Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Phosphine-catalysed intermolecular cyclopropanation reaction between benzyl bromides and activated alkenes

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1. General methods and materials

^{1}H NMR (400 MHz), ^{13}C NMR (100 or 151 MHz), ^{19}F NMR (376 MHz) and ^{31}P NMR (162 MHz) spectra were recorded on Varian INOVA-400/54, Agilent DD2-600/54 or Bruker Ascend^{TM} 400 instruments (Chemical shifts were reported in ppm from tetramethylsilane with the solvent resonance as the internal standard in $CDCl_3$ solution, unless otherwise noted). The following abbreviations were used to explain the multiplicities: s = singlet, d = doublet, t = triplet, q = quartet, dd = double doublet, td = triple doublet; m = multiplet, and coupling constants (*J*) are reported in Hertz (Hz). High resolution mass spectra (HRMS) were recorded on a Waters SYNAPT G2, Agilent G1969-85000 or Shimadzu LCMS-IT-TOF using a time-of-flight mass spectrometer equipped with electrospray ionization (ESI) source. X-ray diffraction experiments were carried out on an Agilent Gemini and the data obtained were deposited at the Cambridge Crystallographic Data Centre (CCDC 2178229). Enantiomeric excess was determined by HPLC (Agilent Technologies: 1220 Infinity II, 1200 Series, 1260 Infinity) analysis on a chiral column in comparison with an authentic racemate, using a Daicel Chiralpak IA Column (250 × 4.6 mm). UV detection was monitored at 254 nm. The melting point was obtained from WRX-4 Mel-Temp apparatus. Column chromatography was performed on silica gel (300–400 mesh) eluting with ethyl acetate (EtOAc)/petroleum ether. TLC was performed on glass-backed silica plates. UV light, I_2, and solution of potassium permanganate were used to visualize products or starting materials. All chemicals were used without purification as commercially available unless otherwise noted. Petroleum ether and EtOAc were distilled. Toluene was freshly distilled from CaH_2 under an atmosphere of dry argon. Dried solvents and liquid reagents were transferred by oven-dried syringe. All benzyl bromides used were commercially available. The α-cyano-α,β-unsaturated ketones **2**,[1] 2-benzylidene-1*H*-indene-1,3(2*H*)-dione **4**,[2] and *tert-butyl* (*Z*)-2-oxo-3-(2-oxo-2-phenylethylidene)-indoline-1-carboxylate **6**[3] were prepared according to the literature procedures, and the spectroscopic data were consistent with the literature report.

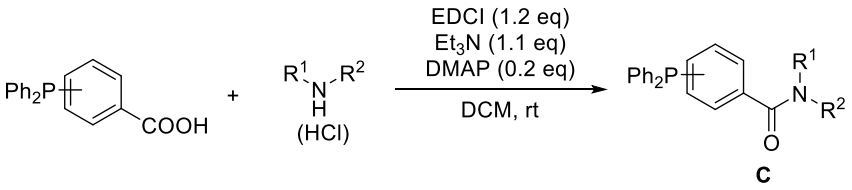
1 (*a*) A. P. Dieskau, M. S. Holzwarth and B. Plietker, Fe-Catalysed Allylic C–C-Bond Activation: Vinylcyclopropanes as Versatile a1,a3,d5-Synthons in Traceless Allylic Substitutions and [3 + 2]-Cycloadditions, *J. Am. Chem. Soc.*, 2012, **134**, 5048–5051; (*b*) R. Maity and S. C. Pan, Dienamine-Mediated Asymmetric Inverse-Electron-Demand Hetero-Diels–Alder Reaction of

Linear Deconjugated Enones: Diversity-Oriented Synthesis of 3,4-Dihydropyrans, *Eur. J. Org. Chem.*, 2017, **4**, 871–874.

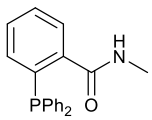
2 G. He, C. Wu, J. Zhou, Q. Yang, C. Zhang, Y. Zhou, H. Zhang and H. Liu, A Method for Synthesis of 3-Hydroxy-1-indanones via Cu-Catalyzed Intramolecular Annulation Reactions, *J. Org. Chem.*, 2018, **83**, 13356−13362.

3 L.-L. Zhang, J.-W. Zhang, S.-H. Xiang, Z. Guo and B. Tan, Remote Control of Axial Chirality: Synthesis of Spirooxindole–Urazoles via Desymmetrization of ATAD, *Org. Lett.*, 2018, **20**, 6022–6026.

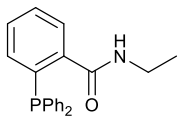
2. Preparation and characterization of phosphine catalysts



To a solution of carboxylic acid (1.0 equiv), amine or amine hydrochloride (1.0 equiv), triethylamine (1.1 equiv) and DMAP (0.2 equiv) in DCM was added EDCI (1.2 equiv). The resultant mixture was stirred at rt overnight. After completion, the solvent was evaporated, and the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether) to give the phosphine catalyst **C**.

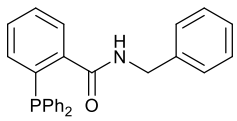


C2: White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.63–7.56 (m, 1H), 7.41–7.27 (m, 12H), 7.00–6.92 (m, 1H), 5.92 (s, 1H), 2.80 (d, J = 4.8 Hz 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 169.6, 141.4 (d, $^{2}J_{PC}$ = 25.3 Hz), 136.8 (d, $^{3}J_{PC}$ = 10.2 Hz), 136.0 (d, $^{2}J_{PC}$ = 19.9 Hz), 134.0, 133.9 (d, $^{2}J_{PC}$ = 20.1 Hz), 130.1, 129.0, 128.8, 128.7 (d, $^{3}J_{PC}$ = 7.1 Hz), 127.9 (d, $^{4}J_{PC}$ = 4.9 Hz), 26.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) –9.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{20}H_{19}NOP^+$ 320.1199; Found 320.1200.

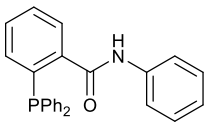


C3: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.63–7.57 (m, 1H), 7.40–7.26 (m, 12H), 6.98–6.90 (m, 1H), 5.83 (s, 1H), 3.32–3,26 (m, 3H), 1.00 (t, J = 7.2 Hz 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.9, 141.7 (d, $^{2}J_{PC}$ = 25.6 Hz),

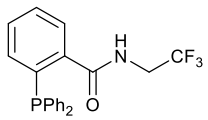
136.9 (d, $^{1}J_{PC}$ = 10.7 Hz), 135.6 (d, $^{2}J_{PC}$ = 20.0 Hz), 134.0, 133.9 (d, $^{2}J_{PC}$ = 20.1 Hz), 130.1, 128.9, 128.8, 128.7 (d, $^{3}J_{PC}$ = 7.1 Hz), 128.0 (d, $^{4}J_{PC}$ = 4.9 Hz), 34.8, 14.4; ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) –10.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{21}NOP^+$ 334.1355; Found 334.1366.



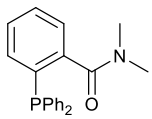
C4: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.65–7.60 (m, 1H), 7.40–7.23 (m, 15H), 7.22–7.16 (m, 2H), 7.00–6.94 (m, 1H), 6.17 (s, 1H), 4.46 (d, *J* = 5.6 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.8, 141.3 (d, $^{2}J_{PC}$ = 25.9 Hz), 137.7, 136.8 (d, $^{2}J_{PC}$ = 10.7 Hz), 136.0 (d, $^{2}J_{PC}$ = 20.7 Hz), 134.1, 133.9 (d, $^{2}J_{PC}$ = 20.2 Hz), 130.3, 128.9, 128.8, 128.7 (d, $^{3}J_{PC}$ = 2.7 Hz), 128.6, 128.1, 128.0 (d, $^{3}J_{PC}$ = 5.0 Hz), 127.5, 44.2; ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) –10.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{26}H_{23}NOP^+$ 396.1512; Found 396.1513.



C5: White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.75–7.70 (m, 1H), 7.60 (s, 1H), 7.47–7.40 (m, 1H), 7.40–7.21 (m, 15H), 7.11–7.05 (m, 1H), 7.04–6.99 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.1, 141.8 (d, $^{2}J_{PC}$ = 26.2 Hz), 137.5, 136.3 (d, $^{1}J_{PC}$ = 10.2 Hz), 135.7 (d, $^{2}J_{PC}$ = 20.0 Hz), 134.1, 134.0 (d, $^{2}J_{PC}$ = 20.1 Hz), 130.5, 129.2, 129.1, 128.9, 128.8 (d, $^{3}J_{PC}$ = 7.3 Hz), 128.5 (d, $^{4}J_{PC}$ = 4.8 Hz), 124.4, 119.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) –10.4; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{21}NOP^+$ 382.1355; Found 382.1362.

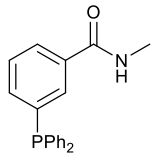


C6: White solid; ^{1}H NMR (400 MHz, CD_3OD): δ (ppm) 7.56–7.51 (m, 1H), 7.46–7.39 (m, 1H), 7.38–7.20 (m, 11H), 7.03–6.97 (m, 1H), 3.84 (q, *J* = 9.4 Hz 2H); ^{13}C NMR (100 MHz, CD_3OD): δ (ppm) 170.8, 140.4 (d, $^{2}J_{PC}$ = 24.9 Hz), 137.3 (d, $^{3}J_{PC}$ = 11.1 Hz), 137.1 (d, $^{2}J_{PC}$ = 21.7 Hz), 133.9, 133.6 (d, $^{2}J_{PC}$ = 20.6 Hz), 130.0, 128.5, 1228.4, 128.1 (d, $^{3}J_{PC}$ = 7.1 Hz), 127.1 (d, $^{3}J_{PC}$ = 4.8 Hz), 124.0 (q, $^{1}J_{FC}$ = 278.3 Hz), 40.1 (q, $^{2}J_{FC}$ = 34.7 Hz); ^{19}F NMR (376 MHz, CD_3OD): δ (ppm) –73.5 (m); ^{31}P NMR (162 MHz, CD_3OD): δ (ppm) –9.6; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{21}H_{18}NF_3OP^+$ 388.1073; Found 388.1070.

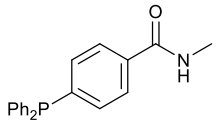


C7: Colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.39–7.26 (m, 13H), 7.16–7.11 (m, 1H), 3.01 (s, 3H), 2.63 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 170.9 (d, $^{3}J_{PC}$ = 3.3 Hz), 143.2 (d, $^{2}J_{PC}$ = 32.9 Hz), 136.5 (d, $^{1}J_{PC}$ = 10.8 Hz), 134.8 (d, $^{2}J_{PC}$ = 16.3 Hz), 134.2, 133.8 (d, $^{2}J_{PC}$ = 19.9 Hz), 129.1, 128.8, 128.7, 128.5 (d, $^{3}J_{PC}$ = 7.0 Hz), 126.3 (d, $^{3}J_{PC}$ =

7.4 Hz), 38.8 (d, $^{5}J_{PC}$ = 2.9 Hz), 34.6; ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) –12.3; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{20}NOPNa^+$ 356.1175; Found 356.1176.



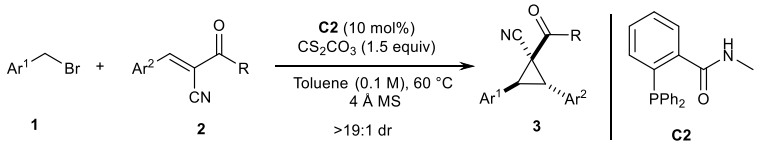
C8: White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.76 (dd, *J* = 7.2, 2.0 Hz 1H), 7.70 (dd, *J* = 8.0, 1.6 Hz 1H), 7.43–7.26 (m, 12H), 6.10 (s, 1H), 2.95 (d, *J* = 4.8 Hz 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 167.9, 138.3 (d, $^{1}J_{PC}$ = 13.0 Hz), 136.5 (d, $^{3}J_{PC}$ = 10.5 Hz), 136.3 (d, $^{2}J_{PC}$ = 15.7 Hz), 134.9 (d, $^{3}J_{PC}$ = 7.2 Hz), 133.8 (d, $^{2}J_{PC}$ = 19.7 Hz), 131.7 (d, $^{2}J_{PC}$ = 23.6 Hz), 129.0, 128.9 (d, $^{4}J_{PC}$ = 5.6 Hz), 128.7 (d, $^{3}J_{PC}$ = 6.9 Hz), 127.6, 26.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) –5.3 (m); HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{18}NOPNa^+$ 342.1018; Found 342.1016.



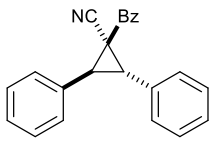
C9: White solid; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.76–7.64 (m, 2H), 7.41–7.26 (m, 12H), 6.29 (s, 1H), 2.98 (d, *J* = 4.8 Hz 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 168.0, 141.9 (d, $^{1}J_{PC}$ = 13.3 Hz), 136.4 (d, $^{1}J_{PC}$ = 10.5 Hz), 134.6, 133.9 (d, $^{2}J_{PC}$ = 19.7 Hz), 133.5 (d, $^{2}J_{PC}$ = 18.8 Hz), 129.1, 128.7 (d, $^{3}J_{PC}$ = 7.1 Hz), 126.8 (d, $^{4}J_{PC}$ = 6.4 Hz), 26.9; ^{31}P NMR (162 MHz, $CDCl_3$): δ (ppm) –5.6 (m); HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{20}H_{18}NOPNa^+$ 342.1018; Found 342.1014.

3. Phosphine-catalysed intermolecular cyclopropanation reactions

3.1 General procedure for synthesis of 3

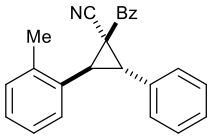


A mixture of benzyl bromide **1** (0.12 mmol, 1.2 equiv), α-cyano-α,β-unsaturated ketone **2** (0.10 mmol, 1.0 equiv), cesium carbonate (0.15 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel to give the product (EtOAc/petroleum ether).

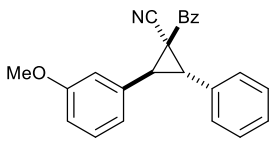


Synthesis of 3a: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenylacrylonitrile **2a** (23.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10

mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3a**: 29.7 mg (0.0920 mmol), as a white solid, 92% yield; mp = 146–148 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.96–7.86 (m, 2H), 7.57–7.51 (m, 1H), 7.49–7.40 (m, 6H), 7.40–7.30 (m, 3H), 7.27–7.18 (m, 3H), 4.33 (d, *J* = 8.8 Hz, 1H), 3.95 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.3, 135.8, 133.8, 133.6, 131.4, 129.0, 128.94, 128.86, 128.7, 128.64, 128.61, 128.58, 128.5, 118.5, 43.0, 35.8, 33.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{17}NONa^+$ 346.1202; Found 346.1205.

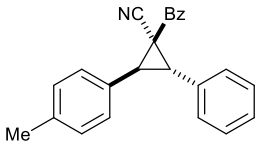


Synthesis of 3b: A mixture of 1-(bromomethyl)-2-methylbenzene **1b** (22.1 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenylacrylonitrile **2a** (23.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 40 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3b**: 30.7 mg (0.0911 mmol), as a white solid, 91% yield; mp = 144–146 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.01–7.91(m, 2H), 7.58–7.52 (m, 1H), 7.50–7.36 (m, 7H), 7.25–7.11 (m, 4H), 4.34 (d, *J* = 9.2 Hz, 1H), 3.91 (d, *J* = 9.2 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.3, 138.0, 136.1, 133.7, 133.5, 130.4, 129.8, 129.0, 128.9, 128.8, 128.7, 128.61, 128.59, 128.5, 126.0, 119.0, 43.1, 36.9, 35.3, 20.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}NO^+$ 338.1539; Found 338.1541.

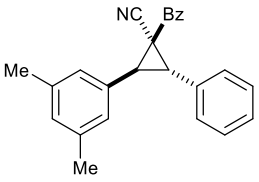


Synthesis of 3c: A mixture of 1-(bromomethyl)-3-methoxybenzene **1c** (24.0 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenylacrylonitrile **2a** (23.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3c**: 30.1 mg (0.0852 mmol), as a colorless oil, 85% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97–7.91 (m, 2H), 7.58–7.52 (m, 1H), 7.49–7.41 (m, 6H), 7.40–7.34 (m, 1H), 7.16 (t, *J* = 8.0 Hz, 1H), 6.94–6.89 (m, 1H), 6.86–6.82 (m, 1H), 6.77–6.72 (m, 1H), 4.29 (d, *J* = 8.8 Hz, 1H), 3.91 (d, *J* = 8.8 Hz, 1H), 3.71 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.2, 159.6, 135.8,

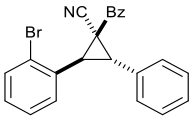
133.8, 133.6, 133.0, 129.7, 129.1, 128.9, 128.63, 128.61, 128.5, 121.2, 118.5, 114.5, 114.2, 55.2, 42.9, 35.7, 33.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{19}NO_2Na^+$ 376.1308; Found 376.1303.



Synthesis of 3d: A mixture of 1-(bromomethyl)-4-methylbenzene **1d** (22.1 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenylacrylonitrile **2a** (23.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/40) to give the product **3d**: 30.7 mg (0.0911 mmol), as a white solid, 91% yield; mp = 142–144 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.00–7.84 (m, 2H), 7.56–7.50 (m, 1H), 7.49–7.29 (m, 7H), 7.26–7.19 (m, 2H), 7.05 (d, *J* = 8.0 Hz, 2H), 4.31 (d, *J* = 8.8 Hz, 1H), 3.93 (d, *J* = 8.8 Hz, 1H), 2.23 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.5, 138.5, 135.9, 133.72, 133.70, 129.4, 129.1, 129.0, 128.74, 128.66, 128.6, 128.4, 128.3, 118.6, 43.1, 35.9, 33.8, 21.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{19}NONa^+$ 360.1359; Found 360.1352.

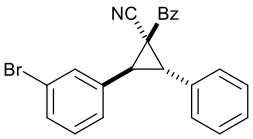


Synthesis of 3e: A mixture of 1-(bromomethyl)-3,5-dimethylbenzene **1e** (23.8 mg, 0.120 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenylacrylonitrile **2a** (23.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 40 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3e**: 30.8 mg (0.0877 mmol), as a white solid, 88% yield; mp = 124–126 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7. 94–7.91 (m, 2H), 7.58–7.51 (m, 1H), 7.50–7.40 (m, 6H), 7.39–7.32 (m, 1H), 6.93 (s, 2H), 6.83 (s, 1H), 4.28 (d, *J* = 8.8 Hz, 1H), 3.88 (d, *J* = 8.8 Hz, 1H), 2.21 (s, 6H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.4, 138.2, 135.9, 133.8, 133.7, 131.3, 130.3, 129.1, 128.9, 128.6, 128.5, 128.4, 126.7, 118.7, 43.2, 35.8, 33.9, 21.2; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{25}H_{22}NO^+$ 352.1696; Found 352.1691.

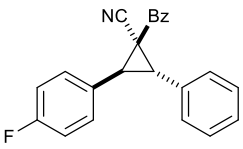


Synthesis of 3f: A mixture of 1-bromo-2-(bromomethyl)benzene **1f** (29.7 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenylacrylonitrile **2a** (23.3 mg, 0.0999

mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 40 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/40) to give the product **3f**: 30.0 mg (0.0748 mmol), as a white solid, 75% yield; mp = 103–105 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.12–8.00 (m, 2H), 7.57–7.51 (m, 2H), 7.49–7.36 (m, 7H), 7.34–7.27 (m, 2H), 7.17–7.11 (m, 1H), 4.33 (d, *J* = 9.2 Hz, 1H), 4.07 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.8, 136.0, 133.6, 133.2, 132.9, 131.2, 130.5, 130.1, 129.3, 129.0, 128.72, 128.69, 128.4, 127.4, 126.5, 118.4, 44.6, 37.1, 36.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{16}{}^{79}BrNONa^+$ 424.0307; Found 424.0310; Calcd for $C_{23}H_{16}{}^{81}BrNONa^+$ 426.0287; Found 426.0292.

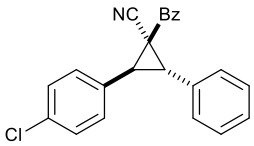


Synthesis of 3g: A mixture of 1-bromo-3-(bromomethyl)benzene **1g** (29.7 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenylacrylonitrile **2a** (23.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3g**: 33.3 mg (0.0830 mmol), as a white solid, 83% yield; mp = 162–164 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.98–7.87 (m, 2H), 7.62–7.54 (m, 1H), 7.52–7.32 (m, 9H), 7.24 (d, *J* = 7.6 Hz, 1H), 7.13–7.02 (m, 1H), 4.27 (d, *J* = 8.8 Hz, 1H), 3.87 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.0, 135.6, 134.0, 133.8, 133.1, 132.1, 131.7, 130.1, 129.0 (2C), 128.7, 128.62, 128.57, 127.4, 122.7, 118.2, 41.2, 35.8, 34.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{16}{}^{79}BrNONa^+$ 424.0307; Found 424.0320; Calcd for $C_{23}H_{16}{}^{81}BrNONa^+$ 426.0287; Found 426.0304.

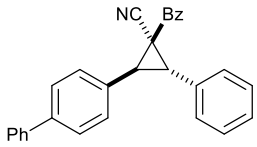


Synthesis of 3h: A mixture of 1-(bromomethyl)-4-fluorobenzene **1h** (22.6 mg, 0.120 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenylacrylonitrile **2a** (23.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 40 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3h**: 30.0 mg (0.0879 mmol), as a white solid, 88% yield; mp = 138–140 °C; ^{1}H NMR (400 MHz,

$CDCl_3$): δ (ppm) 7.98–7.84 (m, 2H), 7.62–7.52 (m, 1H), 7.50–7.35 (m, 7H), 7.34–7.27 (m, 2H), 7.00–6.86 (m, 2H), 4.28 (d, *J* = 8.8 Hz, 1H), 3.92 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.2, 162.3 (d, $^1J_{FC}$ = 247.0 Hz), 135.7, 133.9, 133.3, 130.6 (d, $^3J_{FC}$ = 8.4 Hz), 129.0 (2C), 128.7, 128.60, 128.56, 127.2 (d, $^4J_{FC}$ = 3.4 Hz), 118.4, 115.7 (d, $^2J_{FC}$ = 21.8 Hz), 42.2, 35.8, 34.1; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –112.6 (m); HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{17}FNO^+$ 342.1289; Found 342.1289.

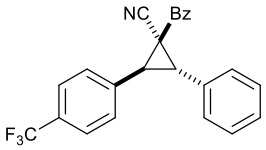


Synthesis of 3i: A mixture of 1-(bromomethyl)-4-chlorobenzene **1i** (24.5 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenylacrylonitrile **2a** (23.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/40) to give the product **3i**: 31.0 mg (0.0868 mmol), as a white solid, 87% yield; mp = 142–144 °C; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.03–7.82 (m, 2H), 7.59–7.53 (m, 1H), 7.51–7.35 (m, 7H), 7.31–7.18 (m, 4H), 4.28 (d, *J* = 8.8 Hz, 1H), 3.89 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.1, 135.6, 134.6, 134.0, 133.2, 130.2, 130.0, 129.0 (2C), 128.9, 128.7, 128.6 (2C), 118.3, 42.1, 35.8, 34.0; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{23}H_{17}{}^{35}ClNO^+$ 358.0993; Found 358.0987; Calcd for $C_{23}H_{17}{}^{37}ClNO^+$ 360.0964; Found 360.0965; $[M + Na]^+$ Calcd for $C_{23}H_{16}{}^{35}ClNONa^+$ 380.0813; Found 380.0808; Calcd for $C_{23}H_{16}{}^{37}ClNONa^+$ 382.0783; Found 382.0786.

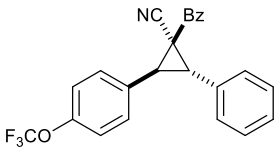


Synthesis of 3j: A mixture of 4-(bromomethyl)-1,1'-biphenyl **1j** (29.5 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenylacrylonitrile **2a** (23.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h and stirred at 80 °C for another 24 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3j**: 37.6 mg (0.0942 mmol), as a white solid, 94% yield; mp = 165–167 °C; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94 (d, *J* = 8.0 Hz, 2H), 7.57–7.51 (m, 1H), 7.51–7.35 (m, 15H), 7.34–7.27 (m, 1H), 4.37 (d, *J* = 8.8 Hz, 1H), 3.98 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.4, 141.3, 140.1, 135.8, 133.8, 133.6, 130.4,

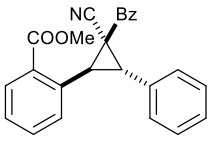
129.3, 129.1, 129.0, 128.8, 128.7, 128.5, 127.6, 127.3, 127.0 (2C), 118.5, 42.9, 36.0, 33.9; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{29}H_{21}NONa^+$ 422.1515; Found 422.1510.



Synthesis of 3k: A mixture of 1-(bromomethyl)-4-(trifluoromethyl)benzene **1k** (28.6 mg, 0.120 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenylacrylonitrile **2a** (23.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 40 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/40) to give the product **3k**: 32.4 mg (0.0828 mmol), as a white solid, 83% yield; mp = 145–147 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.92 (*J* = 8.8 Hz, 2H), 7.60–7.50 (m, 3H), 7.49–7.34 (m, 9H), 4.34 (d, *J* = 8.8 Hz, 1H), 3.95 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.0, 135.61 (d, $^4J_{FC}$ = 1.0 Hz), 135.56, 134.1, 133.0, 130.7 (q, $^2J_{FC}$ = 32.7 Hz), 129.3, 129.05, 128.97, 128.8, 128.7, 128.6, 125.7 (q, $^3J_{FC}$ = 3.8 Hz), 123.8 (d, $^1J_{FC}$ = 272.4 Hz), 118.1, 42.0, 35.8, 34.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –62.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{17}F_3NO^+$ 392.1257; Found 392.1257.

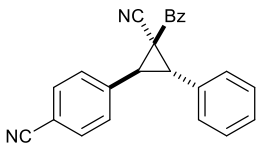


Synthesis of 3l: A mixture of 1-(bromomethyl)-4-(trifluoromethoxy) benzene **1l** (30.6 mg, 0.120 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenyl-acrylonitrile **2a** (23.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 40 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/40) to give the product **3l**: 37.3 mg (0.0916 mmol), as a colorless oil, 92% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.95–7.90 (m, 2H), 7.59–7.54 (m, 1H), 7.48–7.42 (m, 6H), 7.40–7.34 (m, 3H), 7.13–7.08 (m, 2H), 4.29 (d, *J* = 8.8 Hz, 1H), 3.91 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.2, 149.2, 135.7, 134.0, 133.2, 130.4, 130.1, 129.4, 129.01, 128.97, 128.7, 128.63, 128.58, 120.9, 118.2, 41.9, 35.8, 34.2; ^{19}F NMR (376 MHz, $CDCl_3$): δ (ppm) –57.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{16}F_3NO_2Na^+$ 430.1025; Found 430.1026.

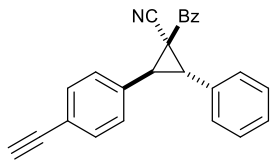


Synthesis of 3m: A mixture of methyl 2-(bromomethyl)benzoate **1m** (27.4 mg, 0.120 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenylacrylonitrile **2a** (23.3 mg,

0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3m**: 15.9 mg (0.0417 mmol), as a white solid, 42% yield; mp = 132–134 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.02–7.96(m, 3H), 7.55–7.33 (m, 11H), 4.56 (d, *J* = 9.6 Hz, 1H), 4.35 (d, *J* = 9.6 Hz, 1H), 3.95 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 189.3, 167.0, 136.2, 133.7, 133.5, 133.4, 132.5, 131.4, 130.4, 130.0, 129.2, 128.9, 128.7, 128.6, 128.5, 128.3, 118.9, 52.5, 43.5, 37.5, 36.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{25}H_{19}NO_3Na^+$ 404.1257; Found 404.1259.

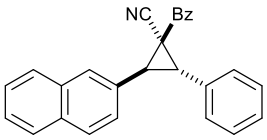


Synthesis of 3n: A mixture of 4-(bromomethyl)benzonitrile **1n** (23.5 mg, 0.120 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenylacrylonitrile **2a** (23.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/30 to 1/20) to give the product **3n**: 30.2 mg (0.0868 mmol), as a white solid, 87% yield; mp = 152–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.94–7.87 (m, 2H), 7.61–7.53 (m, 3H), 7.49–7.37 (m, 9H), 4.30 (d, *J* = 8.8 Hz, 1H), 3.93 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 187.8, 137.0, 135.4, 134.2, 132.7, 132.4, 129.7, 129.1, 129.0, 128.8 (2C), 128.5, 118.2, 117.9, 112.5, 41.8, 35.9, 34.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{17}N_2O^+$ 349.1335; Found 349.1332.

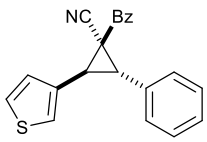


Synthesis of 3o: A mixture of benzyl 1-(bromomethyl)-4-ethynylbenzene **1o** (23.3 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-(furan-2-carbonyl)-3-phenylacrylonitrile **2a** (22.3 mg, 0.100 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 40 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/40) to give the product **3o**: 24.6 mg (0.0709 mmol), as a white solid, 71% yield; mp = 64–66 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.96–7.88 (m, 2H), 7.60–7.35 (m, 10H), 7.34–7.26 (m, 2H), 4.30 (d, *J* = 8.8 Hz, 1H), 3.91 (d, *J* = 8.8 Hz, 1H), 3.05 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.0, 135.6, 134.0, 133.3, 132.4, 132.2, 129.01, 128.98,

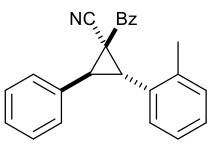
128.8, 128.7, 128.6, 127.5, 122.4, 118.3, 112.6, 82.8, 42.5, 35.9, 33.8; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{25}H_{17}NONa^+$ 370.1202; Found 370.1206.



Synthesis of 3p: A mixture of 2-(bromomethyl)naphthalene **1p** (26.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenylacrylonitrile **2a** (23.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3p**: 36.9 mg (0.0989 mmol), as a white solid, 99% yield; mp = 152–154 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97–7.90 (m, 2H), 7.81–7.75 (m, 2H), 7.74–7.67 (m, 2H), 7.56–7.33 (m, 11H), 4.47 (d, *J* = 8.8 Hz, 1H), 4.10 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.2, 135.7, 133.8, 133.6, 133.1, 133.0, 129.1, 129.0, 128.8, 128.7, 128.6, 128.53, 128.52, 128.2, 128.0, 127.7, 126.6 (2C), 126.3, 118.6, 43.3, 36.0, 34.0; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{27}H_{19}NONa^+$ 396.1359; Found 396.1355.

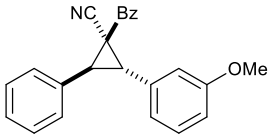


Synthesis of 3q: A mixture of 3-(bromomethyl)thiophene **1q** (21.1 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-(furan-2-carbonyl)-3-phenylacrylonitrile **2a** (22.3 mg, 0.100 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h and 80 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/40) to give the product **3q**: 22.2 mg (0.0674 mmol), as a white solid, 67% yield; mp = 130–132 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.95–7.90 (m, 2H), 7.58–7.53 (m, 1H), 7.47–7.40 (m, 6H), 7.39–7.34 (m, 1H), 7.23–7.20 (m, 1H), 7.19–7.16 (m, 1H), 7.02 (dd, *J* = 4.8, 1.6 Hz, 1H), 4.20 (d, *J* = 8.8 Hz, 1H), 3.89 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.3, 135.6, 133.9, 133.4, 132.4, 129.0, 128.9, 128.7, 128.5, 128.4, 127.6, 126.4, 124.6, 118.3, 38.0, 35.7, 34.6; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{21}H_{15}NOSNa^+$ 352.0767; Found 352.0763.

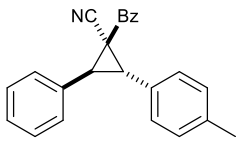


Synthesis of 3r: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-(*o*-tolyl)acrylonitrile **2b** (24.7 mg, 0.100 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10

mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/40) to give the product **3r**: 28.2 mg (0.0836 mmol), as a white solid, 84% yield; mp = 137–139 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.97–7.86 (m, 2H), 7.57–7.50 (m, 1H), 7.47–7.40 (m, 2H), 7.37–7.13 (m, 9H), 4.25 (d, *J* = 8.8 Hz, 1H), 3.99 (d, *J* = 8.8 Hz, 1H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.4, 138.7, 135.7, 133.8, 132.3, 131.5, 130.6, 129.1, 128.9, 128.69, 128.66, 128.63, 128.61, 127.9, 126.3, 118.5, 43.2, 34.8, 32.8, 19.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{19}NONa^+$ 360.1359; Found 360.1363.

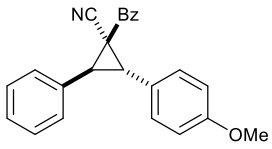


Synthesis of 3s: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-(3-methoxyphenyl)acrylonitrile **2c** (26.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3s**: 27.2 mg (0.0770 mmol), as a white solid, 77% yield; mp = 110–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.98–7.86 (m, 2H), 7.57–7.50 (m, 1H), 7.47–7.39 (m, 2H), 7.38–7.29 (m, 3H), 7.28–7.18 (m, 3H), 7.04 (d, *J* = 8.0 Hz, 1H), 7.01–6.96 (m, 1H), 6.91 (dd, *J* = 8.4, 2.4 Hz, 1H), 4.30 (d, *J* = 8.8 Hz, 1H), 3.93 (d, *J* = 8.8 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.3, 159.9, 135.7, 135.1, 133.8, 131.4, 130.0, 129.1, 128.9, 128.7, 128.61, 128.59, 120.8, 118.5, 114.4, 114.1, 55.4, 43.0, 35.8, 33.8; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{24}H_{20}NO_2^+$ 354.1489; Found 354.1485.

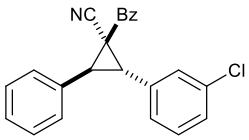


Synthesis of 3t: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-(*p*-tolyl)acrylonitrile **2d** (24.7 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3t**: 28.6 mg (0.0848 mmol), as a white solid, 85% yield; mp = 153–155 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.96–7.88 (m, 2H), 7.56–7.51 (m, 1H), 7.46–7.39 (m, 2H), 7.37–7.30 (m, 4H), 7.28–7.18 (m,

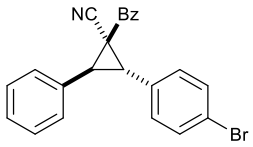
5H), 4.29 (d, *J* = 8.8 Hz, 1H), 3.92 (d, *J* = 8.8 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.4, 138.3, 135.9, 133.7, 131.5, 130.5, 129.6, 129.0, 128.9, 128.64, 128.59, 128.53, 128.48, 118.7, 43.1, 35.9, 33.7, 21.2; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{24}H_{19}NONa^+$ 360.1359; Found 360.1369.



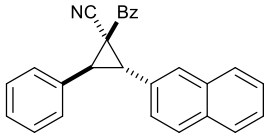
Synthesis of 3u: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-(4-methoxyphenyl)acrylonitrile **2e** (26.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 40 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3u**: 32.5 mg (0.0920 mmol), as a white solid, 92% yield; mp = 81–83 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.91 (dd, *J* = 8.0, 1.6 Hz 2H), 7.57–7.51 (m, 1H), 7.46–7.31 (m, 6H), 7.29–7.18 (m, 3H), 6.96 (d, *J* = 8.4 Hz, 2H), 4.28 (d, *J* = 8.8 Hz, 1H), 3.91 (d, *J* = 8.8 Hz, 1H), 3.82 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.5, 159.7, 135.9, 133.7, 131.5, 129.8, 129.0, 128.9, 128.63, 128.58, 128.5, 125.5, 118.7, 114.4, 55.3, 43.3, 35.9, 33.6; HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{24}H_{19}NO_2Na^+$ 376.1308; Found 376.1308.



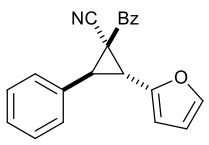
Synthesis of 3v: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-(3-chlorophenyl)acrylonitrile **2f** (26.8 mg, 0.100 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3v**: 24.2 mg (0.0678 mmol), as a white solid, 68% yield; mp = 138–140 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.96–7.84 (m, 2H), 7.59–7.52 (m, 1H), 7.49–7.41 (m, 3H), 7.38–7.29 (m, 5H), 7.28–7.19 (m, 3H), 4.29 (d, *J* = 8.8 Hz, 1H), 3.91 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 187.9, 135.7, 135.5, 134.8, 133.9, 131.0, 130.2, 129.1, 129.0, 128.8, 128.73 (2C), 128.71, 128.66, 126.8, 118.2, 42.8, 35.7, 33.0; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{23}H_{17}{}^{35}ClNO^+$ 358.0993; Found 358.0997; Calcd for $C_{23}H_{17}{}^{37}ClNO^+$ 360.0964; Found 360.0960.



Synthesis of 3w: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-(4-bromophenyl)acrylonitrile **2g** (31.2 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 30 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/40) to give the product **3w**: 34.3 mg (0.0855 mmol), as a white solid, 86% yield; mp = 123–125 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.96–7.80 (m, 2H), 7.60–7.49 (m, 3H), 7.47–7.39 (m, 2H), 7.36–7.19 (m, 7H), 4.26 (d, *J* = 8.8 Hz, 1H), 3.89 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 187.9, 135.6, 133.9, 132.7, 132.1, 131.0, 130.3, 129.1, 128.8, 128.72 (2C), 128.66, 122.6, 118.3, 42.9, 35.7, 33.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{16}{}^{79}BrNONa^+$ 424.0307; Found 424.0314; Calcd for $C_{23}H_{16}{}^{81}BrNONa^+$ 426.0287; Found 426.0284.

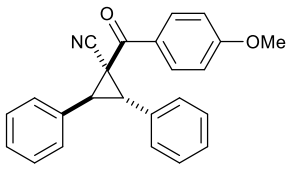


Synthesis of 3x: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-(naphthalen-2-yl)acrylonitrile **2h** (28.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3x**: 26.6 mg (0.0713 mmol), as a white solid, 71% yield; mp = 201–203 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.16 (d, *J* = 8.0 Hz, 1H), 8.05–7.96 (m, 2H), 7.95–7.87 (m, 2H), 7.64–7.37 (m, 9H), 7.32–7.21 (m, 3H), 4.72 (d, *J* = 8.8 Hz, 1H), 4.14 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 188.5, 135.5, 134.0, 133.8, 132.8, 131.5, 130.2, 129.5, 129.3, 128.92, 128.86, 128.8, 128.68, 128.65, 127.2, 126.4, 125.8, 125.2, 123.5, 118.4, 42.7, 35.5, 31.7; HRMS (ESI-TOF) m/z: $[M + H]^+$ Calcd for $C_{27}H_{20}NO^+$ 374.1539; Found 374.1539.

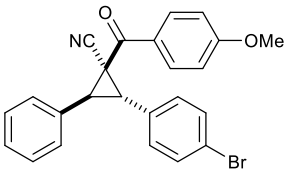


Synthesis of 3y: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-(furan-2-yl)acrylonitrile **2i** (22.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 40 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3y**: 18.1

mg (0.0578 mmol), as a yellow solid, 58% yield; mp = 128–130 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93–7.87 (m, 2H), 7.58–7.52 (m, 1H), 7.48–7.40 (m, 3H), 7.32–7.18 (m, 5H), 6.50 (d, *J* = 3.6 Hz, 1H), 6.43 (dd, *J* = 3.2, 1.6 Hz, 1H), 4.26 (d, *J* = 8.8 Hz, 1H), 4.00 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 187.7, 147.8, 143.2, 135.6, 133.8, 130.7, 129.0, 128.8, 128.7 (2C), 128.6, 118.4, 111.0, 109.3, 42.2, 35.0, 27.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{15}NO_2Na^+$ 336.0995; Found 336.1003.

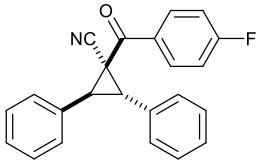


Synthesis of 3z: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-(4-methoxybenzoyl)-3-phenylacrylonitrile **2j** (26.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3z**: 34.7 mg (0.0983 mmol), as a white solid, 98% yield; mp = 116–118 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.98–7.92 (m, 2H), 7.49–7.40 (m, 4H), 7.39–7.34 (m, 1H), 7.32–7.27 (m, 2H), 7.26–7.16 (m, 3H), 6.92–6.86 (m, 2H), 4.29 (d, *J* = 8.8 Hz, 1H), 3.87 (d, *J* = 8.8 Hz, 1H), 3.83 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 186.2, 164.1, 133.8, 131.7, 131.6, 128.9, 128.7, 128.64, 128.61, 128.5, 128.4, 128.3, 118.8, 113.9, 55.5, 42.2, 35.4, 33.2; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{24}H_{19}NO_2Na^+$ 376.1308; Found 376.1313.

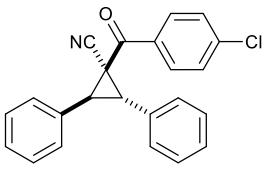


Synthesis of 3aa: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-3-(4-bromophenyl)-2-(4-methoxybenzoyl)acrylonitrile **2k** (34.2 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/40) to give the product **3aa**: 36.3 mg (0.0842 mmol), as a white solid, 84% yield; mp = 139–141 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93 (d, *J* = 8.8 Hz, 2H), 7.55 (d, *J* = 8.4 Hz, 2H), 7.33 (d, *J* = 8.4 Hz, 2H), 7.29–7.19 (m, 5H), 6.89 (d, *J* = 8.8 Hz, 2H), 4.22 (d, *J* = 8.8 Hz, 1H), 3.83 (s, 3H), 3.81 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 185.8, 164.2, 133.0, 132.1, 131.6, 131.3, 130.3, 128.67, 128.66, 128.6, 128.3, 122.5, 118.6, 113.9, 55.6, 42.1, 35.3, 32.5; HRMS (ESI-

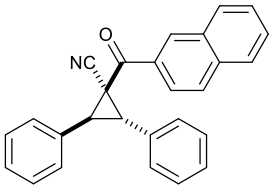
TOF) m/z: [M + Na]$^+$ Calcd for $C_{24}H_{18}{}^{79}BrNO_2Na^+$ 454.0413; Found 454.0421; Calcd for $C_{24}H_{18}{}^{81}BrNO_2Na^+$ 456.0393; Found 456.0403.



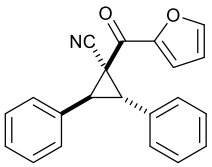
Synthesis of 3ab: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-(4-fluorobenzoyl)-3-phenylacrylonitrile **2l** (25.1 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/40) to give the product **3ab**: 27.3 mg (0.0800 mmol), as a white solid, 80% yield; mp = 110–112 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.95–7.74 (m, 2H), 7.42–7.26 (m, 5H), 7.25–7.11 (m, 5H), 7.06–6.95 (m, 2H), 4.24 (d, *J* = 8.8 Hz, 1H), 3.86 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 186.7, 166.0 (d, $^1J_{FC}$ = 255.1 Hz), 133.5, 132.0 (d, $^4J_{FC}$ = 3.0 Hz), 131.8 (d, $^3J_{FC}$ = 9.5 Hz), 131.3, 129.0, 128.8, 128.71, 128.67, 128.6, 128.5, 118.4, 115.9 (d, $^2J_{FC}$ = 22.0 Hz), 42.9, 35.6, 33.7; ^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) –103.1 (m); HRMS (ESI-TOF) m/z: [M + Na]$^+$ Calcd for $C_{23}H_{16}FNONa^+$ 364.1108; Found 364.1109.



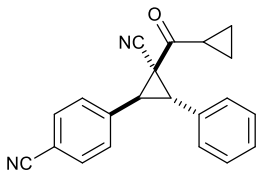
Synthesis of 3ac: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-(4-chlorobenzoyl)-3-phenylacrylonitrile **2m** (26.8 mg, 0.100 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3ac**: 25.9 mg (0.0725 mmol), as a white solid, 73% yield; mp = 134–136 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.00–7.75 (m, 2H), 7.54–7.13 (m, 12H), 4.32 (d, *J* = 8.8 Hz, 1H), 3.95 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 187.1, 140.4, 134.0, 133.4, 131.2, 130.4, 129.03, 128.98, 128.8, 128.73, 128.71, 128.6, 128.5, 118.3, 43.1, 35.7, 33.8; HRMS (ESI-TOF) m/z: [M + H]$^+$ Calcd for $C_{23}H_{17}{}^{35}ClNO^+$ 358.0993; Found 358.0986; Calcd for $C_{23}H_{17}{}^{37}ClNO^+$ 360.0964; Found 360.0967; [M + Na]$^+$ Calcd for $C_{23}H_{16}{}^{35}ClNONa^+$ 380.0813; Found 380.0805; Calcd for $C_{23}H_{16}{}^{37}ClNONa^+$ 382.0783; Found 382.0787.



Synthesis of 3ad: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-(1-naphthoyl)-3-phenylacrylonitrile **2n** (28.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 30 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/40) to give the product **3ad**: 33.0 mg (0.0884 mmol), as a white solid, 88% yield; mp = 127–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.19 (d, *J* = 8.4 Hz, 1H), 8.06–7.89 (m, 2H), 7.87–7.74 (m, 1H), 7.61–7.20 (m, 13H), 4.46 (d, *J* = 9.2 Hz, 1H), 4.05 (d, *J* = 9.2 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 189.9, 133.9, 133.62, 133.57, 133.5, 131.4, 130.2, 129.2, 129.0, 128.8, 128.71, 128.68, 128.64, 128.57, 128.1, 126.7, 125.3, 125.1, 124.2, 118.5, 44.8, 38.2, 35.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{27}H_{19}NONa^+$ 396.1359; Found 396.1357.



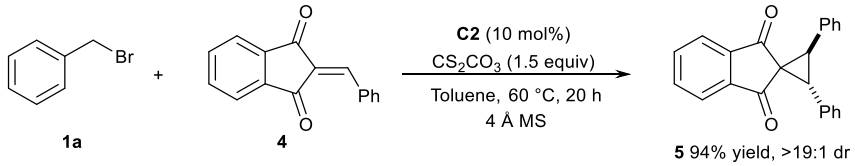
Synthesis of 3ae: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-(furan-2-carbonyl)-3-phenylacrylonitrile **2o** (22.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/50 to 1/40) to give the product **3ae**: 28.5 mg (0.0910 mmol), as a white solid, 91% yield; mp = 135–137 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.66–7.61 (m, 1H), 7.58–7.53 (m, 1H), 7.47–7.36 (m, 5H), 7.28–7.22 (m, 5H), 6.54 (dd, *J* = 3.6, 2.4 Hz, 1H), 4.27 (d, *J* = 8.8 Hz, 1H), 3.89 (d, *J* = 8.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 174.9, 151.0, 147.8, 133.4, 131.3, 129.1, 128.9, 128.7, 128.6, 128.5, 120.6, 118.3, 112.6, 42.8, 34.3, 34.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{15}NO_2Na^+$ 336.0995; Found 336.1000.



Synthesis of 3af: A mixture of 4-(bromomethyl)benzonitrile **1a** (23.5 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-(cyclopropanecarbonyl)-3-phenylacrylonitrile **2p** (19.7 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 80 °C for 40 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30)

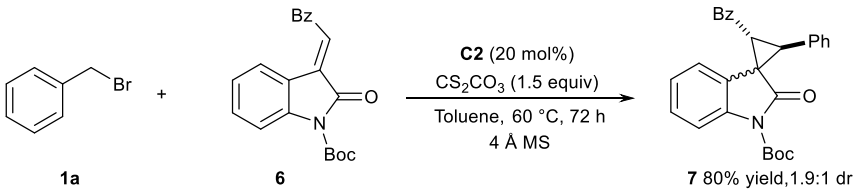
to give the product **3af**: 28.3 mg (0.0907 mmol), as a white solid, 91% yield; mp = 109–111 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.62 (d, *J* = 8.4 Hz, 2H), 7.47–7.35 (m, 7H), 3.98 (d, *J* = 8.8 Hz, 1H), 3.79 (d, *J* = 8.8 Hz, 1H), 2.69–2.61 (m, 1H), 1.14–1.03 (m, 2H), 0.97–0.88 (m, 1H), 0.68–0.60 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 196.6, 137.5, 132.8, 132.2, 130.2, 129.1, 128.8, 128.3, 118.3, 118.1, 112.3, 42.4, 37.6, 36.5, 20.5, 13.3, 12.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{21}H_{16}N_2ONa^+$ 335.1155; Found 335.1154.

3.2 Procedure for synthesis of 5



A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), 2-benzylidene-1*H*-indene-1,3(2*H*)-dione **4** (23.4 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (3.2 mg, 10 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **5**: 30.3 mg (0.0935 mmol), as a yellow solid, 94% yield; mp = 176–178 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.84 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.74 (dd, *J* = 5.6, 3.2 Hz, 2H), 7.46–7.26 (m, 10H), 4.19 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 195.6, 142.1, 134.8, 133.8, 129.3, 128.4, 127.9, 122.6, 48.5, 43.6; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{16}O_2Na^+$ 347.1043; Found 347.1047.

3.3 Procedure for synthesis of 7



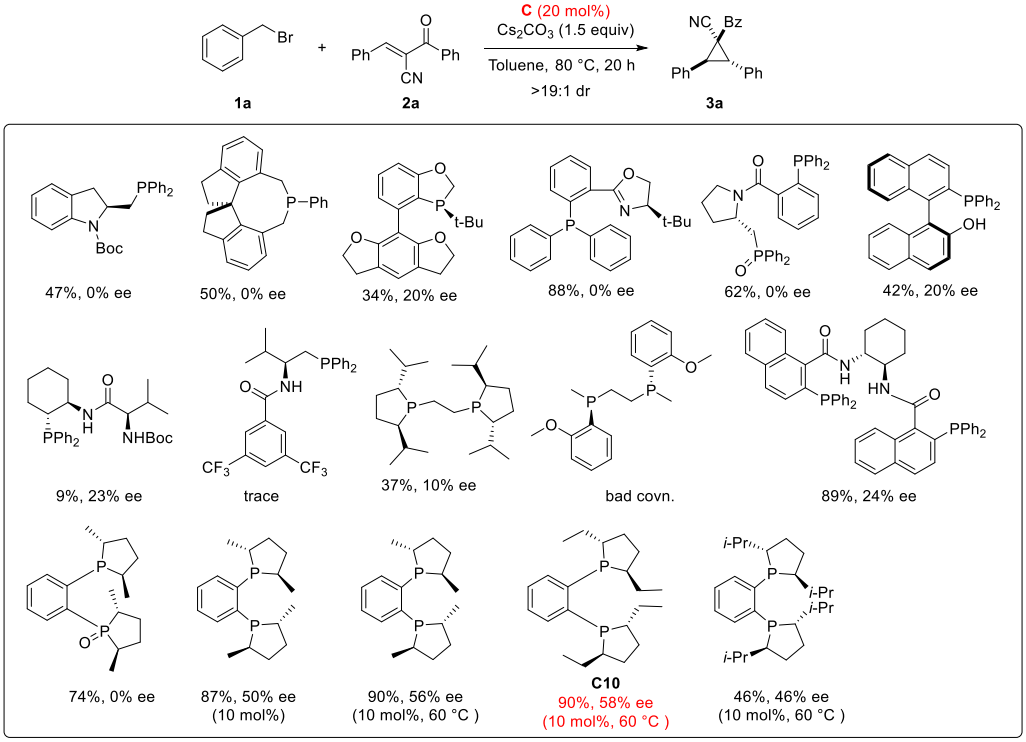
A mixture of benzyl bromide **1a** (28.9 mg, 0.169 mmol, 1.7 equiv), *tert-butyl* (*Z*)-2-oxo-3-(2-oxo-2-phenylethylidene)indoline-1-carboxylate **6** (34.9 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv), **C2** (6.4 mg, 20 mol%) and 4 Å MS (40.0 mg) in distilled toluene (1.0 mL) was stirred at 60 °C for 72 h, and the reaction was monitored by TLC.

After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give separable diastereomers **7a** and **7b** in 80% total yield.

7a: 22.8 mg (0.0519 mmol), as a white solid, 52% yield, mp = 127–129 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.01–7.95 (m, 2H), 7.81 (d, *J* = 8.4 Hz, 1H), 7.59–7.54 (m, 1H), 7.45 (t, *J* = 8.0 Hz, 2H), 7.37–7.22 (m, 7H), 7.10 (td, *J* = 7.6, 1.2 Hz, 1H), 4.34 (d, *J* = 8.8 Hz, 1H), 4.11 (d, *J* = 8.8 Hz, 1H), 1.61 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 192.5, 170.2, 149.0, 139.7, 136.8, 133.9, 132.5, 129.3, 128.9, 128.6, 128.2, 127.8, 127.7, 125.2, 124.4, 121.7, 114.7, 84.6, 42.3, 42.1, 41.6, 28.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{25}NO_4Na^+$ 462.1676; Found 462.1676.

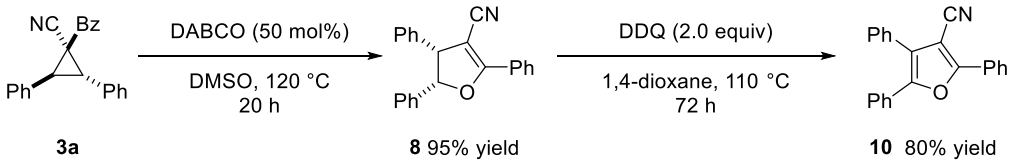
7b: 12.2 mg (0.0278 mmol), as a white solid, 28% yield; mp = 149–151 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.93 (d, *J* = 8.4 Hz, 1H), 7.87–7.79 (m, 2H), 7.57–7.50 (m, 1H), 7.42–7.36 (m, 2H), 7.35–7.26 (m, 4H), 7.25–7.21 (m, 2H), 6.88 (td, *J* = 7.6, 1.0 Hz, 1H), 6.14 (dd, *J* = 7.6, 1.2 Hz, 1H), 4.19 (d, *J* = 8.8 Hz, 1H), 3.63 (d, *J* = 8.8 Hz, 1H), 1.56 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 191.0, 170.7, 149.2, 140.2, 136.4, 133.5, 133.0, 129.9, 128.8, 128.7, 128.4, 128.04, 127.98, 124.4, 123.9, 120.7, 115.0, 84.5, 42.8, 39.9, 39.6, 28.0; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{28}H_{25}NO_4Na^+$ 462.1676; Found 462.1682.

4. Asymmetric intermolecular cyclopropanation exploration



Asymmetric synthesis of 3a: A mixture of benzyl bromide **1a** (20.4 mg, 0.119 mmol, 1.2 equiv), (*E*)-2-benzoyl-3-phenylacrylonitrile **2a** (23.3 mg, 0.0999 mmol, 1.0 equiv), cesium carbonate (48.9 mg, 0.150 mmol, 1.5 equiv) and (*R,R*)-Et-DuPhos **C10** (3.6 mg, 9.9 mol%) in distilled toluene (1.0 mL) was stirred at 60 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was directly purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/40 to 1/30) to give the product **3a**: 29.1 mg (0.0900 mmol), as a white solid, 90% yield; 58% ee, determined by HPLC analysis (Daicel chiralpak IA-H, *n*-hexane/*i*-PrOH = 80/20, flow rate = 1.0 mL/min, l = 254 nm) t_R = 7.22 min (major), t_R = 8.12 min (minor).

5. Transformations of product 3a

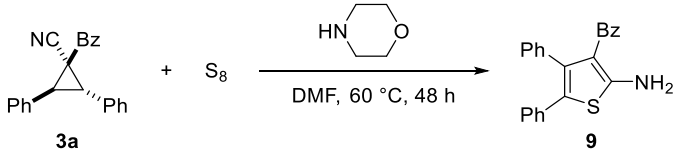


3a **8** 95% yield **10** 80% yield

Synthesis of 8: A solution of **3a** (32.3 mg, 0.0999 mmol, 1.0 equiv) and DABCO (5.6 mg, 0.0499 mmol, 0.5 equiv) in DMSO (1.0 mL) was stirred at 120 °C for 20 h, and the reaction was monitored by TLC. After completion, the mixture was quenched with water (5 mL) and extracted with EtOAc (5 mL x 3), the organic layer was combined, dried with anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/60 to 1/50) to give product **8**: 30.7 mg (0.0950 mmol), as a colorless oil, 95% yield; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.21–8.06 (m, 2H), 7.57–7.47 (m, 3H), 7.46–7.26 (m, 10H), 5.63 (d, *J* = 7.6 Hz, 1H), 4.42 (d, *J* = 7.6 Hz, 1H); ^{13}C NMR (151 MHz, $CDCl_3$): δ (ppm) 166.7, 139.8, 139.7, 131.8, 129.3, 129.0, 128.85, 128.83, 128.2, 127.7, 127.6, 127.4, 125.4, 117.0, 92.1, 84.4, 59.1; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{17}NONa^+$ 346.1202; Found 346.1206. *The relative configuration has been assigned by NOE analysis*.

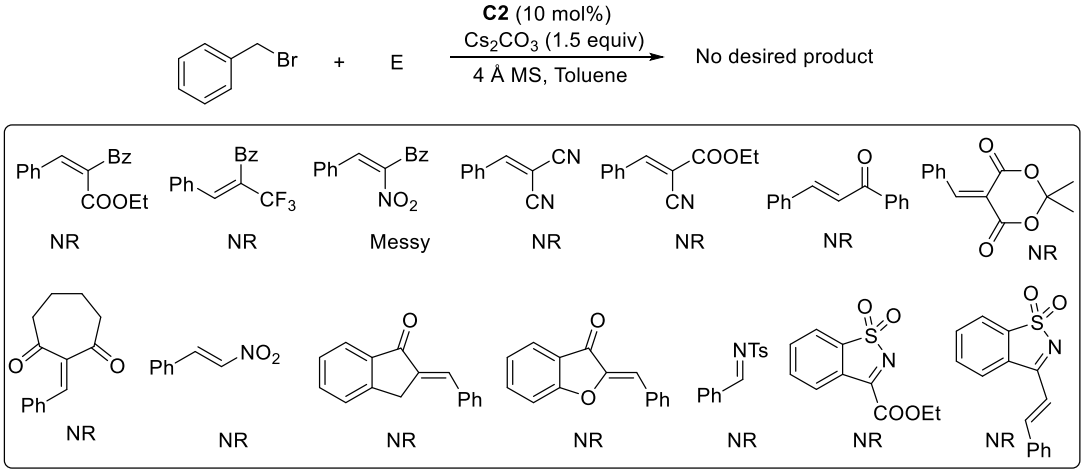
Synthesis of 10: A mixture of **8** (36.0 mg, 0.111 mmol, 1.0 equiv) and DDQ (50.6 mg, 0.223 mmol, 2.0 equiv) in 1,4-dixoane (3.0 mL) was stirred at 110 °C for 72 h, and the reaction was monitored by TLC. After completion, the solvent was evaporated and the residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/90 to 1/70) to give the product **10**: 28.6 mg (0.0891 mmol), as a white solid, 80% yield; mp = 158–160 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 8.16–8.06 (m, 2H), 7.60–7.39 (m, 10H), 7.36–7.27 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): δ

(ppm) 158.4, 148.6, 130.3, 130.2, 129.3, 129.2 (2C), 129.1 (2C), 128.73, 128.67, 128.1, 126.3, 125.5, 124.1, 114.7, 95.7; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{15}NONa^+$ 344.1046; Found 344.1055.



Synthesis of 9: A solution of **3a** (32.3 mg, 0.100 mmol, 1.0 equiv), S_8 (38.5 mg, 0.150 mmol, 1.5 equiv) and morpholine (8.7 mg, 0.0999 mmol, 1.0 equiv) in DMF (1.0 mL) was stirred at 60 °C for 48 h, and the reaction was monitored by TLC. After completion, the solution was washed by water (5 mL) and extracted with EtOAc (5 mL x 3), the organic layer was combined, dried with anhydrous Na_2SO_4, filtered and concentrated *in vacuo*. The residue was purified by flash chromatography on silica gel (EtOAc/petroleum ether = 1/20 to 1/15) to give the product **9**: 24.0 mg (0.0676 mmol), as a yellow solid, 68% yield; mp = 154–156 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 7.27–7.23 (m, 2H), 7.19–7.10 (m, 3H), 7.10–6.99 (m, 3H), 6.98–6.91 (m, 2H), 6.90–6.79 (m, 5H), 6.57 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ (ppm) 193.9, 164.3, 140.1, 136.1, 135.9, 134.0, 130.7, 130.2, 129.3, 128.6, 128.2, 127.6, 127.2, 126.8, 126.5, 120.8, 117.8; HRMS (ESI-TOF) m/z: $[M + Na]^+$ Calcd for $C_{23}H_{17}NOSNa^+$ 378.0923; Found 378.0921.

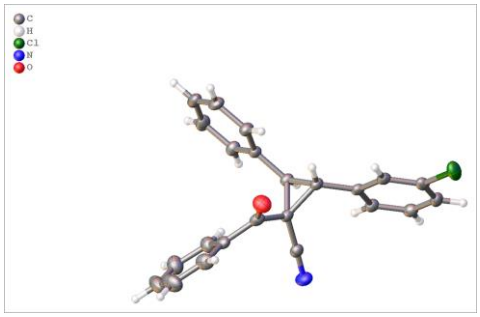
6. More substrate exploration

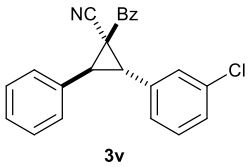


To further expand the substrate scope, other kinds of activated alkenes and imines were tested. Unfortunately, generally no obvious conversions were observed under standard conditions.

7. Crystal data and structural refinement

Procedure for the recrystallization of 3v: To a 10 mL tube containing **3v** (30 mg) were added isopropanol (5.0 mL) and *n*-hexane (5.0 mL). The mixture was heated until a clear solution was formed, which was kept aside and sealed by a piece of weighing paper with a tiny hole at room temperature to obtain crystals. The crystals were subjected for single crystal XRD to determine the absolute configuration of **3v**. The data were collected by an Agilent Gemini equipped with a Mo radiation source (Kα = 0.71073 Å) at 150.15 K. CCDC 2178229 (**3v**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif.



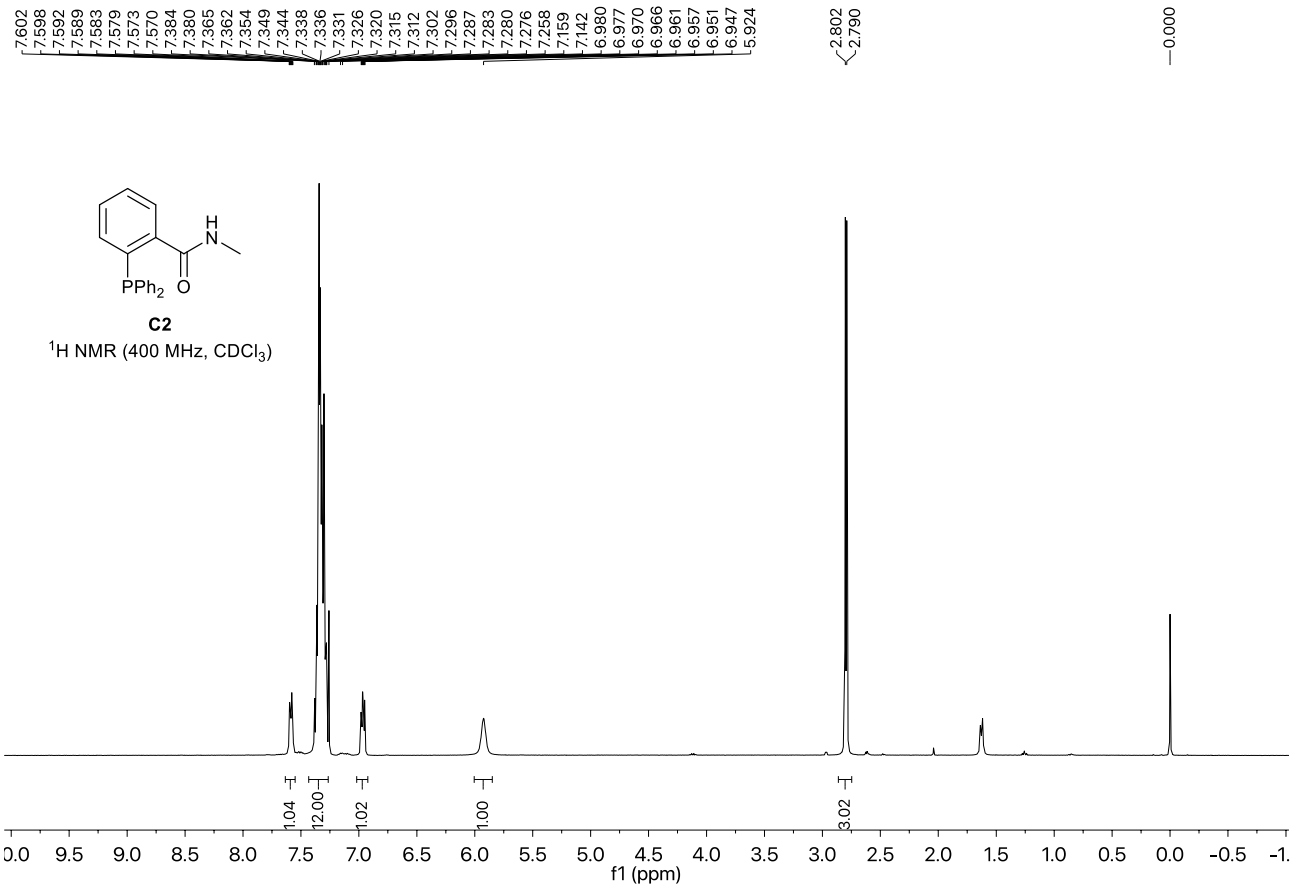


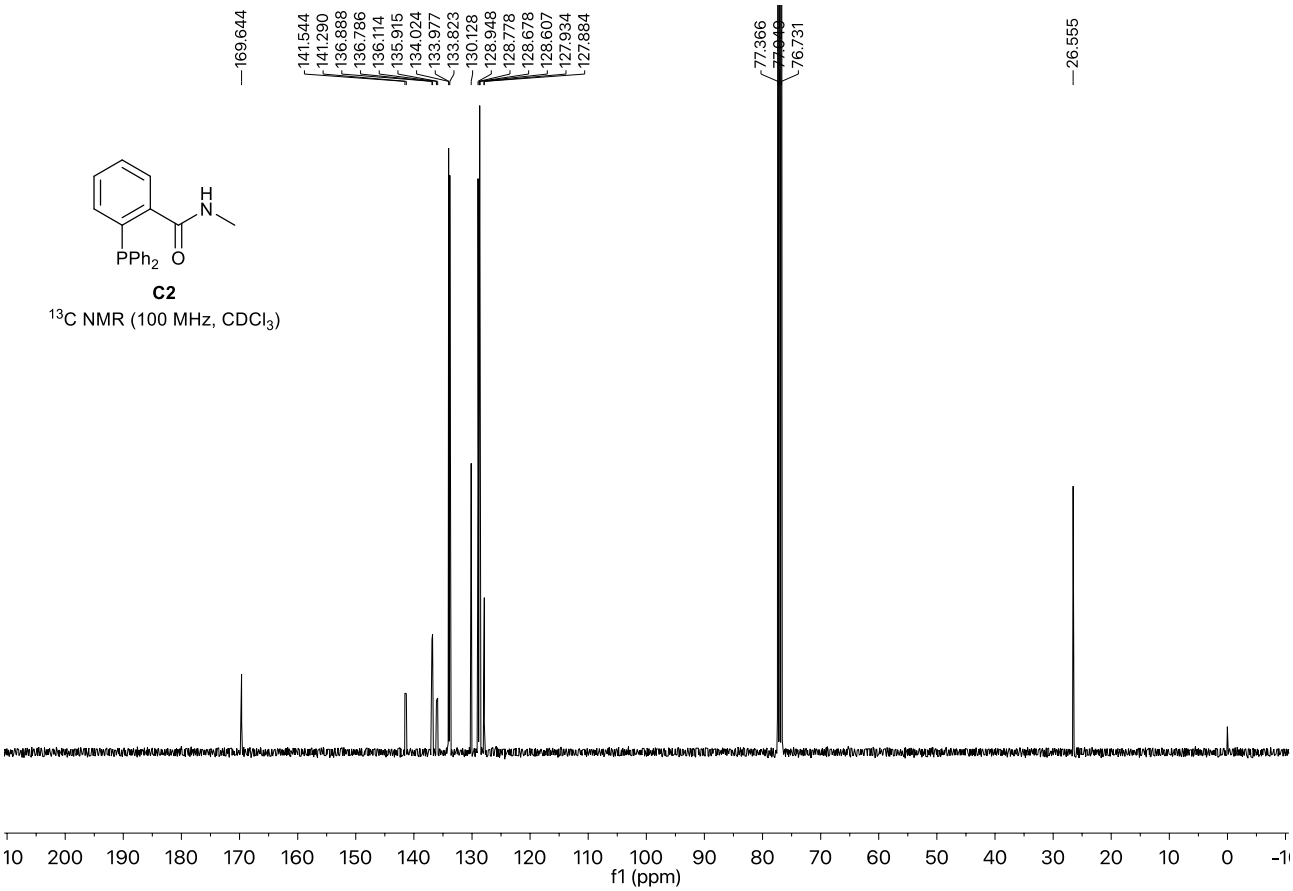
3v

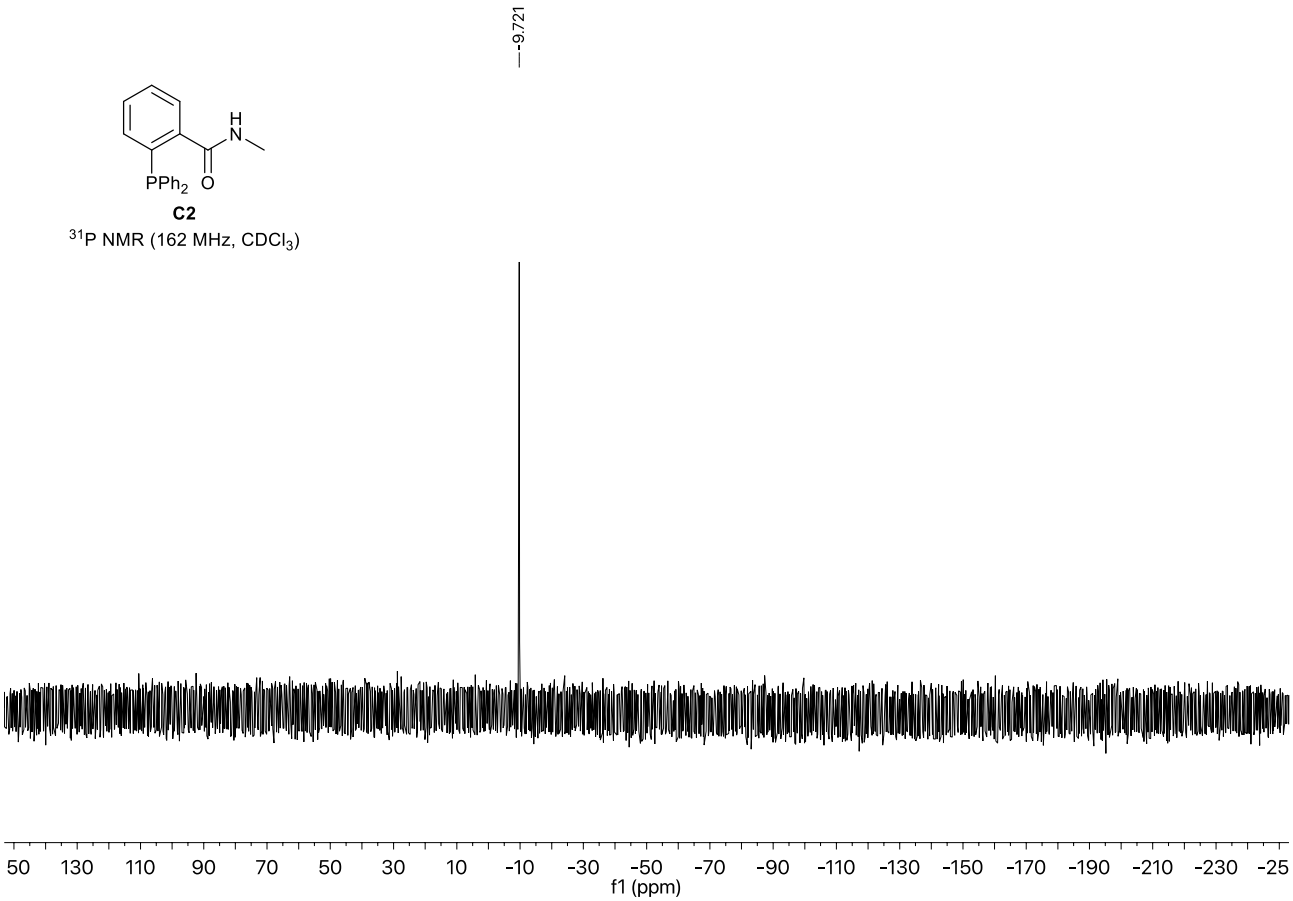
Identification code	**3v**
Empirical formula	$C_{23}H_{16}ClNO$
Formula weight	357.82
Temperature/K	150.15
Crystal system	monoclinic
Space group	I2/c
a/Å	17.725(3)
b/Å	6.1239(8)
c/Å	33.492(6)
α/°	90
β/°	93.999(9)
γ/°	90
Volume/Å^3	3626.6(10)
Z	8

ρ_{calc}g/cm^3	1.311
μ/mm^{-1}	0.222
F(000)	1488.0
Crystal size/mm^3	0.35 × 0.21 × 0.17
Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.608 to 55.026
Index ranges	-23 ≤ h ≤ 23, -7 ≤ k ≤ 7, -43 ≤ l ≤ 43
Reflections collected	31596
Independent reflections	4147 [R_{int} = 0.1463, R_{sigma} = 0.0940]
Data/restraints/parameters	4147/0/235
Goodness-of-fit on F^2	1.033
Final R indexes [I>=2σ (I)]	R_1 = 0.0762, wR_2 = 0.1841
Final R indexes [all data]	R_1 = 0.0957, wR_2 = 0.2005
Largest diff. peak/hole / e Å^{-3}	0.92/-0.70

8. NMR, HRMS spectra and HPLC chromatograms

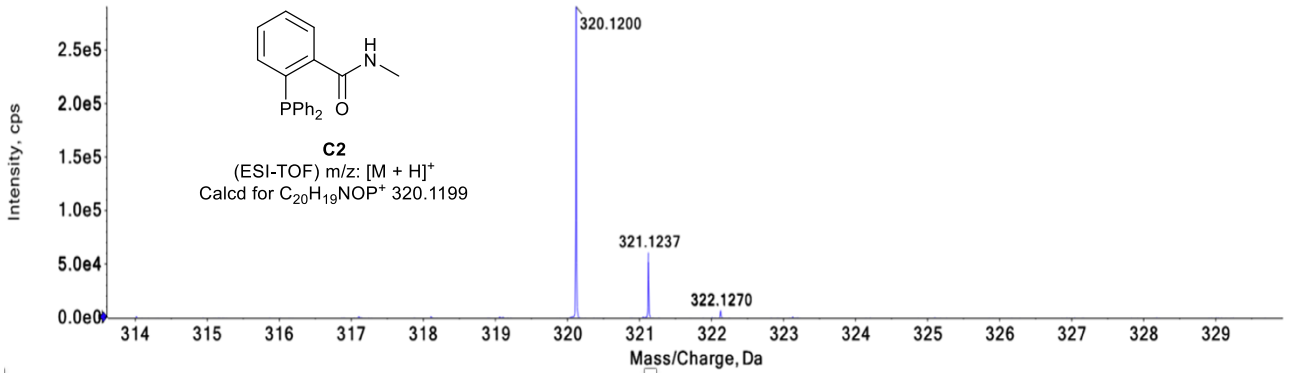






C2

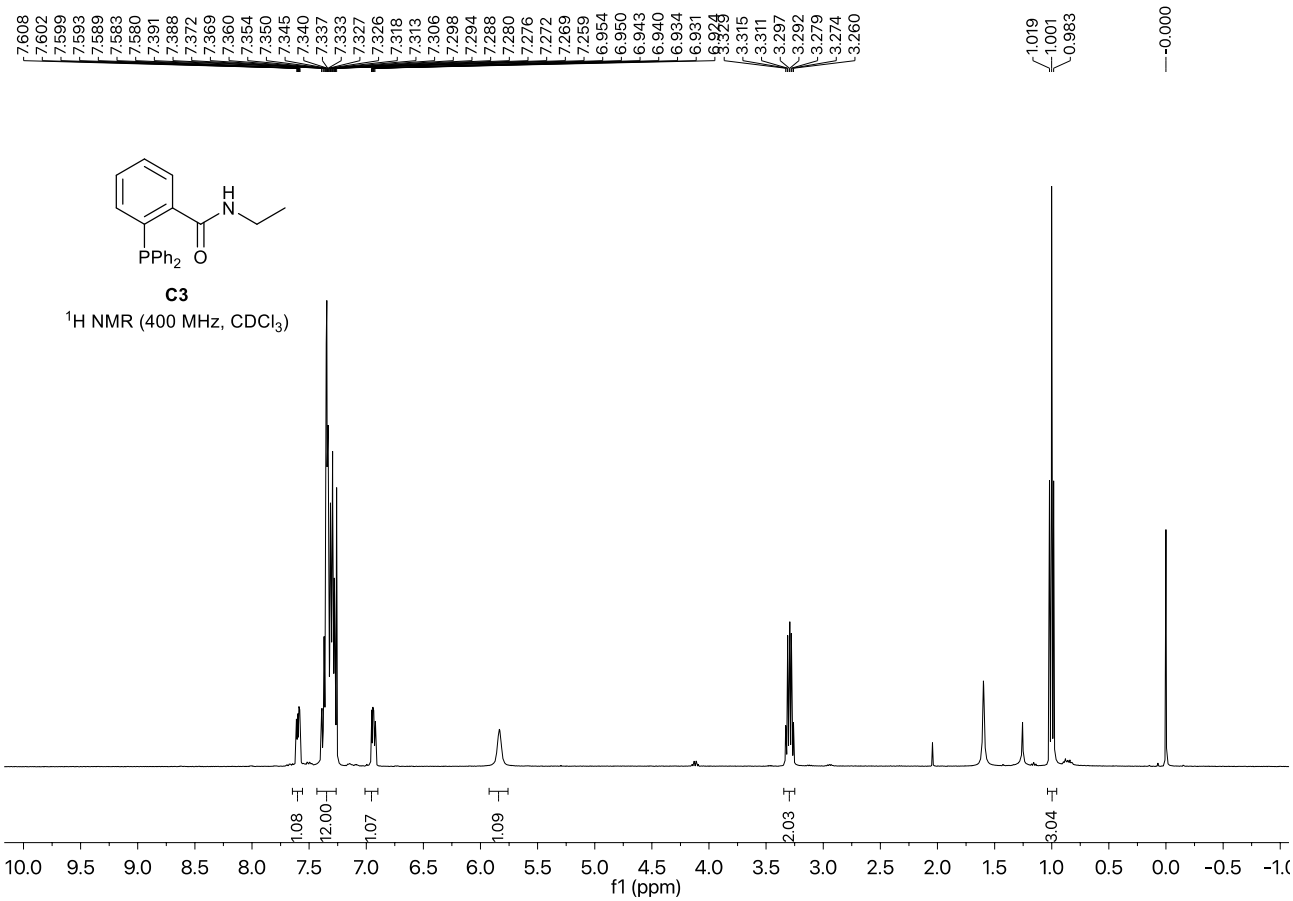
^{31}P NMR (162 MHz, $CDCl_3$)

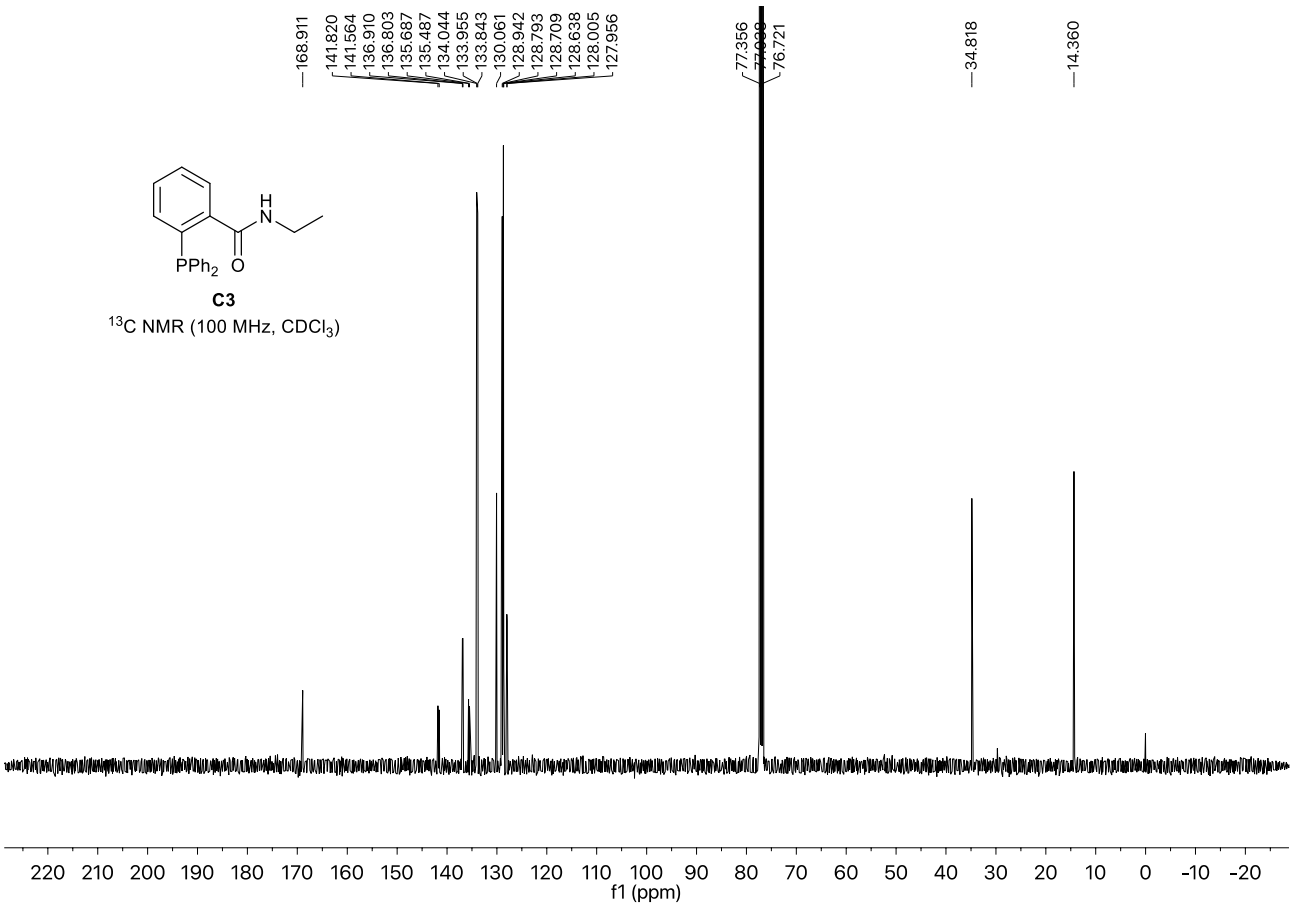


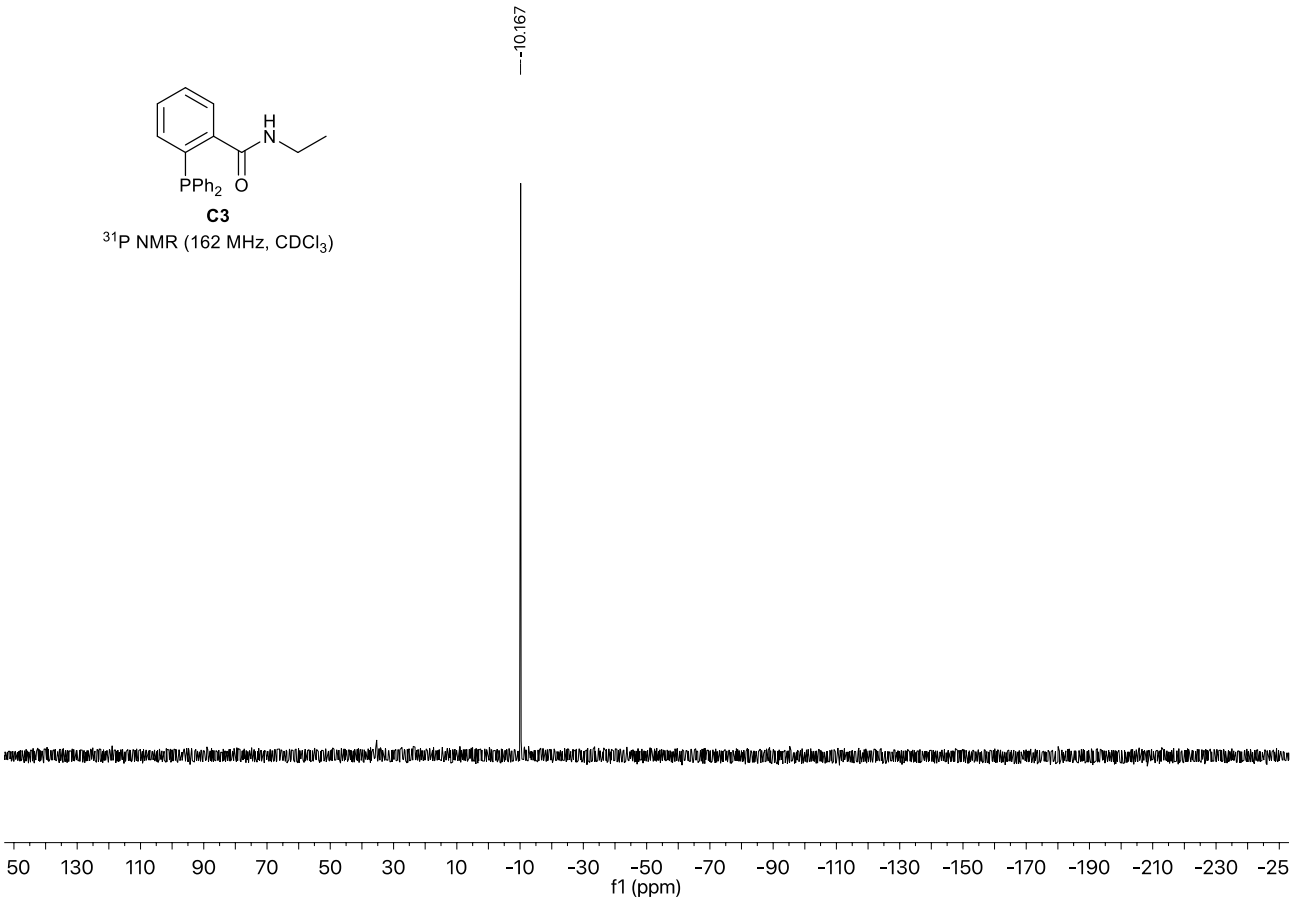
C2

(ESI-TOF) m/z: $[M + H]^+$

Calcd for $C_{20}H_{19}NOP^+$ 320.1199

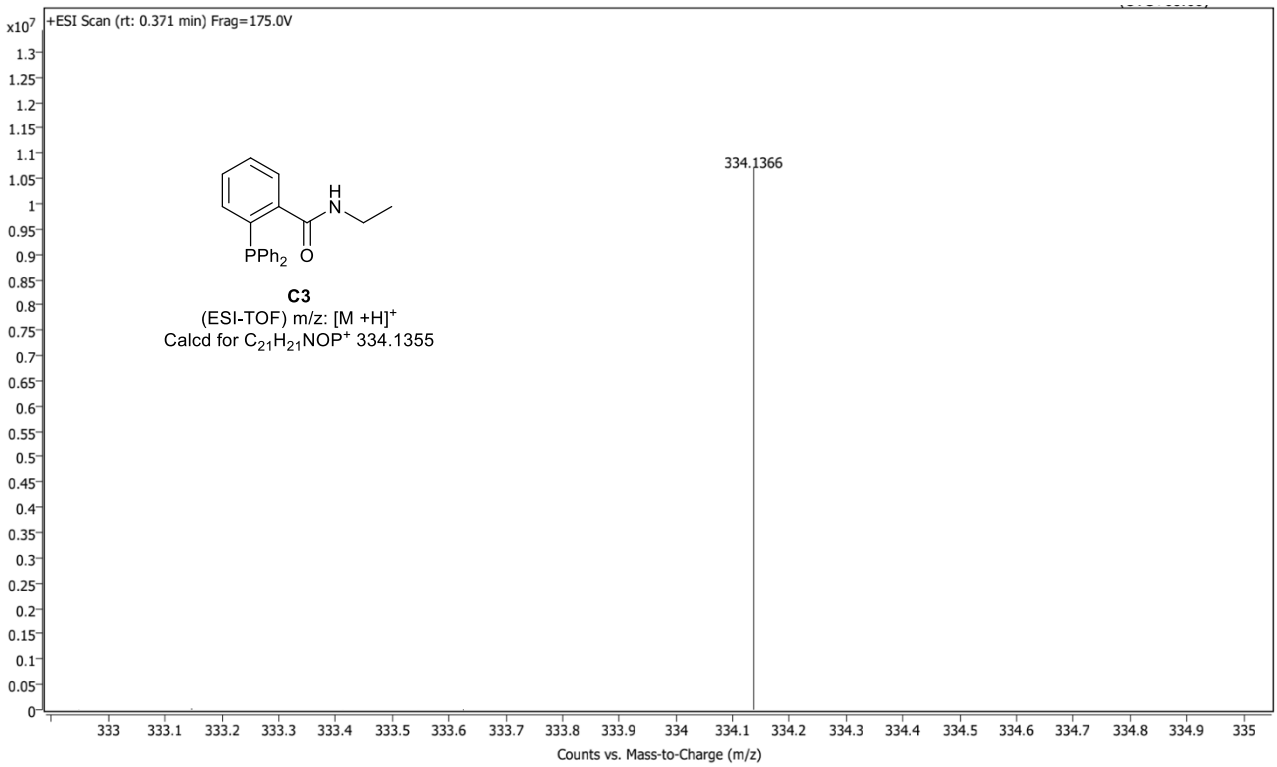

7.608
7.602
7.599
7.593
7.589
7.583
7.580
7.391
7.388
7.372
7.369
7.360
7.354
7.350
7.345
7.340
7.337
7.333
7.327
7.326
7.318
7.313
7.306
7.298
7.294
7.288
7.280
7.276
7.272
7.269
7.259
6.954
6.950
6.943
6.940
6.934
6.931
3.329
3.324
3.315
3.311
3.297
3.292
3.279
3.274
3.260
1.019
1.001
0.983
-0.000
PPh2
O
H
N
C3
1H NMR (400 MHz, CDCl3)
1.08
12.00
1.07
1.09
2.03
3.04
f1 (ppm)


168.911
141.820
141.564
136.910
136.803
135.687
135.487
134.044
133.955
133.843
130.061
128.942
128.793
128.709
128.638
128.005
127.956
77.356
77.000
76.721
34.818
14.360
PPh2
O
H
N
C3
13C NMR (100 MHz, CDCl3)
f1 (ppm)



C3

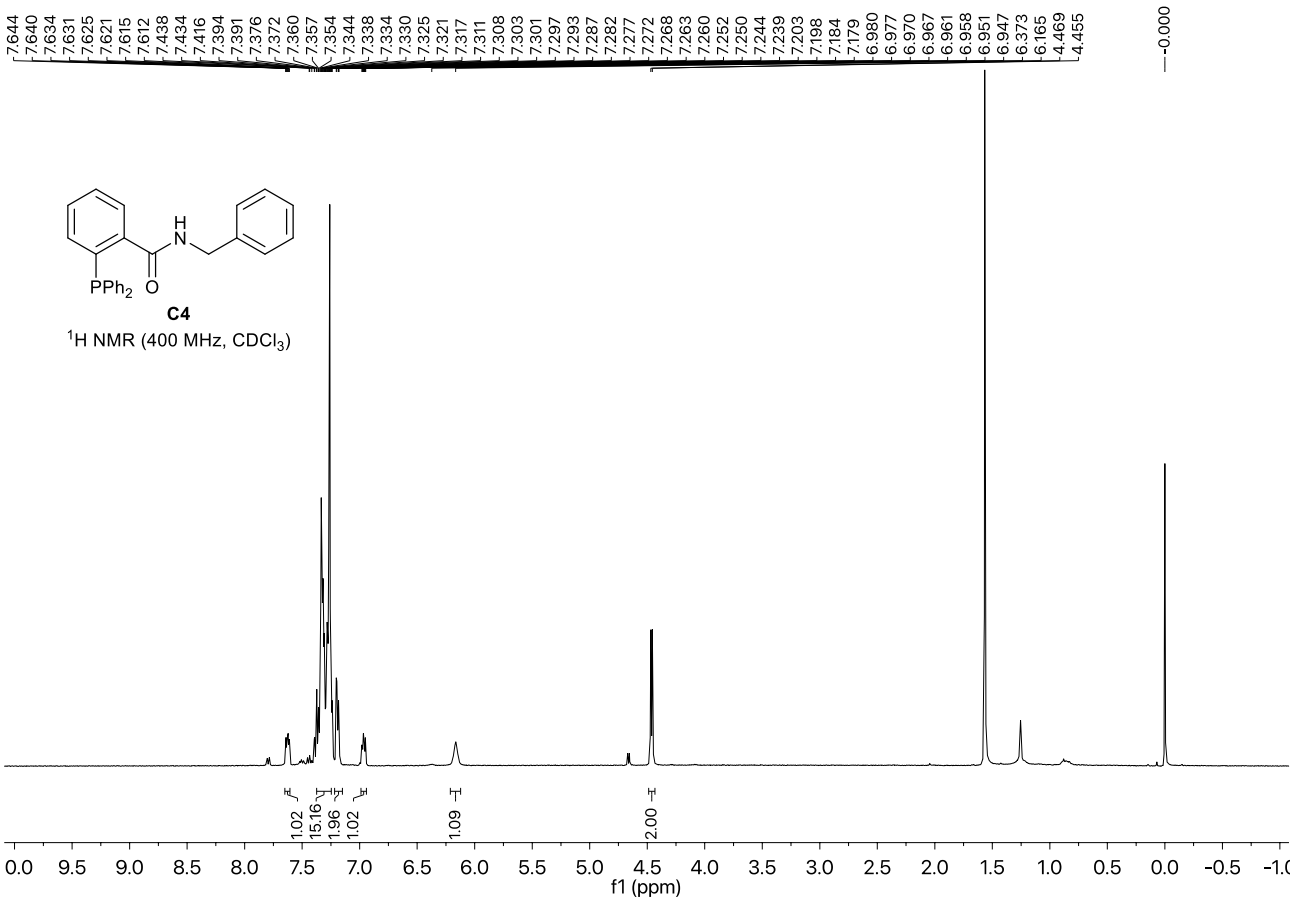
^{31}P NMR (162 MHz, $CDCl_3$)

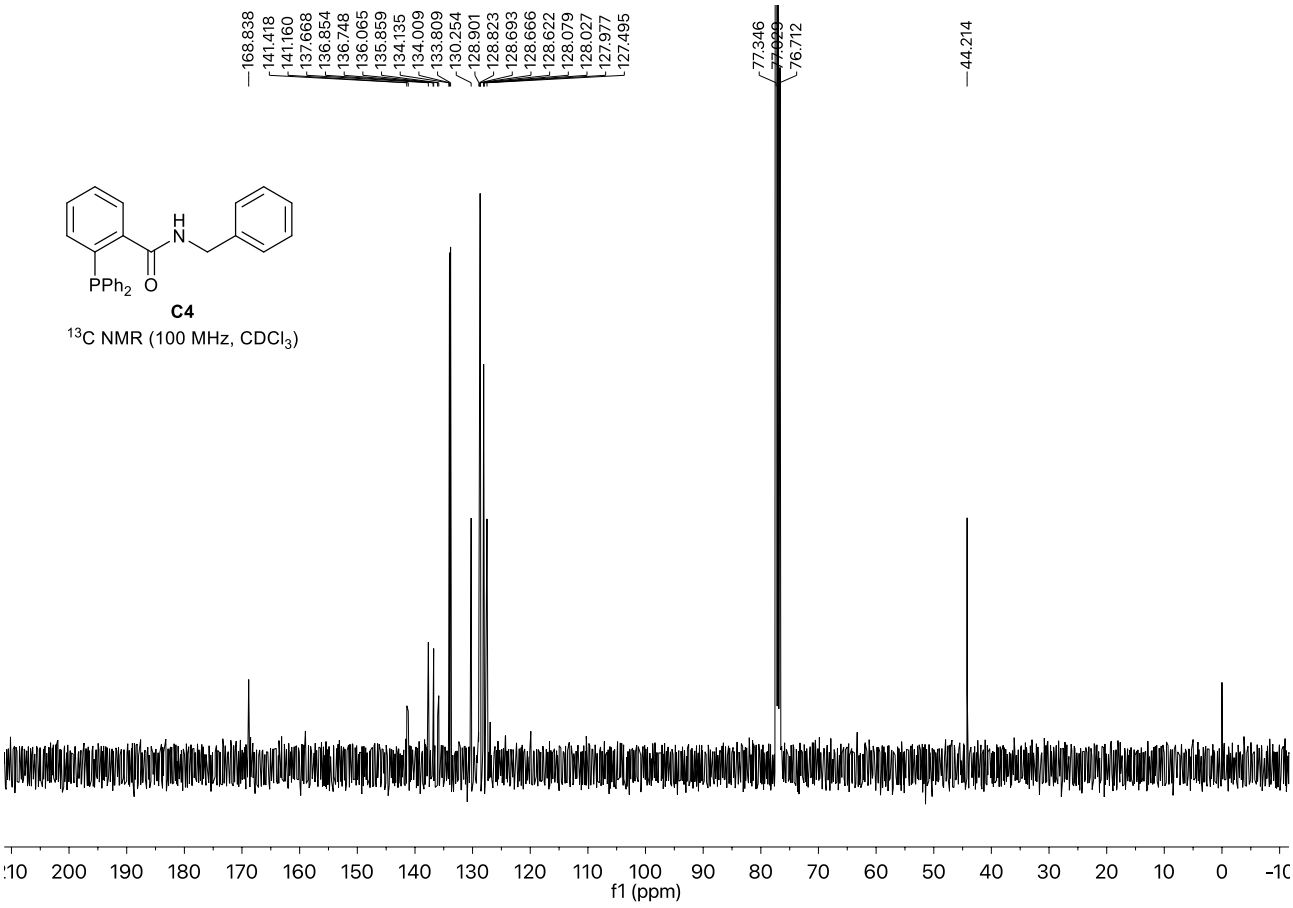


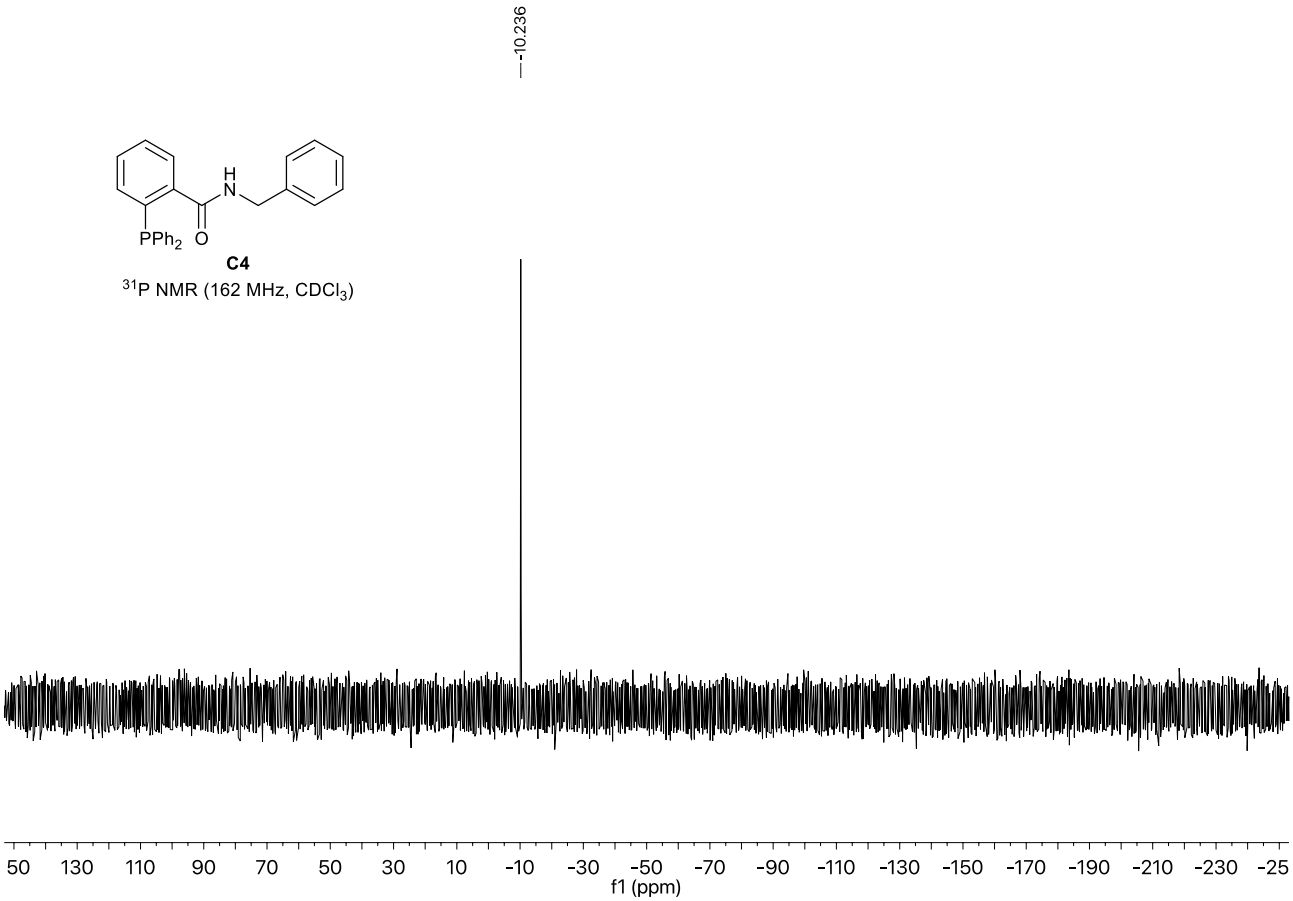
C3

(ESI-TOF) m/z: $[M+H]^+$

Calcd for $C_{21}H_{21}NOP^+$ 334.1355

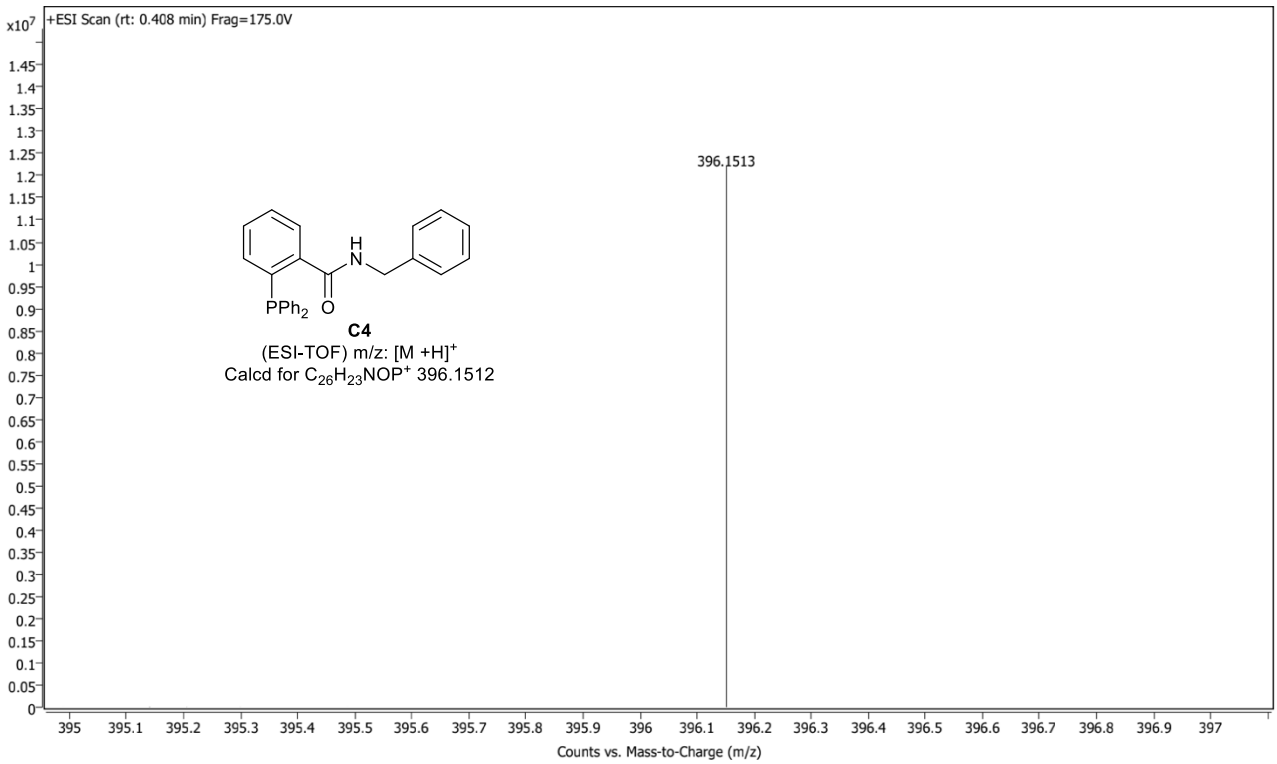

7.644
7.640
7.634
7.631
7.625
7.621
7.615
7.612
7.438
7.434
7.416
7.394
7.391
7.376
7.372
7.360
7.357
7.354
7.344
7.338
7.334
7.330
7.325
7.321
7.317
7.311
7.308
7.303
7.301
7.297
7.293
7.287
7.282
7.277
7.272
7.268
7.263
7.260
7.252
7.250
7.244
7.239
7.203
7.198
7.184
7.179
6.980
6.977
6.970
6.967
6.961
6.958
6.951
6.947
6.373
6.165
4.469
4.455
-0.000
H
N
O
PPh2
C4
1H NMR (400 MHz, CDCl3)
1.02
15.16
1.96
1.02
1.09
2.00
0.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


168.838
141.418
141.160
137.668
136.854
136.748
136.065
135.859
134.135
134.009
133.809
130.254
128.901
128.823
128.693
128.666
128.622
128.079
128.027
127.977
127.495
77.346
77.029
76.712
44.214
H
N
O
PPh2
C4
13C NMR (100 MHz, CDCl3)
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)



C4

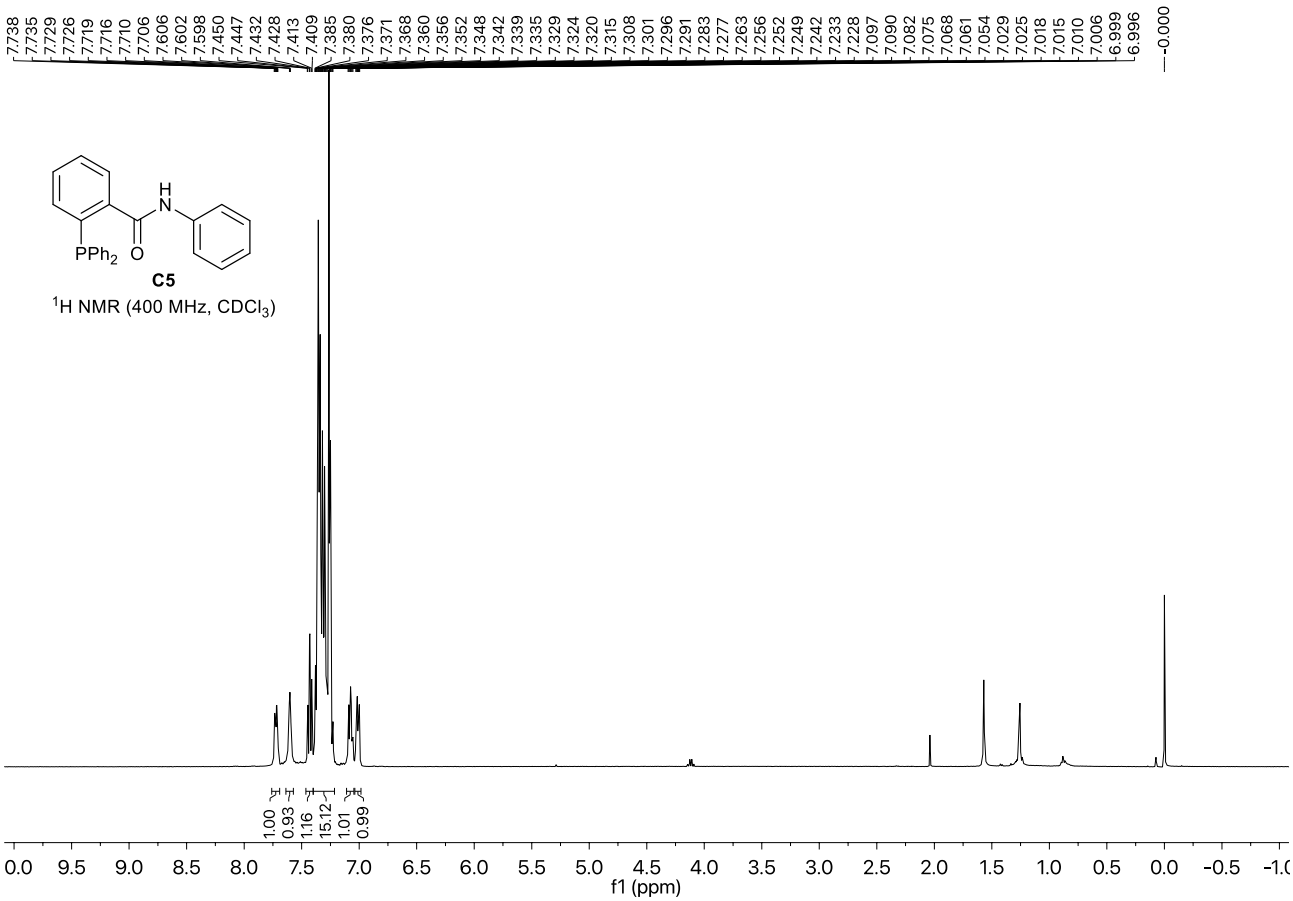
^{31}P NMR (162 MHz, $CDCl_3$)



C4

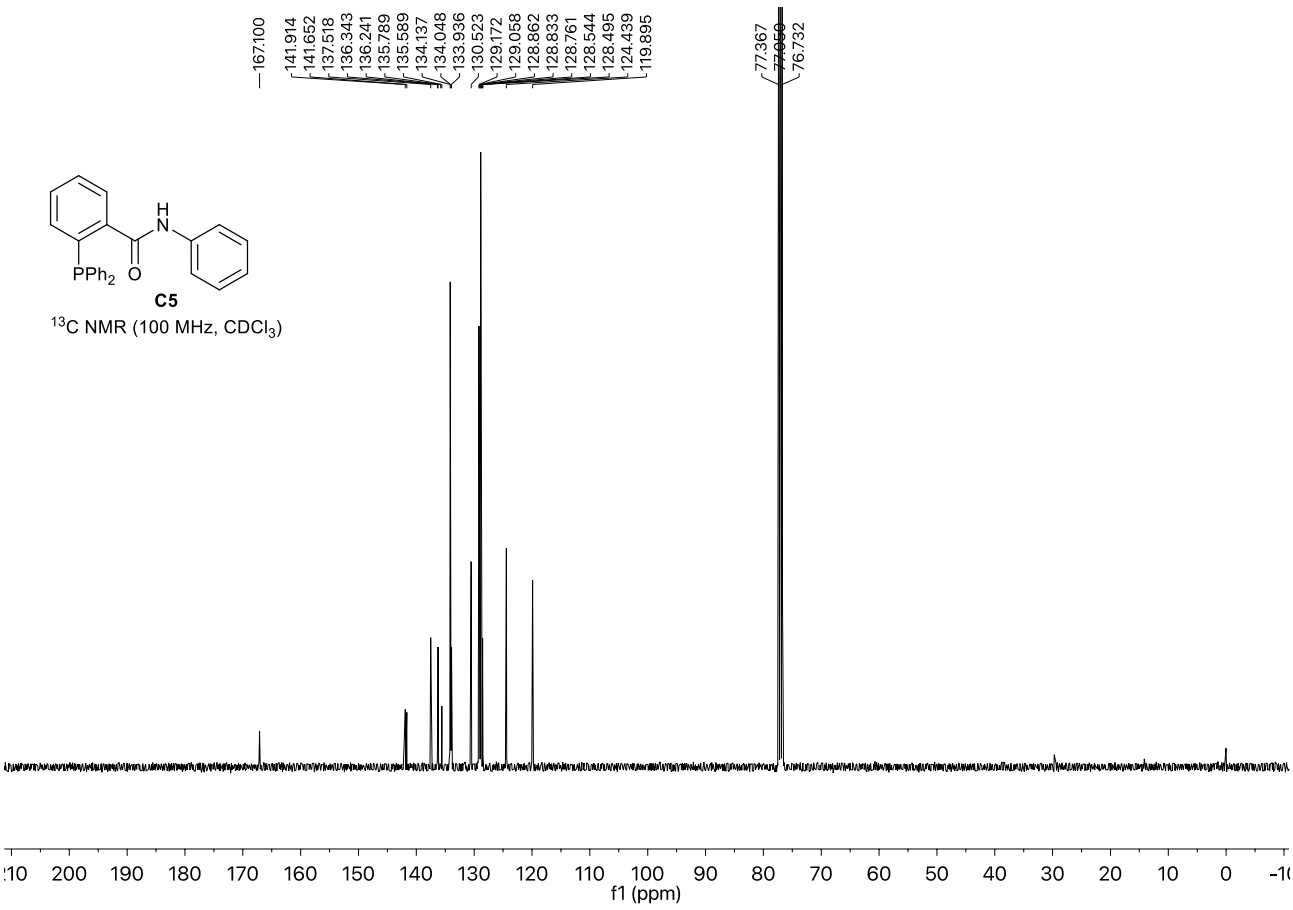
(ESI-TOF) m/z: $[M+H]^+$

Calcd for $C_{26}H_{23}NOP^+$ 396.1512



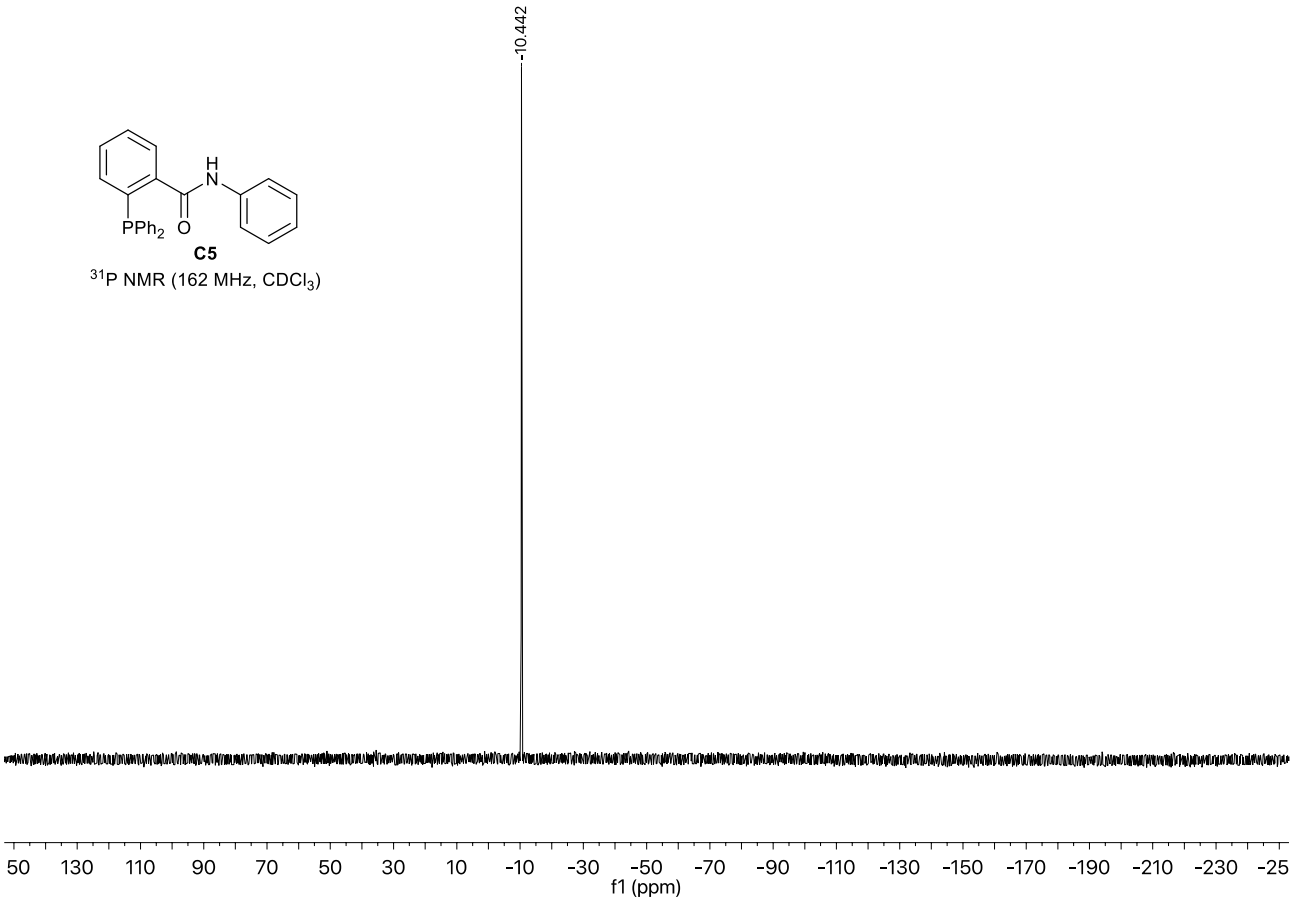
C5

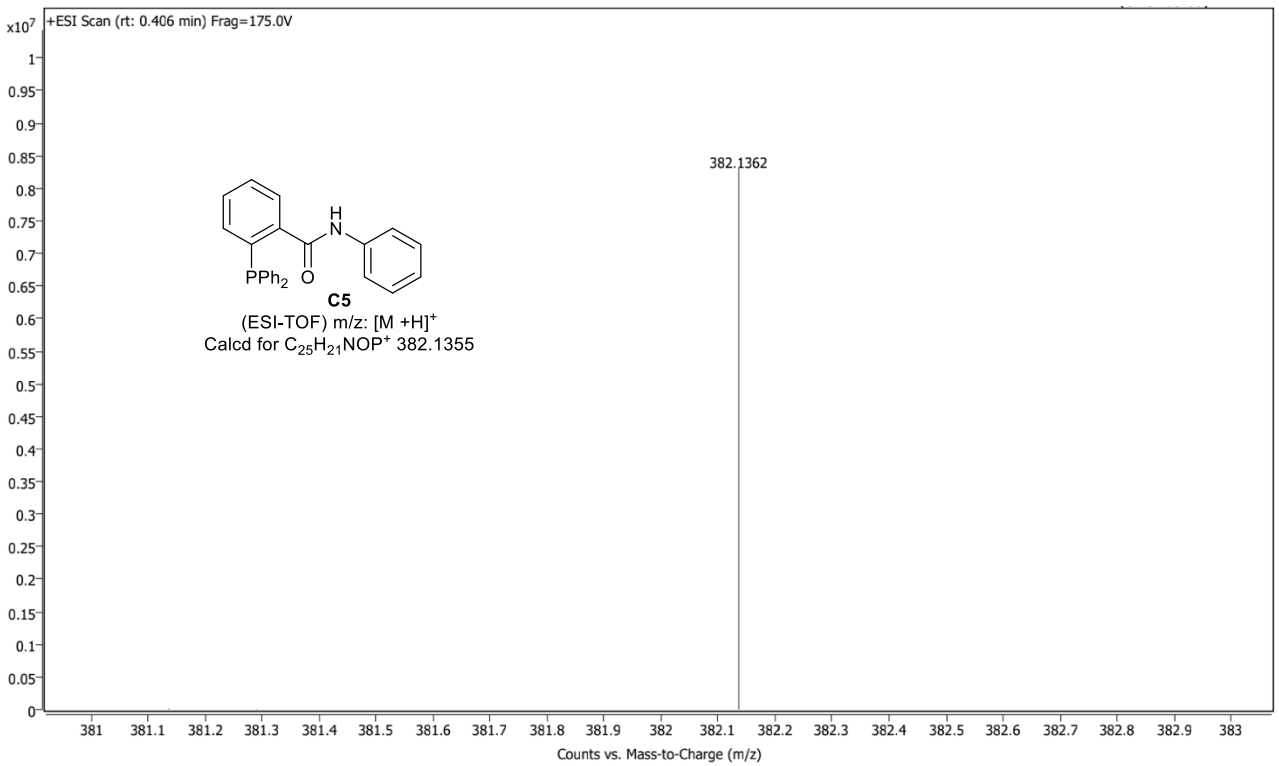
^{1}H NMR (400 MHz, $CDCl_3$)

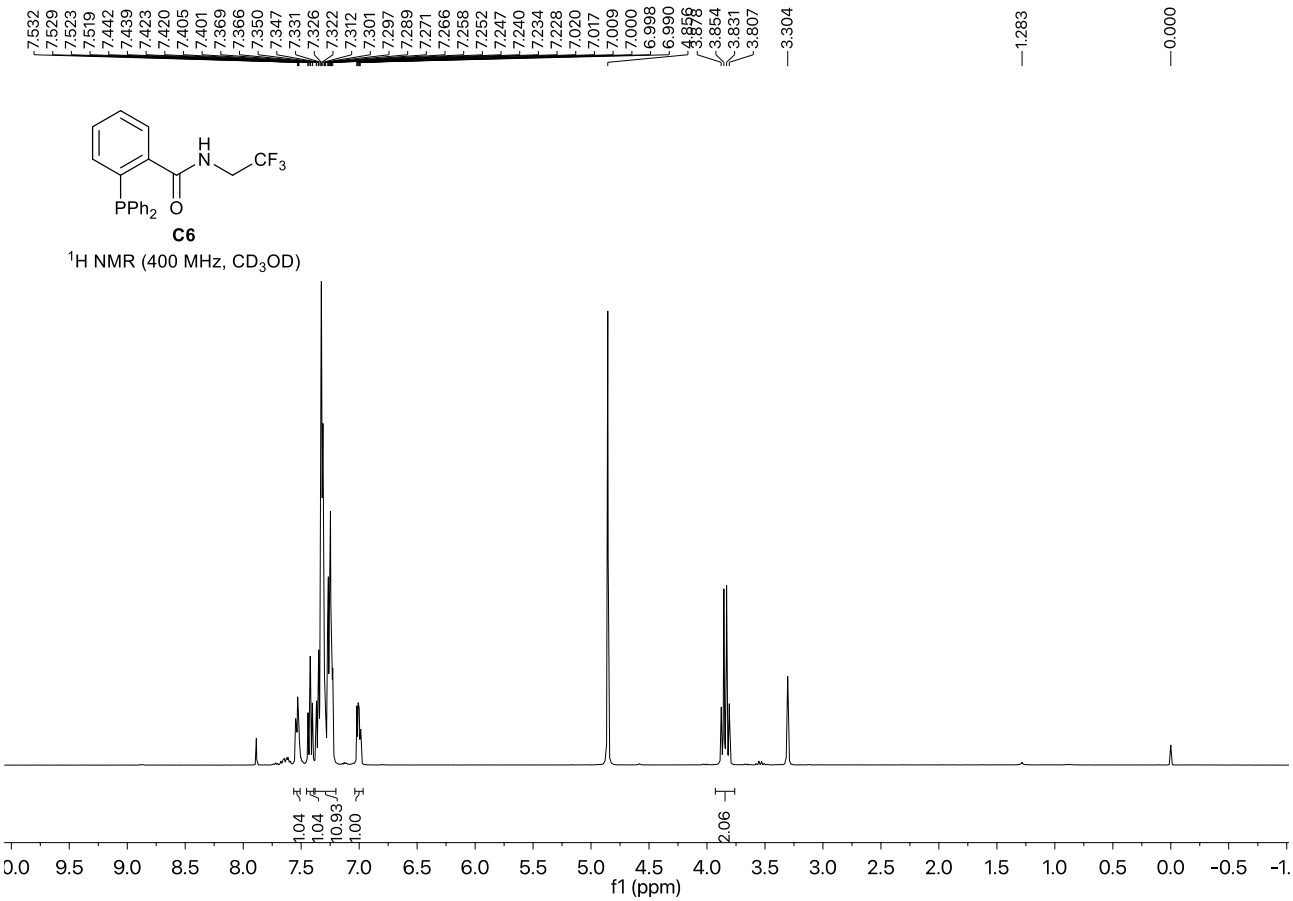


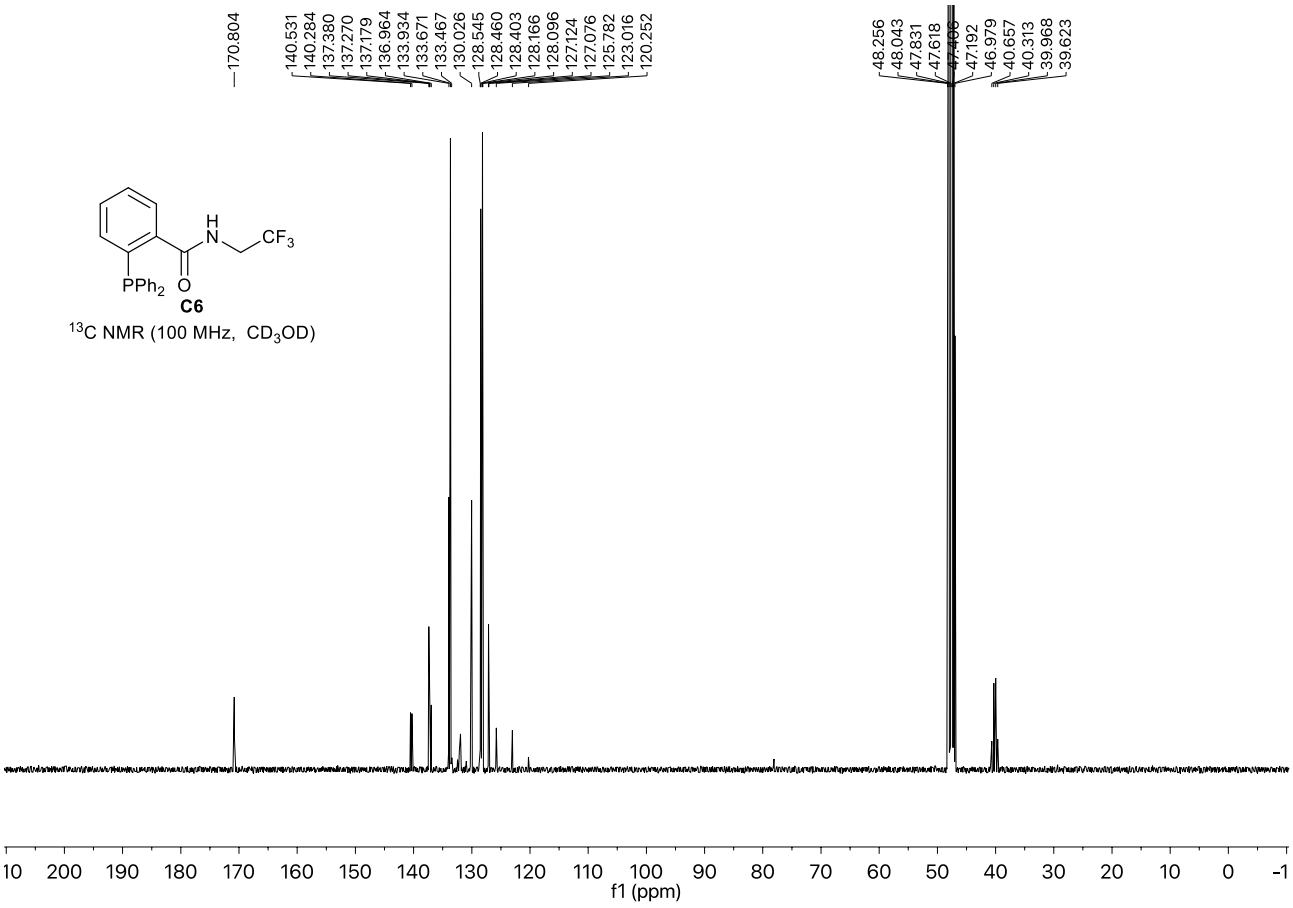
C5

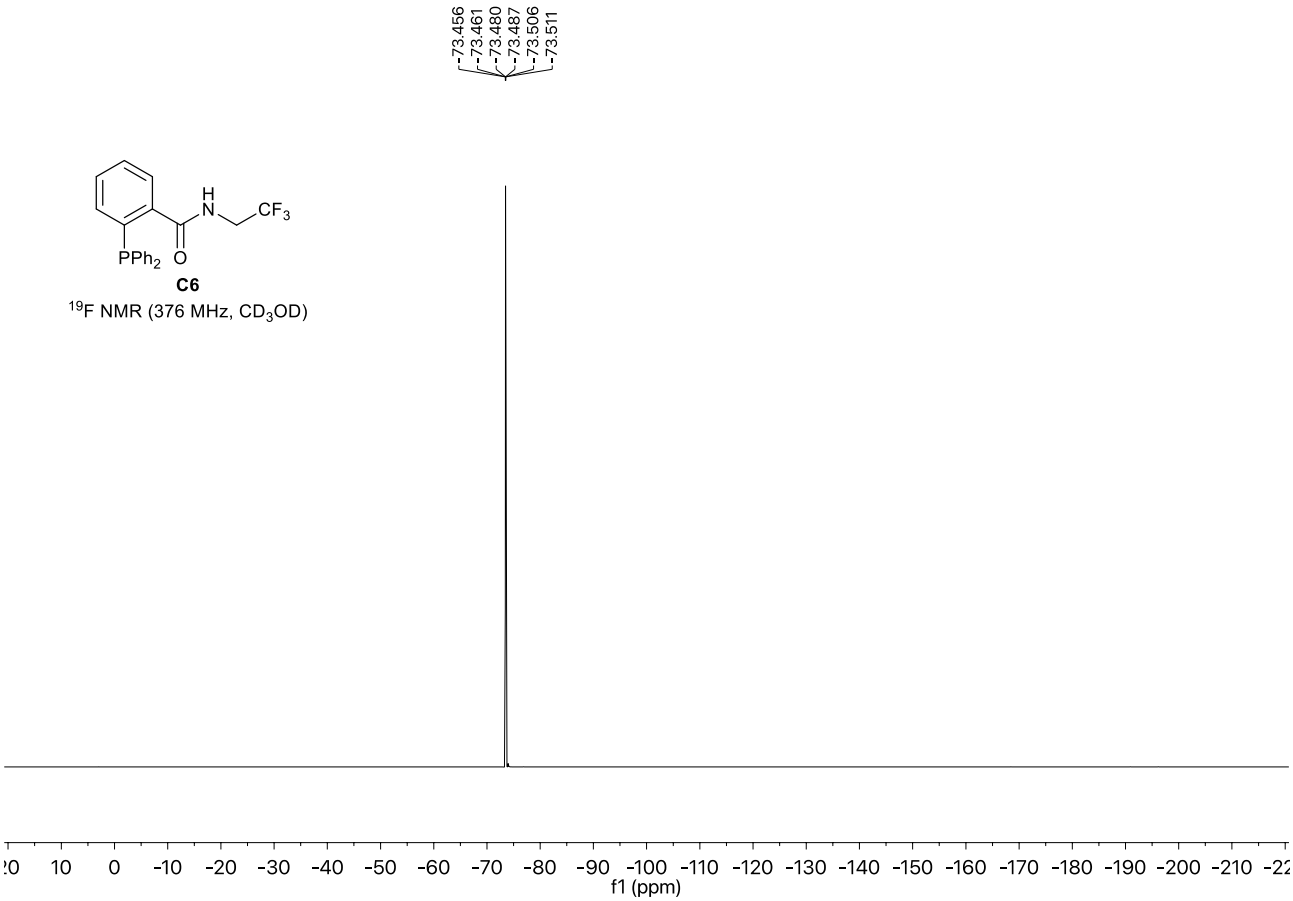
^{13}C NMR (100 MHz, $CDCl_3$)


-10.442
PPh2
O
H
N
C5
31P NMR (162 MHz, CDCl3)
50 130 110 90 70 50 30 10 -10 -30 -50 -70 -90 -110 -130 -150 -170 -190 -210 -230 -25
f1 (ppm)


x10^7
+ESI Scan (rt: 0.406 min) Frag=175.0V
382.1362
PPh2
O
H
N
C5
(ESI-TOF) m/z: [M +H]+
Calcd for C25H21NOP+ 382.1355
Counts vs. Mass-to-Charge (m/z)

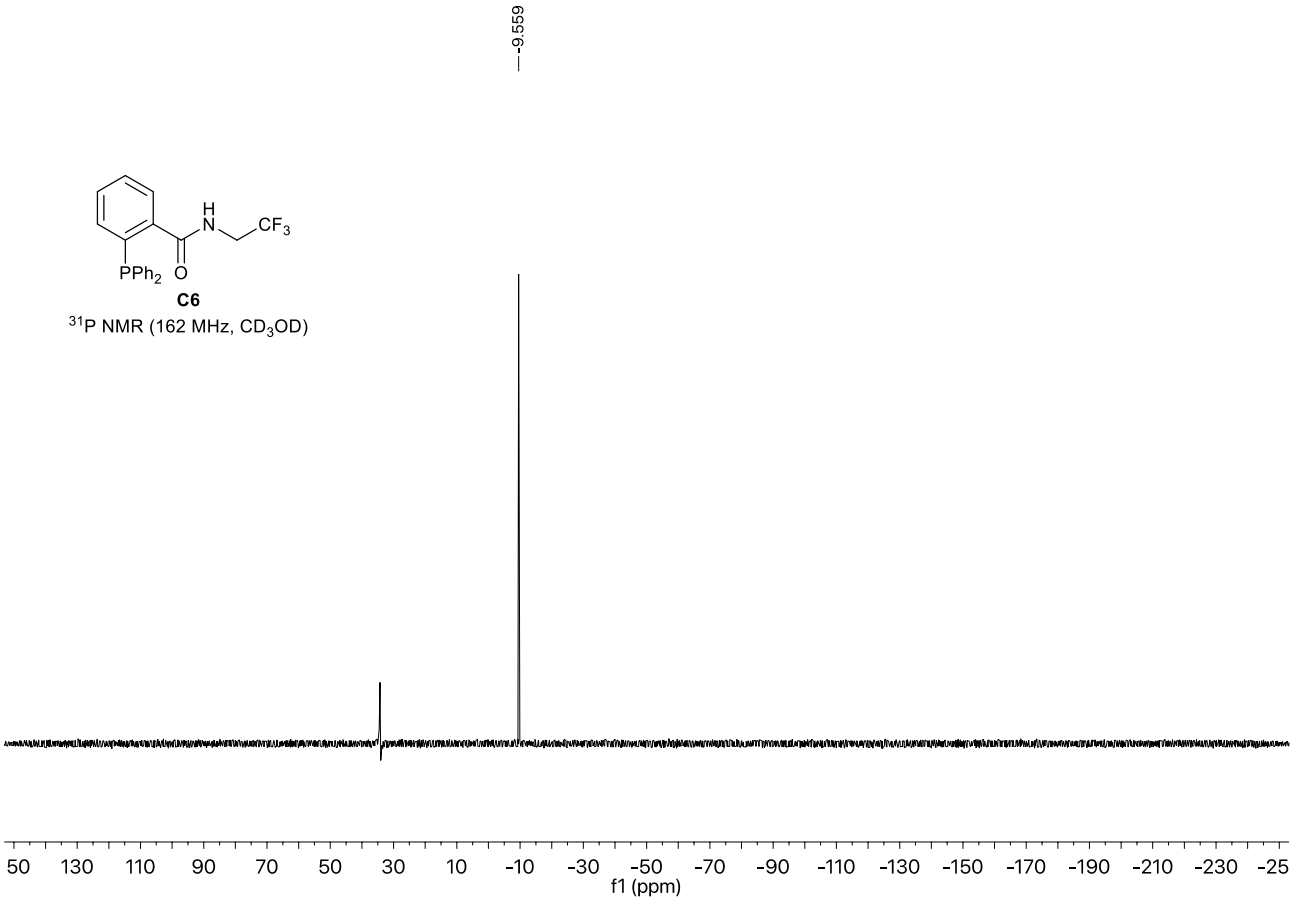

7.532
7.529
7.523
7.519
7.442
7.439
7.423
7.420
7.405
7.401
7.369
7.366
7.350
7.347
7.331
7.326
7.322
7.312
7.301
7.297
7.289
7.271
7.266
7.258
7.252
7.247
7.240
7.234
7.228
7.020
7.017
7.009
7.000
6.998
6.990
3.878
3.854
3.831
3.807
3.304
1.283
0.000
H
N
CF3
PPh2
O
C6
1H NMR (400 MHz, CD3OD)
1.04
1.04
10.93
1.00
2.06
f1 (ppm)


170.804
140.531
140.284
137.380
137.270
137.179
136.964
133.934
133.671
133.467
130.026
128.545
128.460
128.403
128.166
128.096
127.124
127.076
125.782
123.016
120.252
48.256
48.043
47.831
47.618
47.406
47.192
46.979
40.657
40.313
39.968
39.623
H
N
CF3
PPh2
O
C6
13C NMR (100 MHz, CD3OD)
f1 (ppm)



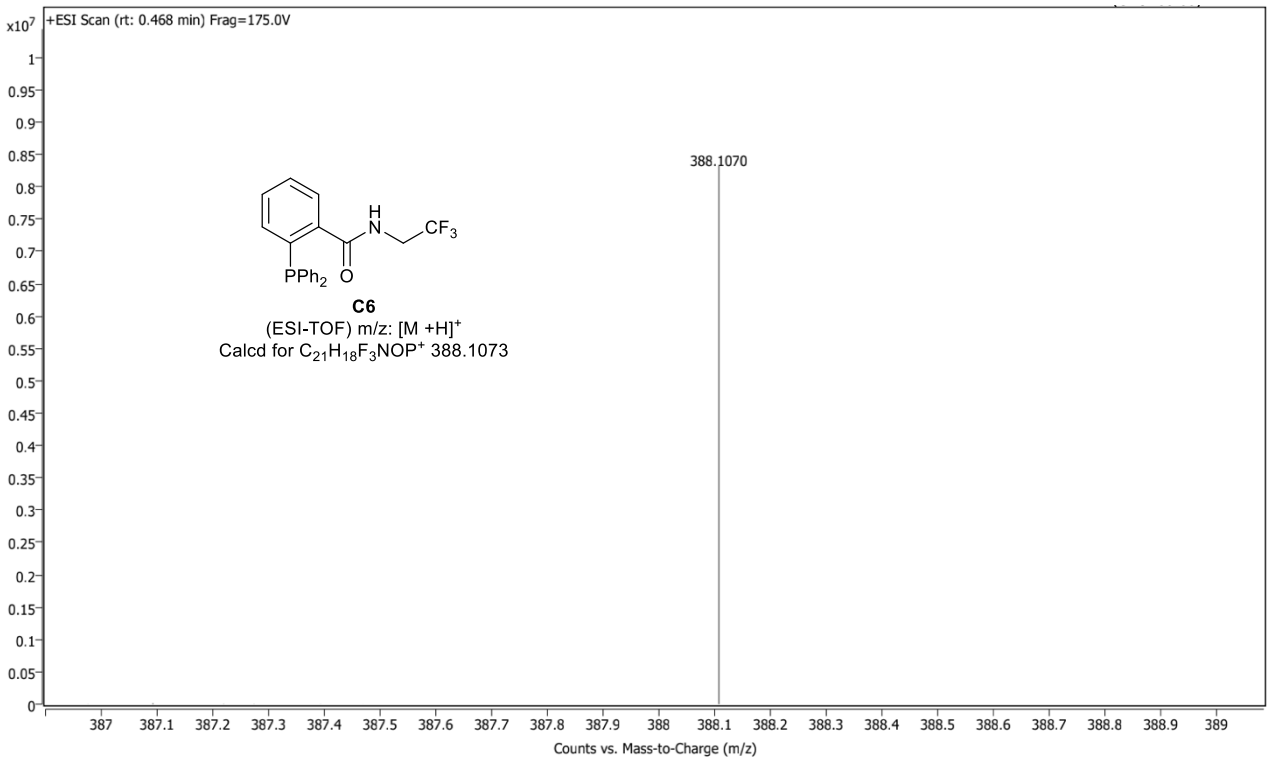
C6

^{19}F NMR (376 MHz, CD_3OD)



C6

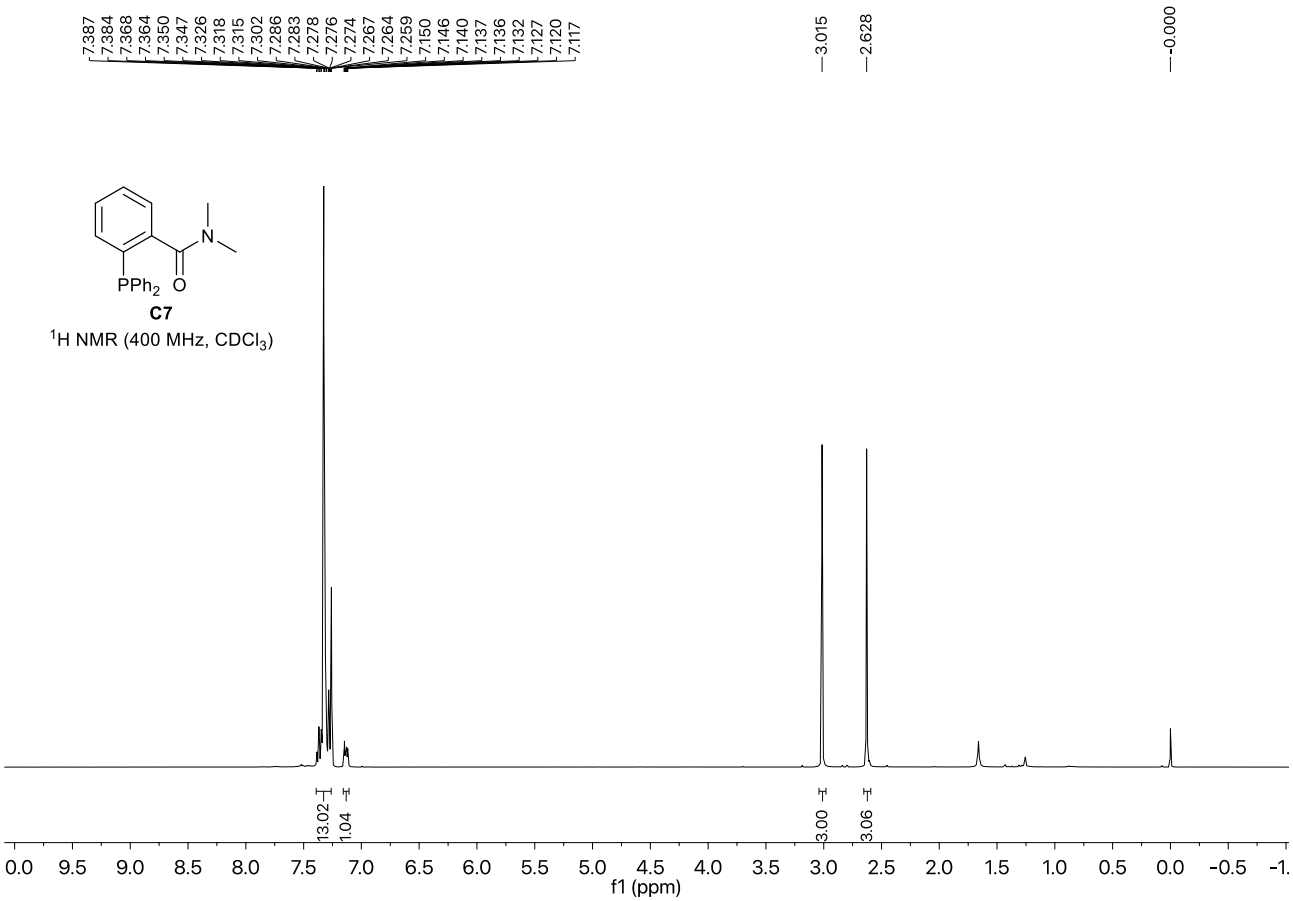
^{31}P NMR (162 MHz, CD_3OD)

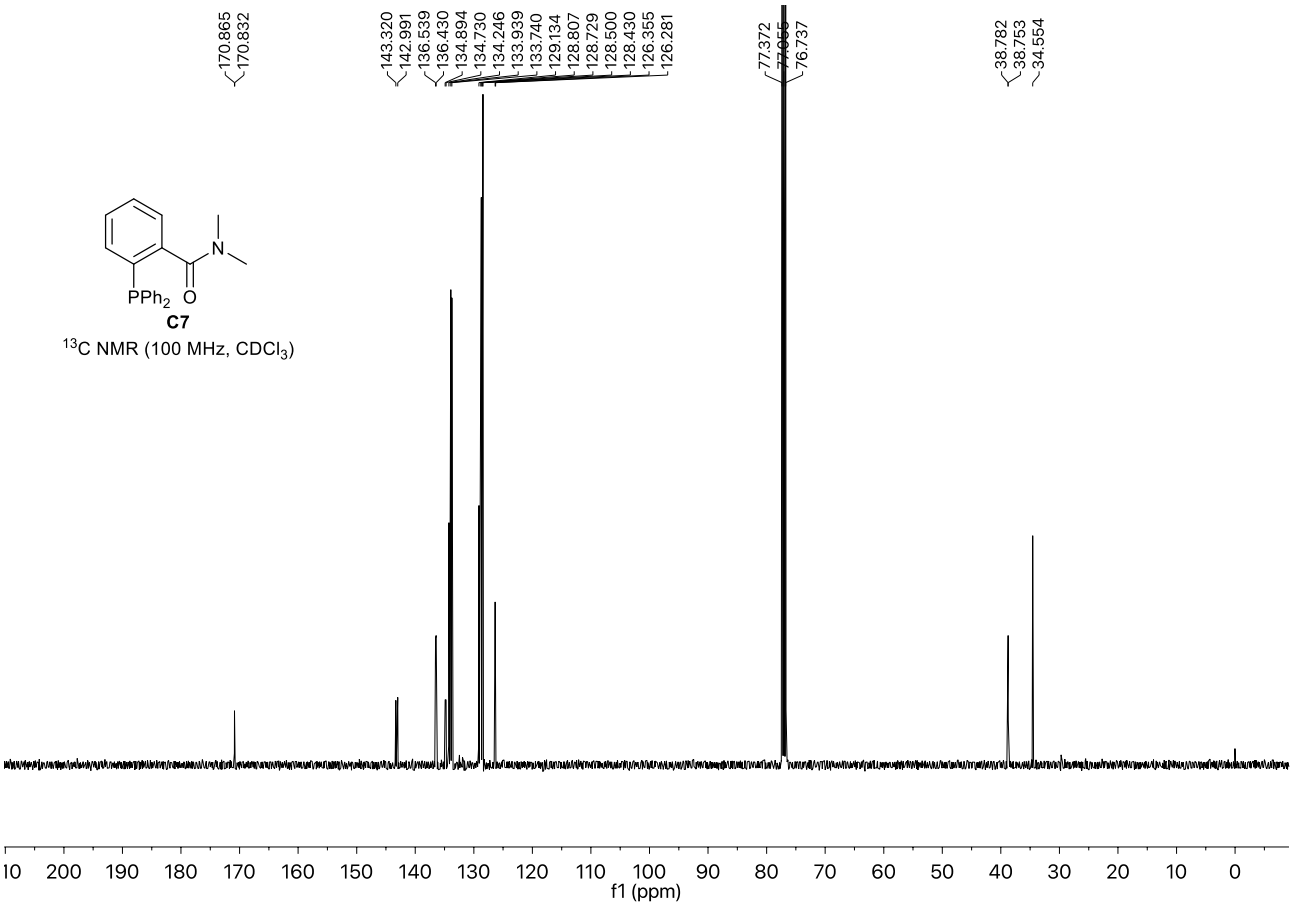


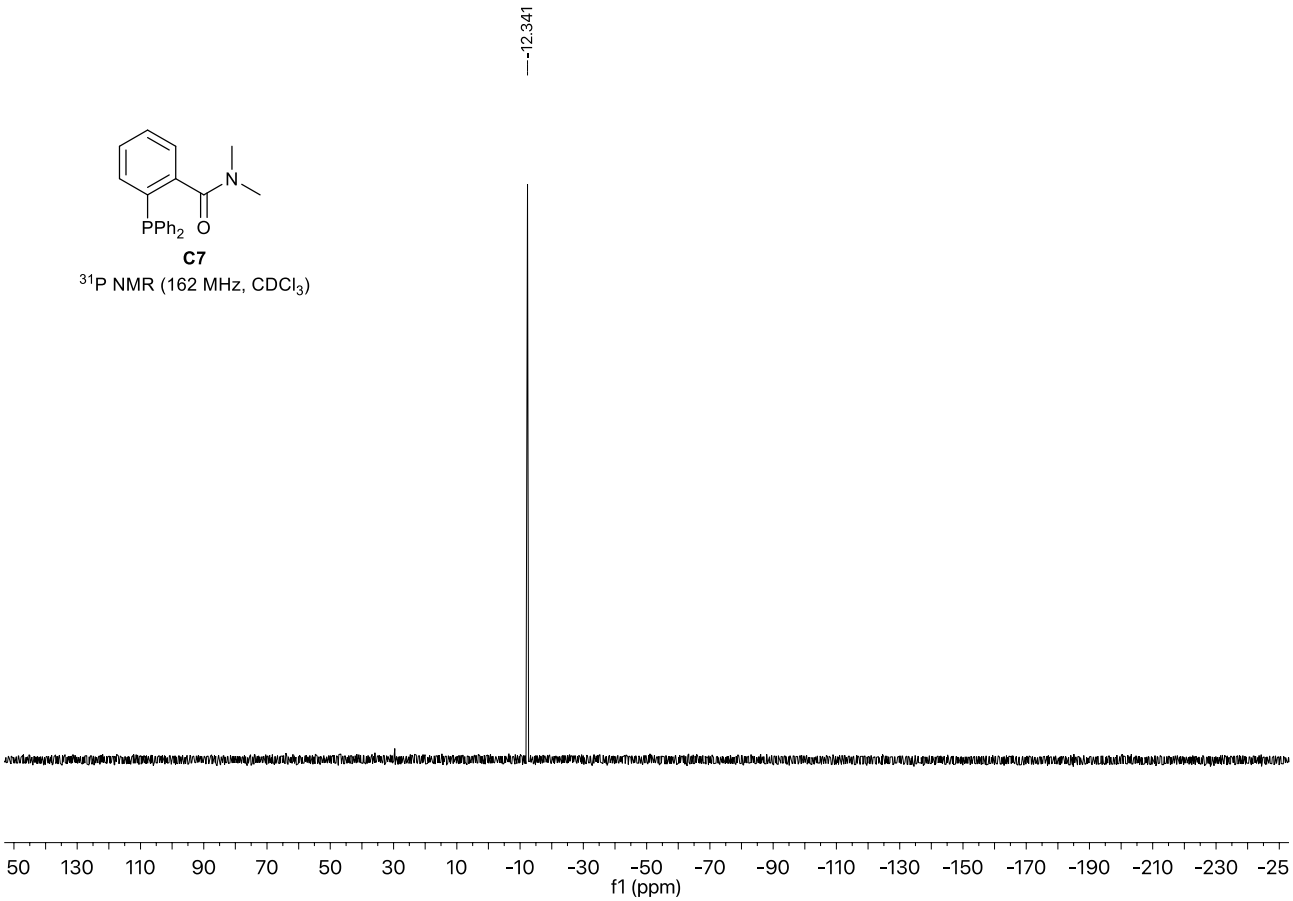
C6

(ESI-TOF) m/z: $[M+H]^+$

Calcd for $C_{21}H_{18}F_3NOP^+$ 388.1073

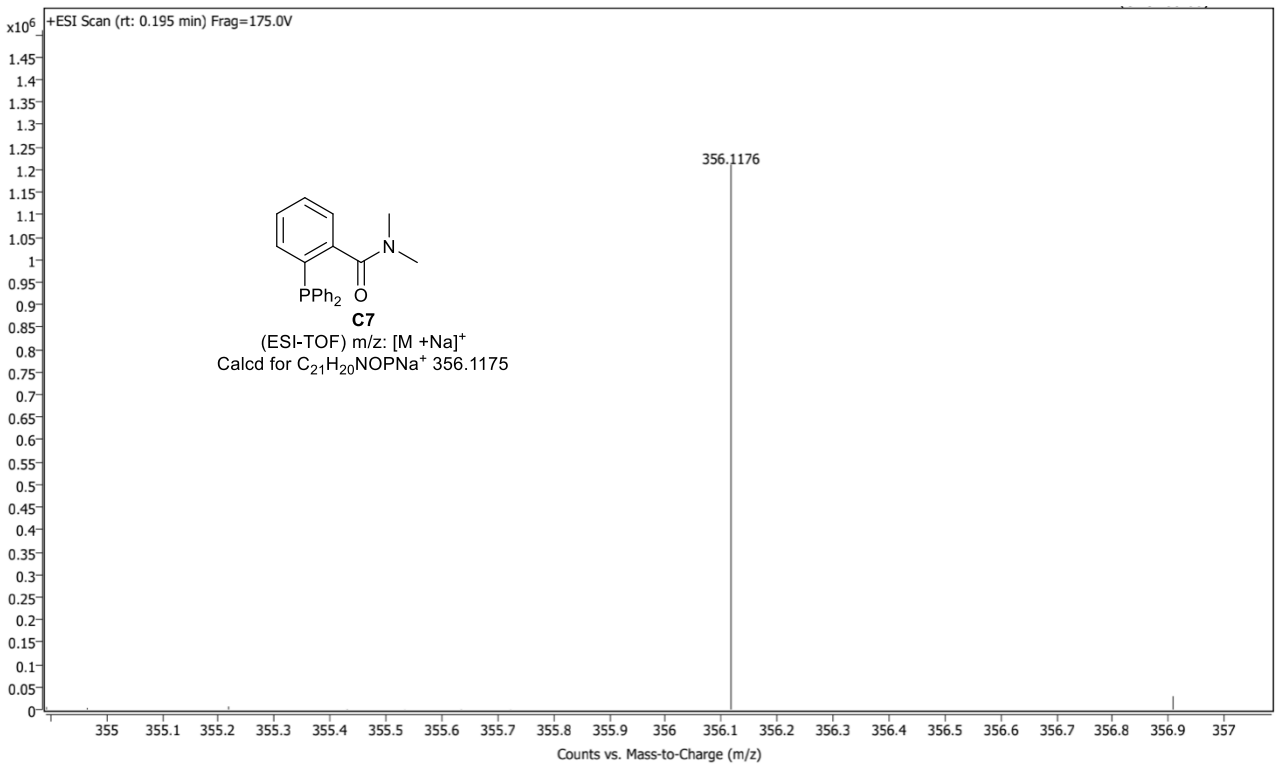

7.387
7.384
7.368
7.364
7.350
7.347
7.326
7.318
7.315
7.302
7.286
7.283
7.278
7.276
7.274
7.267
7.264
7.259
7.150
7.146
7.140
7.137
7.136
7.132
7.127
7.120
7.117
3.015
2.628
0.000
PPh2 O
N
C7
1H NMR (400 MHz, CDCl3)
13.02
1.04
3.00
3.06
f1 (ppm)


170.865
170.832
143.320
142.991
136.539
136.430
134.894
134.730
134.246
133.939
133.740
129.134
128.807
128.729
128.500
128.430
126.355
126.281
77.372
77.055
76.737
38.782
38.753
34.554
PPh2 O
N
C7
13C NMR (100 MHz, CDCl3)
f1 (ppm)



C7

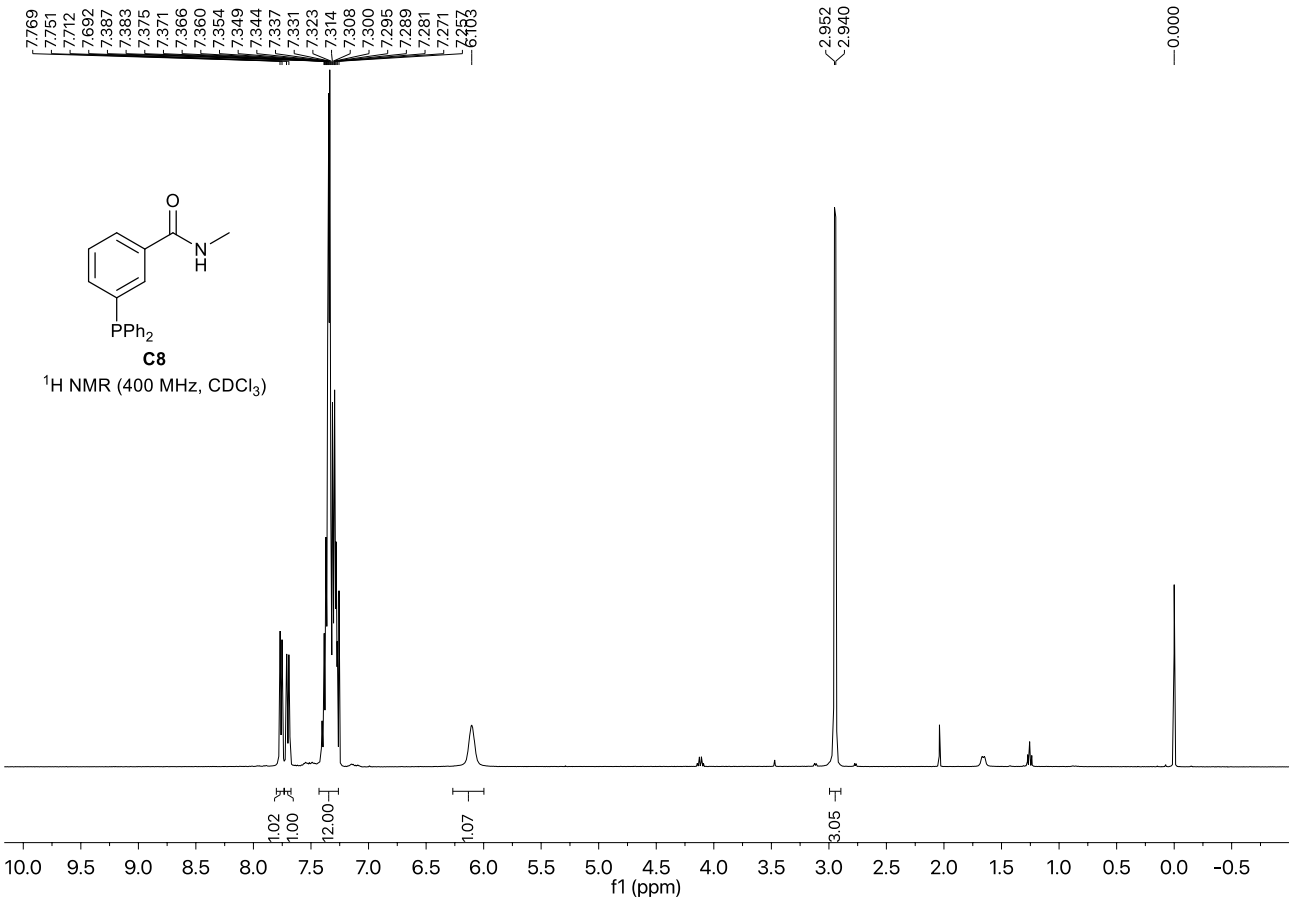
^{31}P NMR (162 MHz, $CDCl_3$)



C7

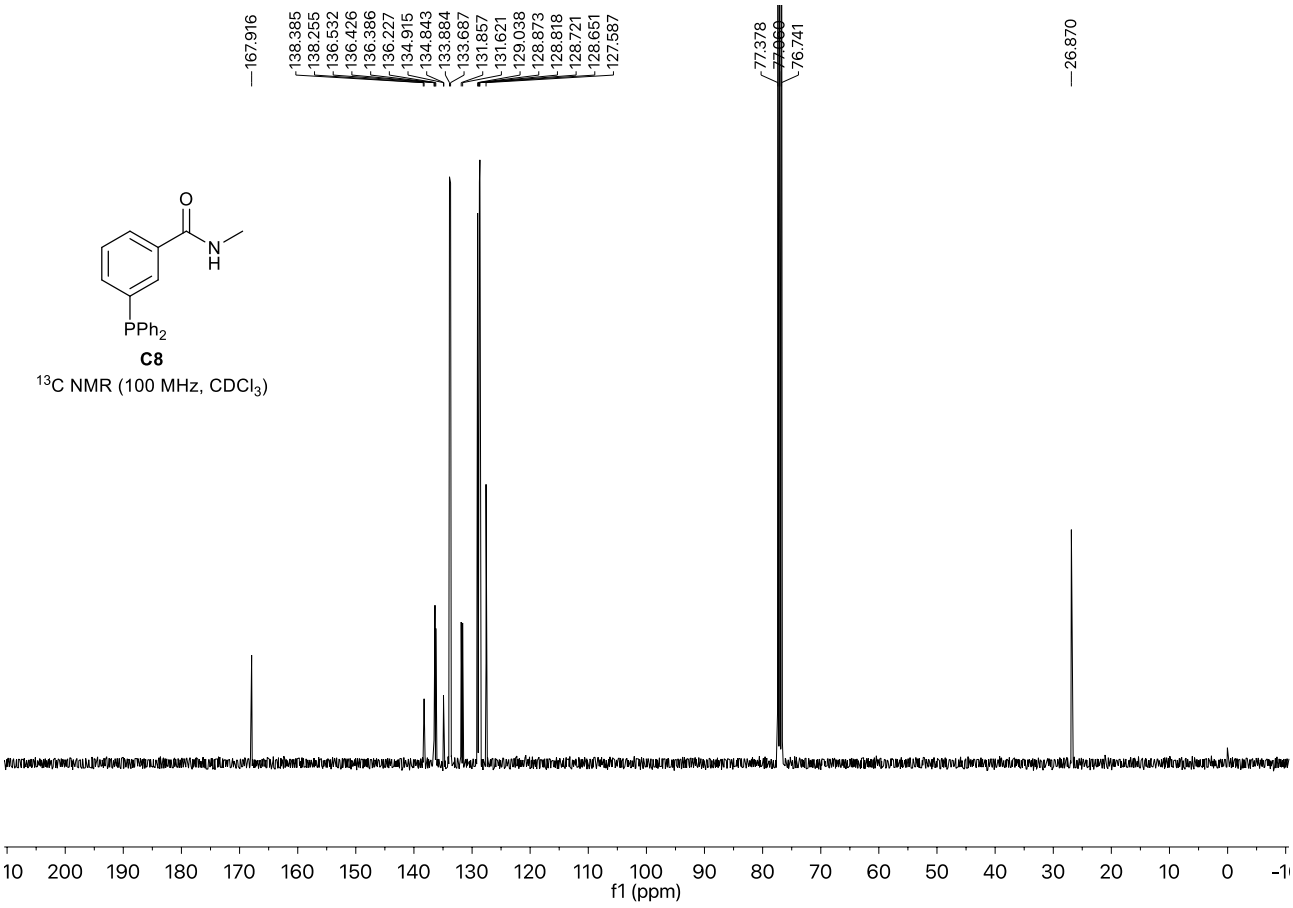
(ESI-TOF) m/z: $[M+Na]^+$

Calcd for $C_{21}H_{20}NOPNa^+$ 356.1175



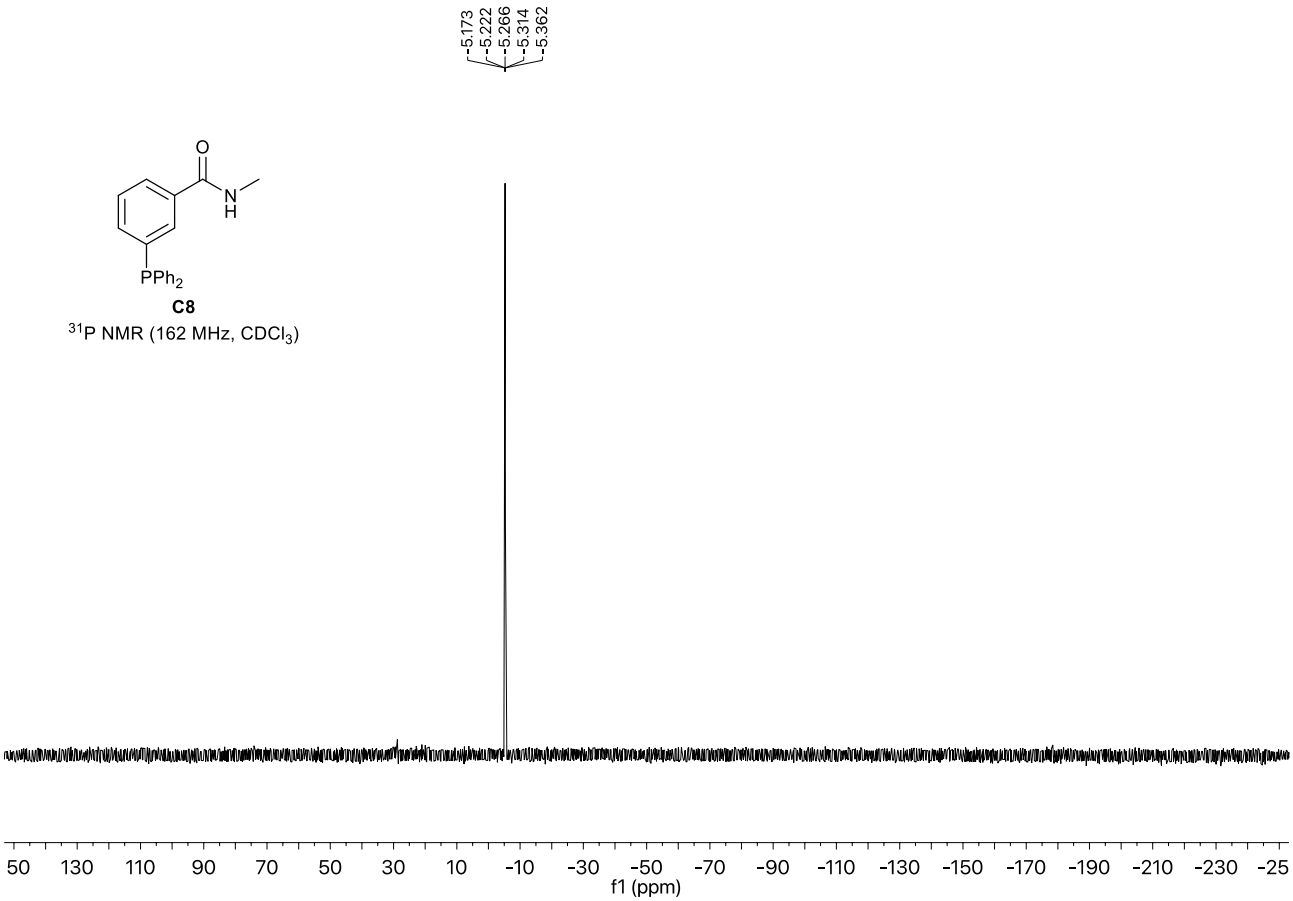
C8

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



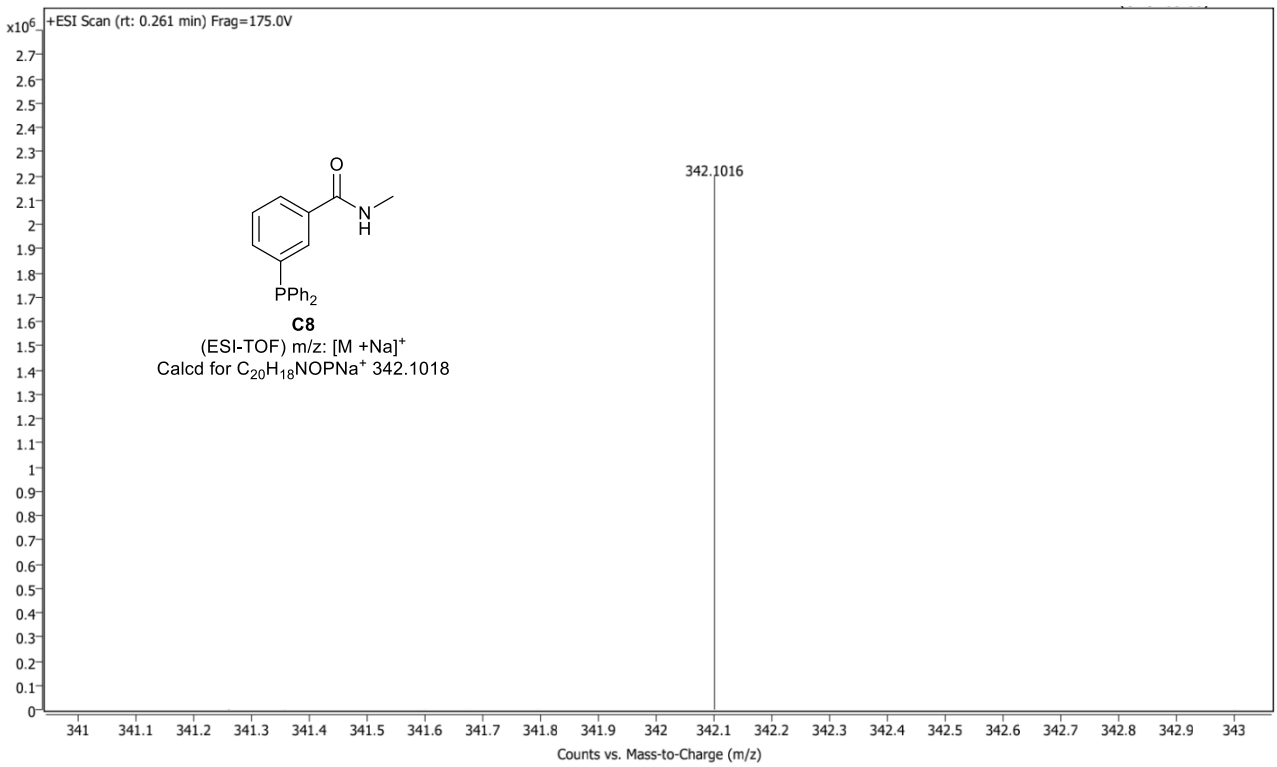
C8

^{13}C NMR (100 MHz, $CDCl_3$)



C8

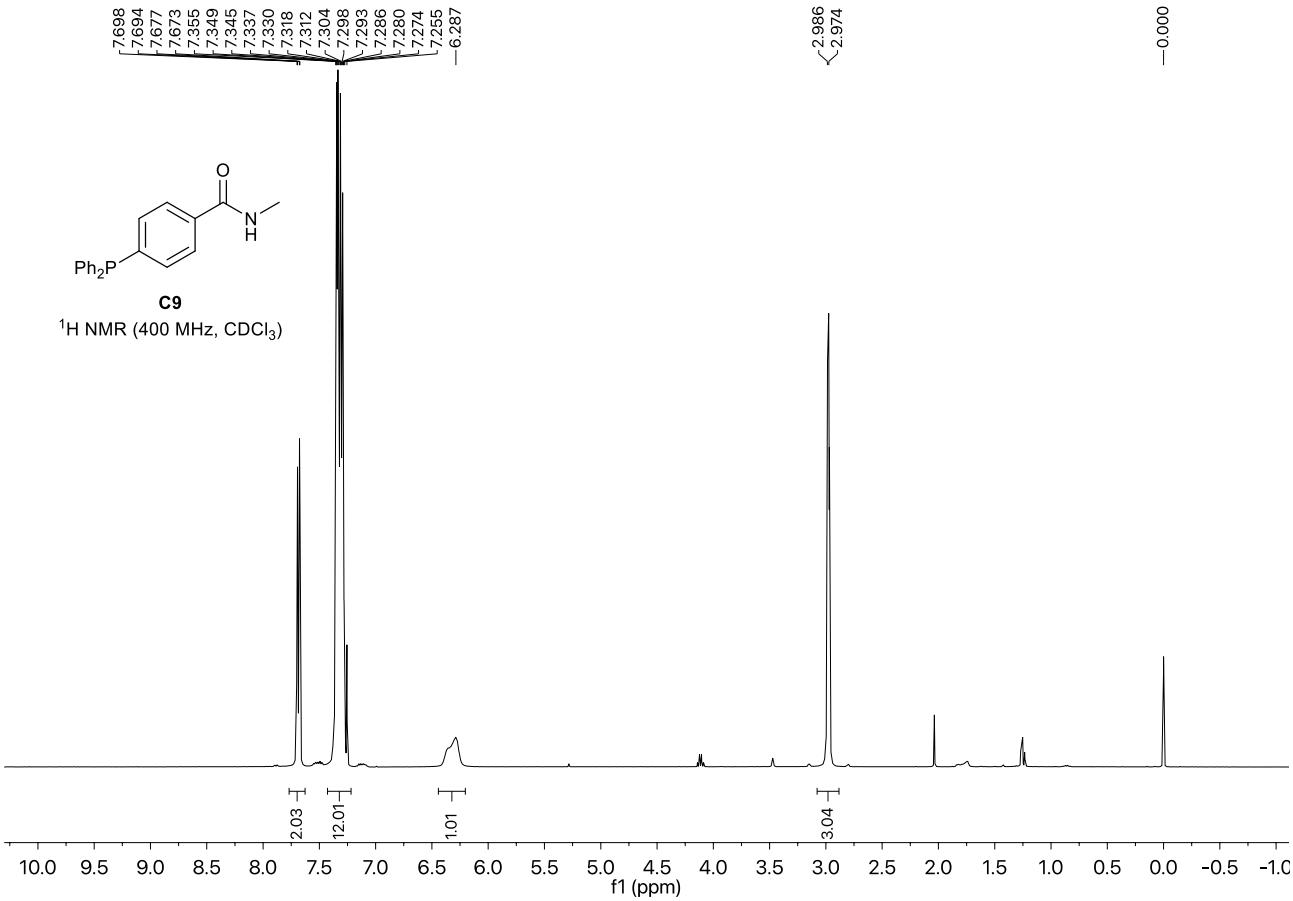
^{31}P NMR (162 MHz, $CDCl_3$)



C8

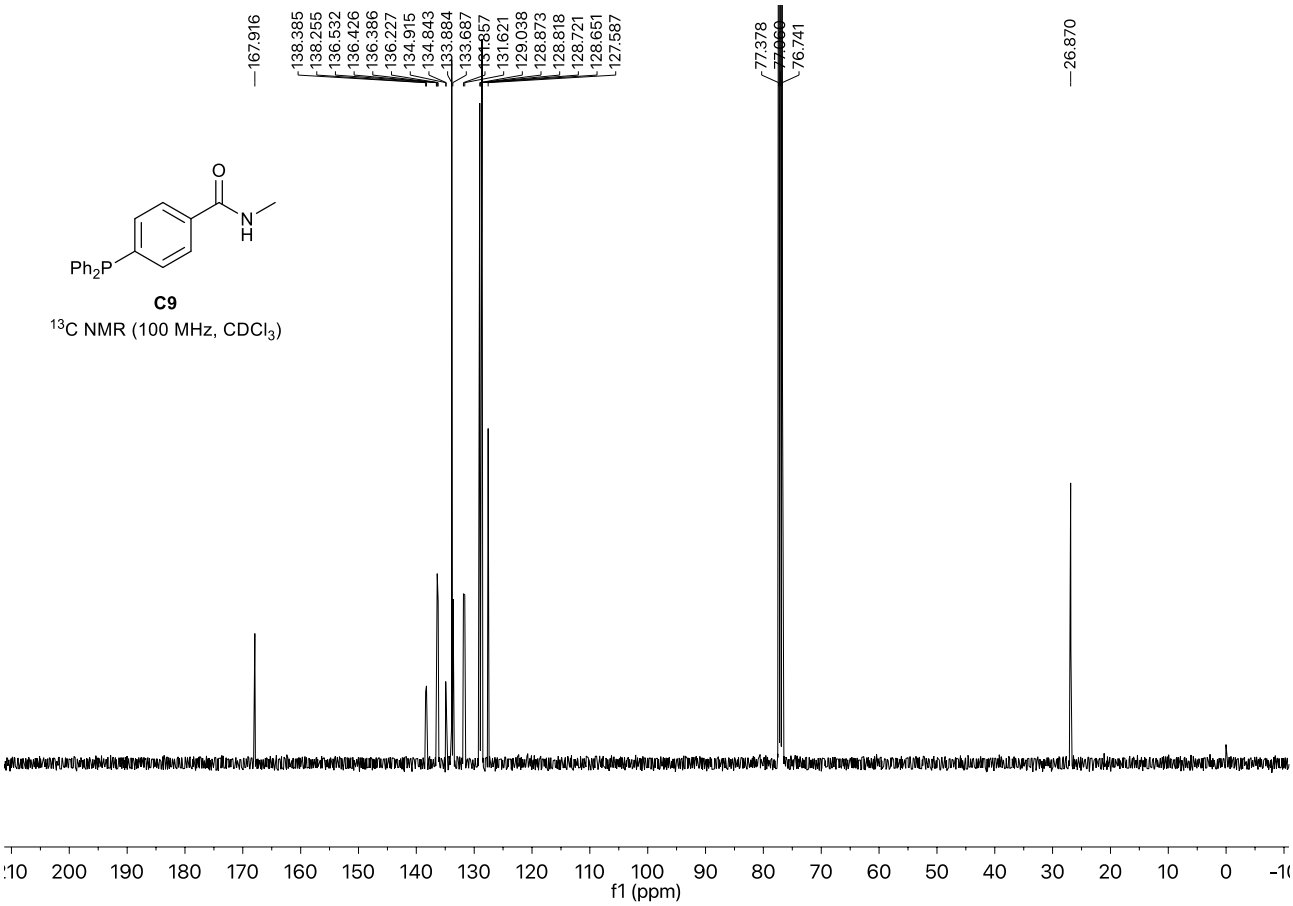
(ESI-TOF) m/z: $[M+Na]^+$

Calcd for $C_{20}H_{18}NOPNa^+$ 342.1018



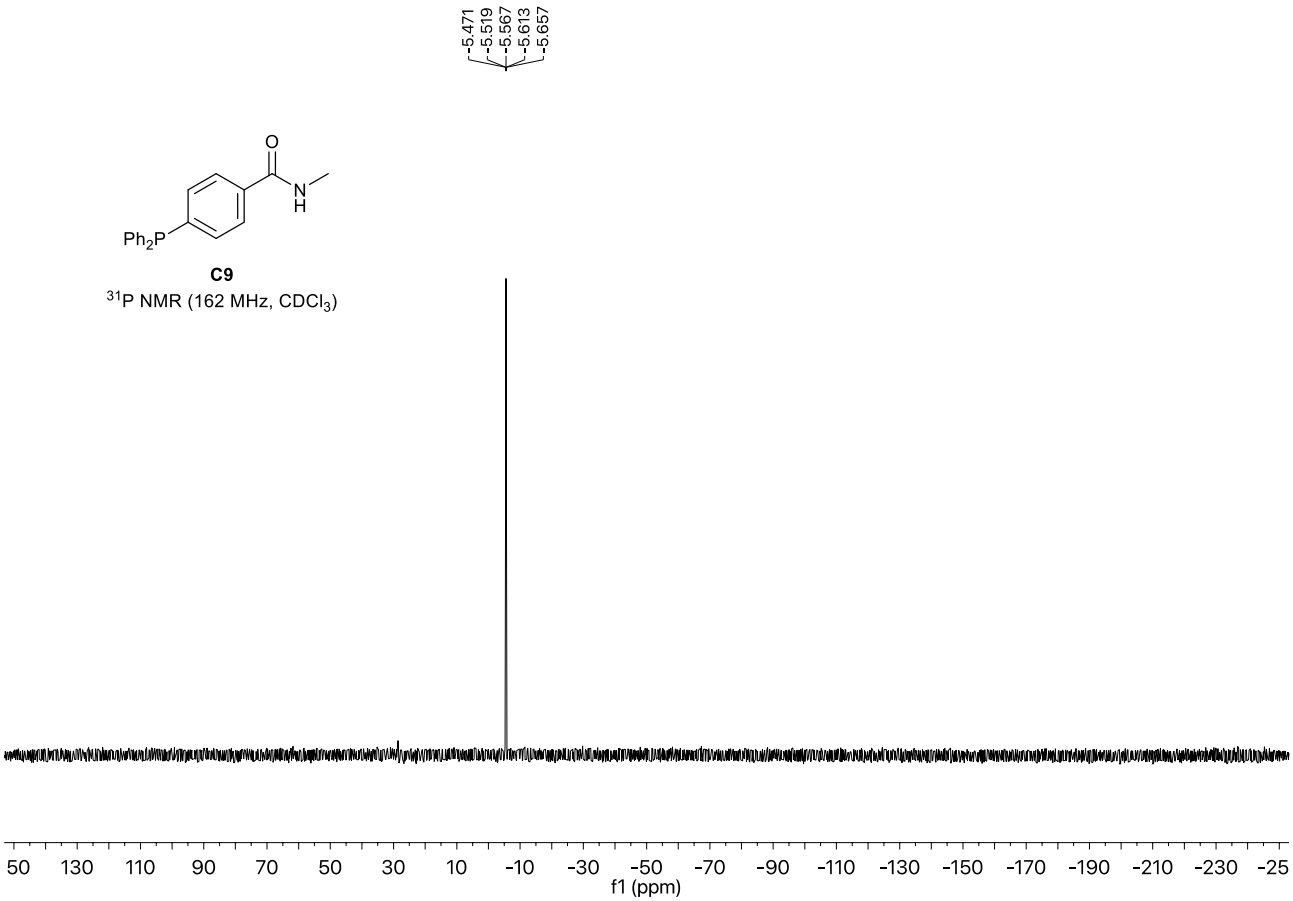
C9

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



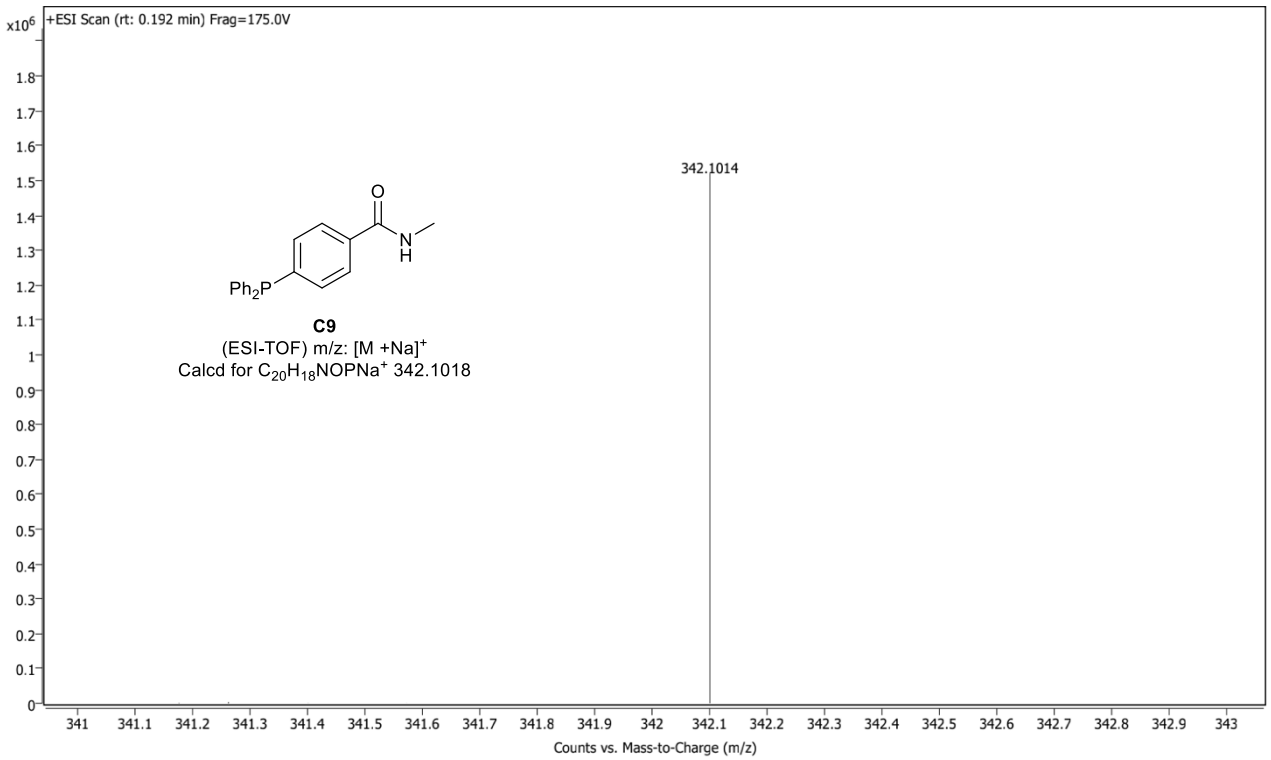
C9

^{13}C NMR (100 MHz, $CDCl_3$)



C9

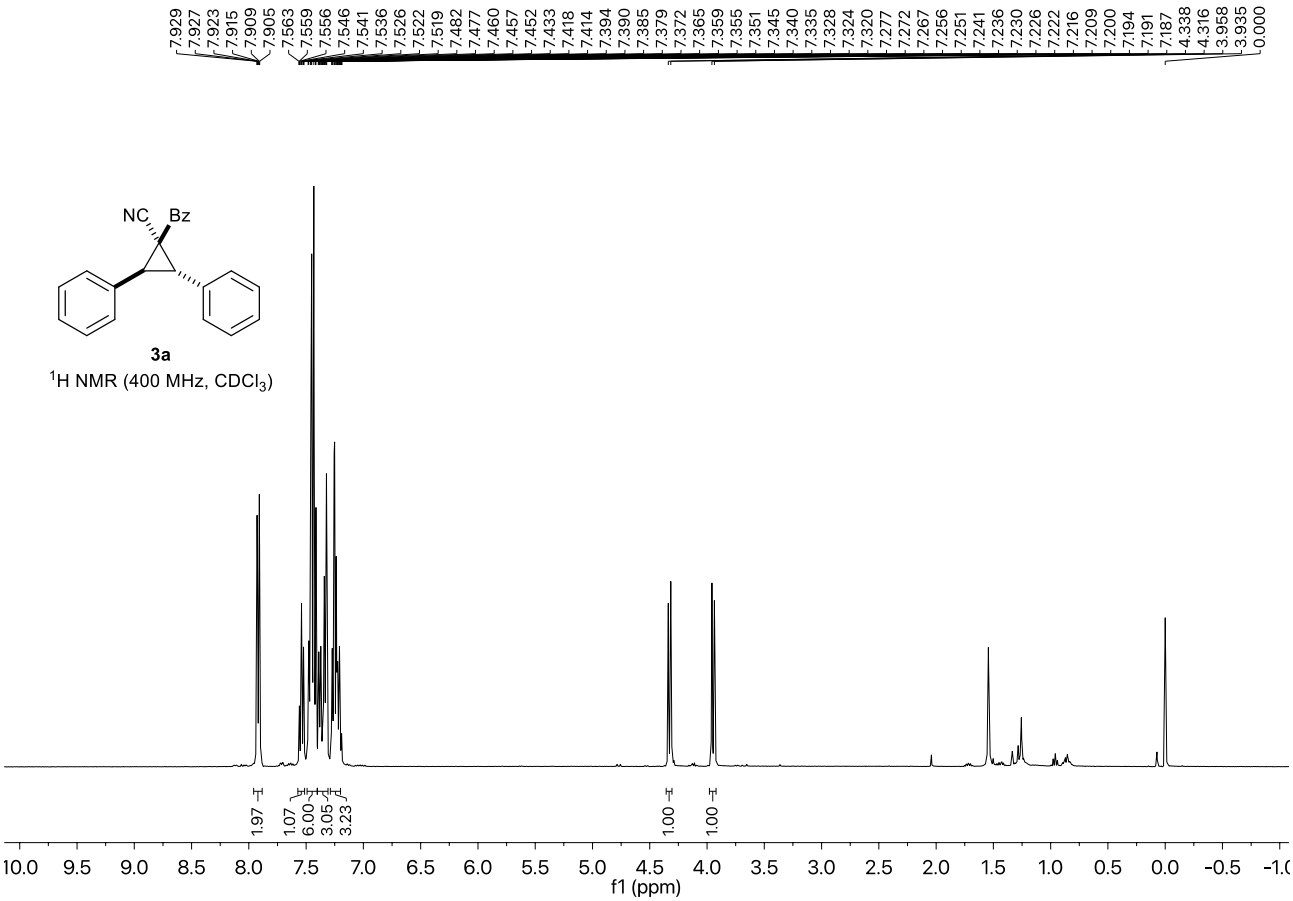
^{31}P NMR (162 MHz, $CDCl_3$)

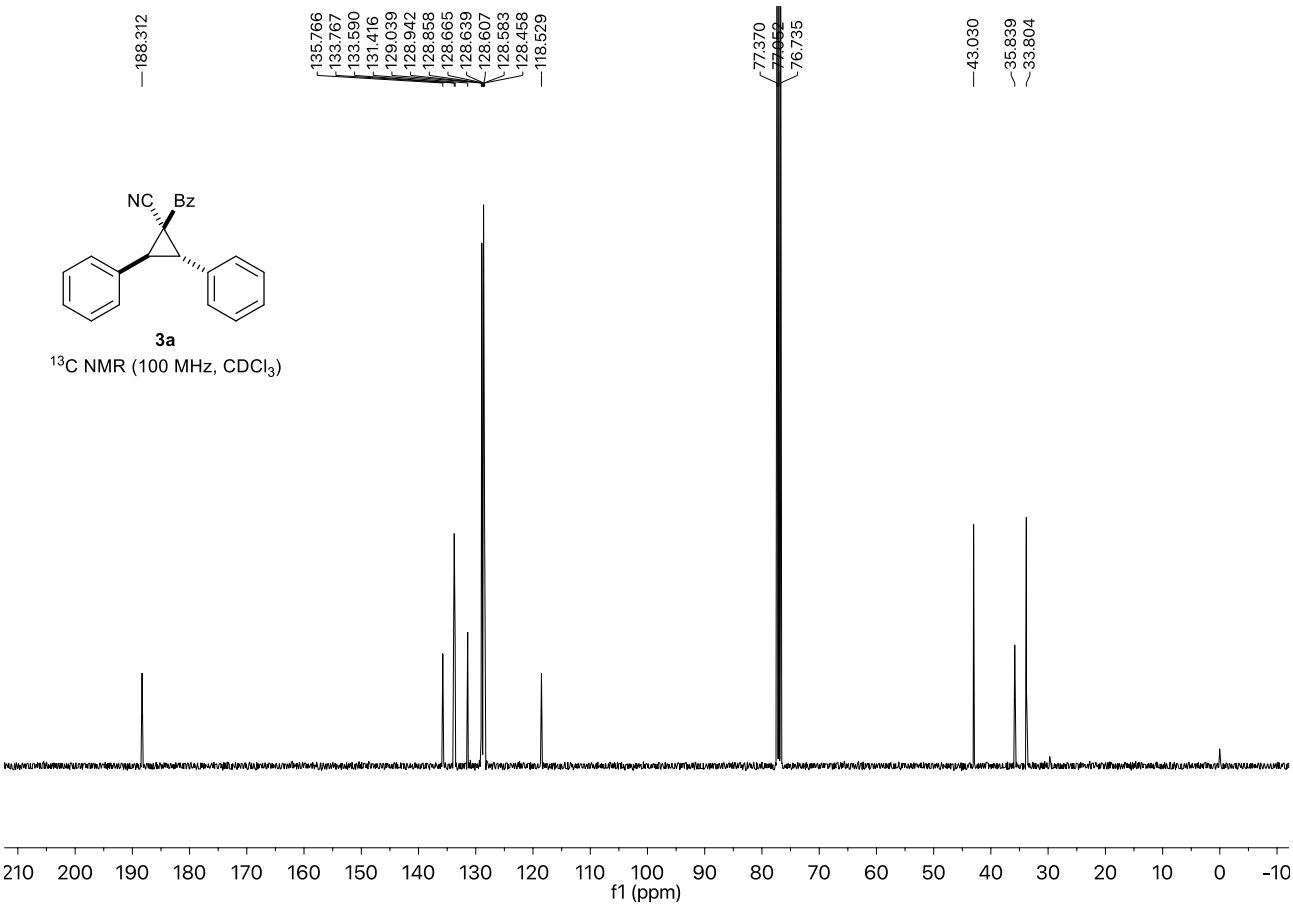


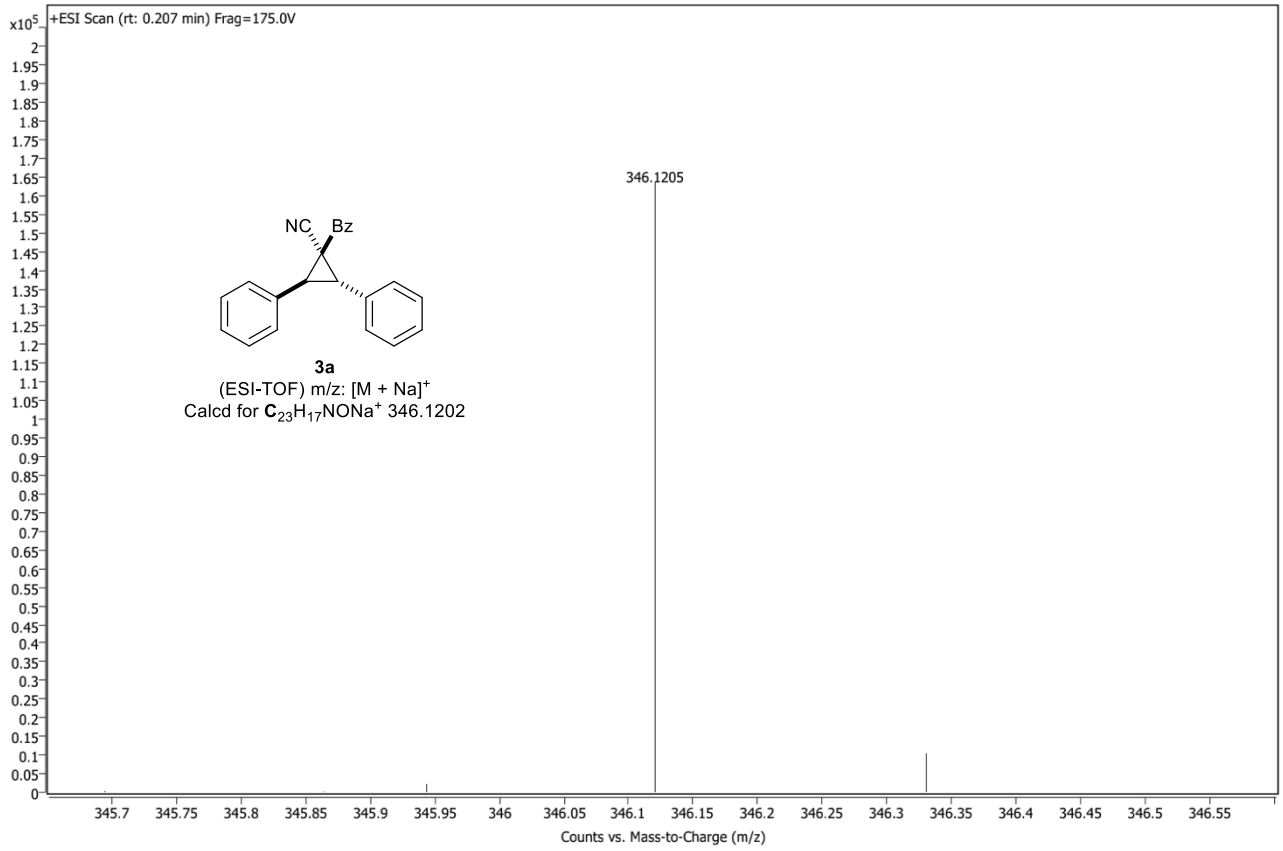
C9

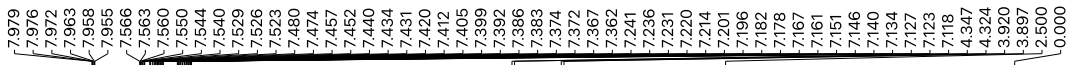
(ESI-TOF) m/z: $[M+Na]^+$

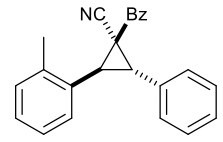
Calcd for $C_{20}H_{18}NOPNa^+$ 342.1018


7.929
7.927
7.923
7.915
7.909
7.905
7.563
7.559
7.556
7.546
7.541
7.536
7.526
7.522
7.519
7.482
7.477
7.460
7.457
7.452
7.433
7.418
7.414
7.394
7.390
7.385
7.379
7.372
7.365
7.359
7.355
7.351
7.345
7.340
7.335
7.328
7.324
7.320
7.277
7.272
7.267
7.256
7.251
7.241
7.236
7.230
7.226
7.222
7.216
7.209
7.200
7.194
7.191
7.187
4.338
4.316
3.958
3.935
0.000
NC
Bz
3a
1H NMR (400 MHz, CDCl3)
1.97
1.07
6.00
3.05
3.23
1.00
1.00
f1 (ppm)


188.312
135.766
133.767
133.590
131.416
129.039
128.942
128.858
128.665
128.639
128.607
128.583
128.458
118.529
77.370
77.052
76.735
43.030
35.839
33.804
NC
Bz
3a
13C NMR (100 MHz, CDCl3)
f1 (ppm)

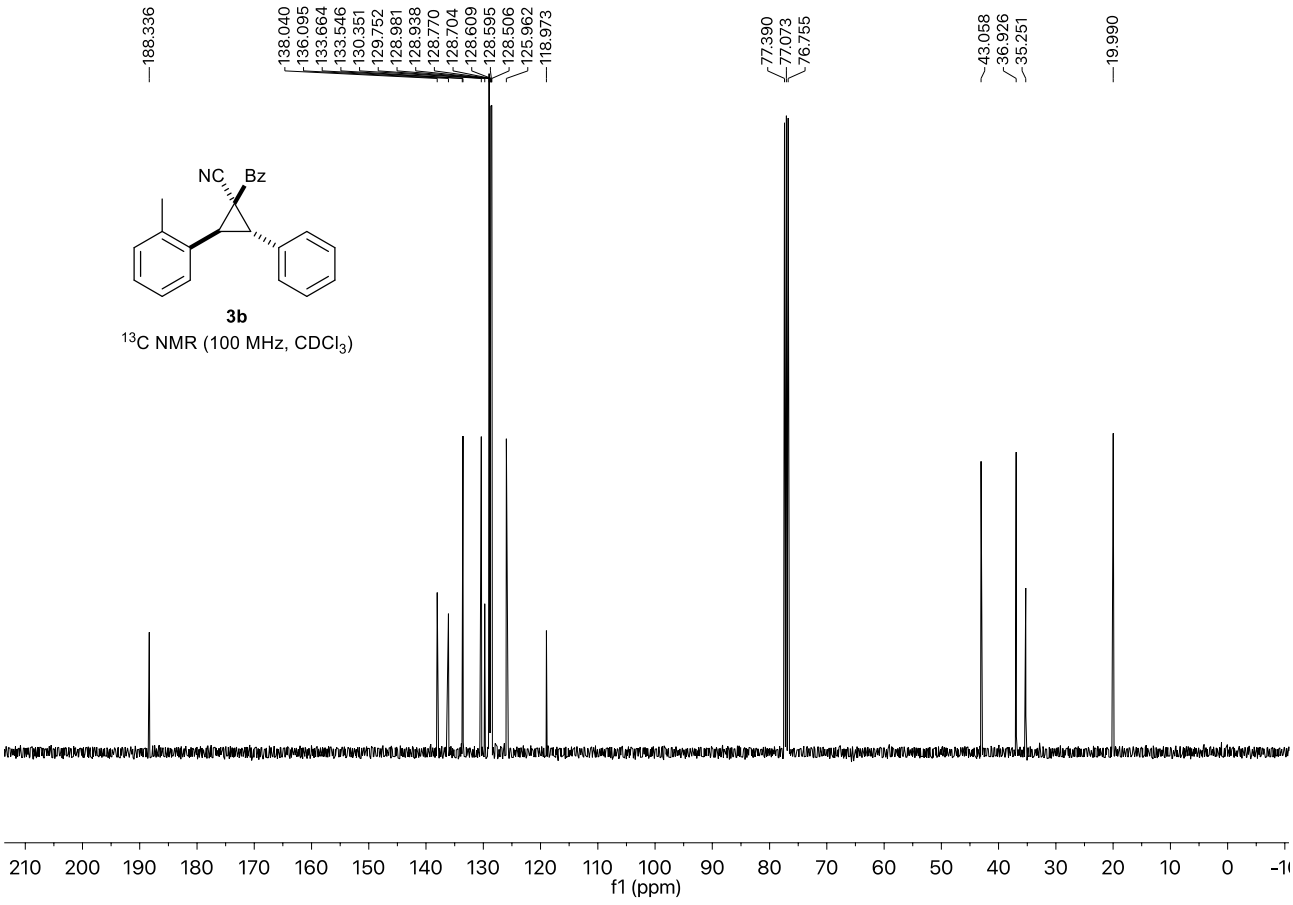

+ESI Scan (rt: 0.207 min) Frag=175.0V
x10^5
346.1205
NC
Bz
3a
(ESI-TOF) m/z: [M + Na]+
Calcd for C23H17NONa+ 346.1202
Counts vs. Mass-to-Charge (m/z)





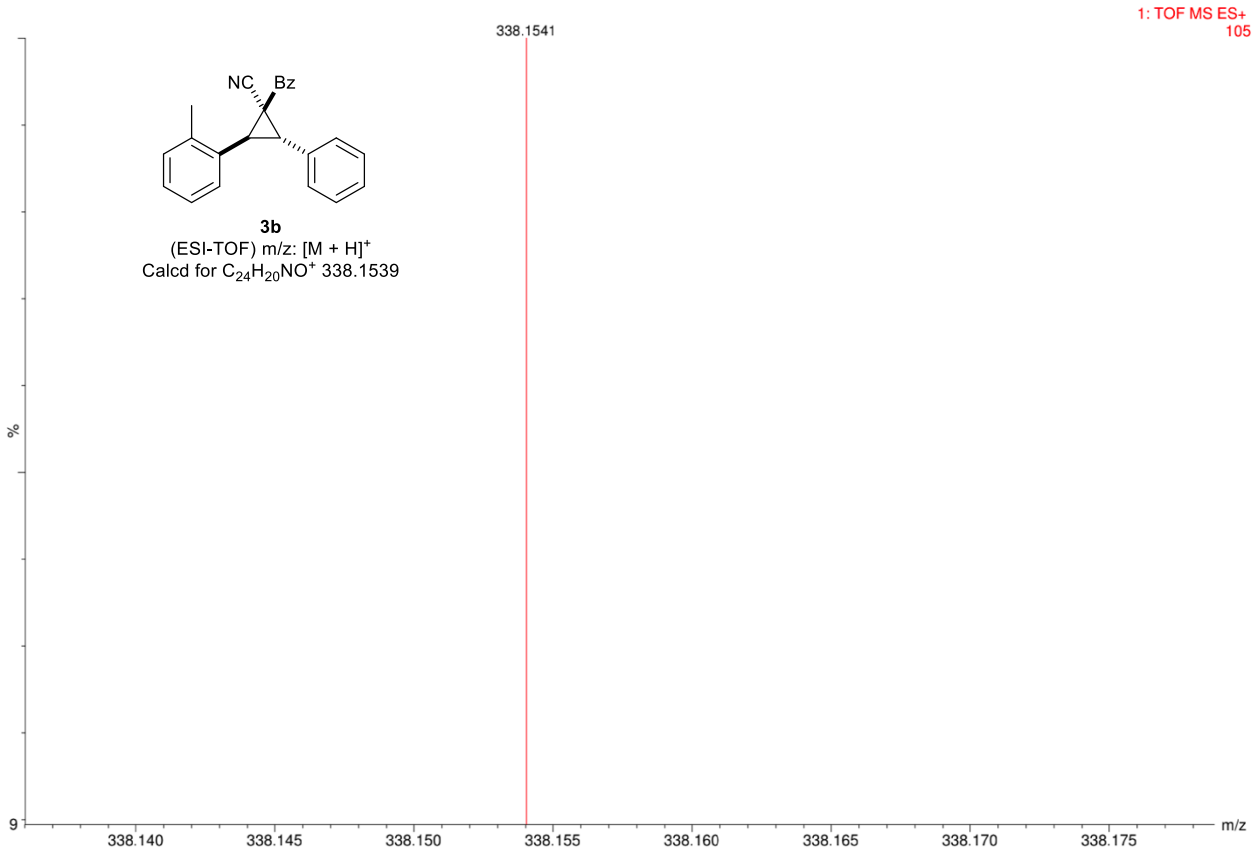
3b

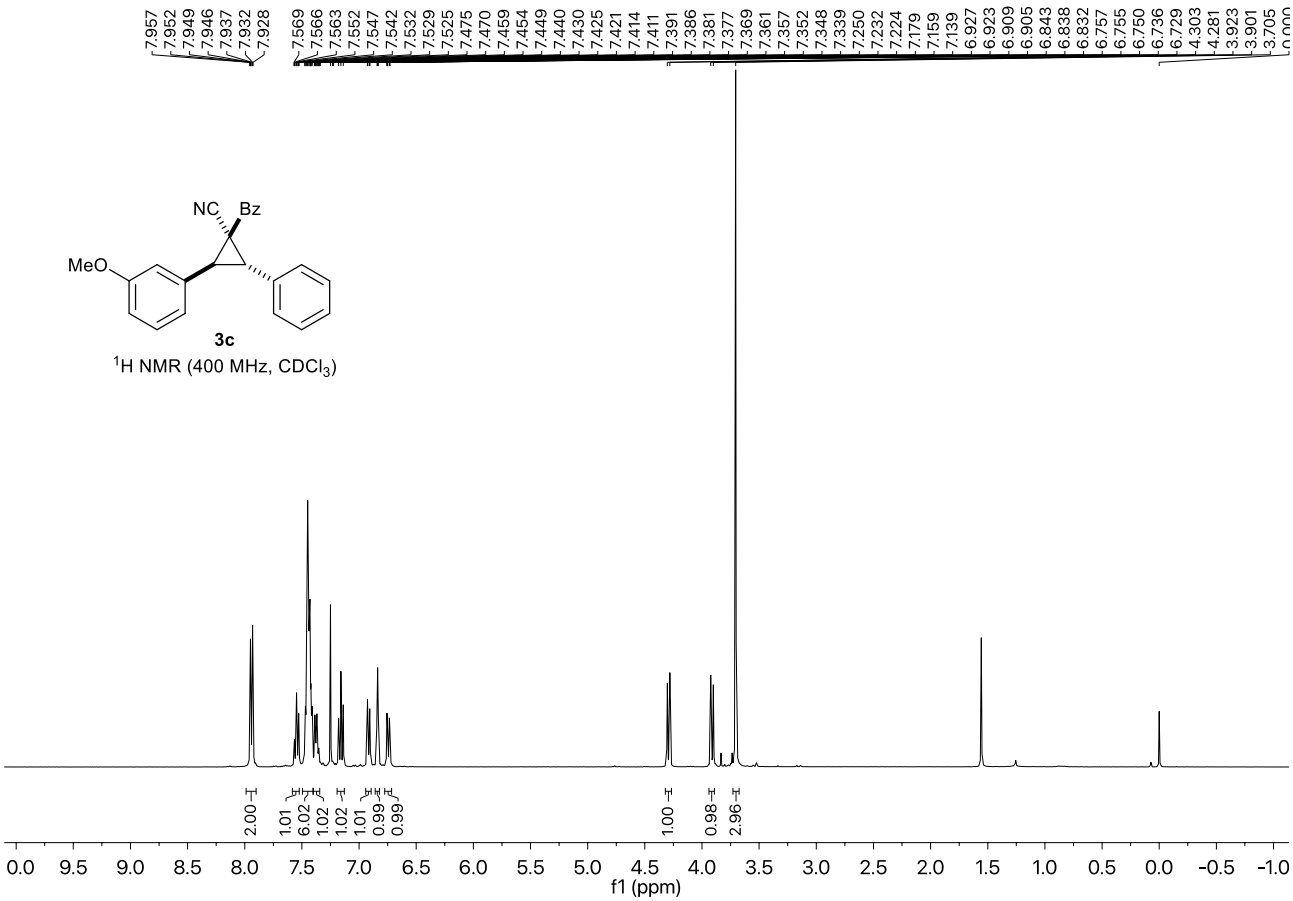
^{1}H NMR (400 MHz, $CDCl_3$)

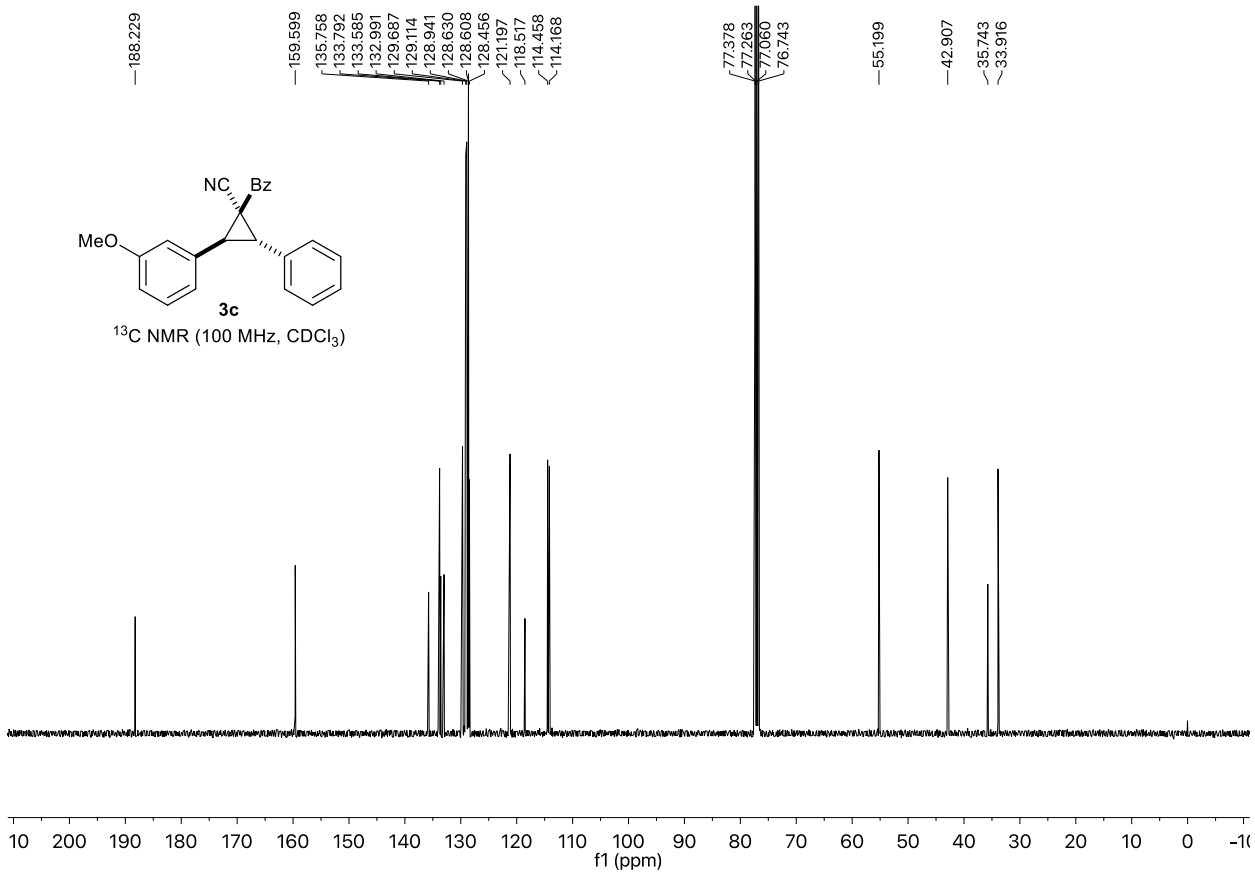


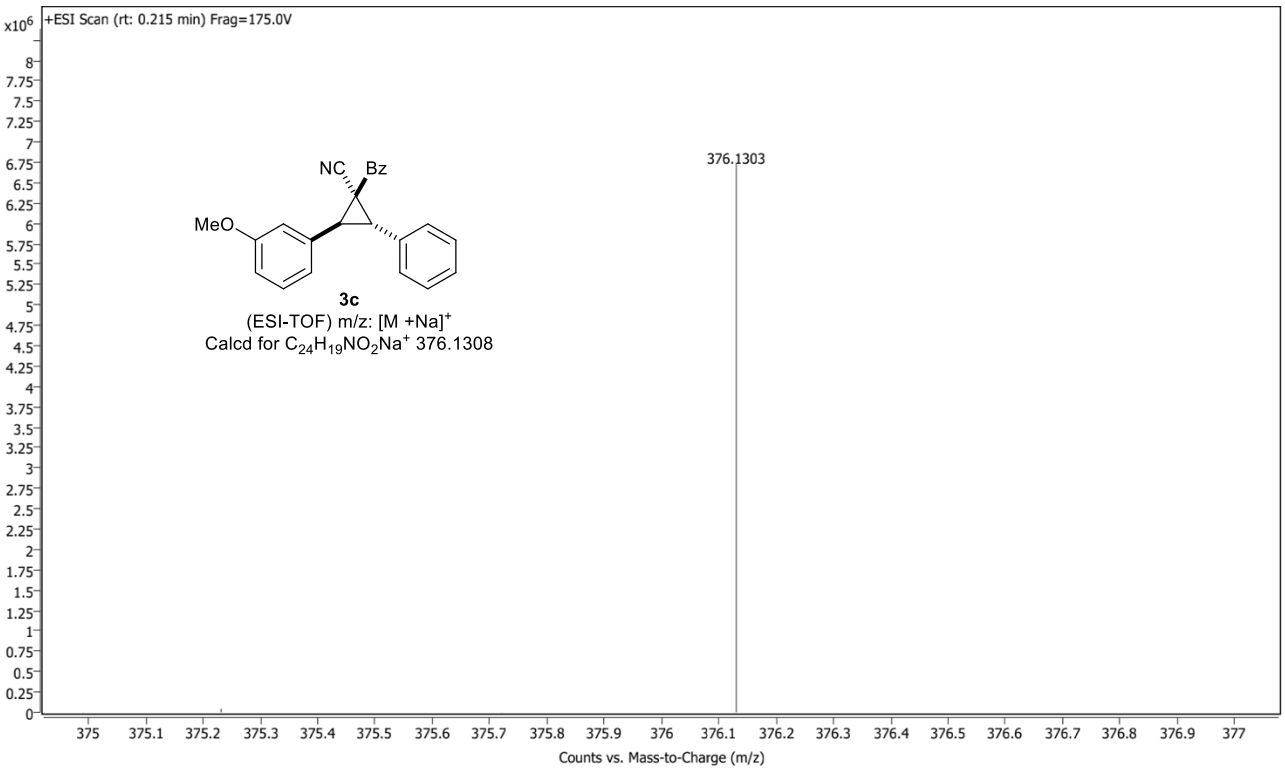
3b

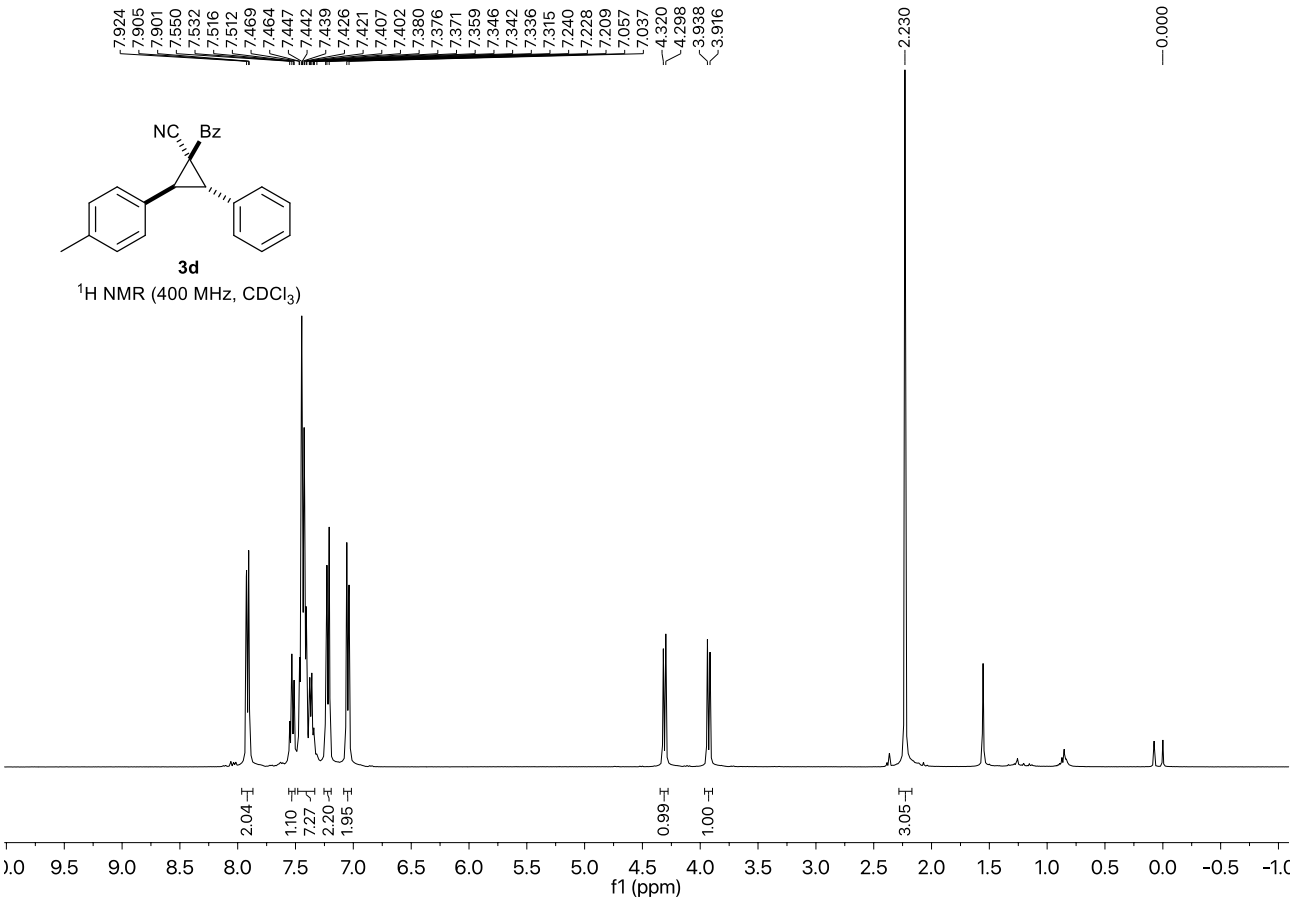
^{13}C NMR (100 MHz, $CDCl_3$)

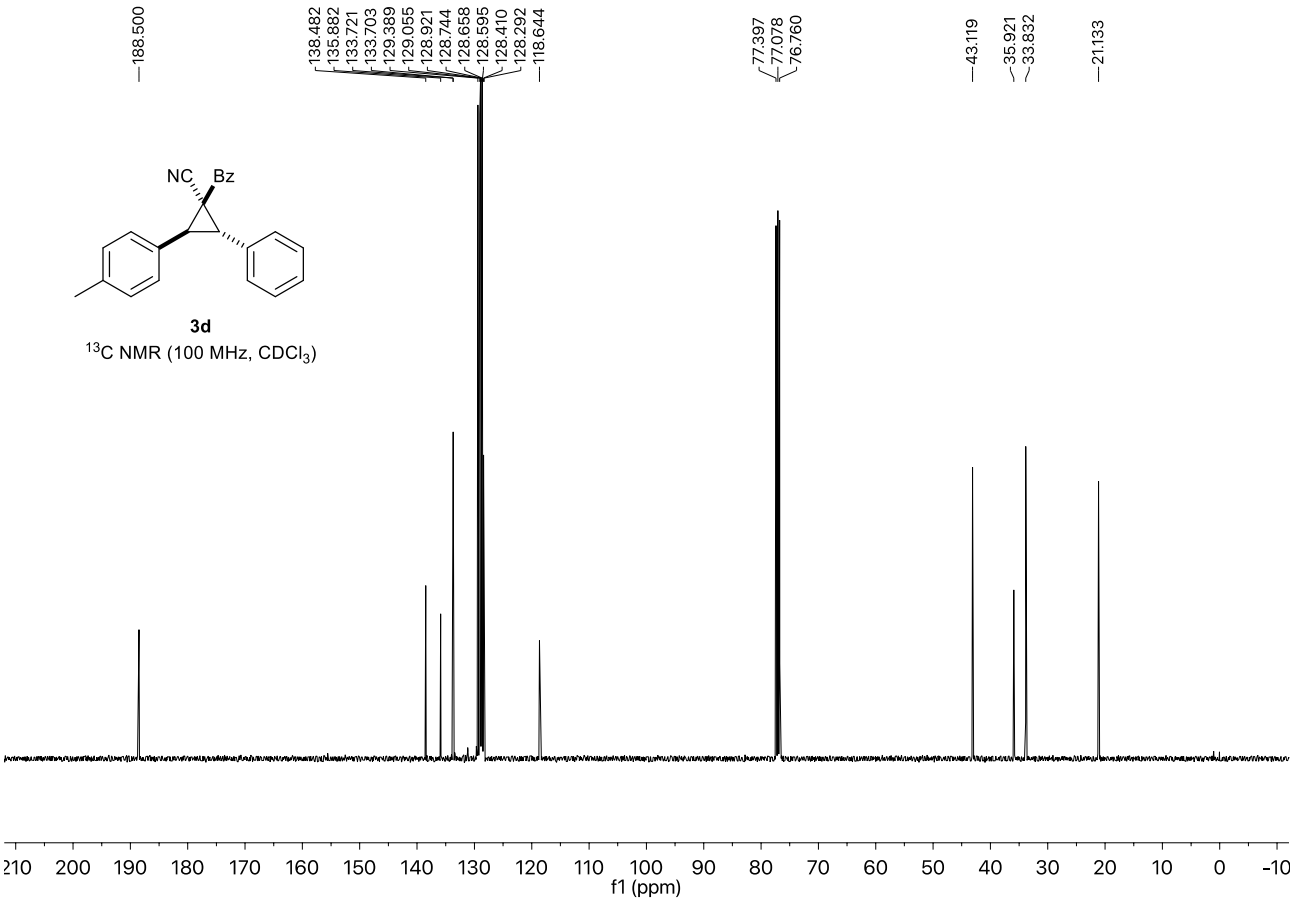

1: TOF MS ES+
105
338.1541
NC
Bz
3b
(ESI-TOF) m/z: [M + H]+
Calcd for C24H20NO+ 338.1539
%
9
338.140
338.145
338.150
338.155
338.160
338.165
338.170
338.175
m/z

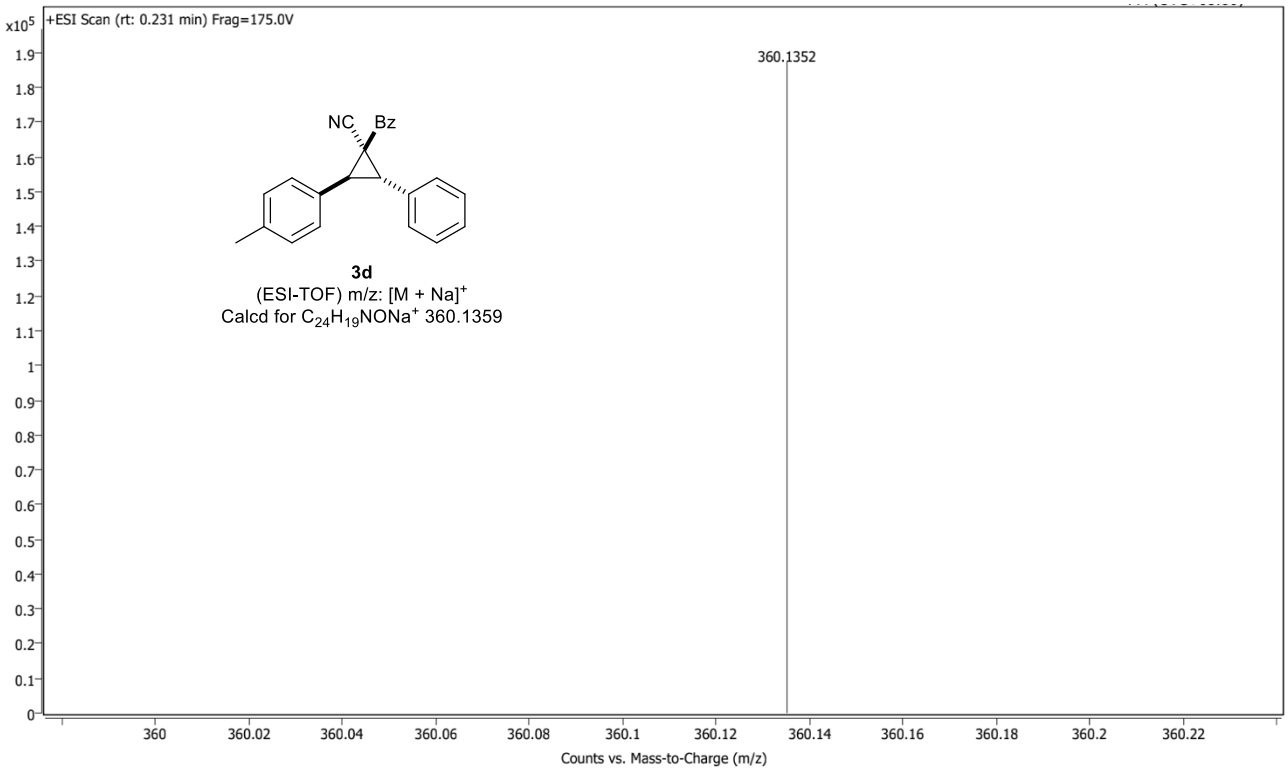

NC
Bz
MeO
3c
^{1}H NMR (400 MHz, $CDCl_3$)
f1 (ppm)

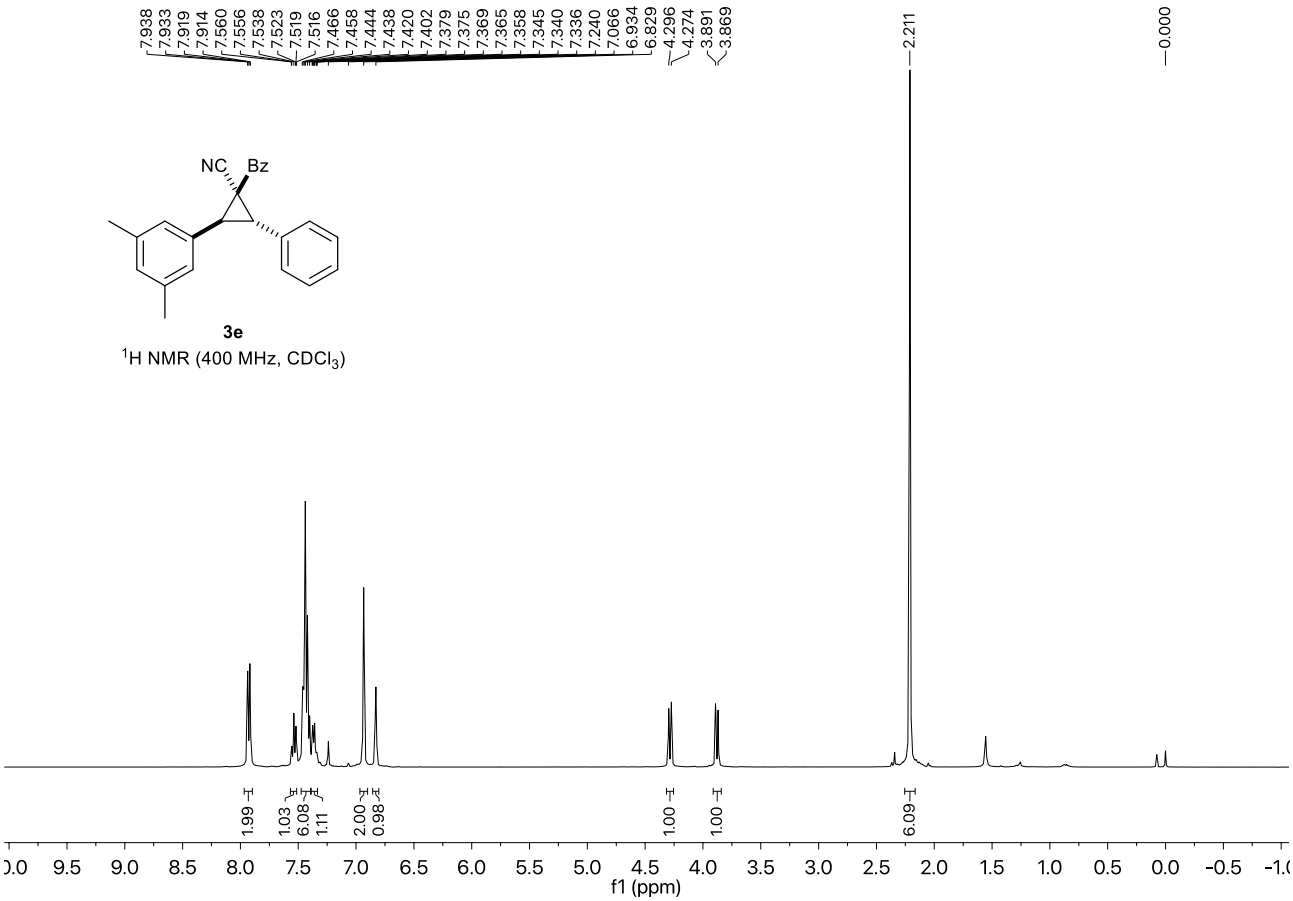

NC
Bz
MeO
3c
^{13}C NMR (100 MHz, $CDCl_3$)
f1 (ppm)


+ESI Scan (rt: 0.215 min) Frag=175.0V
x10^6
376.1303
NC
Bz
MeO
3c
(ESI-TOF) m/z: [M +Na]+
Calcd for C24H19NO2Na+ 376.1308
Counts vs. Mass-to-Charge (m/z)


7.924
7.905
7.901
7.550
7.532
7.516
7.512
7.469
7.464
7.447
7.442
7.439
7.426
7.421
7.407
7.402
7.380
7.376
7.371
7.359
7.346
7.342
7.336
7.315
7.240
7.228
7.209
7.057
7.037
4.320
4.298
3.938
3.916
2.230
0.000
NC
Bz
3d
1H NMR (400 MHz, CDCl3)
2.04
1.10
7.27
2.20
1.95
0.99
1.00
3.05
f1 (ppm)

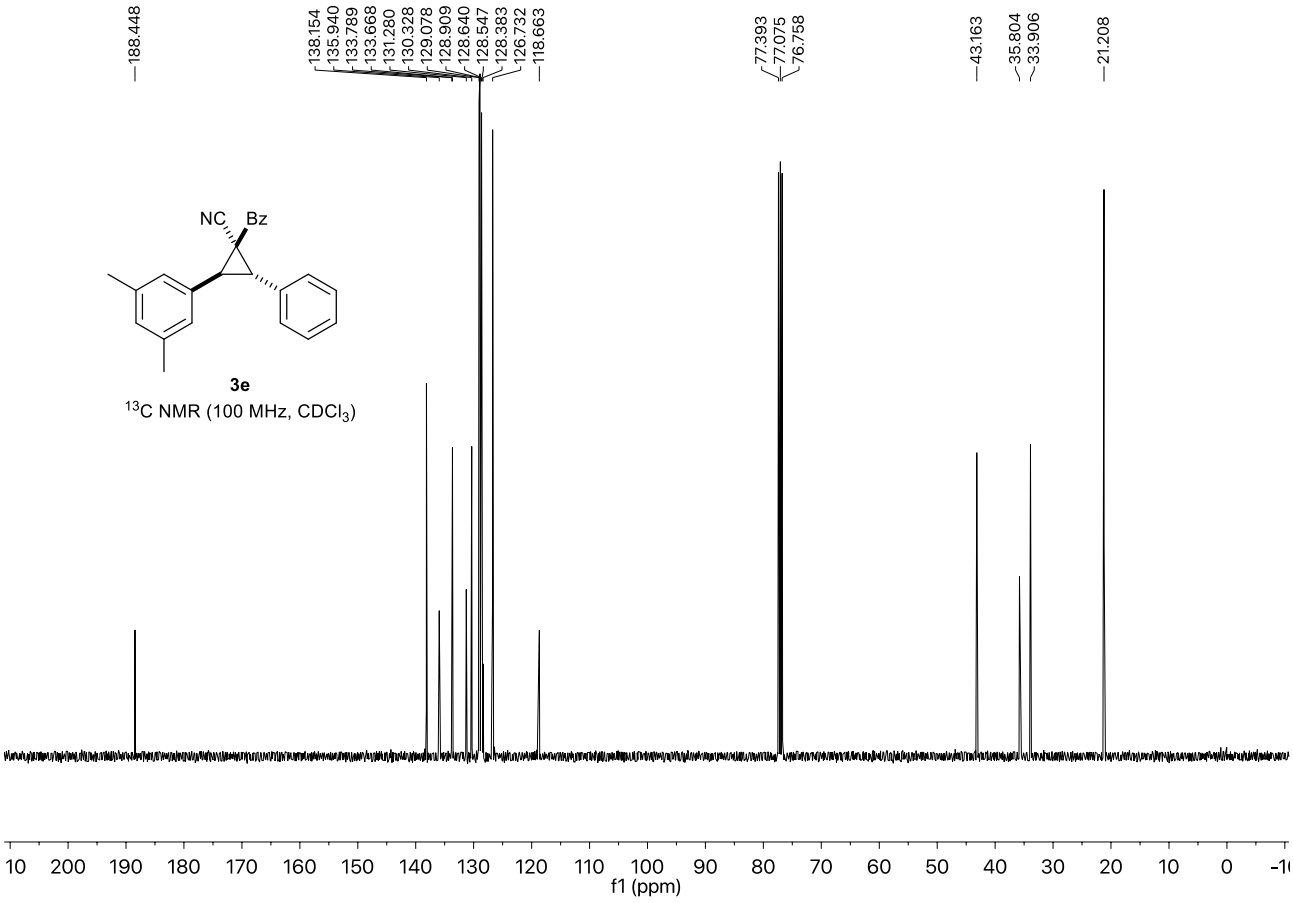

188.500
138.482
135.882
133.721
133.703
129.389
129.055
128.921
128.744
128.658
128.595
128.410
128.292
118.644
77.397
77.078
76.760
43.119
35.921
33.832
21.133
NC
Bz
3d
13C NMR (100 MHz, CDCl3)
f1 (ppm)


+ESI Scan (rt: 0.231 min) Frag=175.0V
x10^5
360.1352
NC
Bz
3d
(ESI-TOF) m/z: [M + Na]+
Calcd for C24H19NONa+ 360.1359
Counts vs. Mass-to-Charge (m/z)



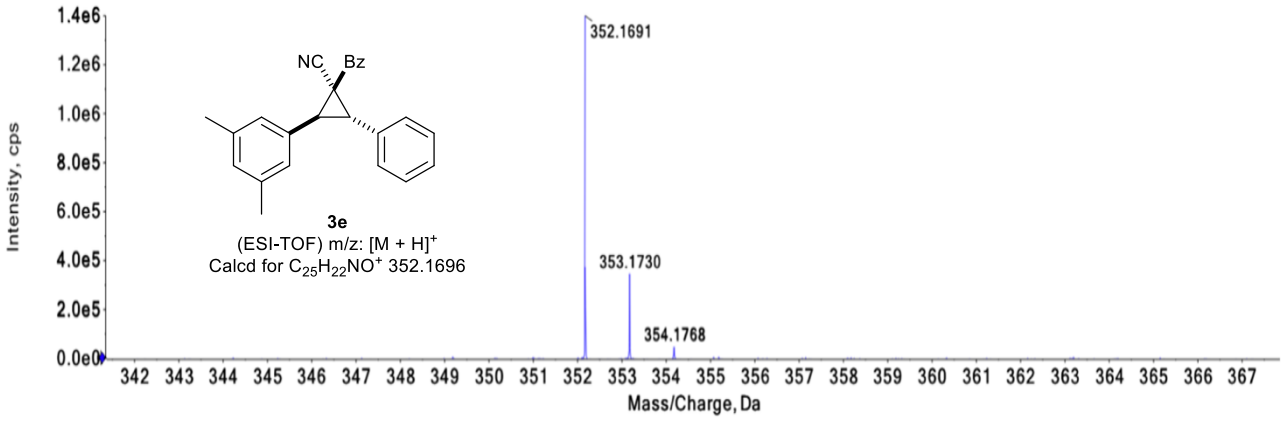
3e

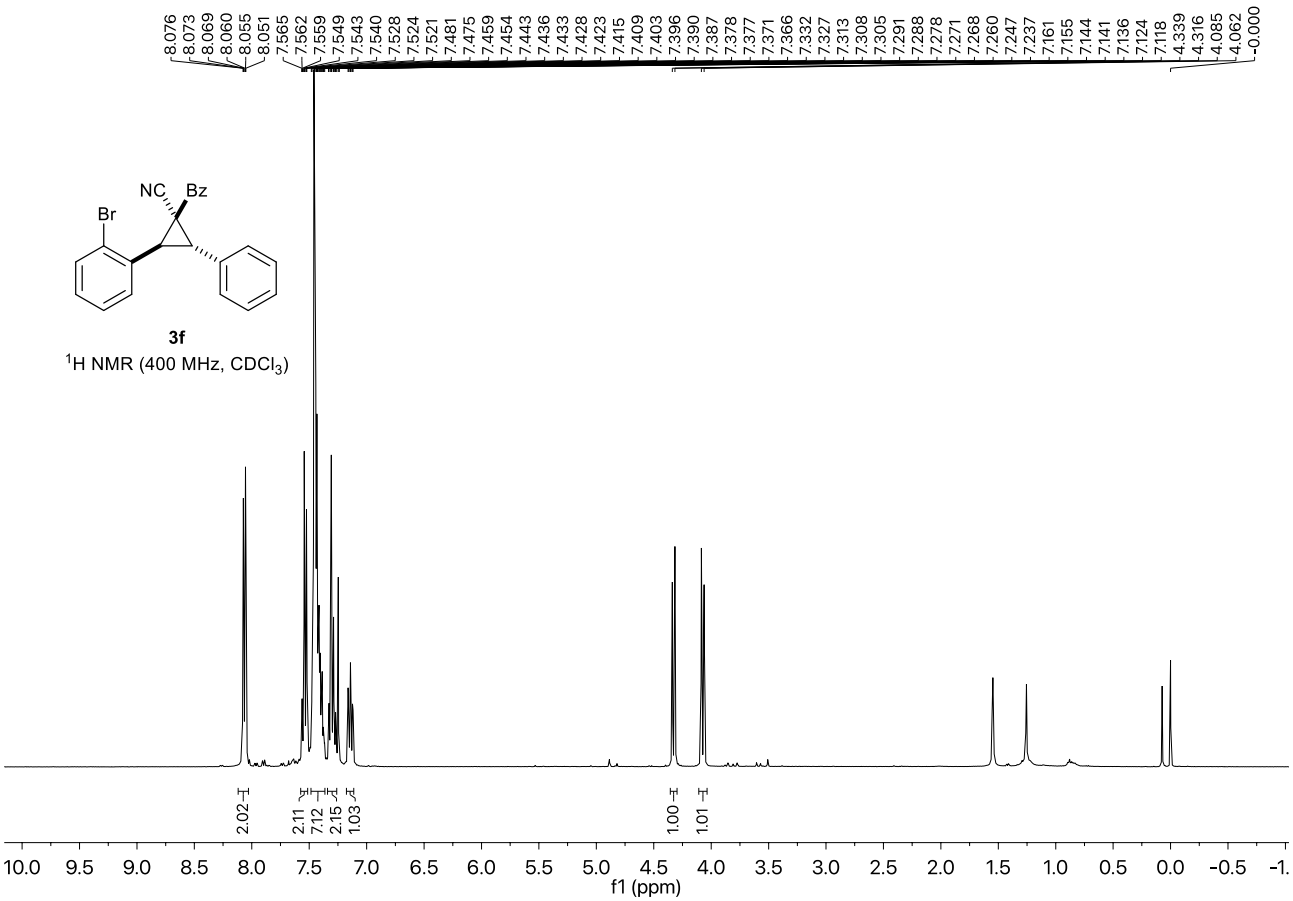
^{1}H NMR (400 MHz, $CDCl_3$)

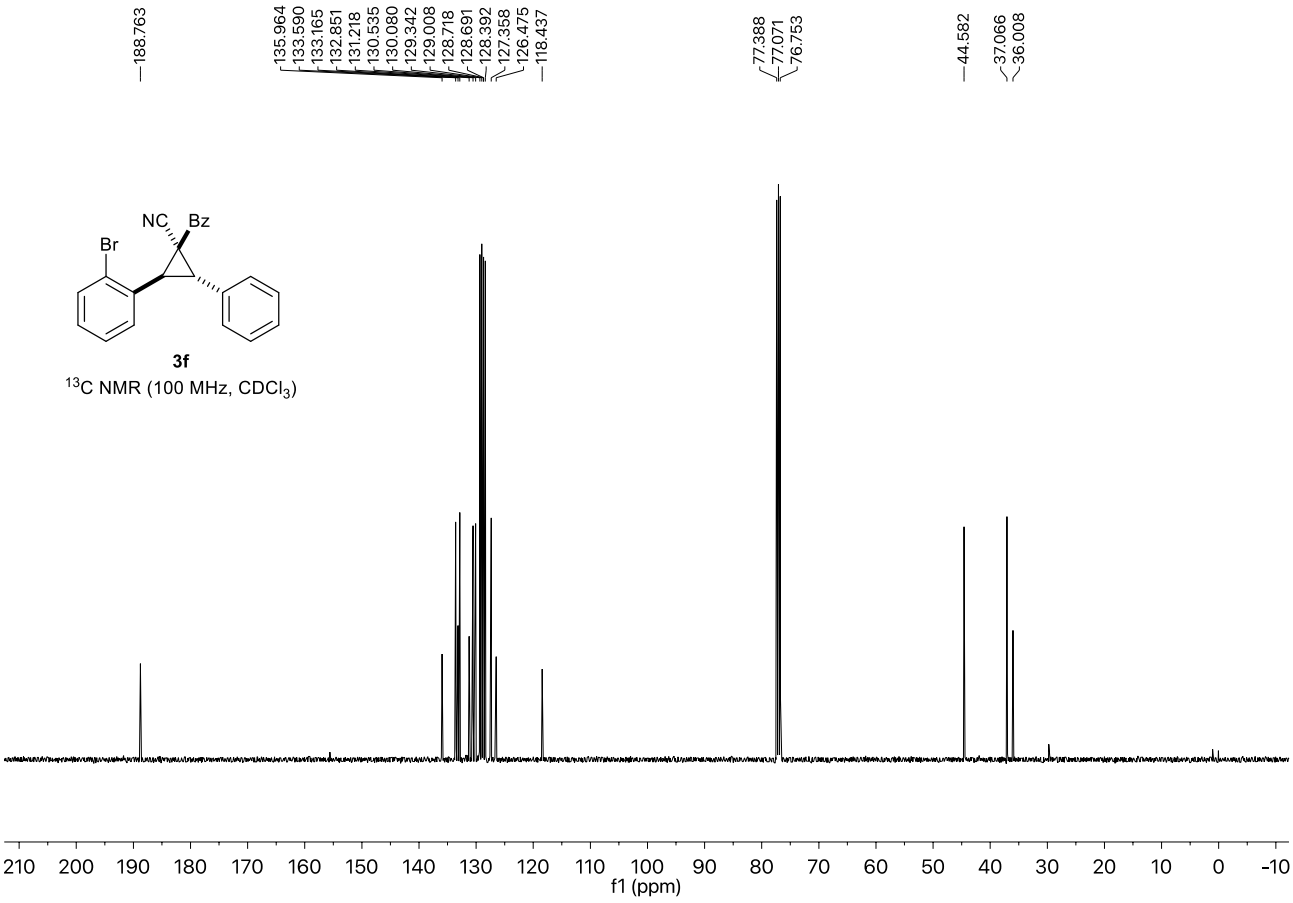


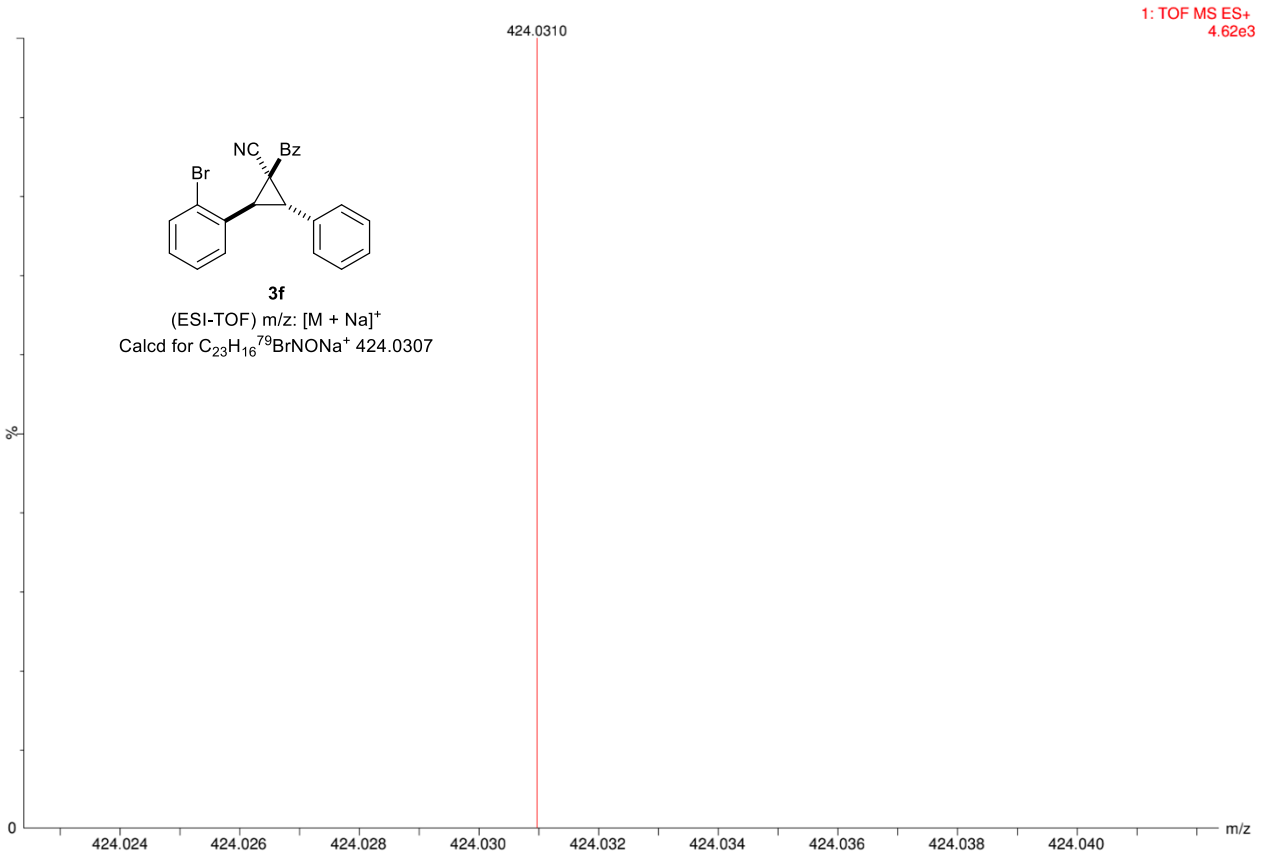
3e

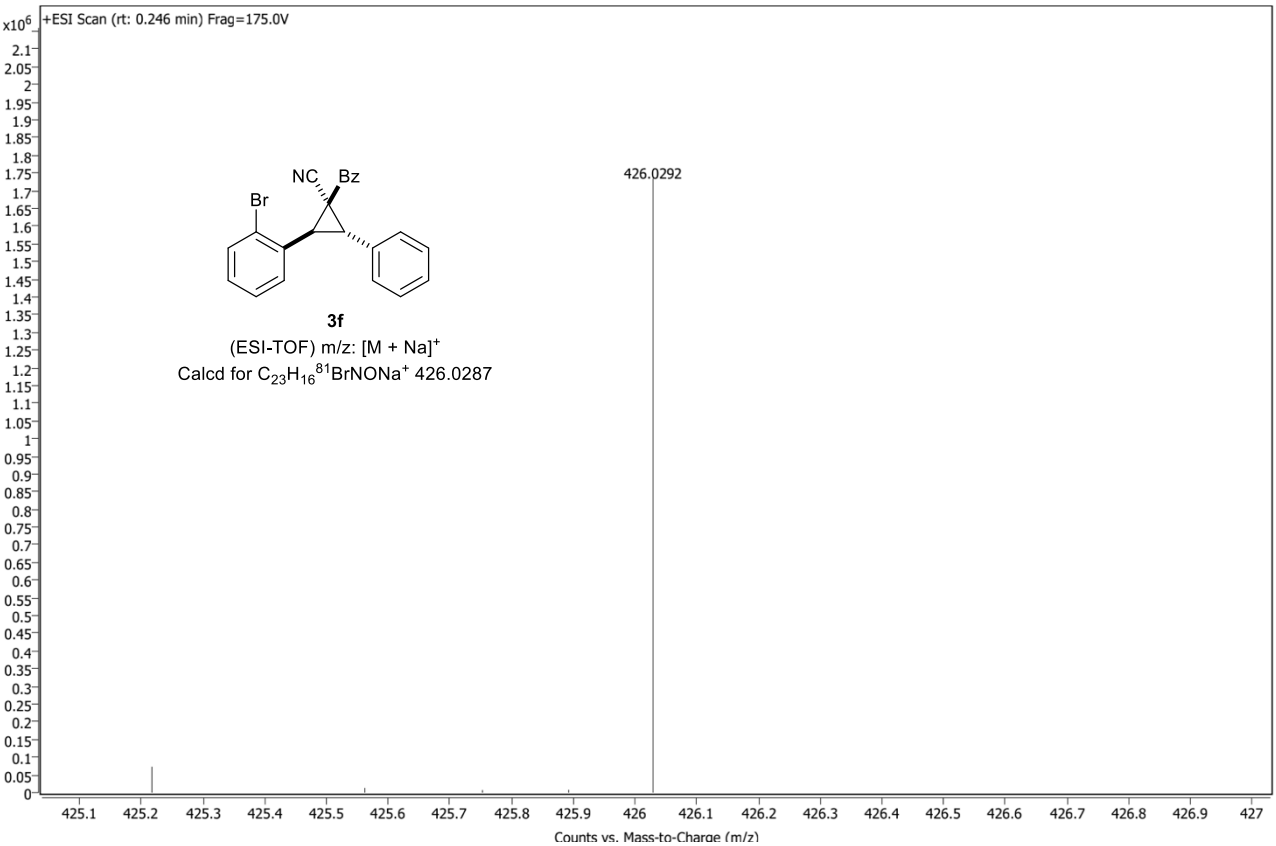
^{13}C NMR (100 MHz, $CDCl_3$)

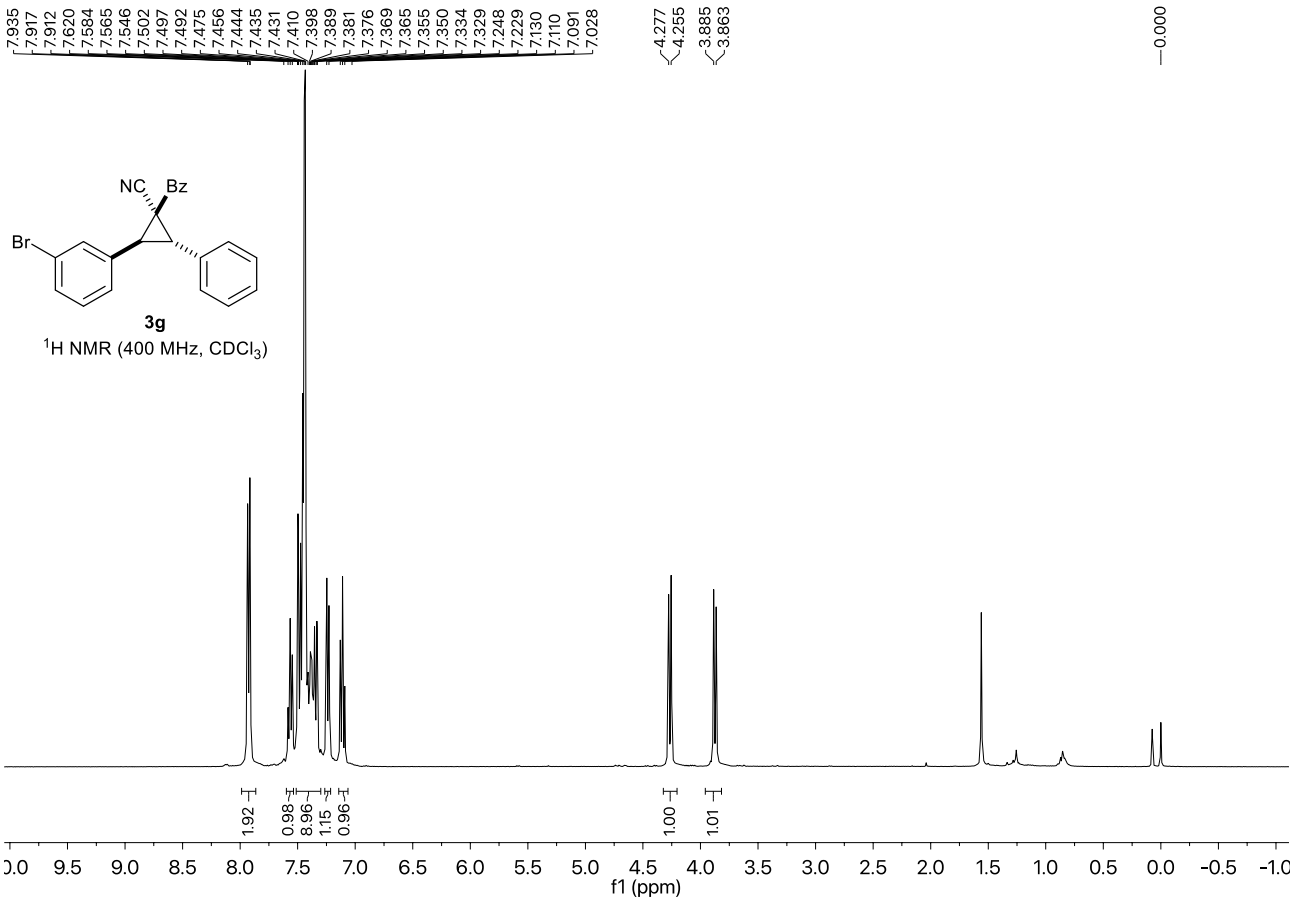

1.4e6
1.2e6
1.0e6
8.0e5
6.0e5
4.0e5
2.0e5
0.0e0
Intensity, cps
NC
Bz
3e
(ESI-TOF) m/z: [M + H]+
Calcd for C25H22NO+ 352.1696
352.1691
353.1730
354.1768
342 343 344 345 346 347 348 349 350 351 352 353 354 355 356 357 358 359 360 361 362 363 364 365 366 367
Mass/Charge, Da


8.076
8.073
8.069
8.060
8.055
8.051
7.565
7.562
7.559
7.549
7.543
7.540
7.528
7.524
7.521
7.481
7.475
7.459
7.454
7.443
7.436
7.433
7.428
7.423
7.415
7.409
7.403
7.396
7.390
7.387
7.378
7.377
7.371
7.366
7.332
7.327
7.313
7.308
7.305
7.291
7.288
7.278
7.271
7.268
7.260
7.247
7.237
7.161
7.155
7.144
7.141
7.136
7.124
7.118
4.339
4.316
4.085
4.062
-0.000
NC
Bz
Br
3f
1H NMR (400 MHz, CDCl3)
2.02
2.11
7.12
2.15
1.03
1.00
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)


188.763
135.964
133.590
133.165
132.851
131.218
130.535
130.080
129.342
129.008
128.718
128.691
128.392
127.358
126.475
118.437
77.388
77.071
76.753
44.582
37.066
36.008
NC
Bz
Br
3f
13C NMR (100 MHz, CDCl3)
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

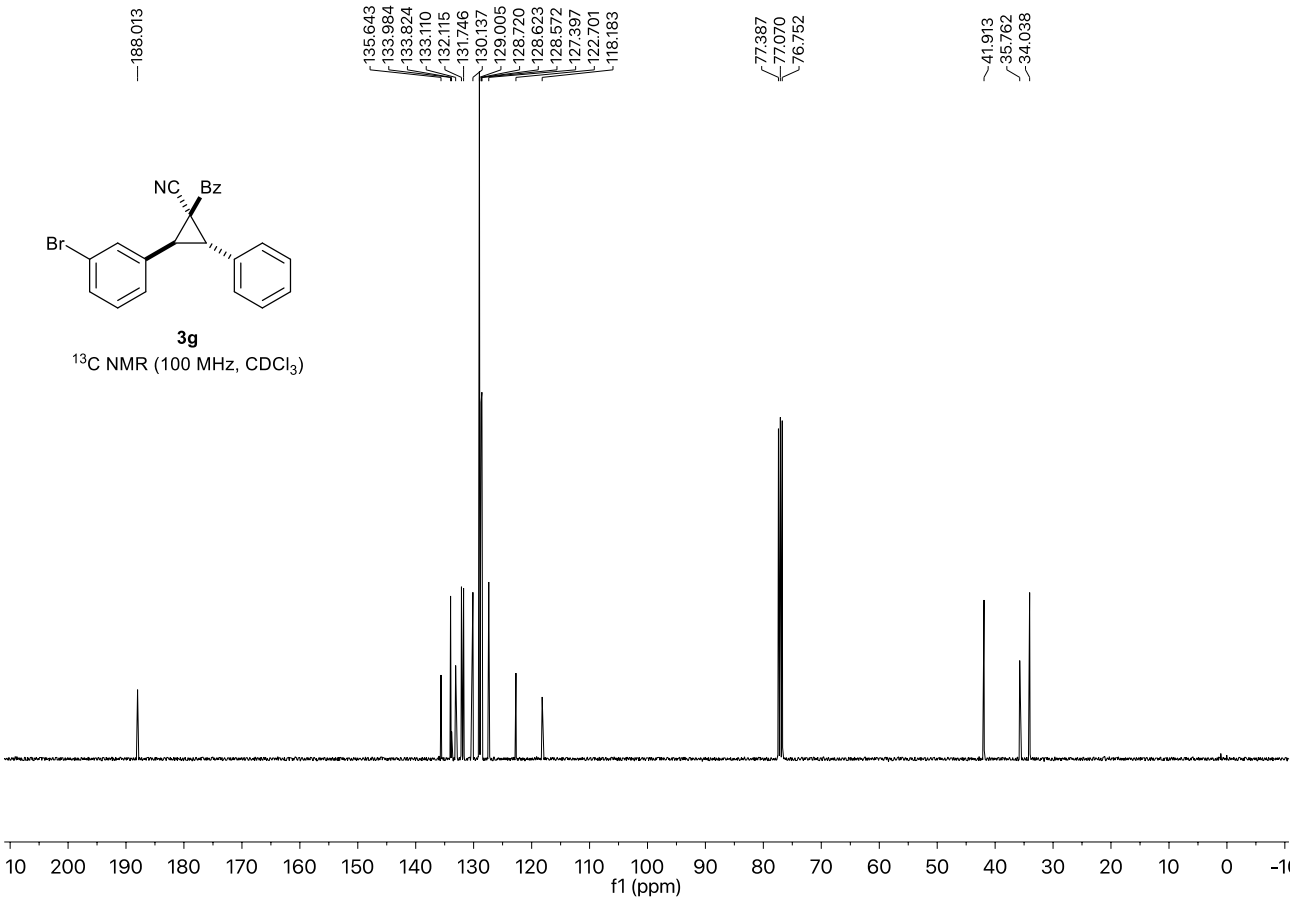

1: TOF MS ES+
4.62e3
424.0310
NC
Bz
Br
3f
(ESI-TOF) m/z: [M + Na]+
Calcd for C23H16 79BrNONa+ 424.0307
%
0
424.024
424.026
424.028
424.030
424.032
424.034
424.036
424.038
424.040
m/z


+ESI Scan (rt: 0.246 min) Frag=175.0V
x10^6
426.0292
NC
Bz
Br
3f
(ESI-TOF) m/z: [M + Na]+
Calcd for C23H16 81BrNONa+ 426.0287
425.1
425.2
425.3
425.4
425.5
425.6
425.7
425.8
425.9
426
426.1
426.2
426.3
426.4
426.5
426.6
426.7
426.8
426.9
427
Counts vs. Mass-to-Charge (m/z)



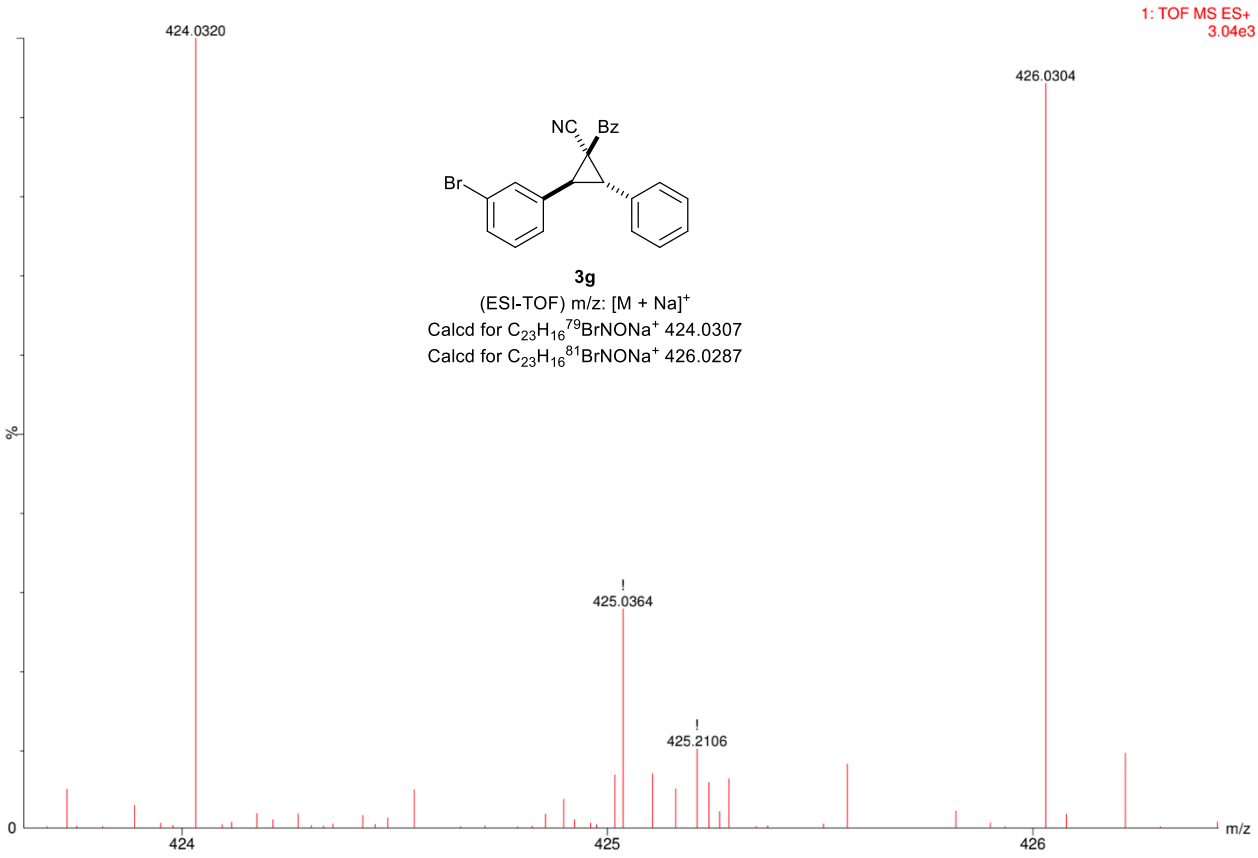
3g

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



3g

^{13}C NMR (100 MHz, $CDCl_3$)

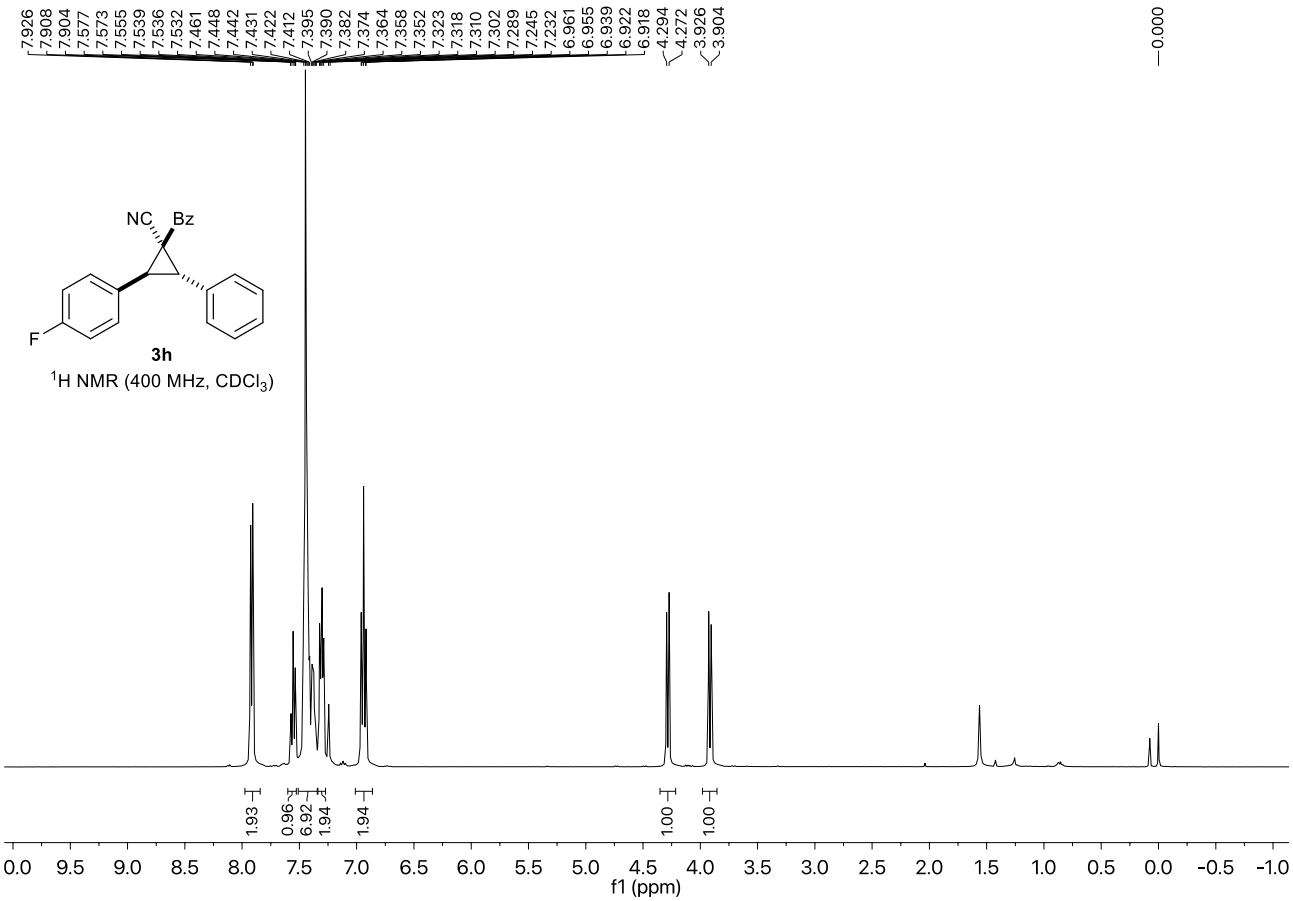


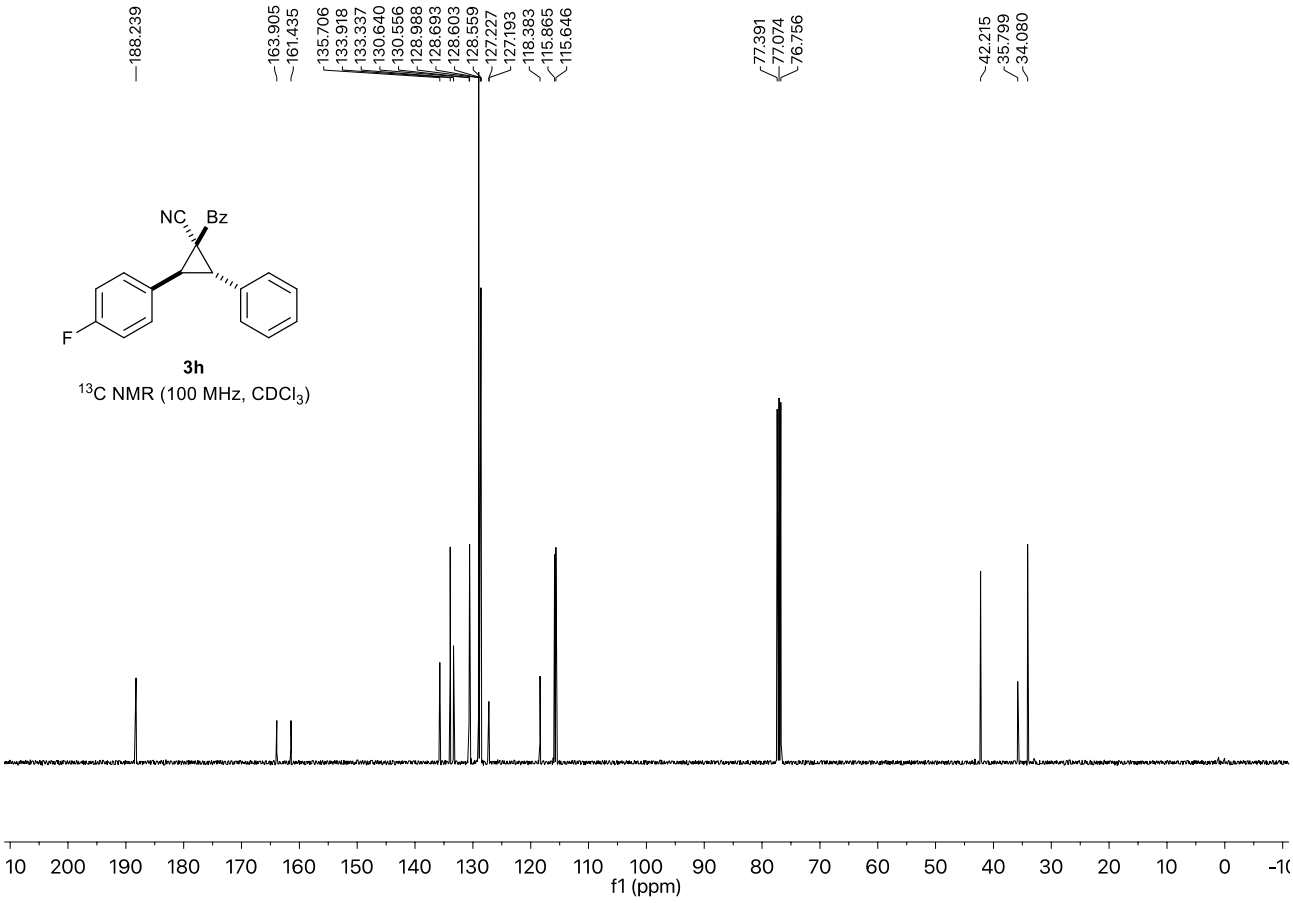
3g

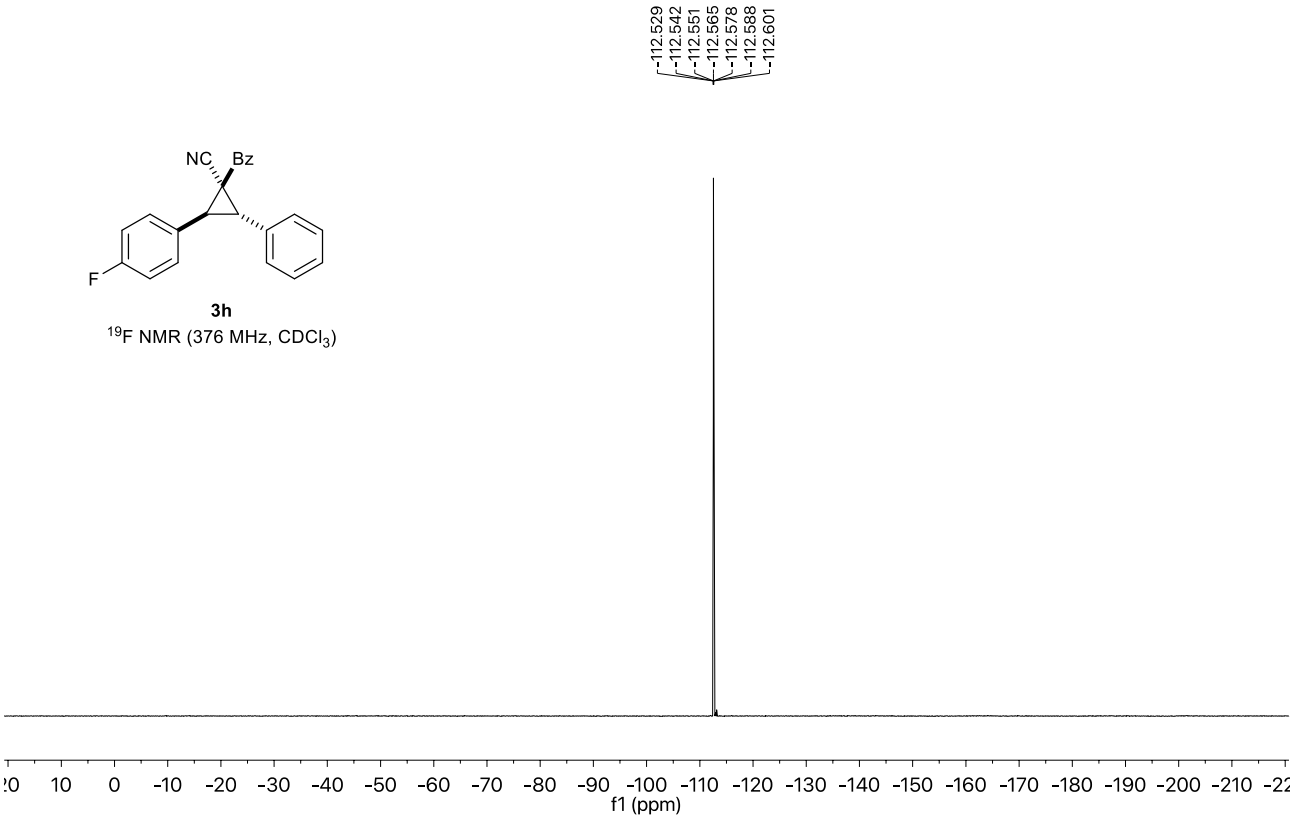
(ESI-TOF) m/z: $[M + Na]^+$

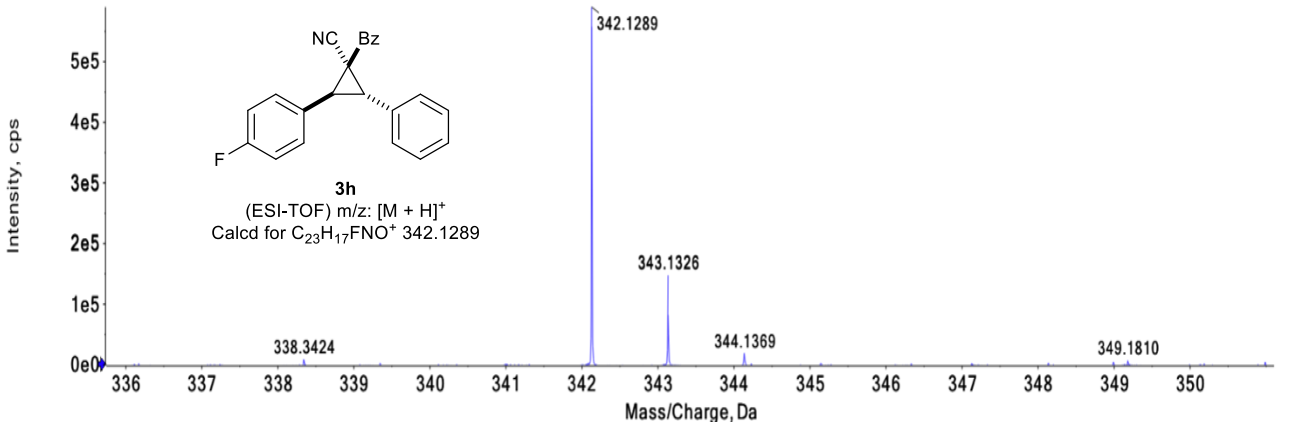
Calcd for $C_{23}H_{16}{}^{79}BrNONa^+$ 424.0307

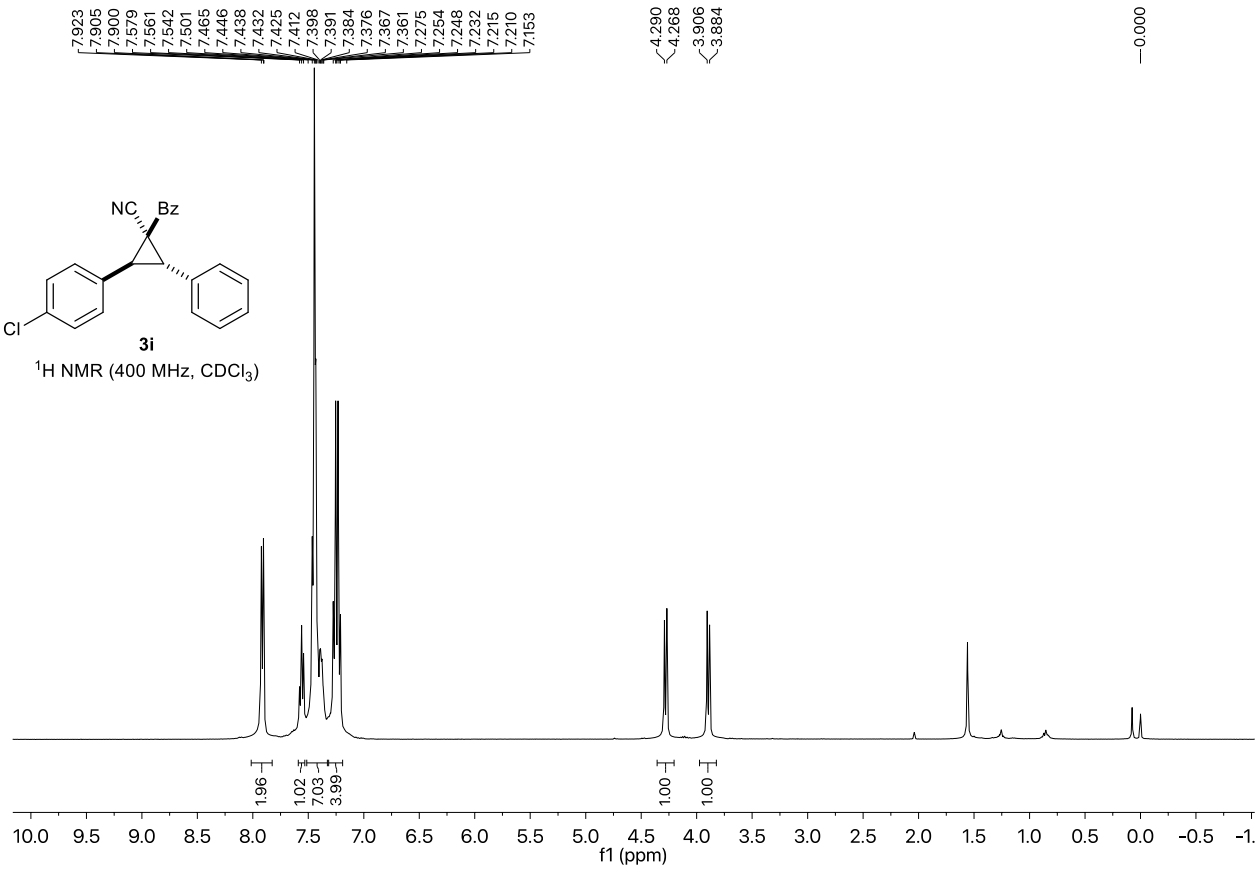
Calcd for $C_{23}H_{16}{}^{81}BrNONa^+$ 426.0287

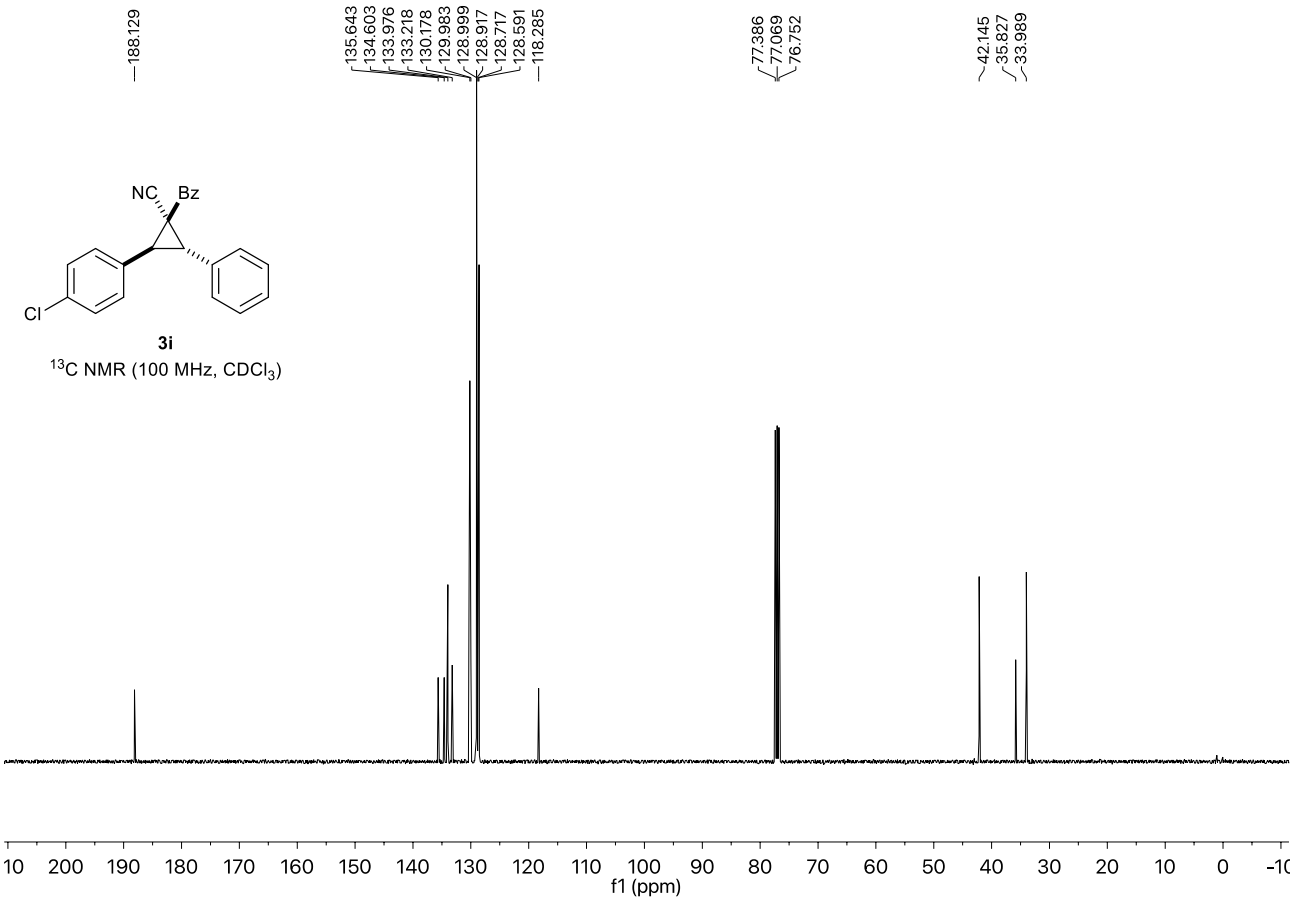

7.926
7.908
7.904
7.577
7.573
7.555
7.539
7.536
7.532
7.461
7.448
7.442
7.431
7.422
7.412
7.395
7.390
7.382
7.374
7.364
7.358
7.352
7.323
7.318
7.310
7.302
7.289
7.245
7.232
6.961
6.955
6.939
6.922
6.918
4.294
4.272
3.926
3.904
0.000
NC
Bz
F
3h
1H NMR (400 MHz, CDCl3)
1.93
0.96
6.92
1.94
1.94
1.00
1.00
f1 (ppm)

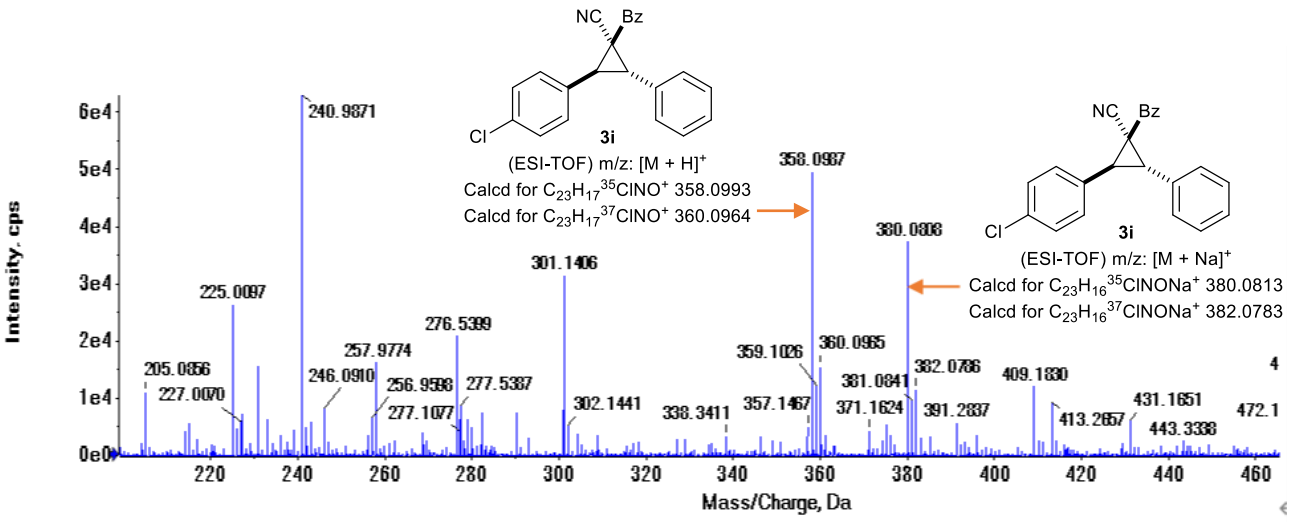

188.239
163.905
161.435
135.706
133.918
133.337
130.640
130.556
128.988
128.693
128.603
128.559
127.227
127.193
118.383
115.865
115.646
77.391
77.074
76.756
42.215
35.799
34.080
NC
Bz
F
3h
13C NMR (100 MHz, CDCl3)
f1 (ppm)

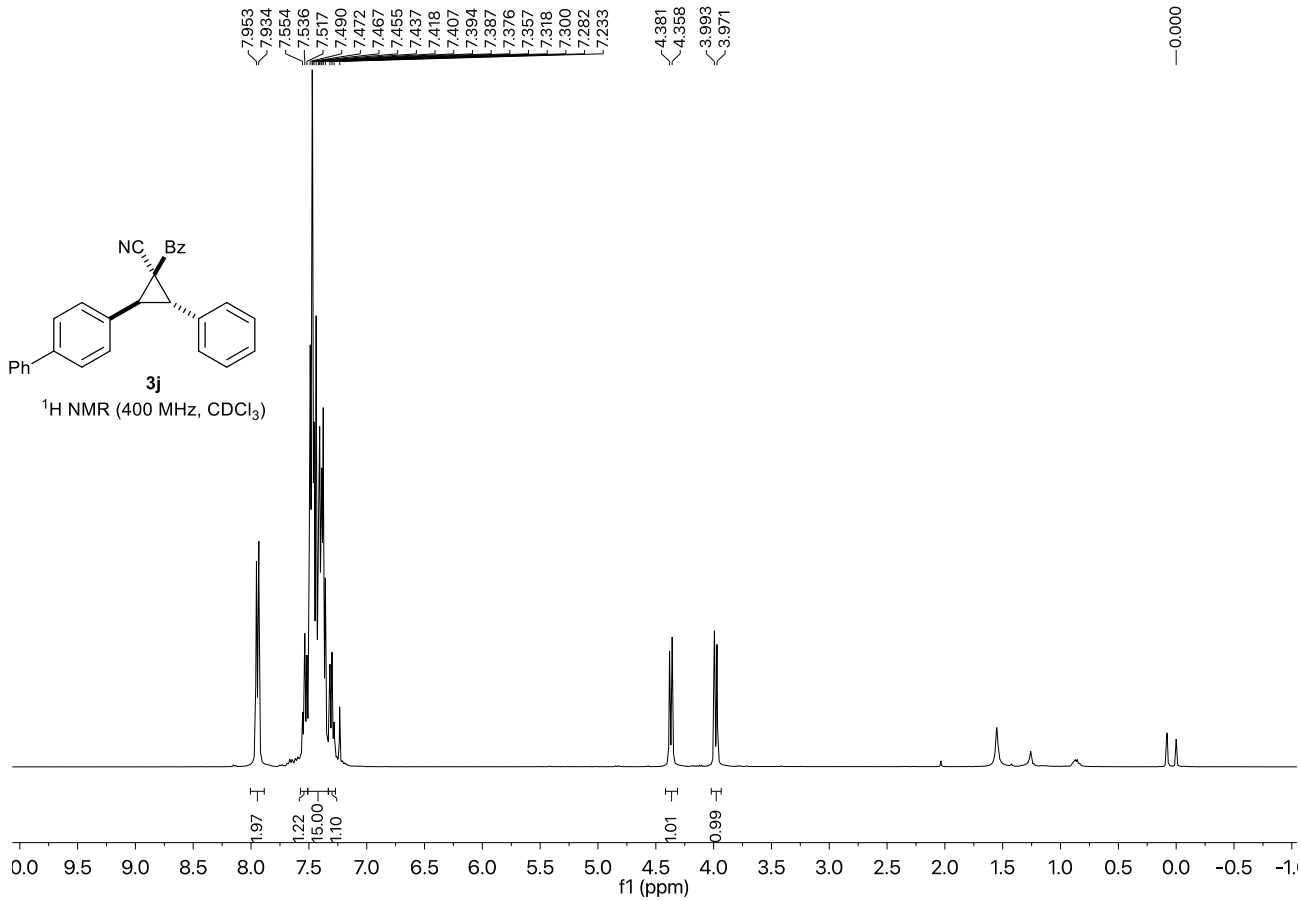

-112.529
-112.542
-112.551
-112.565
-112.578
-112.588
-112.601
NC
Bz
F
3h
19F NMR (376 MHz, CDCl3)
f1 (ppm)


NC
Bz
F
3h
(ESI-TOF) m/z: [M + H]+
Calcd for C23H17FNO+ 342.1289
342.1289
343.1326
344.1369
338.3424
349.1810
Intensity, cps
Mass/Charge, Da


7.923
7.905
7.900
7.579
7.561
7.542
7.501
7.465
7.446
7.438
7.432
7.425
7.412
7.398
7.391
7.384
7.376
7.367
7.361
7.275
7.254
7.248
7.232
7.215
7.210
7.153
4.290
4.268
3.906
3.884
0.000
NC
Bz
Cl
3i
1H NMR (400 MHz, CDCl3)
1.96
1.02
7.03
3.99
1.00
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

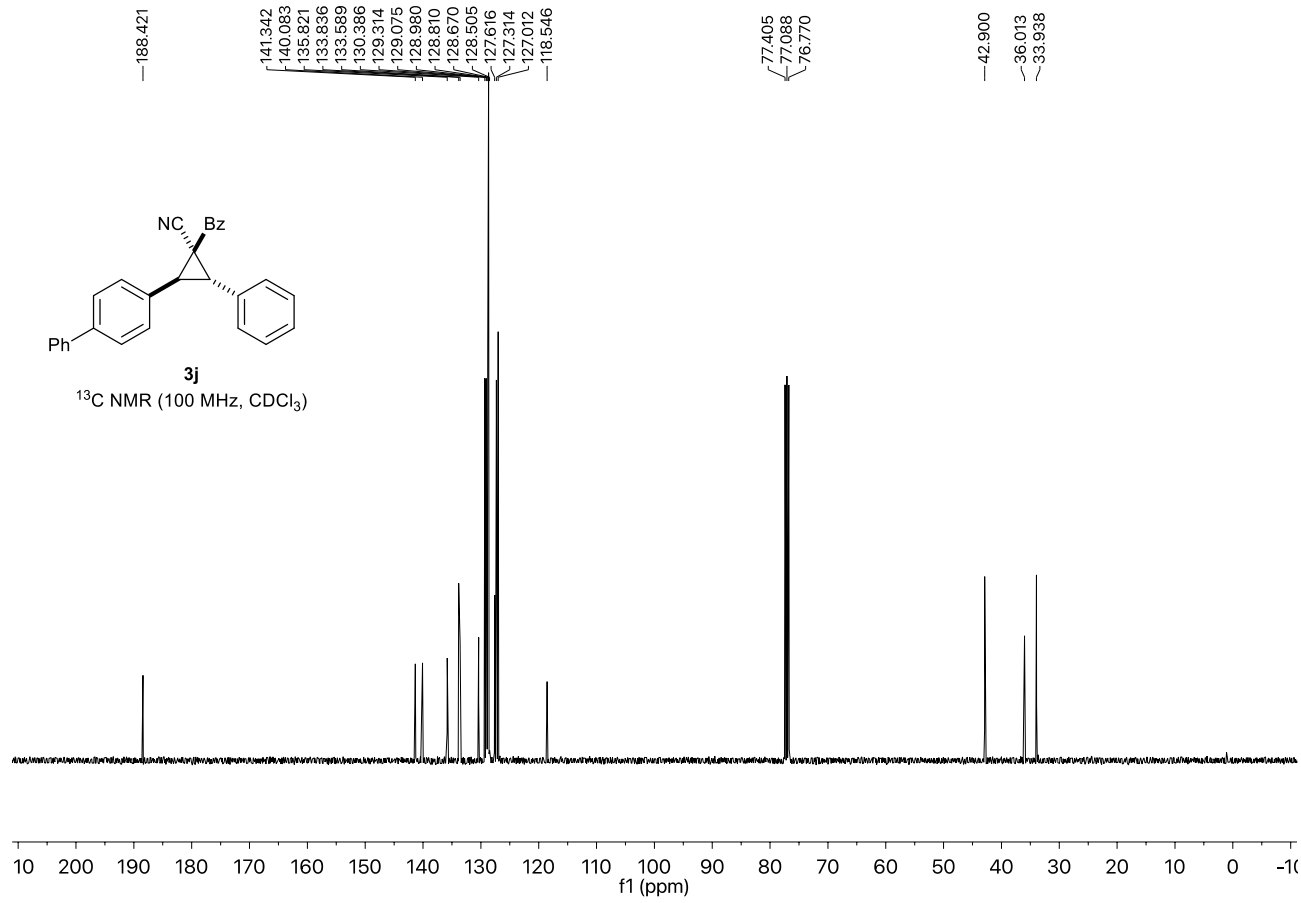

188.129
135.643
134.603
133.976
133.218
130.178
129.983
128.999
128.917
128.717
128.591
118.285
77.386
77.069
76.752
42.145
35.827
33.989
NC
Bz
Cl
3i
13C NMR (100 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


NC
Bz
Cl
3i
(ESI-TOF) m/z: [M + H]+
Calcd for C23H17 35ClNO+ 358.0993
Calcd for C23H17 37ClNO+ 360.0964
NC
Bz
Cl
3i
(ESI-TOF) m/z: [M + Na]+
Calcd for C23H16 35ClNONa+ 380.0813
Calcd for C23H16 37ClNONa+ 382.0783
Intensity, cps
Mass/Charge, Da
240.9871
358.0987
380.0808
301.1406
225.0097
276.5399
257.9774
205.0856
227.0070
246.0910
256.9598
277.5387
277.1077
302.1441
338.3411
359.1026
360.0965
357.1467
382.0786
381.0841
371.1624
391.2837
409.1830
413.2657
431.1651
443.3338
472.1



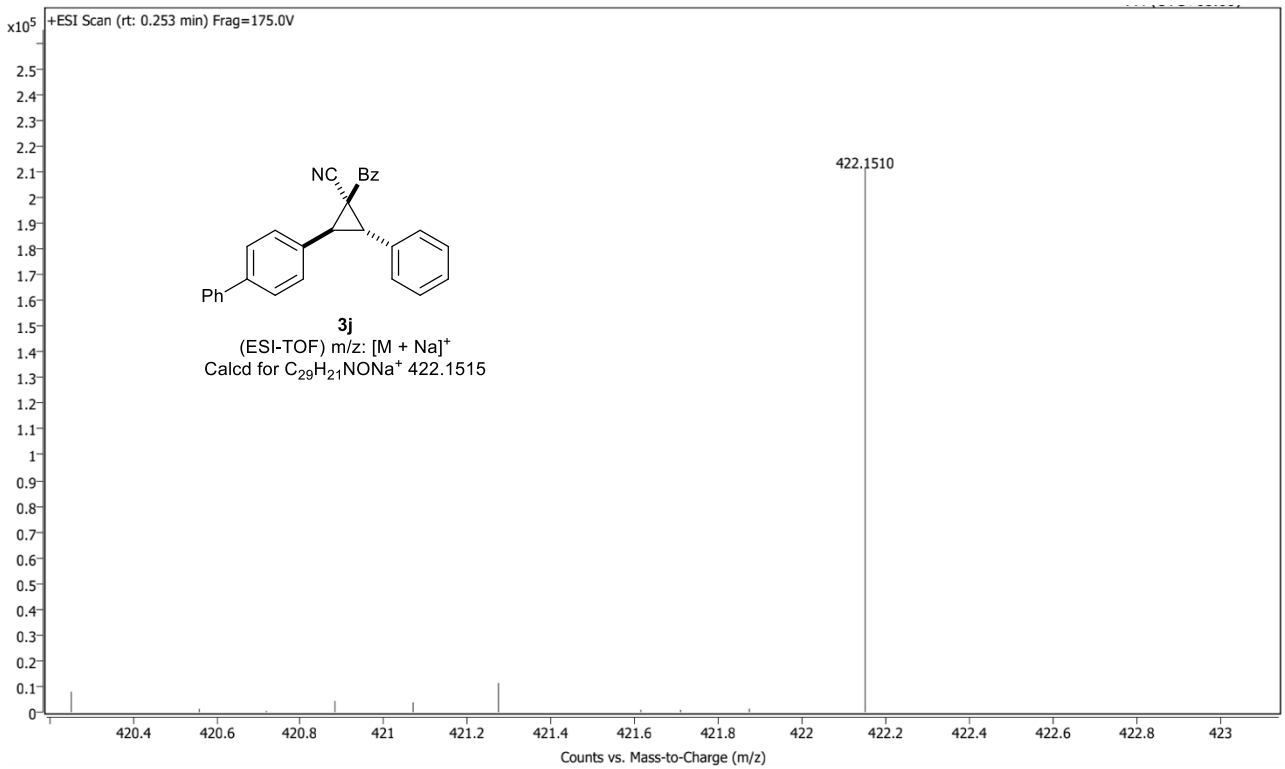
3j

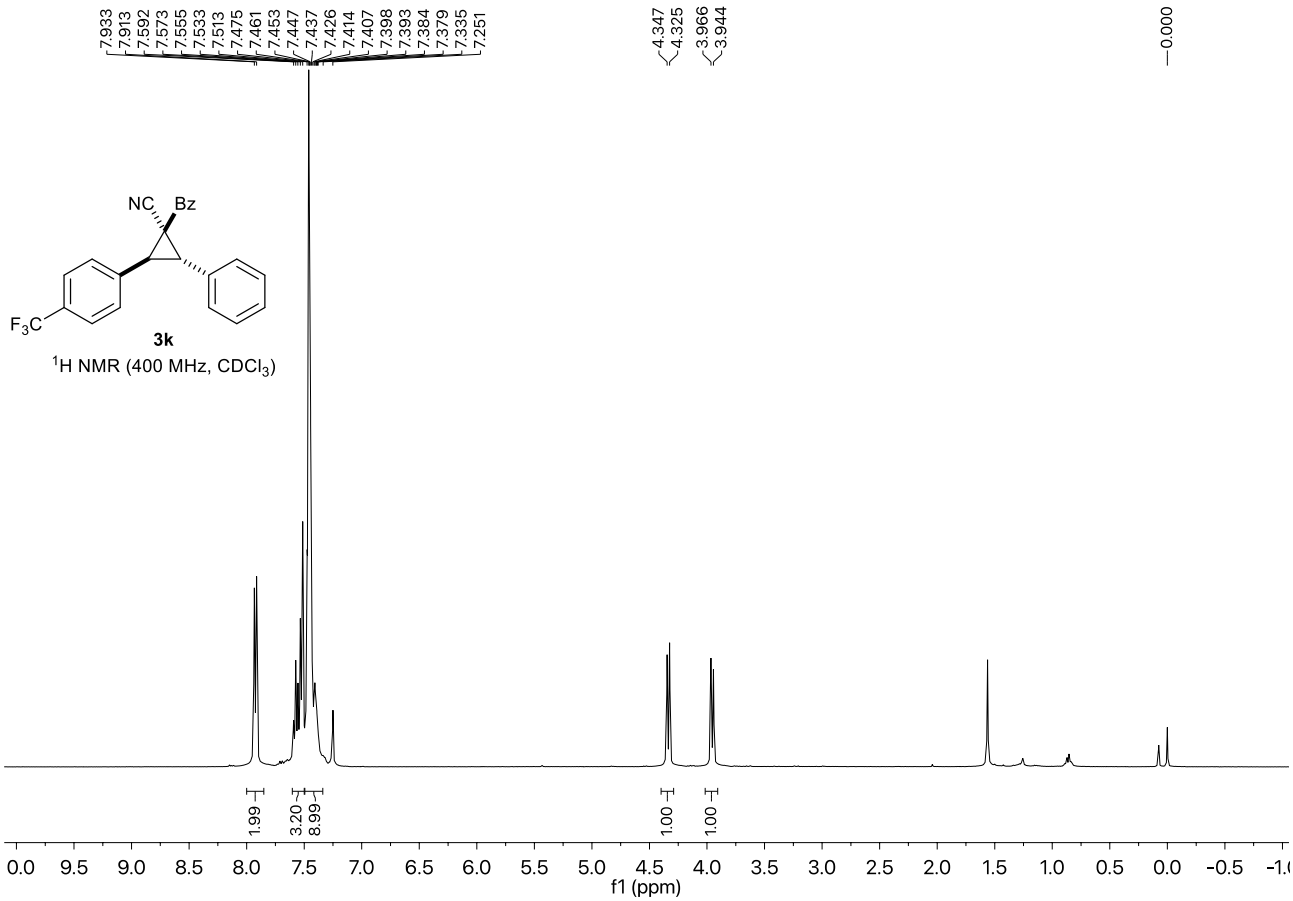
^{1}H NMR (400 MHz, $CDCl_3$)

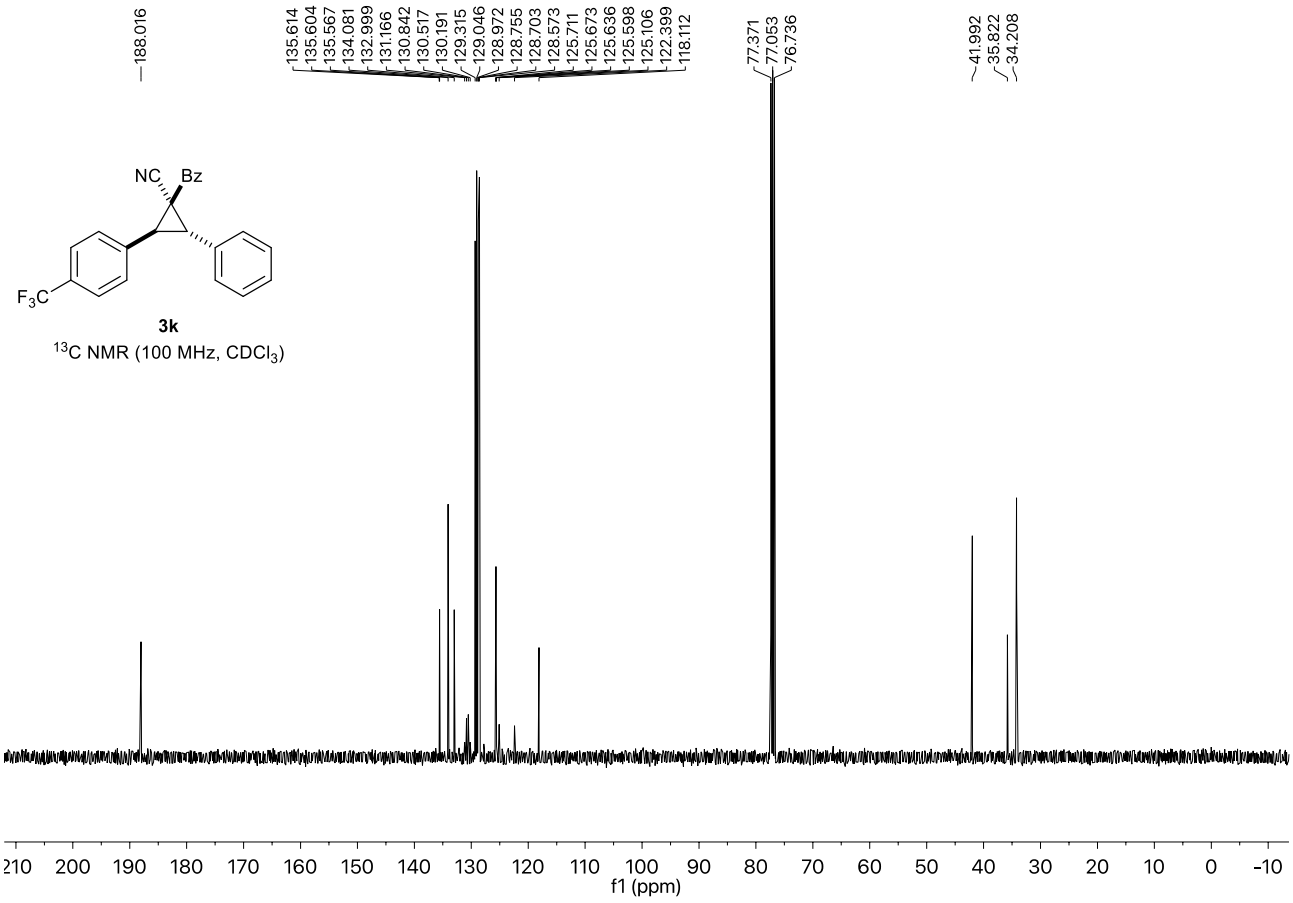


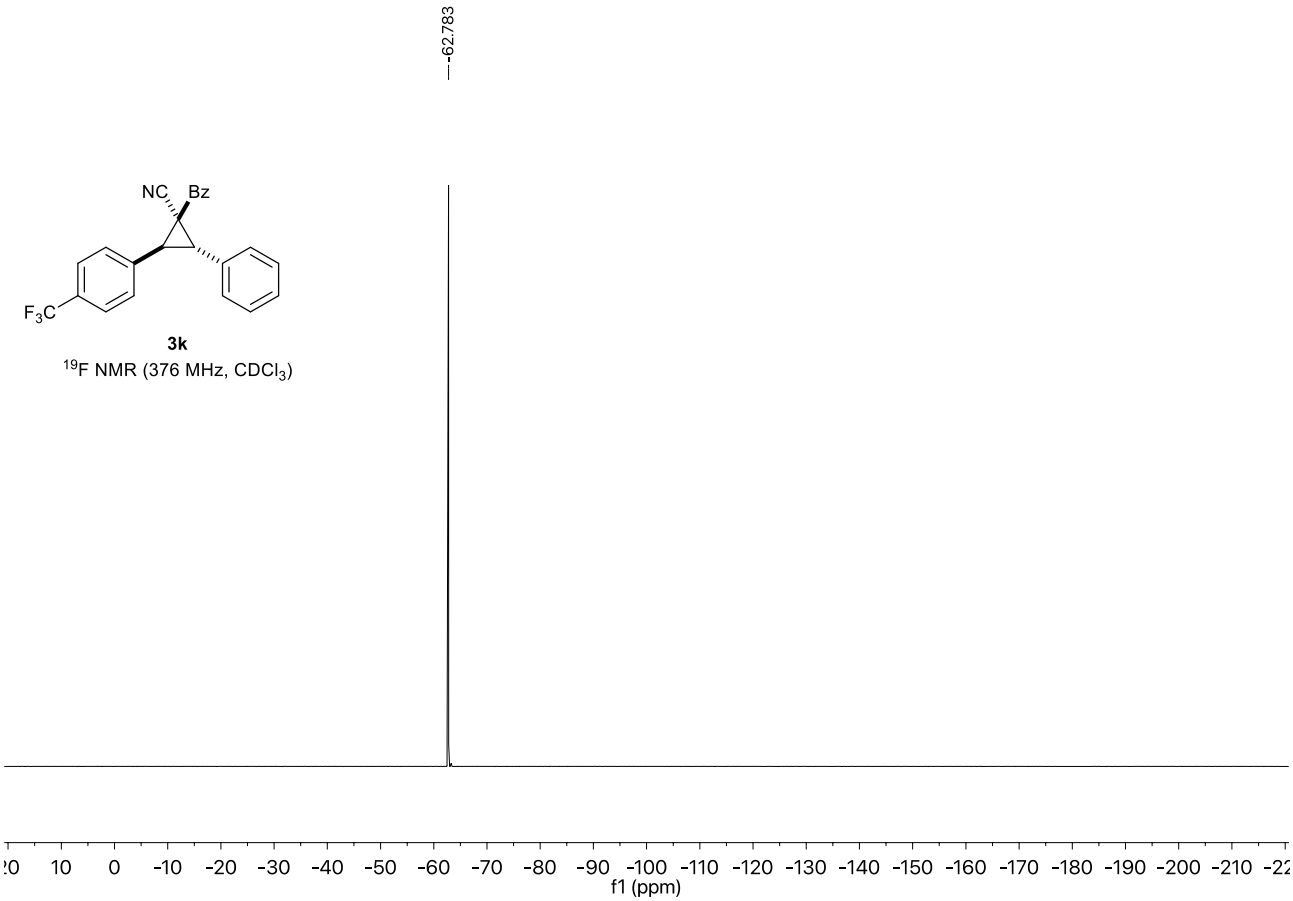
3j

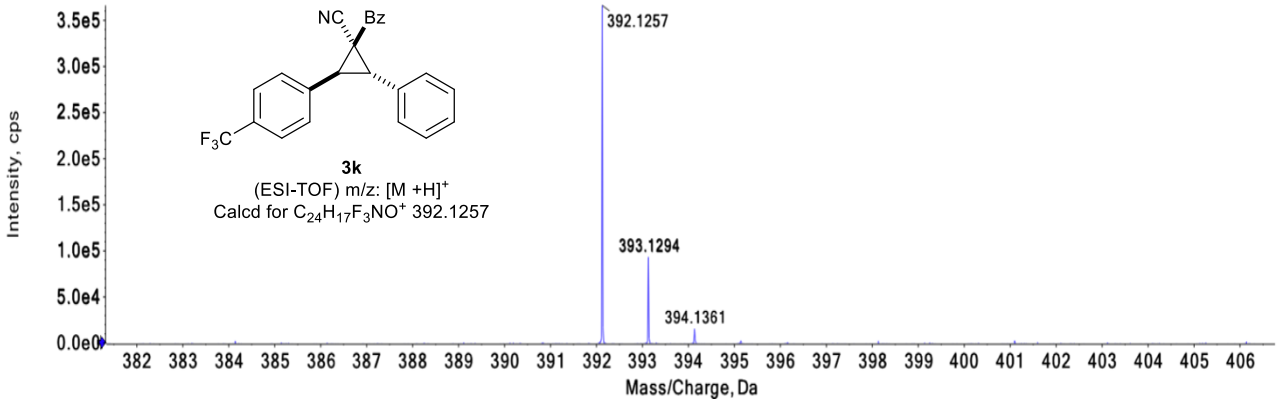
^{13}C NMR (100 MHz, $CDCl_3$)

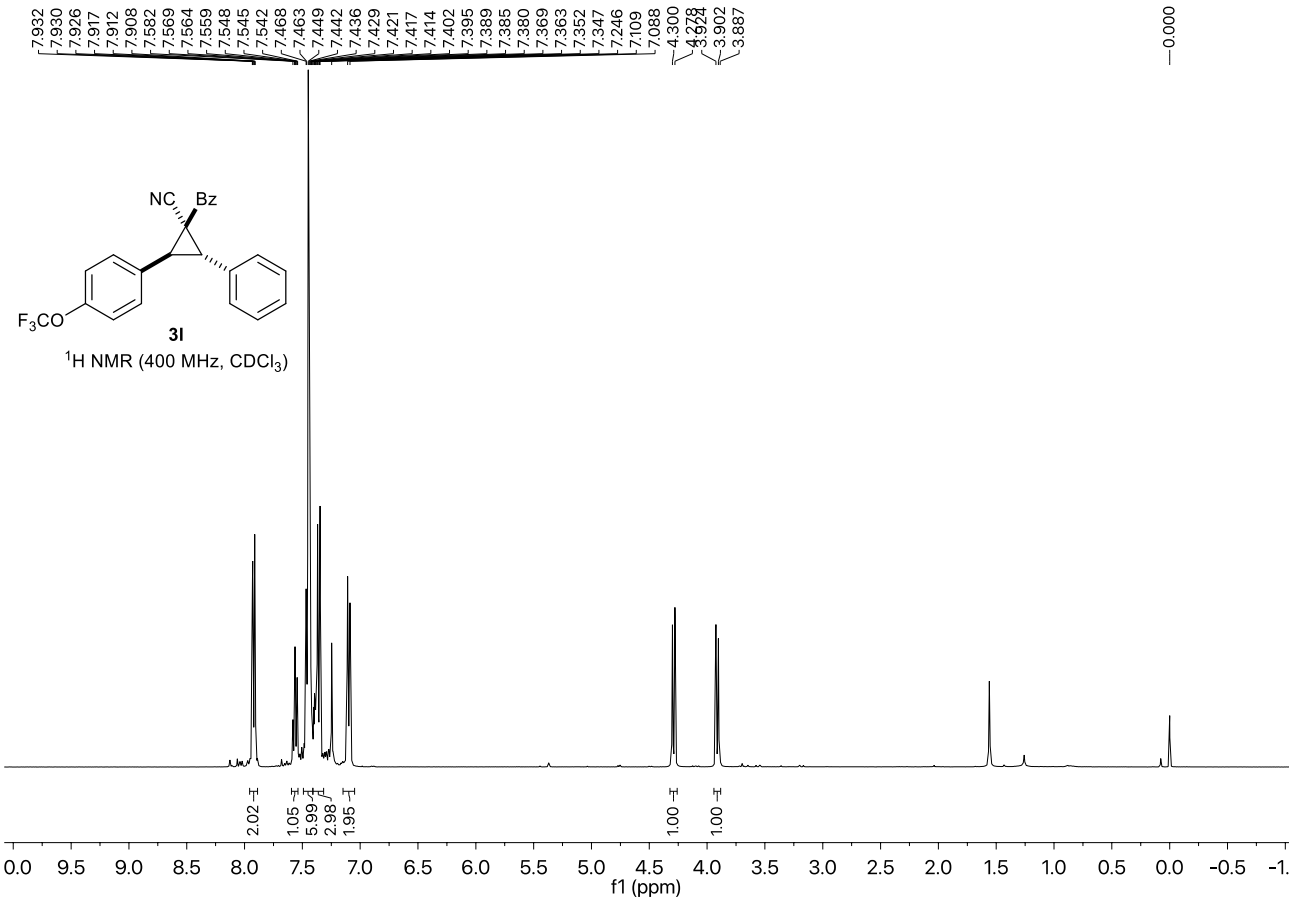

+ESI Scan (rt: 0.253 min) Frag=175.0V
x10^5
422.1510
NC
Bz
Ph
3j
(ESI-TOF) m/z: [M + Na]+
Calcd for C29H21NONa+ 422.1515
Counts vs. Mass-to-Charge (m/z)

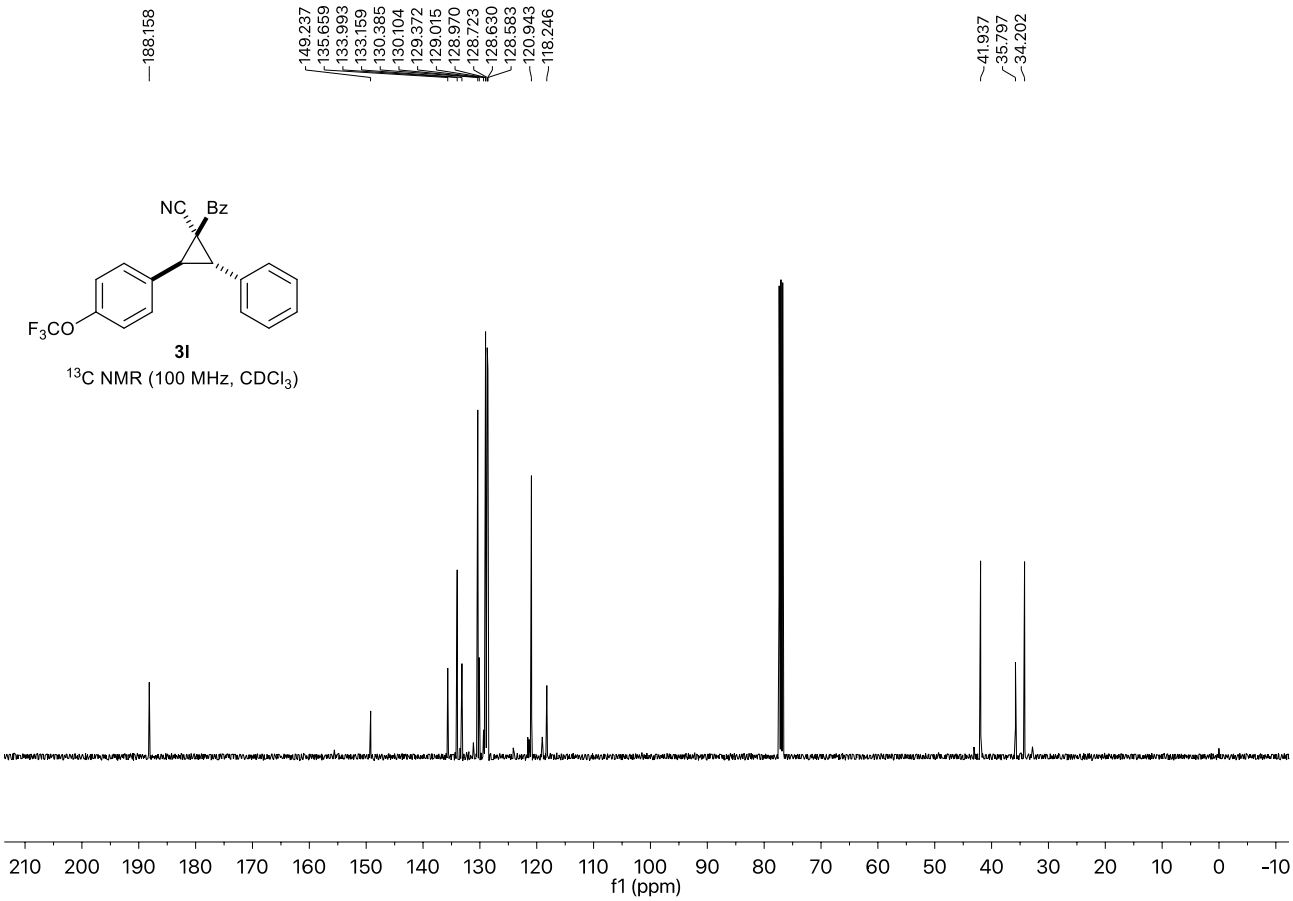

7.933
7.913
7.592
7.573
7.555
7.533
7.513
7.475
7.461
7.453
7.447
7.437
7.426
7.414
7.407
7.398
7.393
7.384
7.379
7.335
7.251
4.347
4.325
3.966
3.944
0.000
NC
Bz
F3C
3k
1H NMR (400 MHz, CDCl3)
1.99
3.20
8.99
1.00
1.00
f1 (ppm)

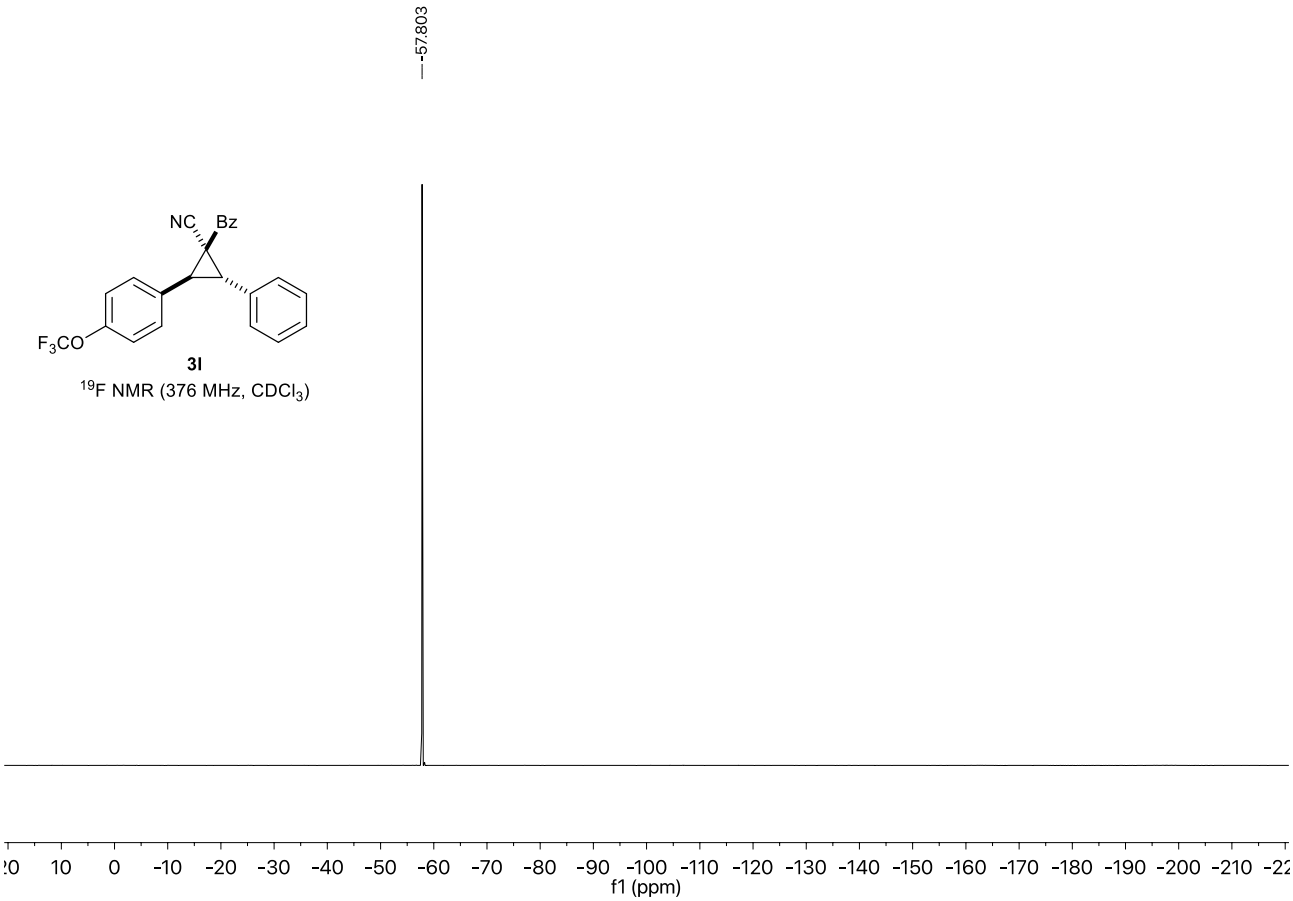

188.016
135.614
135.604
135.567
134.081
132.999
131.166
130.842
130.517
130.191
129.315
129.046
128.972
128.755
128.703
128.573
125.711
125.673
125.636
125.598
125.106
122.399
118.112
77.371
77.053
76.736
41.992
35.822
34.208
NC
Bz
F3C
3k
13C NMR (100 MHz, CDCl3)
f1 (ppm)

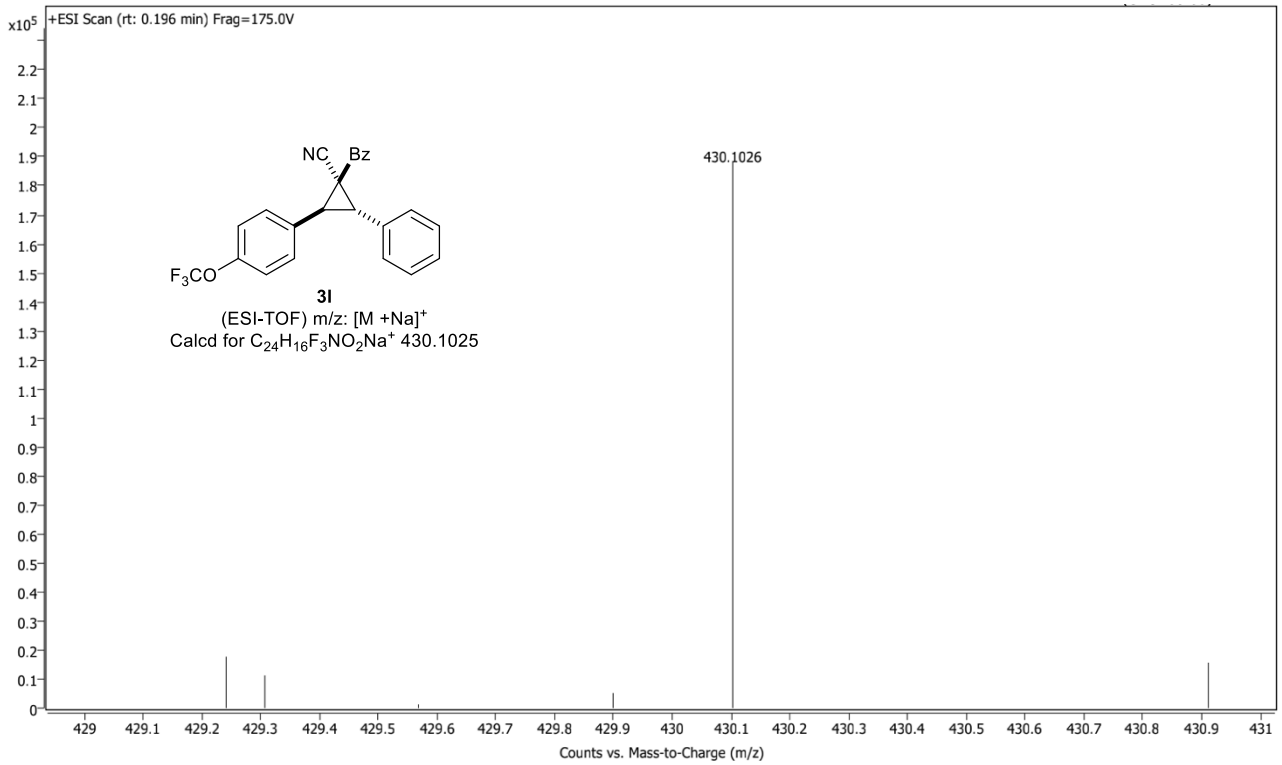

-62.783
NC
Bz
F3C
3k
19F NMR (376 MHz, CDCl3)
f1 (ppm)

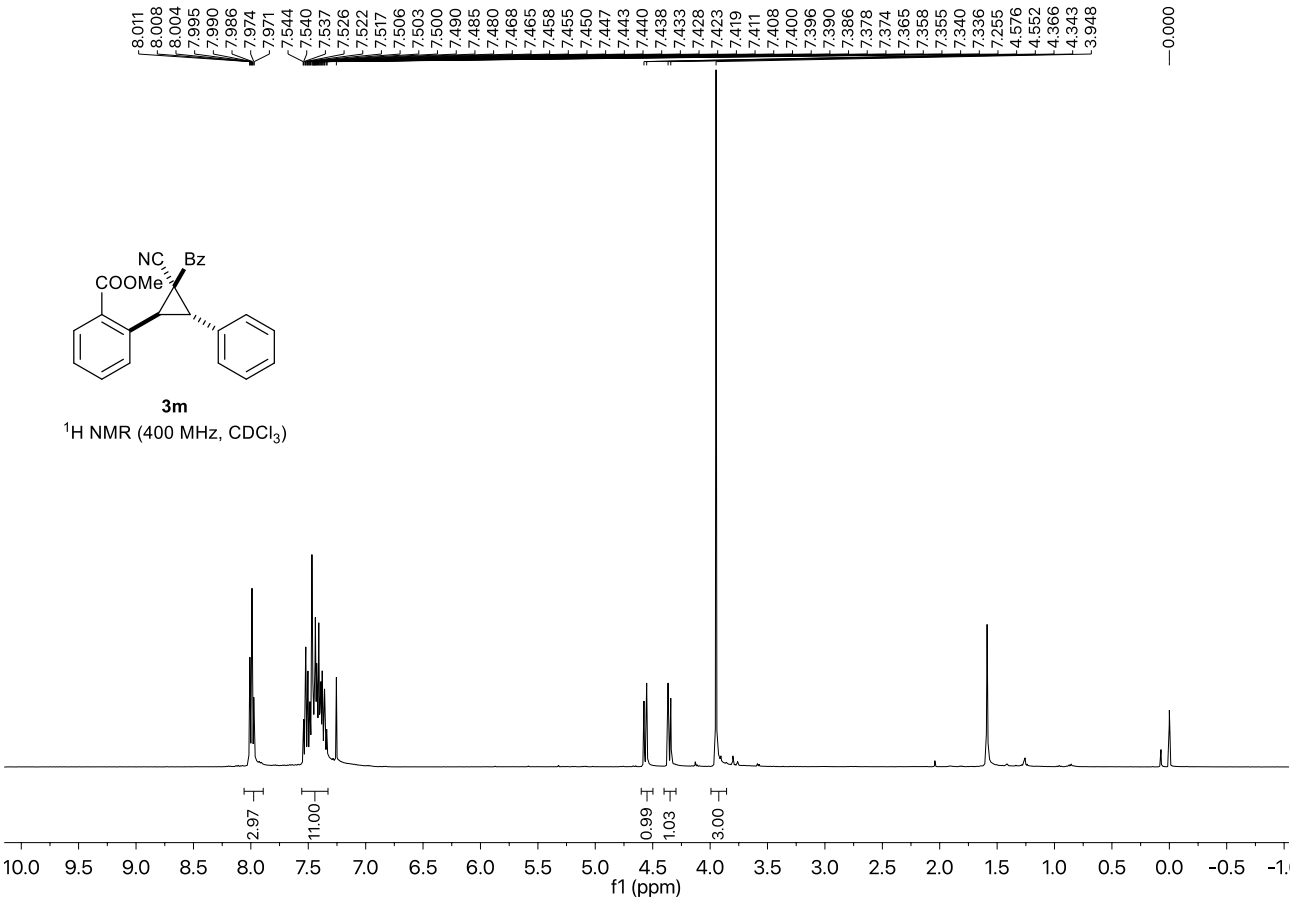

NC
Bz
F3C
3k
(ESI-TOF) m/z: [M +H]+
Calcd for C24H17F3NO+ 392.1257
392.1257
393.1294
394.1361
Intensity, cps
Mass/Charge, Da


7.932
7.930
7.926
7.917
7.912
7.908
7.582
7.569
7.564
7.559
7.548
7.545
7.542
7.468
7.463
7.449
7.442
7.436
7.429
7.421
7.417
7.414
7.402
7.395
7.389
7.385
7.380
7.369
7.363
7.352
7.347
7.246
7.109
7.088
4.300
4.278
3.924
3.902
3.887
0.000
NC
Bz
F3CO
3l
1H NMR (400 MHz, CDCl3)
2.02
1.05
5.99
2.98
1.95
1.00
1.00
f1 (ppm)


188.158
149.237
135.659
133.993
133.159
130.385
130.104
129.372
129.015
128.970
128.723
128.630
128.583
120.943
118.246
41.937
35.797
34.202
NC
Bz
F3CO
3l
13C NMR (100 MHz, CDCl3)
f1 (ppm)

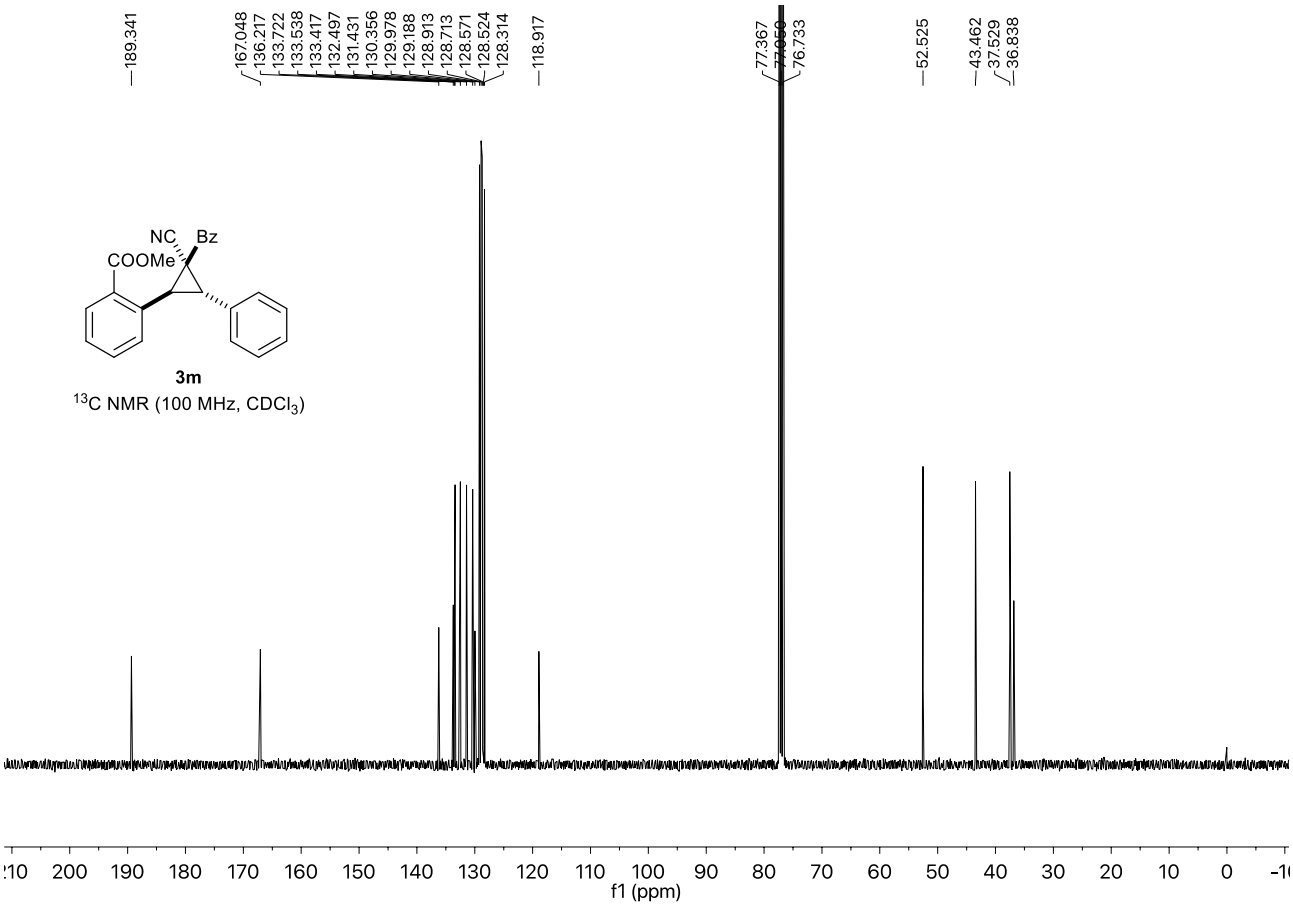

-57.803
NC
Bz
F3CO
3l
19F NMR (376 MHz, CDCl3)
f1 (ppm)


+ESI Scan (rt: 0.196 min) Frag=175.0V
x10^5
NC
Bz
F3CO
3l
(ESI-TOF) m/z: [M +Na]+
Calcd for C24H16F3NO2Na+ 430.1025
430.1026
Counts vs. Mass-to-Charge (m/z)



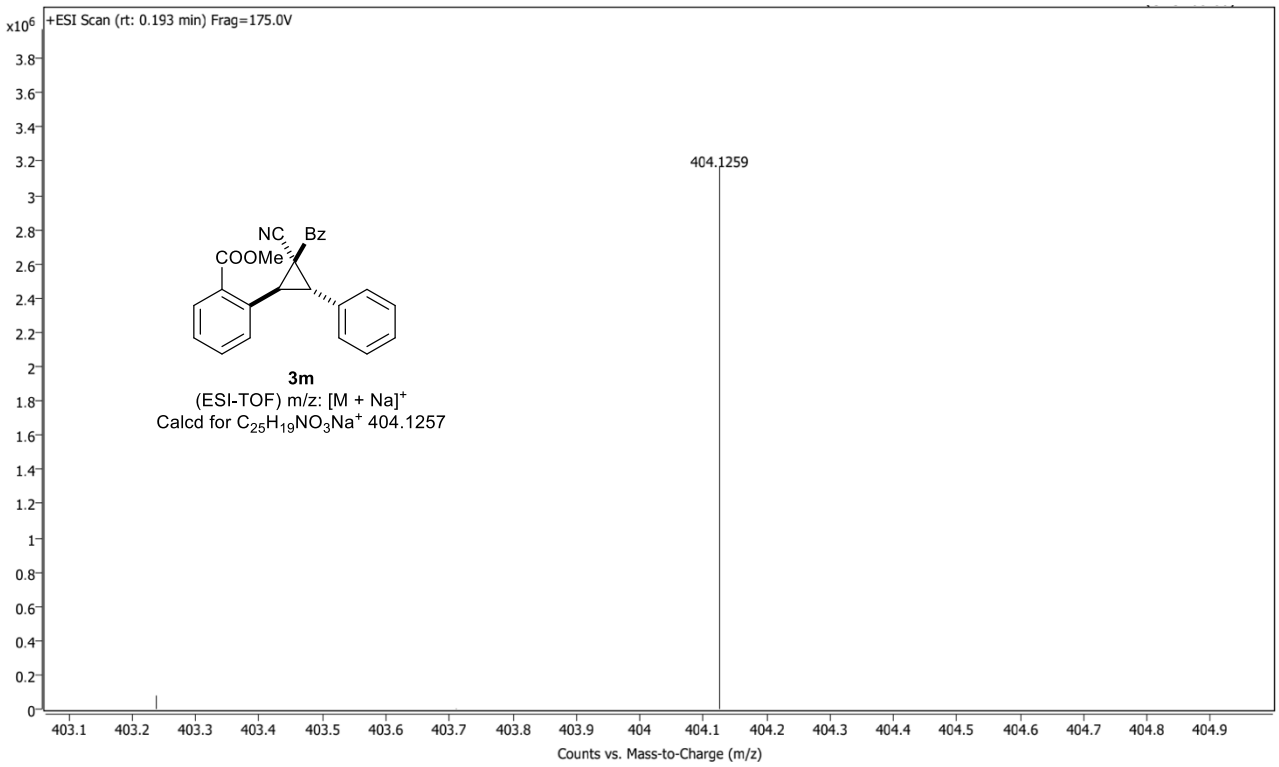
3m

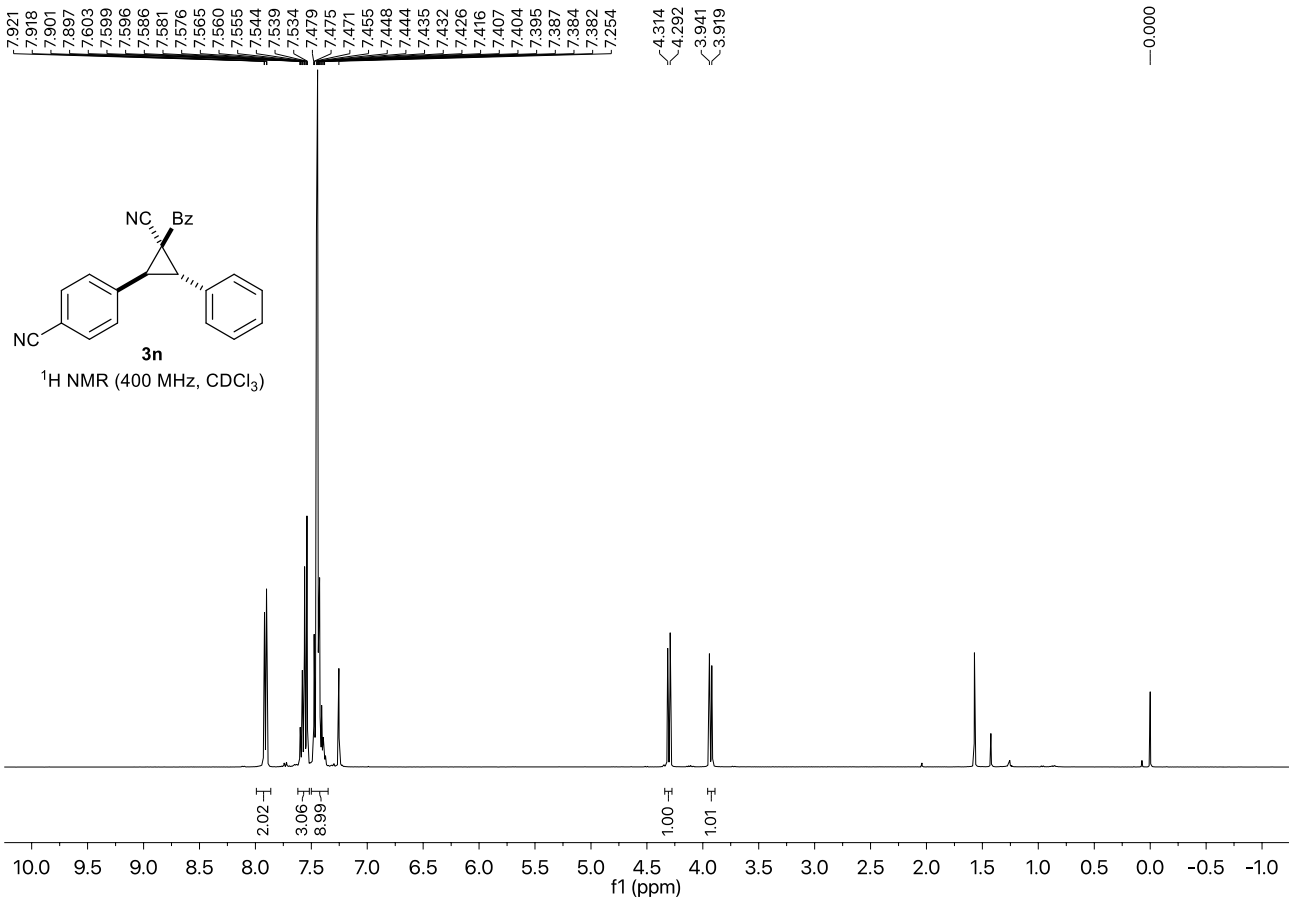
^{1}H NMR (400 MHz, $CDCl_3$)

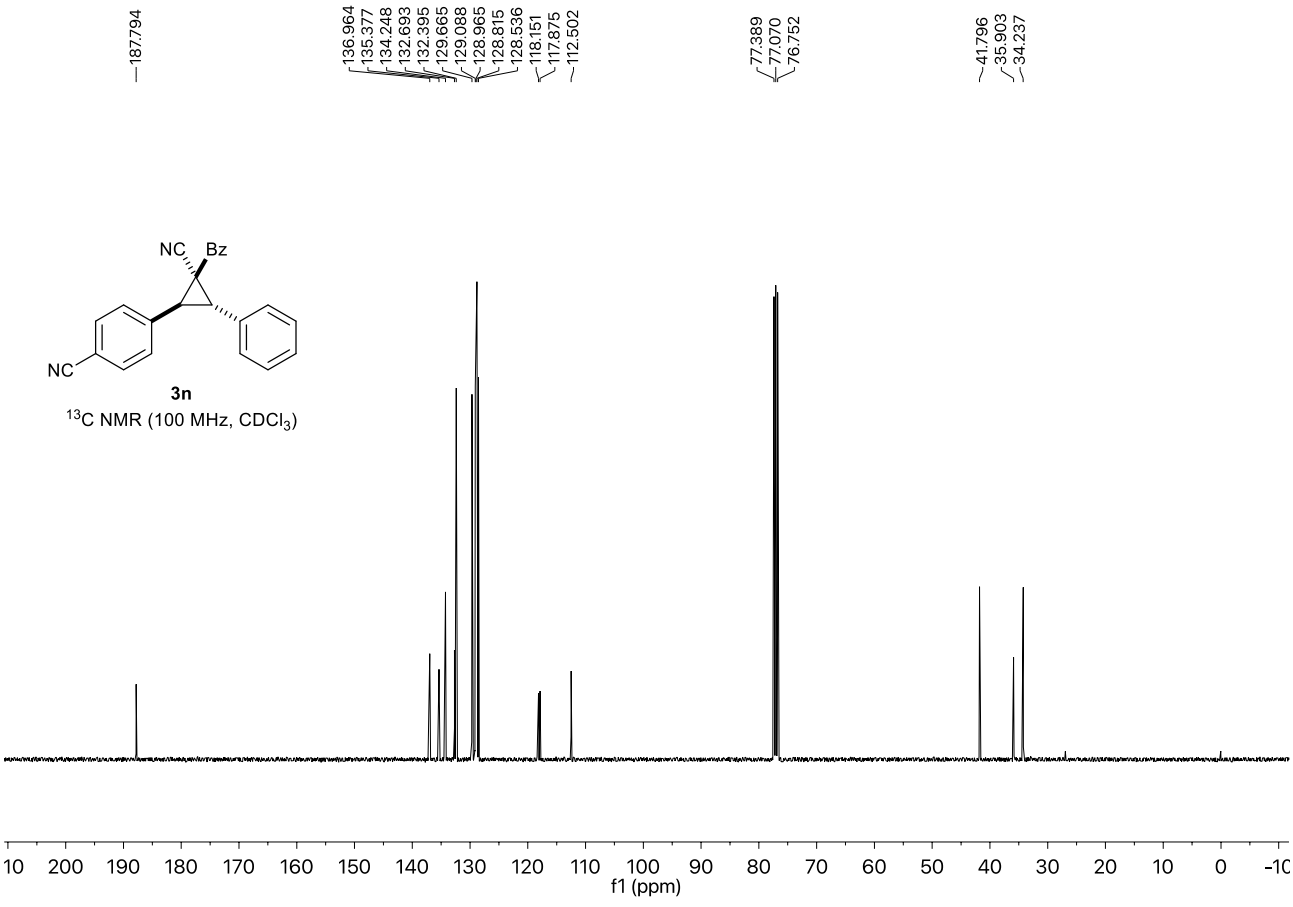


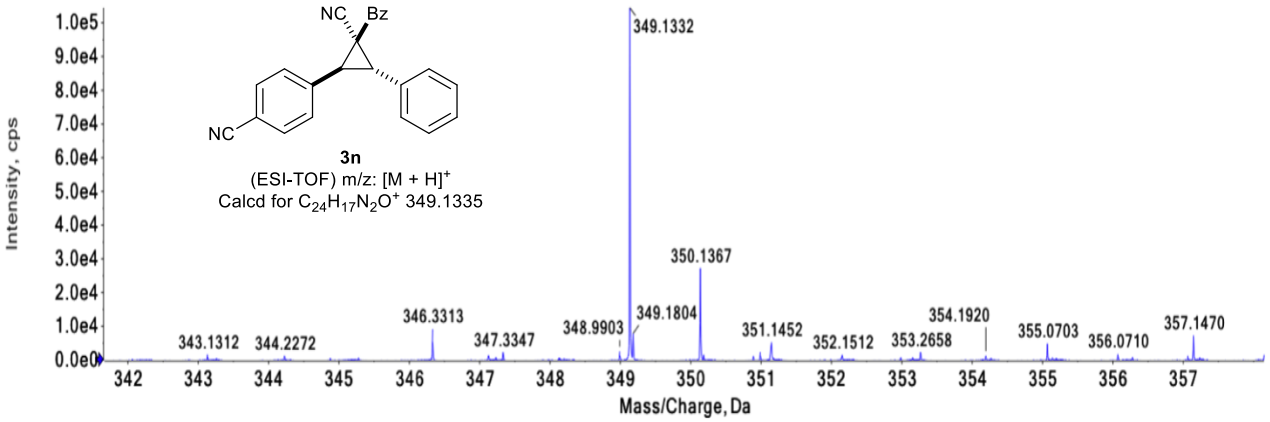
3m

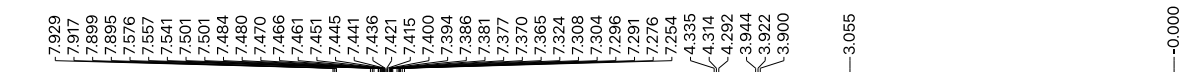
^{13}C NMR (100 MHz, $CDCl_3$)

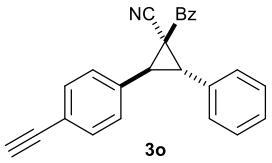

+ESI Scan (rt: 0.193 min) Frag=175.0V
x10^6
404.1259
NC
Bz
COOMe
3m
(ESI-TOF) m/z: [M + Na]+
Calcd for C25H19NO3Na+ 404.1257
Counts vs. Mass-to-Charge (m/z)


7.921
7.918
7.901
7.897
7.603
7.599
7.596
7.586
7.581
7.576
7.565
7.560
7.555
7.544
7.539
7.534
7.479
7.475
7.471
7.455
7.448
7.444
7.435
7.432
7.426
7.416
7.407
7.404
7.395
7.387
7.384
7.382
7.254
4.314
4.292
3.941
3.919
0.000
NC
Bz
NC
3n
1H NMR (400 MHz, CDCl3)
2.02
3.06
8.99
1.00
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


187.794
136.964
135.377
134.248
132.693
132.395
129.665
129.088
128.965
128.815
128.536
118.151
117.875
112.502
77.389
77.070
76.752
41.796
35.903
34.237
NC
Bz
NC
3n
13C NMR (100 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

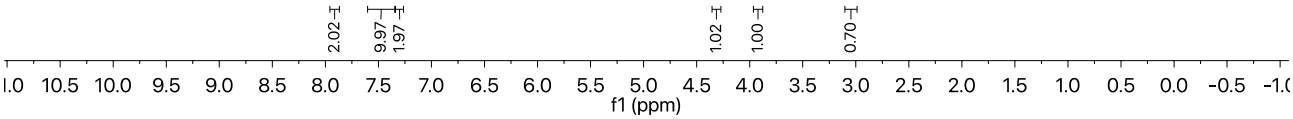

NC
Bz
NC
3n
(ESI-TOF) m/z: [M + H]+
Calcd for C24H17N2O+ 349.1335
Intensity, cps
1.0e5
9.0e4
8.0e4
7.0e4
6.0e4
5.0e4
4.0e4
3.0e4
2.0e4
1.0e4
0.0e0
343.1312
344.2272
346.3313
347.3347
348.9903
349.1332
349.1804
350.1367
351.1452
352.1512
353.2658
354.1920
355.0703
356.0710
357.1470
342
343
344
345
346
347
348
349
350
351
352
353
354
355
356
357
Mass/Charge, Da

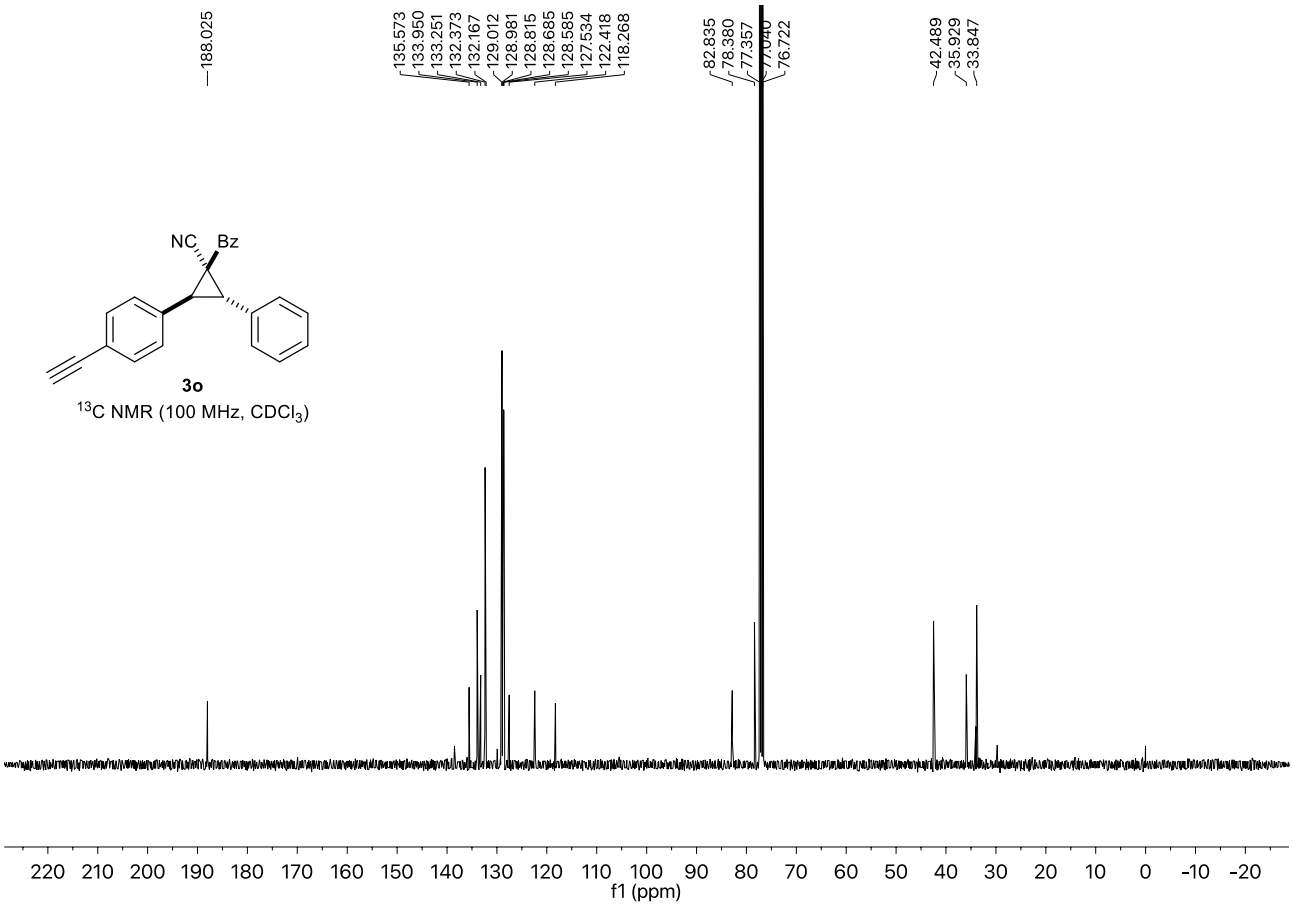




3o

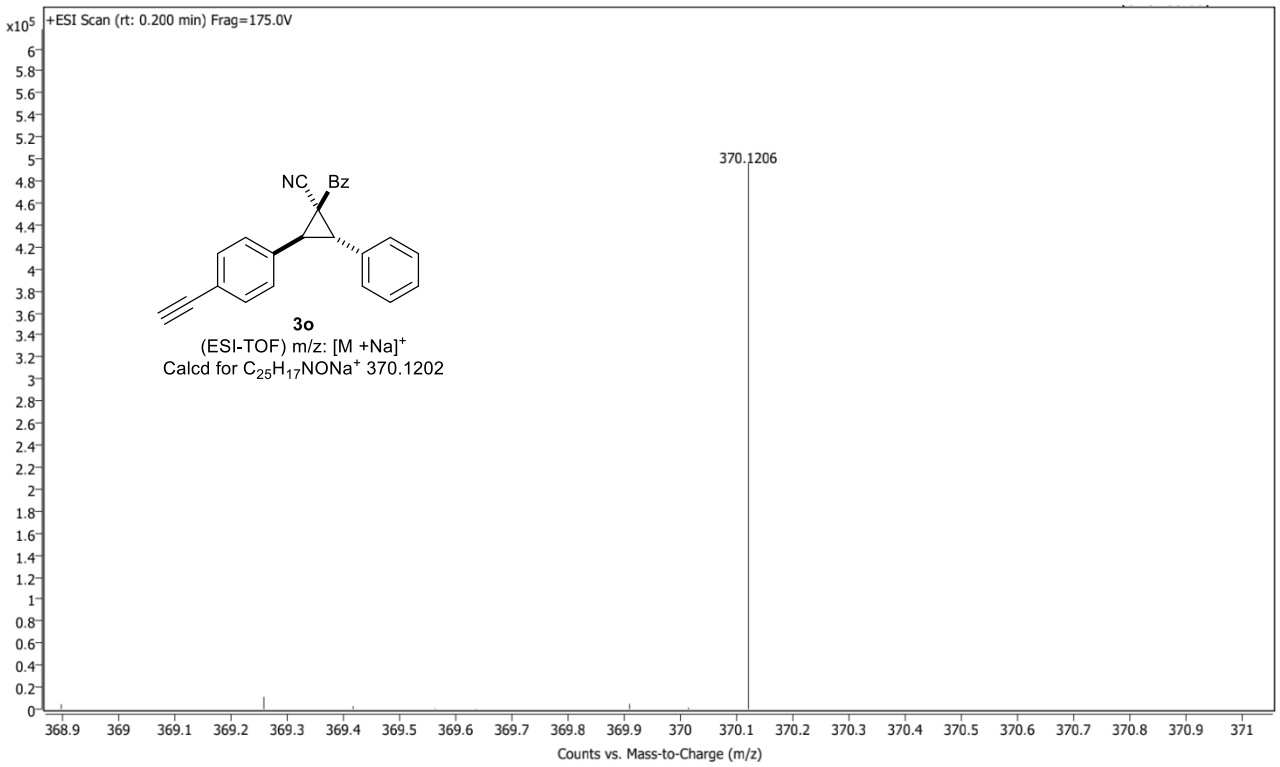
^{1}H NMR (400 MHz, $CDCl_3$)

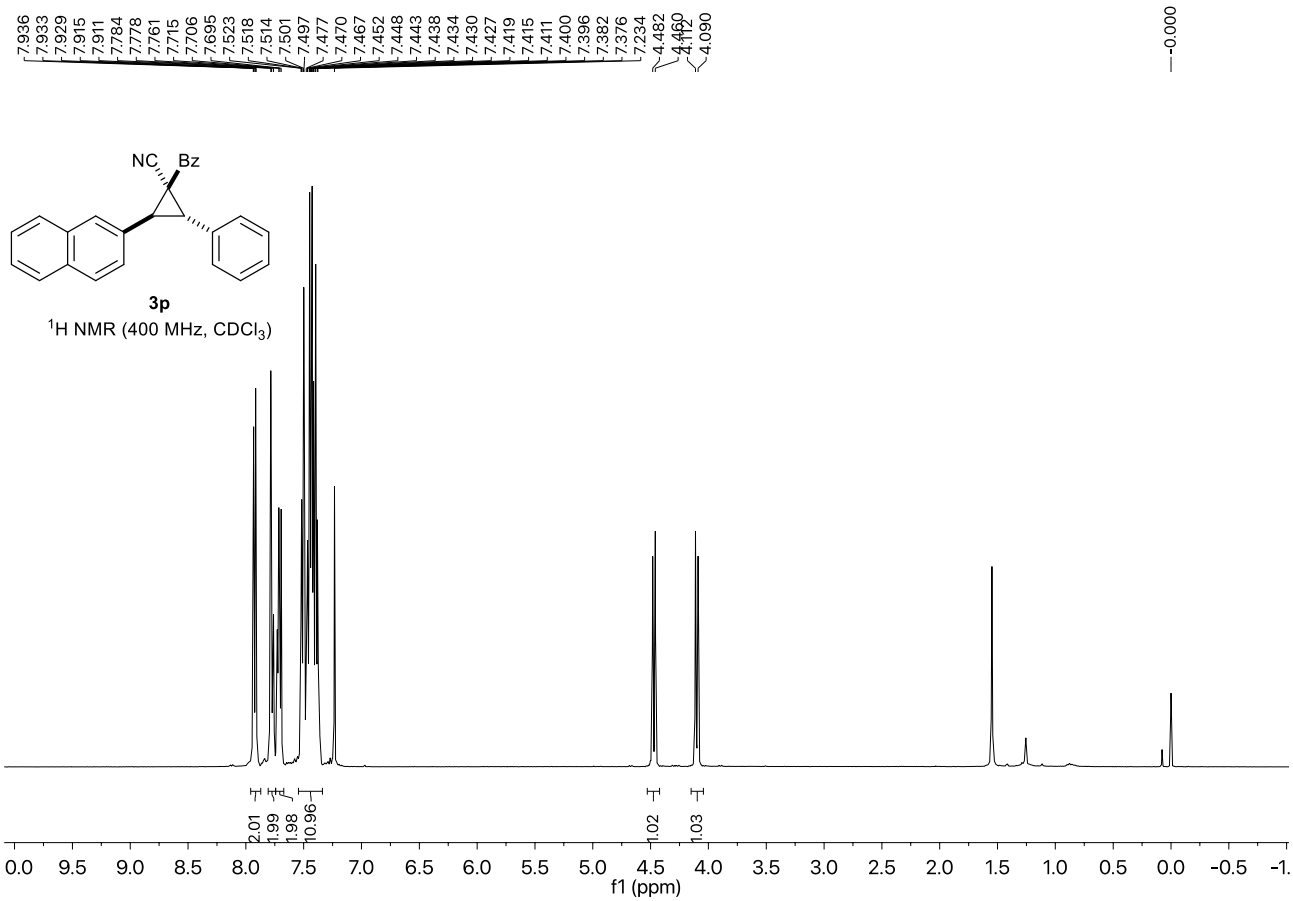


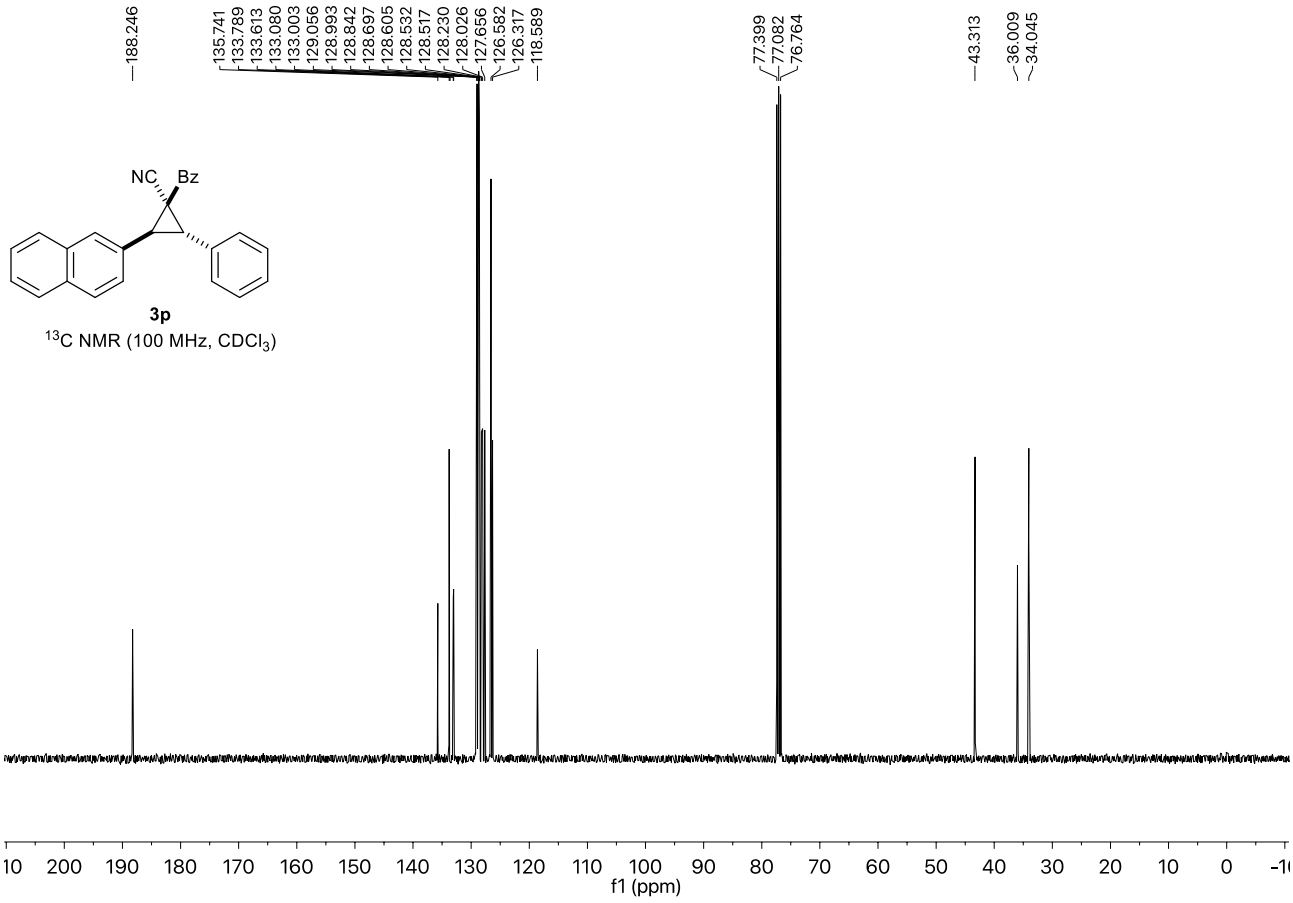


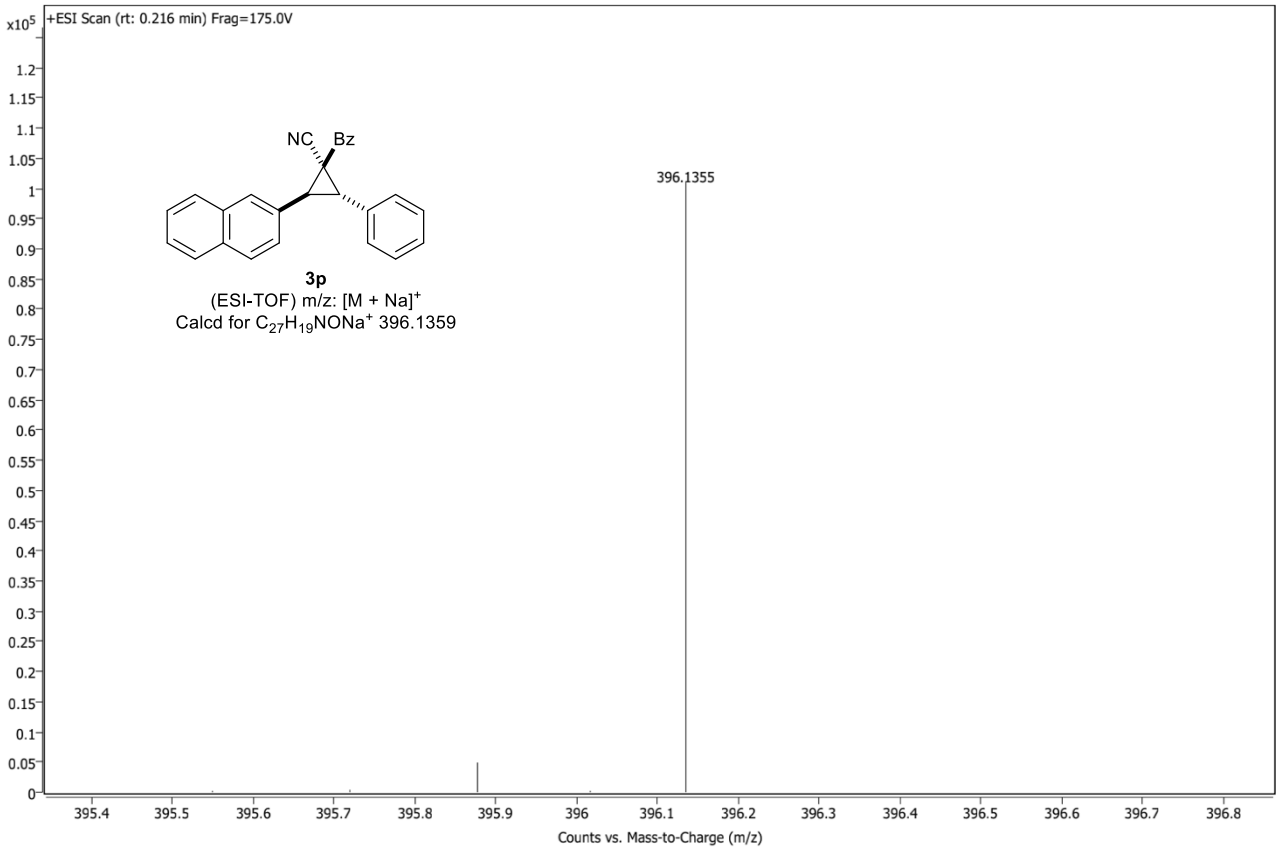
3o

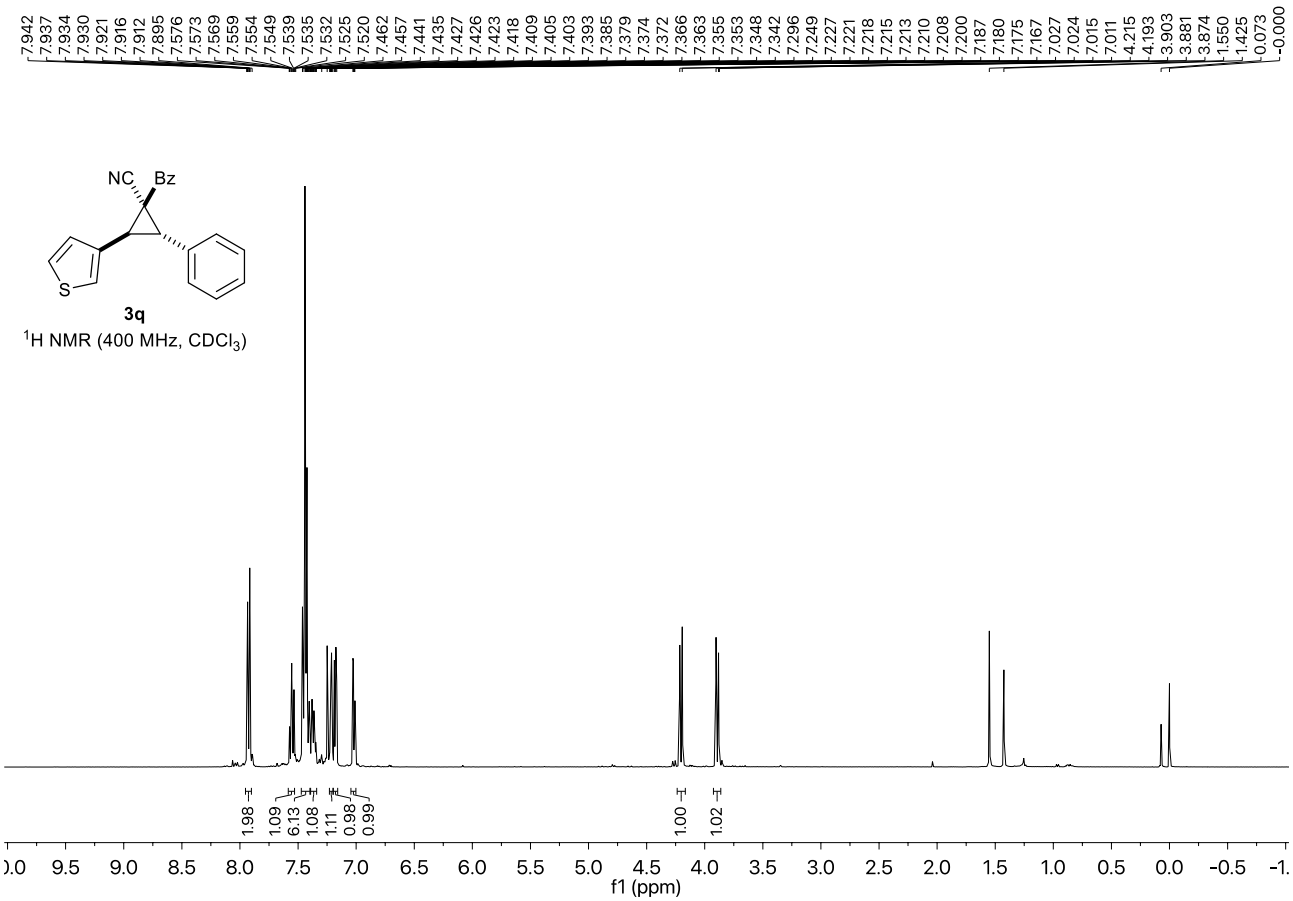
^{13}C NMR (100 MHz, $CDCl_3$)

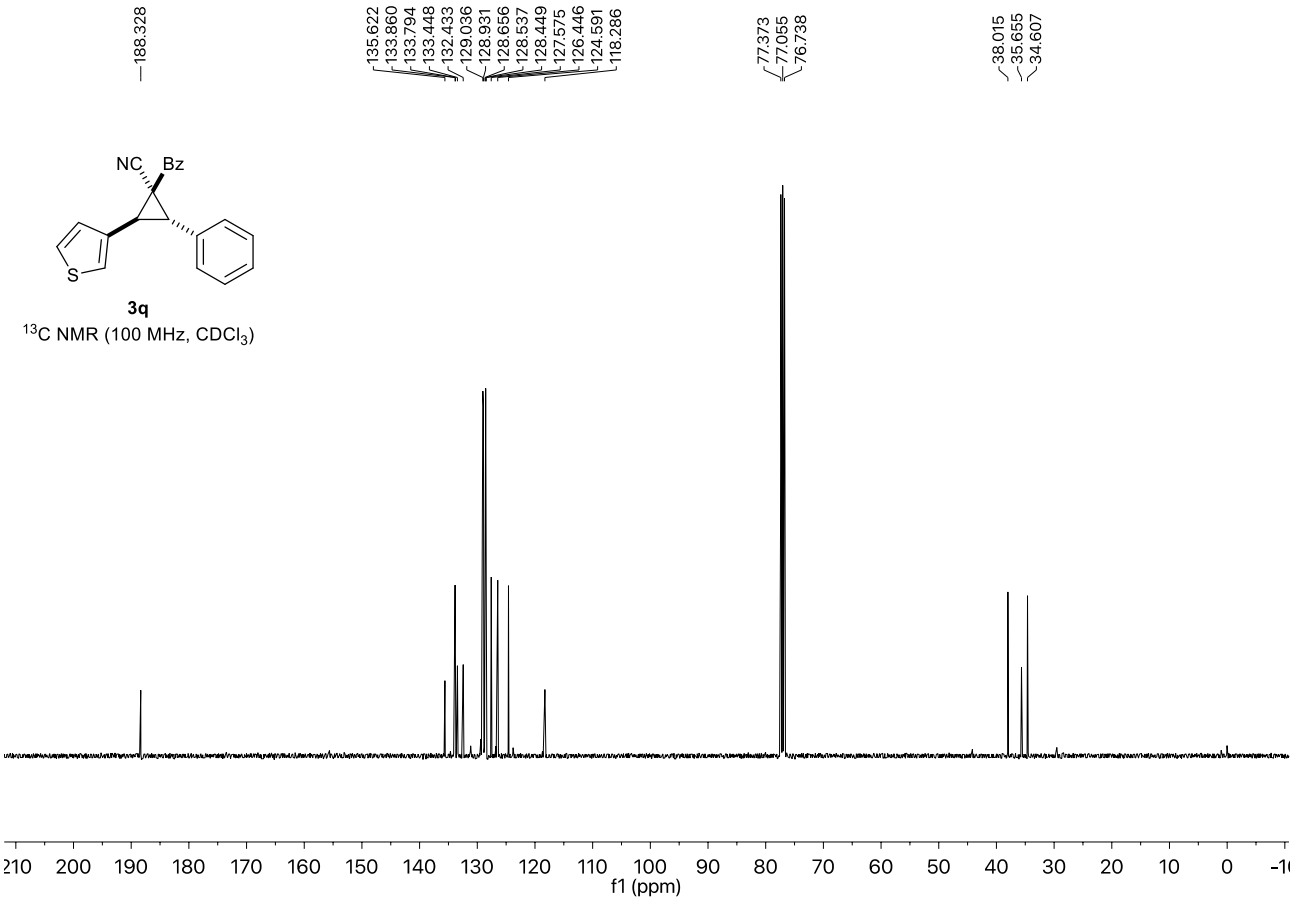

+ESI Scan (rt: 0.200 min) Frag=175.0V
x10^5
370.1206
NC
Bz
3o
(ESI-TOF) m/z: [M +Na]+
Calcd for C25H17NONa+ 370.1202
Counts vs. Mass-to-Charge (m/z)

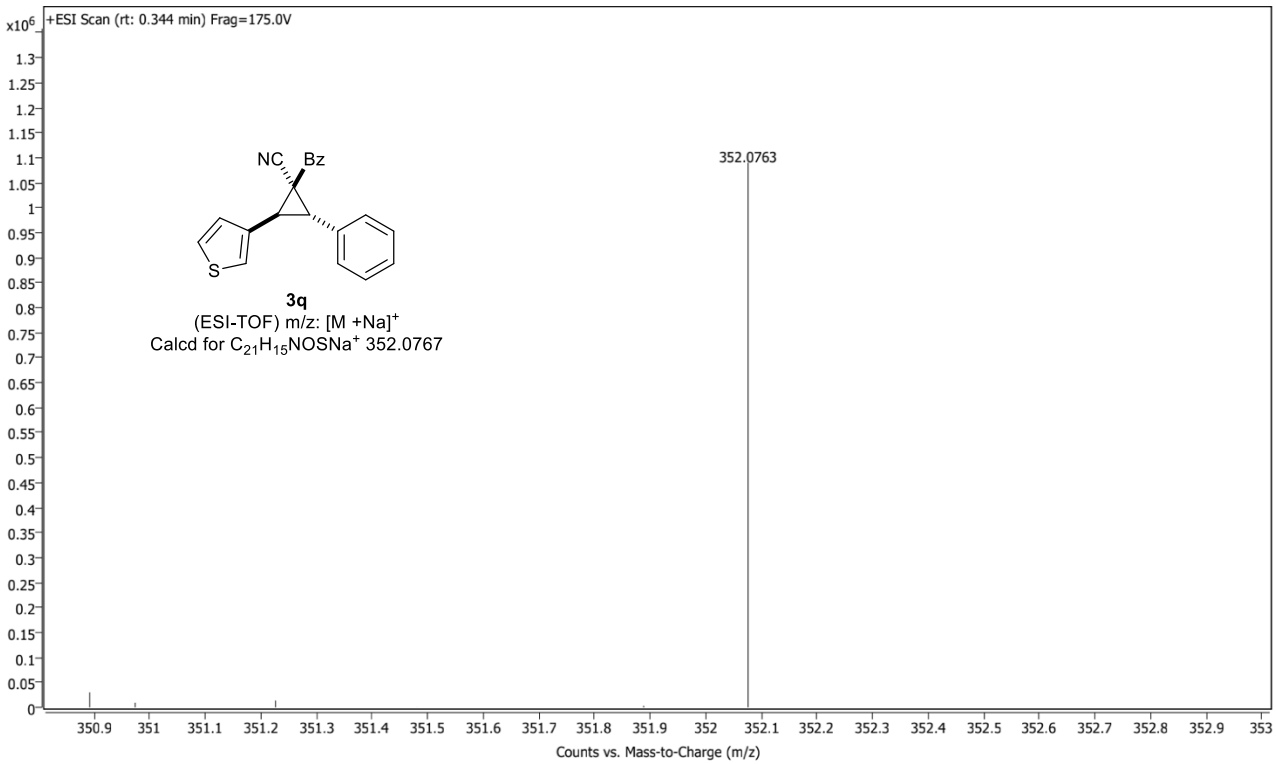

7.936
7.933
7.929
7.915
7.911
7.784
7.778
7.761
7.715
7.706
7.695
7.523
7.518
7.514
7.501
7.497
7.477
7.470
7.467
7.452
7.448
7.443
7.438
7.434
7.430
7.427
7.419
7.415
7.411
7.400
7.396
7.382
7.376
7.234
4.482
4.460
4.112
4.090
0.000
NC
Bz
3p
1H NMR (400 MHz, CDCl3)
2.01
1.99
1.98
10.96
1.02
1.03
f1 (ppm)

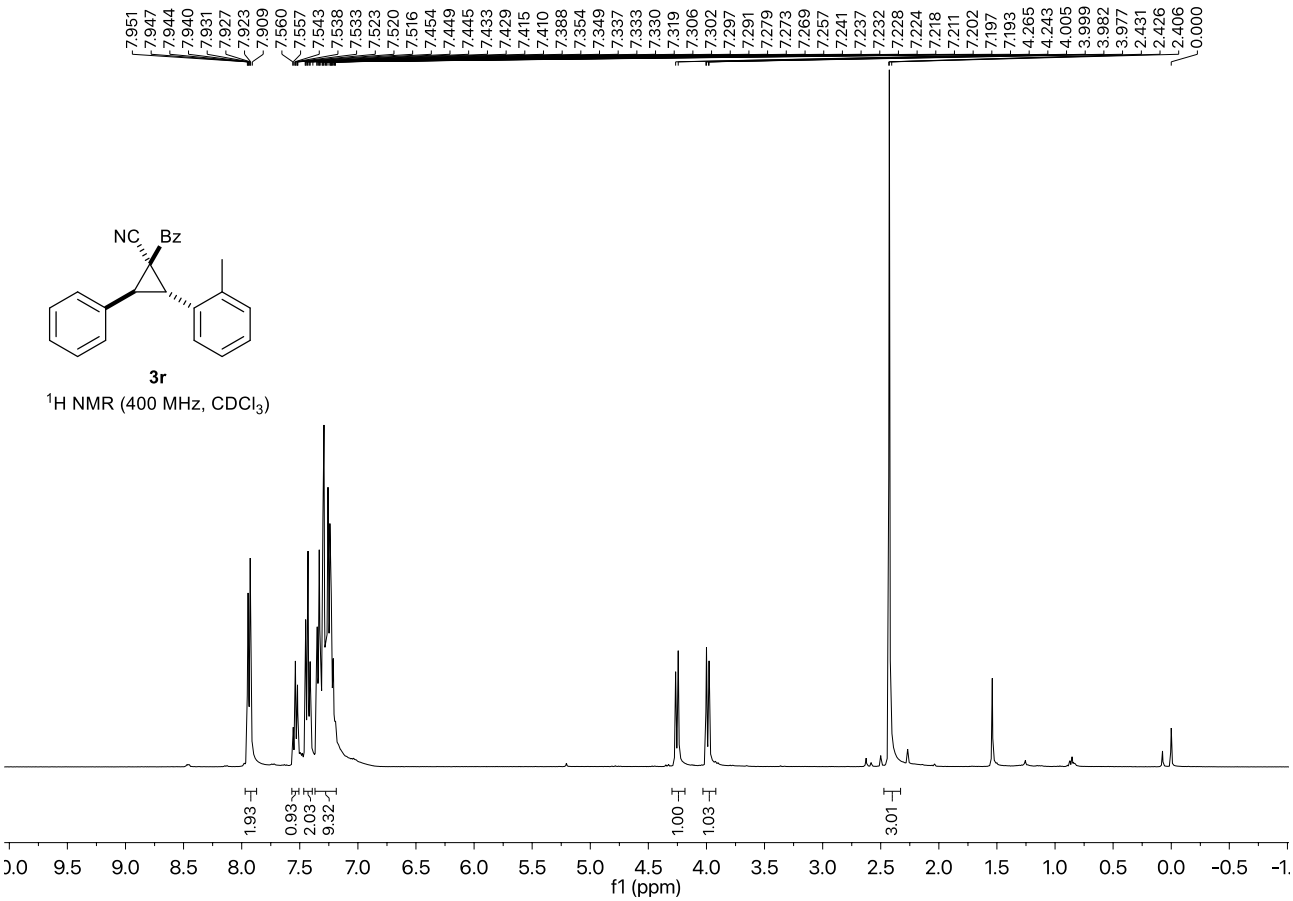

188.246
135.741
133.789
133.613
133.080
133.003
129.056
128.993
128.842
128.697
128.605
128.532
128.517
128.230
128.026
127.656
126.582
126.317
118.589
77.399
77.082
76.764
43.313
36.009
34.045
NC
Bz
3p
13C NMR (100 MHz, CDCl3)
f1 (ppm)

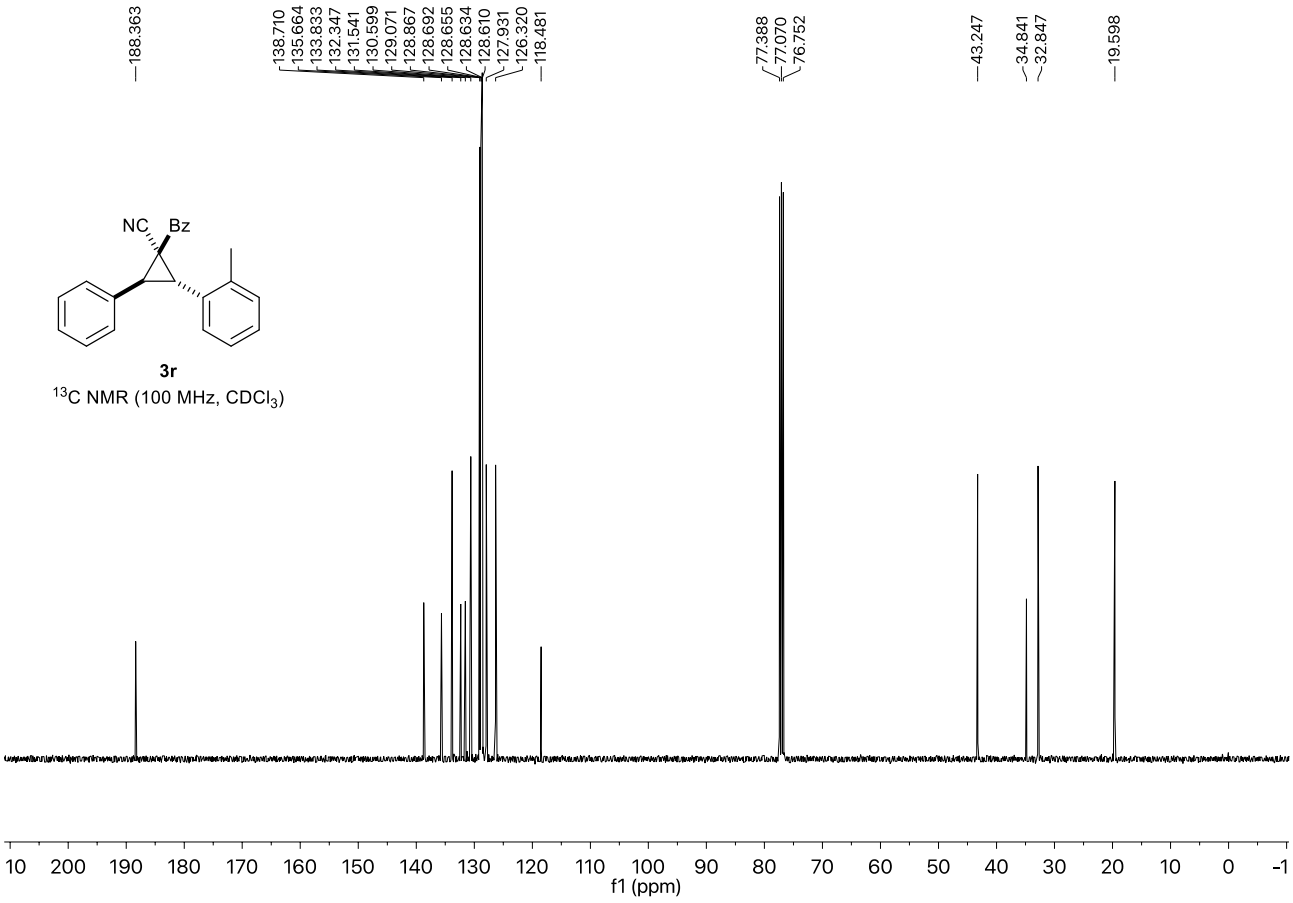

+ESI Scan (rt: 0.216 min) Frag=175.0V
x10^5
NC
Bz
396.1355
3p
(ESI-TOF) m/z: [M + Na]+
Calcd for C27H19NONa+ 396.1359
Counts vs. Mass-to-Charge (m/z)

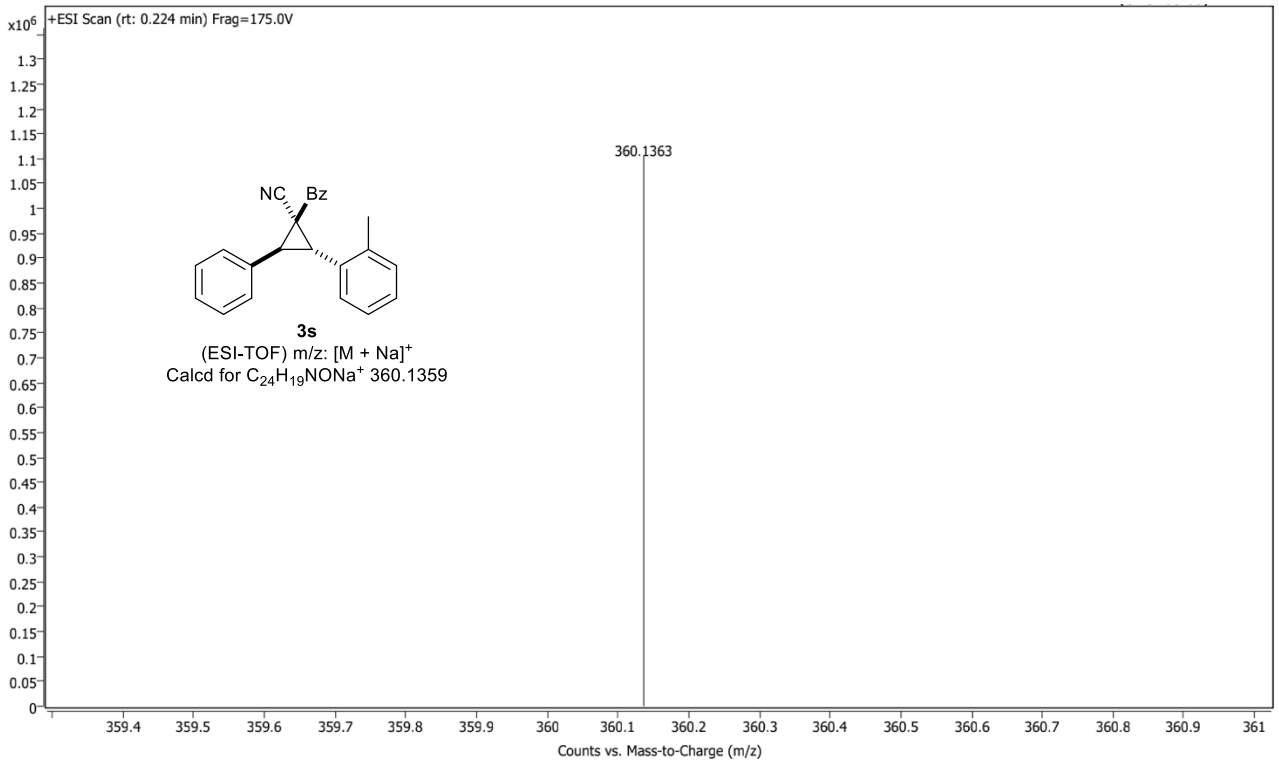

7.942
7.937
7.934
7.930
7.921
7.916
7.912
7.895
7.576
7.573
7.569
7.559
7.554
7.549
7.539
7.535
7.532
7.525
7.520
7.462
7.457
7.441
7.435
7.427
7.426
7.423
7.418
7.409
7.405
7.403
7.393
7.385
7.379
7.374
7.372
7.366
7.363
7.355
7.353
7.348
7.342
7.296
7.249
7.227
7.221
7.218
7.215
7.213
7.210
7.208
7.200
7.187
7.180
7.175
7.167
7.027
7.024
7.015
7.011
4.215
4.193
3.903
3.881
3.874
1.550
1.425
0.073
-0.000
NC
Bz
S
3q
1H NMR (400 MHz, CDCl3)
1.98
1.09
6.13
1.08
1.11
0.98
0.99
1.00
1.02
f1 (ppm)

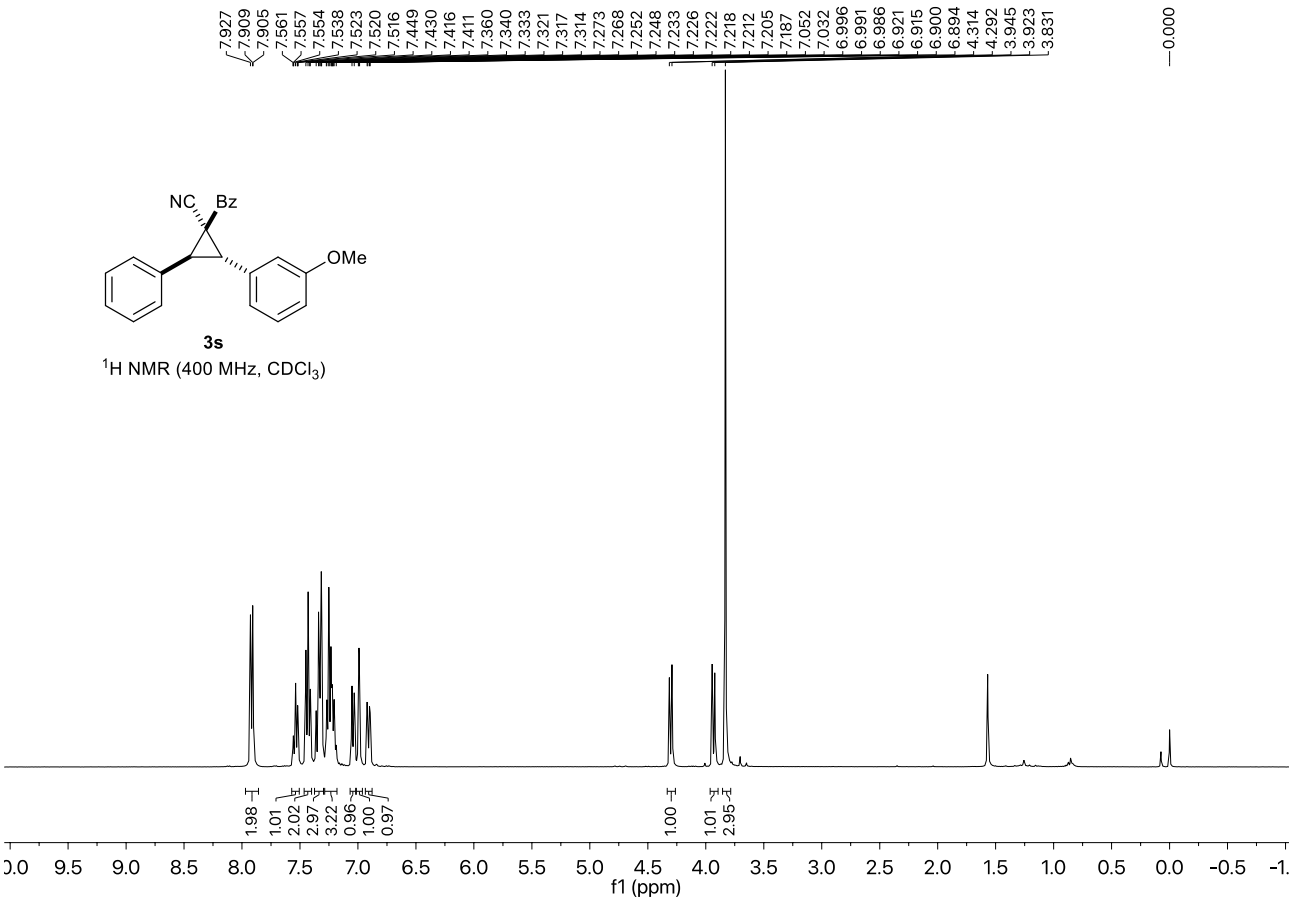

188.328
135.622
133.860
133.794
133.448
132.433
129.036
128.931
128.656
128.537
128.449
127.575
126.446
124.591
118.286
77.373
77.055
76.738
38.015
35.655
34.607
NC
Bz
S
3q
13C NMR (100 MHz, CDCl3)
f1 (ppm)


+ESI Scan (rt: 0.344 min) Frag=175.0V
x10^6
NC
Bz
S
352.0763
3q
(ESI-TOF) m/z: [M +Na]+
Calcd for C21H15NOSNa+ 352.0767
Counts vs. Mass-to-Charge (m/z)


7.951
7.947
7.944
7.940
7.931
7.927
7.923
7.909
7.560
7.557
7.543
7.538
7.533
7.523
7.520
7.516
7.454
7.449
7.445
7.433
7.429
7.415
7.410
7.388
7.354
7.349
7.337
7.333
7.330
7.319
7.306
7.302
7.297
7.291
7.279
7.273
7.269
7.257
7.241
7.237
7.232
7.228
7.224
7.218
7.211
7.202
7.197
7.193
4.265
4.243
4.005
3.999
3.982
3.977
2.431
2.426
2.406
0.000
NC
Bz
3r
1H NMR (400 MHz, CDCl3)
1.93
0.93
2.03
9.32
1.00
1.03
3.01
f1 (ppm)

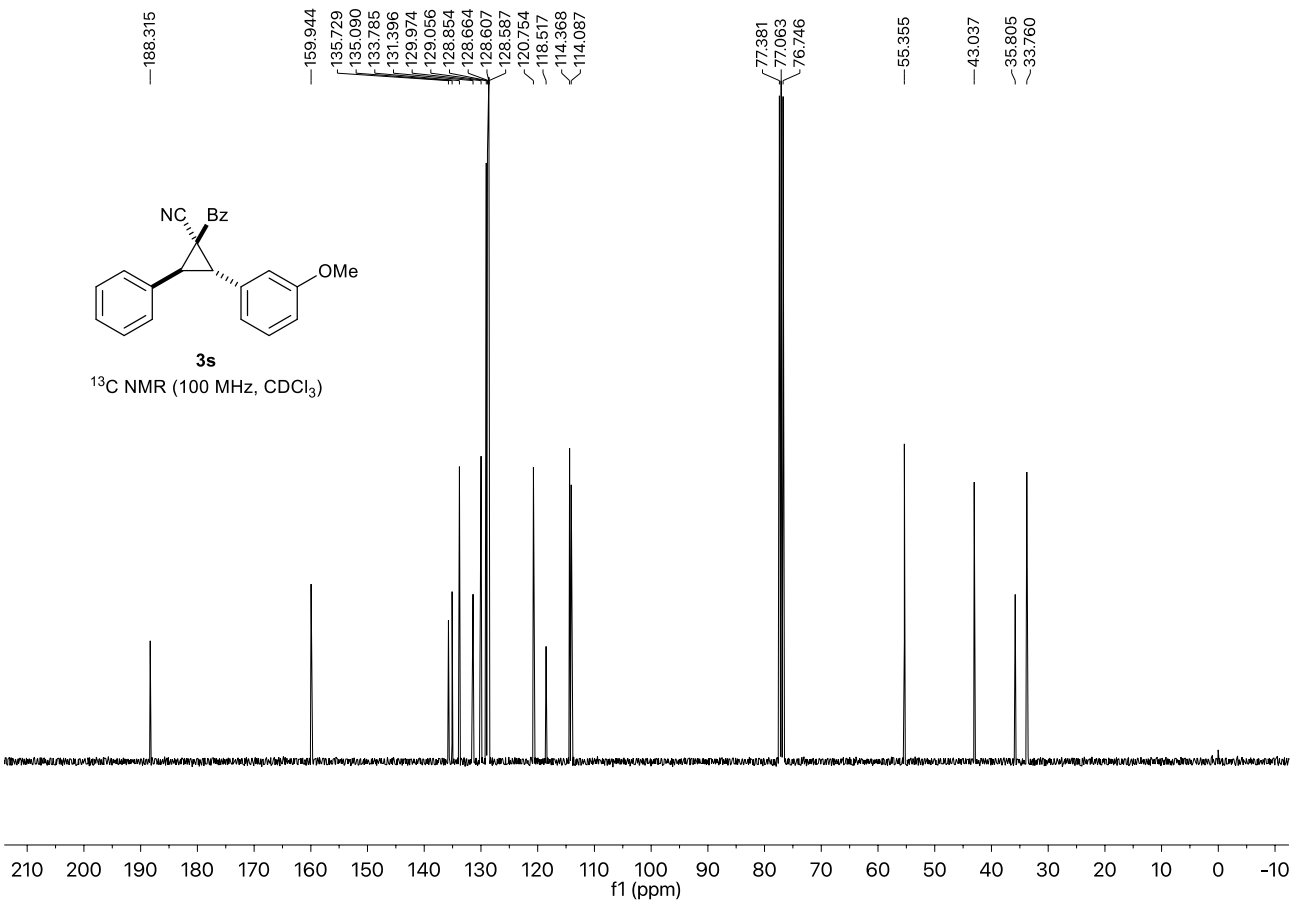

188.363
138.710
135.664
133.833
132.347
131.541
130.599
129.071
128.867
128.692
128.655
128.634
128.610
127.931
126.320
118.481
77.388
77.070
76.752
43.247
34.841
32.847
19.598
NC
Bz
3r
13C NMR (100 MHz, CDCl3)
f1 (ppm)


+ESI Scan (rt: 0.224 min) Frag=175.0V
x10^6
360.1363
NC
Bz
3s
(ESI-TOF) m/z: [M + Na]+
Calcd for C24H19NONa+ 360.1359
Counts vs. Mass-to-Charge (m/z)



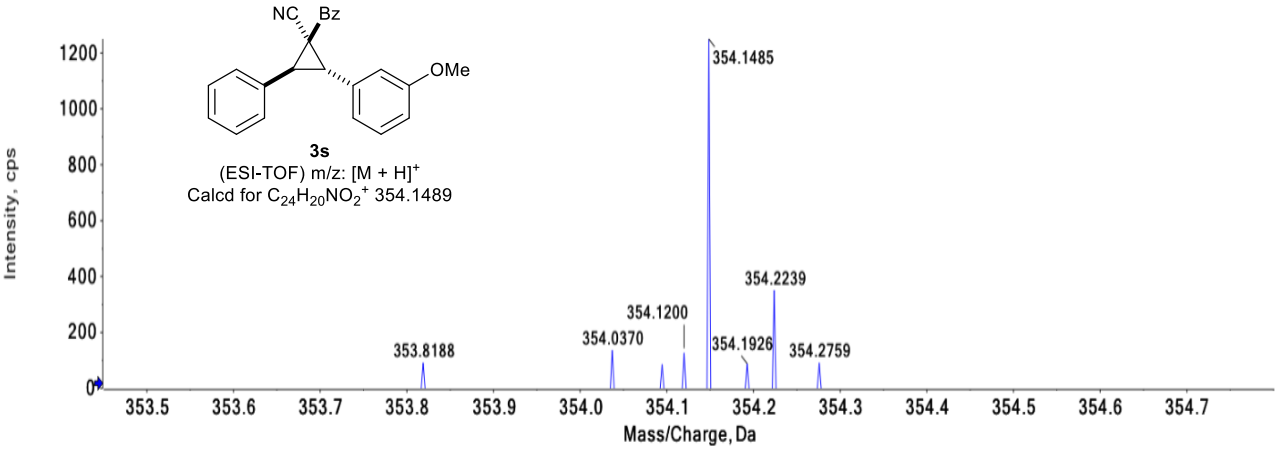
3s

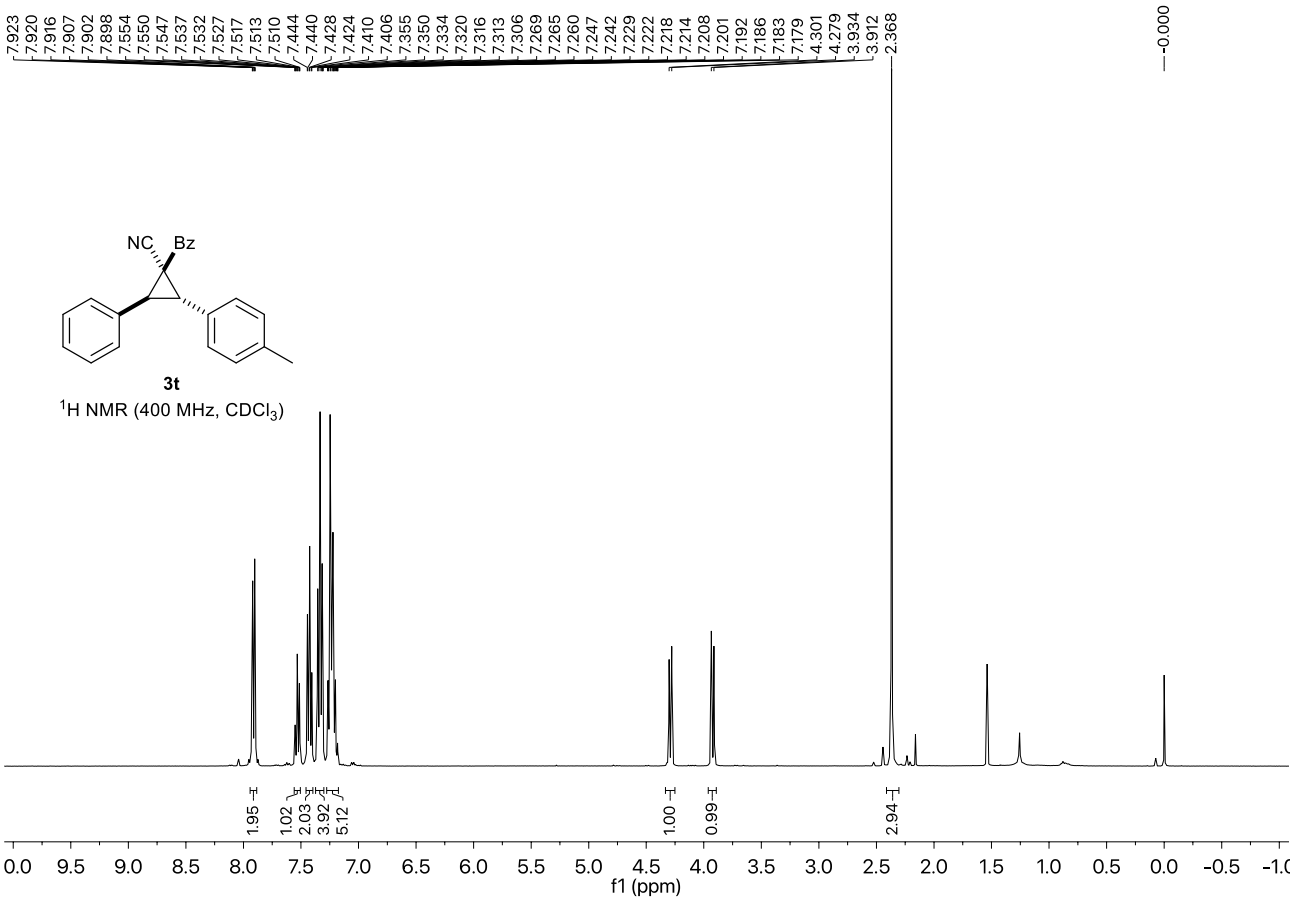
^{1}H NMR (400 MHz, $CDCl_3$)

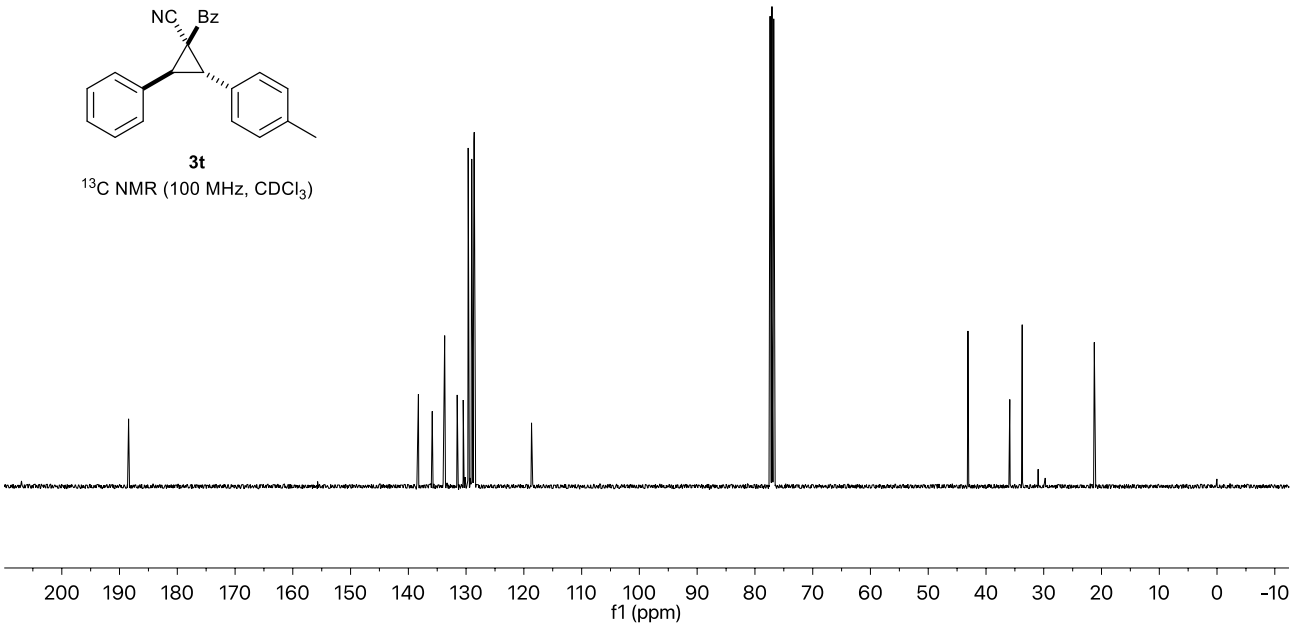


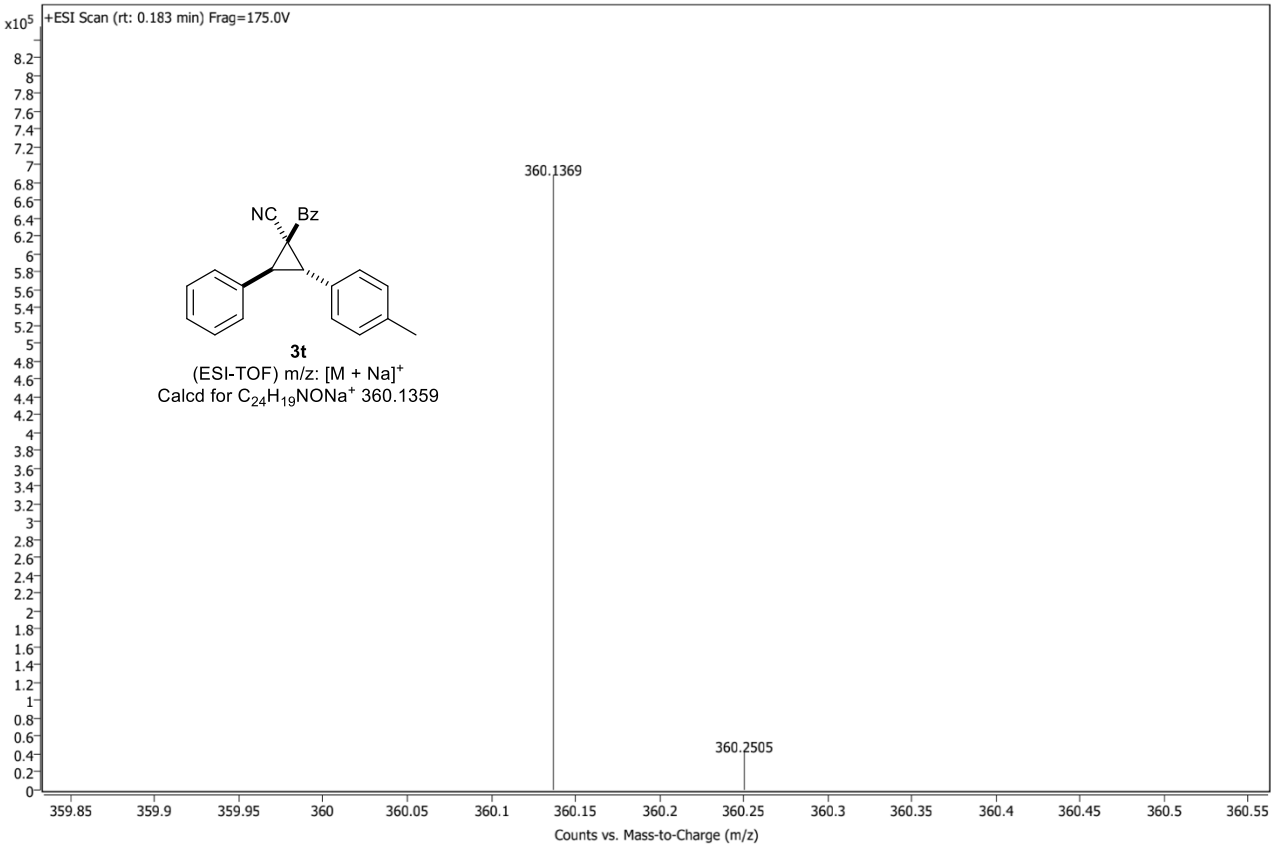
3s

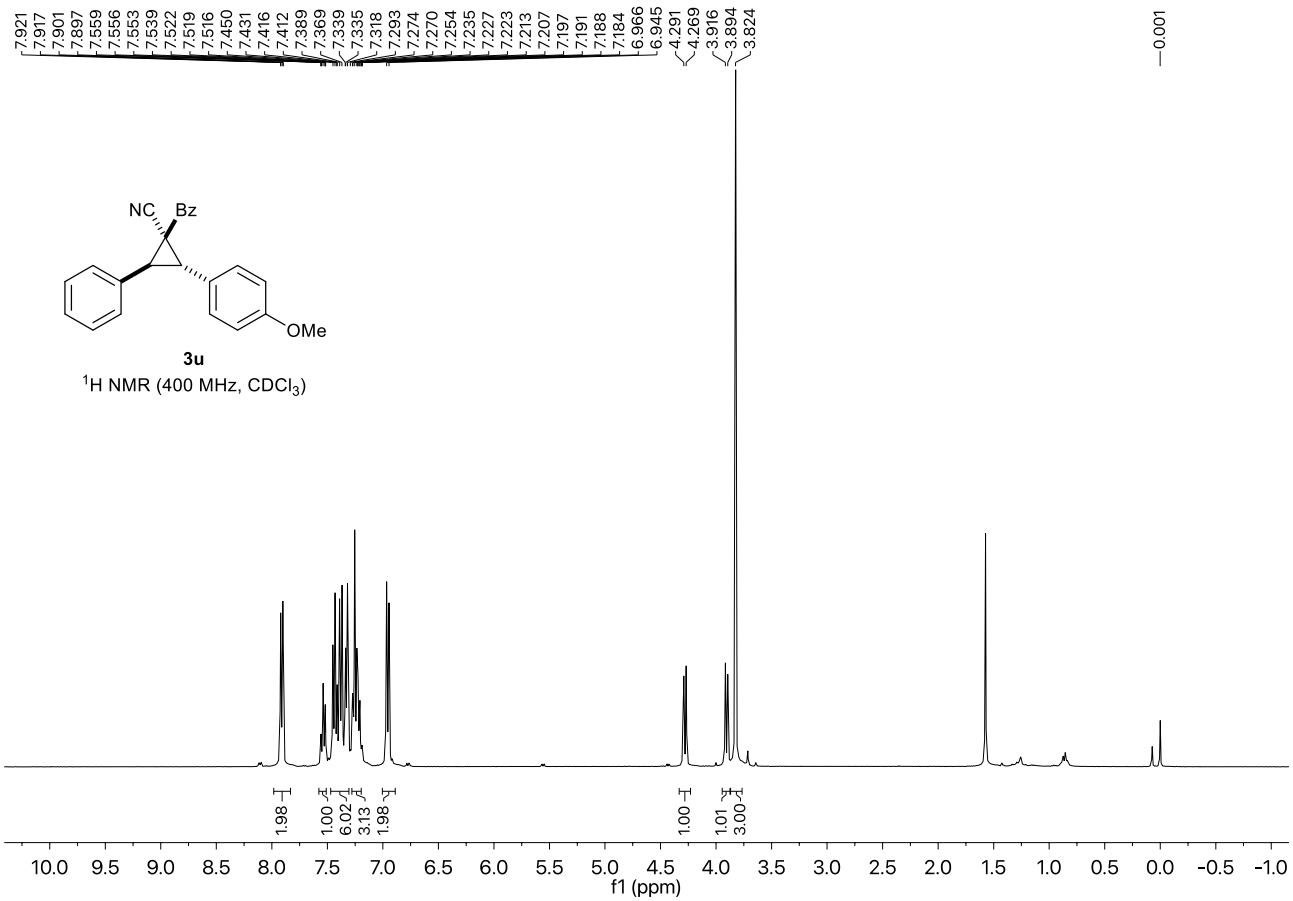
^{13}C NMR (100 MHz, $CDCl_3$)


NC
Bz
OMe
3s
(ESI-TOF) m/z: [M + H]+
Calcd for C24H20NO2+ 354.1489
Intensity, cps
Mass/Charge, Da
354.1485
354.2239
354.1200
354.0370
354.1926
354.2759
353.8188


NC
Bz
3t
1H NMR (400 MHz, CDCl3)
f1 (ppm)

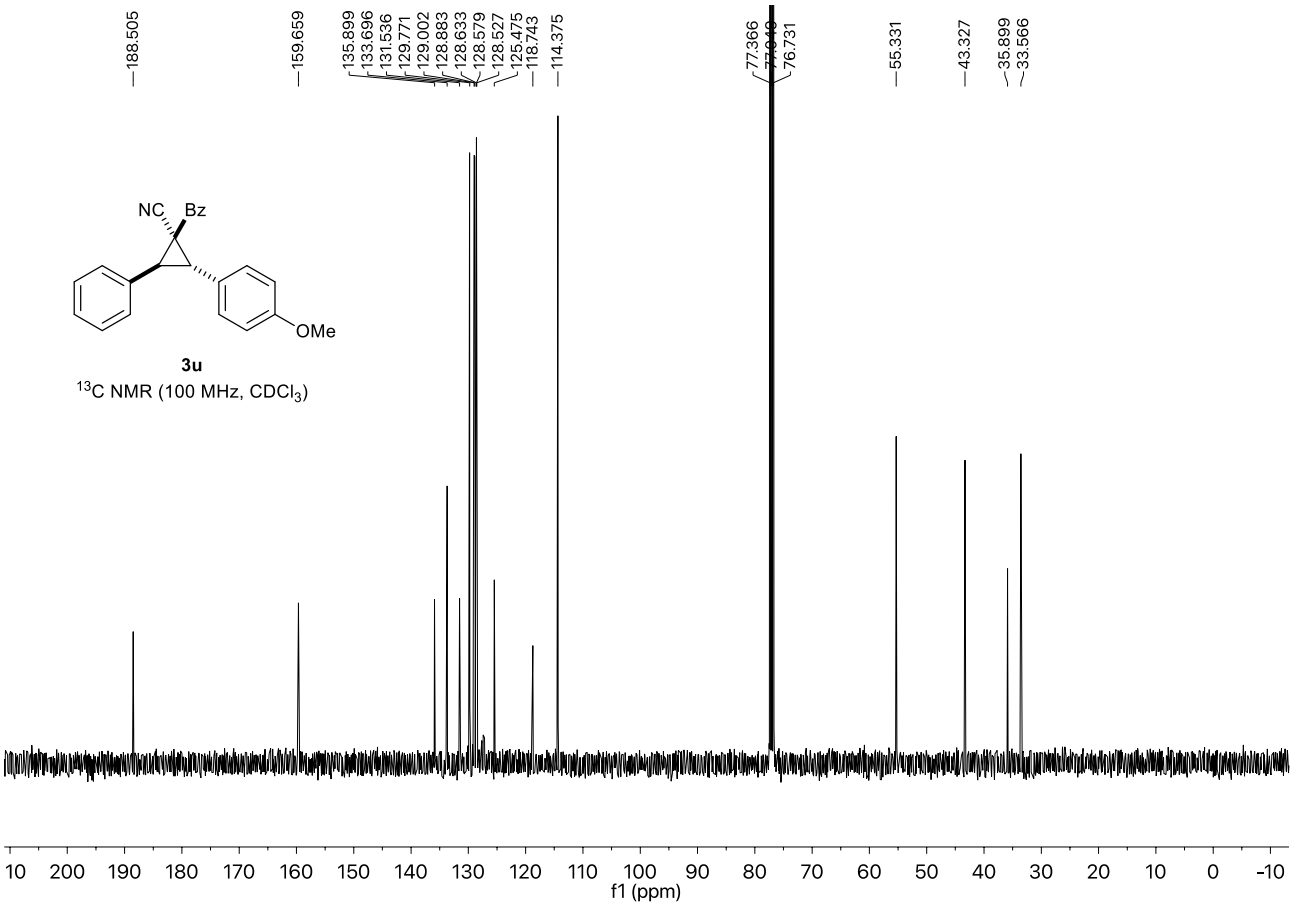

NC
Bz
3t
13C NMR (100 MHz, CDCl3)
f1 (ppm)


+ESI Scan (rt: 0.183 min) Frag=175.0V
x10^5
360.1369
360.2505
NC
Bz
3t
(ESI-TOF) m/z: [M + Na]+
Calcd for C24H19NONa+ 360.1359
Counts vs. Mass-to-Charge (m/z)



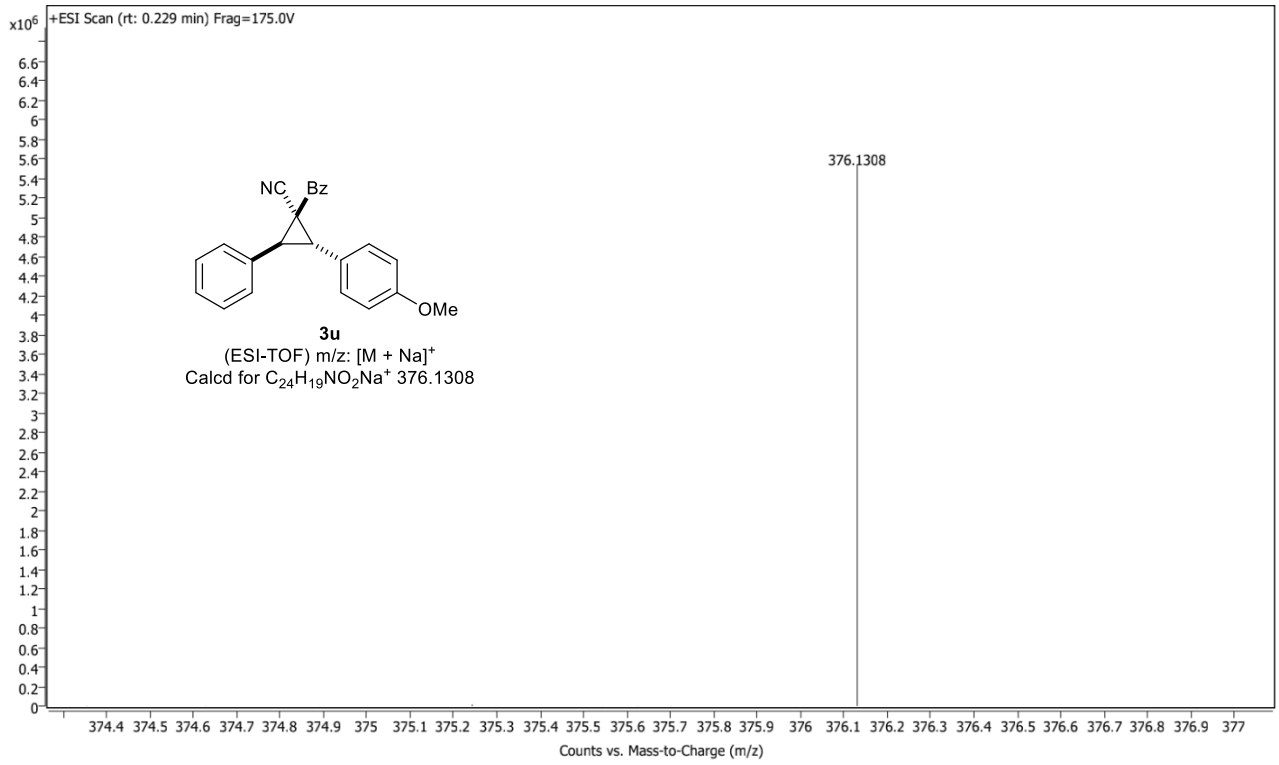
3u

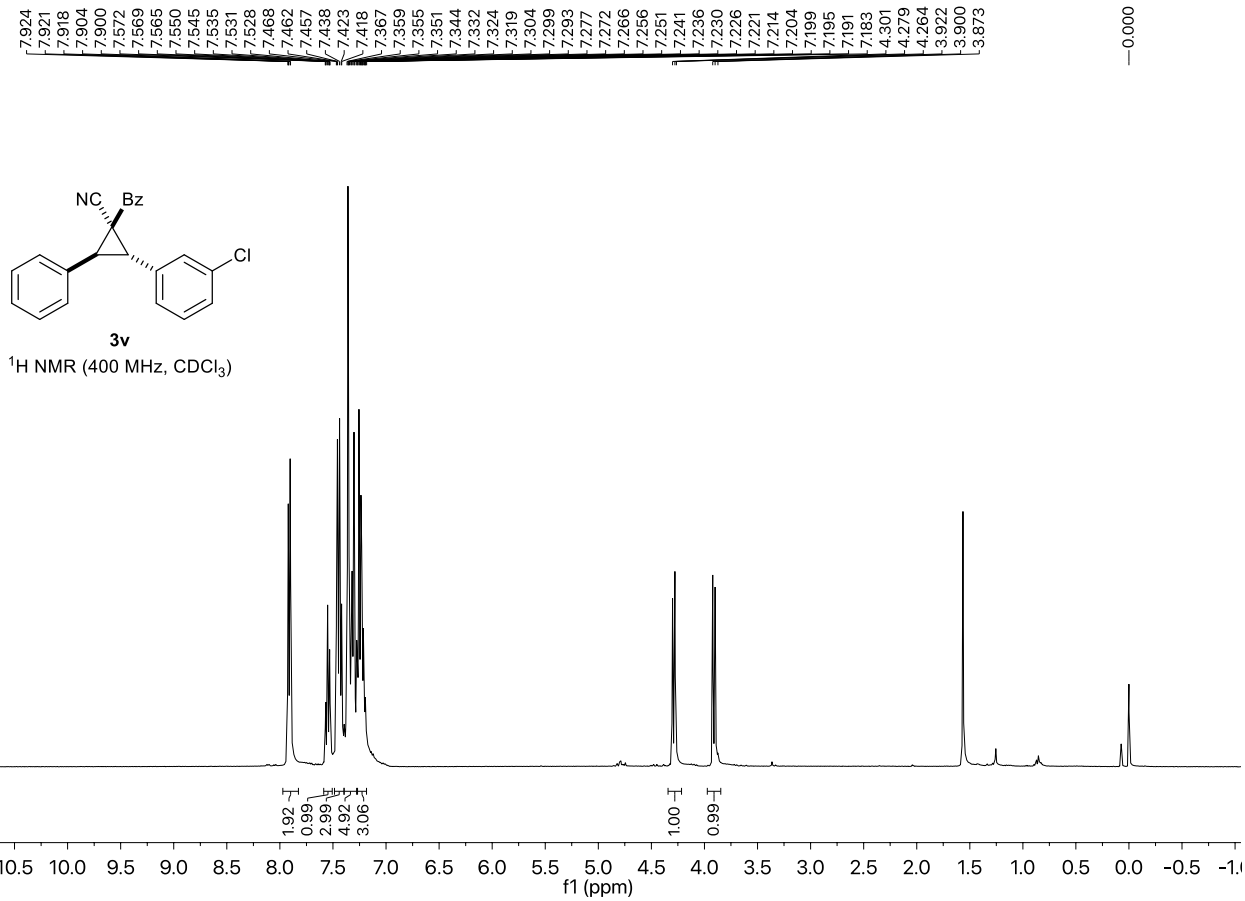
^{1}H NMR (400 MHz, $CDCl_3$)

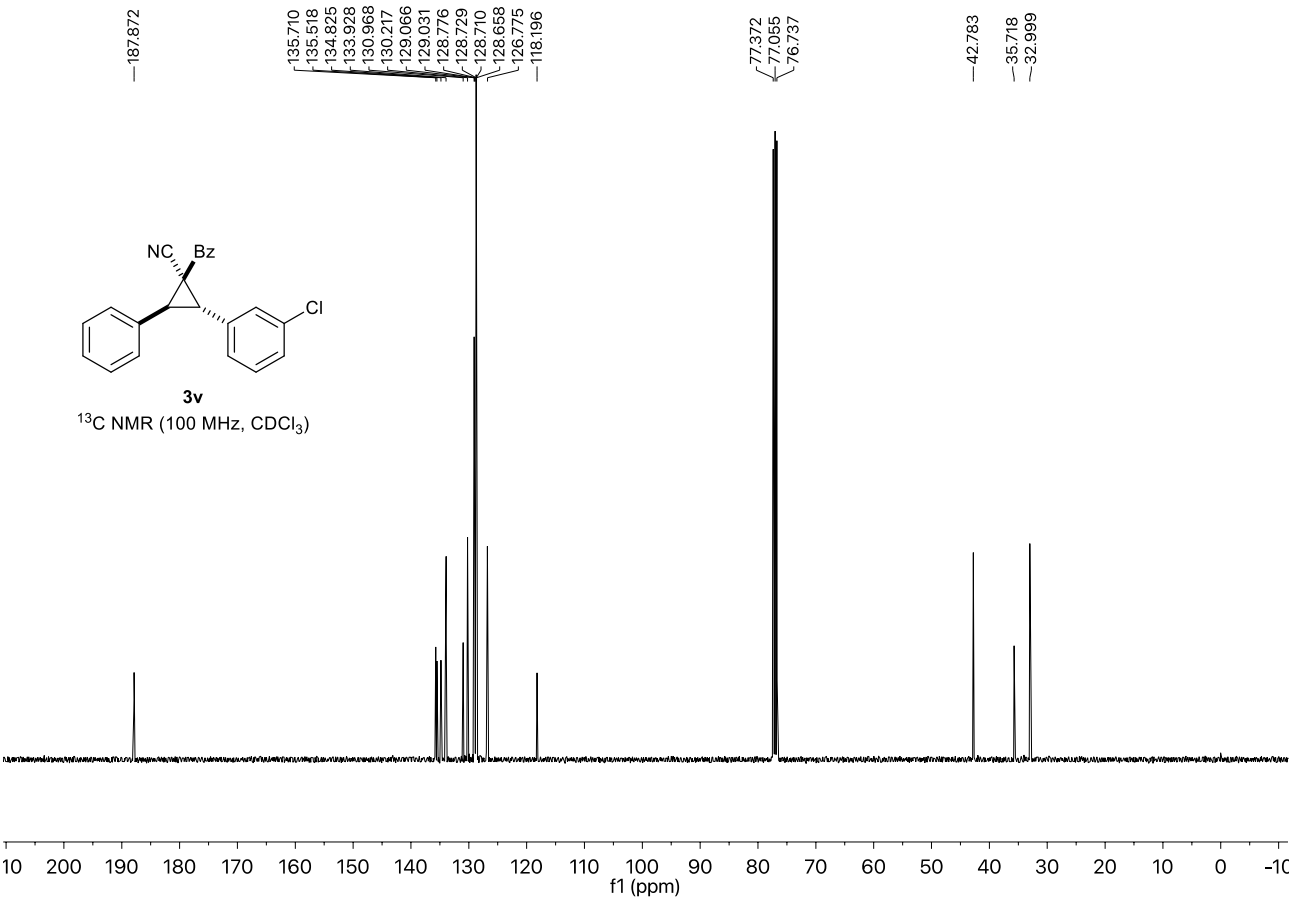


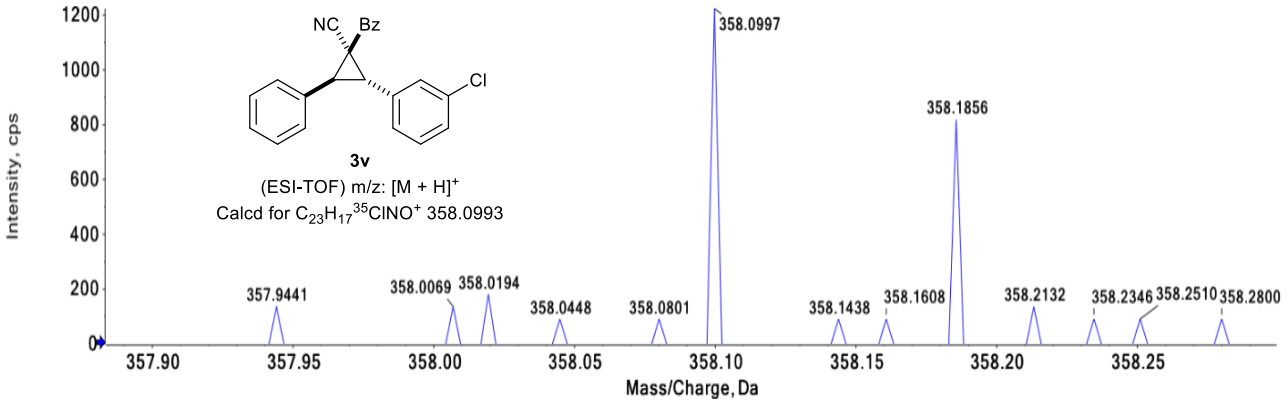
3u

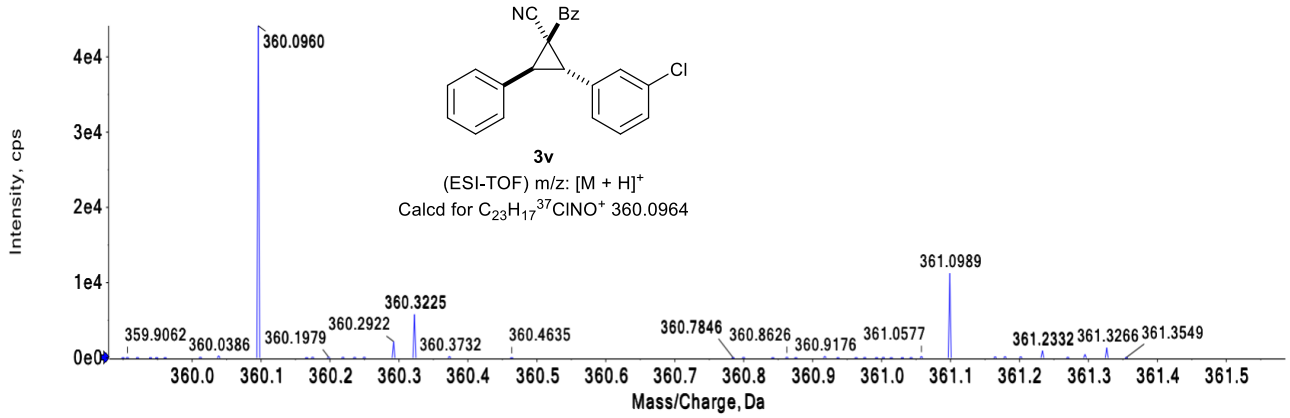
^{13}C NMR (100 MHz, $CDCl_3$)

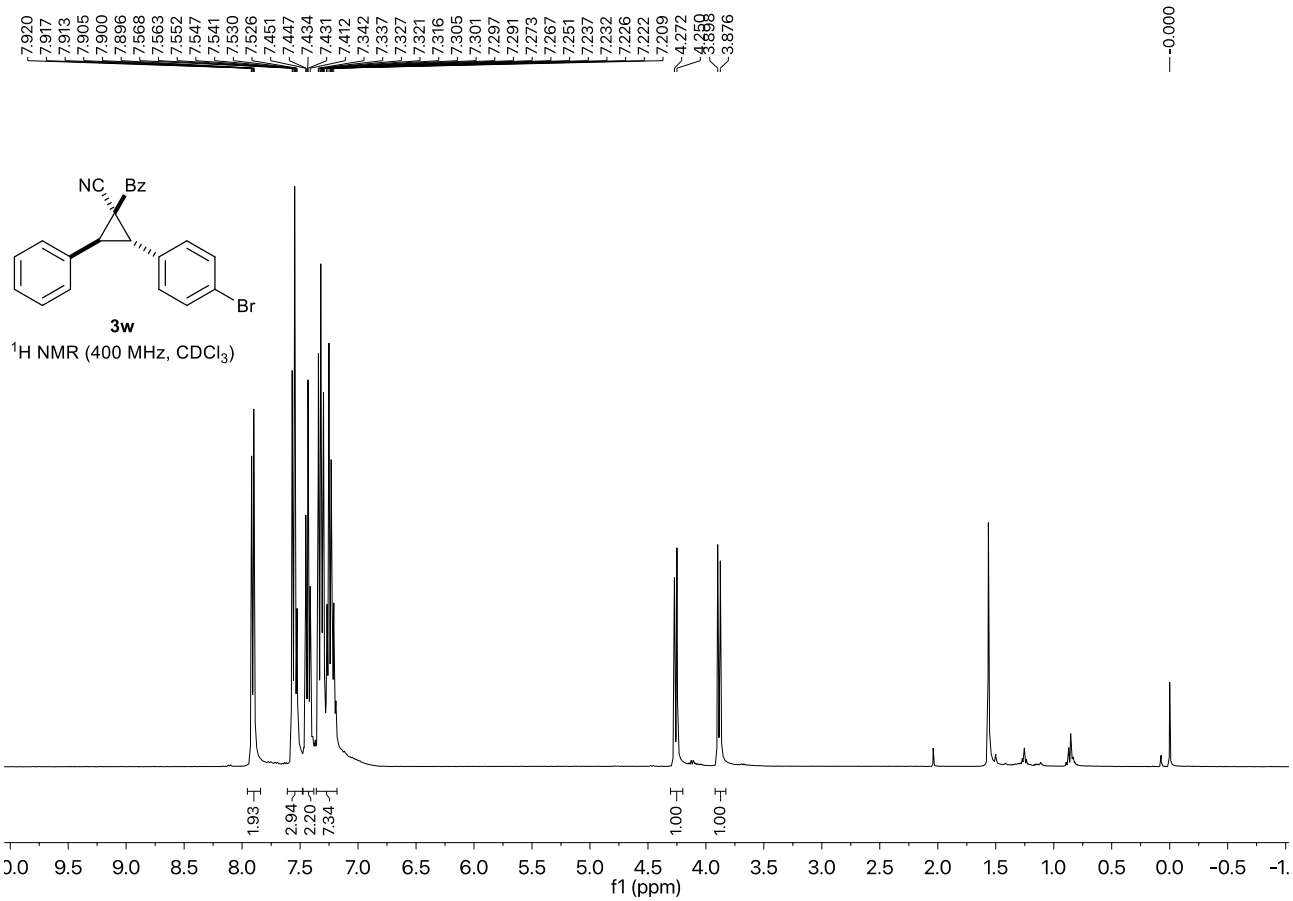

+ESI Scan (rt: 0.229 min) Frag=175.0V
x10^6
376.1308
NC
Bz
OMe
3u
(ESI-TOF) m/z: [M + Na]+
Calcd for C24H19NO2Na+ 376.1308
Counts vs. Mass-to-Charge (m/z)

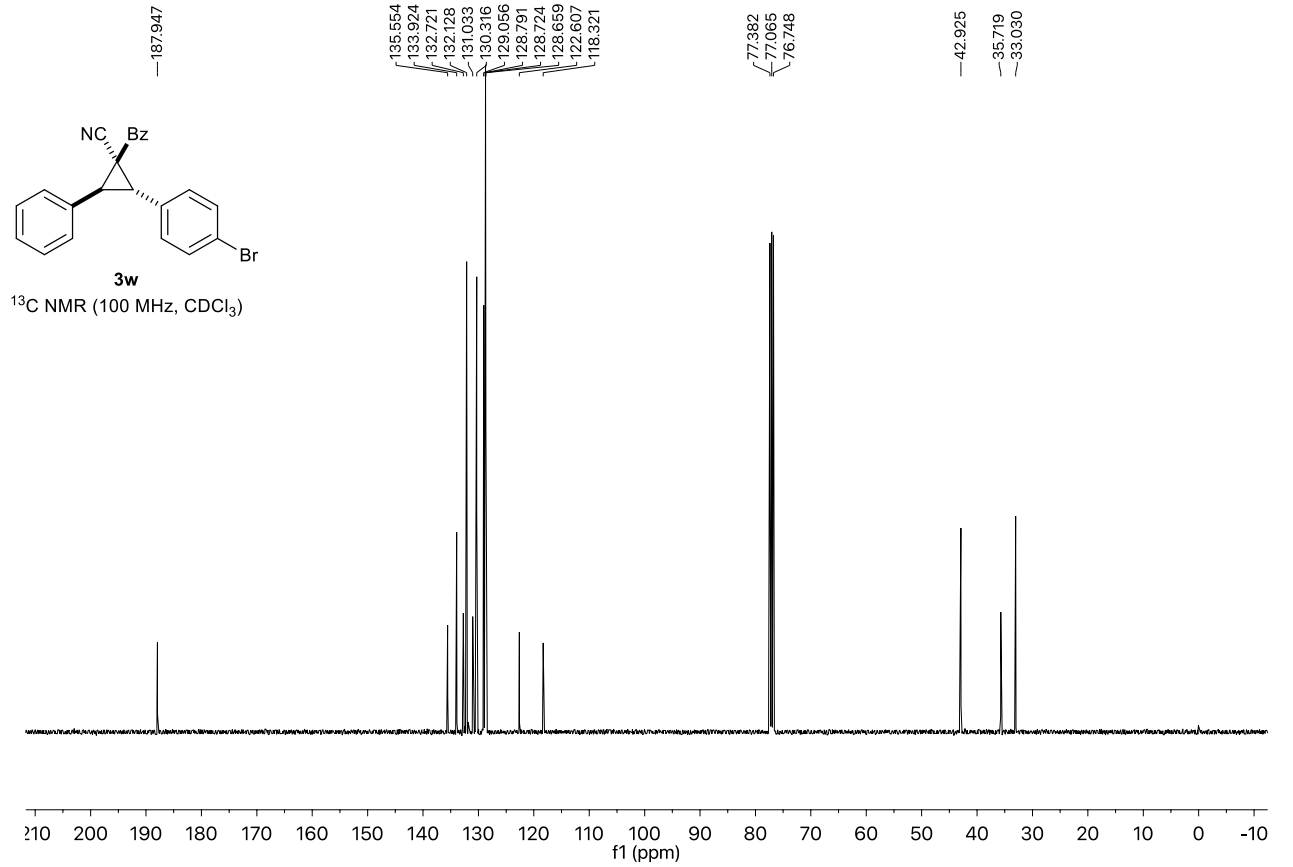

7.924
7.921
7.918
7.904
7.900
7.572
7.569
7.565
7.550
7.545
7.535
7.531
7.528
7.468
7.462
7.457
7.438
7.423
7.418
7.367
7.359
7.355
7.351
7.344
7.332
7.324
7.319
7.304
7.299
7.293
7.277
7.272
7.266
7.256
7.251
7.241
7.236
7.230
7.226
7.221
7.214
7.204
7.199
7.195
7.191
7.183
4.301
4.279
4.264
3.922
3.900
3.873
0.000
NC
Bz
Cl
3v
1H NMR (400 MHz, CDCl3)
1.92
0.99
2.99
4.92
3.06
1.00
0.99
f1 (ppm)

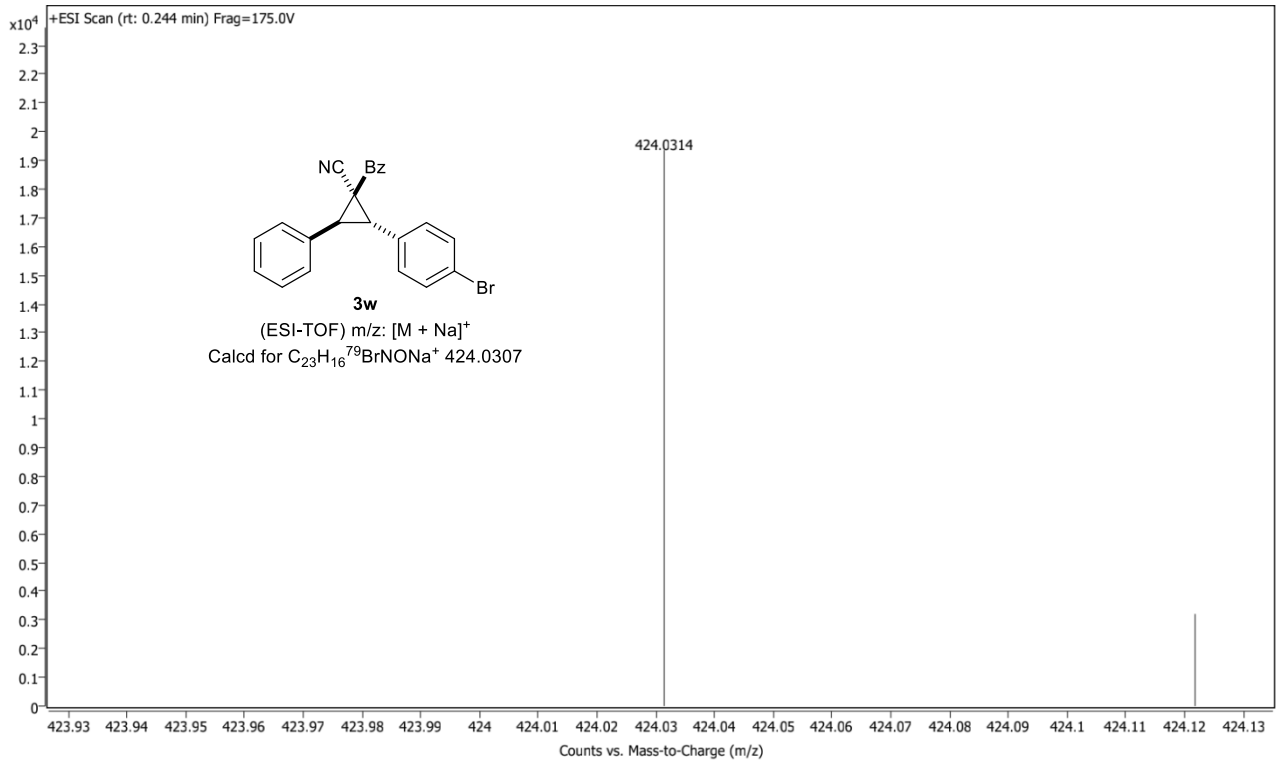

187.872
135.710
135.518
134.825
133.928
130.968
130.217
129.066
129.031
128.776
128.729
128.710
128.658
126.775
118.196
77.372
77.055
76.737
42.783
35.718
32.999
NC
Bz
Cl
3v
13C NMR (100 MHz, CDCl3)
f1 (ppm)

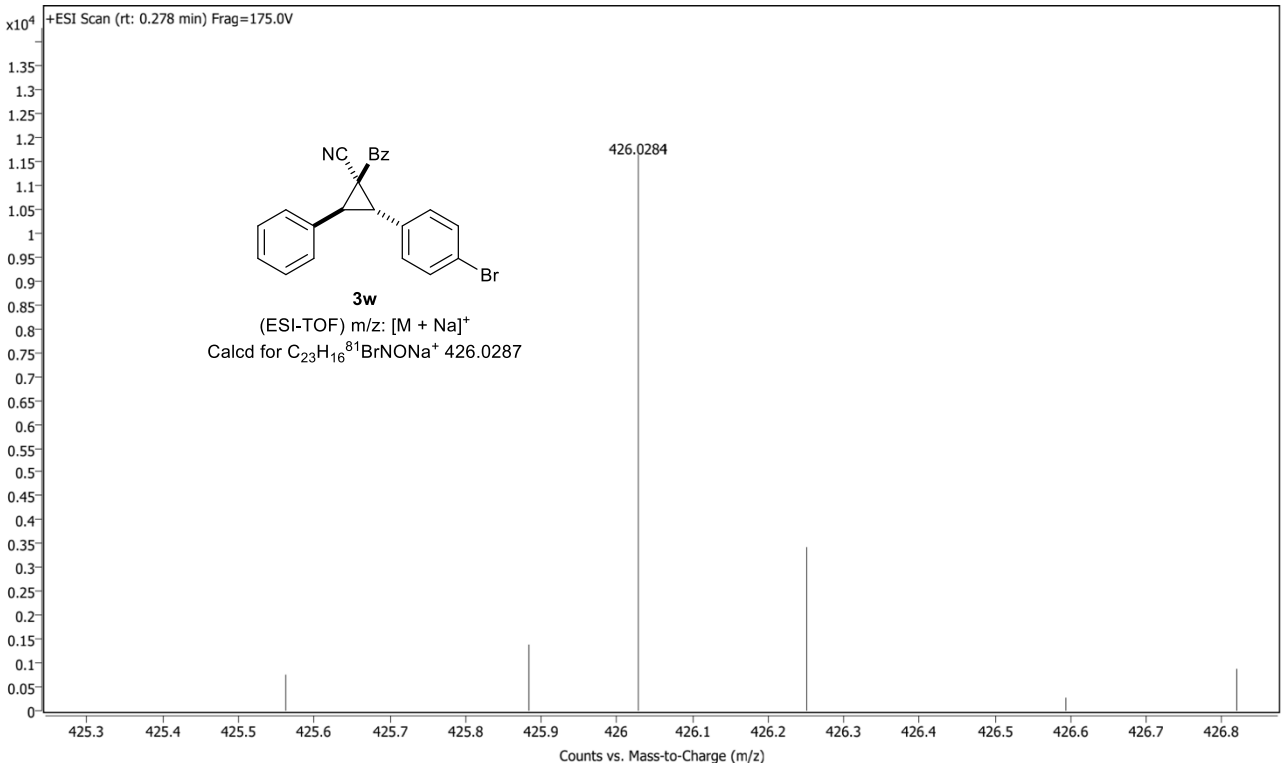

NC
Bz
Cl
3v
(ESI-TOF) m/z: [M + H]+
Calcd for C23H17 35ClNO+ 358.0993
Intensity, cps
Mass/Charge, Da
358.0997
358.1856
357.9441
358.0069
358.0194
358.0448
358.0801
358.1438
358.1608
358.2132
358.2346
358.2510
358.2800

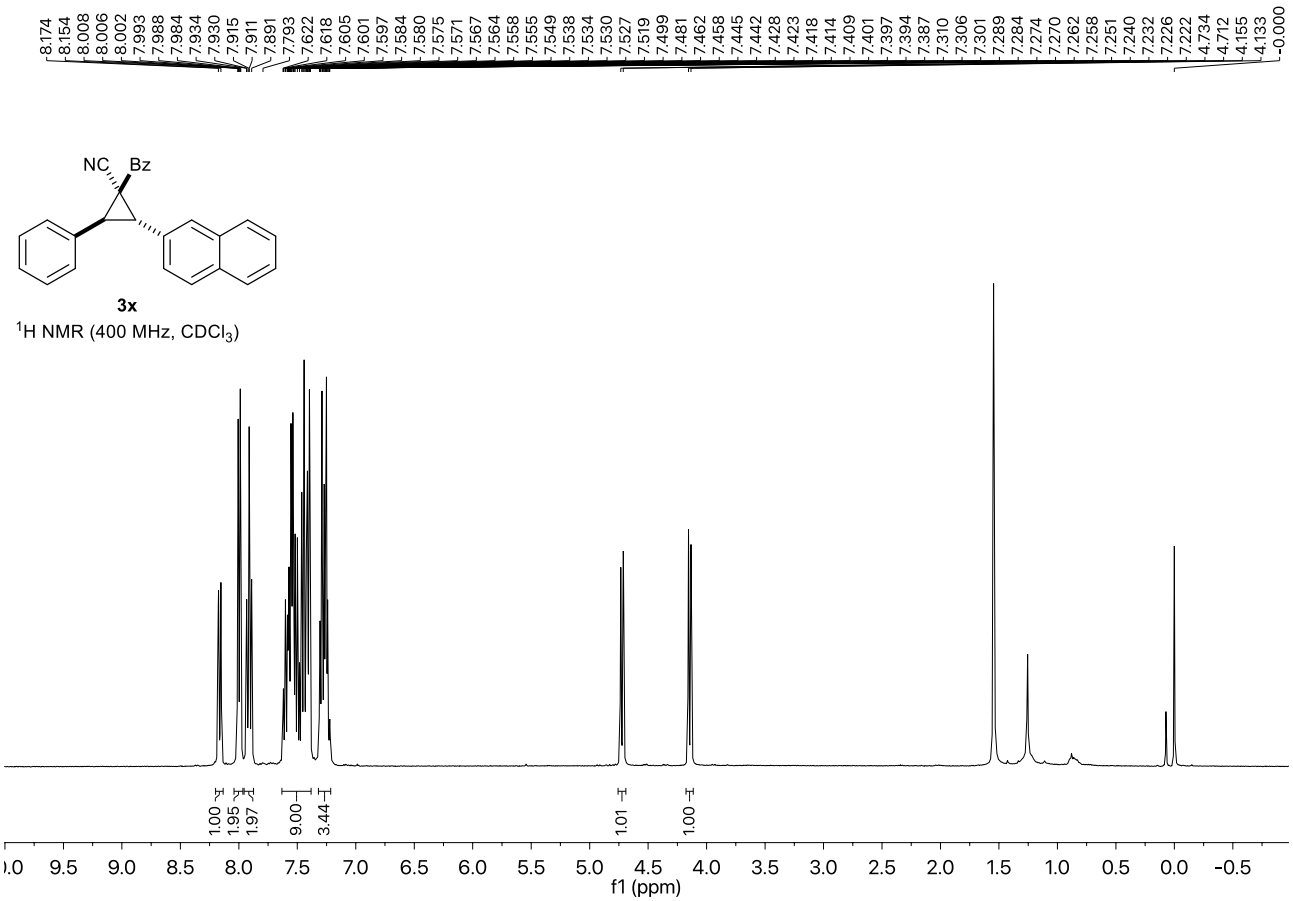

NC
Bz
Cl
3v
(ESI-TOF) m/z: [M + H]+
Calcd for C23H17 37ClNO+ 360.0964
Intensity, cps
Mass/Charge, Da
360.0960
361.0989
360.3225
359.9062
360.0386
360.1979
360.2922
360.3732
360.4635
360.7846
360.8626
360.9176
361.0577
361.2332
361.3266
361.3549

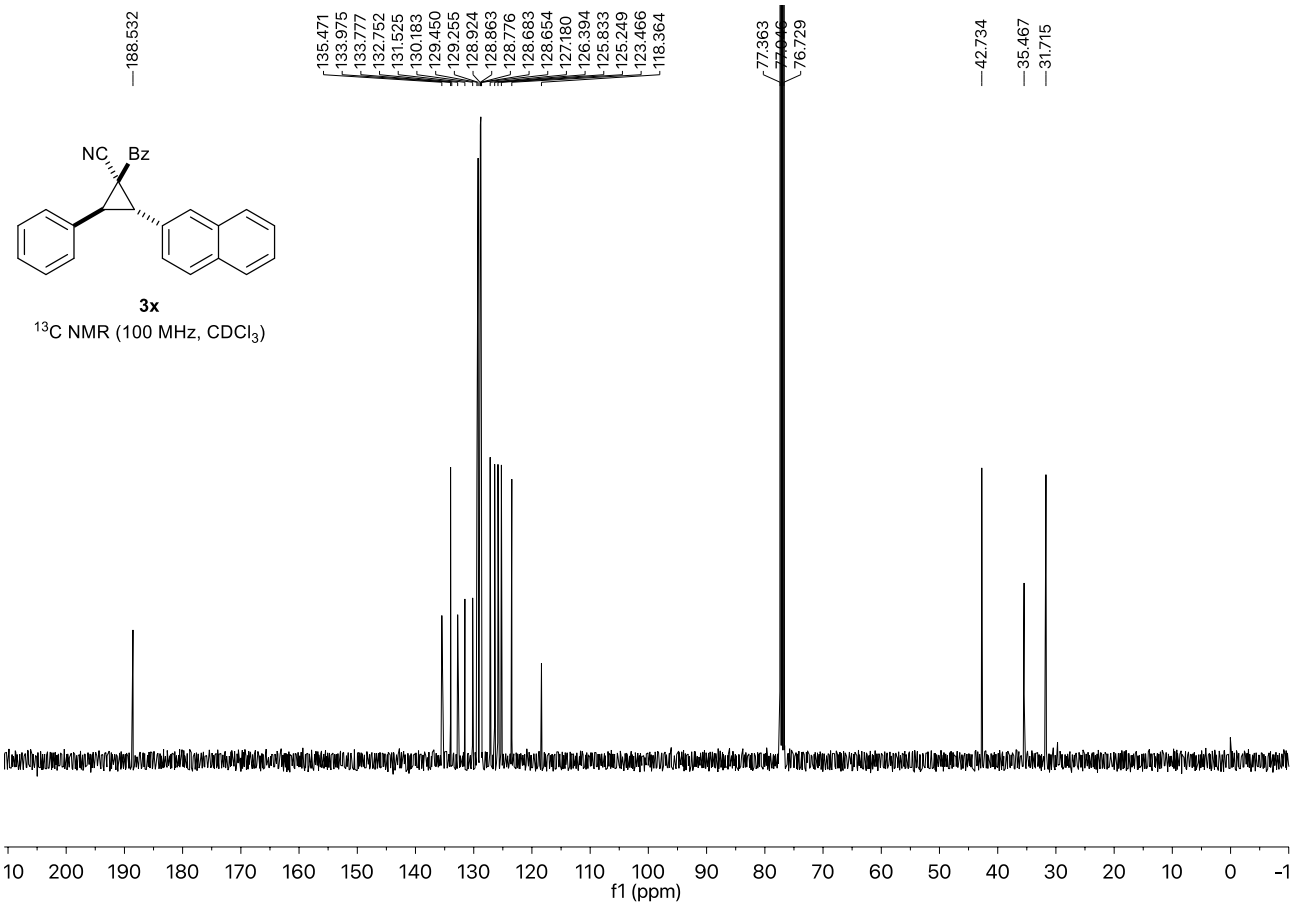

7.920
7.917
7.913
7.905
7.900
7.896
7.568
7.563
7.552
7.547
7.541
7.530
7.526
7.451
7.447
7.434
7.431
7.412
7.342
7.337
7.327
7.321
7.316
7.305
7.301
7.297
7.291
7.273
7.267
7.251
7.237
7.232
7.226
7.222
7.209
4.272
3.898
3.876
0.000
NC
Bz
Br
3w
1H NMR (400 MHz, CDCl3)
1.93
2.94
2.20
7.34
1.00
1.00
f1 (ppm)

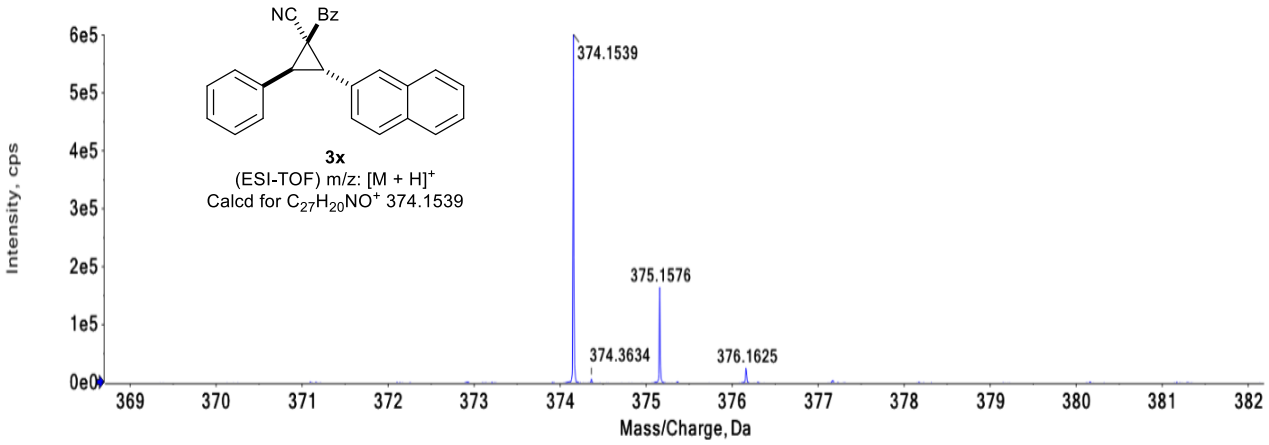

187.947
135.554
133.924
132.721
132.128
131.033
130.316
129.056
128.791
128.724
128.659
122.607
118.321
77.382
77.065
76.748
42.925
35.719
33.030
NC
Bz
Br
3w
13C NMR (100 MHz, CDCl3)
f1 (ppm)

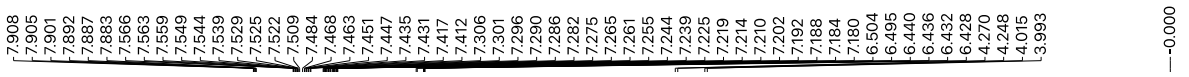

+ESI Scan (rt: 0.244 min) Frag=175.0V
x10^4
424.0314
NC
Bz
Br
3w
(ESI-TOF) m/z: [M + Na]+
Calcd for C23H16 79BrNONa+ 424.0307
Counts vs. Mass-to-Charge (m/z)

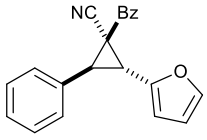

+ESI Scan (rt: 0.278 min) Frag=175.0V
x10^4
426.0284
NC
Bz
Br
3w
(ESI-TOF) m/z: [M + Na]+
Calcd for C23H16 81BrNONa+ 426.0287
Counts vs. Mass-to-Charge (m/z)


NC
Bz
3x
1H NMR (400 MHz, CDCl3)
1.00
1.95
1.97
9.00
3.44
1.01
1.00
f1 (ppm)


NC
Bz
3x
13C NMR (100 MHz, CDCl3)
f1 (ppm)

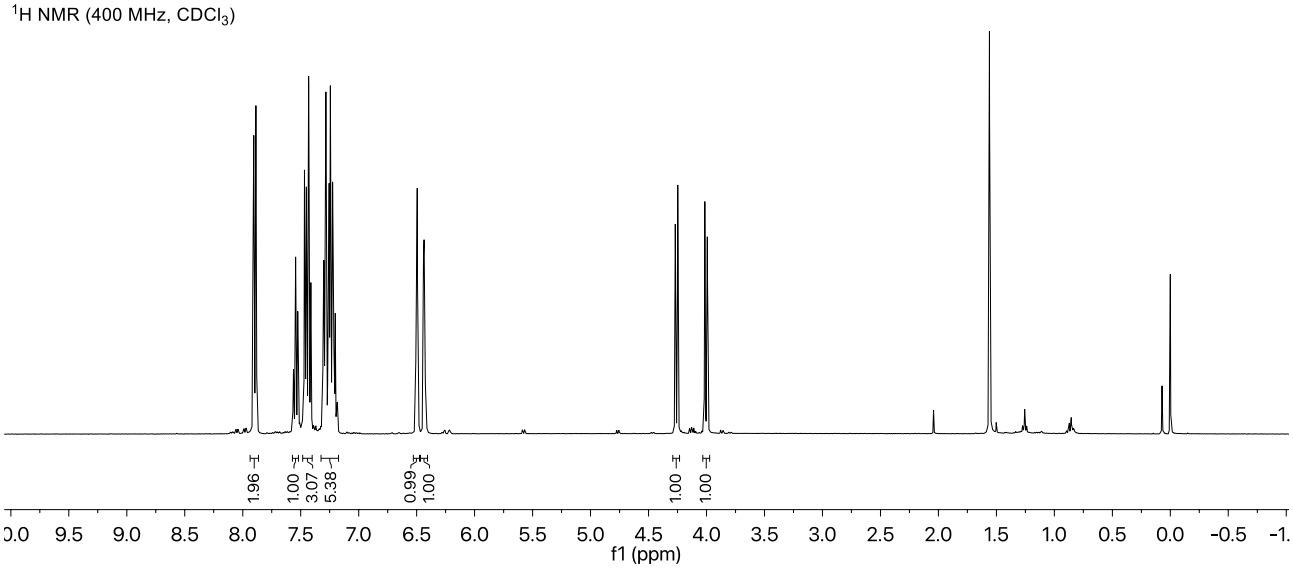

NC
Bz
3x
(ESI-TOF) m/z: [M + H]+
Calcd for C27H20NO+ 374.1539
Intensity, cps
6e5
5e5
4e5
3e5
2e5
1e5
0e0
374.1539
375.1576
374.3634
376.1625
369
370
371
372
373
374
375
376
377
378
379
380
381
382
Mass/Charge, Da

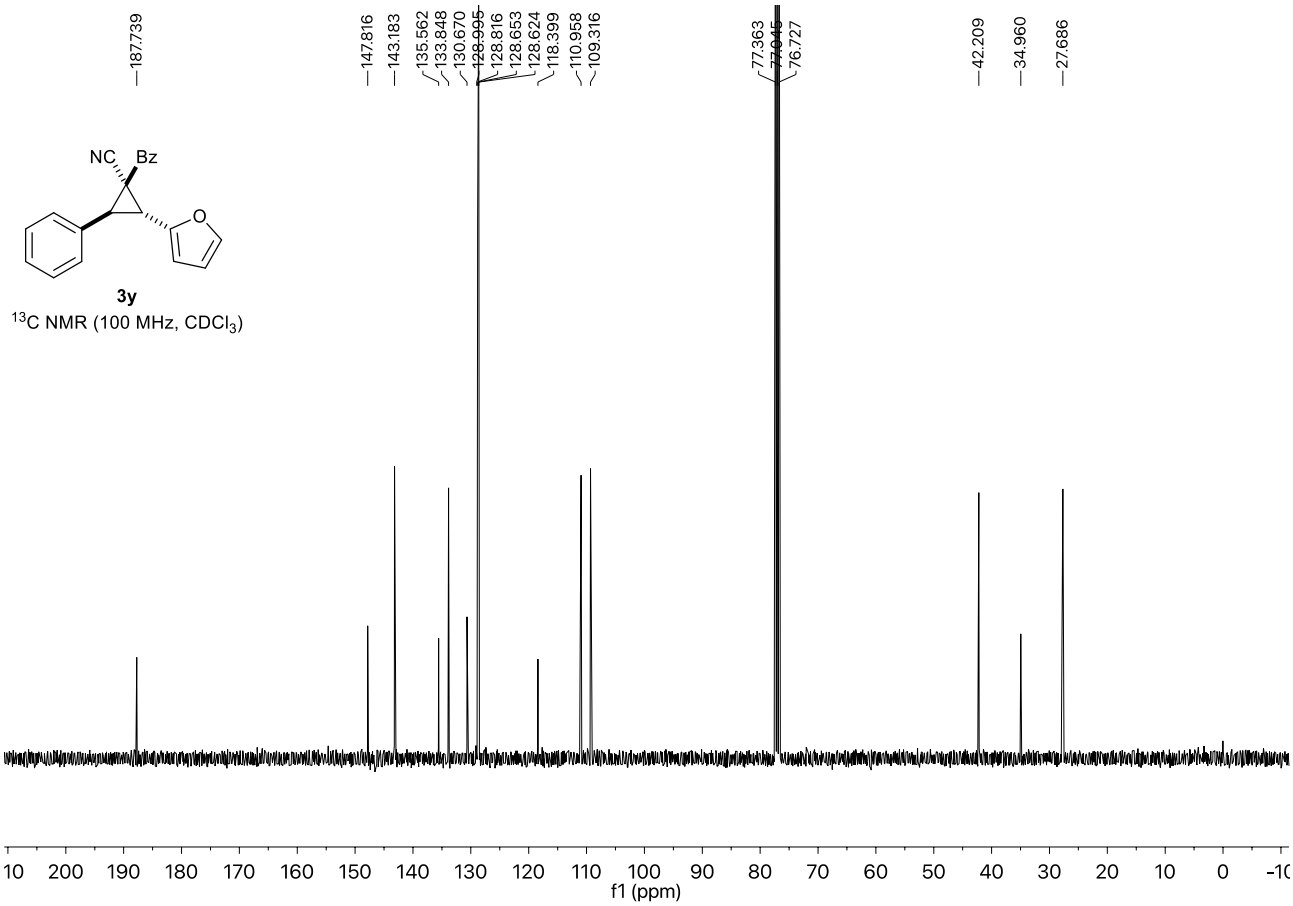




3y

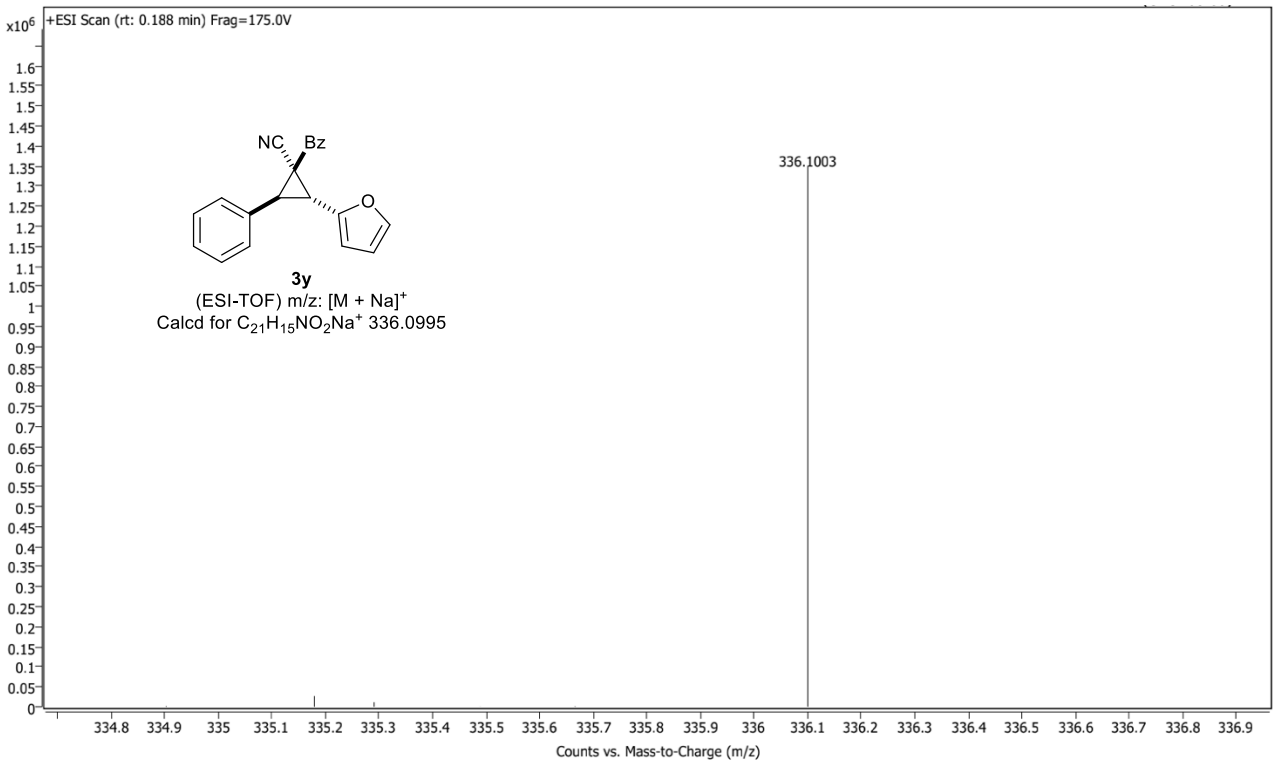
^{1}H NMR (400 MHz, $CDCl_3$)

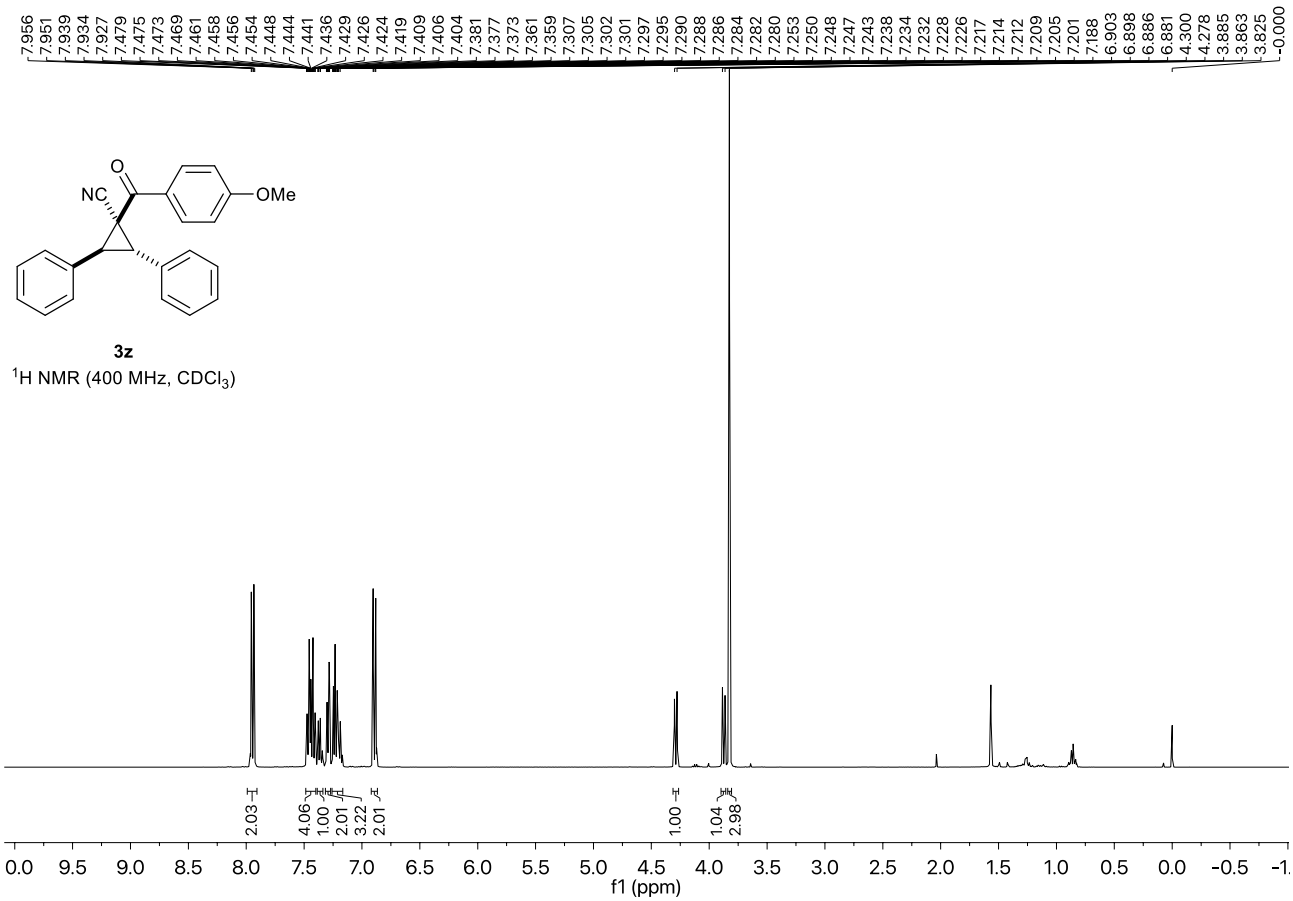




3y

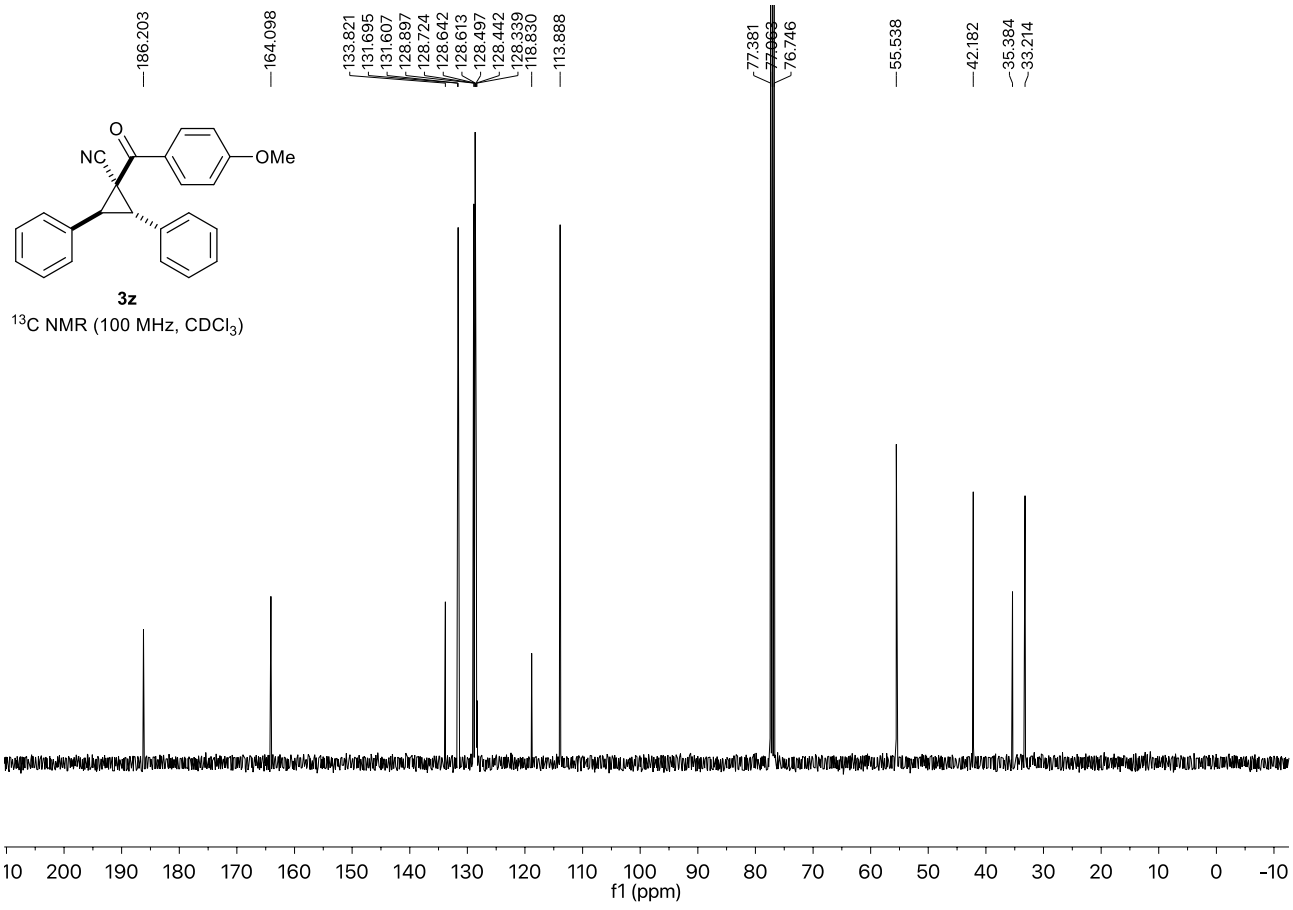
^{13}C NMR (100 MHz, $CDCl_3$)


+ESI Scan (rt: 0.188 min) Frag=175.0V
x10^6
NC
Bz
O
336.1003
3y
(ESI-TOF) m/z: [M + Na]+
Calcd for C21H15NO2Na+ 336.0995
Counts vs. Mass-to-Charge (m/z)



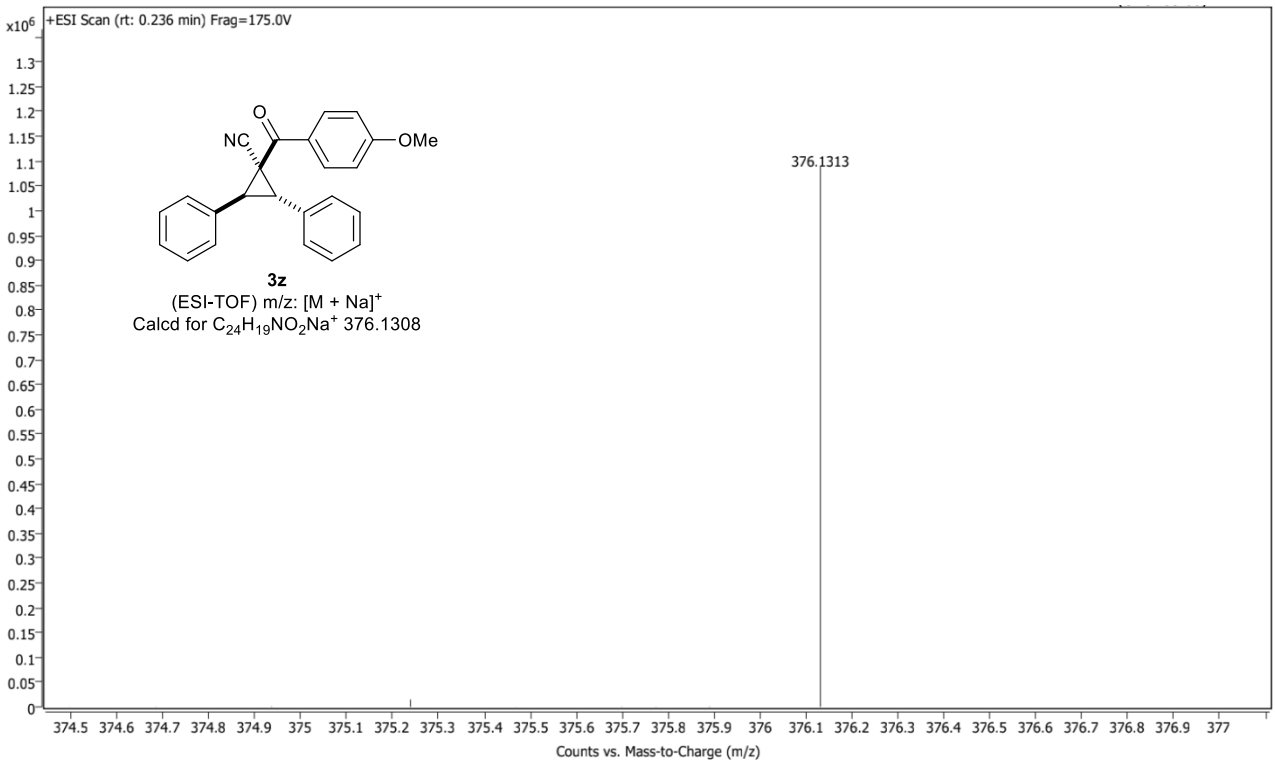
3z

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



3z

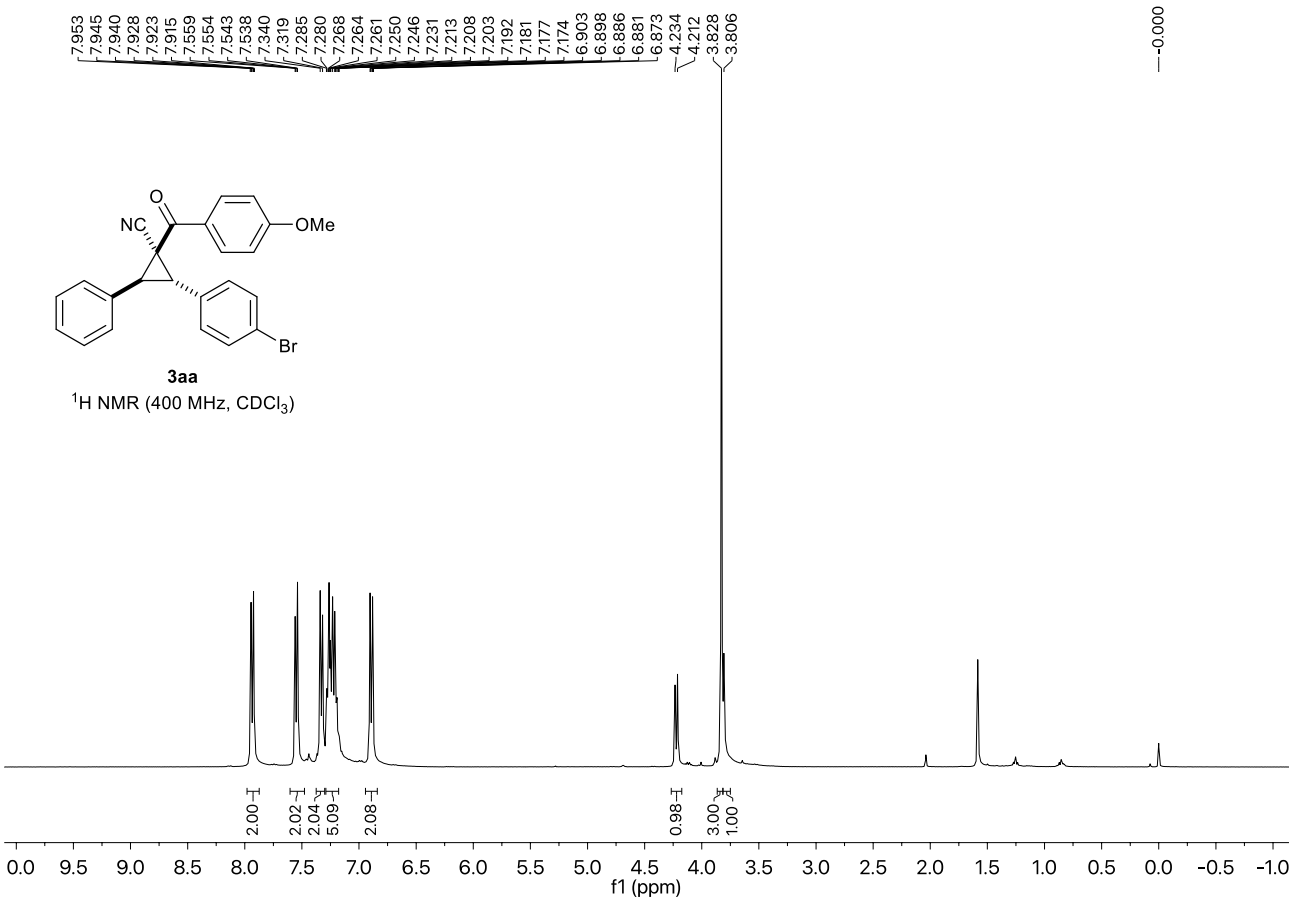
^{13}C NMR (100 MHz, $CDCl_3$)



3z

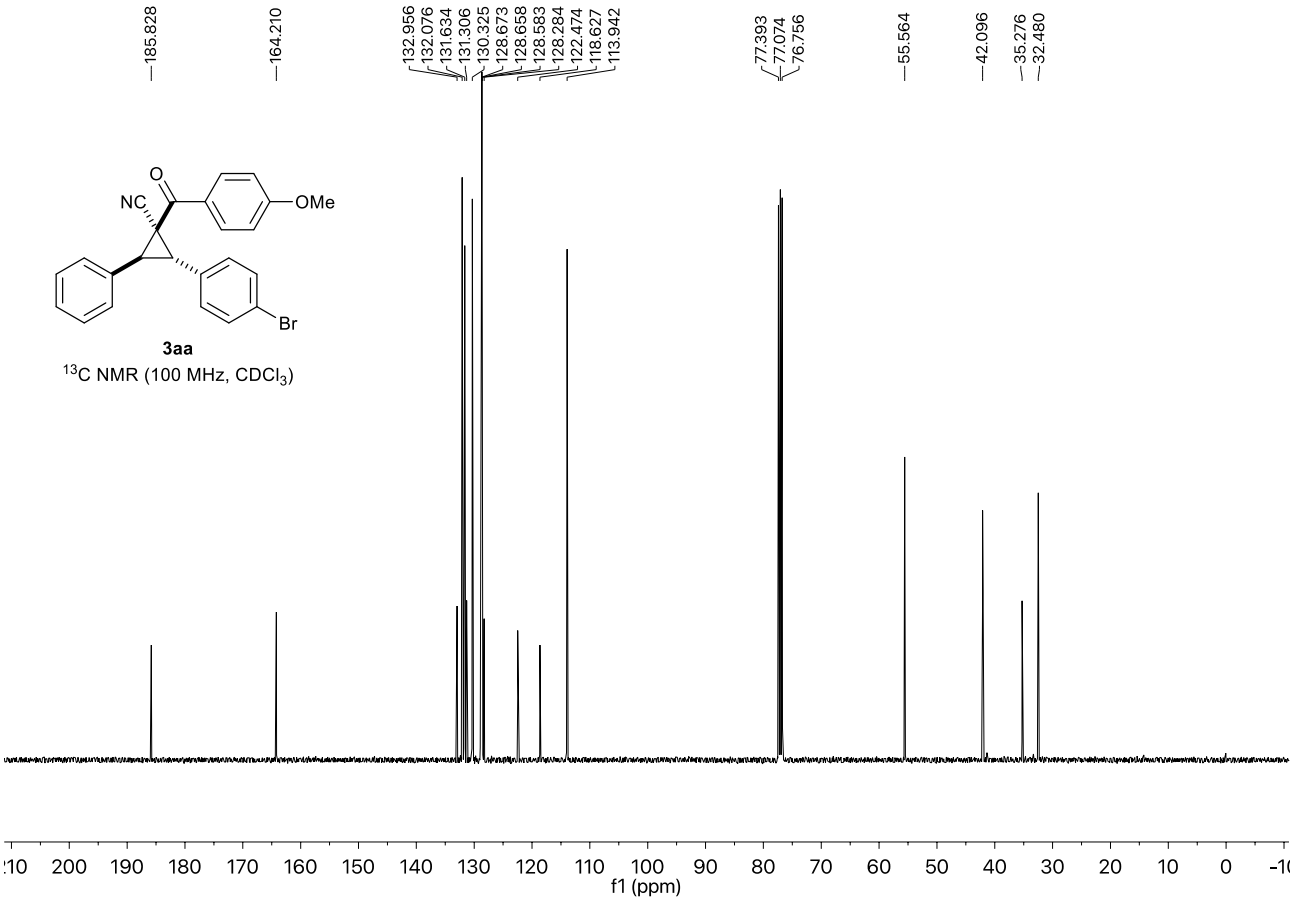
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{24}H_{19}NO_2Na^+$ 376.1308



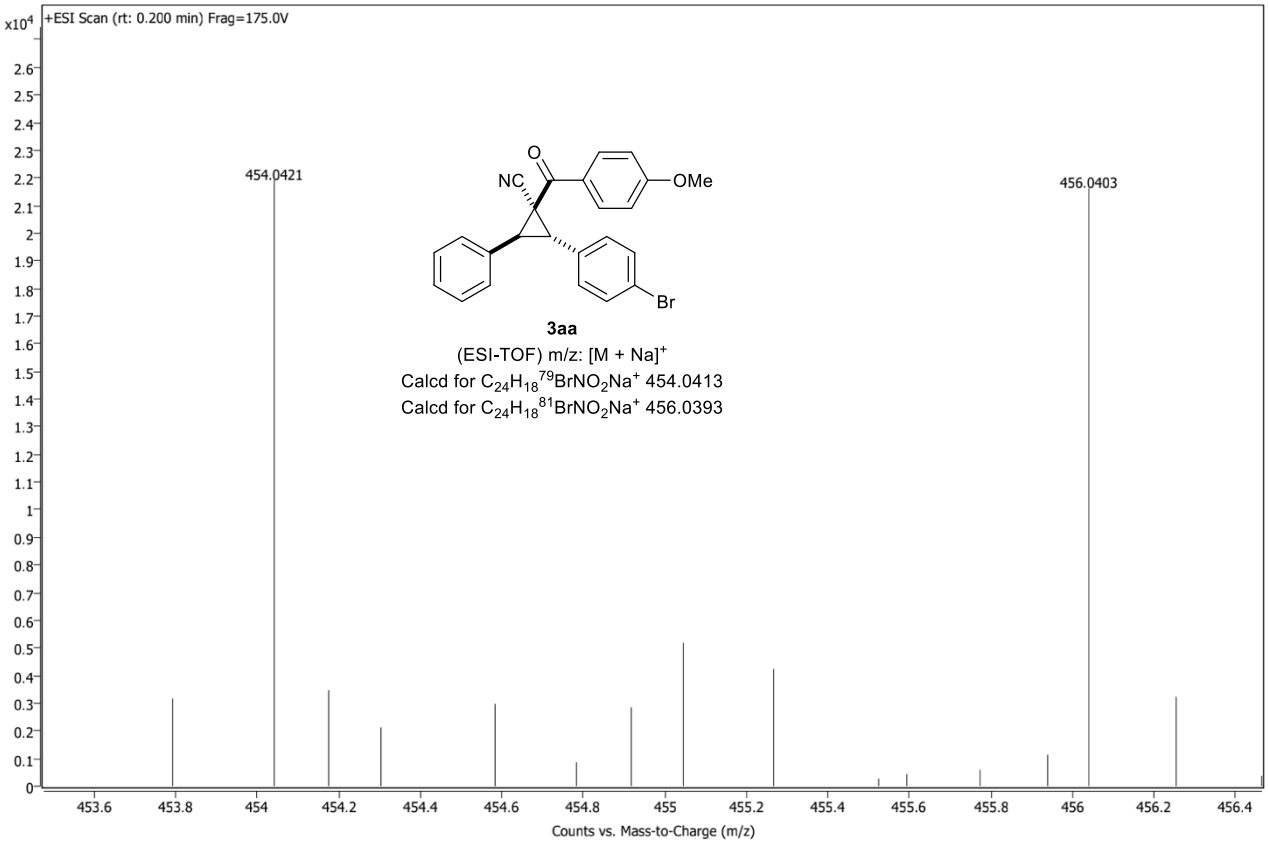
3aa

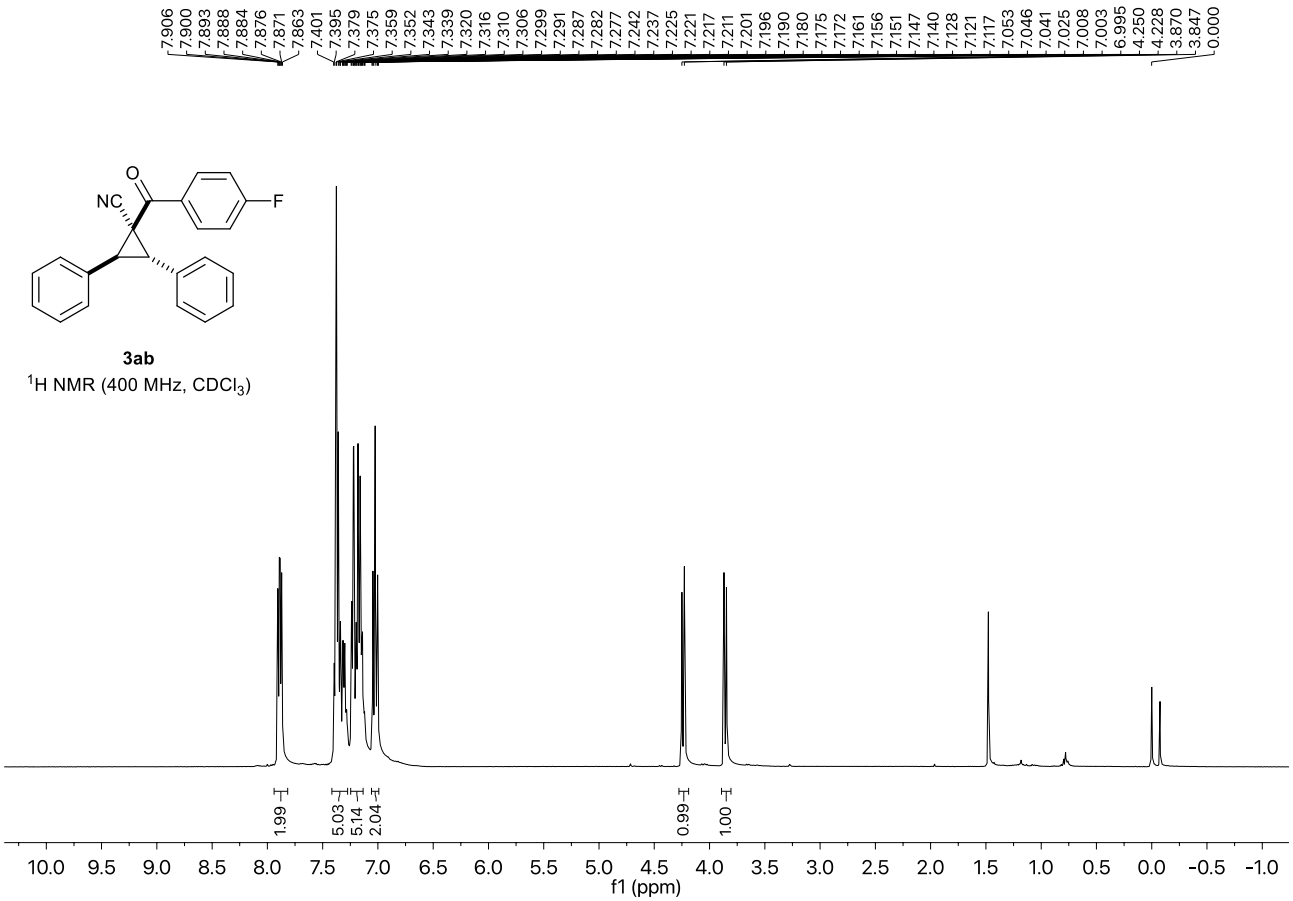
^{1}H NMR (400 MHz, $CDCl_3$)

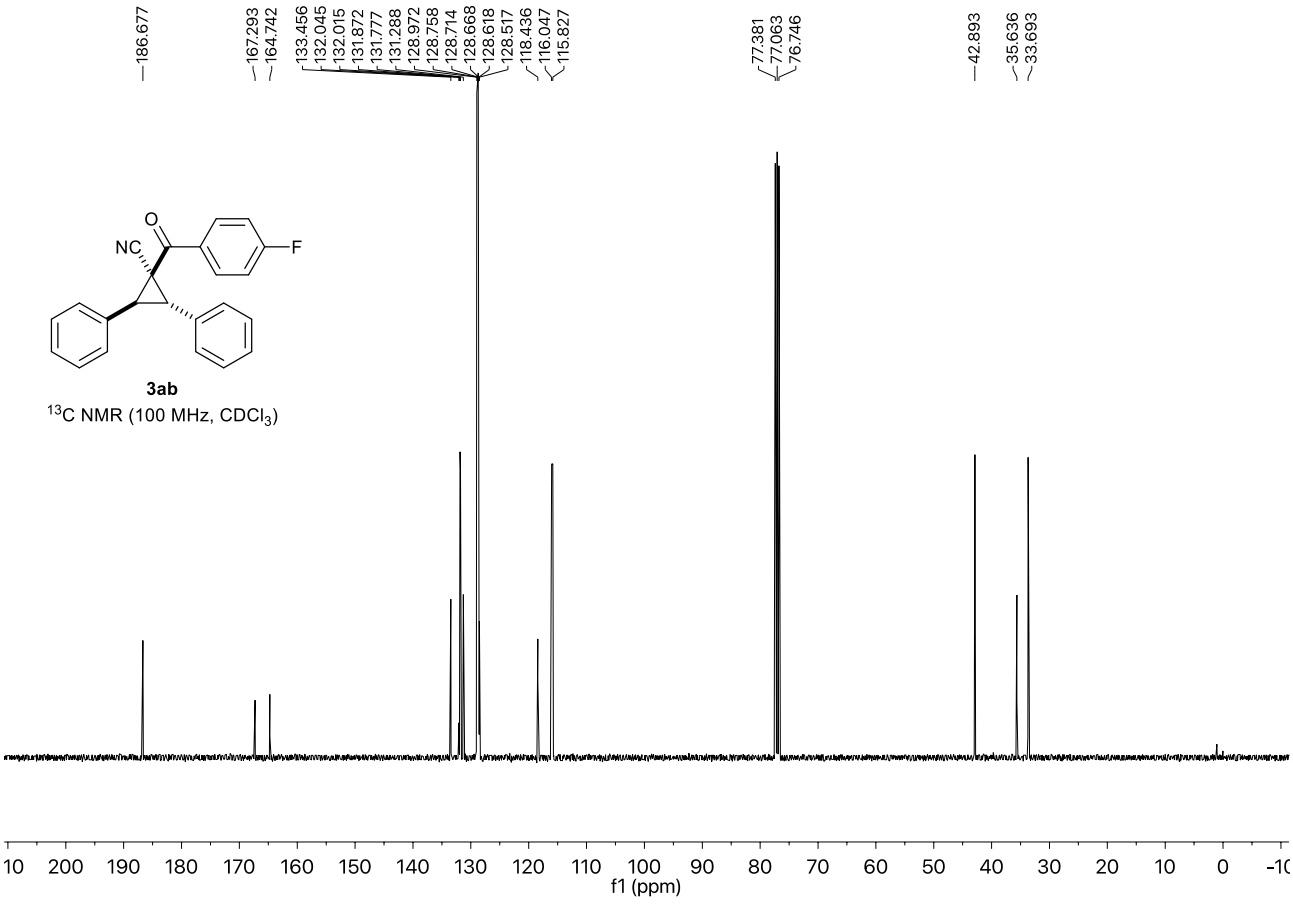


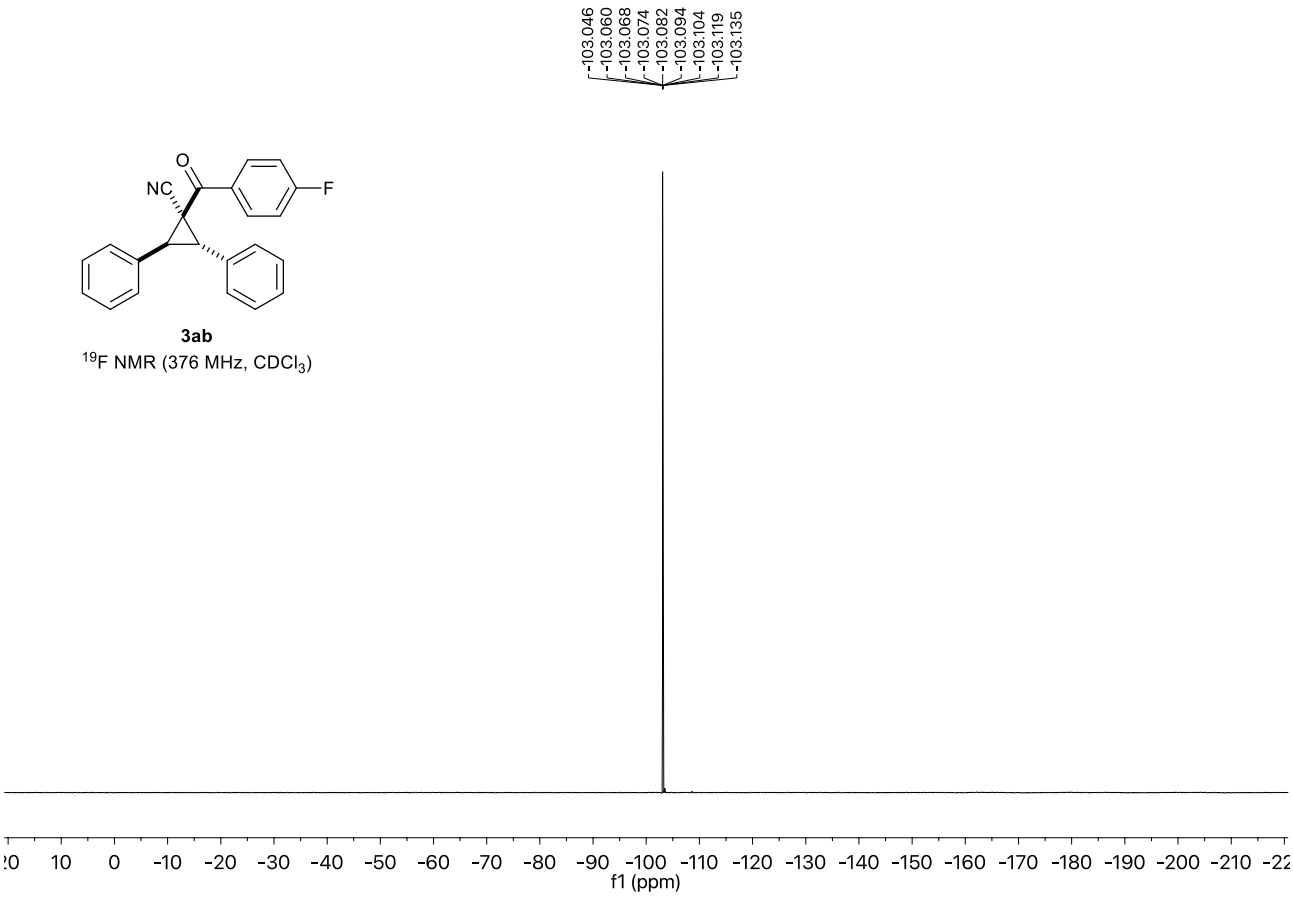
3aa

^{13}C NMR (100 MHz, $CDCl_3$)


+ESI Scan (rt: 0.200 min) Frag=175.0V
x10^4
454.0421
456.0403
NC
O
OMe
Br
3aa
(ESI-TOF) m/z: [M + Na]+
Calcd for C24H18 79BrNO2Na+ 454.0413
Calcd for C24H18 81BrNO2Na+ 456.0393
Counts vs. Mass-to-Charge (m/z)

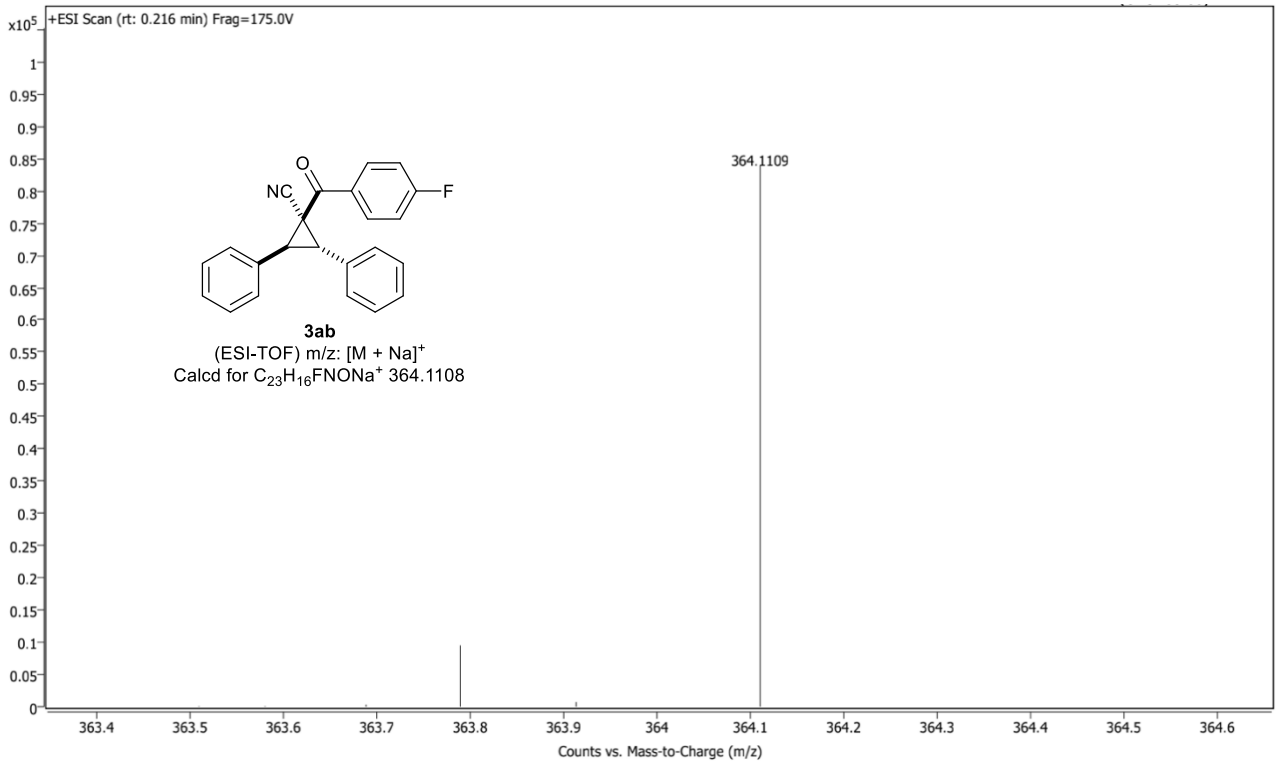

7.906
7.900
7.893
7.888
7.884
7.876
7.871
7.863
7.401
7.395
7.379
7.375
7.359
7.352
7.343
7.339
7.320
7.316
7.310
7.306
7.299
7.291
7.287
7.282
7.277
7.242
7.237
7.225
7.221
7.217
7.211
7.201
7.196
7.190
7.180
7.175
7.172
7.161
7.156
7.151
7.147
7.140
7.128
7.121
7.117
7.053
7.046
7.041
7.025
7.008
7.003
6.995
4.250
4.228
3.870
3.847
0.000
O
NC
F
3ab
1H NMR (400 MHz, CDCl3)
1.99
5.03
5.14
2.04
0.99
1.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.0
f1 (ppm)


186.677
167.293
164.742
133.456
132.045
132.015
131.872
131.777
131.288
128.972
128.758
128.714
128.668
128.618
128.517
118.436
116.047
115.827
77.381
77.063
76.746
42.893
35.636
33.693
O
NC
F
3ab
13C NMR (100 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



3ab

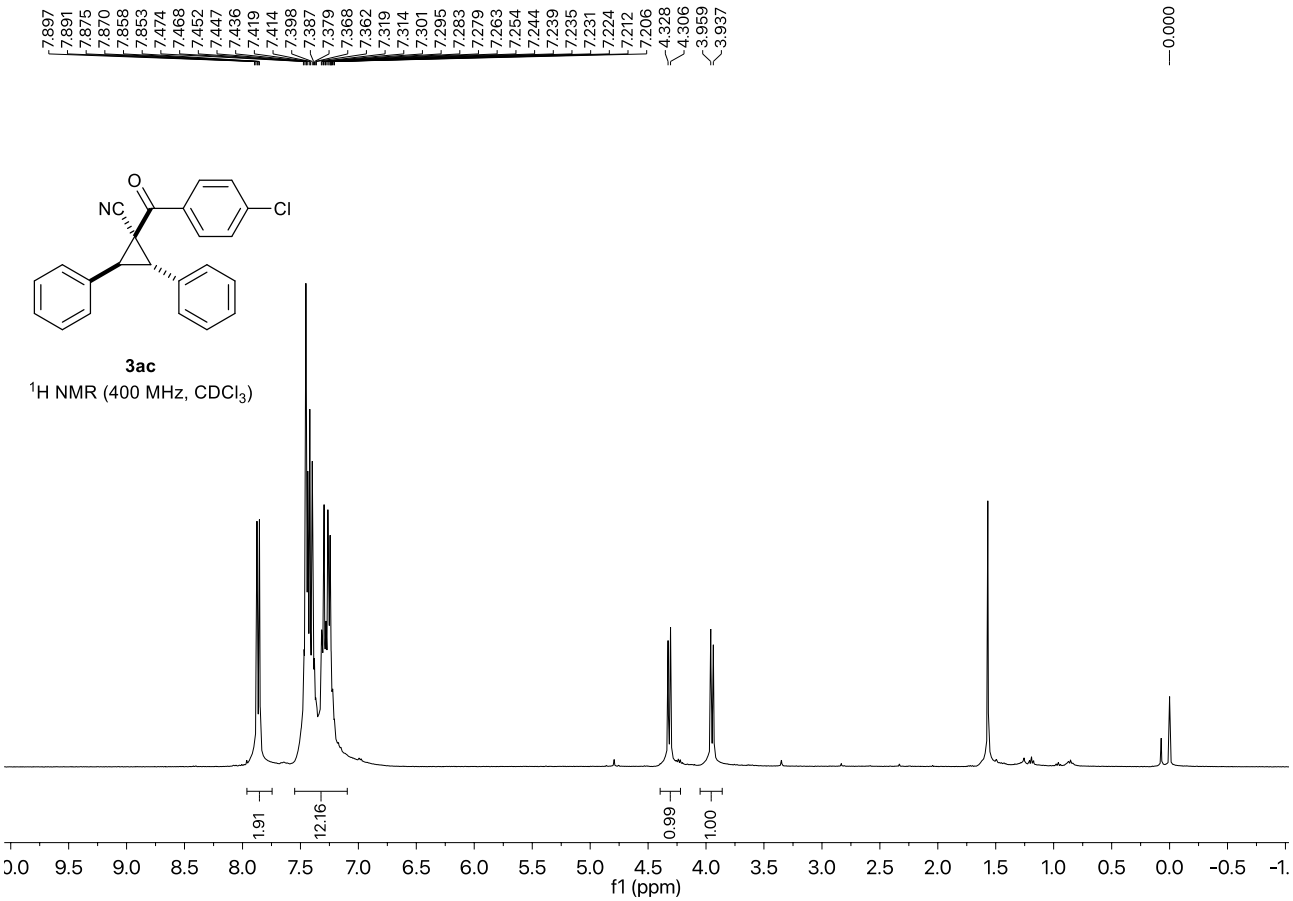
^{19}F NMR (376 MHz, $CDCl_3$)

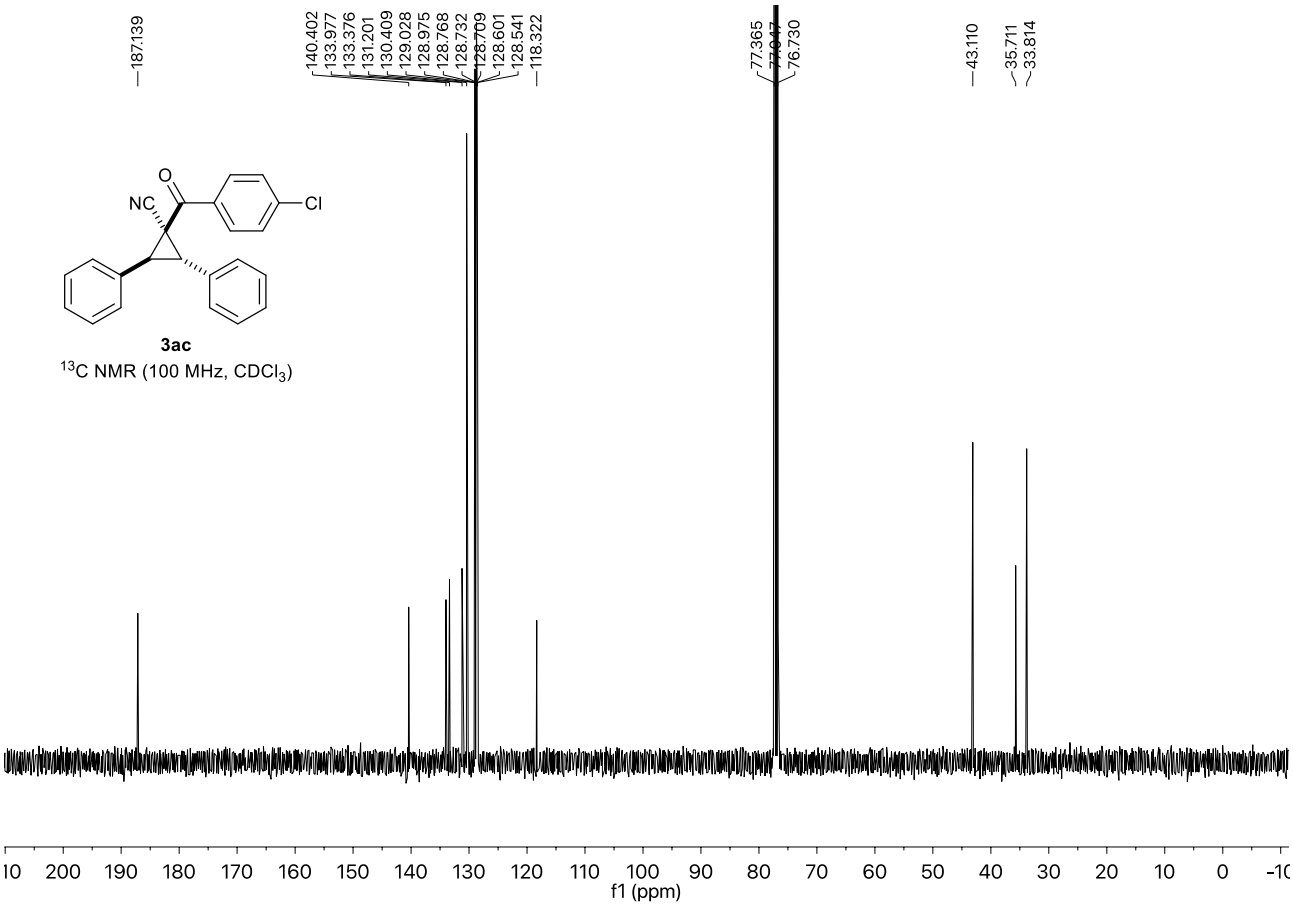


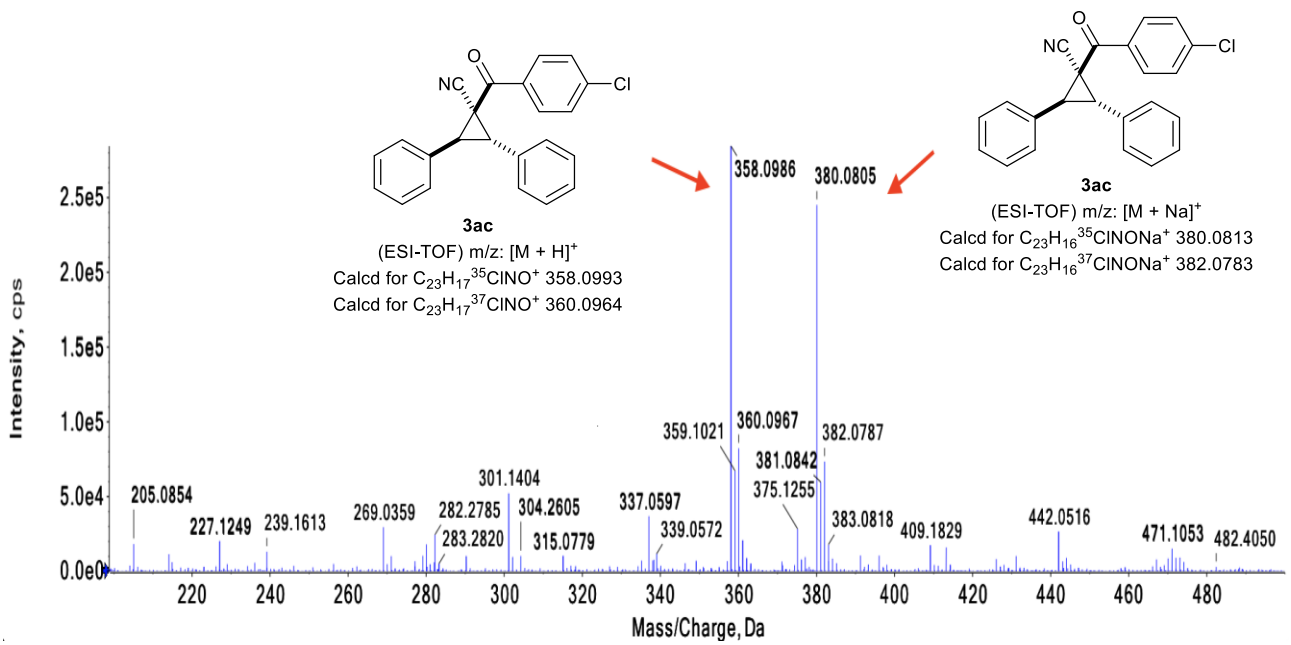
3ab

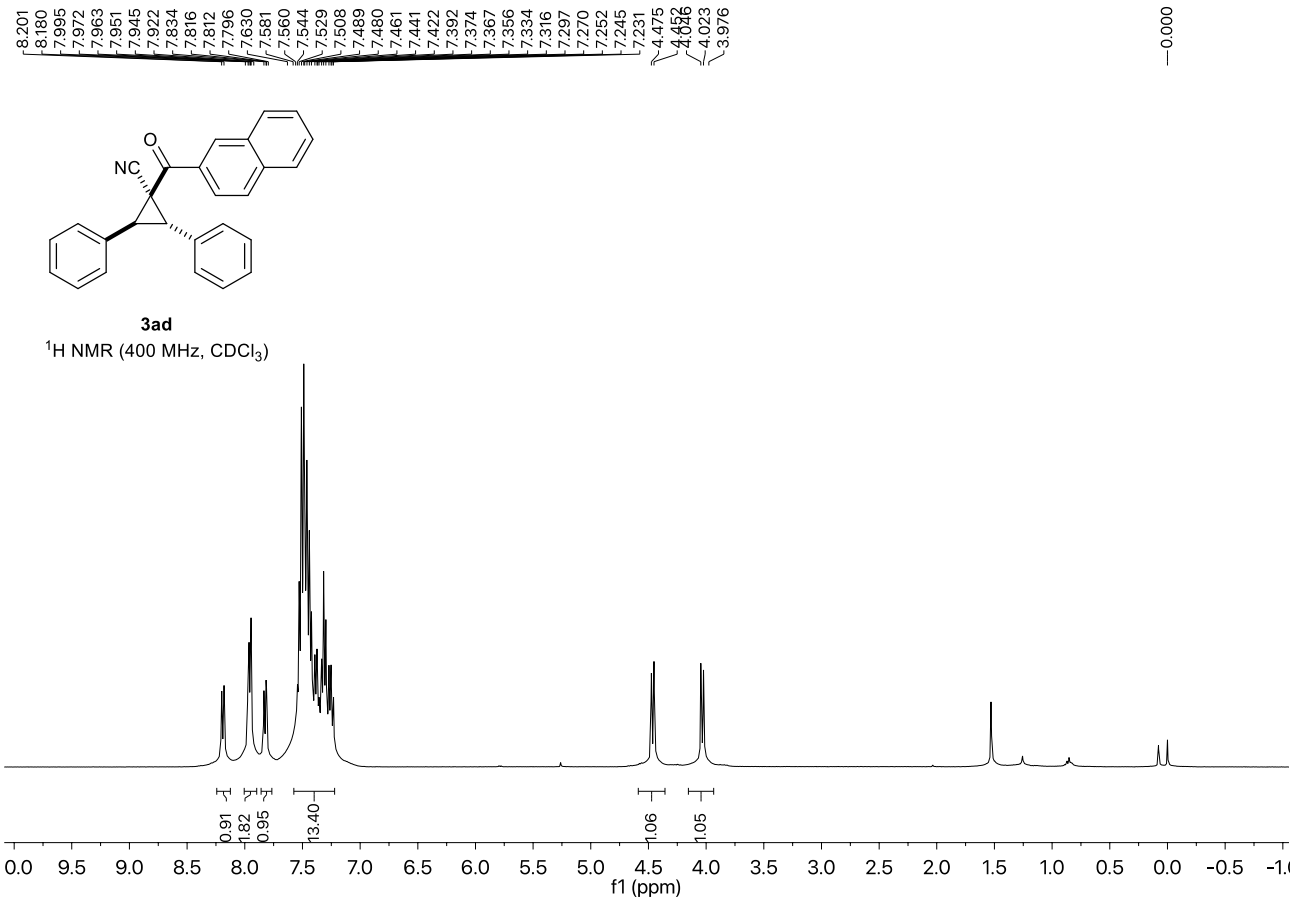
(ESI-TOF) m/z: $[M + Na]^+$

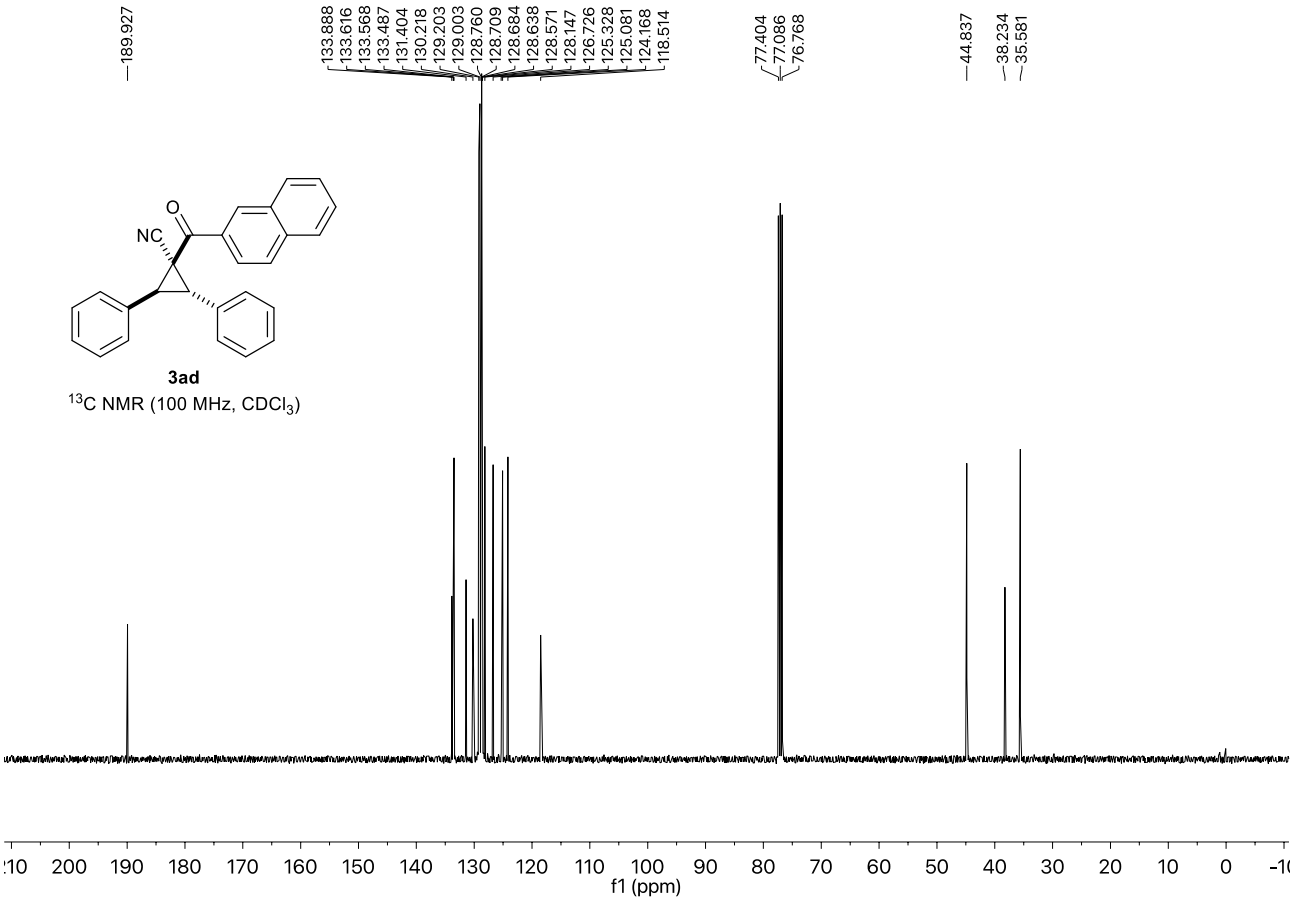
Calcd for $C_{23}H_{16}FNONa^+$ 364.1108

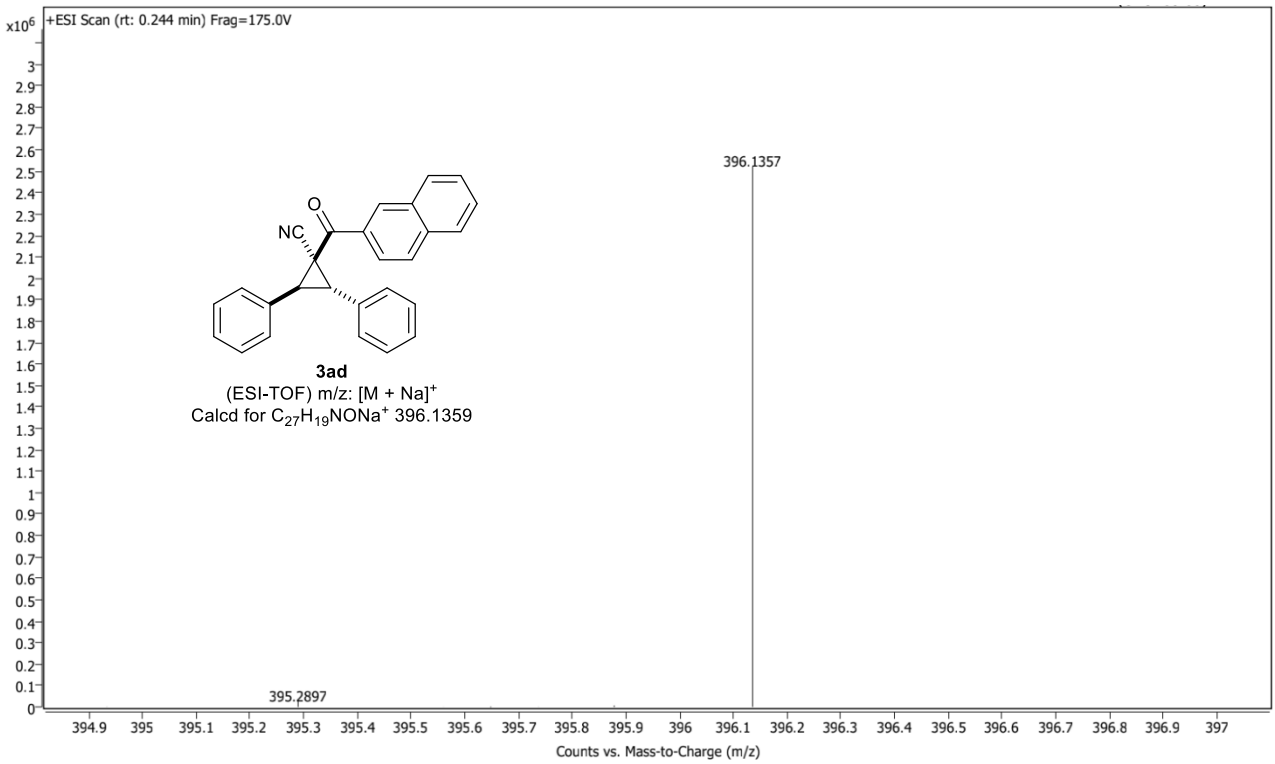

7.897
7.891
7.875
7.870
7.858
7.853
7.474
7.468
7.452
7.447
7.436
7.419
7.414
7.398
7.387
7.379
7.368
7.362
7.319
7.314
7.301
7.295
7.283
7.279
7.263
7.254
7.244
7.239
7.235
7.231
7.224
7.212
7.206
4.328
4.306
3.959
3.937
0.000
O
NC
Cl
3ac
1H NMR (400 MHz, CDCl3)
1.91
12.16
0.99
1.00
f1 (ppm)

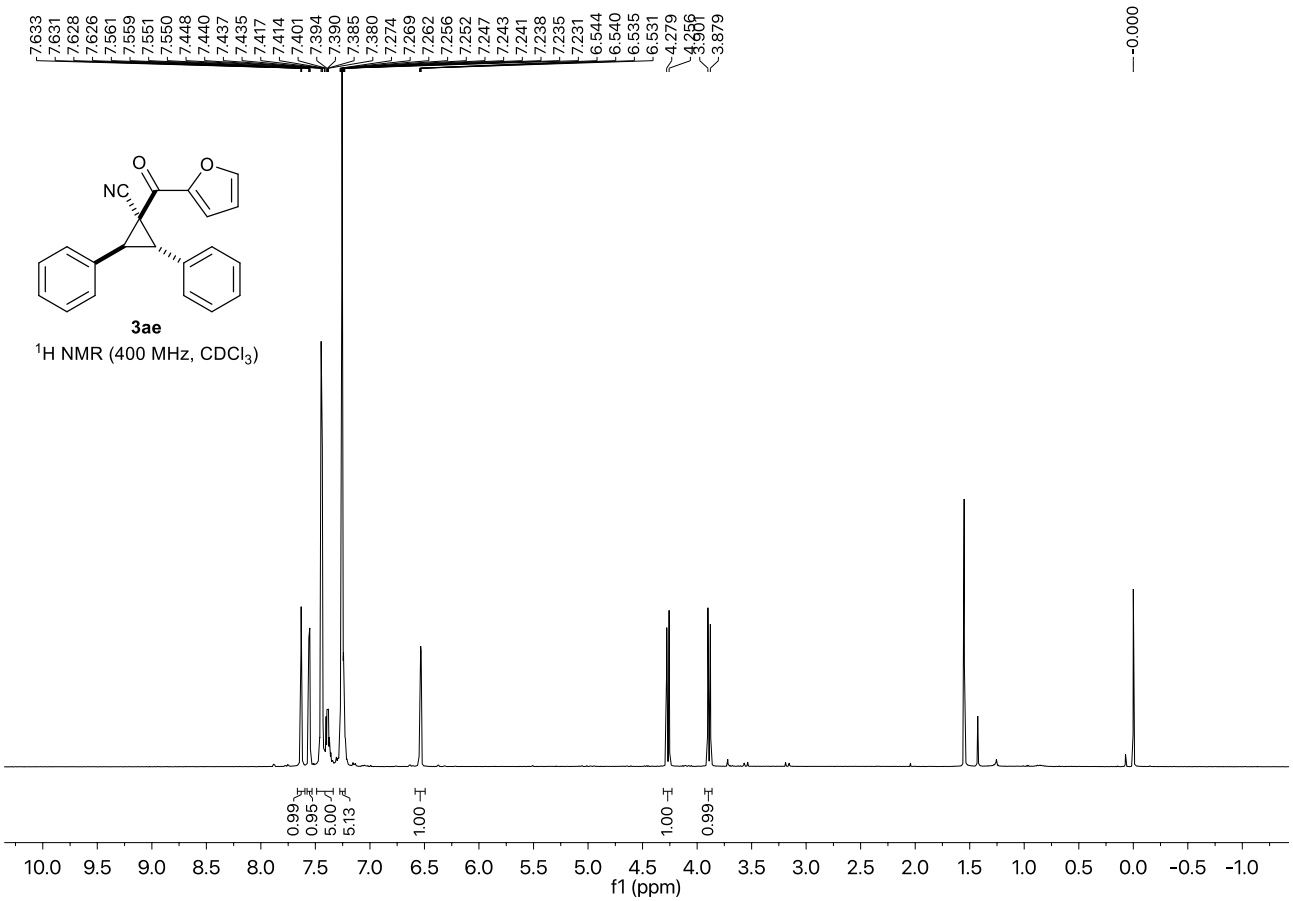

187.139
140.402
133.977
133.376
131.201
130.409
129.028
128.975
128.768
128.732
128.709
128.601
128.541
118.322
77.365
77.047
76.730
43.110
35.711
33.814
O
NC
Cl
3ac
13C NMR (100 MHz, CDCl3)
f1 (ppm)


3ac
(ESI-TOF) m/z: [M + H]+
Calcd for C23H17 35ClNO+ 358.0993
Calcd for C23H17 37ClNO+ 360.0964
3ac
(ESI-TOF) m/z: [M + Na]+
Calcd for C23H16 35ClNONa+ 380.0813
Calcd for C23H16 37ClNONa+ 382.0783
Intensity, cps
Mass/Charge, Da
358.0986
380.0805
359.1021
360.0967
382.0787
381.0842
375.1255
301.1404
304.2605
282.2785
283.2820
315.0779
337.0597
339.0572
205.0854
227.1249
239.1613
269.0359
383.0818
409.1829
442.0516
471.1053
482.4050


8.201
8.180
7.995
7.972
7.963
7.951
7.945
7.922
7.834
7.816
7.812
7.796
7.630
7.581
7.560
7.544
7.529
7.508
7.489
7.480
7.461
7.441
7.422
7.392
7.374
7.367
7.356
7.334
7.316
7.297
7.270
7.252
7.245
7.231
4.475
4.452
4.046
4.023
3.976
0.000
O
NC
3ad
1H NMR (400 MHz, CDCl3)
0.91
1.82
0.95
13.40
1.06
1.05
f1 (ppm)

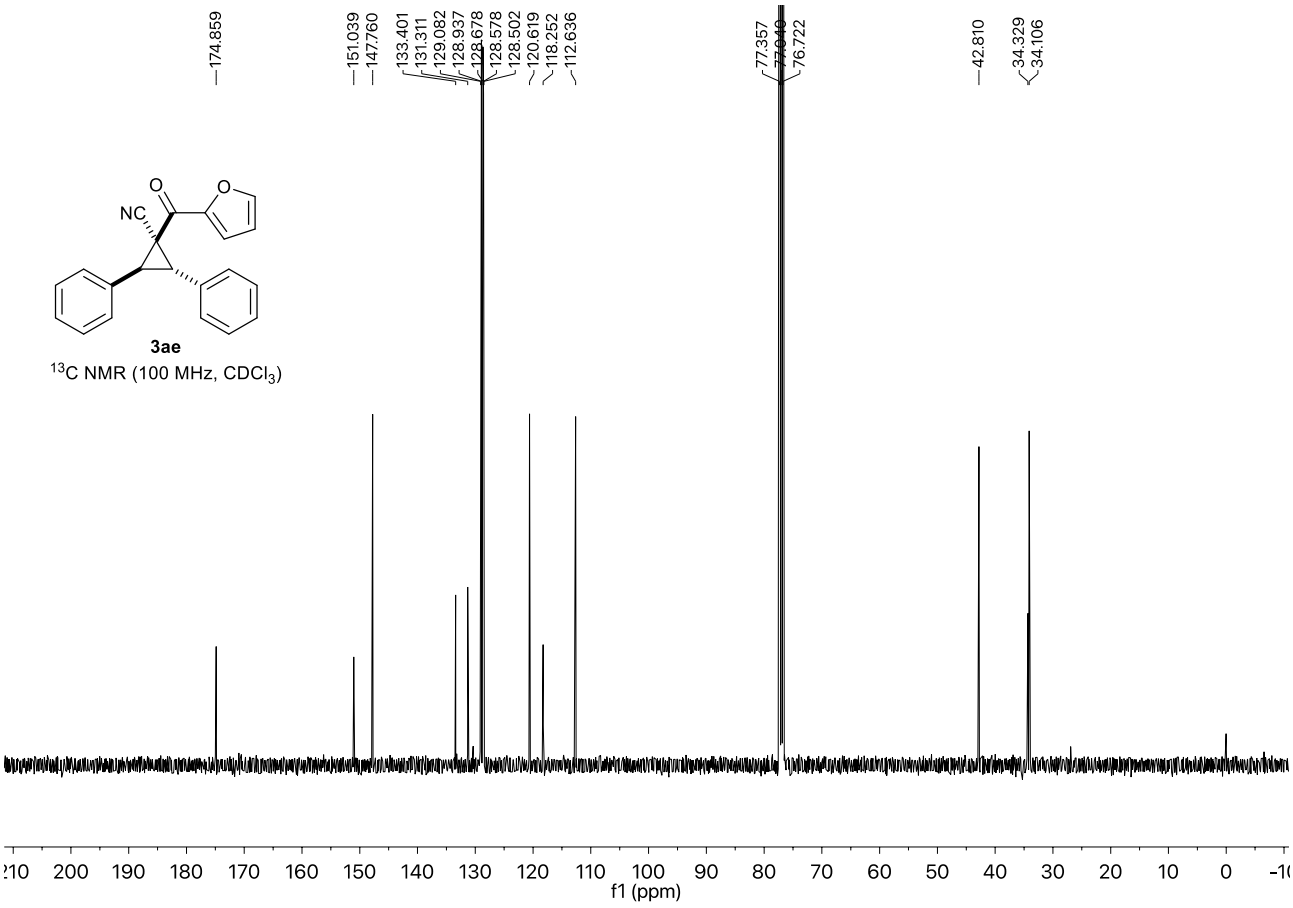

189.927
133.888
133.616
133.568
133.487
131.404
130.218
129.203
129.003
128.760
128.709
128.684
128.638
128.571
128.147
126.726
125.328
125.081
124.168
118.514
77.404
77.086
76.768
44.837
38.234
35.581
O
NC
3ad
13C NMR (100 MHz, CDCl3)
f1 (ppm)


+ESI Scan (rt: 0.244 min) Frag=175.0V
x10^6
396.1357
395.2897
O
NC
3ad
(ESI-TOF) m/z: [M + Na]+
Calcd for C27H19NONa+ 396.1359
Counts vs. Mass-to-Charge (m/z)



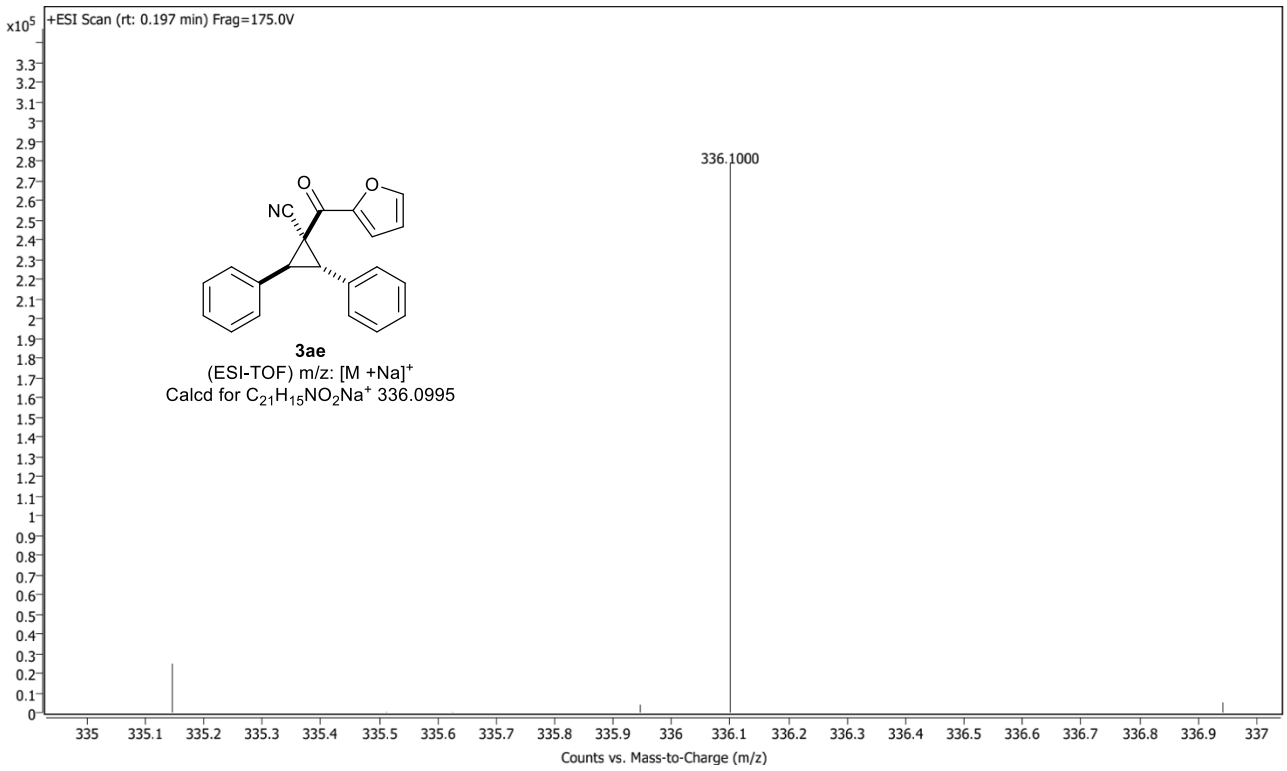
3ae

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



3ae

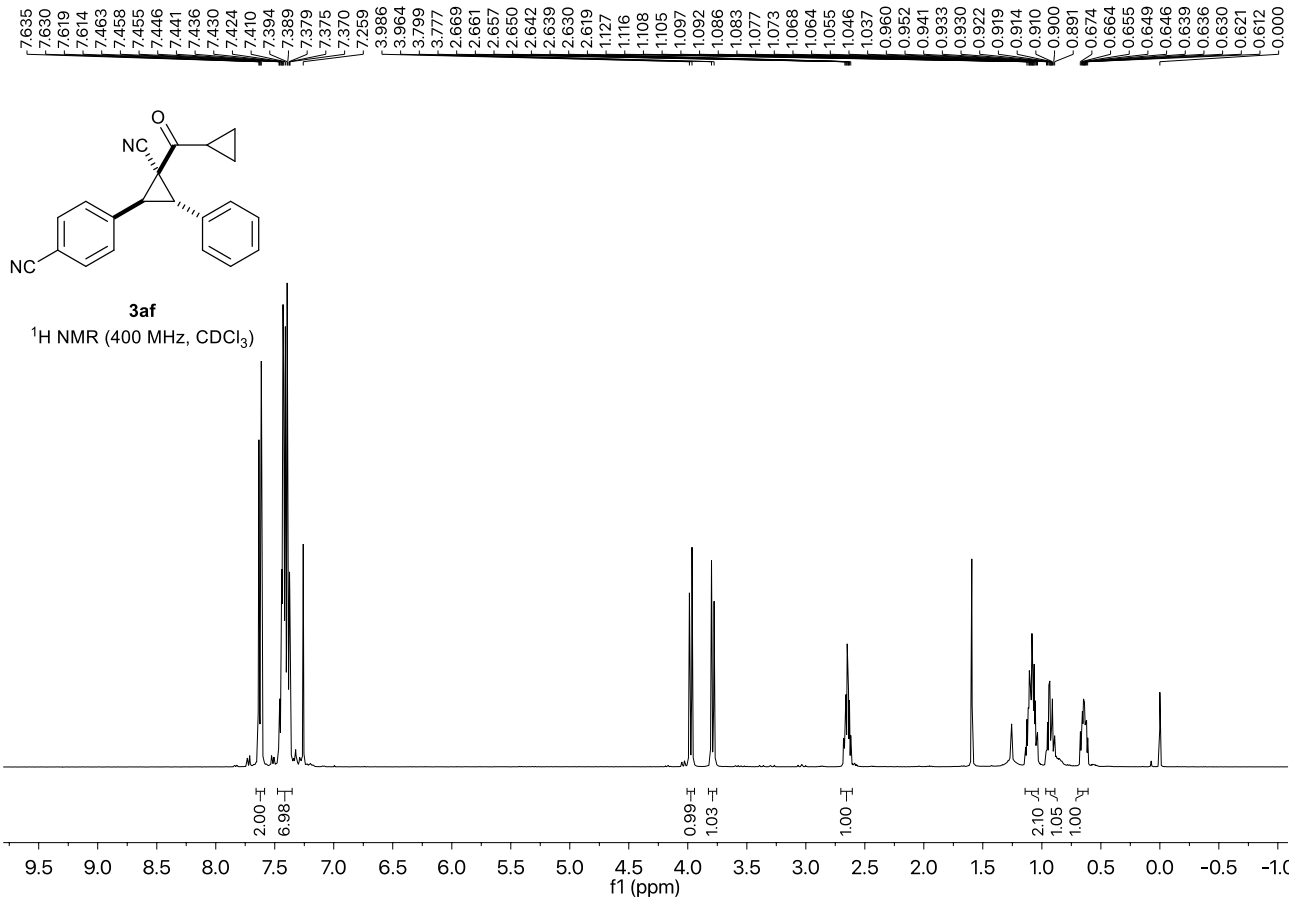
^{13}C NMR (100 MHz, $CDCl_3$)

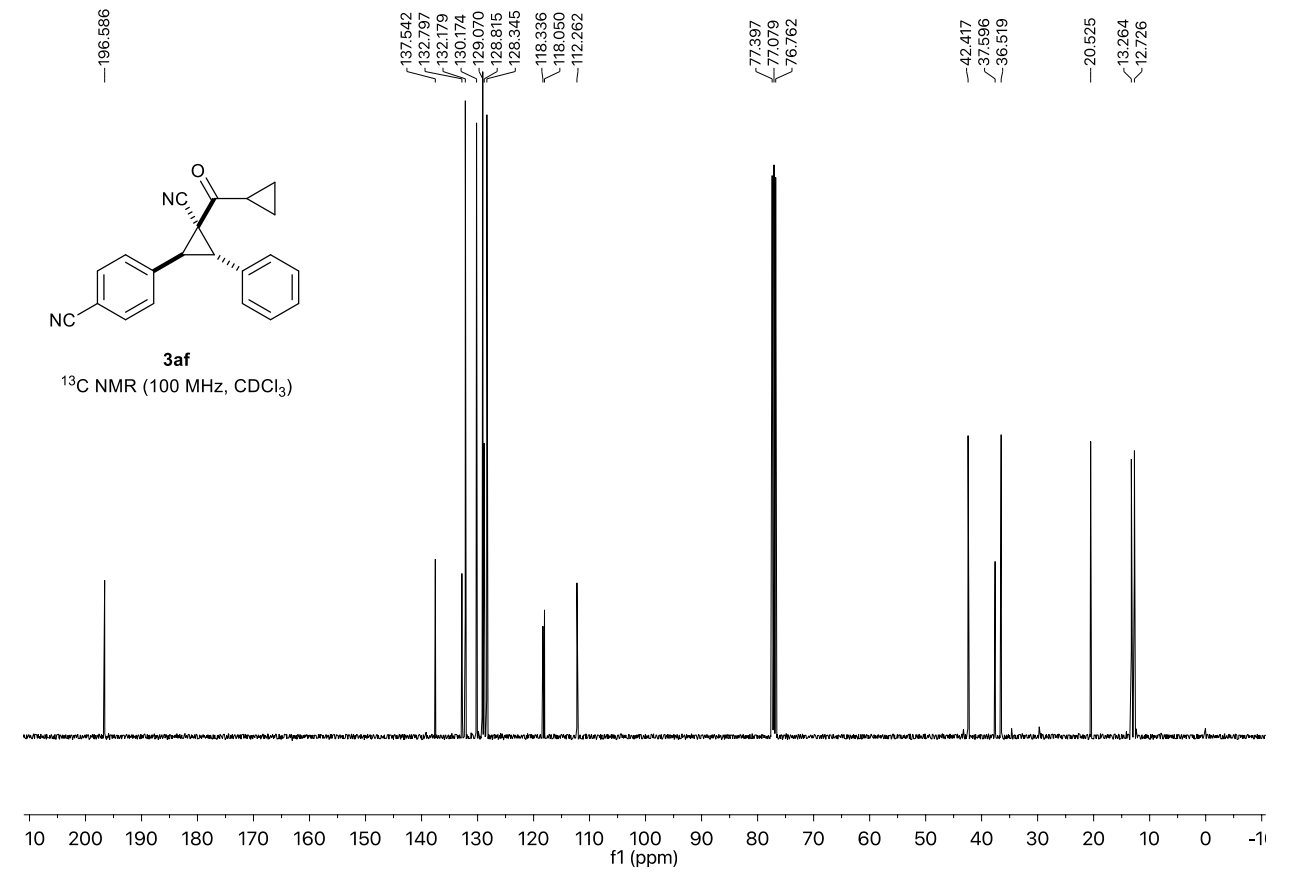


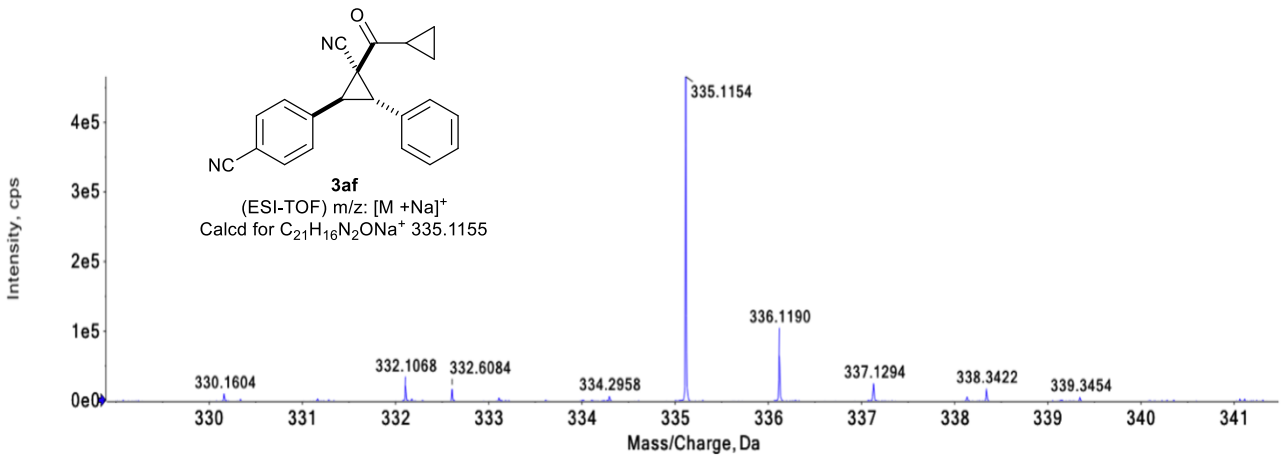
3ae

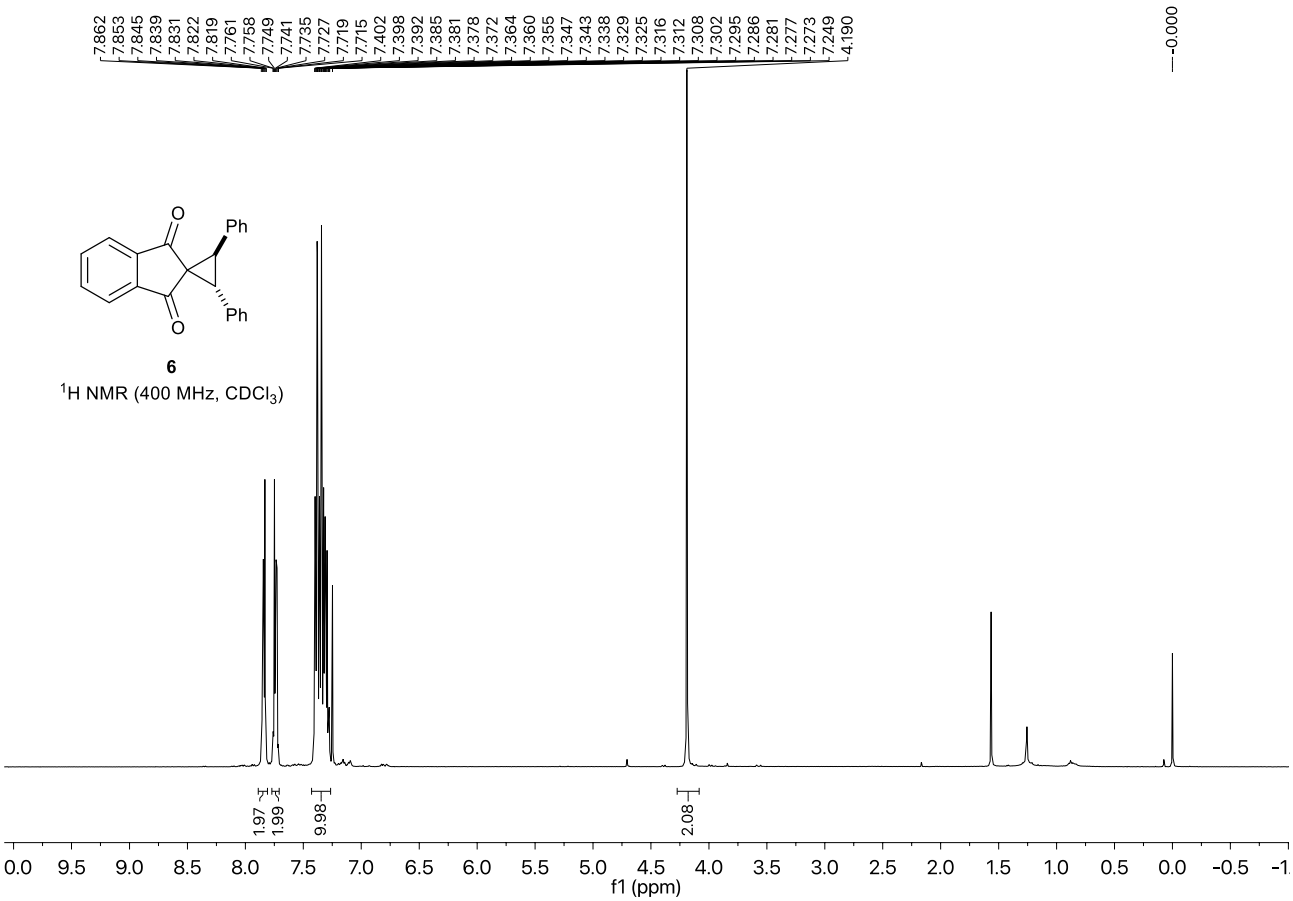
(ESI-TOF) m/z: $[M+Na]^+$

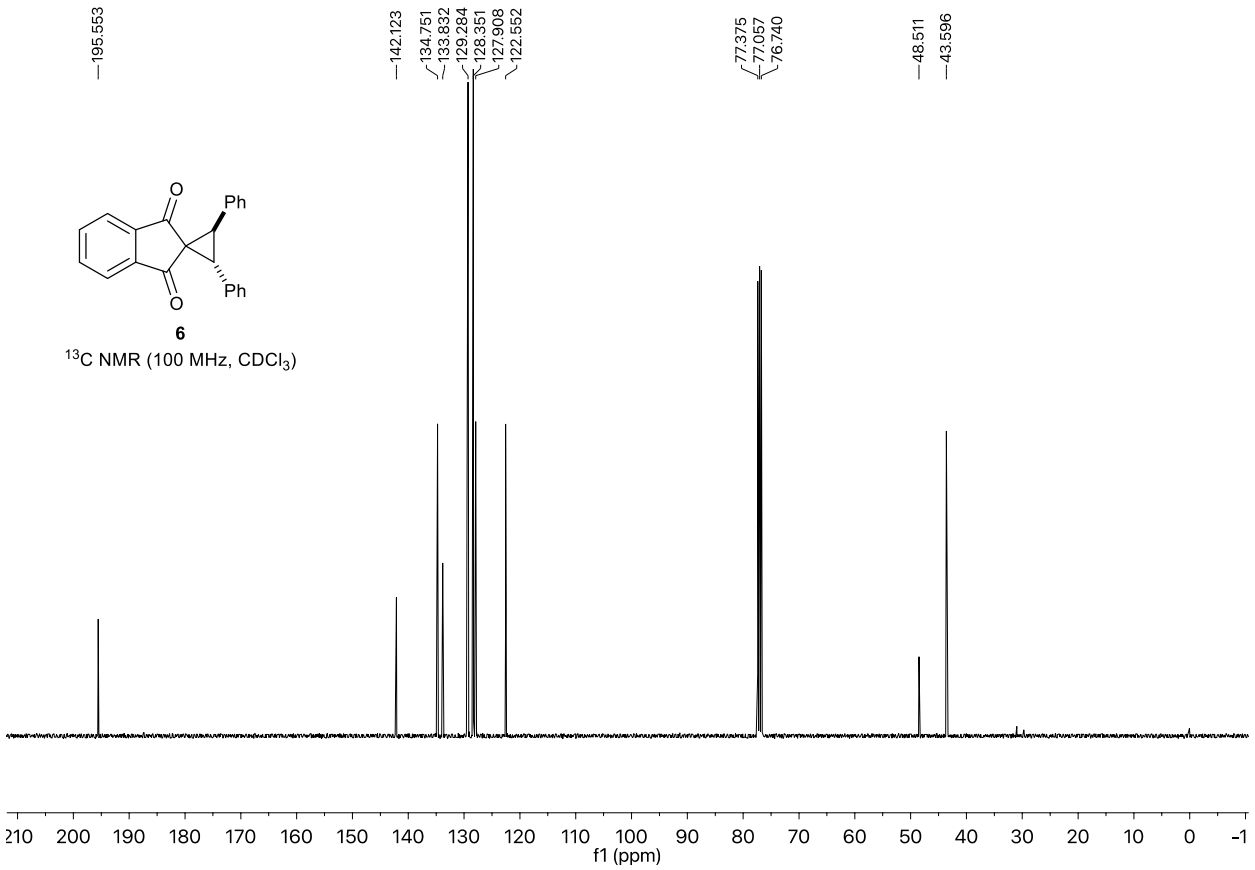
Calcd for $C_{21}H_{15}NO_2Na^+$ 336.0995

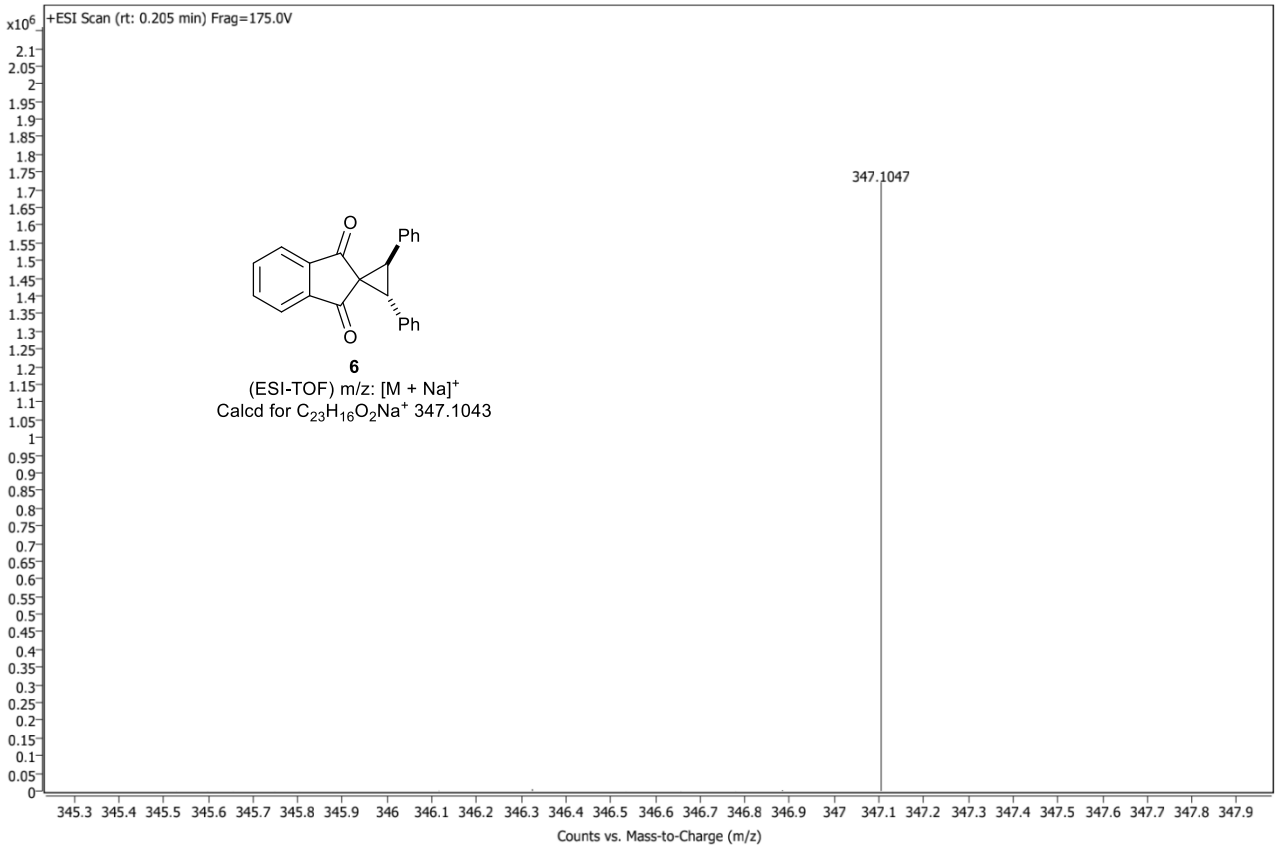

7.635
7.630
7.619
7.614
7.463
7.458
7.455
7.446
7.441
7.436
7.430
7.424
7.410
7.394
7.389
7.379
7.375
7.370
7.259
3.986
3.964
3.799
3.777
2.669
2.661
2.657
2.650
2.642
2.639
2.630
2.619
1.127
1.116
1.108
1.105
1.097
1.092
1.086
1.083
1.077
1.073
1.068
1.064
1.055
1.046
1.037
0.960
0.952
0.941
0.933
0.930
0.922
0.919
0.914
0.910
0.900
0.891
0.674
0.664
0.655
0.649
0.646
0.639
0.636
0.630
0.621
0.612
0.000
O
NC
NC
3af
1H NMR (400 MHz, CDCl3)
2.00
6.98
0.99
1.03
1.00
2.10
1.05
1.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


196.586
137.542
132.797
132.179
130.174
129.070
128.815
128.345
118.336
118.050
112.262
77.397
77.079
76.762
42.417
37.596
36.519
20.525
13.264
12.726
O
NC
NC
3af
13C NMR (100 MHz, CDCl3)
10 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


O
NC
NC
3af
(ESI-TOF) m/z: [M +Na]+
Calcd for C21H16N2ONa+ 335.1155
Intensity, cps
4e5
3e5
2e5
1e5
0e0
330.1604
332.1068
332.6084
334.2958
335.1154
336.1190
337.1294
338.3422
339.3454
330
331
332
333
334
335
336
337
338
339
340
341
Mass/Charge, Da


7.862
7.853
7.845
7.839
7.831
7.822
7.819
7.761
7.758
7.749
7.741
7.735
7.727
7.719
7.715
7.402
7.398
7.392
7.385
7.381
7.378
7.372
7.364
7.360
7.355
7.347
7.343
7.338
7.329
7.325
7.316
7.312
7.308
7.302
7.295
7.286
7.281
7.277
7.273
7.249
4.190
0.000
O
Ph
Ph
O
6
1H NMR (400 MHz, CDCl3)
1.97
1.99
9.98
2.08
f1 (ppm)

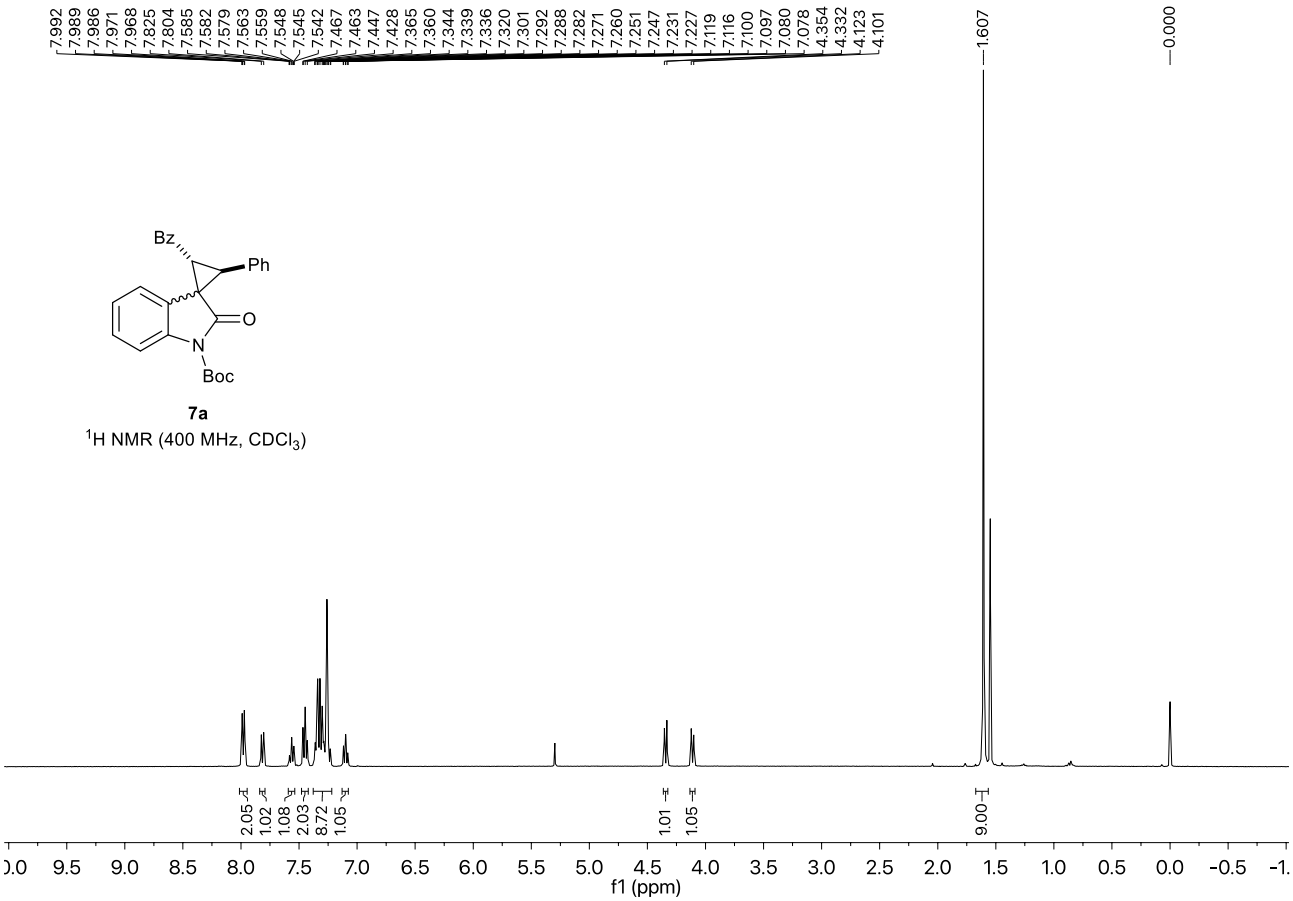

195.553
142.123
134.751
133.832
129.284
128.351
127.908
122.552
77.375
77.057
76.740
48.511
43.596
O
Ph
Ph
O
6
13C NMR (100 MHz, CDCl3)
f1 (ppm)



6

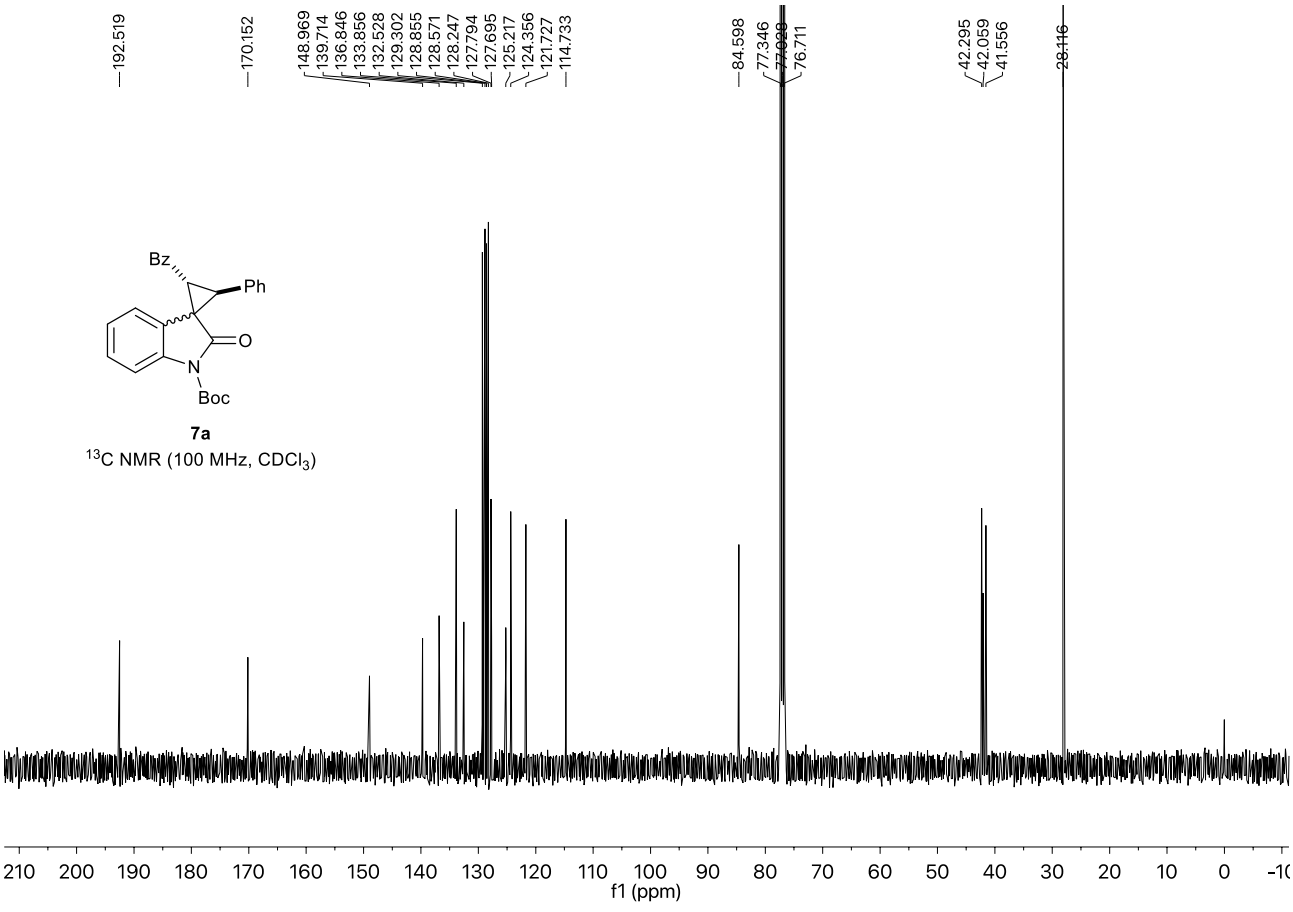
(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{23}H_{16}O_2Na^+$ 347.1043



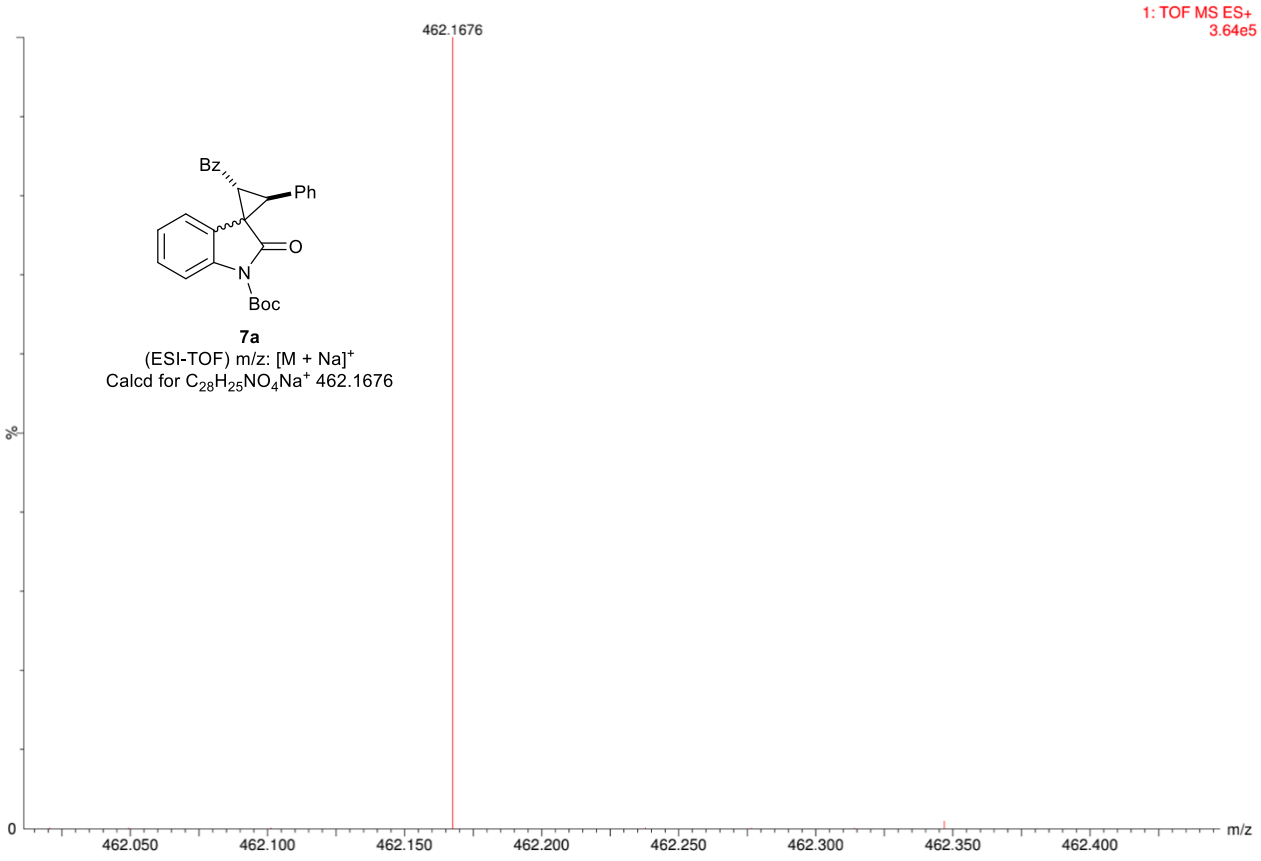
7a

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



7a

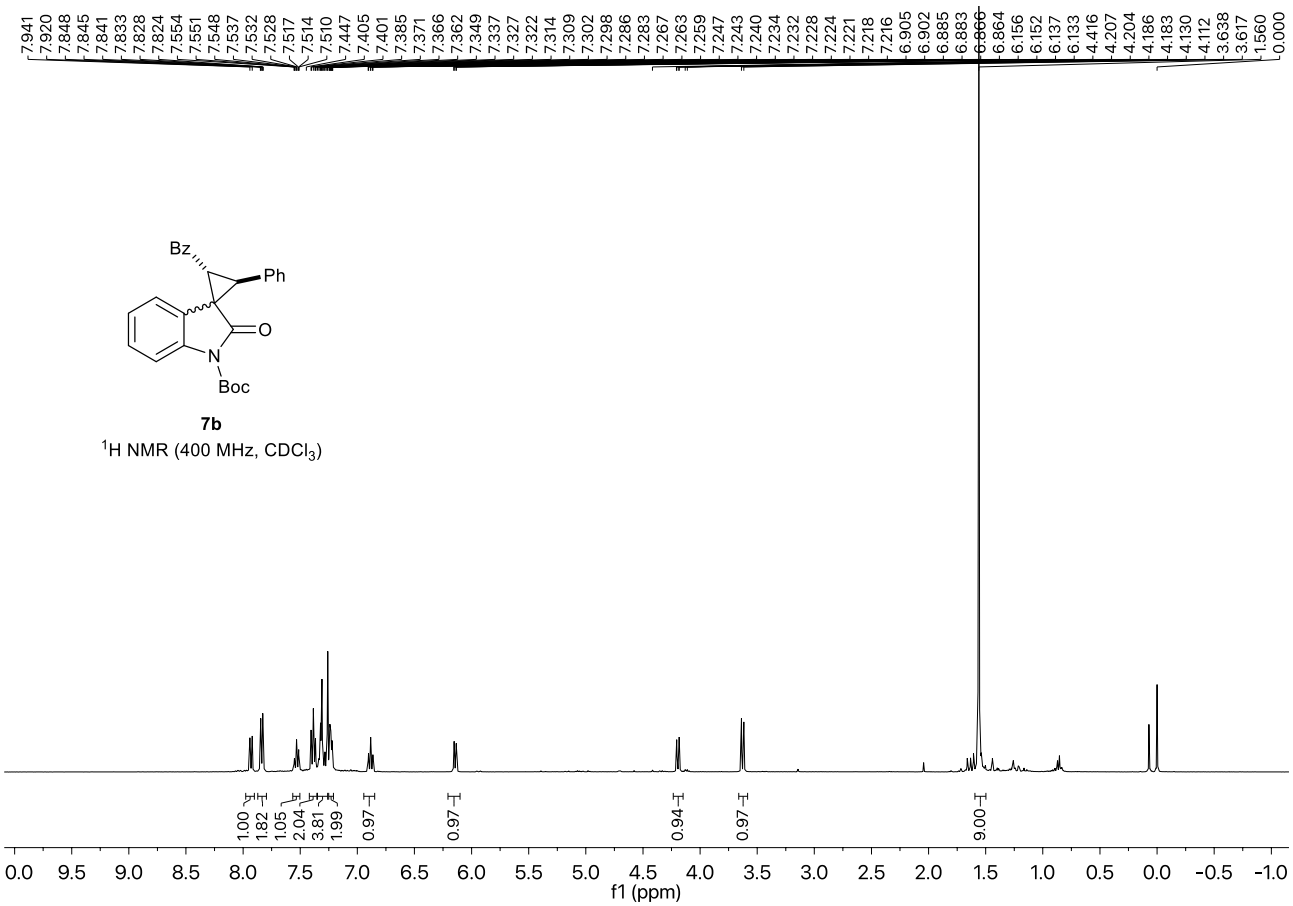
^{13}C NMR (100 MHz, $CDCl_3$)

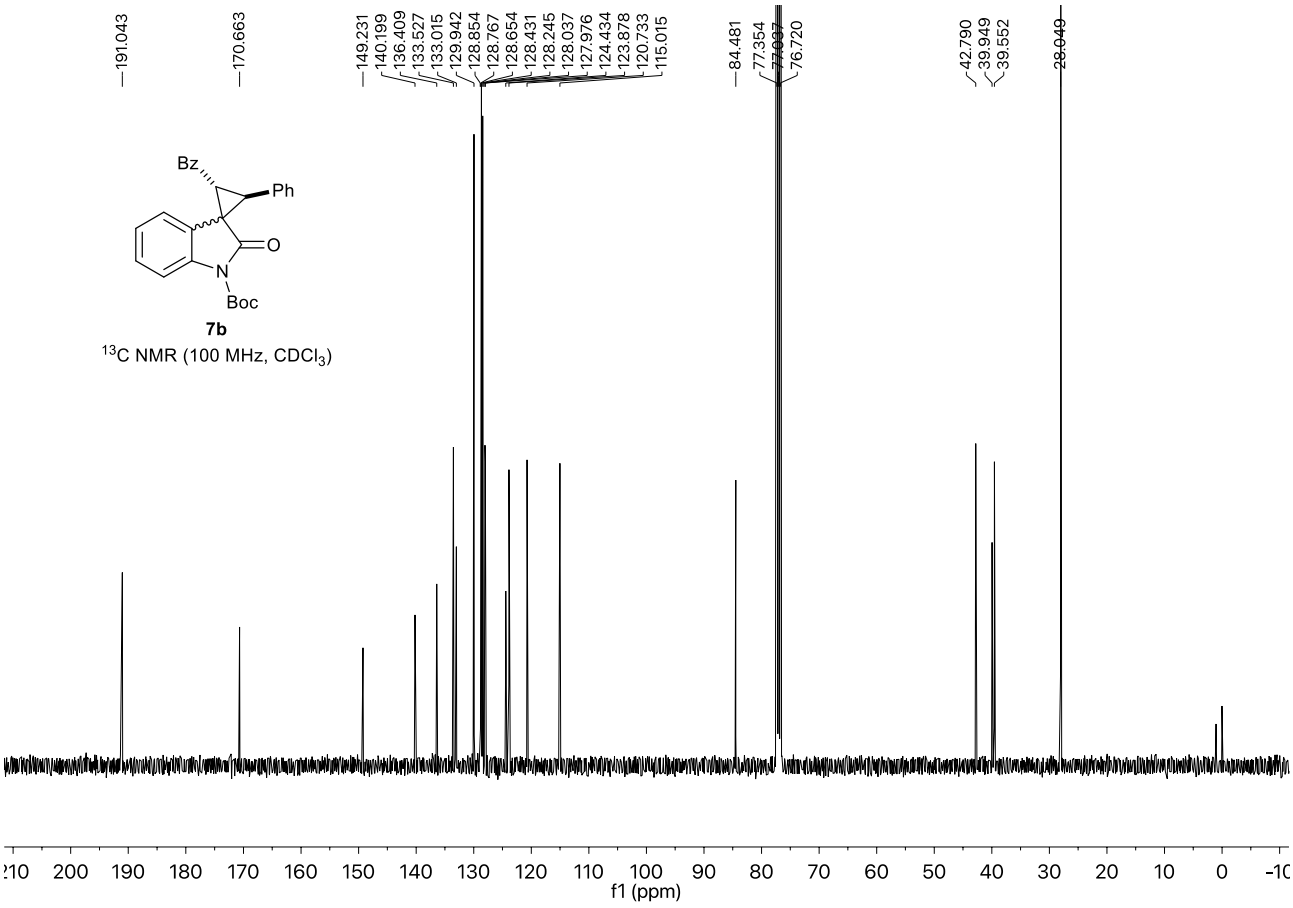


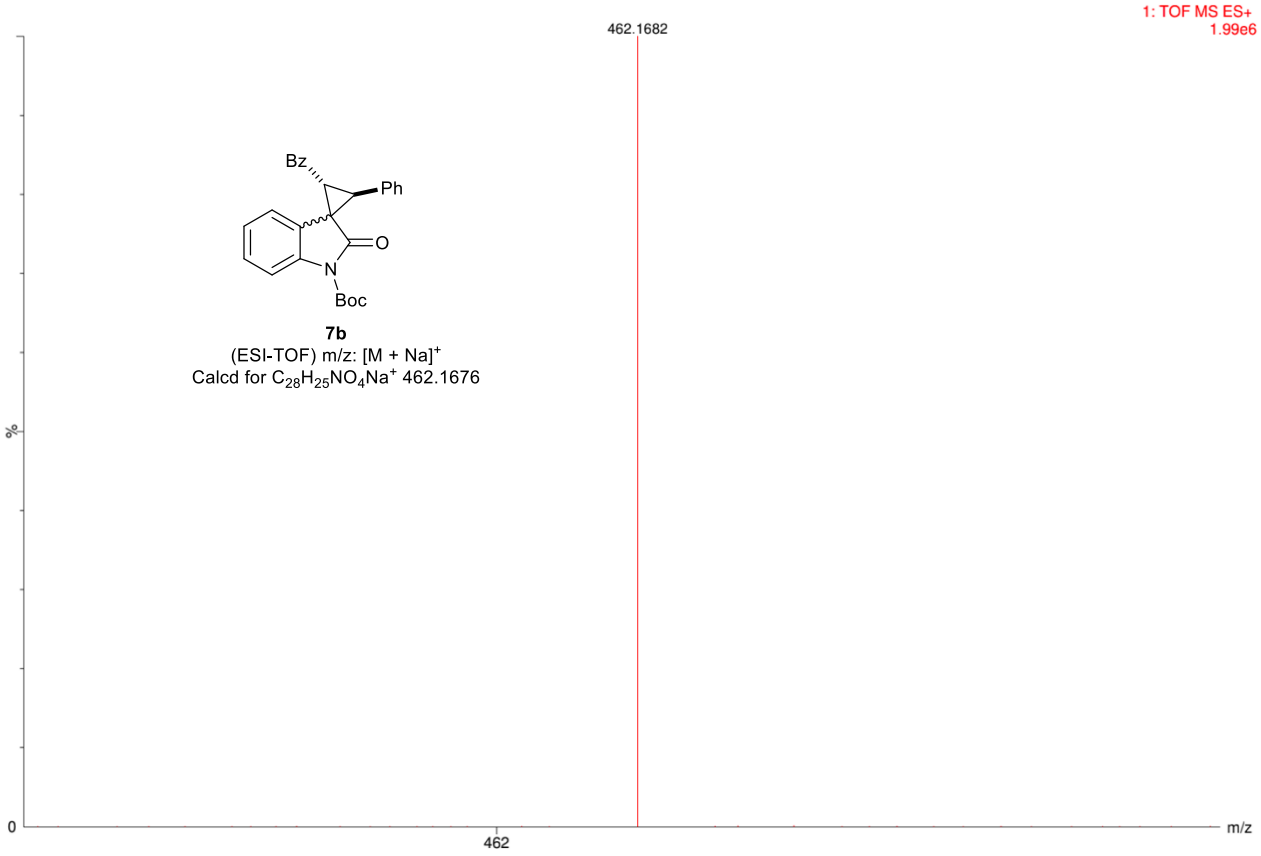
7a

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{28}H_{25}NO_4Na^+$ 462.1676


Bz
Ph
O
N
Boc
7b
1H NMR (400 MHz, CDCl3)
f1 (ppm)

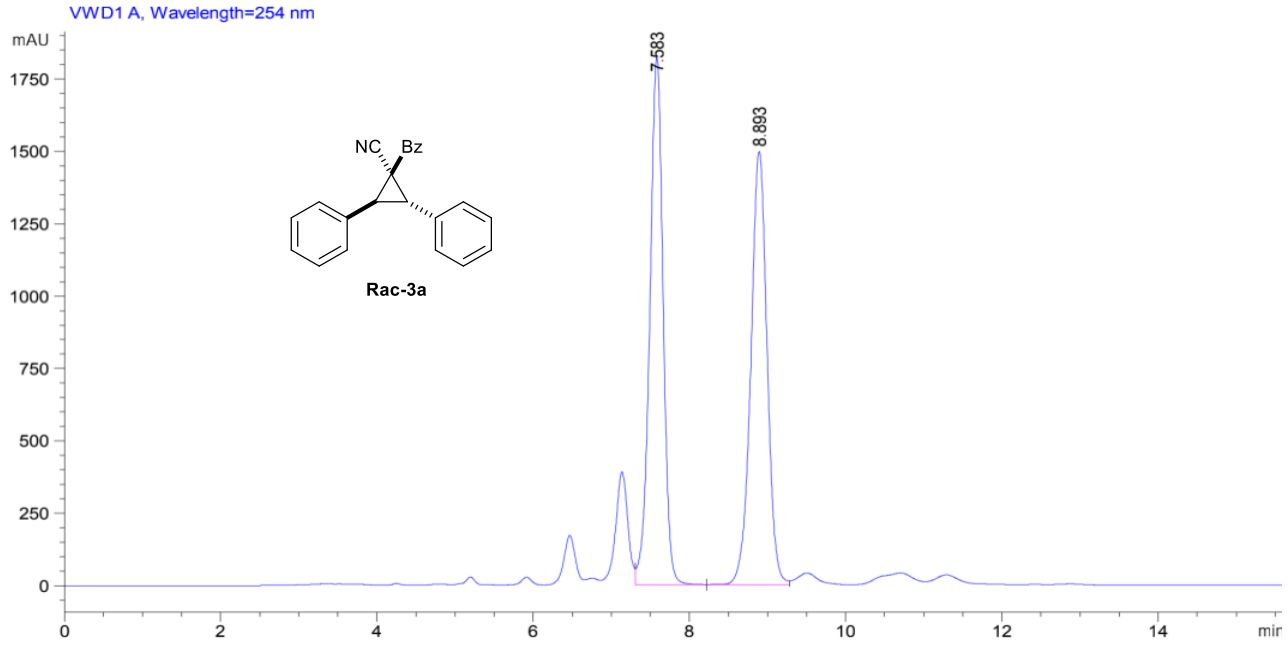

Bz
Ph
O
N
Boc
7b
13C NMR (100 MHz, CDCl3)
f1 (ppm)



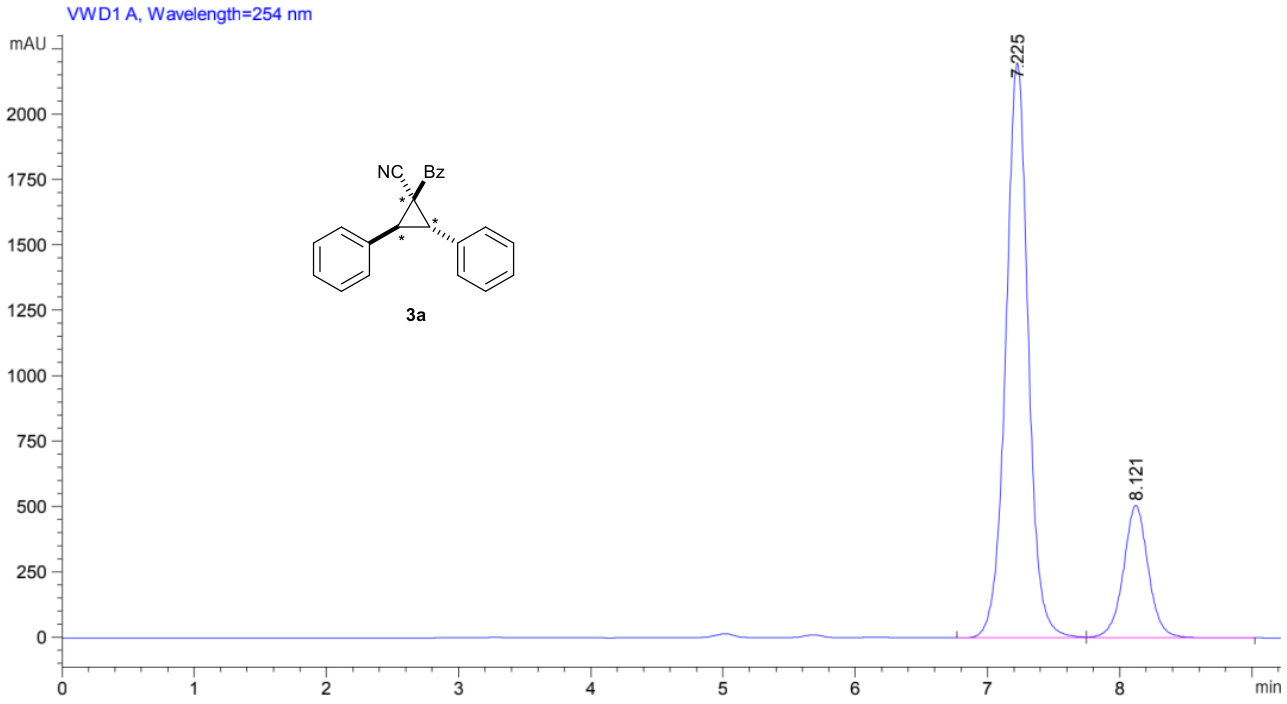
7b

(ESI-TOF) m/z: $[M + Na]^+$

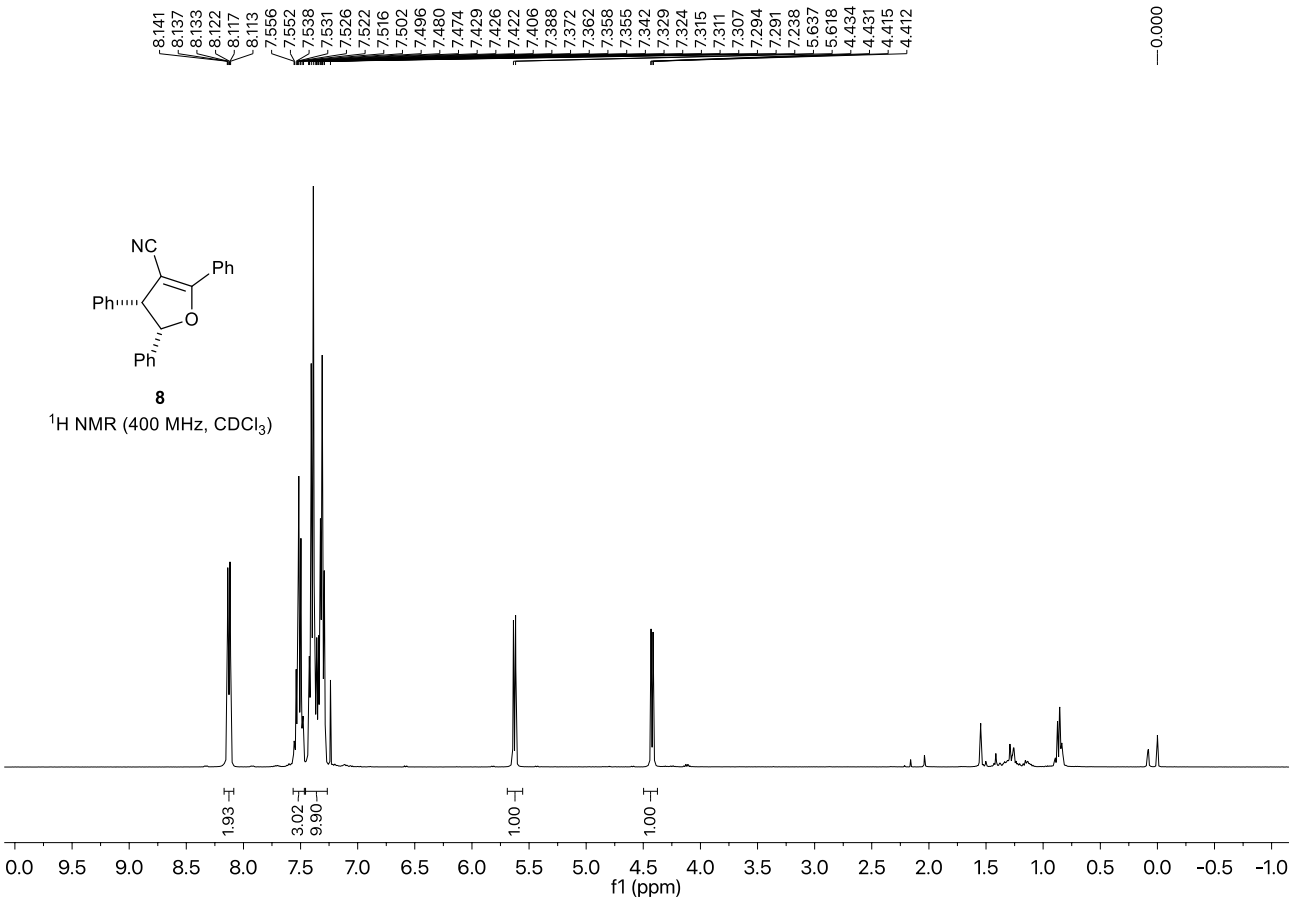
Calcd for $C_{28}H_{25}NO_4Na^+$ 462.1676

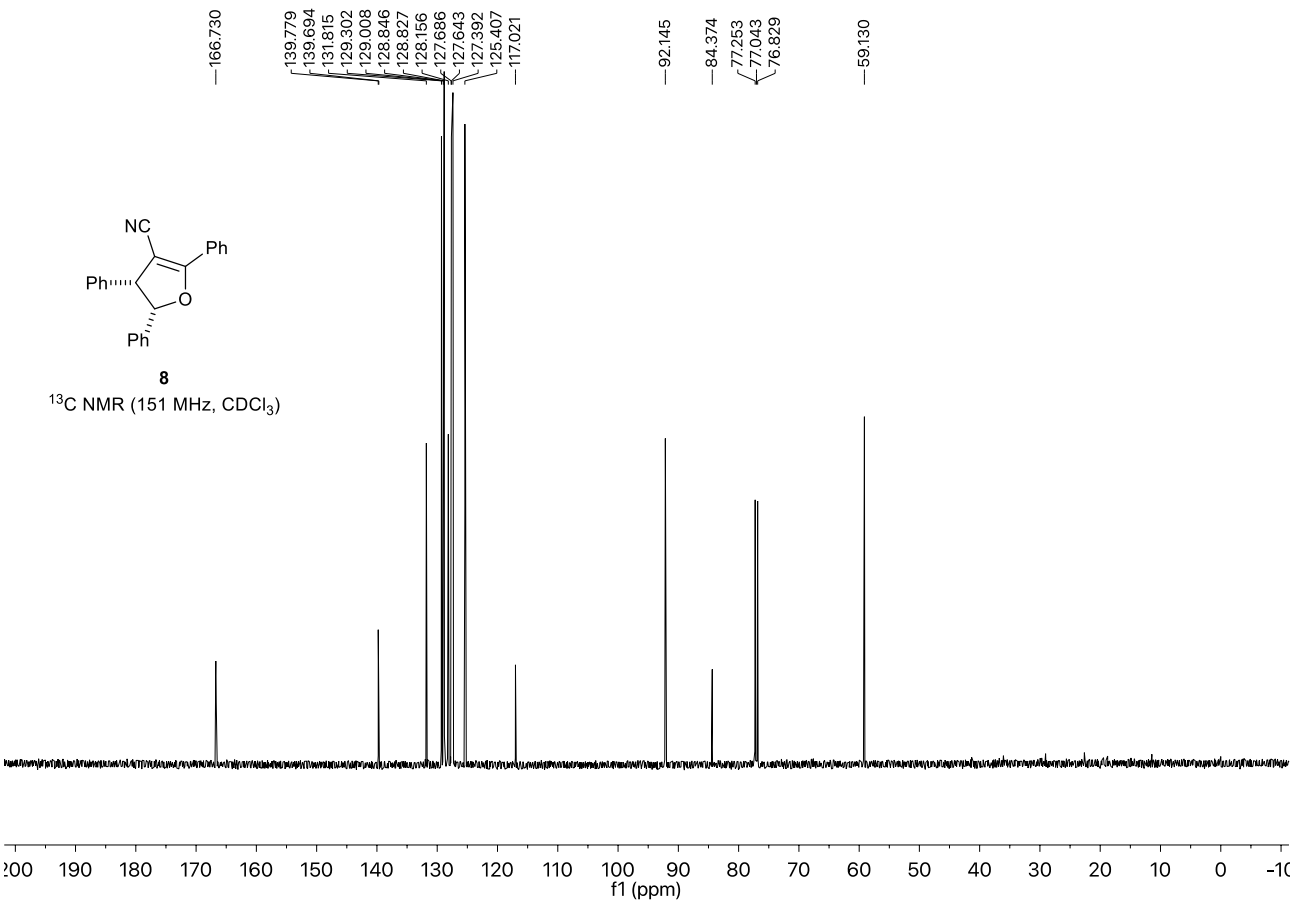


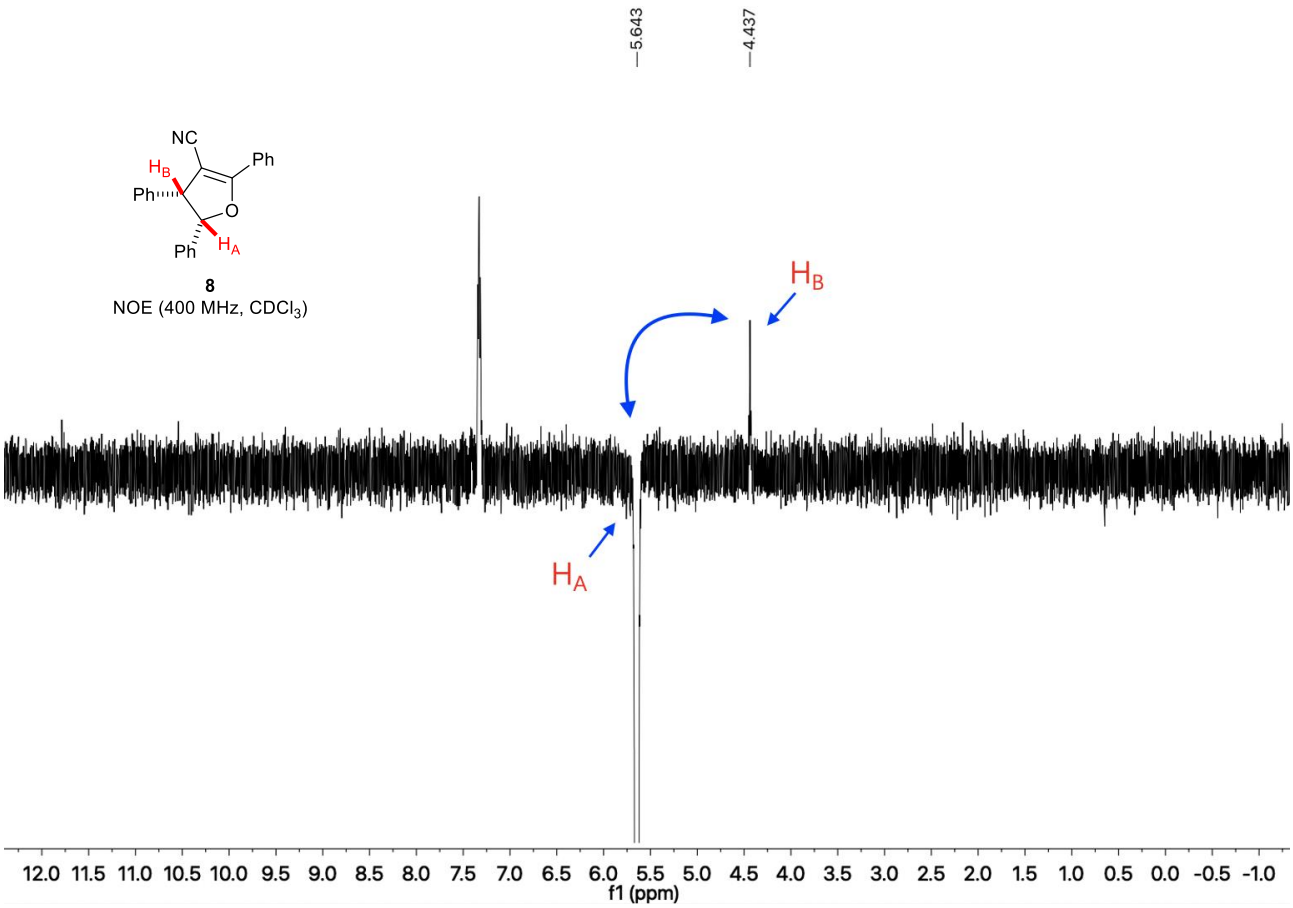
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.583	VB	0.1824	2.16473e4	1820.24963	50.0068
2	8.893	BV	0.2240	2.16414e4	1496.57874	49.9932



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	7.225	BV	0.1798	2.59170e4	2198.23340	79.5827
2	8.121	VBA	0.1999	6649.12598	506.10809	20.4173

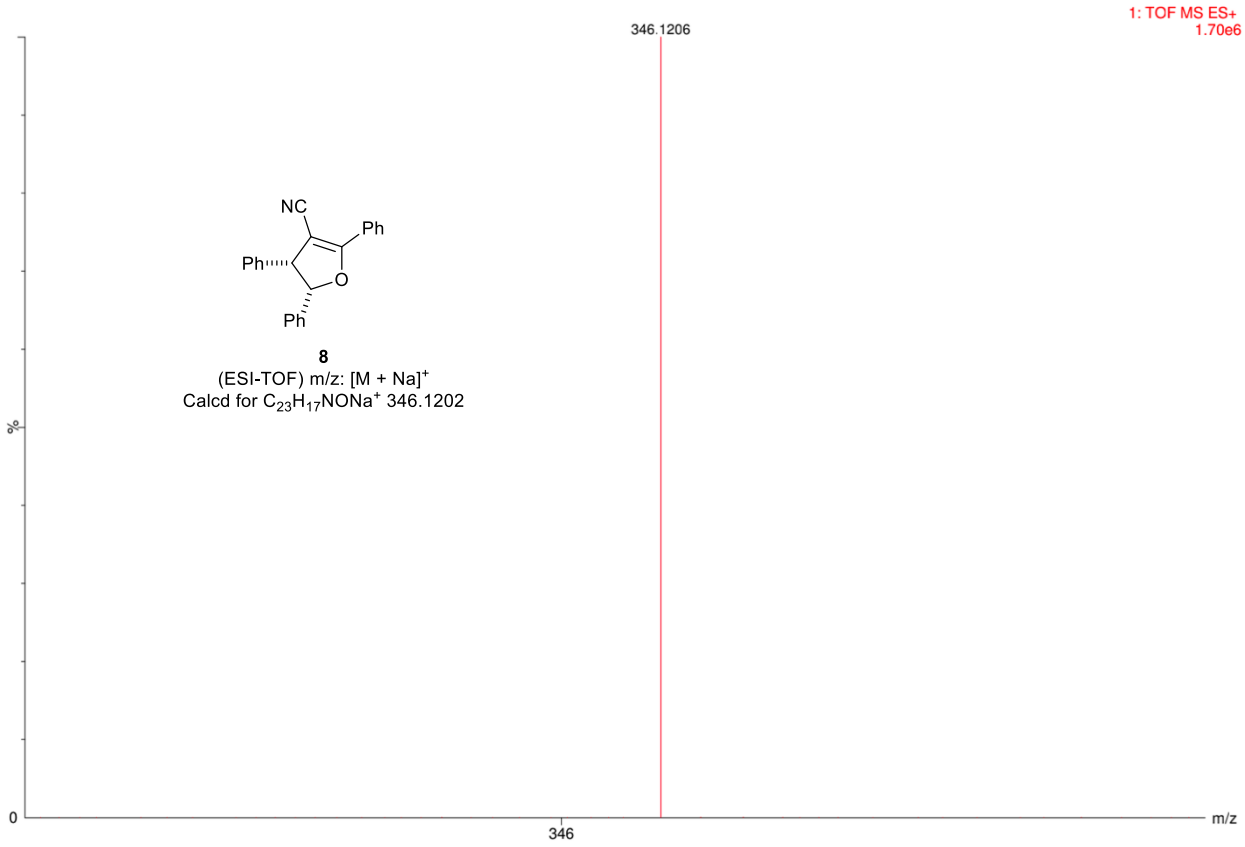

8.141
8.137
8.133
8.122
8.117
8.113
7.556
7.552
7.538
7.531
7.526
7.522
7.516
7.502
7.496
7.480
7.474
7.429
7.426
7.422
7.406
7.388
7.372
7.362
7.358
7.355
7.342
7.329
7.324
7.315
7.311
7.307
7.294
7.291
7.238
5.637
5.618
4.434
4.431
4.415
4.412
0.000
NC
Ph
Ph
O
Ph
8
1H NMR (400 MHz, CDCl3)
1.93
3.02
9.90
1.00
1.00
f1 (ppm)


166.730
139.779
139.694
131.815
129.302
129.008
128.846
128.827
128.156
127.686
127.643
127.392
125.407
117.021
92.145
84.374
77.253
77.043
76.829
59.130
NC
Ph
Ph
O
Ph
8
13C NMR (151 MHz, CDCl3)
f1 (ppm)



8

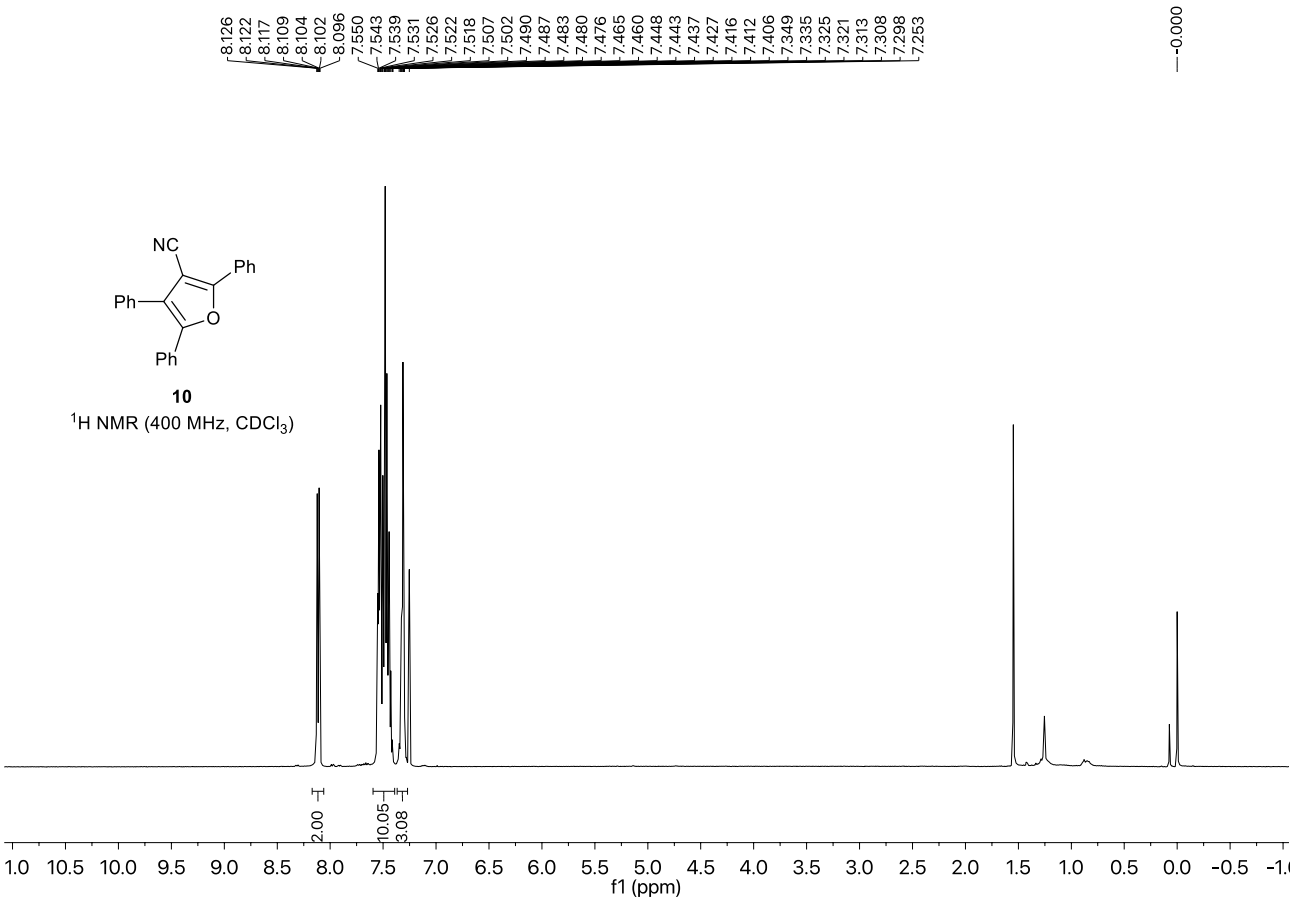
NOE (400 MHz, $CDCl_3$)

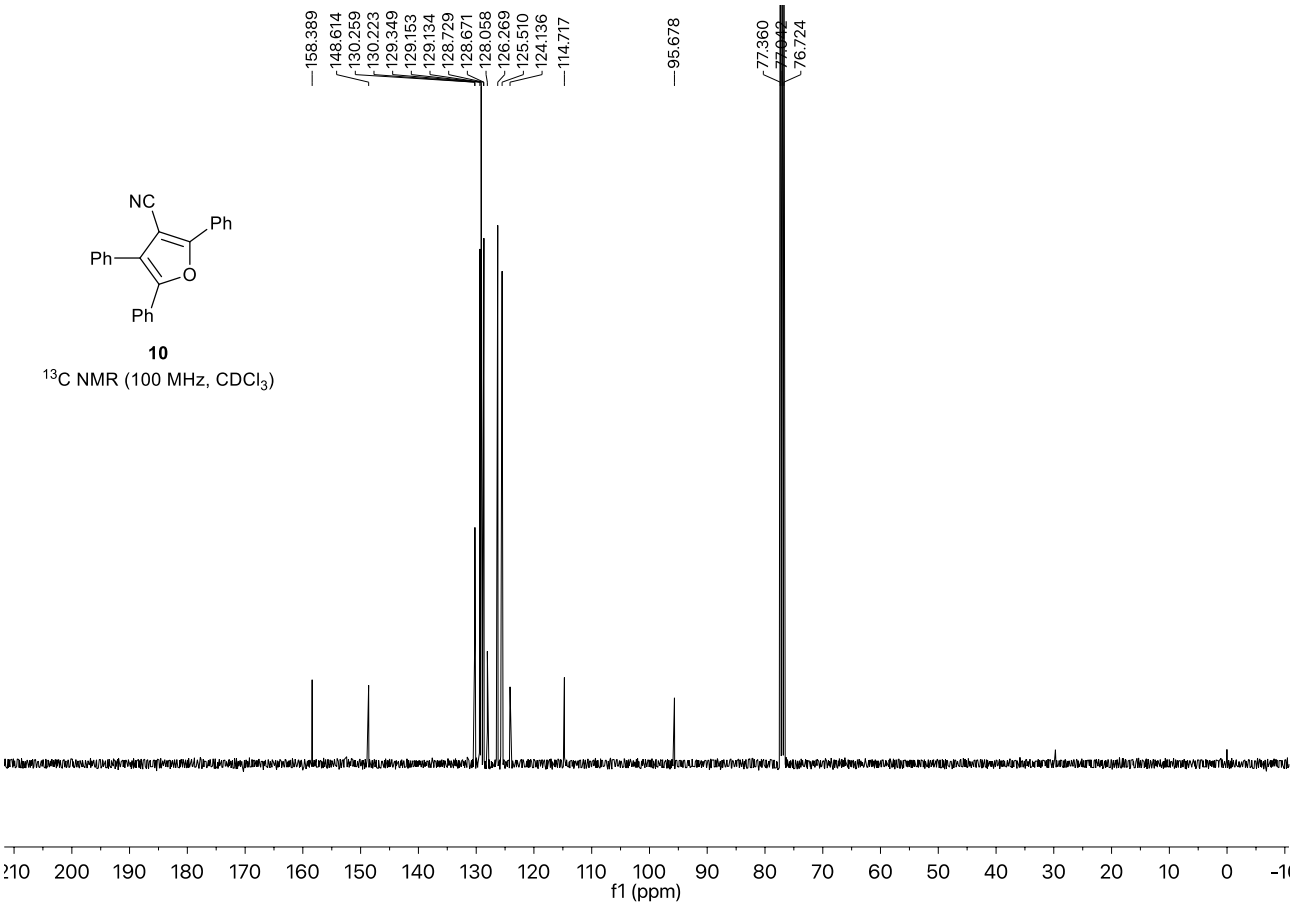


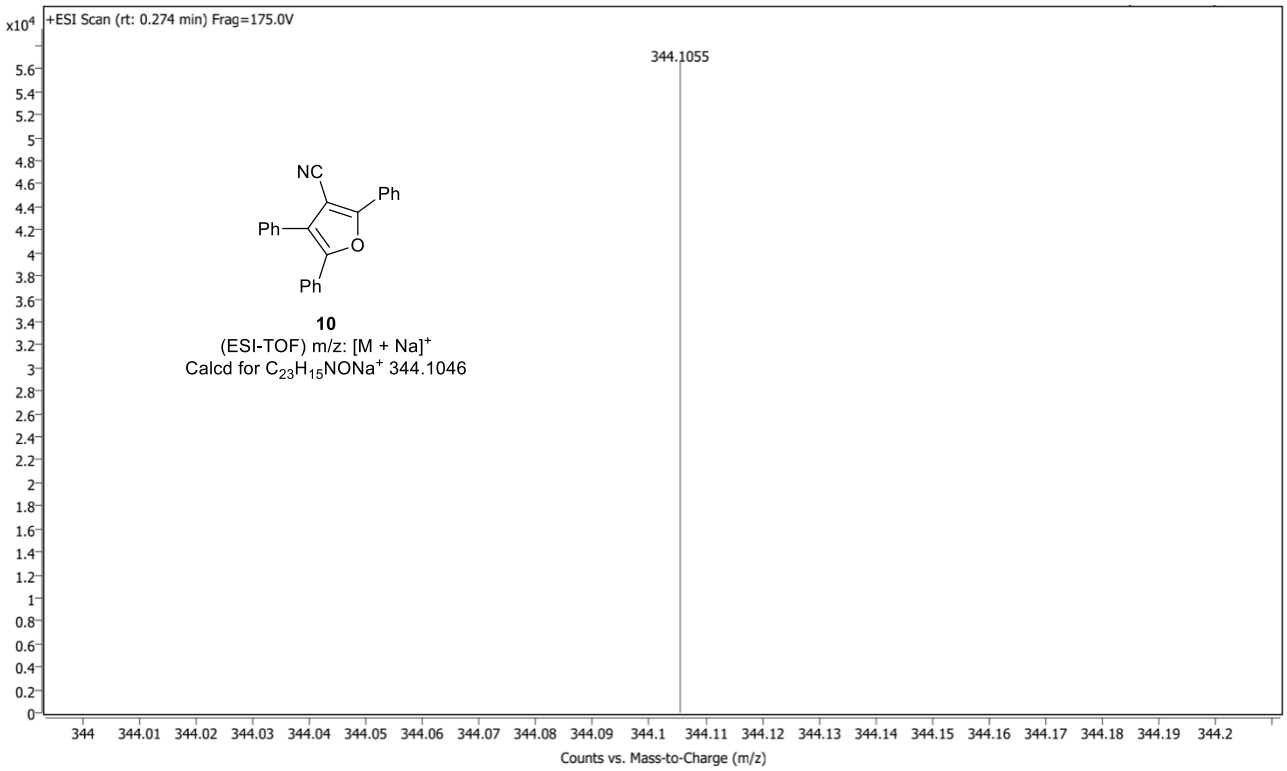
8

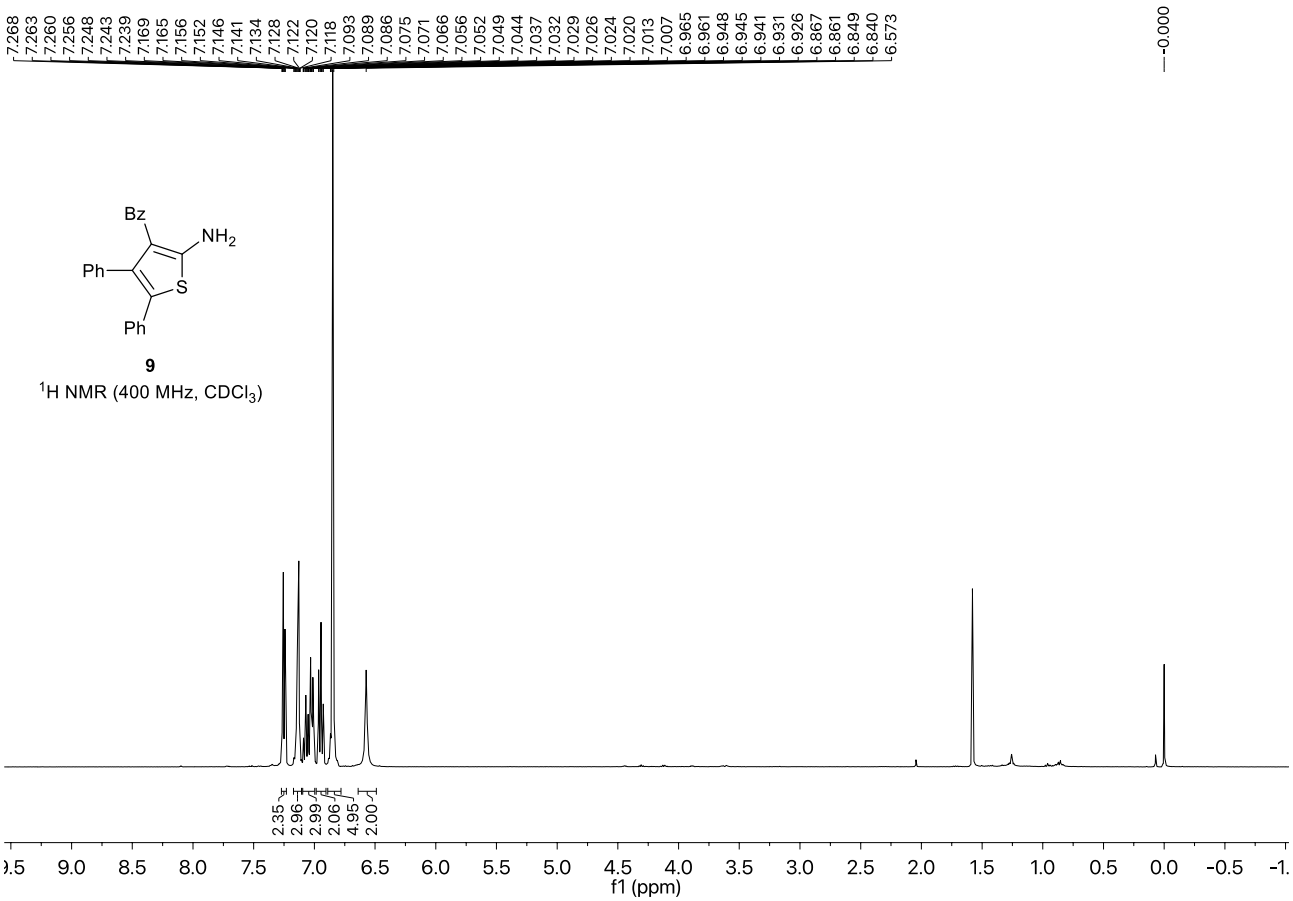
(ESI-TOF) m/z: $[M + Na]^+$

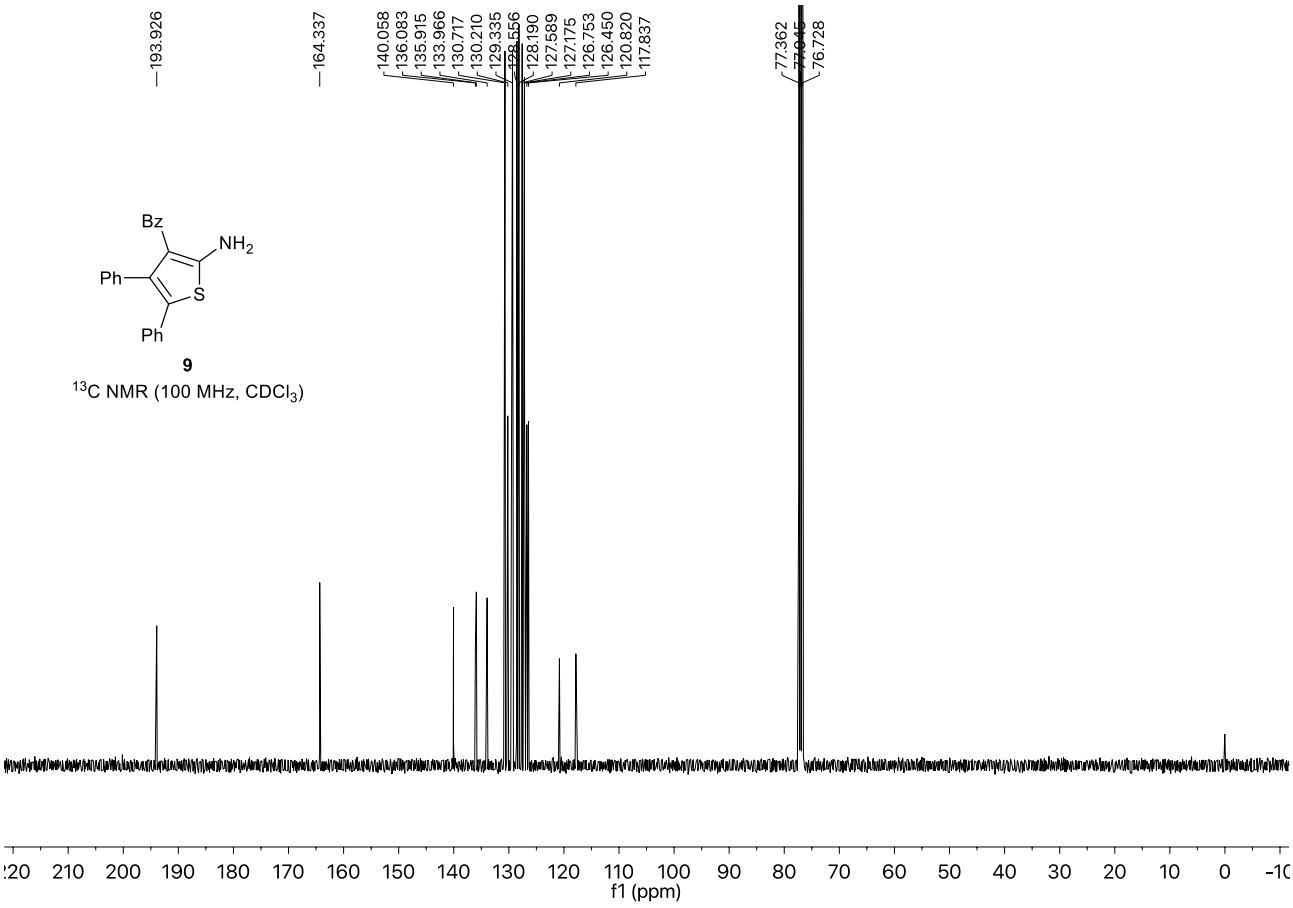
Calcd for $C_{23}H_{17}NONa^+$ 346.1202

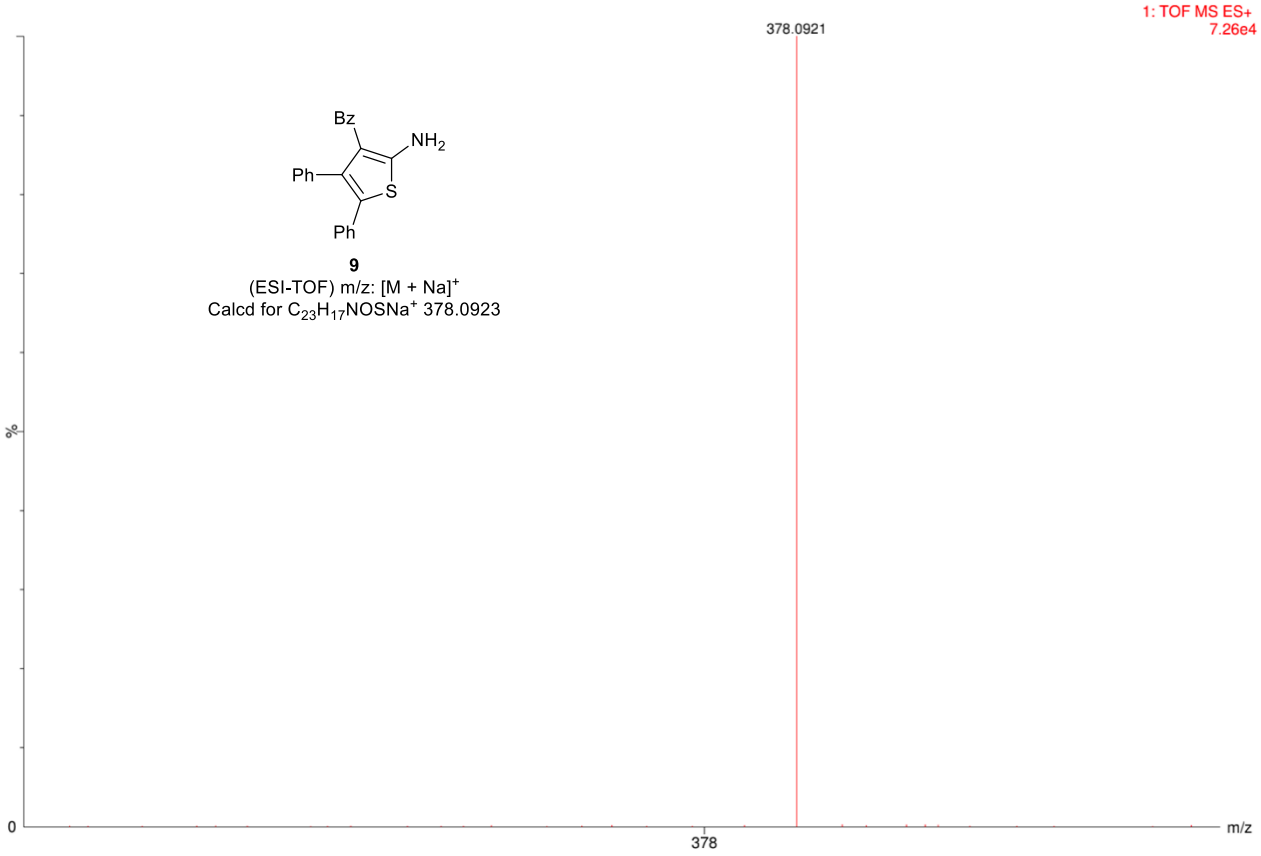

8.126
8.122
8.117
8.109
8.104
8.102
8.096
7.550
7.543
7.539
7.531
7.526
7.522
7.518
7.507
7.502
7.490
7.487
7.483
7.480
7.476
7.465
7.460
7.448
7.443
7.437
7.427
7.416
7.412
7.406
7.349
7.335
7.325
7.321
7.313
7.308
7.298
7.253
0.000
NC
Ph
Ph
O
Ph
10
1H NMR (400 MHz, CDCl3)
2.00
10.05
3.08
f1 (ppm)


158.389
148.614
130.259
130.223
129.349
129.153
129.134
128.729
128.671
128.058
126.269
125.510
124.136
114.717
95.678
77.360
77.042
76.724
NC
Ph
Ph
O
Ph
10
13C NMR (100 MHz, CDCl3)
f1 (ppm)


+ESI Scan (rt: 0.274 min) Frag=175.0V
x10^4
344.1055
NC
Ph
Ph
O
Ph
10
(ESI-TOF) m/z: [M + Na]+
Calcd for C23H15NONa+ 344.1046
Counts vs. Mass-to-Charge (m/z)


7.268
7.263
7.260
7.256
7.248
7.243
7.239
7.169
7.165
7.156
7.152
7.146
7.141
7.134
7.128
7.122
7.120
7.118
7.093
7.089
7.086
7.075
7.071
7.066
7.056
7.052
7.049
7.044
7.037
7.032
7.029
7.026
7.024
7.020
7.013
7.007
6.965
6.961
6.948
6.945
6.941
6.931
6.926
6.867
6.861
6.849
6.840
6.573
0.000
Bz
NH2
Ph
S
Ph
9
1H NMR (400 MHz, CDCl3)
2.35
2.96
2.99
2.06
4.95
2.00
f1 (ppm)


193.926
164.337
140.058
136.083
135.915
133.966
130.717
130.210
129.335
128.556
128.190
127.589
127.175
126.753
126.450
120.820
117.837
77.362
77.045
76.728
Bz
NH2
Ph
S
Ph
9
13C NMR (100 MHz, CDCl3)
f1 (ppm)



9

(ESI-TOF) m/z: $[M + Na]^+$

Calcd for $C_{23}H_{17}NOSNa^+$ 378.0923