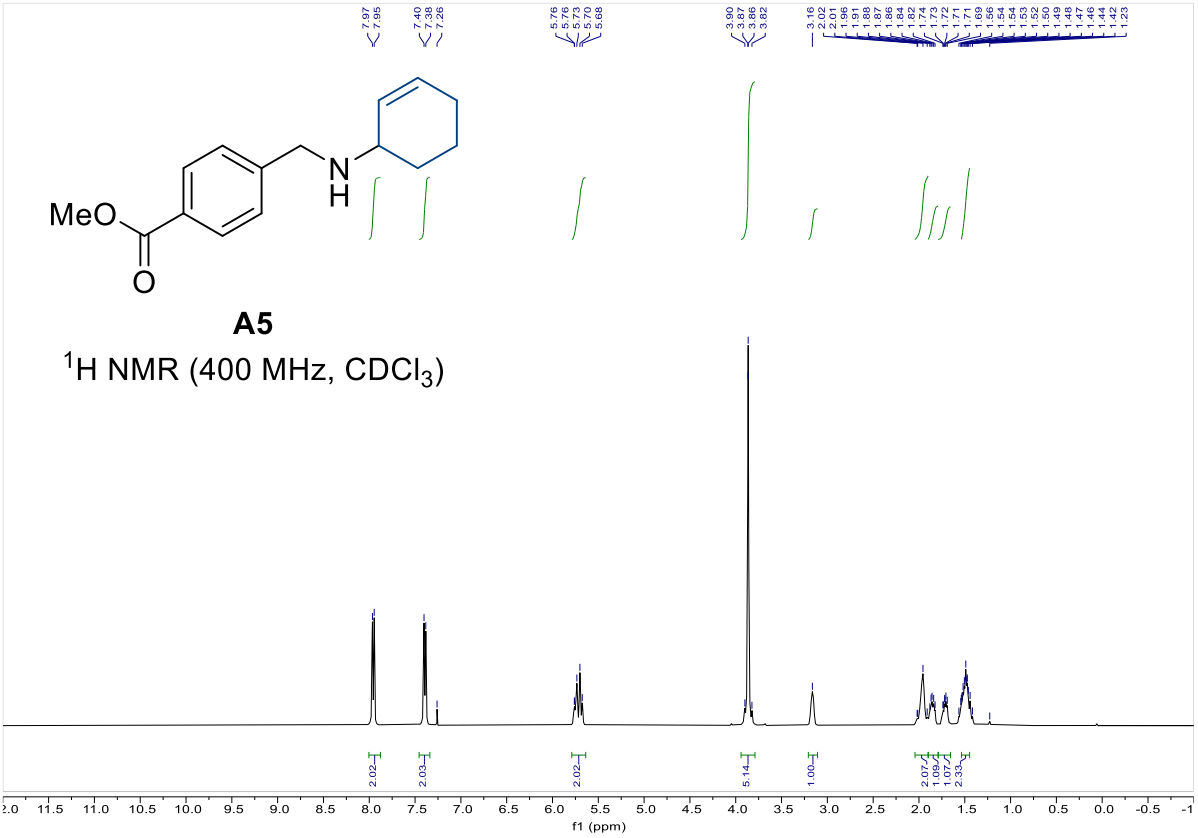
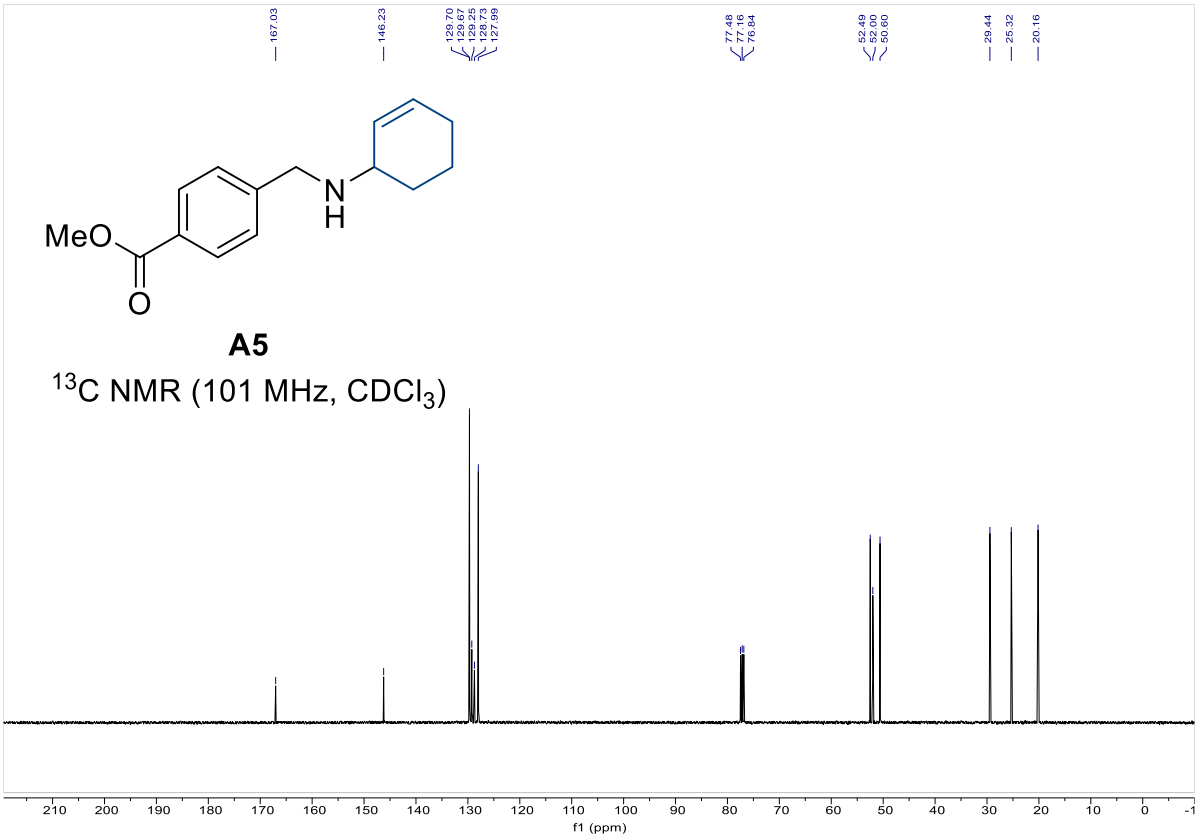
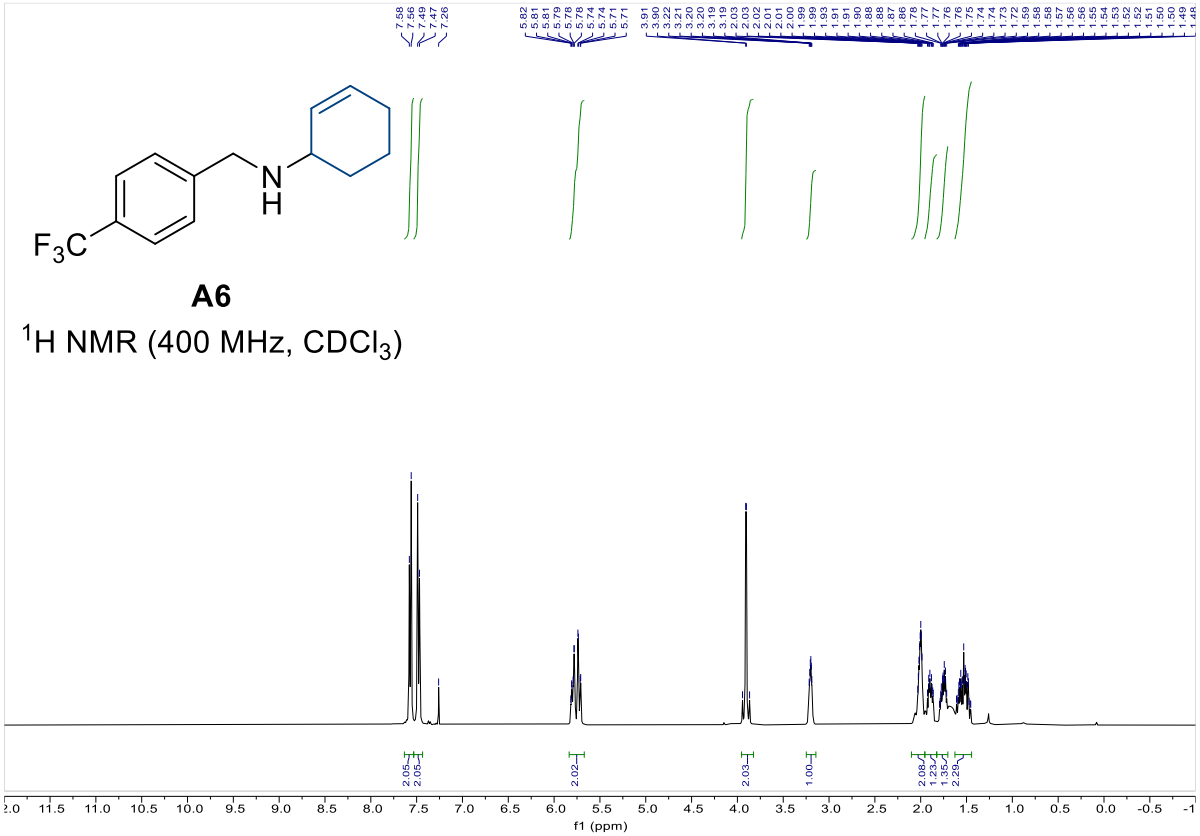

Br
N
H
A4
13C NMR (101 MHz, CDCl3)
f1 (ppm)

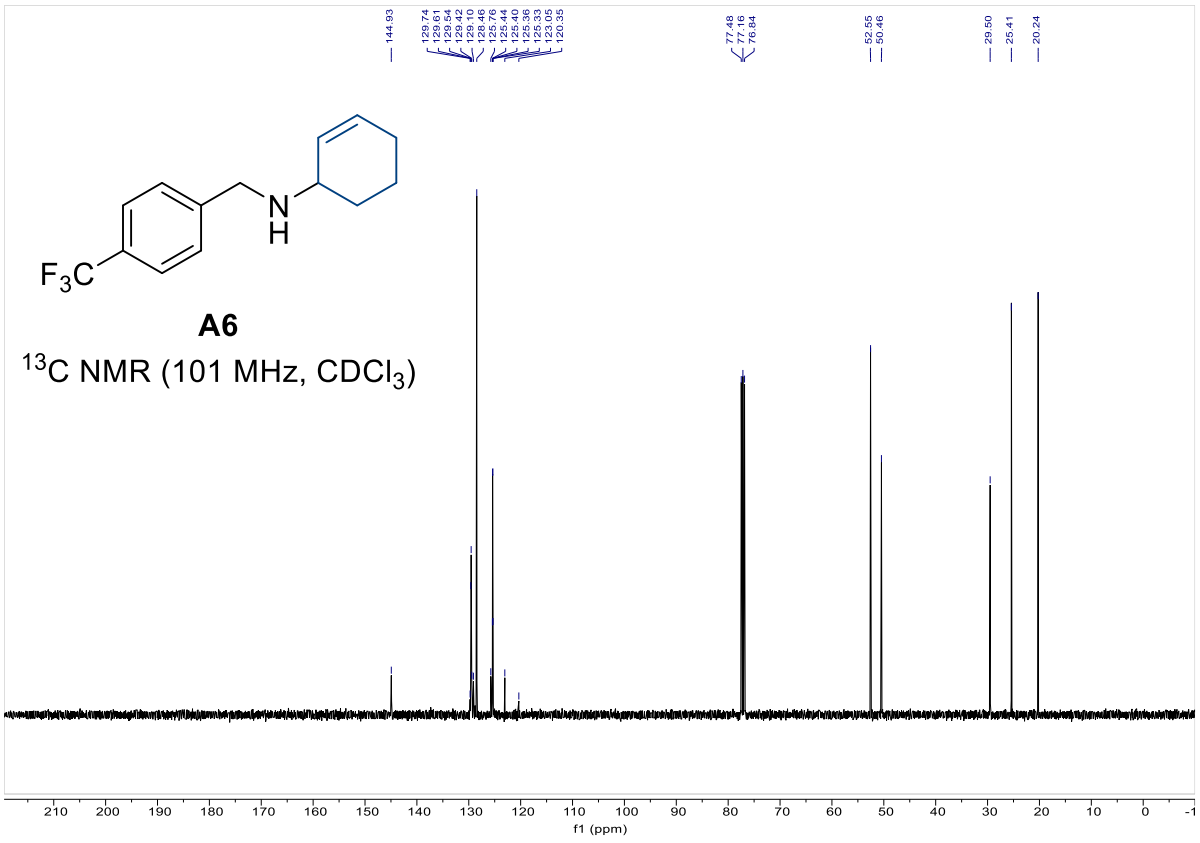

MeO
O
N
H
A5
1H NMR (400 MHz, CDCl3)
f1 (ppm)


MeO
O
N
H
A5
13C NMR (101 MHz, CDCl3)
f1 (ppm)



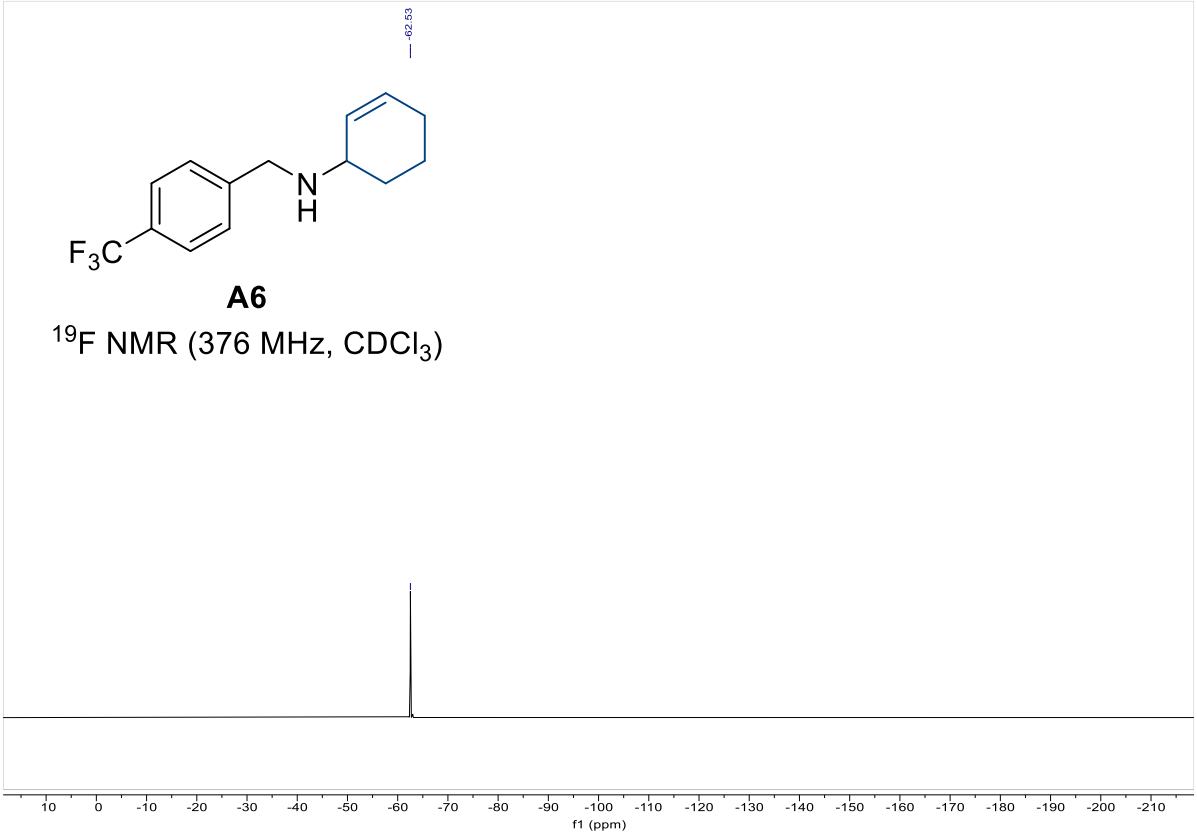
A6

^{1}H NMR (400 MHz, $CDCl_3$)



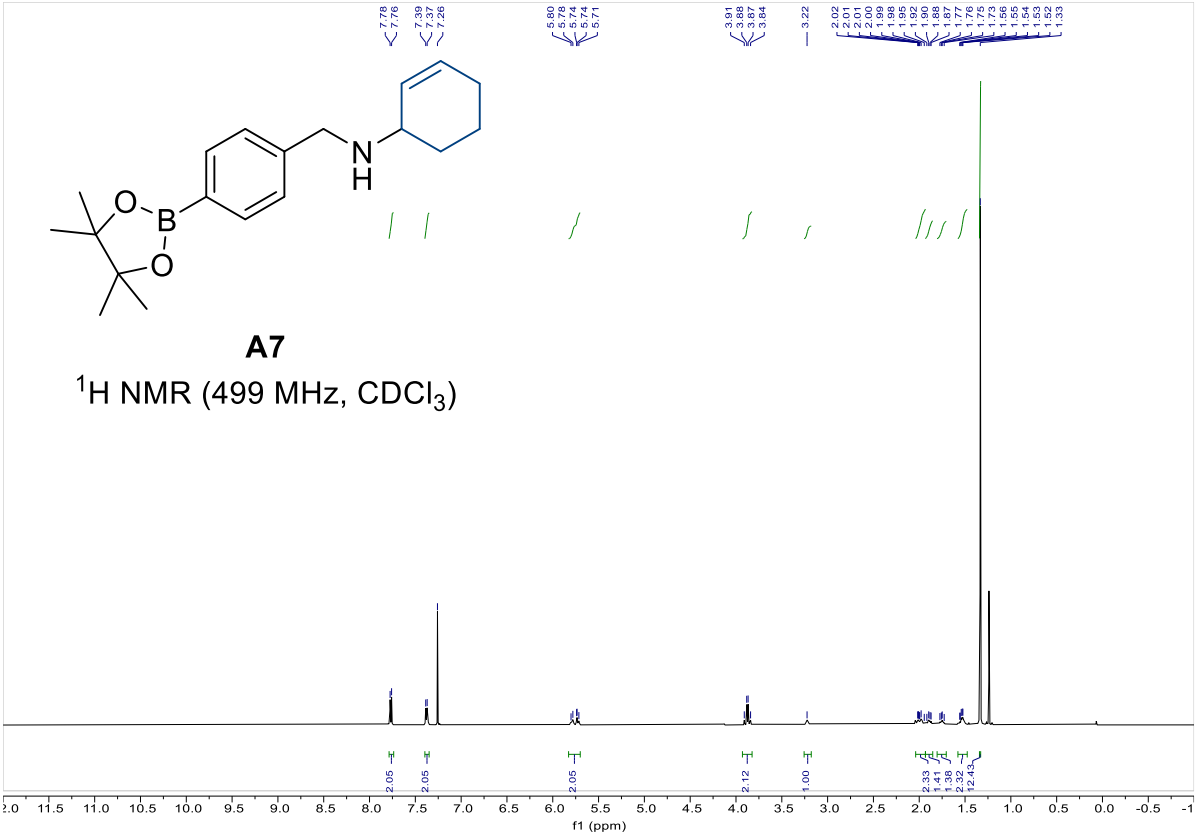
A6

^{13}C NMR (101 MHz, $CDCl_3$)



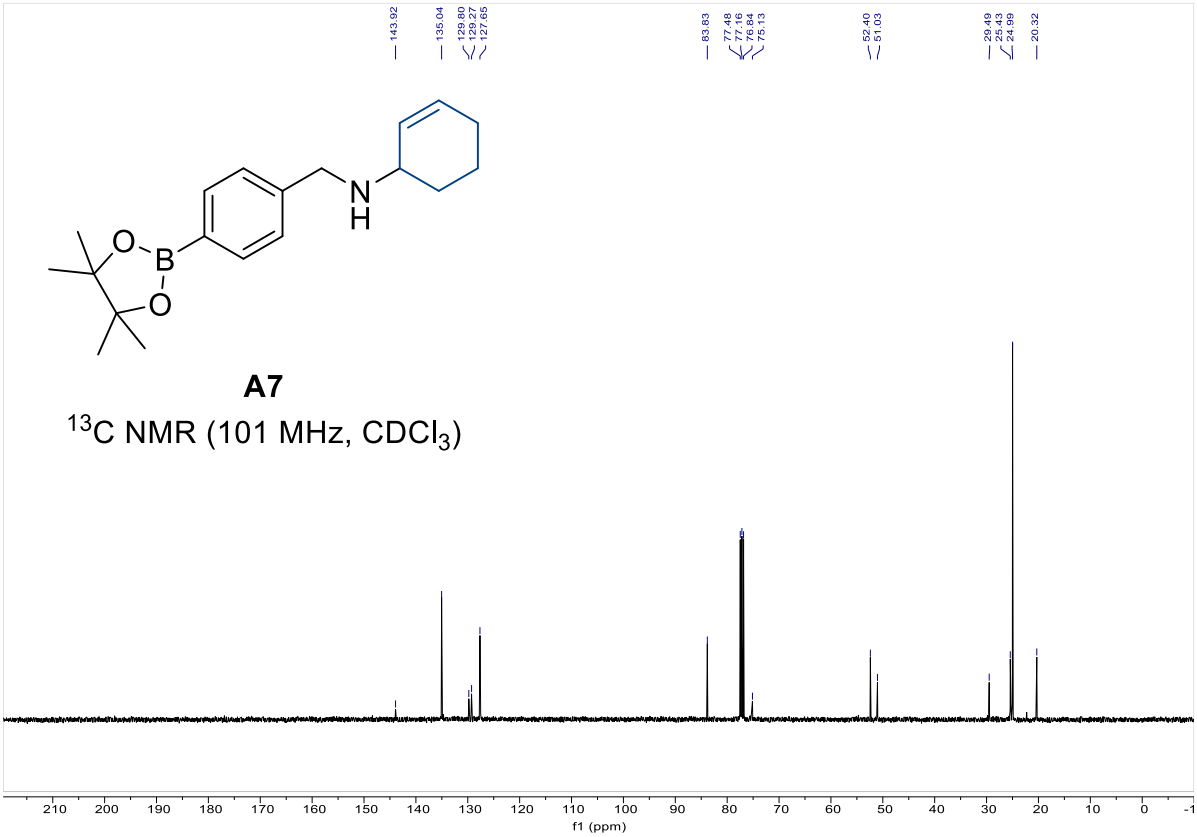
A6

^{19}F NMR (376 MHz, $CDCl_3$)



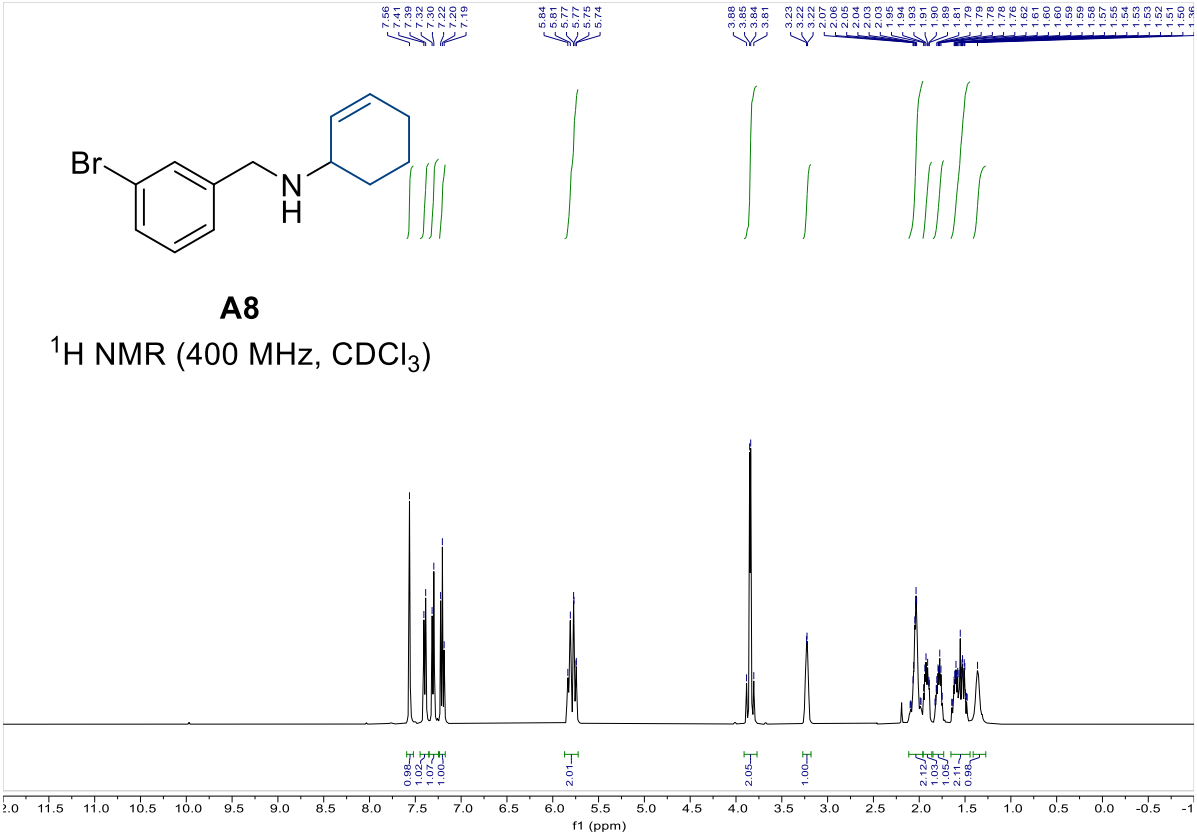
A7

^{1}H NMR (499 MHz, $CDCl_3$)



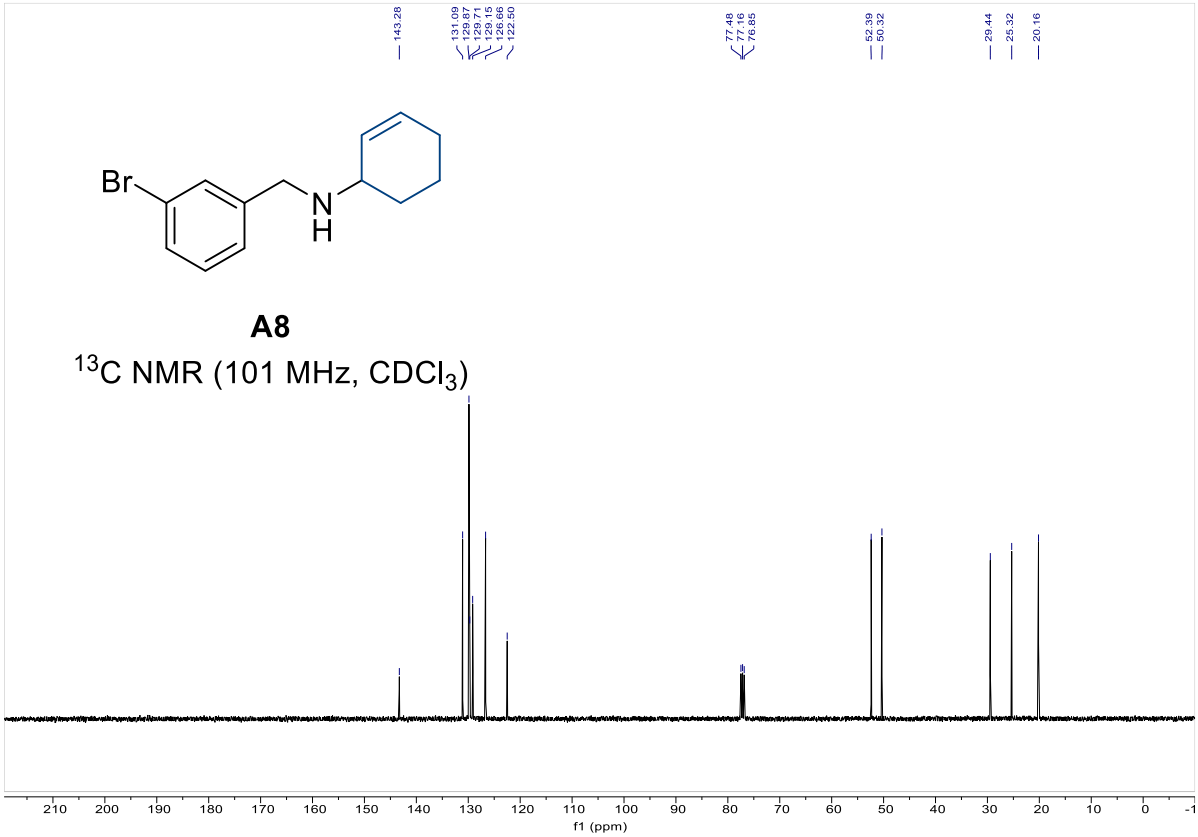
A7

^{13}C NMR (101 MHz, $CDCl_3$)



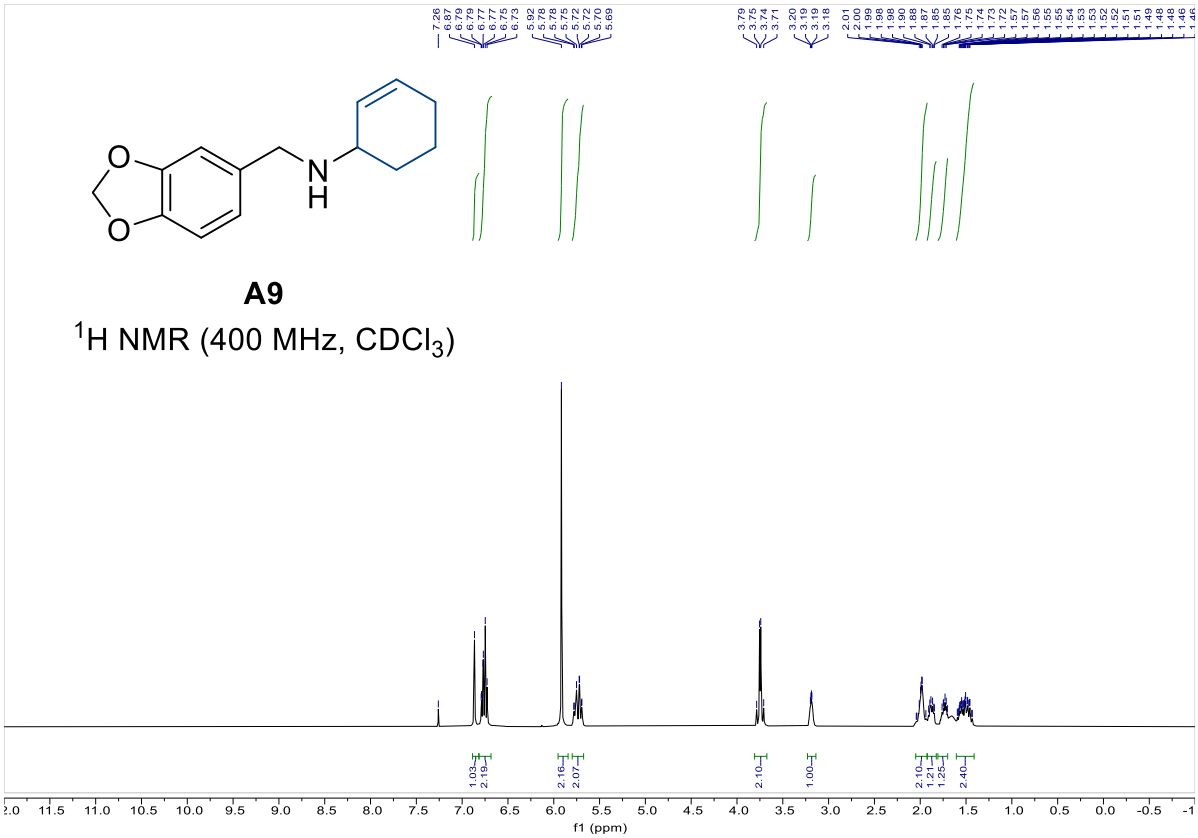
A8

^{1}H NMR (400 MHz, $CDCl_3$)



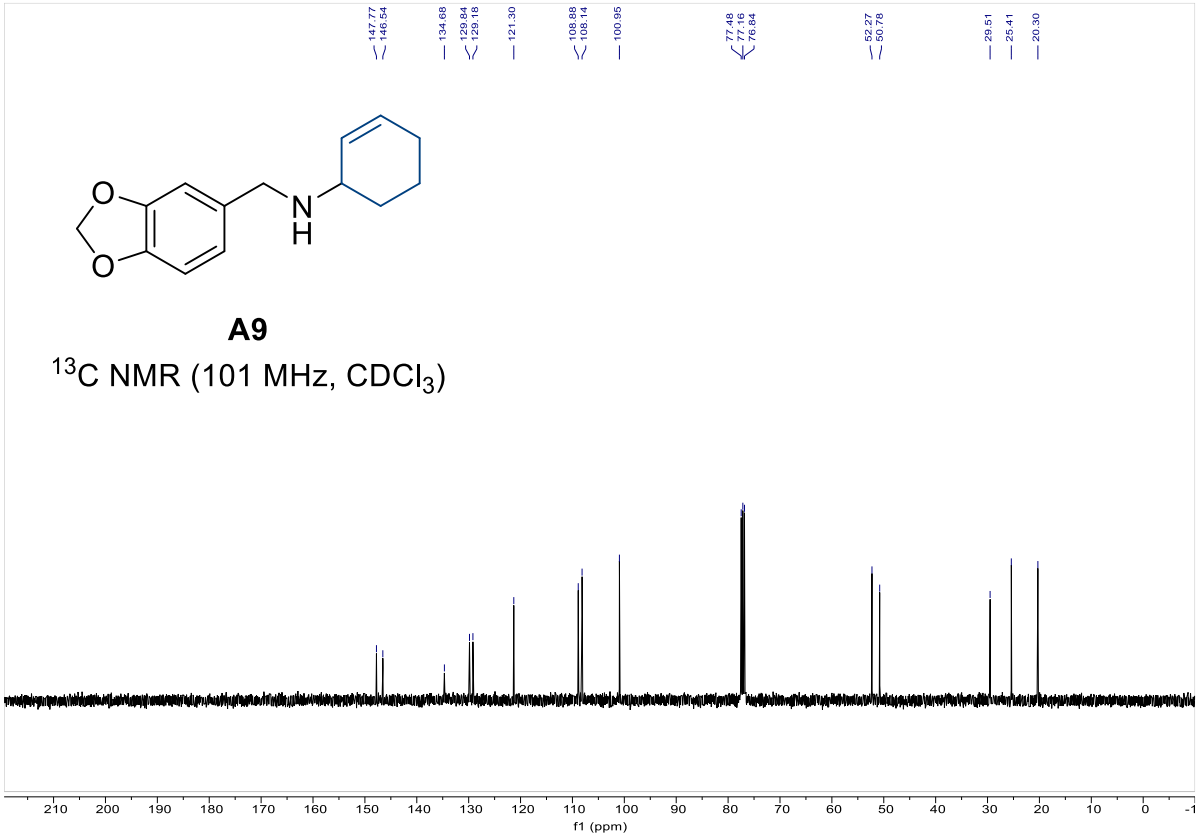
A8

^{13}C NMR (101 MHz, $CDCl_3$)



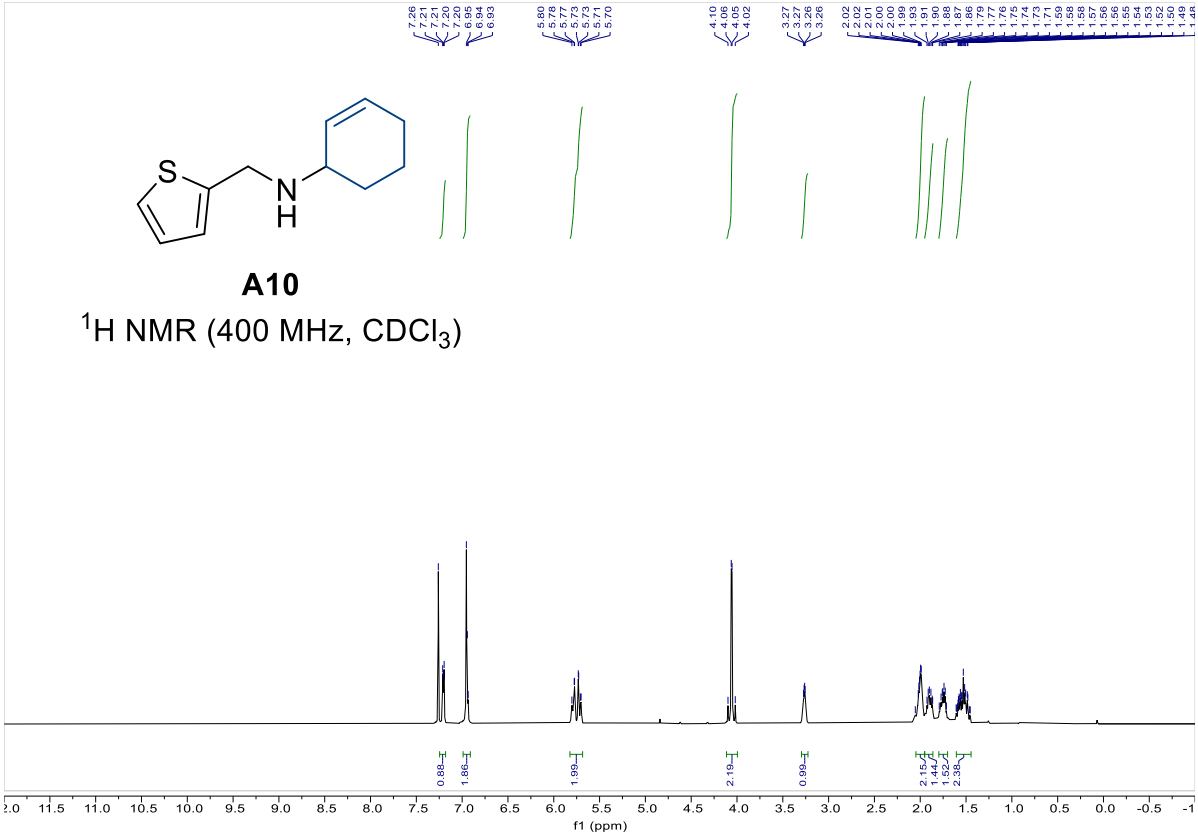
A9

^{1}H NMR (400 MHz, $CDCl_3$)



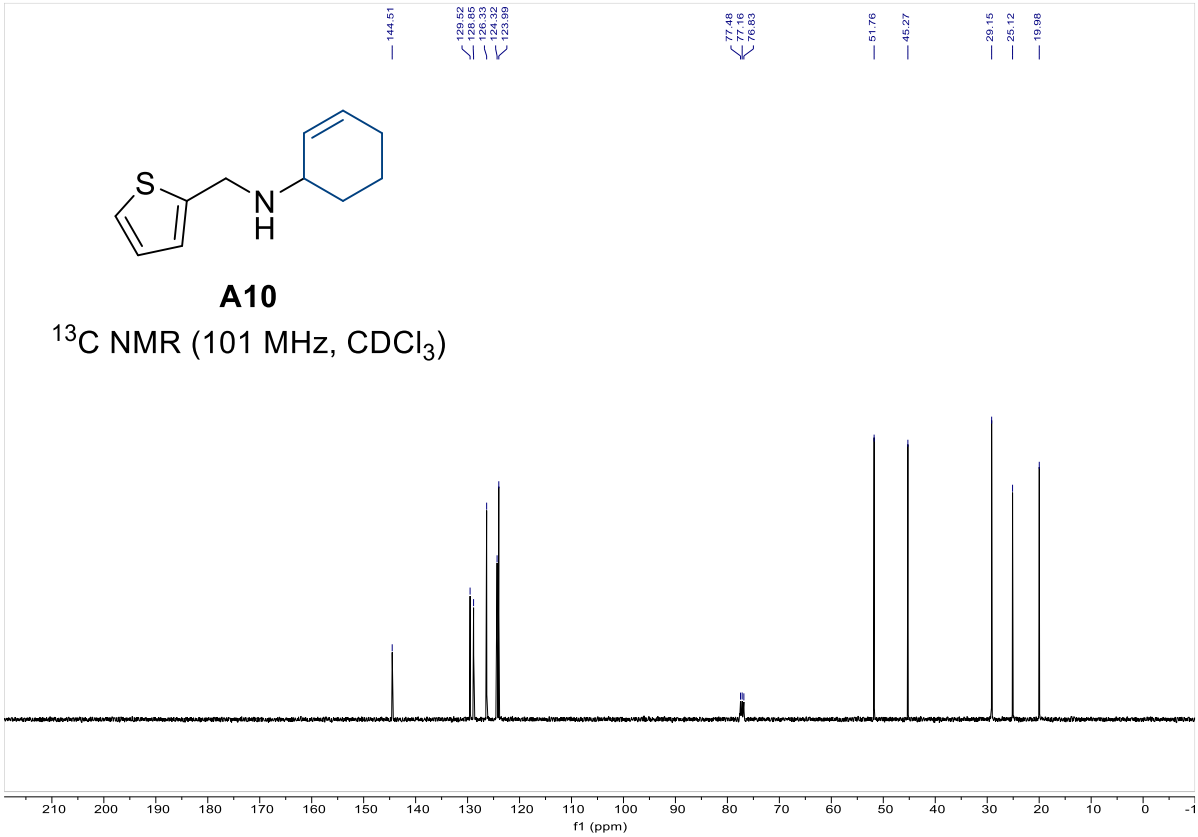
A9

^{13}C NMR (101 MHz, $CDCl_3$)



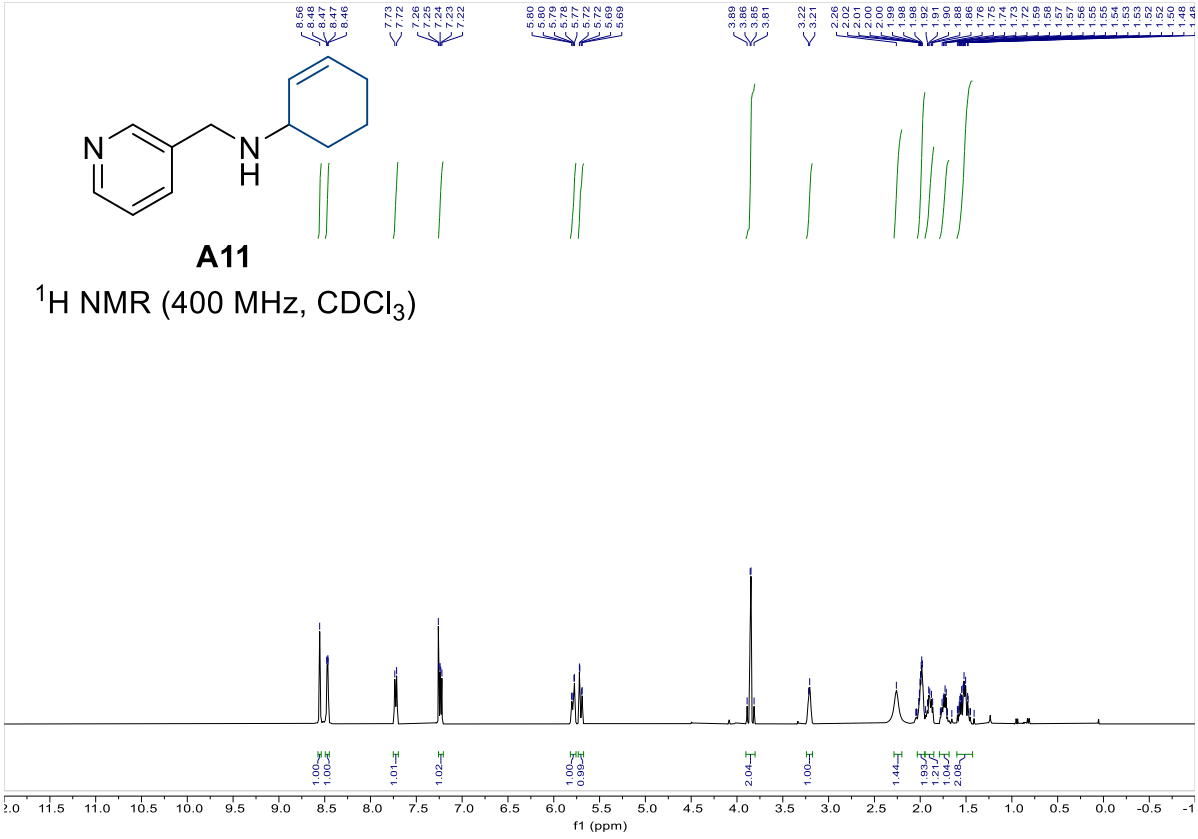
A10

^{1}H NMR (400 MHz, $CDCl_3$)



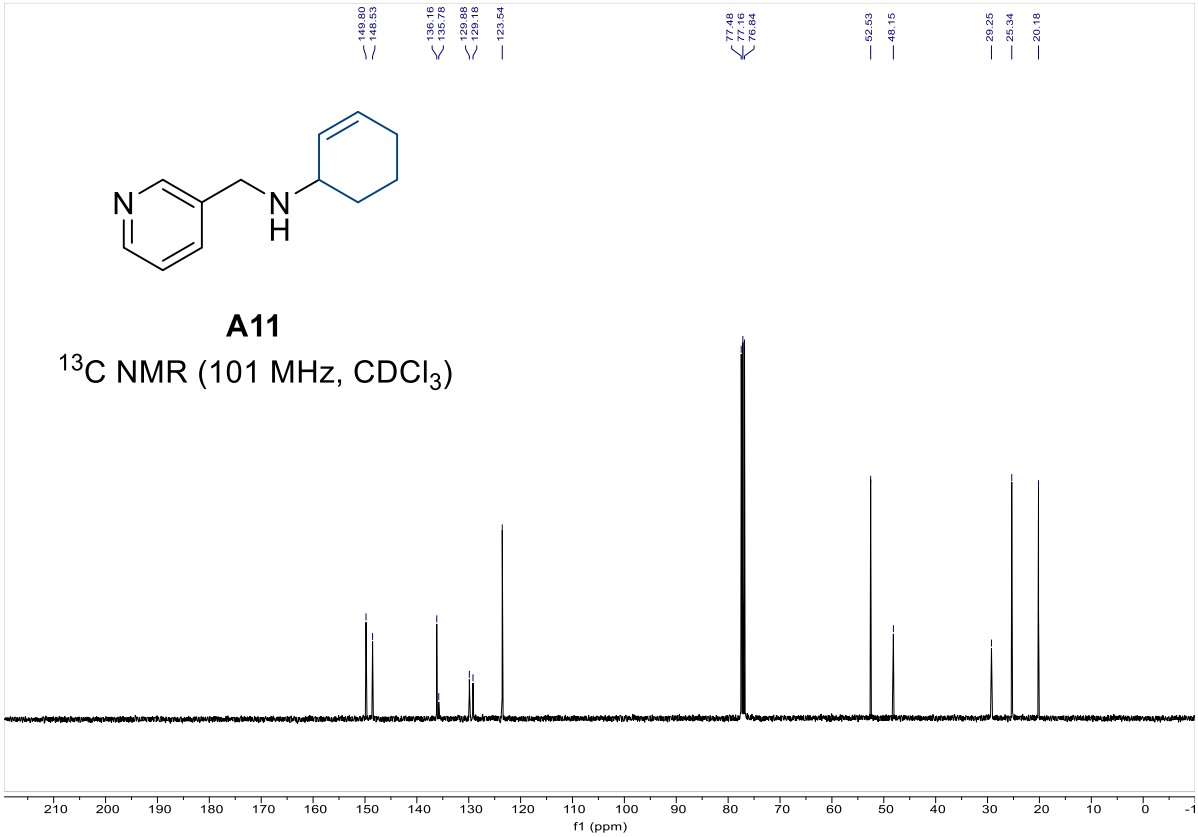
A10

^{13}C NMR (101 MHz, $CDCl_3$)



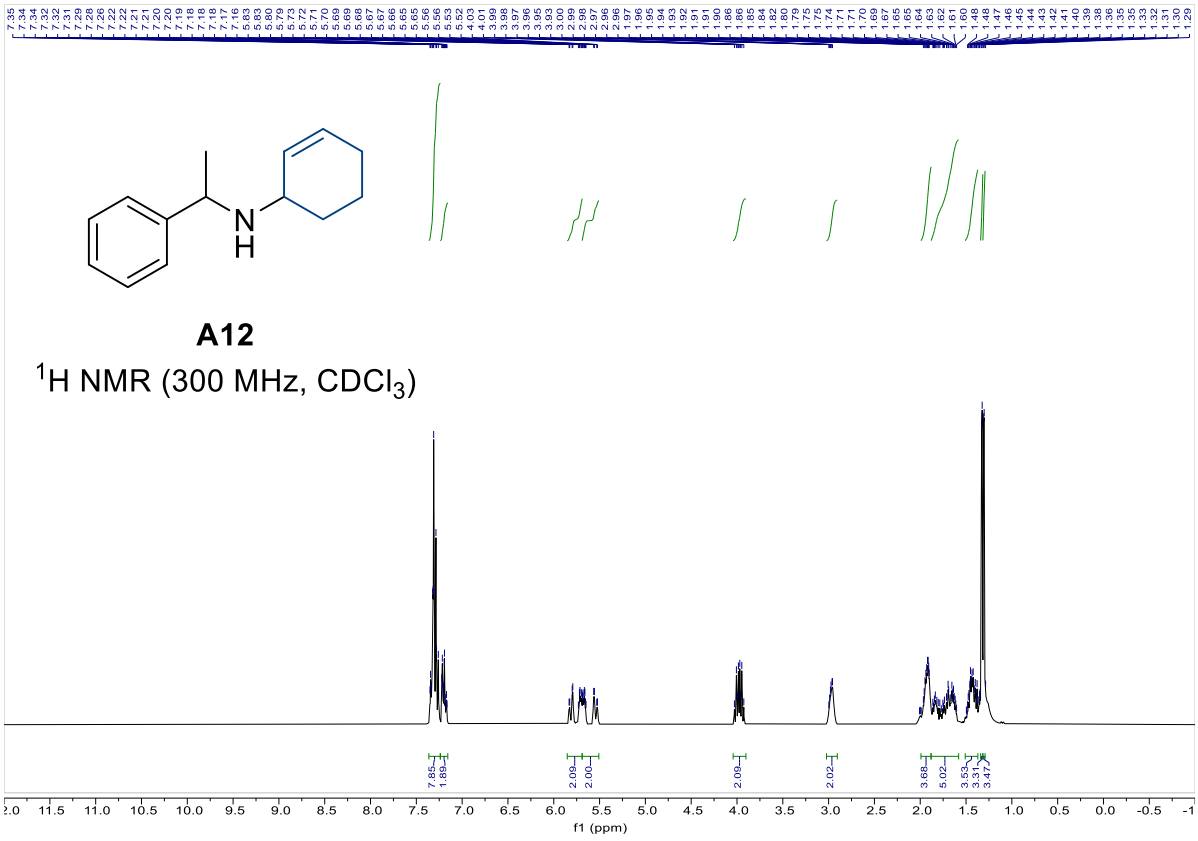
A11

^{1}H NMR (400 MHz, $CDCl_3$)



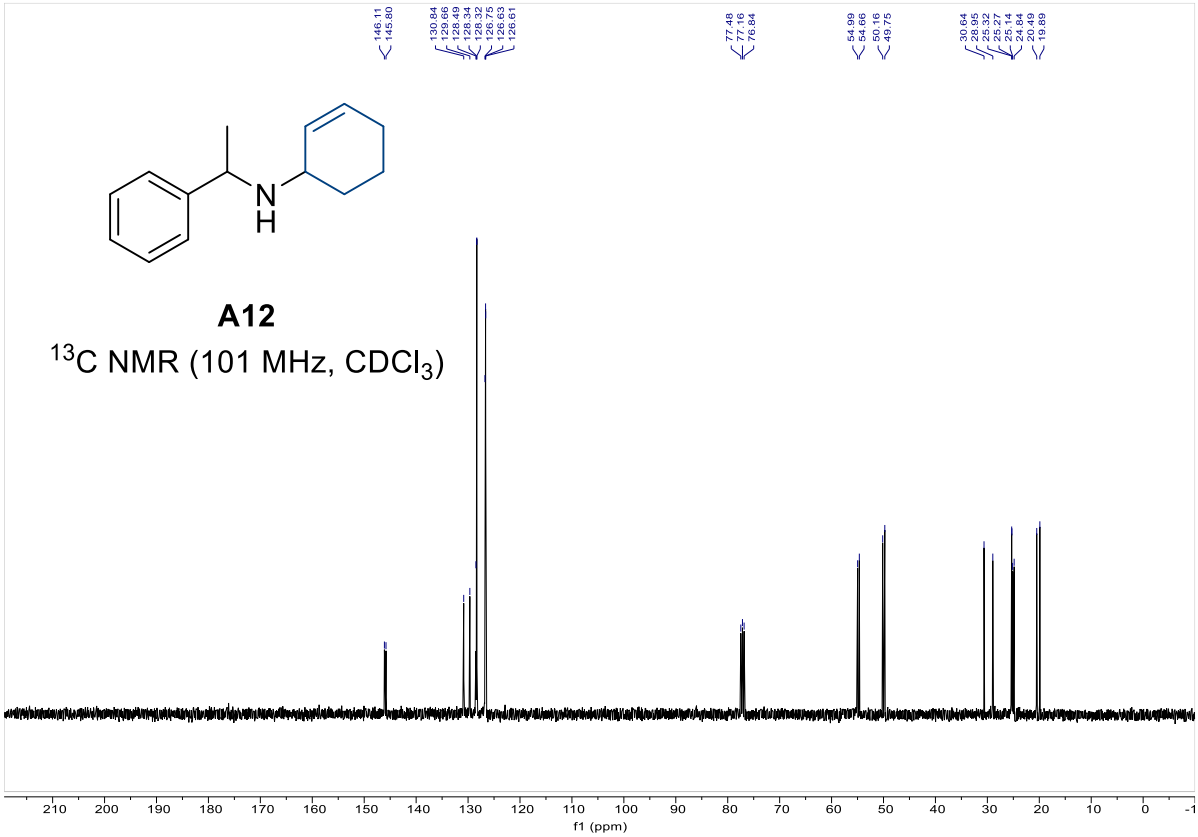
A11

^{13}C NMR (101 MHz, $CDCl_3$)



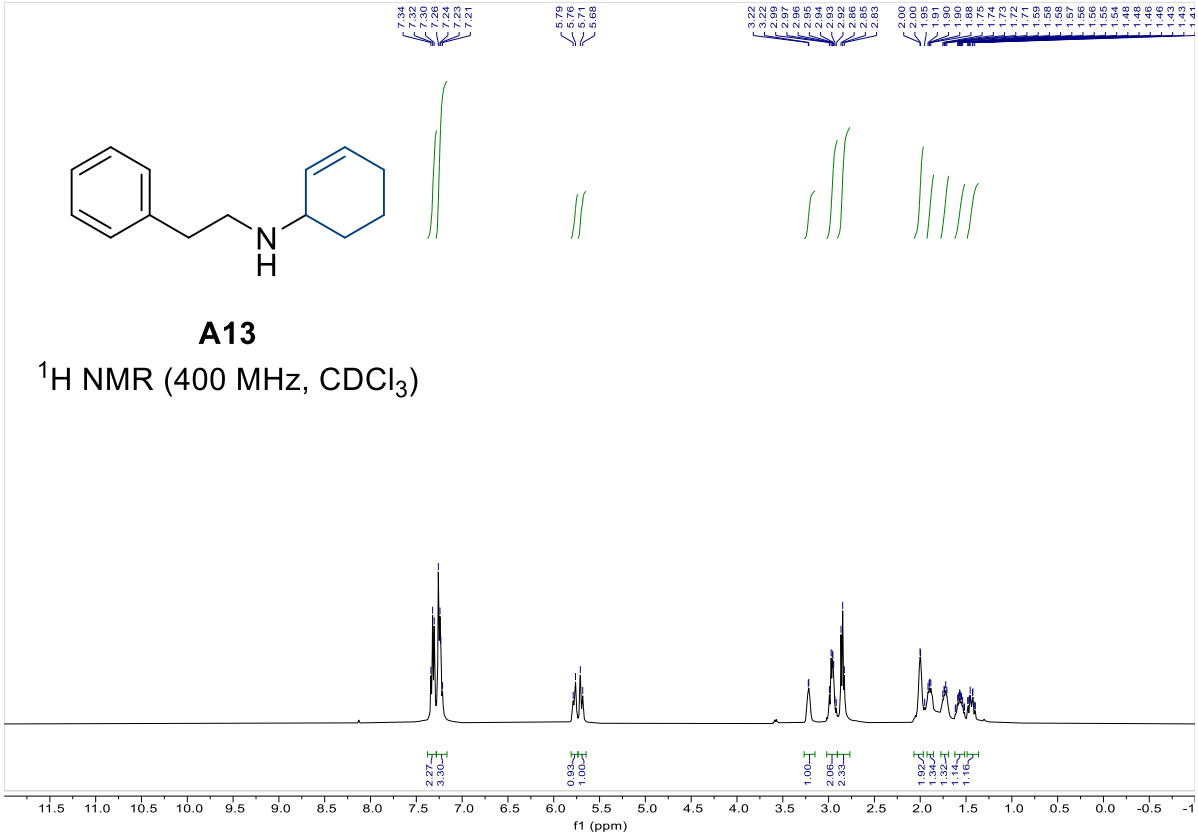
A12

^{1}H NMR (300 MHz, $CDCl_3$)



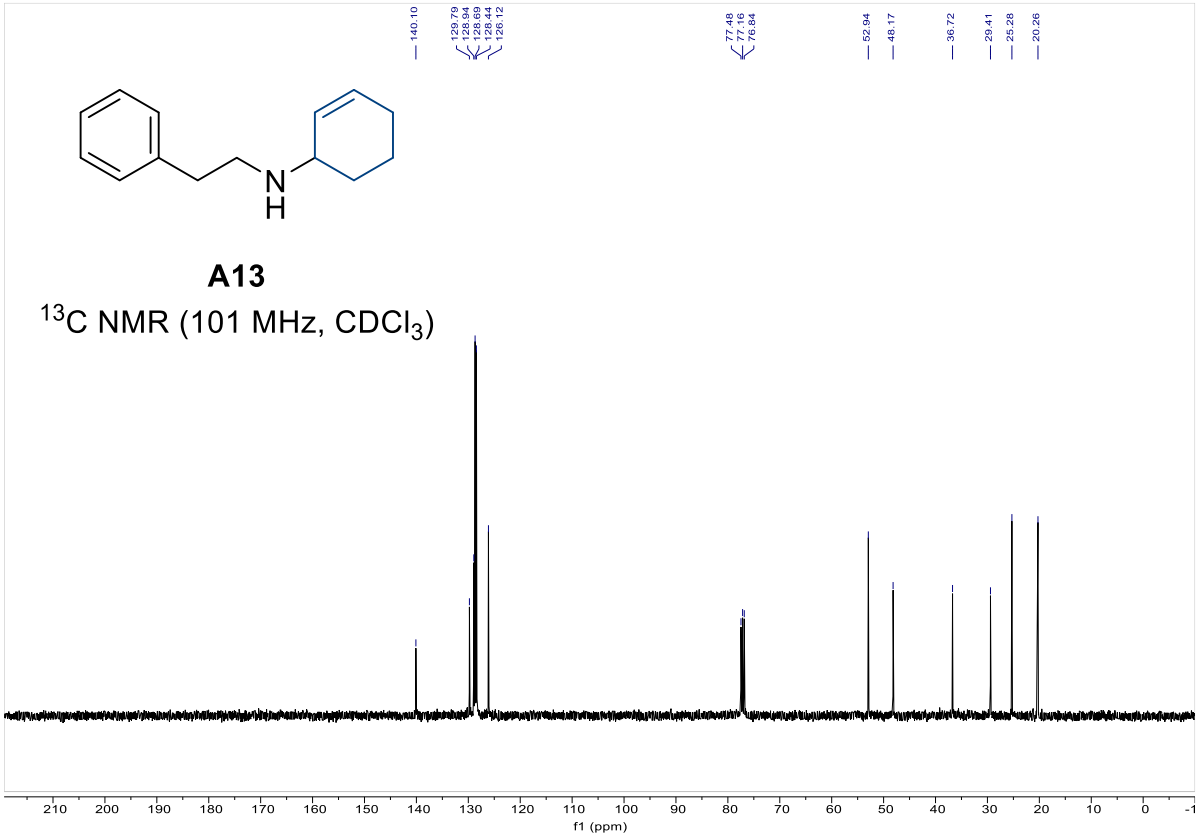
A12

^{13}C NMR (101 MHz, $CDCl_3$)



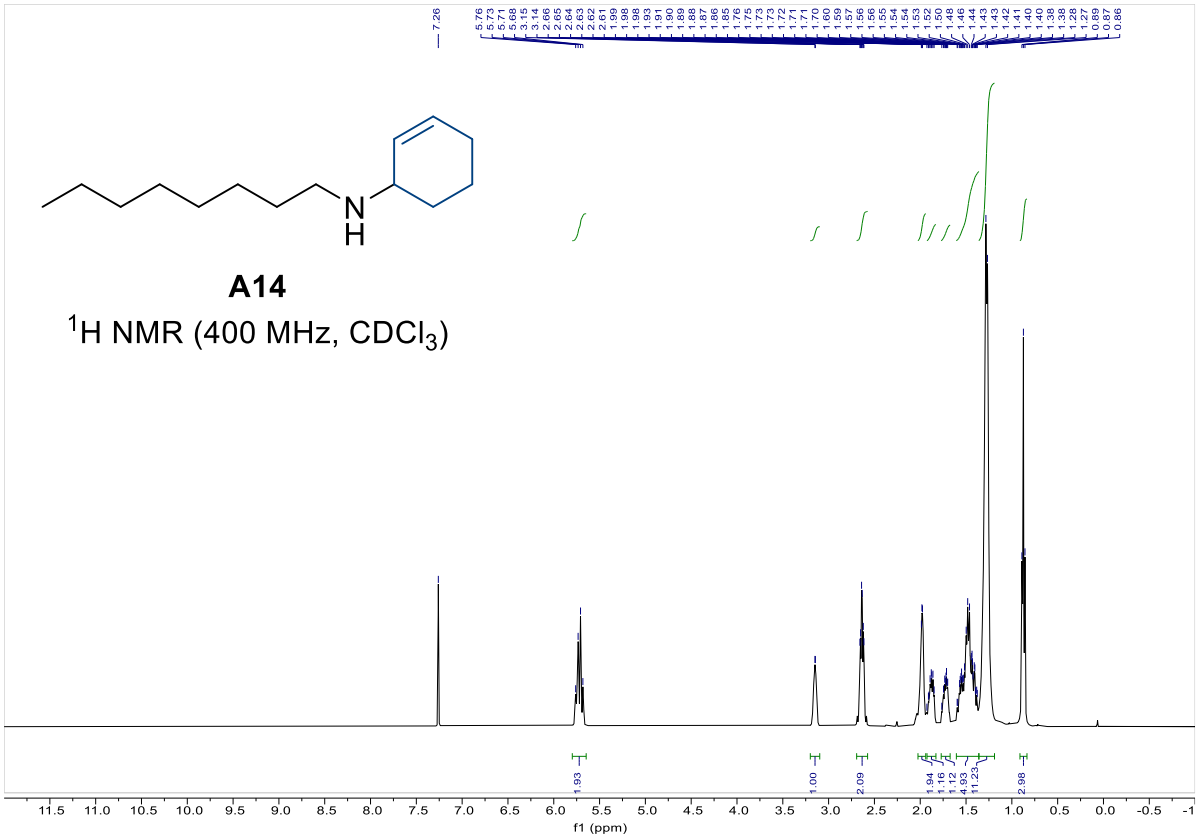
A13

^{1}H NMR (400 MHz, $CDCl_3$)



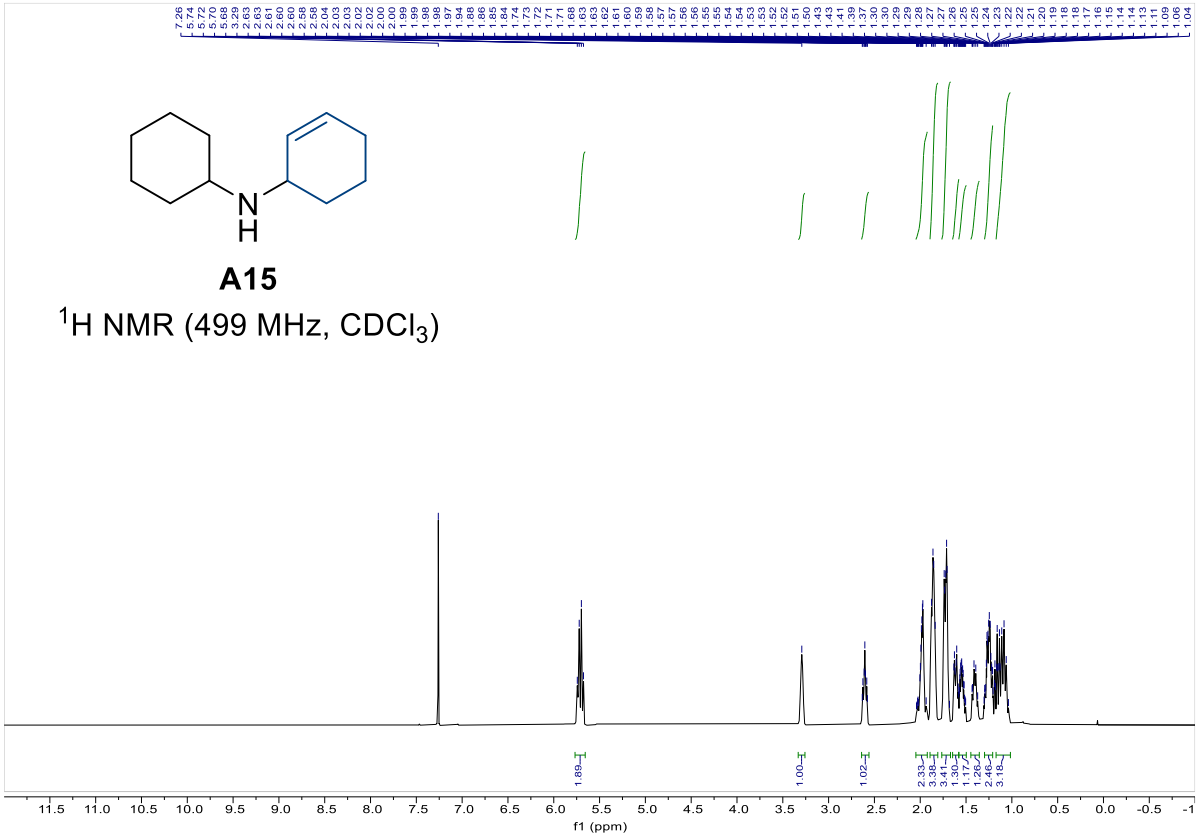
A13

^{13}C NMR (101 MHz, $CDCl_3$)



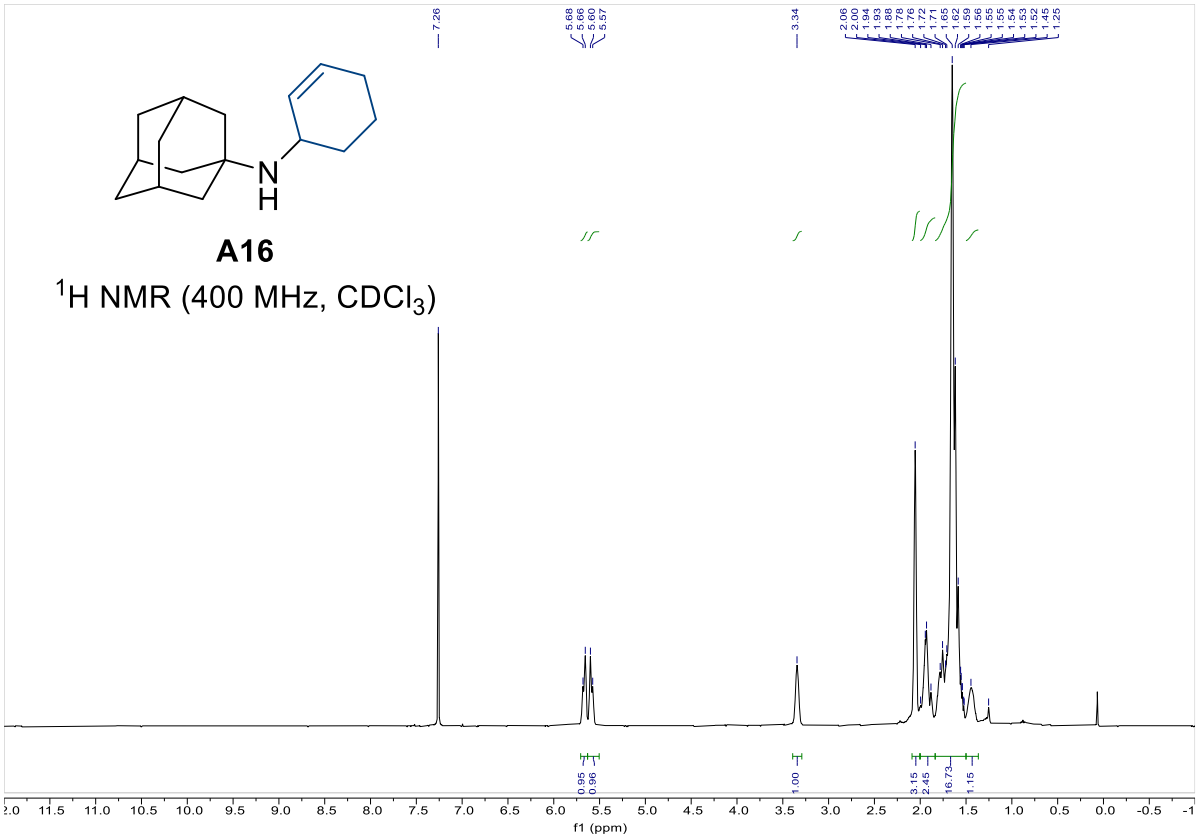
A14

^{1}H NMR (400 MHz, $CDCl_3$)



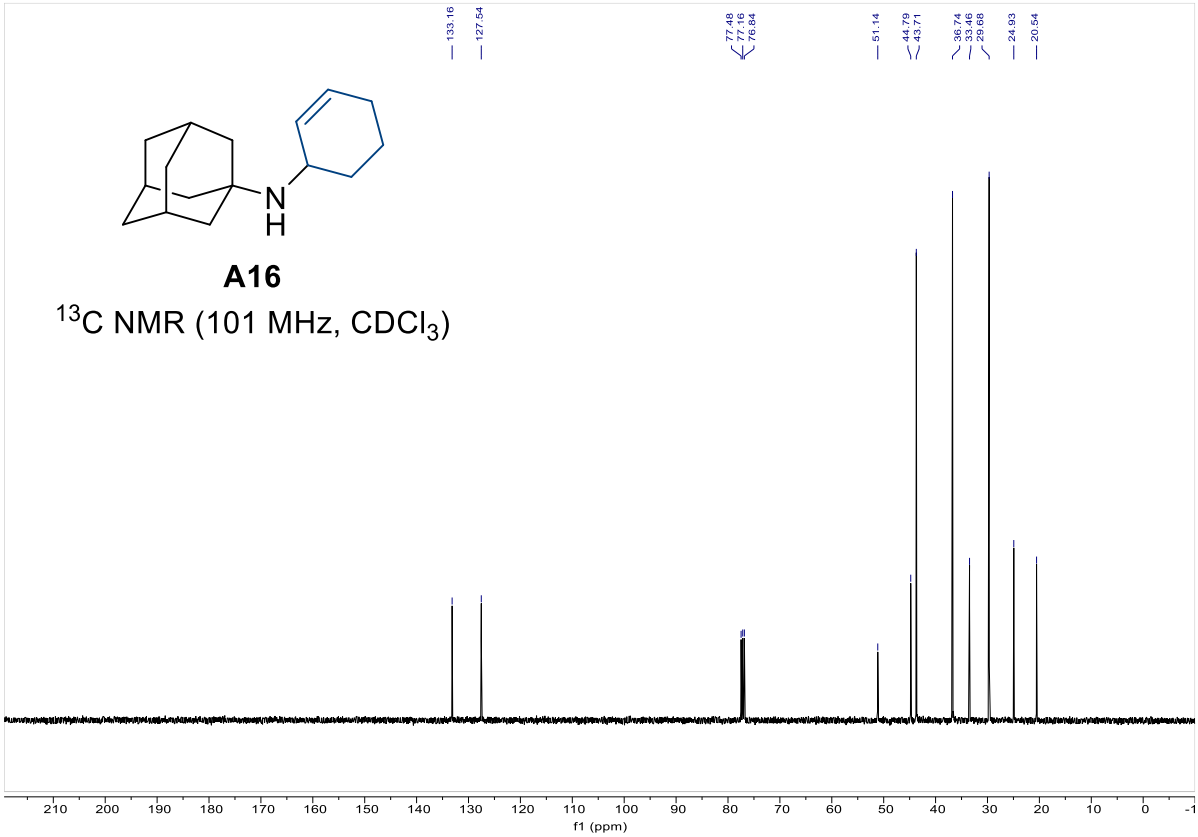
A15

^{1}H NMR (499 MHz, $CDCl_3$)



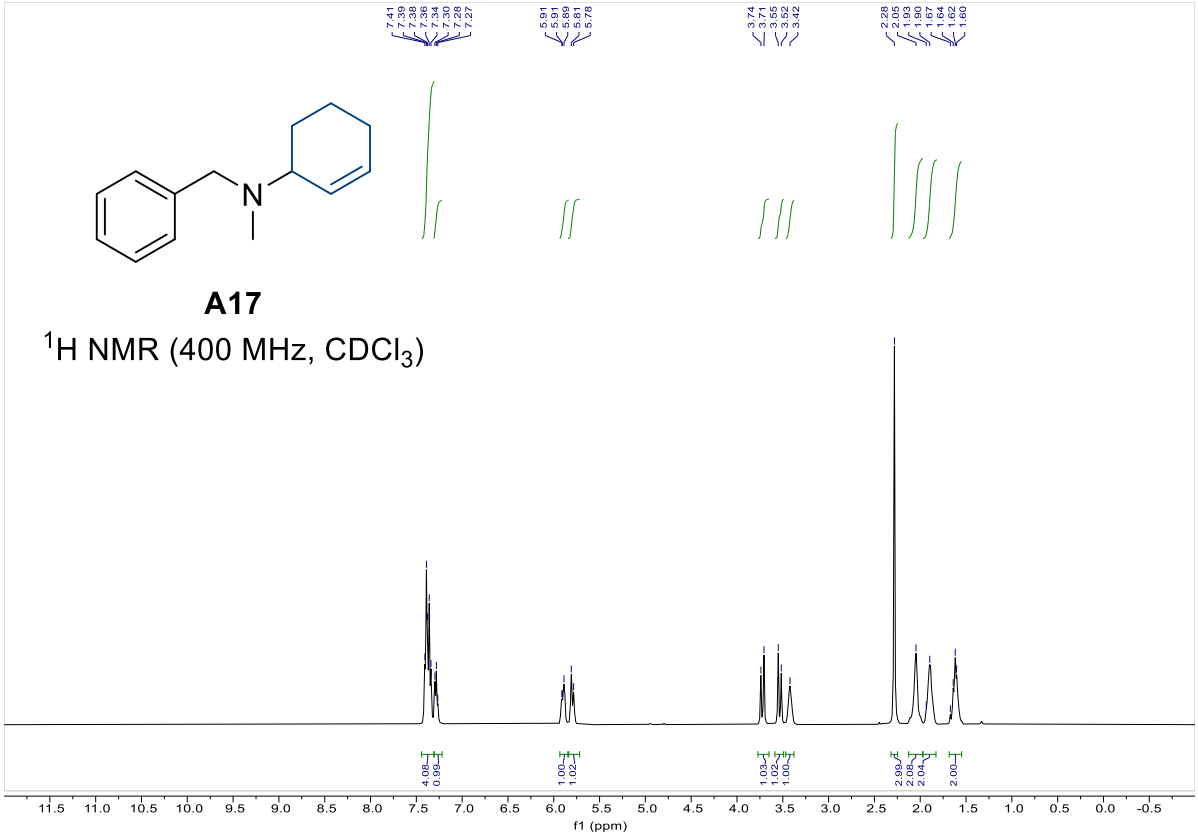
A16

^{1}H NMR (400 MHz, $CDCl_3$)



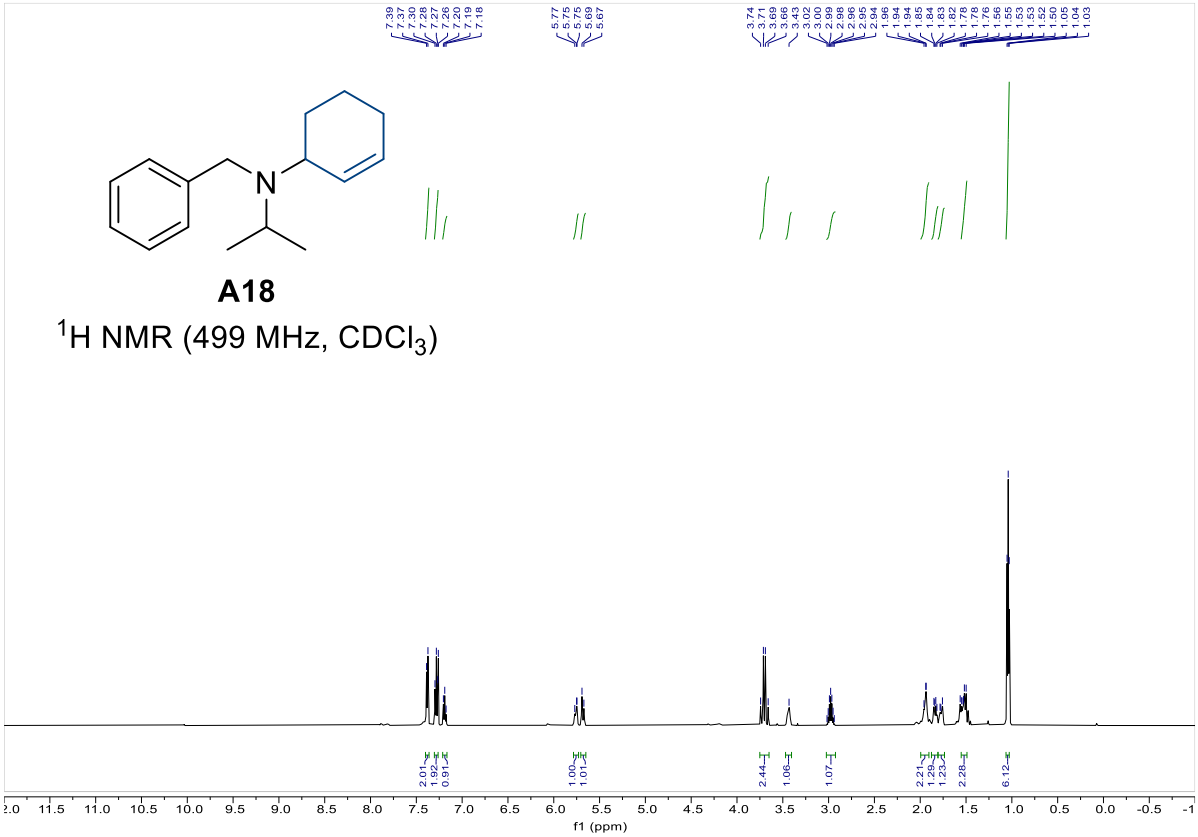
A16

^{13}C NMR (101 MHz, $CDCl_3$)



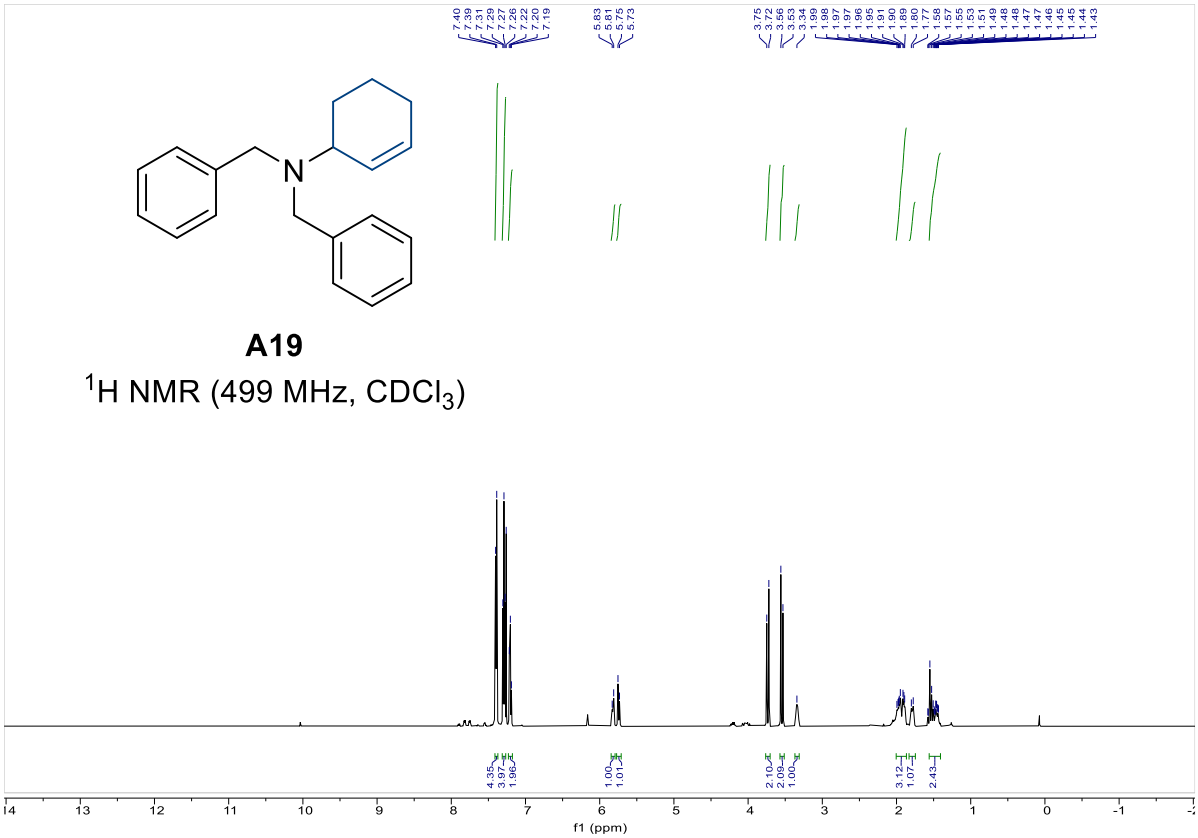
A17

^{1}H NMR (400 MHz, $CDCl_3$)



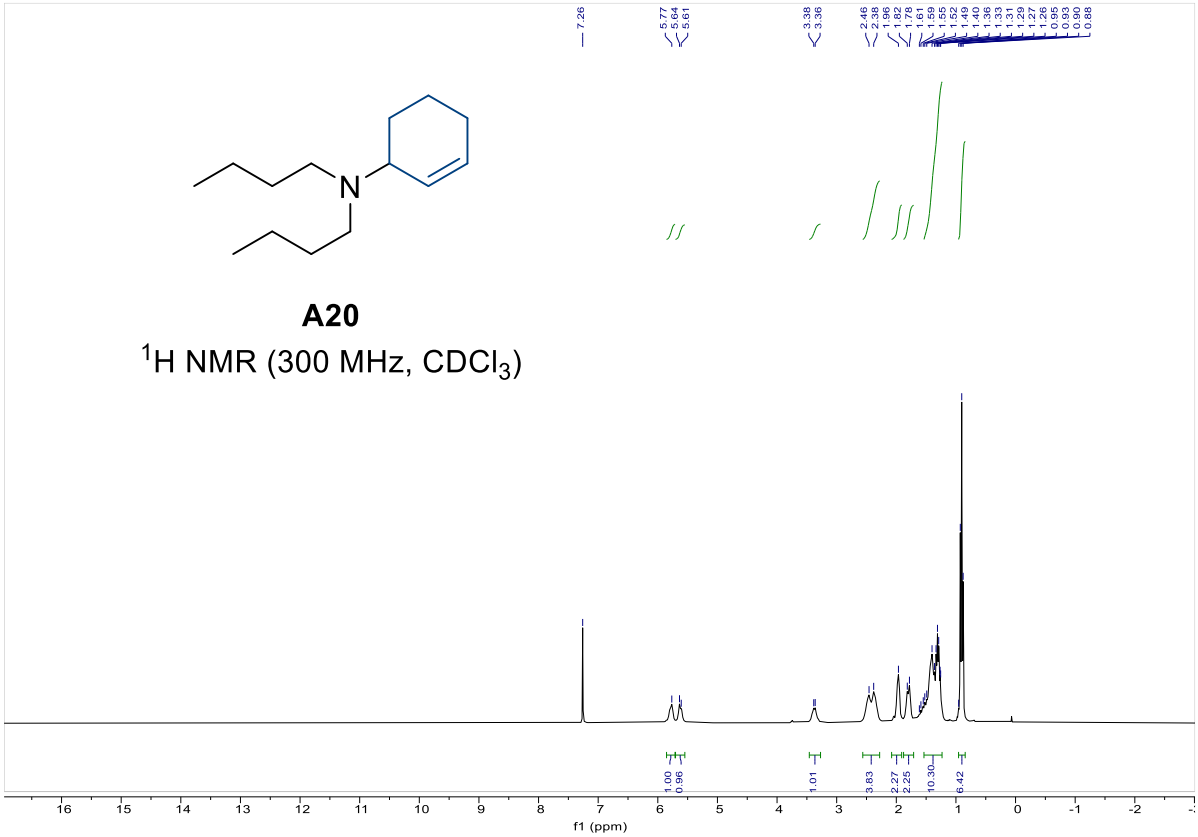
A18

^{1}H NMR (499 MHz, $CDCl_3$)



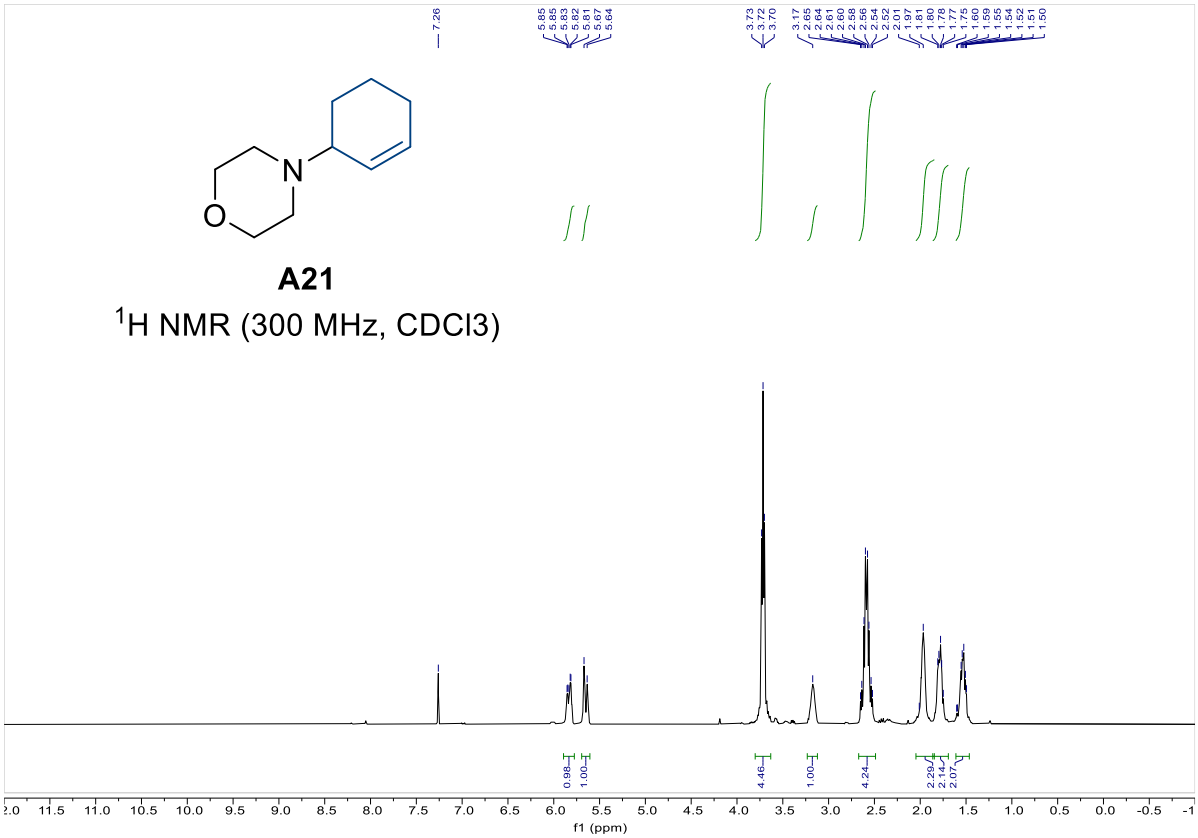
A19

^{1}H NMR (499 MHz, $CDCl_3$)



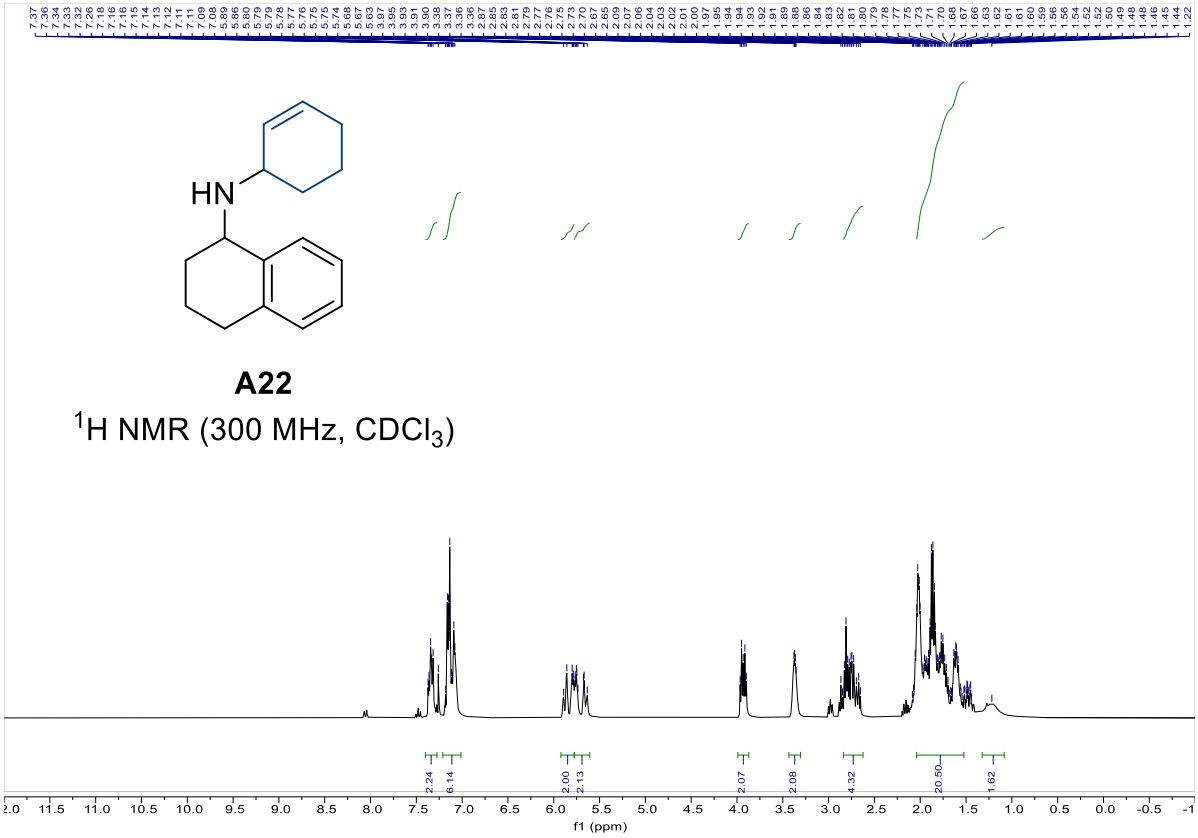
A20

^{1}H NMR (300 MHz, $CDCl_3$)



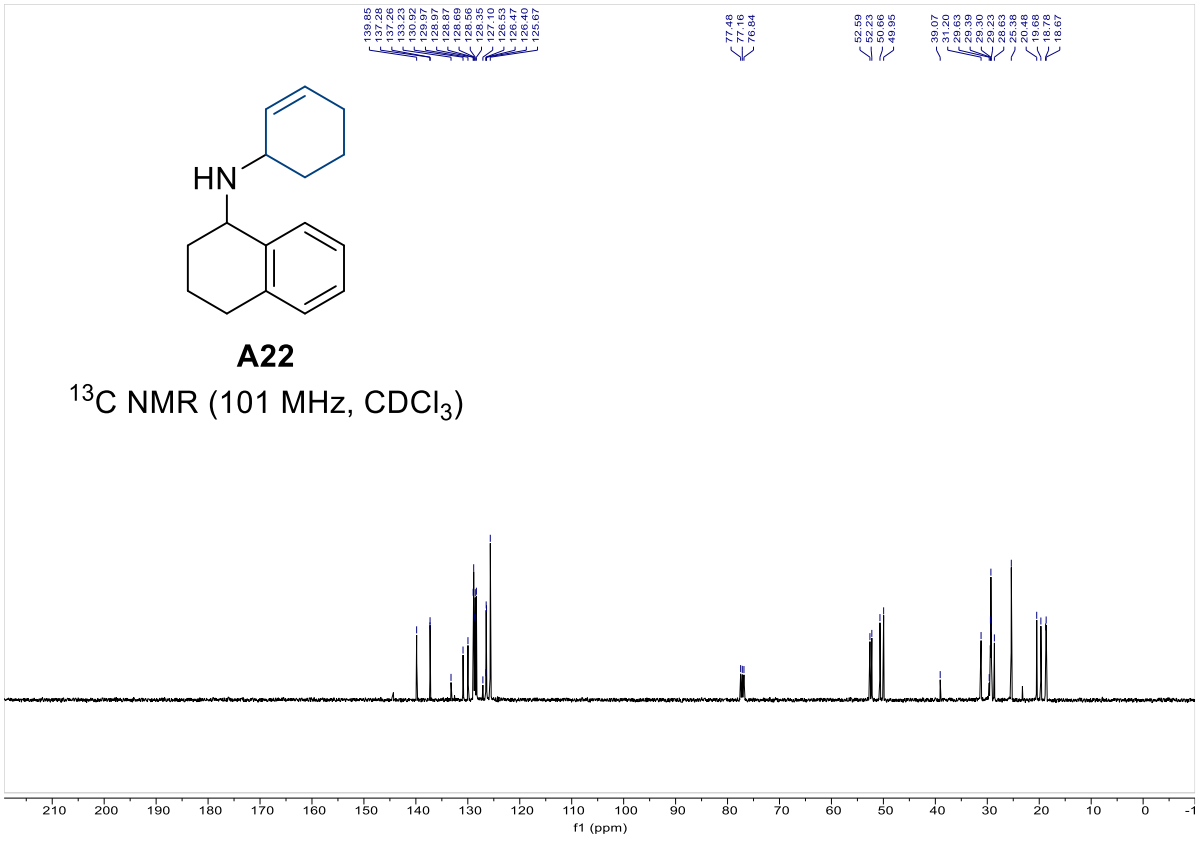
A21

^{1}H NMR (300 MHz, CDCl3)



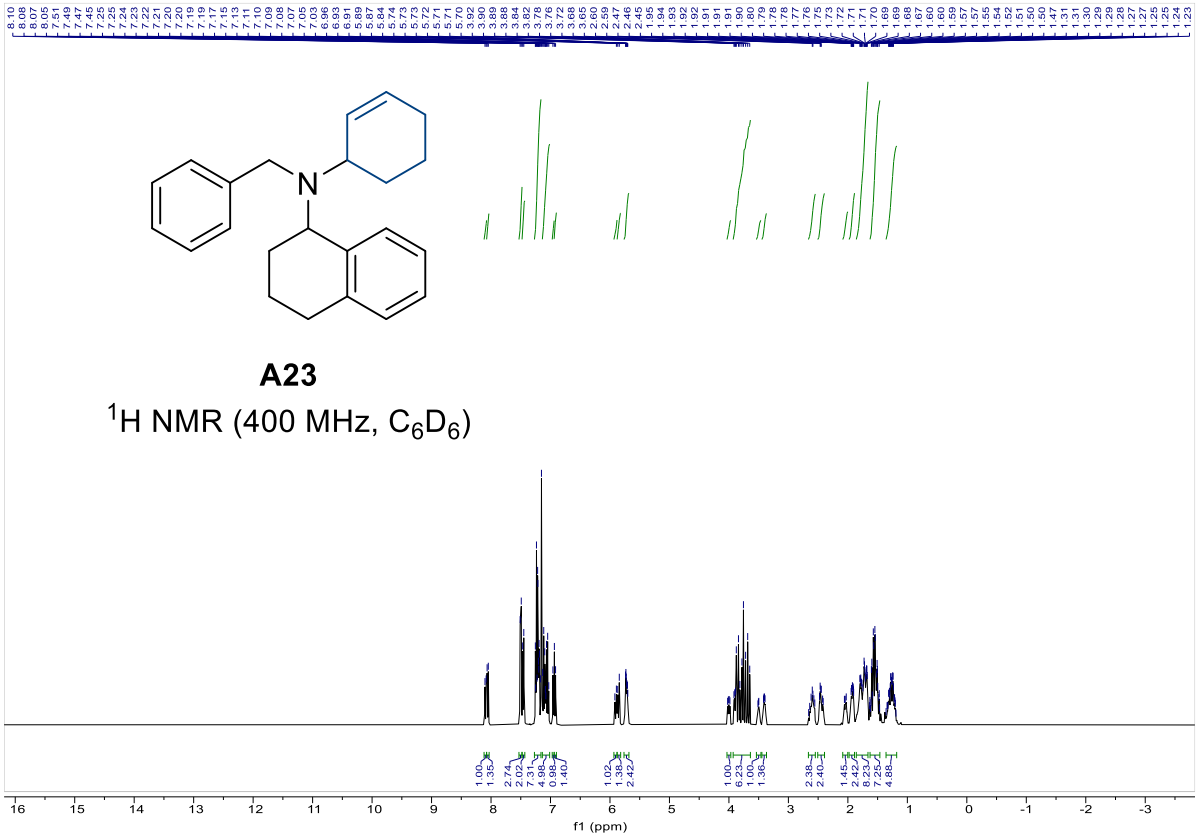
A22

^{1}H NMR (300 MHz, $CDCl_3$)



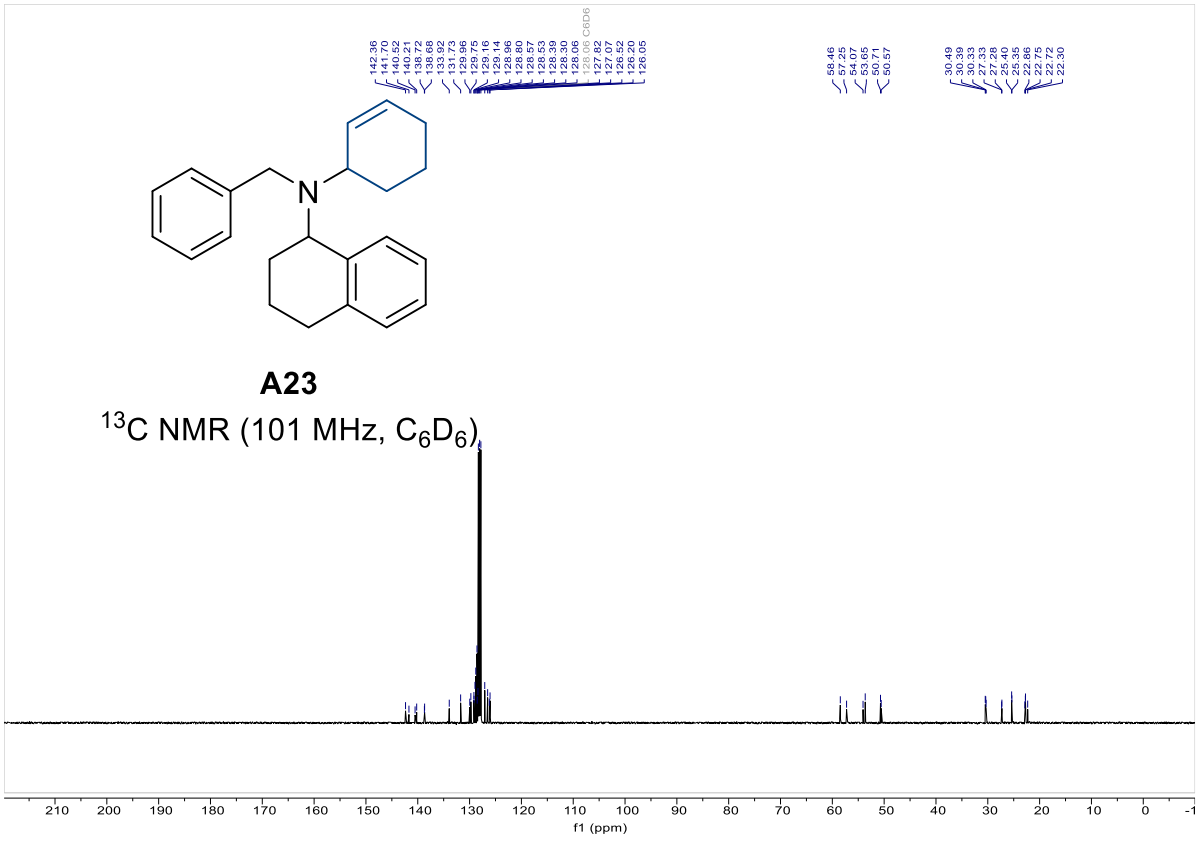
A22

^{13}C NMR (101 MHz, $CDCl_3$)



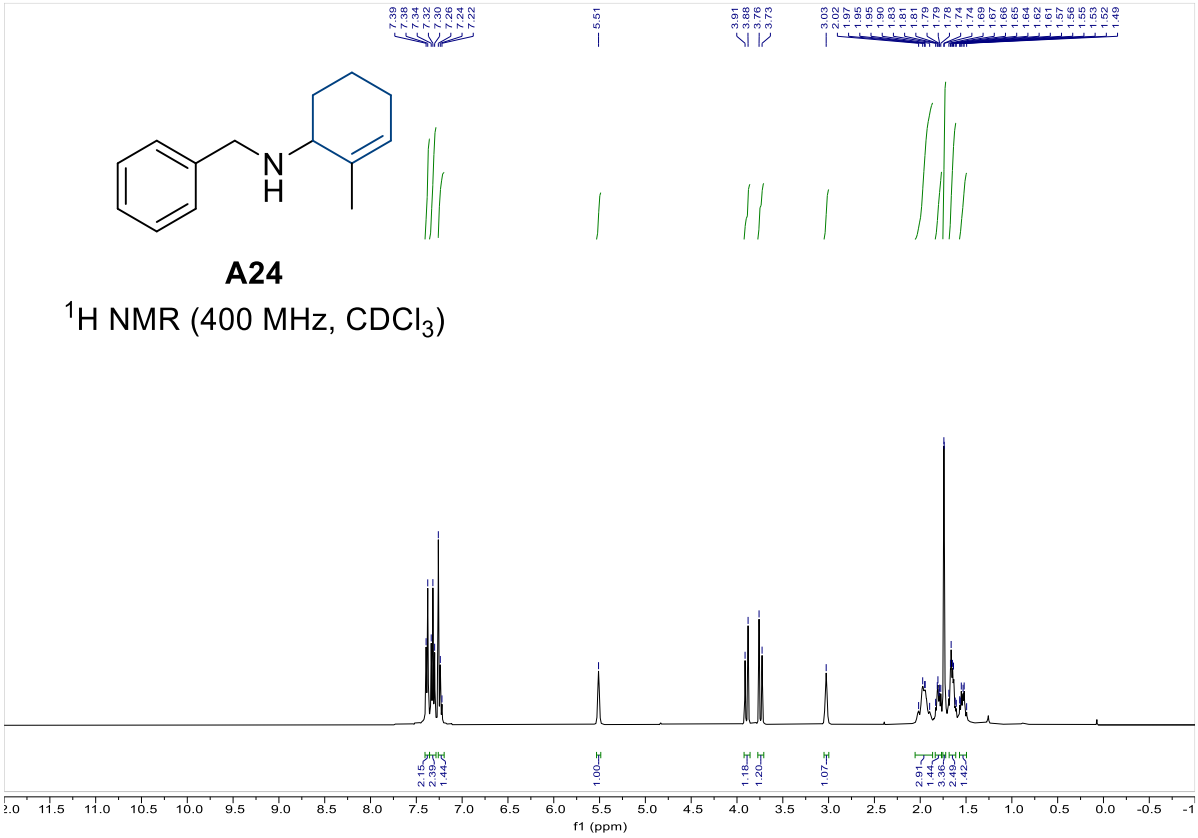
A23

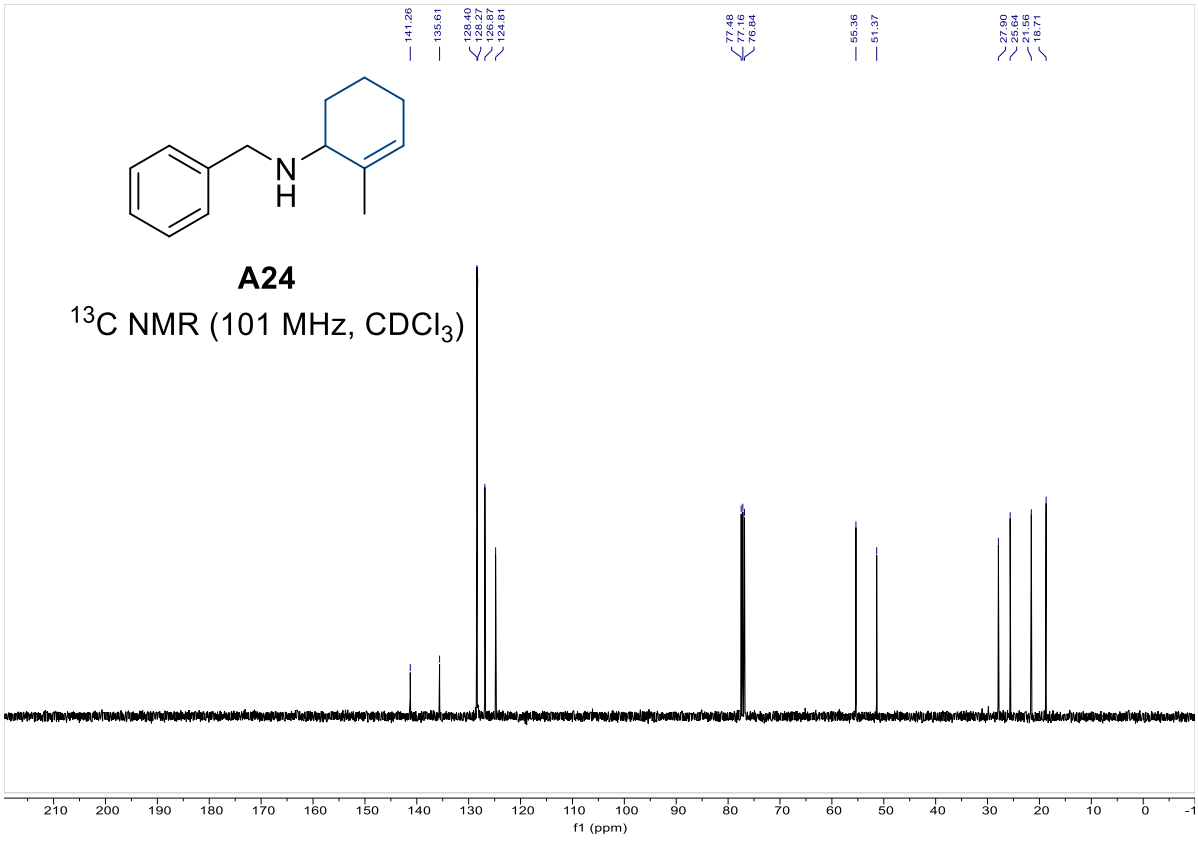
^{1}H NMR (400 MHz, C_6D_6)

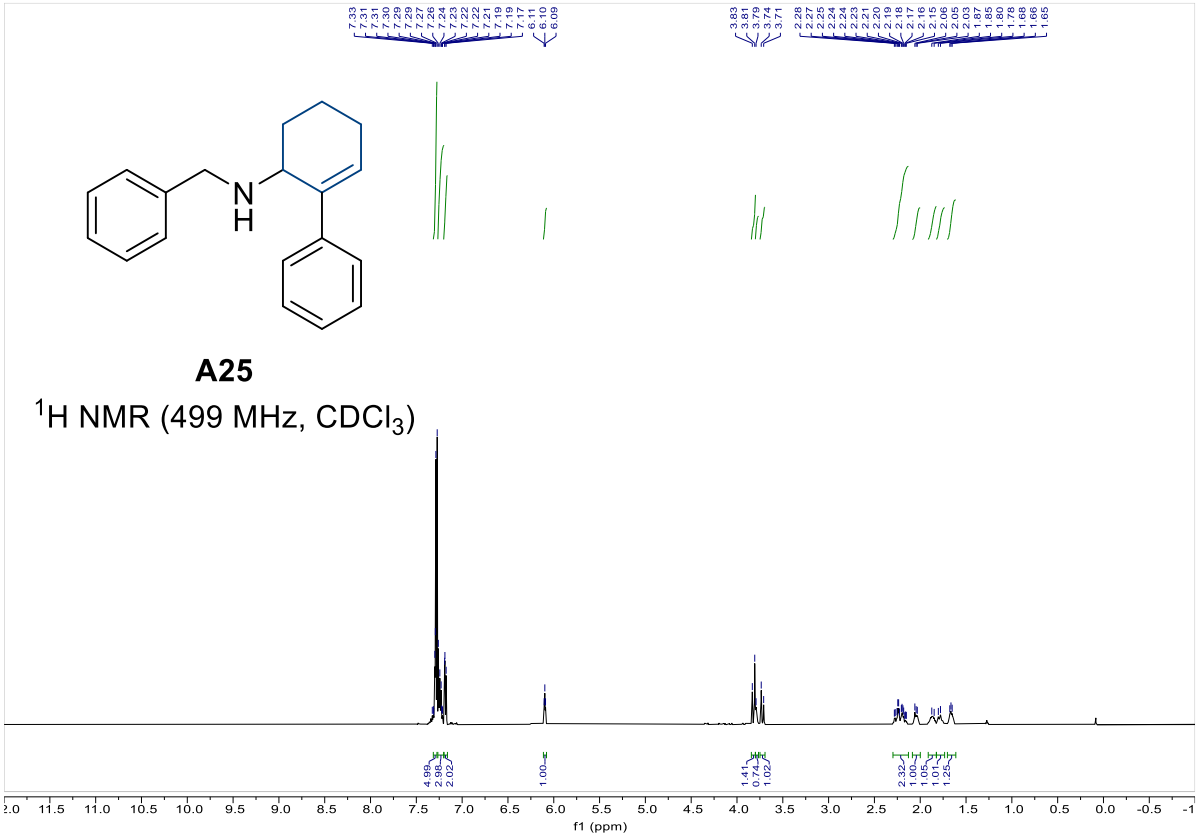


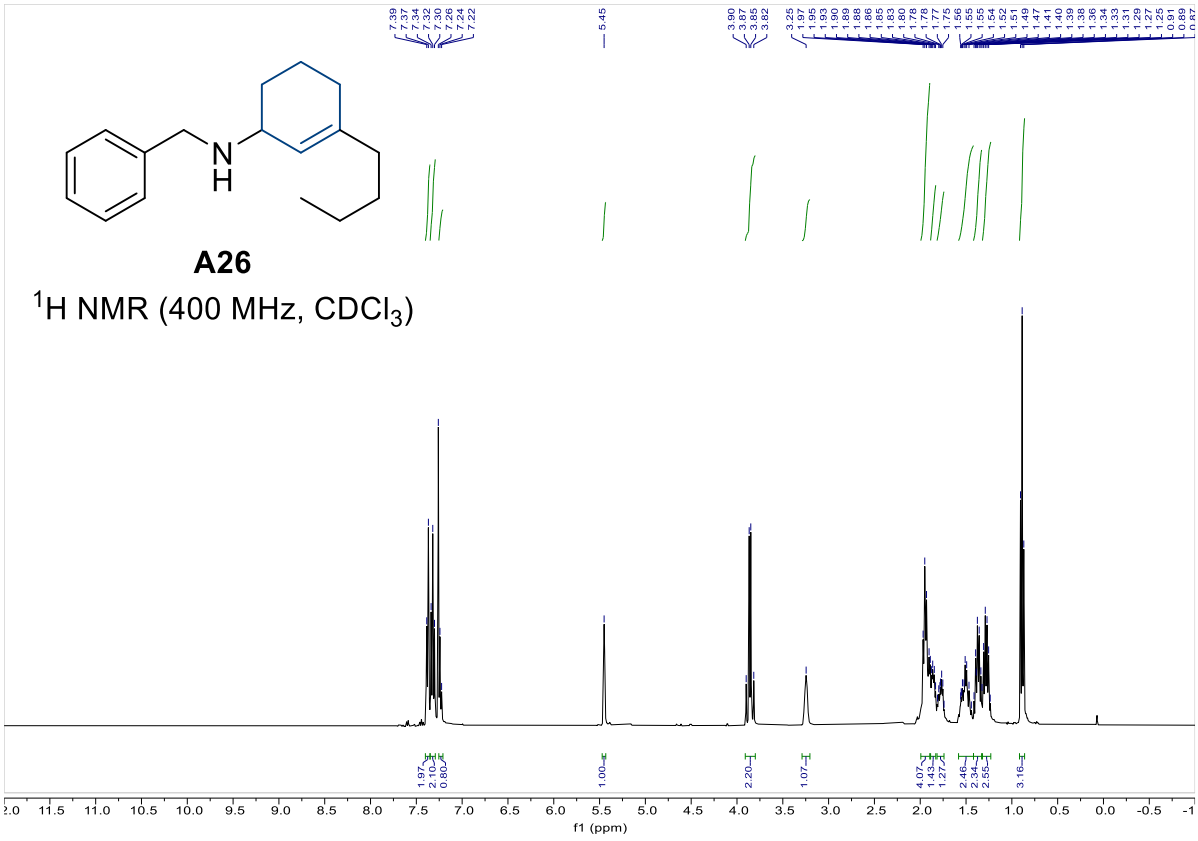
A23

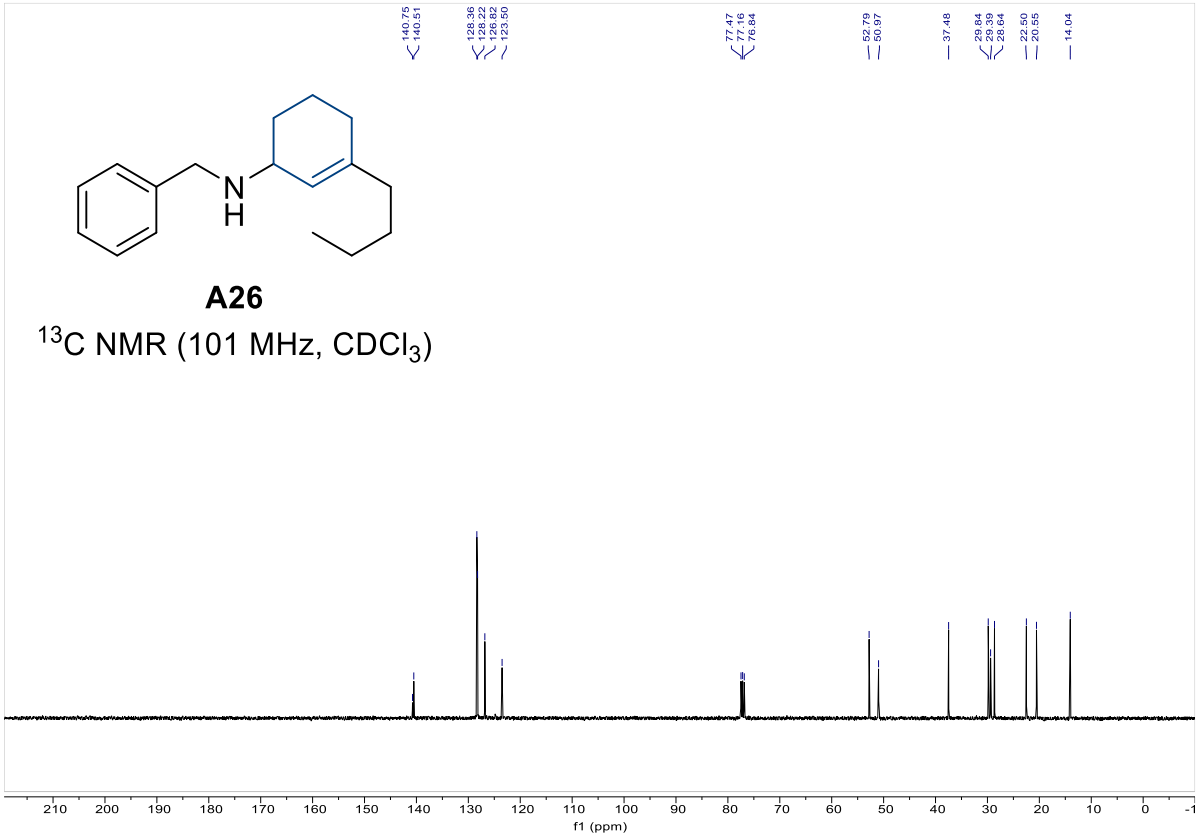
^{13}C NMR (101 MHz, C_6D_6)


A24
1H NMR (400 MHz, CDCl3)
f1 (ppm)


A24
13C NMR (101 MHz, CDCl3)
f1 (ppm)

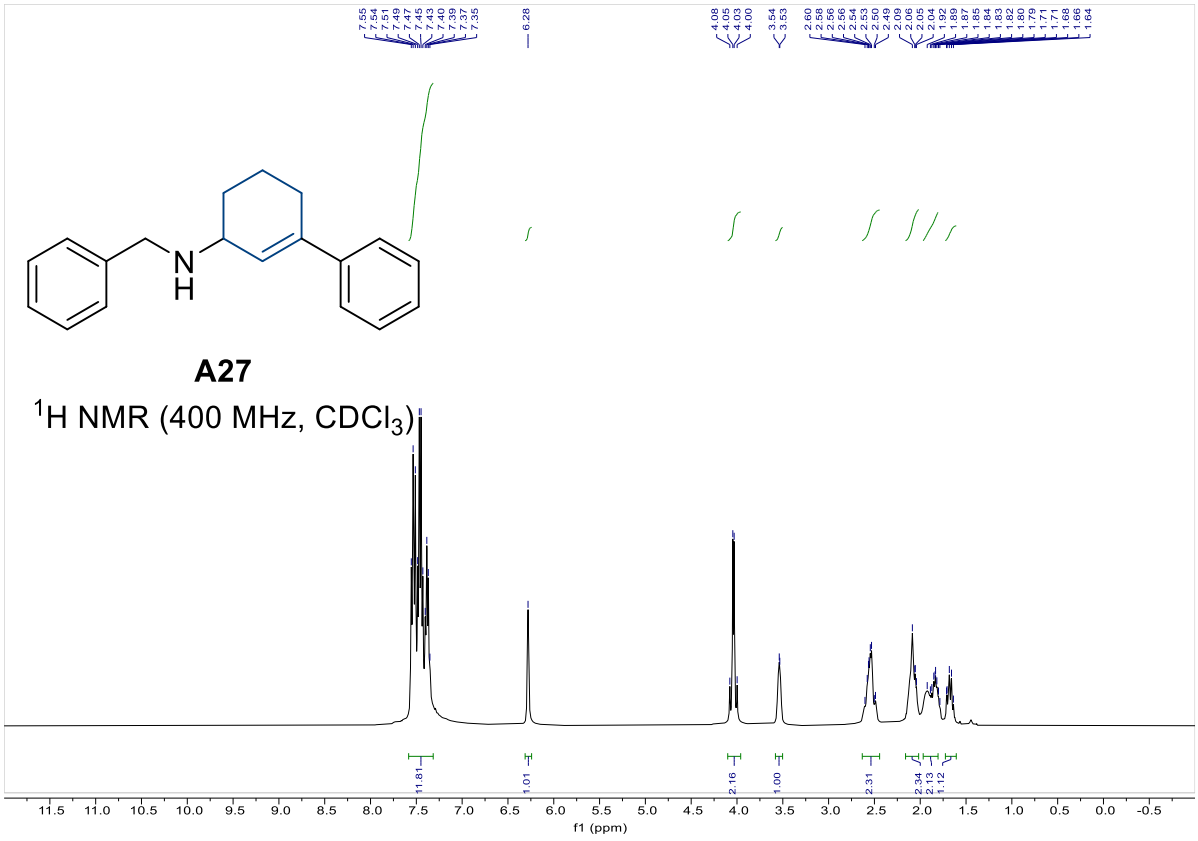

A25
1H NMR (499 MHz, CDCl3)
f1 (ppm)


A26
1H NMR (400 MHz, CDCl3)
f1 (ppm)



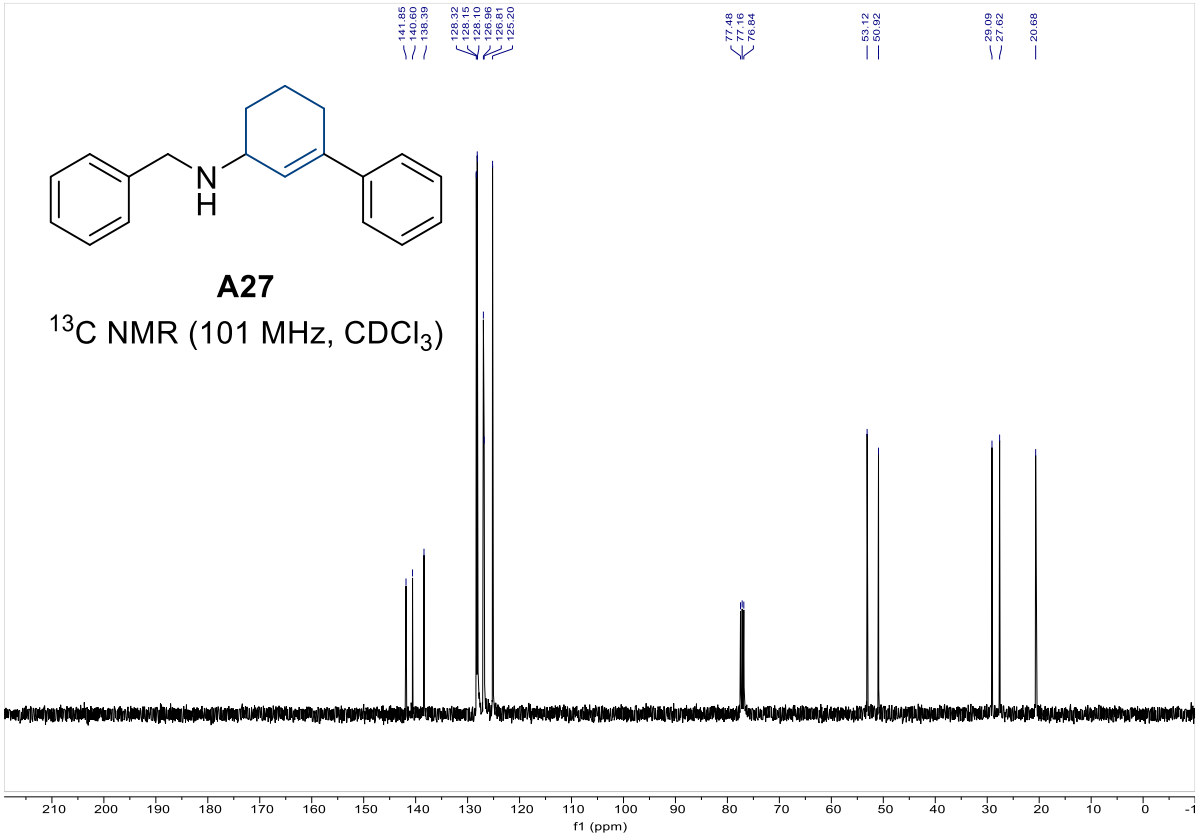
A26

^{13}C NMR (101 MHz, $CDCl_3$)



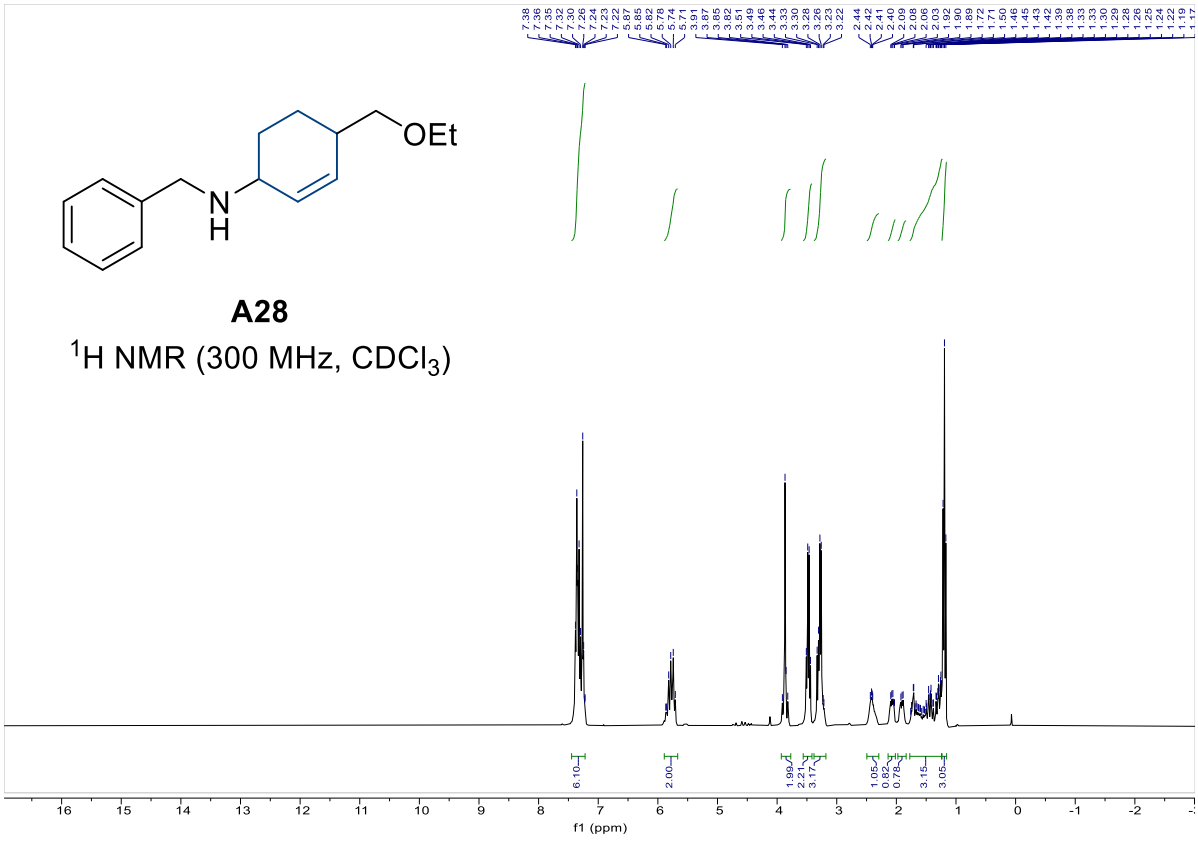
A27

^{1}H NMR (400 MHz, $CDCl_3$)



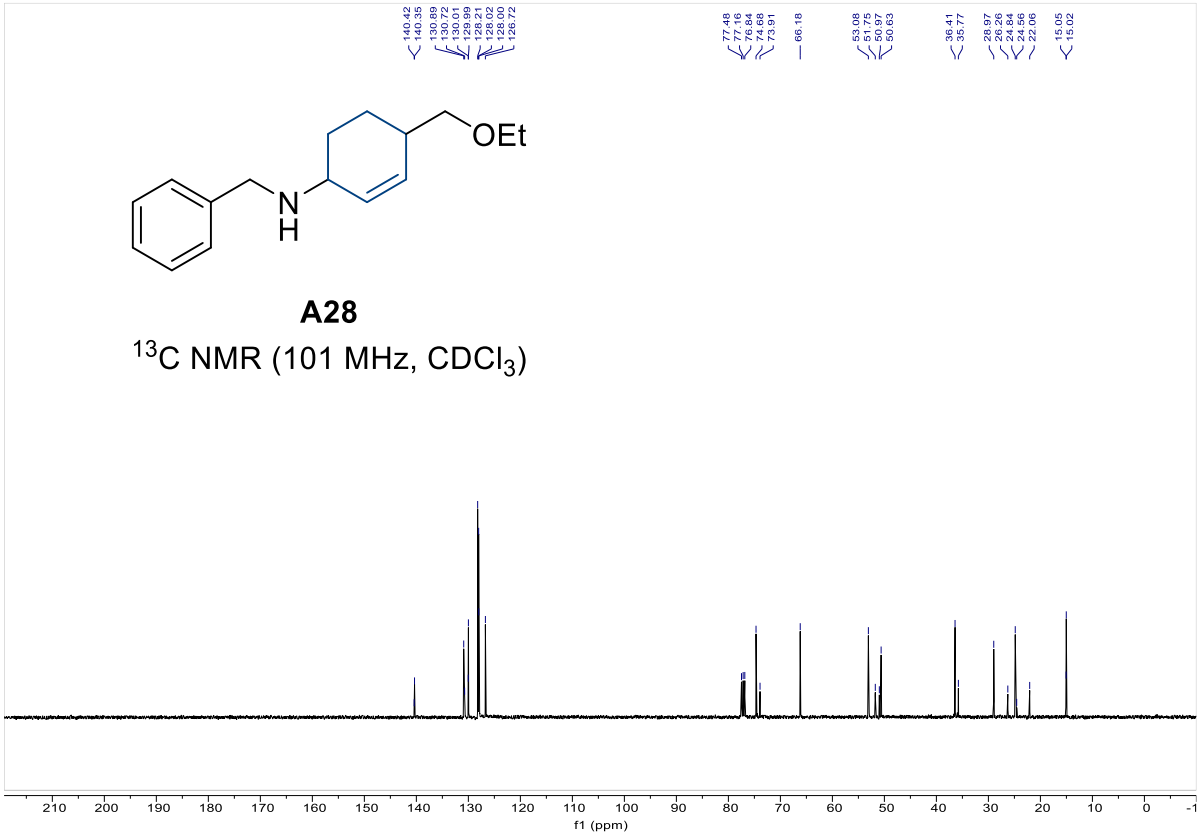
A27

^{13}C NMR (101 MHz, $CDCl_3$)



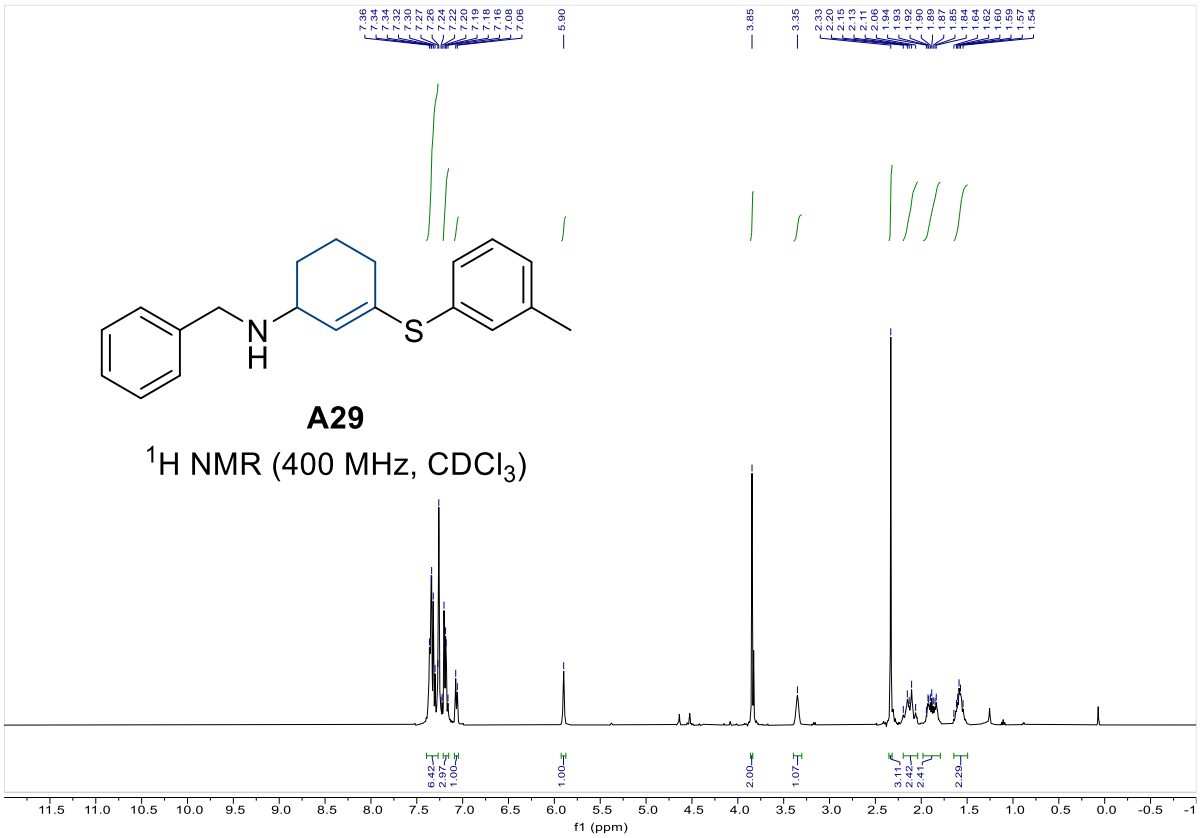
A28

^{1}H NMR (300 MHz, $CDCl_3$)



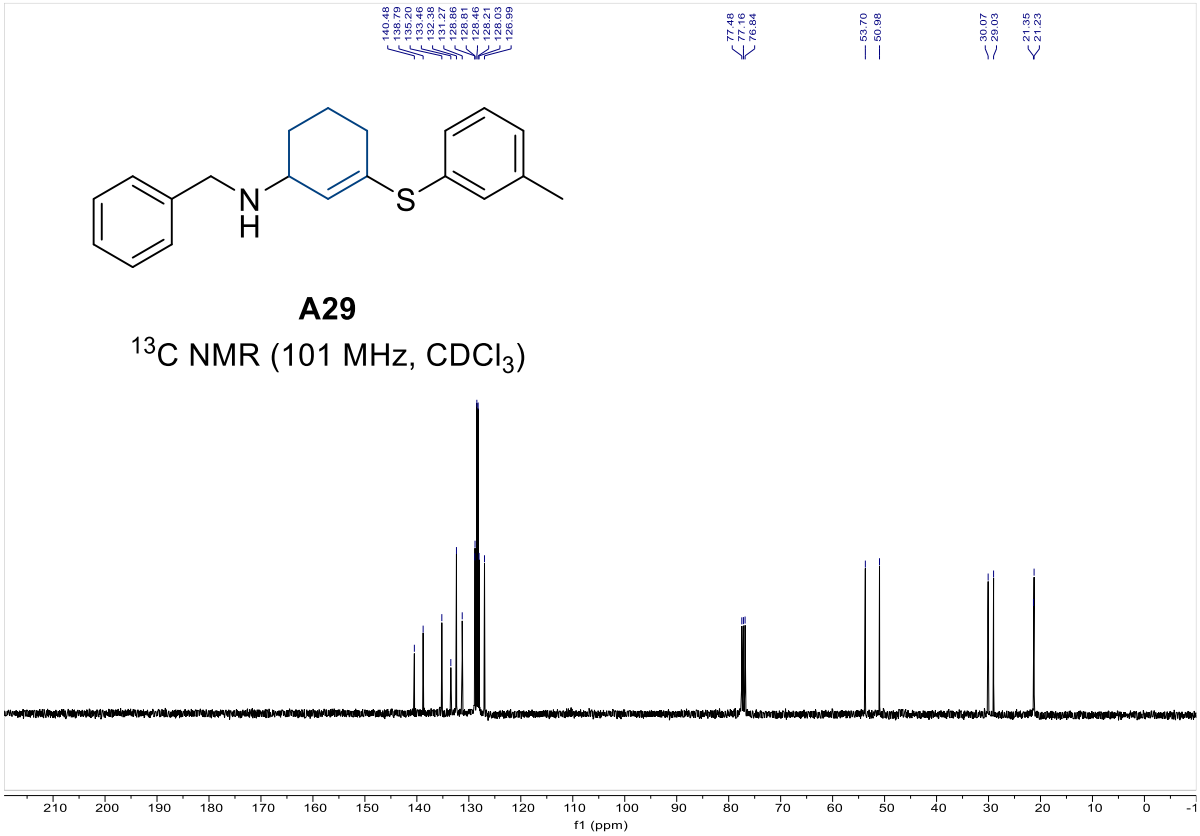
A28

^{13}C NMR (101 MHz, $CDCl_3$)



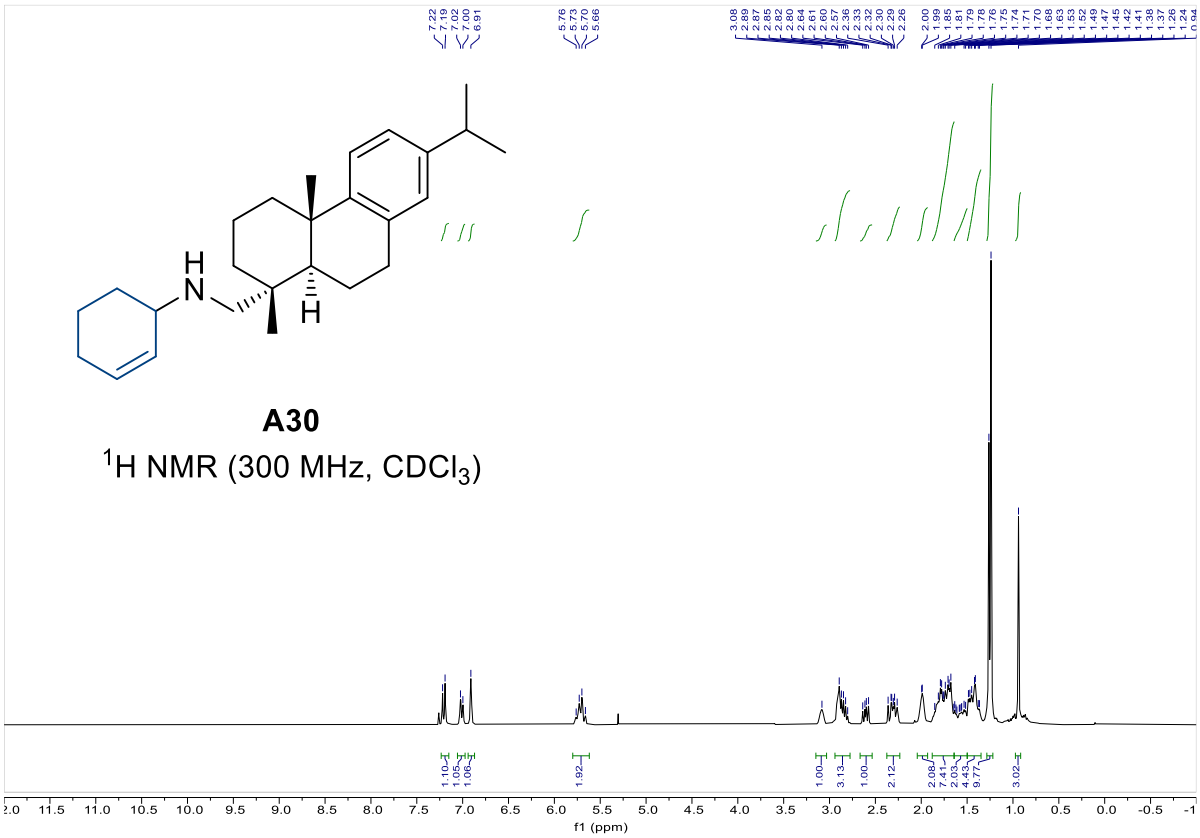
A29

^{1}H NMR (400 MHz, $CDCl_3$)



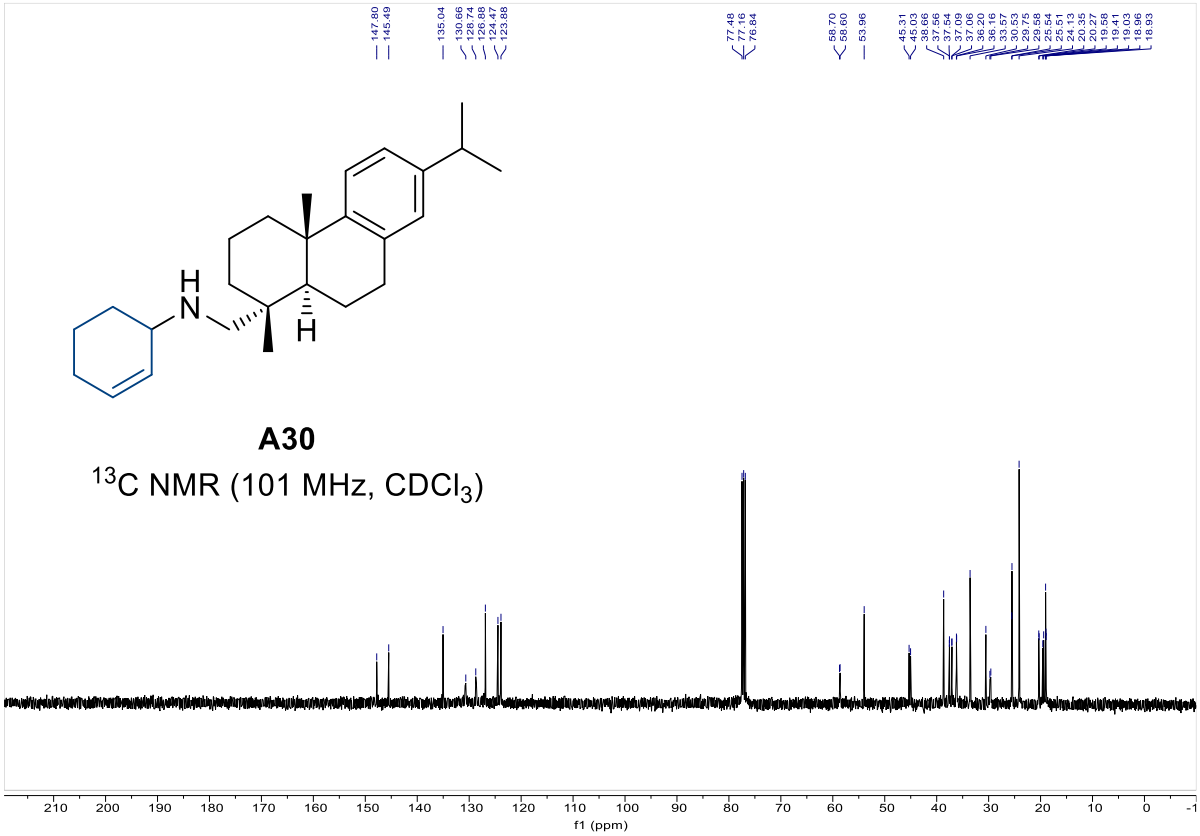
A29

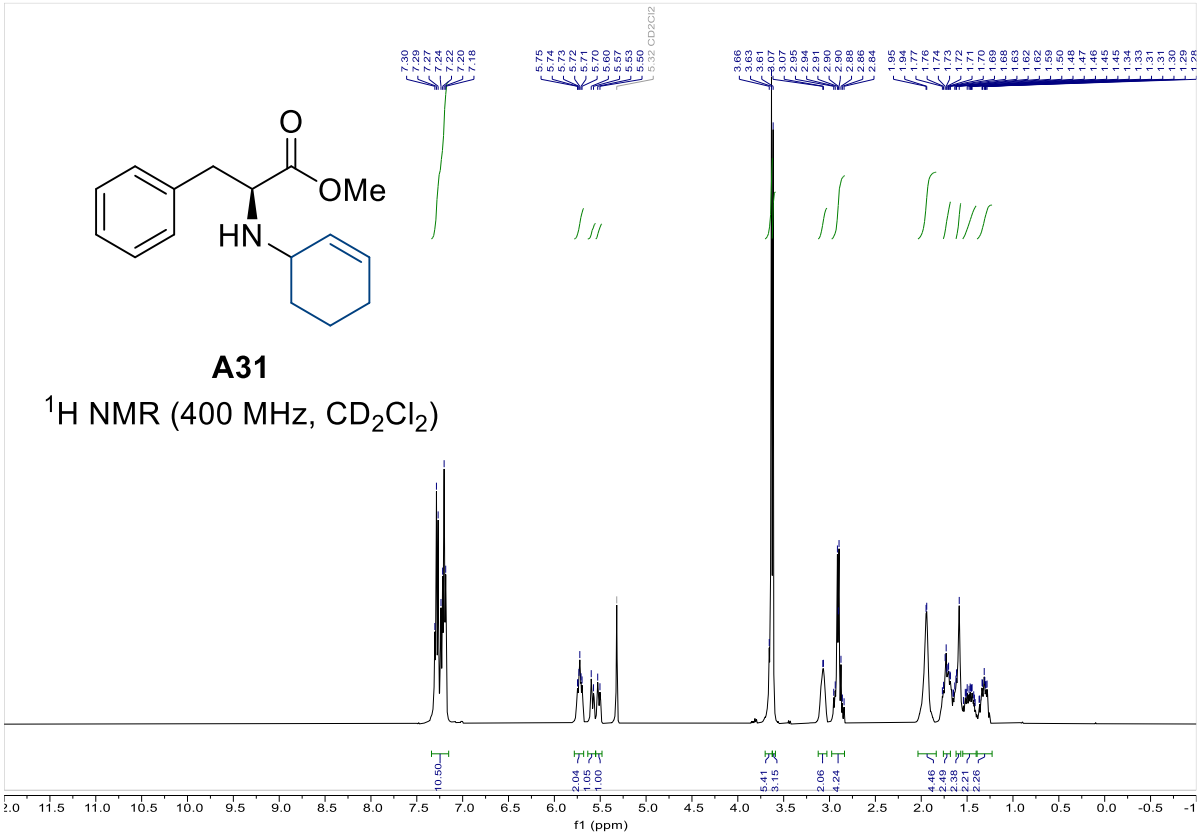
^{13}C NMR (101 MHz, $CDCl_3$)

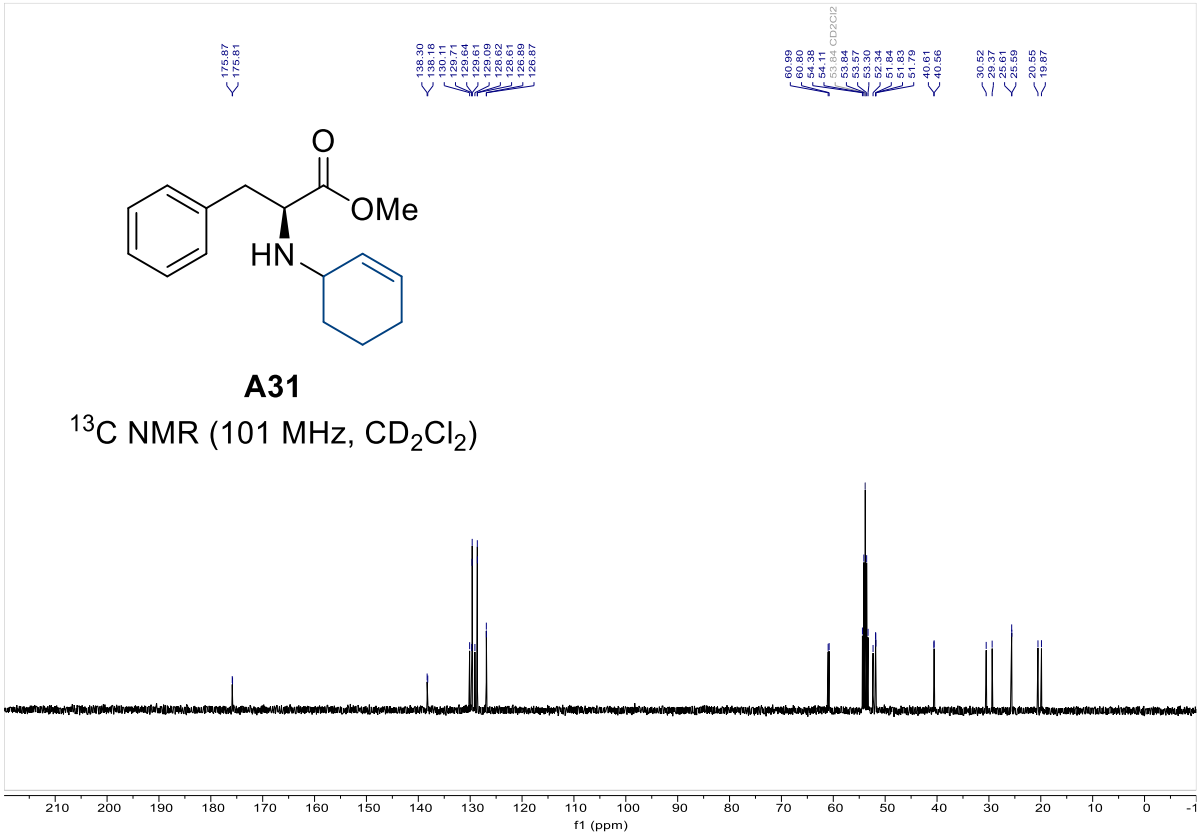


A30

^{1}H NMR (300 MHz, $CDCl_3$)

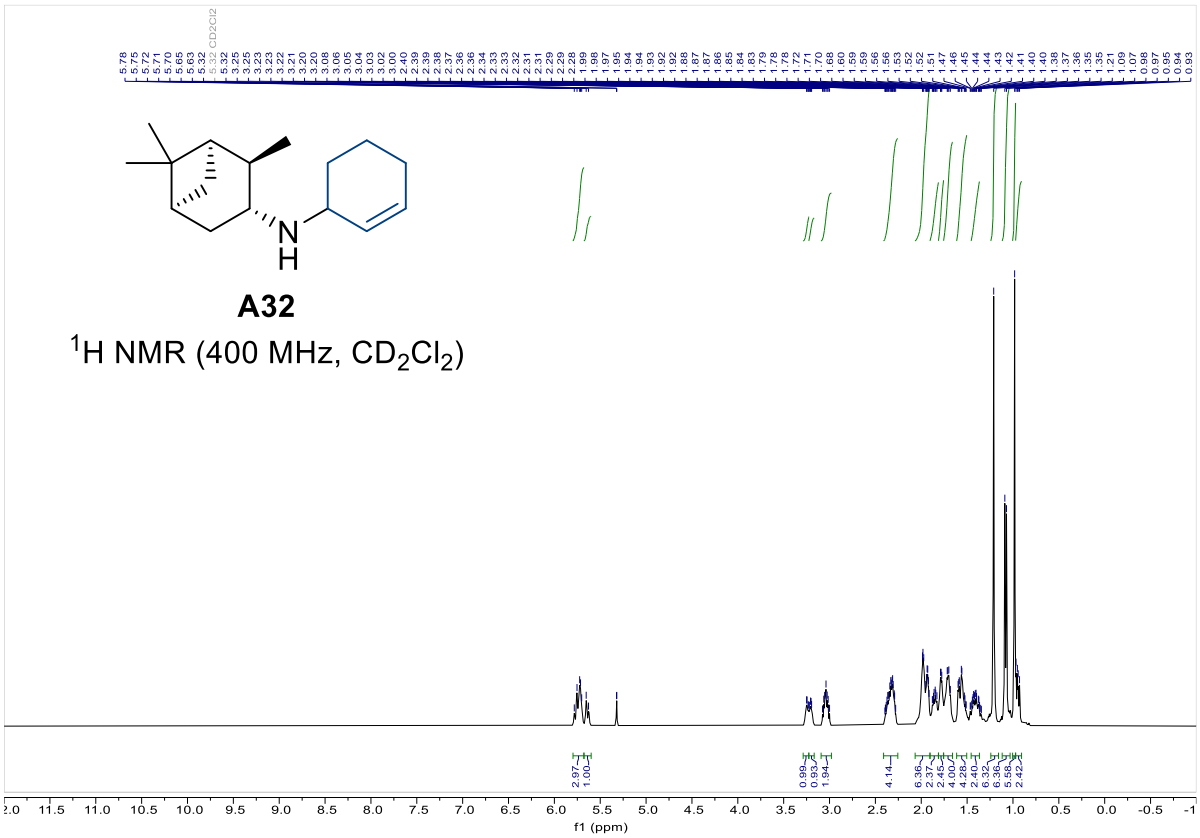

H
N
H
A30
13C NMR (101 MHz, CDCl3)
f1 (ppm)


O
OMe
HN
A31
1H NMR (400 MHz, CD2Cl2)
f1 (ppm)



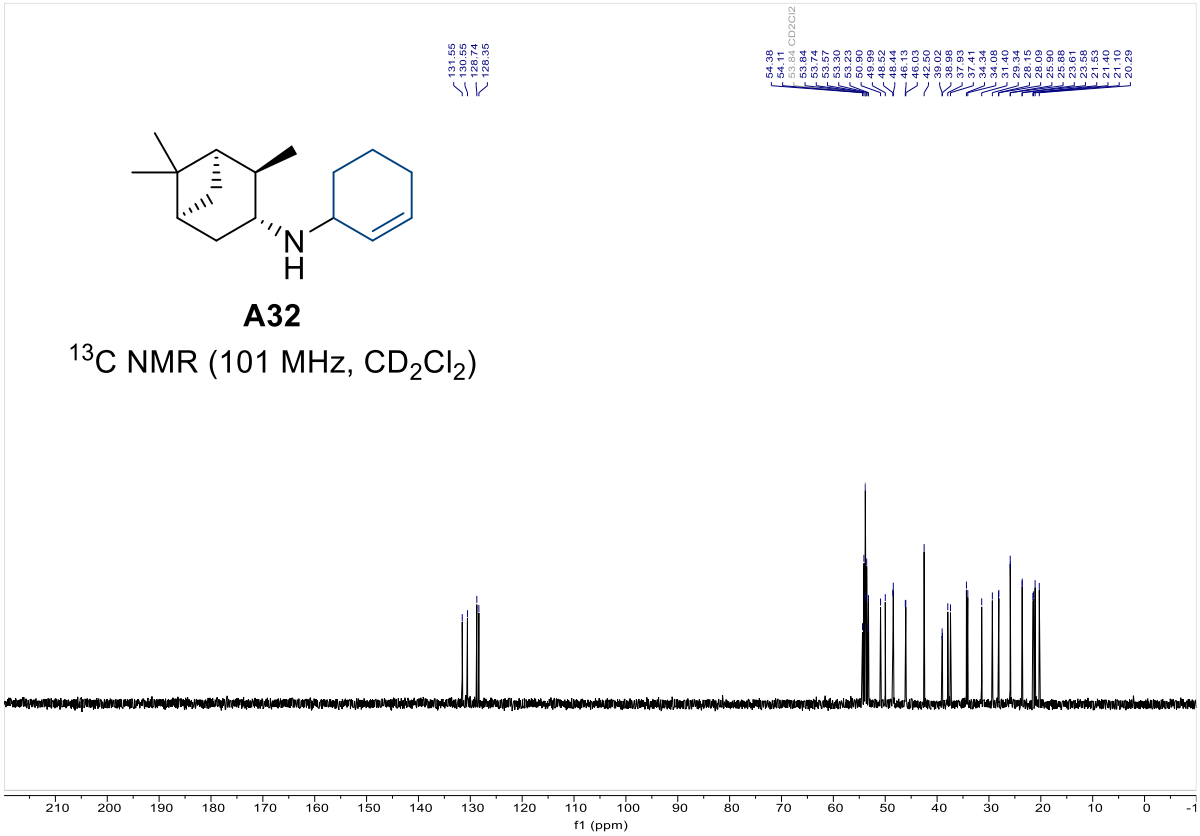
A31

^{13}C NMR (101 MHz, CD_2Cl_2)



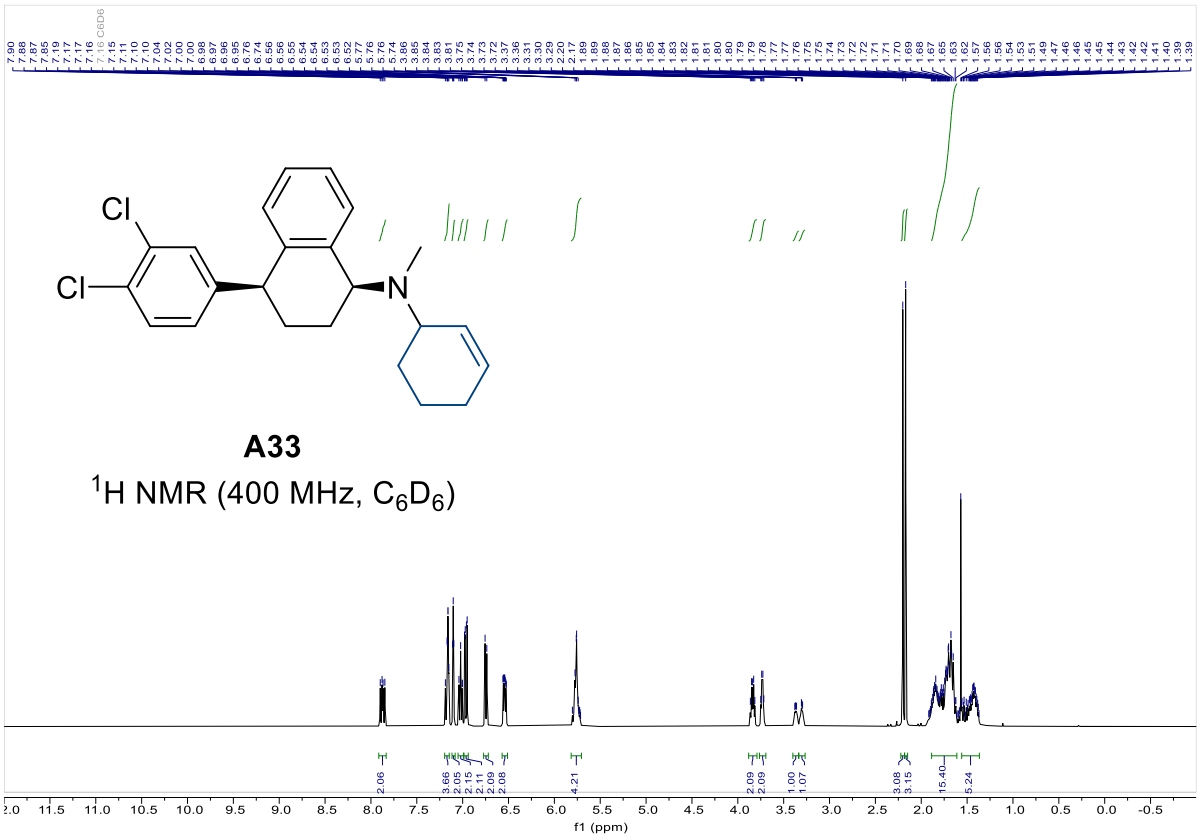
A32

^{1}H NMR (400 MHz, CD_2Cl_2)



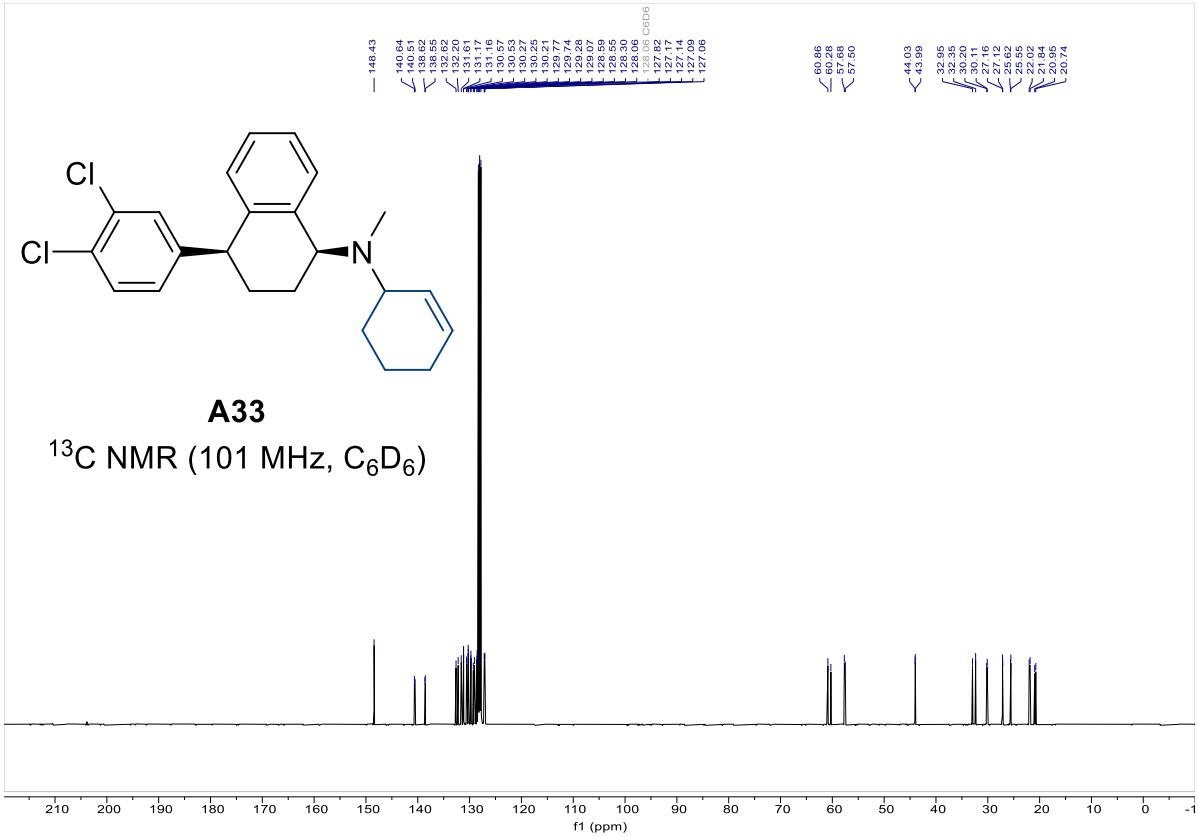
A32

^{13}C NMR (101 MHz, CD_2Cl_2)



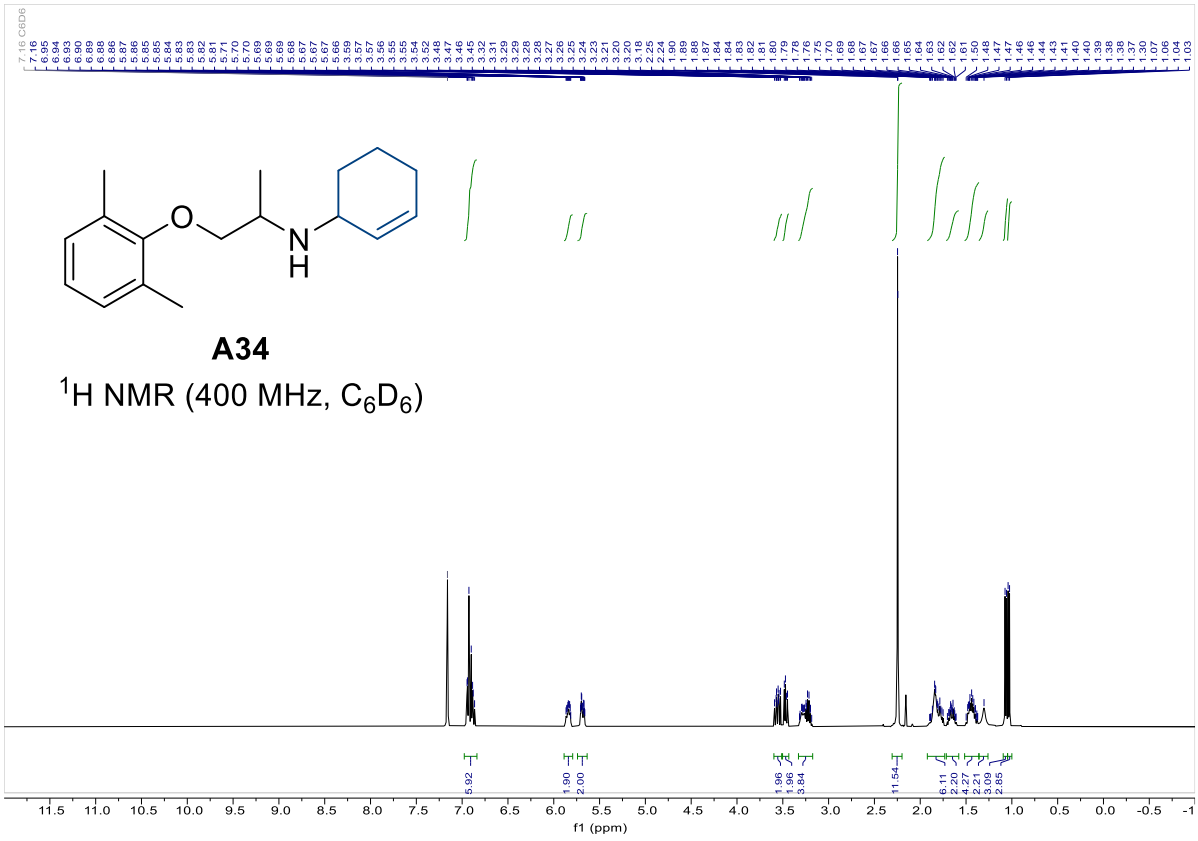
A33

^{1}H NMR (400 MHz, C_6D_6)



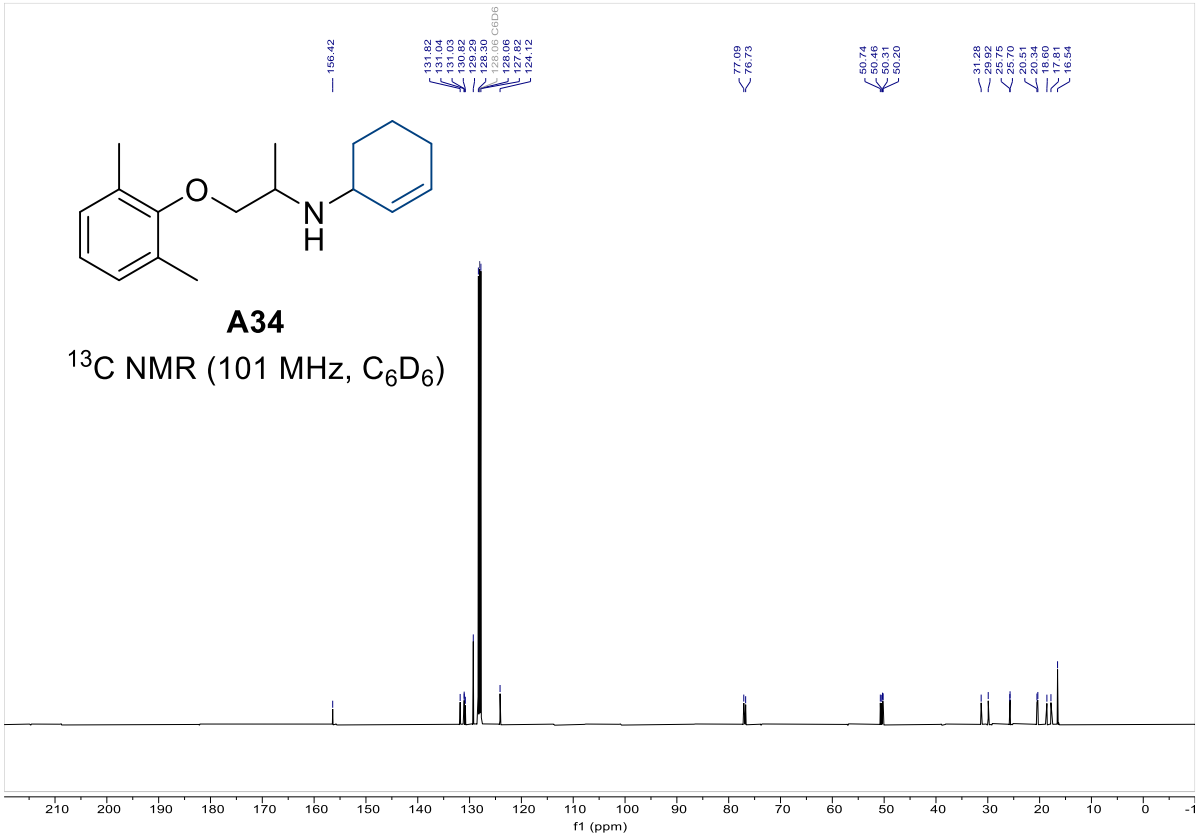
A33

^{13}C NMR (101 MHz, C_6D_6)



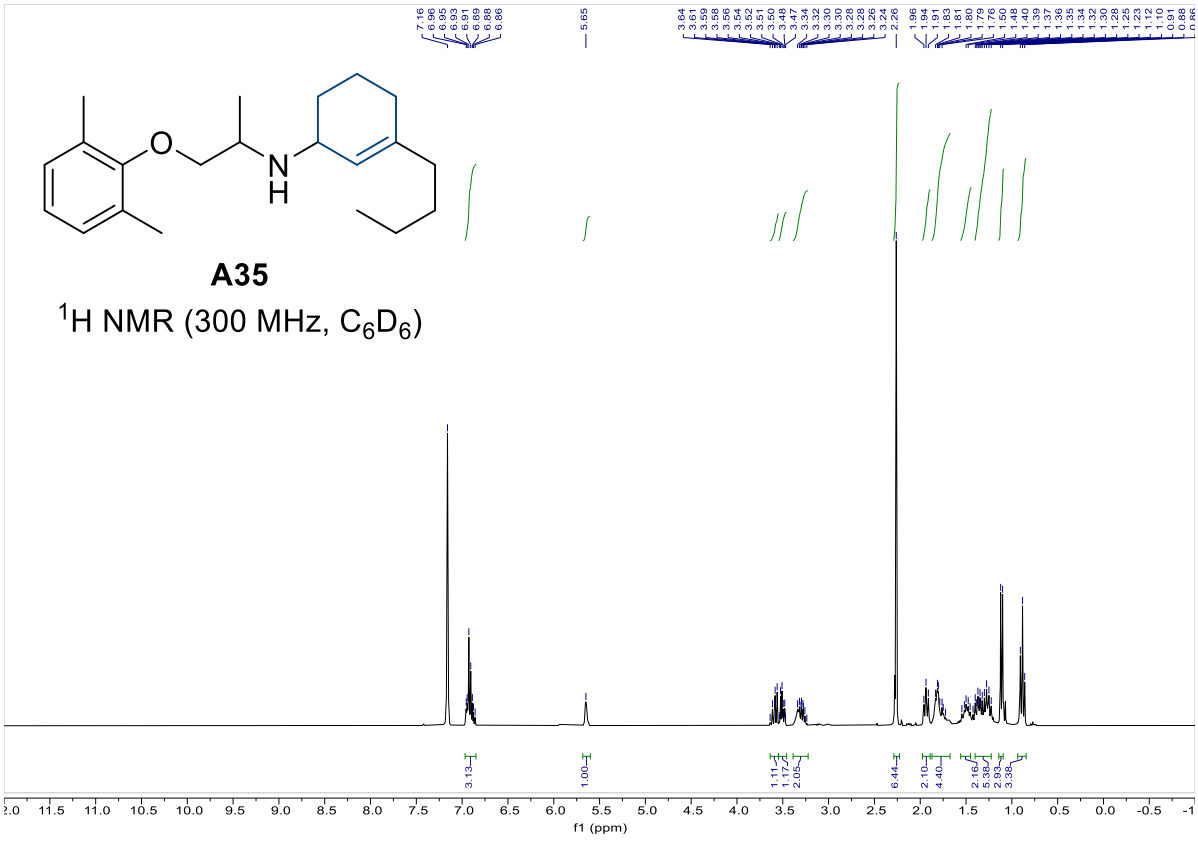
A34

^{1}H NMR (400 MHz, C_6D_6)



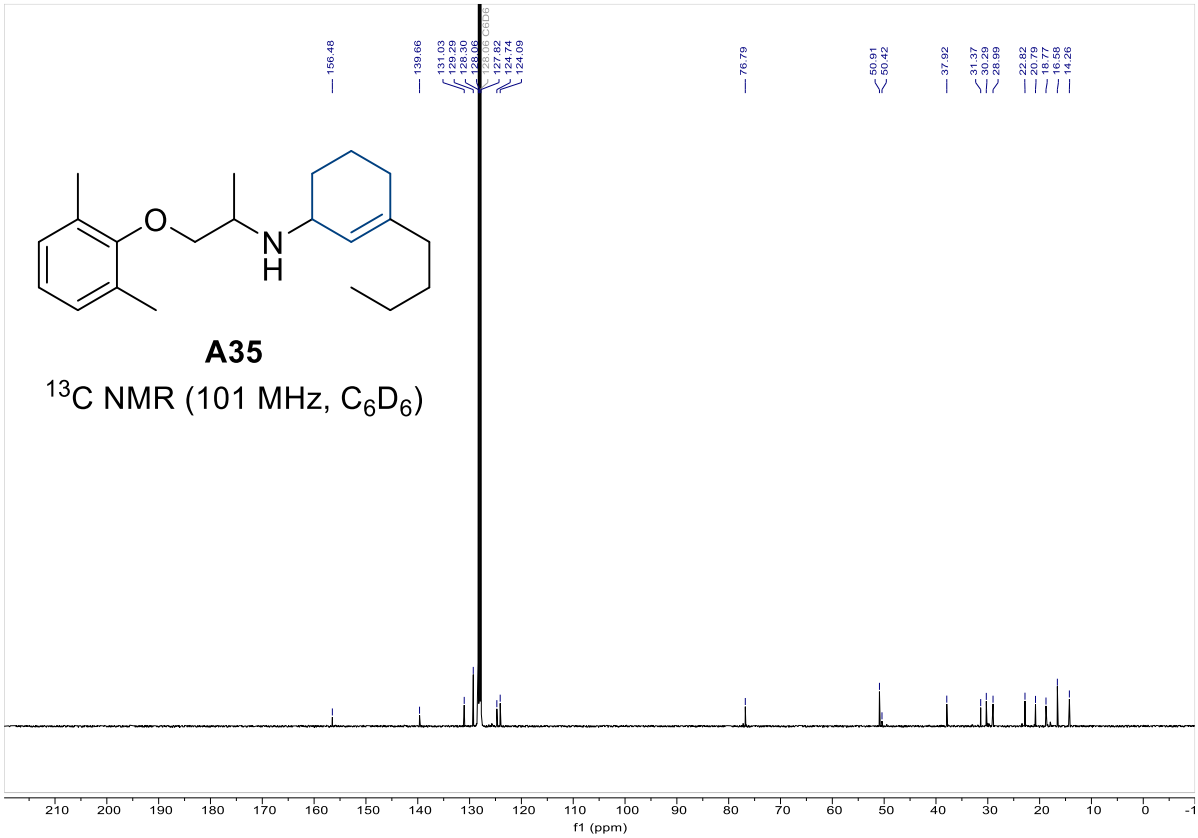
A34

^{13}C NMR (101 MHz, C_6D_6)



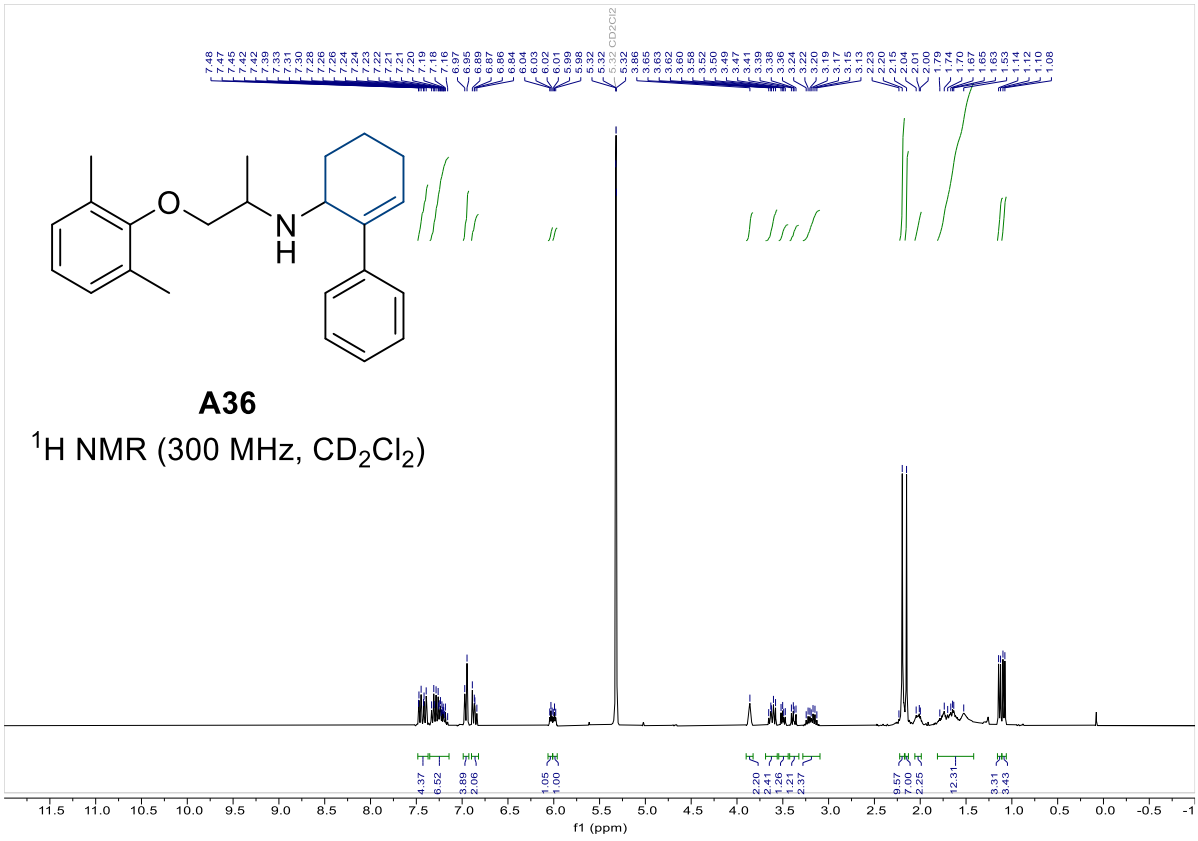
A35

^{1}H NMR (300 MHz, C_6D_6)



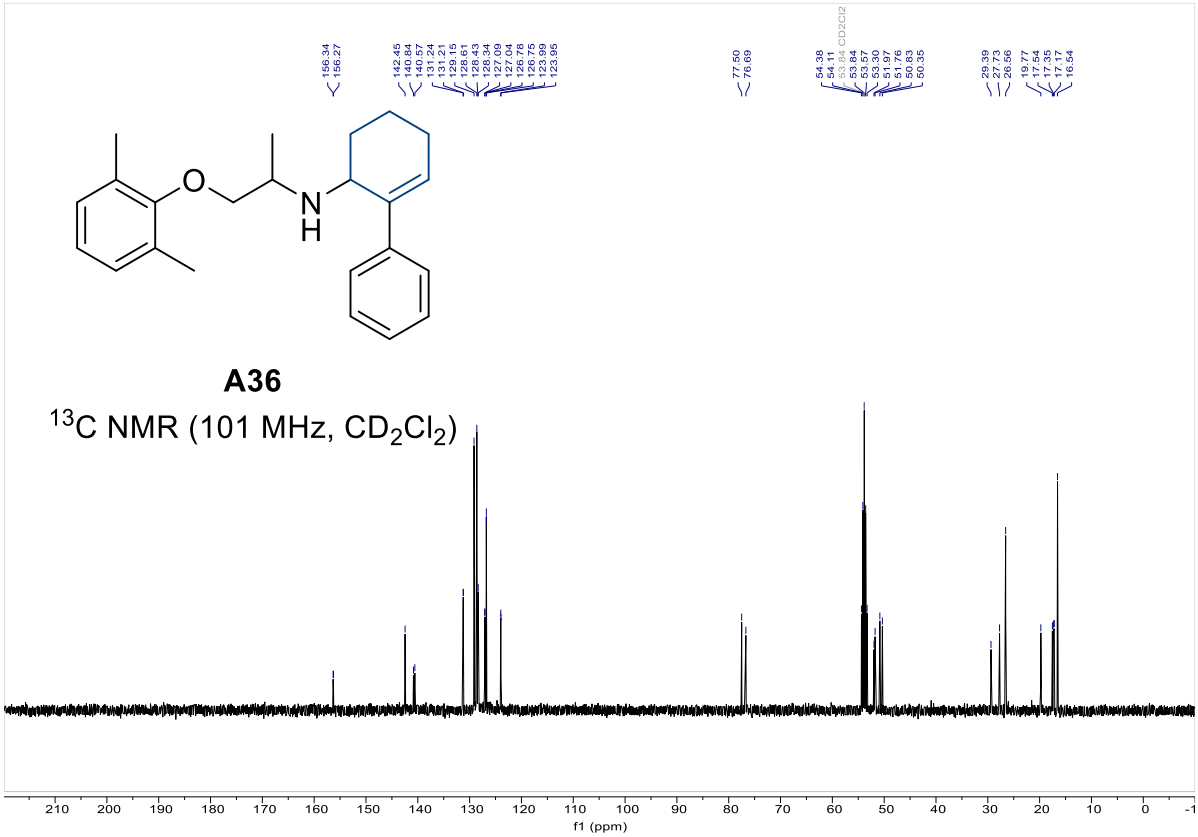
A35

^{13}C NMR (101 MHz, C_6D_6)



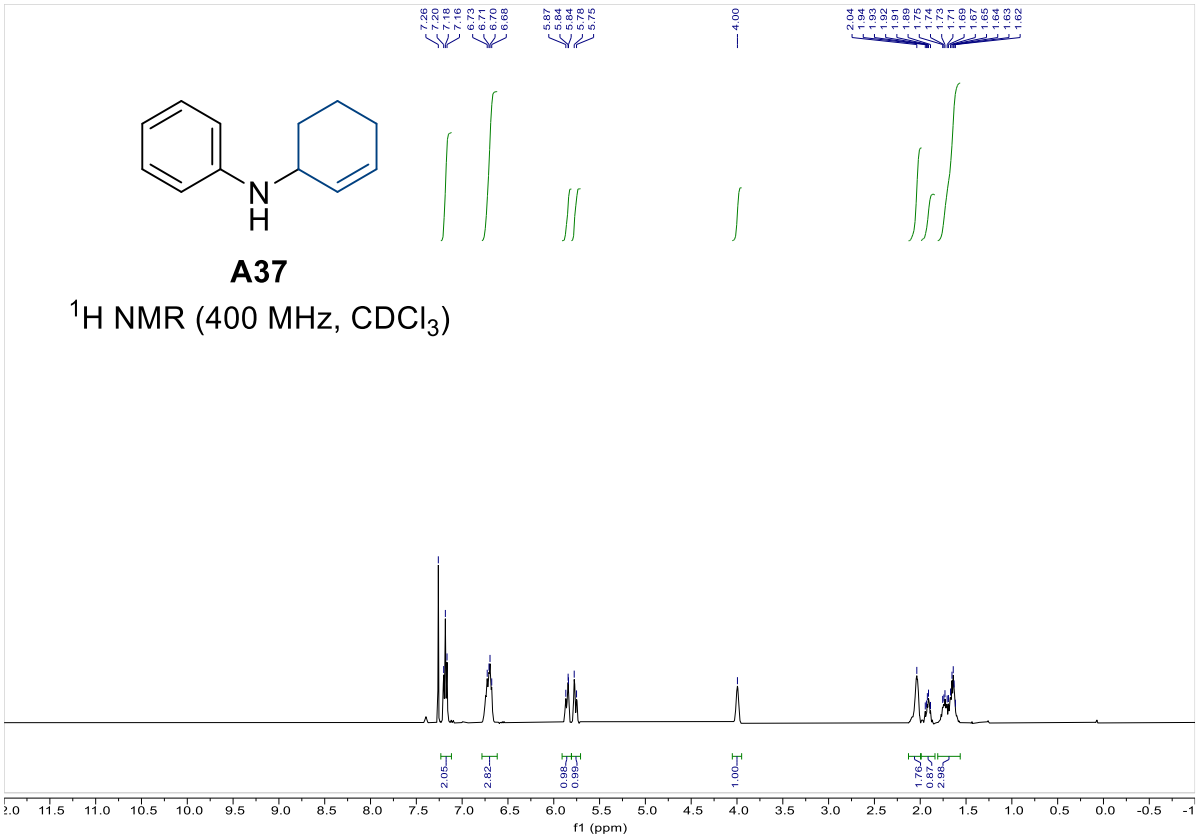
A36

^{1}H NMR (300 MHz, CD_2Cl_2)



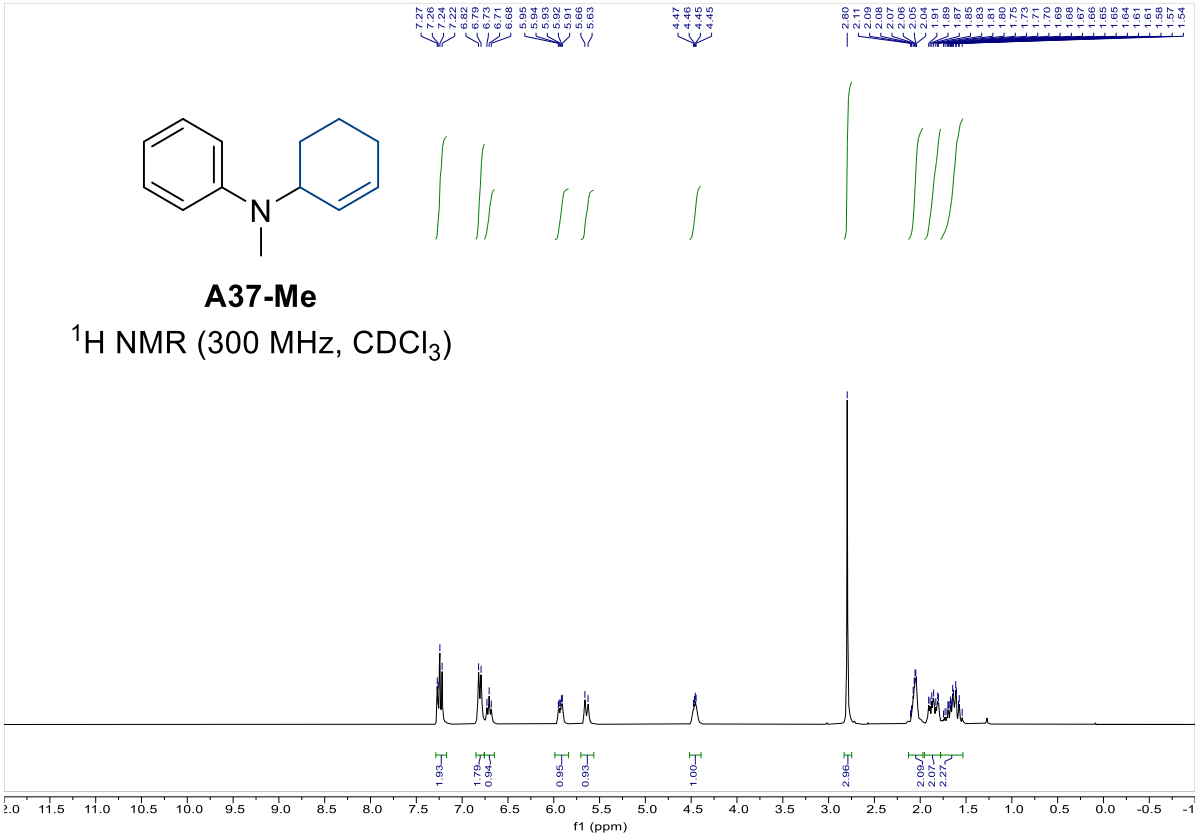
A36

^{13}C NMR (101 MHz, CD_2Cl_2)



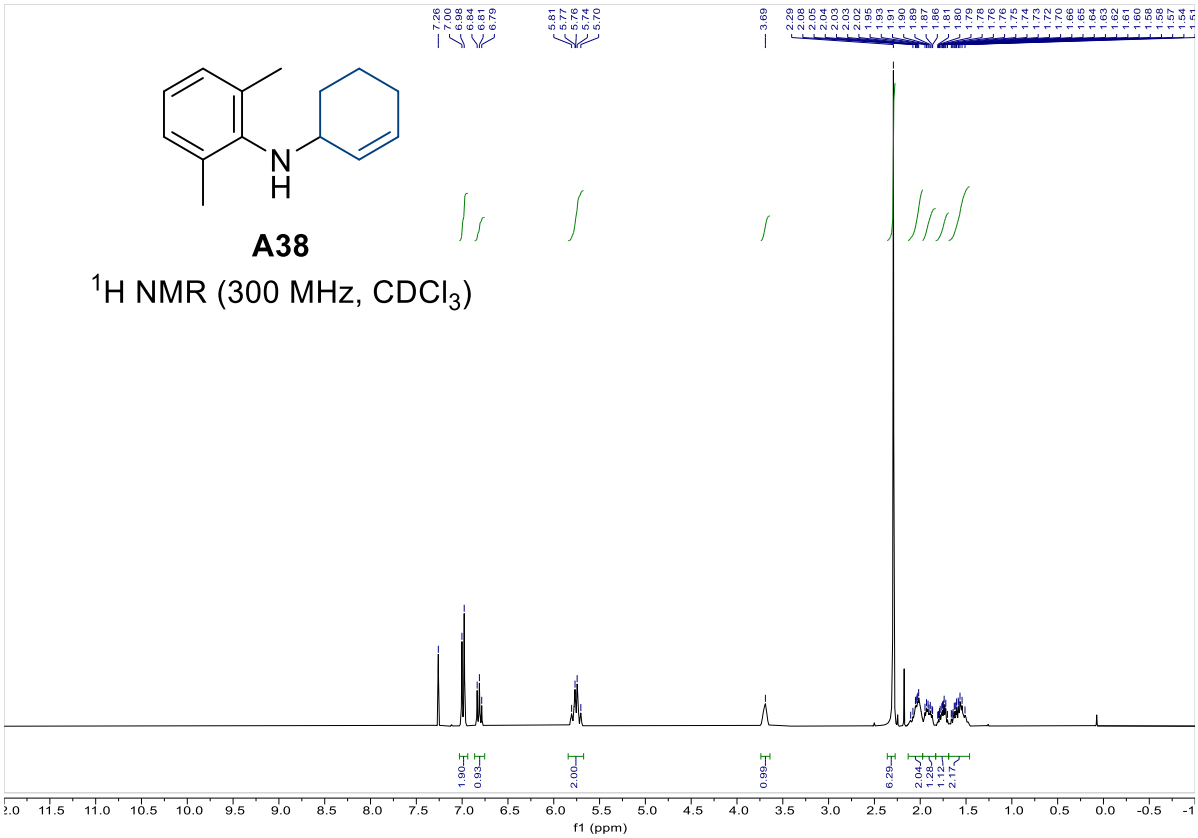
A37

^{1}H NMR (400 MHz, $CDCl_3$)



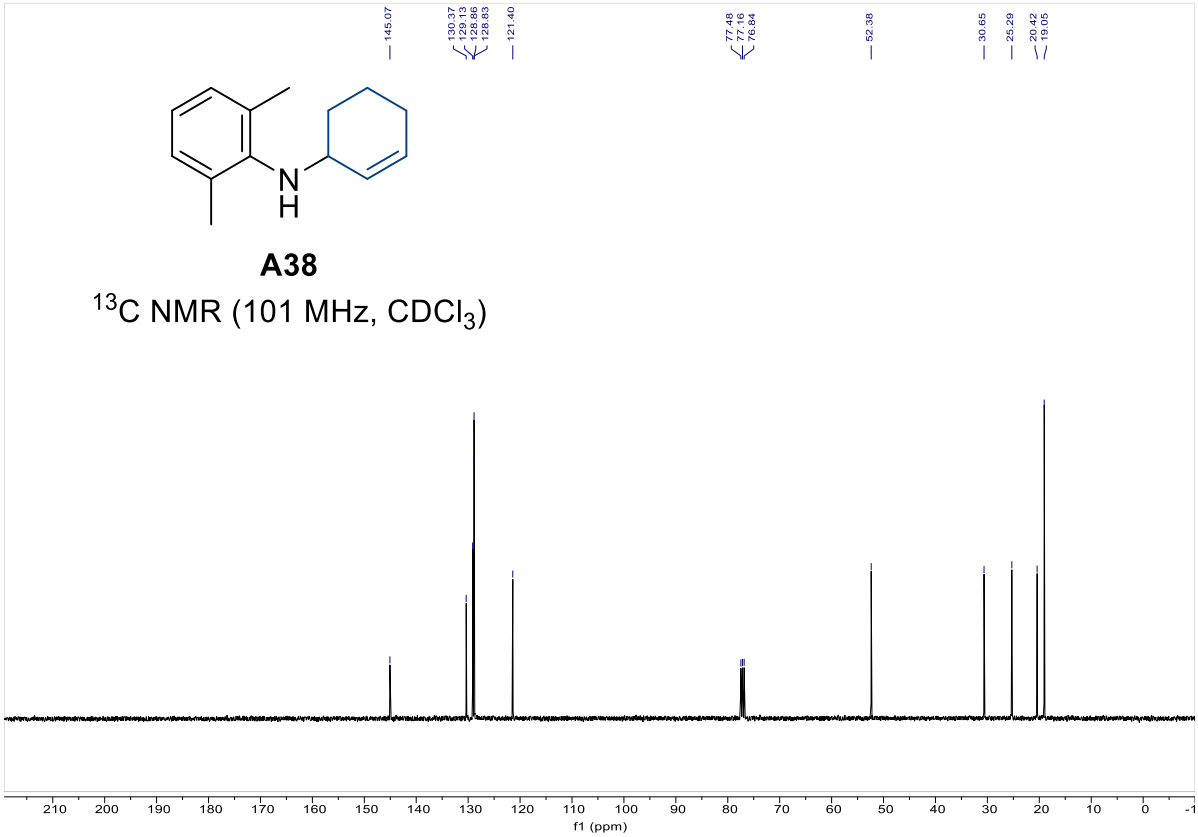
A37-Me

^{1}H NMR (300 MHz, $CDCl_3$)



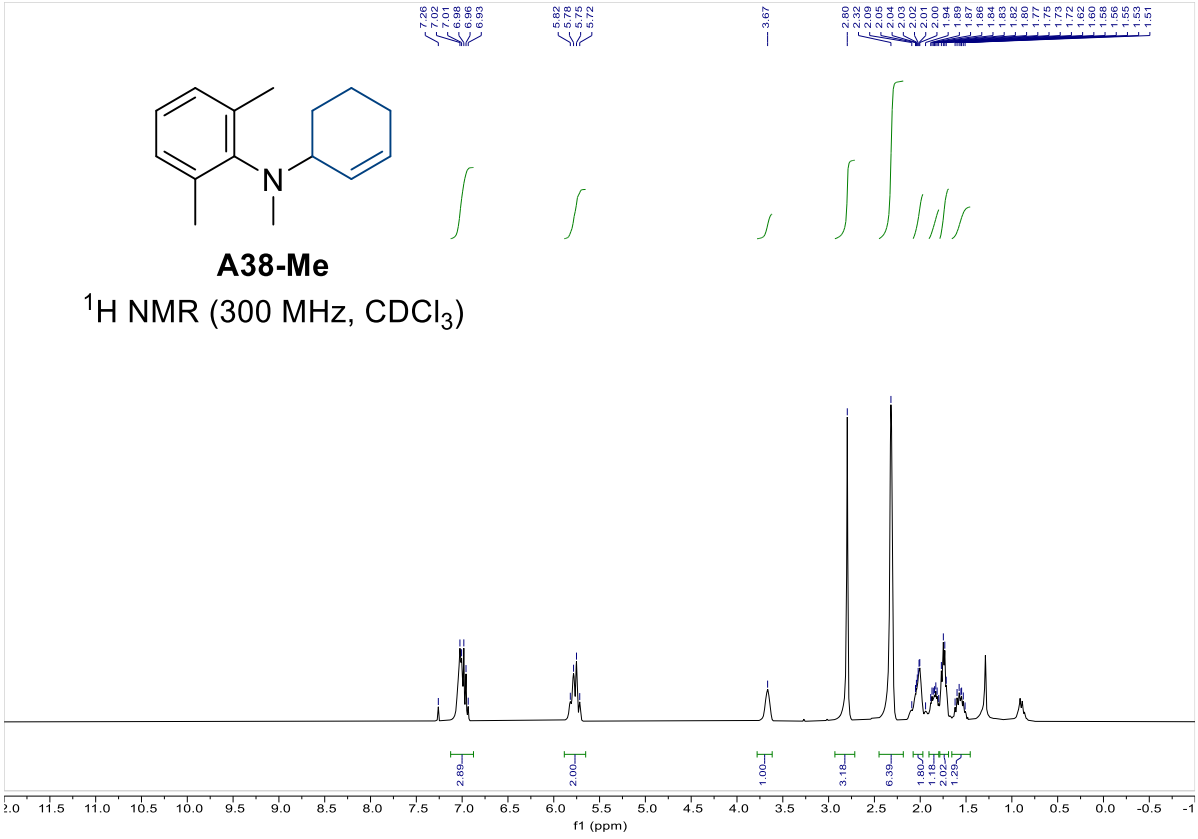
A38

^{1}H NMR (300 MHz, $CDCl_3$)



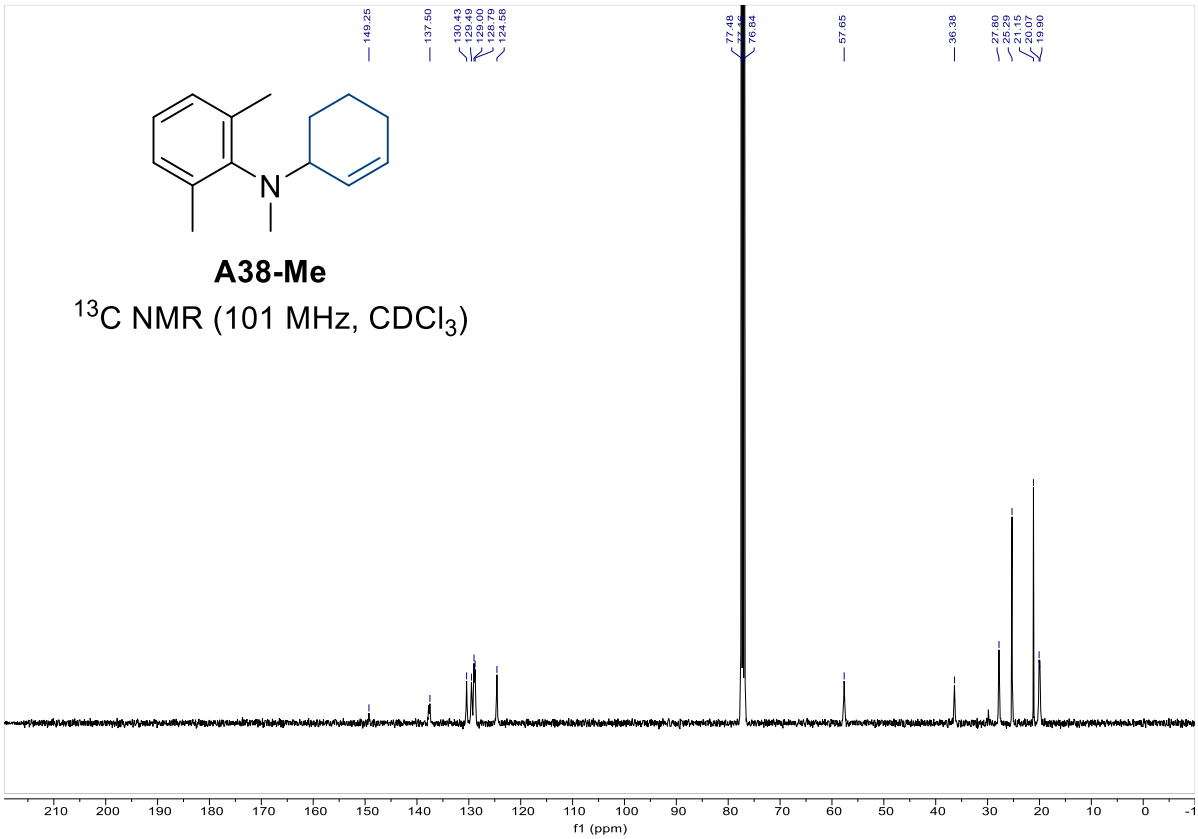
A38

^{13}C NMR (101 MHz, $CDCl_3$)



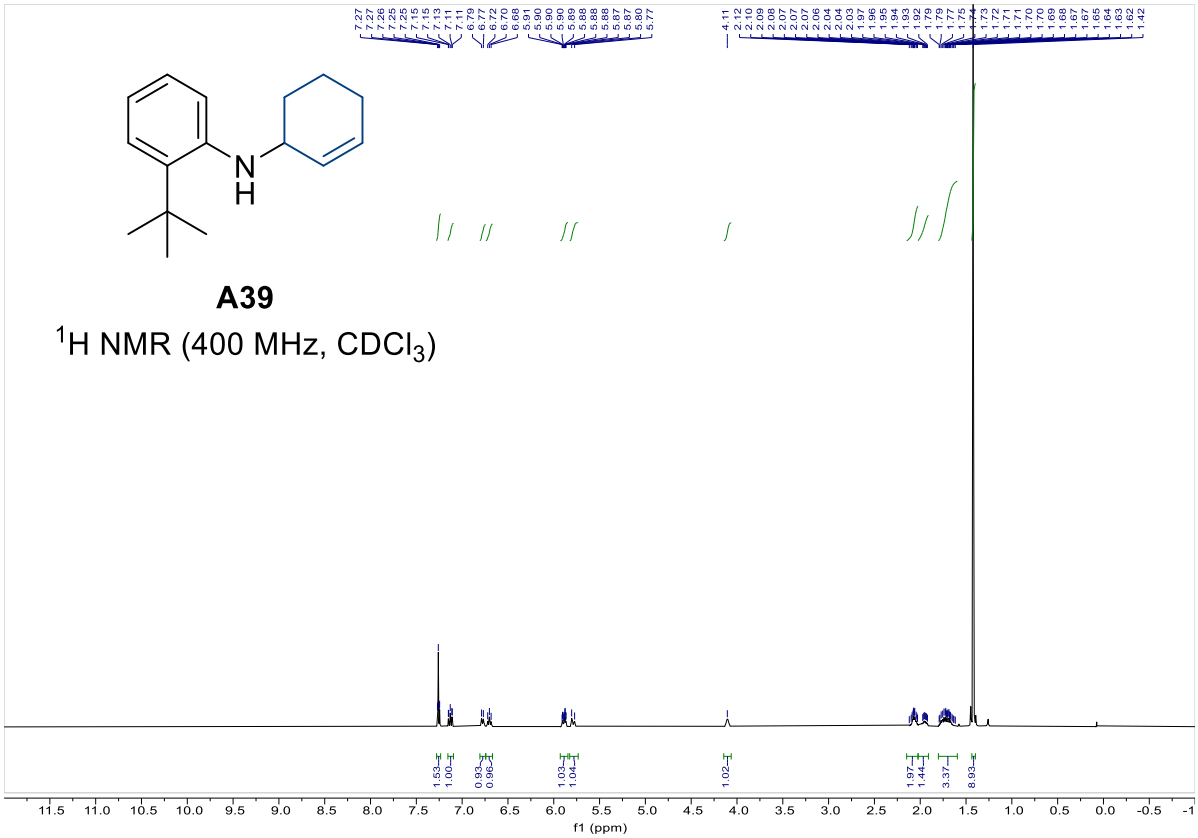
A38-Me

^{1}H NMR (300 MHz, $CDCl_3$)



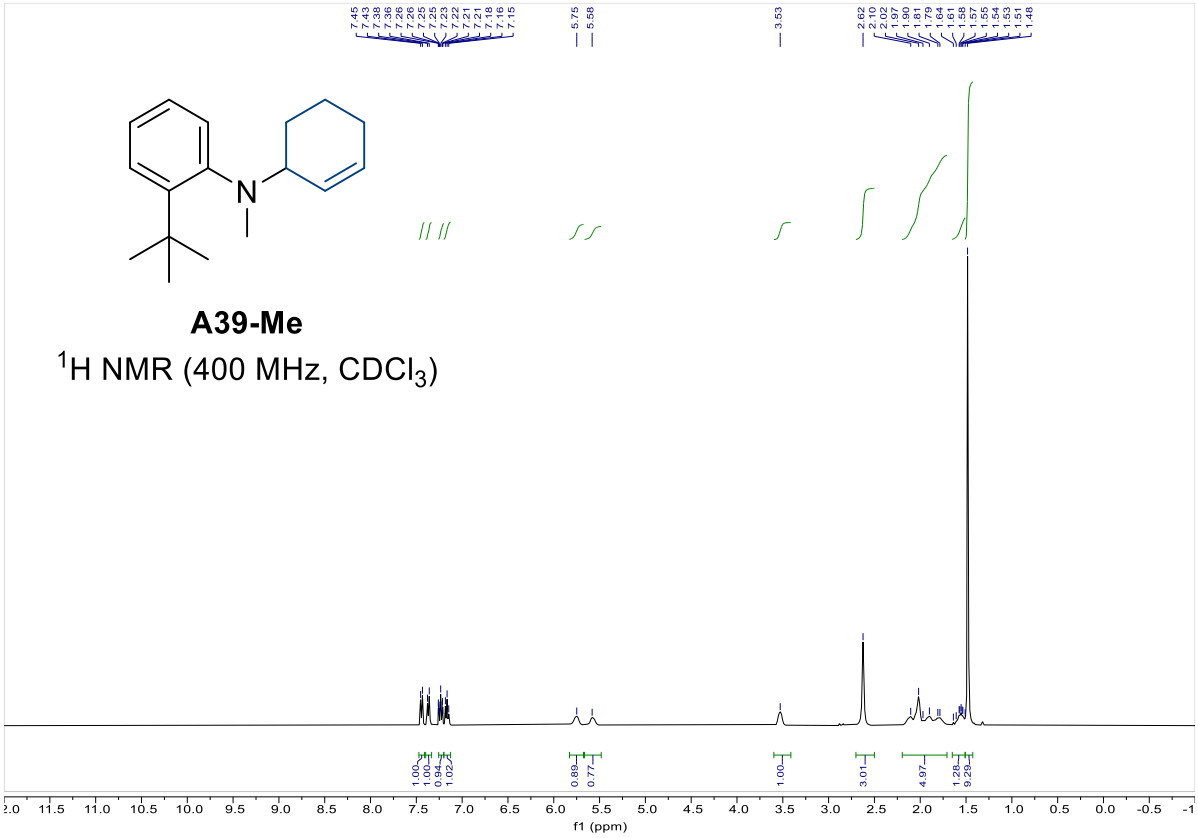
A38-Me

^{13}C NMR (101 MHz, $CDCl_3$)



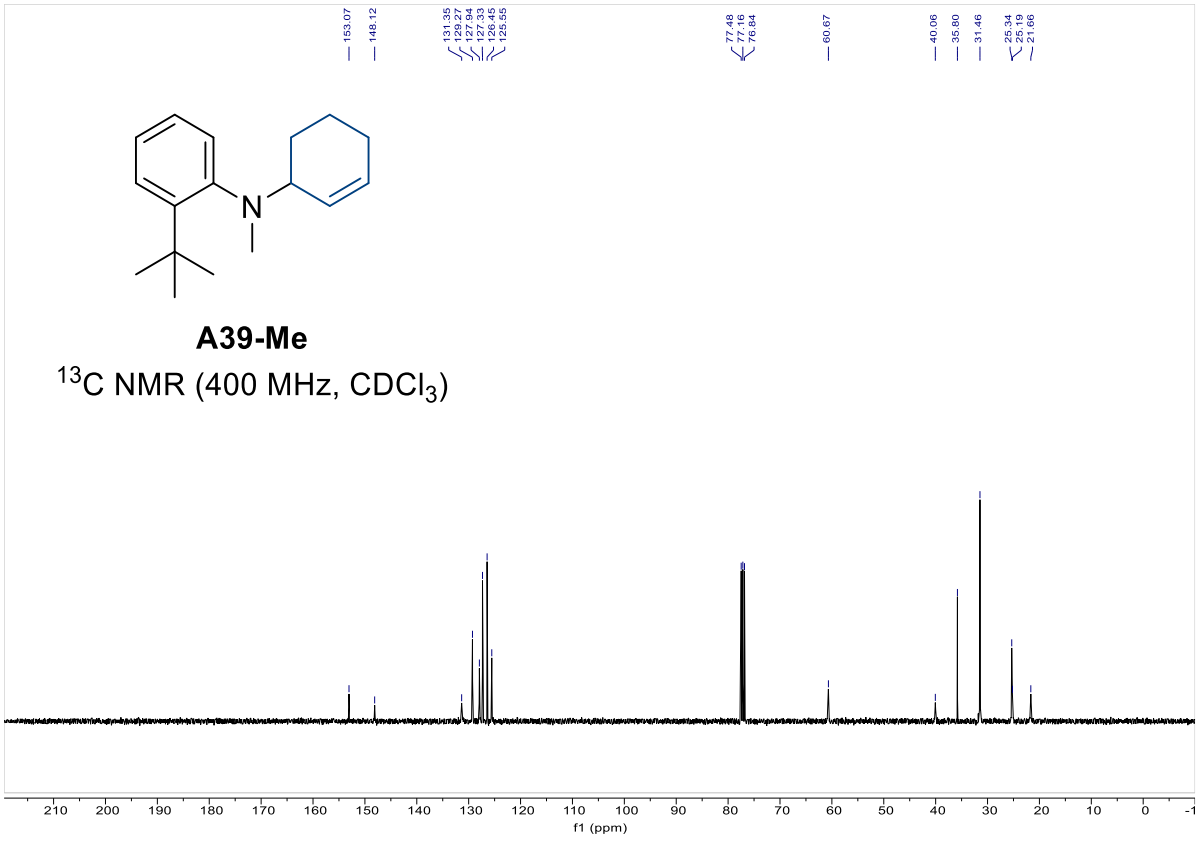
A39

^{1}H NMR (400 MHz, $CDCl_3$)



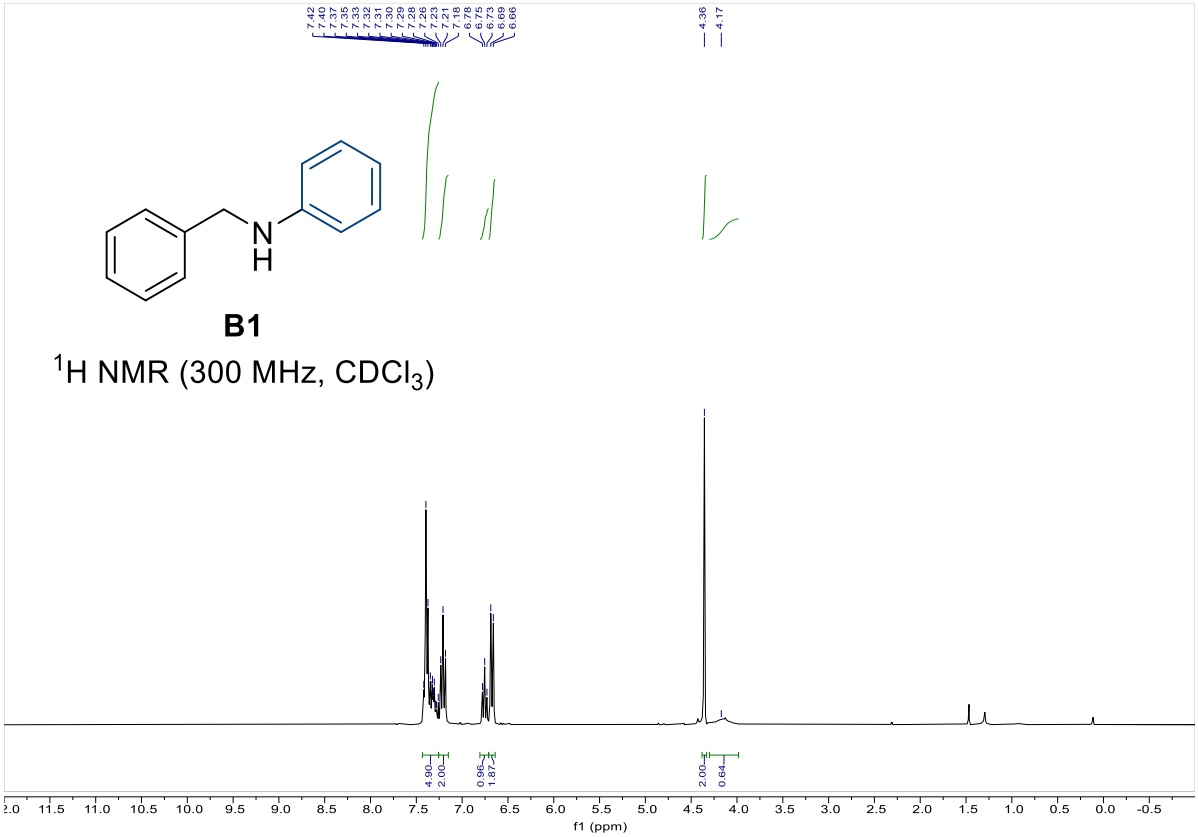
A39-Me

^{1}H NMR (400 MHz, $CDCl_3$)



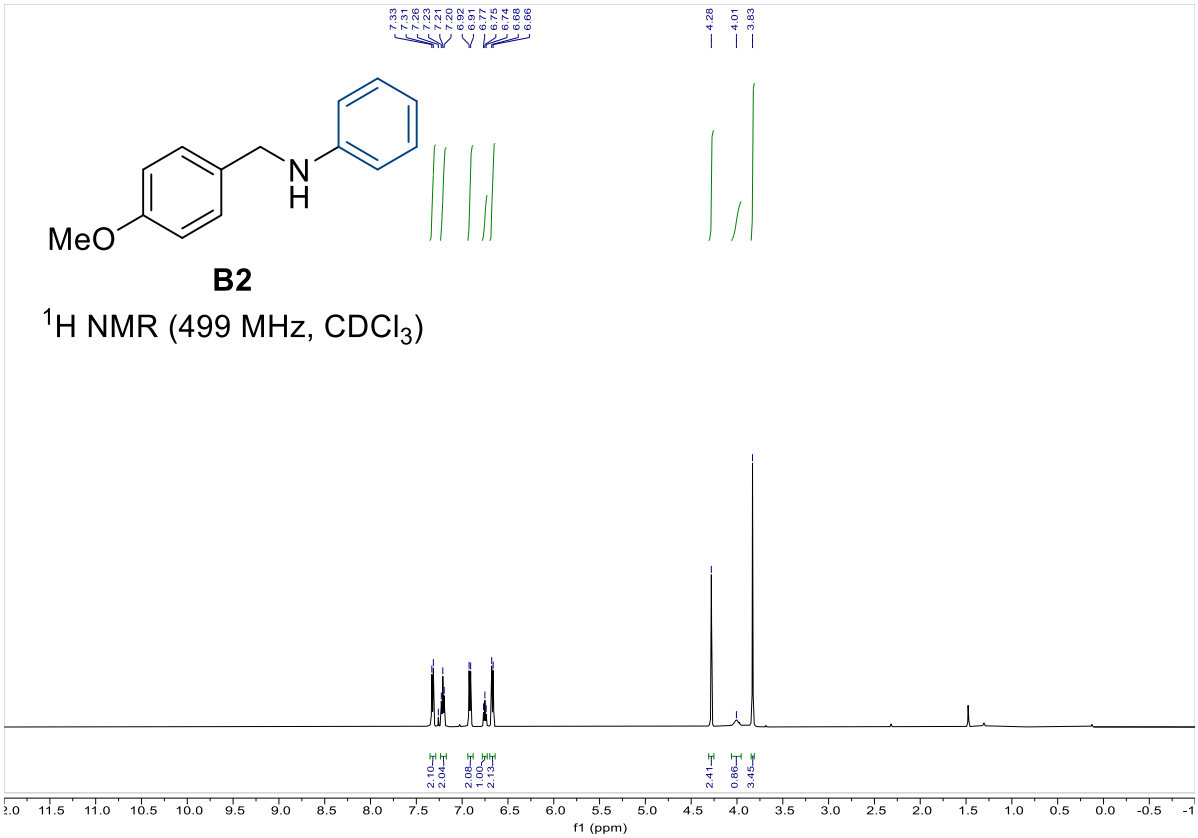
A39-Me

^{13}C NMR (400 MHz, $CDCl_3$)



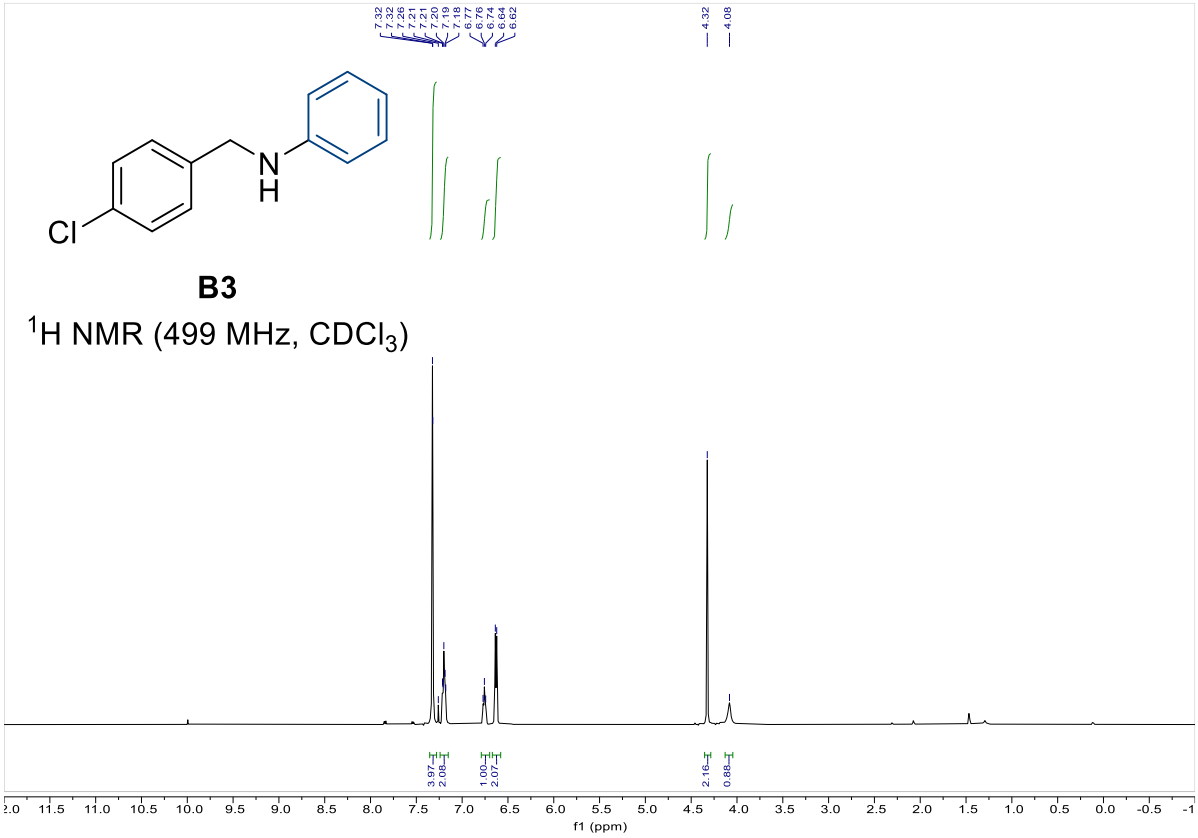
B1

^{1}H NMR (300 MHz, $CDCl_3$)



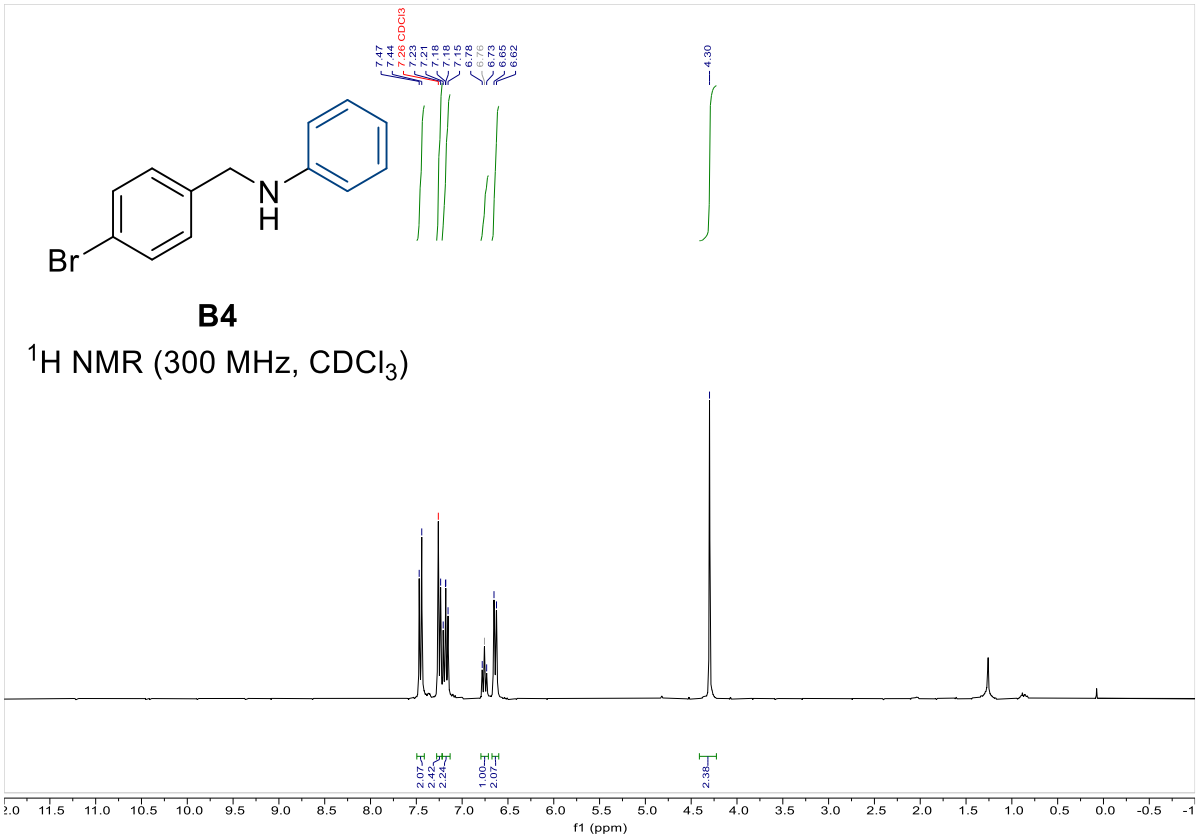
B2

^{1}H NMR (499 MHz, $CDCl_3$)



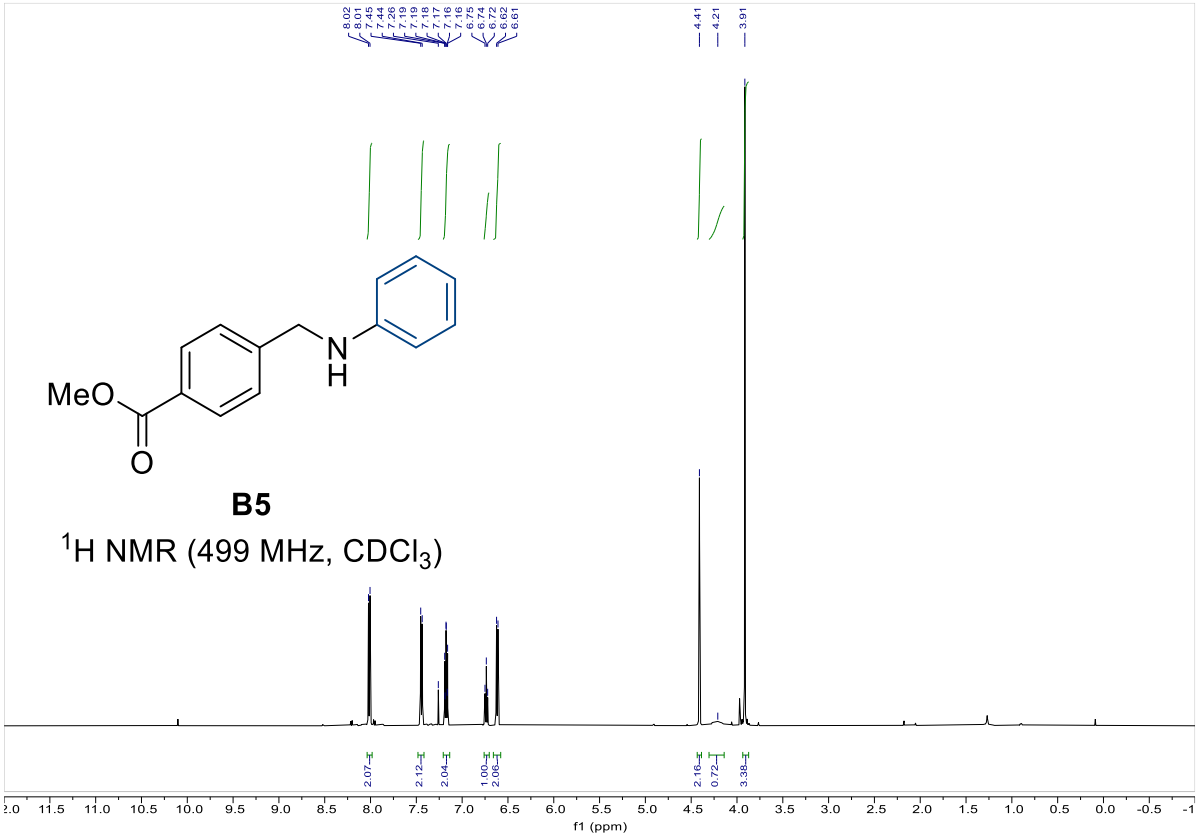
B3

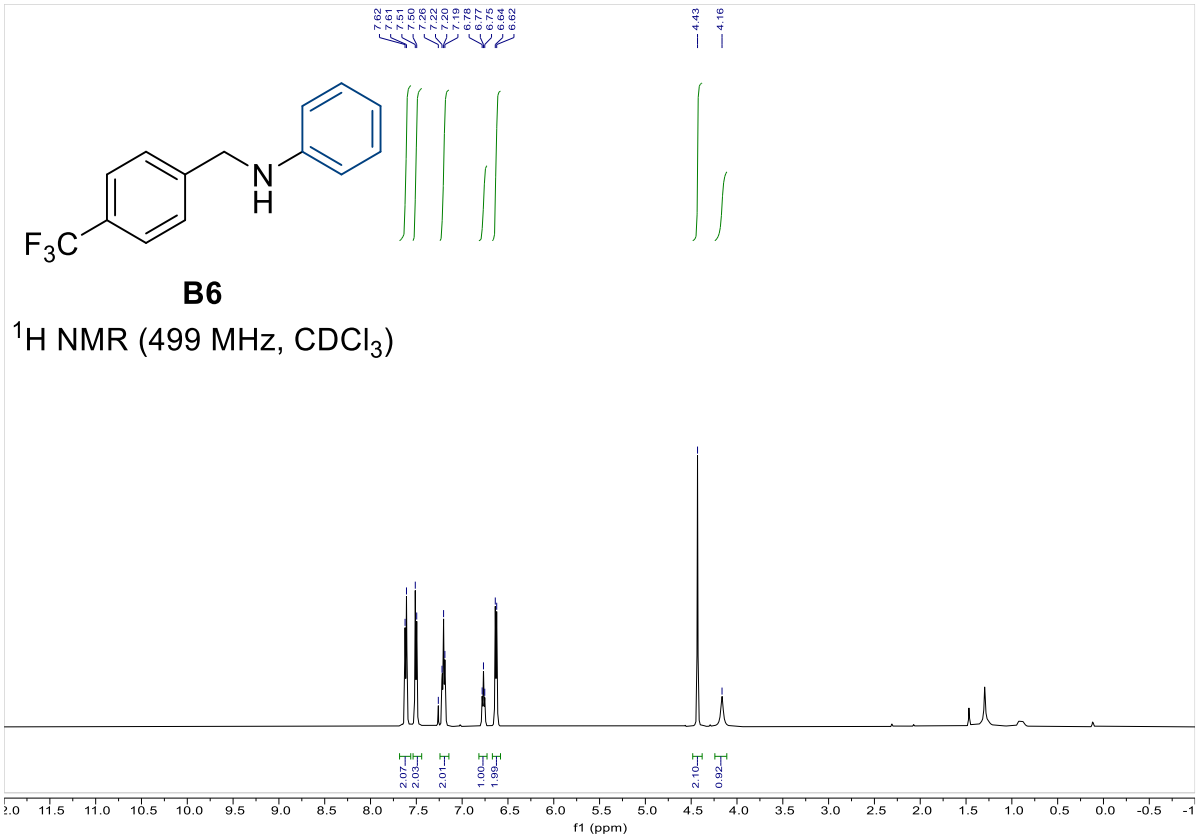
^{1}H NMR (499 MHz, $CDCl_3$)

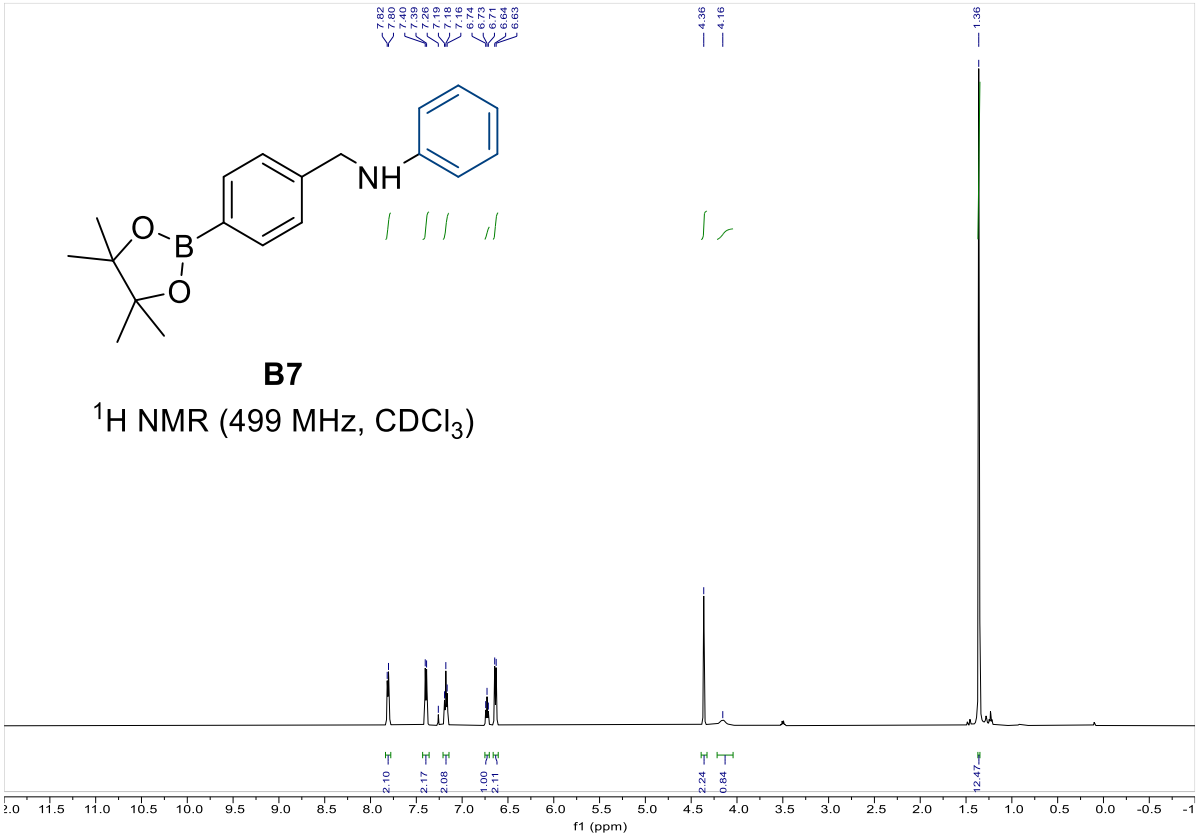


B4

^{1}H NMR (300 MHz, $CDCl_3$)

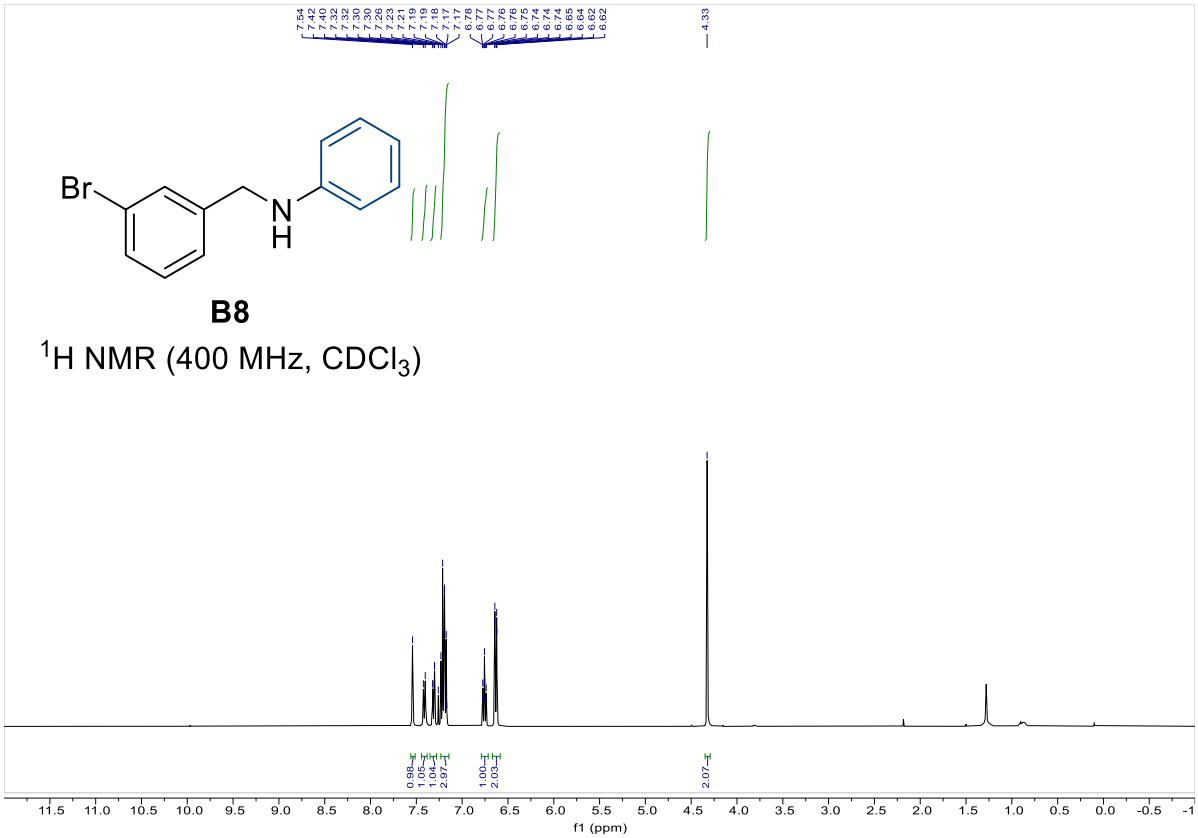

MeO
O
N
H
B5
1H NMR (499 MHz, CDCl3)
f1 (ppm)


F3C
N
H
B6
1H NMR (499 MHz, CDCl3)
f1 (ppm)



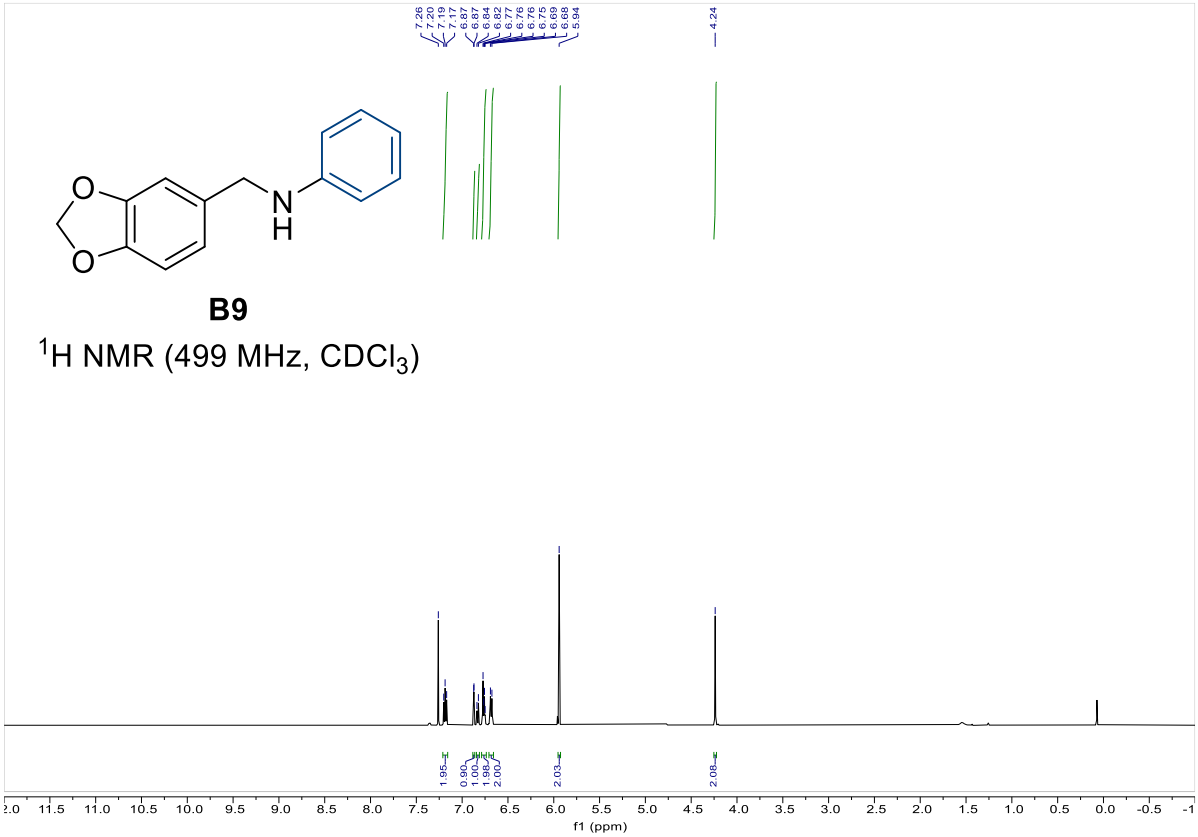
B7

^{1}H NMR (499 MHz, $CDCl_3$)



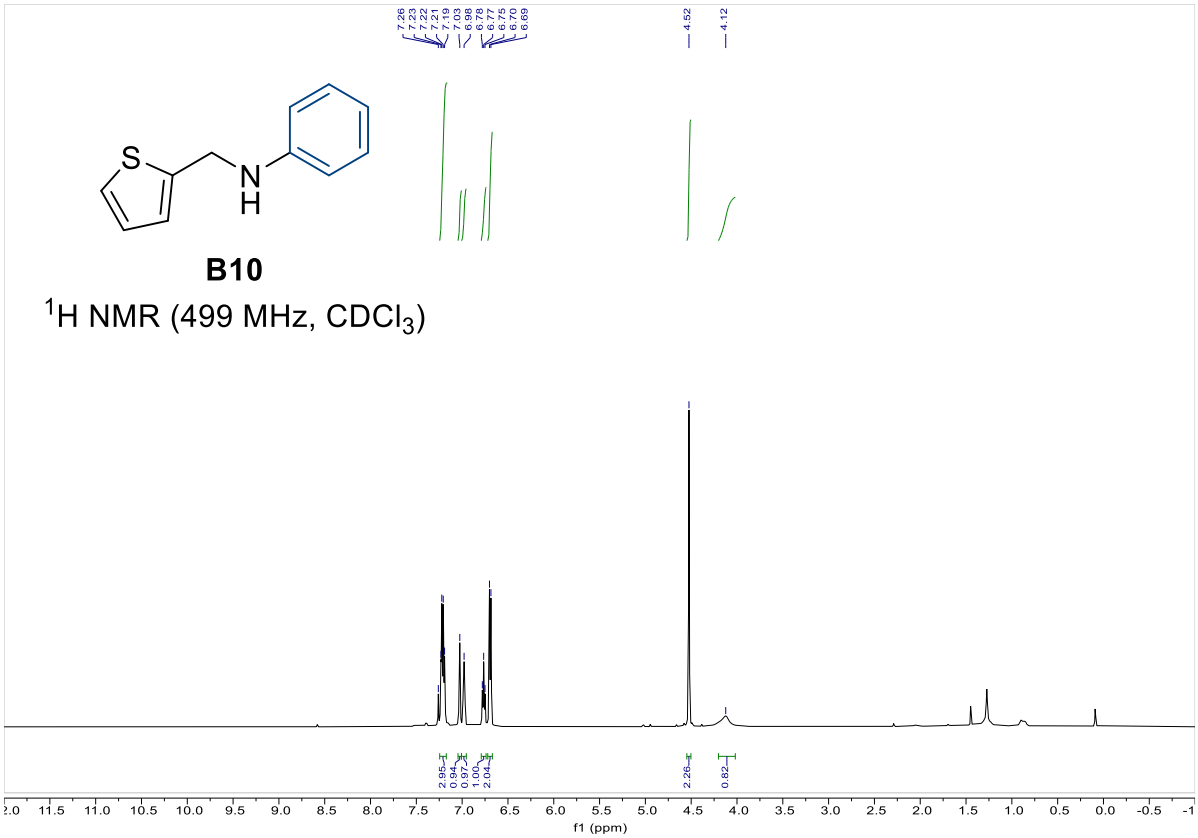
B8

^{1}H NMR (400 MHz, $CDCl_3$)



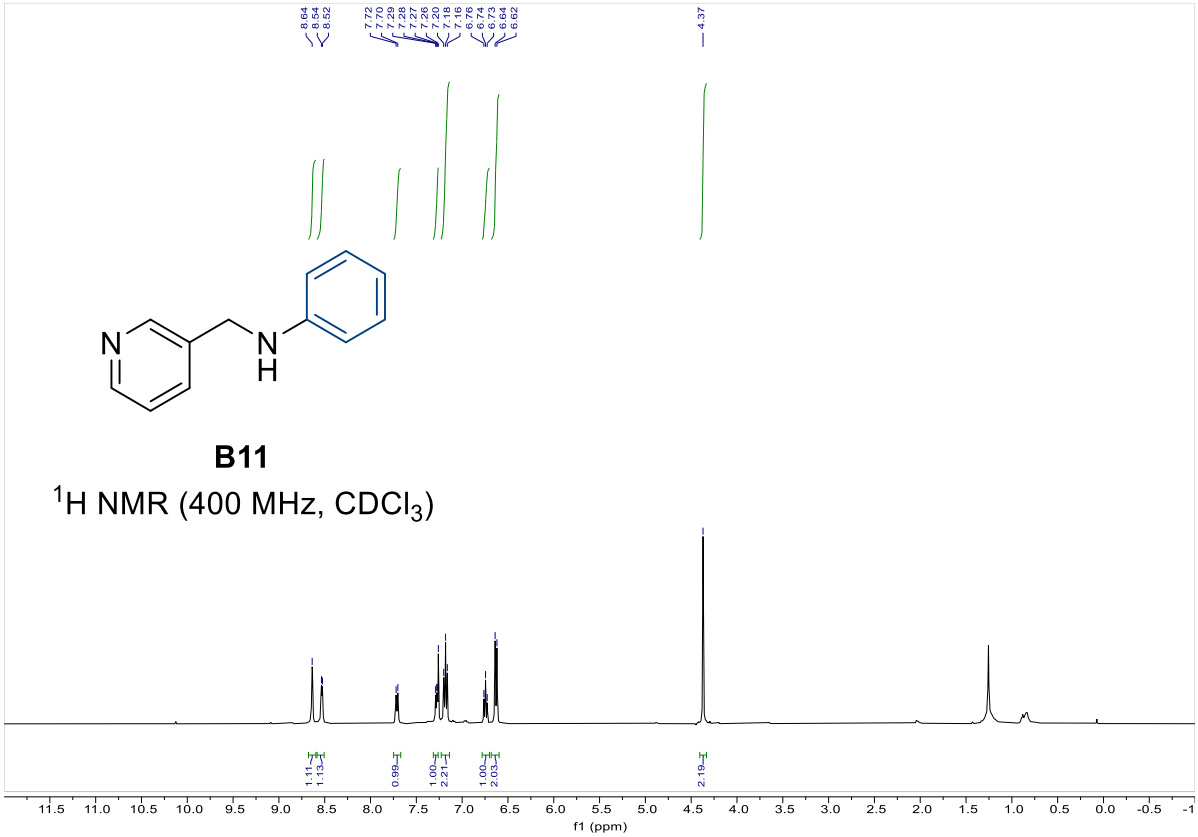
B9

^{1}H NMR (499 MHz, $CDCl_3$)



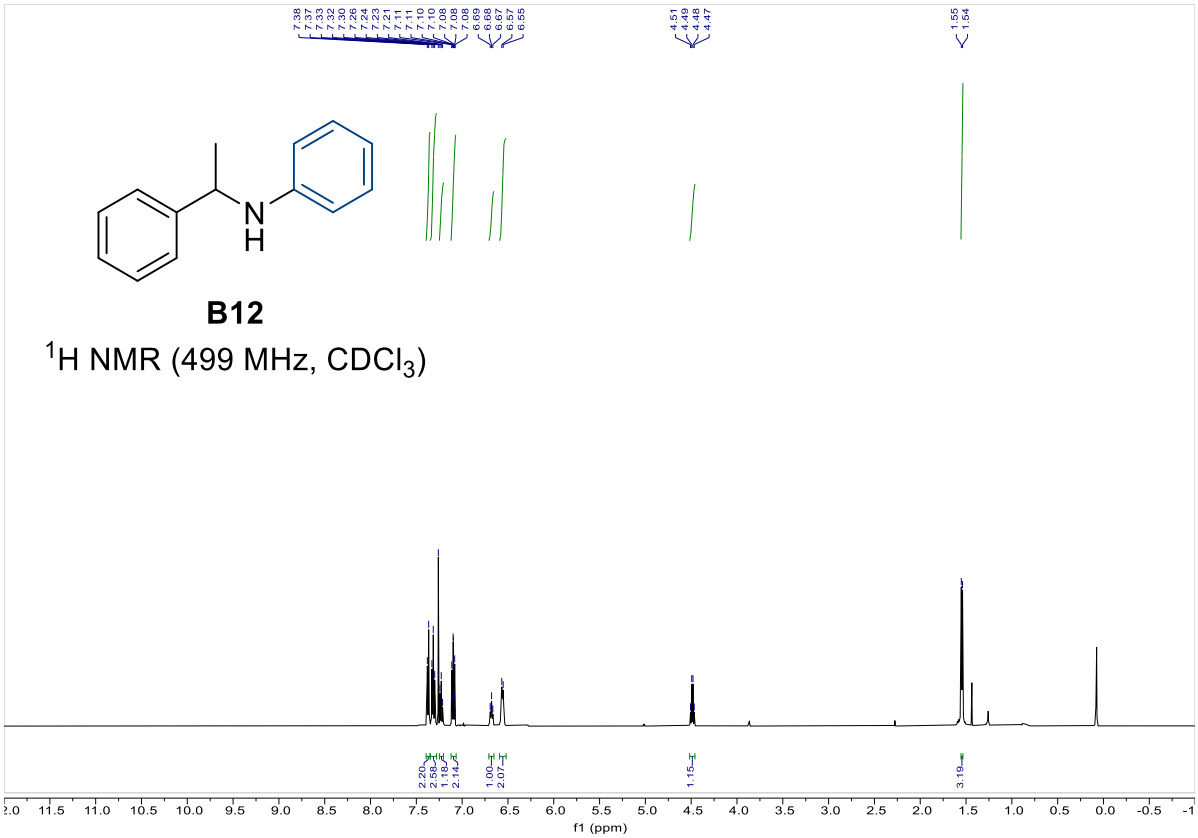
B10

^{1}H NMR (499 MHz, $CDCl_3$)



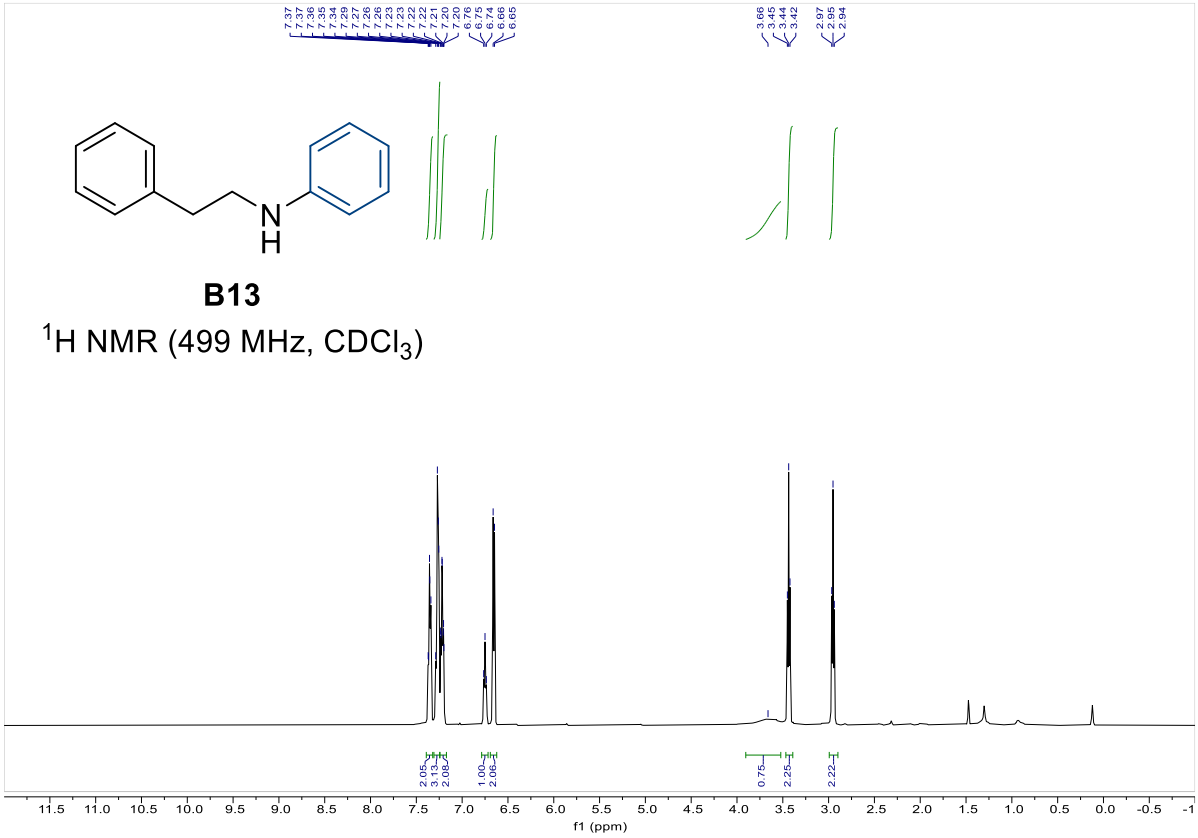
B11

^{1}H NMR (400 MHz, $CDCl_3$)



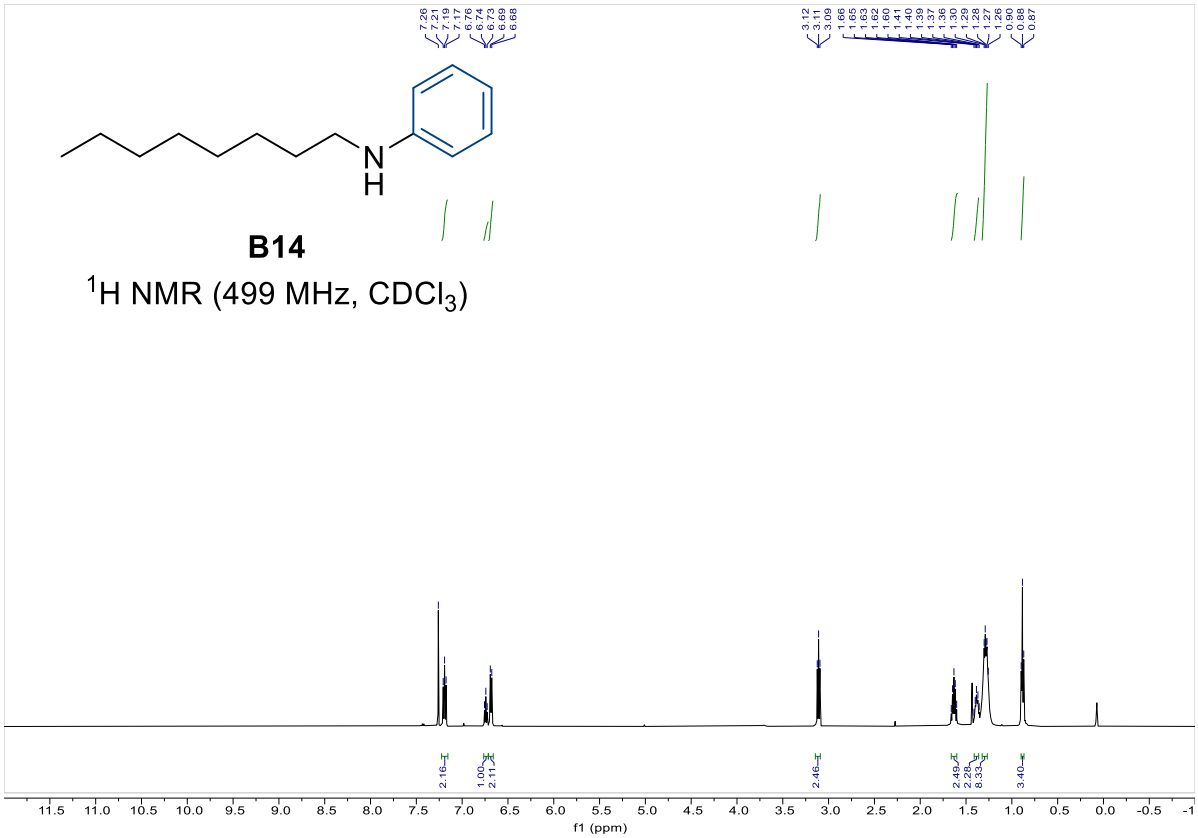
B12

^{1}H NMR (499 MHz, $CDCl_3$)



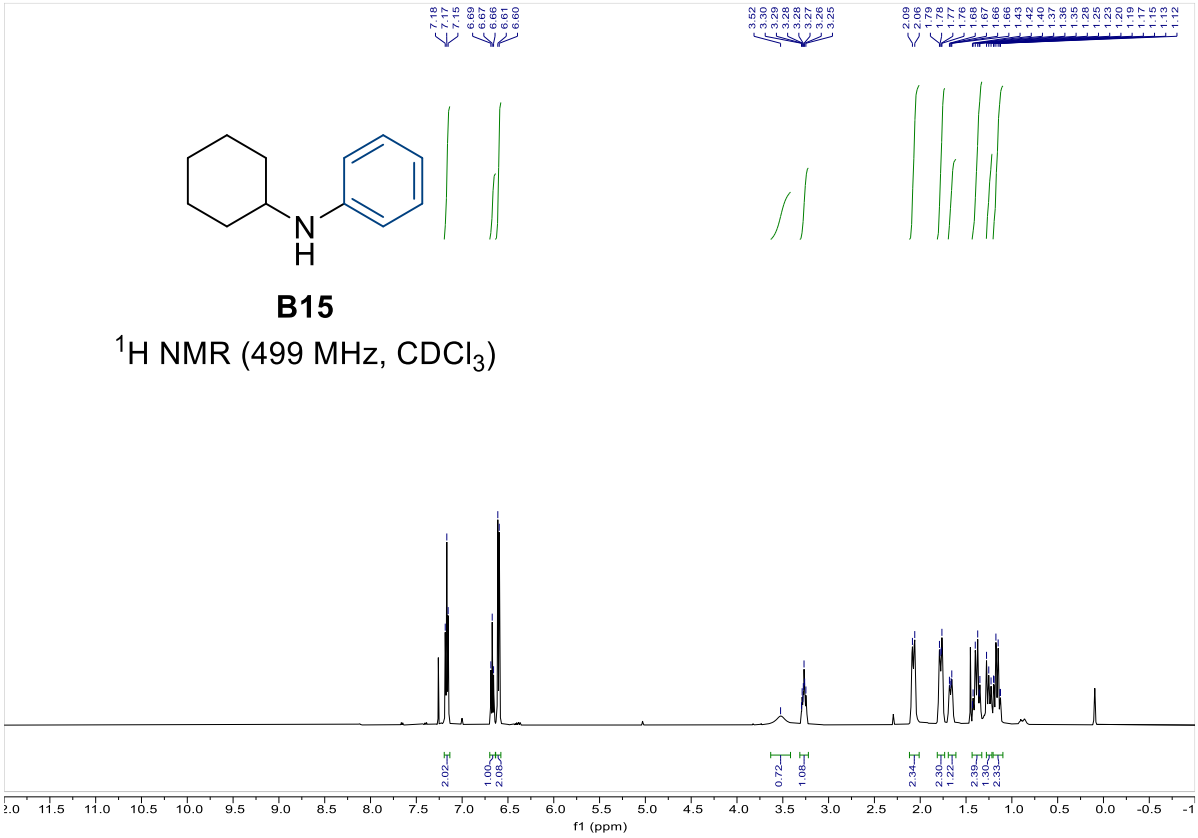
B13

^{1}H NMR (499 MHz, $CDCl_3$)



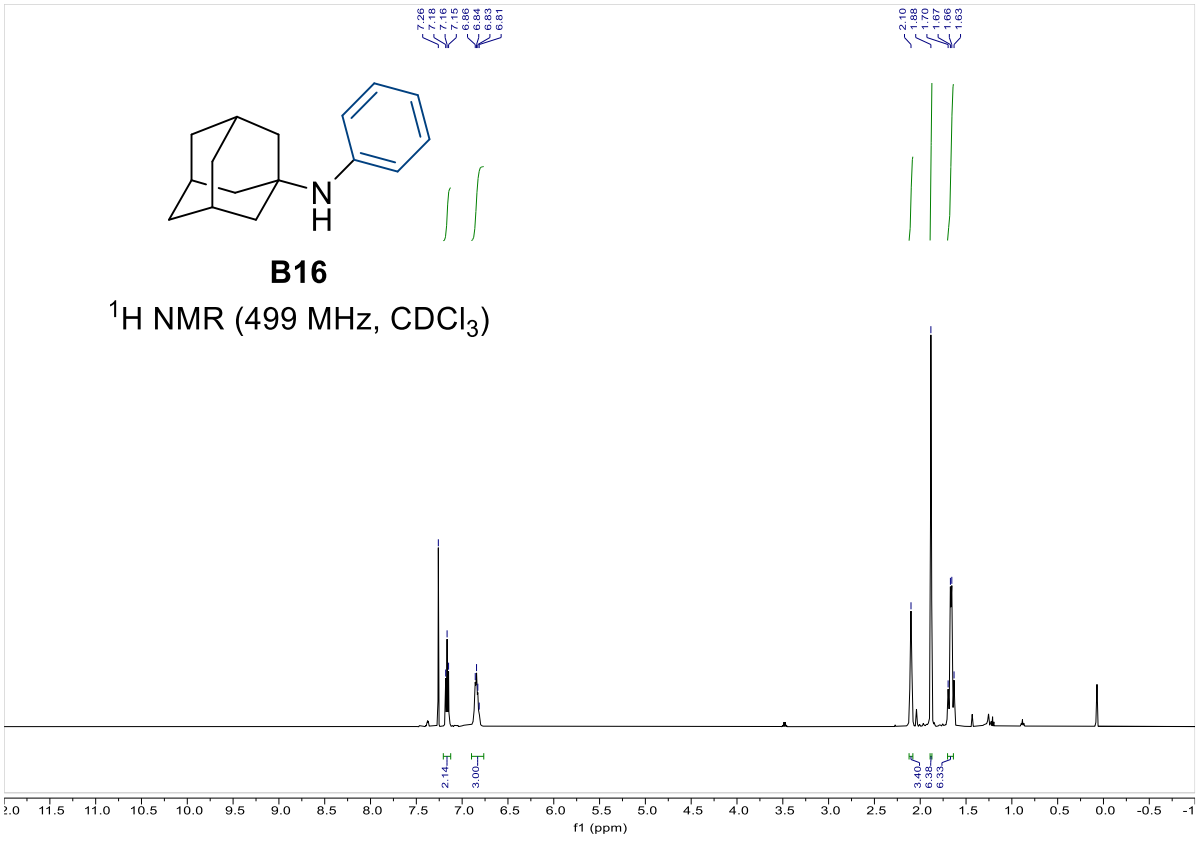
B14

^{1}H NMR (499 MHz, $CDCl_3$)



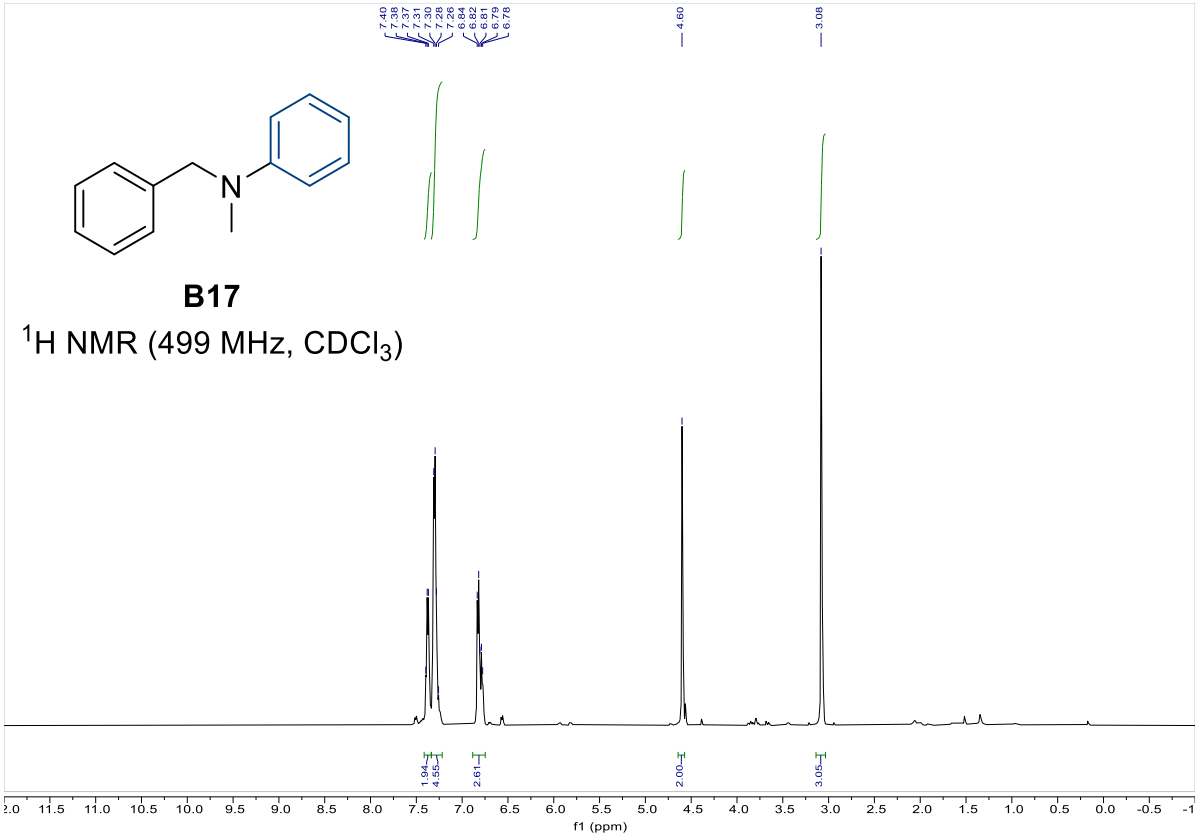
B15

^{1}H NMR (499 MHz, $CDCl_3$)



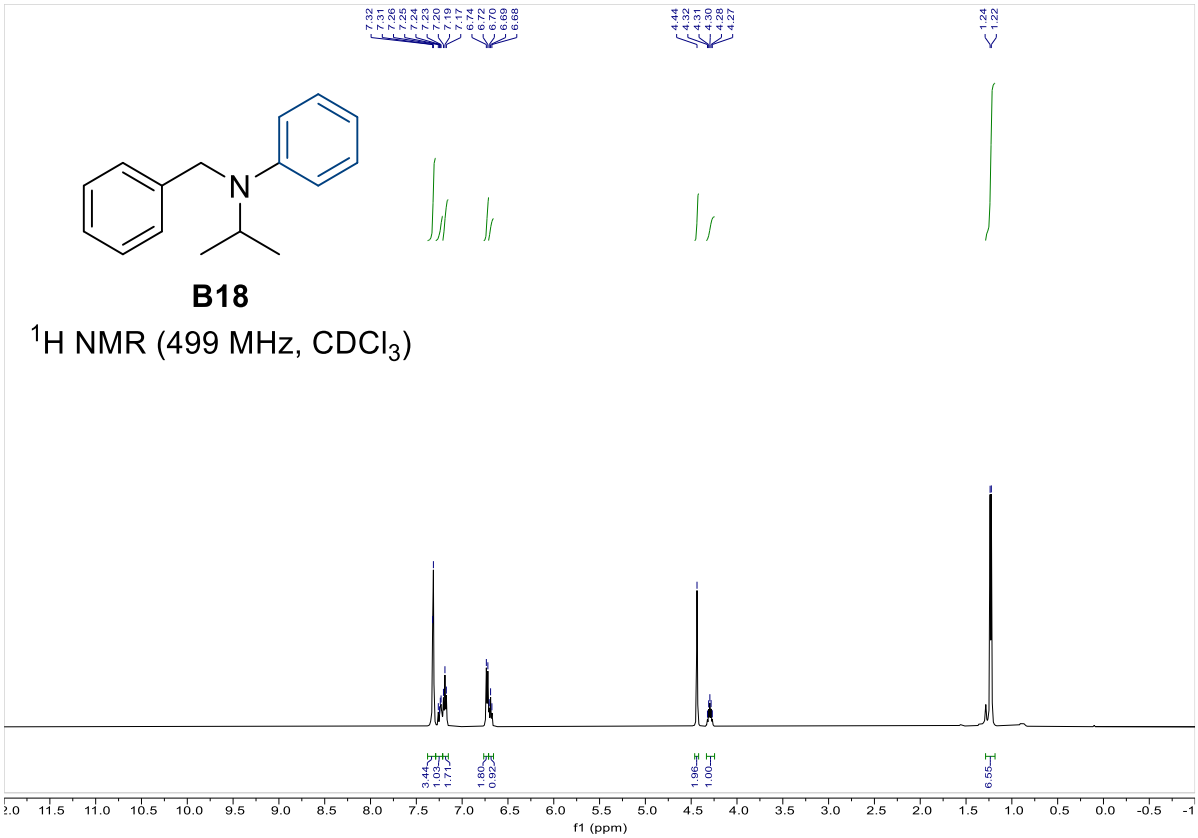
B16

^{1}H NMR (499 MHz, $CDCl_3$)



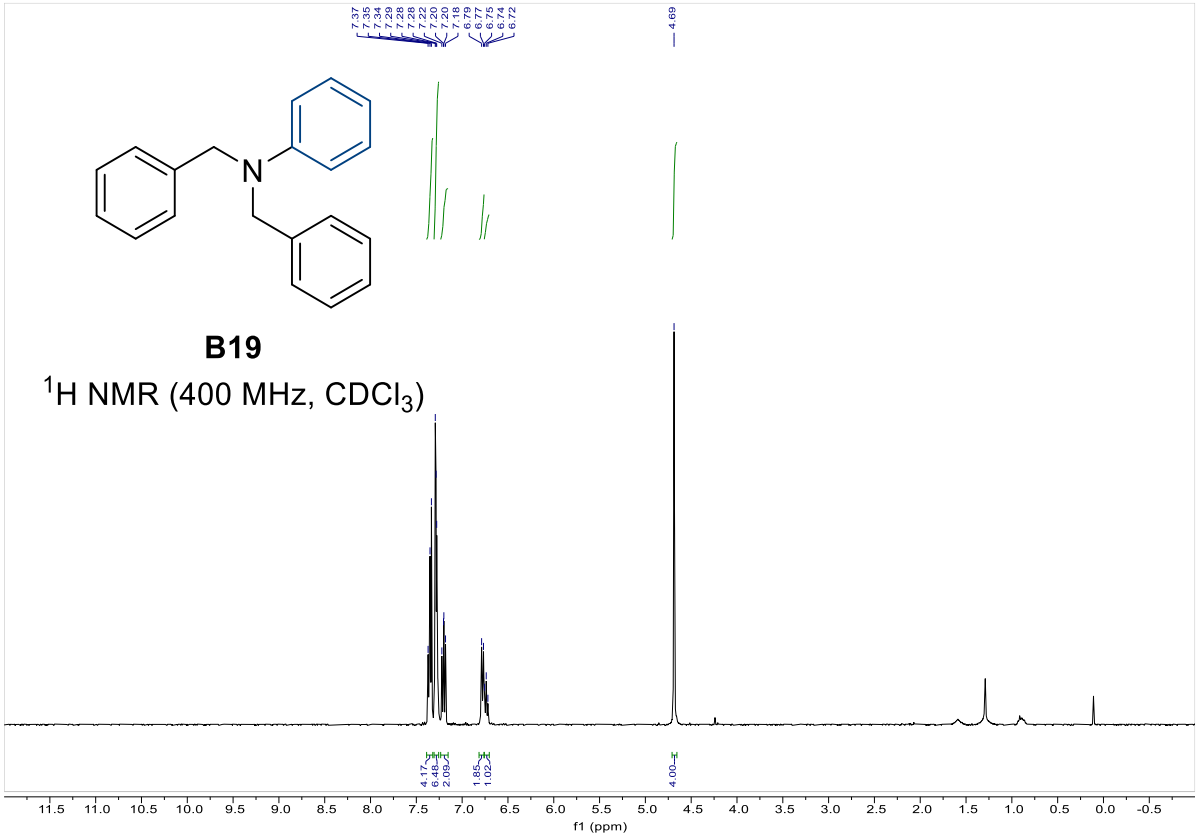
B17

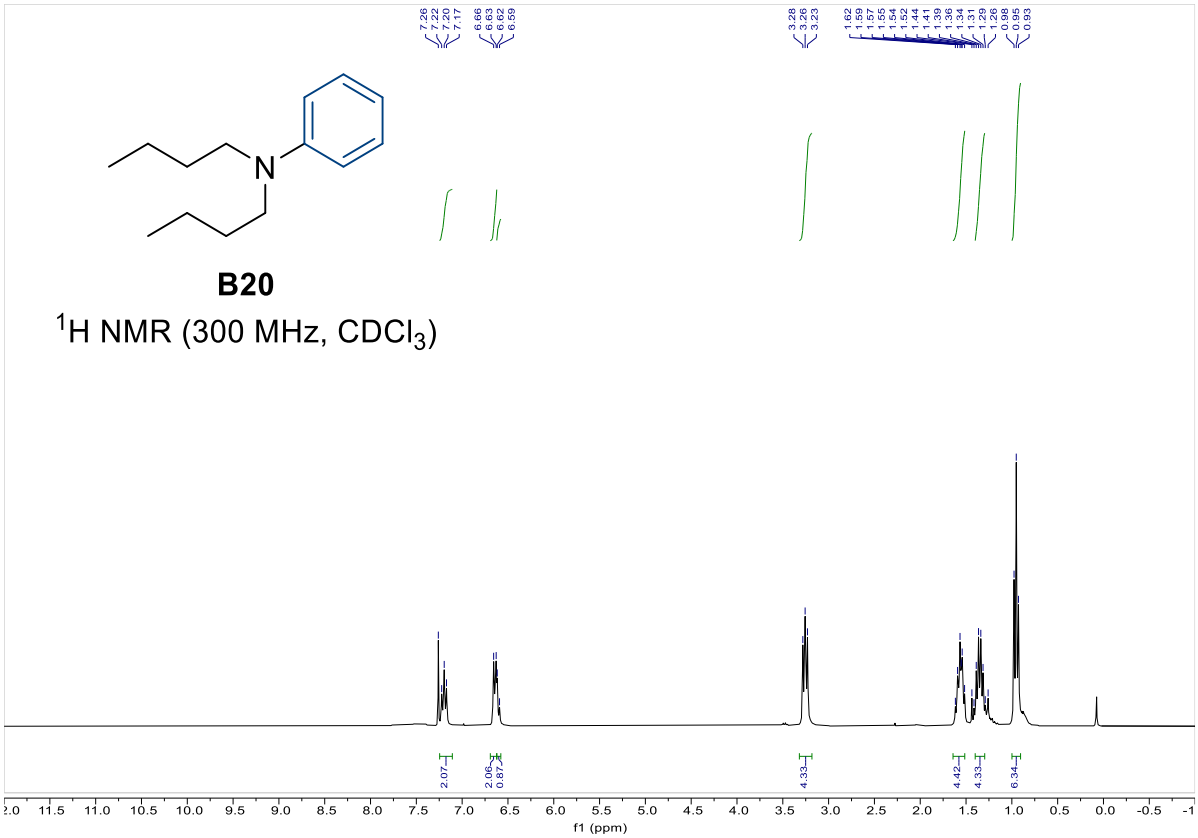
^{1}H NMR (499 MHz, $CDCl_3$)

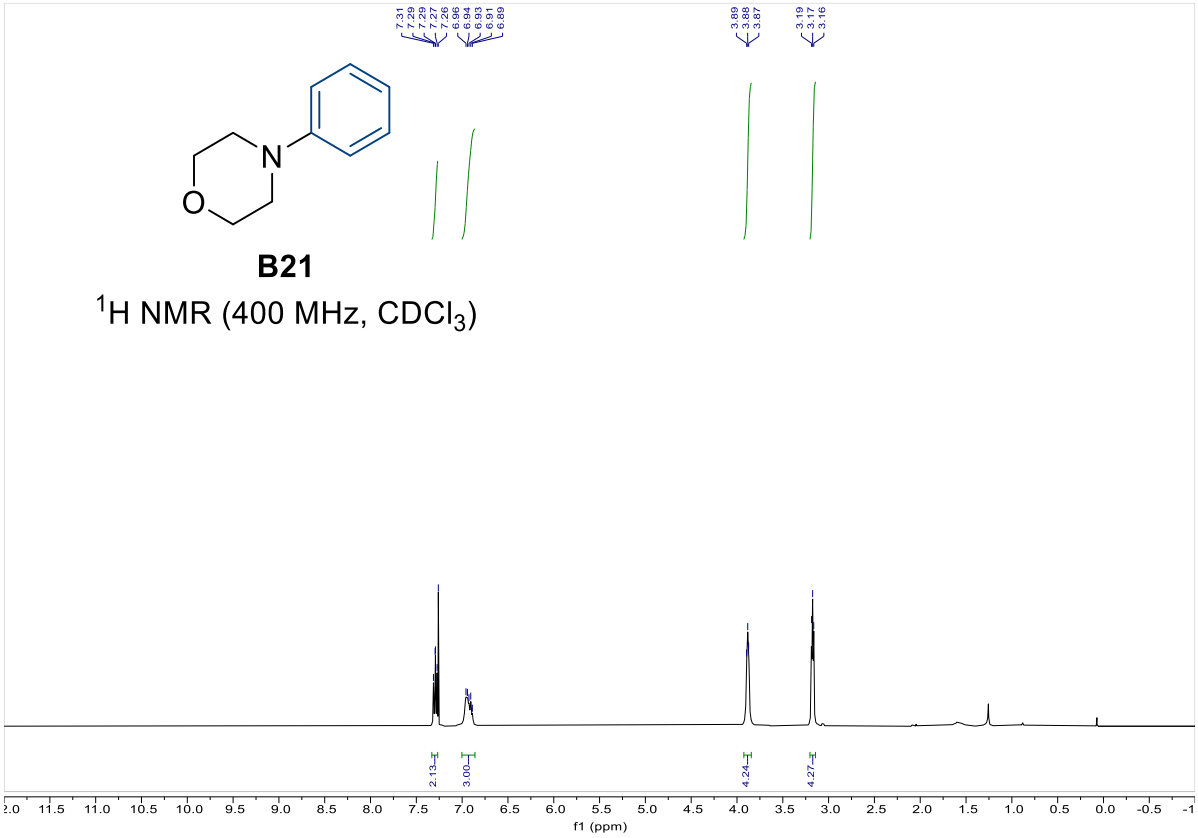


B18

^{1}H NMR (499 MHz, $CDCl_3$)

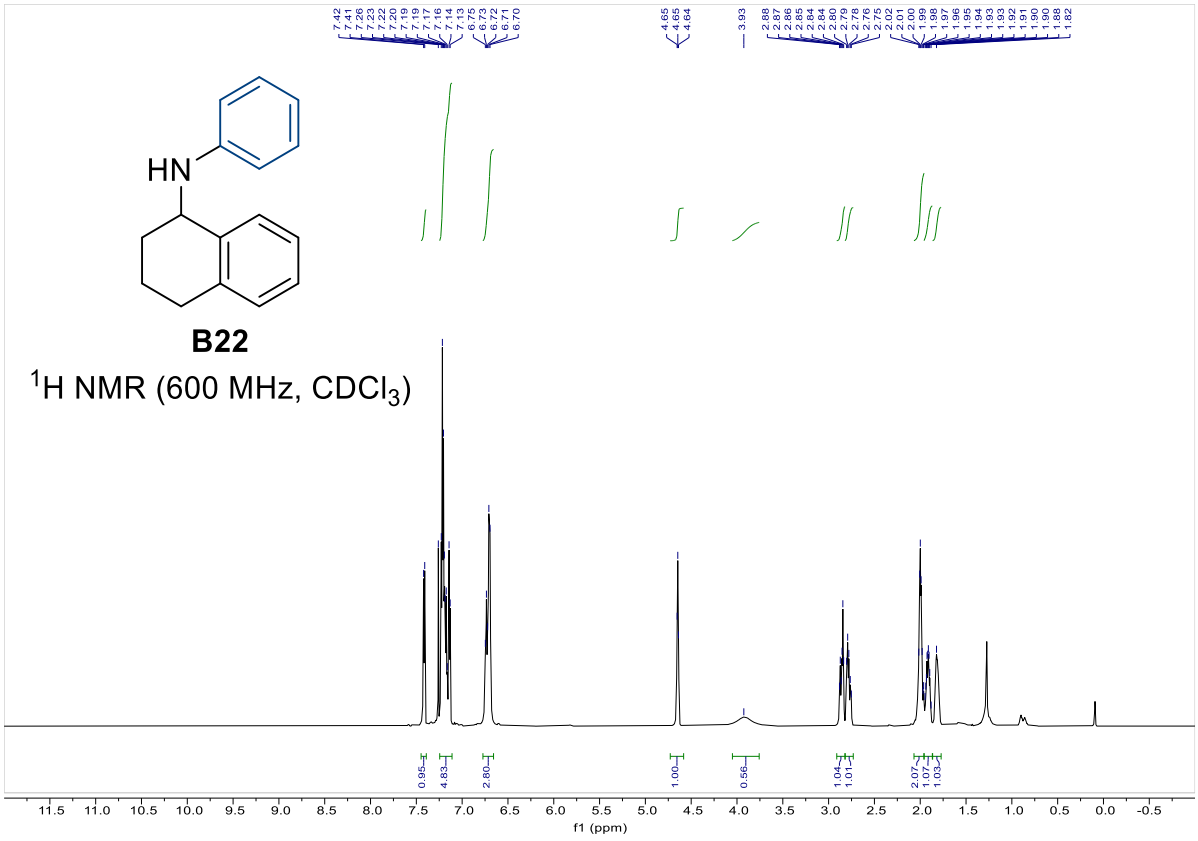

N
B19
1H NMR (400 MHz, CDCl3)
f1 (ppm)


N
B20
1H NMR (300 MHz, CDCl3)
f1 (ppm)



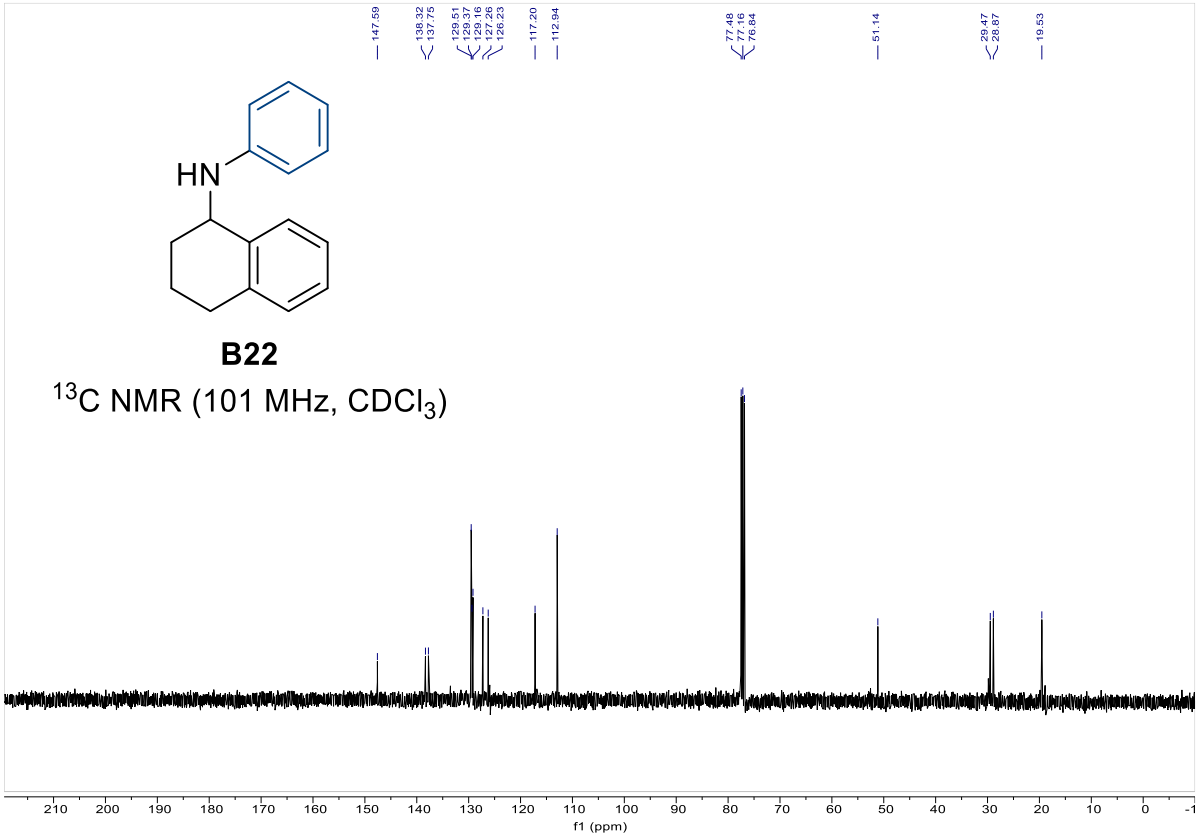
B21

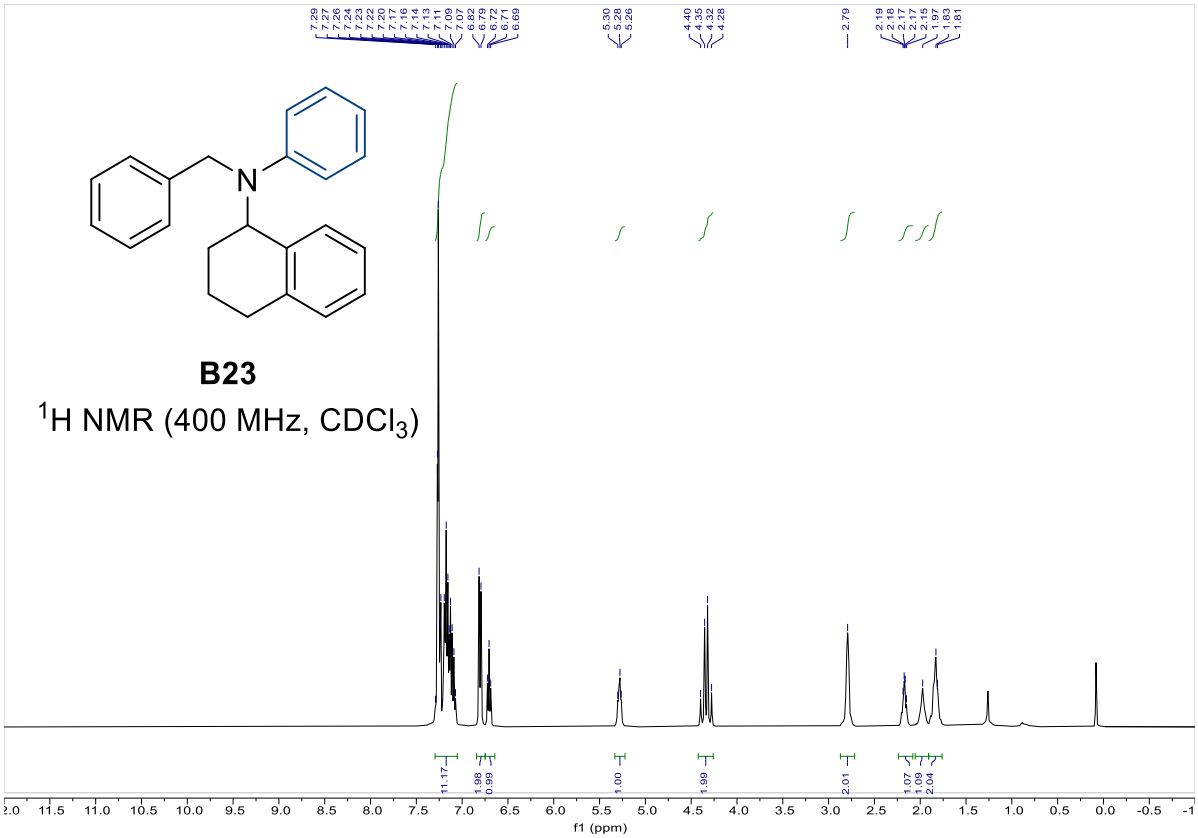
^{1}H NMR (400 MHz, $CDCl_3$)

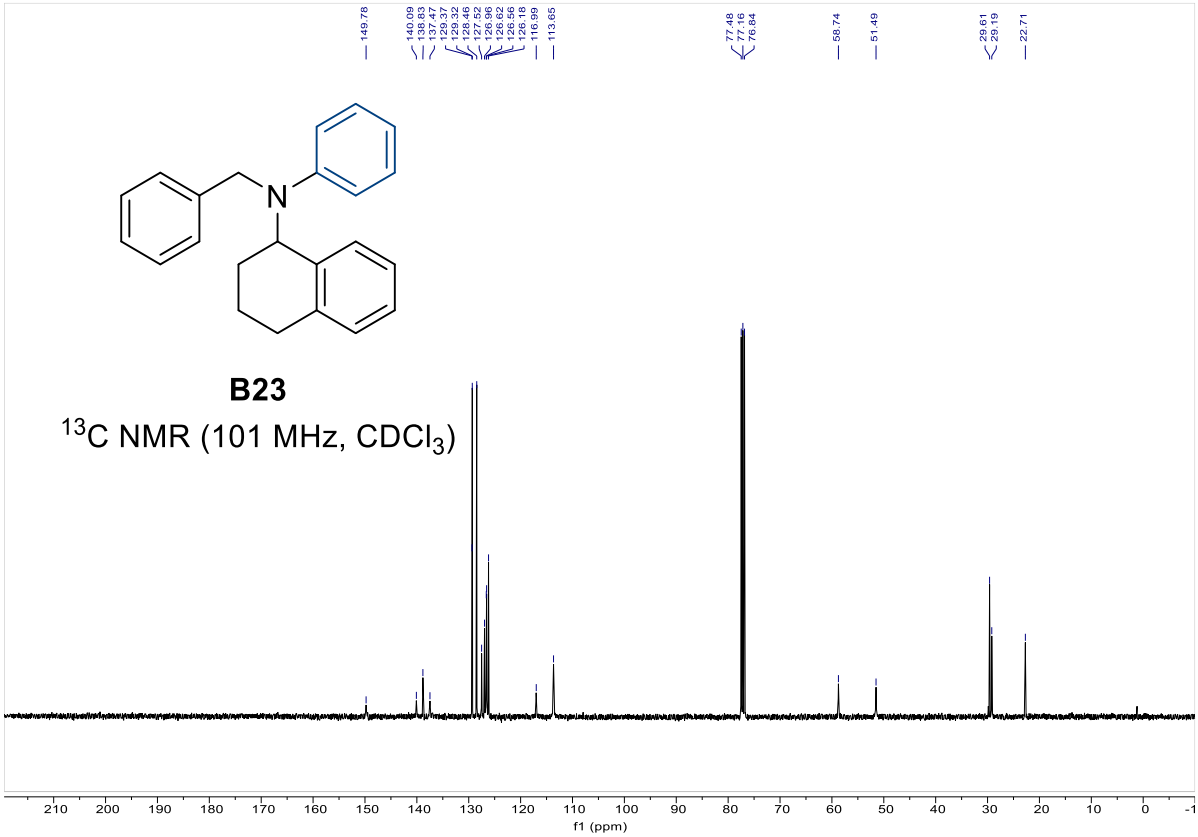


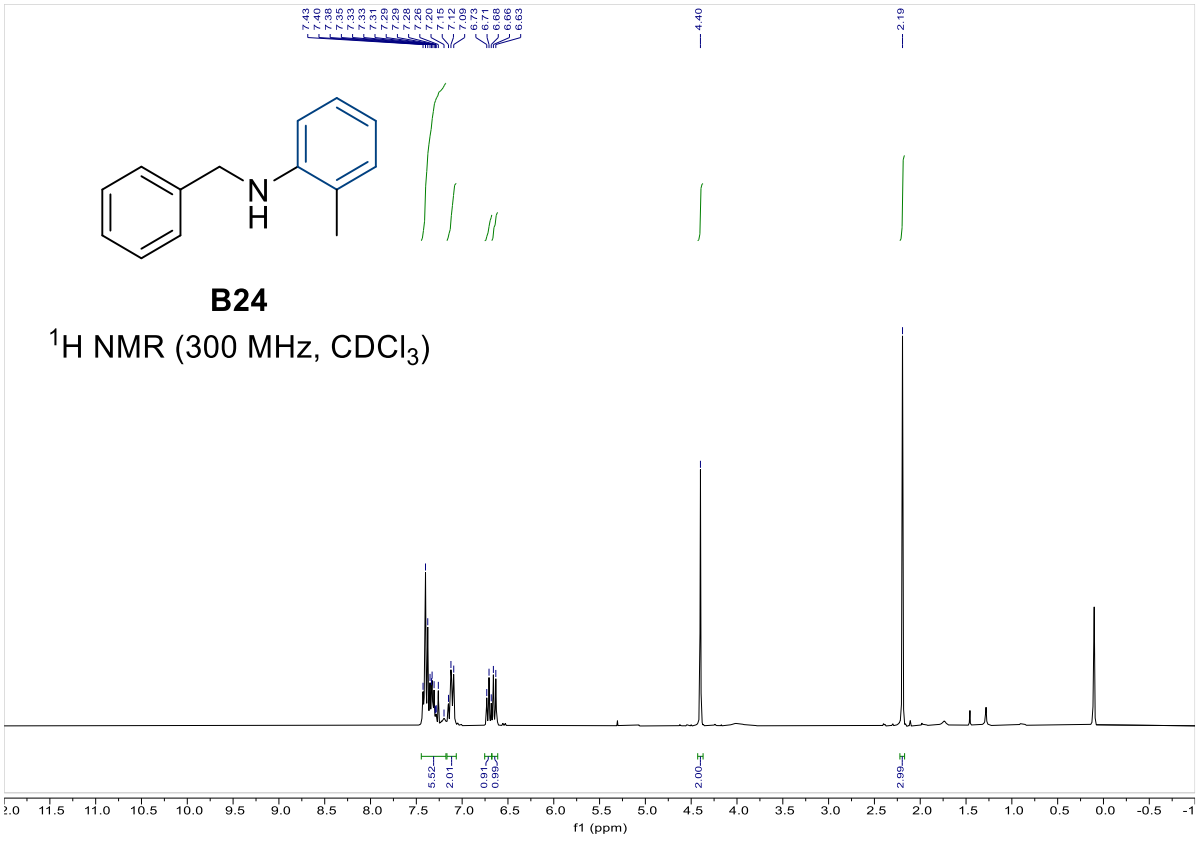
B22

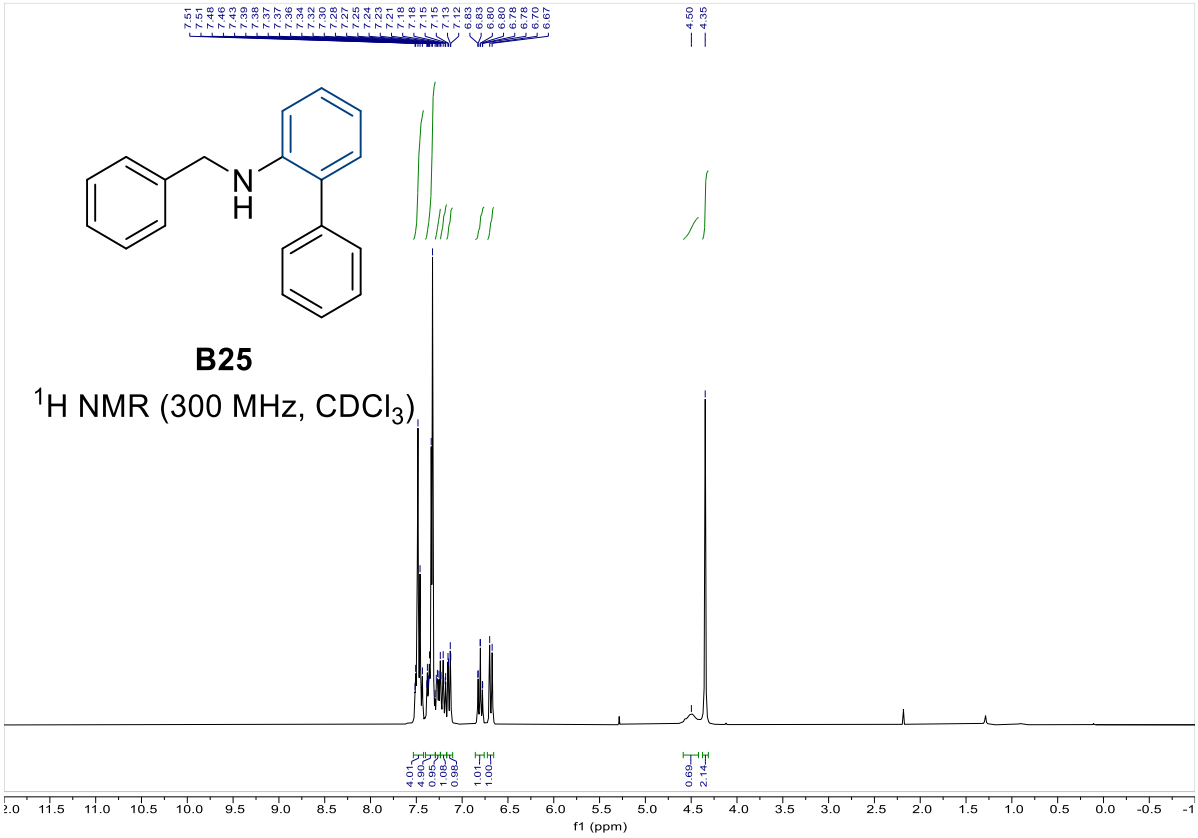
^{1}H NMR (600 MHz, $CDCl_3$)


147.59
138.32
137.75
129.51
129.37
129.16
127.26
126.23
117.20
112.94
77.48
77.16
76.84
51.14
29.47
28.87
19.53
HN
B22
13C NMR (101 MHz, CDCl3)
f1 (ppm)


7.29
7.27
7.26
7.24
7.23
7.22
7.20
7.17
7.16
7.14
7.13
7.11
7.09
7.07
6.92
6.89
6.72
6.71
6.69
5.30
5.28
5.26
4.40
4.35
4.32
4.28
2.79
2.19
2.18
2.17
2.17
2.15
1.97
1.83
1.81
N
B23
1H NMR (400 MHz, CDCl3)
11.17
1.98
0.99
1.00
1.99
2.01
1.07
1.09
2.04
f1 (ppm)

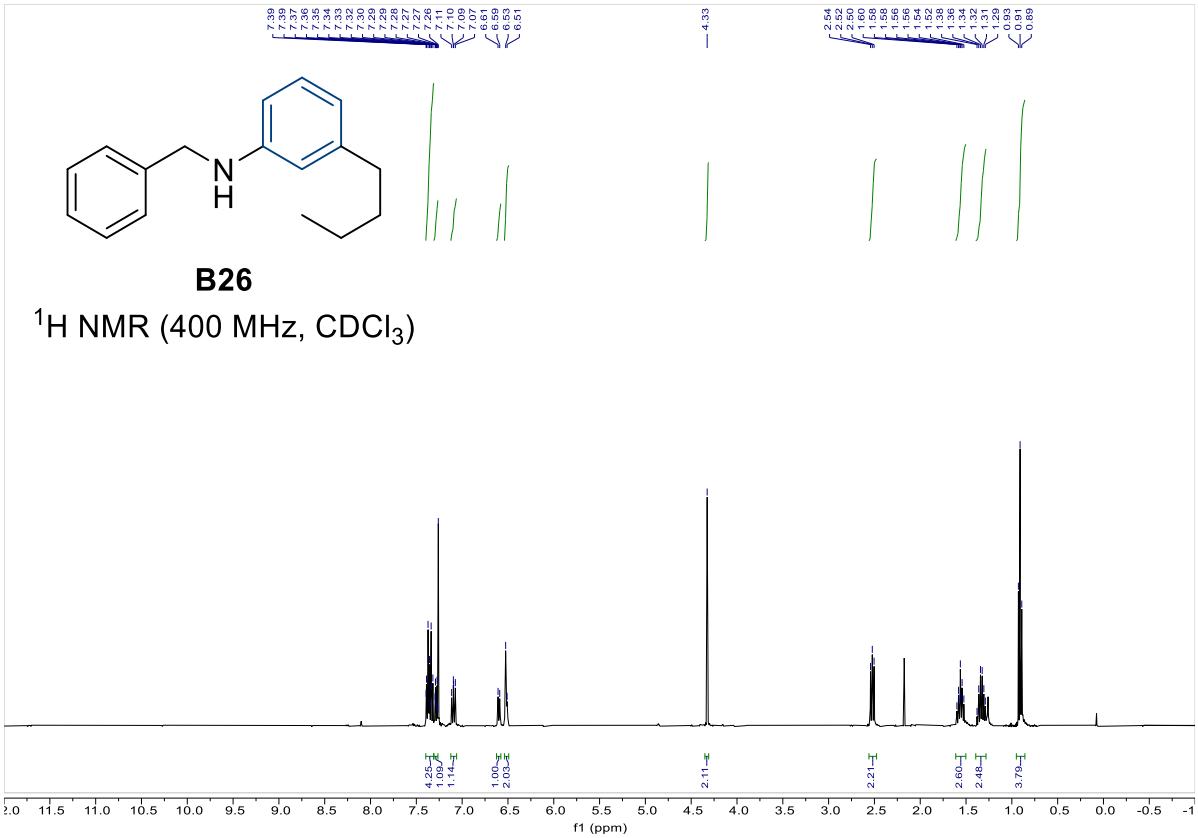

149.78
140.09
138.83
137.47
129.37
129.22
128.46
127.52
126.96
126.62
126.55
126.18
116.99
113.65
77.48
77.16
76.84
58.74
51.49
29.61
29.19
22.71
N
B23
13C NMR (101 MHz, CDCl3)
f1 (ppm)


7.43
7.40
7.38
7.35
7.33
7.31
7.29
7.28
7.26
7.20
7.15
7.12
7.09
6.73
6.71
6.68
6.66
6.63
4.40
2.19
N
H
B24
1H NMR (300 MHz, CDCl3)
5.52
2.01
0.91
0.99
2.00
2.99
f1 (ppm)



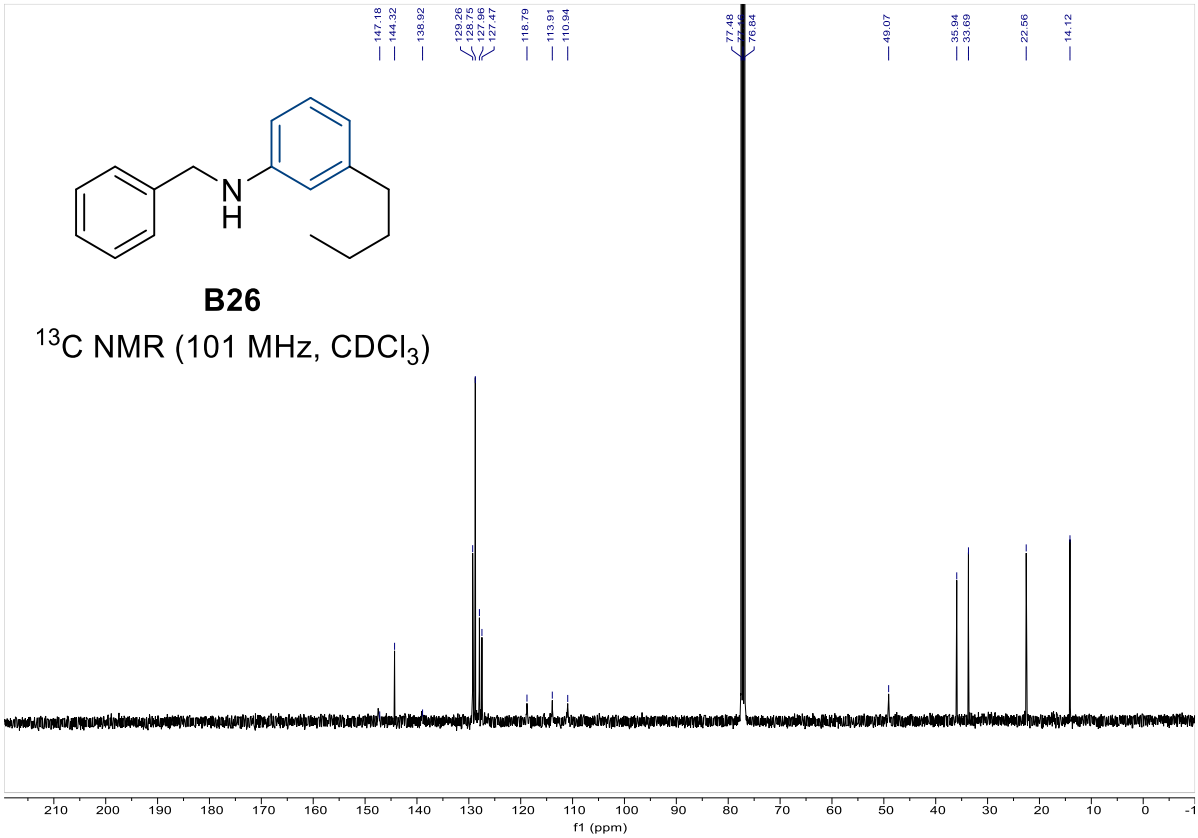
B25

^{1}H NMR (300 MHz, $CDCl_3$)



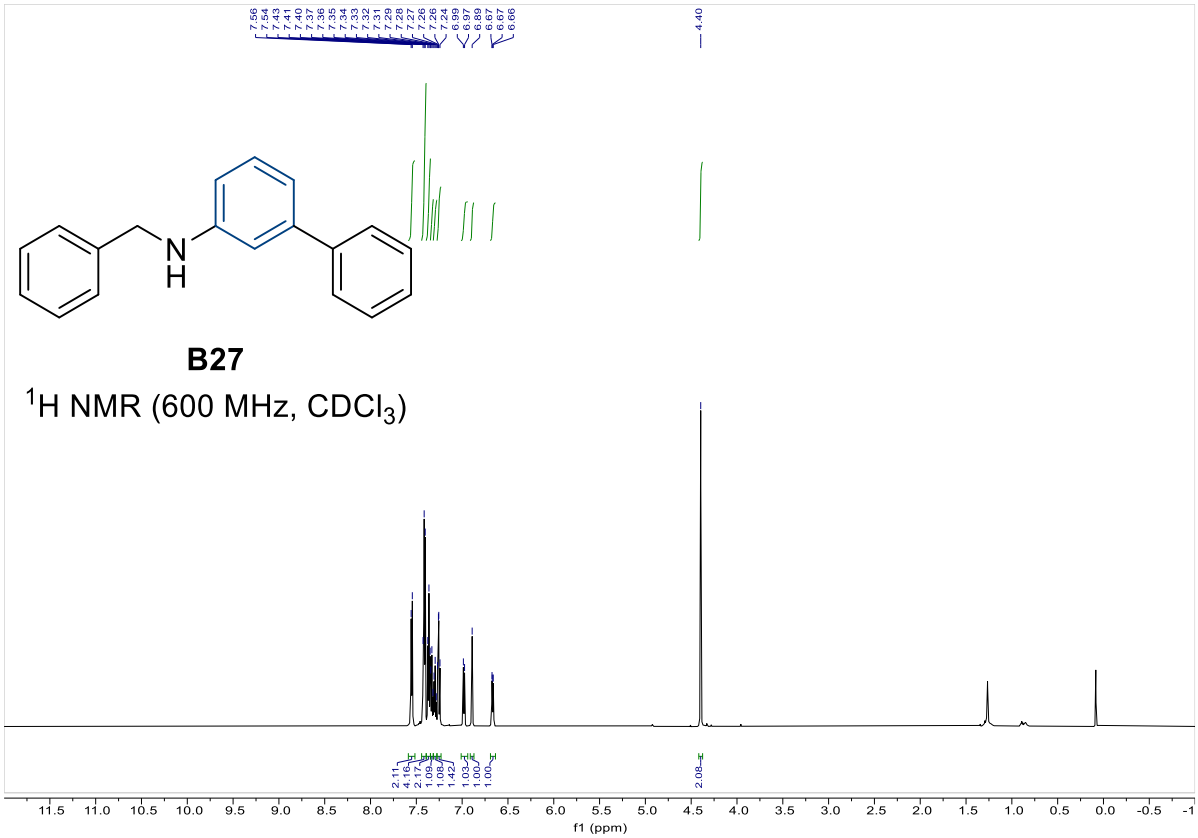
B26

^{1}H NMR (400 MHz, $CDCl_3$)



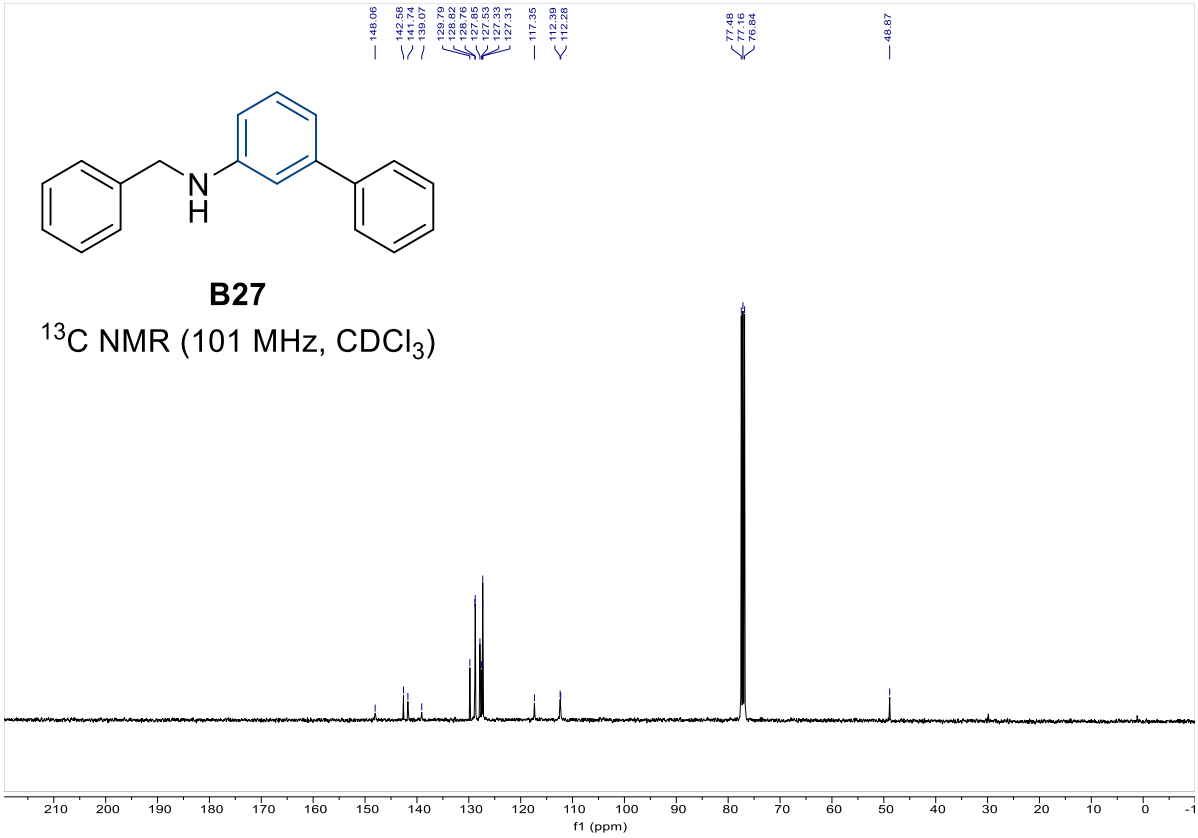
B26

^{13}C NMR (101 MHz, $CDCl_3$)



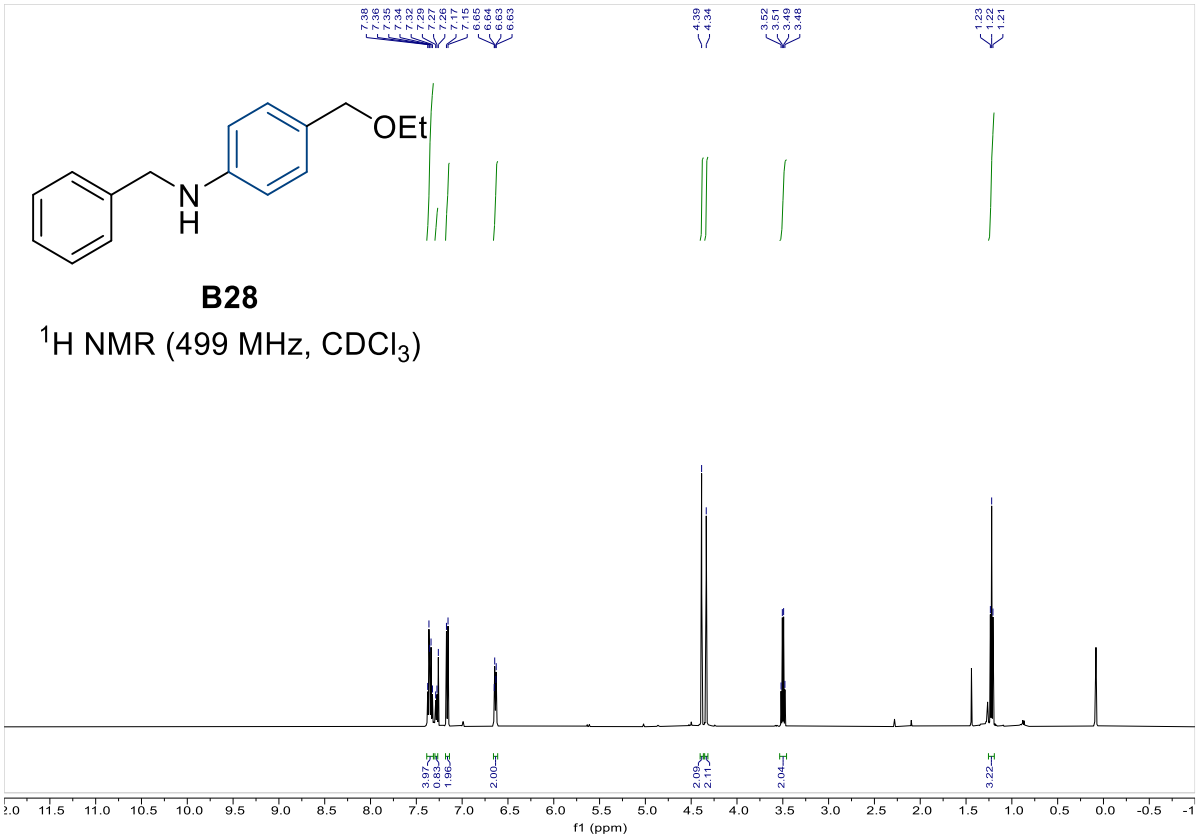
B27

^{1}H NMR (600 MHz, $CDCl_3$)



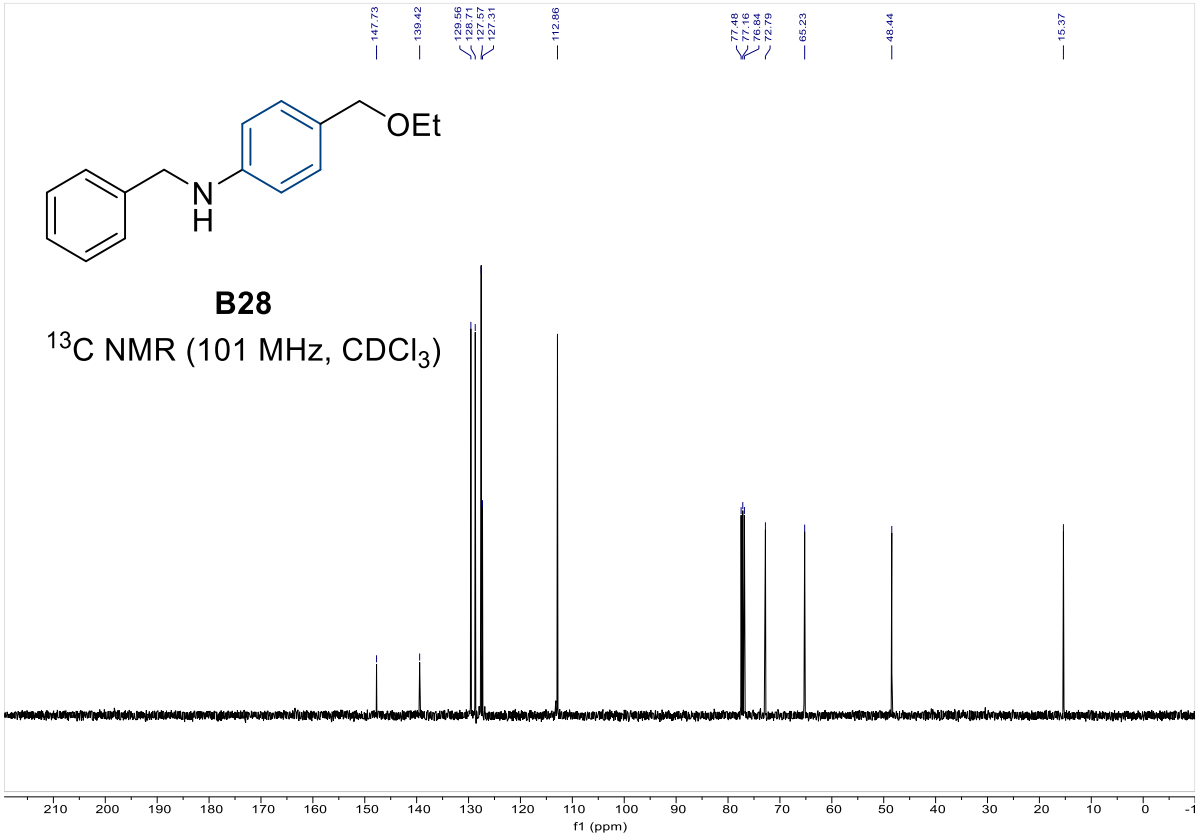
B27

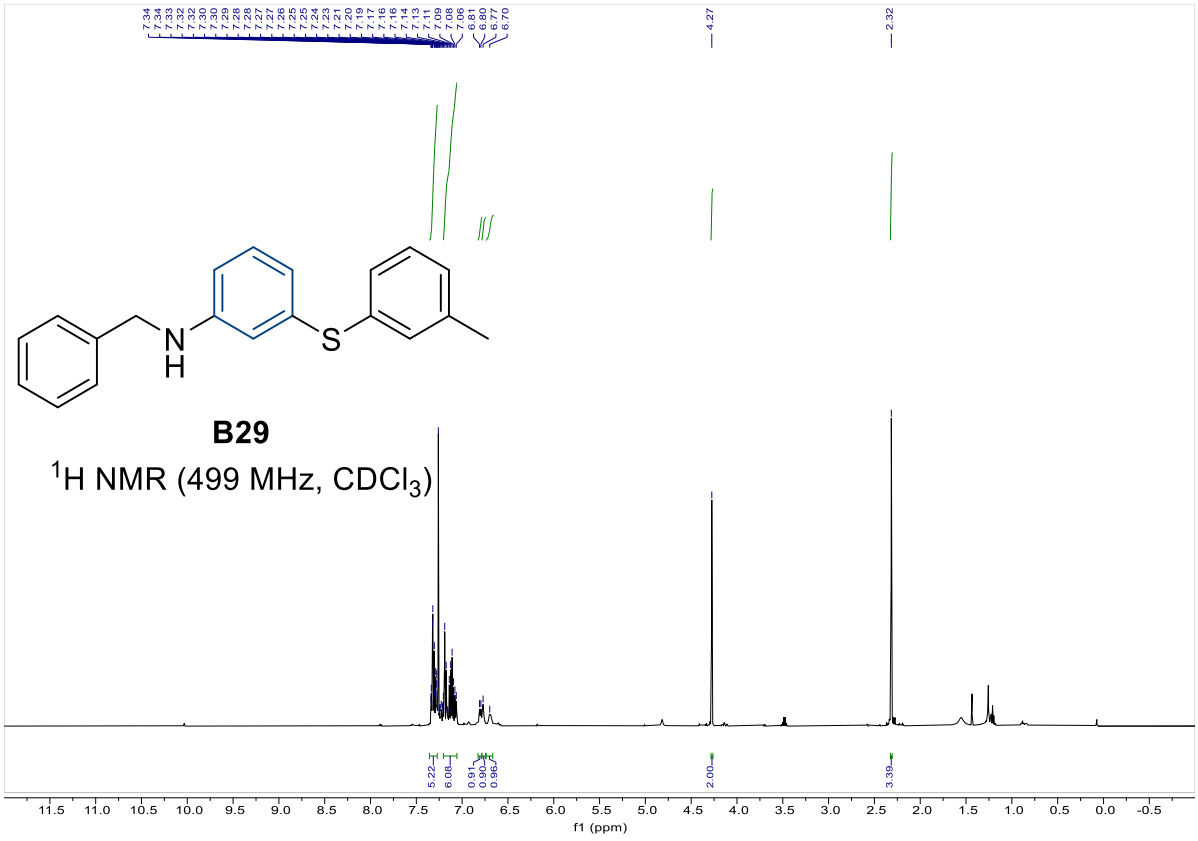
^{13}C NMR (101 MHz, $CDCl_3$)

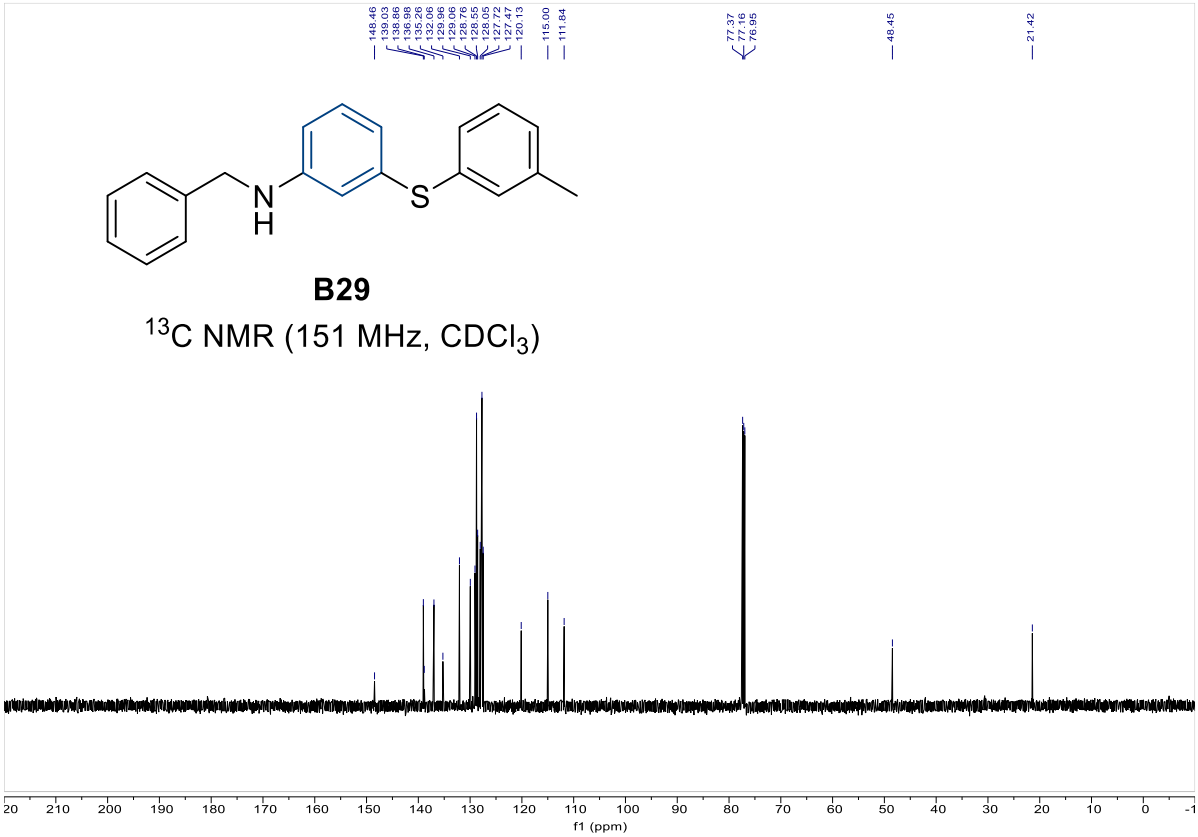


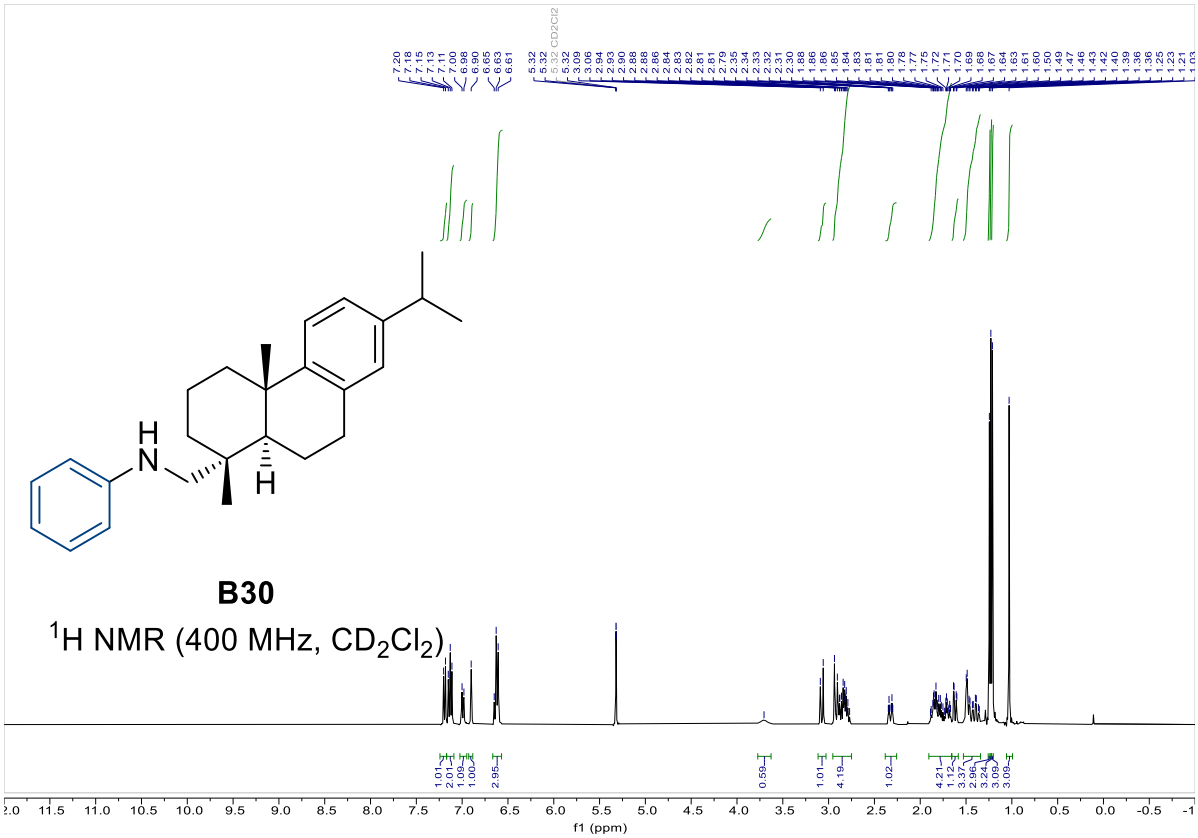
B28

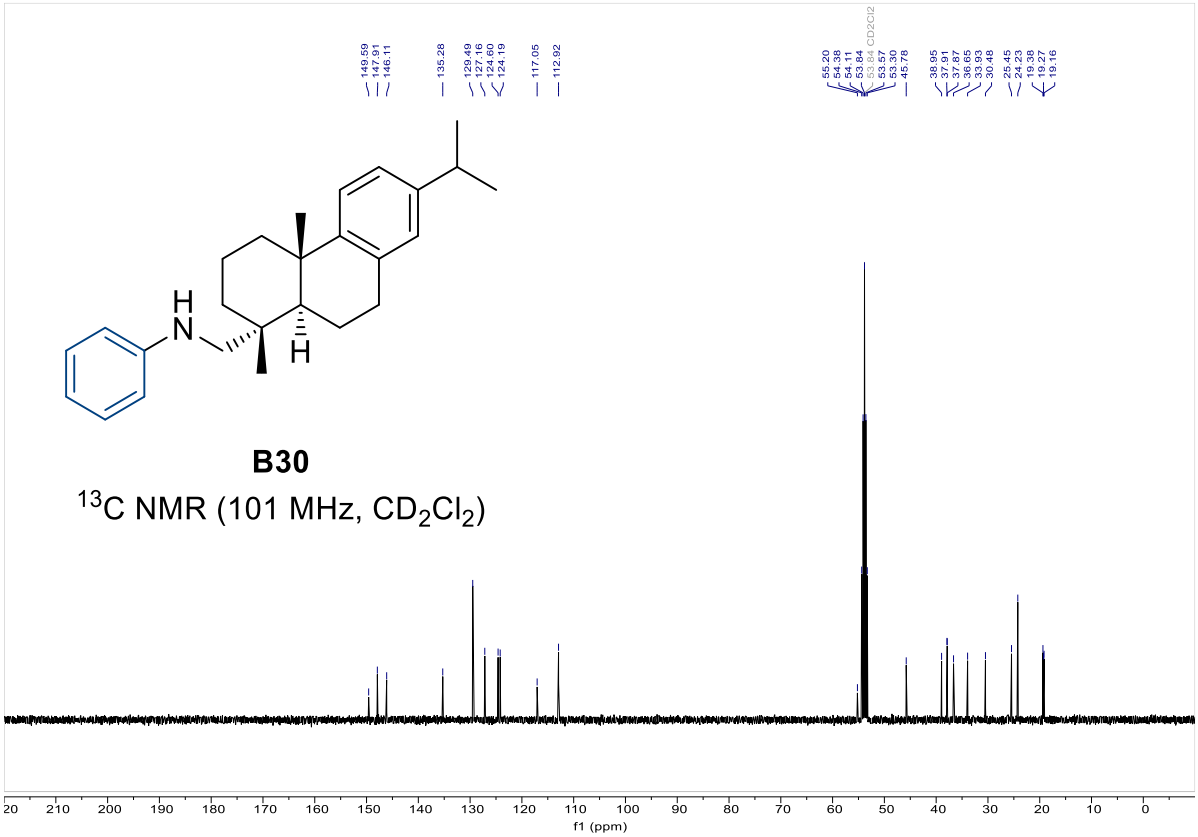
^{1}H NMR (499 MHz, $CDCl_3$)


147.73
139.42
129.56
129.11
127.57
127.31
112.86
77.48
77.16
76.84
72.79
65.23
48.44
15.37
OEt
N
H
B28
13C NMR (101 MHz, CDCl3)
f1 (ppm)


7.34
7.34
7.33
7.32
7.32
7.30
7.30
7.29
7.28
7.28
7.27
7.27
7.26
7.25
7.25
7.24
7.23
7.21
7.20
7.19
7.17
7.16
7.16
7.14
7.13
7.11
7.09
7.08
7.06
6.81
6.80
6.77
6.70
4.27
2.32
N
H
S
B29
1H NMR (499 MHz, CDCl3)
5.22
6.08
0.91
0.90
0.96
2.00
3.39
f1 (ppm)

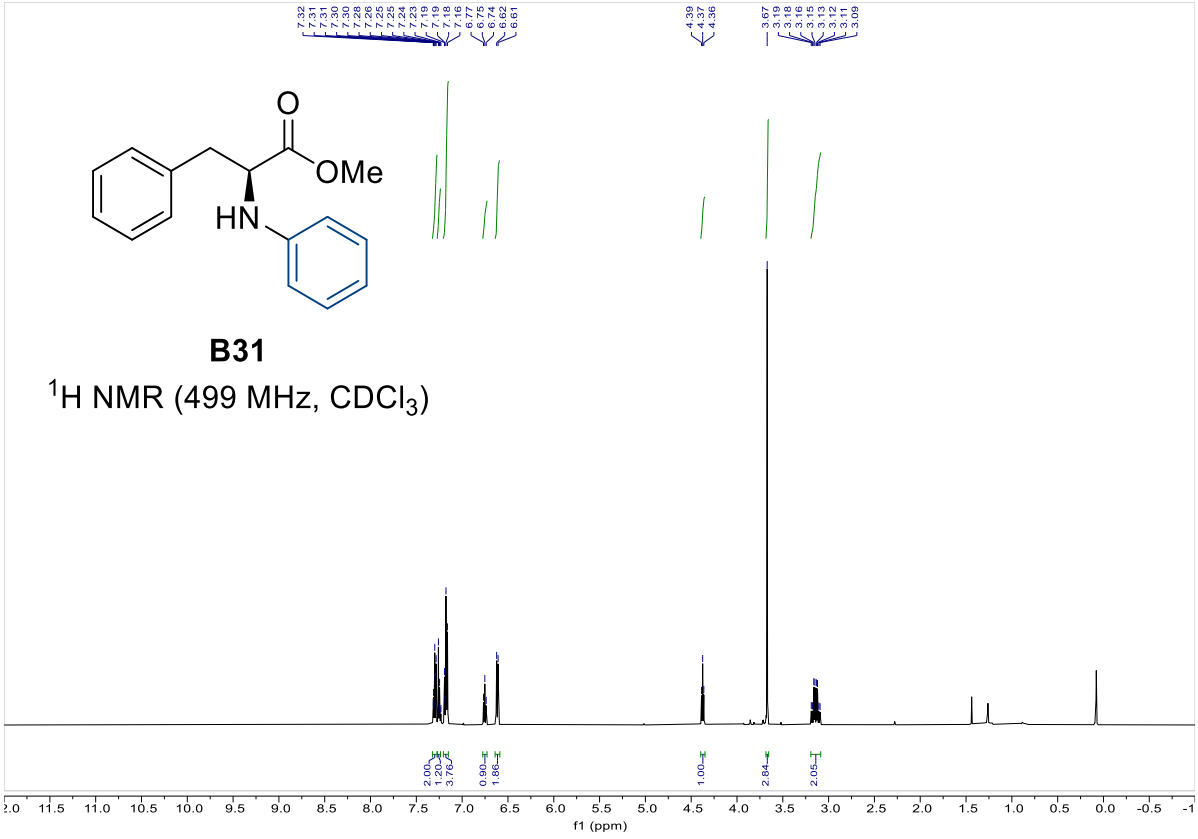

148.46
139.03
138.86
136.98
135.26
132.06
129.96
129.06
128.76
128.55
128.05
127.72
127.47
120.13
115.00
111.84
77.37
77.16
76.95
48.45
21.42
N
H
S
B29
13C NMR (151 MHz, CDCl3)
f1 (ppm)


7.20
7.18
7.15
7.13
7.11
7.00
6.98
6.90
6.65
6.63
6.61
5.32
CD2Cl2
3.09
3.06
2.94
2.93
2.90
2.88
2.86
2.84
2.83
2.82
2.81
2.79
2.36
2.34
2.33
2.32
2.31
2.30
1.88
1.86
1.85
1.84
1.83
1.81
1.80
1.78
1.77
1.75
1.72
1.71
1.70
1.69
1.68
1.67
1.64
1.63
1.61
1.60
1.50
1.49
1.47
1.46
1.43
1.42
1.40
1.39
1.36
1.25
1.23
1.21
1.03
H
N
H
B30
1H NMR (400 MHz, CD2Cl2)
1.01
2.01
1.09
1.00
2.95
0.59
1.01
4.19
1.02
4.21
1.12
3.37
2.96
3.24
3.09
3.09
f1 (ppm)



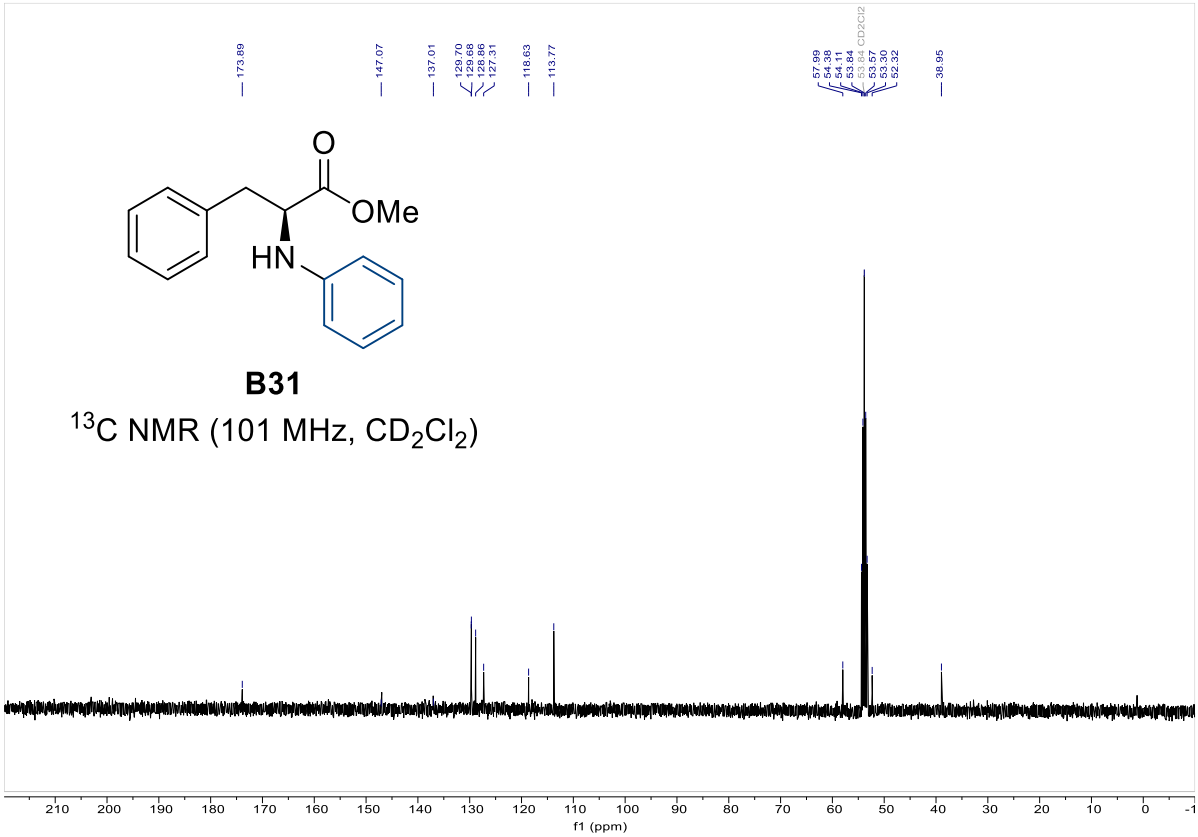
B30

^{13}C NMR (101 MHz, CD_2Cl_2)



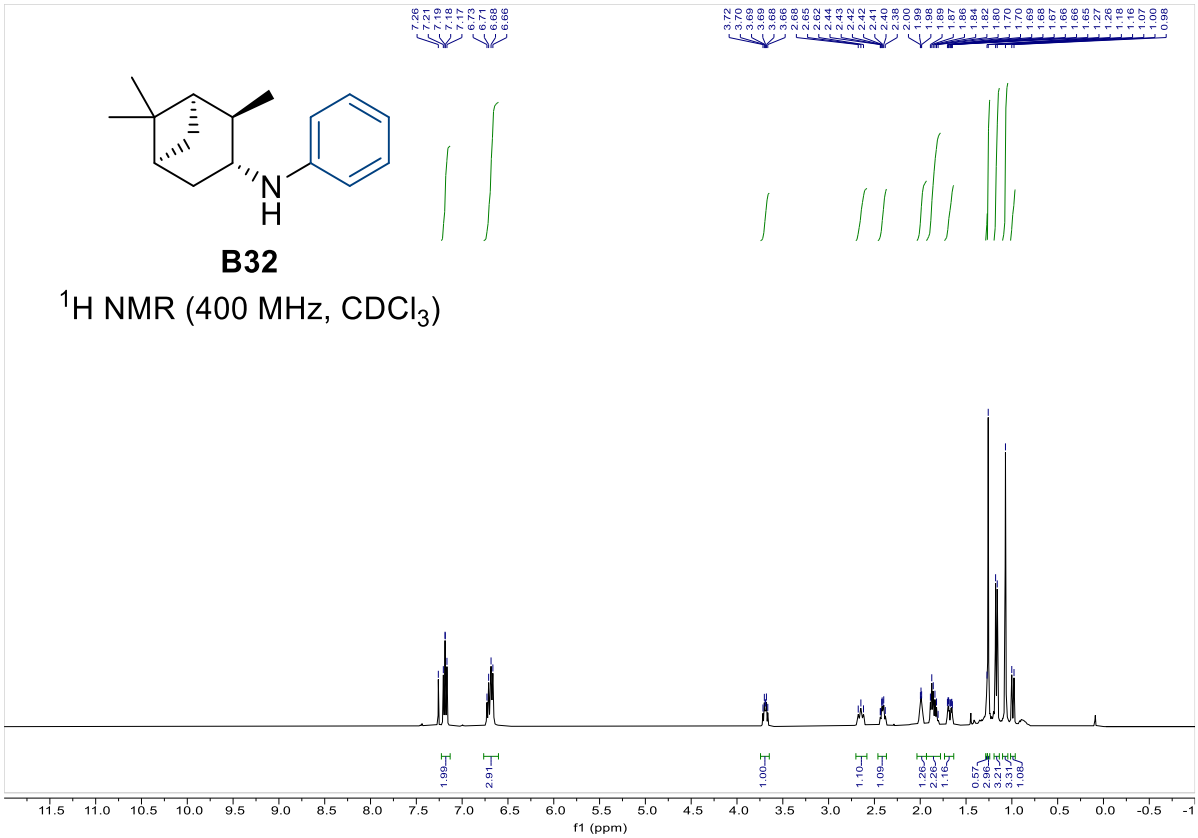
B31

^{1}H NMR (499 MHz, $CDCl_3$)



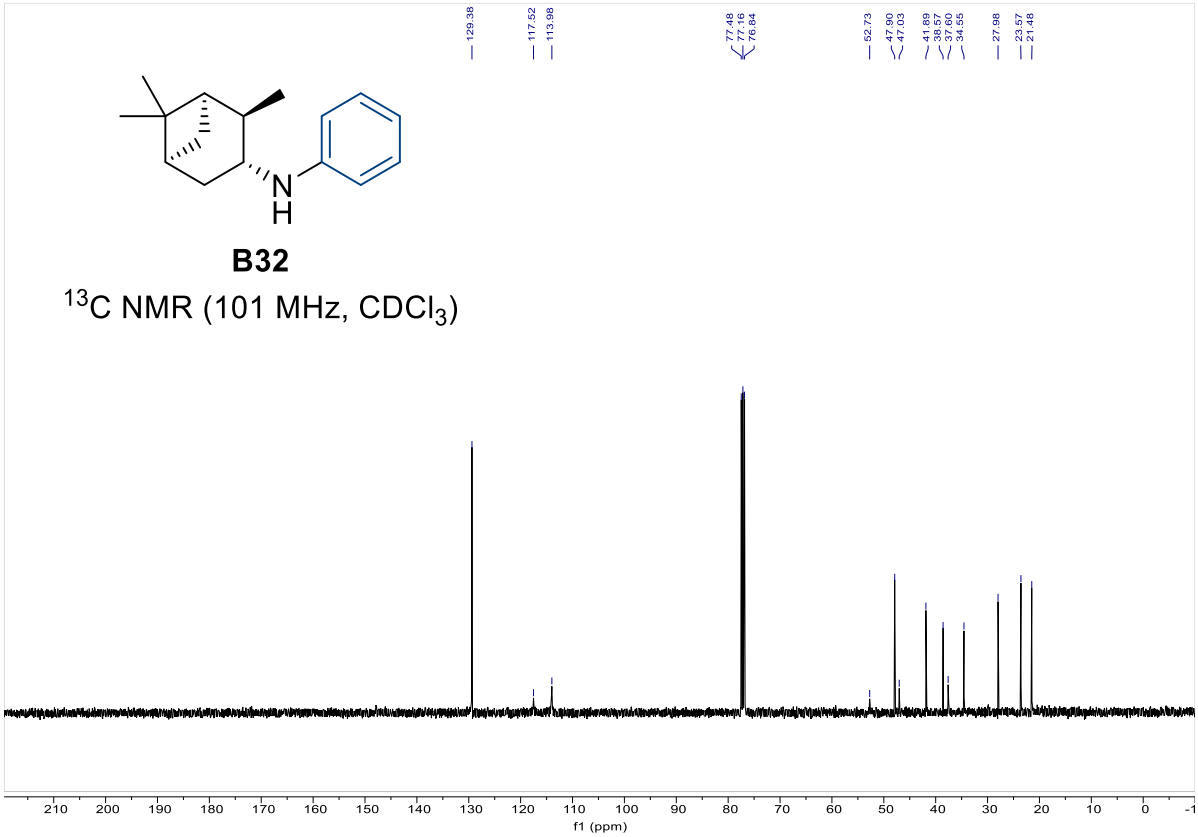
B31

^{13}C NMR (101 MHz, CD_2Cl_2)



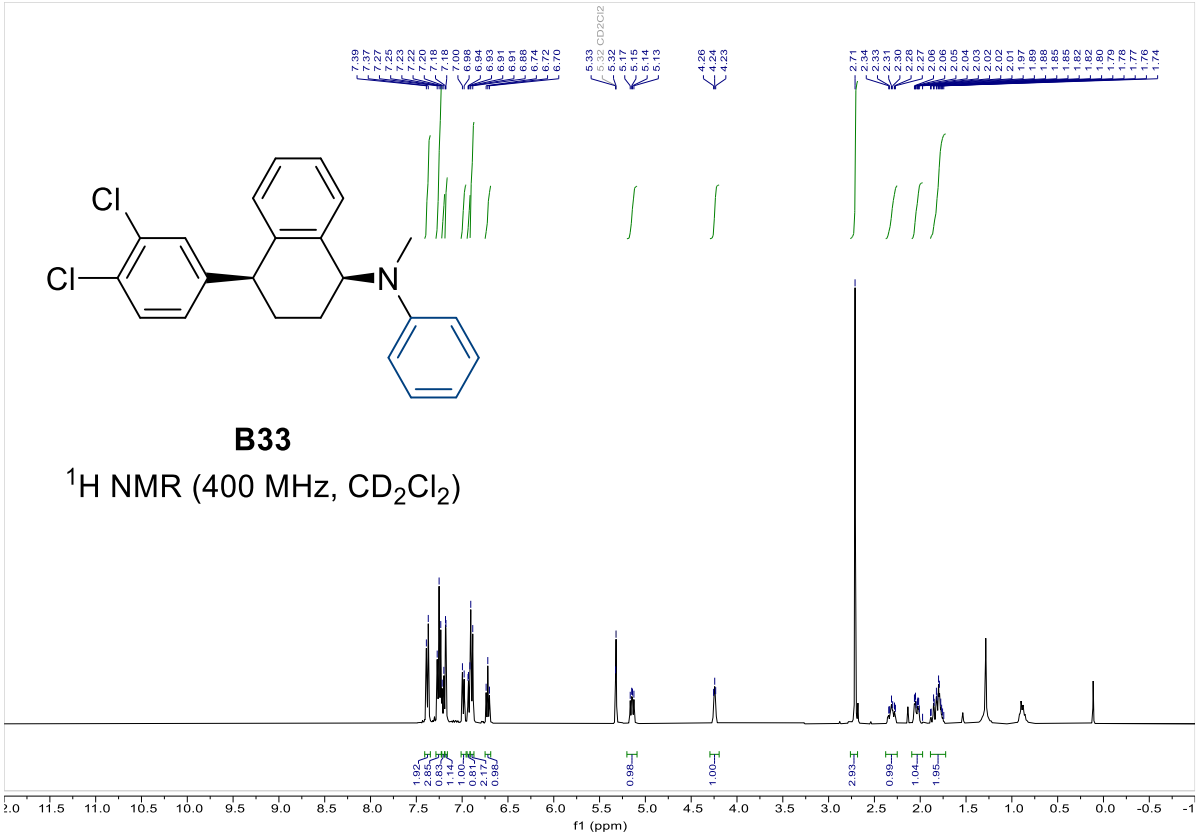
B32

^{1}H NMR (400 MHz, $CDCl_3$)



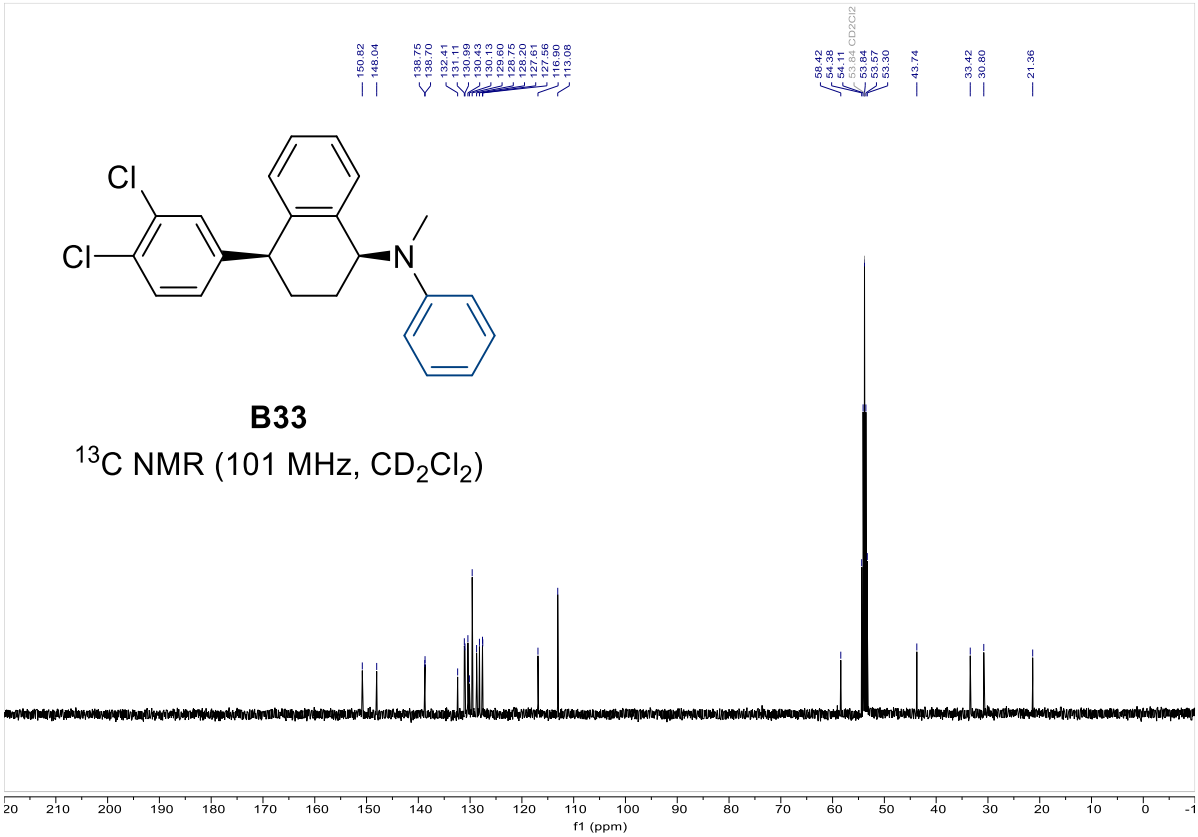
B32

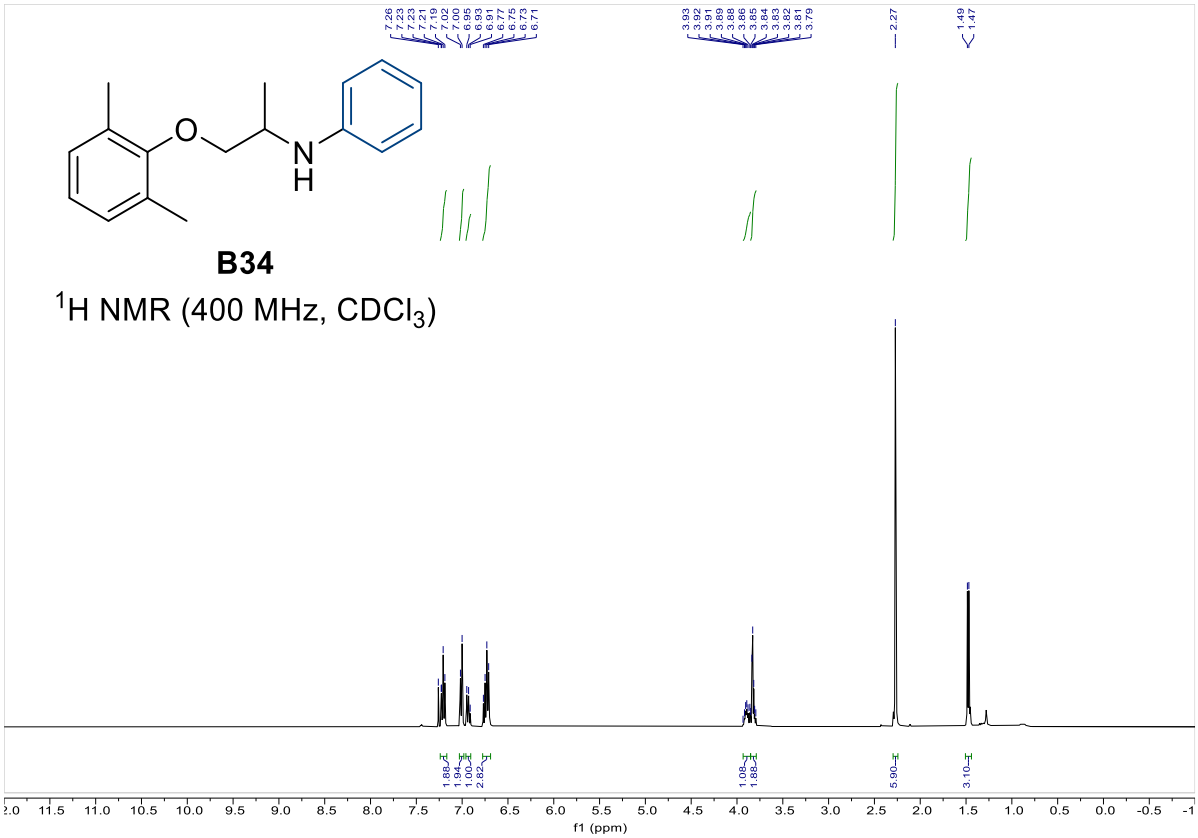
^{13}C NMR (101 MHz, $CDCl_3$)

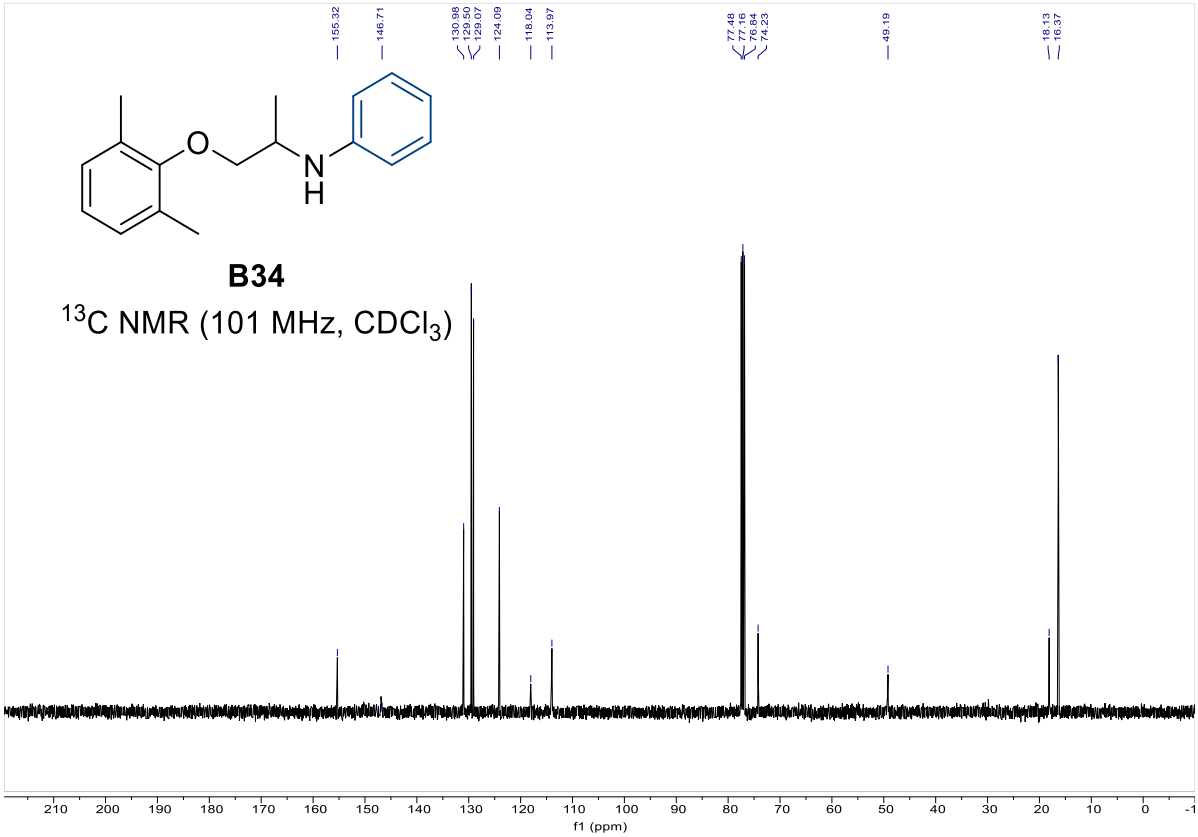


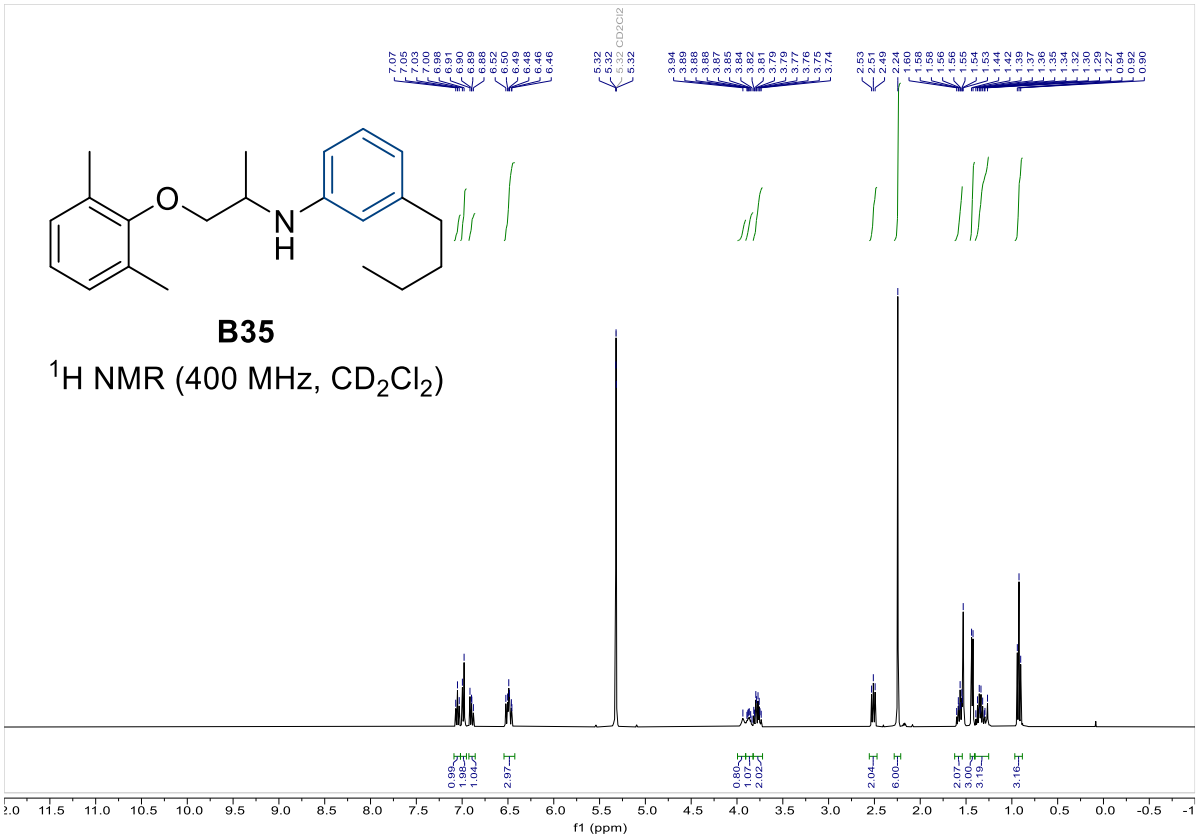
B33

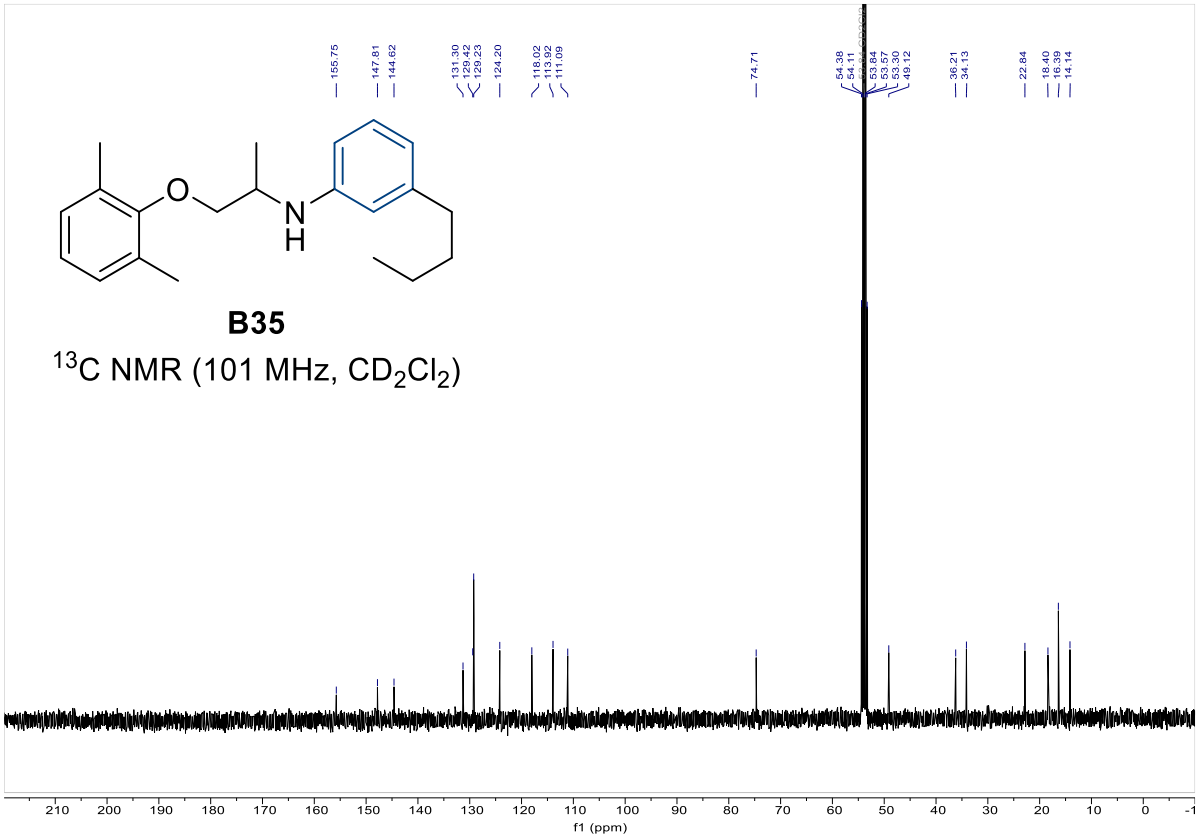
^{1}H NMR (400 MHz, CD_2Cl_2)


Cl
Cl
N
B33
13C NMR (101 MHz, CD2Cl2)
f1 (ppm)


O
N
H
B34
1H NMR (400 MHz, CDCl3)
f1 (ppm)

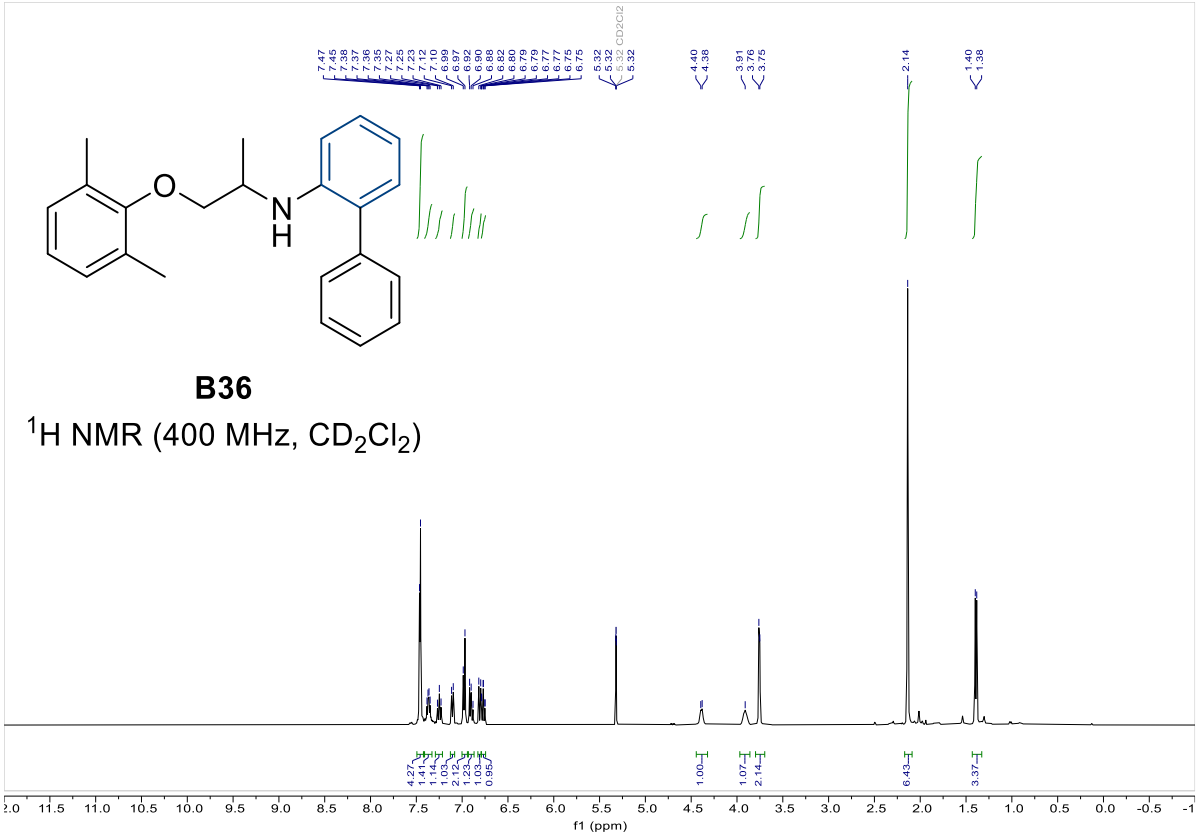

155.32
146.71
130.98
129.50
129.07
124.09
118.04
113.97
77.48
77.16
76.84
74.23
49.19
18.13
16.37
O
N
H
B34
13C NMR (101 MHz, CDCl3)
f1 (ppm)


7.07
7.05
7.03
7.00
6.98
6.91
6.90
6.89
6.88
6.52
6.50
6.49
6.48
6.46
6.46
5.32
5.32
5.32 CD2Cl2
5.32
3.94
3.89
3.88
3.88
3.87
3.85
3.84
3.82
3.81
3.79
3.79
3.77
3.77
3.76
3.75
3.74
2.53
2.51
2.49
2.24
1.60
1.58
1.58
1.56
1.56
1.55
1.54
1.53
1.44
1.42
1.39
1.37
1.36
1.35
1.34
1.32
1.30
1.29
1.27
0.94
0.92
0.90
0.99
1.98
1.04
2.97
0.80
1.07
2.02
2.04
6.00
2.07
3.00
3.19
3.16
O
N
H
B35
1H NMR (400 MHz, CD2Cl2)
f1 (ppm)



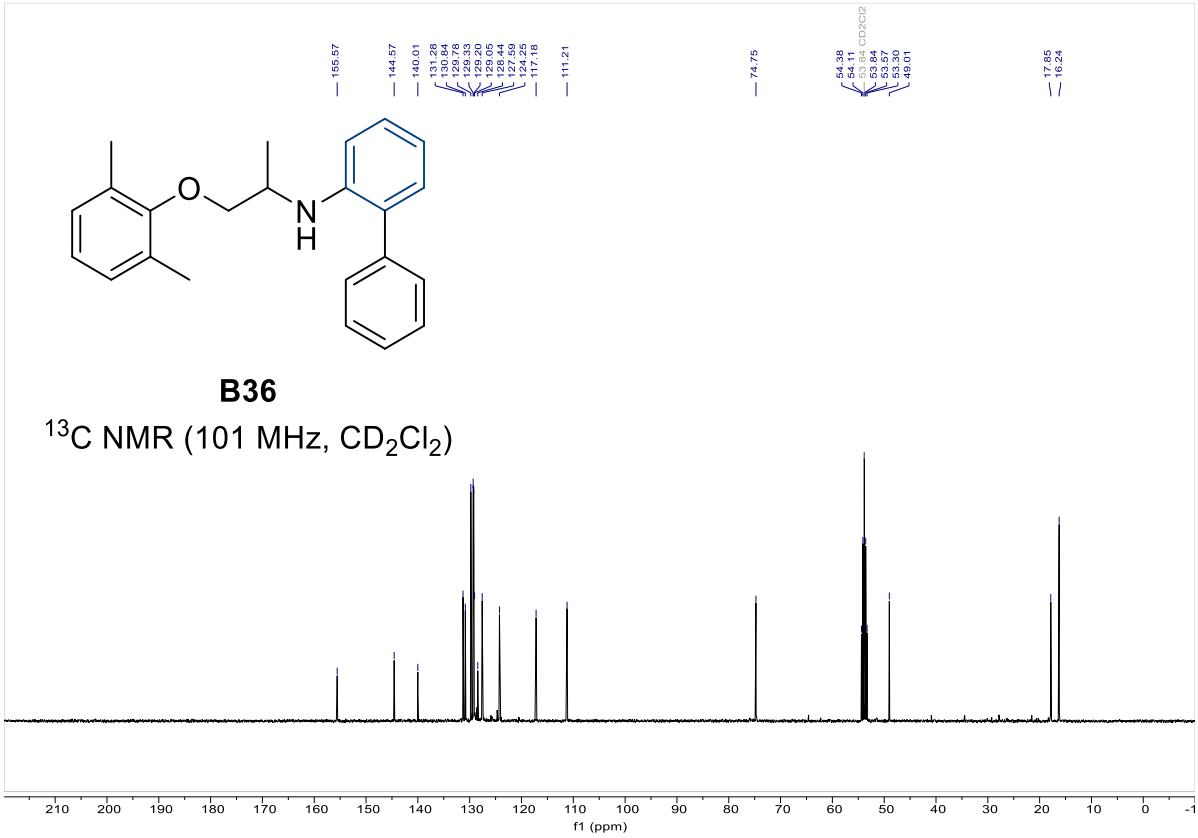
B35

^{13}C NMR (101 MHz, CD_2Cl_2)



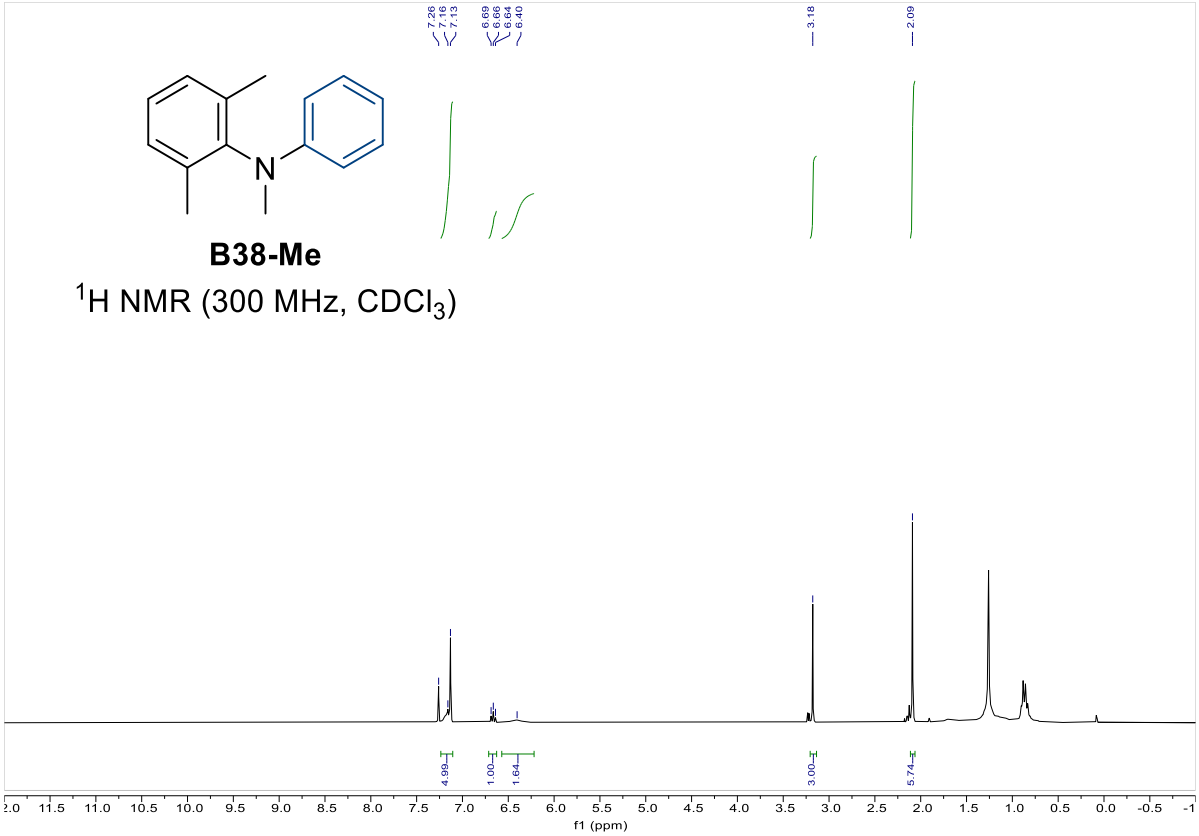
B36

^{1}H NMR (400 MHz, CD_2Cl_2)



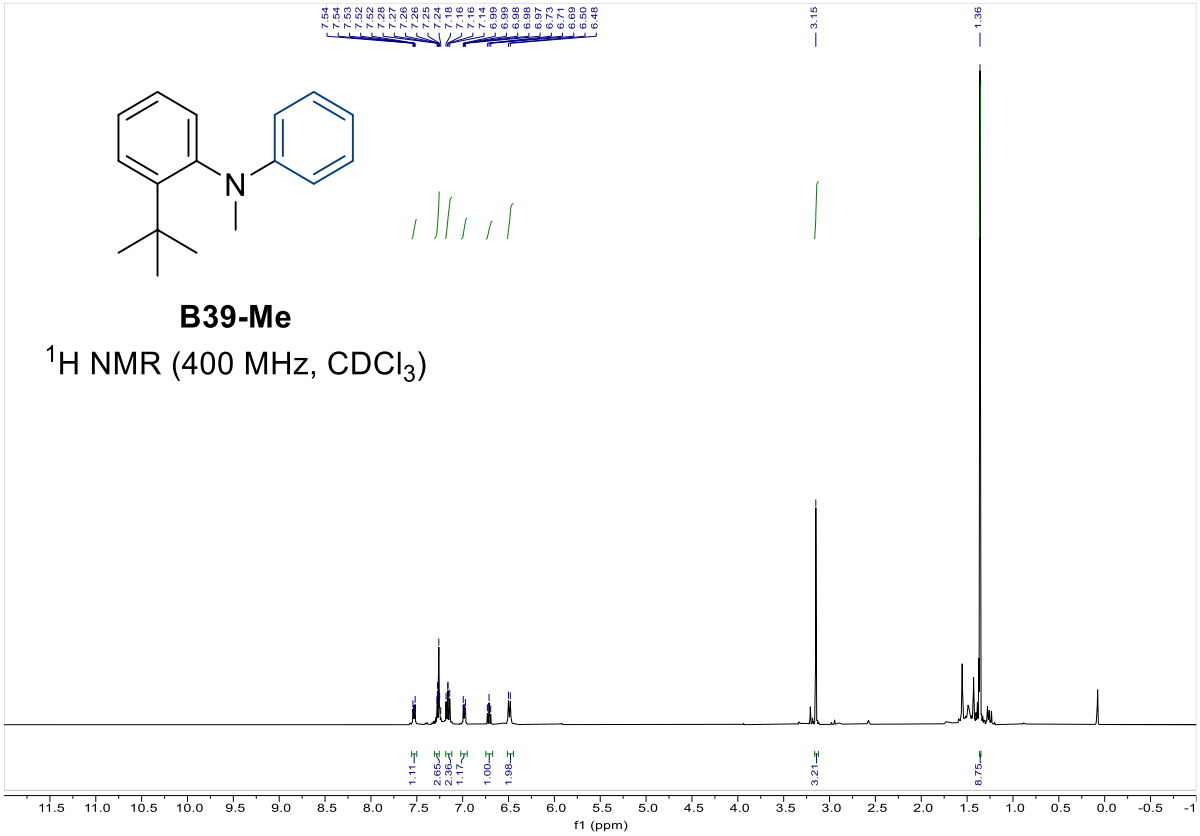
B36

^{13}C NMR (101 MHz, CD_2Cl_2)



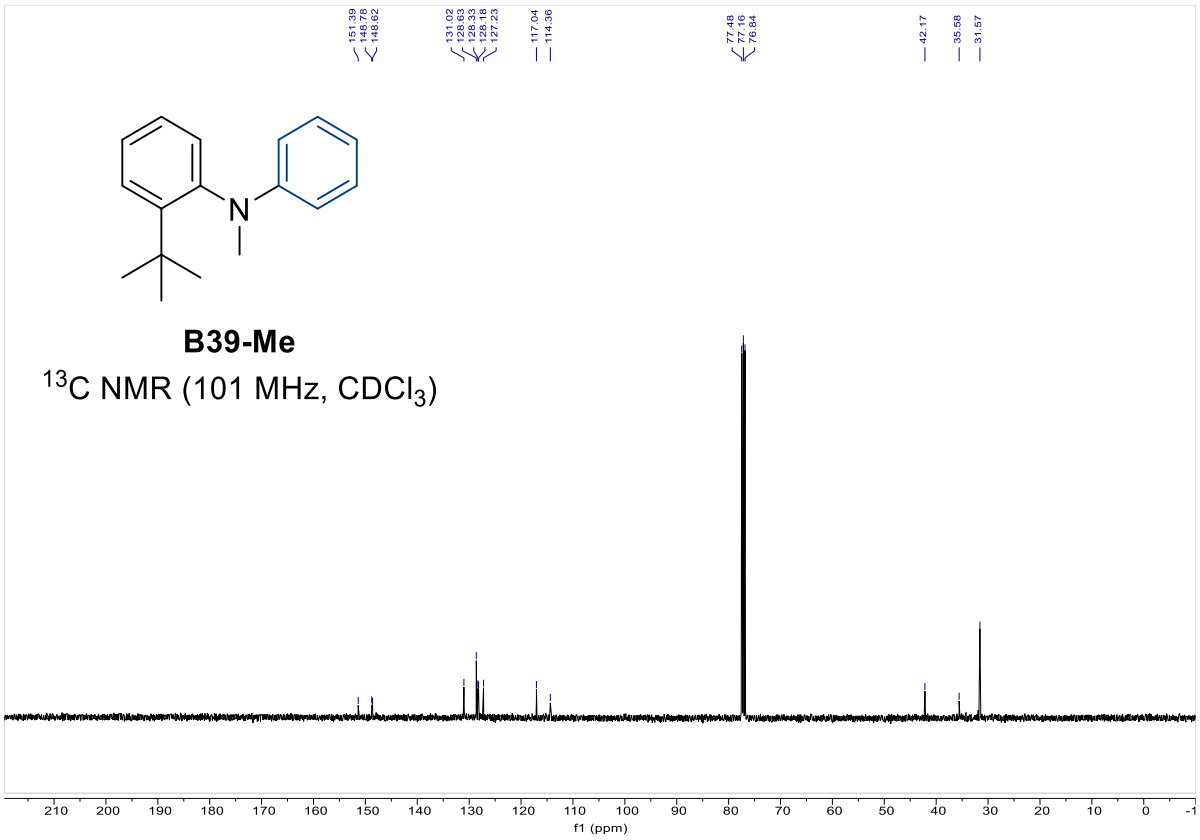
B38-Me

^{1}H NMR (300 MHz, $CDCl_3$)



B39-Me

^{1}H NMR (400 MHz, $CDCl_3$)



B39-Me

^{13}C NMR (101 MHz, $CDCl_3$)