Rhodium(I)-Catalyzed Cascade C(sp^2)–H Bond Alkylation – Amidation of Anilines: Phosphorus as Traceless Directing Group

Marie Peng,[a] Denis Ari,[a] Thierry Roisnel,[a] Henri Doucet,[a] and Jean-François Soulé*[b]

[a] Univ. Rennes, CNRS, ISCR UMR 6226, 35000 Rennes, France

[b] Chimie ParisTech, PSL University, CNRS, Institute of Chemistry for Life and Health Sciences, 75005 Paris, France , France

E-mail: jean-francois.soule@chimieparistech.psl.eu

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1. General Information

All reactions were carried out under argon atmosphere with standard Schlenk techniques or set up in glovebox (Mbraun, MB10-Compact). All reagents were obtained from commercial sources and used as supplied unless stated otherwise. *N,N*-Dimethylformamide was distilled with $MgSO_4$ under argon and stored in the glovebox before use. ^{1}H NMR spectra were recorded on Bruker AV III 400 MHz spectrometer fitted with a BBFO probe. Chemical shifts (δ) are reported in parts per million relatives to residual chloroform (7.26 ppm for ^{1}H; 77.16 ppm for ^{13}C). Coupling constants are reported in Hertz. ^{1}H NMR assignment abbreviations are the following: singlet (s), doublet (d), triplet (t), quartet (q), doublet of doublets (dd), doublet of triplets (dt), doublet of doublet of doublets (ddd), multiplet (m). ^{13}C NMR spectra were recorded at 100 MHz on the same spectrometer and reported in ppm. ^{19}F NMR spectra were recorded at 376 MHz on the same spectrometer and reported in ppm. ^{31}P NMR spectra were recorded at 162 MHz on the same spectrometer and reported in ppm. GC analyses were performed with a gas chromatograph (GC-2014 Shimadzu) instrument equipped with a capillary column (UptibondTM UB5P- 5% phenyl-95% dimethyl polysiloxane), which was coupled to a flame ionization detector (FID). The following GC conditions were used: flow rate (77.7 kPa, N_2), Injector (250°C), Detector (280°C), Int. T. (50 °C), Int. T. (2 min), Rate (20 °C /min), Fin. T. (280 °C), Fin. T. (20 min).

Mass spectroscopy were recorded on a Waters Q-Tof 2 mass spectrometer or a Bruker Ultraflex III mass spectrometer at the corresponding facilities of the CRMPO, Centre Régional de Mesures Physiques de l'Ouest, Université de Rennes 1.

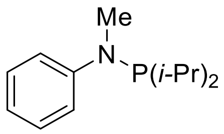
Column chromatography was carried out on a Teledyne ISCO CombiFlash NextGen 300 using FlashPure silica flash columns (4, 12, 25 g; 35–45 µm). Substrates were purified using heptane and ethyl acetate on a gradient of 100:0 to 0:100 with flow rates of 13 – 400 mL/min depending on the size of column and ΔRf.

Complex (2,2,6,6-tetramethyl-3,5-heptanedionato)-(1,5- cyclooctadiene) rodium [Rh(COD)(**L6**)] was already reported and prepared according to the literature.[S1]

2. General Procedure for Starting Materials 1a-1g and Compounds Characterizations

Procedure: To a solution of aniline (1.5 mmol, 1 equiv.) in anhydrous THF (4.5 mL) was added *n*-BuLi (1.1 M in hexanes, 1.6 mL, 1.8 mmol, 1.2 equiv.) dropwise at -78 °C. The reaction was warmed up to room temperature and stirred over 1h. Then, Cl-P(*i*-Pr)$_2$ (310 µL, 1.95 mmol, 1.6 equiv.) was added dropwise at -78 °C, the mixture was warmed up to room temperature and stirred overnight. The crude product was concentrated and the residue was dissolved in pentane. The precipitate was filtered off over celite and the filtrate was concentrated. Then, the crude product was heated at 60°C under vacuum over 3h to remove the excess of Cl-P(*i*-Pr)$_2$ to afford pure phosphanamines which were stored in a glovebox.

1,1-Diisopropyl-*N*-methyl-*N*-phenylphosphanamine (1a)



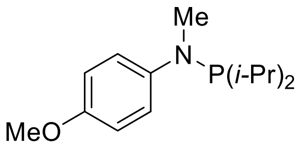
Following the general procedure using *N*-methylaniline (180 µL, 1.5 mmol, 1 equiv.), the product was obtained in 95% yield (318 mg, 1.4 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.28 – 7.16 (m, 4H), 6.78 (tt, *J* = 6.5, 1.8 Hz, 1H), 2.97 (d, *J* = 1.4 Hz, 3H), 2.08 (hept.d, *J* = 7.0, 3.6 Hz, 2H), 1.13 (dd, *J* = 16.7, 6.9 Hz, 6H), 1.03 (dd, *J* = 16.7, 6.9 Hz, 6H).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ (ppm) 72.2.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 153.1 (d, *J* = 20.4 Hz), 128.7 (d, *J* = 1.8 Hz), 118.4 (d, *J* = 1.8 Hz), 116.5 (d, *J* = 16.5 Hz), 34.4 (d, *J* = 7.5 Hz), 26.8 (d, *J* = 15.1 Hz), 19.7 (d, *J* = 10.3 Hz), 19.5 (d, *J* = 25.9 Hz).

1,1-Diisopropyl-*N*-(4-methoxyphenyl)-*N*-methylphosphanamine (1b)



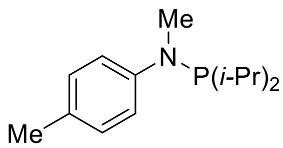
Following the general procedure using 4-methoxy-*N*-methylaniline (206 mg, 1.5 mmol, 1 equiv.), the product was obtained in 70 % yield (266 mg, 1.05 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.16 – 7.13 (m, 2H), 6.82 – 6.79 (m, 2H), 3.76 (s, 3H), 2.96 (d, *J* = 0.8 Hz, 3H), 2.06 (hept.d, J = 7.2, 3.0 Hz, 2H), 1.15 – 1.03 (m, 12H).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ (ppm) 73.9.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 152.6 (d, *J* = 2.0 Hz), 147.0 (d, *J* = 20.8 Hz), 118.0 (d, *J* = 14.8 Hz), 114.1, 55.7, 34.9 (d, *J* = 7.2 Hz), 26.7 (d, *J* = 15.2 Hz), 19.7 (d, *J* = 10.1 Hz), 19.5 (d, *J* = 25.4 Hz).

1,1-Diisopropyl-*N*-methyl-*N*-(*p*-tolyl)phosphanamine (1c)



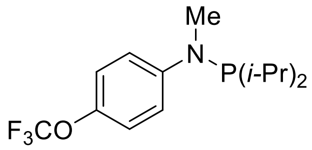
Following the general procedure using *N*-methyl-*para*-toluidine (190 µL, 1.5 mmol, 1 equiv.), the product was obtained in 78% yield (277 mg, 1.17 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.19 – 7.10 (m, 2H), 7.08 – 6.99 (m, 2H), 2.96 (d, *J* = 1.6 Hz, 3H), 2.27 (s, 3H), 2.08 (hept.d, *J* = 7.0, 3.6 Hz, 2H), 1.13 (dd, *J* = 16.6, 7.0 Hz, 6H), 1.04 (dd, *J* = 12.0, 7.0 Hz, 6H).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ (ppm) 72.2.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 150.7 (d, *J* = 20.4 Hz), 129.2 (d, *J* = 1.3 Hz), 127.6 (d, *J* = 1.7 Hz), 116.5 (d, *J* = 15.8 Hz), 34.5 (d, *J* = 7.4 Hz), 26.8 (d, *J* = 15.2 Hz), 20.4, 19.7 (d, *J* = 10.1 Hz), 19.5 (d, *J* = 25.8 Hz).

1,1-Diisopropyl-*N* -(4-(trifluoromethoxy)phenyl)-*N*-methyl-phosphanamine (1d)



Following the general procedure using *N*-methyl-4-(trifluoromethoxy)aniline (231 µL, 1.5 mmol, 1 equiv.), the product was obtained in 77% yield (355 mg, 1.16 mmol).

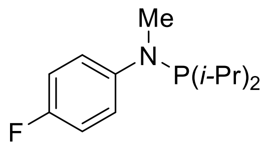
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.23 – 7.20 (m, 2H), 7.06 – 7.04 (m, 2H), 2.96 (d, *J* = 1.3 Hz, 3H), 2.07 (hept.d, *J* = 7.0, 3.5 Hz, 2H), 1.13 (dd, *J* = 16.8, 7.0 Hz, 6H), 1.03 (dd, *J* = 12.1, 7.0 Hz, 6H).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ (ppm) 73.6.

^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$) δ (ppm) -58.3.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 151.8 (d, *J* = 21.1 Hz), 141.2 (t, *J* = 2.2 Hz), 120.8 (q, *J* = 255.3 Hz), 121.5, 116.7 (d, *J* = 17.1 Hz), 34.4 (d, *J* = 7.8 Hz), 26.8 (d, *J* = 15.3 Hz), 19.7 (d, *J* = 10.0 Hz), 19.4 (d, *J* = 25.7 Hz).

1,1-Diisopropyl-*N*-(4-fluorophenyl) -*N*-methylphosphanamine (1e)



Following the general procedure using 4-fluoro-*N*-methylaniline (180 µL, 1.5 mmol, 1 equiv.), the product was obtained in 85% yield (308 mg, 1.28 mmol).

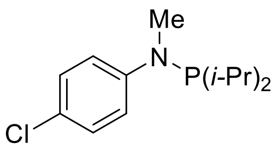
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.22 – 7.15 (m, 2H), 6.96 – 6.88 (m, 2H), 2.96 (d, *J* = 1.5 Hz, 3H), 2.09 (hept.d, *J* = 7.0, 3.5 Hz, 2H), 1.15 (dd, *J* = 16.6, 7.0 Hz, 6H), 1.06 (dd, *J* = 12.0, 7.0 Hz, 6H).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ(ppm) 74.1.

^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$) δ (ppm) -127.0.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 156.2 (dd, *J* = 237.0, 2.4 Hz), 149.3 (dd, *J* = 21.0, 2.1 Hz), 117.4 (dd, *J* = 16.0, 7.3 Hz), 114.8 (d, *J* = 21.8 Hz), 34.5 (d, *J* = 7.6 Hz), 26.7 (d, *J* = 15.2 Hz), 19.6 (d, *J* = 10.1 Hz), 19.3 (d, *J* = 25.7 Hz).

***N*-(4-Chlorophenyl)-1,1-diisopropyl-*N*-methylphosphanamine (1f)**



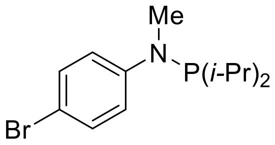
Following the general procedure using 4-chloro-*N*-methylaniline (181 µL, 1.5 mmol, 1 equiv.), the product was obtained in 85% yield (329 mg, 1.28 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.34 – 7.05 (m, 4H), 2.94 (d, *J* = 1.3 Hz, 3H), 2.08 (hept.d, *J* = 7.0, 3.5 Hz, 2H), 1.15 (dd, *J* = 16.8, 7.0 Hz, 6H), 1.04 (dd, *J* = 12.1, 7.0 Hz, 6H).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ (ppm) 73.0.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 151.6 (d, *J* = 20.9 Hz), 128.3 (d, *J* = 1.5 Hz), 123.0 (d, *J* = 2.8 Hz), 117.2 (d, *J* = 17.1 Hz), 34.2 (d, *J* = 7.7 Hz), 26.6 (d, *J* = 15.4 Hz), 19.5 (d, *J* = 10.1 Hz), 19.3 (d, *J* = 25.9 Hz).

N-(4-Bromophenyl)-1,1-diisopropyl-N-methylphosphanamine (1g)



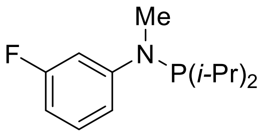
Following the general procedure using 4-bromo-*N*-methylaniline (170 µL, 1.5 mmol, 1 equiv.), the product was obtained in 80% yield (361 mg, 1.2 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.32 – 7.26 (m, 2H), 7.17 – 7.12 (m, 2H), 2.95 (d, *J* = 1.2 Hz, 3H), 2.09 (hept.d, *J* = 7.0, 3.6 Hz, 2H), 1.14 (dd, *J* = 16.8, 6.9 Hz, 6H), 1.03 (dd, *J* = 12.1, 7.0 Hz, 6H).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ (ppm) 72.9.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 148.4, 131.9, 114.0, 108.8, 30.8, 25.5, 24.8, 16.3, 15.1 (d, *J* = 3.2 Hz).

1,1-Diisopropyl- N-(3-fluorophenyl)-N-methylphosphanamine (1h)



Following the general procedure using 3-fluoro-*N*-methylaniline (170 µL, 1.5 mmol, 1 equiv.), the product was obtained in 63% yield (228 mg, 0.95 mmol).

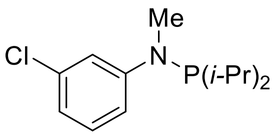
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.13 (td, *J* = 8.2, 7.0 Hz, 1H), 7.07 – 6.91 (m, 2H), 6.46 (tdd, *J* = 8.2, 2.4, 0.9 Hz, 1H), 2.94 (d, *J* = 1.2 Hz, 3H), 2.08 (hept.d, *J* = 7.0, 3.6 Hz, 2H), 1.13 (dd, *J* = 16.8, 6.9 Hz, 6H), 1.02 (dd, *J* = 16.8, 6.9 Hz, 6H).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ (ppm) 72.7.

^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$) δ (ppm) -113.0.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 163.6 (dd, *J* = 241.9, 1.6 Hz), 155.0 (dd, *J* = 21.5, 10.4 Hz), 130.0 (dd, *J* = 10.1, 1.6 Hz), 111.7 (dd, *J* = 18.0, 2.4 Hz), 104.7 (dd, *J* = 21.6, 1.5 Hz), 103.1 (dd, *J* = 25.8, 17.3 Hz), 34.3 (d, *J* = 7.7 Hz), 26.7 (d, *J* = 15.5 Hz), 19.5 (d, *J* = 10.1 Hz), 19.3 (d, *J* = 26.1 Hz).

N-(3-Chlorophenyl)-1,1-diisopropyl-N-methylphosphanamine (1i)



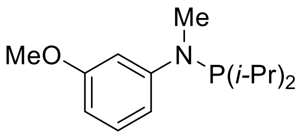
Following the general procedure using 3-chloro-*N*-methylaniline (181 µL, 1.5 mmol, 1 equiv.), the product was obtained in 72% yield (278 mg, 1.08 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.24 – 7.06 (m, 3H), 6.74 (dd, *J* = 7.6, 1.9, 1.1 Hz, 1H), 2.93 (d, *J* = 1.2 Hz, 3H), 2.07 (hept.d, *J* = 7.0, 3.6 Hz, 2H), 1.12 (dd, *J* = 16.8, 7.0 Hz, 6H), 1.01 (dd, *J* = 16.8, 7.0 Hz, 6H).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ (ppm) 72.8.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 154.4 (d, *J* = 21.0 Hz), 134.6, 129.5 (d, *J* = 1.7 Hz), 118.2 (d, *J* = 1.6 Hz), 116.0 (d, *J* = 16.6 Hz), 115.0 (d, *J* = 18.6 Hz), 34.3 (d, *J* = 7.8 Hz), 26.8 (d, *J* = 15.4 Hz), 19.7 (d, *J* = 10.1 Hz), 19.4 (d, *J* = 26.0 Hz).

1,1-Diisopropyl-*N*-(3-methoxyphenyl)-*N*-methylphosphanamine (1j)



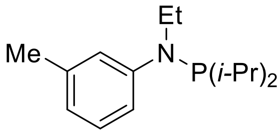
Following the general procedure using 3-methoxy-*N*-methylaniline (206 mg, 1.5 mmol, 1 equiv.), the product was obtained in 80% yield (304 mg, 1.2 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.11 (t, *J* = 8.2 Hz, 1H), 6.89 (dt, *J* = 8.3, 2.4 Hz, 1H), 6.80 (q, *J* = 2.5 Hz, 1H), 6.35 (dd, *J* = 8.0, 2.3 Hz, 1H), 3.79 (s, 3H), 2.95 (d, *J* = 1.2 Hz, 3H), 2.07 (hept.d, *J* = 7.0, 3.5 Hz, 2H), 1.12 (dd, *J* = 16.7, 6.9 Hz, 6H), 1.02 (dd, *J* = 12.0, 7.0 Hz, 6H).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ (ppm) 72.0.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 160.3, 154.5 (d, *J* = 20.7 Hz), 129.2, 109.4 (d, *J* = 17.8 Hz), 103.3, 102.7 (d, *J* = 16.7 Hz), 55.3, 34.5 (d, *J* = 7.5 Hz), 26.8 (d, *J* = 15.5 Hz), 19.7 (d, *J* = 10.1 Hz), 19.5 (d, *J* = 26.1 Hz).

1,1-Diisopropyl-*N*-ethyl-*N*-(*m*-tolyl)phosphanamine (1k)



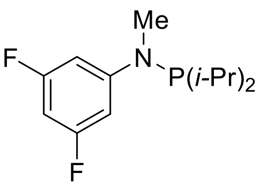
Following the general procedure using *N*-ethyl-*meta*-toluidine (190 µL, 1.5 mmol, 1 equiv.), the product was obtained in 90% yield (339 mg, 1.35 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.09 (t, *J* = 7.8 Hz, 1H), 7.03 – 6.92 (m, 2H), 6.63 (d, *J* = 7.4 Hz, 1H), 3.52 (qd, *J* = 7.0, 2.6 Hz, 2H), 2.30 (s, 3H), 2.09 (hept.d, *J* = 7.0, 3.1 Hz, 2H), 1.15 – 1.05 (m, 15H).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ (ppm) 80.9.

^{13}C NMR (101 MHz, CDCl$_3$) δ (ppm) 150.1 (d, *J* = 17.1 Hz), 137.9, 128.2, 120.3, 120.1, 116.3 (d, *J* = 12.3 Hz), 42.1, 26.7 (d, *J* = 16.6 Hz), 21.7, 19.7 (d, *J* = 11.3 Hz), 19.4 (d, *J* = 24.9 Hz), 14.0.

***N*-(3,5-Difluorophenyl)-1,1-diisopropyl-*N*-methylphosphanamine (1l)**



Following the general procedure using 3,5-difluoro-*N*-methylaniline (176 µL, 1.5 mmol, 1 equiv.), the product was obtained in 75% yield (291 mg, 1.13 mmol).

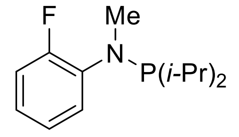
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 6.79 – 6.75 (m, 2H), 6.20 (tt, *J* = 8.9, 2.2 Hz, 1H), 2.90 (d, *J* = 1.0 Hz, 3H), 2.06 (hept.d, *J* = 7.0, 3.5 Hz, 2H), 1.12 (dd, *J* = 17.0, 6.9 Hz, 6H), 1.00 (dd, *J* = 12.2, 7.0 Hz, 6H).

^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$) δ (ppm) 73.2.

^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$) δ (ppm) -110.7.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 163.6 (ddd, *J* = 242.7, 16.1, 1.8 Hz), 155.6 (dt, *J* = 22.9, 12.9 Hz), 98.7 (dd, *J* = 29.3, 18.7 Hz), 93.3 (t, *J* = 26.2 Hz), 34.3 (d, *J* = 8.0 Hz), 26.7 (d, *J* = 15.5 Hz), 19.6 (d, *J* = 10.2 Hz), 19.3 (d, *J* = 26.1 Hz).

1,1-Diisopropyl-*N*-(2-fluorophenyl)-*N*-methylphosphanamine (1m)



Following the general procedure using 2-fluoro-*N*-methylaniline (180 µL, 1.5 mmol, 1 equiv.), the product was obtained in 90% yield (325 mg, 1.35 mmol).

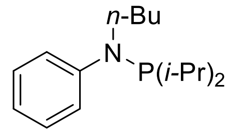
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.20 (tt, *J* = 8.2, 1.9 Hz, 1H), 7.04 – 6.81 (m, 3H), 3.01 (dd, *J* = 2.6, 1.6 Hz, 3H), 2.07 (hept.d, *J* = 7.0, 3.3 Hz, 2H), 1.32 – 0.98 (m, 12H).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ (ppm) 84.0 (d, *J* = 32.6 Hz).

^{19}F{^{1}H} NMR (376 MHz, $CDCl_3$) δ (ppm) -120.4 (d, *J* = 32.4 Hz).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 156.9 (dd, *J* = 245.9, 3.5 Hz), 141.4 (dd, *J* = 20.9, 9.0 Hz), 126.1 (dd, *J* = 12.4, 3.3 Hz), 124.1 (d, *J* = 3.4 Hz), 122.8 (dd, *J* = 7.7, 1.7 Hz), 116.4 (d, *J* = 21.2 Hz), 36.6 (t, *J* = 5.7 Hz), 26.5 (d, *J* = 15.5 Hz), 19.7 (d, *J* = 10.0 Hz), 19.3 (d, *J* = 24.4 Hz).

1,1-Diisopropyl-*N*-ethyl-*N*-phenylphosphanamine (1n)



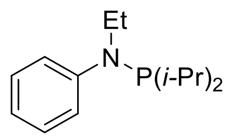
Following the general procedure using *N*-butylaniline (240 µL, 1.5 mmol, 1 equiv.), the product was obtained in 87% yield (346 mg, 1.31 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.26 – 7.13 (m, 4H), 3.47 – 3.41 (m, 2H), 2.12 (hept.d, *J* = 7.0, 3.5 Hz, 2H), 1.58 – 1.47 (m, 2H), 1.32 (dt, *J* = 14.4, 7.3 Hz, 2H), 1.20 – 1.03 (m, 12H), 0.94 (t, *J* = 7.3 Hz, 3H).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ (ppm) 82.0.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 150.7 (d, *J* = 16.3 Hz), 128.6, 119.5 (d, *J* = 12.4 Hz), 112.7, 32.0, 26.9 (d, *J* = 16.5 Hz), 22.8, 20.6, 19.9 (d, *J* = 11.3 Hz), 19.5 (d, *J* = 24.7 Hz), 14.2.

1,1-Diisopropyl-*N*-ethyl-*N*-phenylphosphanamine (1o)



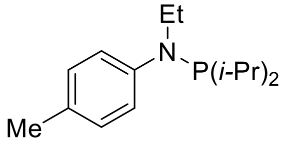
Following the general procedure using *N*-ethylaniline (189 µL, 1.5 mmol, 1 equiv.), the product was obtained in 90 % yield (320 mg, 1.35 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.24 – 7.12 (m, 4H), 6.81-6.78 (1H, m), 6.84 – 6.78 (m, 1H), 3.54 (qd, *J* = 7.0, 2.7 Hz, 2H), 2.10 (hept.d, *J* = 7.0, 3.5 Hz, 2H), 1.17 – 1.04 (m, 15H).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ (ppm) 81.4.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 150.3 (d, *J* = 17.0 Hz), 128.7, 119.5 (d, *J* = 12.8 Hz), 119.3 (d, *J* = 1.7 Hz), 42.5, 26.9 (d, *J* = 16.4 Hz), 19.9 (d, *J* = 11.1 Hz), 19.6 (d, *J* = 24.8 Hz), 14.1.

1,1-Diisopropyl-*N*-ethyl-*N*-(*p*-tolyl)phosphanamine (1p)



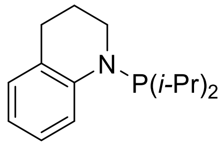
Following the general procedure using *N*-ethyl-*para*-toluidine (190 µL, 1.5 mmol, 1 equiv.), the product was obtained in 88% yield (332 mg, 1.32 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.10 – 6.98 (m, 4H), 3.52 (qd, *J* = 7.0, 2.9 Hz, 2H), 2.26 (s, 3H), 2.08 (hept.d, *J* = 7.0, 3.0 Hz, 2H), 1.17 – 1.04 (m, 15H).

$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ (ppm) 81.4.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 147.8 (d, *J* = 16.5 Hz), 129.3, 128.7 (d, *J* = 1.7 Hz), 119.8 (d, *J* = 11.9 Hz), 42.8, 26.9 (d, *J* = 16.2 Hz), 20.6, 19.9 (d, *J* = 11.1 Hz), 19.6 (d, *J* = 24.7 Hz), 14.2.

1-(Diisopropylphosphaneyl)-1,2,3,4-tetrahydroquinoline (1q)



Following the general procedure using 1,2,3,4-tetrahydroquinolinone (189 µL, 1.5 mmol, 1 equiv.), the product was obtained in 64% yield (239 mg, 0.96 mmol).

^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.72 (s, 1H), 7.07 – 6.98 (m, 2H), 6.70 – 6.60 (m, 1H), 3.37 (t, *J* = 5.5 Hz, 2H), 2.78 (t, *J* = 6.5 Hz, 2H), 2.22 – 2.07 (m, 2H), 1.91 (quint., *J* = 6.4 Hz, 2H), 1.19 – 1.03 (m, 12H).

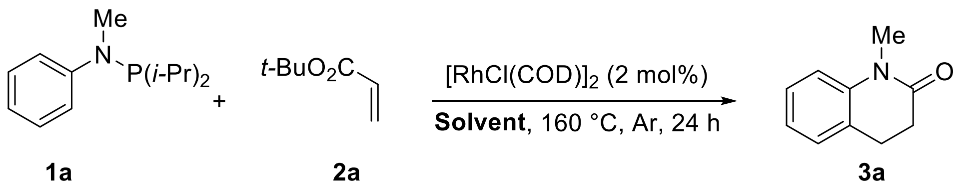
$^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$) δ (ppm) 64.0.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 129.6 (d, *J* = 1.3 Hz), 126.3 (d, *J* = 2.6 Hz), 124.1, 117.6, 117.3, 117.0, 28.2, 25.8 (d, *J* = 15.3 Hz), 23.1, 19.9 (d, *J* = 10.8 Hz), 19.6 (d, *J* = 25.5 Hz).

3. Optimization of the Reaction Conditions

Procedure: In a glovebox, an oven-dried Schlenk tube was charged with phosphanamine **1a** (44 mg, 0.2 mmol, 1 equiv.). Then the Schlenk tube was closed and removed from the glovebox. Under argon atmosphere, the catalyst (0.006 mmol, 2 mol%), additive (n. equiv.), *tert*-butyl acrylate **2a** (87 µL, 0.6 mmol, 3 equiv.) and solvent (1 mL) were added. The resulting mixture was stirred at 160 °C over 24 h. The crude product was then cooled down, diluted with ethyl acetate and injected in a calibrated GC-FID using *n*-dodecane (10 µL) as an internal standard to give the corresponding yields : t_R (min) 8.2 (*n*-dodecane), 10.7 (product **3a**).

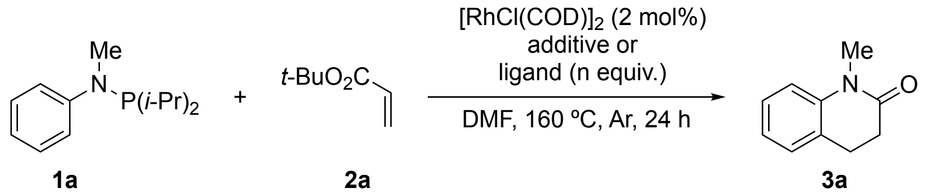
Table S1. Screening of Solvents.



Entry	Solvent	Yield **3a** (%)
1	Toluene	42[a]
2	Xylene	29[a]
3	1,2-Dichloroethane	24
4	Dimethyl carbonate	35
5	*N,N*-Dimethylformamide	40
6	*N,N*-Dimethylacetamide	27
7	1,4-Dioxane	12[a]

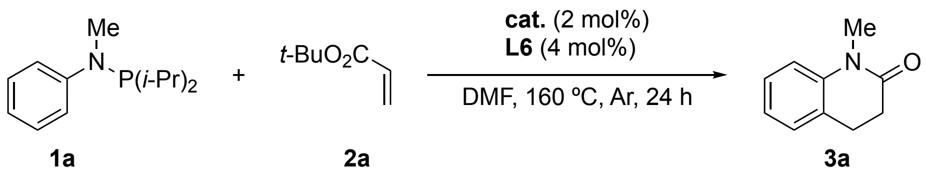
[a]Yield obtained after acid hydrolysis HCl 1 N at 80 °C.

Table S2. Screening of additives or ligands.



Entry	Additive or Ligand (n equiv.)	Yield **3a** (%)
1	-	40
2	NaOAc (0.3 equiv.)	30
3	$AlMe_3$ (0.3 equiv)	34
4	*N*-acetyl-DL alanine (**L1**) (0.04 equiv.)	54
5	*N*-acetyl-DL leucine (0.04 equiv)	38
6	PPh_3 (0.04 equiv)	30
7	Dppb (**L2**)(0.04 equiv)	36
8	BINOL (**L3**) (0.04 equiv)	46
9	Bathophenanthroline (0.04 equiv)	32
10	Acetylacetone (**L4**) (0.04 equiv)	45
11	1,1,1-Trifluoropentane-2,4-dione (**L5**) (0.04 equiv)	22
12	2,2,6,6-Tetramethylheptane-3,5-dione (**L6**)(0.04 equiv)	58

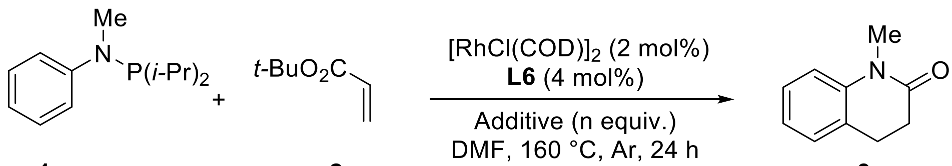
Table S3. Screening of catalysts.



Entry	Catalyst	Yield **3a** (%)
1	$[RhCl(COD)]_2$	58
2	$[IrCl(COD)]_2$	22
3	$[Rh(Cp^*)Cl_2]_2$	n.d.[a]
4	$[Ru(p\text{-Cymene})Cl_2]_2$	n.d.[a]
5	$[Rh(OAc)(COD)]_2$	traces
6	$[RhCl(NBD)]_2$	45
7	$[RhCl(COE)_2]_2$	39
8	$[RhOH(COD)]_2$	17
9	Rh(acac)(COD)	17
10	$[Rh(OMe)(COD)]_2$	32
11	$RhCl(PPh_3)_3$	17

[a]Reaction set up in the presence of $AgSbF_6$ (8 mol%) as additive.

Table S4. Control of Water Amount.



1a **2a** **3a**

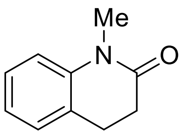
Entry	Additive (n equiv.)	Yield **3a** (%)
1	MS 4 Å (50 mg)	58
2	H_2O (1)	60
3	H_2O (2)	62
4	H_2O (4)	67
5	H_2O (6)	75
6	H_2O (8)	77
7	H_2O (10)	90 (81)
8	H_2O (20)	54
9	H_2O (10)	35[a]

[a]Reaction was performed without **L6**. Isolated yield is shown in parentheses.

4. Representative Procedure for the Synthesis of 3a-3s and Compound Characterizations

Procedure: In a glovebox, an oven-dried Schlenk tube was charged with *N*-arylphosphanamines **1** (0.3 mmol, 1 equiv.) and distilled DMF (1.5 mL). Then, the Schlenk tube was closed and removed from the glovebox. Under argon atmosphere, $[RhCl(COD)]_2$ (3 mg, 0.006 mmol, 2 mol%), 2,2,6,6-tetramethylheptane-3,5-dione **L6** (3 µL, 0.012 mmol, 4 mol%), water (54 µL, 3 mmol, 10 equiv.) and acrylate derivative **2** (0.9 mmol, 3 equiv.) were added. The resulting mixture was stirred at 160 °C over 24 h. The crude product was purified on flash chromatography on silica gel using heptane and ethyl acetate as eluents to provide the pure products.

1-Methyl-3,4-dihydroquinolin-2(1H)-one (3a)



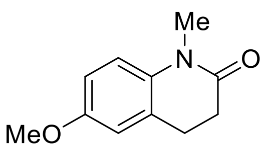
Following the general procedure using **1a** (67 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3a** as a white solid in 81% yield (39 mg, 0.24 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.27 – 7.21 (m, 1H), 7.16 – 7.13 (m, 1H), 7.03 – 6.94 (m, 2H), 3.34 (s, 3H), 2.93 – 2.83 (m, 2H), 2.68 – 2.55 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 170.6, 140.8, 127.8, 127.6, 126.4, 122.9, 114.8, 31.9, 29.7, 25.5.

HRMS m/z (ESI) calcd for $C_{10}H_{11}NONa$ $[M+Na]^+$ 184.0733, found 184.0733.

6-Methoxy-1-methyl-3,4-dihydroquinolin-2(1H)-one (3b)



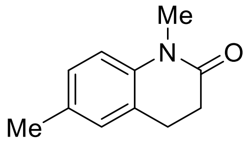
Following the general procedure using **1b** (76 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3b** as a yellow oil in 78% yield (45 mg, 0.23 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.90 (d, *J* = 8.7 Hz, 1H), 6.78 (dd, *J* = 8.7, 2.9 Hz, 1H), 6.73 (d, *J* = 2.9 Hz, 1H), 3.79 (s, 3H), 3.33 (s, 3H), 2.91 – 2.84 (m, 2H), 2.66 – 2.59 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 170.2, 155.4, 134.4, 127.9, 115.7, 114.0, 112.0, 55.7, 31.9, 29.8, 25.8.

HRMS m/z (ESI) calcd for $C_{11}H_{13}NO_2Na$ $[M+Na]^+$ 214,0839 found 214.0839.

1,6-Dimethyl-3,4-dihydroquinolin-2(1H)-one (3c)



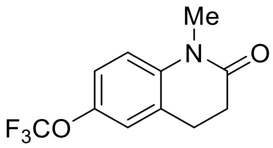
Following the general procedure using **1c** (71 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3c** as an orange oil in 79 % yield (41 mg, 0.24 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.05 (d, *J* = 8.2 Hz, 1H), 6.98 (s, 1H), 6.86 (d, *J* = 8.2 Hz, 1H), 3.33 (s, 3H), 2.90 – 2.80 (m, 2H), 2.69 – 2.59 (m, 2H), 2.30 (s, 3H).

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 170.4, 138.3, 132.3, 128.5, 127.8, 126.1, 114.6, 31.8, 29.5, 25.4, 20.6.

HRMS m/z (ESI) calcd for $C_{11}H_{13}NONa$ $[M+Na]^+$ 198.0889, found 198.0889.

1-Methyl-6-(trifluoromethoxy)-3,4-dihydroquinolin-2(1H)-one (3d)



Following the general procedure using **1d** (92 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3d** as a yellow oil in 60% yield (44 mg, 0.18 mmol).

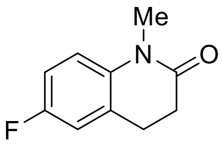
^{1}H RMN (400 MHz, $CDCl_3$) δ (ppm) 7.13 – 7.07 (m, 1H), 7.03 (s, 1H), 6.95 (d, *J* = 8.8 Hz, 1H), 3.34 (s, 3H), 2.93 – 2.87 (m, 2H), 2.67 – 2.62 (m, 2H).

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ (ppm) -58.2.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 170.1, 144.3 (d, *J* = 2.1 Hz), 139.5, 128.0, 120.7, 120.0, 119.9 (q, *J* = 256.2 Hz), 115.6, 31.4, 29.8, 25.4.

HRMS m/z (ESI) calcd for $C_{11}H_{10}NO_2F_3Na$ $[M+Na]^+$ 268.0556, found 268.0557.

6-Fluoro-1-methyl-3,4-dihydroquinolin-2(1H)-one (3e)



Following the general procedure using **1e** (72 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3e** as an orange solid in 85% yield (46 mg, 0.25 mmol).

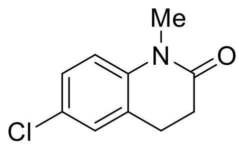
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 6.96 – 6.85 (m, 3H), 3.34 (s, 3H), 2.84 (m, 2H), 2.68 – 2.56 (m, 2H).

$^{19}F\{^{1}H\}$ NMR (376 MHz, $CDCl_3$) δ (ppm) -121.0.

$^{13}C\{^{1}H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 170.1, 158.6 (d, *J* = 242.9 Hz), 128.4 (d, *J* = 7.6 Hz), 115.9 (d, *J* = 8.1 Hz), 114.9 (d, *J* = 22.9 Hz), 113.8, 113.6, 31.6, 29.9, 25.6.

HRMS m/z (ESI) calcd for $C_{10}H_{10}NOFNa$ $[M+Na]^+$ 202.0639, found 202.0640.

6-Chloro-1-methyl-3,4-dihydroquinolin-2(1H)-one (3f)



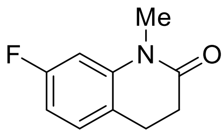
Following the general procedure using **1f** (77 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3f** as an orange solid in 78% yield (46 mg, 0.23 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.21 (dd, *J* = 8.6, 2.4 Hz, 1H), 7.15 (s, 1H), 6.89 (d, *J* = 8.6 Hz, 1H), 3.33 (s, 3H), 2.91 – 2.83 (m, 2H), 2.70 – 2.58 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 170.2, 139.4, 128.1, 128.0, 127.8, 127.4, 115.9, 31.5, 29.8, 25.3.

HRMS m/z (ESI) calcd for $C_{10}H_{10}NOClNa$ [M+Na]$^+$ 218.0343, found 218.0343.

7-Fluoro-1-methyl-3,4-dihydroquinolin-2(1H)-one (3h)



Following the general procedure using **1h** (72 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3h** as an orange oil in 54% yield (29 mg, 0.16 mmol).

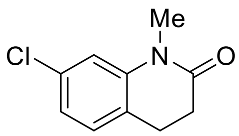
^{1}H RMN (400 MHz, $CDCl_3$) δ (ppm) 7.12 – 7.06 (m, 1H), 6.72 (s, 1H), 6.71 – 6.68 (m, 1H), 3.32 (s, 3H), 2.89 – 2.85 (m, 2H), 2.68 – 2.60 (m, 2H).

^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ (ppm) -114.1.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 170.4, 162.4 (d, *J* = 243.3 Hz), 142.1 (d, *J* = 10.1 Hz), 128.7 (d, *J* = 9.3 Hz), 121.7 (d, *J* = 3.2 Hz), 109.0 (d, *J* = 21.2 Hz), 102.9 (d, *J* = 26.6 Hz), 31.9, 29.7, 24.9.

HRMS m/z (ESI) calcd for $C_{10}H_{10}NOFNa$ [M+Na]$^+$ 202.0638 found 202.0638.

7-Chloro-1-methyl-3,4-dihydroquinolin-2(1H)-one (3i)



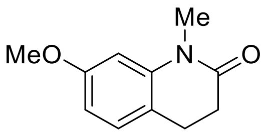
Following the general procedure using **1i** (77 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3i** as a yellow solid in 65% yield (38 mg, 0.19 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.08 (d, *J* = 7.8 Hz, 1H), 7.01 – 6.93 (m, 2H), 3.33 (s, 3H), 2.93 – 2.83 (m, 2H), 2.69 – 2.61 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 170.3, 141.9, 133.2, 128.8, 124.6, 122.6, 115.2, 31.6, 29.7, 25.0.

HRMS m/z (ESI) calcd for $C_{10}H_{10}NOClNa$ [M+Na]$^+$ 218.0343 found 218.0343.

7-Methoxy-1-methyl-3,4-dihydroquinolin-2(1H)-one (3j)



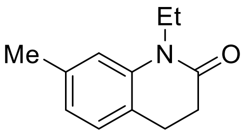
Following the general procedure using **1j** (76 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3j** as a yellow solid in 62% yield (36 mg, 0.19 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.06 (d, J = 8.3 Hz, 1H), 6.64 – 6.41 (m, 2H), 3.81 (s, 3H), 3.33 (s, 3H), 2.89 – 2.79 (m, 2H), 2.71 – 2.56 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 170.8, 159.3, 141.8, 128.3, 118.6, 106.6, 102.6, 55.6, 32.2, 29.7, 24.7.

HRMS m/z (ESI) calcd for $C_{11}H_{13}NO_2Na$ $[M+Na]^+$ 214.0838, found 214.0838.

1-Ethyl-7-methyl-3,4-dihydroquinolin-2(1H)-one (3k)



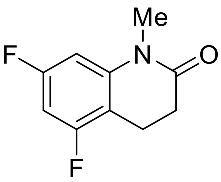
Following the general procedure using **1k** (75 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3k** as a yellow oil in 68% yield (39 mg, 0.20 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.04 (d, J = 7.4 Hz, 1H), 6.85 – 6.77 (m, 2H), 3.97 (q, J = 7.1 Hz, 2H), 2.86 – 2.80 (m, 2H), 2.64 – 2.57 (m, 2H), 2.36 (s, 3H), 1.26 (t, J = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 170.2, 139.6, 137.3, 127.9, 123.6, 123.3, 115.5, 37.5, 32.2, 25.3, 21.7, 13.0

HRMS m/z (ESI) calcd for $C_{12}H_{15}NONa$ $[M+Na]^+$ 212.1046, found 212.1046.

5,7-Difluoro-1-methyl-3,4-dihydroquinolin-2(1H)-one (3l)



Following the general procedure using **1l** (78 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3l** as a yellow oil in 72% yield (43 mg, 0.22 mmol).

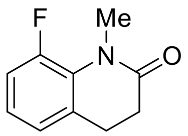
^{1}H RMN (400 MHz, $CDCl_3$) δ (ppm) 6.66 – 6.35 (m, 2H), 3.31 (s, 3H), 2.90 – 2.86 (m, 2H), 2.67 – 2.60 (m, 2H).

^{19}F{1H} NMR (376 MHz, $CDCl_3$) δ (ppm) -111.2 (d, J = 6.9 Hz), -114.8 (d, J = 6.8 Hz).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 170.0, 162.1 (dd, J = 244.8, 14.7 Hz), 159.6 (dd, J = 244.8, 14.5 Hz), 143.2 (dd, J = 12.3, 9.1 Hz), 109.0 (dd, J = 22.2, 3.8 Hz), 98.9 (dd, J = 26.6, 3.5 Hz), 98.1 (dd, J = 26.7, 25.4 Hz), 30.8, 29.9, 17.3 (d, J = 3.5 Hz).

HRMS m/z (ESI) calcd for $C_{10}H_9NOF_2Na$ $[M+Na]^+$ 220.0544, found 220.0546.

8-Fluoro-1-methyl-3,4-dihydroquinolin-2(1H)-one (3m)



Following the general procedure using **1m** (72 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 85:15) to afford **3m** as an orange solid in 42% yield (23 mg, 0.13 mmol).

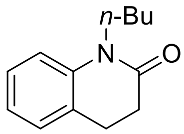
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.09 – 6.87 (m, 3H), 3.44 (d, *J* = 6.4 Hz, 3H), 2.91 – 2.86 (m, 2H), 2.63 – 2.58 (m, 2H).

^{19}F{^{1}H} NMR (376 MHz, CDCl$_3$) δ (ppm) -122.5.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 171.3, 152.2 (d, *J* = 247.1 Hz), 131.3 (d, *J* = 2.0 Hz), 127.7 (d, *J* = 27.5 Hz), 124.3 (d, *J* = 8.4 Hz), 123.1 (d, *J* = 3.1 Hz), 115.9 (d, *J* = 22.0 Hz), 33.5 (d, *J* = 11.3 Hz), 32.2, 26.1 (d, *J* = 2.5 Hz).

HRMS m/z (ESI) calcd for $C_{10}H_{10}NOFNa$ $[M+Na]^+$ 202.0638, found 202.0636.

1-Butyl-3,4-dihydroquinolin-2(1H)-one (3n)



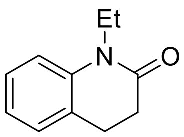
Following the general procedure using **1n** (71 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3n** as a yellow oil in 83% yield (51 mg, 0.25 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.30 – 7.22 (m, 1H), 7.21 – 7.14 (m, 1H), 7.05 – 6.97 (m, 2H), 3.93 (t, *J* = 7.5 Hz, 2H), 2.94 – 2.85 (m, 2H), 2.69 – 2.62 (m, 2H), 1.79 – 1.52 (m, 2H), 1.48 – 1.20 (m, 2H), 0.98 (t, *J* = 7.3 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 170.2, 139.7, 128.1, 127.5, 126.7, 122.7, 114.9, 42.0, 32.1, 29.4, 25.7, 20.3, 13.9.

HRMS m/z (ESI) calcd for $C_{13}H_{17}NONa$ $[M+Na]^+$ 226.1202, found 226.1201.

1-Ethyl-3,4-dihydroquinolin-2(1H)-one (3o)



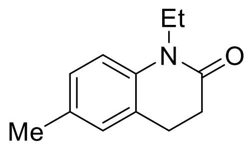
Following the general procedure using **1o** (71 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3o** as a yellow oil in 75% yield (39 mg, 0.22 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.26 – 7.22 (m, 1H), 7.16 (dd, *J* = 7.3, 1.3 Hz, 1H), 7.04 – 6.95 (m, 2H), 3.99 (q, *J* = 7.1 Hz, 2H), 3.00 – 2.80 (m, 2H), 2.76 – 2.33 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 170.0, 139.7, 128.1, 127.6, 126.7, 122.8, 114.7, 37.5, 32.1, 25.7, 12.9.

HRMS m/z (ESI) calcd for $C_{11}H_{13}NONa$ $[M+Na]^+$ 198.0889, found 198.0888.

1-Ethyl-6-methyl-3,4-dihydroquinolin-2(1H)-one (3p)



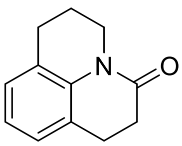
Following the general procedure using **1p** (75 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3p** as an orange oil in 81% yield (46 mg, 0.24 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.04 (d, *J* = 8.2 Hz, 1H), 6.98 (s, 1H), 6.90 (d, *J* = 8.2 Hz, 1H), 3.97 (q, *J* = 7.1 Hz, 2H), 2.88 – 2.78 (m, 2H), 2.65 – 2.52 (m, 2H), 2.30 (s, 3H), 1.24 (t, *J* = 7.1 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 169.9, 137.2, 132.3, 128.9, 127.9, 126.6, 114.6, 37.4, 32.1, 25.7, 20.6, 12.9.

HRMS m/z (ESI) calcd for $C_{12}H_{15}NONa$ [M+Na]$^+$ 212.1046, found 212.1048.

2,3,6,7-Tetrahydro-*1H,5H*-pyrido[3,2,1-ij]quinolin-5-one (3q)



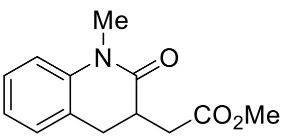
Following the general procedure using **1q** (72 mg, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3q** as a yellow oil in 70% yield (39 mg, 0.21 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.02 – 6.96 (m, 2H), 6.93 – 6.88 (m, 1H), 3.90 – 3.85 (m, 2H), 2.91 – 2.84 (m, 2H), 2.79 (t, *J* = 6.3 Hz, 2H), 2.68 – 2.61 (m, 2H), 1.97 – 1.90 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 169.7, 136.2, 127.9, 125.8, 125.5, 125.4, 122.5, 41.0, 31.6, 27.4, 25.4, 21.6.

HRMS m/z (ESI) calcd for $C_{12}H_{13}NONa$ [M+Na]$^+$ 210.0889, found 210.0891.

Methyl 2-(1-methyl-2-oxo-1,2,3,4-tetrahydroquinolin-3-yl)acetate (3r)



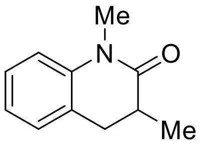
Following the general procedure using **1a** (67 mg, 0.3 mmol, 1 equiv.) and dimethyl itaconate **2b** (142 mg, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 70:30) to afford **3r** as an orange oil in 57% yield (40 mg, 0.17 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.31 – 7.22 (m, 1H), 7.21 – 7.13 (m, 1H), 7.07 – 6.94 (m, 2H), 3.72 (s, 3H), 3.36 (s, 3H), 3.09 – 2.77 (m, 4H), 2.46 (dd, *J* = 16.1, 6.8 Hz, 1H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 172.8, 171.2, 140.4, 127.9, 127.8, 125.6, 123.1, 114.8, 52.0, 37.6, 34.9, 31.2, 30.1.

HRMS m/z (ESI) calcd for $C_{13}H_{15}NO_3Na$ [M+Na]$^+$ 256.0944, found 256.0945.

1,3-Dimethyl-3,4-dihydroquinolin-2(1H)-one (3s)



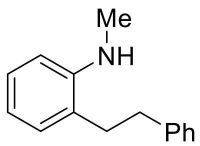
Following the general procedure using **1a** (67 mg, 0.3 mmol, 1 equiv.) and methyl methacrylate **2c** (96 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3s** as a yellow oil in 60% yield (32 mg, 0.18 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.28 – 7.23 (m, 1H), 7.17 – 7.15 (m, 1H), 7.03 – 6.95 (m, 2H), 3.36 (s, 3H), 2.93 (dd, *J* = 14.5, 4.8 Hz, 1H), 2.73 – 2.62 (m, 2H), 1.26 (d, *J* = 6.6 Hz, 3H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 173.4, 140.6, 128.0, 127.5, 125.9, 122.8, 114.6, 35.7, 33.5, 29.9, 15.8.

HRMS m/z (ESI) calcd for $C_{11}H_{13}NONa$ $[M+Na]^+$ 198.0889, found 198.0891.

***N*-Methyl-2-phenethylaniline (5a)**



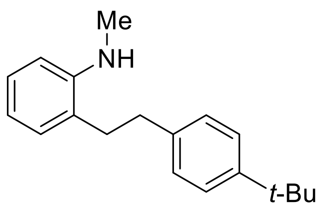
Following the general procedure using **1a** (66 mg, 0.3 mmol, 1 equiv.) and styrene **2d** (99 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 95:5) to afford **5a** as a colorless oil in 60% yield (38 mg, 0.18 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.35 – 7.29 (m, 2H), 7.26 – 7.17 (m, 4H), 7.09 (d, *J* = 7.3 Hz, 1H), 6.74 (t, *J* = 7.3 Hz, 1H), 6.67 (d, *J* = 8.0 Hz, 1H), 2.97 – 2.93 (m, 2H), 2.83 (s, 3H), 2.81 – 2.74 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 146.8, 142.1, 128.9, 128.6, 128.5, 127.5, 126.2, 125.8, 117.4, 110.1, 35.3, 33.3, 31.1.

HRMS m/z (ESI) calcd for $C_{15}H_{18}N$ $[M+H]^+$ 212.1433, found 212.1431.

2-(4-(Tert-butyl)phenethyl)-*N*-methylaniline (5b)



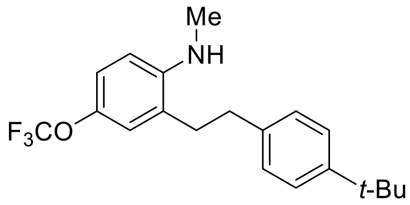
Following the general procedure using **1a** (66 mg, 0.3 mmol, 1 equiv.) and 4-*tert*-butyl-styrene **2e** (163 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 95:5) to afford **5b** as a colorless oil in 73% yield (59 mg, 0.22 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.43 – 7.37 (m, 2H), 7.25 – 7.19 (m, 3H), 7.17 (d, *J* = 7.4 Hz, 1H), 6.79 (t, *J* = 7.4 Hz, 1H), 6.69 (d, *J* = 8.0 Hz, 1H), 3.00 – 2.93 (m, 2H), 2.83 (s, 3H), 2.83 – 2.77 (m, 2H), 1.39 (s, 9H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 149.0, 147.0, 139.0, 128.8, 128.1, 127.5, 125.9, 125.5, 117.3, 109.9, 34.8, 34.5, 33.3, 31.6, 31.0.

HRMS m/z (ESI) calcd for $C_{19}H_{26}N$ $[M+H]^+$ 268.2060, found 268.2061.

2-(4-*Tert*-butyl)phenethyl)-*N*-methyl-4-(trifluoromethoxy)aniline (5c)



Following the general procedure using **1d** (92 mg, 0.3 mmol, 1 equiv.) and 4-*tert*-butyl-styrene **2e** (163 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 90:10) to afford **5c** as a colorless oil in 65% yield (69 mg, 0.19 mmol).

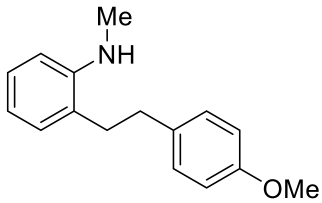
^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.36 (d, *J* = 8.3 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 7.07 – 7.02 (m, 1H), 6.98 – 6.94 (m, 1H), 6.56 (d, *J* = 8.8 Hz, 1H), 2.97 – 2.86 (m, 2H), 2.79 (s, 3H), 2.78 – 2.67 (m, 2H), 1.36 (s, 9H).

^{19}F NMR (376 MHz, CDCl$_3$) δ (ppm) -58.3.

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 149.3, 145.8, 140.4 (d, *J* = 2.0 Hz), 138.4, 128.2, 126.9, 125.6, 122.1, 120.9 (q, *J* = 255.0 Hz), 120.1, 109.9, 34.6, 34.5, 33.1, 31.5, 31.1.

HRMS m/z (ESI) calcd for $C_{20}H_{24}NOF_3Na$ [M+Na]$^+$ 374.1707, found 374.1706.

2-(4-Methoxyphenethyl)-*N*-methylaniline (5d)



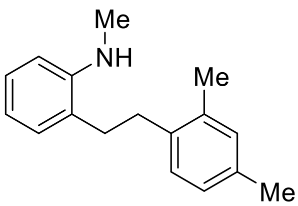
Following the general procedure using **1a** (66 mg, 0.3 mmol, 1 equiv.) and 4-vinylanisole **2f** (120 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 90:10) to afford **5d** as a colorless oil in 75% yield (54 mg, 0.22 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.27 – 7.23 (m, 2H), 7.20 – 7.14 (m, 1H), 7.12 – 7.07 (m, 2H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 3.85 (s, 3H), 2.94 – 2.86 (m, 2H), 2.83 (s, 3H), 2.77 – 2.68 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 158.1, 147.0, 134.2, 129.4, 128.9, 127.5, 125.8, 117.2, 114.0, 109.9, 55.5, 34.4, 33.6, 31.1.

HRMS m/z (ESI) calcd for $C_{16}H_{19}NONa$ [M+Na]$^+$ 264.1358 found 264.1357.

2-(2,4-Dimethylphenethyl)-*N*-methylaniline (5e)



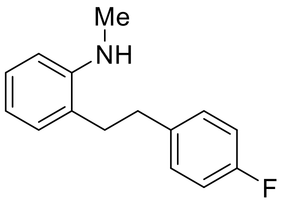
Following the general procedure using **1a** (66 mg, 0.3 mmol, 1 equiv.) and 2,4-dimethyl-styrene **2g** (131 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 95:5) to afford **5e** as a colorless oil in 67% yield (48 mg, 0.20 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.25 – 7.19 (m, 1H), 7.16 – 7.06 (m, 2H), 7.04 – 6.96 (m, 2H), 6.82 – 6.74 (m, 1H), 6.70 – 6.63 (m, 1H), 2.94 – 2.89 (m, 2H), 2.85 (s, 3H), 2.77 – 2.69 (m, 2H), 2.35 (s, 3H), 2.30 (s, 3H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 146.9, 137.1, 135.8, 135.7, 131.1, 129.2, 128.7, 127.4, 126.8, 125.9, 117.1, 109.8, 32.1, 32.3, 30.9, 20.9, 19.2.

HRMS m/z (ESI) calcd for $C_{17}H_{22}N$ $[M+H]^+$ 240.1746, found 240.1745.

2-(4-Fluorophenethyl)-*N*-methylaniline (5f)



Following the general procedure using **1a** (66 mg, 0.3 mmol, 1 equiv.) and 4-fluorostyrene **2h** (99 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 95:5) to afford **5f** as a colorless oil in 32% yield (22 mg, 0.09 mmol).

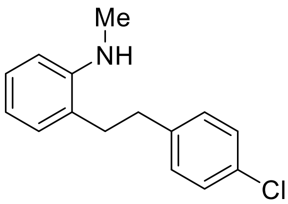
^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.22 – 7.11 (m, 3H), 7.05 – 6.94 (m, 3H), 6.71 (t, *J* = 7.4 Hz, 1H), 6.65 (d, *J* = 8.0 Hz, 1H), 2.94 – 2.88 (m, 2H), 2.84 (s, 3H), 2.78 – 2.71 (m, 2H).

^{19}F NMR (376 MHz, $CDCl_3$) δ (ppm) -117.4.

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 161.5 (d, *J* = 243.7 Hz), 146.9, 137.6 (d, *J* = 3.3 Hz), 129.9 (d, *J* = 7.8 Hz), 128.9, 127.6, 125.3, 117.3, 115.3 (d, *J* = 21.2 Hz), 110.0, 34.3, 33.4, 31.0.

HRMS m/z (ESI) calcd for $C_{15}H_{17}NF$ $[M+H]^+$ 230.1339, found 230.1337.

2-(4-Chlorophenethyl)-*N*-methylaniline (5g)



Following the general procedure using **1a** (66 mg, 0.3 mmol, 1 equiv.) and 4-chlorostyrene **2i** (108 µL, 0.9 mmol, 3 equiv.), the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 90:10) to afford **5g** as a colorless oil in 42% yield (31 mg, 0.17 mmol).

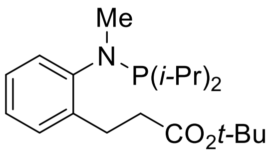
^1H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.27 – 7.23 (m, 2H), 7.20 – 7.14 (m, 1H), 7.12 – 7.07 (m, 2H), 7.01 (d, *J* = 7.4 Hz, 1H), 6.70 (t, *J* = 7.3 Hz, 1H), 6.64 (d, *J* = 8.0 Hz, 1H), 2.94 – 2.86 (m, 2H), 2.83 (s, 3H), 2.77 – 2.68 (m, 2H).

$^{13}C\{^1H\}$ NMR (101 MHz, $CDCl_3$) δ (ppm) 146.7, 140.3, 131.8, 129.8, 128.8, 128.5, 127.5, 125.1, 117.2, 109.9, 34.3, 33.0, 30.9.

HRMS m/z (ESI) calcd for $C_{15}H_{17}NCl$ $[M+H]^+$ 246.1044, found 246.1045.

5. Procedure for C-H Alkylation of Phosphanamine for Preparation of 4a and Compound Characterization

***Tert*-butyl 3-(2-((diisopropylphosphaneyl)(methyl)amino)phenyl)propanoate (4a)**



In a glovebox, an oven-dried Schlenk tube was charged with phosphanamine **1a** (66 mg, 0.3 mmol, 1 equiv.). The Schlenk tube was closed and removed from the glovebox. Under argon atmosphere, $[RhCl(COD)]_2$ (3 mg, 0.006 mmol, 2 mol%), toluene (1.5 mL), 2,2,6,6-tetramethylheptane-3,5-dione **L6** (3 µL, 0.012 mmol, 4 mol%) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.) were added. The resulting mixture was stirred at 160 °C over 24 h. The residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 70:30) to afford **4a** as a colorless oil in 21% yield (22 mg, 0.063 mmol).

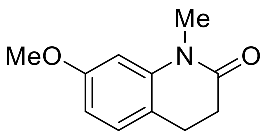
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.20 (d, *J* = 7.9 Hz, 1H), 7.16 – 7.09 (m, 2H), 7.02 – 6.97 (m, 1H), 3.06 – 3.04 (m, 2H), 2.99 (d, *J* = 1.9 Hz, 3H), 2.56 – 2.52 (m, 2H), 2.10 (pent.d, *J* = 7.1, 2.7 Hz, 2H), 1.44 (s, 9H), 1.24 (dd, *J* = 11.8, 7.1 Hz, 6H), 1.12 (dd, *J* = 15.1, 7.0 Hz, 6H).

^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$) δ (ppm) 79.8.

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 172.8, 151.7 (d, *J* = 17.3 Hz), 136.3 (d, *J* = 3.4 Hz), 126.6 (d, *J* = 7.3 Hz), 123.9, 80.2, 38.3 (d, *J* = 6.5 Hz), 36.8, 28.3, 27.4 (d, *J* = 7.1 Hz), 26.7, 26.6, 20.4 (d, *J* = 11.6 Hz), 19.8, 19.6.

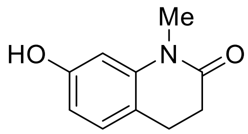
6. Large Scale Reaction and Application to the Synthesis of Aripiprazole *N*-Methylated Analog

6-Methoxy-1-methyl-3,4-dihydroquinolin-2(1H)-one (3j)



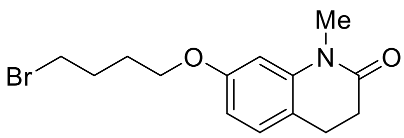
In a glovebox, an oven-dried Schlenk tube was charged with **1j** (1.27 g, 5 mmol, 1 equiv.) and distilled DMF (33 mL). Then, the Schlenk tube was closed and removed from the glovebox. Under argon atmosphere, $[RhCl(COD)]_2$ (25 mg, 0.05 mmol, 1 mol%), 2,2,6,6-tetramethylheptane-3,5-dione **L6** (27 µL, 0.1 mmol, 2 mol%), water (9 mL, 50 mmol, 10 equiv.) and *tert*-butyl acrylate (2 mL, 15 mmol, 3 equiv.) were added. The resulting mixture was stirred at 160 °C over 24 h. The crude product was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **3j** in 57% yield (0.54 g, 2.85 mmol).

6-Hydroxy-1-methyl-3,4-dihydroquinolin-2(1H)-one (6)



To a 0 °C solution of **3j** (0.54 g, 2.85 mmol, 1 equiv.) in CH_2Cl_2 (10 mL) was added dropwise BBr_3 (1 M in CH_2Cl_2, 5.7 mL, 5.7 mmol, 2 equiv.). Then the resulting mixture was slowly warmed up to room temperature and stirred over 14 h. The reaction mixture was concentrated under reduced pressure. The crude product was purified by flash chromatography (EtOAc/CH_2Cl_2/Hexanes = 1:1:1) to afford the product **6** as a yellow solid in 38% yield (0.19 g, 1.08 mmol). NMR datas were consistent with those in the literature.[S2]

6-(4-Bromobutoxy)-1-methyl-3,4-dihydroquinolin-2(1H)-one (7)



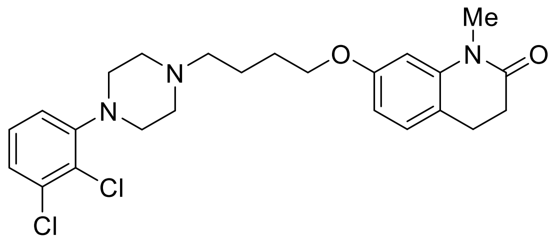
1,4-Dibromobutane (259 µL, 2.16 mmol, 2 equiv.) was added to a solution of **6** (0.19 g, 1.08 mmol, 1 equiv.) and potassium carbonate (135 mg, 1.96 mmol, 2 equiv.) in acetone (6 mL). The resulting mixture was refluxed over 6 h. After cooling to room temperature, the mixture was filtered, the solvent was evaporated under reduced pressure. The crude product was purified by flash column chromatography on silica gel (Heptane/EtOAc = 50:50) to afford **7** as a white solid in 56% yield (0.19 g, 0.60 mmol).

^{1}H NMR (400 MHz, CDCl$_3$) δ (ppm) 7.00 (d, *J* = 8.1 Hz, 1H), 6.57 – 6.43 (m, 2H), 3.96 (t, *J* = 6.0 Hz, 2H), 3.45 (t, *J* = 6.6 Hz, 2H), 3.28 (s, 3H), 2.83 – 2.74 (m, 2H), 2.66 – 2.47 (m, 2H), 2.11 – 1.98 (m, 2H), 1.98 – 1.83 (m, 2H).

^{13}C{^{1}H} NMR (101 MHz, CDCl$_3$) δ (ppm) 170.5, 158.4, 141.6, 128.1, 118.4, 107.0, 102.9, 67.0, 33.4, 32.0, 29.5, 29.4, 27.9, 24.5.

HRMS m/z (ESI) calcd for $C_{14}H_{19}BrNO_2$ $[M+H]^+$ 312.0594, found 312.0593.

7-(4-(4-(2,3-Dichlorophenyl)piperazin-1-yl)butoxy)-1-methyl-3,4-dihydroquinolin-2(1H)-one (8)



To a solution of **7** (0.19 g, 0.60 mmol, 1 equiv.) in acetonitrile (5 mL) was added potassium iodide (200 mg, 1.2 mmol, 2 equiv.). The mixture was refluxed at 85 °C over 30 min. Then the reaction was cooled to room temperature, triethylamine (167 µL, 1.2 mmol, 2 equiv.) and 1-(2,3-dichlorophenyl)piperazine hydrochloride (241 mg, 0.9 mmol, 1.5 equiv.) were added. The reaction mixture was refluxed at 85 °C over 8 h. After cooling to room temperature, the mixture was filtered, the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography on silica gel (EtOAc = 1) to afford **8** as a white solid in 70% yield (0.19 g, 0.42 mmol).

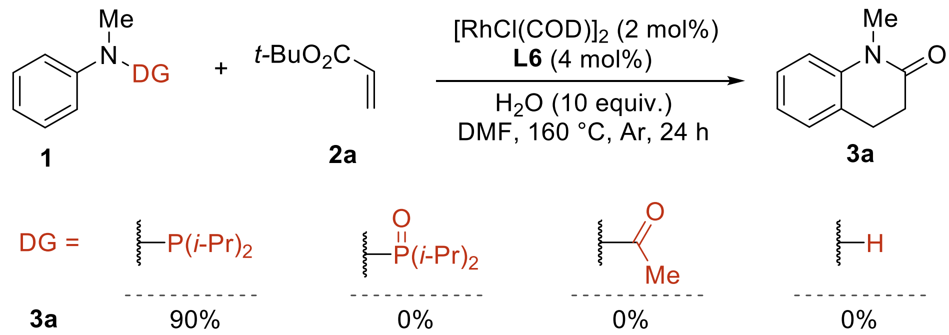
^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.20 – 7.12 (m, 2H), 7.05 (d, *J* = 8.1 Hz, 1H), 6.97 (dd, *J* = 7.0, 2.6 Hz, 1H), 6.60 – 6.50 (m, 2H), 4.01 (t, *J* = 5.9 Hz, 2H), 3.33 (s, 3H), 3.19 – 3.09 (m, 4H), 2.90 – 2.80 (m, 2H), 2.67 – 2.59 (m, 4H), 1.92 – 1.74 (m, 8H).

^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$) δ (ppm) 170.8, 158.7, 150.9, 141.8, 134.3, 128.4, 128.3, 127.7, 125.1, 118.9, 118.6, 107.3, 103.1, 67.9, 58.2, 53.3, 50.7, 32.2, 29.7, 27.4, 24.8, 23.1.

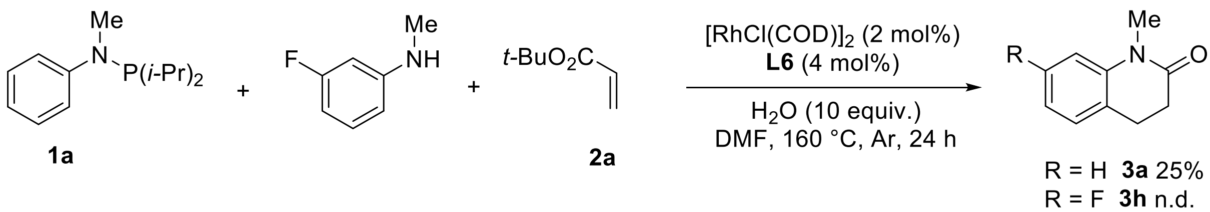
HRMS m/z (ESI) calcd for $C_{24}H_{30}Cl_2N_3O_2$ $[M+H]^+$ 462.1710, found 462.1712.

7. Mechanistic Studies

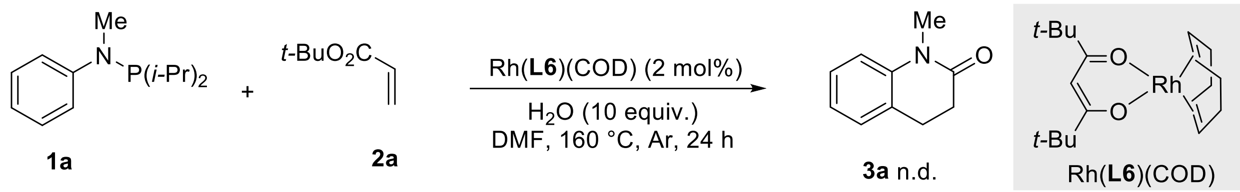
1. Control Experiments



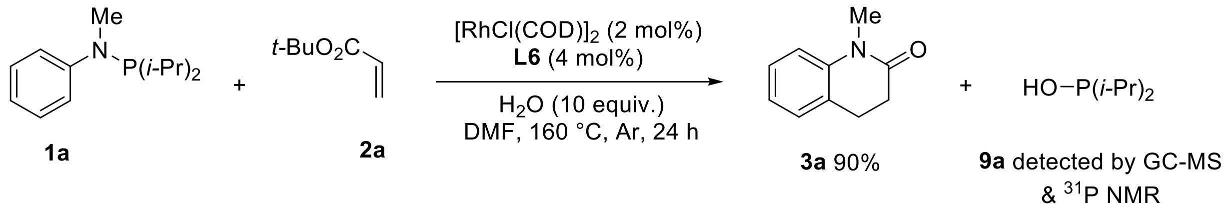
Procedure: Under argon atmosphere, an oven-dried Schlenk tube was charged with starting material **1** (0.3 mmol, 1 equiv.), $[RhCl(COD)]_2$ (3 mg, 0.006 mmol, 2 mol%), distilled DMF (1.5 mL), 2,2,6,6-tetramethylheptane-3,5-dione **L6** (3 µL, 0.012 mmol, 4 mol%), water (54 µL, 3 mmol, 10 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.). The resulting mixture was stirred at 160 °C over 24 h. The crude product was then cooled down, diluted with ethyl acetate and injected in a calibrated GC-FID using *n*-dodecane (10 µL) as an internal standard to give the corresponding yields: t_R (min) 8.2 (*n*-dodecane), 10.7 (product **3a**).



Procedure: In a glovebox, an oven-dried Schlenk tube was charged with **1a** (66 mg, 0.3 mmol, 1 equiv.) and distilled DMF (1.5 mL). Then, the Schlenk tube was closed and removed from the glovebox. Under argon atmosphere, $[RhCl(COD)]_2$ (3 mg, 0.006 mmol, 2 mol%), 2,2,6,6-tetramethylheptane-3,5-dione (3 µL, 0.012 mmol, 4 mol%), water (54 µL, 3 mmol, 10 equiv.), 3-fluoro-*N*-methylaniline (40 µL, 0.3 mmol, 1 equiv.) and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.) were added. The resulting mixture was stirred at 160 °C over 24 h. The crude product was then cooled down, diluted with ethyl acetate and injected in a calibrated GC-MS.

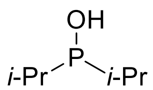


Procedure: In a glovebox, an oven-dried Schlenk tube was charged with phosphanamine **1a** (66 mg, 0.3 mmol, 1 equiv.) and distilled DMF (1.5 mL). Then, the Schlenk tube was closed and removed from the glovebox. Under argon atmosphere, [Rh**L6**(COD)]$_2$ (2.4 mg, 0.006 mmol, 2 mol%), water (54 µL, 3 mmol, 10 equiv.), and *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.) were added. The resulting mixture was stirred at 160 °C over 24 h. The crude product was then cooled down, diluted with ethyl acetate and injected in GC-MS.



Procedure: In a glovebox, an oven-dried Schlenk tube was charged with phosphanamine **1a** (66 mg, 0.3 mmol, 1 equiv.) and distilled DMF (1.5 mL). Then, the Schlenk tube was closed and removed from the glovebox. Under argon atmosphere, [RhCl(COD)]$_2$ (3 mg, 0.006 mmol, 2 mol%), 2,2,6,6-tetramethylheptane-3,5-dione (3 µL, 0.012 mmol, 4 mol%), water (54 µL, 3 mmol, 10 equiv.), *tert*-butyl acrylate **2a** (131 µL, 0.9 mmol, 3 equiv.) were added. The resulting mixture was stirred at 160 °C over 24 h. The crude product was then cooled down, diluted with ethyl acetate and injected in GC-MS. Products were identified according to their retention time (t_R) and mass-to-charge ratio (m/z): t_R (min) 5.9 (hydroxydiisopropylphosphane **9a**), 6.2 (*n*-dodecane), 9.2 (product **3a**).

Hydroxydiisopropylphosphane (9a)



According to Zargarian's work,[S3] hydroxydiisopropylphosphane was synthesized as followed. To a solution of chlorodiisopropylphosphine (318 µL, 2 mmol, 1 equiv.) in THF (5 mL) was added water (72 µL, 4 mmol, 2 equiv.). The resulting solution was stirred at room temperature over 2 h. Then Et_3N (245 µL, 2.2 mmol, 1.1 equiv.) was carefully added under stirring, followed by $MgSO_4$ and 5 mL of diethyl ether. The precipitate was filtered off by cannula filtration. The resulting filtrate was evaporated under reduced pressure to provide the pure product **9a** as a colorless liquid.

NMR datas were consistent with those in the literature. Mass-to-charge ratio (m/z = 134) was determined after GC-MS analysis.

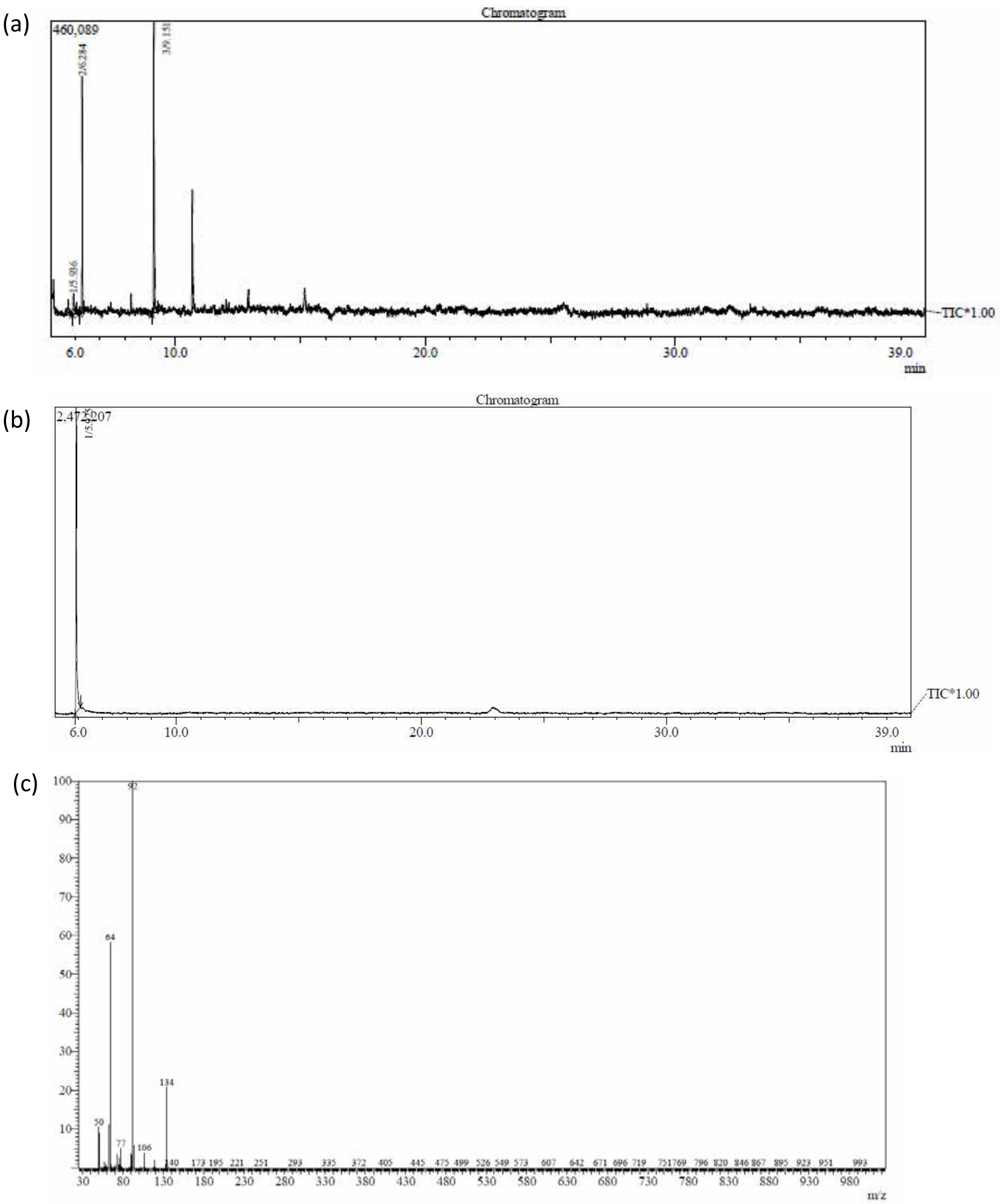
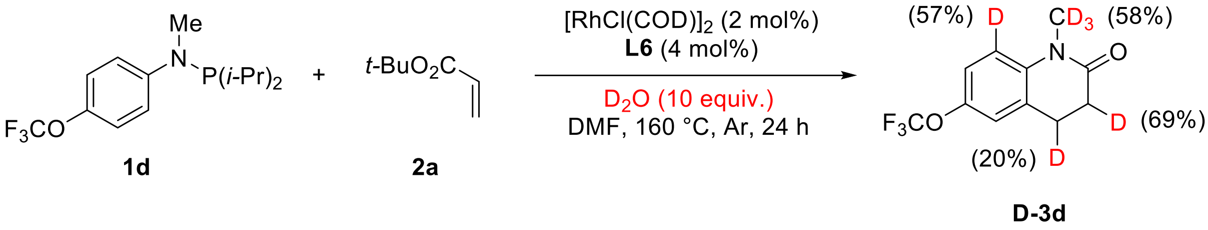


Figure S1. a) Gas Chromatogram of the Crude Mixture. b) Gas Chromatogram of Hydroxydiisopropylphosphane **9a**. c) Mass Spectrum of Hydroxydiisopropylphosphane **9a** (m/z = 134).

2. Deuterium Labelling Experiments



Procedure: In a glovebox, an oven-dried Schlenk tube was charged with phosphanamine **1d** (92 mg, 0.3 mmol, 1 equiv.) and distilled DMF (1.5 mL). The Schlenk tube was closed and removed from the glovebox. Under argon atmosphere, $[RhCl(COD)]_2$ (3 mg, 0.006 mmol, 2 mol%), 2,2,6,6-tetramethylheptane-3,5-dione **L6** (3 μL, 0.012 mmol, 4 mol%), deuterium oxide (54 μL, 3 mmol, 10 equiv.) and *tert*-butyl acrylate **2a** (131 μL, 0.9 mmol, 3 equiv.) were added. The resulting mixture was stirred at 160 °C over 24 h. the residue was purified by flash chromatography on silica gel (Heptane/Ethyl Acetate = 80:20) to afford **D-3d**.

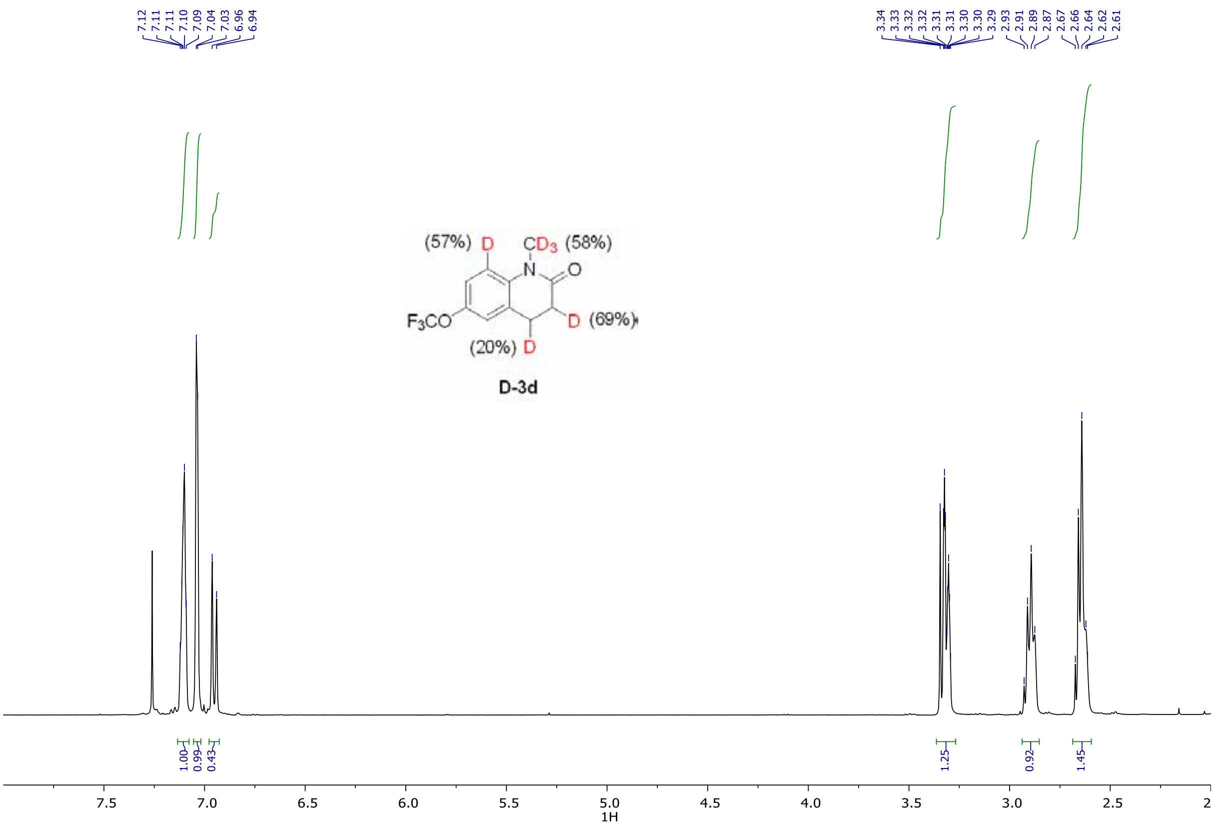
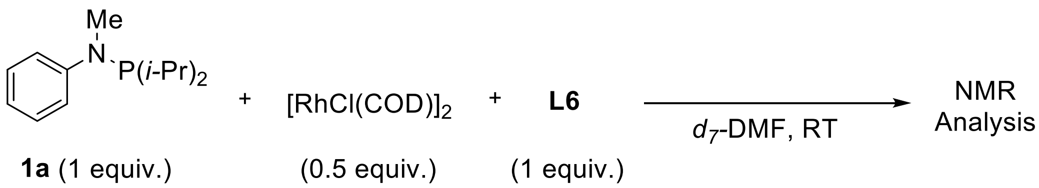


Figure S2. ^{1}H NMR Spectra of **D-3d**.

3. Stochiometric Reactions



Procedure: In a glovebox, to a 5 mL vial was added $[RhCl(COD)]_2$ (10 mg, 0.02 mmol, 1 equiv.), phosphanamine **1a** (9 mg, 0.04 mmol, 2 equiv.), 2,2,6,6-tetramethylheptane-3,5-dione **L6** (8.5 µL, 0.04 mmol, 2 equiv.) in d_7-DMF (0.75 mL). The reaction was stirred at room temperature over 2 h or 24 h in a glovebox. The crude solution was directly used for NMR analyses using a Young NMR tube.

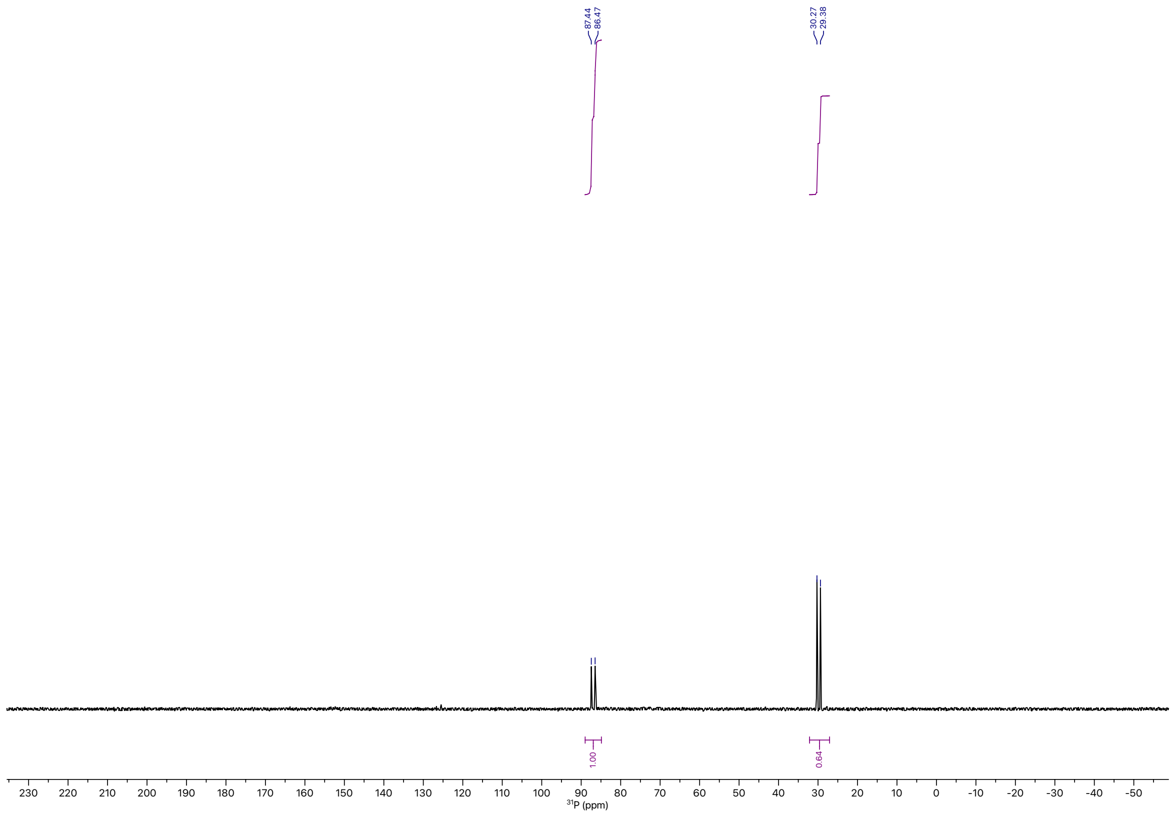
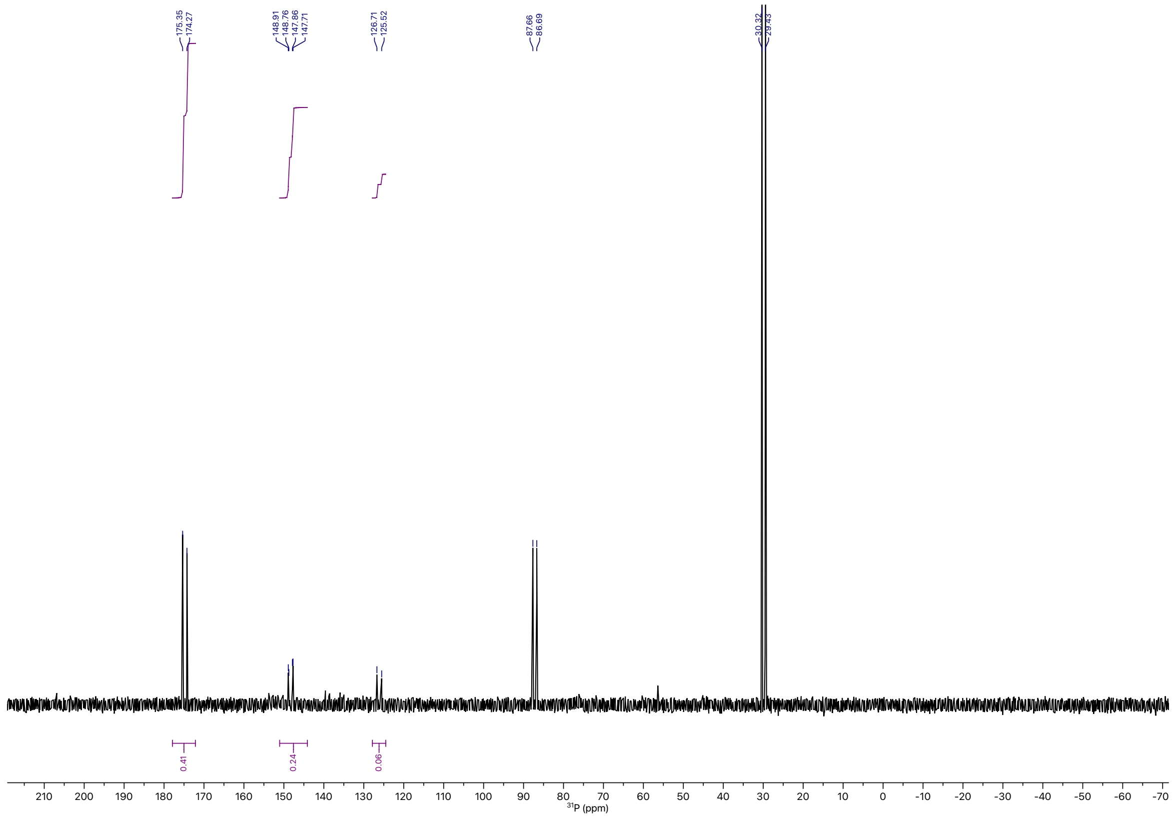


Figure S3. 31P NMR Chart After 2h Reaction.



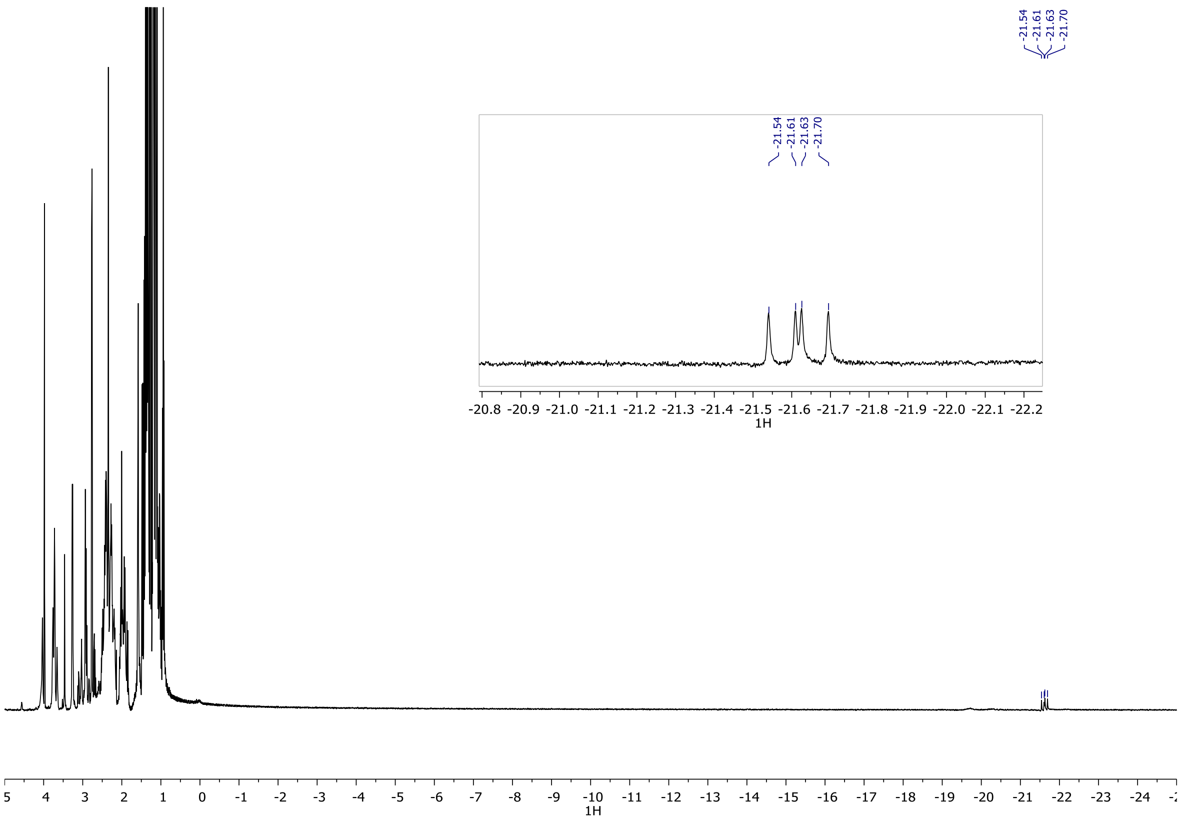
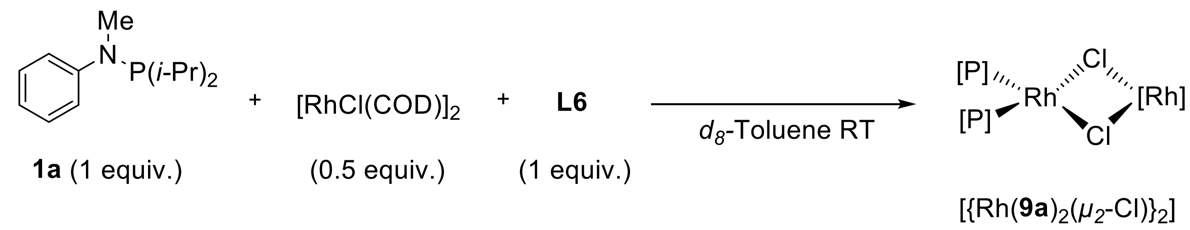
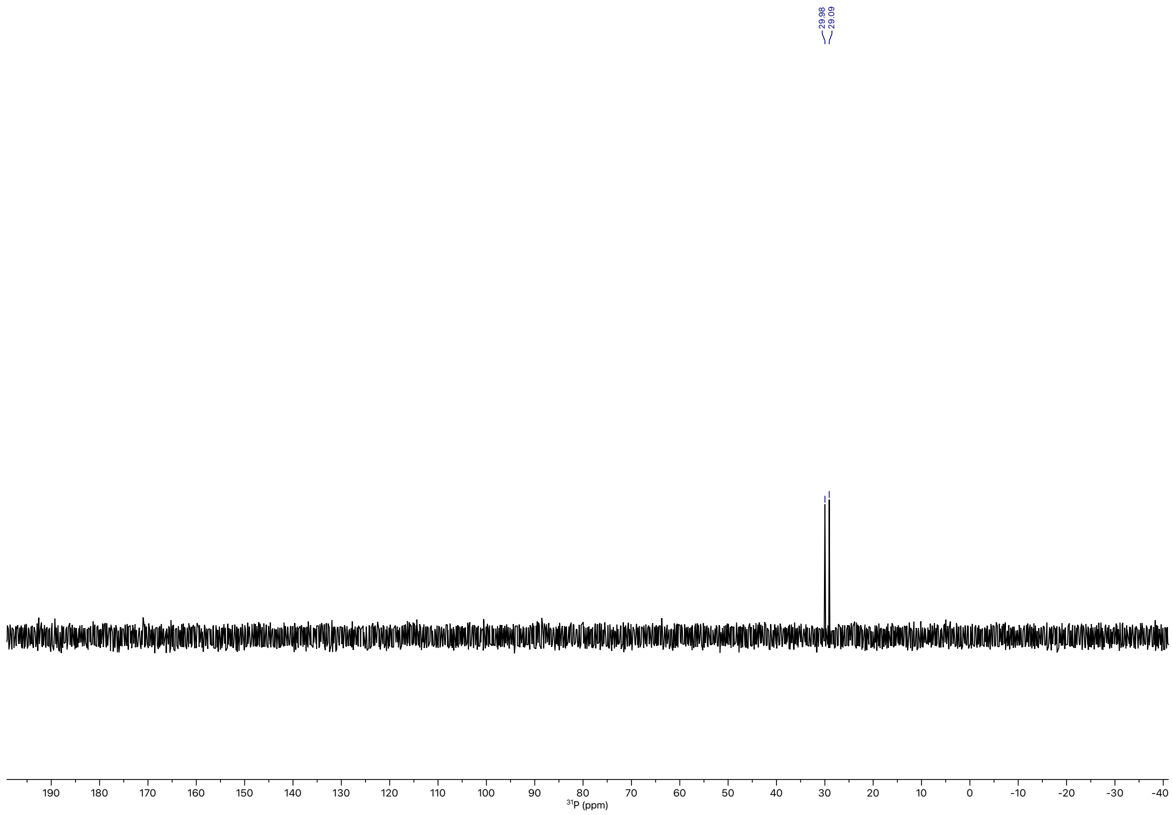


Figure S4. ^{31}P and ^{1}H NMR Charts After 24h Reaction.



Procedure: In a glovebox, to a 5 mL vial was added $[RhCl(COD)]_2$ (10 mg, 0.02 mmol, 1 equiv.), phosphanamine **1a** (9 mg, 0.04 mmol, 2 equiv.), 2,2,6,6-tetramethylheptane-3,5-dione **L6** (8.5 µL, 0.04 mmol, 2 equiv.) in *d*$_8$-Toluene (0.75 mL). The reaction was stirred over 10 min then the crude solution was removed from glovebox and concentrated under vacuum. The resulting product was diluted in CH_2Cl_2, filtered over a plug of Al_2O_3 and concentrated under vacuum.



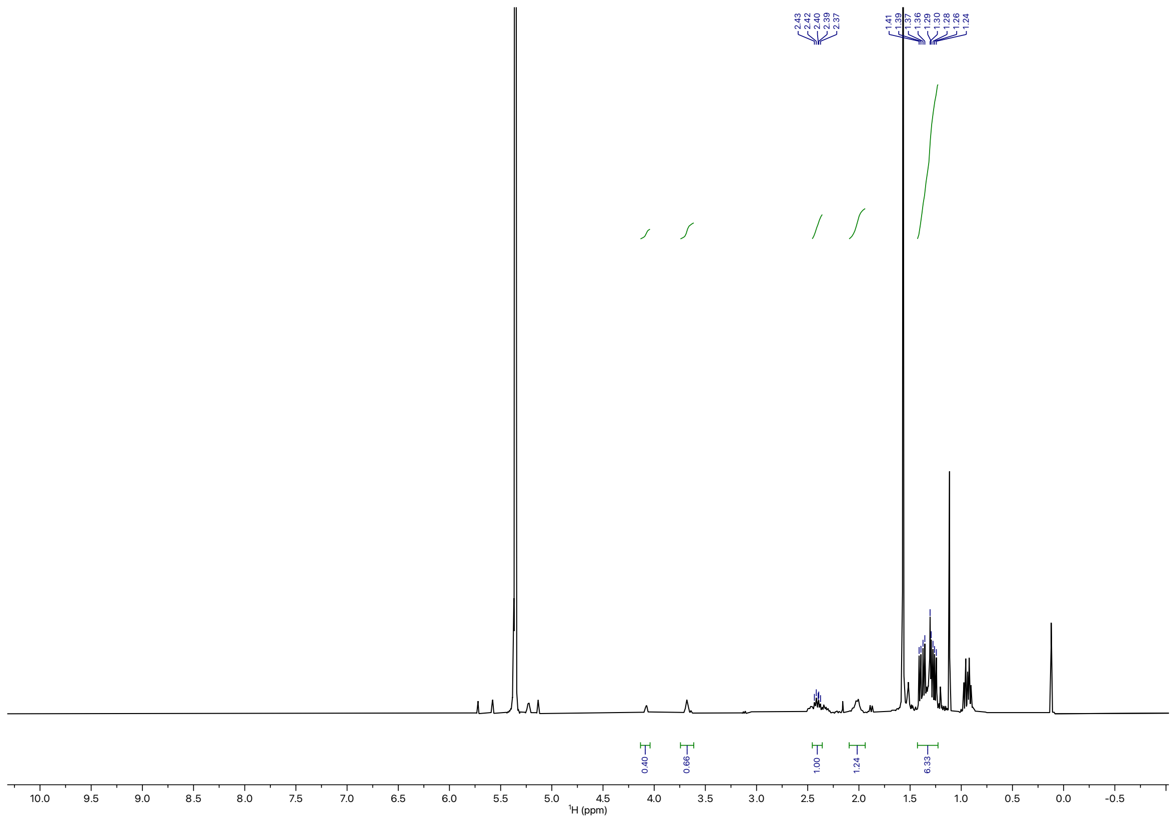


Figure S5. ^{31}P and ^{1}H NMR Charts of [{Rh(**9a**)$_2$(μ_2-Cl)}$_2$].

8. Kinetic Study

1. Kinetic Reaction Profile

Procedure: In a glovebox, a three-necked round bottom flask was charged with phosphanamine **1a** (88 mg, 0.4 mmol, 1 equiv.) and distilled DMF (2 mL). Then the flask was closed and removed from the glovebox. Under argon atmosphere, $[RhCl(COD)]_2$ (4 mg, 0.012 mmol, 2 mol%), 2,2,6,6-tetramethylheptane-3,5-dione **L6** (4 µL, 0.024 mmol, 4 mol%), water (72 µL, 4 mmol, 10 equiv.) and *tert*-butyl acrylate **2a** (174 µL, 1.2 mmol, 3 equiv.) were added. The reaction was initiated by placing the flask into a preheated bath at 160 °C. Reaction progress was followed by NMR spectroscopy analyses. The reaction was sampled by withdrawing 50 µL aliquots of the reaction solution, which was quenched with a solution of $CDCl_3$ (0.6 mL). Final concentrations of **1a** and **4a** were determined by ^{31}P NMR spectroscopy analysis using triphenylphosphine (0.038 mmol) as external standard. Final concentration of **3a** was determined by ^{1}H NMR spectroscopy analysis using dichloroethane (0.063 mmol) as external standard.

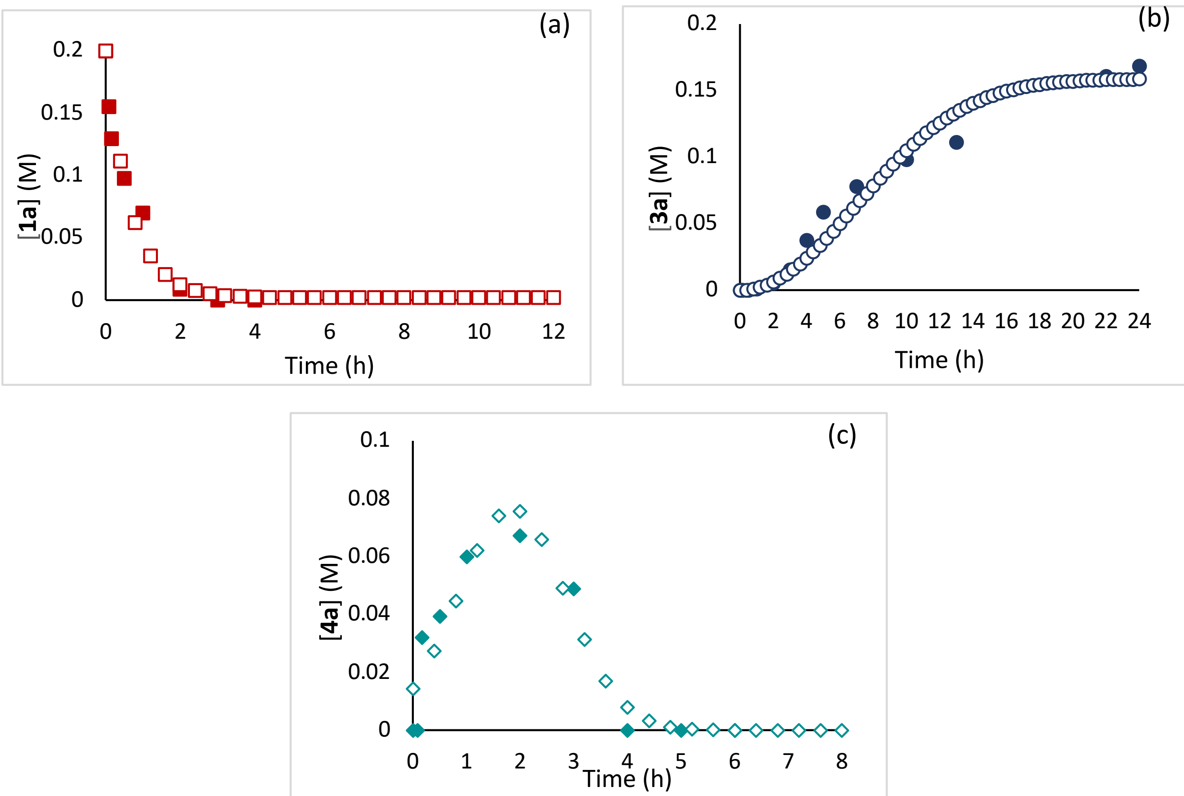


Figure S6. a) Consumption of Phosphanamine [**1a**] (M) *vs.* Time (h). Experimental datas are shown in red filled dots, fitting datas are shown in red empty dots and were obtained using exponential decay function. b) Formation of Final Product **3a** (M) *vs.* Time (h). Experimental datas are shown in blue filled dots, fitting datas are shown in blue empty dots and were obtained using sigmoidal Boltzmann function. c) Formation and Consumption of Intermediate [**4a**] (M) *vs.* Time (h). Experimental datas are shown in green filled dots, fitting datas are shown in green empty dots and were obtained using Gaussian function.

2. Same "Excess" Experiments

In Reaction Progress Kinetic Analysis (RPKA), "excess" indicates the difference between the initial concentrations of the starting materials. A series of experiments were performed following the conditions in Table 2.5 with same "excess" of **1a** and **2a**.

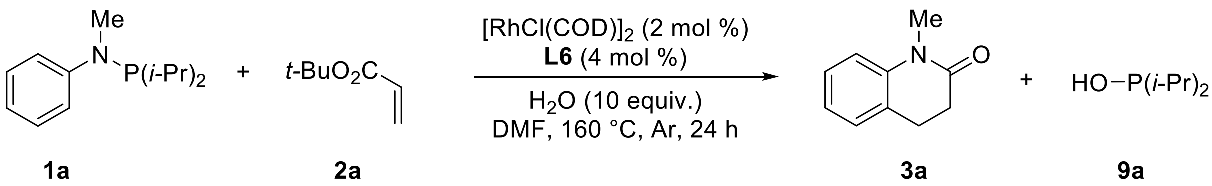


Table S5. Reaction Conditions for the Same "Excess" Experiments.

Reaction	[**1a**]$_0$ (M)	[**2a**]$_0$ (M)	[**3a**]$_0$ (M)	[**9a**]$_0$ (M)
1	0.2	0.6	0	0
2	0.12	0.52	0	0
3	0.12	0.52	0.08	0
4	0.12	0.52	0	0.08

The results reveal that the same "excess" experiments with added product **3a** and **9a** (Reactions **3** and **4**) exhibit the same rate as the same "excess" experiment (Reaction **2**), providing evidence that no product inhibition occurred. Therefore, the lack of overlay between the standards conditions (Reaction **1**) and the time-adjusted same "excess" conditions (Reaction **2**) indicates that catalyst deactivation might occur.

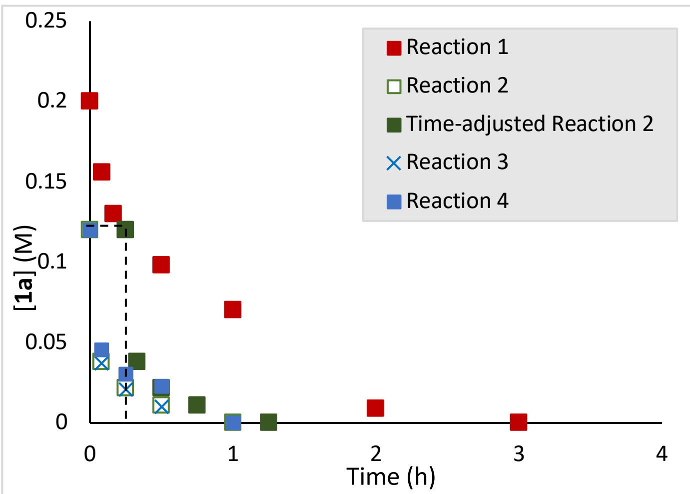


Figure S7. Same "Excess" Reaction Profile.

3. Effect of Water

Procedure: In a glovebox, a three-necked round bottom flask was charged with phosphanamine **1a** (88 mg, 0.4 mmol, 1 equiv.) and distilled DMF (2 mL). Then the flask was closed and removed from the glovebox. Under argon atmosphere, $[RhCl(COD)]_2$ (4 mg, 0.008 mmol, 2 mol%), 2,2,6,6-tetramethylheptane-3,5-dione **L6** (4 µL, 0.016 mmol, 4 mol%), water (0.4 mmol – 2 mmol – 4 mmol) and *tert*-butyl acrylate **2a** (174 µL, 1.2 mmol, 3 equiv.) were added. The reaction was initiated by placing the flask into a preheated bath at 160 °C. Reaction progress was followed by NMR spectroscopy analysis. The reaction was sampled by withdrawing 50 µL aliquots of the reaction solution, which was quenched with a solution of $CDCl_3$ (0.6 mL). Final concentrations of **1a** and **4a** were determined by ^{31}P NMR spectroscopy analysis using triphenylphosphine (0.038 mmol) as external standard. Final concentration of **3a** was determined by ^{1}H NMR spectroscopy analysis using dichloroethane (0.063 mmol) as external standard.

Table S6. Kinetic Data for Rate Dependance on Initial Concentration of Water.

Initial $[H_2O]$ (M)	Rate of **1a** consumption (M/h)	Rate of **3a** formation (M/h)
0.2	- 0.096	0.0019
1	- 0.097	0.0028
2	- 0.1	0.0072

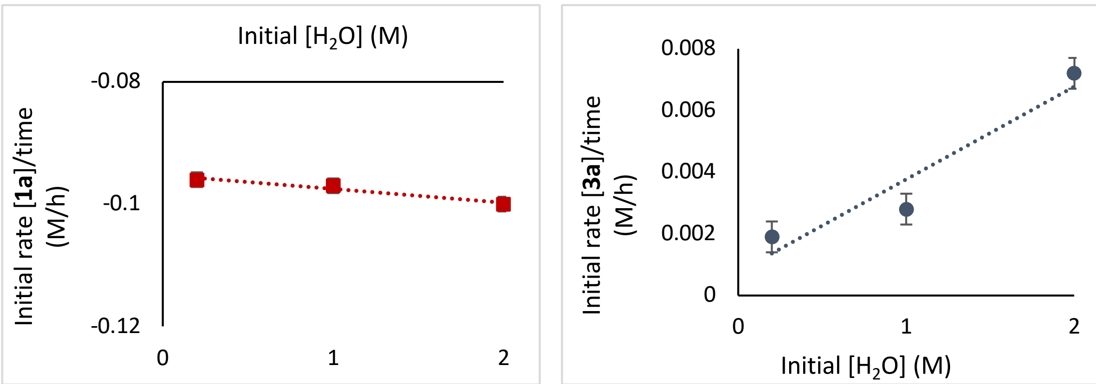


Figure S8. Kinetic Plot for Rate Dependance on Initial Concentration of Water.

4. Kinetic Order of Reagents

Procedure: In a glovebox, a three-necked round bottom flask was charged with phosphanamine **1a** (88 mg, 0.4 mmol, 1 equiv.) and distilled DMF (2 mL). Then the flask was closed and removed from the glovebox. Under argon atmosphere, $[RhCl(COD)]_2$ (0.004 mmol – 0.008 mmol – 0.012 mmol), 2,2,6,6-tetramethylheptane-3,5-dione **L6** (0.008 mmol – 0.016 mmol – 0.024 mmol), water (72 µL, 4 mmol, 10 equiv.) and *tert*-butyl acrylate **2a** (174 µL, 1.2 mmol, 3 equiv.) were added. The reaction was initiated by placing the flask into a preheated bath at 160 °C. Reaction progress was followed by NMR spectroscopy analysis. The reaction was sampled by withdrawing 50 µL aliquots of the reaction solution, which was quenched with a solution of $CDCl_3$ (0.6 mL). Final concentrations of **1a** and **4a** were determined by ^{31}P NMR spectroscopy analysis using triphenylphosphine (0.038 mmol) as external standard. Final concentration of **3a** was determined by ^{1}H NMR spectroscopy analysis using dichloroethane (0.063 mmol) as external standard.

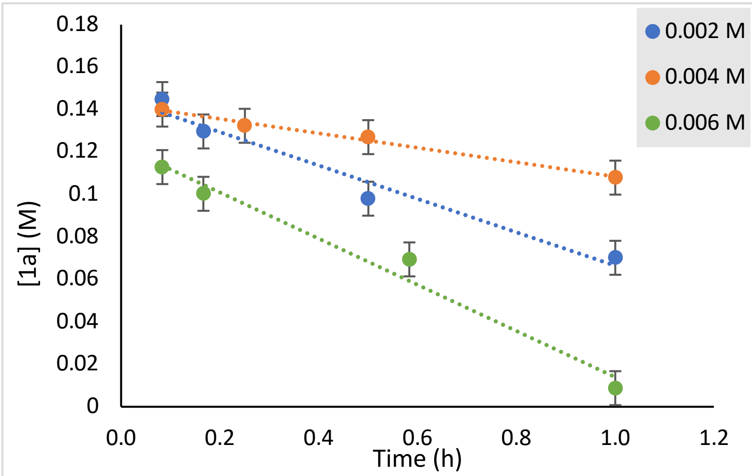


Figure S9. Kinetic Plot of Phosphanamine [**1a**] (M) *vs.* Time (h) for a Series of Initial Concentration of Rhodium.

Table S7. Kinetic Data for Rate Dependance on Initial Concentration of Rhodium.

Initial [Rh] (M)	Rate of **1a** consumption (M/h)
0.002	- 0.034
0.004	- 0.0787
0.006	- 0.1087

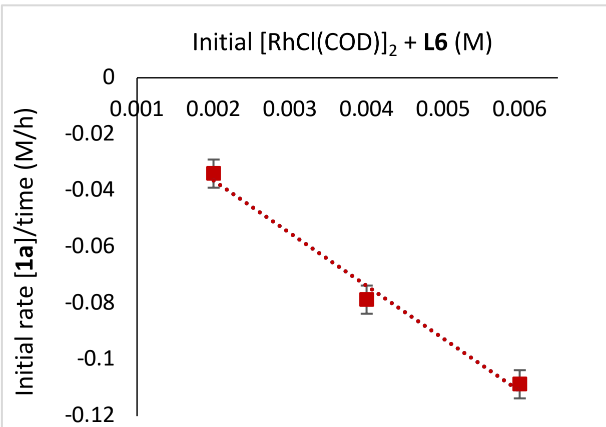


Figure S10. Kinetic Plot for Rate Dependance on Initial Concentration of Rhodium.

Procedure: In a glovebox, a three-necked round bottom flask was charged with phosphanamine **1a** (88 mg, 0.4 mmol, 1 equiv.) and distilled DMF (2 mL). Then the flask was closed and removed from the glovebox. Under argon atmosphere, $[RhCl(COD)]_2$ (4 mg, 0.008 mmol, 2 mol%), 2,2,6,6-tetramethylheptane-3,5-dione **L6** (4 µL, 0.016 mmol, 4 mol%), water (72 µL, 4 mmol, 10 equiv.) and *tert*-butyl acrylate **2a** (0.4 mmol – 0.8 mmol – 1.2 mmol – 2 mmol) were added. The reaction was initiated by placing the flask into a preheated bath at 160 °C. Reaction progress was followed by NMR spectroscopy analysis. The reaction was sampled by withdrawing 50 µL aliquots of the reaction solution, which was quenched with a solution of $CDCl_3$ (0.6 mL). Final concentrations of **1a** and **4a** were determined by ^{31}P NMR spectroscopy analysis using triphenylphosphine (0.038 mmol) as external standard. Final concentration of **3a** was determined by ^{1}H NMR spectroscopy analysis using dichloroethane (0.063 mmol) as external standard.

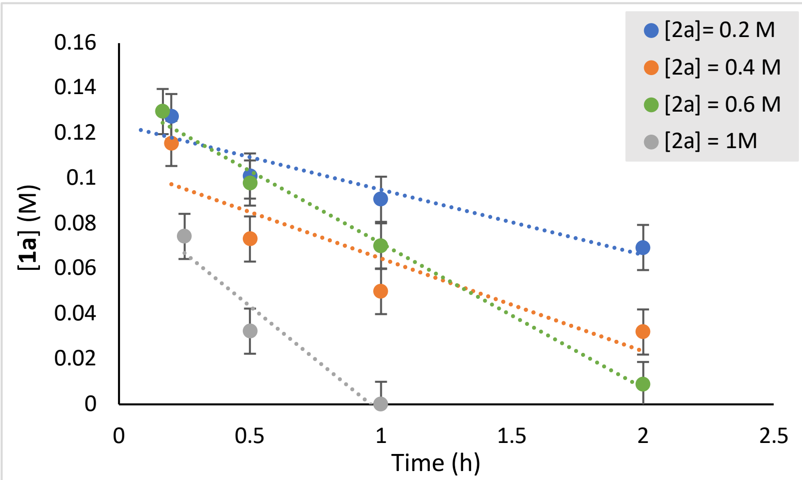


Figure S11. Kinetic Plot of [**1a**] (M) *vs.* Time (h) for a Series of Initial Concentration of *Tert*-butyl Acrylate **2a**.

Table S8. Kinetic Data for Rate Dependance on Initial Concentration of *Tert*-butyl Acrylate **2a**.

Initial [**2a**] (M)	Rate of **1a** consumption (M/h)
0.2	- 0.0288
0.4	- 0.0411
0.6	- 0.064
1	- 0.0942

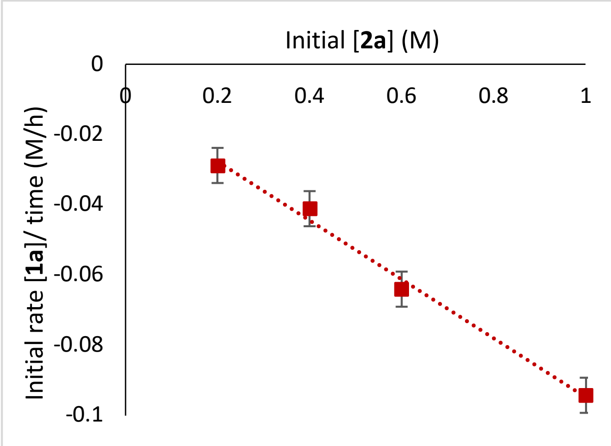


Figure S12. Kinetic Plot for Rate Dependance on Initial Concentration of *Tert*-butyl Acrylate **2a**.

Procedure: In a glovebox, a three-necked round bottom flask was charged with phosphanamine **1a** (0.1 mmol – 0.8 mmol) and distilled DMF (2 mL). Then the flask was closed and removed from the glovebox. Under argon atmosphere, $[RhCl(COD)]_2$ (4 mg, 0.008 mmol, 2 mol%), 2,2,6,6-tetramethylheptane-3,5-dione **L6** (4 µL, 0.016 mmol, 4 mol%), water (72 µL, 4 mmol, 10 equiv.) and *tert*-butyl acrylate **2a** (174 µL, 1.2 mmol, 3 equiv.) were added. The reaction was initiated by placing the flask into a preheated bath at 160 °C. Reaction progress was followed by NMR spectroscopy analysis. The reaction was sampled by withdrawing 50 µL aliquots of the reaction solution, which was quenched with a solution of $CDCl_3$ (0.6 mL). Final concentrations of **1a** and **4a** were determined by ^{31}P NMR spectroscopy analysis using triphenylphosphine (0.038 mmol) as external standard. Final concentration of **3a** was determined by ^{1}H NMR spectroscopy analysis using dichloroethane (0.063 mmol) as external standard.

Table S9. Kinetic Data for Rate Dependance on Initial Concentration of Phosphanamine **1a**.

Initial [**1a**] (M)	Rate of **1a** consumption (M/h)
0.05	- 0.0633
0.01	-0.0441
0.2	- 0.0309
0.4	- 0.029

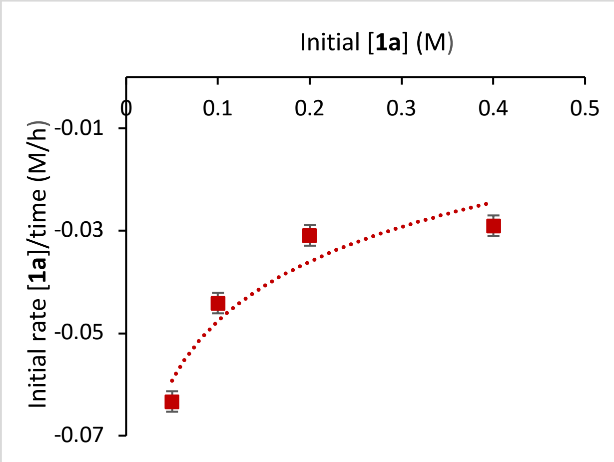


Figure S13. Kinetic Plot for Rate Dependance on Initial Concentration of Phosphanamine **1a**.

9. X-Ray Crystallographic Datas

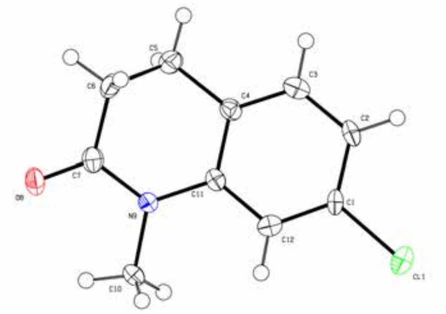


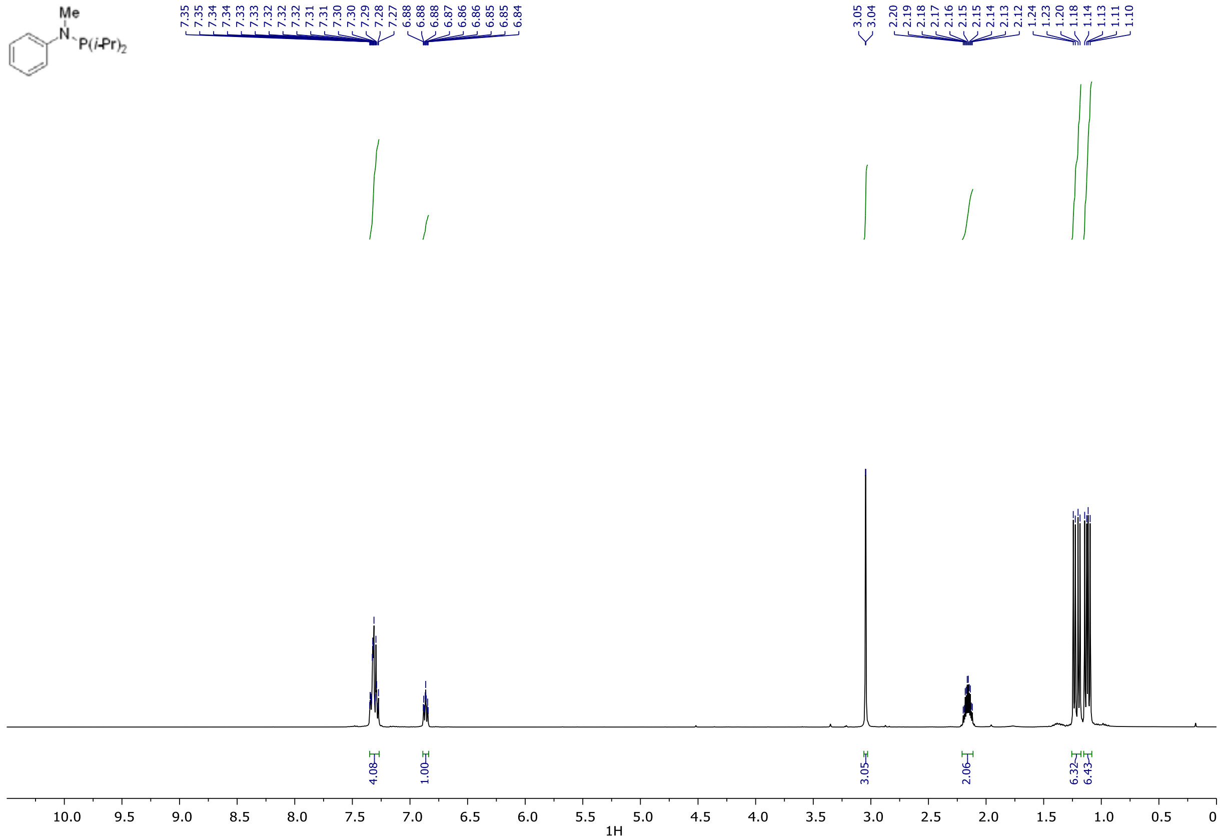
Table S10. Crystal Data and Structure for **3i**.

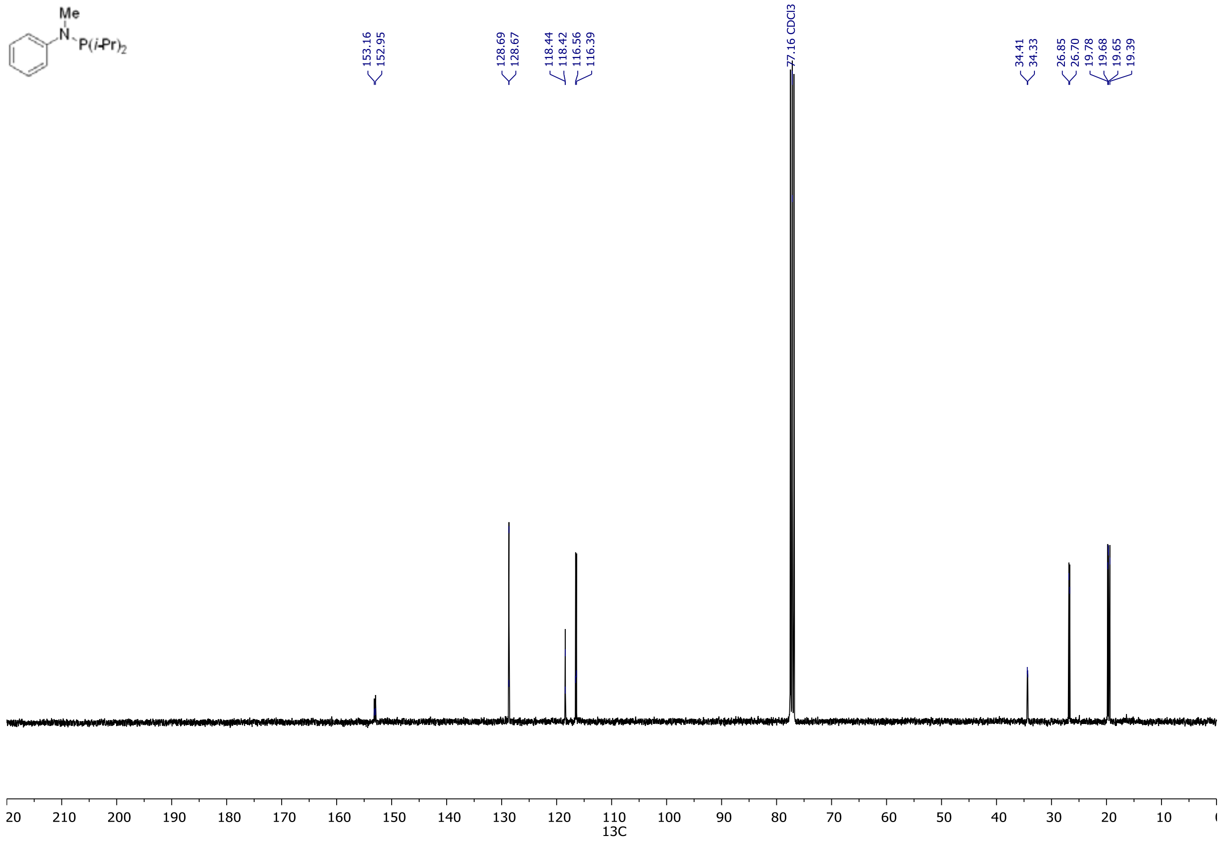
Empirical formula	$C_{10}H_{10}ClNO$
Formula weight	195.64 g/mol
Temperature	150(2) K
Radiation type	Mo-Kα
Wavelength	0.71073 Å
Crystal system, space group	monoclinic, P $2_{1/n}$
Unit cell dimensions	a = 10.4075(13) Å
	b = 6.8598(8) Å
	c = 12.7321(15) Å
	β = 101.950(6) °
Volume	4288.2(5) $Å^3$
Z, Calculated density	4, 1.461 g/ cm^{-3}
Absorption coefficient	0.383 mm^{-1}
F(000)	408
Crystal size	0.320 x 0.170 x 0.060 mm
Crystal color	colourless
Crystal description	plate
Diffractometer	APEXII Kappa-CCD (Bruker-AXS)
θ range for data collection	3.271 to 27.478 °
(sinθ/λ)max ($Å^{-1}$)	0.649

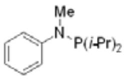
h_{min}, h_{max}	-13.9
k_{min}, k_{max}	-8.8
l_{min}, l_{max}	-16.16
Reflections collected / unique	5583/2024 [$^{\alpha}$R(int) = 0.0273]
Reflections [I > 2σ]	1555
Completeness to θ_{max}	0.992
Absorption correction type	multi-scan
Max. and min. transmission	0.977, 0.874
Refinement method	Full-matrix least-squares on F^2
H-atom treatment	H-atom parameters constrained
Data / restraints / parameters	2024 / 0 / 119
Goodness-of-fit	1.121
Final R indices [I>2σ]	R_1 = 0.0374, ωR_2 = 0.0838
R indices (all data)	R_1 = 0.0582, ωR_2 = 0.0930
Largest diff. peak and hole	0.328 and -0.244 e.Å^{-3}

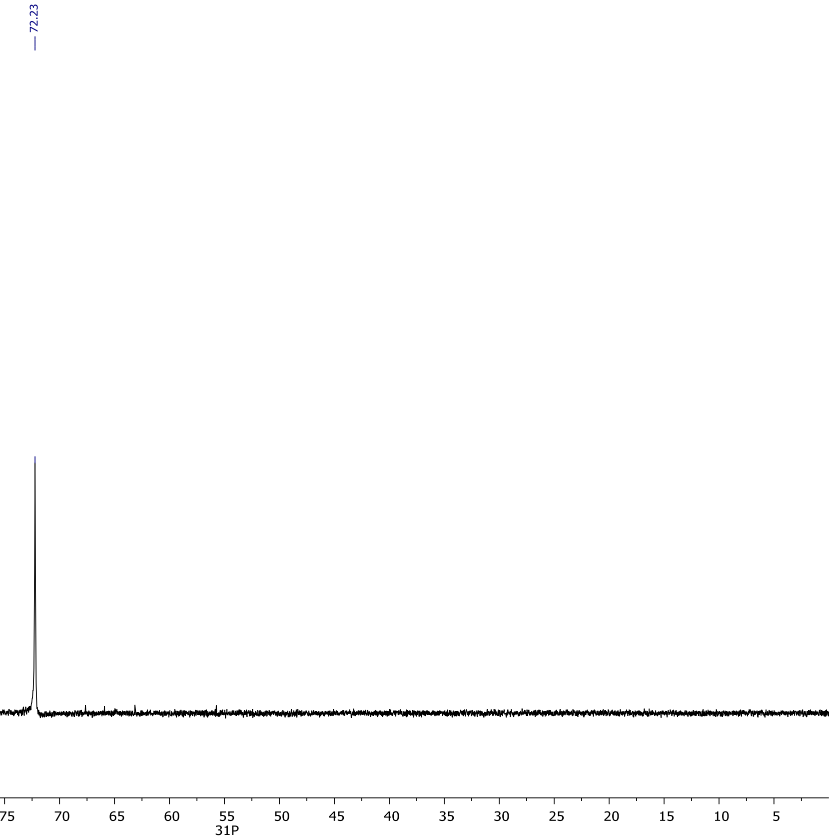
10. NMR Datas of Starting Materials and Products

1a

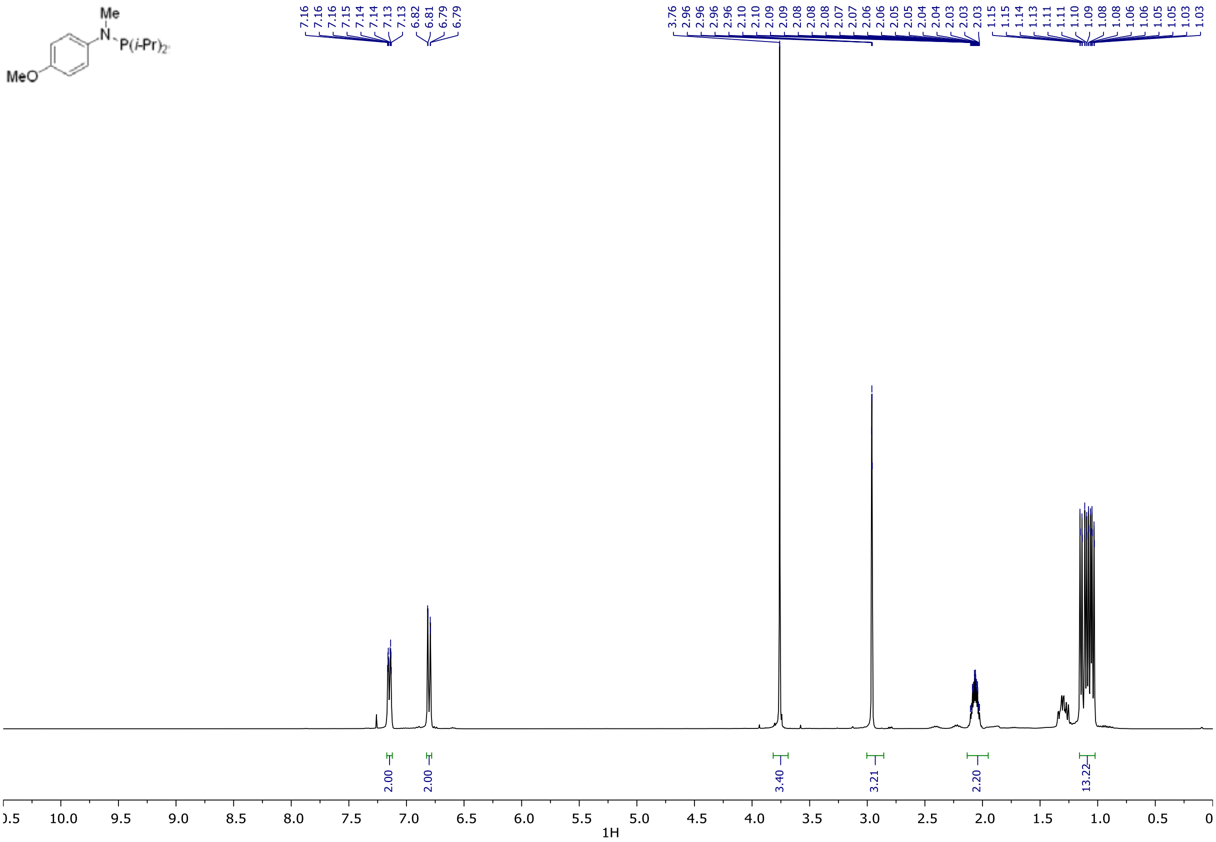


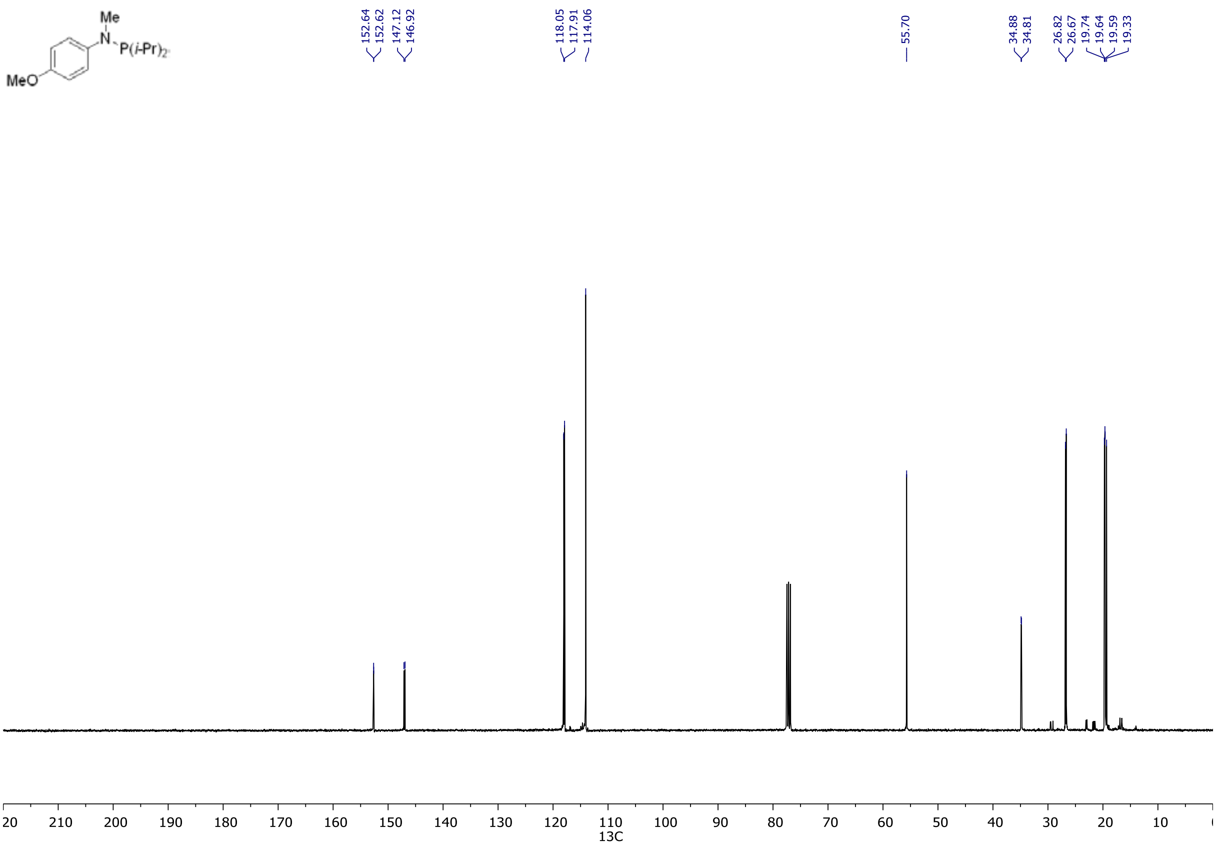


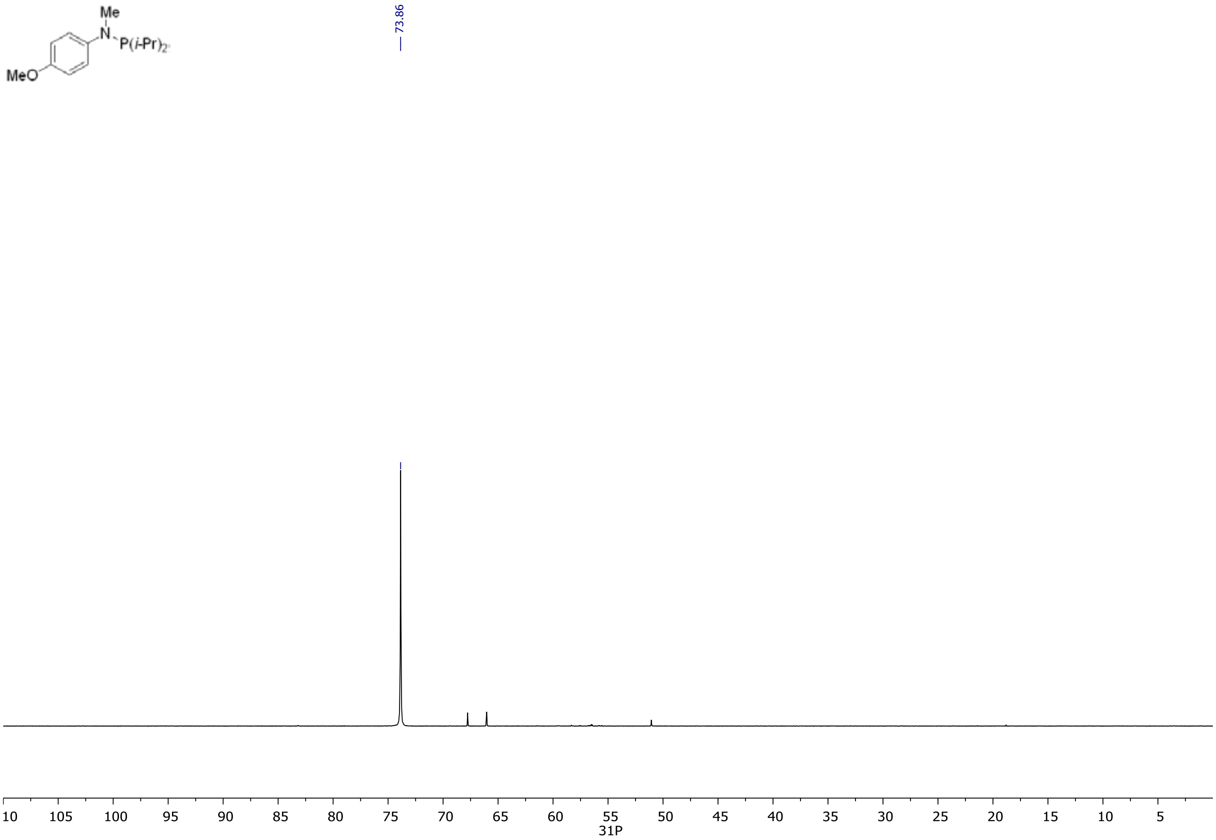

Me
N
P(i-Pr)2


72.23
10
105
100
95
90
85
80
75
70
65
60
55
31P
50
45
40
35
30
25
20
15
10
5

1b



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60
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31P
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45
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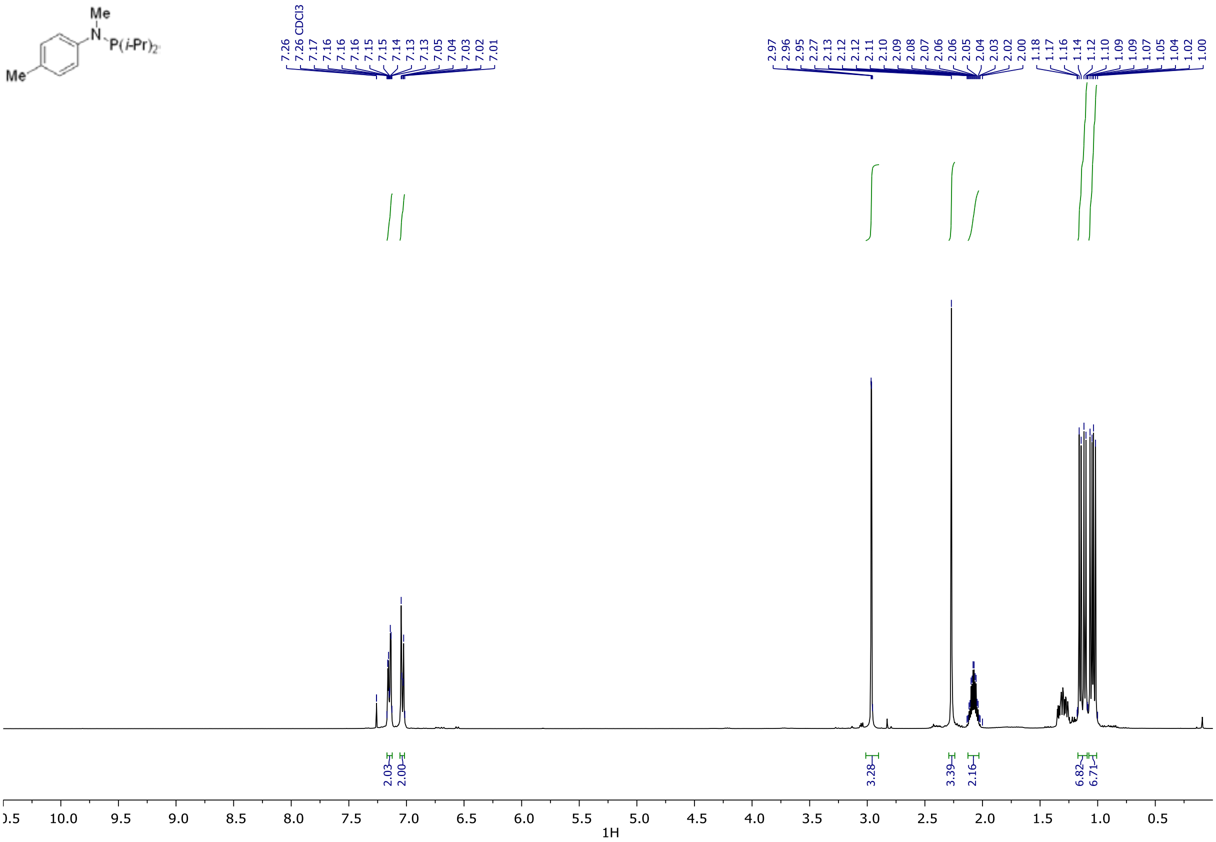
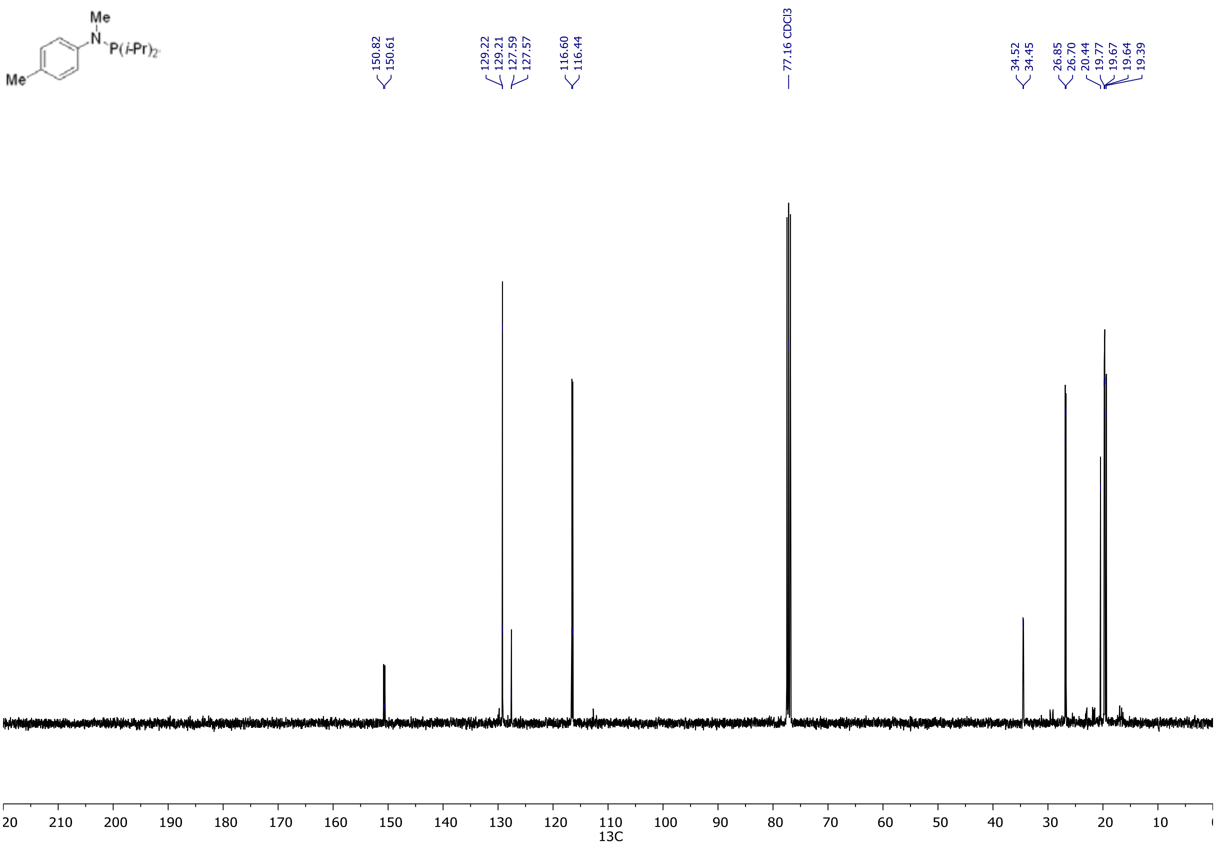
35
30
25
20
15
10
5

1c


Me
N
P(i-Pr)2
Me
7.26 CDCl3
7.26
7.17
7.16
7.16
7.16
7.15
7.15
7.14
7.13
7.13
7.05
7.04
7.03
7.02
7.01
2.97
2.96
2.95
2.27
2.13
2.12
2.12
2.11
2.10
2.09
2.08
2.07
2.06
2.06
2.05
2.04
2.03
2.02
2.00
1.18
1.17
1.16
1.14
1.12
1.10
1.09
1.09
1.07
1.05
1.04
1.02
1.00
2.03
2.00
3.28
3.39
2.16
6.82
6.71
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
1H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P(i-Pr)2
Me
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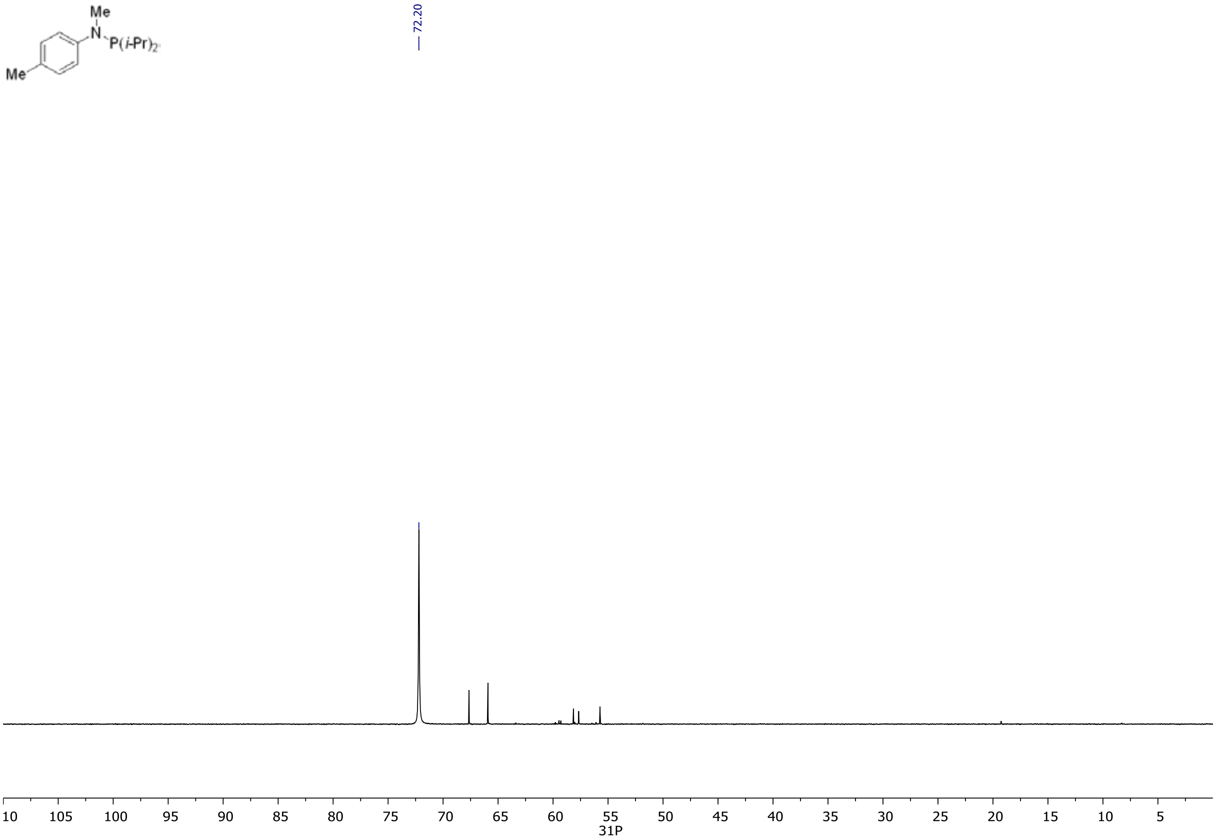
150.61
129.22
129.21
127.59
127.57
116.60
116.44
77.16 CDCl3
34.52
34.45
26.85
26.70
20.44
19.77
19.67
19.64
19.39
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
13C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P(i-Pr)2
Me
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10
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100
95
90
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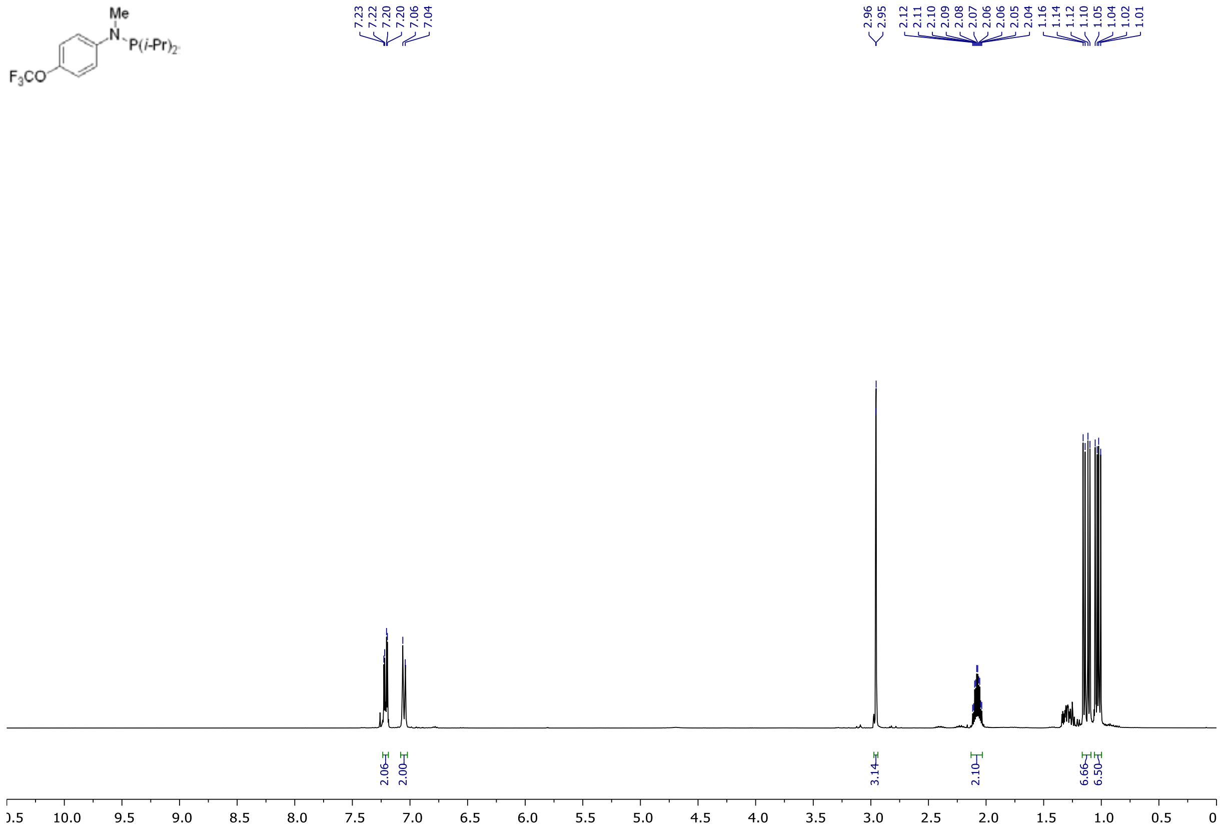
70
65
60
55
50
45
40
35
30
25
20
15
10
5
31P

1d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P(i-Pr)2
F3CO
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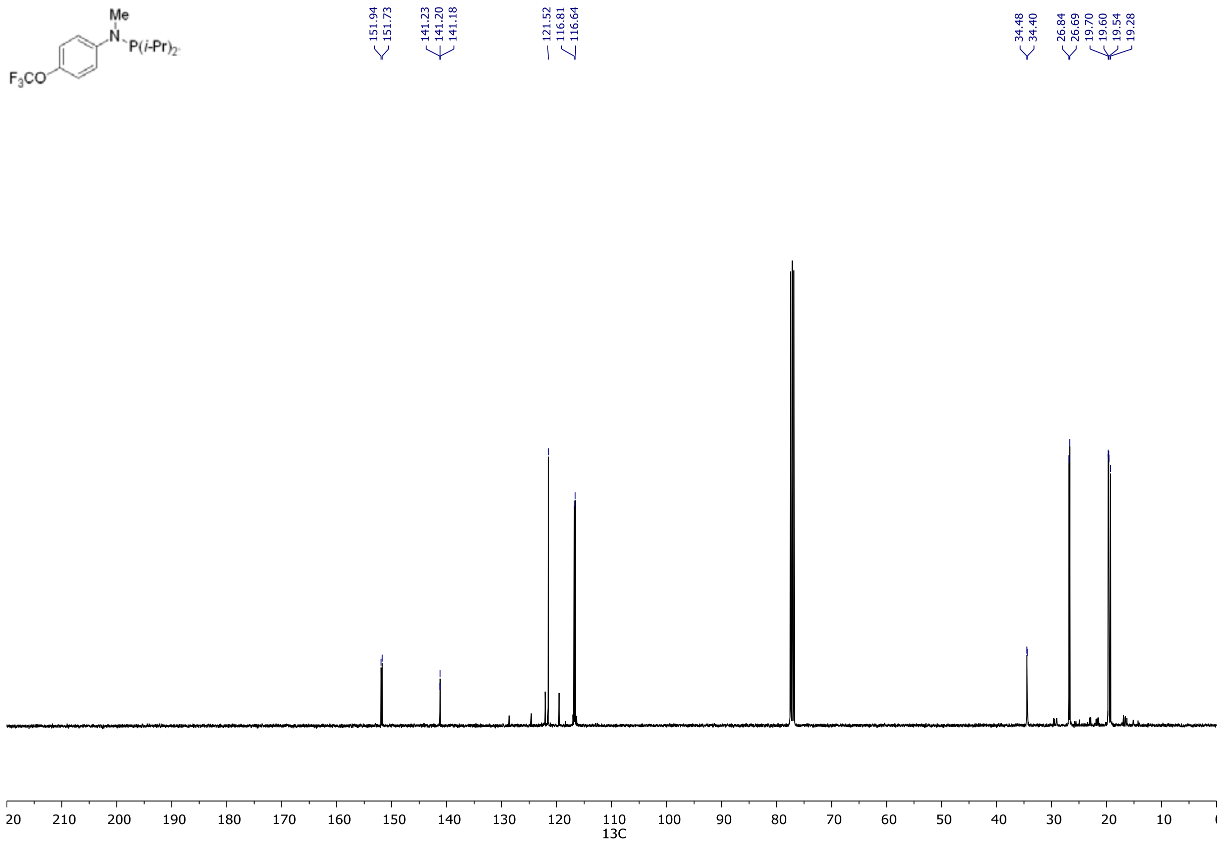
7.22
7.20
7.20
7.06
7.04
2.96
2.95
2.12
2.11
2.10
2.09
2.08
2.07
2.06
2.06
2.05
2.04
1.16
1.14
1.12
1.10
1.05
1.04
1.02
1.01
2.06
2.00
3.14
2.10
6.66
6.50
1H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141.20
141.18
121.52
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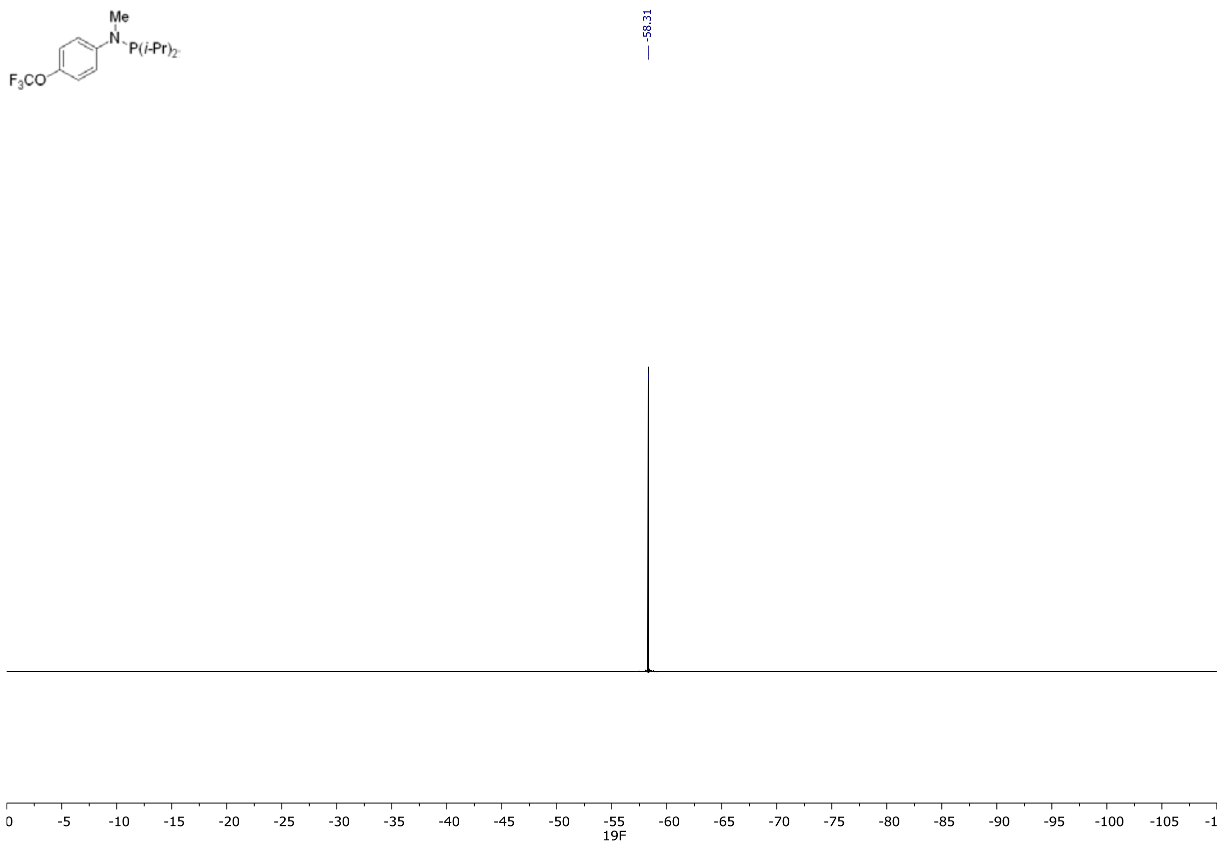
19.54
19.28
13C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P(i-Pr)2
F3CO
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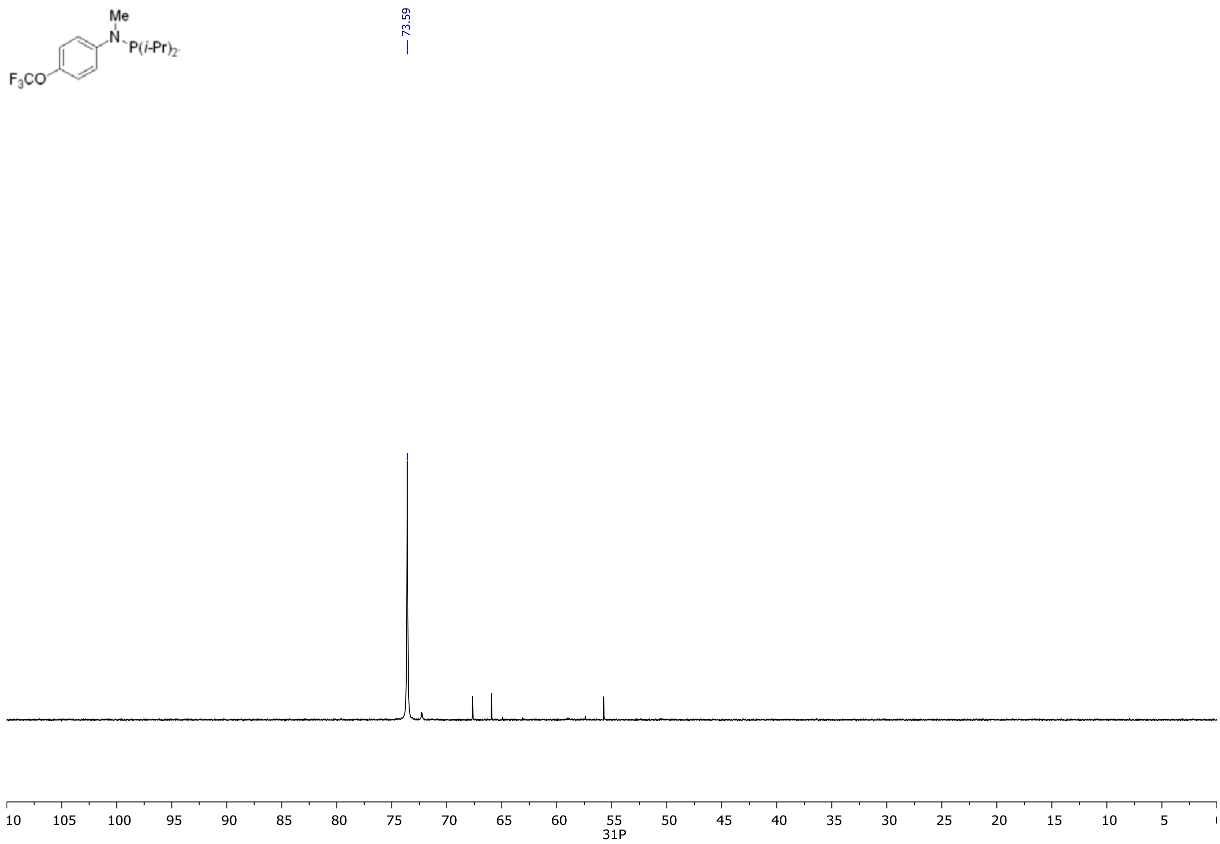
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105
19F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P(i-Pr)2
F3CO
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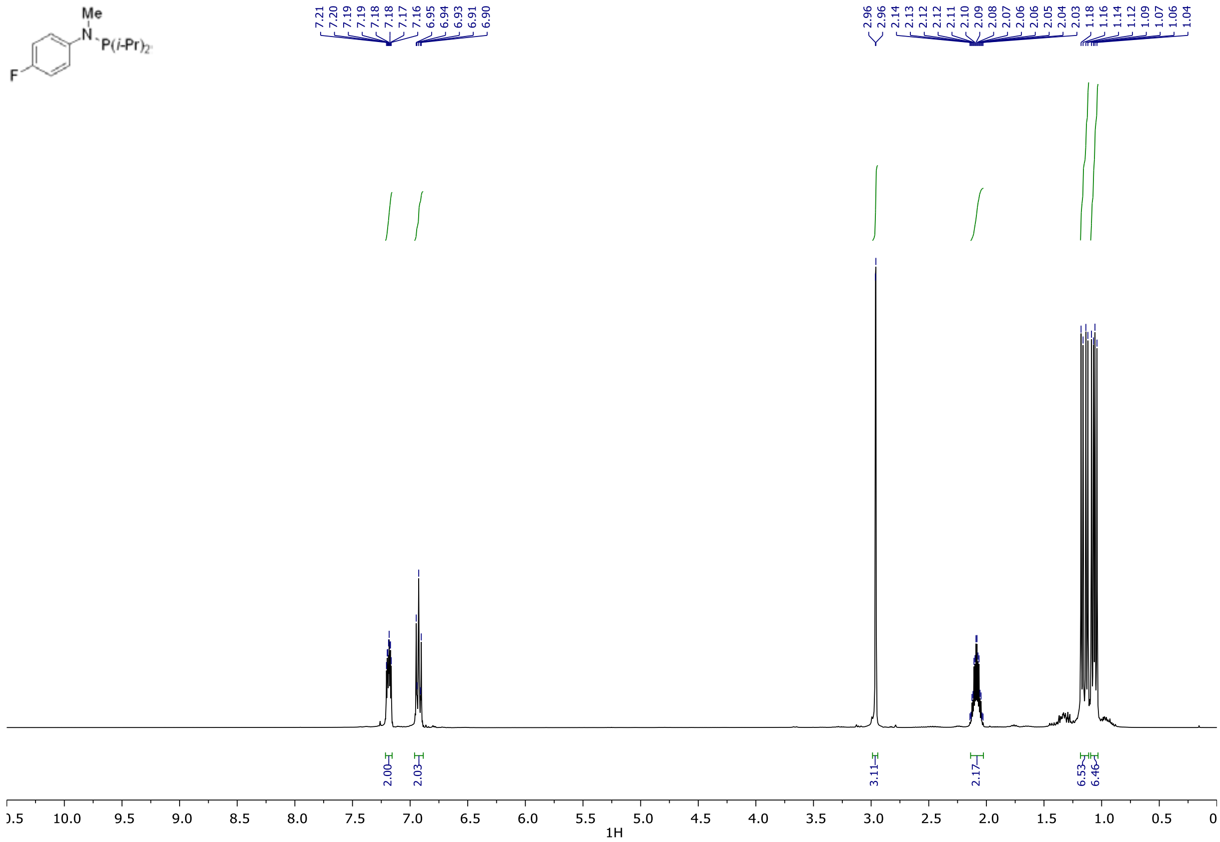
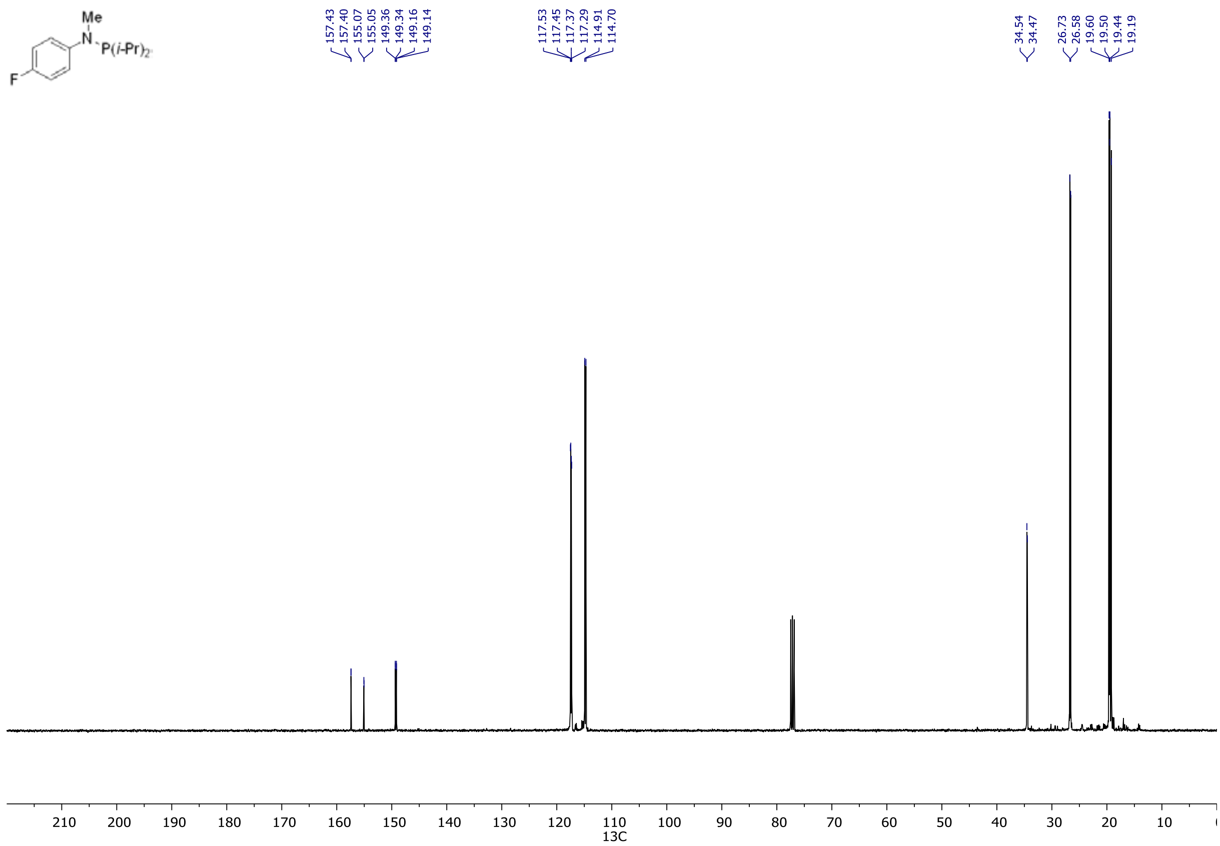
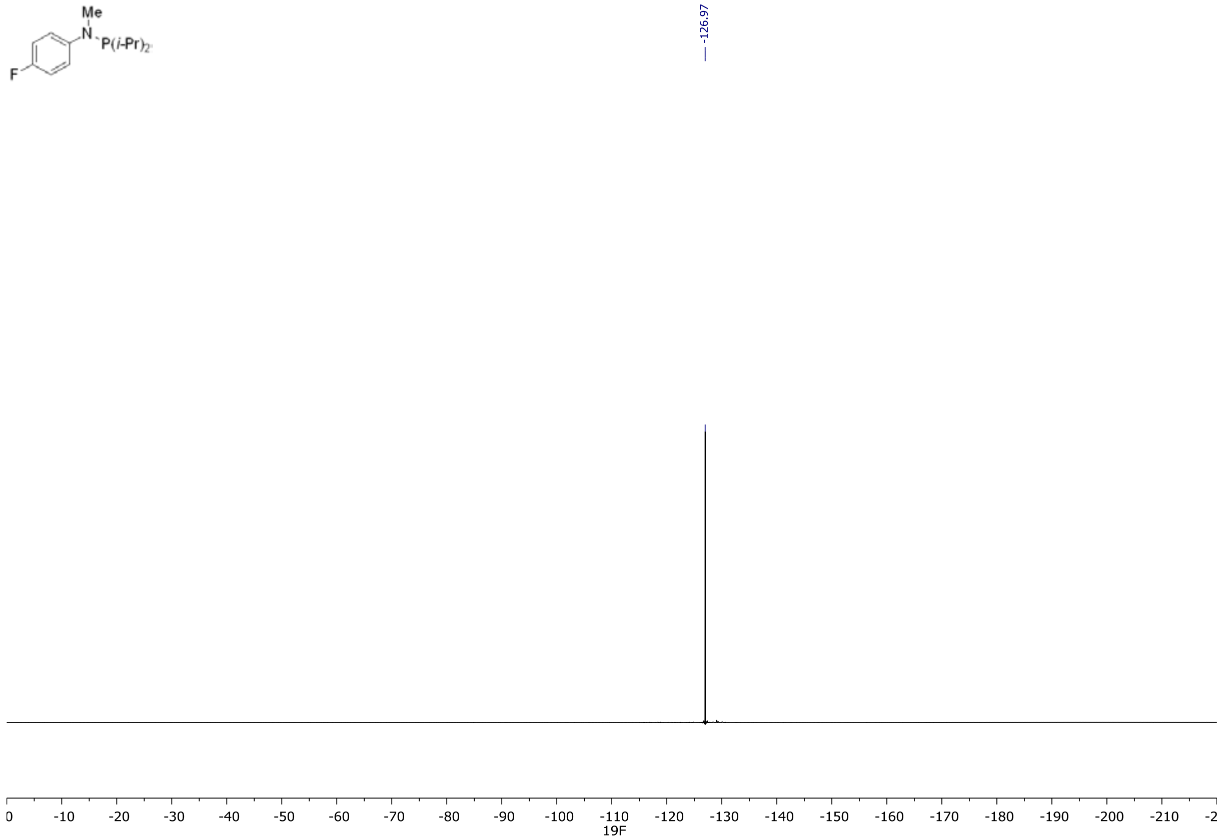
105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
31P

1e



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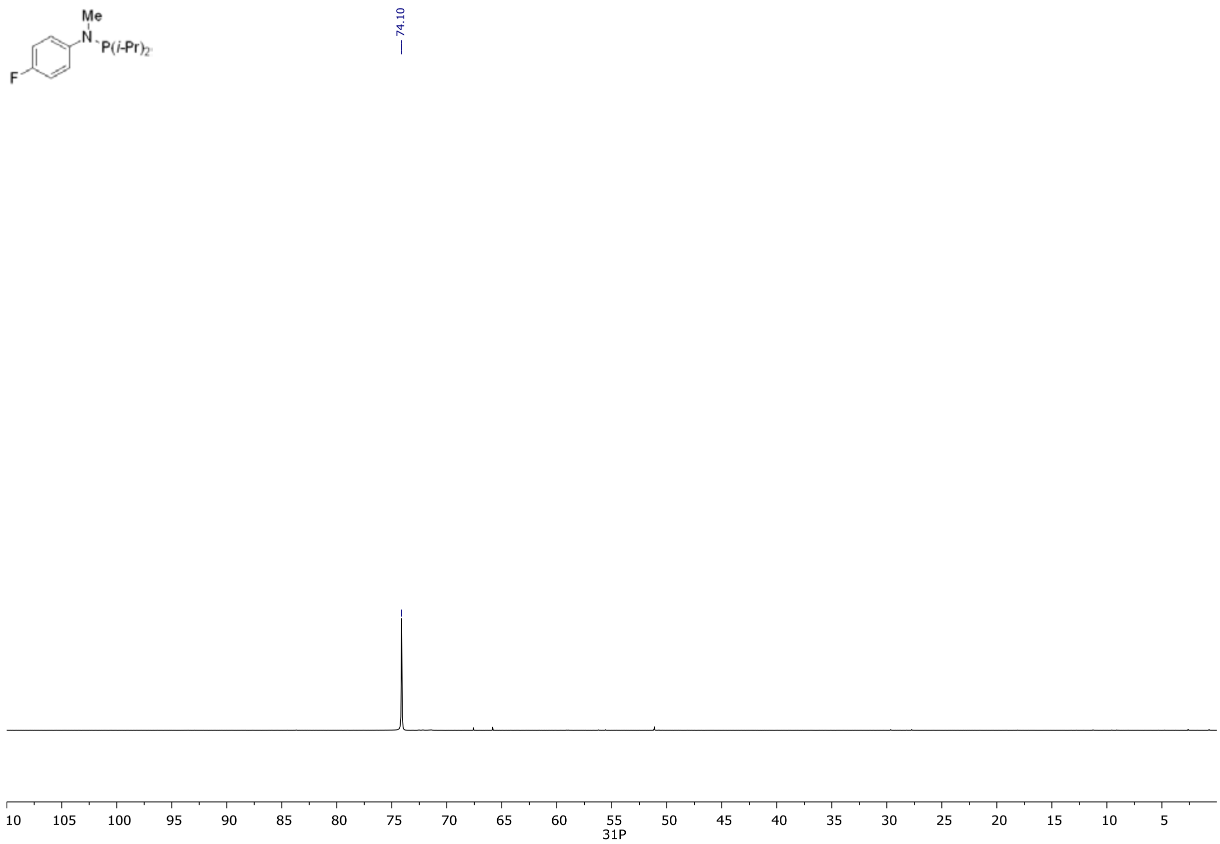
19F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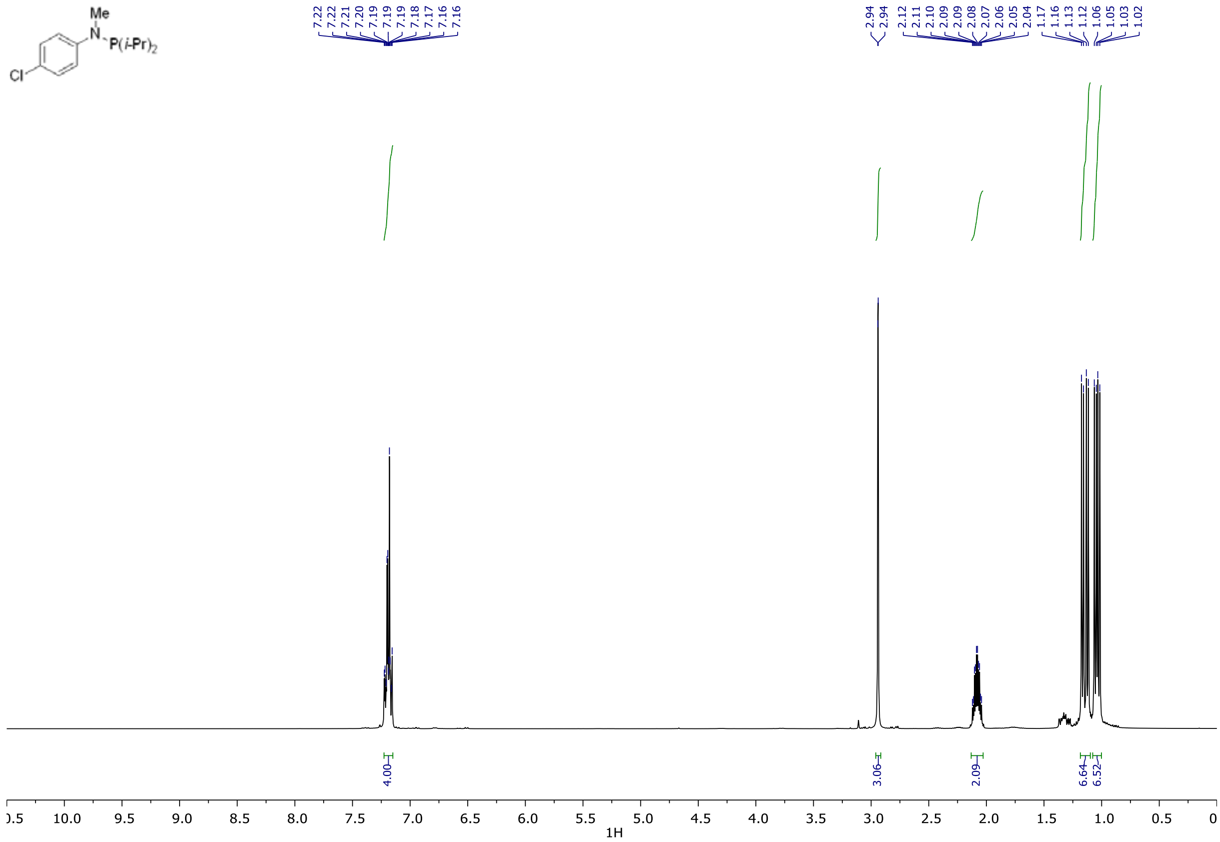
31P

1f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P(i-Pr)2
Cl
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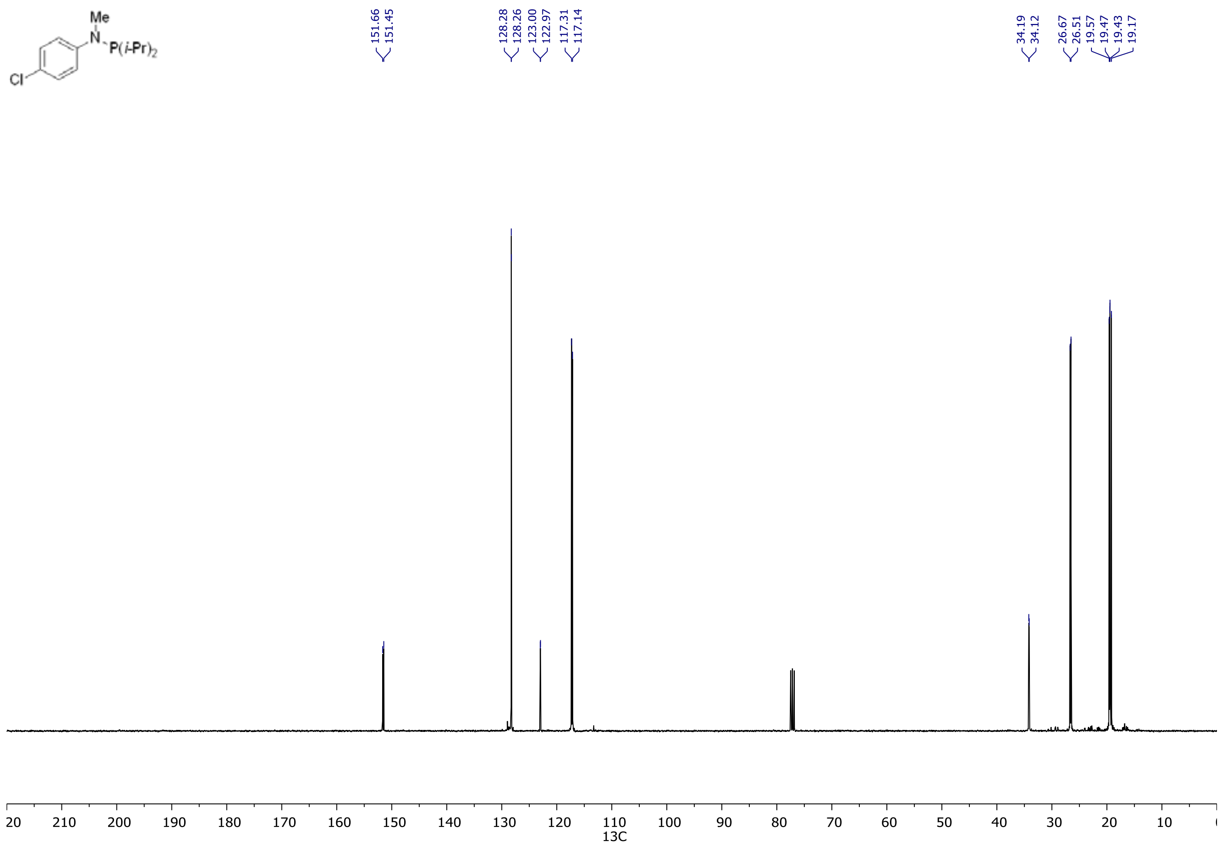
7.22
7.21
7.20
7.19
7.19
7.19
7.18
7.17
7.16
7.16
2.94
2.94
2.12
2.11
2.10
2.09
2.09
2.08
2.07
2.06
2.05
2.04
1.17
1.16
1.13
1.12
1.06
1.05
1.03
1.02
4.00
3.06
2.09
6.64
6.52
1H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N
P(i-Pr)2
Cl
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151.45
128.28
128.26
123.00
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117.14
34.19
34.12
26.67
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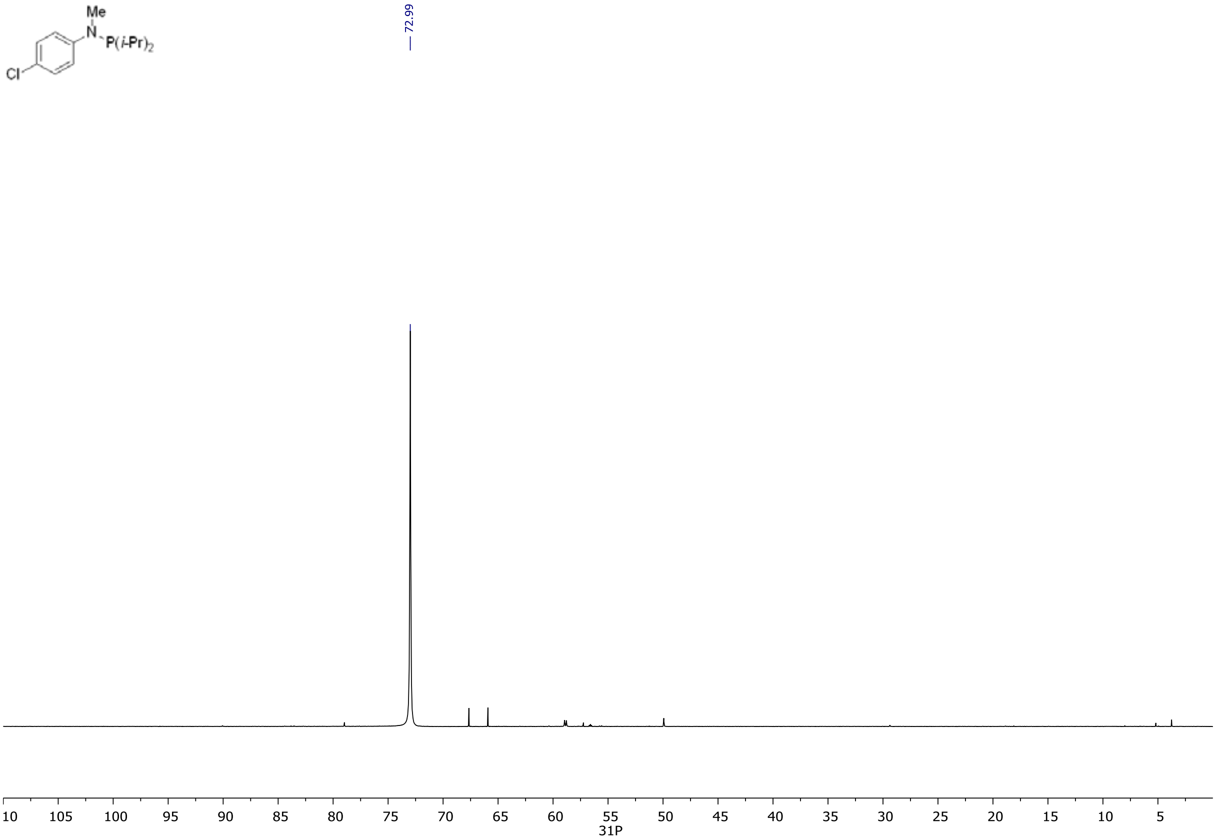
19.57
19.47
19.43
19.17
13C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Cl
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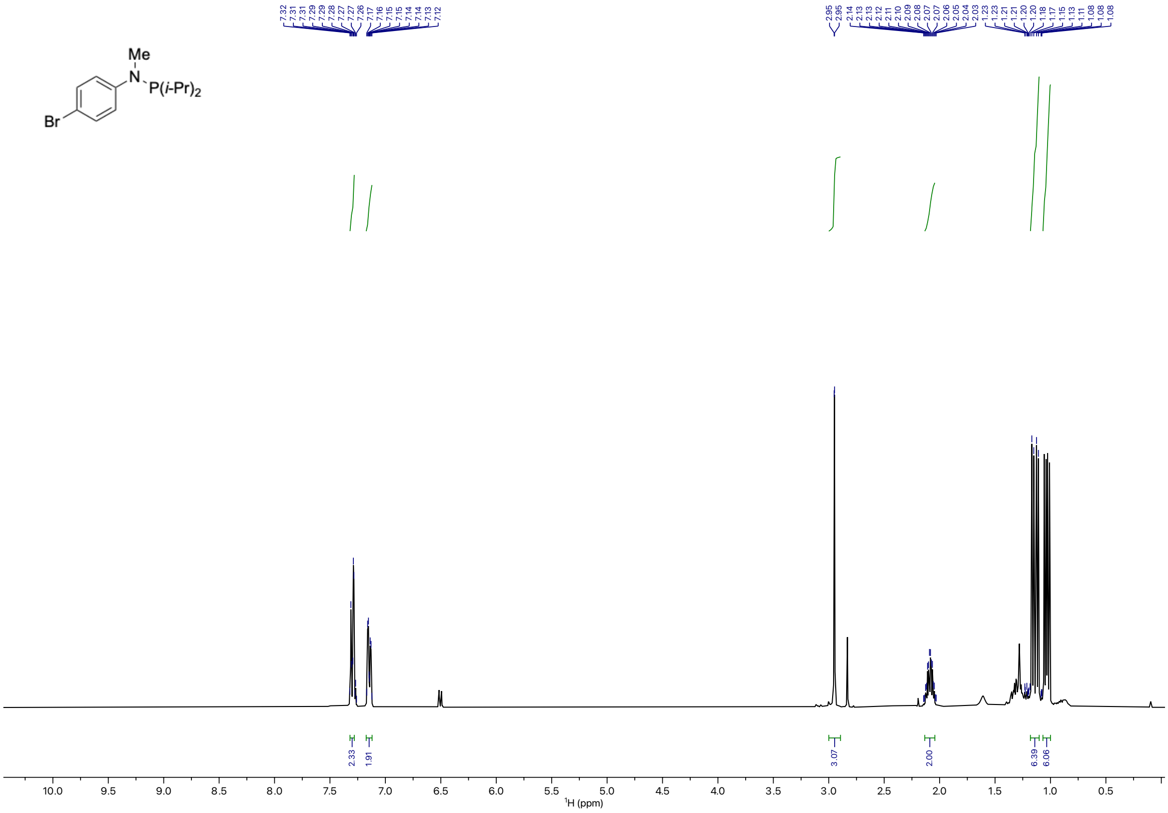
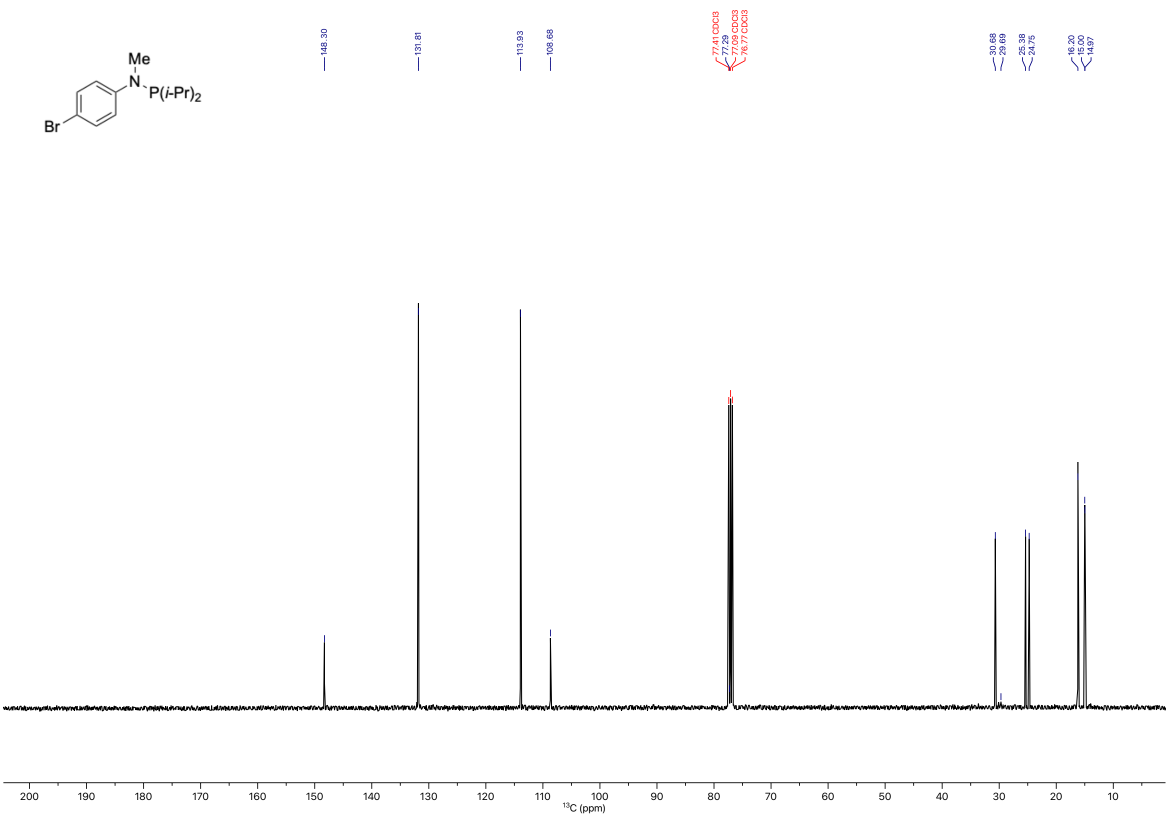
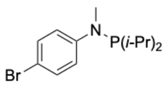
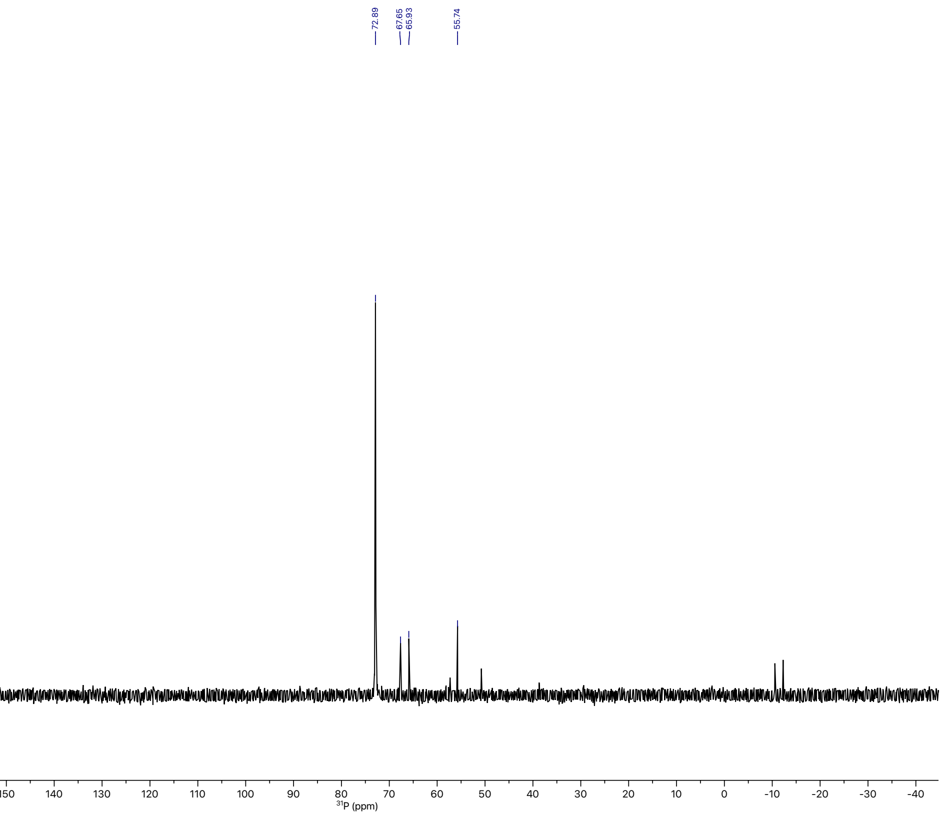
31P

1g






N
P(i-Pr)2
Br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67.65
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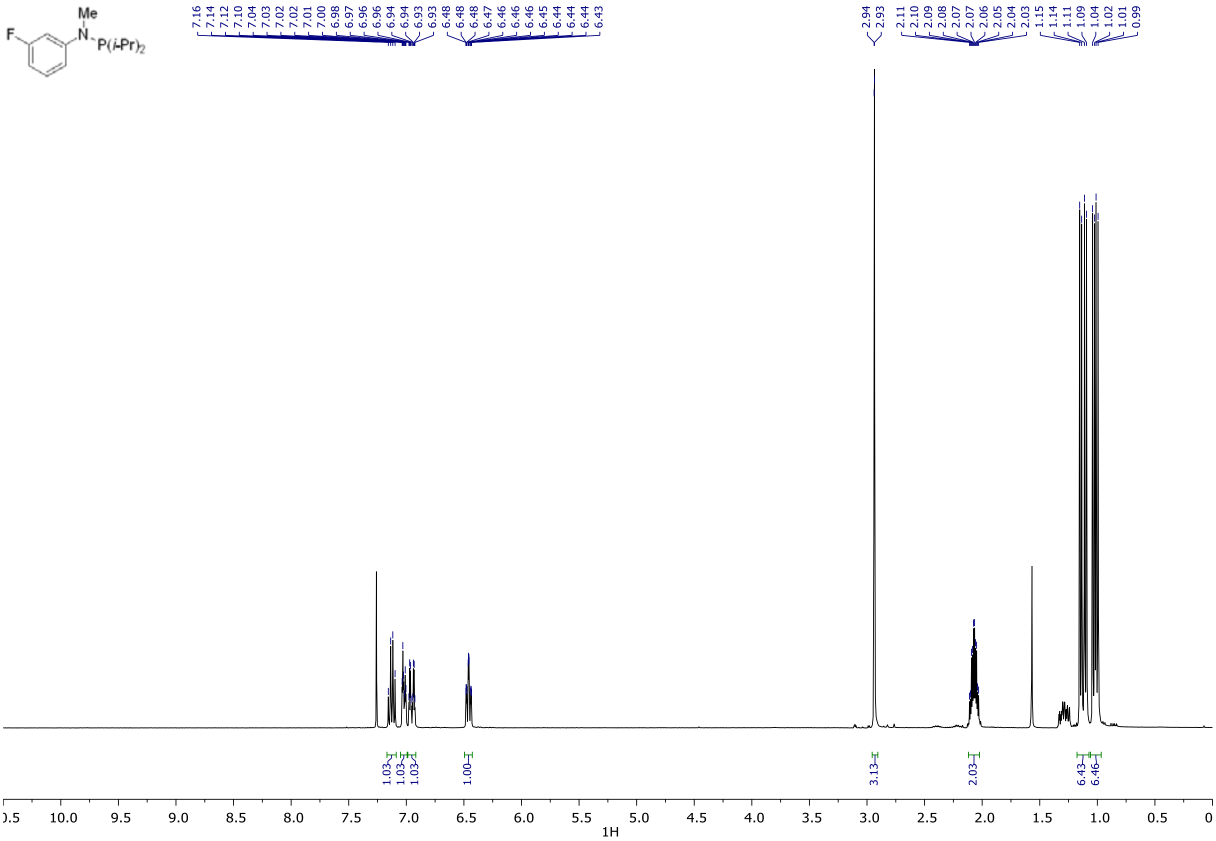
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
-20
-30
-40
31P (ppm)

1h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N
F
P(i-Pr)2
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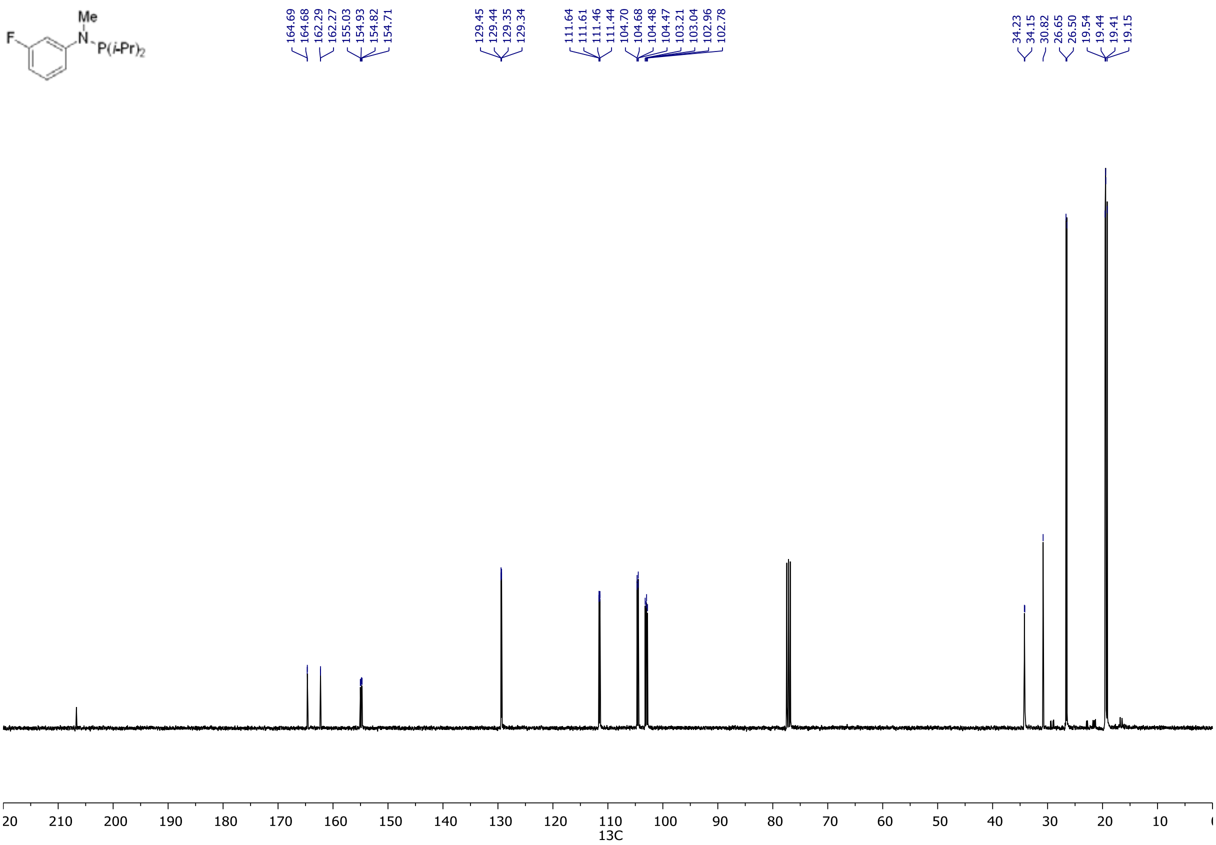
2.94 2.93 2.11 2.10 2.09 2.08 2.07 2.07 2.06 2.05 2.04 2.03 1.15 1.14 1.11 1.09 1.04 1.02 1.01 0.99
1.03 1.03 1.03 1.00 3.13 2.03 6.43 6.46
1H


Me
N
F
P(i-Pr)2
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129.45 129.44 129.35 129.34
111.64 111.61 111.46 111.44 104.70 104.68 104.48 104.47 103.21 103.04 102.96 102.78
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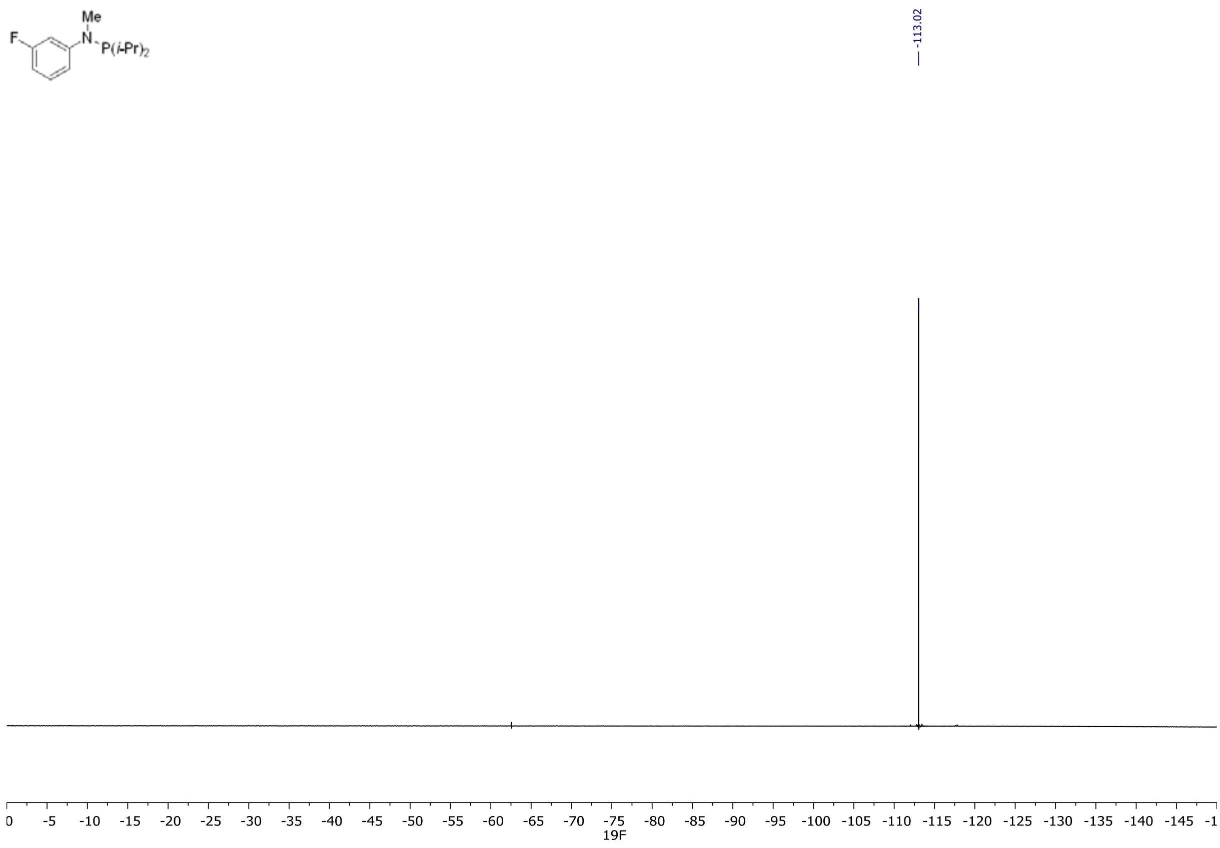
13C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P(i-Pr)2
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0
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-10
-15
-20
-25
-30
-35
-40
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-50
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-60
-65
-70
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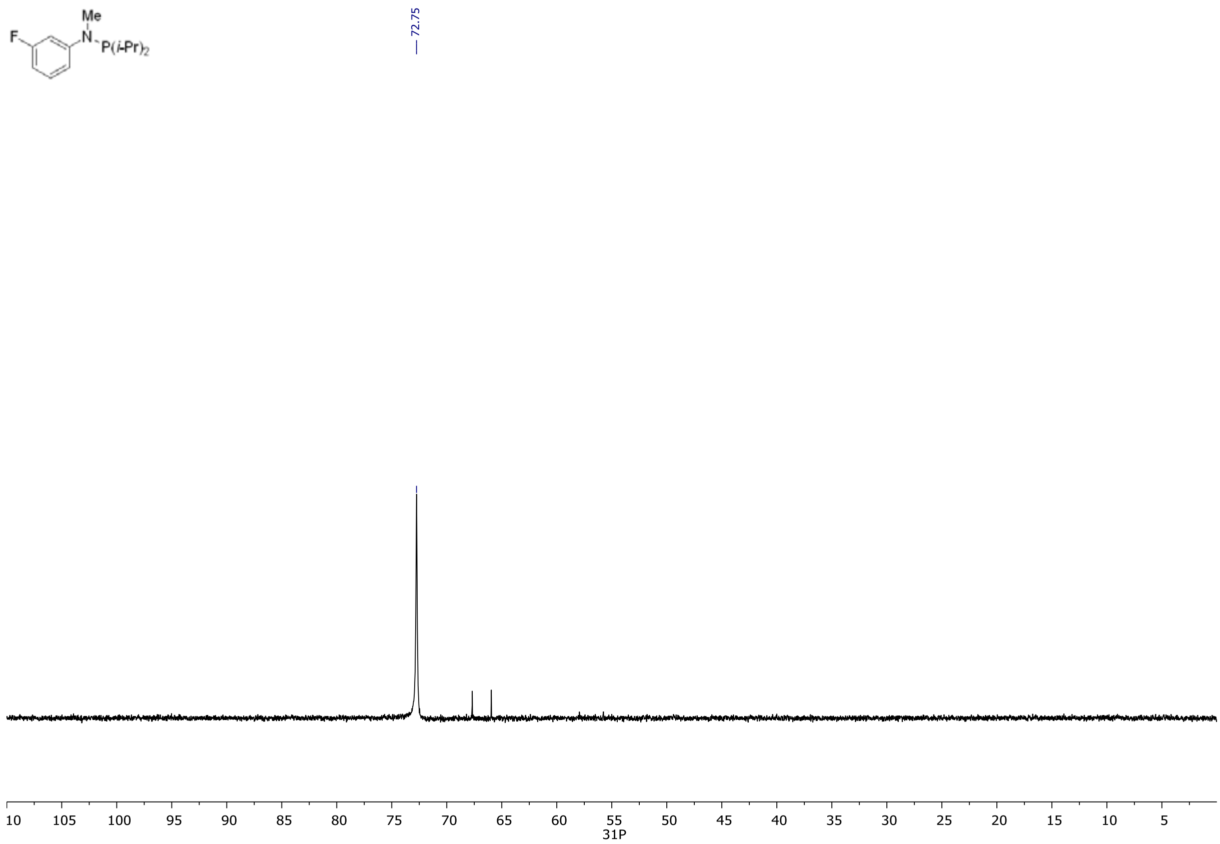
-135
-140
-145
19F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F
N
P(i-Pr)2
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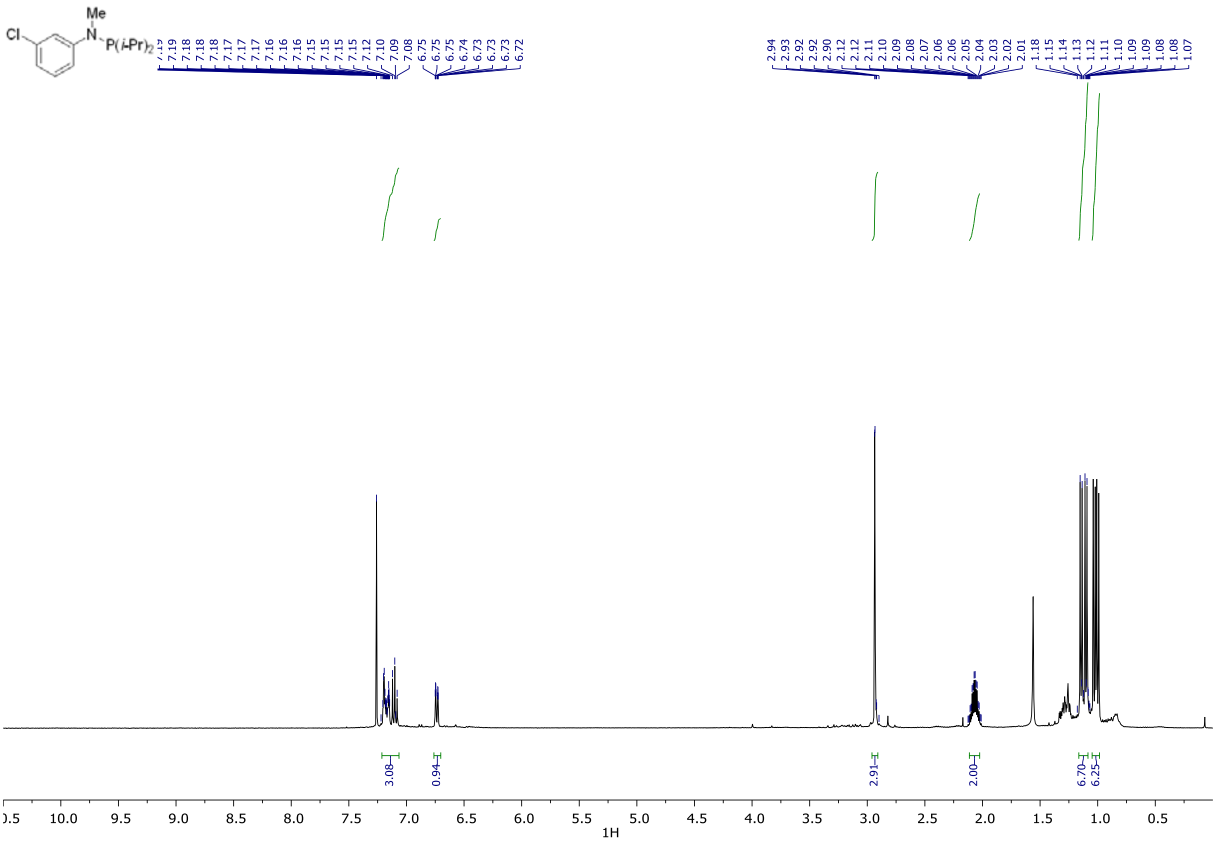
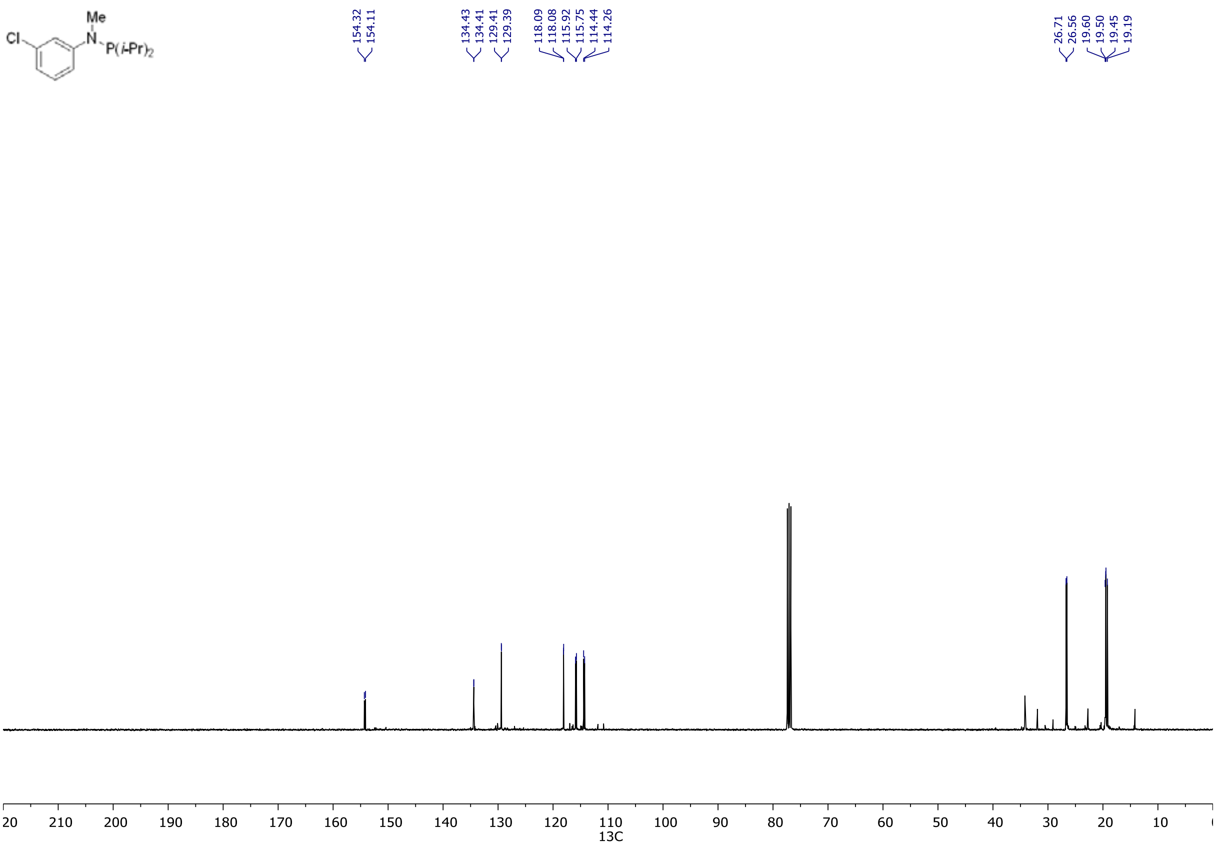
10
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
31P

1i


Cl
Me
N
P(i-Pr)2
7.19 7.19 7.18 7.18 7.18 7.17 7.17 7.17 7.16 7.16 7.15 7.15 7.15 7.15 7.12 7.10 7.09 7.08 6.75 6.75 6.75 6.74 6.73 6.73 6.73 6.72
2.94 2.93 2.92 2.92 2.90 2.12 2.12 2.11 2.10 2.09 2.08 2.07 2.06 2.05 2.04 2.03 2.02 2.01 1.18 1.15 1.14 1.13 1.12 1.11 1.10 1.09 1.09 1.08 1.08 1.07
3.08
0.94
2.91
2.00
6.70
6.25
1H


Cl
Me
N
P(i-Pr)2
154.32 154.11
134.43 134.41 129.41 129.39
118.09 118.08 115.92 115.75 114.44 114.26
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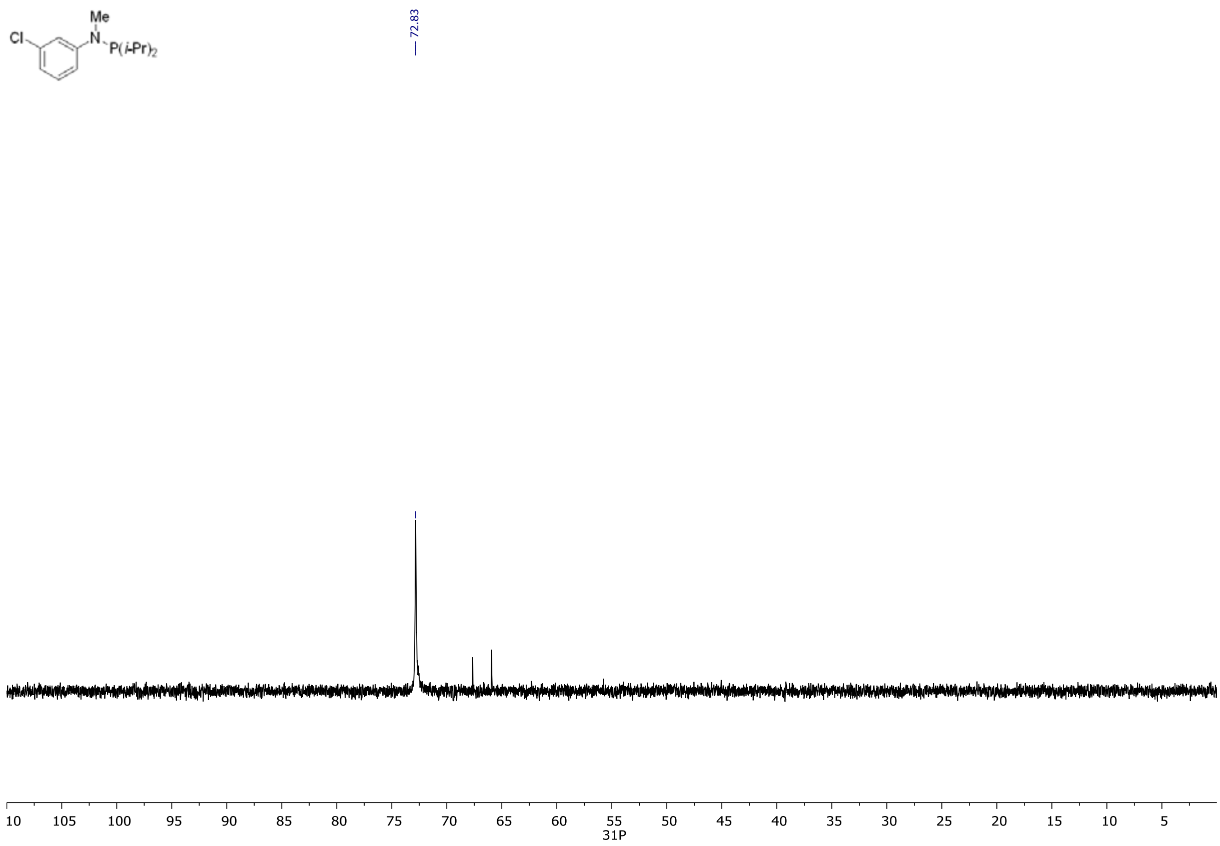
13C


Me
Cl
N
P(i-Pr)2
72.83
10
105
100
95
90
85
80
75
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65
60
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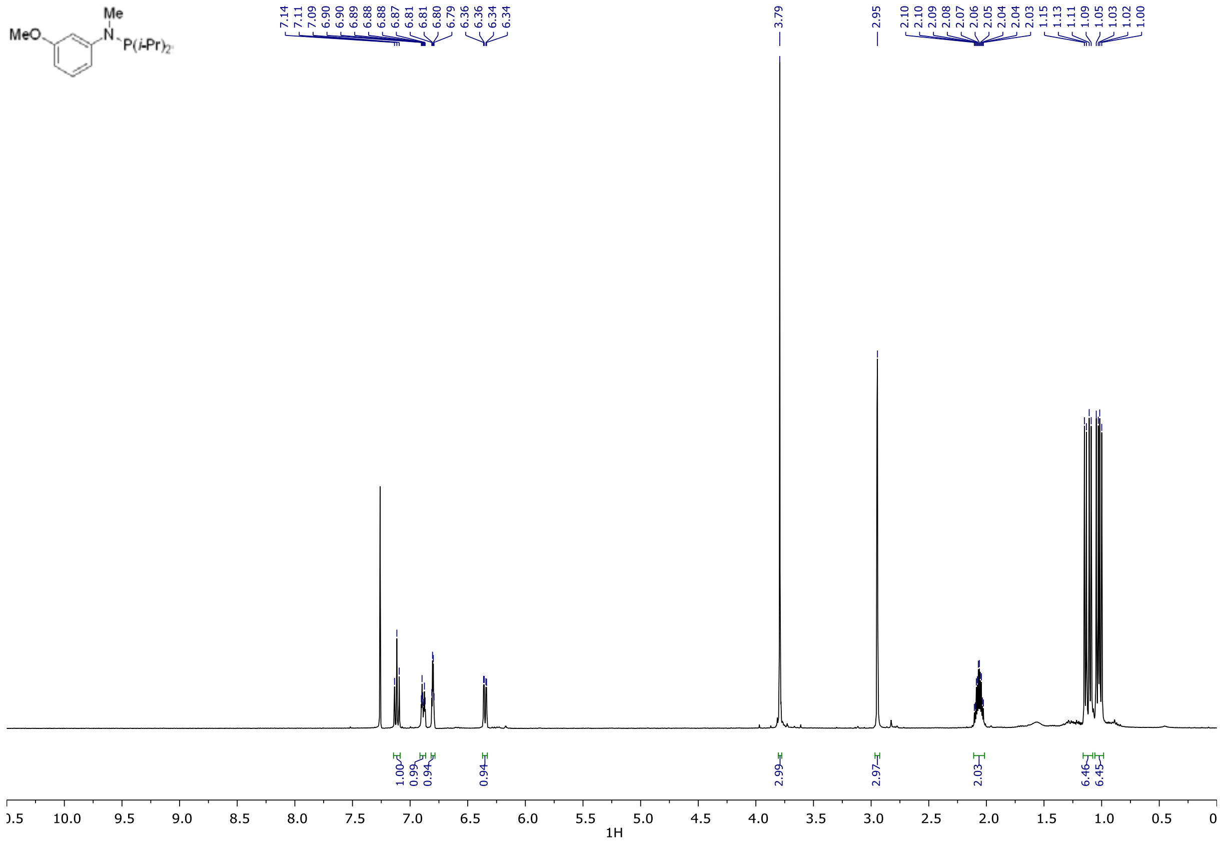
45
40
35
30
25
20
15
10
5
31P

1j


MeO
Me
N
P(i-Pr)2
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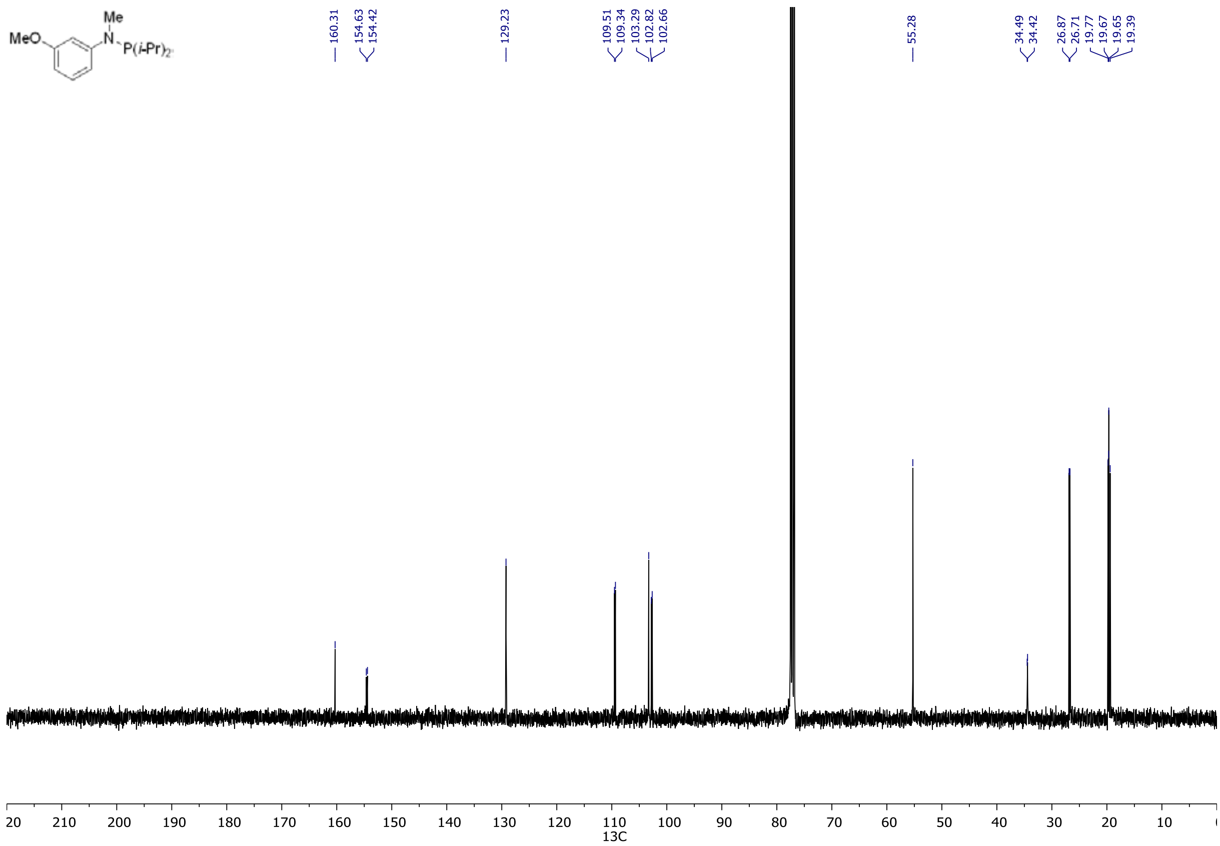
3.79
2.95
2.10 2.10 2.09 2.08 2.07 2.06 2.05 2.04 2.04 2.03 1.15 1.13 1.11 1.09 1.05 1.03 1.02 1.00
1.00 0.99 0.94 0.94 2.99 2.97 2.03 6.46 6.45
1H


MeO
Me
N
P(i-Pr)2
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129.23
109.51 109.34 103.29 102.82 102.66
55.28
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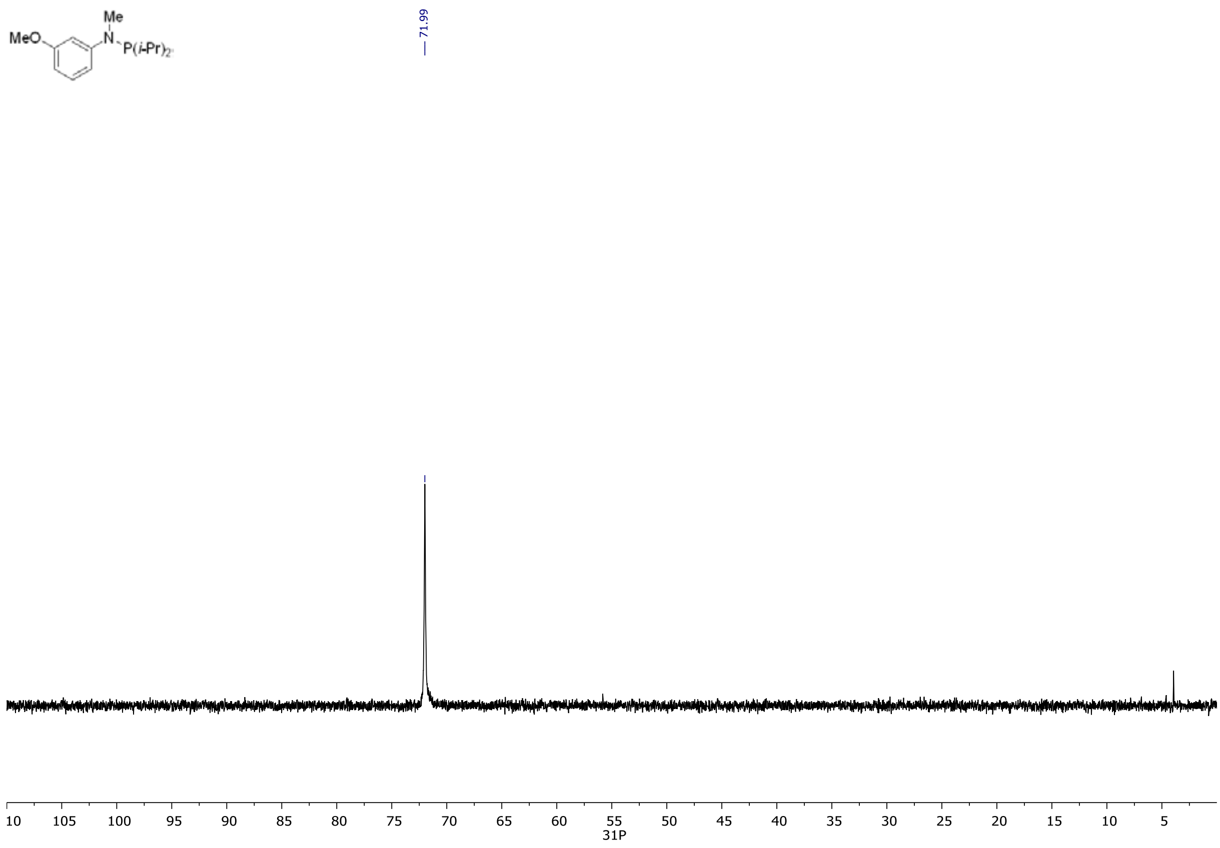
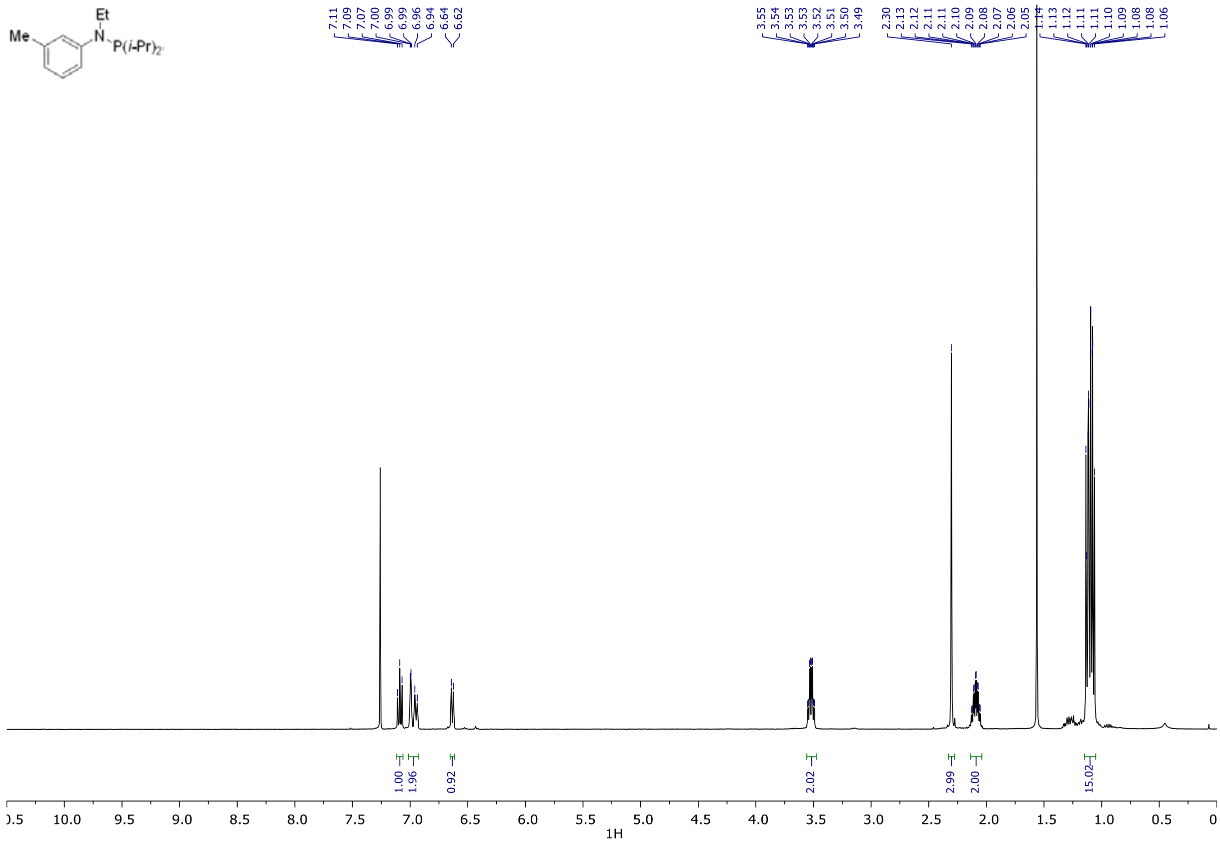
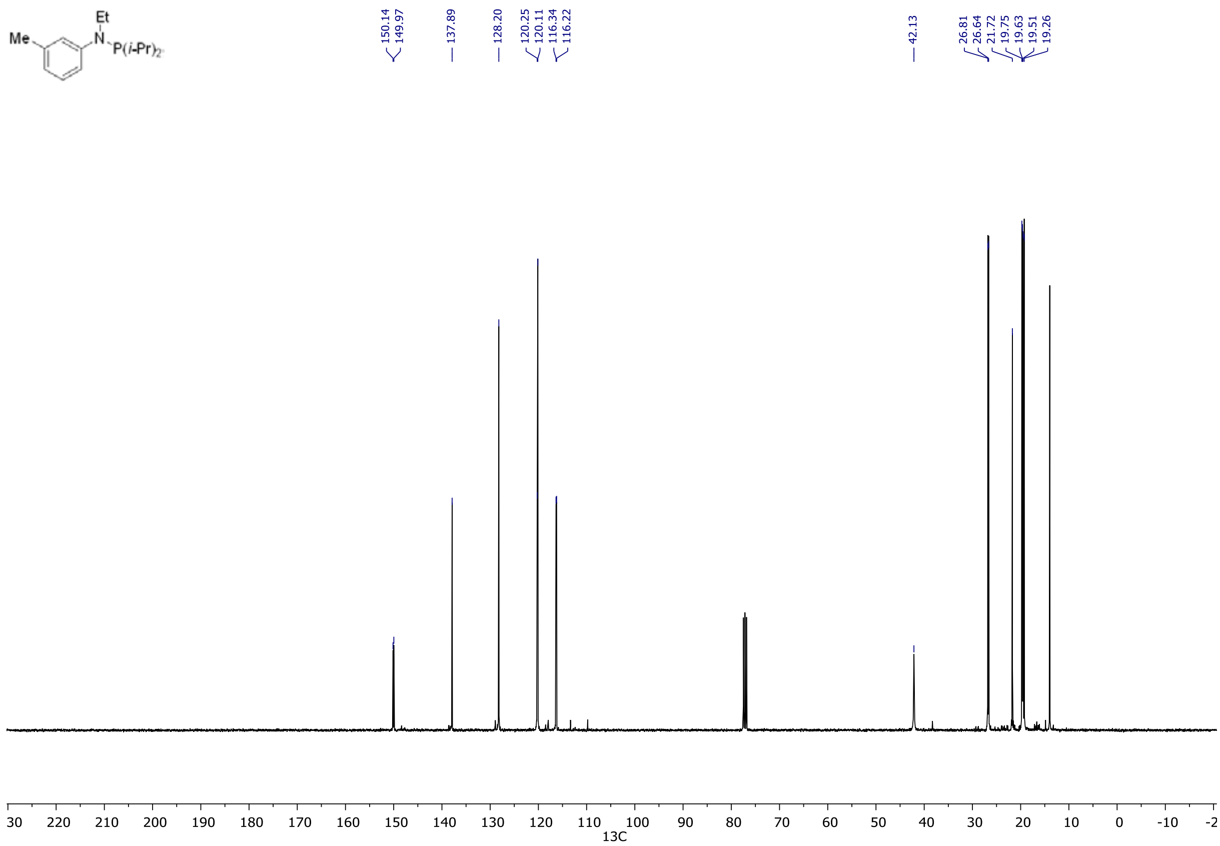
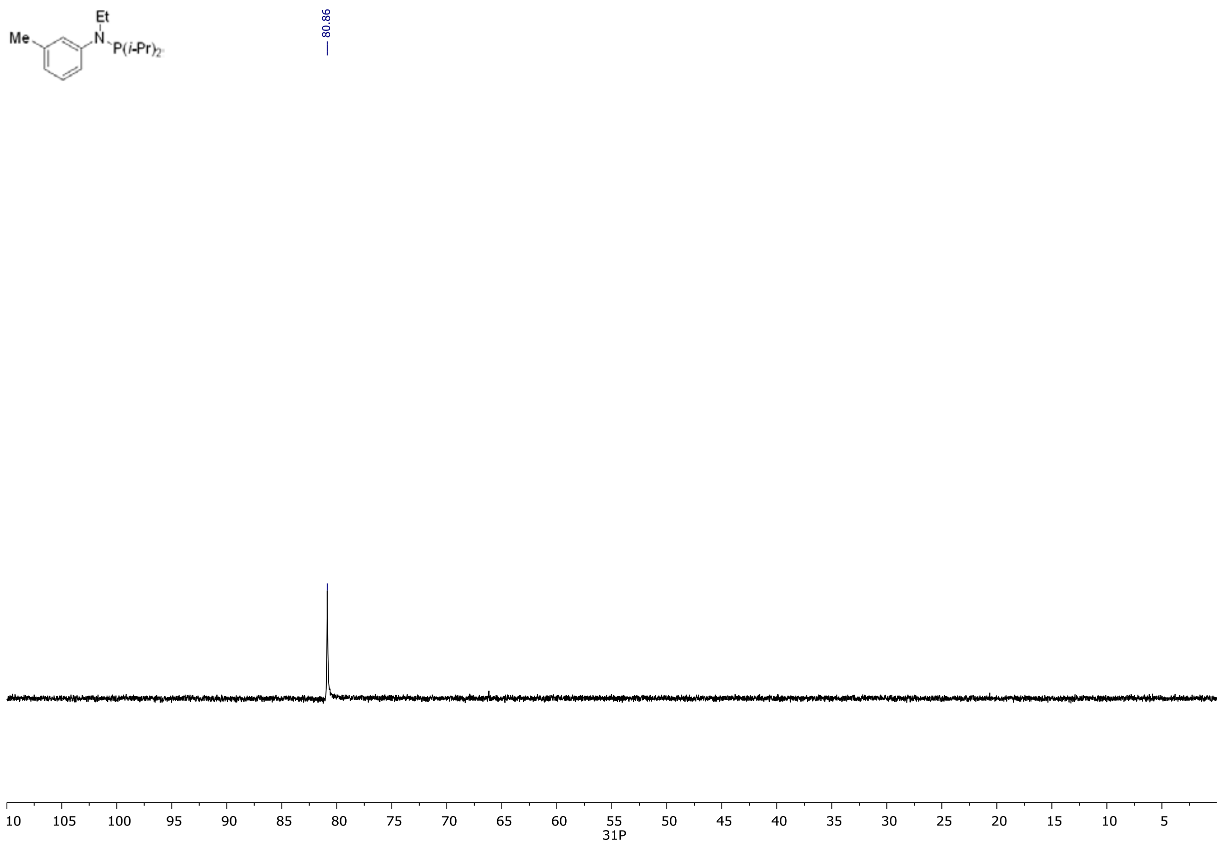
13C


MeO
Me
N
P(i-Pr)2
71.99
10 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
31P

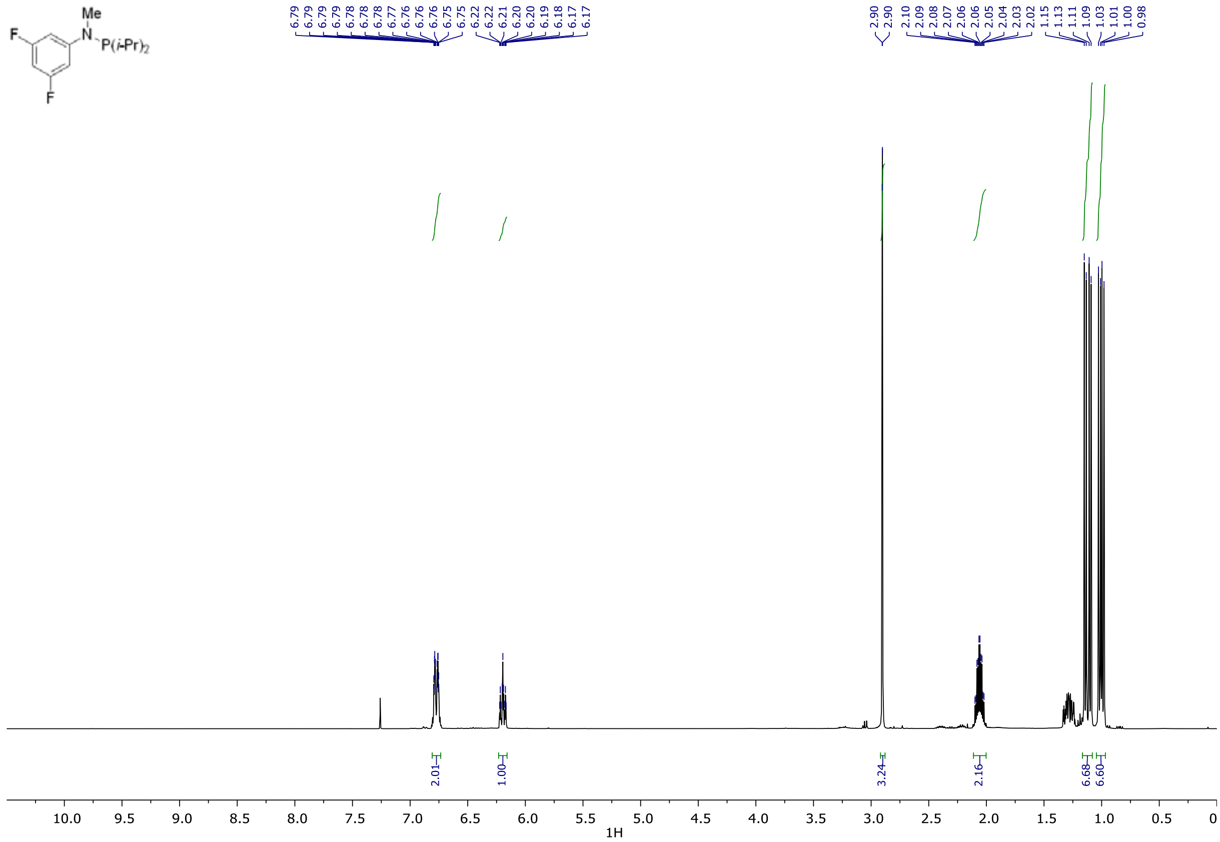
1k

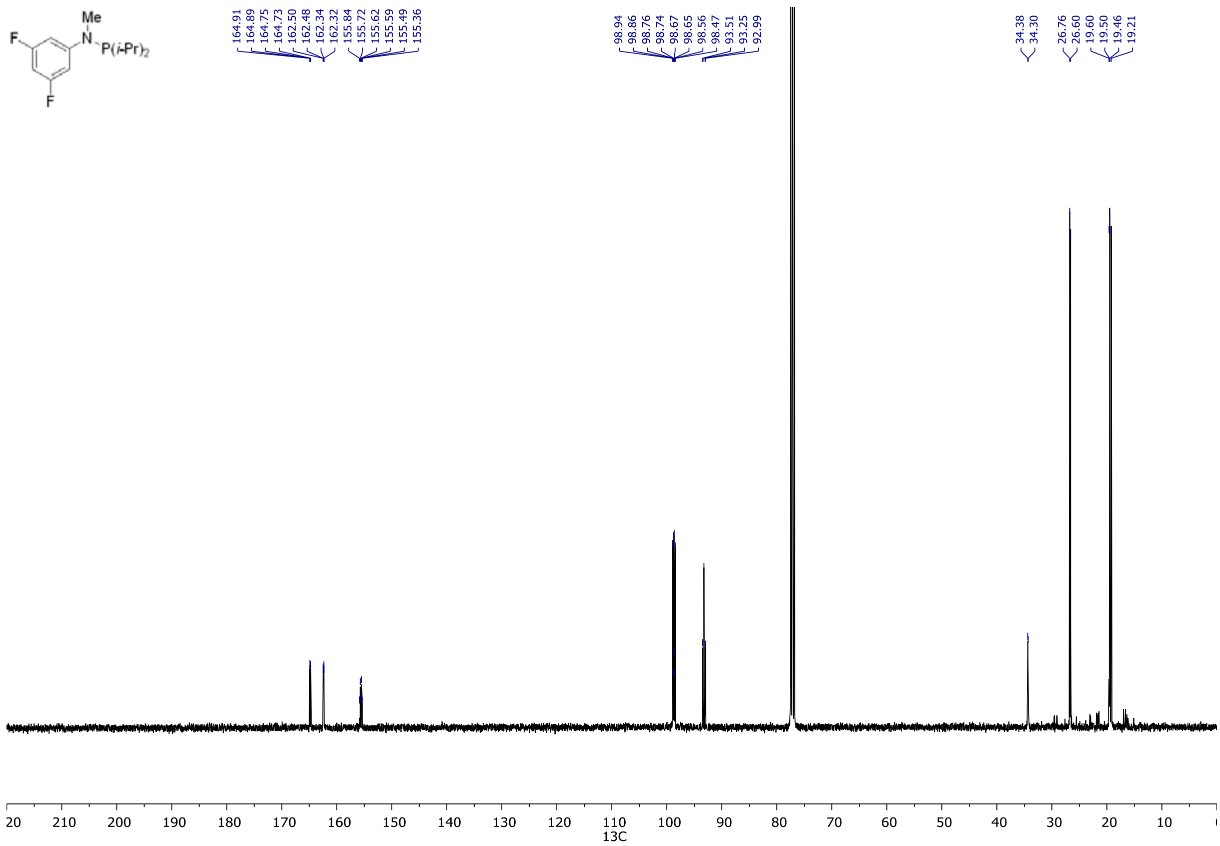


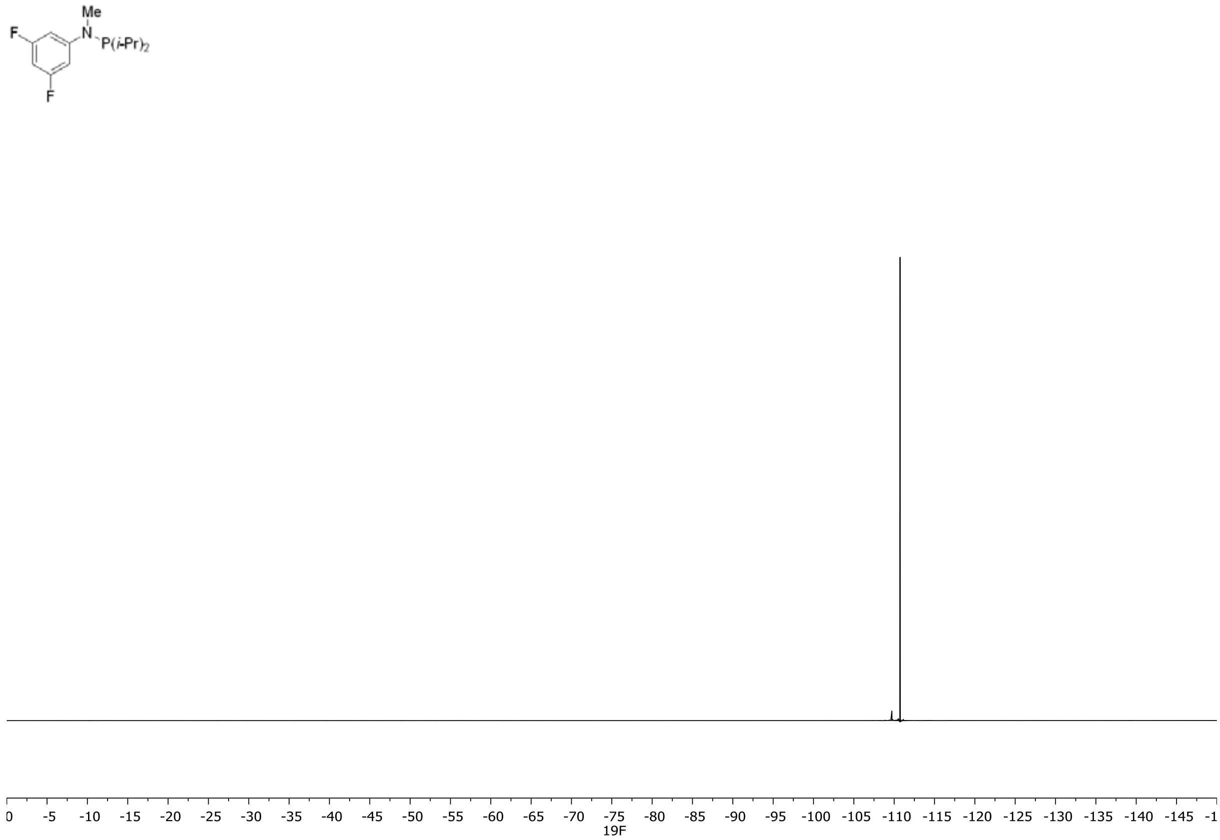



Et
Me
N
P(i-Pr)2
80.86
10 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
31P

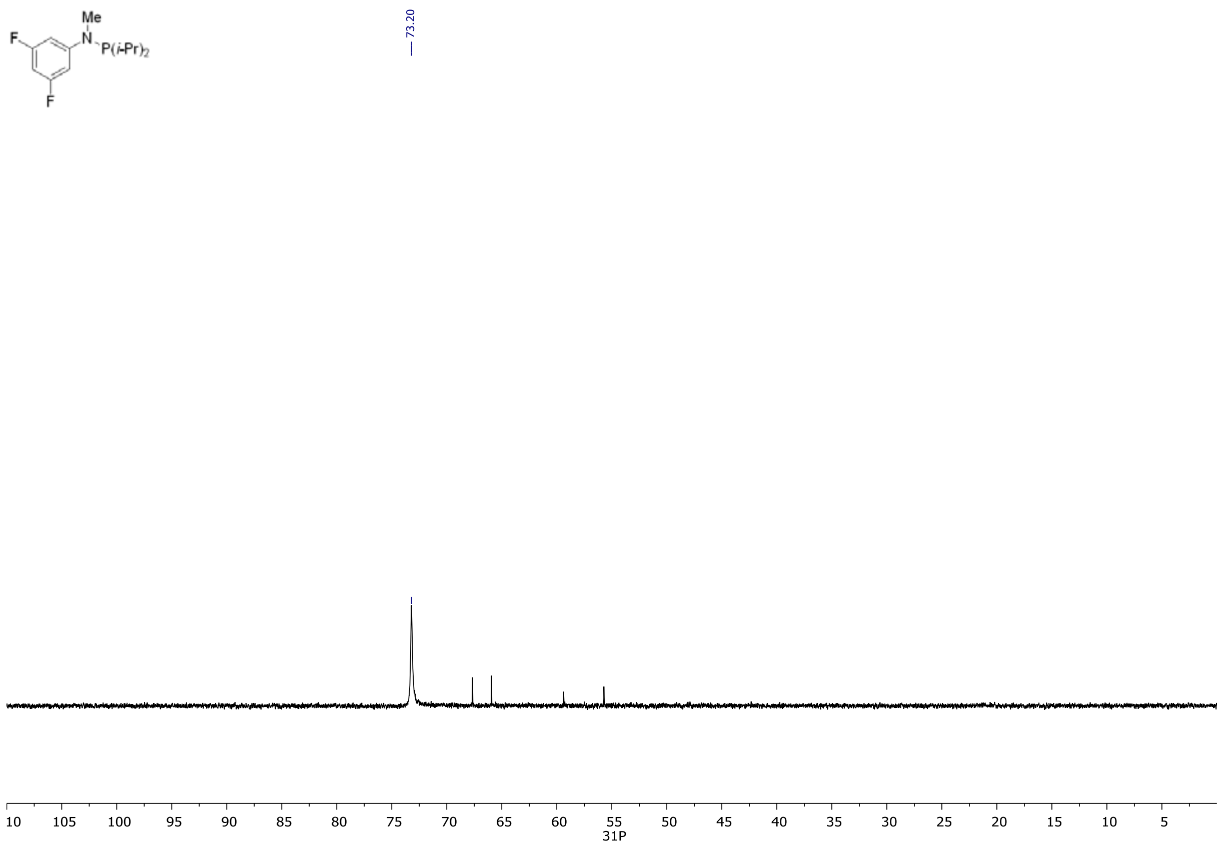
1l







Me
N
P(i-Pr)2
F
F
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145
19F



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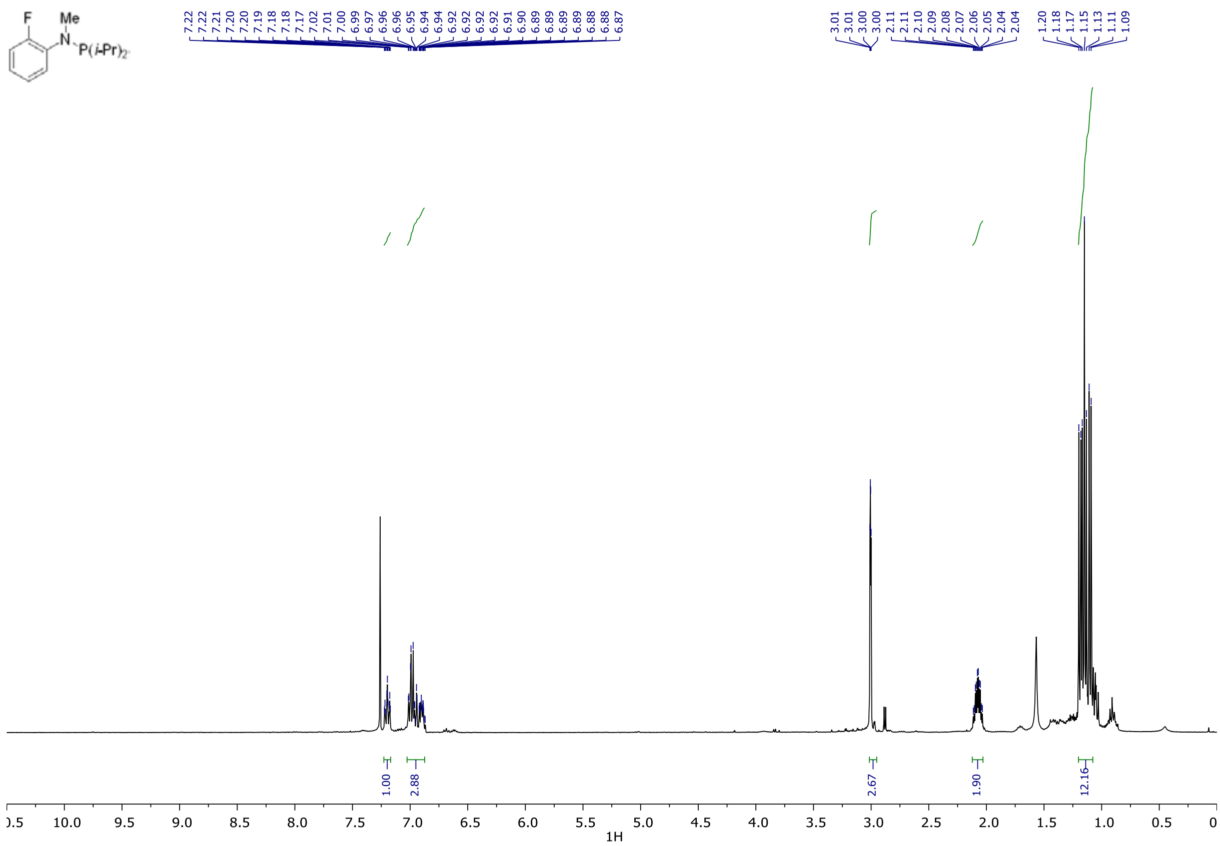
F
F
73.20
105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
31P

1m


F
Me
N
P(i-Pr)2
7.22 7.22 7.21 7.20 7.20 7.19 7.18 7.18 7.17 7.02 7.01 7.00 6.99 6.97 6.96 6.96 6.95 6.94 6.94 6.92 6.92 6.92 6.91 6.90 6.89 6.89 6.89 6.89 6.88 6.88 6.87
3.01 3.01 3.00 3.00 2.11 2.11 2.10 2.09 2.08 2.07 2.06 2.05 2.04 2.04
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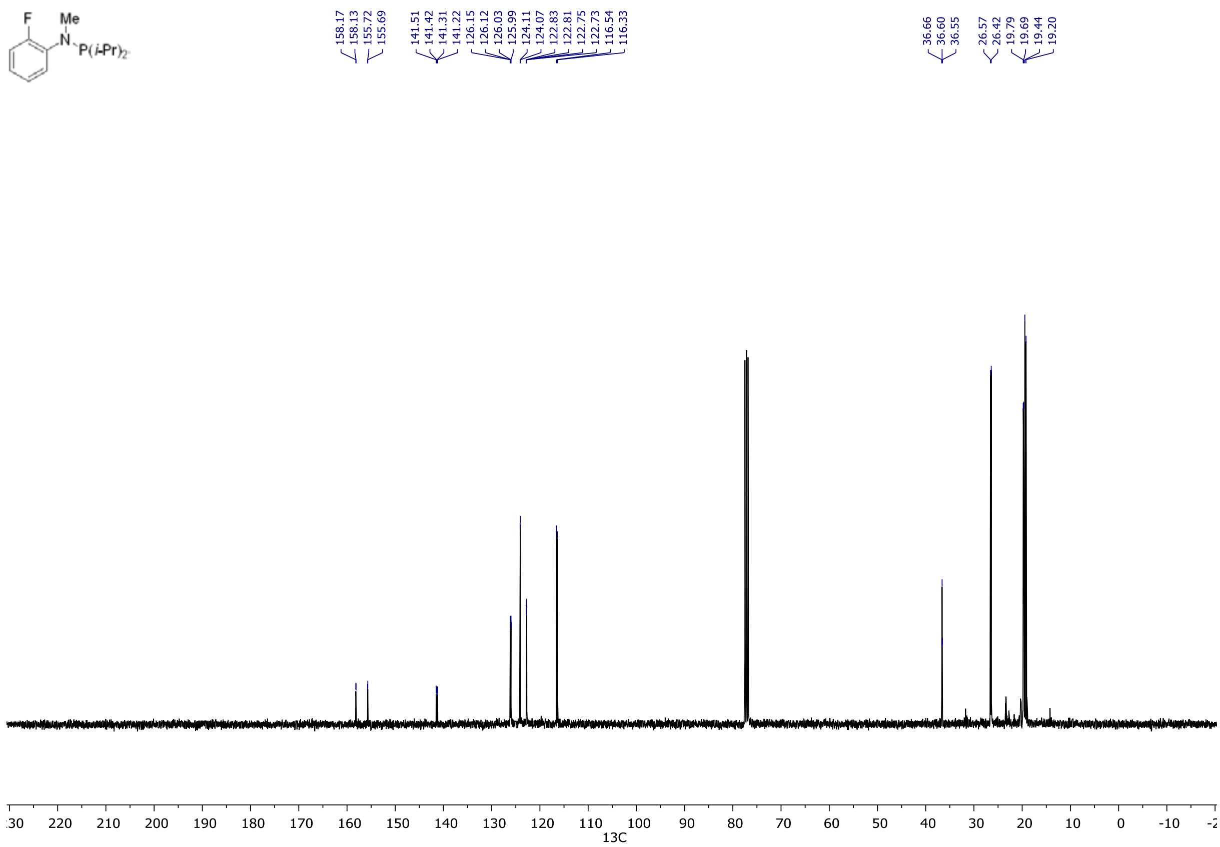
1.00
2.88
2.67
1.90
12.16
1H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Me
N
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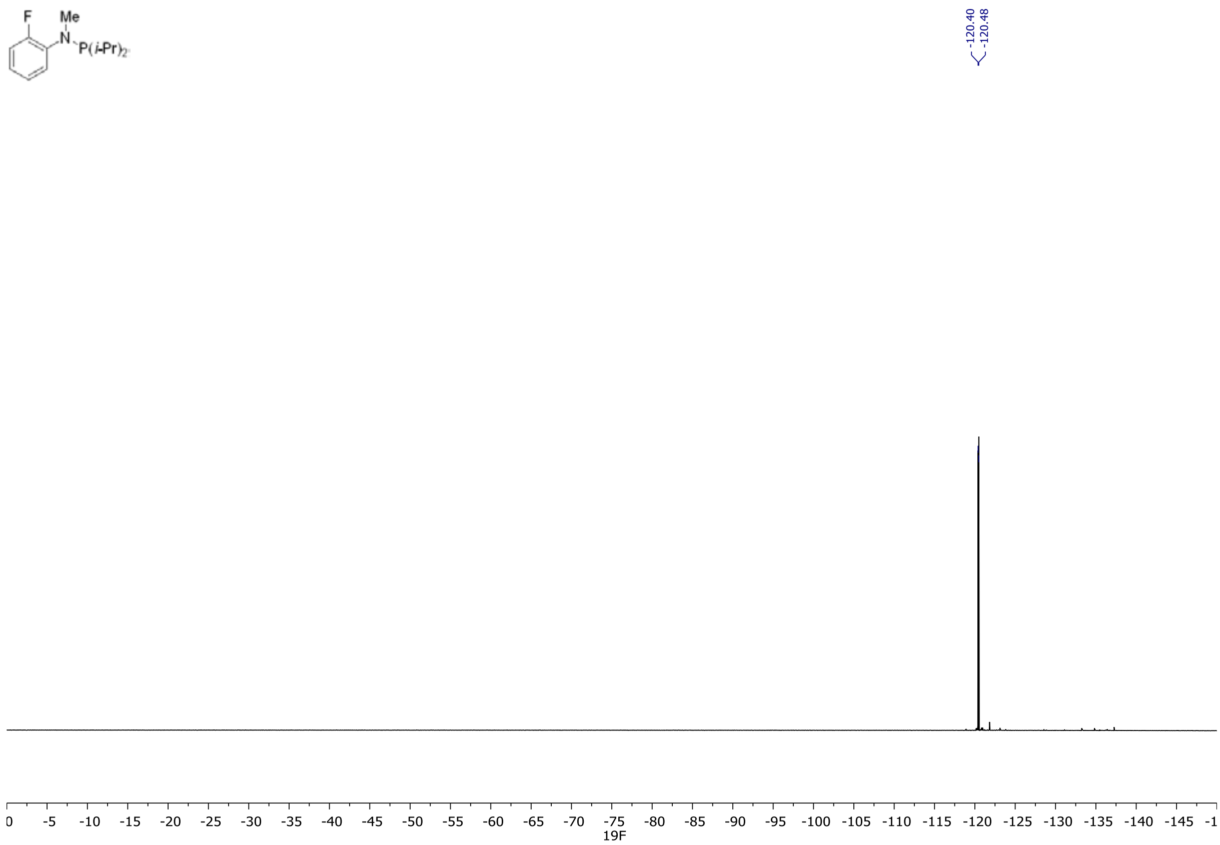
158.17 158.13 155.72 155.69
141.51 141.42 141.31 141.22 126.15 126.12 126.03 125.99 124.11 124.07 122.83 122.81 122.75 122.73 116.54 116.33
36.66 36.60 36.55
26.57 26.42 19.79 19.69 19.44 19.20
13C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Me
N
P(i-Pr)2
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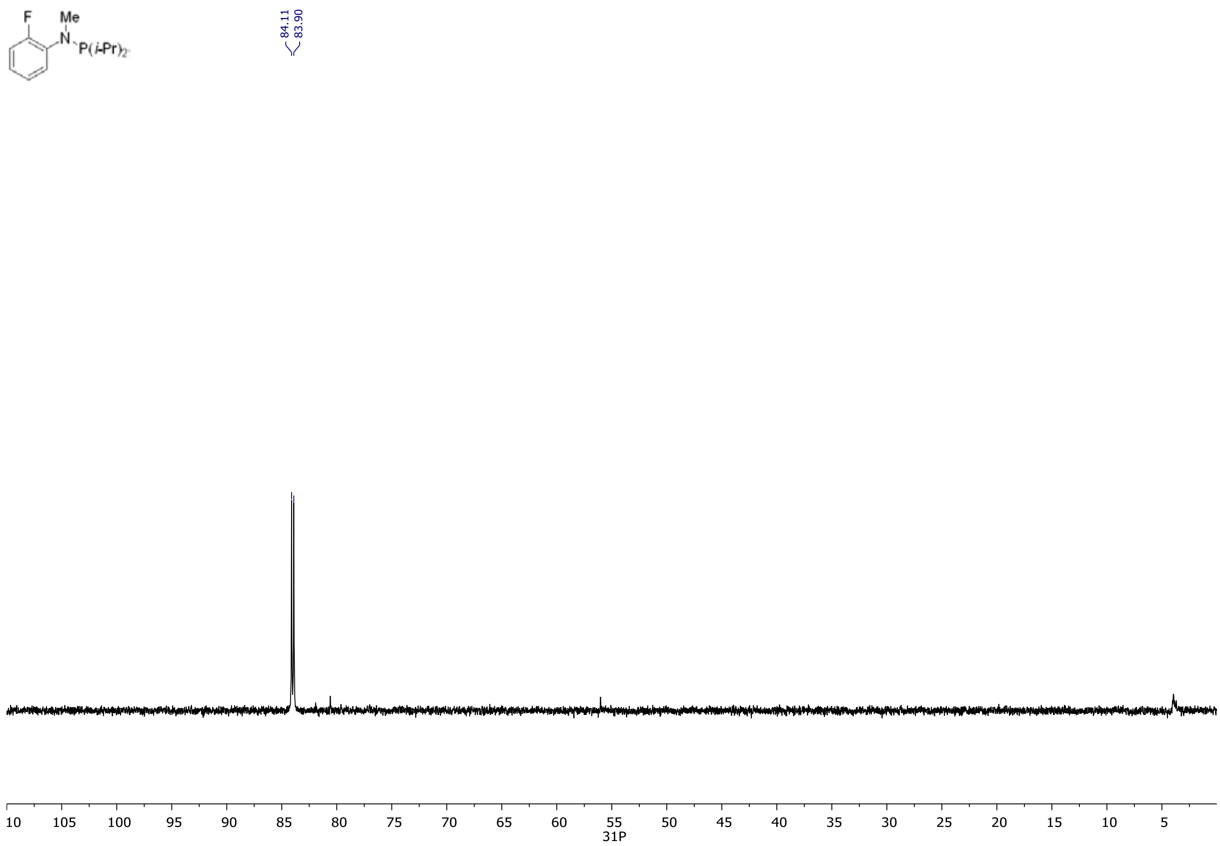
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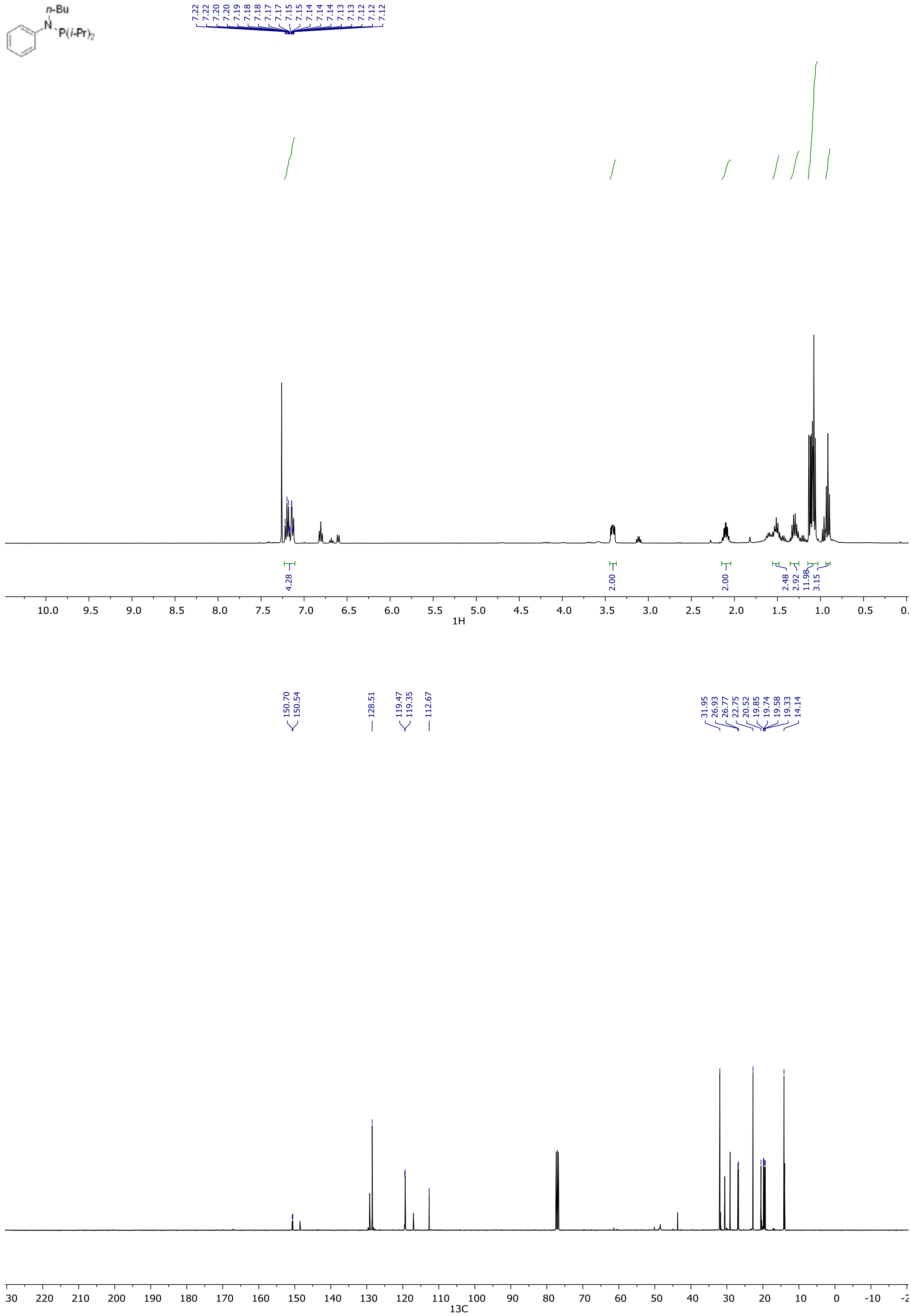
N
P(i-Pr)2
84.11
83.90
31P

1n


n-Bu
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P(i-Pr)2
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7.20
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7.19
7.18
7.18
7.17
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7.15
7.14
7.14
7.14
7.13
7.13
7.12
7.12
7.12
4.28
2.00
2.00
2.48
2.92
11.98
3.15
1H
150.70
150.54
128.51
119.47
119.35
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26.77
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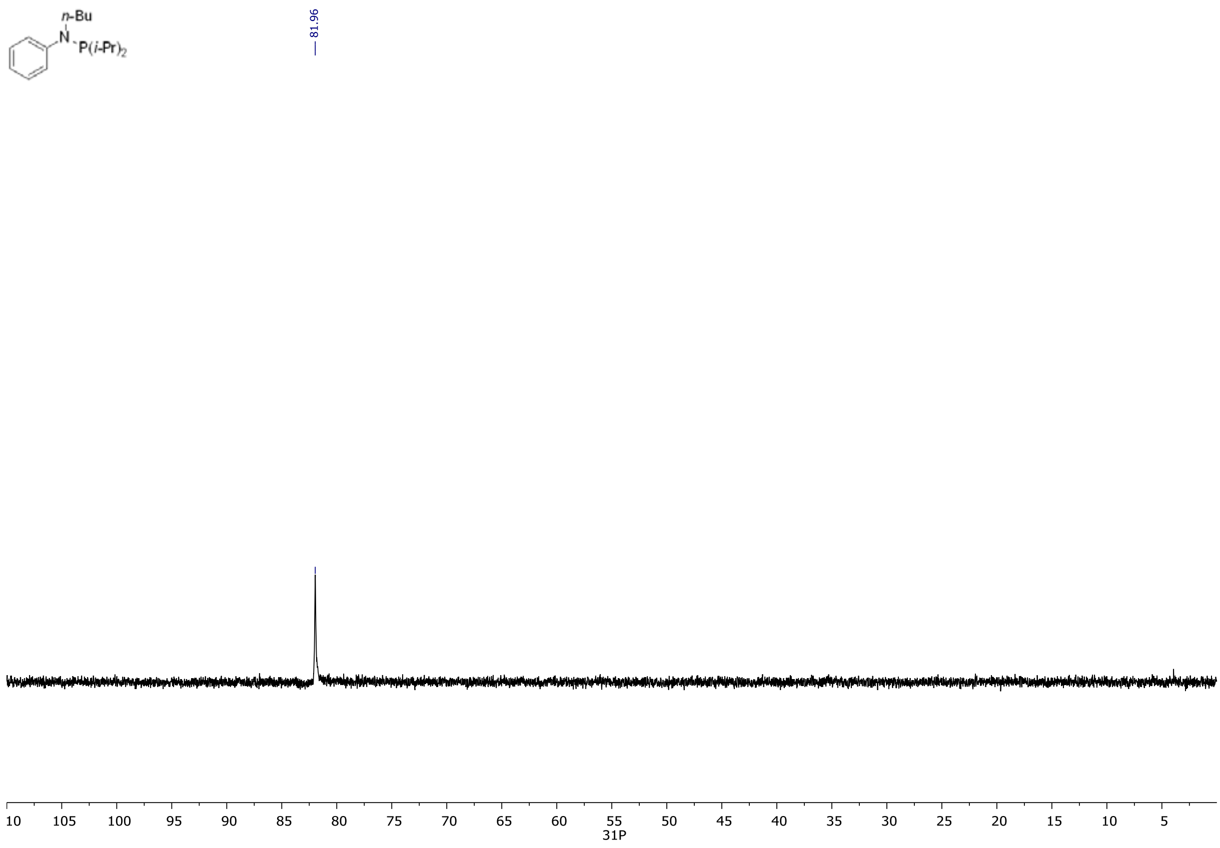
14.14
13C


n-Bu
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P(i-Pr)2
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105
100
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31P
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25
20
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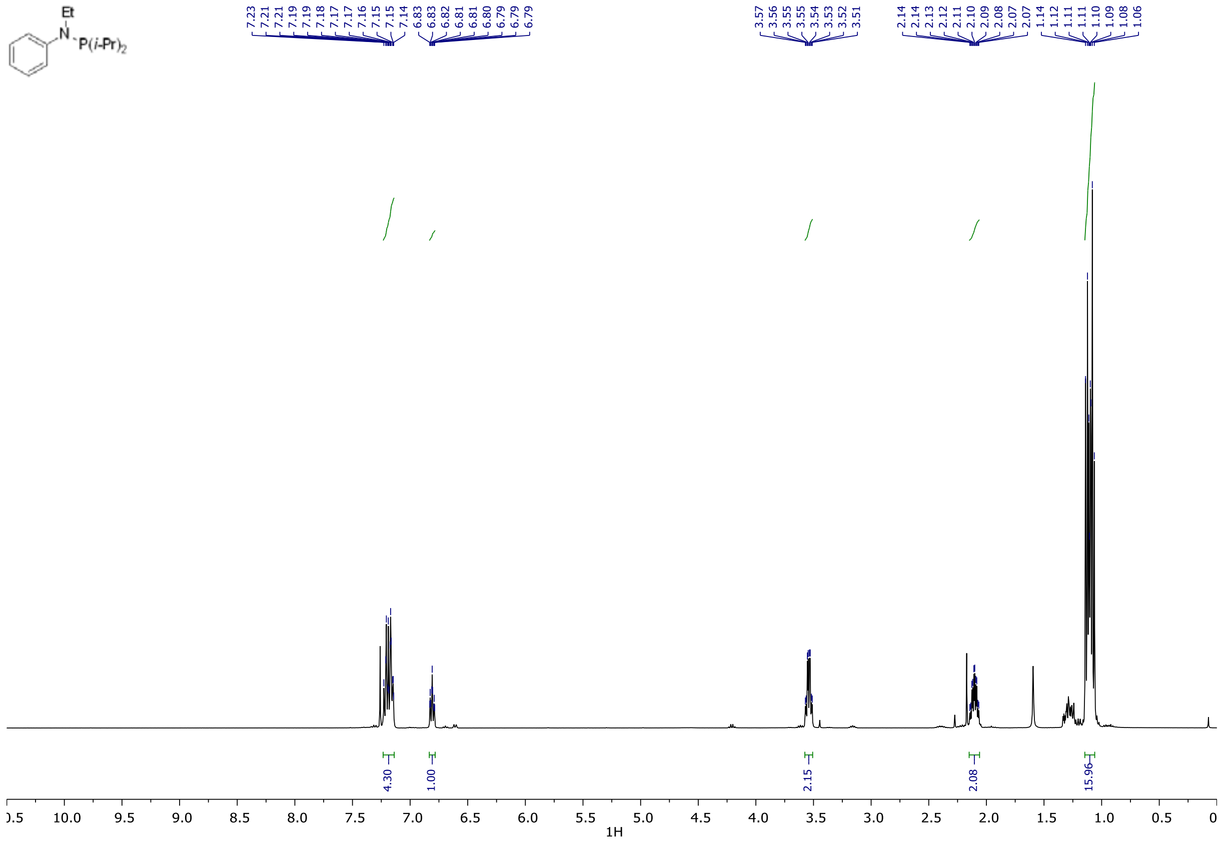
10
5

1o



Et
N
P(i-Pr)2
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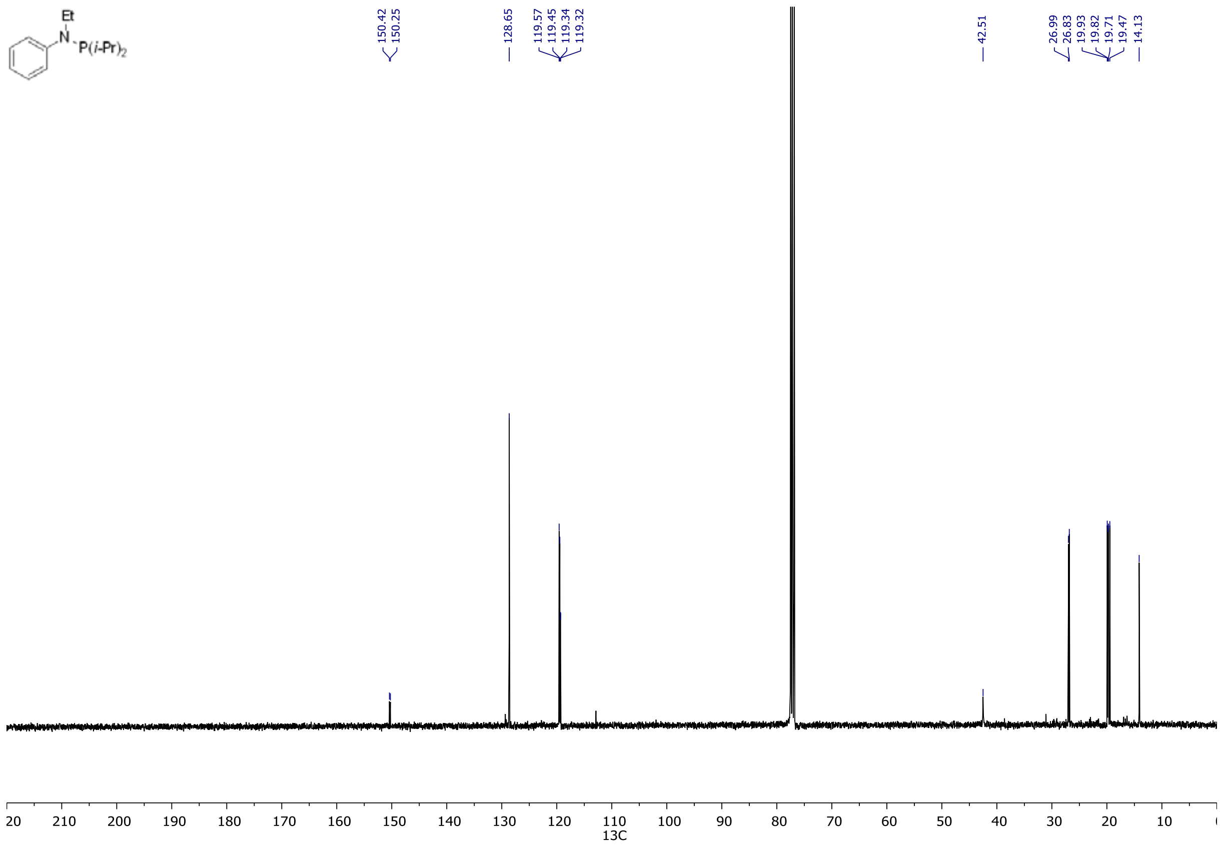
7.21
7.19
7.19
7.18
7.17
7.17
7.16
7.15
7.15
7.14
6.83
6.83
6.82
6.81
6.81
6.80
6.79
6.79
6.79
3.57
3.56
3.55
3.55
3.54
3.53
3.52
3.51
2.14
2.14
2.13
2.12
2.11
2.10
2.09
2.08
2.07
2.07
1.14
1.12
1.11
1.11
1.10
1.09
1.08
1.06
4.30
1.00
2.15
2.08
15.96
1H



Et
N
P(i-Pr)2
150.42
150.25
128.65
119.57
119.45
119.34
119.32
42.51
26.99
26.83
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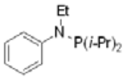
19.47
14.13
13C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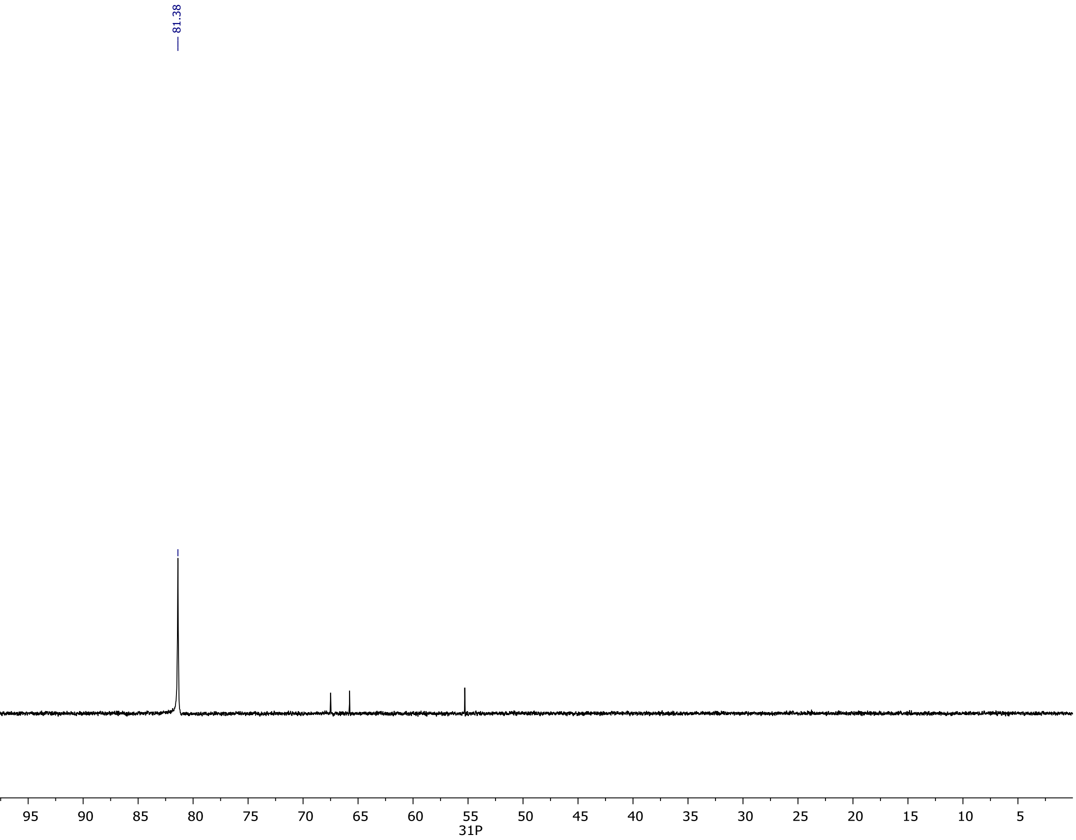
N
P(i-Pr)2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10
105
100
95
90
85
80
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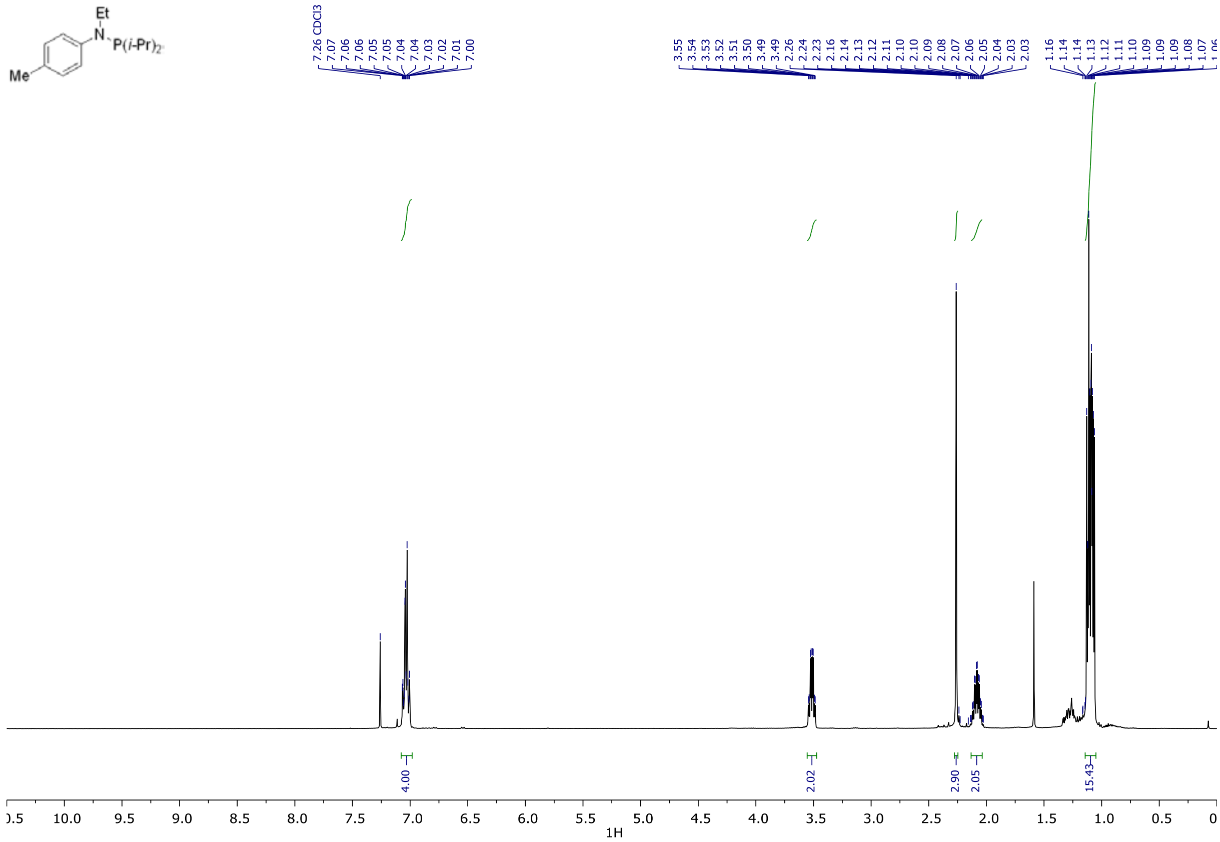
70
65
60
55
31P
50
45
40
35
30
25
20
15
10
5

1p


Et
N
P(i-Pr)2
Me
7.26 CDCl3
7.07
7.06
7.06
7.05
7.04
7.04
7.03
7.02
7.01
7.00
3.55
3.54
3.53
3.52
3.51
3.50
3.49
3.49
2.26
2.24
2.23
2.16
2.14
2.13
2.12
2.11
2.10
2.10
2.09
2.08
2.07
2.06
2.05
2.04
2.03
2.03
1.16
1.14
1.14
1.13
1.12
1.11
1.10
1.09
1.09
1.09
1.08
1.07
4.00
2.02
2.90
2.05
15.43
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
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3.0
2.5
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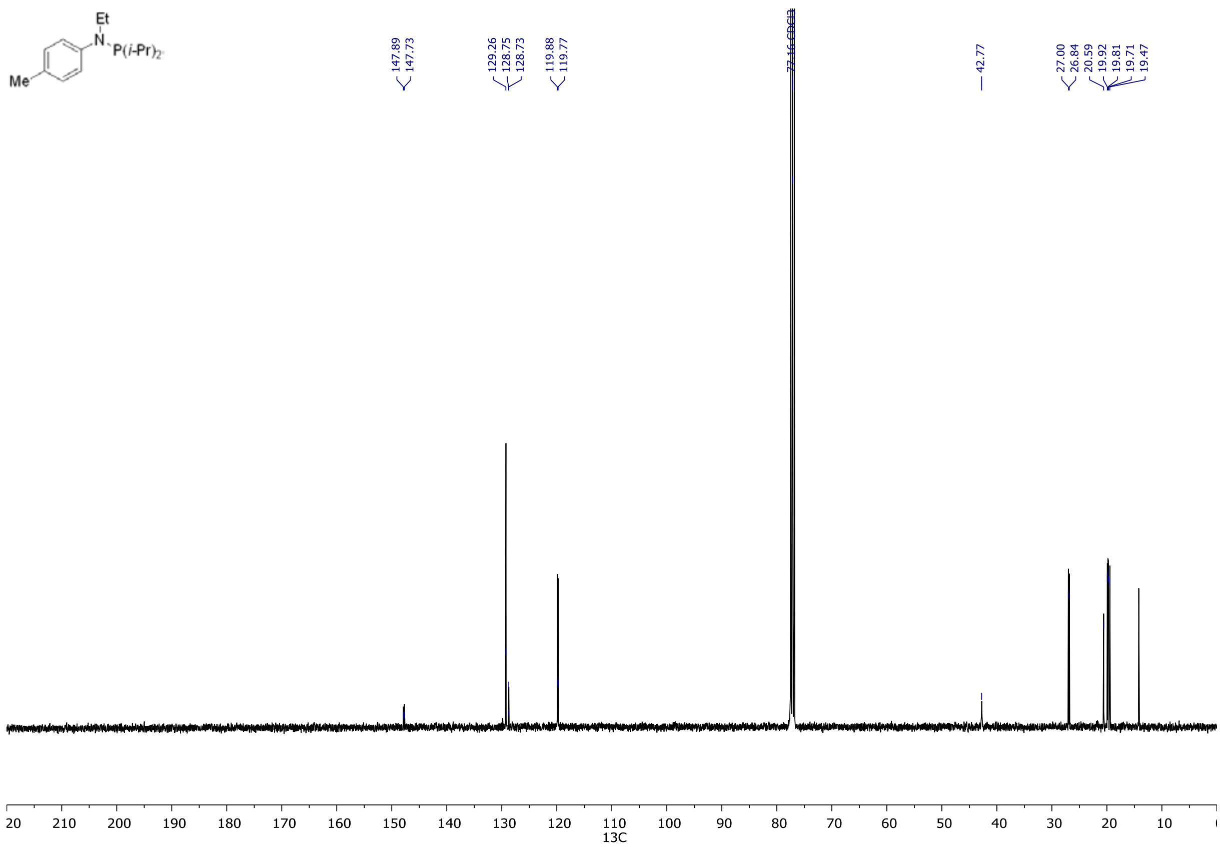
1.5
1.0
0.5
0
1H


Et
N
P(i-Pr)2
Me
147.89
147.73
129.26
128.75
128.73
119.88
119.77
77.16 CDCl3
42.77
27.00
26.84
20.59
19.92
19.81
19.71
19.47
210
200
190
180
170
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150
140
130
120
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100
90
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70
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50
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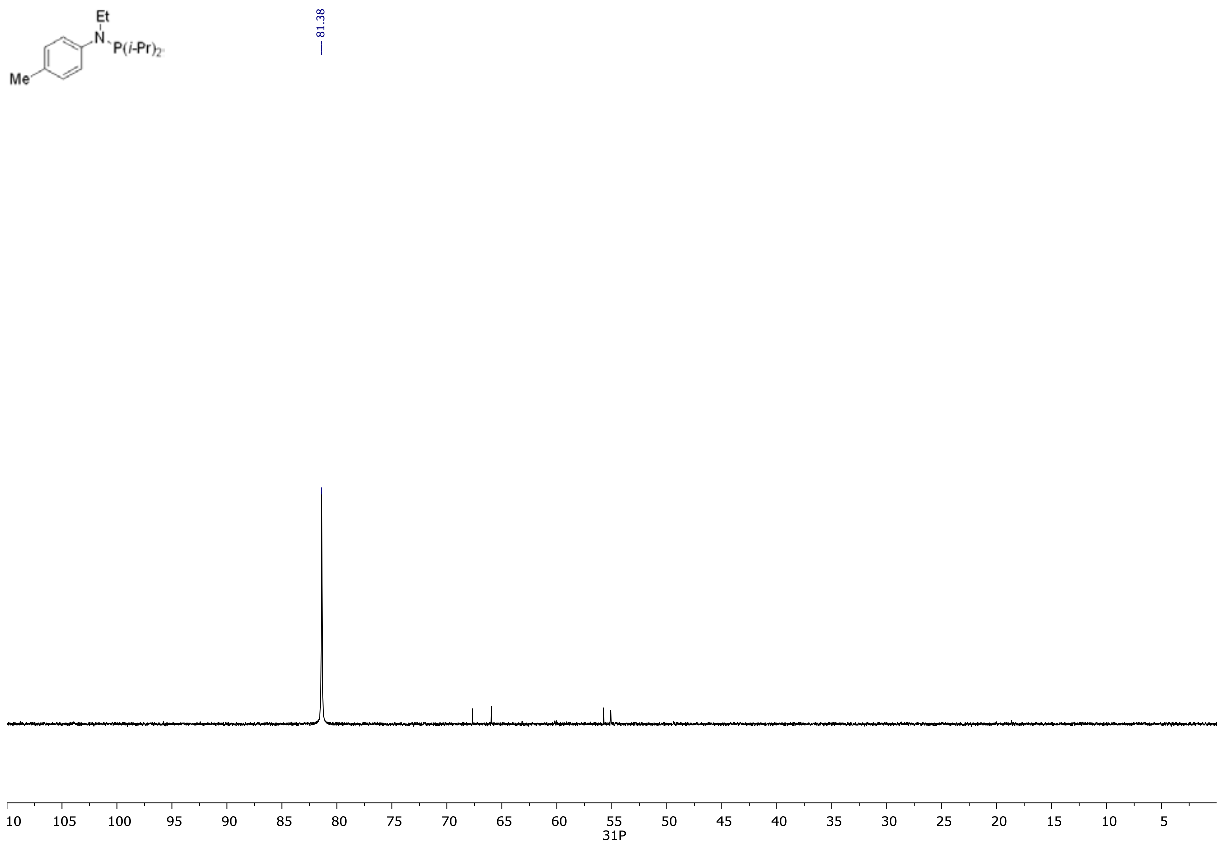
30
20
10
13C


Et
N
P(i-Pr)2
Me
81.38
10
105
100
95
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60
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31P
50
45
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35
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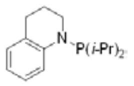
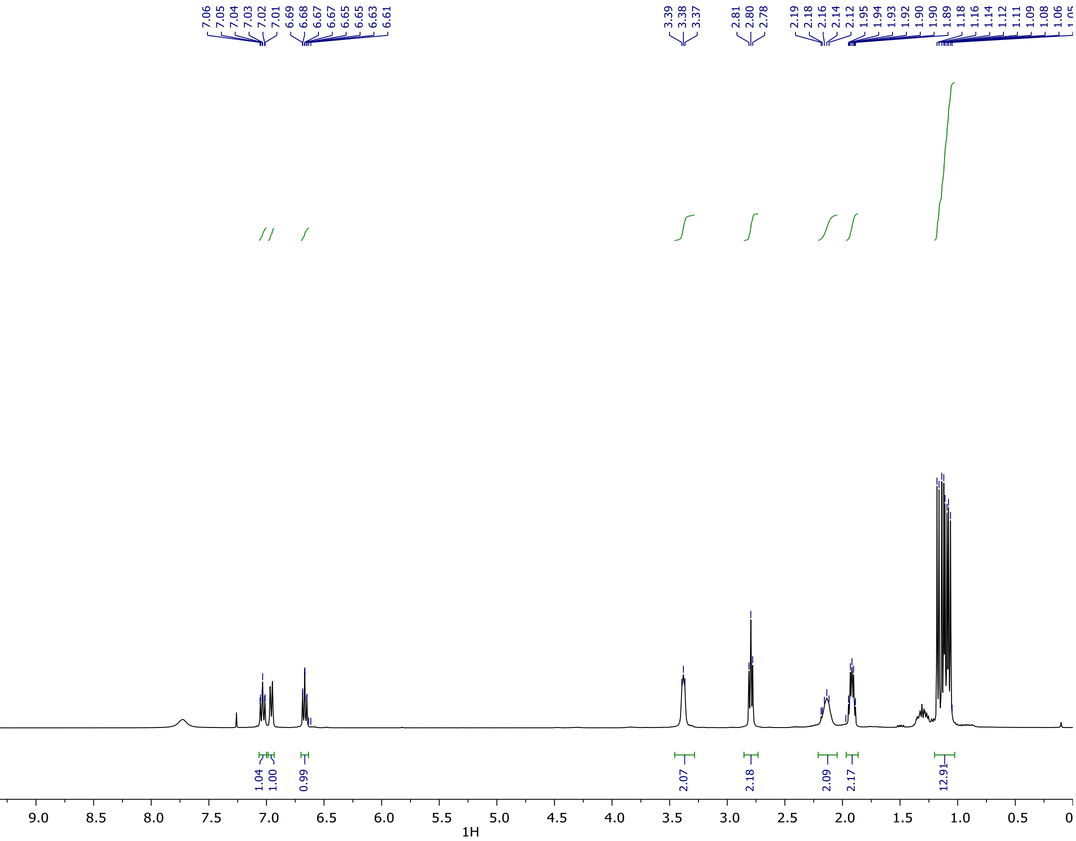
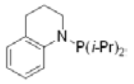
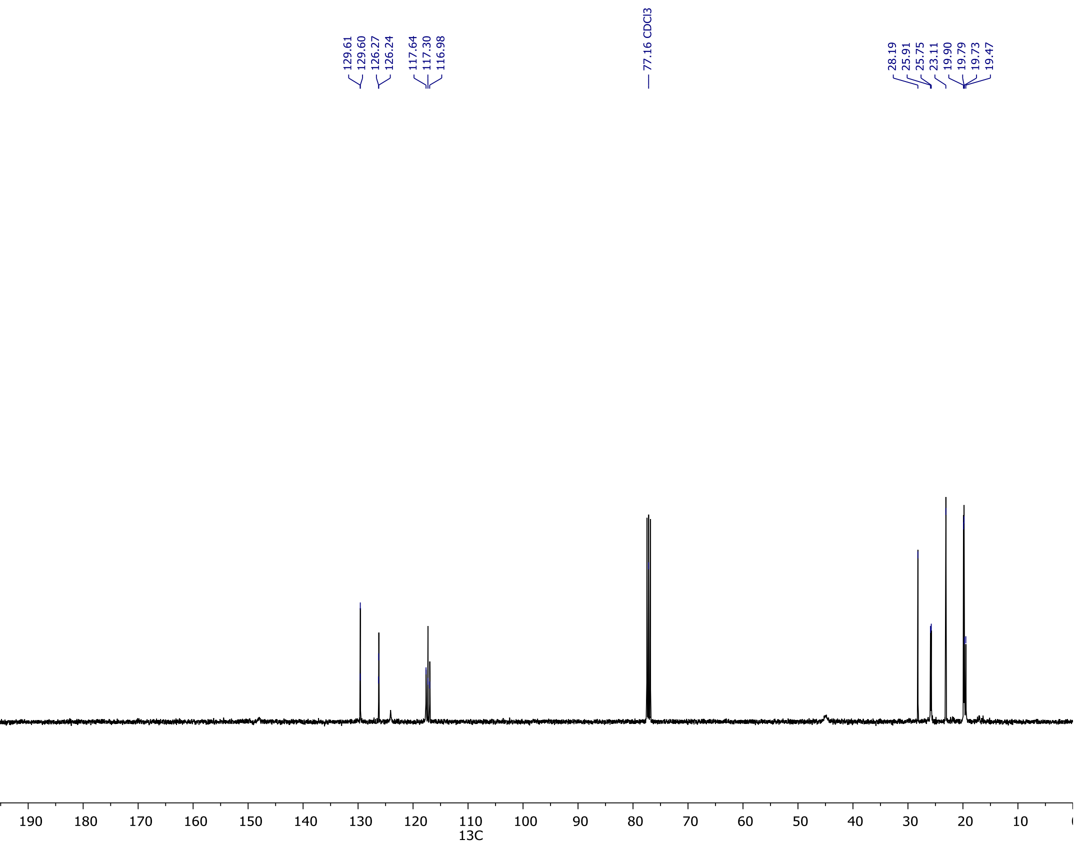
25
20
15
10
5

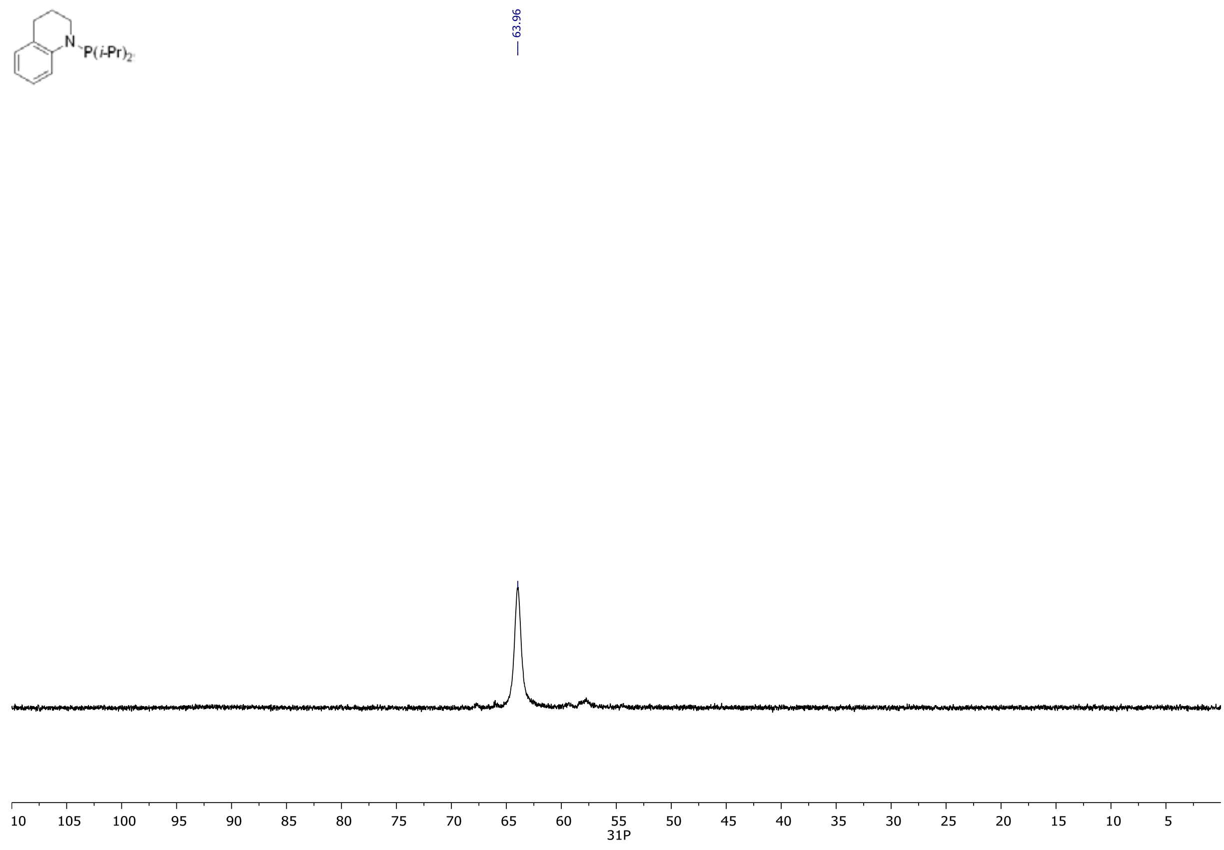
1q



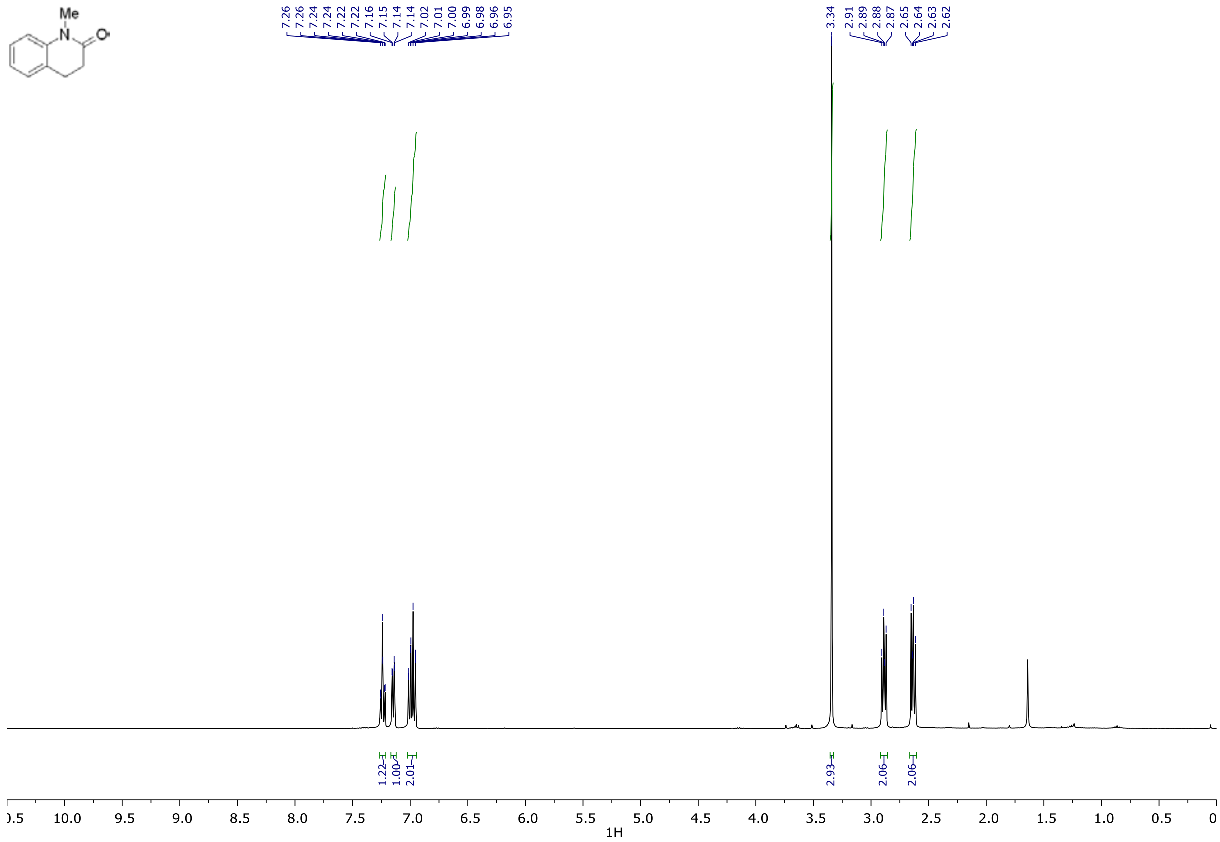







N
P(i-Pr)2
63.96
10 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
31P

3a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O
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7.24
7.24
7.22
7.22
7.16
7.15
7.14
7.14
7.02
7.01
7.00
6.99
6.98
6.96
6.95
3.34
2.91
2.89
2.88
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2.64
2.63
2.62
1.22
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2.01
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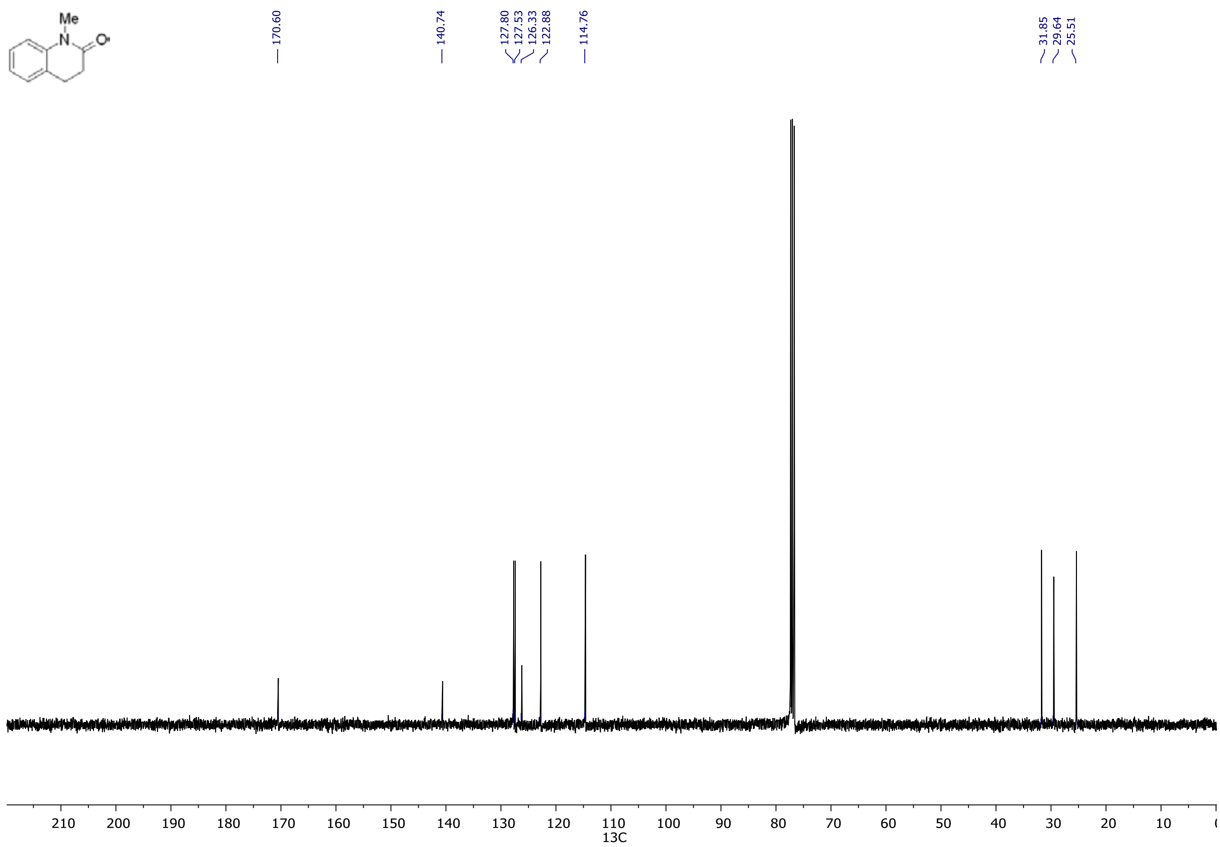
2.06
2.06
1H


Me
N
O
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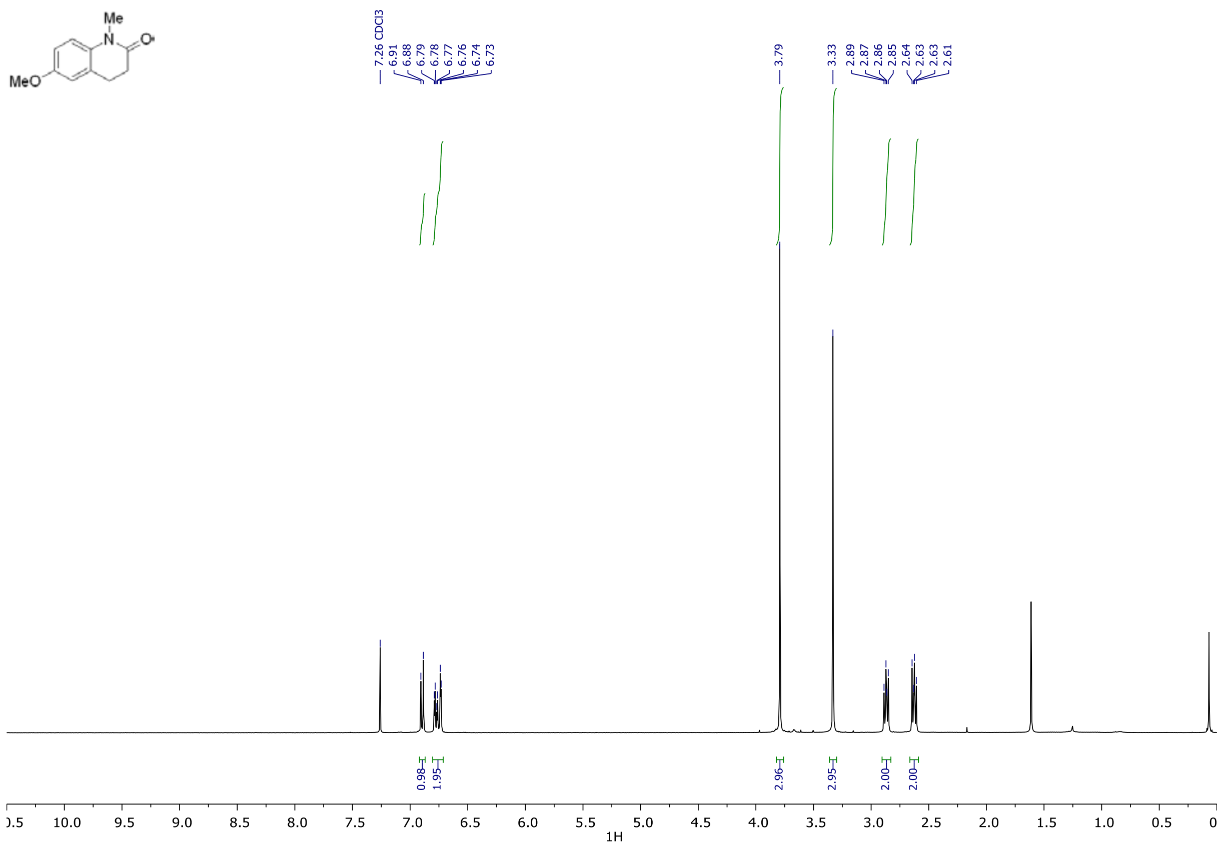
31.85
29.64
25.51
13C

3b



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N
O
MeO
7.26 CDCl3
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6.77
6.76
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6.73
3.79
3.33
2.89
2.87
2.86
2.85
2.64
2.63
2.63
2.61
0.98
1.95
2.96
2.95
2.00
2.00
10.0
9.5
9.0
8.5
8.0
7.5
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6.5
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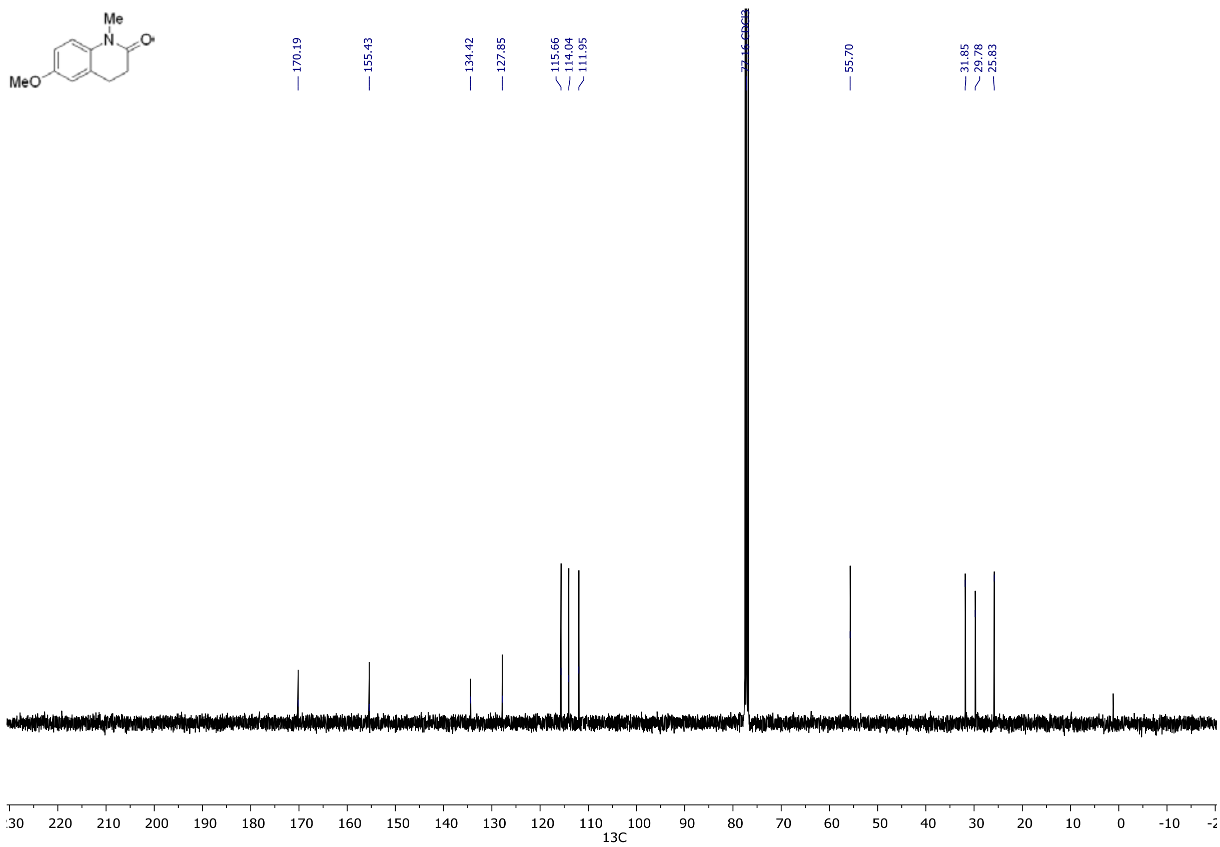

Me
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MeO
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134.42
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114.04
111.95
77.16 CDCl3
55.70
31.85
29.78
25.83
220
210
200
190
180
170
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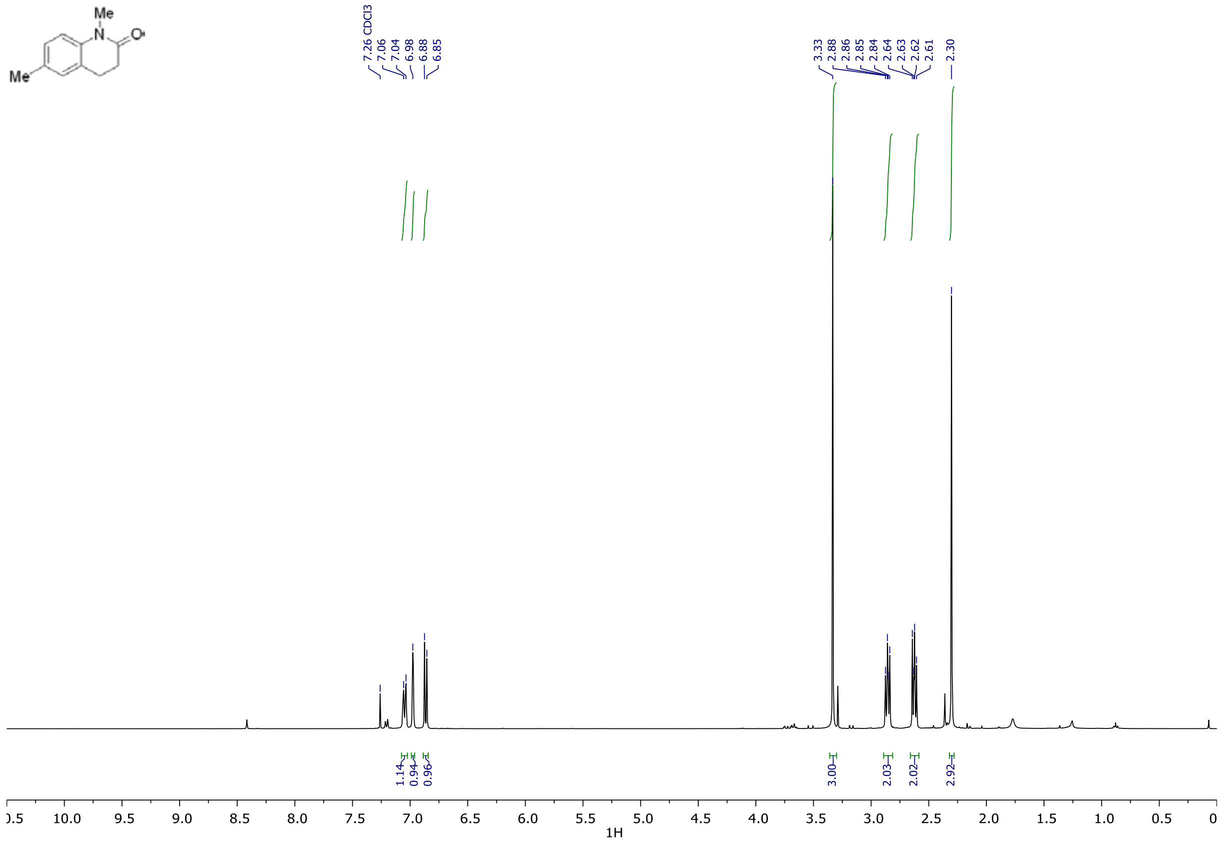
-10
13C

3c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O
Me
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2.84
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2.30
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3.00
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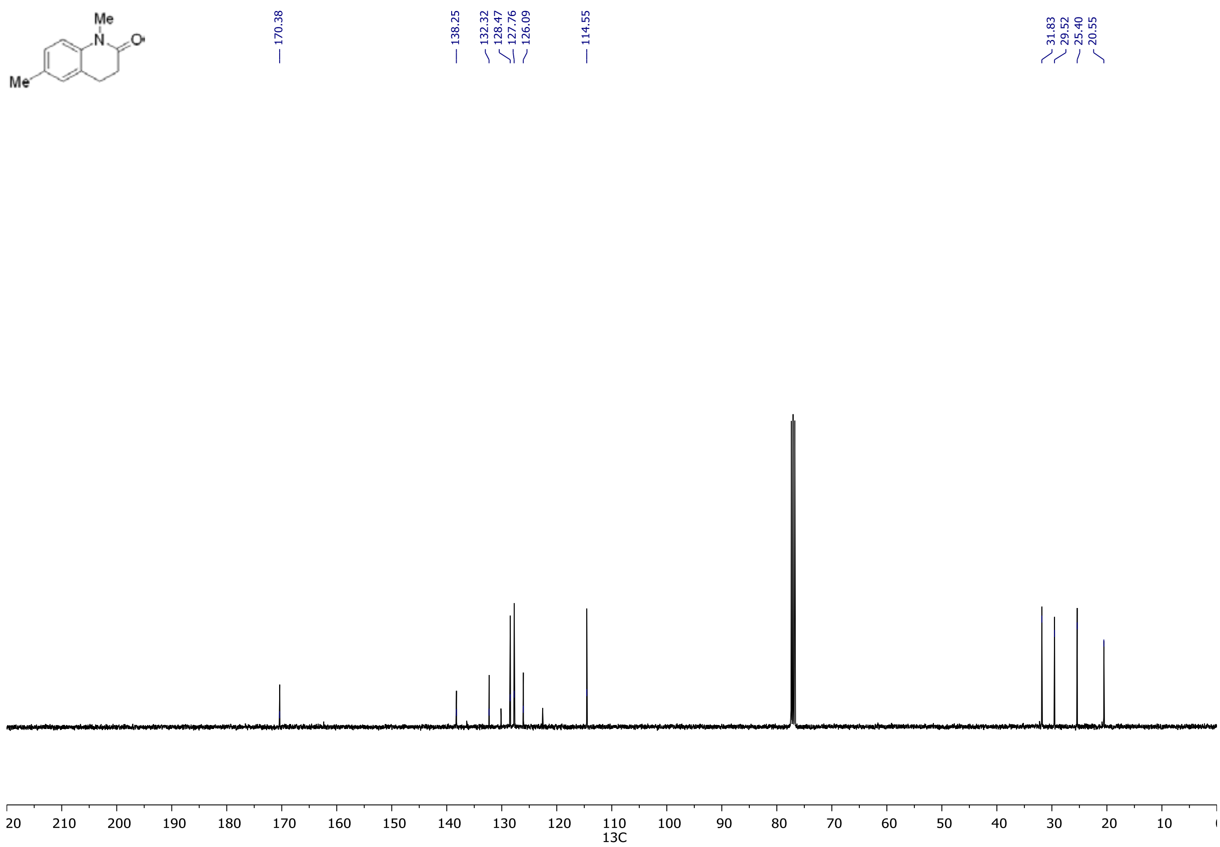
2.92
1H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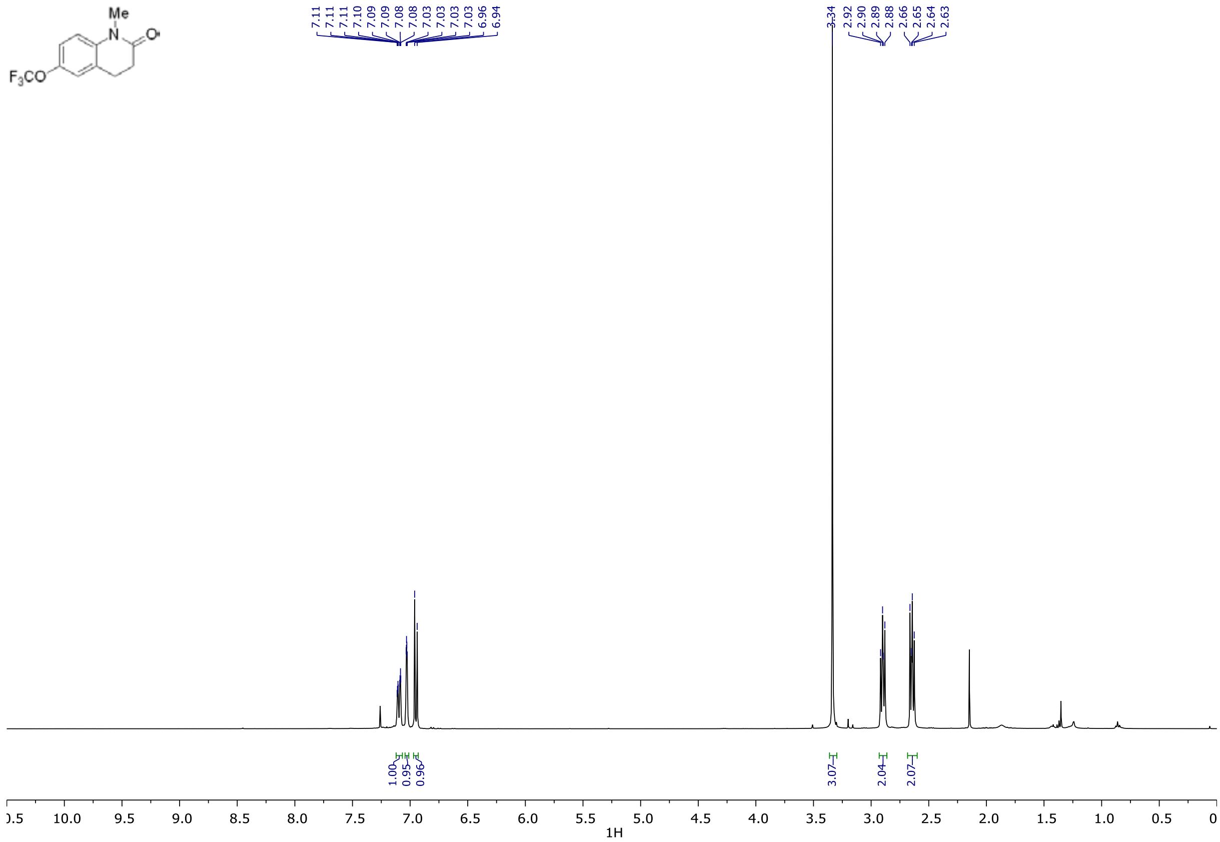
13C

3d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7.08
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6.96
6.94
3.34
2.92
2.90
2.89
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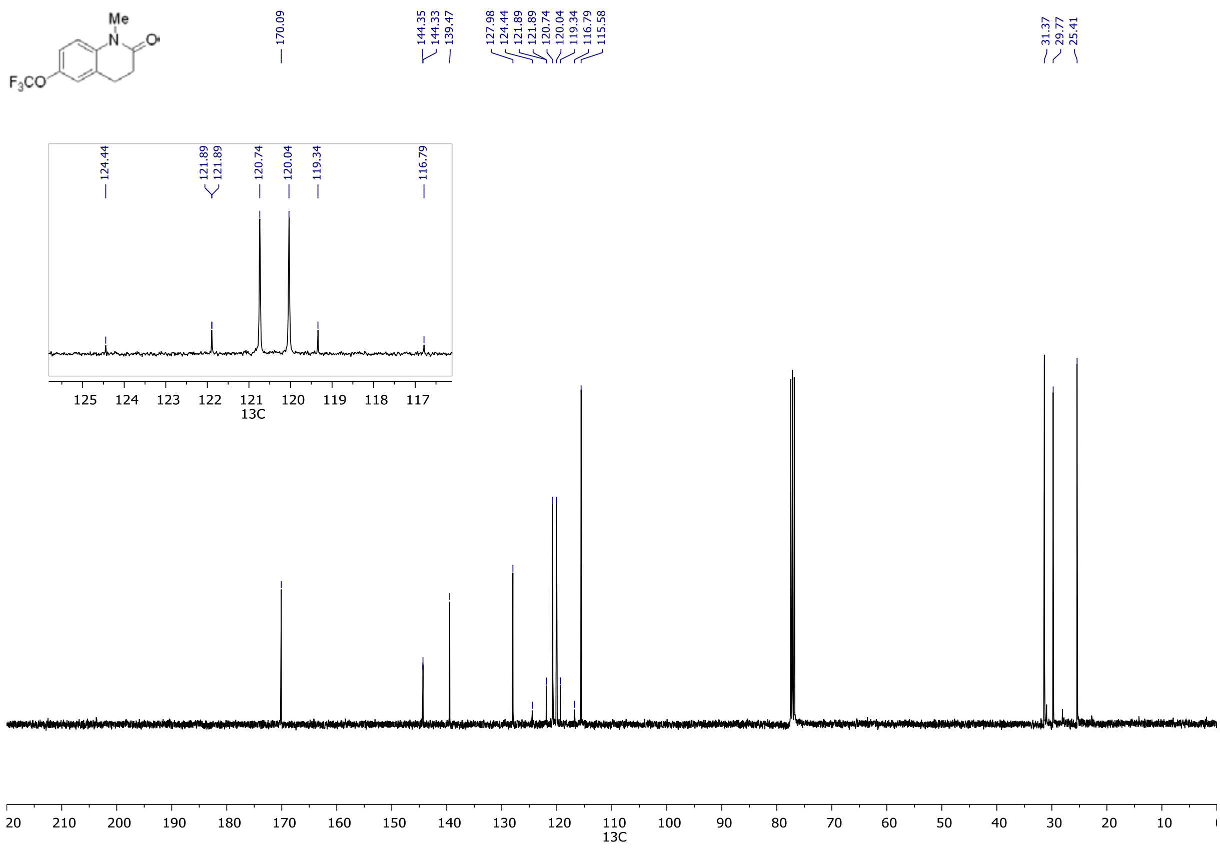
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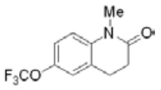

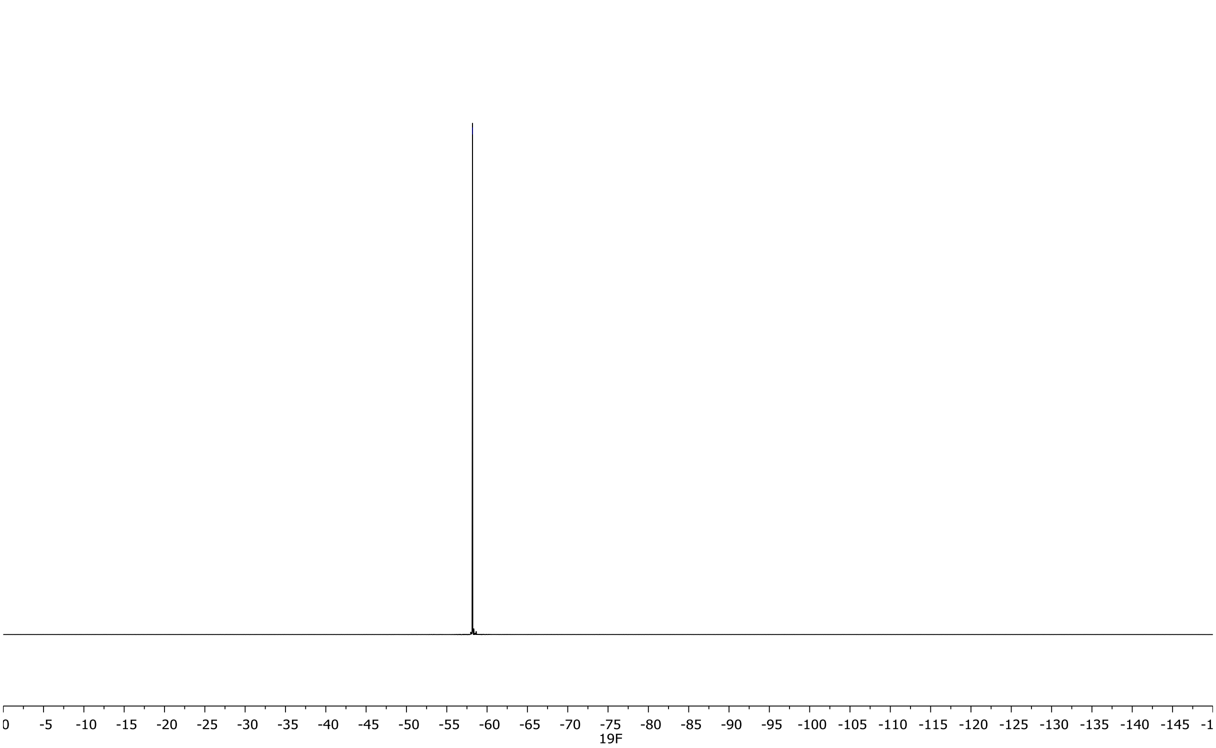
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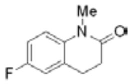
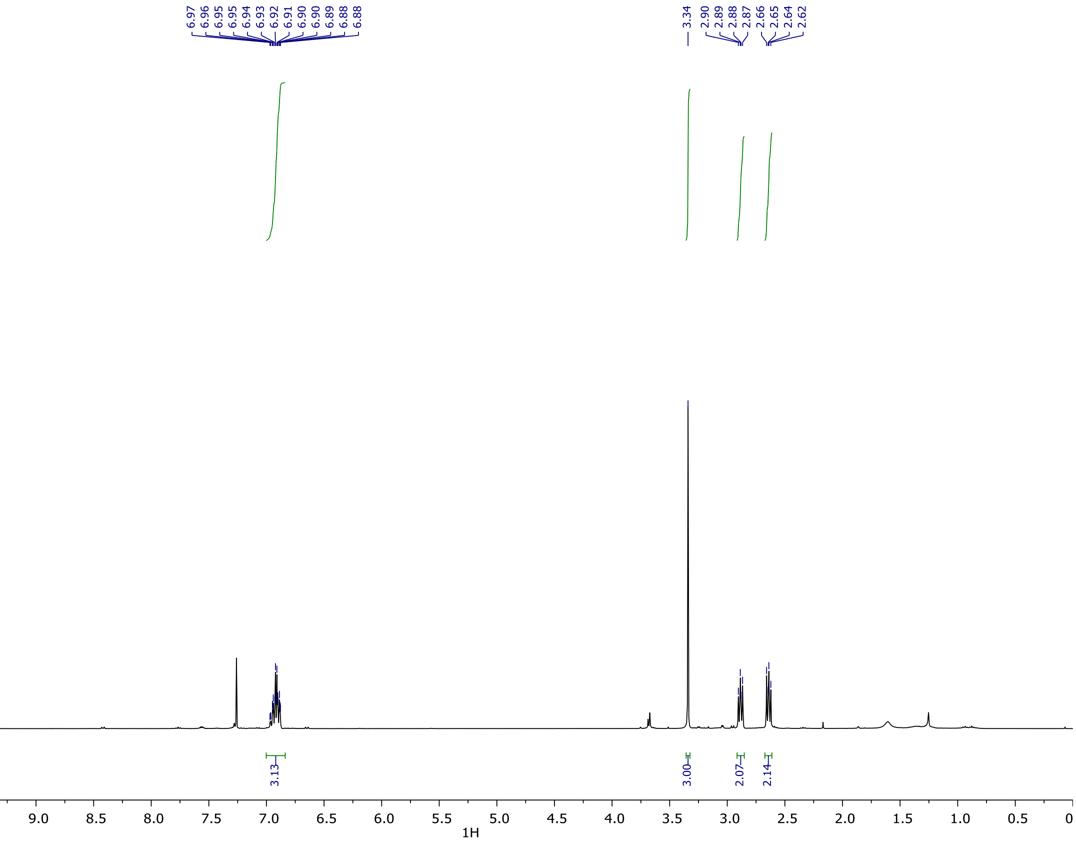
-130
-135
-140
-145
19F

3e


Me
N
O
F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2.07
2.14
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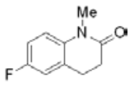
1H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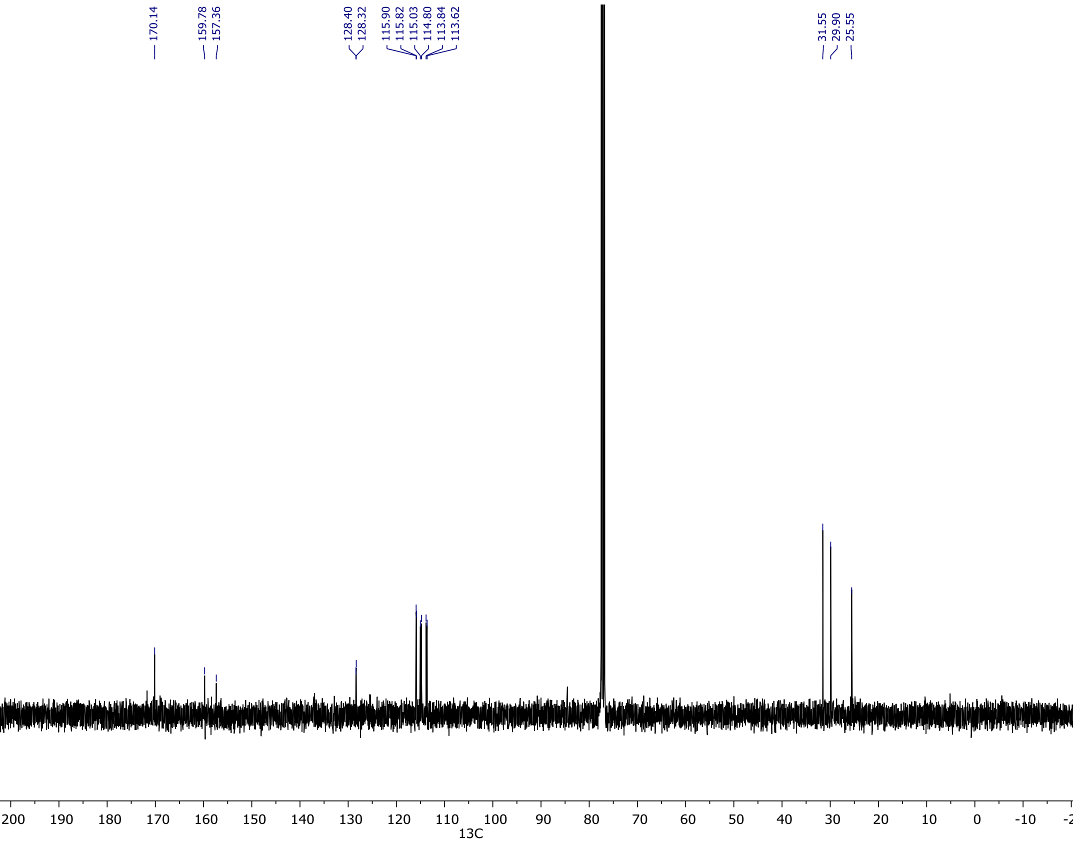
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200
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180
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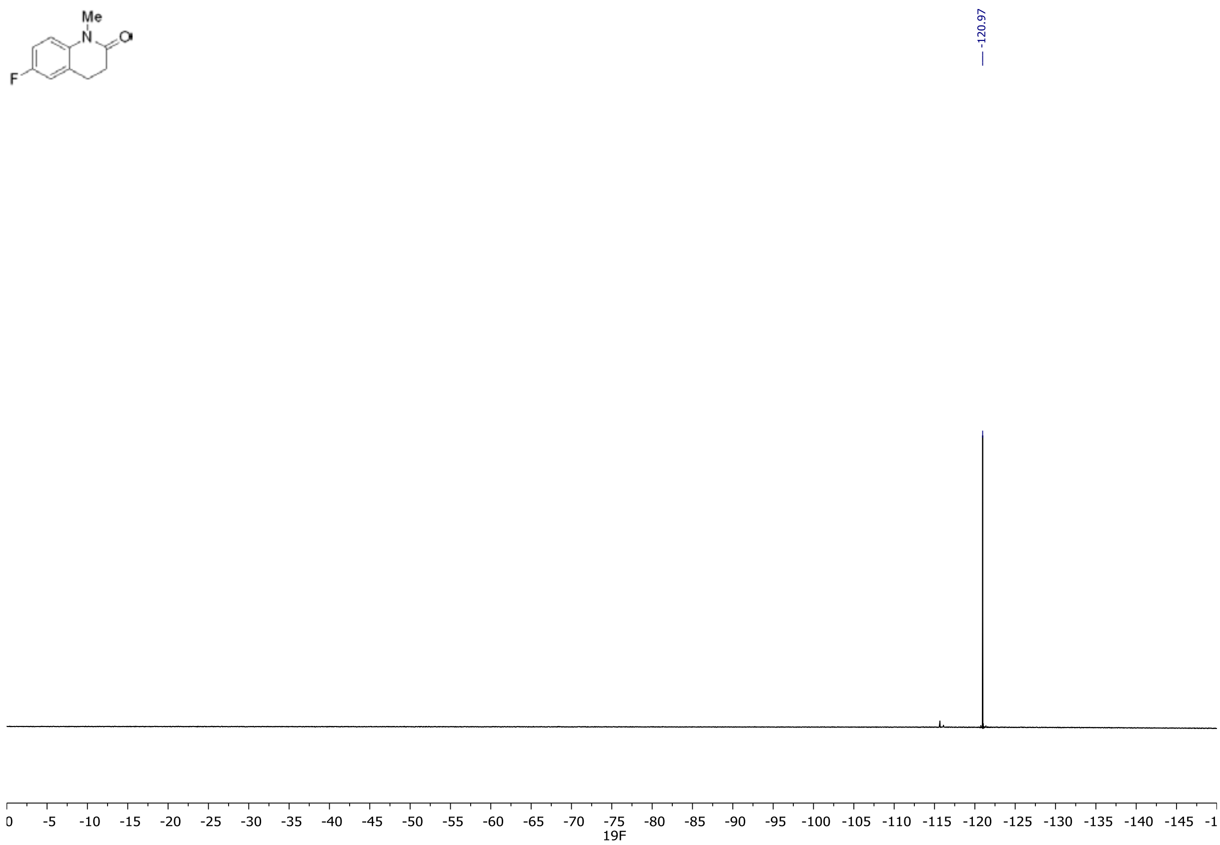
-10
13C



Me
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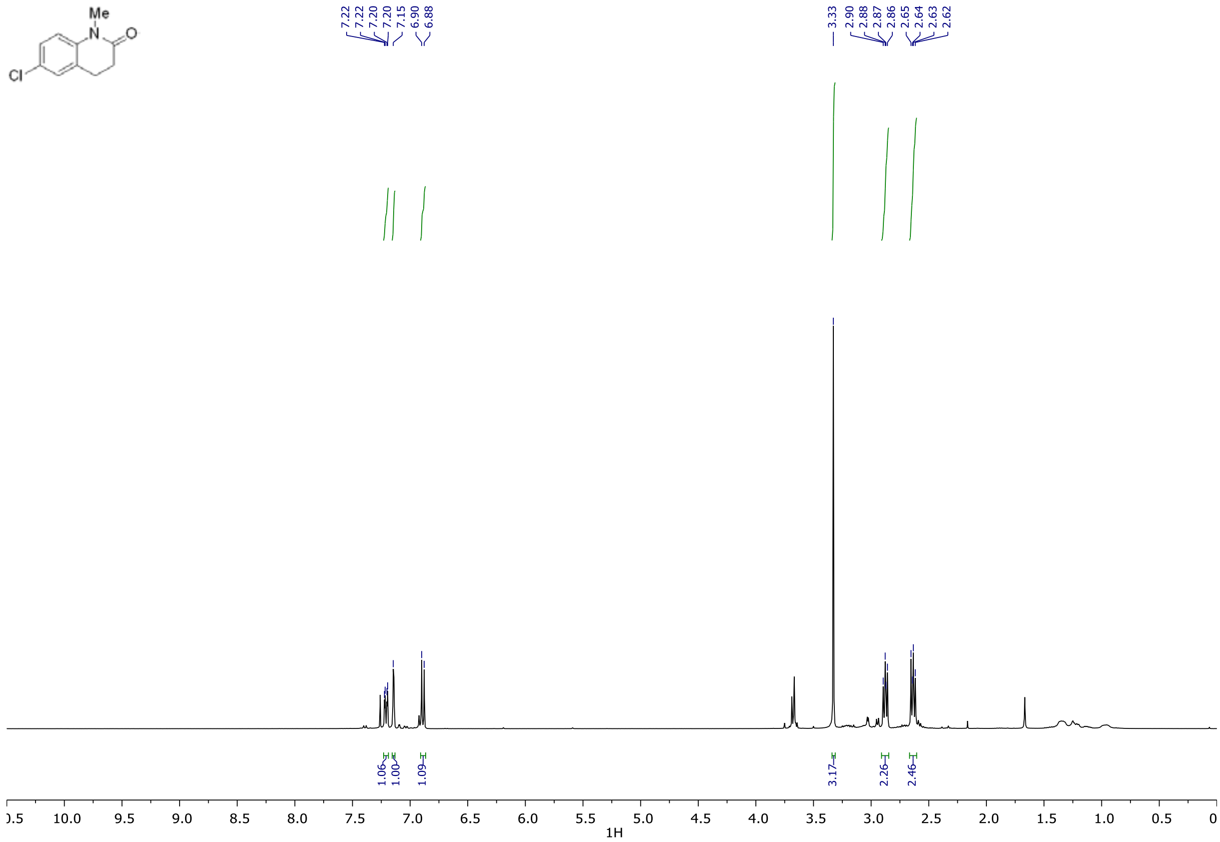
O
F
-120.97
0 -5 -10 -15 -20 -25 -30 -35 -40 -45 -50 -55 -60 -65 -70 -75 -80 -85 -90 -95 -100 -105 -110 -115 -120 -125 -130 -135 -140 -145 -1
19F

3f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7.20
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2.87
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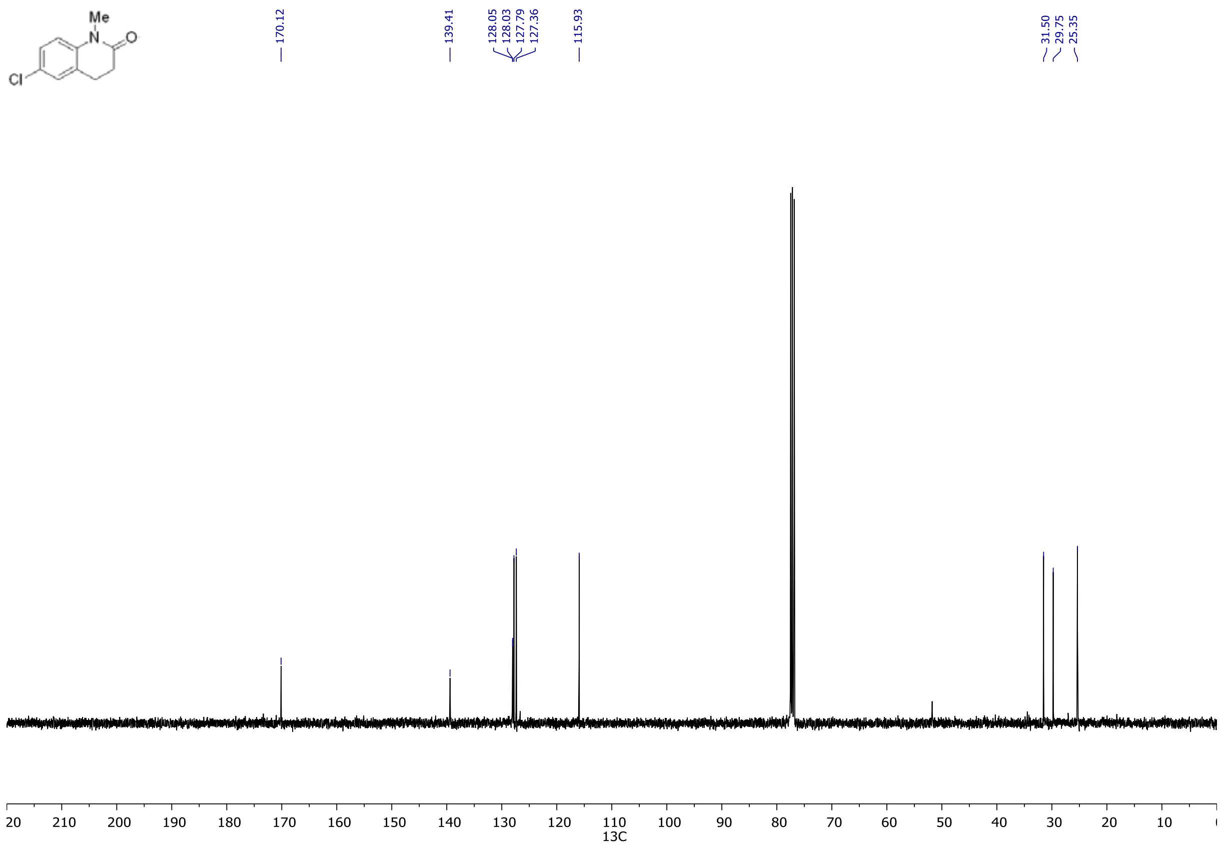
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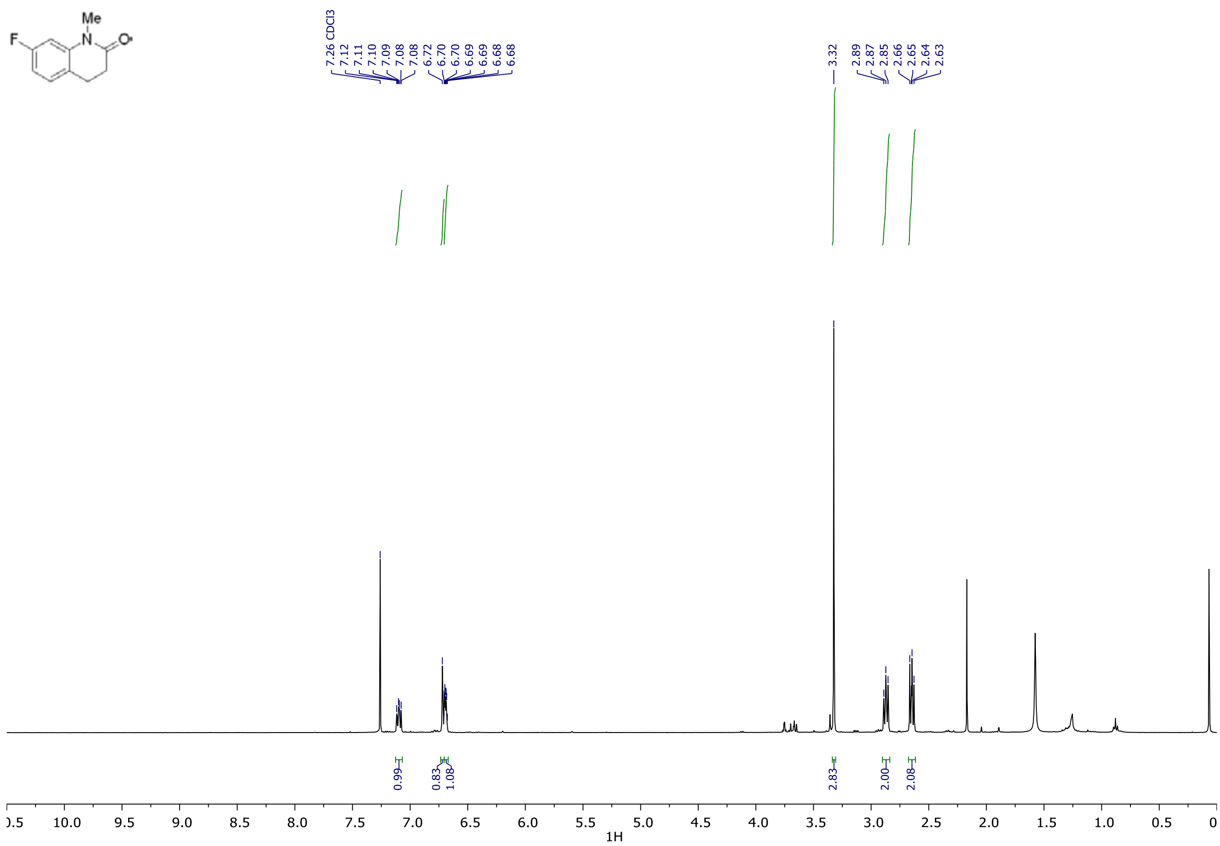
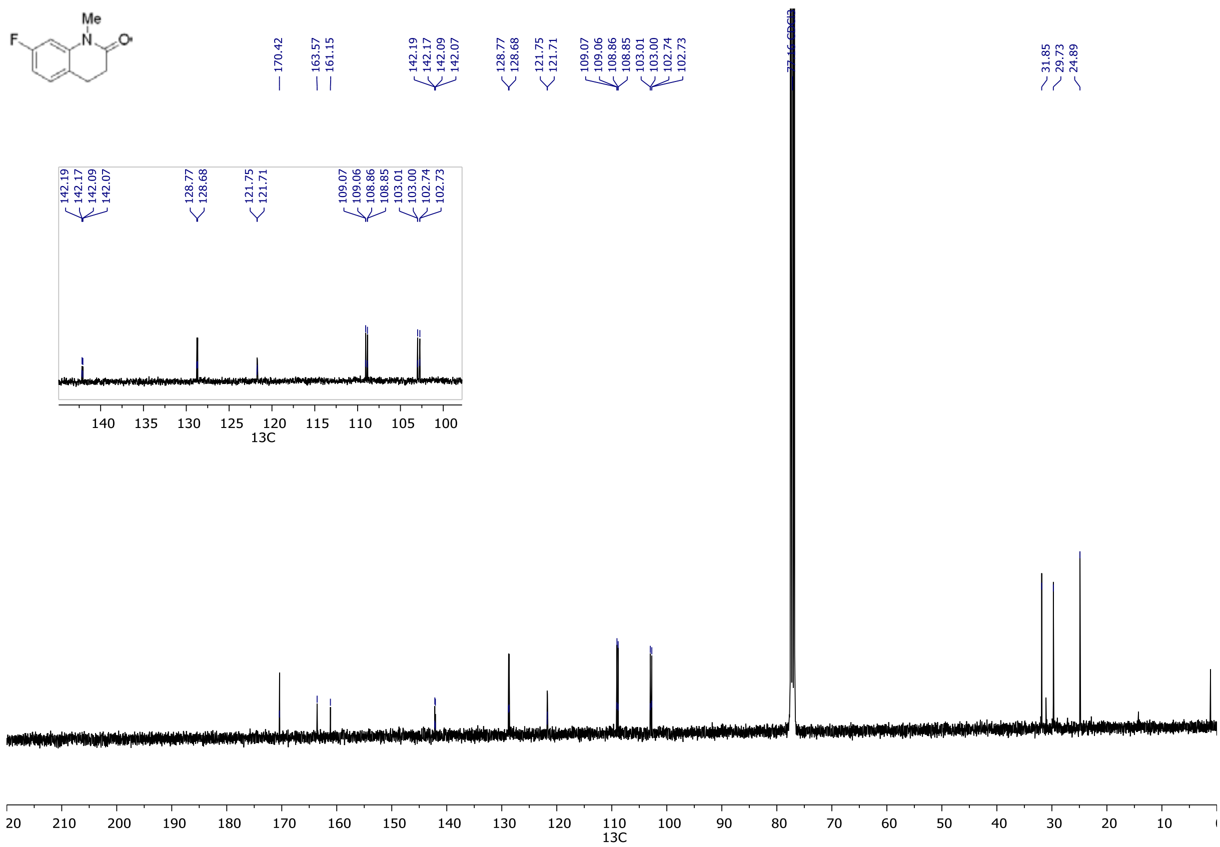
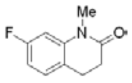
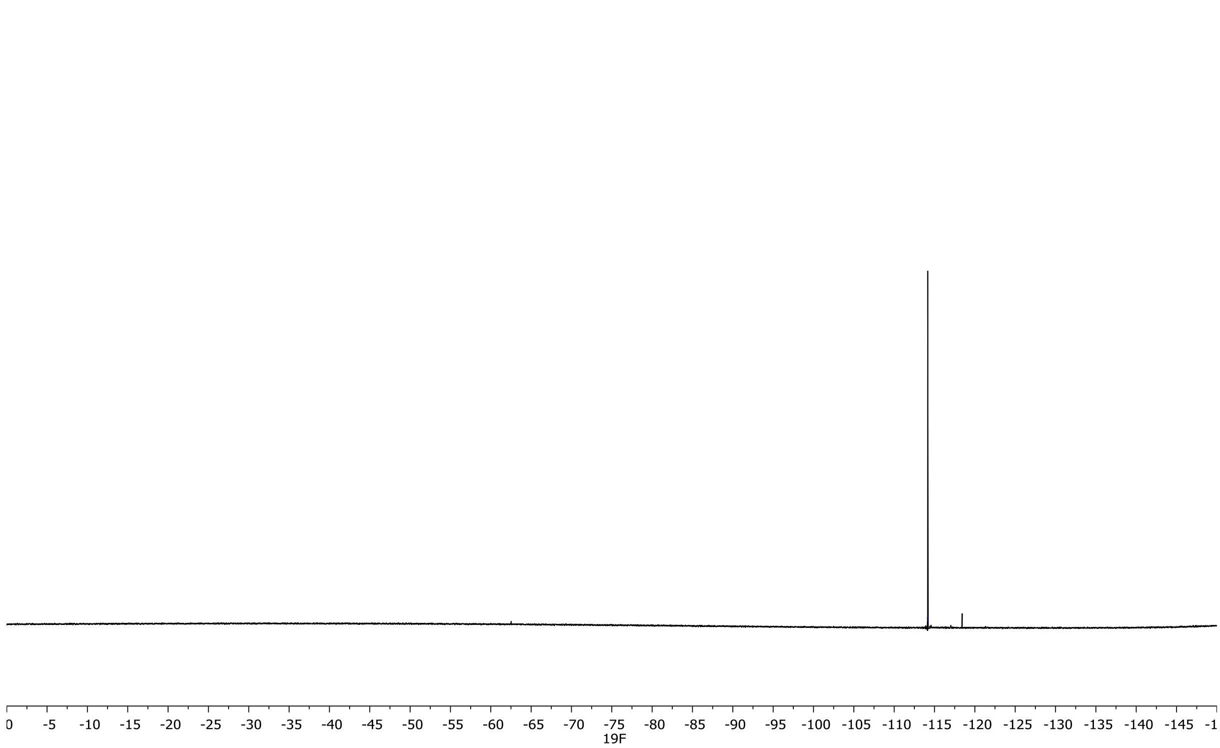
13C

3h





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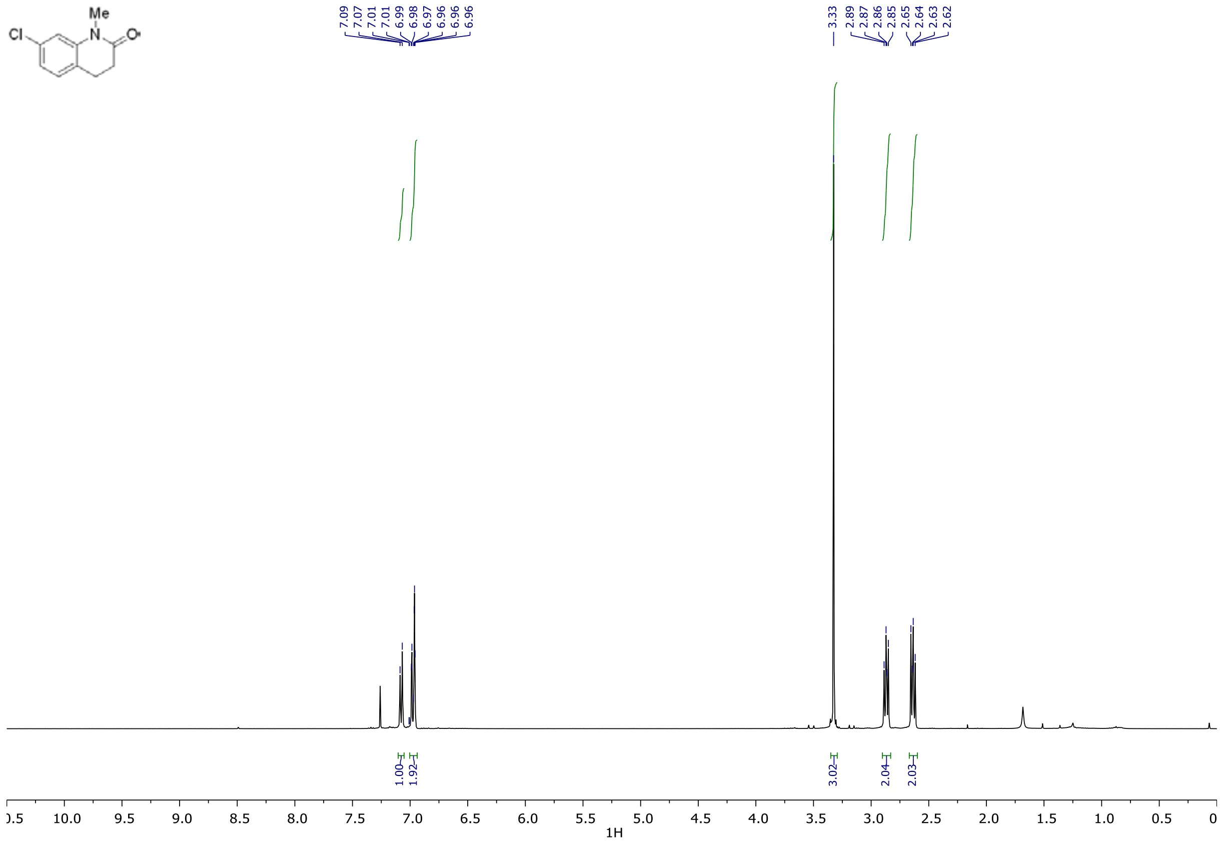
19F

3i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2.87
2.86
2.85
2.65
2.64
2.63
2.62
1.00
1.92
3.02
2.04
2.03
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
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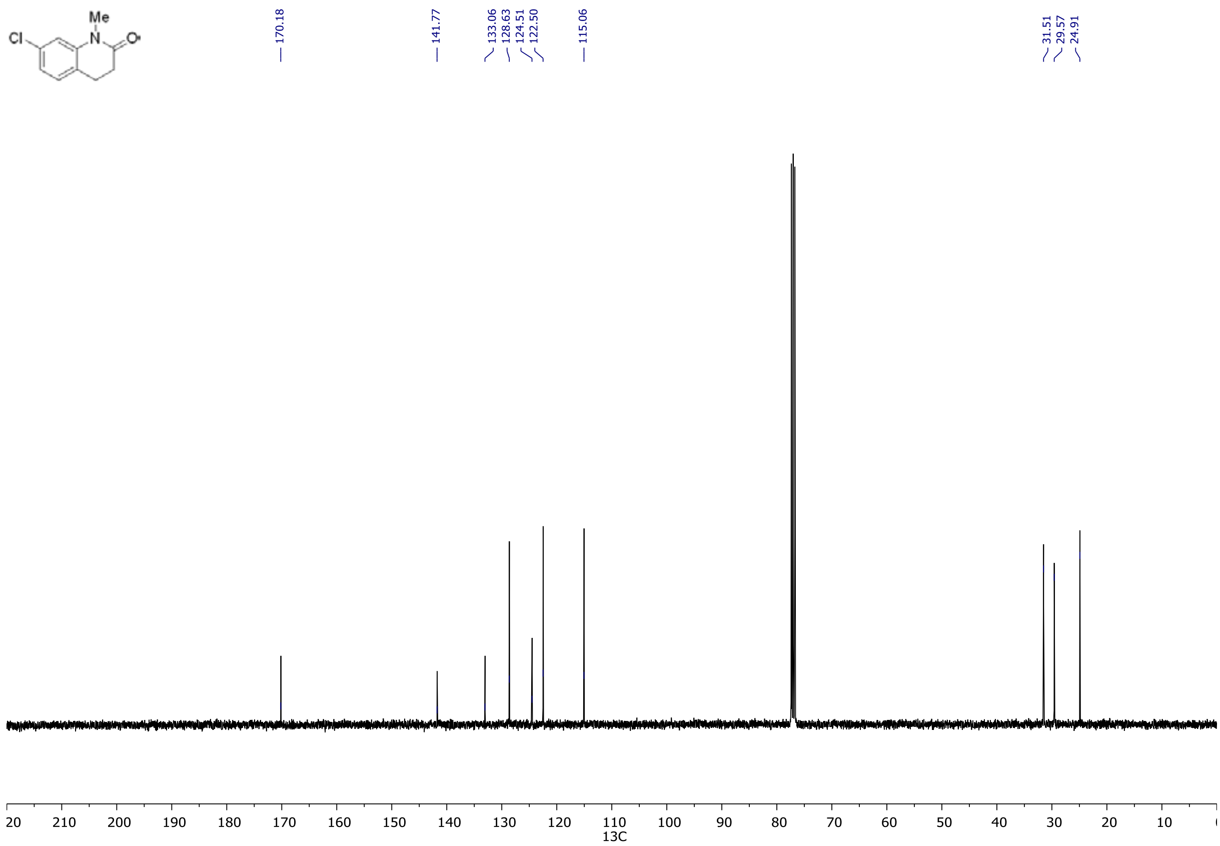
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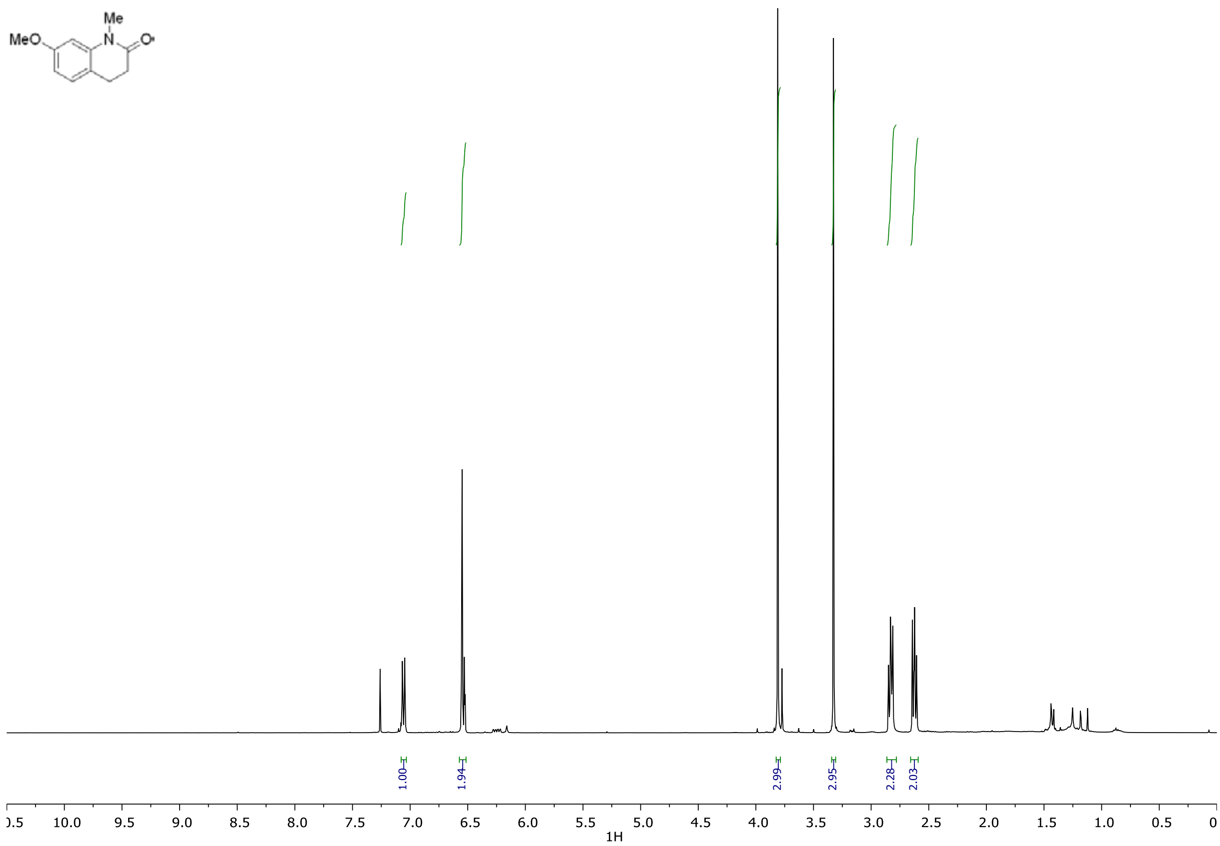
3j



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O
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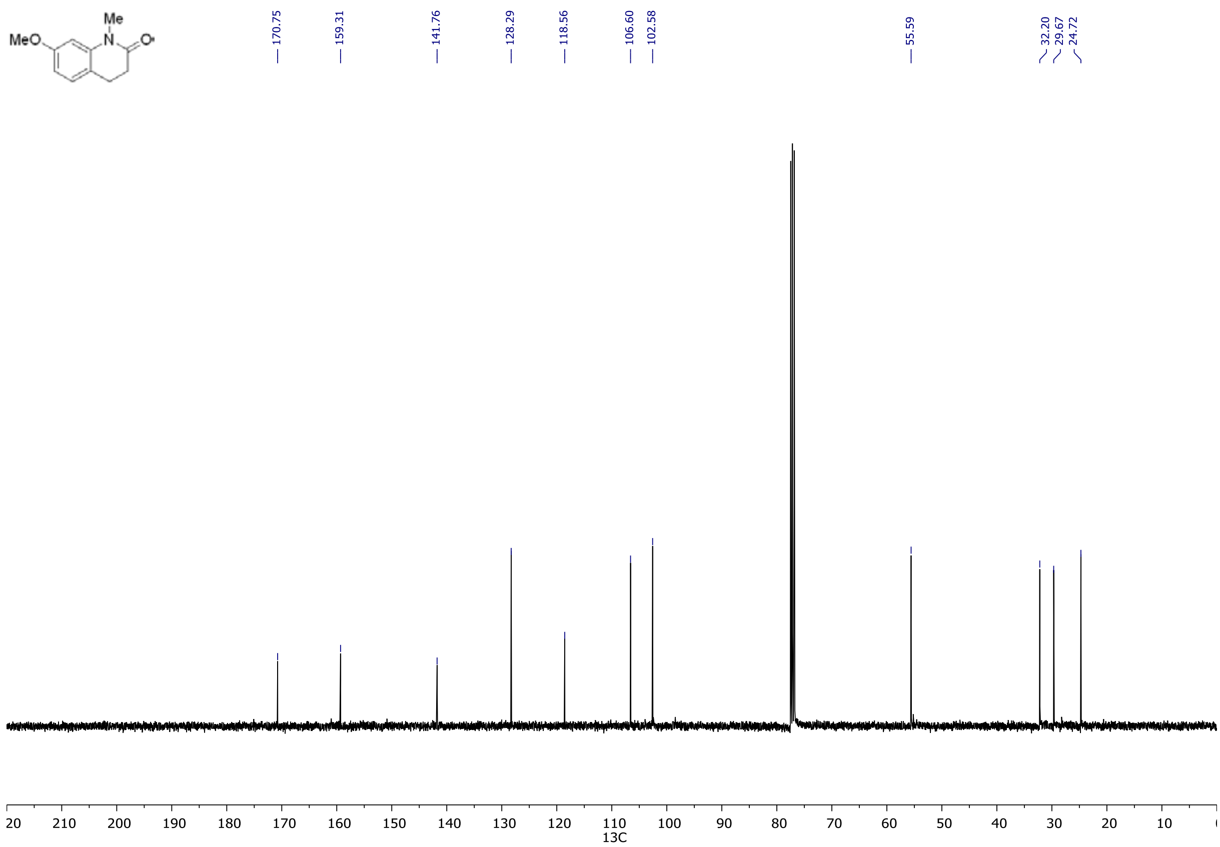

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13C

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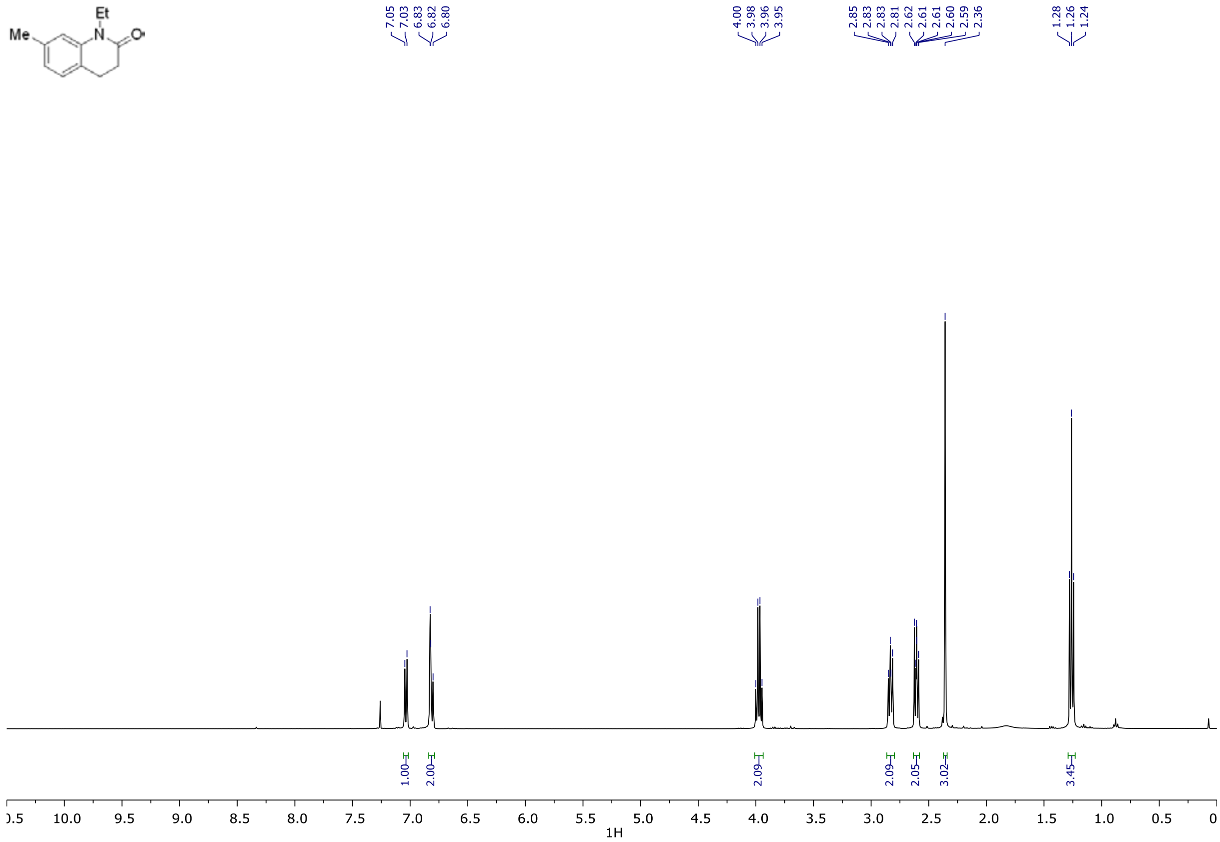
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1.28 1.26 1.24
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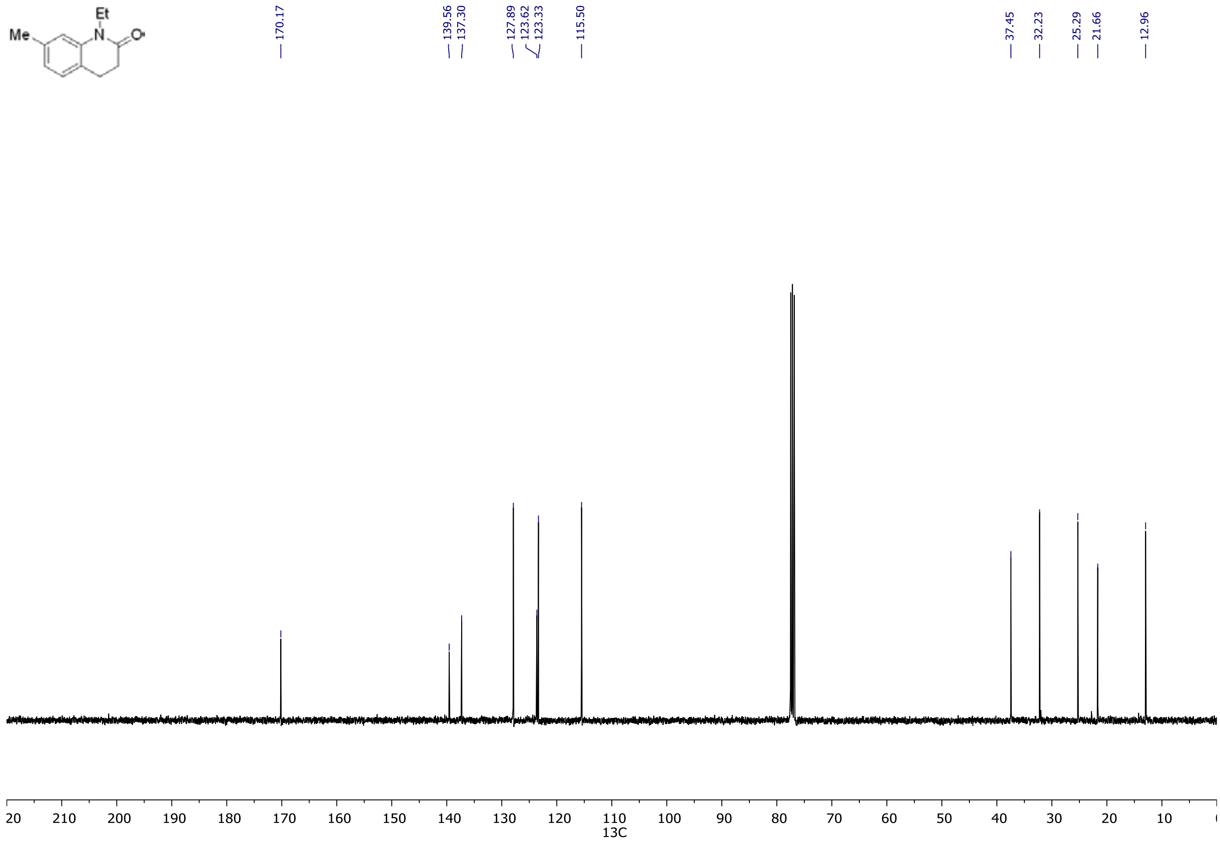
1H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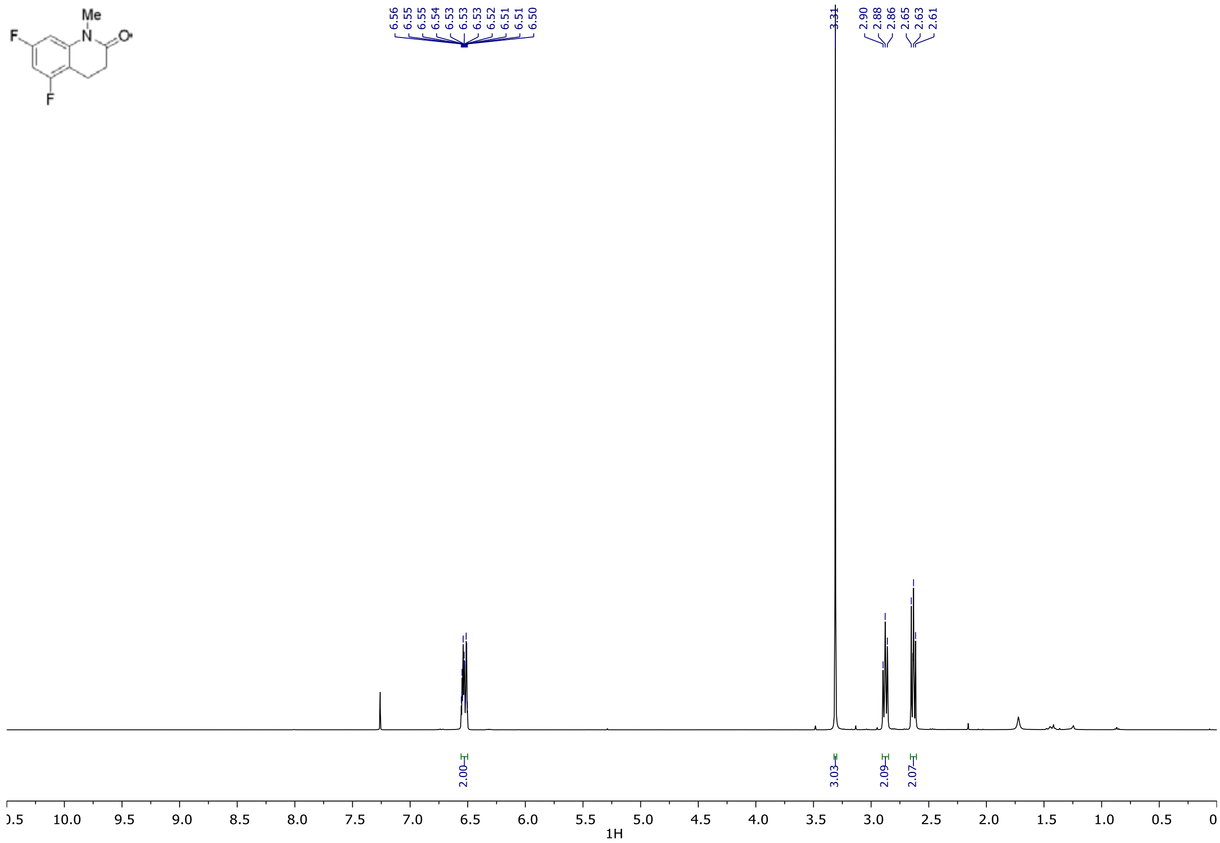
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6.51
6.50
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2.86
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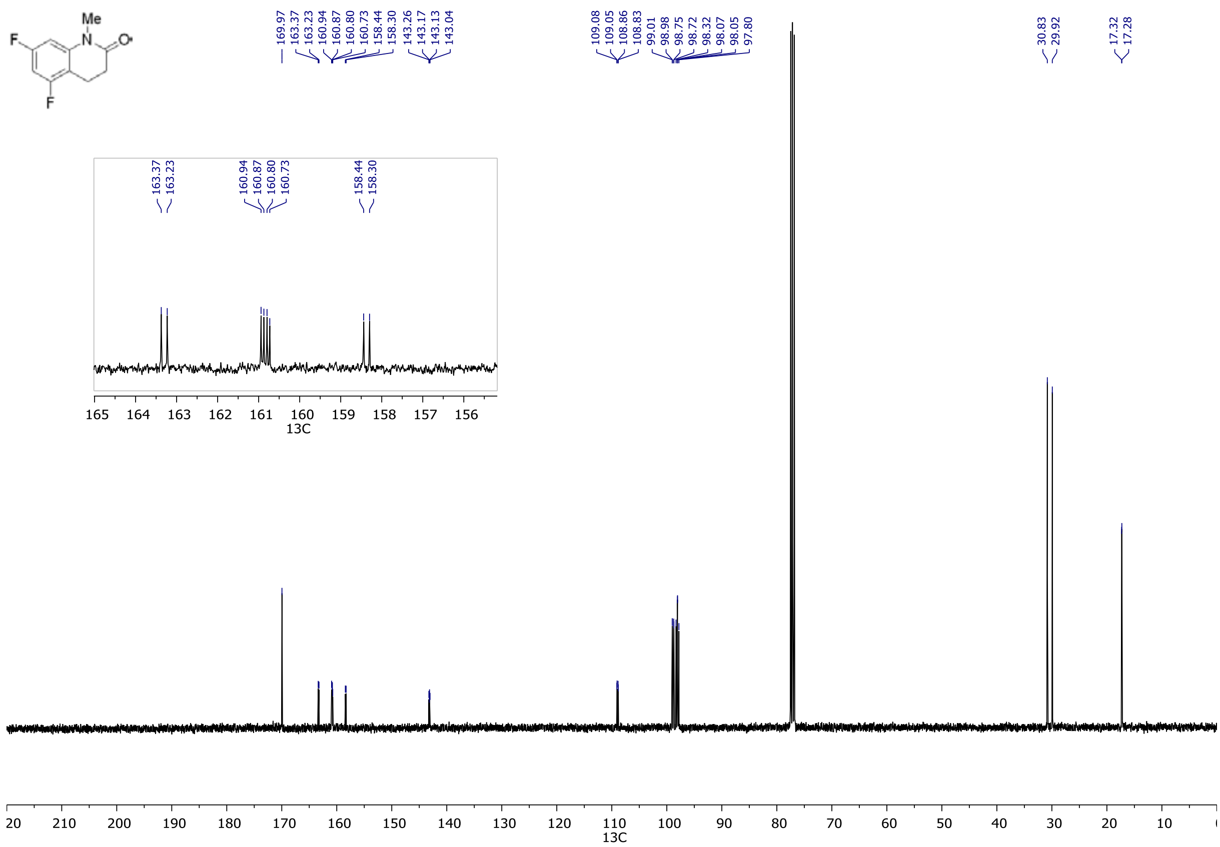
2.63
2.61
2.00
3.03
2.09
2.07
1H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143.17
143.13
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109.08
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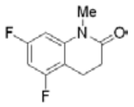
13C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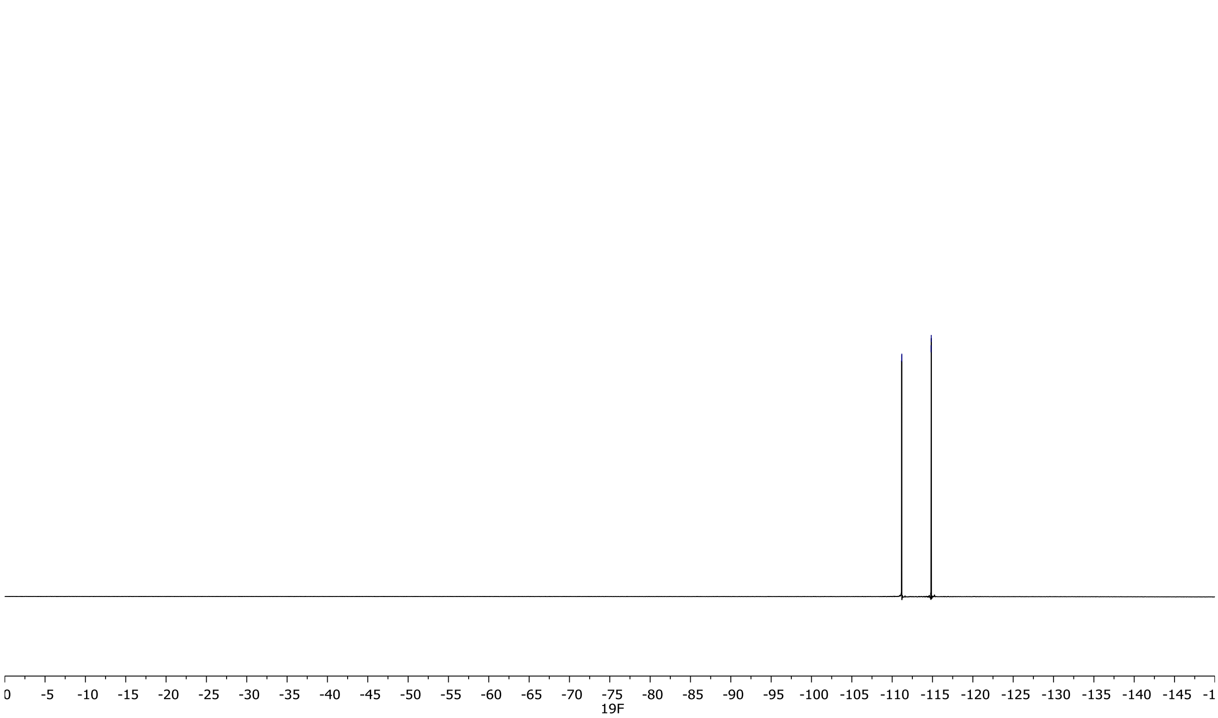
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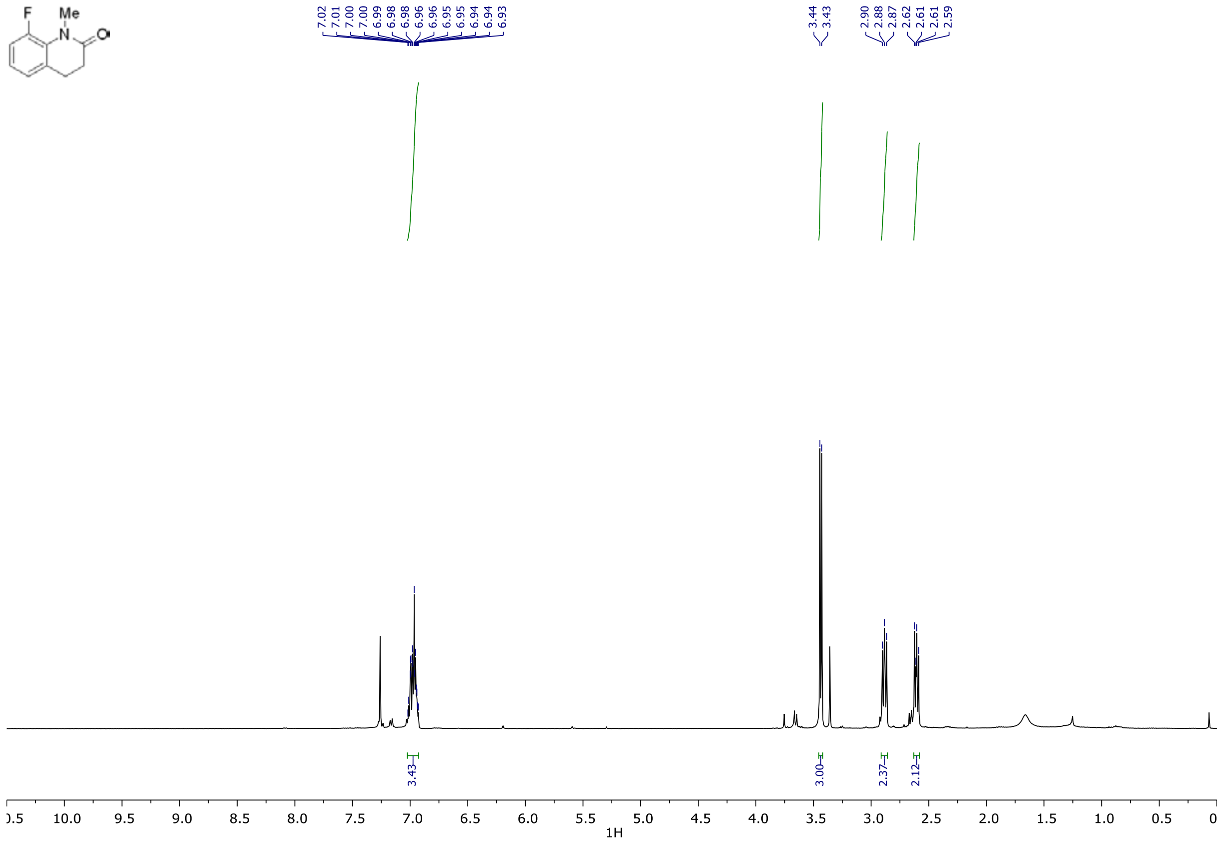
19F

3m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Me
N
O
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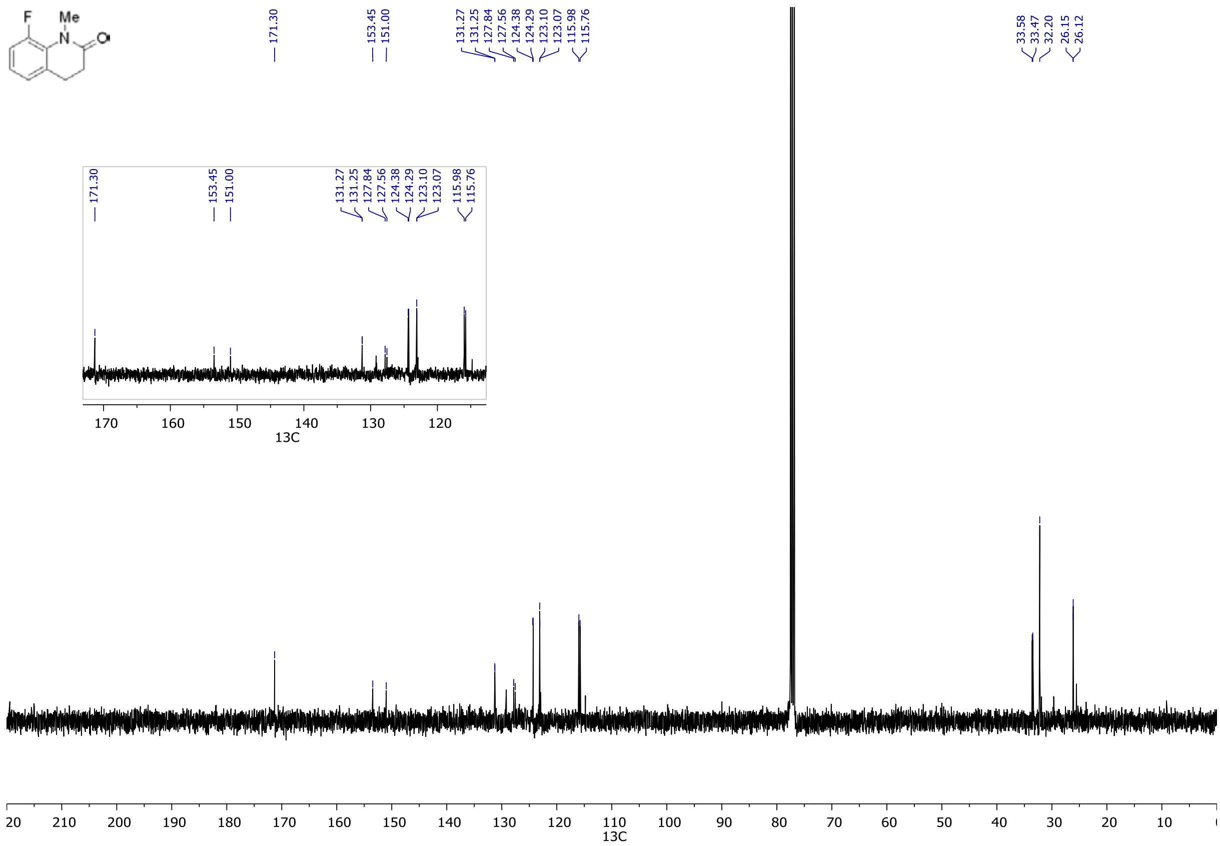
3.44 3.43
2.90 2.88 2.87 2.62 2.61 2.61 2.59
3.43
3.00
2.37
2.12
0.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
1H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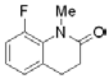
13C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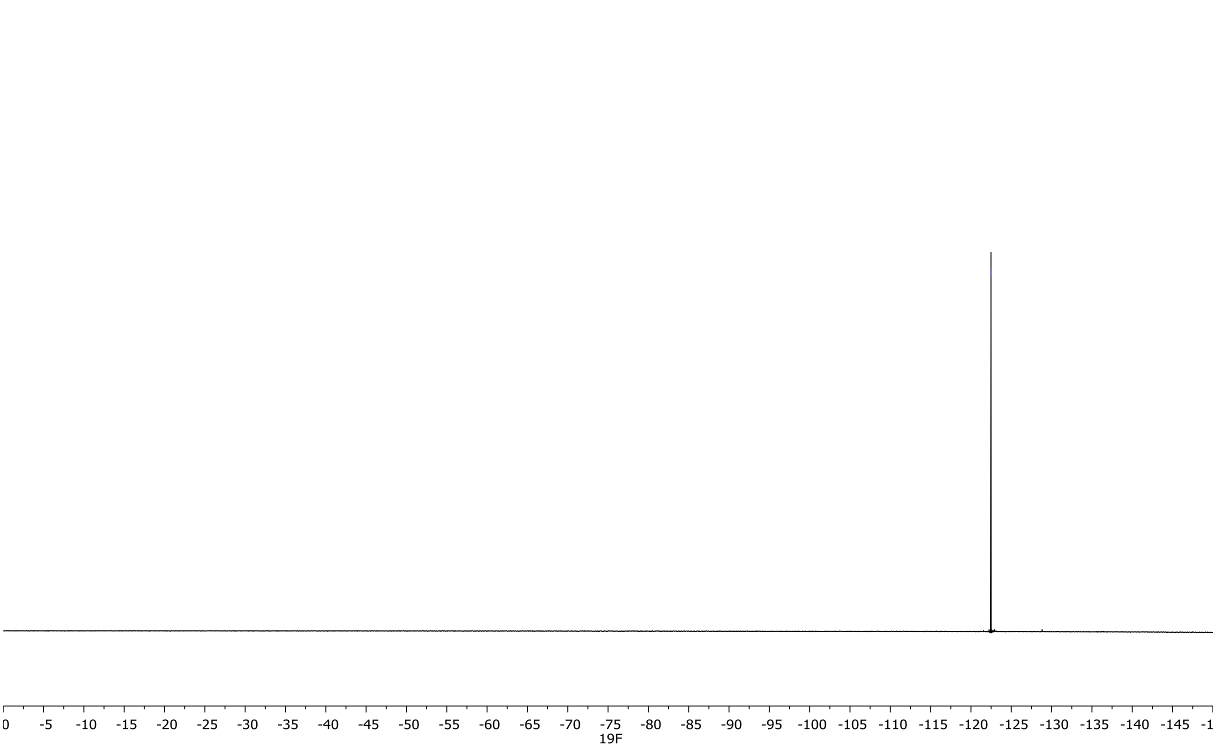
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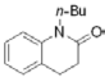
3n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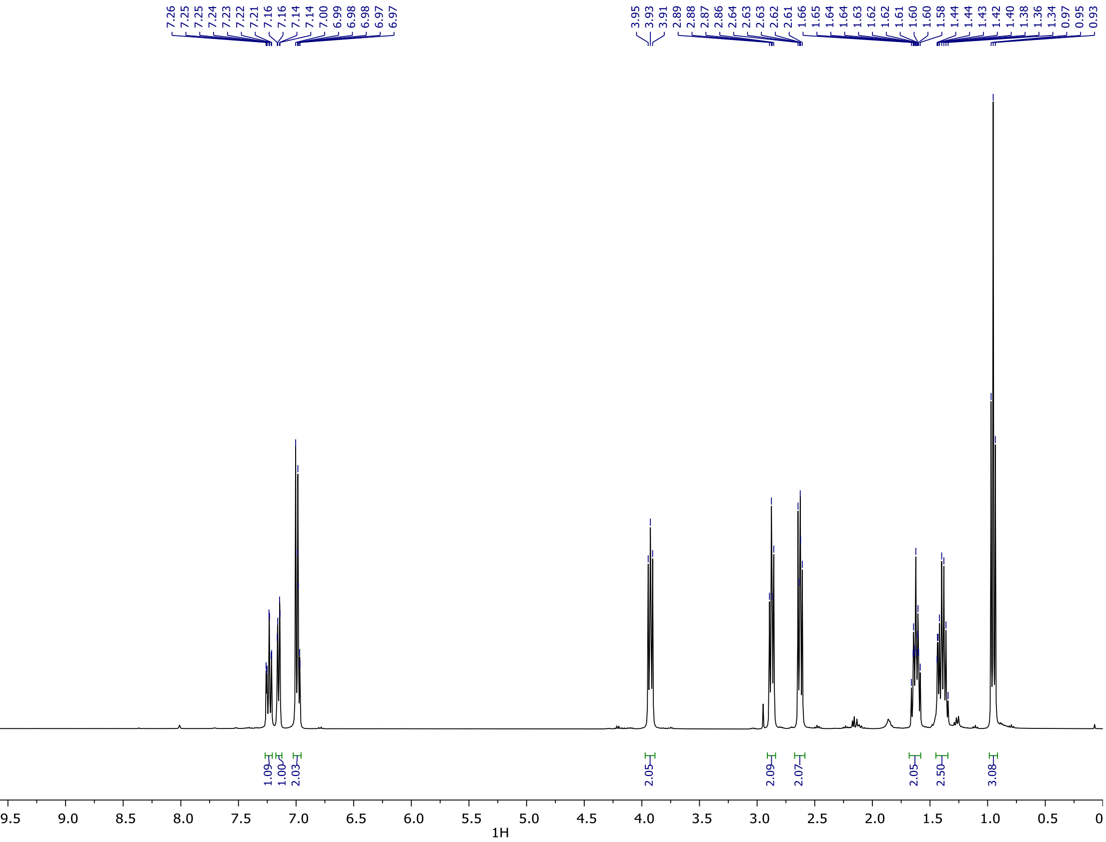
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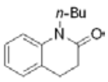
1.09 1.00 2.03 2.05 2.09 2.07 2.05 2.50 3.08
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
1H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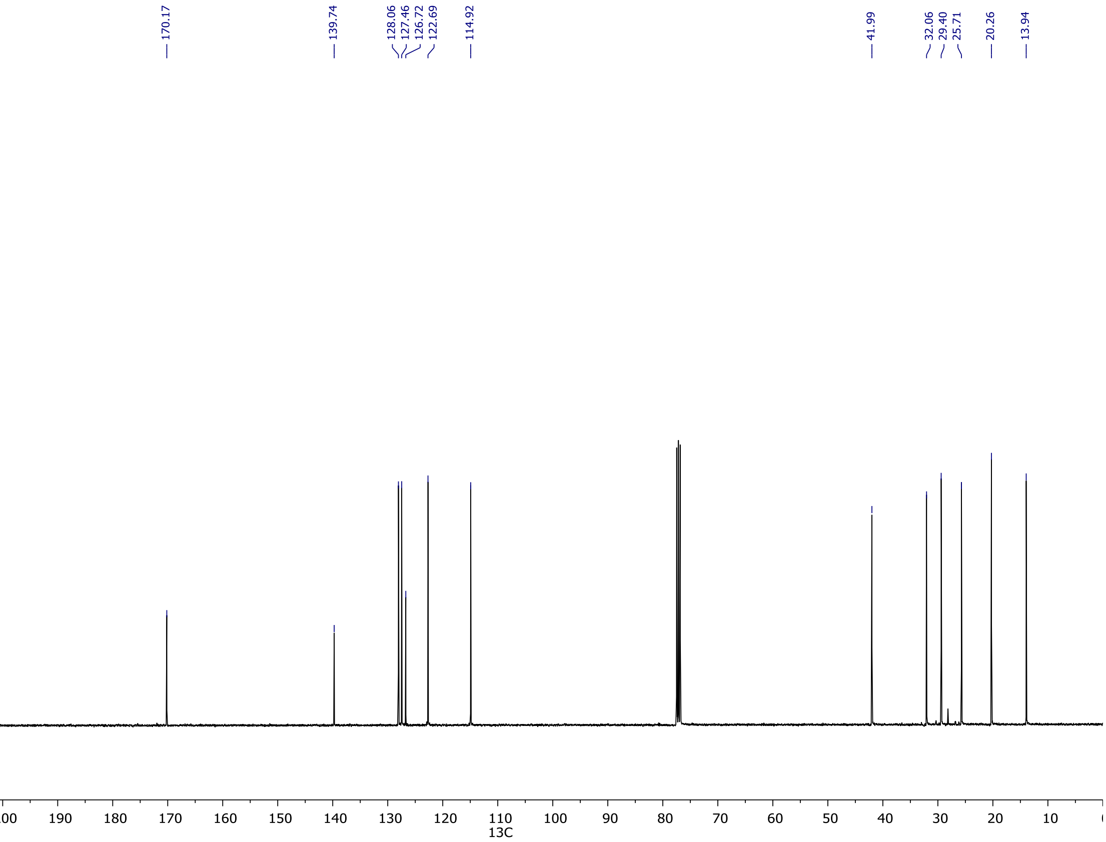
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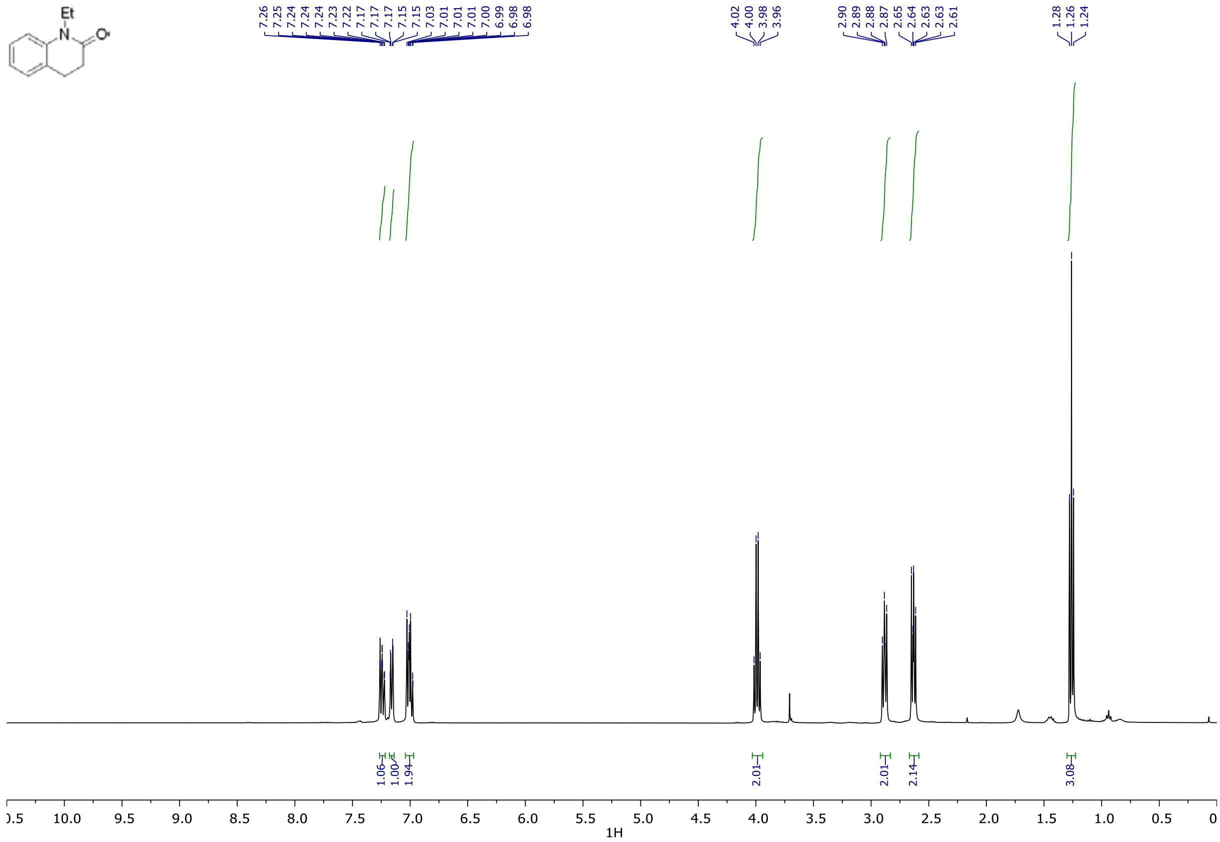
3o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O
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4.02 4.00 3.98 3.96
2.90 2.89 2.88 2.87 2.65 2.64 2.63 2.63 2.61
1.28 1.26 1.24
1.06 1.00 1.94 2.01 2.01 2.14 3.08
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
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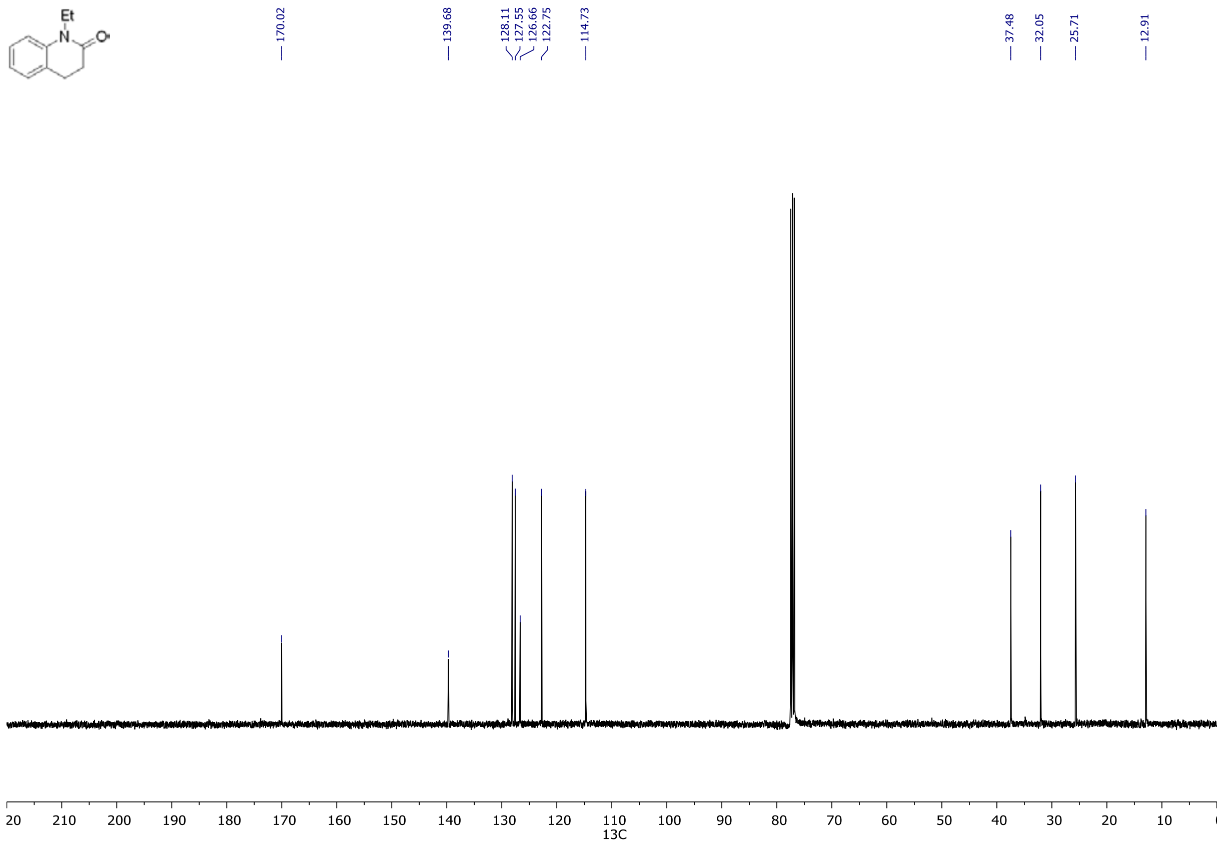
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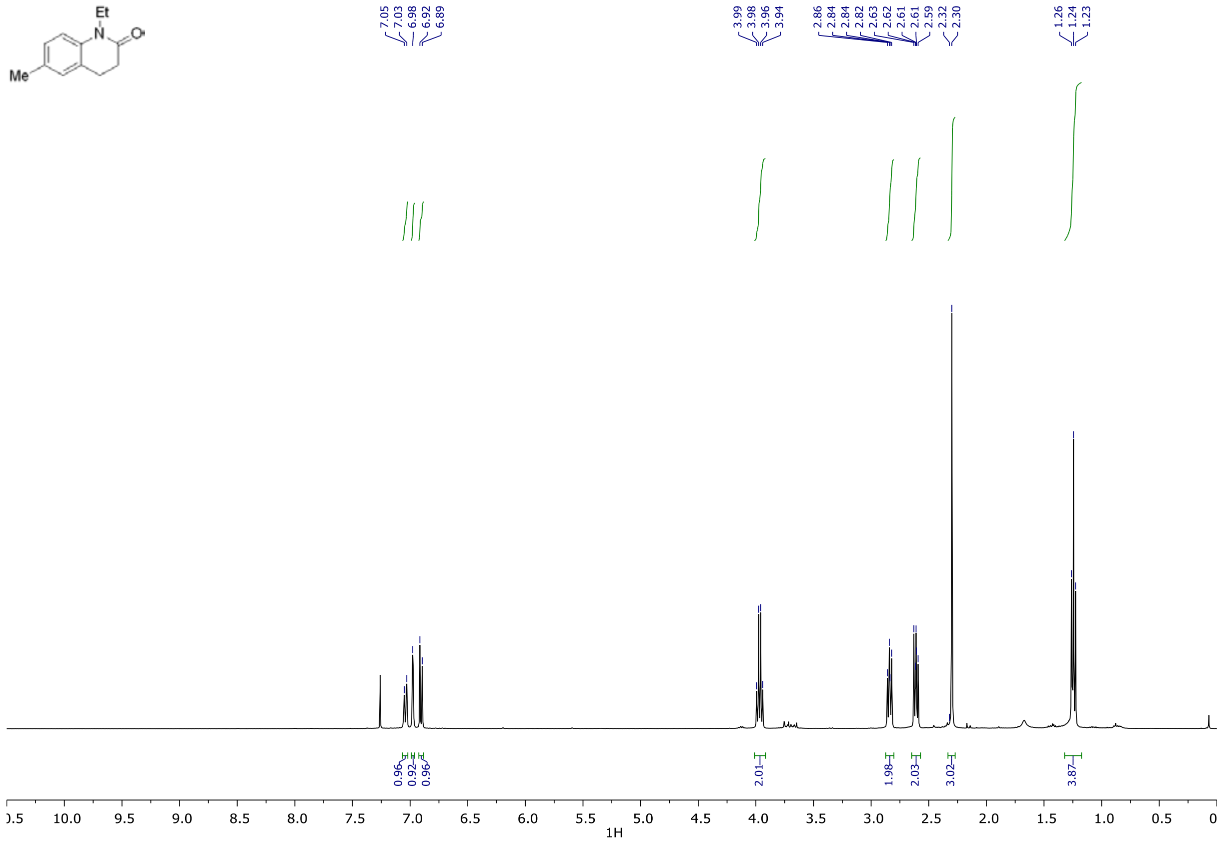
3p



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2.61
2.61
2.59
2.32
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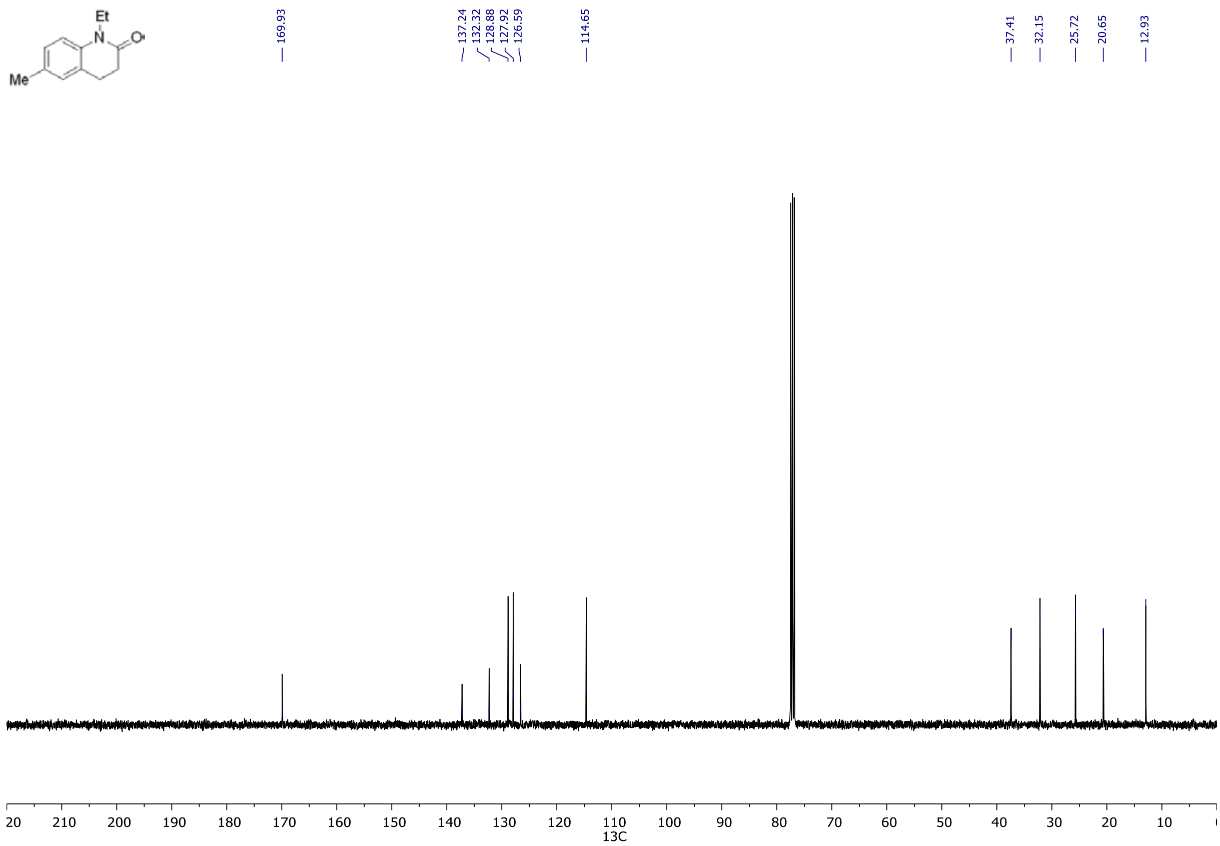

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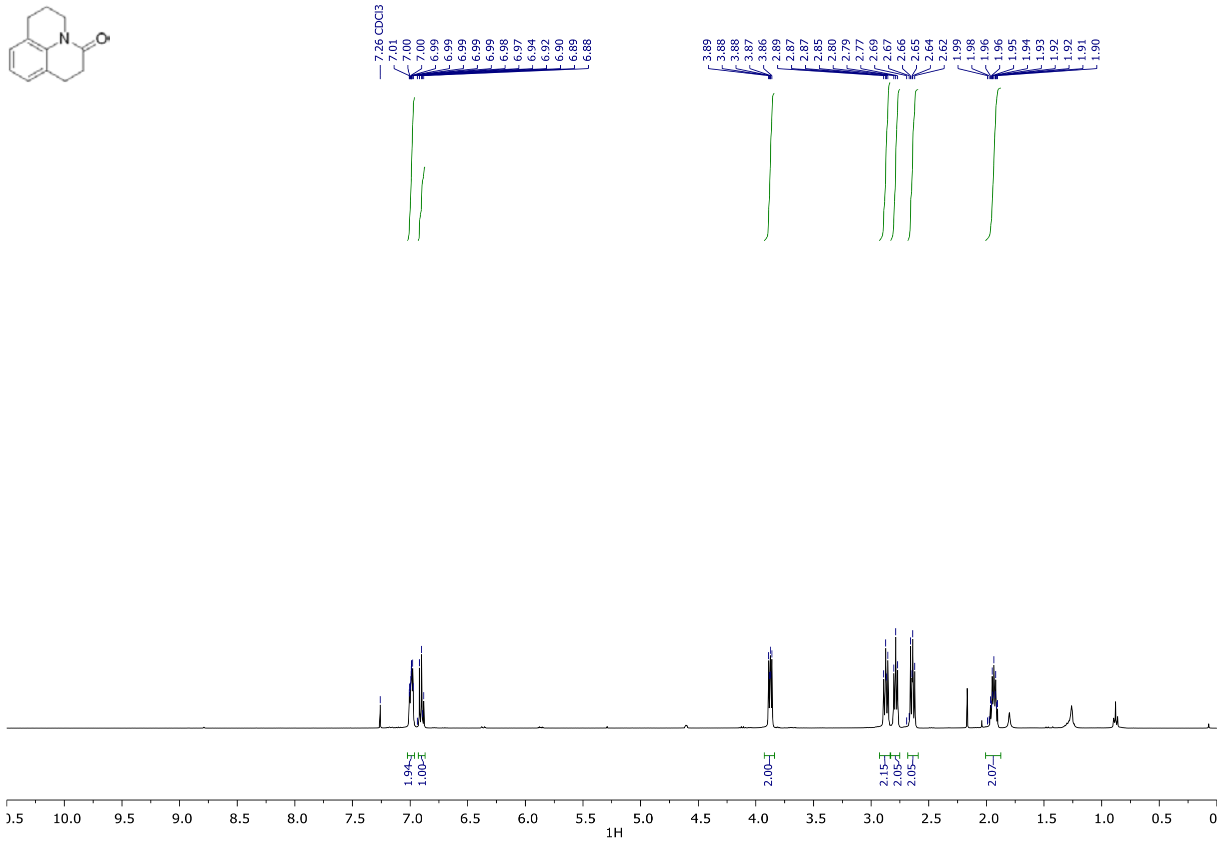
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2.62
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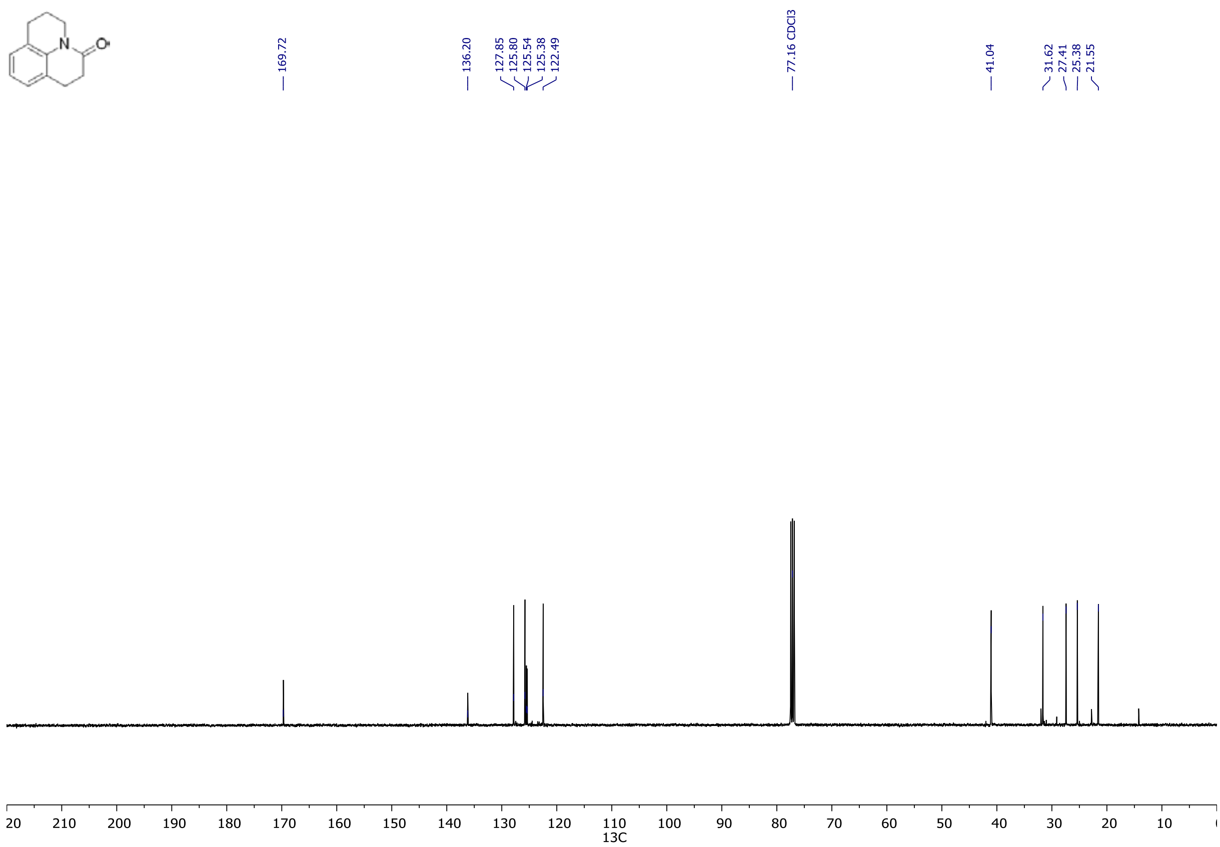
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21.55
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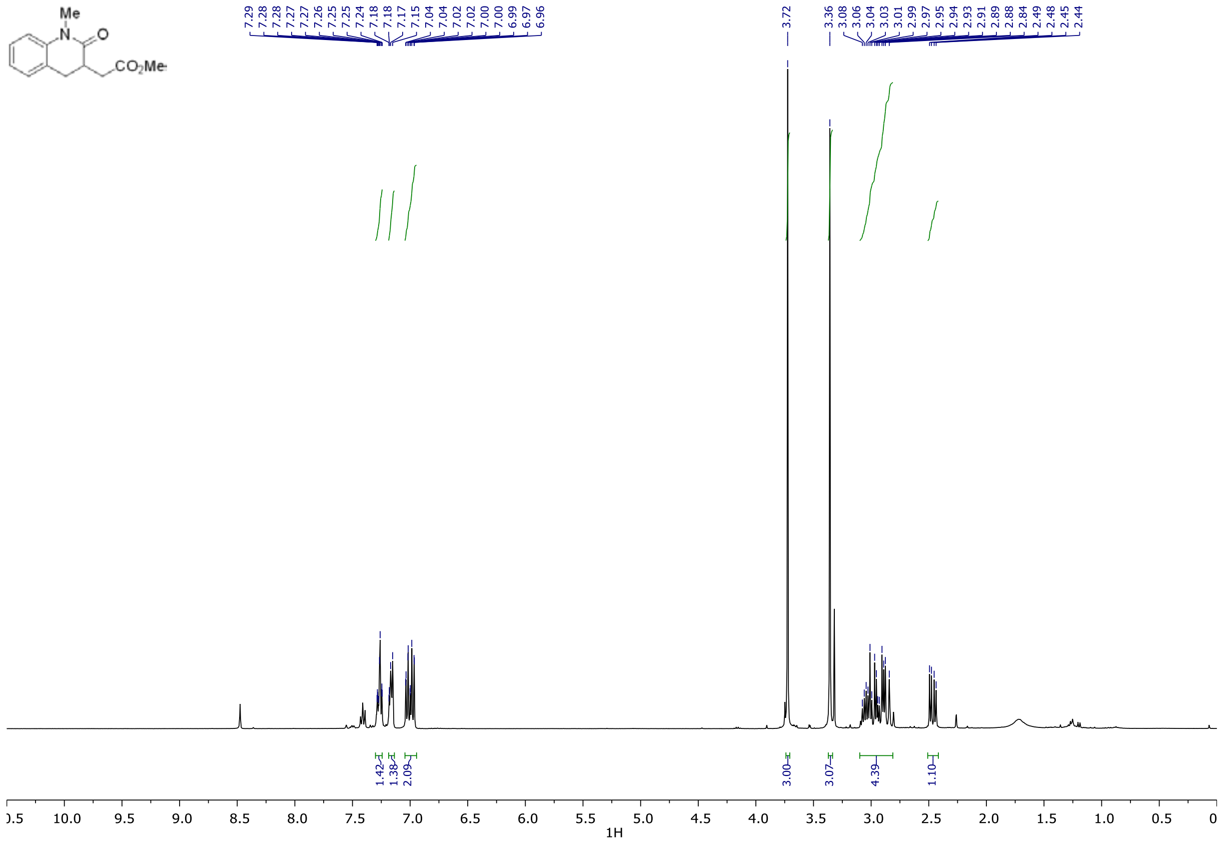
3r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3.72
3.36 3.08 3.06 3.04 3.04 3.03 3.01 2.99 2.97 2.95 2.94 2.93 2.91 2.89 2.88 2.84 2.49 2.48 2.45 2.44
1.42 1.38 2.09 3.00 3.07 4.39 1.10
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0
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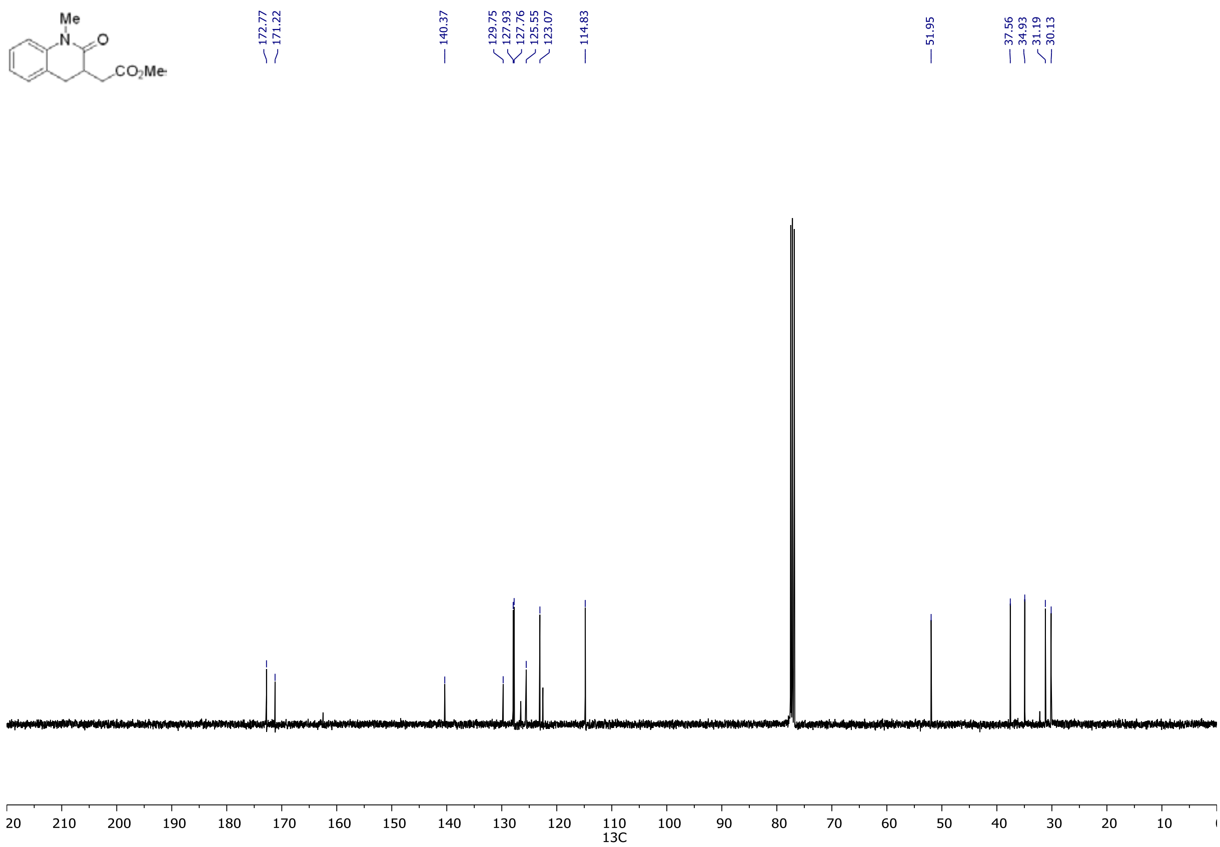
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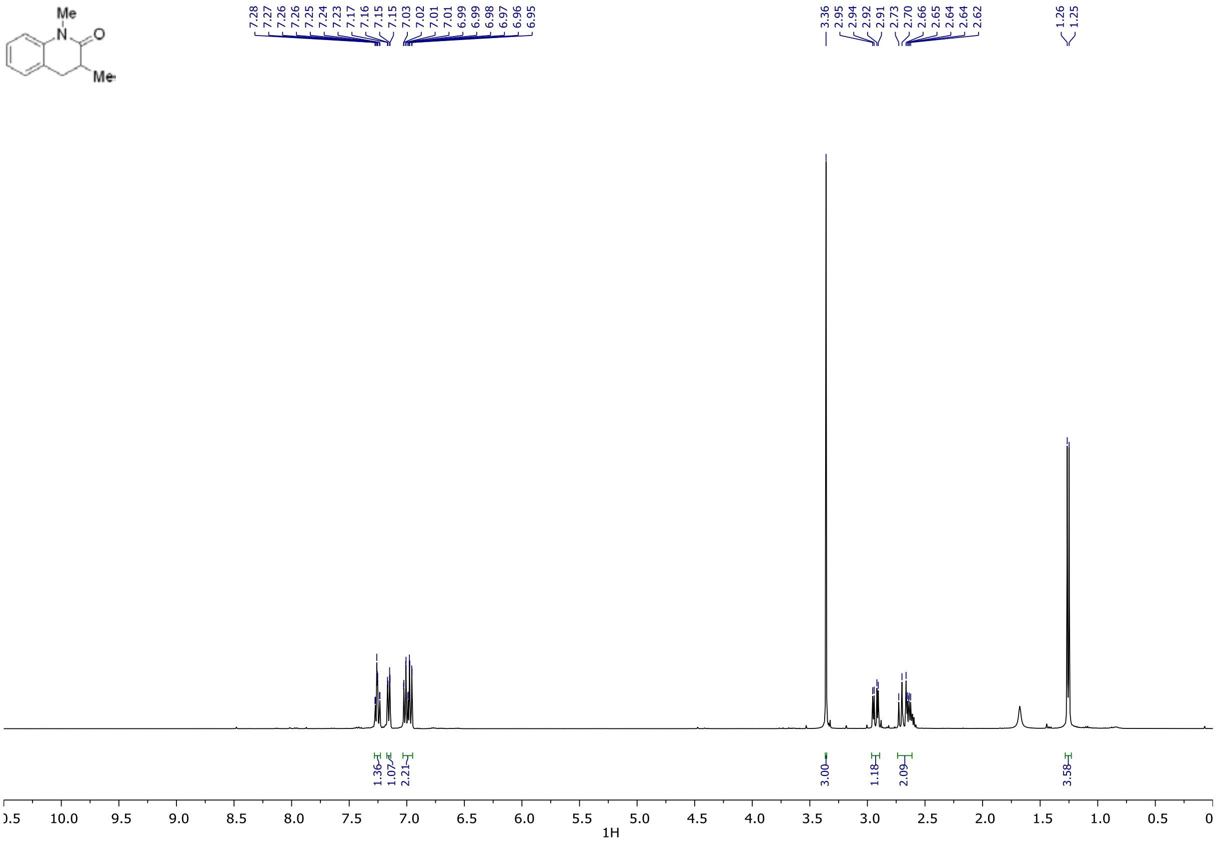
13C

3s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7.17
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7.15
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7.02
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7.01
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6.95
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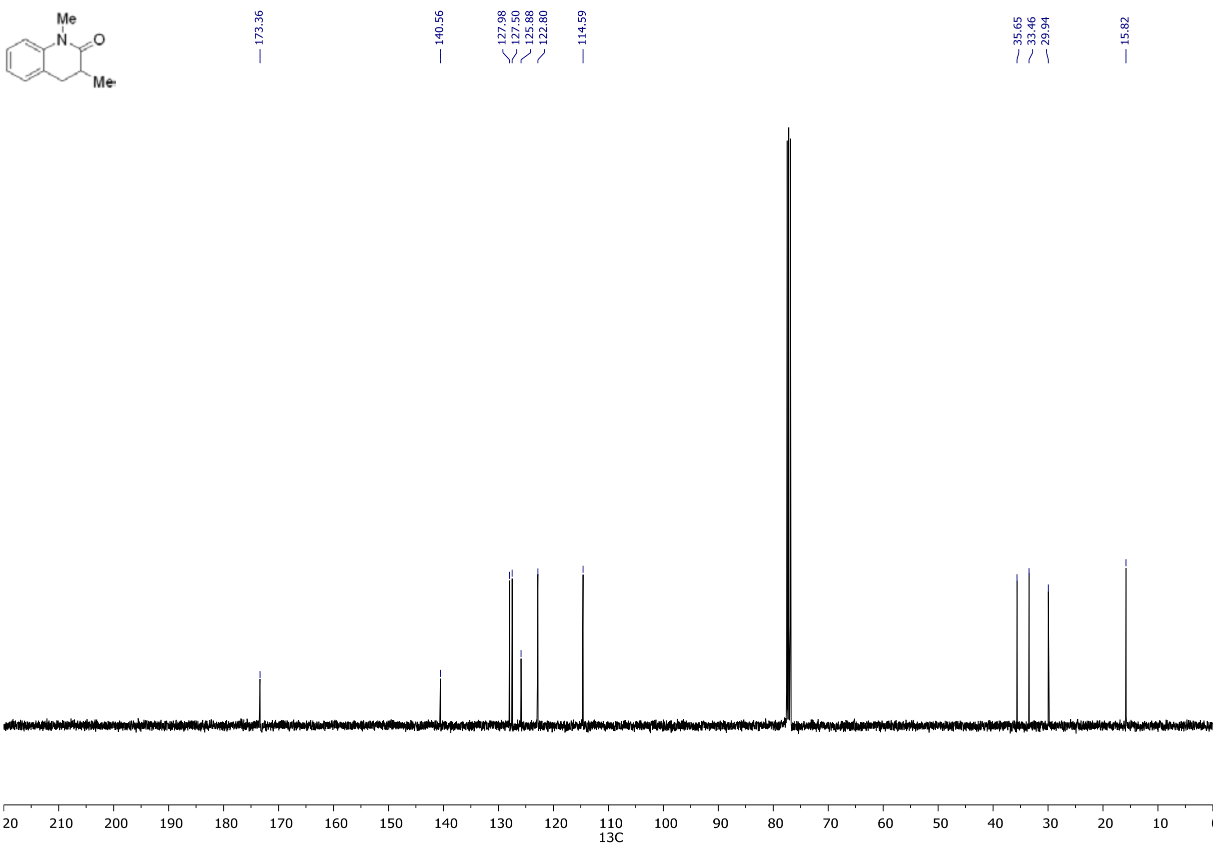
1H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O
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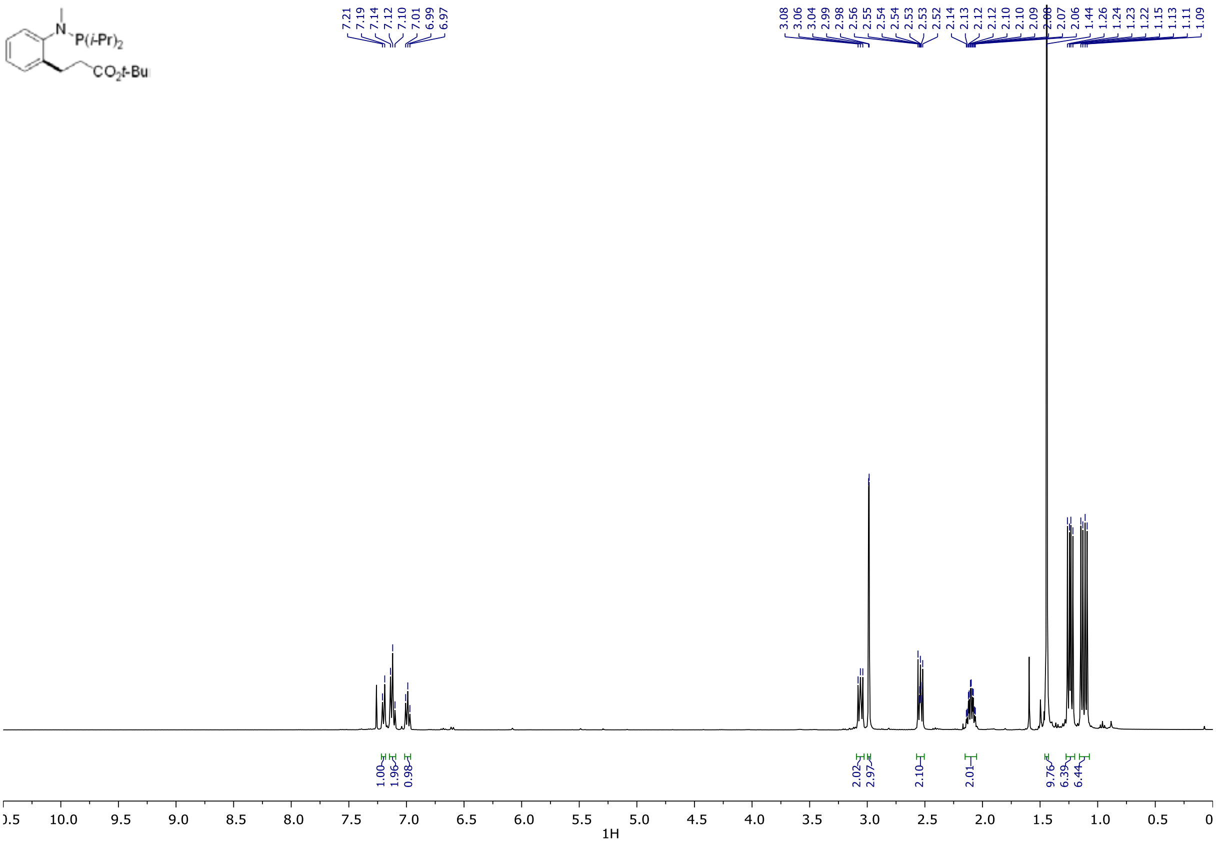
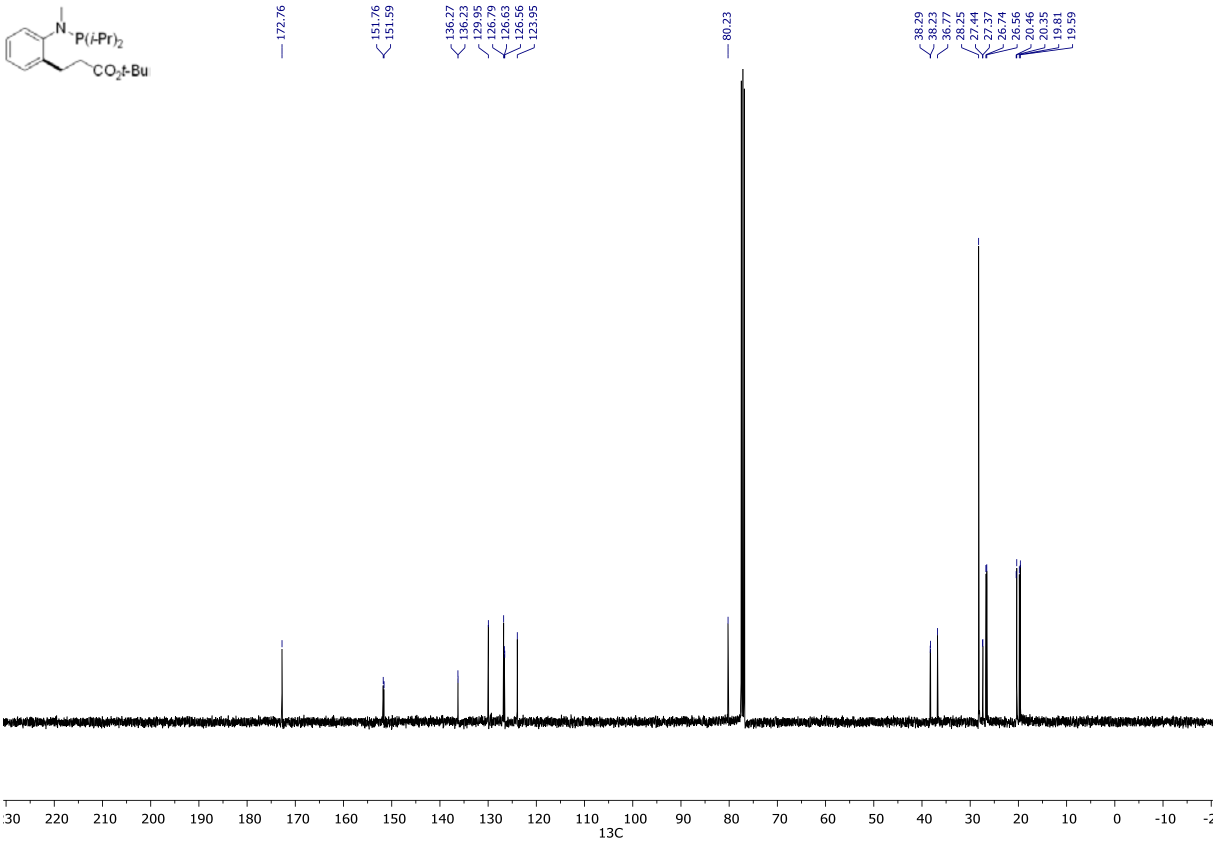
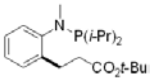
33.46
29.94
15.82
13C

4a



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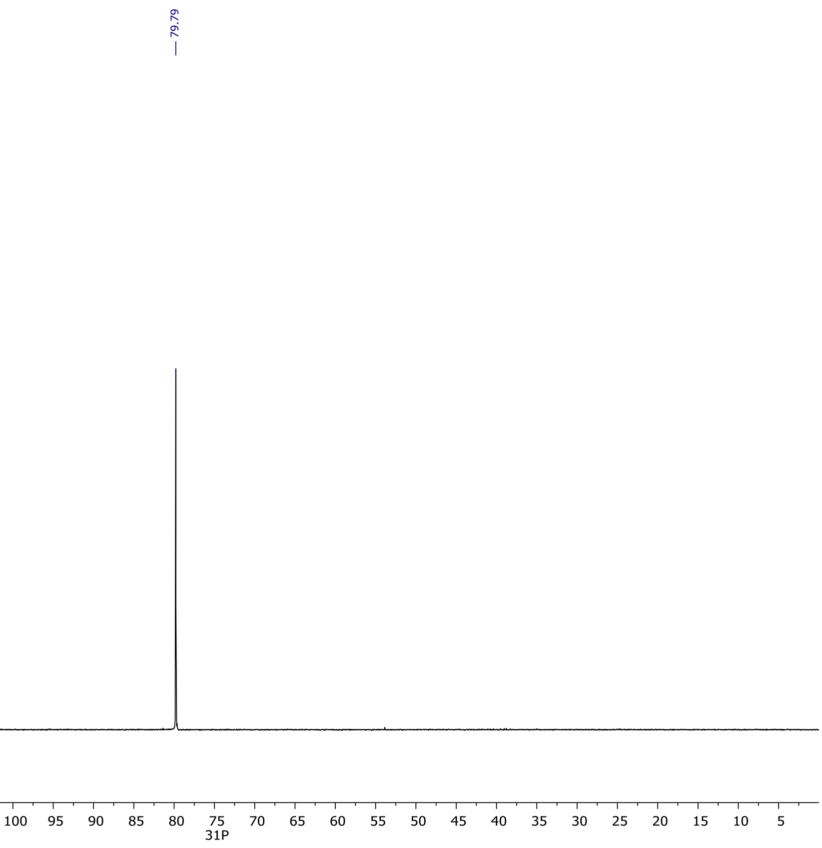
P(i-Pr)2
CO2t-Bu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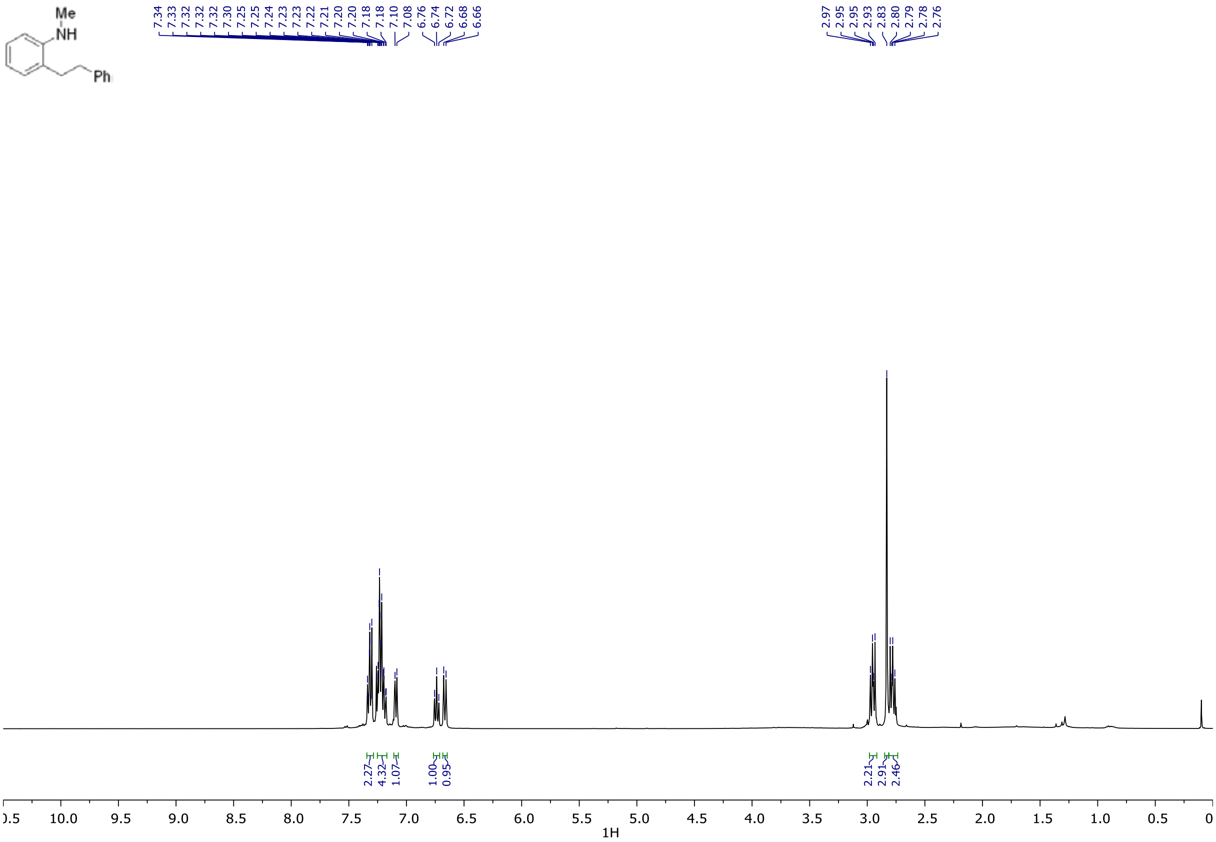
31P

5a


Me
NH
Ph
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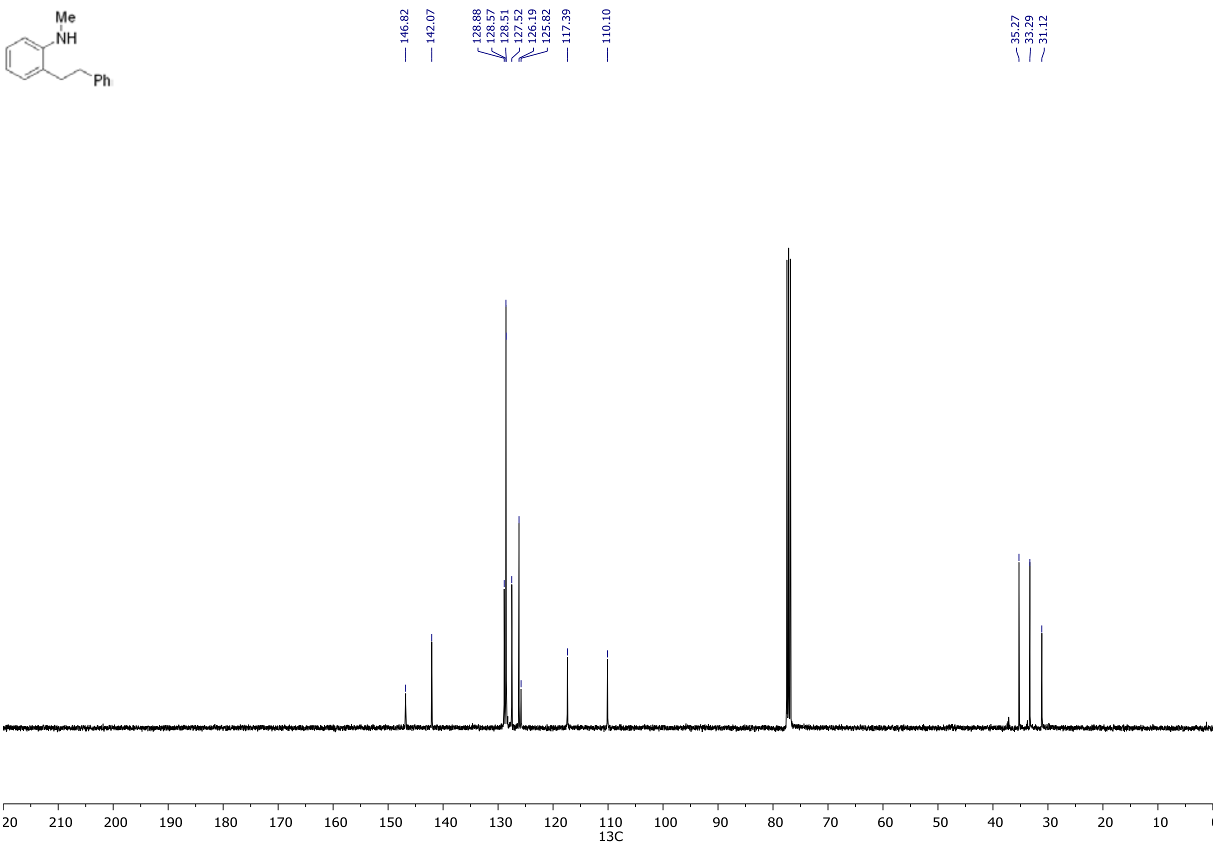
2.27 4.32 1.07 1.00 0.95
2.21 2.91 2.46
1H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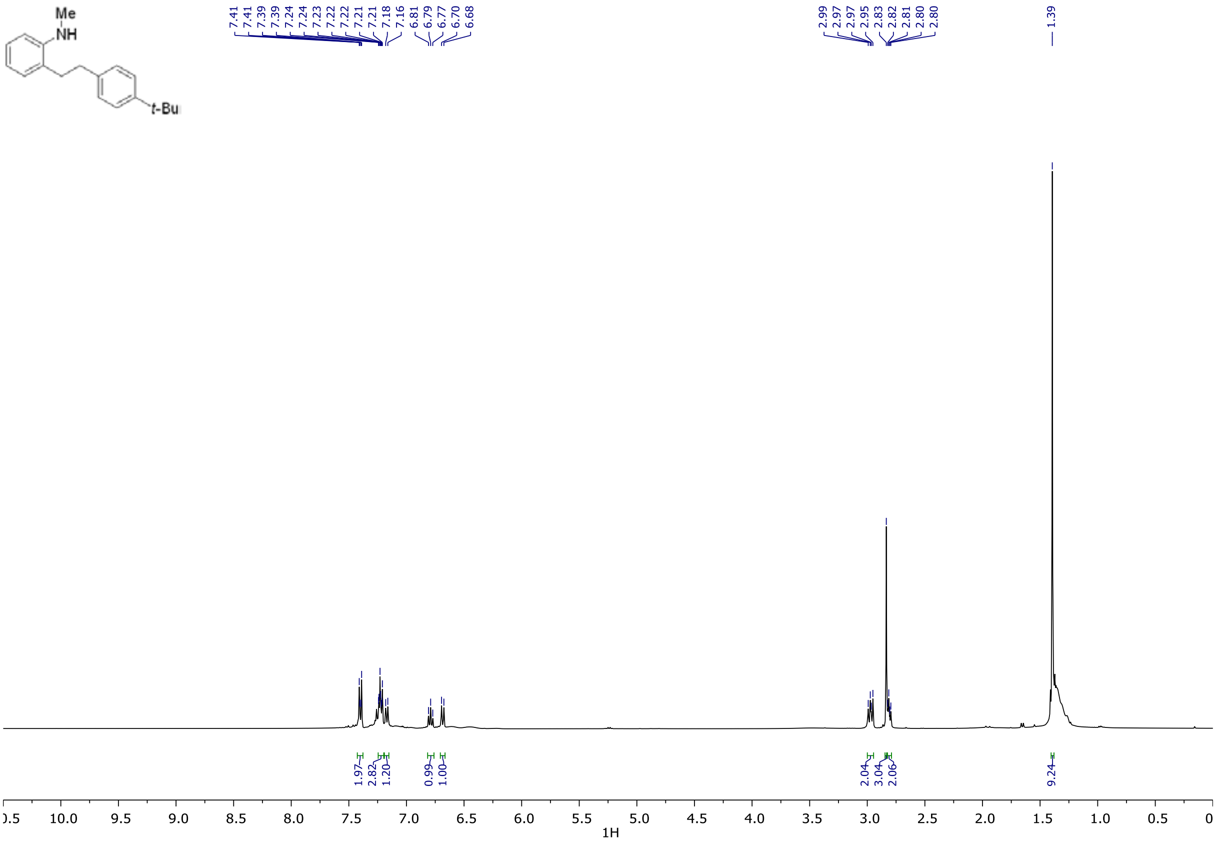
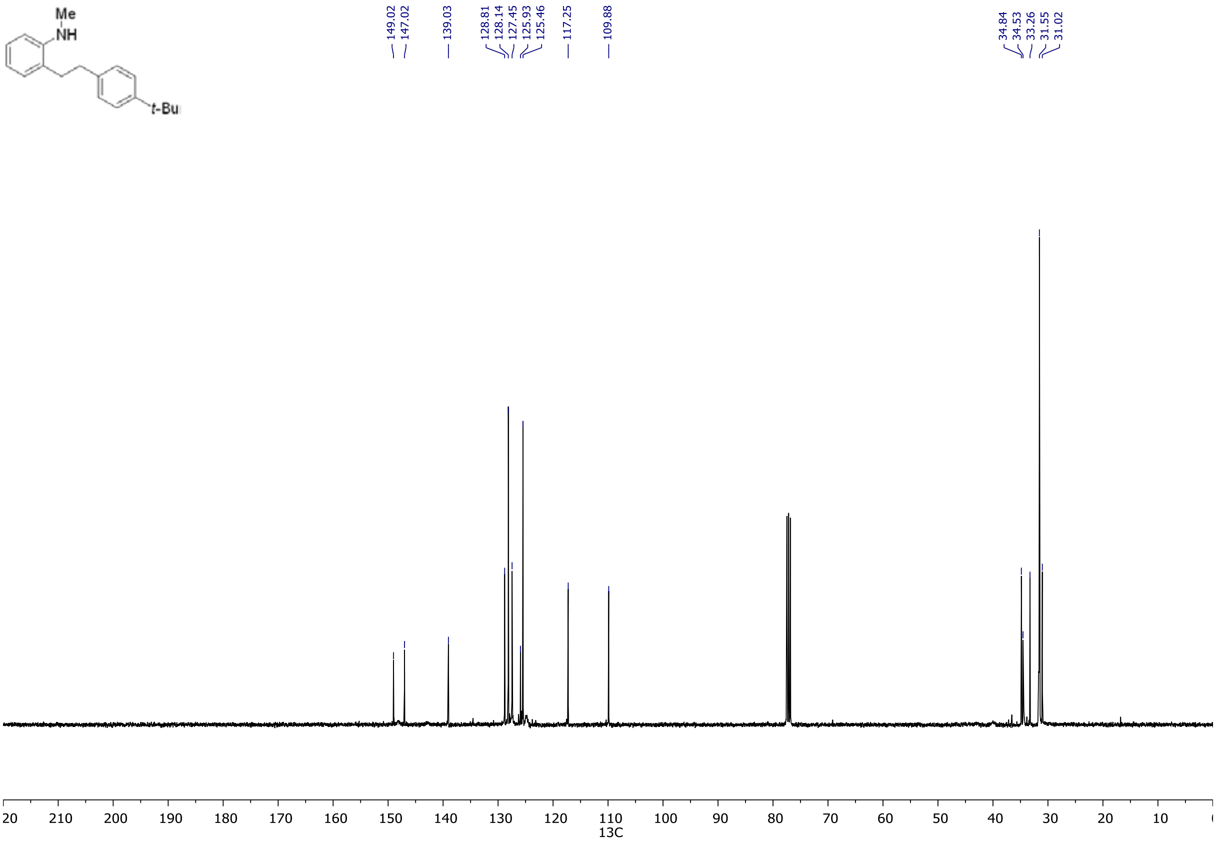
13C

5b





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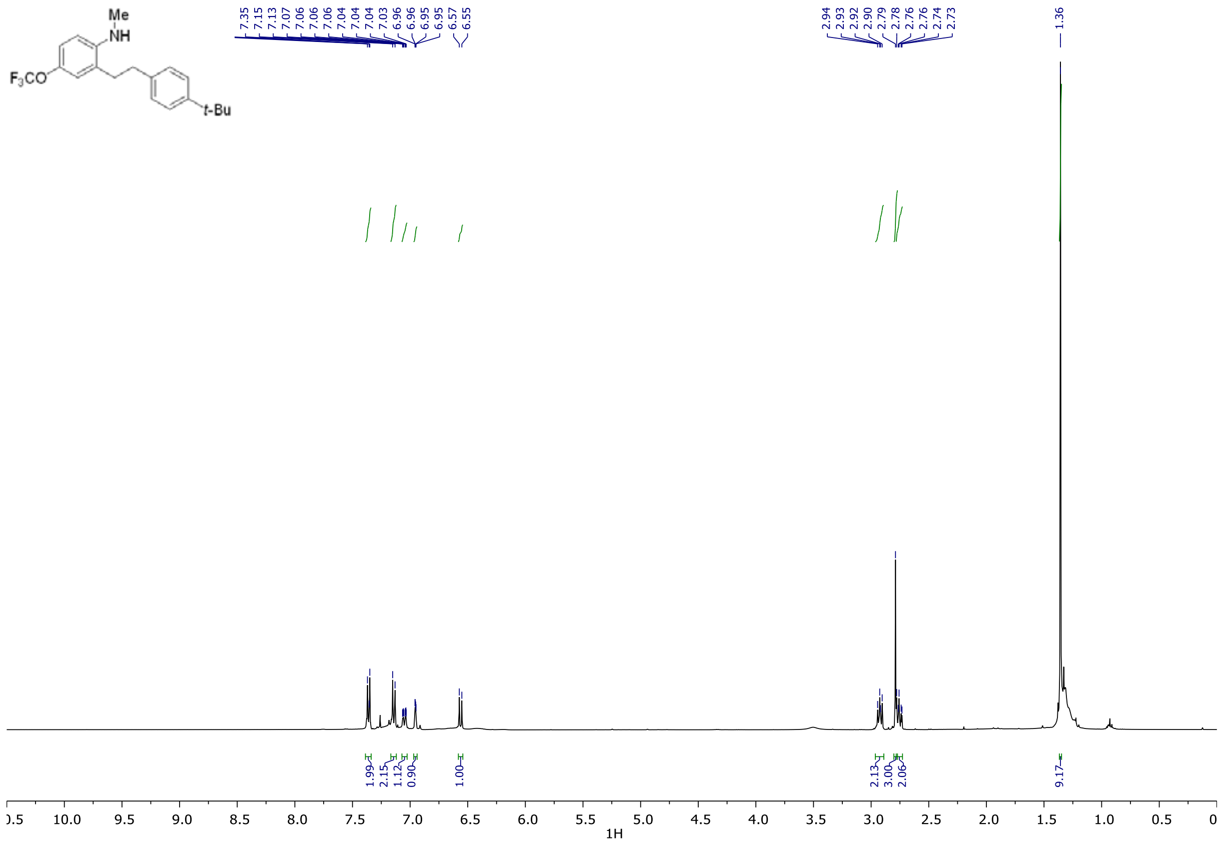

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NH
F3CO
t-Bu
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7.15
7.13
7.07
7.06
7.06
7.06
7.04
7.04
7.04
7.03
6.96
6.96
6.95
6.95
6.57
6.55
2.94
2.93
2.92
2.90
2.79
2.78
2.76
2.74
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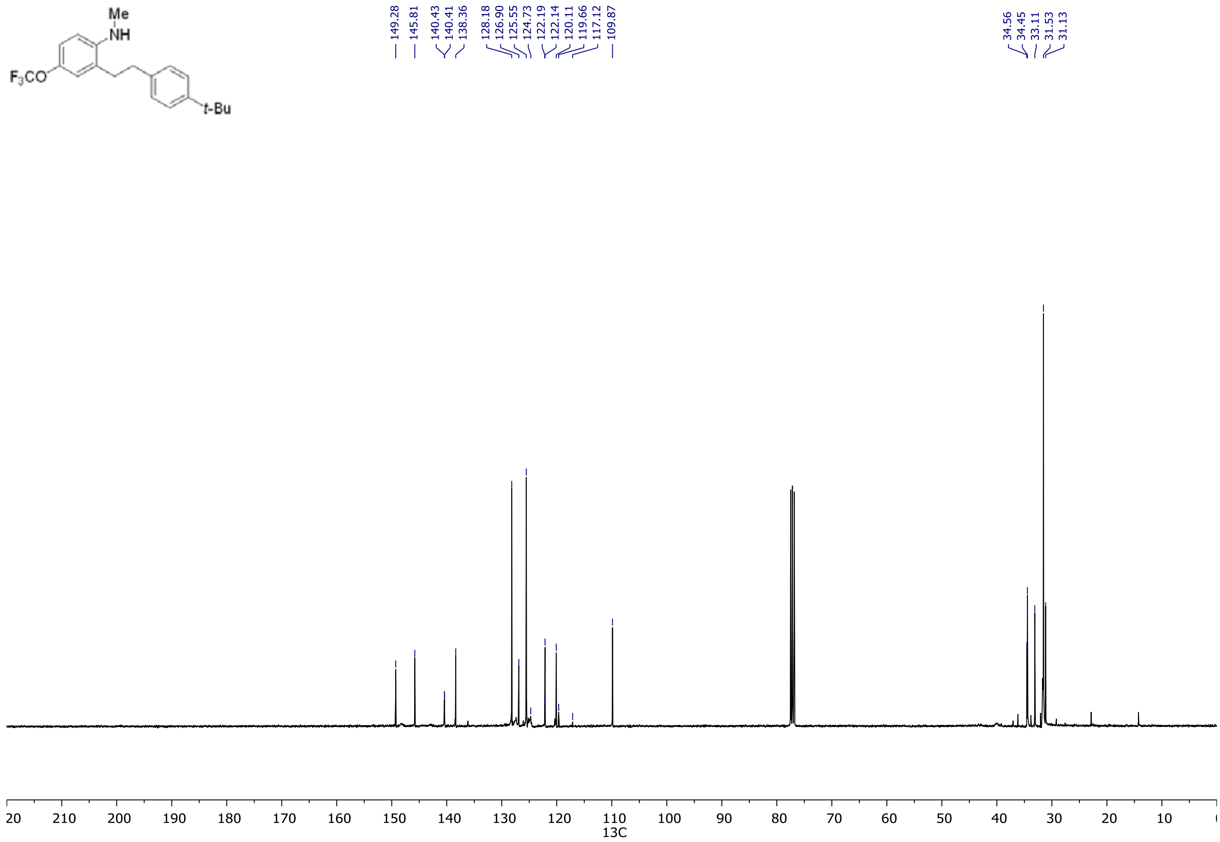
2.13
3.00
2.06
9.17
1H



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t-Bu
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138.36
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124.73
122.19
122.14
120.11
119.66
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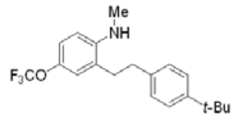
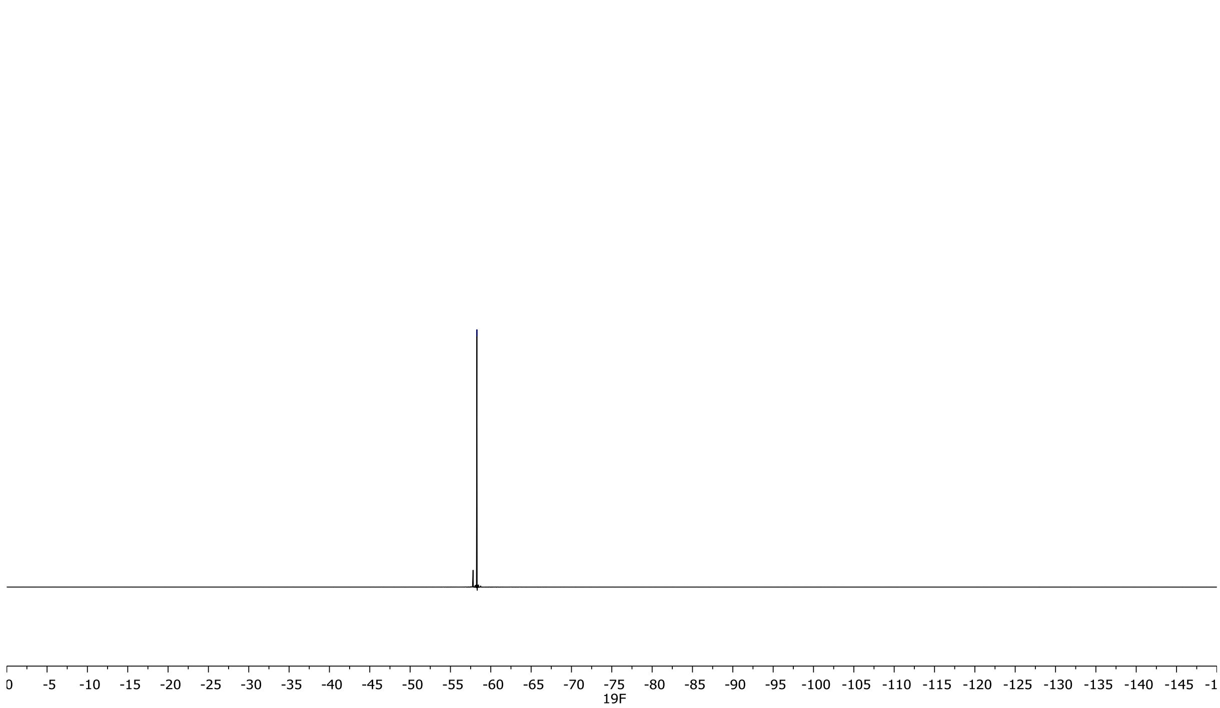
109.87
34.56
34.45
33.11
31.53
31.13
13C

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-70
-75
-80
-85
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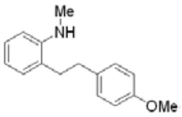
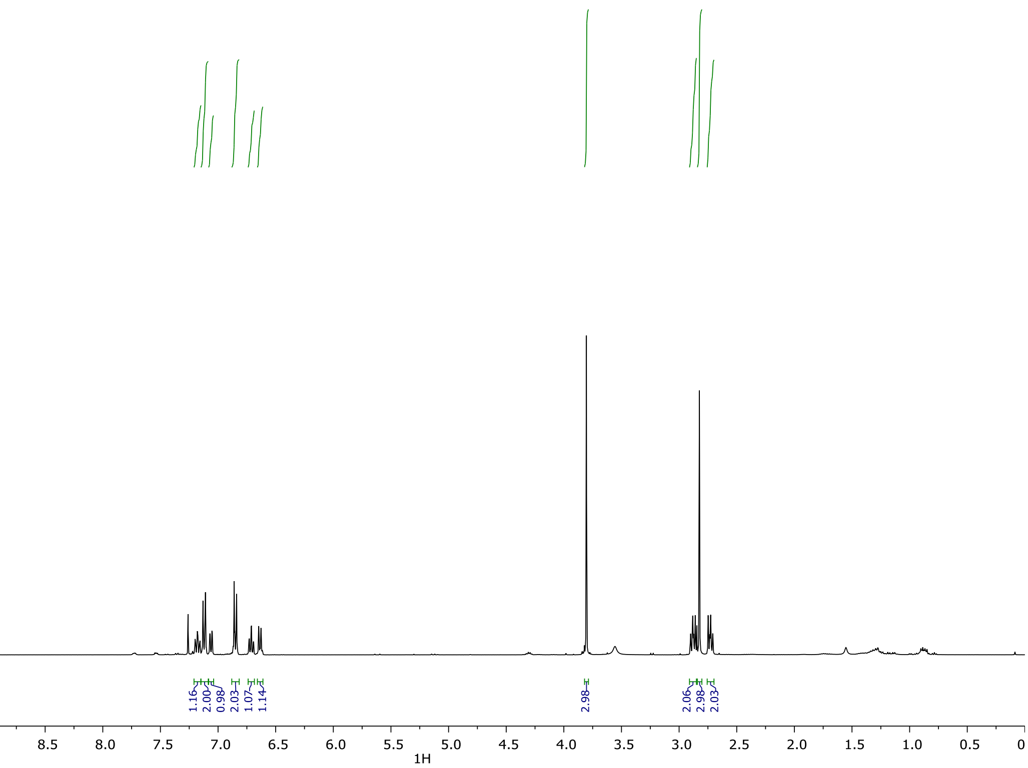
-105
-110
-115
-120
-125
-130
-135
-140
-145
-1
19F

5d

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2.00
0.98
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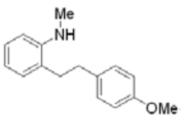
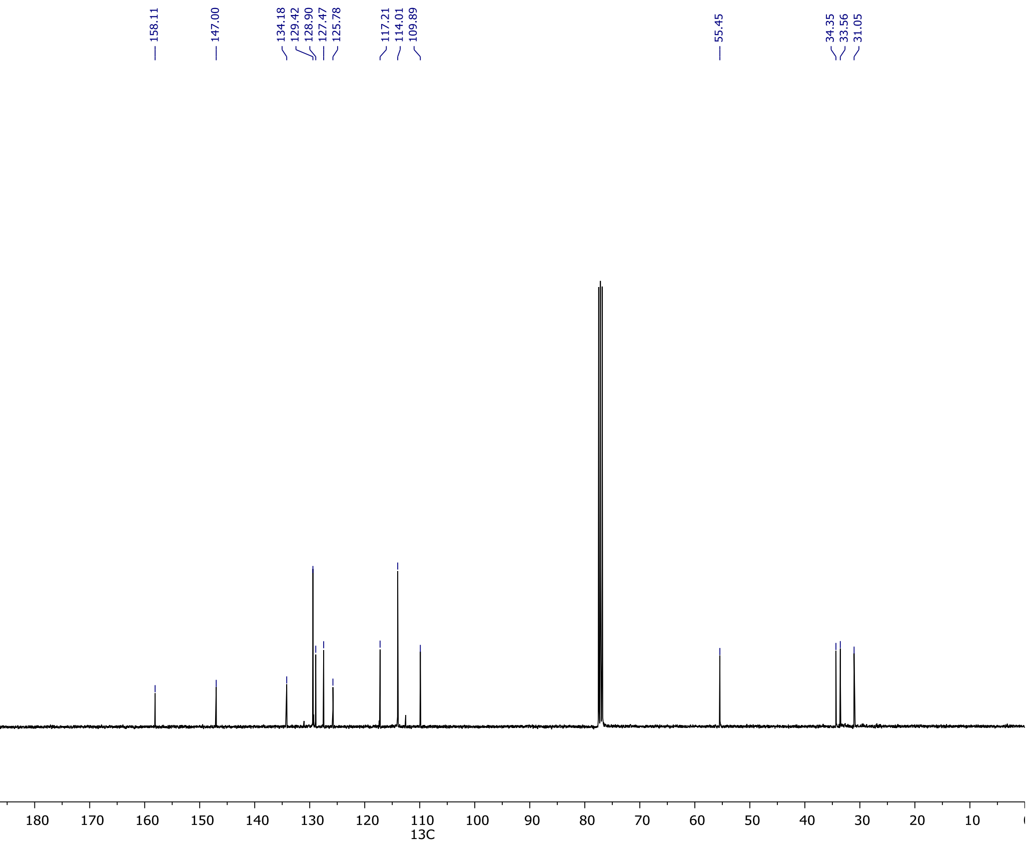
1.14
2.98
2.06
2.98
2.03
1H

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134.18
129.42
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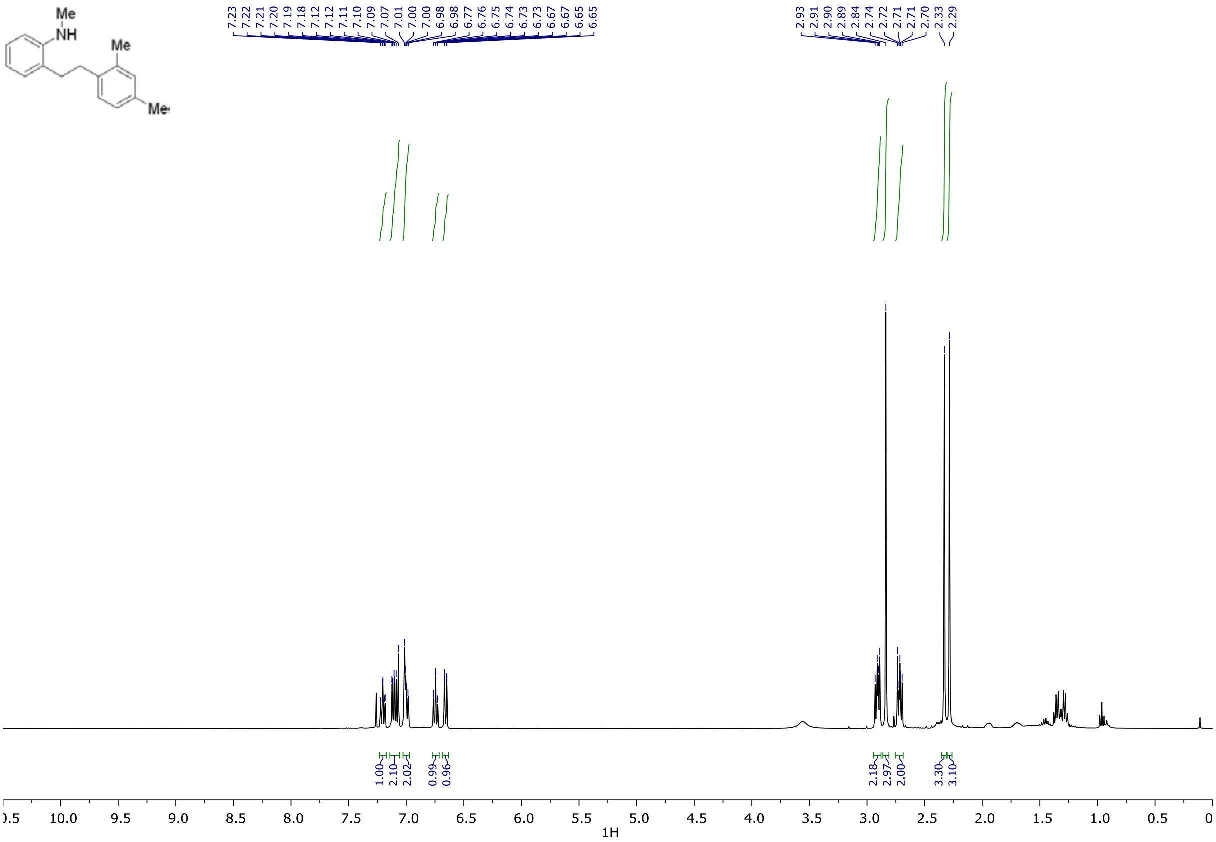
127.47
125.78
117.21
114.01
109.89
55.45
34.35
33.56
31.05
13C

5e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NH
Me
Me
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7.22
7.21
7.20
7.19
7.18
7.12
7.12
7.11
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7.09
7.07
7.01
7.00
7.00
6.98
6.98
6.77
6.76
6.75
6.74
6.73
6.73
6.67
6.65
6.65
2.93
2.91
2.90
2.89
2.84
2.74
2.72
2.71
2.71
2.70
2.33
2.29
1.00
2.10
2.02
0.99
0.96
2.18
2.97
2.00
3.30
3.10
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
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4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0
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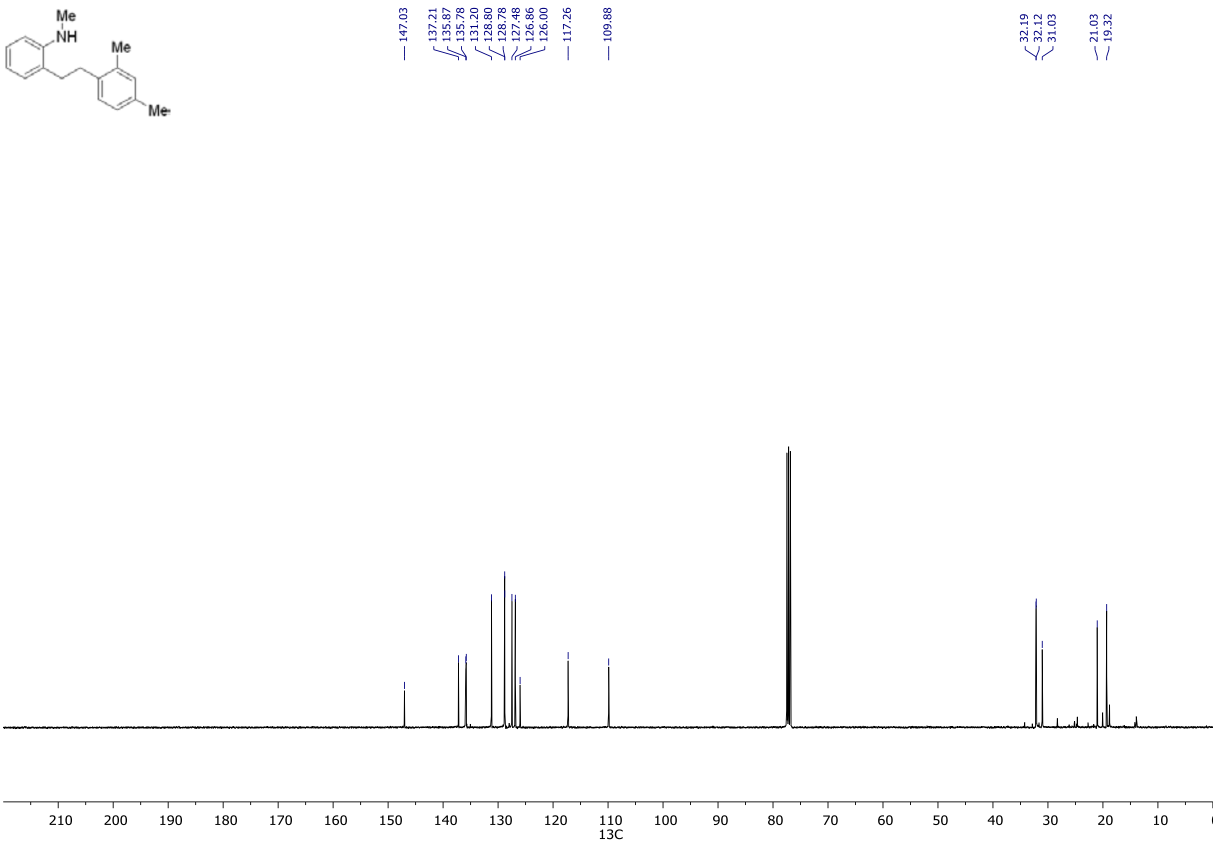
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NH
Me
Me
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128.80
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127.48
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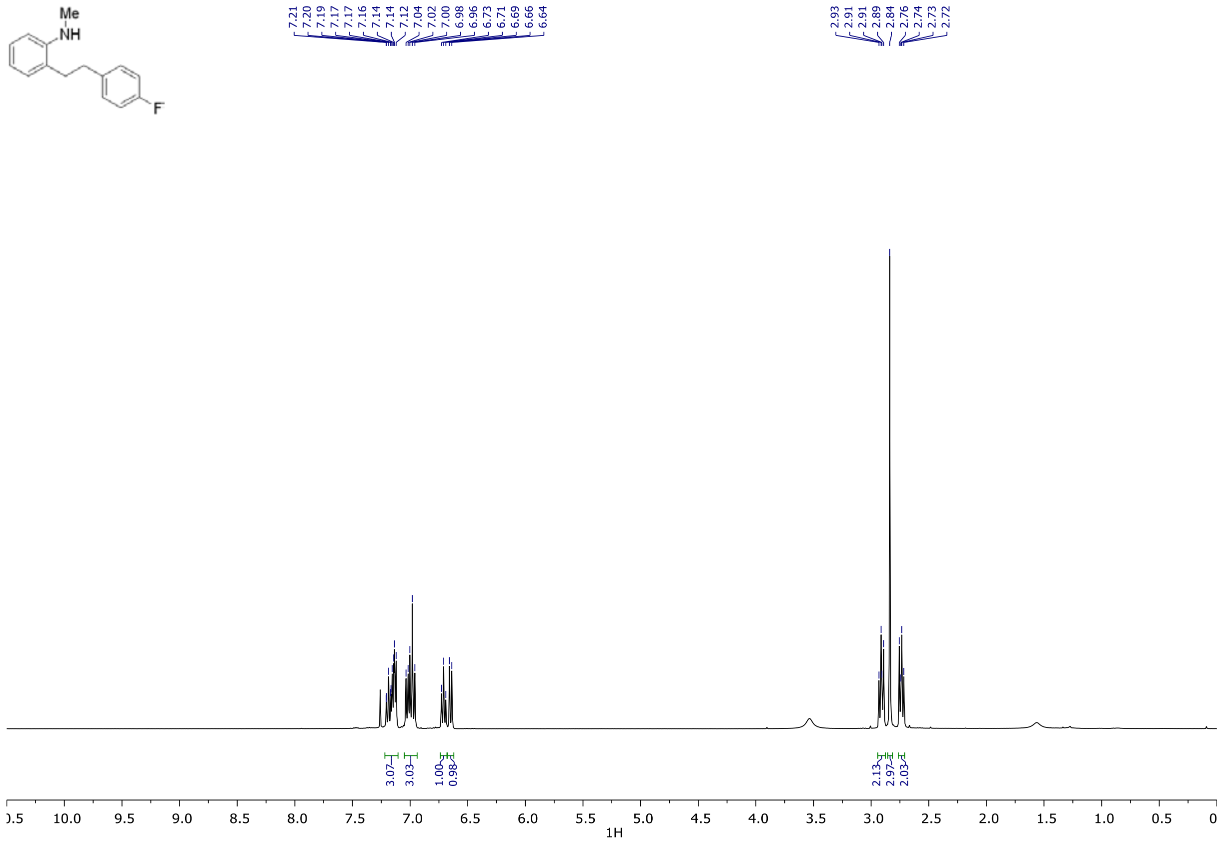
126.00
117.26
109.88
32.19
32.12
31.03
21.03
19.32
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
13C

5f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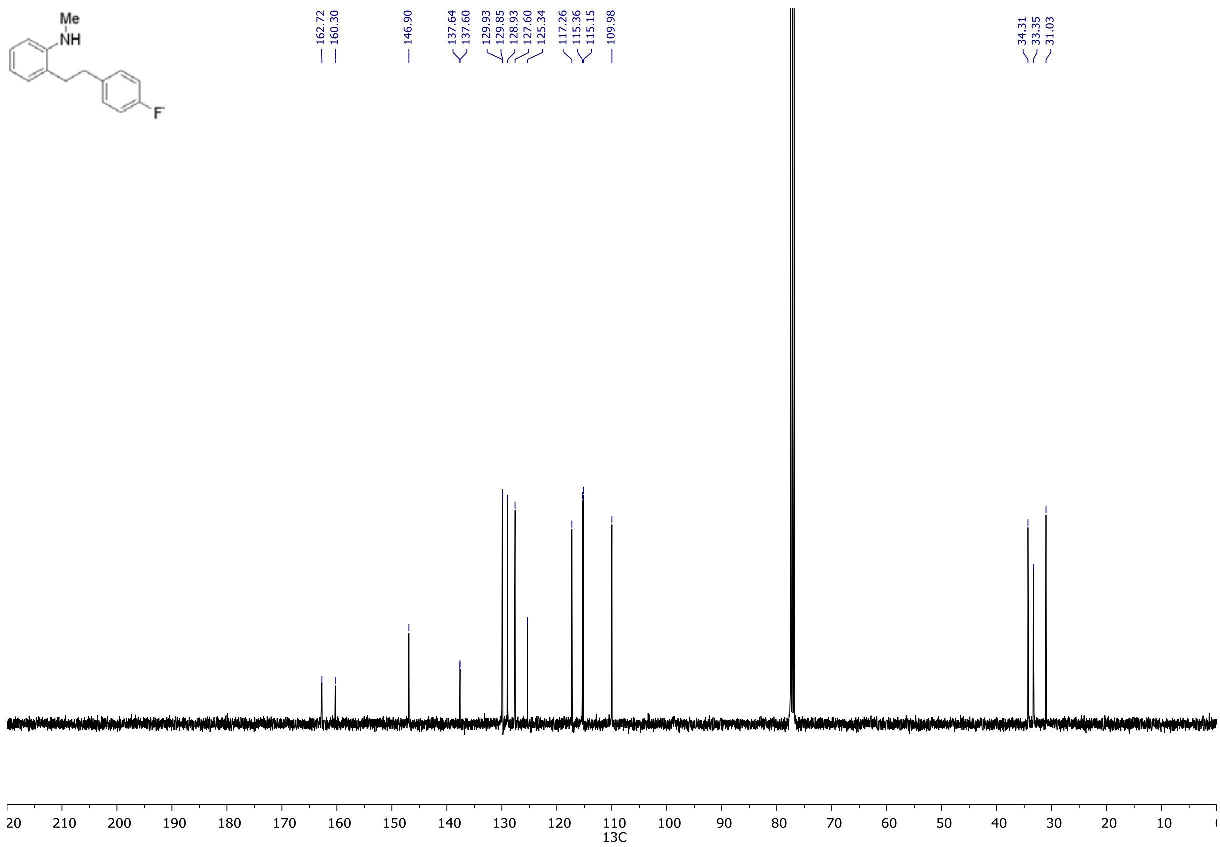
7.20
7.19
7.17
7.17
7.16
7.14
7.14
7.12
7.04
7.02
7.00
6.98
6.96
6.73
6.71
6.69
6.66
6.64
2.93
2.91
2.91
2.89
2.84
2.76
2.74
2.73
2.72
3.07
3.03
1.00
0.98
2.13
2.97
2.03
1H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125.34
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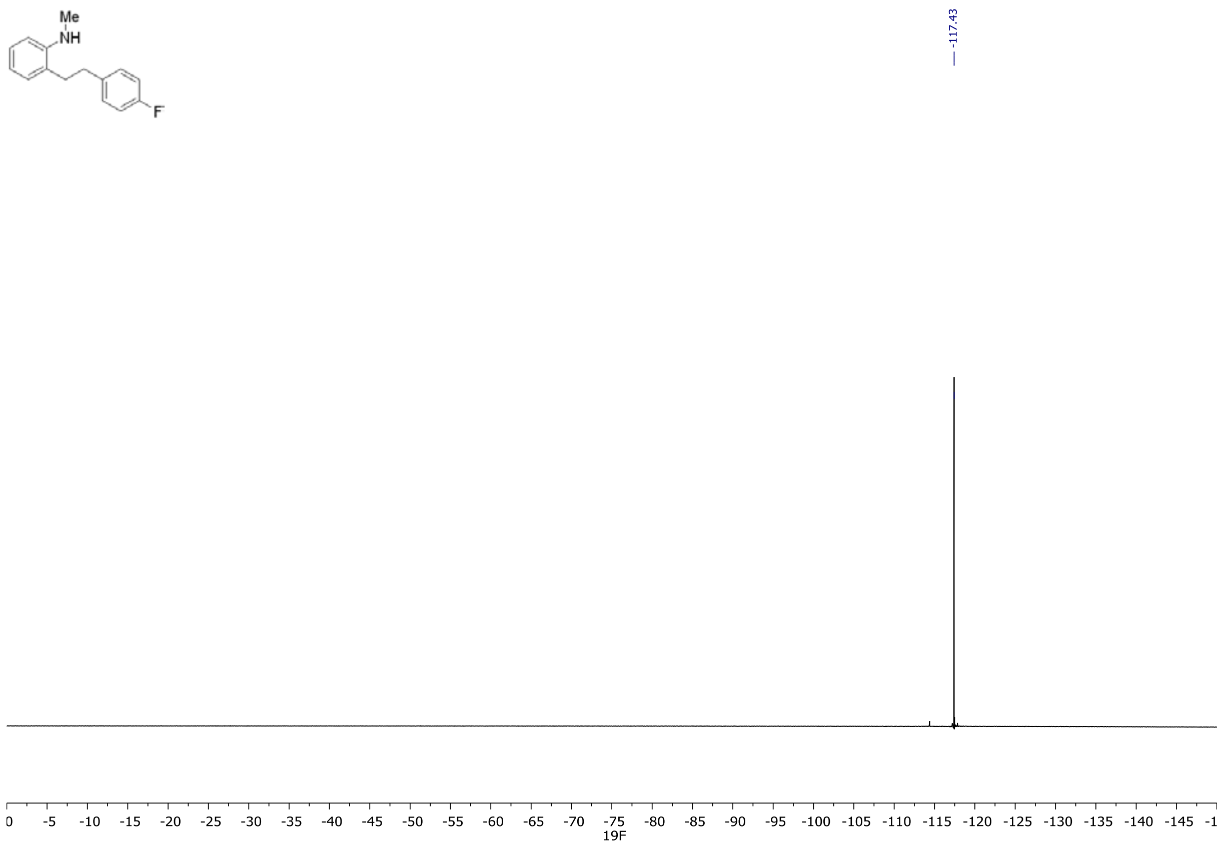
115.36
115.15
109.98
34.31
33.35
31.03
13C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-70
-75
-80
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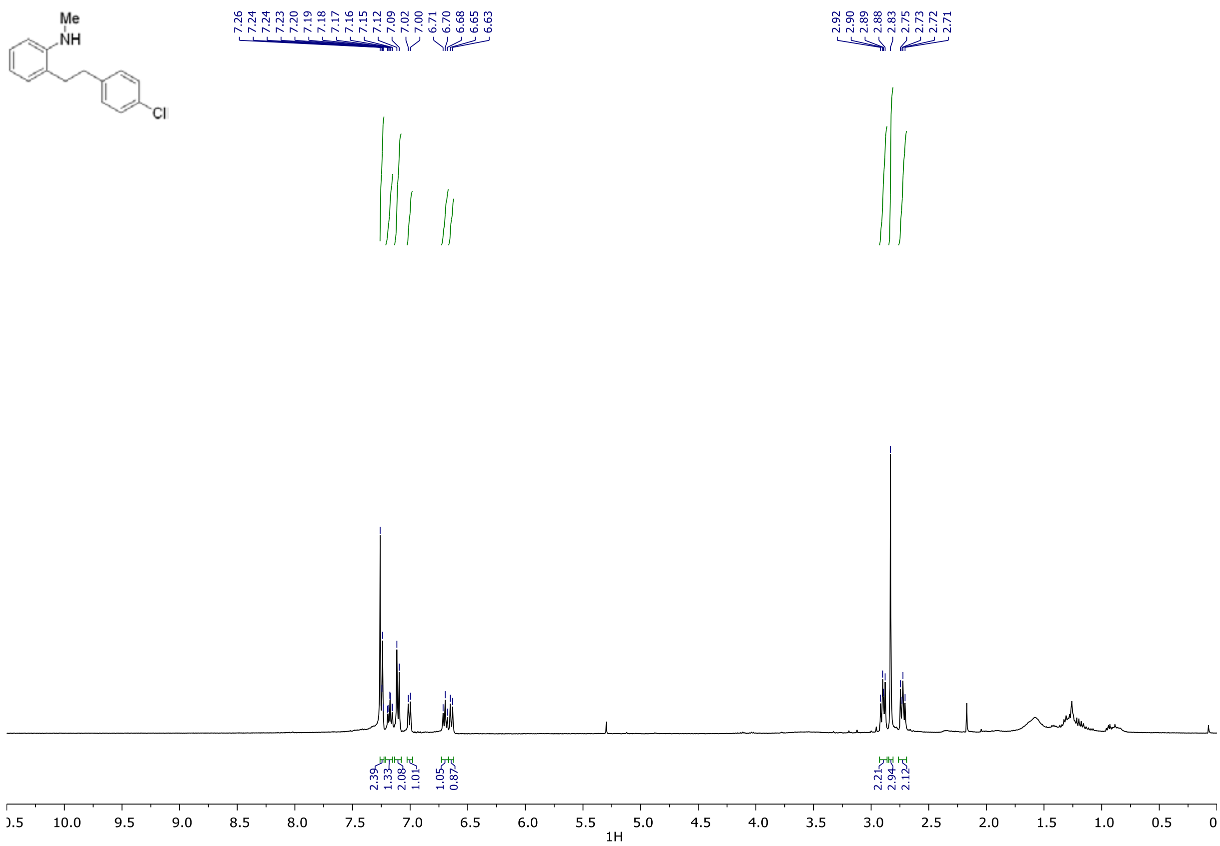
-130
-135
-140
-145
19F

5g


Me
NH
Cl
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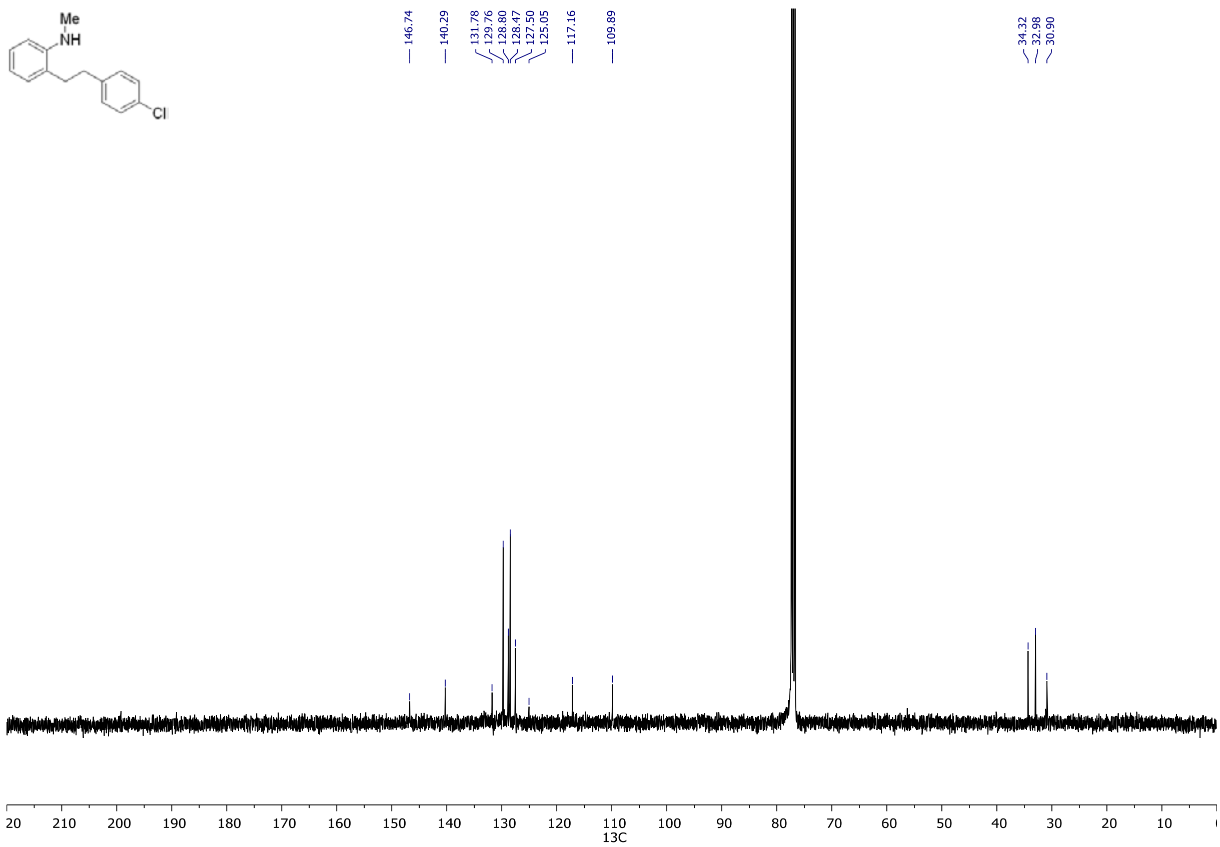
2.92 2.90 2.89 2.88 2.83 2.75 2.73 2.72 2.71
2.39 1.33 2.08 1.01 1.05 0.87
2.21 2.94 2.12
1H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Cl
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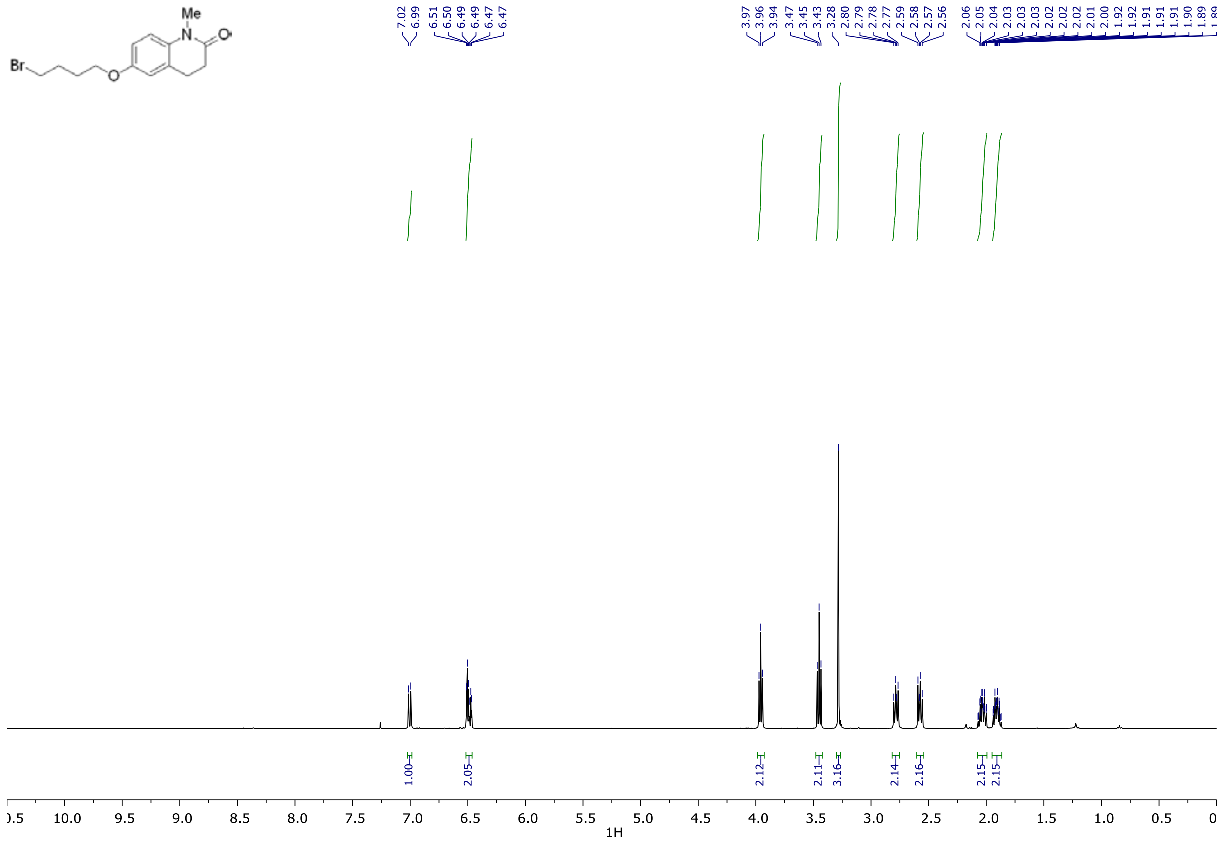
34.32 32.98 30.90
13C

7



Me
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O
Br
O
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3.96
3.94
3.47
3.45
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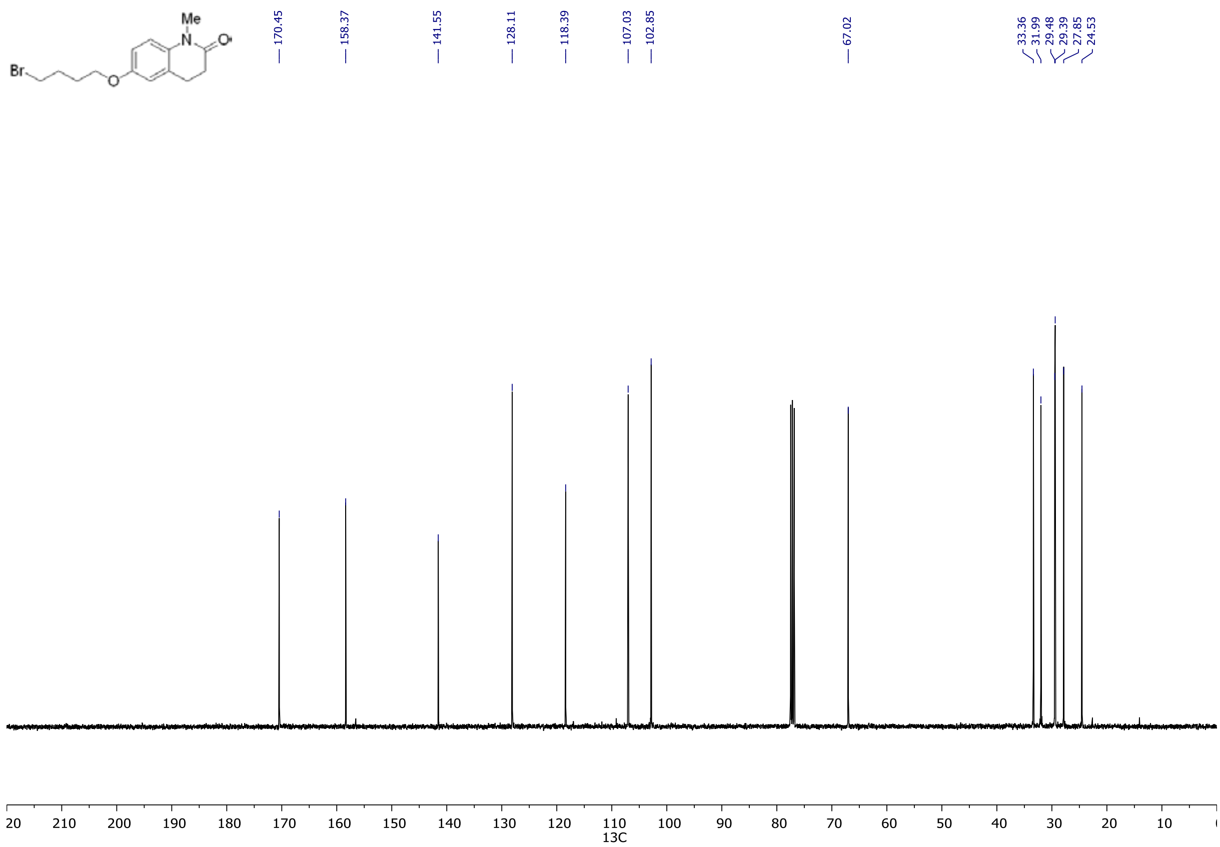

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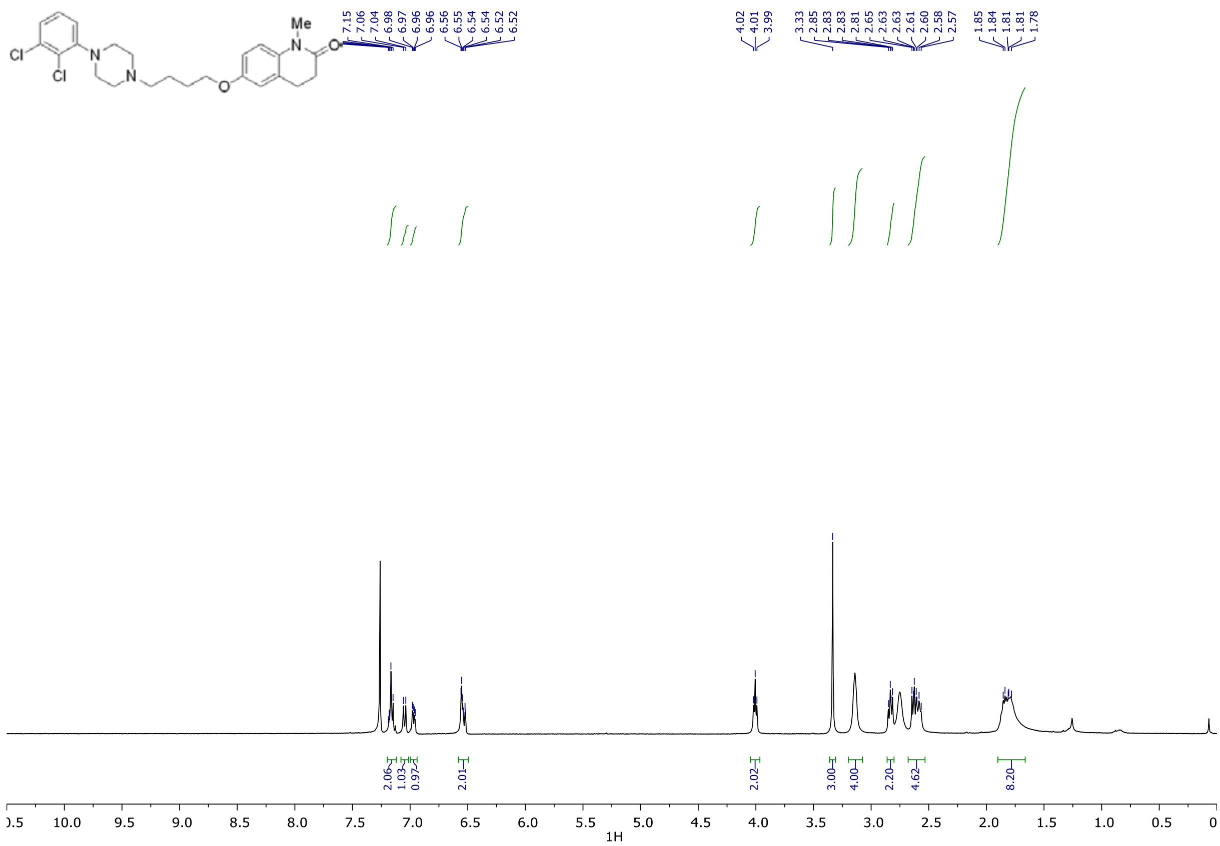
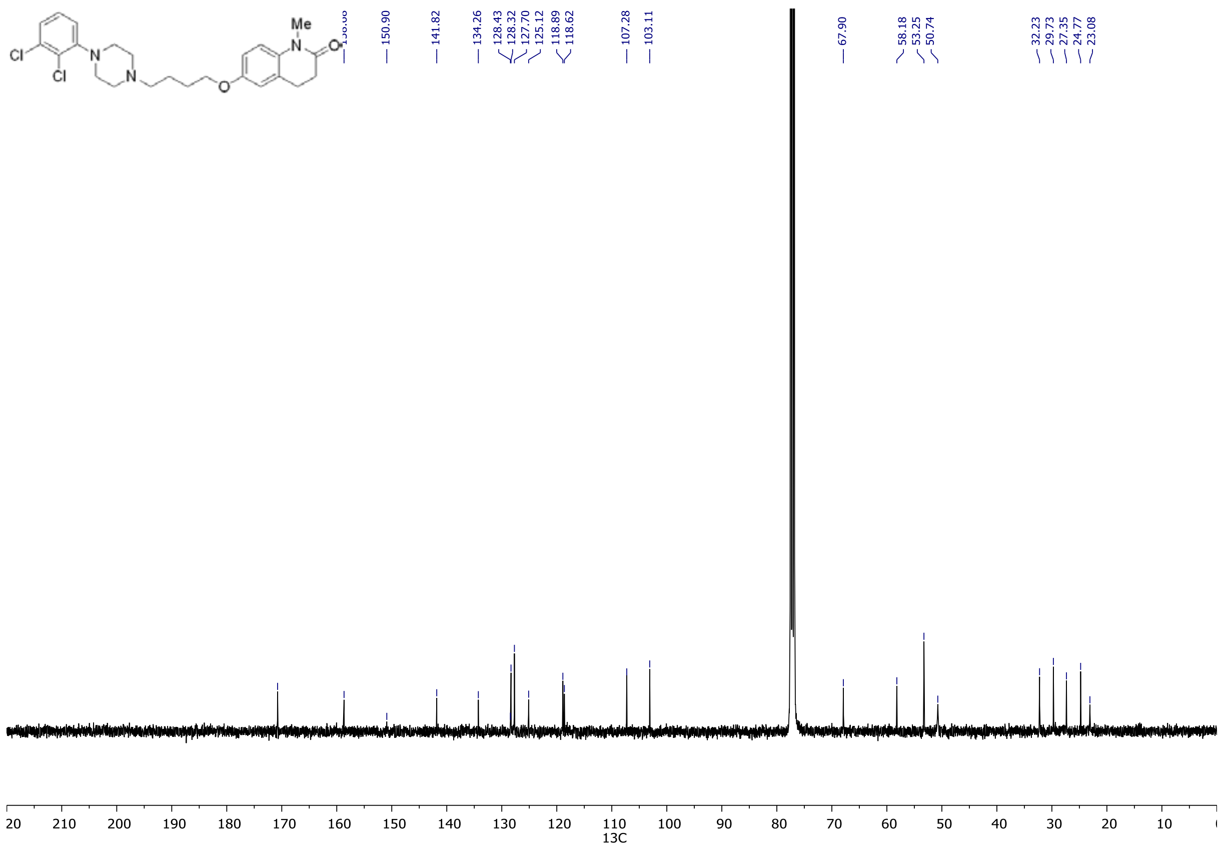
10
13C

8





11. References

[S1] Stemmler, R. T.; Bolm, C. *Adv. Synth. Catal.* **2007**, *349*, 1185–1198.

[S2] Chen, Y.; Turlik, A.; Newhouse, T. R. *J. Am. Chem. Soc.* **2016**, *138*, 1166–1169.

[S3] Mangin, L. P.; Michaud, G.; Zargarian, D. *Organometallics* **2020**, *39*, 4006–4018