Supporting Information for

Efficient Synthesis of Chiral γ-Aminobutyric Esters via direct Rhodium-Catalyzed Enantioselective Hydroaminomethylation of acrylates

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Table of contents

SI. General Considerations

General: All the reactions were carried out using Schlenk-line inert atmosphere techniques or glovebox techniques. Anhydrous solvents were collected from the system Braun MB SPS-800 except from 1,2-dichloroethane, which was dried over CaH_2, and stored under inert atmosphere.

Reagents: Commercially available reagents and solvents were purchased at the highest commercial quality from Sigma-Aldrich, Fluka, Alfa Aesar, Fluorochem, Strem and were used as received, without further purification, unless otherwise stated.

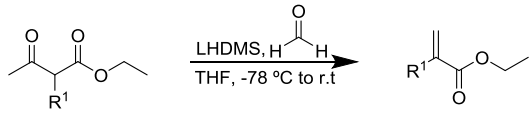
Analytical methods: ^{1}H, $^{13}C\{^{1}H\}$ and $^{31}P\{^{1}H\}$ NMR spectra were recorded using a Varian Mercury VX 400 (400, 100.6, and 161.97 MHz respectively). Chemical shift values (δ) are reported in ppm relative to TMS (^{1}H and $^{13}C\{^{1}H\}$) or H_3PO_4 ($^{31}P\{^{1}H\}$), and coupling constants are reported in Hertz. The following abbreviations are used to indicate the multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; bs, broad signal. High-resolution mass spectra (HRMS) were recorded on an Agilent Time-of-Flight 6210 using ESI-TOF (electrospray ionization-time of flight). Samples were introduced to the mass spectrometer ion source by direct injection using a syringe pump and were externally calibrated using sodium formate. The instrument was operating in the positive ion mode. Reactions were monitored by TLC carried out on 0.25 mm E. Merck silica gel 60 F_{254} glass or aluminum plates. Developed TLC plates were visualized under a short-wave UV lamp (254 nm) and by heating plates that were dipped in potassium permanganate. Flash column chromatography was carried out using forced flow of the indicated solvent on Merck silica gel 60 (230-400 mesh).

The enantiomeric excess of γ-aminobutyric esters **6** or analogous aminoalcohols **17** was determined by ^{1}H NMR spectroscopy using Eu(hcf)$_3$, and HPLC analysis on chiral stationary phase performed on a Waters ACQUITY® UPC^2 instrument, employing Daicel Chiralpak IA, IG, IC or OD-H chiral columns, and Trefoil CEL2 chiral column. The exact conditions for the analyses are specified within the supporting information section. HPLC traces were compared to racemic samples prepared performing the reactions in the presence of di-*tert*-butylphenylphosphine.

Catalysis: The Rh-catalyzed HAM reaction was set up in a CAT24 autoclave from HEL Inc. and was stirred with a teflon-coated magnetic stir bar.

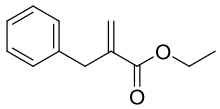
SII. Synthesis of α-alkyl acrylates

General Procedure A: Synthesis of α-alkyl acrylates (1b-d)



The reaction was carried out in an oven dried, argon purged, schlenck fitted with a argon inlet and septum and following a modified literature procedure.[1] To a stirred solution of ethyl 2-alkylacetoacetate (17 mmol, 1.0 eq) in THF (136 mL) was added LiHMDS 1.0 M in THF (19 mL, 19 mmol, 1.1 eq) at -78 °C. The solution was left stirring for 30 min then paraformaldehyde (3g, excess) was added as a solid in one portion. The suspension was allowed to reach room temperature and left stirring for 16h. The mixture was filtrated through a pad of Celite to remove the excess of paraformaldehyde. The filtrate was concentrated *in vacuo* and purified by flash chromatography to afford the α-alkyl acrylate **1**.

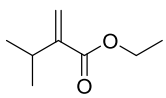
Ethyl 2-benzylacrylate (1b)[1]



General procedure A was followed employing ethyl 2-benzyl-3-oxobutanoate as starting material. Purification by flash chromatography eluting with hexane/EtOAc (20:1) afforded **1b** (3.0 g, 93%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.22 (t, $J_{H,H}$ = 7.2 Hz, 3H), 3.59 (s, 2H), 4.14 (q, $J_{H,H}$ = 7.2 Hz, 2H), 5.41 (bs, 1H), 6.19 (bs, 1H), 7.15-7.27 (m, 5H, *Ar*). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 14.2 (1C), 38.1 (1C), 60.8 (1C), 126.0 (1C), 126.3-138.8 (6C, *Ar*), 140.4 (1C), 167.0 (1C). These signals are in agreement with those reported in the literature.

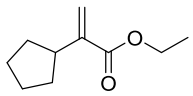
Ethyl 3-methyl-2-methylenebutanoate (1c)[1]



General procedure A was followed employing ethyl 2-acetyl-3-methylbutanoate as starting material. Purification by flash chromatography eluting with hexane/EtOAc (20:1) afforded **1c** (2.2 g, 54%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.07 (d, $J_{H,H}$ = 8 Hz, 6H), 1.30 (t, $J_{H,H}$ = 8 Hz, 3H), 2.80 (m, 1H), 4.21 (q, $J_{H,H}$ = 8 Hz, 2H), 5.50 (bs, 1H), 6.11 (bs, 1H). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 14.3 (1C), 21.9 (2C), 29.4 (1C), 60.6 (1C), 121.6 (1C), 147.5 (1C), 167.6 (1C). Peaks in agreement with those reported in the literature.

Ethyl 2-cyclopentylacrylate (1d)



General procedure A was followed employing ethyl 2-cyclopentyl-3-oxobutanoate (10 mmol) as starting material. Purification by flash chromatography eluting with hexane/EtOAc (30:1) afforded **1d** (850 mg, 51%) as colorless oil.

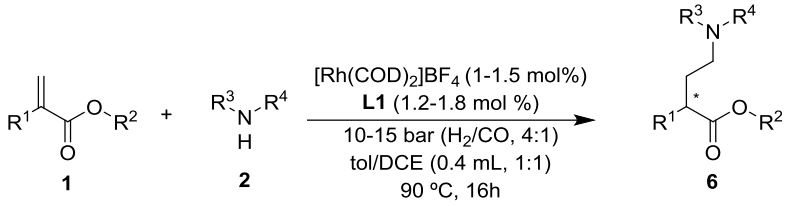
^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.26 (t, $J_{H,H}$ = 8 Hz, 3H), 1.58 (m, 2H), 1.64 (m, 5H), 1.70 (m, 1H), 2.84 (m, 1H), 4.20 (q, $J_{H,H}$ = 8 Hz, 2H), 5.51 (bs, 1H), 6.10

(bs, 1H).**^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 14.3 (1C), 25.0 (2C), 31.2 (2C), 41.5 (1C), 60.5 (1C), 121.6 (1C), 144.8 (1C), 167.7 (1C). **ESI-HRMS:** Calculated for $C_{10}H_{16}O_2$. Exact: (M: 168.1150, M+H: 169.1229); Experimental: (M+H: 169.1221).

[1] Wang, X.; Buchwald, S. L. Rh-Catalyzed Asymmetric Hydro-formylation of Functionalized 1,1-Disubstituted Olefins. J. Am. Chem. Soc. 2011, 133, 19080-19083.

SIII. General procedure for Rh-catalyzed Asymmetric HAM with secondary amines

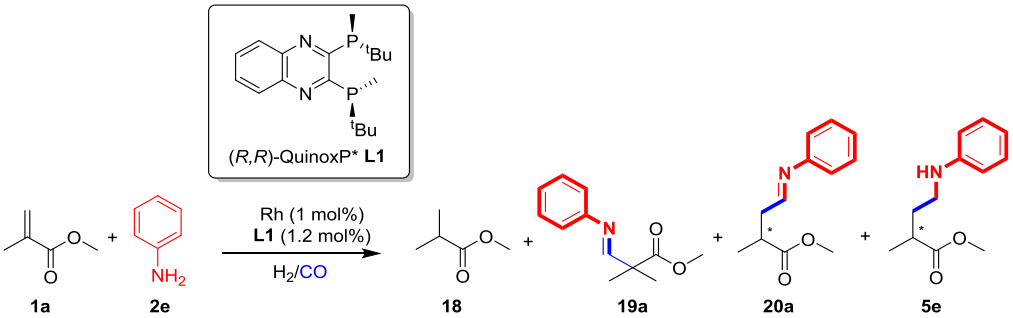
General procedure B: rhodium catalyzed asymmetric hydroaminomethylation of α-alkyl acrylates with secondary amines.



A 2 mL glassware reactor tube was charged with α-alkyl acrylate **1** (0.5 mmol), amine (0.5 mmol), bis(1,5-cyclooctadiene)rhodium (I) tetrafluoroborate (2 mg, 0.005 mmol) in DCE (0.2 mL) and chiral ligand (*R*,*R*)-QuinoxP*__L1__ (2 mg, 0.006 mmol) in toluene (0.2 mL). The reaction tube was placed in the reactor which was pressurized at the desired pressure, heated to 90 °C and left stirring at 900 rpm. The reaction was stopped after 16 h by cooling the reactor in an ice bath for 20 min followed by venting of the system. The mixture was purified by chromatographic column and the enantiomeric excess of the resulting α-alkyl-γ-aminobutyric esters **6** analyzed by chiral HPLC or ^{1}H NMR using $Eu(hcf)_3$.

SIV. Optimization of Reaction Conditions with Aniline

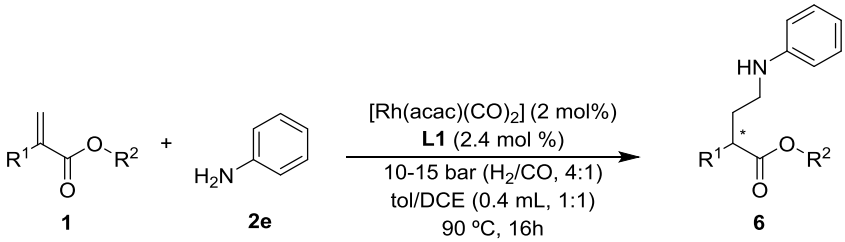
Table S1: Optimization of reaction conditions for the asymmetric hydroaminomethylation of methyl methacrylate **1a** with aniline **2e**.



Entry[a]	Rh	Conv. [%][b]	**18**[b]	**19a**[b]	**20a**[b]	**6e** [IY] [b]	ee [%][c]
1[d]	$[Rh(COD)_2]BF_4$	22	16	-	6	-	-
2	$[Rh(acac)(CO)_2]$	>99	69	11	18	-	-
3[d]	$[Rh(acac)(CO)_2]$	>99	66	6	16	12 [11]	60
4[e]	$[Rh(acac)(CO)_2]$	>99	51	6	16	26 [19]	60
5[f]	$[Rh(COD)_2]BF_4$	77	28	16	17	16 [15]	40

[a] Reaction conditions: **1a** (0.5 mmol), **2e** (0.5 mmol), Rh (1 mol%), **L1** (1.2 mol %), P = 10 bar (H_2/CO, 4:1), toluene (0.4 ml), T = 90°C, t = 16h. [b] % conversion and yield determined by ^{1}H NMR using naphthalene as internal standard, values in bracket refer to isolated yields. [c] ee determined by HPLC. [d] tol/DCE (1:1, 0.4 ml). [e] Rh (2 mol%), **L1** (2.4 mol%), tol/DCE (1:1, 0.4 ml). [f] NEt_3 (0.5 mol%), tol/DCE (1:1, 0.4 mL).

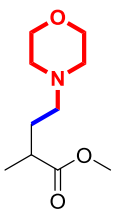
General procedure C: rhodium catalyzed asymmetric HAM of α-alkyl acrylates 1 with aniline 2e.



A 2 mL glassware reactor tube was charged with α-alkyl acrylate **1** (0.5 mmol), aniline **2e** (0.5 mmol), dicarbonyl(acetylacetonato)rhodium (I) (2.6 mg, 0.01 mmol) in DCE (0.2 mL) and chiral ligand (*R*,*R*)-QuinoxP* **L1** (4 mg, 0.012 mmol) in toluene (0.2 mL). The reaction tube was placed in the reactor which was pressurized with 10 bar of H_2/CO (4:1), heated to 90°C and left stirring at 900 rpm. The reaction was stopped after 16 h by cooling the reactor in an ice bath for 20 min followed by venting of the system. The mixture was purified by chromatographic column and the enantiomeric excess of the resulting α-alkyl-γ-aminobutyric esters **6** analyzed by chiral HPLC.

SV. Synthesis of γ-aminobutyric esters via Rh-catalyzed HAM

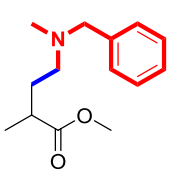
Methyl 2-methyl-4-morpholinobutanoate (6a)



General procedure B was followed employing methyl methacrylate **1a** (53.5 µL, 0.5 mmol) and morpholine (44 µL, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (2:1) afforded **6a** (60 mg, 60%) as colorless oil. The enantiomeric excess was determined to be 73% by UPC[2] analysis on a Acquity Trefoil Cel2 column with a gradient 90:10 CO_2/Acetonitrile with 0.1% of diethylamine as additive, flow rate 2mL/min, λ = 230 nm: $t_{r\ minor}$ = 2.0 min, $t_{r\ major}$ = 1.5 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.15 (d, $J_{H,H}$ = 7.2 Hz, 3H), 1.55 (m, 1H), 1.90 (m, 1H), 2.31 (dt, $J_{H,H}$ = 2, 8 Hz, 2H), 2.49 (bs, 4H), 2.52 (m, 1H), 3.66 (s, 3H), 3.69 (t, $J_{H,H}$ = 4.4, 4H). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 17.4 (1C), 30.5 (1C), 37.9 (1C), 51.7 (1C), 53.8 (2C), 56.8 (1C), 67.1 (2C), 177.1 (1C). **ESI-HRMS:** Calculated for $C_{10}H_{19}NO$. Exact: (M: 201.1365, M+H: 202.1443); Experimental: (M+H: 202.1435).

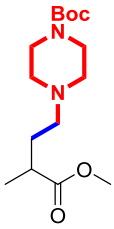
Methyl 4-(benzyl(methyl)amino)-2-methylbutanoate (6b)



General procedure B was followed employing **1a** (53.5 µL, 0.5 mmol) and N-Benzylmethylamine (66.5 µL, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (3:1) afforded **6b** (57 mg, 50%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.12 (d, $J_{H,H}$ = 7.2 Hz, 3H), 1.59 (m, 1H), 1.94 (m, 1H), 2.17 (s, 3H), 2.37 (t, $J_{H,H}$ = 6.8 Hz, 2H), 2.55 (m, 1H), 3.47 (bs, 2H), 3.64 (s, 3H), 7.24-7.31 (m, 5H, *Ar*). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 17.3 (1C), 31.4 (1C), 37.5 (1C), 42.2 (1C), 51.7 (1C), 55.0 (1C), 62.6 (1C), 112.7-148.1 (6C, *Ar*) 177.4 (1C). **ESI-HRMS:** Calculated for $C_{14}H_{21}NO_2$. Exact: (M: 235.1572, M+H: 236.1651); Experimental: (M+H: 236.1647).

Methyl 4-(*tert*-butyl piperazine-1-carboxylate)-2-methylbutanoate (6c)

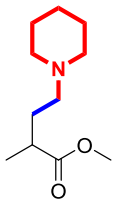


General procedure B was followed employing **1a** (53.5 µL, 0.5 mmol) and N-Boc-piperazine (93.1 mg, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (2:1) afforded **6c** (75.1 mg, 50%) as colorless oil. The enantiomeric excess was determined to be 69 % by UPC^2 analysis on a Daicel Chiralpak IG column with a gradient 90:10 CO_2/MeOH with 0.1% of diethylamine as additive, flow rate 2mL/min, λ = 230 nm: $t_{r\ minor}$ = 2.2 min, $t_{r\ major}$ = 2.3 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.16 (d, $J_{H,H}$ = 7.2 Hz, 3H), 1.45 (s, 9H), 1.57 (m, 1H), 1.91 (m, 1H), 2.33 (m, 6H), 2.50 (m, 1H), 3.40 (t, $J_{H,H}$ = 4.8 Hz, 4H), 3.66

(s, 3H). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 17.3 (1C), 28.4 (3C), 30.6 (1C), 37.8 (1C), 43.0 (2C), 51.6 (1C), 52.9 (2C), 56.2 (1C), 79.6 (1C), 154.7(1C), 176.9 (1C). **ESI-HRMS:** Calculated for $C_{15}H_{28}N_2O_4$. Exact: (M: 300.2049, M+H: 301.2127); Experimental: (M+H: 301.2126).

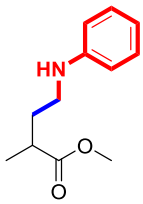
Methyl 2-methyl-4-(piperidin-1-yl)butanoate (6d)



General procedure B was followed employing **1a** (53.5 µL, 0.5 mmol) and piperidine (49.5 µL, 0.5 mmol). Purification by flash chromatography eluting with Et_2O afforded **6d** (50 mg, 50%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.15 (d, $J_{H,H}$ = 7.2 Hz, 3H), 1.44 (bs, 2H), 1.56 (m, 5H), 1.90 (m, 1H), 2.25 (m, 2H), 2.34 (bs, 4H), 2.45 (m, 1H), 3.66 (s, 3H). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 17.2 (1C), 24.4 (1C), 25.9 (2C), 30.9 (1C), 37.9 (1C), 51.5 (1C), 54.6 (1C), 57.0 (2C), 177.1 (1C). **ESI-HRMS:** Calculated for $C_{21}H_{21}NO_2$. Exact: (M: 199.1572, M+H: 200.1651); Experimental: (M+H: 200.1660).

Methyl 2-methyl-4-(phenylamino)butanoate (6e)

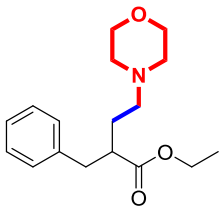


General procedure C was followed employing **1a** (53.5 µL, 0.5 mmol) and aniline (46 µL, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (2:1) afforded **6e** (19 mg, 19%) as colorless oil. The enantiomeric excess was determined to be 60% by UPC[2] analysis on a Daicel Chiralpak IA column with a gradient 95:05 CO_2/EtOH with 0.1% of diethylamine as additive, flow rate 3mL/min, λ = 240 nm: $t_{r\ minor}$ = 1.2 min, $t_{r\ major}$ = 1.1 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.21 (d, $J_{H,H}$ = 7.2 Hz, 3H), 1.76 (m, 1H), 1.99 (m, 1H), 2.61 (m, 1H), 3.16 (t, $J_{H,H}$ = 7.2 Hz, 2H), 3.68 (s, 3H), 6.59 (m, 2H, *Ar*), 6.7 (tt, $J_{H,H}$ = 7.2, 1.2 Hz, 1H, *Ar*), 7.18 (m, 2H, *Ar*). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 17.3 (1C), 33.3 (1C), 37.4 (1C), 41.8 (1C), 51.7 (1C), 112.7-148.1

(6C, *Ar*), 176.9 (1C). **ESI-HRMS:** Calculated for $C_{12}H_{17}NO_2$. Exact: (M: 207.1259, M+H: 208.1338); Experimental: (M+H: 208.1331).

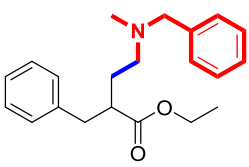
Ethyl 2-benzyl-4-morpholinobutanoate (6f)



General procedure B was followed employing **1b** (95 mg, 0.5 mmol) and morpholine (44 µL, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (1:2) afforded **6f** (70 mg, 48%) as colorless oil. The enantiomeric excess was determined to be 75 % by UPC^2 analysis on a Daicel Chiralpak IG column with a gradient 95:05 CO_2/Methanol with 0.1% of diethylamine as additive, flow rate 2mL/min, λ = 210 nm: $t_{r\ minor}$ = 4.7 min, $t_{r\ major}$ = 3.9 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.08 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.56 (m, 1H), 1.80 (m, 1H), 2.27 (m, 6H), 2.65 (m, 2H), 2.87 (m, 1H), 3.59 (m, 4H), 4.0 (m, 2H), 7.08-7.22 (m, 5H, *Ar*). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 14.2 (1C), 28.5 (1C), 38.7 (1C), 45.9 (1C), 53.7 (2C), 56.8 (1C), 60.3 (1C), 67.0 (2C), 126.4-139.4 (6C, *Ar*), 175.4 (1C). **ESI-HRMS:** Calculated for $C_{17}H_{25}NO_3$. Exact: (M: 291.1834, M+H: 292.1913); Experimental: (M+H: 292.1907).

Ethyl 2-benzyl-4-(benzyl(methyl)amino)butanoate (6g)

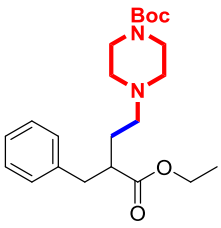


General procedure B was followed employing **1b** (95 mg, 0.5 mmol) and N-benzylmethylamine (66.5 µL, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (4:1) afforded **6g** (58 mg, 37%) as colorless oil. The enantiomeric excess was determined to be 69 % by UPC^2 analysis on a CEL2 column with a gradient 98:02 CO_2/Methanol with 0.1% of diethylamine as additive, flow rate 2mL/min, λ = 210 nm: $t_{r\ minor}$ = 5.7 min, $t_{r\ major}$ = 4.9 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.04 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.61 (m, 1H), 1.81 (m, 1H), 2.05 (s, 3H), 2.29 (m, 2H), 2.68 (m, 2H), 2.84 (m, 1H), 3.36 (bs, 2H),

3.94 (q, $J_{H,H}$ = 7.2 Hz, 2H), 7.07-7.23 (m, 10H, *Ar*). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 14.2 (1C), 29.4 (1C), 38.6 (1C), 42.0 (1C), 45.5 (1C), 55.0 (1C), 60.2 (1C), 62.5 (1C), 126.3-139.3 (12C, *Ar*), 175.5 (1C). **ESI-HRMS:** Calculated for $C_{21}H_{27}NO_2$. Exact: (M: 325.2042, M+H: 326.2120); Experimental: (M+H: 326.2116).

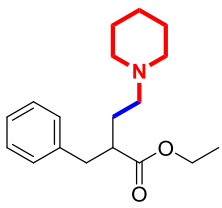
Tert-butyl 4-(3-benzyl-4-ethoxy-4-oxobutyl)piperazine-1-carboxylate (6h)



General procedure B was followed employing **1b** (95 mg, 0.5 mmol) and N-Boc-piperazine (94 mg, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (1:1) afforded **6h** (97 mg, 50%) as colorless oil. The enantiomeric excess was determined to be 71 % by UPC[2] analysis on a Daicel Chiralpak IG column with a gradient 85:15 CO_2/Methanol, flow rate 2mL/min, λ = 205 nm: $t_{r\ minor}$ = 2.5 min, $t_{r\ major}$ = 2.7 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.07 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.38 (s, 9H), 1. 60 (m, 1H), 1.80 (m, 1H), 2.24 (m, 6H), 2.64 (m, 2H), 2.88 (dd, $J_{H,H}$ = 13.2, 7.6 Hz, 1H), 3.30 (m, 4H), 3.99 (m, 2H), 7.08-7.20 (m, 5H, *Ar*). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 14.2 (1C), 28.4 (3C), 28.7 (1C), 38.7 (1C), 45.9 (2C), 52.9 (2C), 56.4 (1C), 60.3 (1C), 79.6 (1C), 126.4-139.1 (6C, *Ar*), 154.8 (1C), 175.4 (1C). **ESI-HRMS:** Calculated for $C_{22}H_{34}NO_2$. Exact: (M: 390.2519, M+H: 391.2597); Experimental: (M+H: 391.2596).

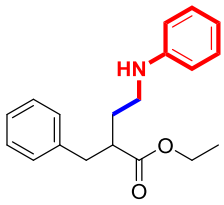
Ethyl 2-benzyl-4-(piperidin-1-yl)butanoate (6i)



General procedure B was followed employing **1b** (95 mg, 0.5 mmol) and piperidine (49.5 µL, 0.5 mmol). Purification by flash chromatography with Al_2O_3 eluting with pentane/Et_2O (20:1) afforded **6i** (40 mg, 28%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.07 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.33 (m, 2H), 1.47 (m, 4H), 1.67 (m, 1H), 1.82 (m, 1H), 2.21 (m, 6H), 2.59 (m, 1H), 2.68 (dd, $J_{H,H}$ = 13.2, 6.8 Hz, 1H), 2.68 (dd, $J_{H,H}$ = 13.6, 8.4 Hz, 1H), 3.98 (q, $J_{H,H}$ = 7.2 Hz, 2H), 7.08-7.21 (m, 5H, *Ar*). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 14.2 (1C), 24.4 (1C), 25.9 (2C), 29.0 (1C), 38.7 (1C), 46.1 (1C), 54.6 (2C), 57.1 (1C), 60.2 (1C), 126.2-139.2 (6C, *Ar*), 175.4 (1C). **ESI-HRMS:** Calculated for $C_{18}H_{27}NO_2$. Exact: (M: 289.2042, M+H: 290.2120); Experimental: (M+H: 290.2119).

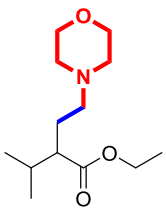
Ethyl 2-benzyl-4-(phenylamino)butanoate (6j)



General procedure C was followed employing **1b** (95 mg, 0.5 mmol) and aniline (46.0 µL, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (4:1) afforded **6j** (26 mg, 18%) as colorless oil. The enantiomeric excess was determined to be 66 % by UPC^2 analysis on a Daicel Chiralpak IA column with a gradient 90:10 CO_2/Methanol, flow rate 3mL/min, λ = 241 nm: $t_{r\ minor}$ = 1.5 min, $t_{r\ major}$ = 1.7 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.14 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.81 (m, 1H), 1.97 (m, 1H), 2.77 (m, 2H), 3.01 (m, 1H), 3.15 (m, 2H), 4.06 (q, $J_{H,H}$ = 7.2 Hz, 3H), 6.55 (d, $J_{H,H}$ = 8.4 Hz, 2H, *Ar*), 6.67 (t, $J_{H,H}$ = 7.2 Hz, 1H, *Ar*), 7.14-7.30 (m, 7H, *Ar*). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 14.2 (1C), 31.4 (1C), 38.6 (1C), 42.0 (1C), 45.5 (1C), 60.5 (1C), 112.7-148.0 (12C, *Ar*), 175.3 (1C). **ESI-HRMS:** Calculated for $C_{19}H_{23}NO_2$. Exact: (M: 297.1729, M+H: 298.1807); Experimental (M+H: 298.1802).

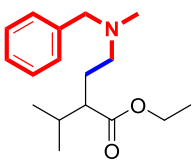
Ethyl 2-isopropyl-4-morpholinobutanoate (6k)



General procedure B was followed employing **1c** (71 mg, 0.5 mmol) and morpholine (44 µL, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (1:1) afforded **6k** (117 mg, 96%) as colorless oil. The enantiomeric excess was determined to be 84% by UPC[2] analysis on a Daicel Chiralpak IG column with a gradient 95:5 CO_2/Acetonitrile with 0.1% of diethylamine as additive, flow rate 2mL/min, λ = 230 nm: $t_{r\ minor}$ = 1.8 min, : $t_{r\ major}$ = 1.7 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.92 (t, $J_{H,H}$ = 6.8 Hz, 6H), 1.26 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.65 (m, 1H), 1.82 (m, 2H), 2.11 (m, 1H) 2.26 (m, 2H), 2.41 (bs, 4H), 3.68 (t, $J_{H,H}$ = 4.8 Hz, 4H), 4.14 (m, 2H). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 14.5 (1C), 20.3 (1C), 20.5 (1C), 26.4 (1C), 30.9 (1C), 51.0 (1C), 53.9 (2C), 57.6 (1C), 60.1 (1C), 67.1 (2C), 175.6 (1C). **ESI-HRMS:** Calculated for $C_{13}H_{25}NO_3$. Exact: (M: 243.1834, M+H: 244.1913); Experimental: (M+H: 244.1907).

Ethyl 4-(benzyl(methyl)amino)-2-isopropylbutanoate (6l)

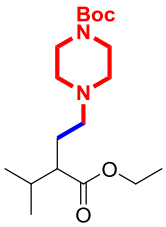


General procedure B was followed employing **1c** (71 mg, 0.5 mmol) and N-benzylmethylamine (66.5 µL, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (1:3) afforded **6l** (98 mg, 70%) as colorless oil. The enantiomeric excess was determined to be >80% by ^{1}H NMR using $Eu(hfc)_3$.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.92 (t, $J_{H,H}$ = 7.2 Hz, 6H), 1.23 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.69 (m, 1H), 1.81 (m, 1H), 1.86 (m, 1H), 2.15 (s, 3H), 2.19 (m, 1H), 2.29 (m, 1H), 2.37 (m, 1H), 3.40 (d, $J_{H,H}$ = 12.8 Hz, 1H), 3.50 (d, $J_{H,H}$ = 12.8 Hz, 1H), 4.09 (m, 2H), 7.26-7.30 (m, 5H, *Ar*). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 14.3 (1C), 20.1 (1C), 20.4 (1C), 27.1 (1C), 30.7 (1C), 42.0 (1C) 50.4 (1C), 55.7 (1C), 59.9 (1C), 62.5 (1C), 126.8-139.1 (6C, *Ar*), 175.5 (1C). **ESI-HRMS:**

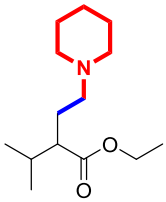
Calculated for $C_{17}H_{27}NO_2$. Exact: (M: 277.2042, M+H: 278.2120); Experimental: (M+H: 278.2115).

Tert-butyl 4-(3-(ethoxycarbonyl)-4-methylpentyl)piperazine-1-carboxylate (6m)



General procedure B was followed employing **1c** (71 mg, 0.5 mmol) and N-Boc-piperazine (93.1 mg, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (1:1) afforded **6m** (94 mg, 55%) as colorless oil The enantiomeric excess was determined to be >90% by ^{1}H NMR using Eu(hfc)$_3$. **^{1}H NMR** (400 MHz, $CDCl_3$) δ: 0.91 (t, $J_{H,H}$ = 7.2 Hz, 6H), 1.25 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.44 (s, 9H), 1.63 (m, 1H), 1.83 (m, 1H), 2.12 (m, 1H), 2.23 (m, 1H), 2.30 (m, 1H), 2.34 (bs, 4H), 3.39 (t, $J_{H,H}$ = 4.8 Hz, 4H), 4.13 (m, 2H). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 14.5 (1C), 20.2 (1C), 20.5 (1C), 26.5 (1C), 28.4 (3C), 30.7 (1C), 43.1 (1C), 43.8 (1C), 50.9 (1C), 53.0 (2C), 57.0 (1C), 59.9 (1C), 79.5 (1C),154.7 (1C), 175.4 (1C). **ESI-HRMS:** Calculated for $C_{18}H_{34}N_2O_4$. Exact: (M: 342.2519, M+H: 343.2597); Experimental: (M+H: 343.2595).

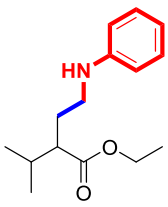
Ethyl 2-isopropyl-4-(piperidin-1-yl)butanoate (6n)



General procedure B was followed employing **1c** (71 mg, 0.5 mmol) and piperidine (49.5 µL, 0.5 mmol). Purification by flash chromatography eluting with Et_2O afforded the **6n** (111 mg, 92%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.92 (dd, $J_{H,H}$ = 8, 6.8 Hz, 6H), 1.26 (t, $J_{H,H}$ = 6.8 Hz, 3H), 1.41 (m, 2H), 1.55 (m, 4H), 1.68 (m, 2H), 1.84 (m, 1H)6, 2.09 (m, 1H), 2.18 (m, 1H), 2.30 (m, 1H), 2.34 (bs, 4H), 4.13 (m, 2H). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 14.4 (1C), 20.1 (1C), 20.5 (1C), 24.4 (1C), 26.0 (2C), 26.8 (1C), 30.8 (1C), 51.2 (1C), 54.7 (2C), 57.8 (1C), 59.9 (1C), 175.6 (1C). **ESI-HRMS:** Calculated for $C_{14}H_{27}NO_2$. Exact: (M: 241.2042, M+H: 242.2120); Experimental: (M+H: 242.2109).

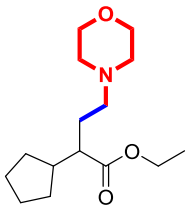
Ethyl 2-isopropyl-4-(phenylamino)butanoate (6o)



General procedure C was followed employing **1c** (71 mg, 0.5 mmol) and aniline (46 µL, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (1:1) afforded **6o** (68.7 mg, 55%) as colorless oil. The enantiomeric excess was determined to be 77% by UPC[2] analysis on a Daicel Chiralpak IG column with a gradient 85:15 CO_2/Acetonitrile with 0.1% of diethylamine as additive, flow rate 3 mL/min, λ = 243 nm: $t_{r\ minor}$ = 2.3 min, $t_{r\ major}$ = 1.8 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.93 (dd, $J_{H,H}$ = 6.6, 2.4, 6H), 1.25 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.81 (m, 1H), 1.93 (m, 2H), 2.23 (m, 1H), 3.10 (m, 2H), 4.14 (m, 2H), 6.58 (m, 2H, *Ar*), 6.59 (tt, $J_{H,H}$ = 7.2, 1.2 Hz, 1H, *Ar*), 7.16 (m, 2H, *Ar*). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 14.5 (1C), 20.2 (1C), 20.5 (1C), 29.2 (1C), 30.9 (1C), 42.7 (1C), 50.6 (1C), 60.4 (1C) 112.8-148.2 (6C, *Ar*), 175.6 (1C). **ESI-HRMS:** Calculated for $C_{15}H_{23}NO_2$. Exact: (M: 249.1729, M+H: 250.1807); Experimental: (M+H: 250.1796).

Ethyl 2-cyclopentyl-4-morpholinobutanoate (6p)

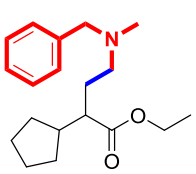


General procedure B was followed employing **1d** (84.1 mg, 0.5 mmol) and morpholine (44 µL, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (1:1) afforded **6p** (101 mg, 75%) as colorless oil. The enantiomeric excess was determined to be 85% by UPC[2] analysis on a Daicel Chiralpak IG column with a gradient 96:4 CO_2/MeOH with 0.1% of diethylamine as additive, flow rate 2 mL/min, λ = 230 nm: $t_{r\ minor}$ = 3.7 min, $t_{r\ major}$ = 3.5 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.14 (tt, $J_{H,H}$ = 6.8, 2Hz, 1H), 1.22 (t, $J_{H,H}$ = 7.2 Hz, 1H), 1.26 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.50-1.69 (m, 6H), 1.82 (m, 2H), 1.96 (m, 1H), 2.12 (m, 1H), 2.22 (m, 1H), 2.31 (m, 1H), 2.40 (bs, 4H), 3.68 (bs, 4H), 4.13 (m, 2H). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 14.5 (1C), 25.1 (1C), 28.6 (1C),

30.8 (1C), 31.0 (1C), 43.0 (1C), 50.0 (1C), 53.9 (2C), 54.1 (1C), 57.4 (1C), 60.1 (1C), 67.1 (2C), 176.0 (1C). **ESI-HRMS:** Calculated for $C_{15}H_{27}NO_3$. Exact: (M: 269.1991, M+H: 270.2069); Experimental: (M+H: 270.2065).

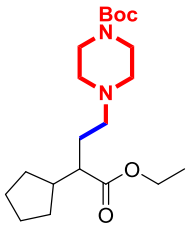
Ethyl 4-(benzyl(methyl)amino)-2-cyclopentylbutanoate (6q)



General procedure B was followed employing **1d** (84.1 mg, 0.5 mmol) and morpholine N-benzylmethylamine (66.5 µL, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (1:1) afforded **6q** (82 mg, 55%) as colorless oil.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.14 (m, 2H), 1.22 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.50-1.83 (m, 8H), 1.97 (m, 1H), 2.14 (s, 3H), 2.25 (m, 2H), 2.39 (m, 1H), 3.41 (d, $J_{H,H}$ = 12.8 Hz, 1H), 3.50 (d, $J_{H,H}$ = 12.8 Hz, 1H), 4.10 (m, 2H), 7.22-7.31 (m, 5H, *Ar*). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 14.4 (1C), 25.1 (2C), 29.4 (1C), 30.7 (1C), 31.0 (1C), 42.1 (1C) 43.0 (1C), 49.5 (1C), 55.7 (1C), 60.0 (1C), 62.6 (1C), 127.0-139.3 (6C, *Ar*), 176.0 (1C). **ESI-HRMS:** Calculated for $C_{19}H_{29}NO_3$. Exact: (M: 303.2198, M+H: 304.2277); Experimental: (M+H: 304.2280).

Tert-butyl 4-(3-cyclopentyl-4-ethoxy-4-oxobutyl)piperazine-1-carboxylate (6r)

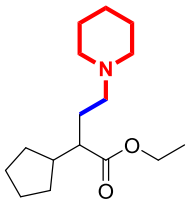


General procedure B was followed employing **1d** (84.1 mg, 0.5 mmol) and 1-Boc-piperazine (93.1 mg, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (4:1) afforded **6r** (136.4 mg, 74%) as colorless oil. The enantiomeric excess was determined to be 84% by UPC[2] analysis on a Daicel Chiralpak IG column with a gradient 90:10 CO_2/MeOH with 0.1% of diethylamine as additive, flow rate 2 mL/min, λ = 230 nm: $t_{r\ minor}$ = 3.2 min, $t_{r\ major}$= 3.7 min.

^{1}H NMR (400 MHz, CD_2Cl_2) δ: 1.03 (m, 1H), 1.15 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.15 (m, 1H), 1.35 (s, 9H), 1.43 (m, 6H), 1.51 (m, 2H), 1.85 (m, 1H), 2.14 (m, 1H), 2.25 (m, 2H), 2.33 (m, 4H), 2.45 (m, 1H), 3.39 (m, 4H), 4.10(m, 2H). **^{13}C NMR**

(100.6 MHz, CD_2Cl_2) δ:14.2 (1C), 15.9 (1C), 25.0 (1C), 28.1 (3C), 28.6 (1C), 30.5 (1C), 30.8 (1C), 42.9 (2C), 49.9 (1C), 53.0 (2C), 56.8 (1C), 60.0 (1C), 64.7 (1C), 79.7 (1C), 154.5 (1C), 175.6 (1C). **ESI-HRMS:** Calculated for $C_{20}H_{37}N_2O_4$. Exact: (M: 368.2675, M+H: 369.2753); Experimental: (M+H: 369.2696).

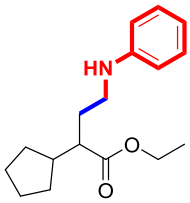
Ethyl 2-cyclopentyl-4-(piperidin-1-yl)butanoate (6s)



General procedure B was followed employing **1d** (84.1 mg, 0.5 mmol) and piperidine (49.5 µL, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (1:1) afforded **6s** (67 mg, 50%) as colorless oil. The enantiomeric excess was determined to be 84% by UPC[2] analysis on a Daicel Chiralpak IC column with a gradient 90:10 CO_2/EtOH, with 0.1% of diethylamine as additive, flow rate 2 mL/min, λ = 230 nm: $t_{r\ minor}$ = 3.5 min, $t_{r\ major}$ = 3.8 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.15 (m, 2H), 1.24 (m, 1H), 1.25 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.43 (bs, 2H), 1.51 (m, 2H), 1.60 (bs, 7H), 1.84 (m, 3H), 1.96 (m, 1H), 2.13 (td, $J_{H,H}$ = 10, 3.6 Hz, 1H), 2.24 (m, 1H), 2.40 (bs, 4H), 4.13 (m, 2H). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ:14.5 (1C), 24.5 (1C), 25.1 (1C), 25.9 (2C), 28.8 (1C), 30.8 (1C), 30.9 (1C) 43.0 (2C), 50.1 (1C), 54.7 (2C), 57.6 (1C), 60.0 (1C), 175.8 (1C). **ESI-HRMS:** Calculated for $C_{16}H_{29}NO_2$. Exact: (M: 267.2198, M+H: 268.2277); Experimental: (M+H: 268.2285).

Ethyl 2-cyclopentyl-4-(piperidin-1-yl) butanoate (6t)

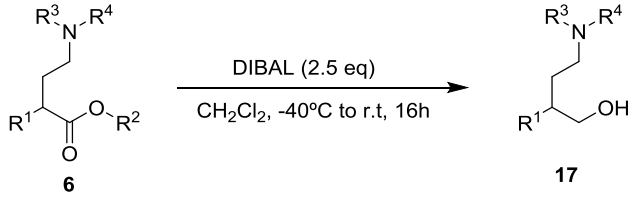


General procedure C was followed employing **1d** (84.1 mg, 0.5 mmol) and aniline (46.0 µL, 0.5 mmol). Purification by flash chromatography eluting with pentane/Et_2O (1:1) afforded **6t** (68.9 mg, 50%) as colorless oil. The enantiomeric excess was determined to be 84% by UPC^2 analysis on a Daicel Chiralpak IG column with a gradient 80:20 CO_2/MeOH, with 0.1% of diethylamine as additive, flow rate 3 mL/min, λ = 243 nm: $t_{r\ minor}$ = 3.4 min, $t_{r\ major}$ = 2.8 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 1.11 (m, 1H), 1.20 (m, 1H), 1.24 (t, $J_{H,H}$ = 7.2 Hz, 3H), 1.56 (m, 6H), 1.84 (m, 3H), 2.01 (m, 1H), 2.26 (m, 1H), 3.11 (m, 2H), 4.14 (q, $J_{H,H}$ = 7.2 Hz, 2H), 6.59 (m, 2H, *Ar*), 6.69 (t, $J_{H,H}$ = 7.6 Hz, 1H, *Ar*), 7.16 (m, 2H, *Ar*). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ:14.3 (1C), 25.0 (2C), 30.7 (1C), 30.8 (1C), 31.2 (1C), 42.4 (1C), 42.8 (1C), 49.5 (1C), 60.3 (1C), 112.8-148.1 (6C, *Ar*), 175.9 (1C). **ESI-HRMS:** Calculated for $C_{17}H_{25}NO_2$. Exact: (M: 275.1885, M+H: 276.1964); Experimental: (M+H: 276.1962).

SVI. Reduction of γ-aminobutyric esters to alcohols

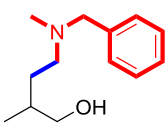
General procedure D: reduction of α-alkyl-γ-aminobutyric esters 6 into the corresponding aminoalcohols 17



Diisobutylaluminum hydride (DIBAL) solution 1.0 M in DCM (2.5 eq) was added dropwise to a solution of the corresponding amino ester **6** (1 eq) in CH_2Cl_2 (2.0 mL) at -40°C. The reaction was left stirring at -40°C for 1h, then

allowed to reach room temperature and left stirring overnight. The reaction was quenched by addition of NH_4Cl sat. solution (2 mL) at 0°C and the mixture was left stirring for 2h. Then, the aqueous phase was extracted with CH_2Cl_2 (3 x 2 mL), the organic phases were dried with $MgSO_4$, filtrated and concentrated under vacuum. The residue was finally purified by chromatographic column using Al_2O_3 to afford the corresponding **17**.

4-(benzyl(methyl)amino)-2-methylbutan-1-ol (17a)

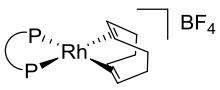


General procedure D was followed employing **6c** (31 mg, 0.13 mmol) and DIBAL (325 µL, 0.33 mmol). Purification by flash chromatography eluting with CH_2Cl_2 and 1% of MeOH afforded **17a** (26 mg, 95 %) as colorless oil. The enantiomeric excess was determined to be 62% by HPLC analysis on a Chiralpack IG column with a gradient 95:05 CO_2/MeOH, with 0.1% of diethylamine as additive, flow rate 2 mL/min, λ = 210 nm: $t_{r\ minor}$ = 7.4 min, $t_{r\ major}$ = 7.7 min.

^{1}H NMR (400 MHz, $CDCl_3$) δ: 0.86 (d, $J_{H,H}$ = 6.8 Hz, 3H), 1.55 (m, 1H), 1.64 (m, 1H), 1.75 (m, 1H), 2.13 (s, 3H), 2.43 (m, 1H), 2.52 (m, 1H), 3.29 (dd, $J_{H,H}$ = 11.4, 8.4 Hz, 1H), 3.47 (d, $J_{H,H}$ = 12.4 Hz, 1H), 3.51 (dd, $J_{H,H}$ = 11.6, 1.2 Hz, 2H), 3.56 (d, $J_{H,H}$ = 12.4 Hz, 1H), 7.27 (m, 5H, *Ar*). **^{13}C NMR** (100.6 MHz, $CDCl_3$) δ: 18.3 (1C), 34.0 (1C), 36.9 (1C), 41.1 (1C), 56.5 (1C), 62.7 (1C), 68.7 (1C), 127.5-137.4 (6C, *Ar*). **ESI-HRMS:** Calculated for $C_{13}H_{22}NO$. Exact: (M: 207.1623, M+H: 208.1701); Experimental: (M+H: 208.1698).

SVII. Synthesis and characterization of Rhodium complexes

[Rh(COD)(L1)]BF_4 (7)



Bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate (40 mg, 0.1 mmol) was dissolved in anhydrous dichloromethane (5 mL) and cooled to -20 °C. Then, (*R,R*)-QuinoxP* **L1** (33.4 mg, 0.1 mmol) in anhydrous dichloromethane (5 mL) was added dropwise for 30 min. The

reaction was left stirring at -20 °C for 1h and then left stirring at room temperature for another 1h. After that, the crude was concentrated under vacuum, and the complex was precipitated with anhydrous diethyl ether at 0°C. The precipitated was filtrated, and washed with anhydrous hexane to afford the desired complex **7** (49 mg, 78 %) as orange solid.

^{1}H NMR (400 MHz, CD_2Cl_2) δ: 1.10 (d, $J_{P,H}$ = 15.2 Hz, 18H), 1.86 (d, $J_{P,H}$ = 8.0 Hz, 6H), 2.23 (m, 4H), 2.56 (m, 2H), 2.67 (m, 2H), 5.03 (m, 2H), 6.12 (m, 2H), 7.99 (dd, $J_{H,H}$ = 6.4, 3.2 Hz, 2H, *Ar*), 8.29 (dd, $J_{H,H}$ = 6.4, 3.2 Hz, 2H, *Ar*). **^{13}C NMR** (100.6 MHz, CD_2Cl_2) δ: 4.0 (t, $J_{P,C}$ = 10.3 Hz, 2C), 26.2 (2C), 28.4 (6C), 35.8 (2C), 38.4 (t, $J_{P,C}$ = 12.8 Hz, 2C), 92.4 (m, 2C), 107.2 (dt, $J_{Rh,C}$ = 7.8 Hz, $J_{P,C}$ = 2.2 Hz, 2C), 130.2-142.8 (6C, *Ar*), 154.4 (td, $J_{P,C}$ = 53.3 Hz, $J_{Rh,C}$ = 2.4 Hz, 2C*, Ar*). **^{31}P NMR** (161.97 MHz, CD_2Cl_2) δ: 41.6 (d, $J_{Rh,P}$ = 148.2 Hz, 2P). **ESI-HRMS:** Calculated for $C_{26}H_{40}N_2P_2Rh$. Exact: (M+: 545.1716); Experimental: (M+: 545.1715).

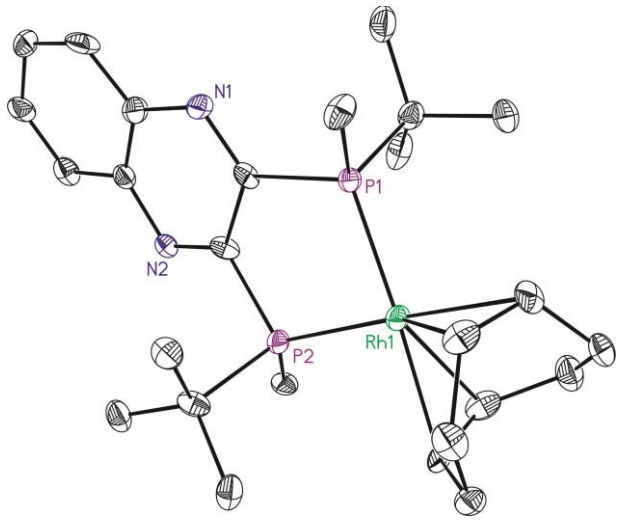
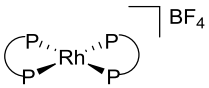


Figure S1: ORTEP drawing of the complex [Rh(COD)(**L1**)]BF_4 **7** (with ellipsoid at 50% probability). Solvent molecules, H, B and F atoms are omitted for clarity and only partial labelling scheme is illustrated.

Table S2: Selected bond lengths (Å) and angles (°) for complex **7**.

Bond lengths			
Rh-P(1)	2.258 (3)	Rh-C(20)	2.304 (11)
Rh-P(2)	2.267 (3)	Rh-C(23)	2.236 (10)
Rh-C(19)	2.204 (13)	Rh-C(24)	2.292 (10)
Angles			
P(1)-Rh-P(2)	85.43 (10)	C(20)-Rh-(C24)	86.8 (4)
C(19)-Rh-(C23)	95.9 (4)		

$[Rh(L1)_2]BF_4$ (8)



Bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate (40 mg, 0.1 mmol) was dissolved in anhydrous CH_2Cl_2 (2 mL). Then, (*R,R*)-QuinoxP* **L1** (100 mg, 0.3 mmol) in anhydrous dichloromethane (2 mL) was added dropwise, and the reaction was left stirring for 1h. After that, the crude was concentrated under vacuum, and the complex was precipitated with anhydrous diethyl ether at 0 °C. The precipitated was filtrated, and washed with anhydrous hexane to afford the desired complex **8** (73 mg, 85 %) as orange solid.

^{1}H NMR (400 MHz, CD_2Cl_2) δ: 1.07 (t, $J_{P,H}$ = 7.2 Hz, 36H), 2.23 (s, 12H), 7.99 (dd, $J_{H,H}$ = 6.4, 3.2 Hz, 4H, *Ar*), 8.32 (dd, $J_{H,H}$ = 6.4, 3.2 Hz, 4H, *Ar*). **^{13}C NMR** (100.6 MHz, CD_2Cl_2) δ: 9.5 (t, $J_{P,C}$ = 6.9 Hz, 4C), 28.4 (12C), 38.3 (t, $J_{P,C}$ = 6.4 Hz, 4C), 130.0-142.5 (12C, *Ar*), 155.8 (td, $J_{P,C}$ = 26.8 Hz, $J_{Rh,C}$ = 1.4 Hz, 4C, *Ar*). **^{31}P NMR** (161.97 MHz, CD_2Cl_2) δ: 38.9 (d, $J_{Rh,P}$ = 130.4 Hz, 2P). **ESI-HRMS:** Calculated for $C_{36}H_{56}N_4P_4Rh^+$. Exact: (M+: 771.2505); Experimental: (M+: 771.2539).

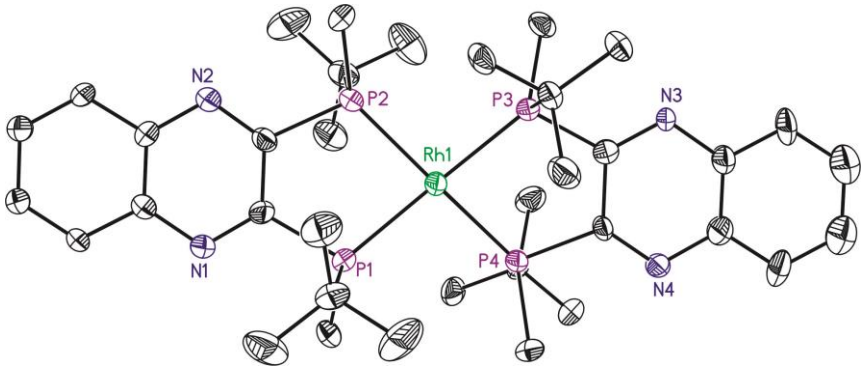
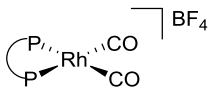


Figure S2: ORTEP drawing of the complex [Rh(**L1**)$_2$]BF$_4$ **8** (with ellipsoid at 50% probability). Solvent molecules, H, B and F atoms are omitted for clarity and only partial labelling scheme is illustrated.

Table S3: Selected bond lengths (Å) and angles (°) for complex **8**.

Bond lengths			
Rh-P(1)	2.317 (17)	Rh-P(3)	2.305(9)
Rh-P(2)	2.316 (17)	Rh-P(4)	2.294(9)
Angles			
P(1)-Rh-P(2)	84.79(6)	P(2)-Rh-P(4)	160.79(19)
P(1)-Rh-P(3)	163.5(2)	P(3)-Rh-P(4)	85.5(3)
P(1)-Rh-P(4)	98.15(19)		
P(2)-Rh-P(3)	97.02(2)		

[Rh(CO)$_2$(L1)]BF$_4$ (9)

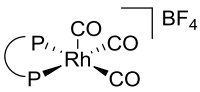


Complex [Rh(COD)(**L1**)]BF$_4$ **7** (20 mg, 0.035 mmol) was dissolved in anhydrous CH_2Cl_2 (5 mL). Then, CO was bubbled into the previous solution for 1h. After that, the solvent was evaporated under vacuum, and the residue was washed with Et_2O (3 x 1 mL) to afford the desired complex **9** (20 mg, 97 %) as yellow solid.

^{1}H NMR (400 MHz, CD_2Cl_2) δ: 1.24 (d, $J_{P,H}$ = 17.2 Hz, 18H), 2.13 (dd, $J_{P,H}$ = 10.0 Hz, $J_{Rh,H}$ = 1.2 Hz, 6H), 8.12 (dd, $J_{H,H}$ = 6.4, 3.6 Hz, 2H, *Ar*), 8.38 (dd, $J_{H,H}$ = 6.4, 3.6 Hz, 2H, *Ar*). **^{13}C NMR** (100.6 MHz, CD_2Cl_2) δ: 7.5 (t, $J_{P,C}$ = 13.5 Hz,

2C), 27.8 (6C), 36.5 (t, $J_{P,C}$ = 13.8 Hz, 2C) , 130.0-142.7 (6C, *Ar*), 152.3 (td, $J_{P,C}$ = 57.8 Hz, $J_{Rh,C}$ = 2.6 Hz, 2C, *Ar*), 184.6 (m, 2C, CO). **^{31}P NMR** (161.97 MHz, CD_2Cl_2) δ: 47.2 (d, $J_{Rh,P}$ = 114.7 Hz, 2P). **IR** (neat): *ν* (CO) = 2097, 2051 cm^{-1}

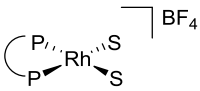
$[Rh(CO)_3(L1)]BF_4$ (10)



Bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate (6 mg, 0.015 mmol) dissolved in anhydrous dichloroethane (0.25 mL), and (*R,R*)-QuinoxP* **L1** (6 mg, 0.018 mmol) in anhydrous deuterated toluene (0.25 mL) were mixed inside a sapphire NMR tube inside the glovebox. Then, the tube was sealed and removed from the glovebox. After that, the tube was pressurized with 30 bar CO, heated at 90 ºC and the reaction was left stirring for 16h. After that, the crude was analysed by NMR.

^{1}H NMR (400 MHz, tol-d) δ: 0.95 (d, $J_{P,H}$ = 14.3 Hz, 18H), 1.81 (d, $J_{P,H}$ = 6.9 Hz, 6H), 7.72 (dd, $J_{H,H}$ = 6.4, 3.5 Hz, 2H, *Ar*), 8.09 (dd, $J_{H,H}$ = 6.4, 3.5 Hz, 2H, *Ar*). **^{13}C NMR** (100.6 MHz, tol-d) δ: 7.9 (m, 2C), 27.4 (m, 6C), 36.3 (m, 2C) , 126.2-142.7 (6C, *Ar*), 153.1 (t, $J_{P,C}$ = 57.8 Hz, 2C, *Ar*). **^{31}P NMR** (161.97 MHz, CD_2Cl_2) δ: 48.7 (d, $J_{Rh,P}$ = 116 Hz). **IR** (neat): *ν* (CO) = 2120, 2086, 2041 cm^{-1}

$[Rh(Solv.)_2(L1)]BF_4$ (11)



Bis(1,5-cyclooctadiene)rhodium(I) tetrafluoroborate (6 mg, 0.015 mmol) dissolved in anhydrous dichloroethane (0.25 mL), and (*R,R*)-QuinoxP* **L1** (6 mg, 0.018 mmol) in anhydrous deuterated toluene (0.25 mL) were mixed inside a sapphire NMR tube inside the glovebox. Then, the tube was sealed and removed from the glovebox. After that, the tube was pressurized with 8 bar H_2, and then the reaction was left stirring for 1h at room temperature. After that, the crude was analysed by NMR.

^{1}H NMR (400 MHz, tol-d) δ: 0.80 (d, $J_{P,H}$ = 15.3 Hz, 18H), 1.77 (d, $J_{P,H}$ = 8.5 Hz, 6H), 7.55 (dd, $J_{H,H}$ = 6.6, 3.5 Hz, 2H, *Ar*), 7.96 (dd, $J_{H,H}$ = 6.5, 3.5 Hz, 2H, *Ar*). **^{31}P NMR** (161.97 MHz, CD_2Cl_2) δ: 60.1 (d, $J_{Rh,P}$ = 200 Hz).

SVIII. Selected NMR and IR spectra from in situ HP NMR studies

A. [Rh(COD)$_2$]BF$_4$ in the presence of L1 under CO pressure

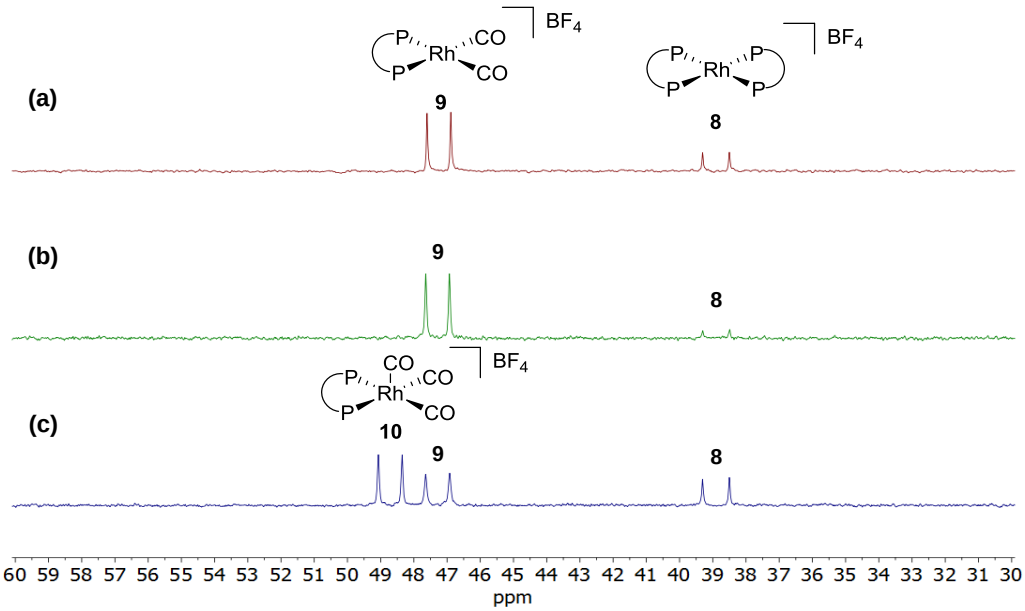


Figure S3: ^{31}P{^{1}H} NMR spectra of [Rh(COD)$_2$]BF$_4$ and **L1** in tol-d^{8}/DCE at variable CO pressures and temperatures: a) 10 bar of CO for 16h at room temperature, b) 30 bar CO for 96h at rt, c) 10 bar at rt for 16h, then 10 bar of CO at 90 °C for 16 h.

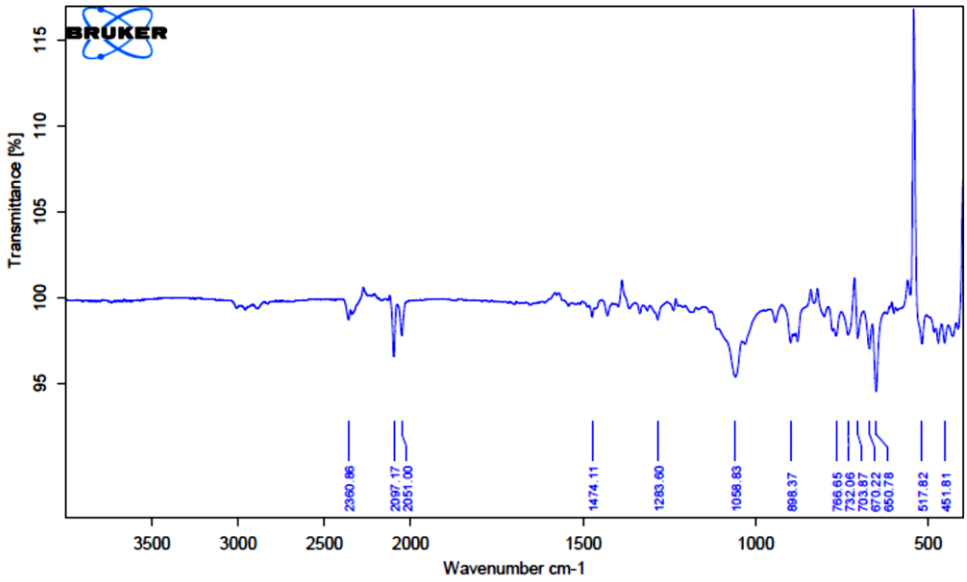


Figure S4: IR spectra of the resulting solution of mixing $[Rh(COD)_2]BF_4$ and **L1** in tol-d^8/DCE under 10 bar of CO for 16h at room temperature.

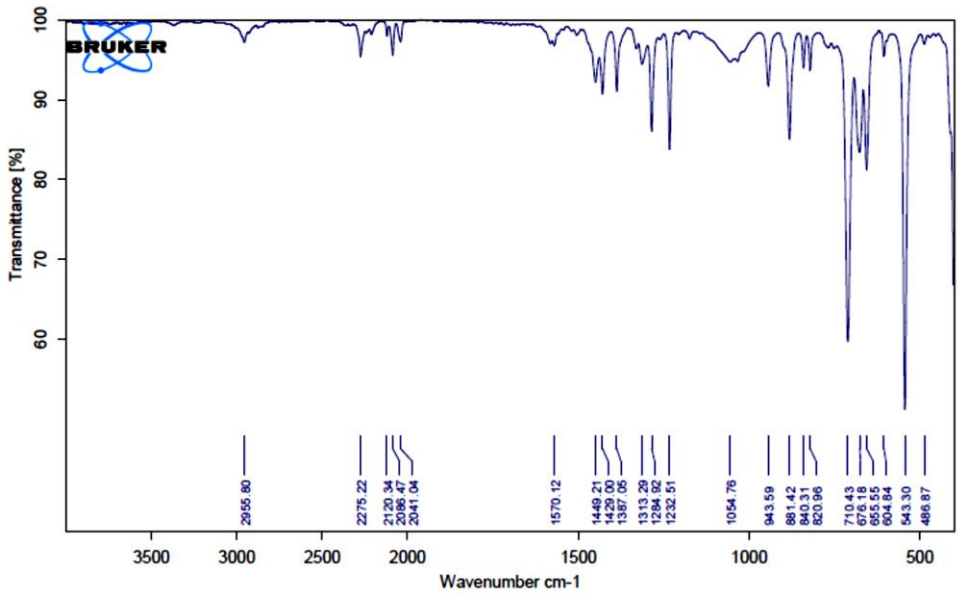


Figure S5: IR spectra of the resulting solution of mixing $[Rh(COD)_2]BF_4$ and **L1** in tol-d^8/DCE under 10 bar of CO for 16h at 90 °C.

B. [Rh(COD)$_2$]BF$_4$ in the presence of L1 under H$_2$ pressure

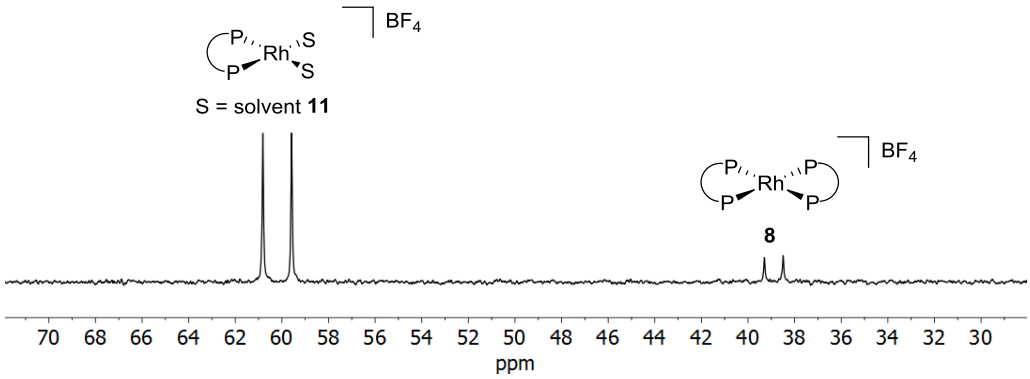


Figure S6: $^{31}P\{^{1}H\}$ NMR spectra of [Rh(COD)$_2$]BF$_4$ and **L1** in tol-d^8/DCE at 8 bar of H$_2$ at room temperature.

C. [Rh(COD)$_2$]BF$_4$ in the presence of L1 under H$_2$/CO pressure

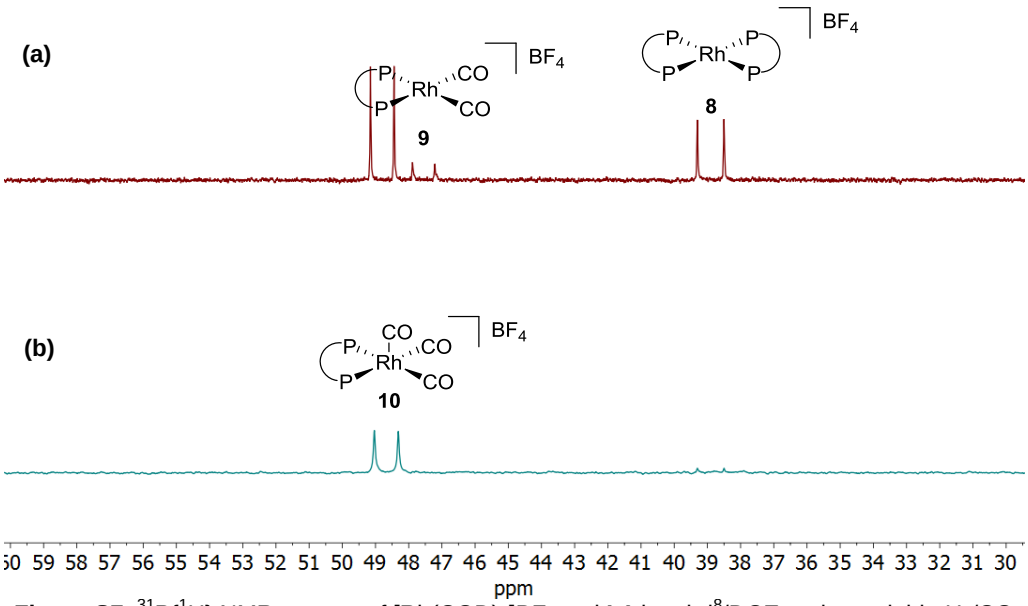


Figure S7: $^{31}P\{^{1}H\}$ NMR spectra of [Rh(COD)$_2$]BF$_4$ and **L1** in tol-d^8/DCE under variable H$_2$/CO pressures and at 90°C: a) 10 bar (H$_2$/CO, 4:1) for 24h, b) 20 bar (H$_2$/CO, 4:1) for 48 h.

D. Characterization of species 12 and 13

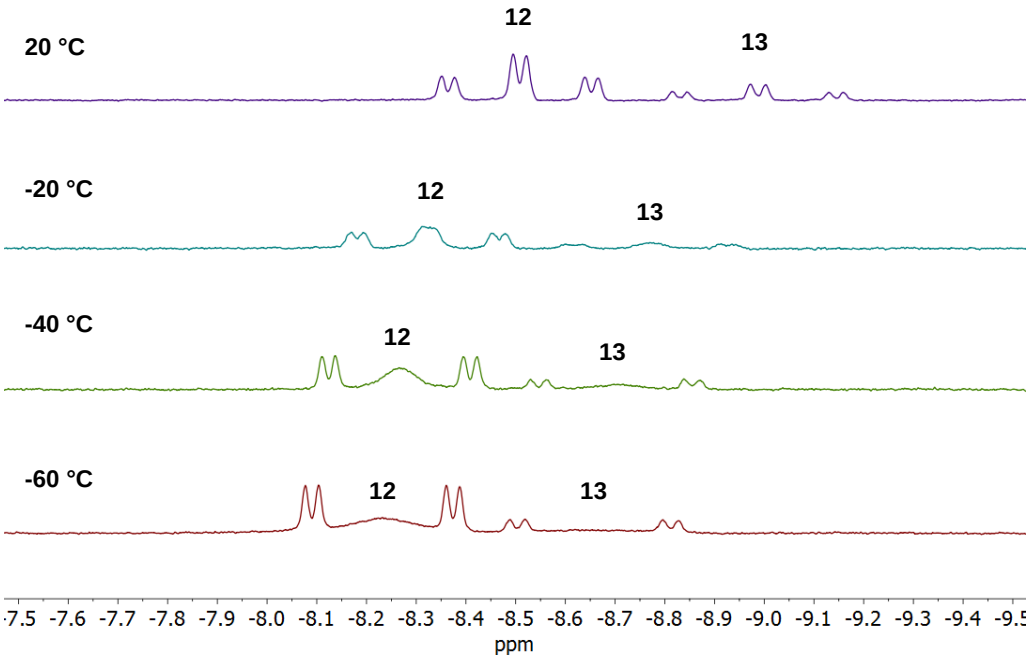


Figure S8: ^{1}H NMR spectra of [Rh(acac)(CO)$_2$] in the presence **L1** under 10 bar (H_2/CO, 4:1) and at 90°C for 16 h recorded at variable temperature.

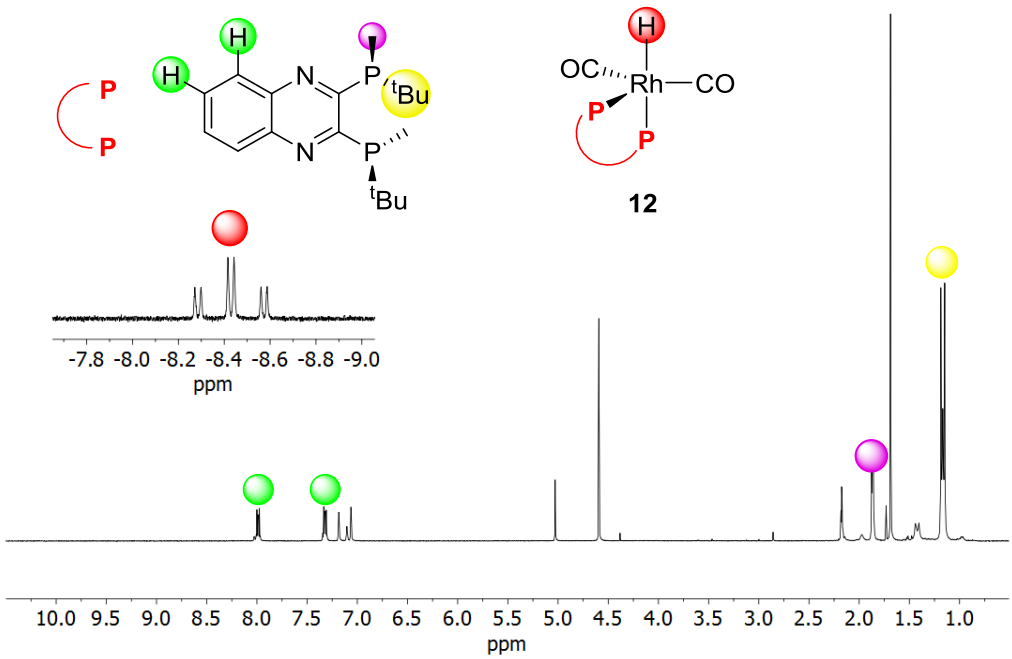


Figure S9: ^{1}H NMR spectra of [Rh(acac)(CO)$_2$] in the presence of **L1** under 10 bar (H_2/CO, 4:1) and at room temperature. Inset: hydride region.

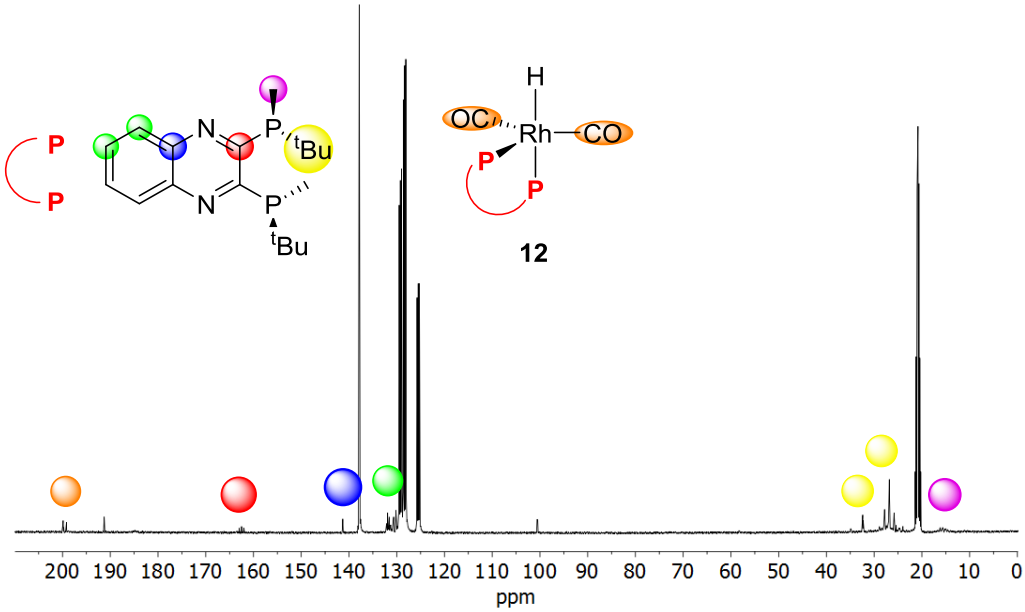


Figure S10: ^{13}C{^{1}H} NMR spectra of [Rh(acac)(CO)$_2$] in the presence of **L1** under 10 bar (H_2/CO, 4:1) and at room temperature for 16 h.

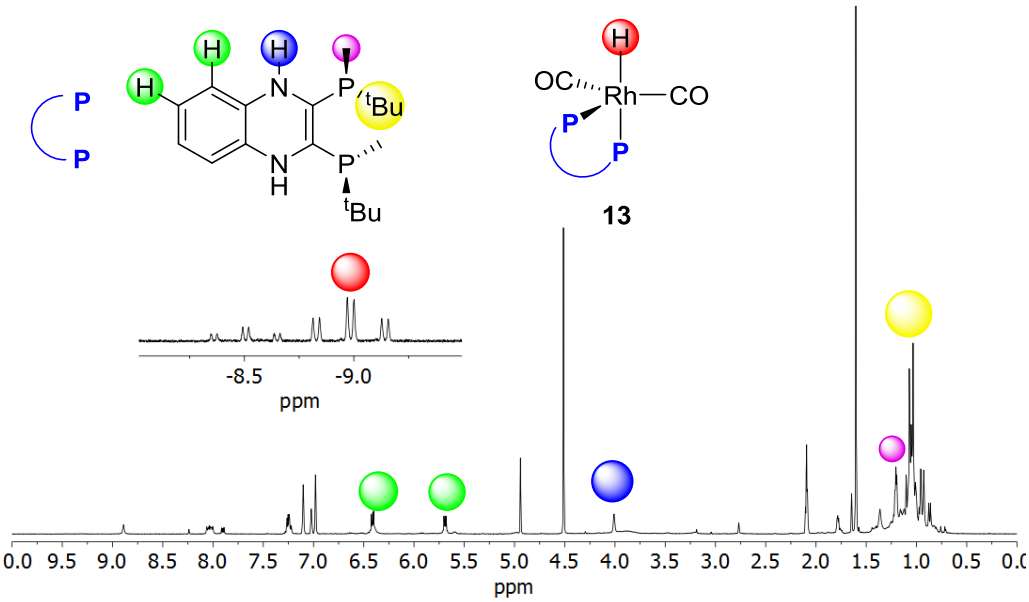


Figure S11: ^{1}H NMR spectra of [Rh(acac)(CO)$_2$] in the presence **L1** under 20 bar (H$_2$/CO, 4:1) and at 90°C for 16 h. Signals corresponding to species **13** emphasized. Inset: hydride region.

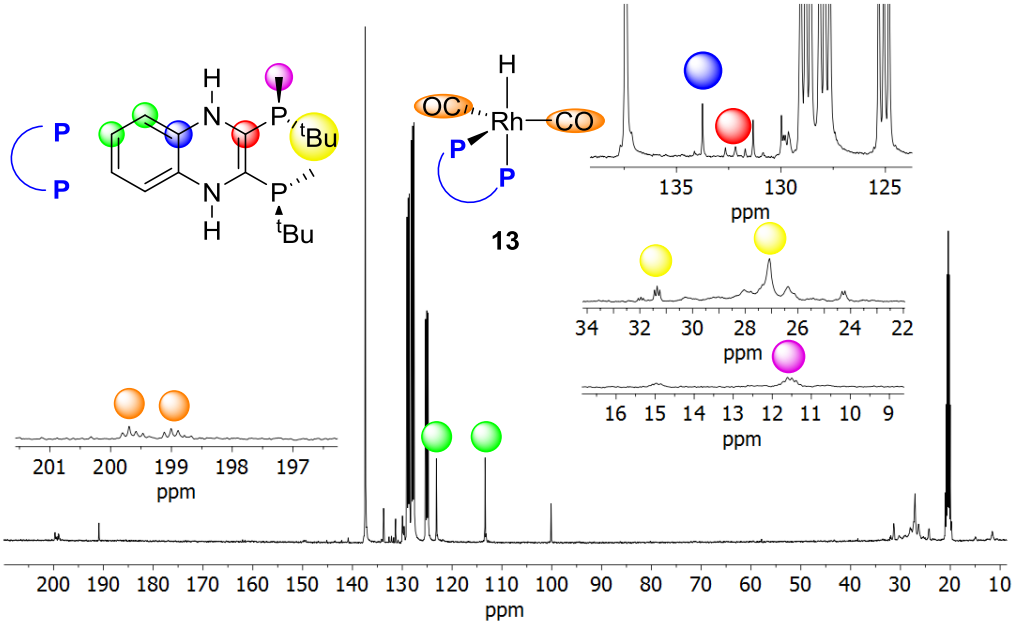


Figure S12: ^{13}C{^{1}H} NMR spectra of [Rh(acac)(CO)$_2$] in the presence **L1** under 20 bar (H$_2$/CO, 4:1) and at 90 °C for 16 h. Signals corresponding to species **13** emphasized. Inset: different areas of the spectra.

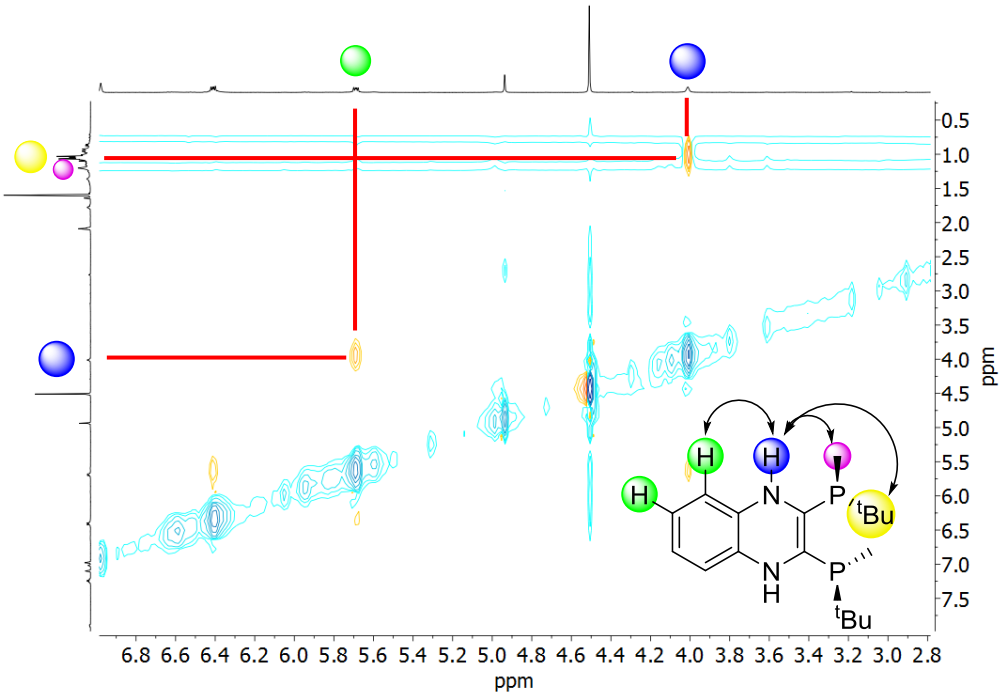


Figure S13: ^{1}H-^{1}H NOESY NMR spectra of [Rh(acac)(CO)$_2$] in the presence **L1** under 20 bar (H_2/CO, 4:1) and at 90 °C for 16 h. Signals corresponding to species **13** emphasized

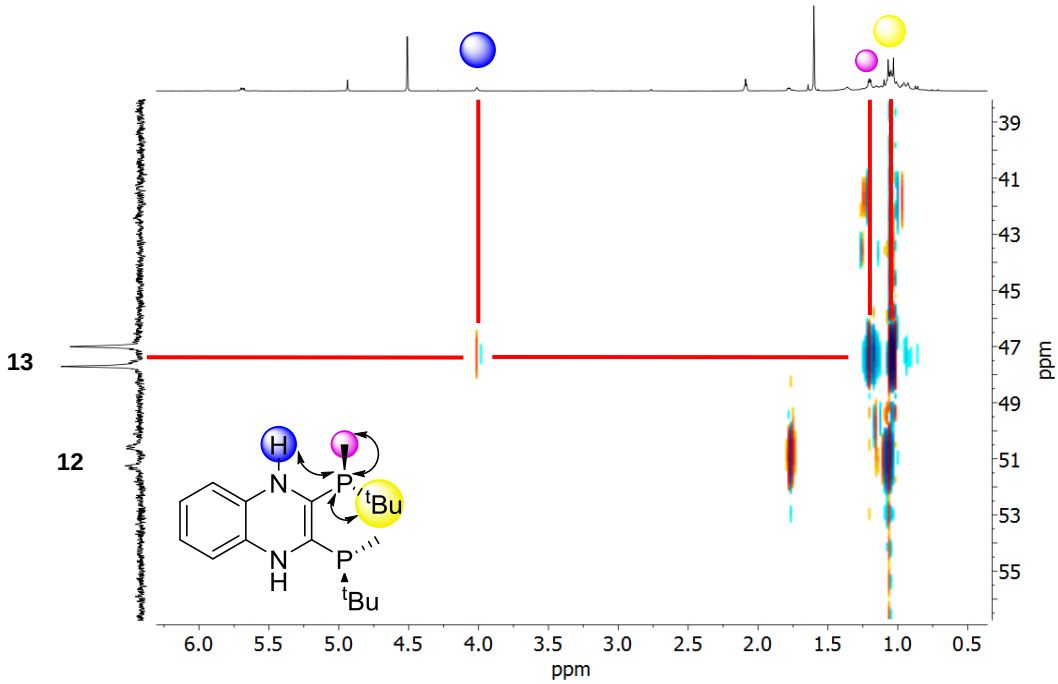


Figure S14: ^{1}H-^{31}P HMBC NMR spectra of [Rh(acac)(CO)$_2$] in the presence **L1** under 20 bar (H_2/CO, 4:1) and at 90°C for 16 h. Signals corresponding to species **13** emphasized

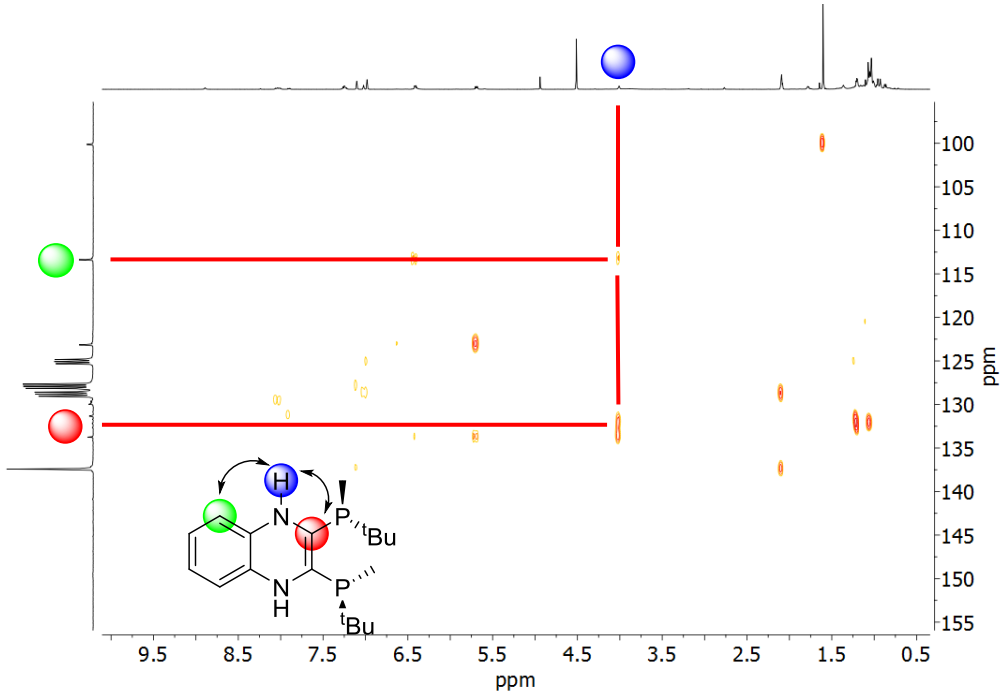


Figure S15: ^{1}H-^{13}C HMBC NMR spectra of [Rh(acac)$(CO)_2$] in the presence of **L1** under 20 bar (H_2/CO, 4:1) and at 90°C for 16 h. Signals corresponding to species **13** emphasized.

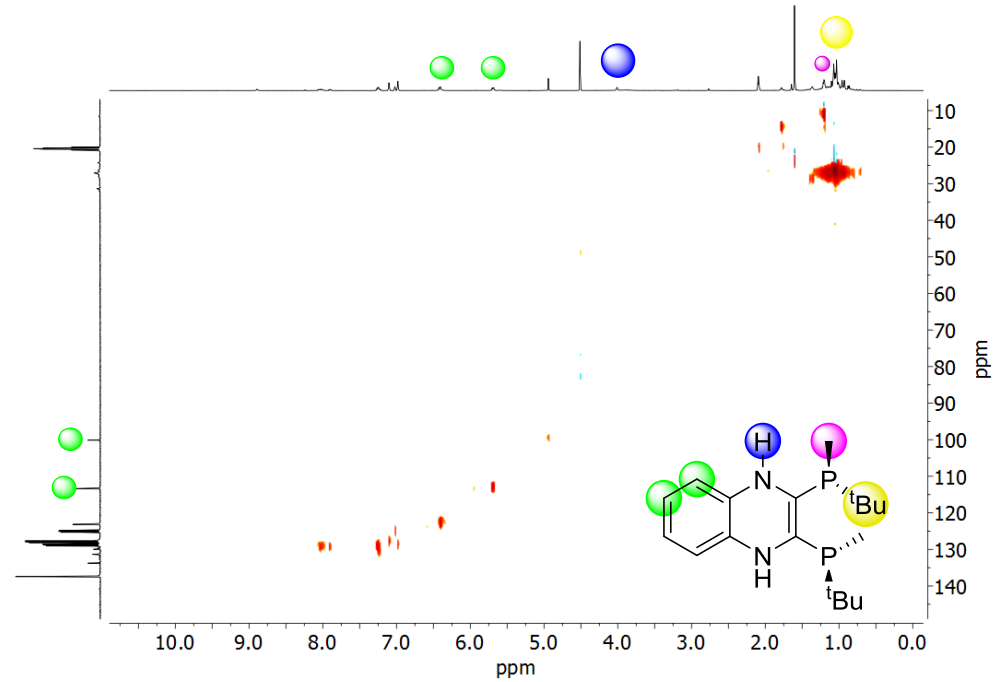
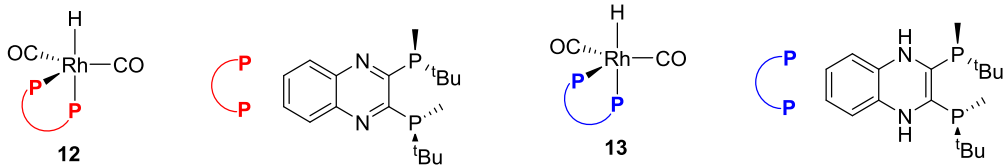


Figure S16: ^{1}H-^{13}C HSQC NMR spectra of [Rh(acac)$(CO)_2$] in the presence of **L1** under 20 bar (H_2/CO, 4:1) at 90°C for 16 h. Signals corresponding to species **13** emphasized.

Table S4: Selected spectroscopic data of the rhodium coordination sphere from rhodium complexes **12** and **13**.



	δ ^{31}P ppm	δ ^{1}H ppm	δ ^{13}CO ppm
12	51.6 (d, $J_{Rh,P}$ = 114.7 Hz)	- 8.5 (td, $J_{Rh,H}$ = 10.4 Hz, $J_{P,H}$ = 57.6 Hz)	199 (dt, $J_{P,C}$ = 10.8 Hz, $J_{Rh,C}$ = 68.8 Hz)
13	48.9 (d, $J_{Rh,P}$ = 115.5 Hz)	- 9.0 (td, $J_{Rh,H}$ = 12.4 Hz, $J_{P,H}$ = 62.8 Hz)	199 (dt, $J_{P,C}$ = 11.6 Hz, $J_{Rh,C}$ = 69.7 Hz)

Table S5: Selected spectroscopic data corresponding to the quinaxoline backbone of rhodium complexes **12** and **13**.

12		**13**	
δ ^{1}H ppm	**δ ^{13}C ppm**	**δ ^{1}H ppm**	**δ ^{13}C ppm**
1.05 (C(C$\underline{H}_3$)$_3$)	28 (C($\underline{C}$H$_3$)$_3$), 31.9 (t, $J_{P,C}$ = 9.4 Hz, $\underline{C}$(CH$_3$)$_3$)	1.05 (C(C$\underline{H}_3$)$_3$)	28 (C($\underline{C}$H$_3$)$_3$), 31.3 (t, $J_{P,C}$ = 9.9 Hz, $\underline{C}$(CH$_3$)$_3$)
1.79 (C$\underline{H}_3$)	14.9 ($\underline{C}$H$_3$)	1.20 (C$\underline{H}_3$)	11.6 (C$\underline{H}_3$)
-	162.5 (t, $J_{P,C}$ = 47.9 Hz, C)	-	132.2 (t, $J_{P,C}$ = 48.1 Hz, C)
-	-	4 (N$\underline{H}$)	-
-	141.2 (C)	-	133.8 (C)
7.3 (C$\underline{H}$)	131.3 ($\underline{C}$H)	5.7 (C$\underline{H}$)	113.1 ($\underline{C}$H)
7.9 (C$\underline{H}$)	129.9 ($\underline{C}$H)	6.4 (C$\underline{H}$)	123.0 ($\underline{C}$H)

E. Experiments to control the formation of hydrides 12 and 13

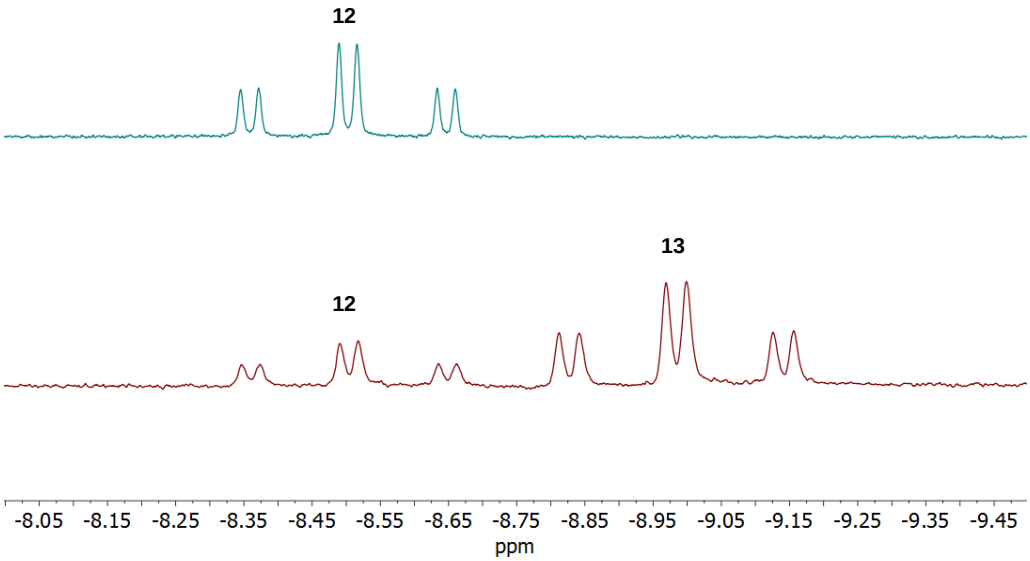


Figure S17: ^{1}H NMR spectra of [Rh(acac)(CO)$_2$] in the presence of **L1** under 10 bar (H_2/CO, 4:1) at variable temperature. Top: 20 °C. Bottom: 90 °C.

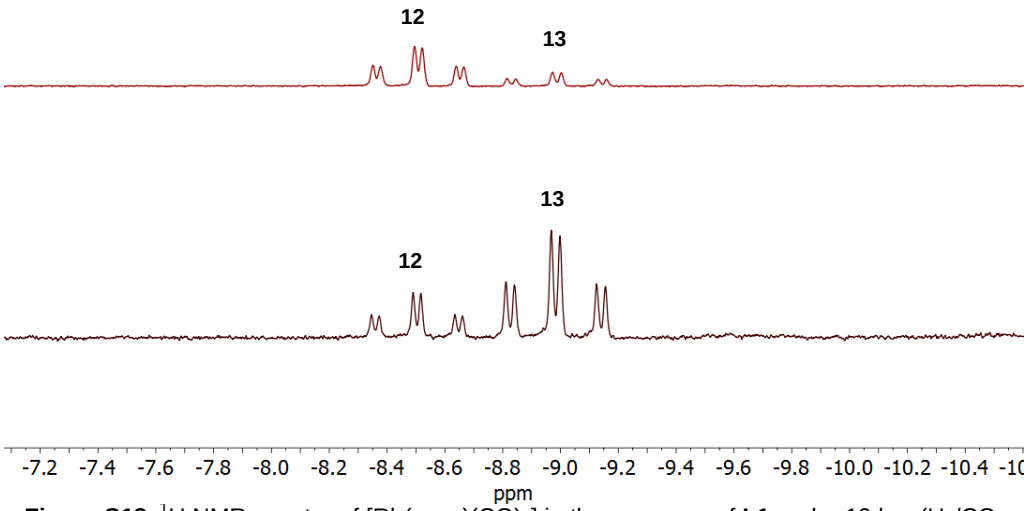


Figure S18: ^{1}H NMR spectra of [Rh(acac)(CO)$_2$] in the presence of **L1** under 10 bar (H_2/CO, 4:1) at 90°C using different concentrations. Top: [Rh] = 0.0125M Bottom: [Rh] = 0.0375M.

F. Reaction monitoring experiments

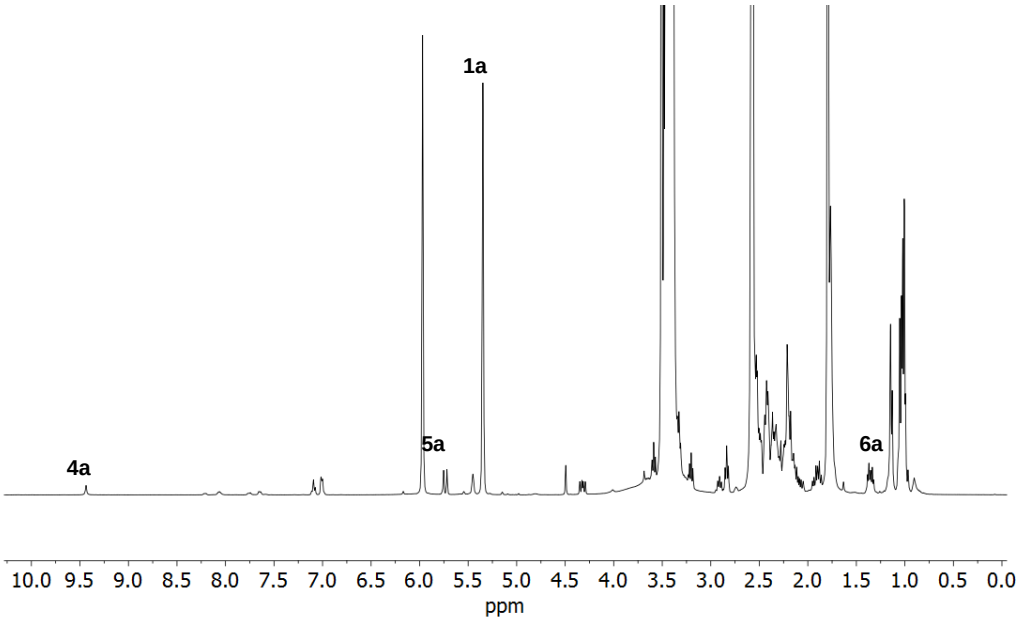


Figure S19: ^{1}H NMR spectra of $[Rh(COD)_2]BF_4$ in the presence of **L1**, methyl methacrylate **1a** and morpholine **2a** under 10 bar (H_2/CO, 4:1) at 90°C in tol-d8/DCE.

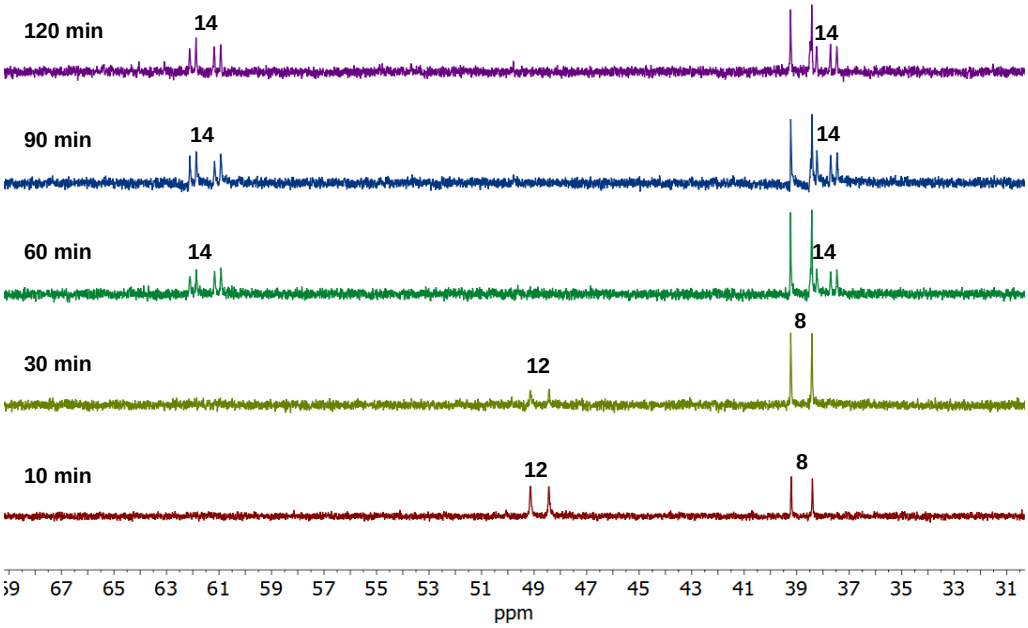


Figure S20: ^{31}P NMR spectra of $[Rh(COD)_2]BF_4$ in the presence of **L1**, methyl methacrylate **1a** and morpholine **2a** under 10 bar (H_2/CO, 4:1) at 90°C in tol-d8/DCE.

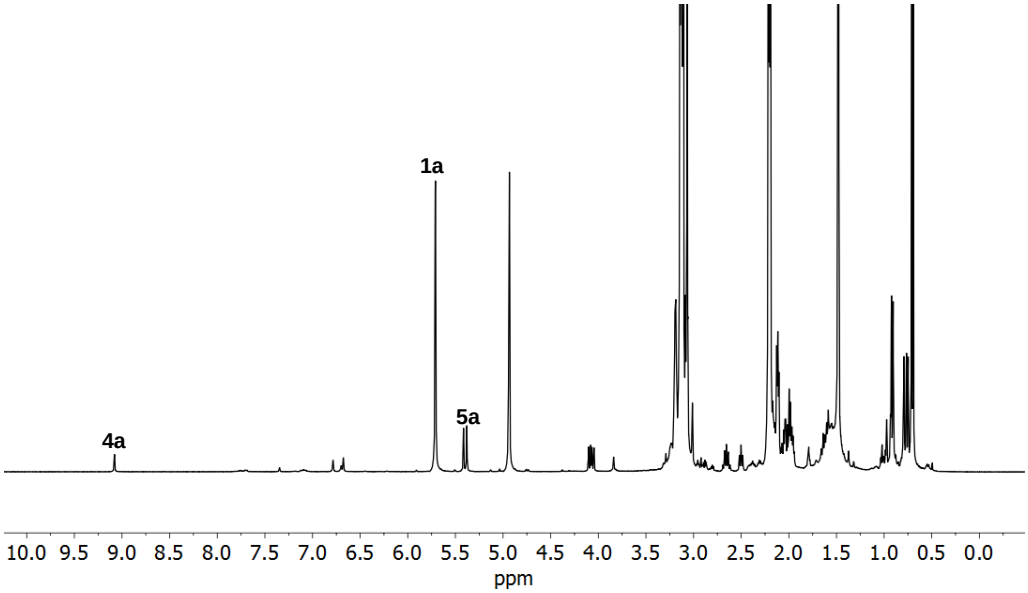


Figure S21: ^{1}H NMR spectra of [Rh(acac)(CO)$_2$] in the presence of **L1**, methyl methacrylate **1a** and morpholine **2a** under 10 bar (H$_2$/CO, 4:1) at 90°C in tol-d8.

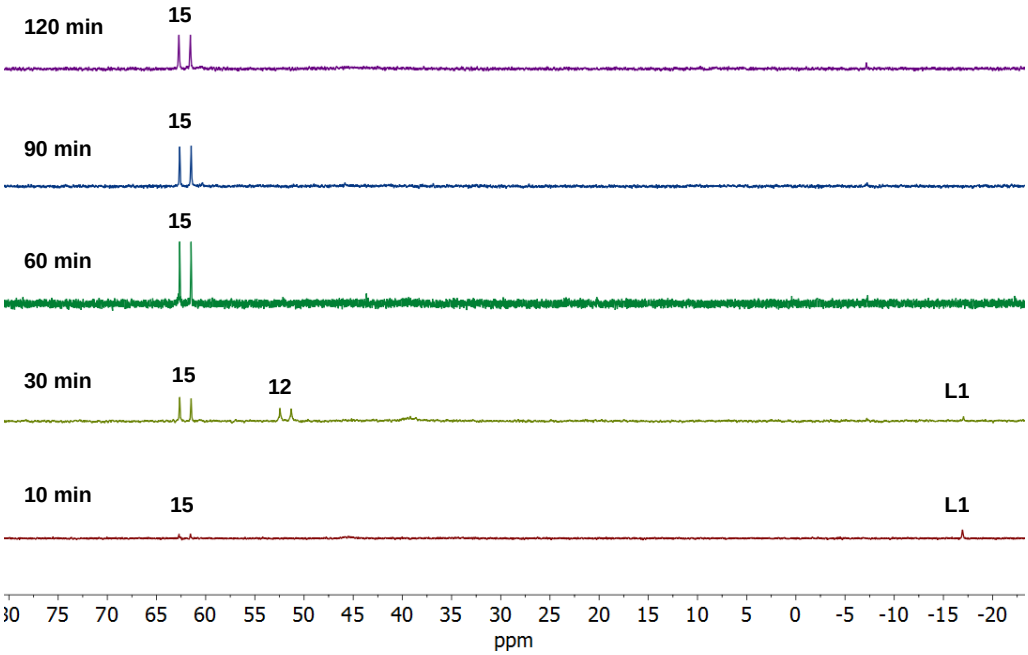


Figure S22: ^{31}P NMR spectra of [Rh(acac)(CO)$_2$] in the presence of **L1**, methyl methacrylate **1a** and morpholine **2a** under 10 bar (H$_2$/CO, 4:1) at 90°C in tol-d8.

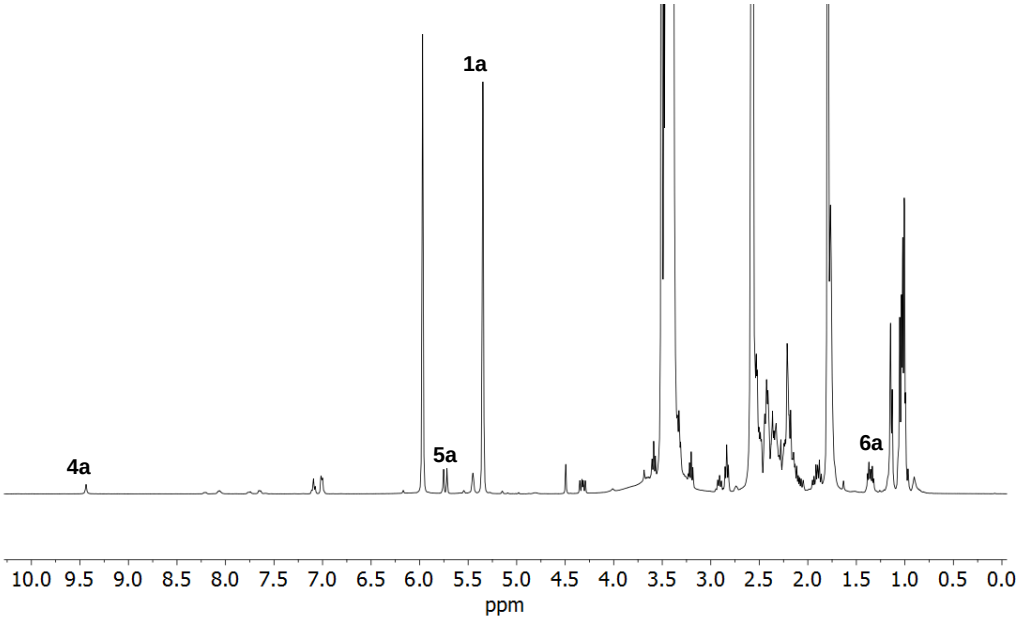


Figure S23: ^{1}H NMR spectra of [Rh(acac)(CO)$_2$] in the presence of **L1**, methyl methacrylate **1a** and morpholine **2a** under 10 bar (H$_2$/CO, 4:1) at 90°C in tol-d8/DCE.

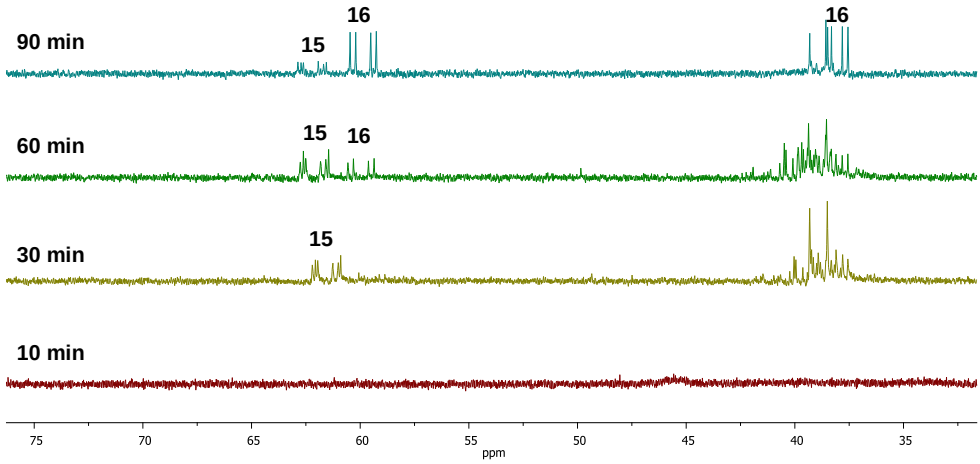


Figure S24: ^{31}P NMR spectra of [Rh(acac)(CO)$_2$] in the presence of **L1**, methyl methacrylate **1a** and morpholine **2a** under 10 bar (H$_2$/CO, 4:1) at 90°C in tol-d8/DCE.

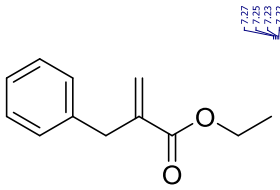
SIX. Selected spectroscopic data

Table S6: Selected spectroscopic data of the rhodium species detected by HP-NMR.

Species	δ ^{31}P ppm	IR (νCO)
[Rh(COD)(**L1**)]BF_4 **7**	41.6 (d, $J_{Rh,P}$ = 148 Hz)	-
[Rh(**L1**)$_2$]BF_4 **8**	38.9 (d, $J_{Rh,P}$ = 130 Hz)	-
[Rh(CO)$_2$(**L1**)]BF_4 **9**	47.2 (d, $J_{Rh,P}$ = 115 Hz)	2097, 2051
[Rh(CO)$_3$(**L1**)]BF_4 **10**	48.7 (d, $J_{Rh,P}$ = 116 Hz)	2120, 2086, 2041
[Rh(Solvent)$_2$(**L1**)]BF_4 **11**	60.1 (d, $J_{Rh,P}$ = 200 Hz)	-
[Rh(**5a**)(**L1**)]BF_4 **14**	38 ppm ($J_{Rh,P}$ = 123.5 Hz, $J_{P,P}$ = 38.7 Hz) 61.5 ppm ($J_{Rh,P}$ = 151.7 Hz, $J_{P,P}$ = 38.5 Hz)	-
[Rh(acac)(**L1**)] **15**	62.0 ppm ($J_{Rh,P}$ = 187.6 Hz)	-
[Rh(**5a**)(**L1**)]acac **16**	38 ppm ($J_{Rh,P}$ = 123 Hz, $J_{P,P}$ = 41 Hz) 59.8 ppm ($J_{Rh,P}$ = 154 Hz, $J_{P,P}$ = 41 Hz)	-

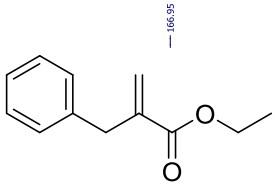
SX. Spectra of novel compounds

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



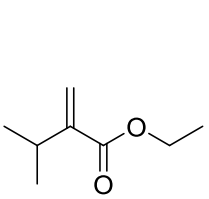
1b

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)



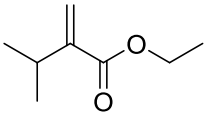
1b

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



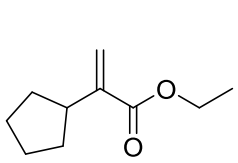
1c

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)



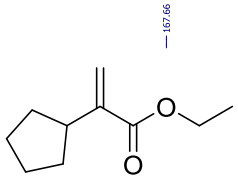
1c

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



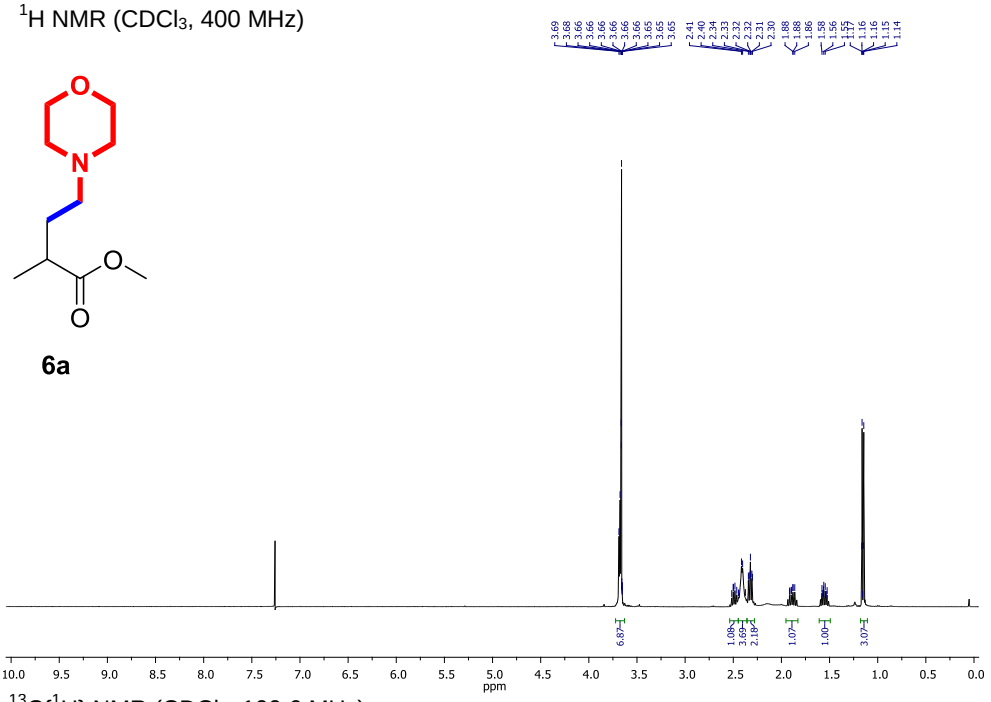
1d

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)



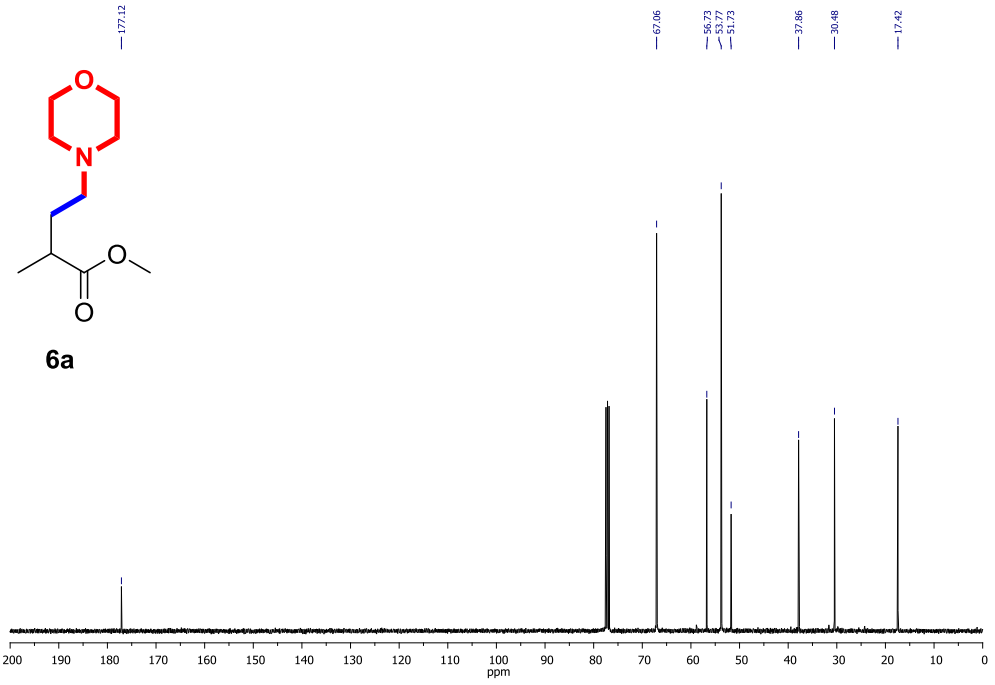
1d

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



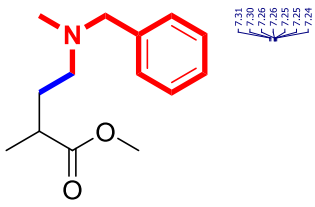
6a

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)

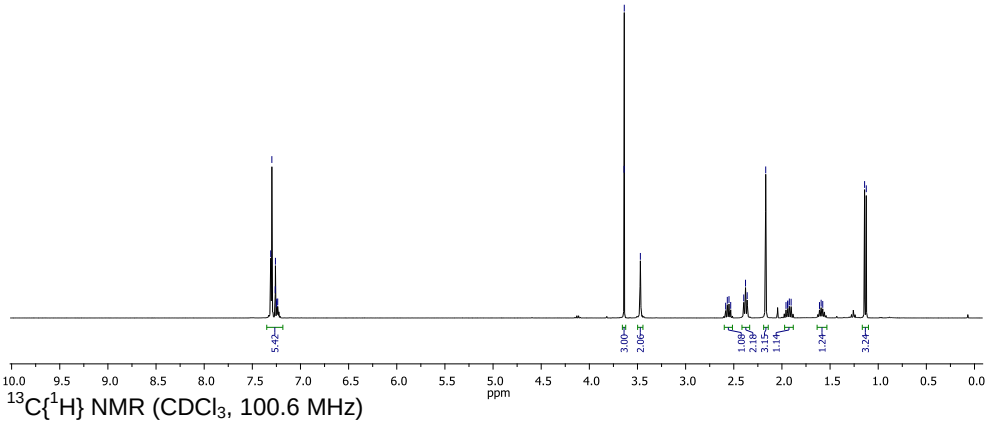


6a

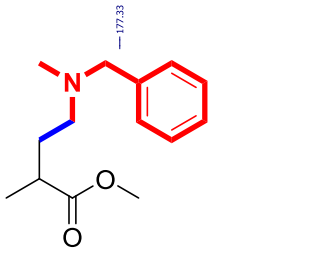
^{1}H NMR ($CDCl_3$, 400 MHz)



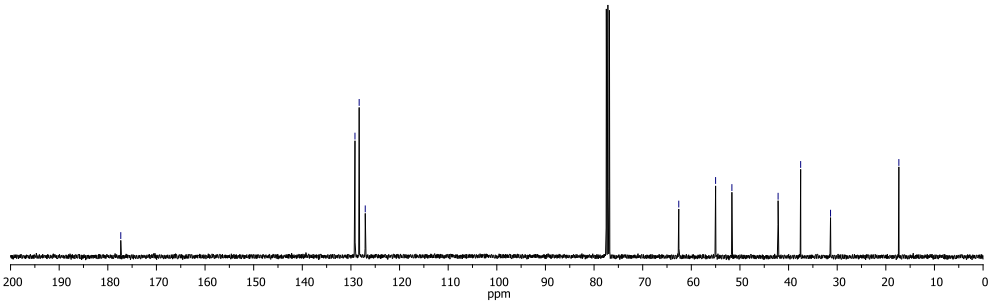
6b



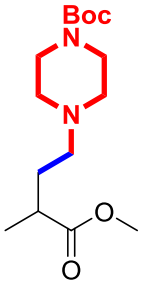
^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)



6b

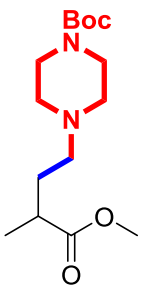


^{1}H NMR ($CDCl_3$, 400 MHz)



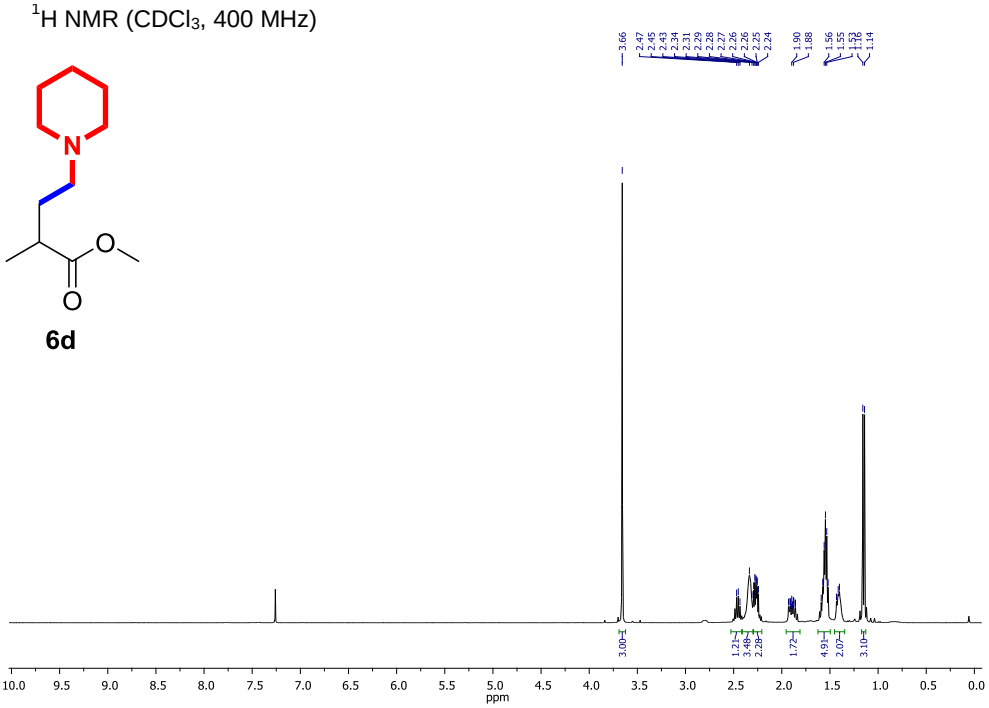
6c

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)



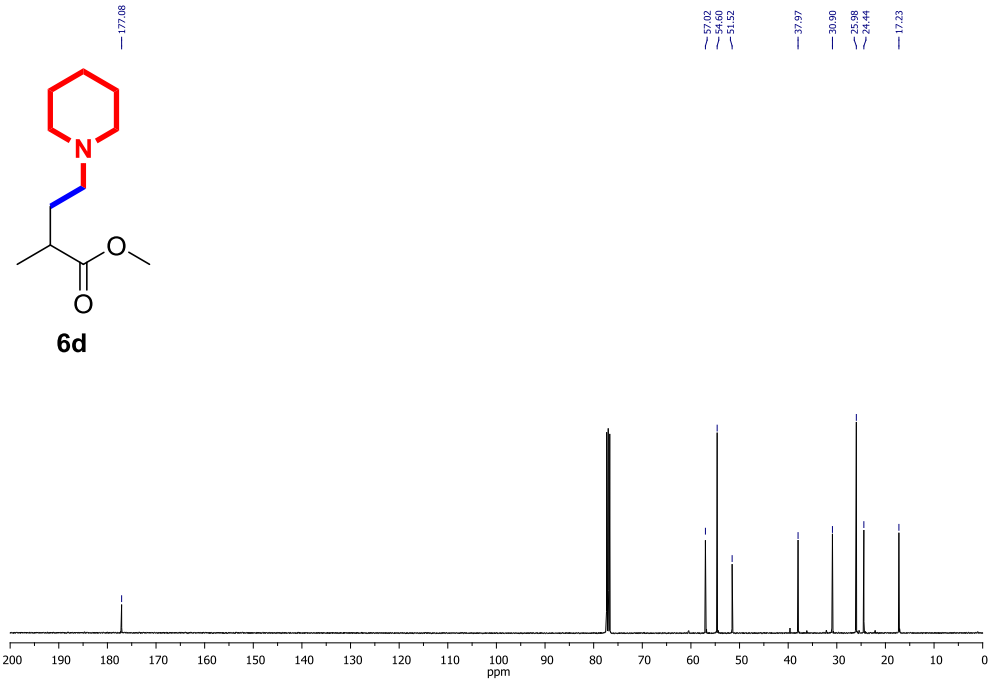
6c

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



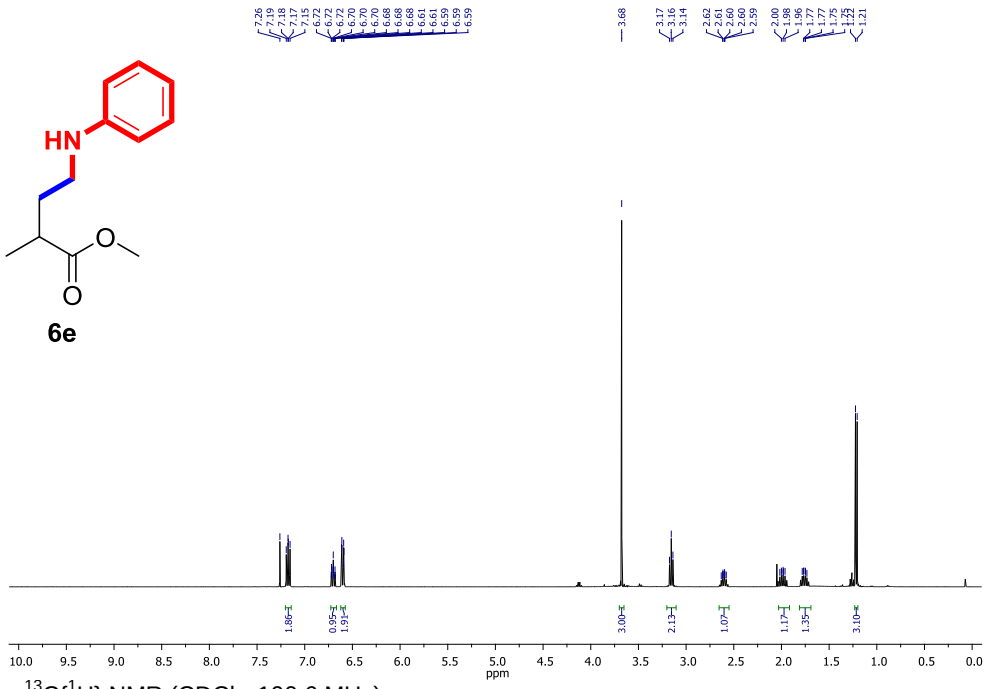
6d

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)



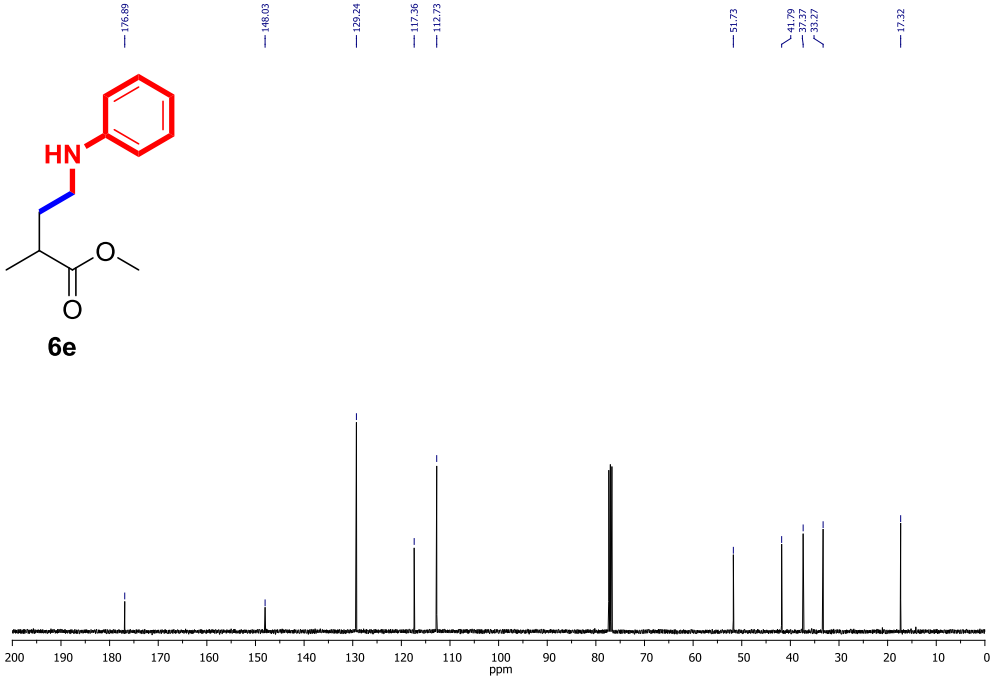
6d

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



6e

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)



6e

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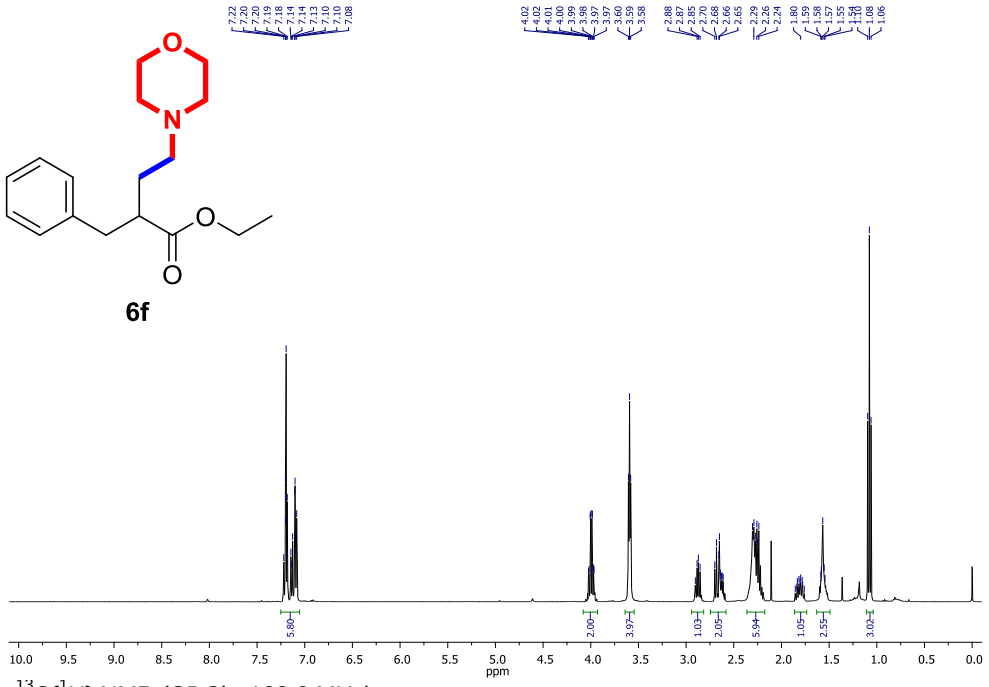
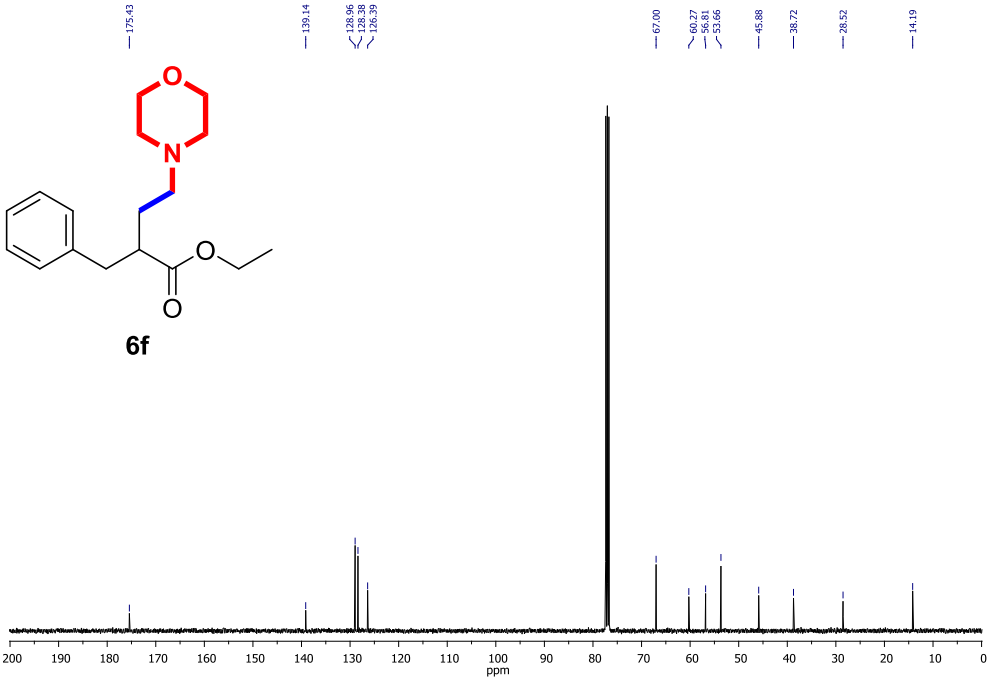


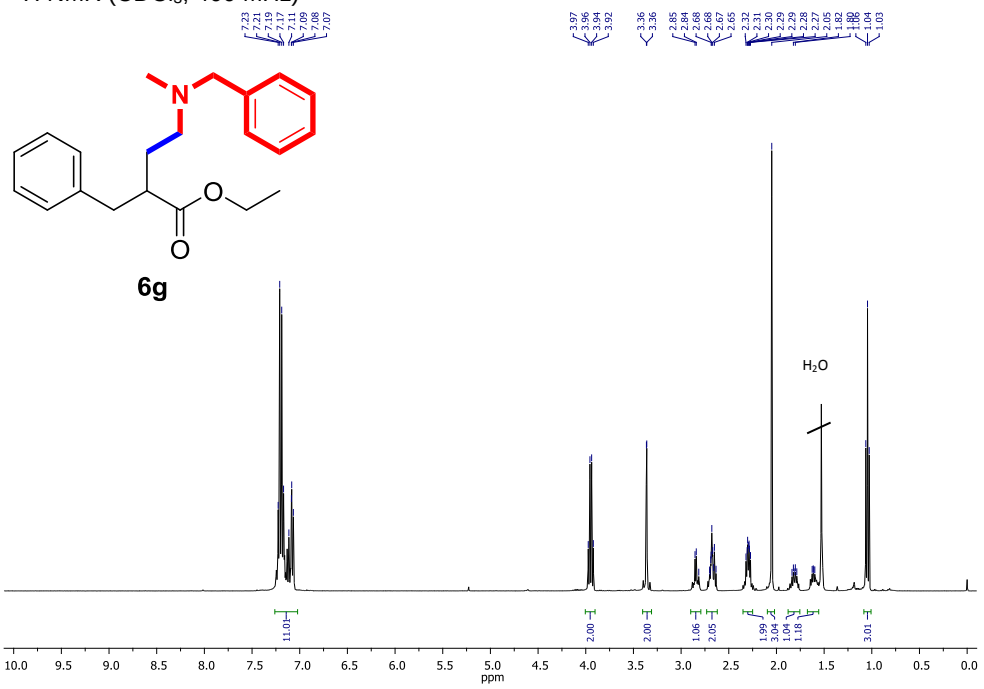
6f

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)



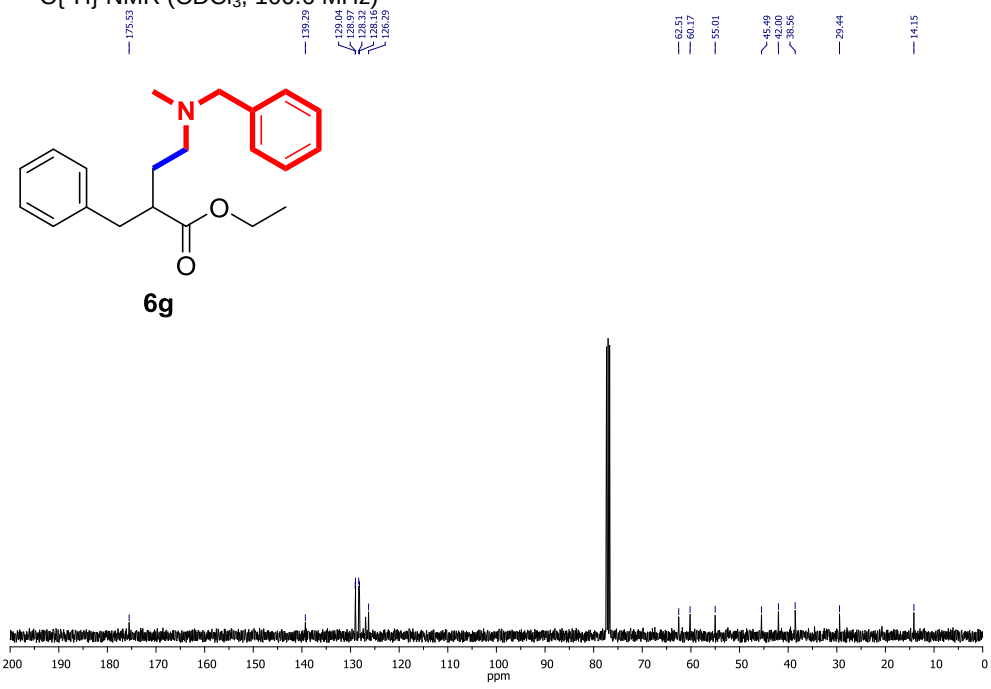
6f

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



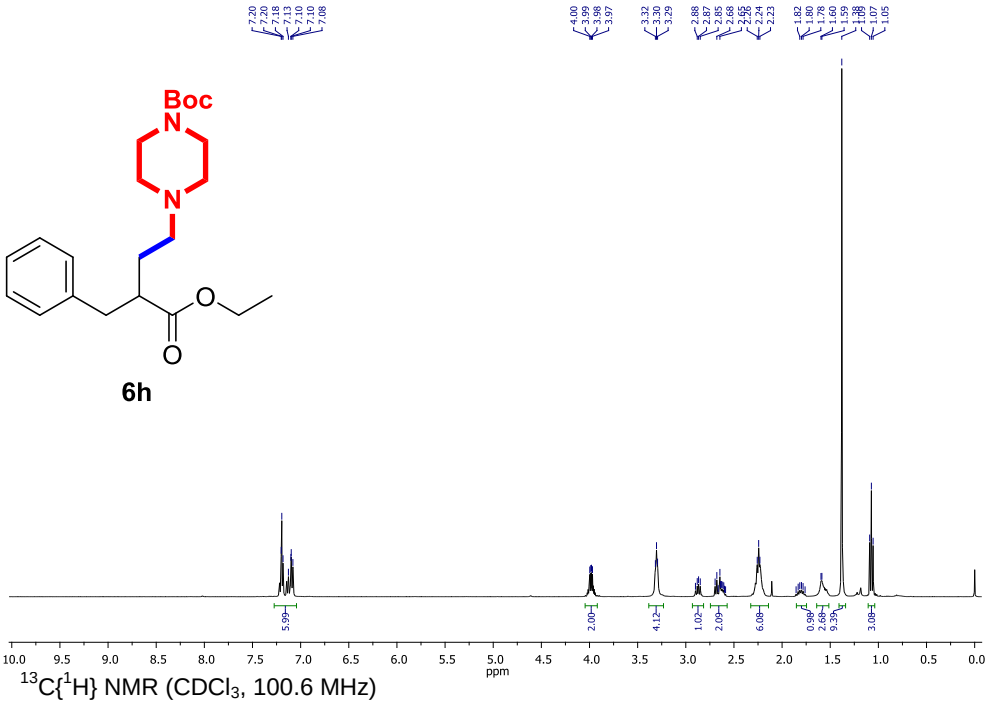
6g

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)

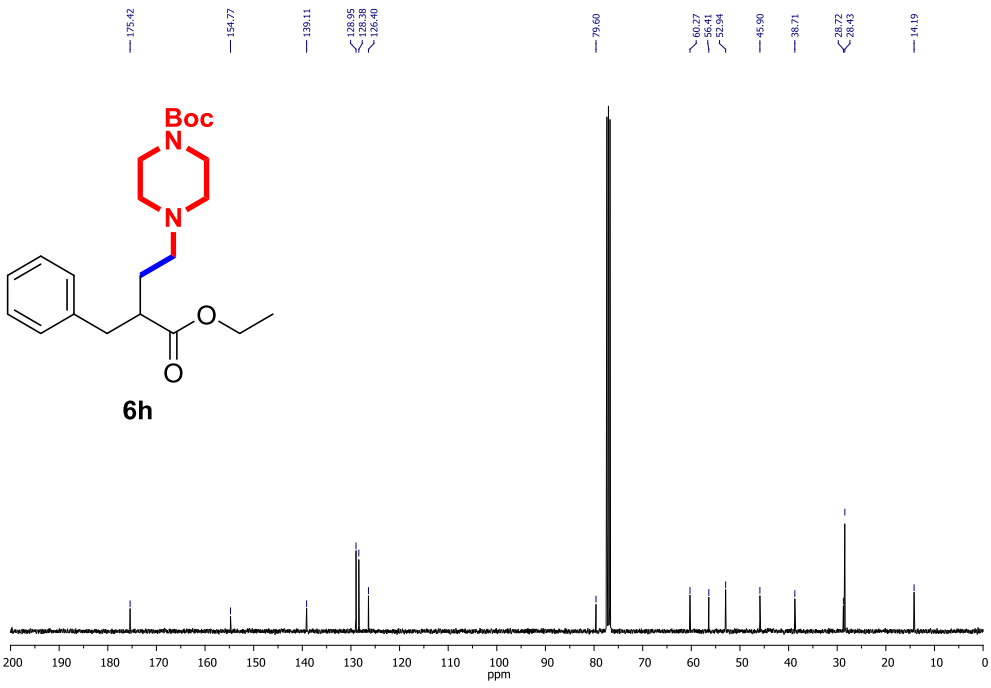


6g

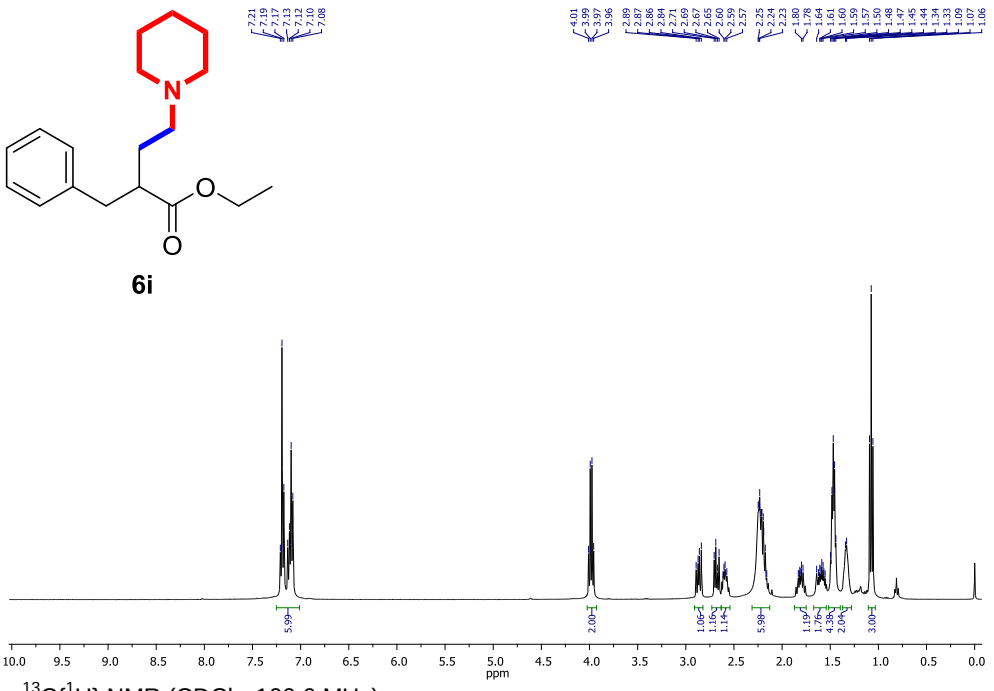
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)

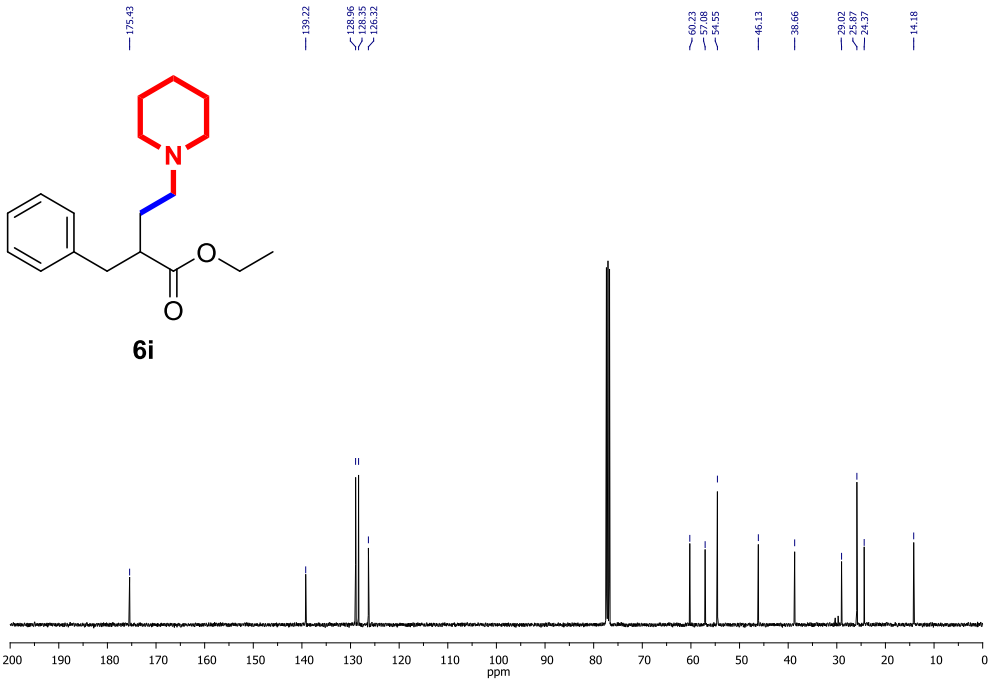


^{1}H NMR ($CDCl_3$, 400 MHz)



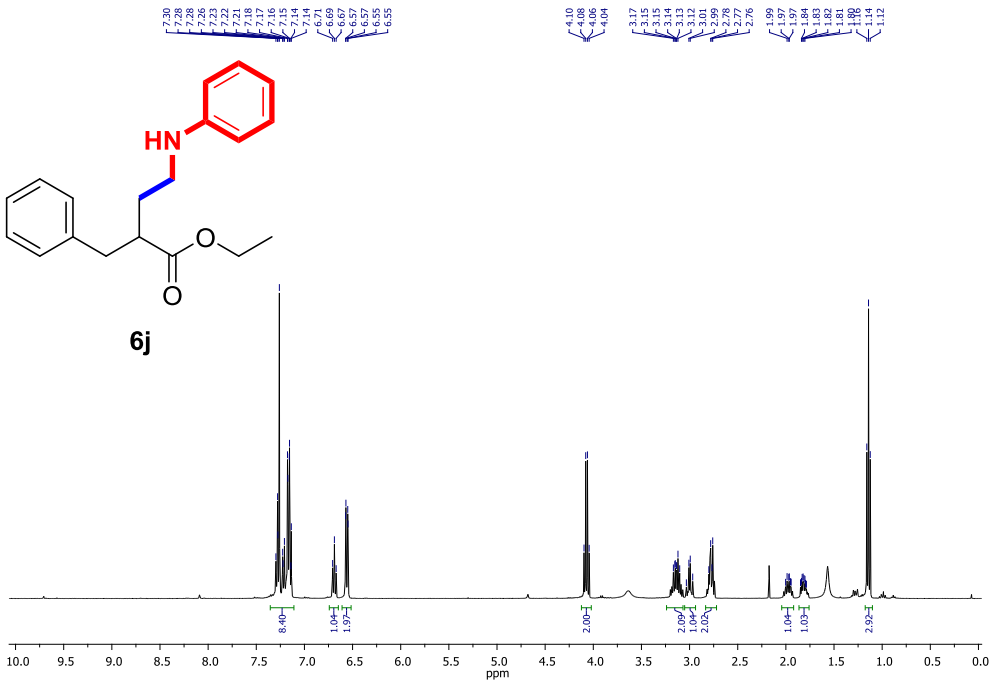
6i

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)

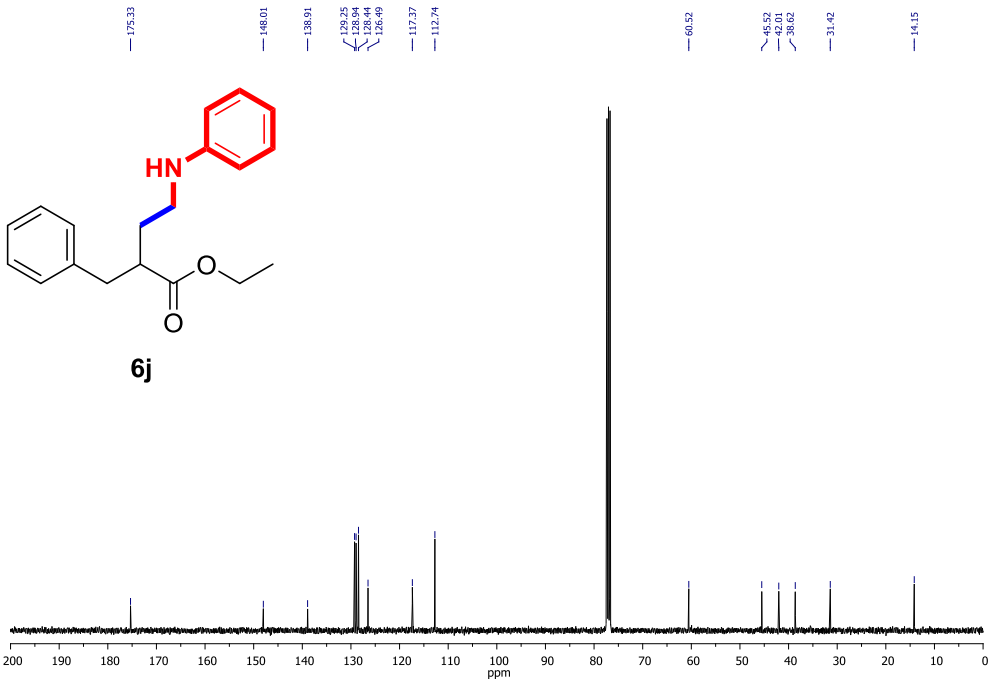


6i

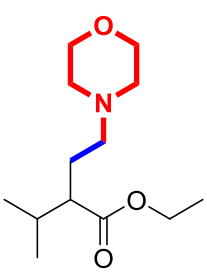
^{1}H NMR ($CDCl_3$, 400 MHz)



$^{13}C\{^{1}H\}$ NMR ($CDCl_3$, 100.6 MHz)

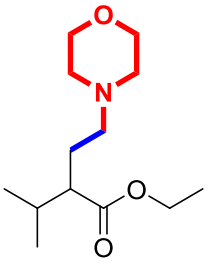


^{1}H NMR ($CDCl_3$, 400 MHz)



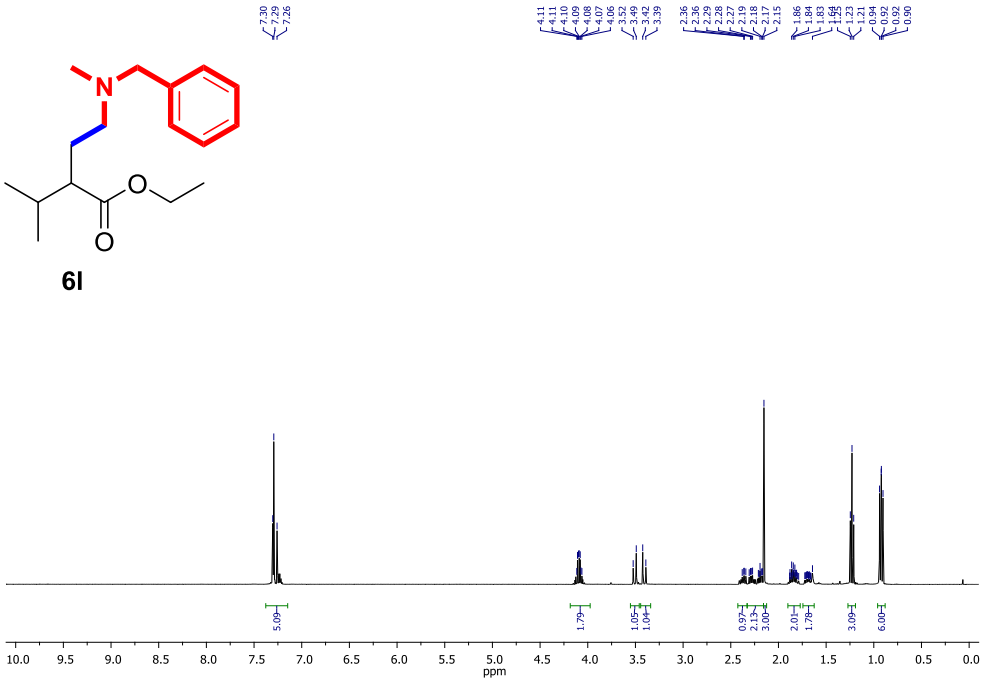
6k

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)



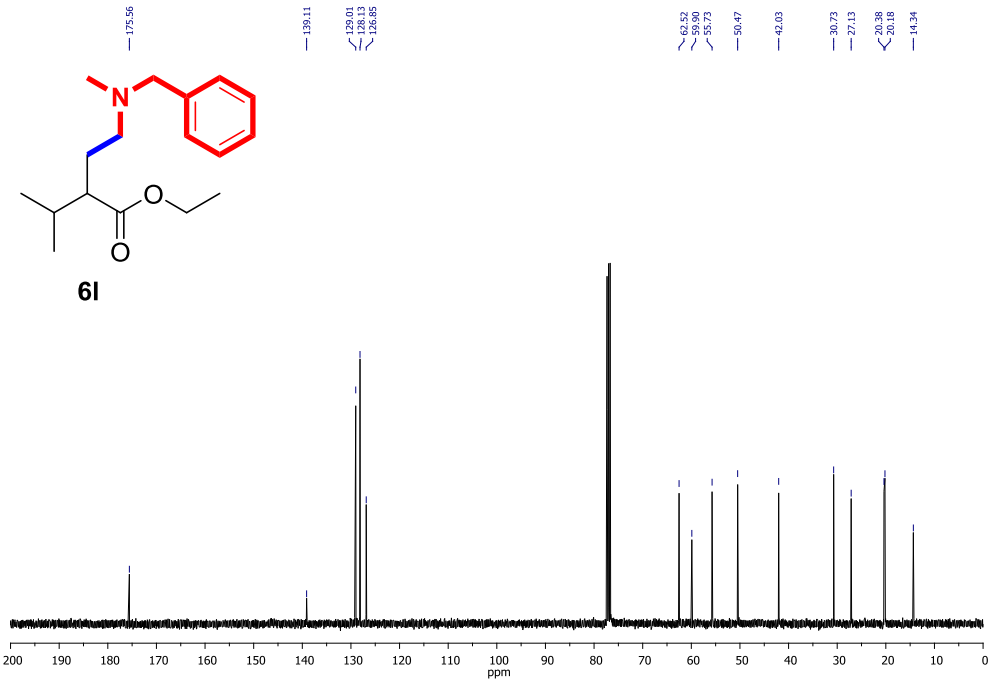
6k

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



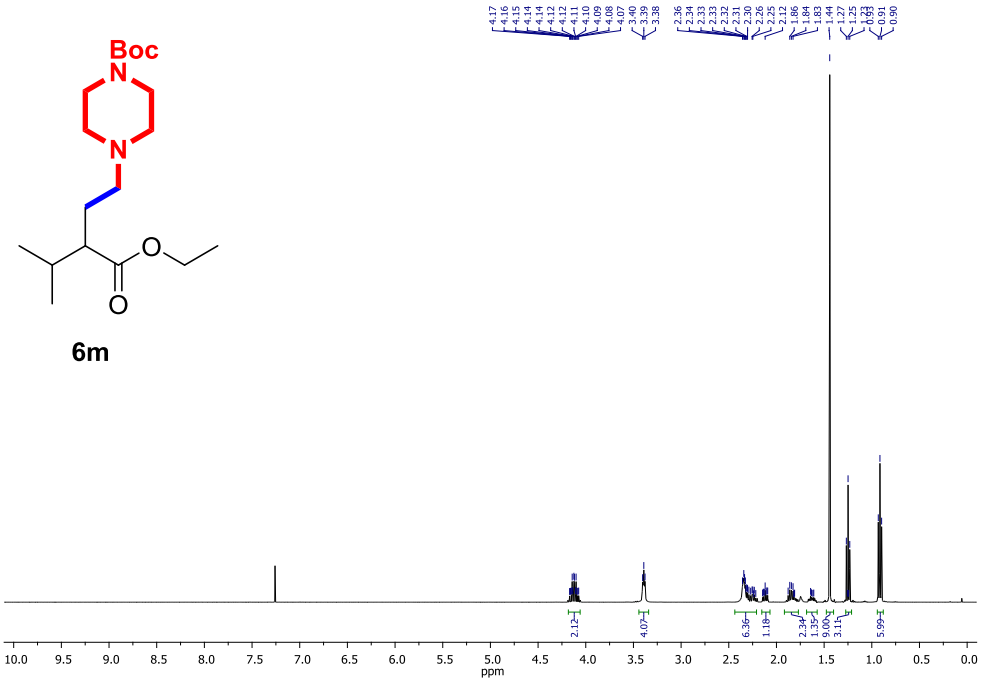
6l

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)

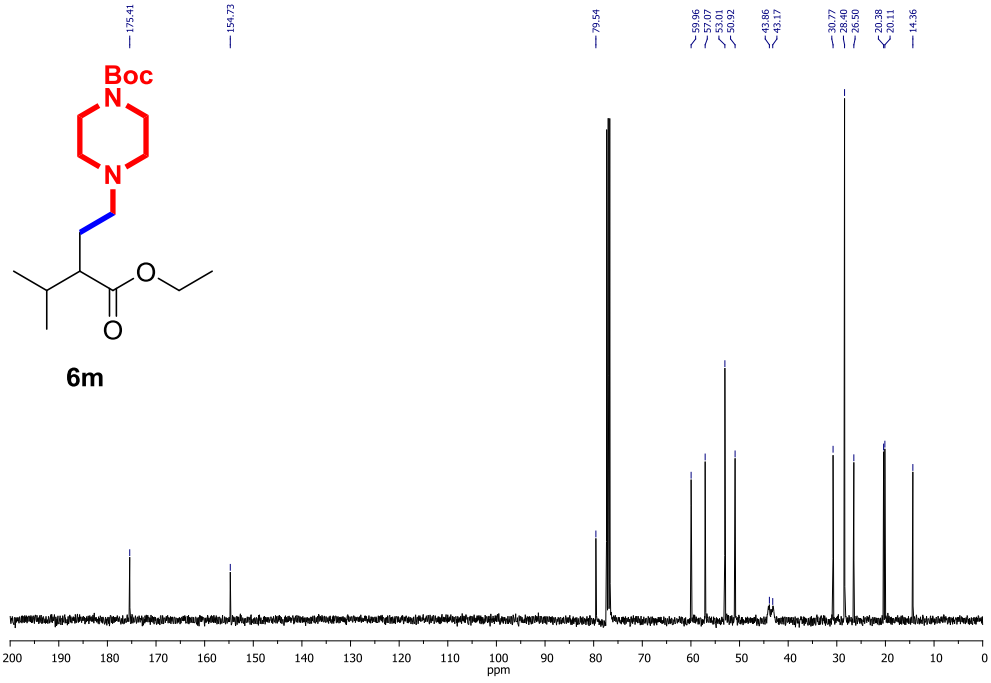


6l

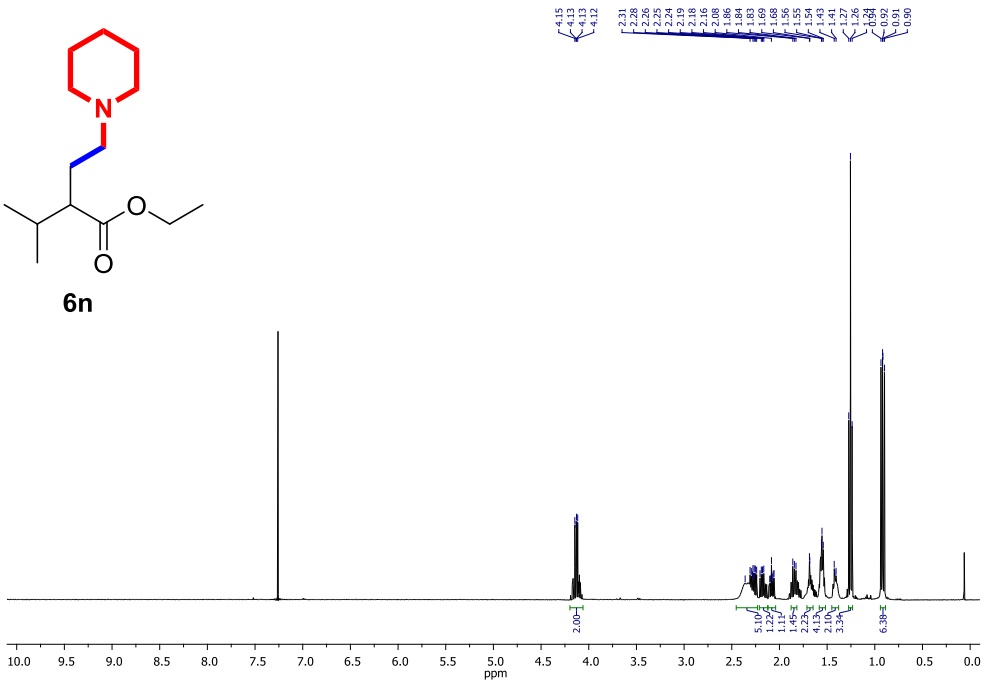
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)

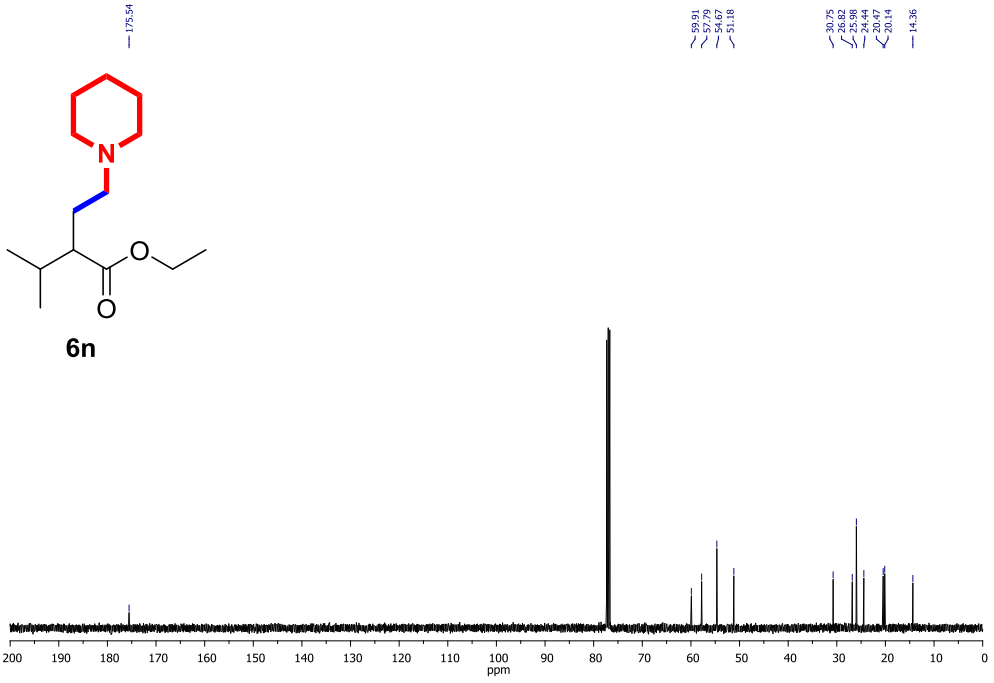


^{1}H NMR ($CDCl_3$, 400 MHz)



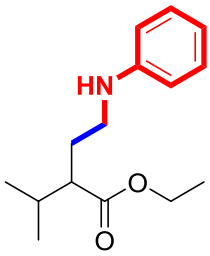
6n

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)

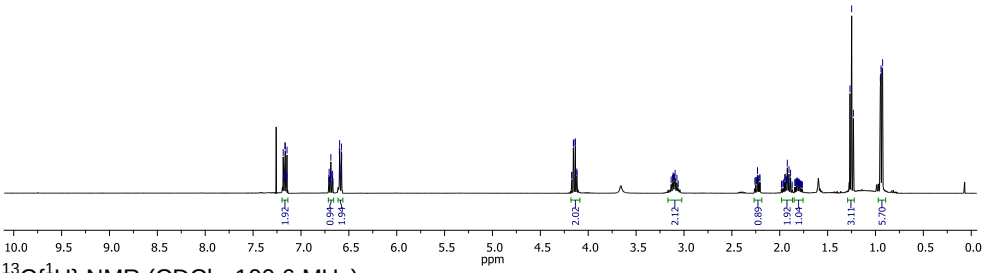


6n

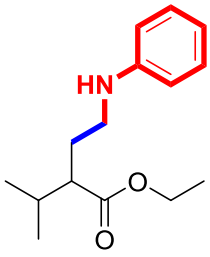
^{1}H NMR ($CDCl_3$, 400 MHz)



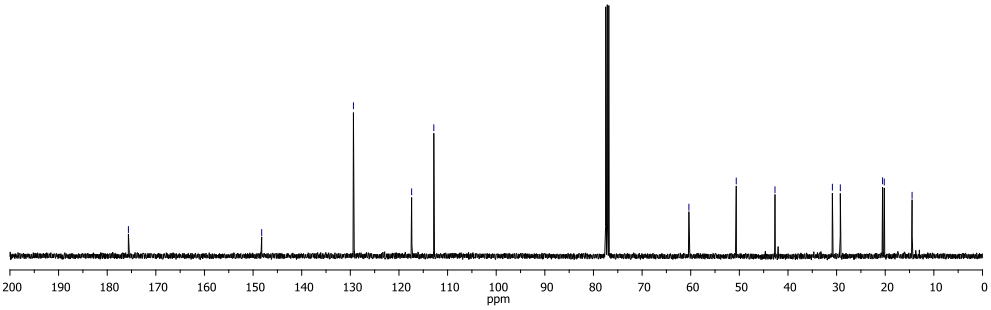
6o



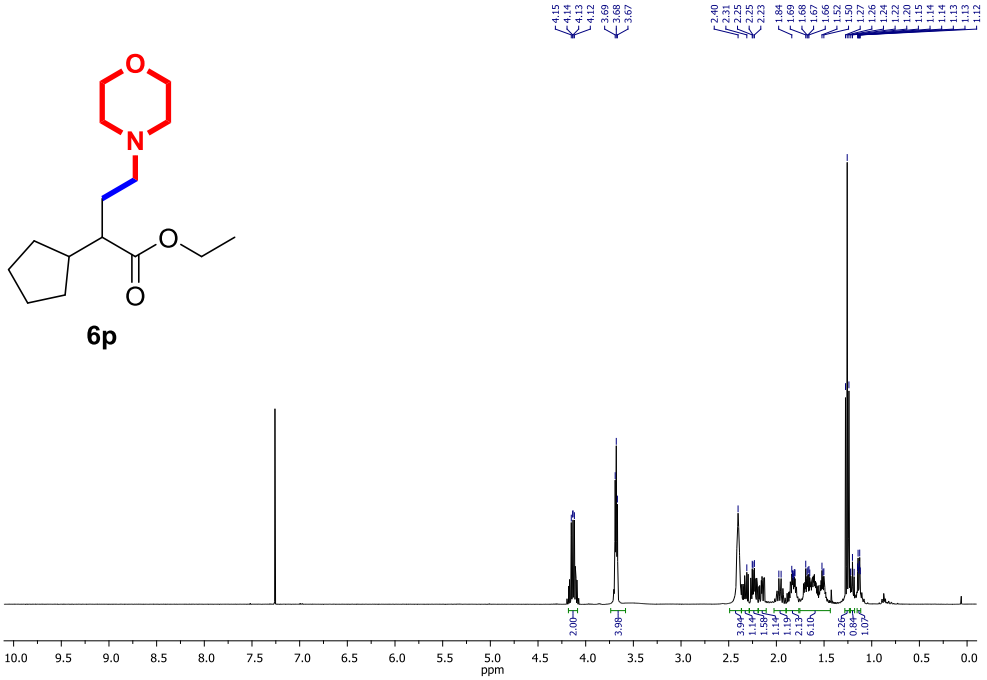
^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)



6o

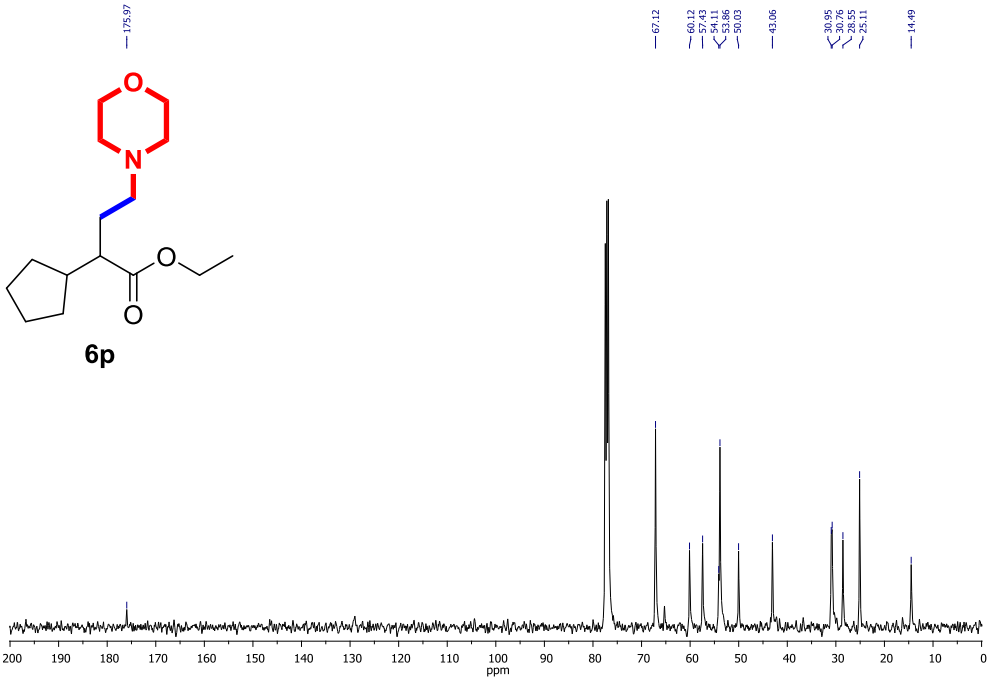


^{1}H NMR ($CDCl_3$, 400 MHz)



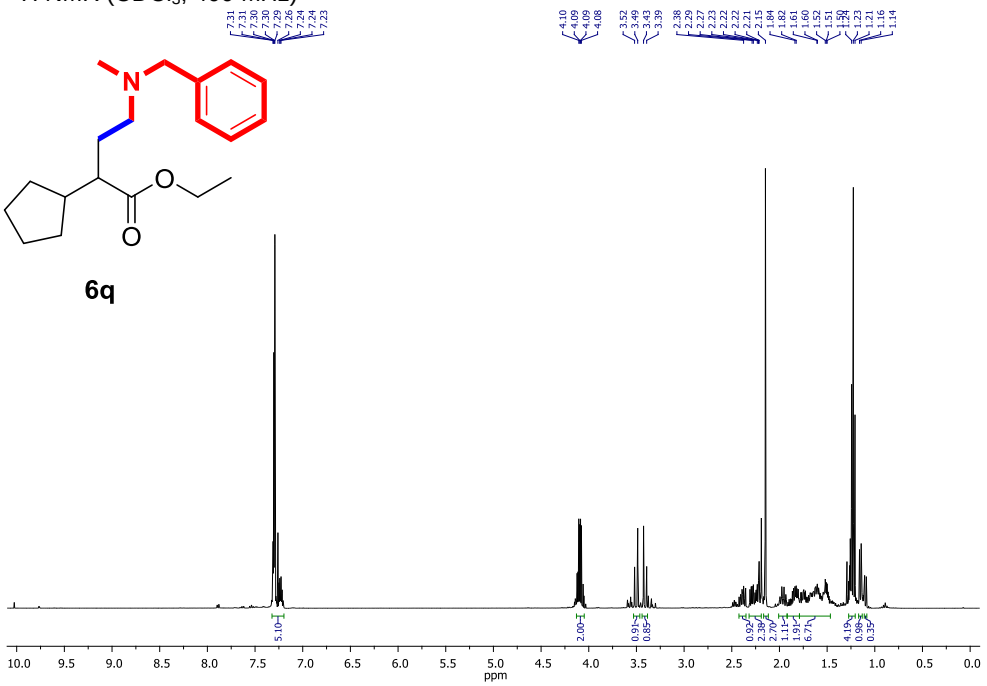
6p

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)



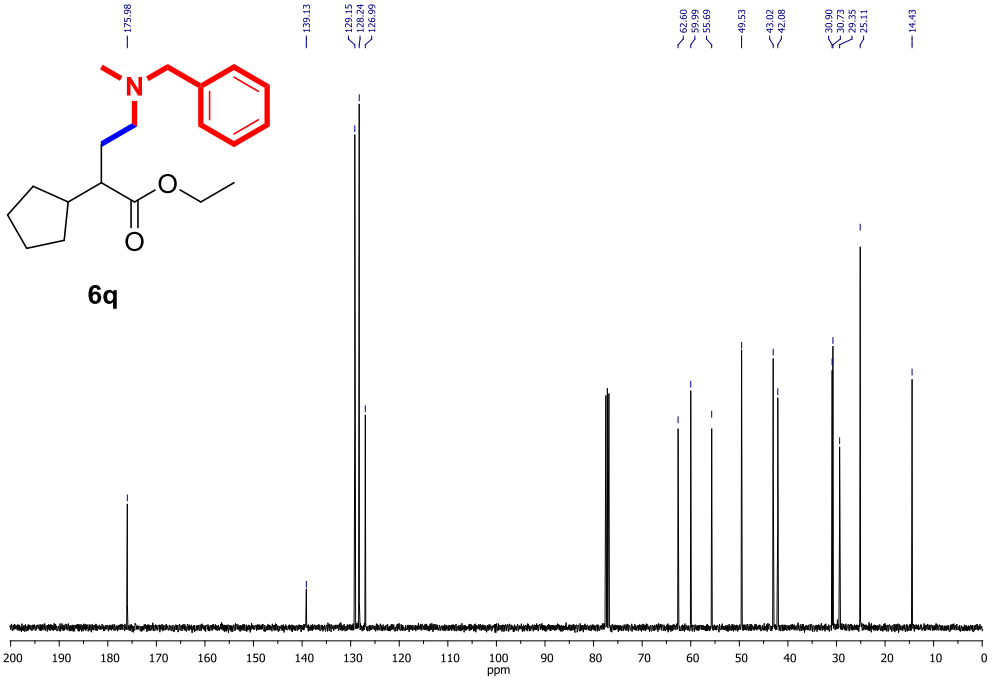
6p

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



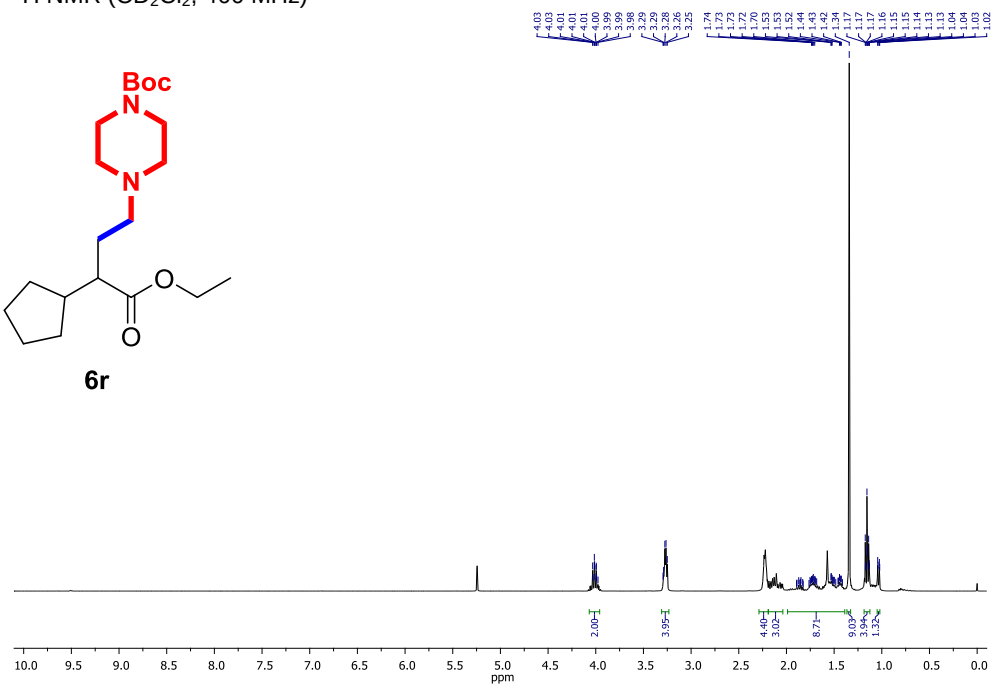
6q

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)



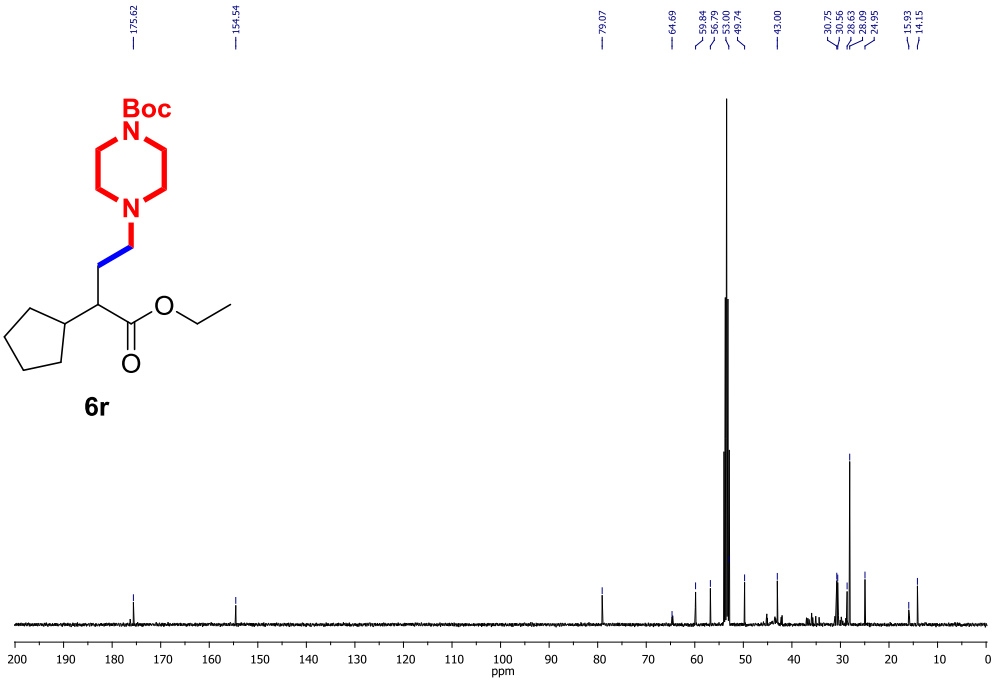
6q

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



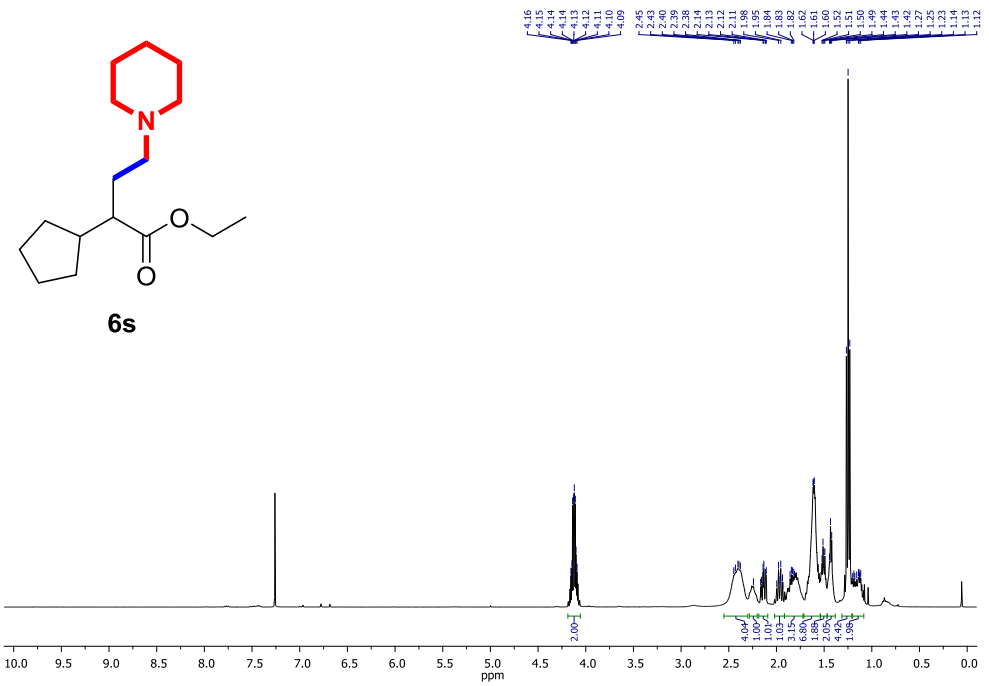
6r

^{13}C{^{1}H} NMR (CD_2Cl_2, 100.6 MHz)



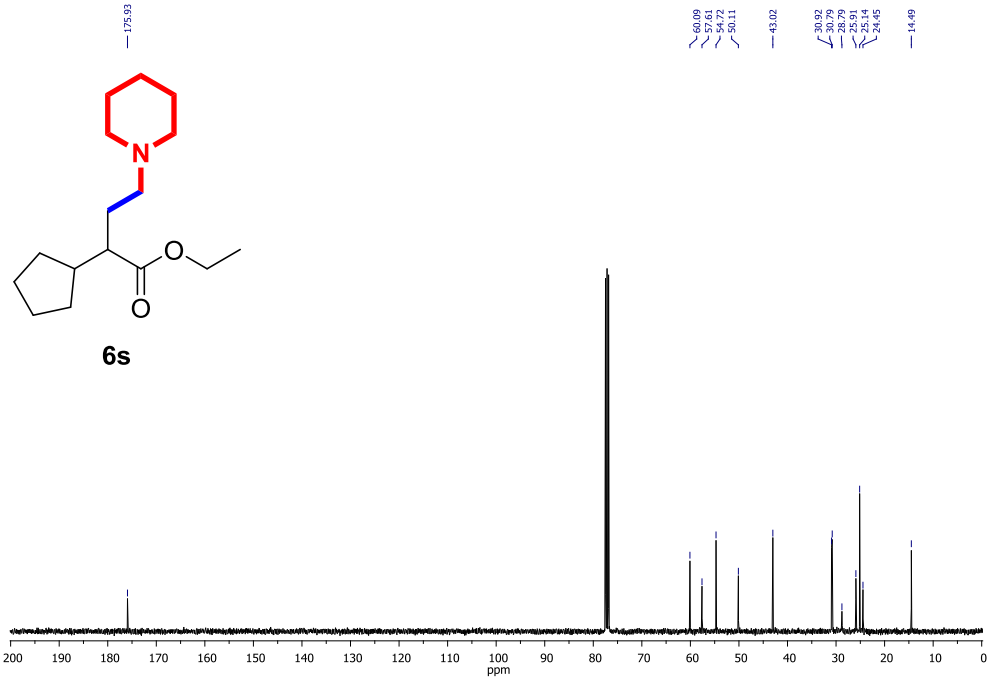
6r

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



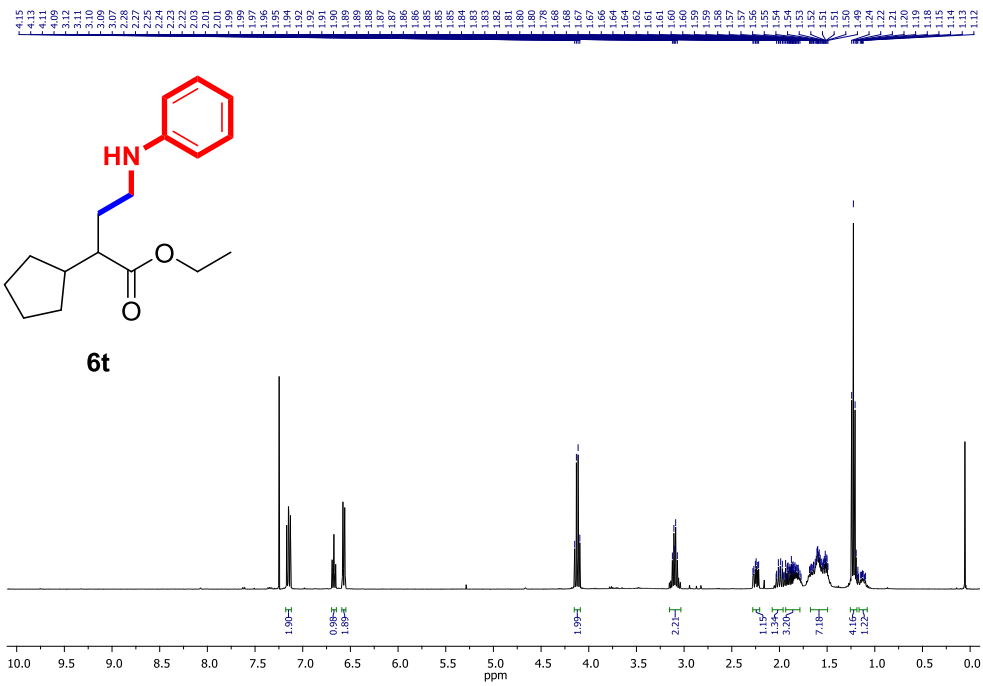
6s

^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)

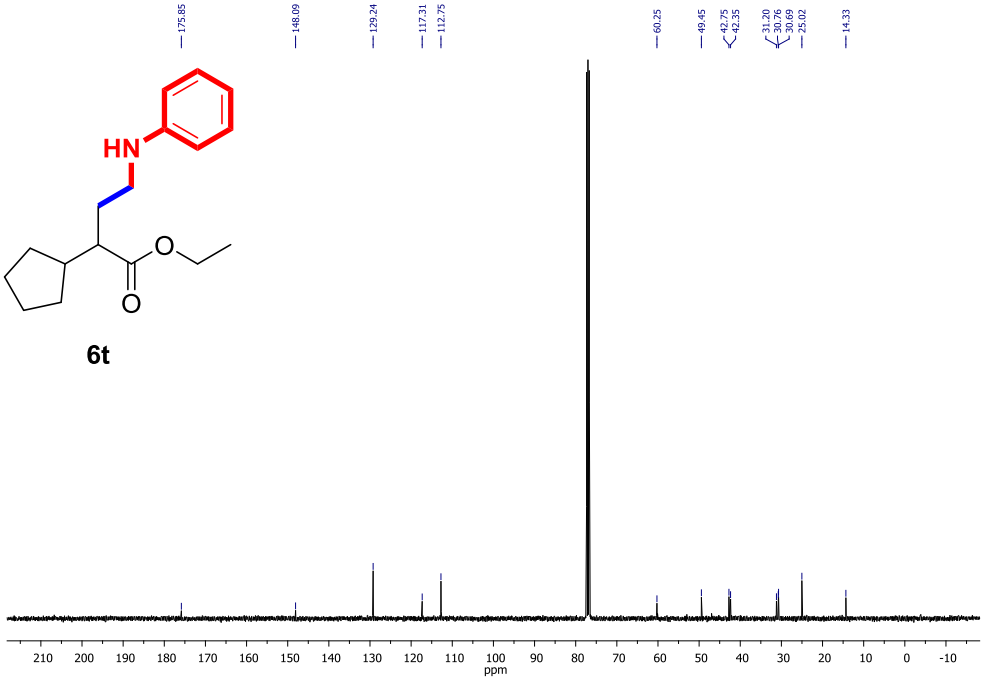


6s

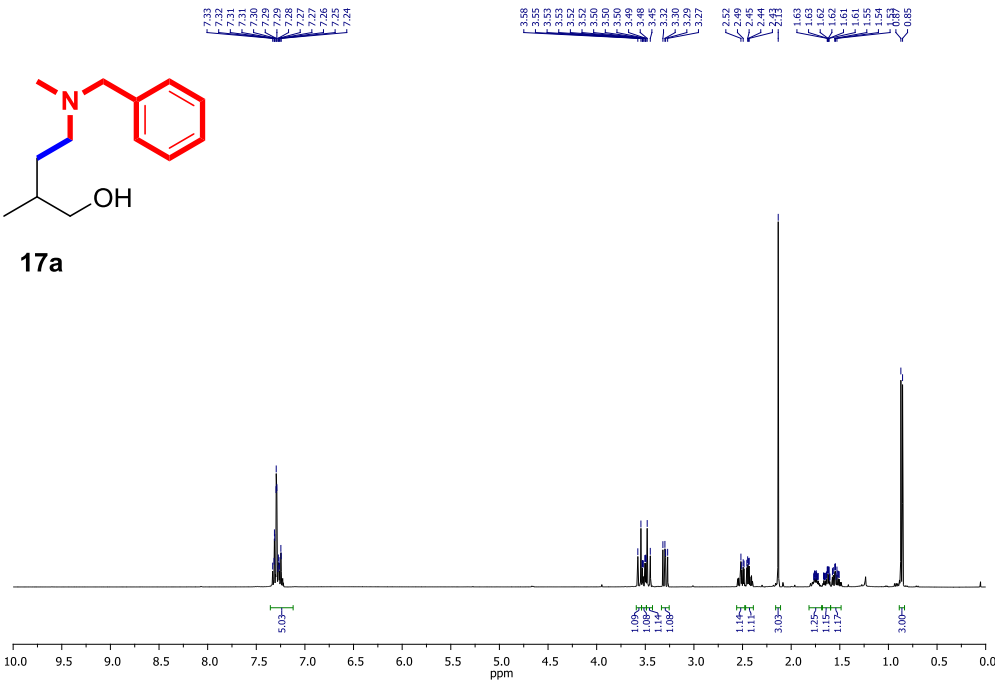
^{1}H NMR ($CDCl_3$, 400 MHz)



^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)

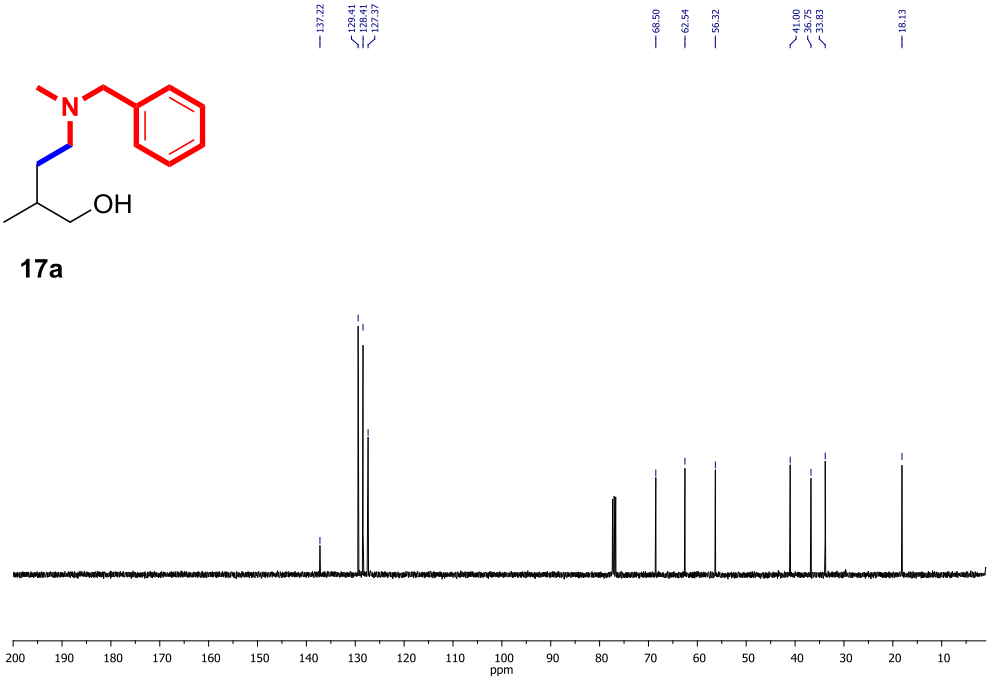


^{1}H NMR ($CDCl_3$, 400 MHz)



17a

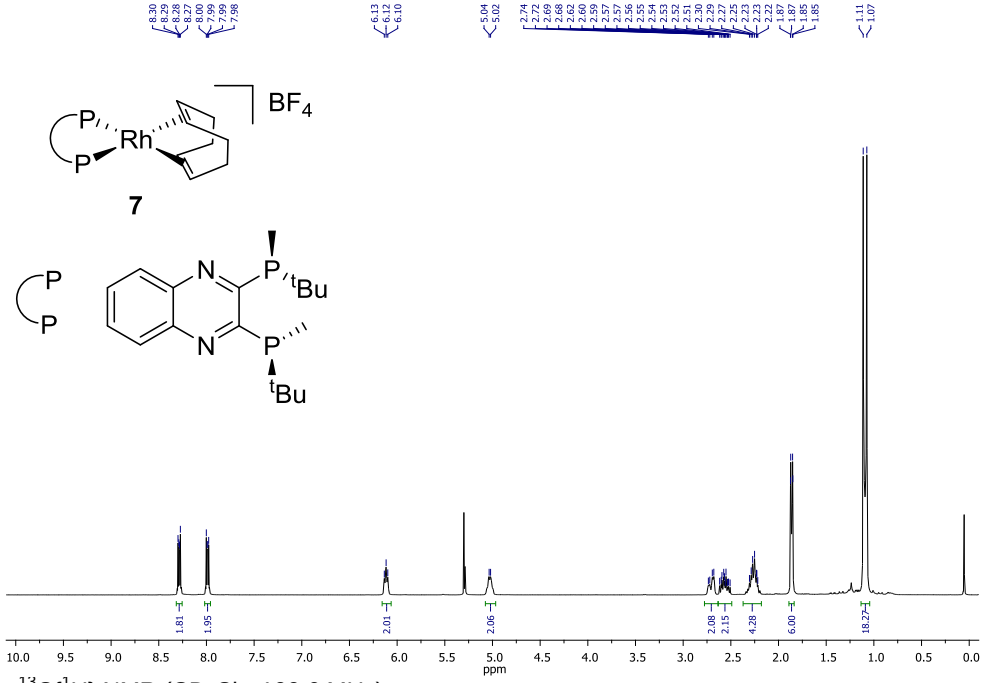
^{13}C{^{1}H} NMR ($CDCl_3$, 100.6 MHz)



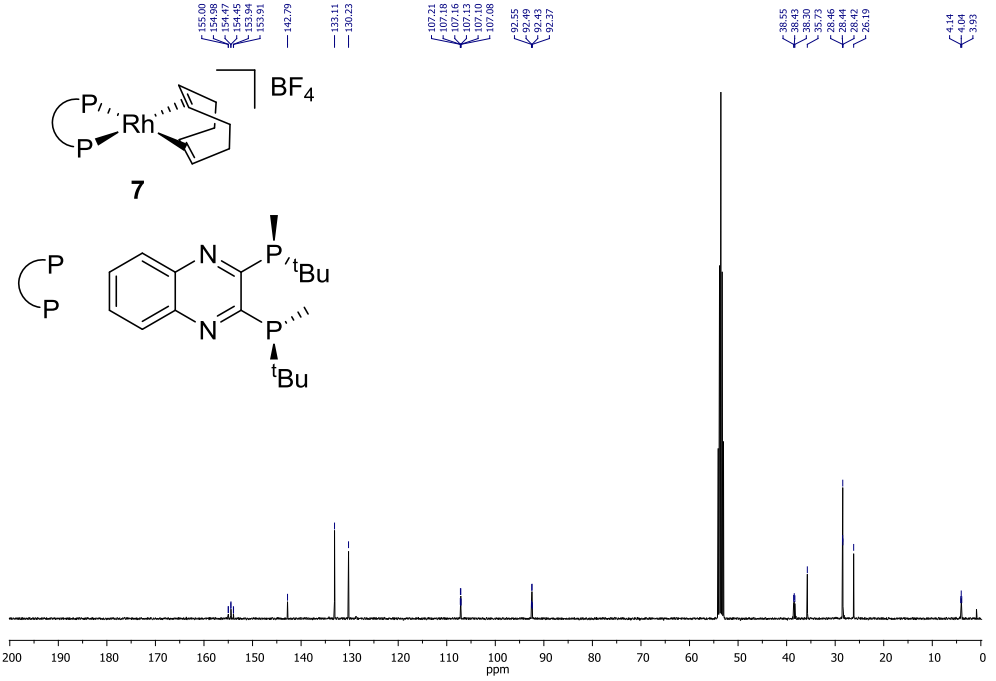
17a

SXI. Spectroscopic data of rhodium complexes 7, 8 and 9

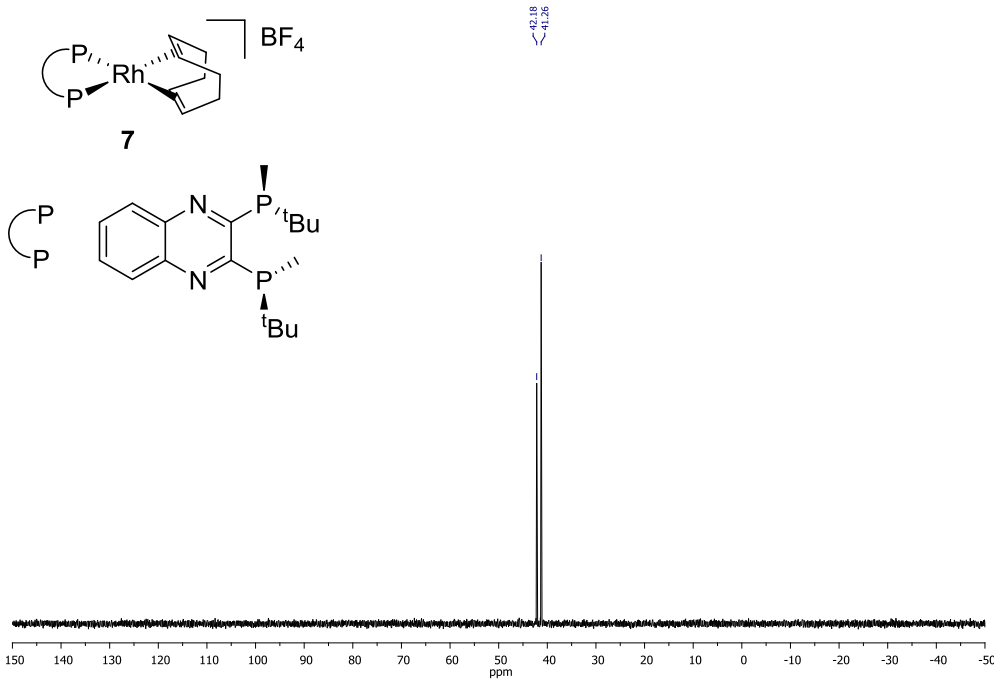
^{1}H NMR (CD_2Cl_2, 400 MHz)



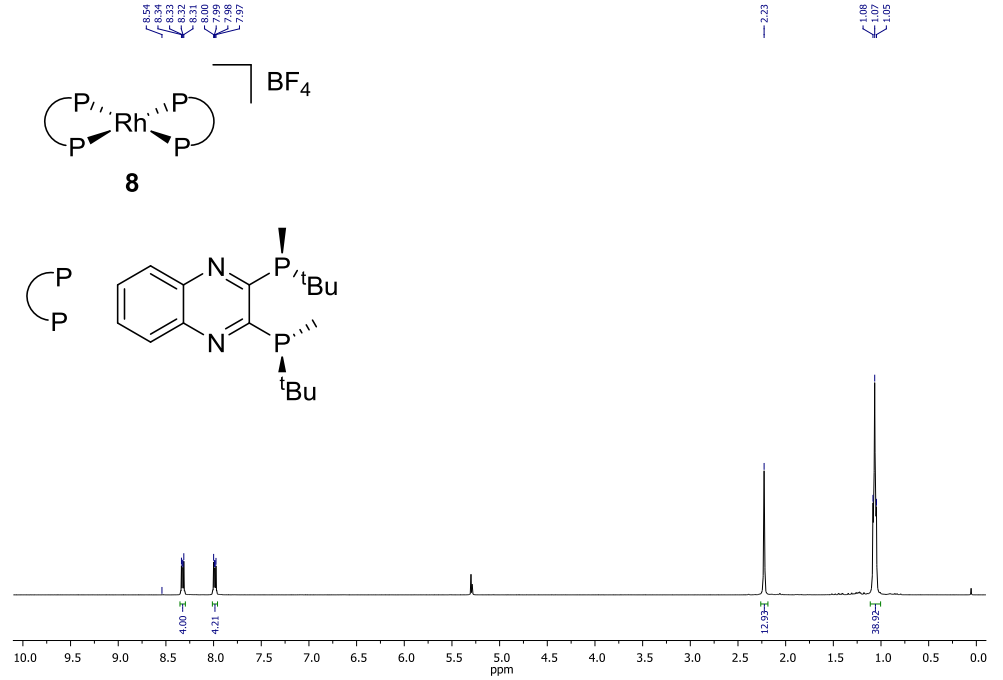
^{13}C{^{1}H} NMR (CD_2Cl_2, 100.6 MHz)



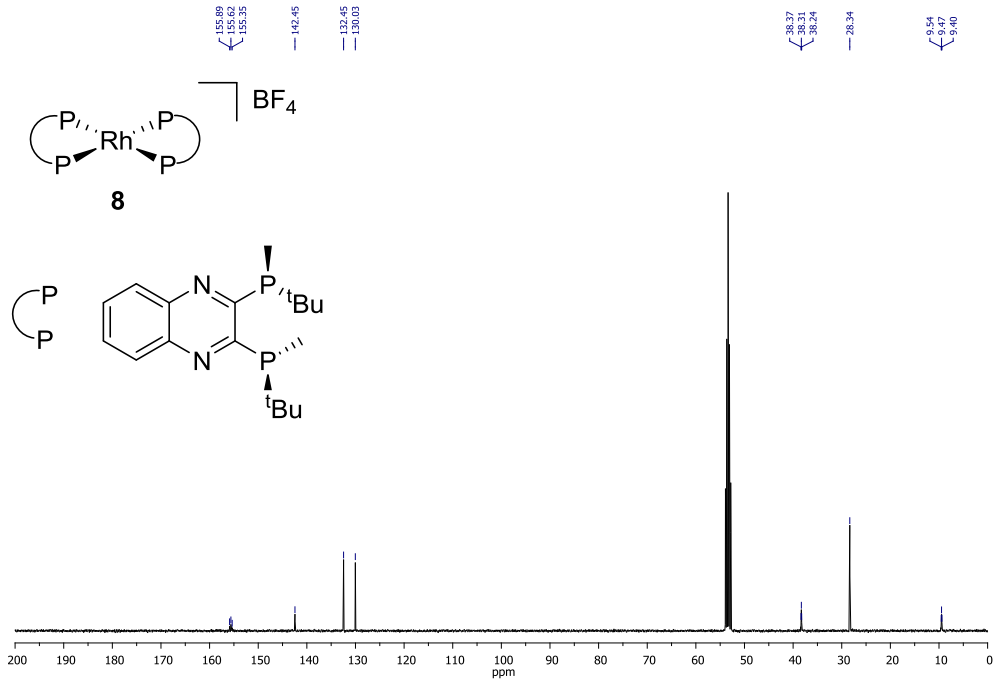
$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 161.97 MHz)



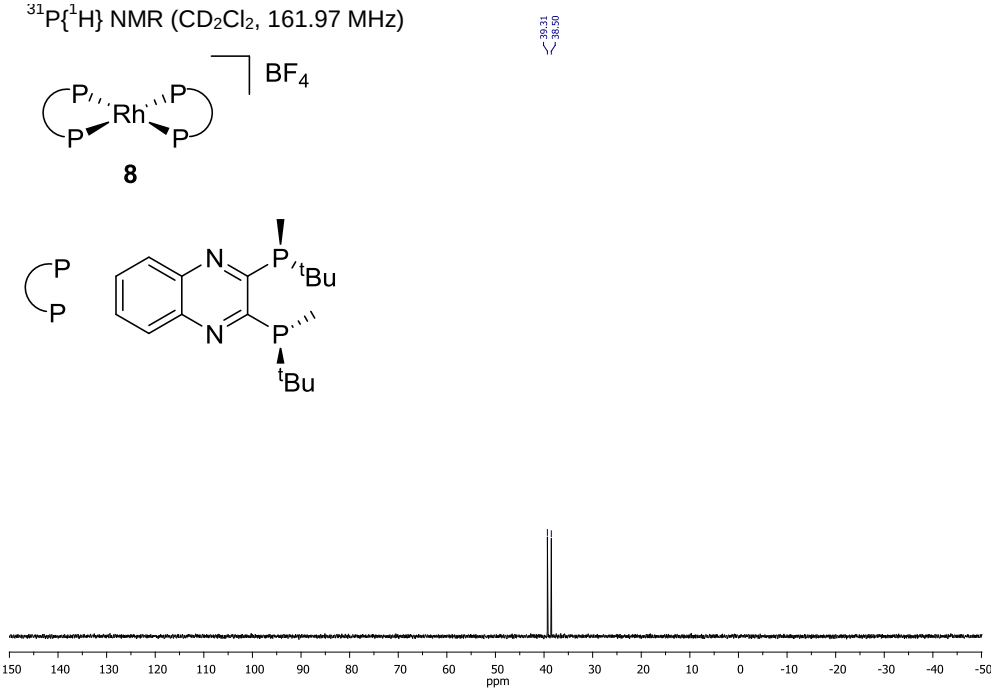
^{1}H NMR (CD_2Cl_2, 400 MHz)



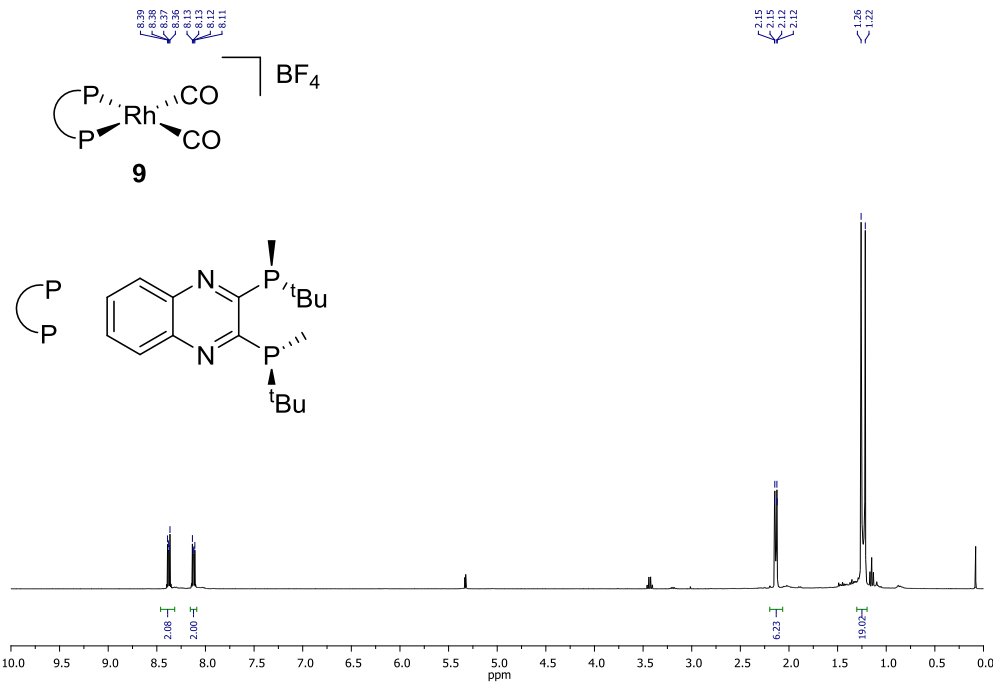
$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100.6 MHz)



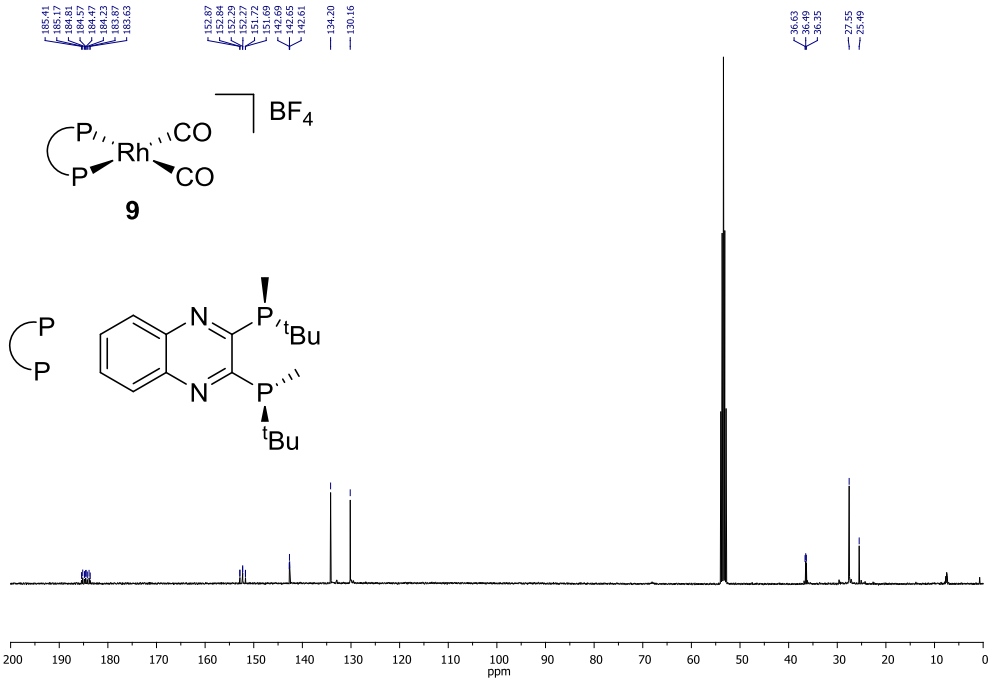
$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 161.97 MHz)



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

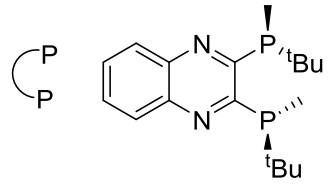


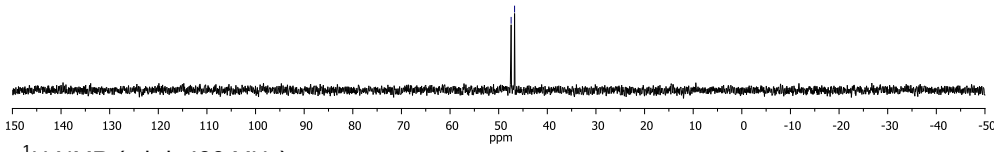
$^{13}C\{^{1}H\}$ NMR (CD_2Cl_2, 100.6 MHz)



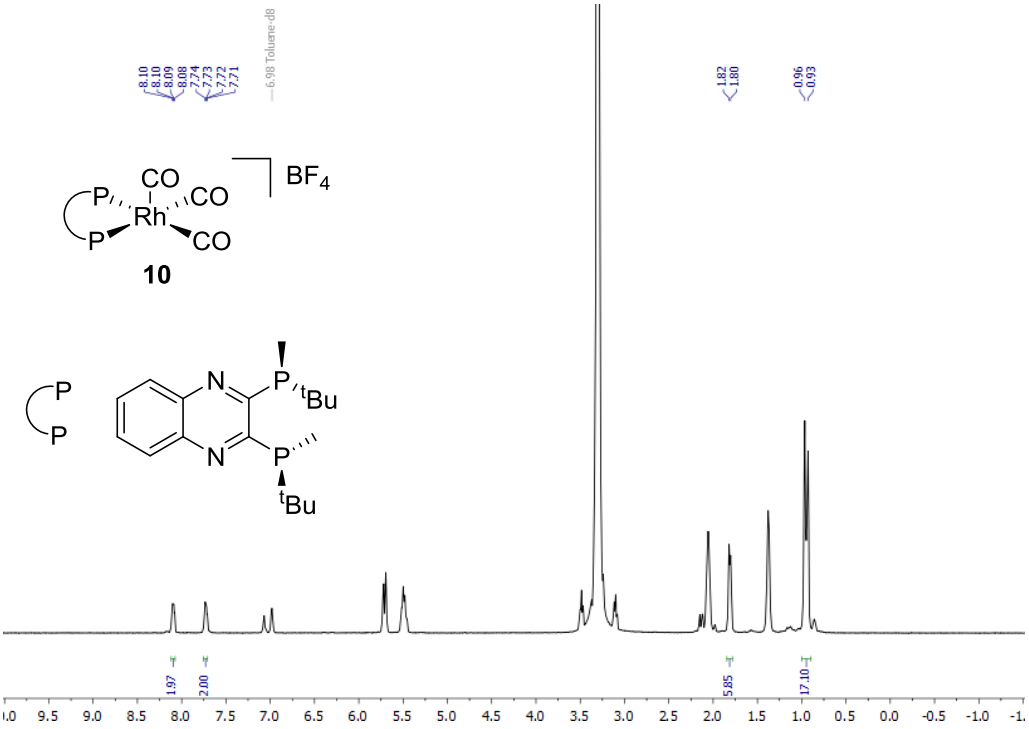
$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 161.97 MHz)

9



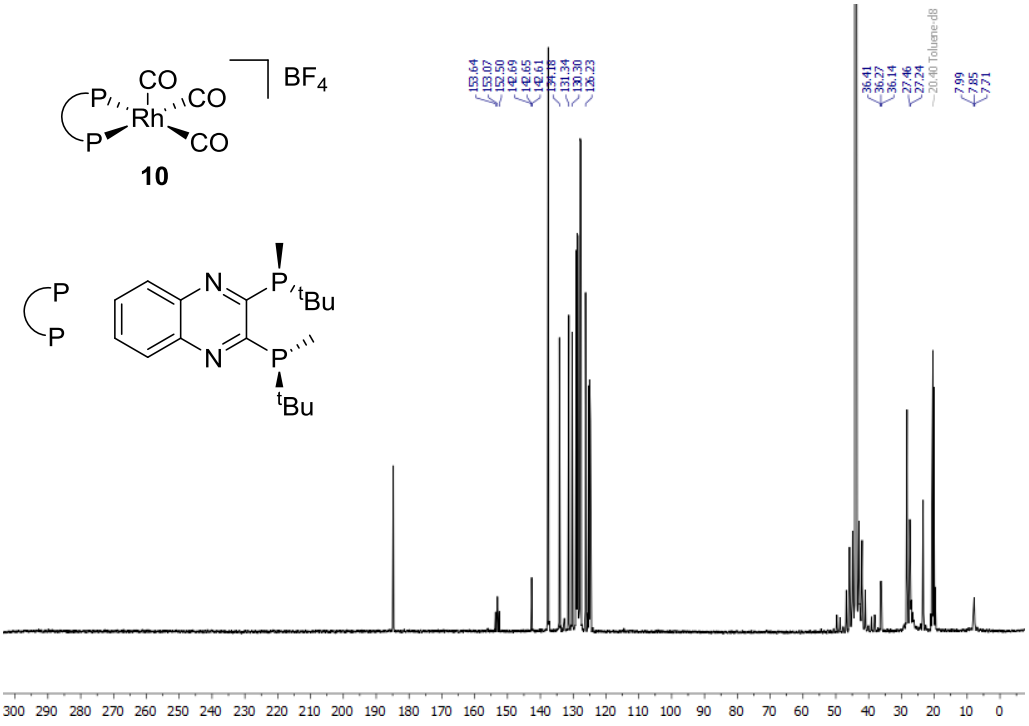


^{1}H NMR (tol-d, 400 MHz)

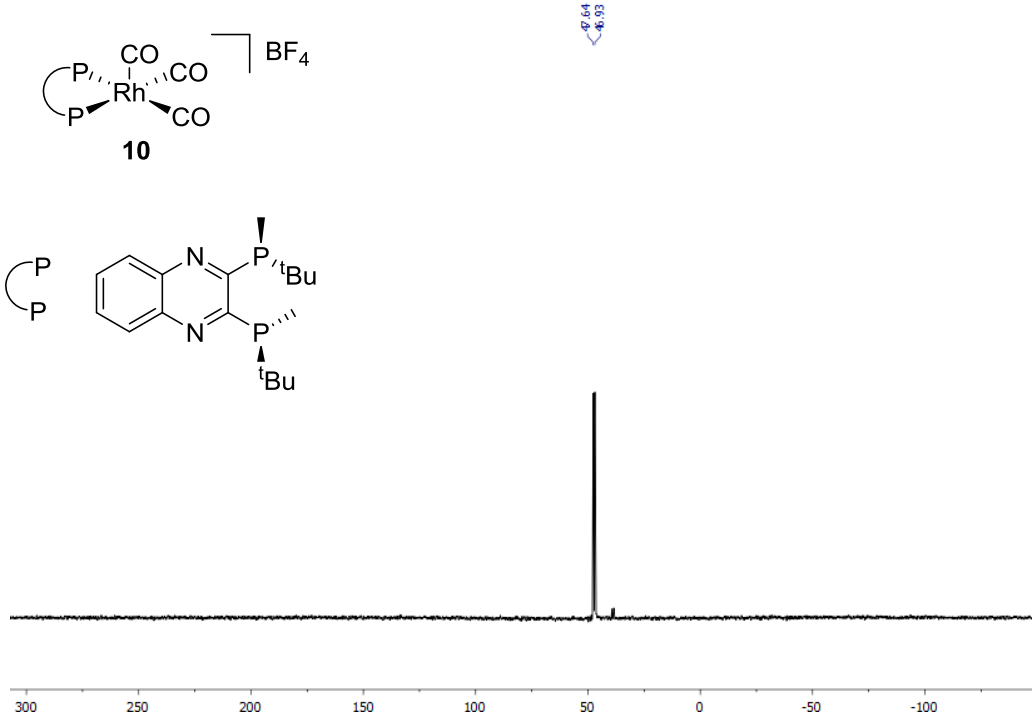


10

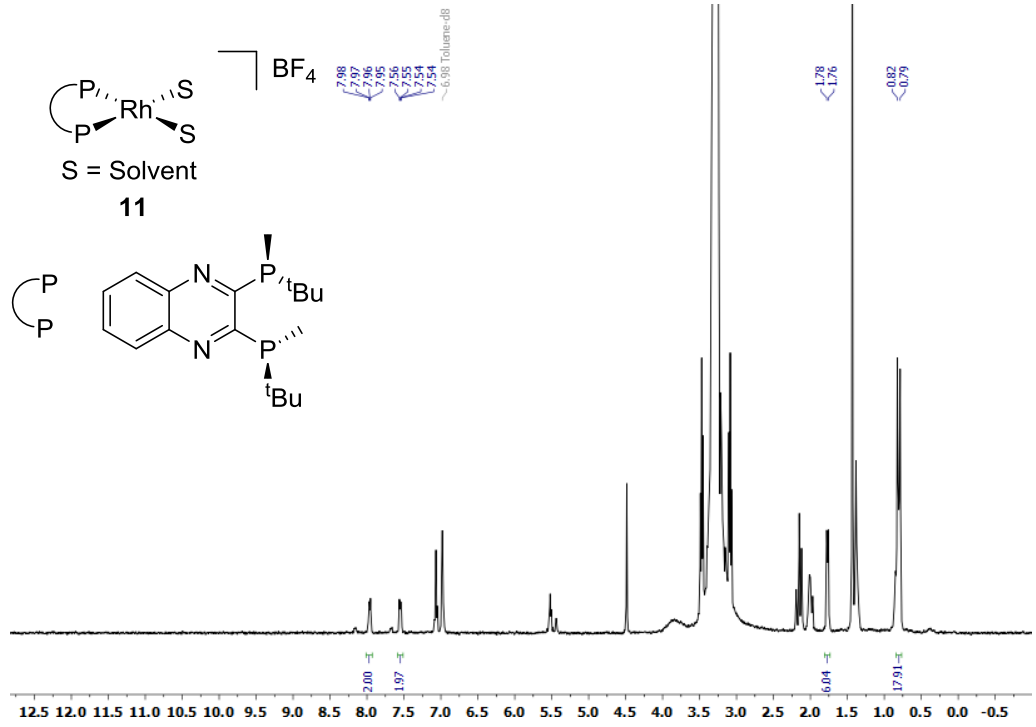
$^{13}C\{^{1}H\}$ NMR (tol-d, 100.6 MHz)



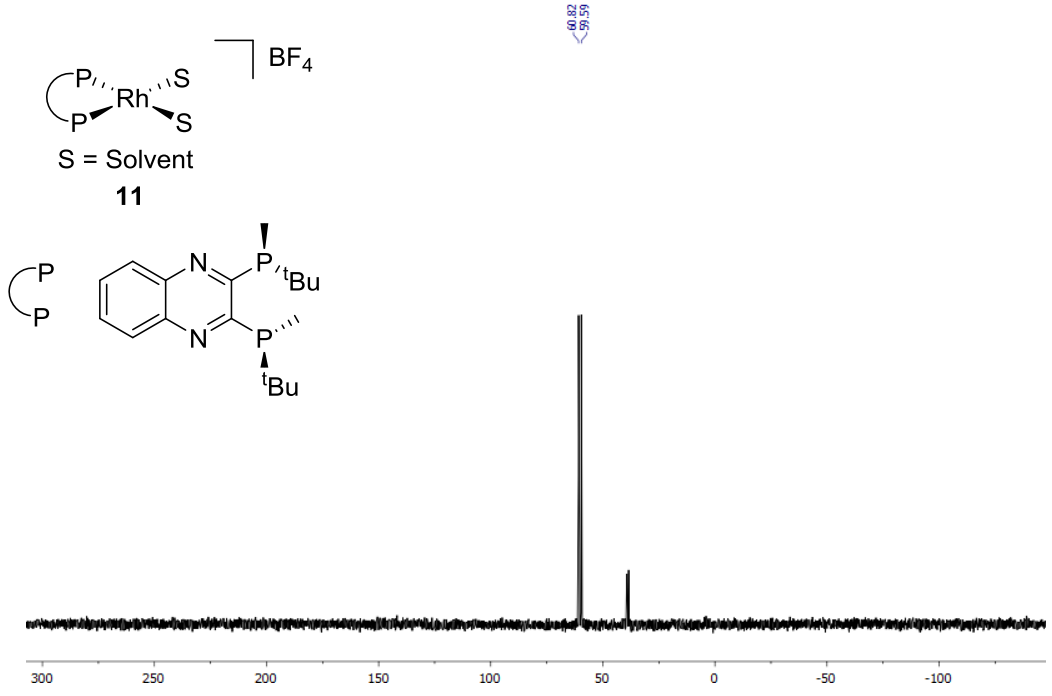
$^{31}P\{^{1}H\}$ NMR (CD_2Cl_2, 161.97 MHz)



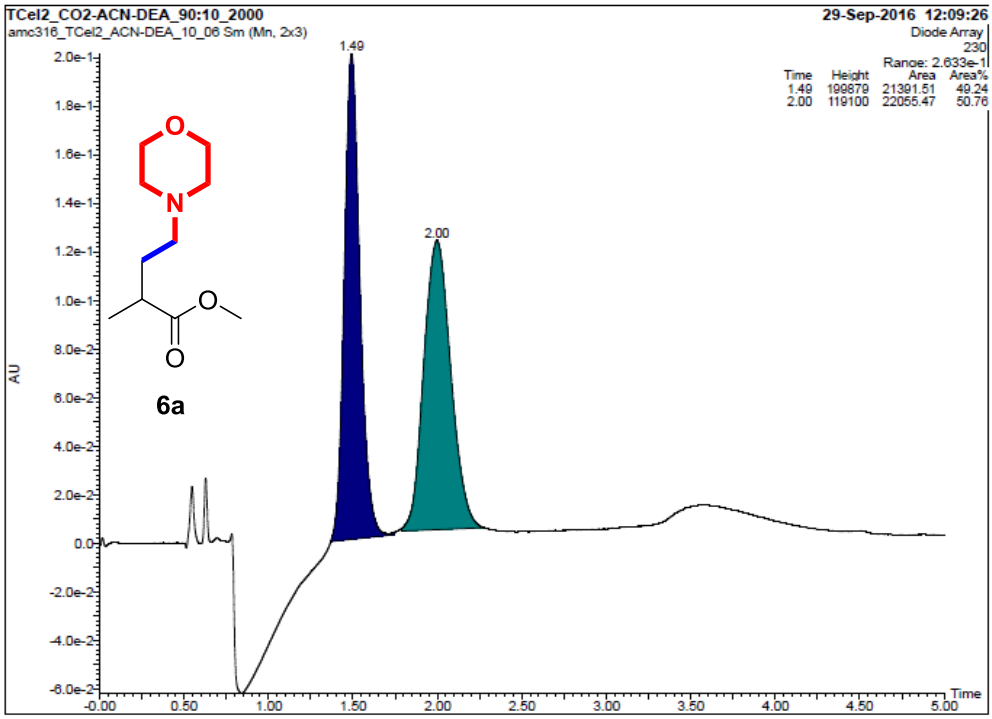
^{1}H NMR (tol-d, 400 MHz)

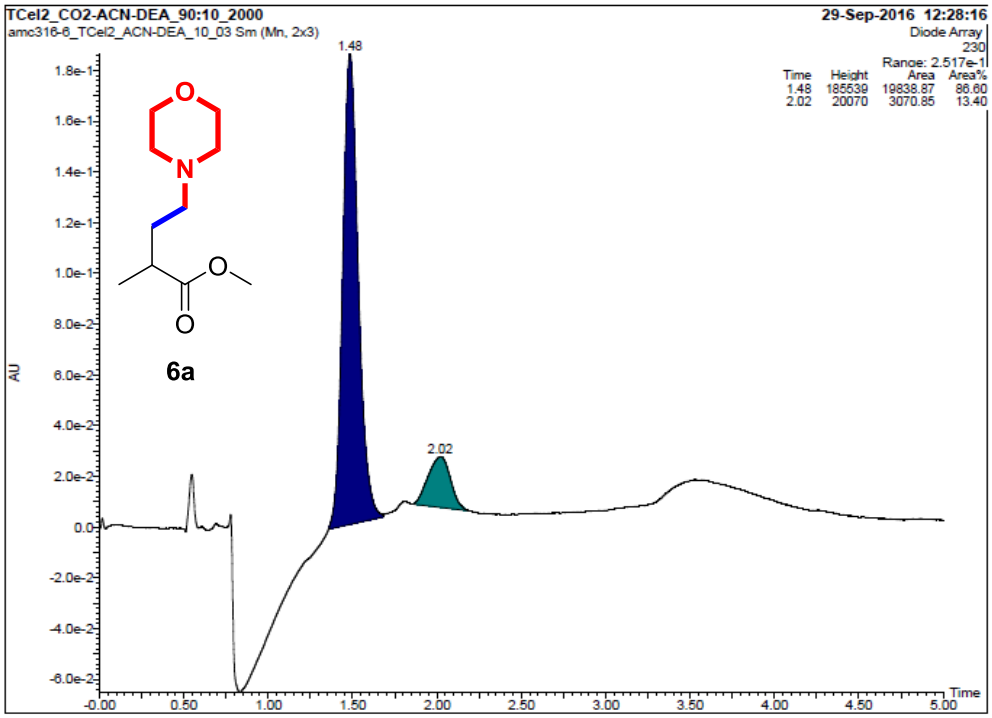


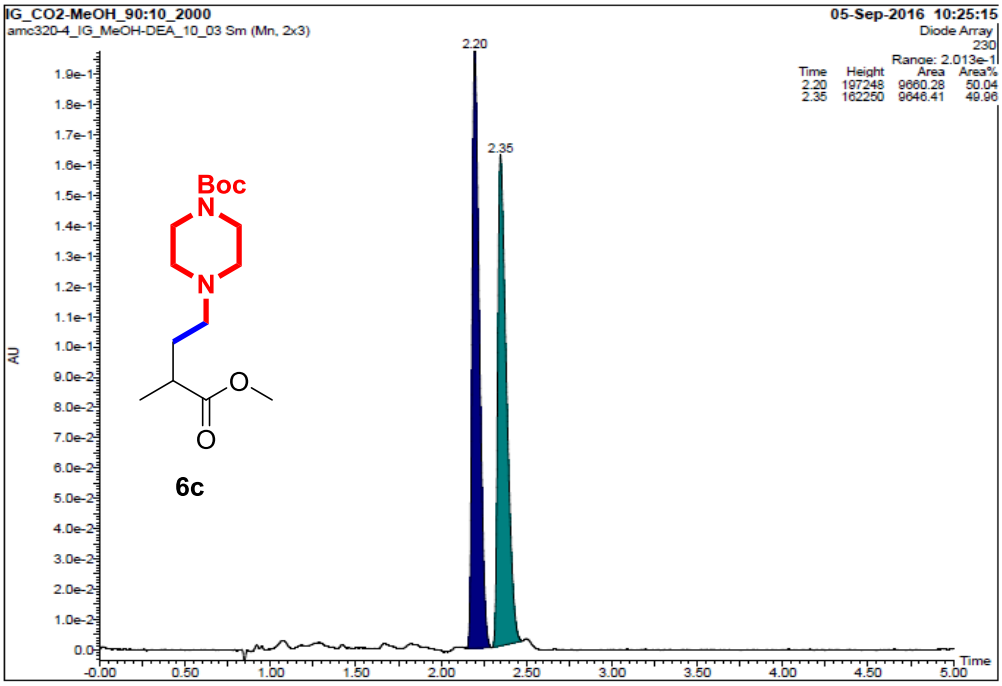
^{31}P{^{1}H} NMR (tol-d, 161.97 MHz)

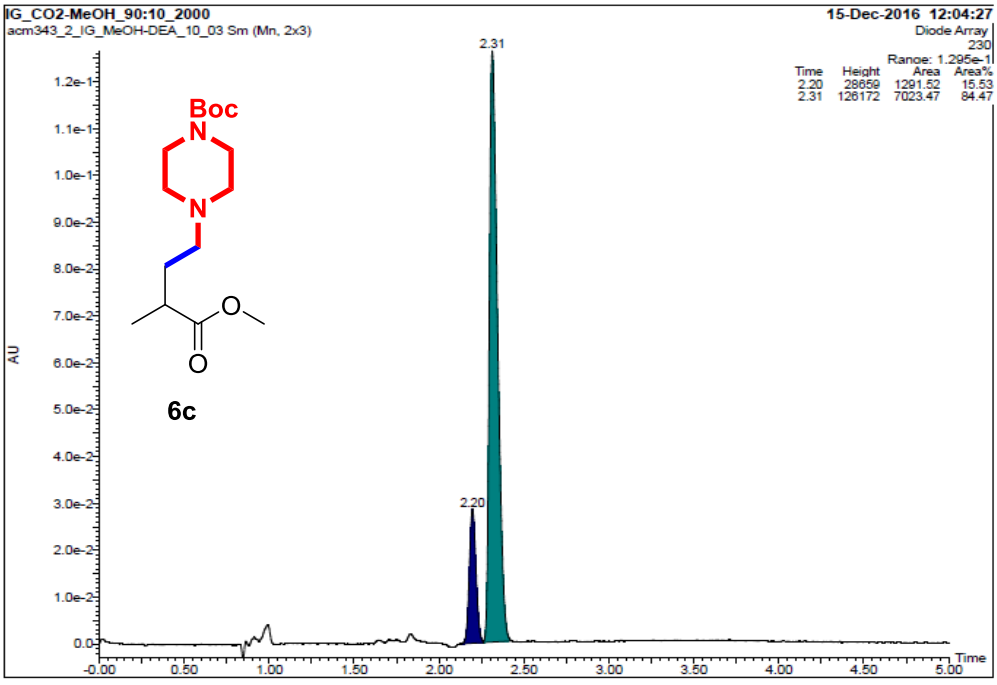


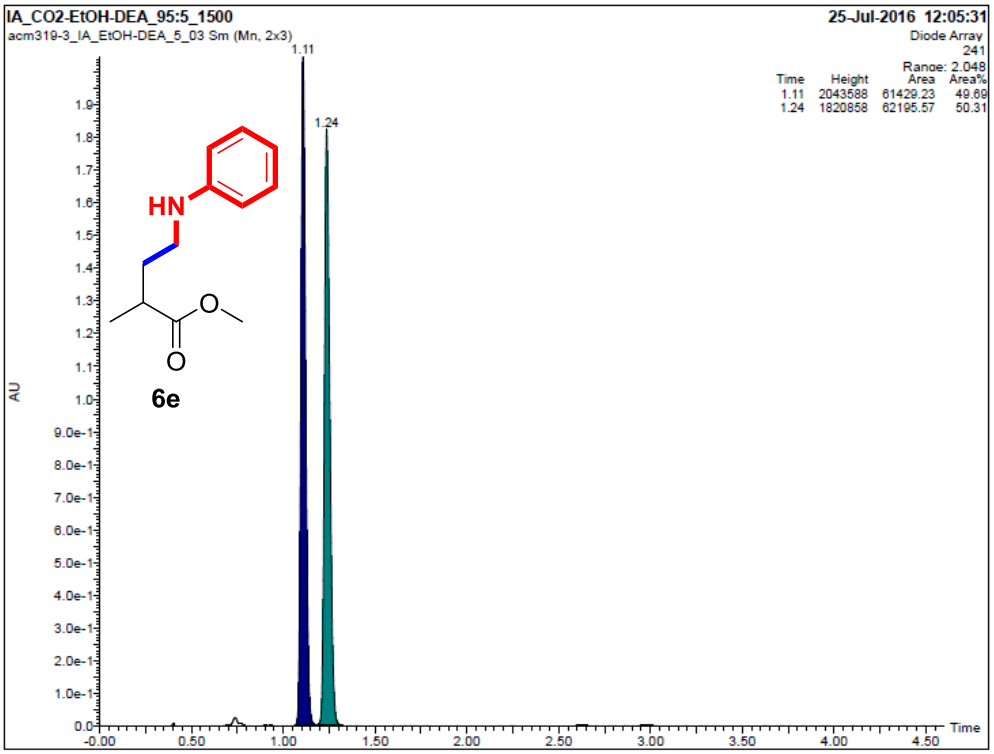
SXII. Enantiomeric excess determination

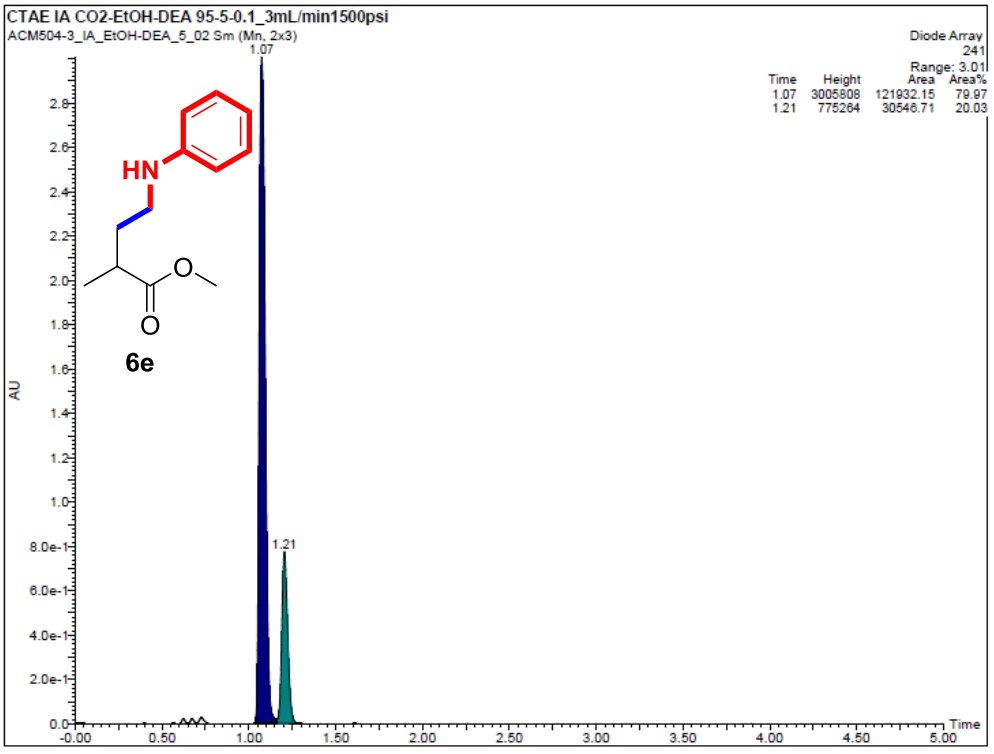


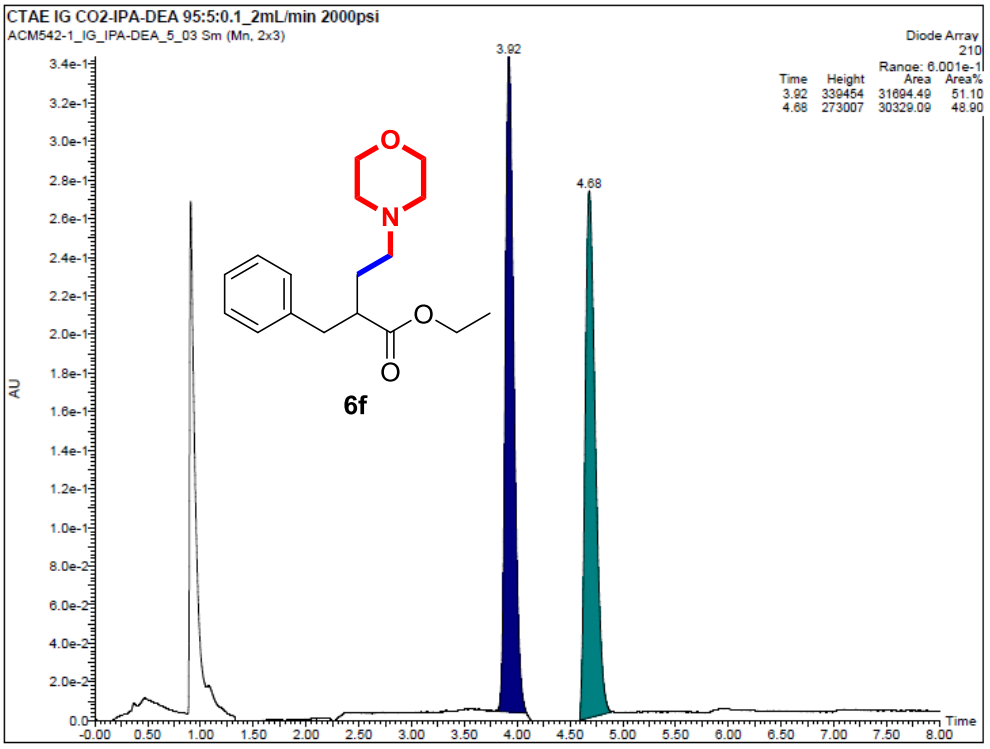


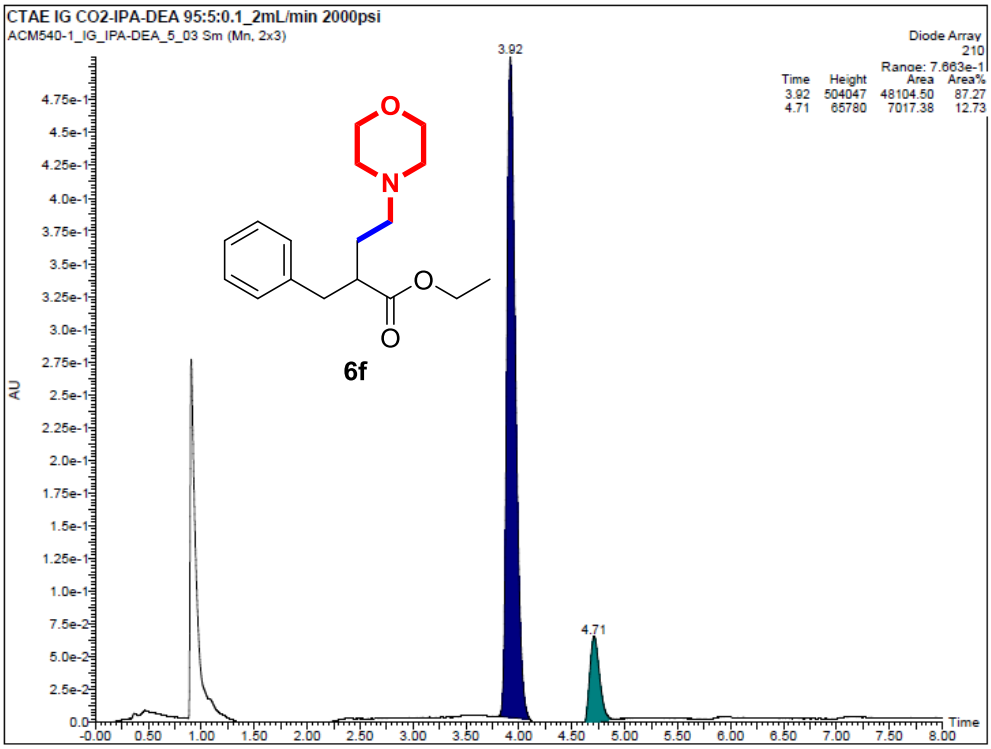

IG_CO2-MeOH_90:10_2000
amc320-4_IG_MeOH-DEA_10_03 Sm (Mn, 2x3)
05-Sep-2016 10:25:15
Diode Array
230
Range: 2.013e-1
Time Height Area Area%
2.20 197248 9660.28 50.04
2.35 162250 9646.41 49.96
2.20
2.35
Boc
N
N
O
O
6c
AU
Time

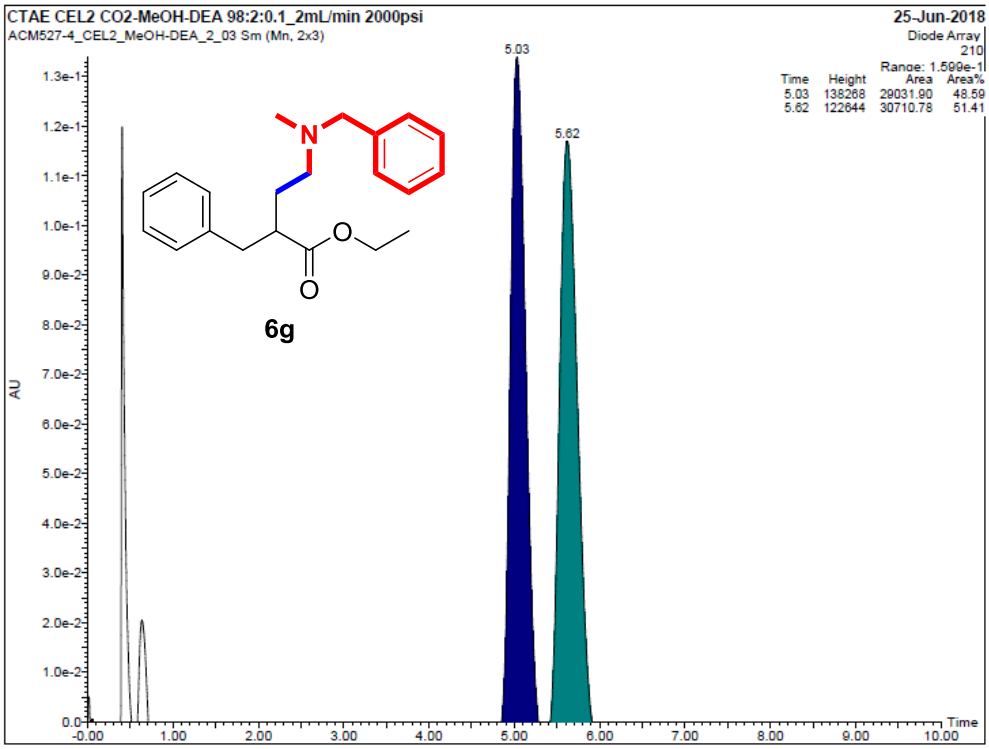

IG_CO2-MeOH_90:10_2000
acm343_2_IG_MeOH-DEA_10_03 Sm (Mn, 2x3)
15-Dec-2016 12:04:27
Diode Array
230
Range: 1.295e-1
Time Height Area Area%
2.20 28659 1291.52 15.53
2.31 126172 7023.47 84.47
2.31
2.20
Boc
N
N
O
O
6c
AU
Time

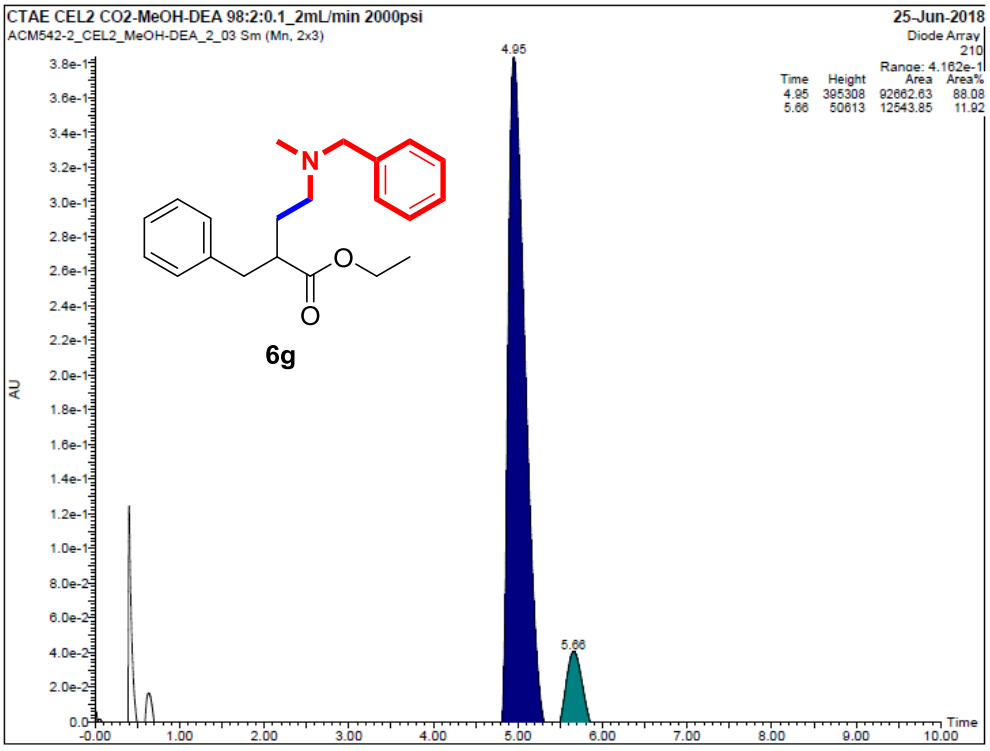

IA_CO2-EtOH-DEA_95:5_1500
25-Jul-2016 12:05:31
acm319-3_IA_EtOH-DEA_5_03 Sm (Mn, 2x3)
Diode Array
241
Range: 2.048
Time Height Area Area%
1.11 2043588 61429.23 49.69
1.24 1820858 62195.57 50.31
1.11
1.24
HN
O
O
6e
AU
Time

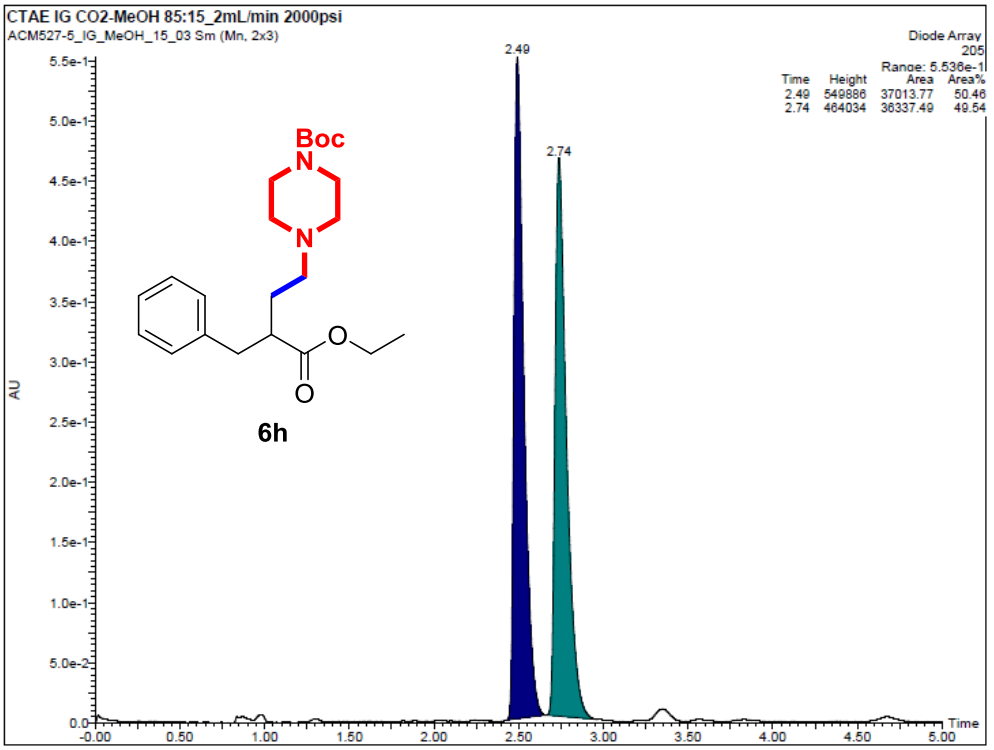

CTAE IA CO2-EtOH-DEA 95-5-0.1_3mL/min1500psi
ACM504-3_IA_EtOH-DEA_5_02 Sm (Mn, 2x3)
Diode Array
241
Range: 3.01
Time Height Area Area%
1.07 3005808 121932.15 79.97
1.21 775264 30546.71 20.03
1.07
1.21
HN
O
O
6e
AU
Time

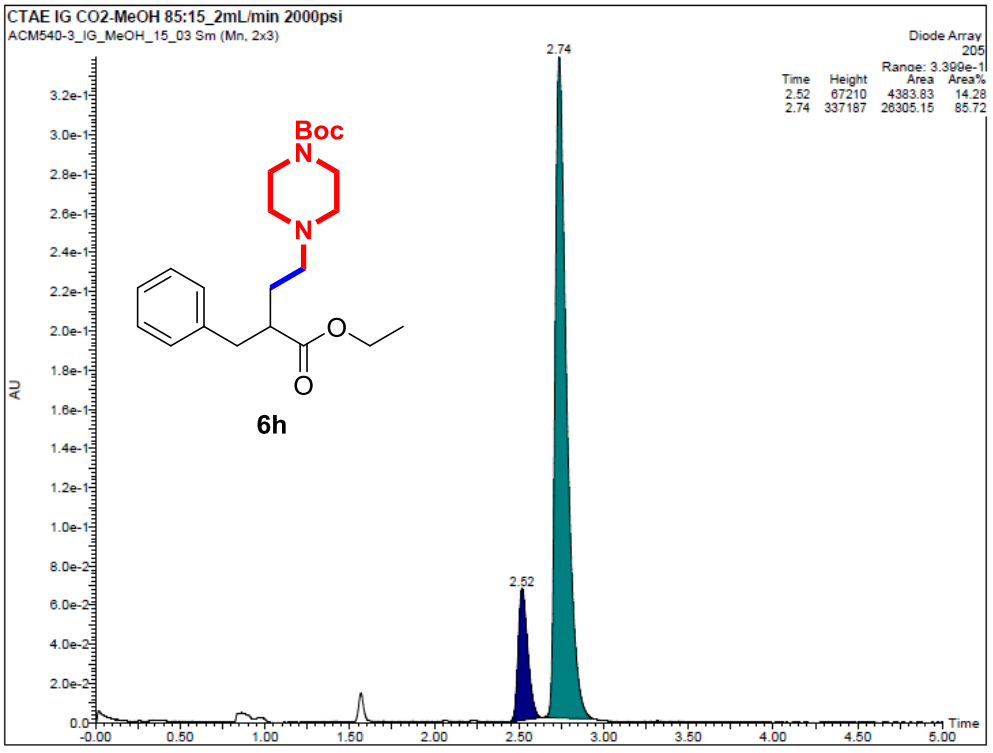

CTAE IG CO2-IPA-DEA 95:5:0.1_2mL/min 2000psi
ACM542-1_IG_IPA-DEA_5_03 Sm (Mn, 2x3)
Diode Array
210
Range: 6.001e-1
Time Height Area Area%
3.92 339454 31694.49 51.10
4.68 273007 30329.09 48.90
3.92
4.68
AU
Time
6f

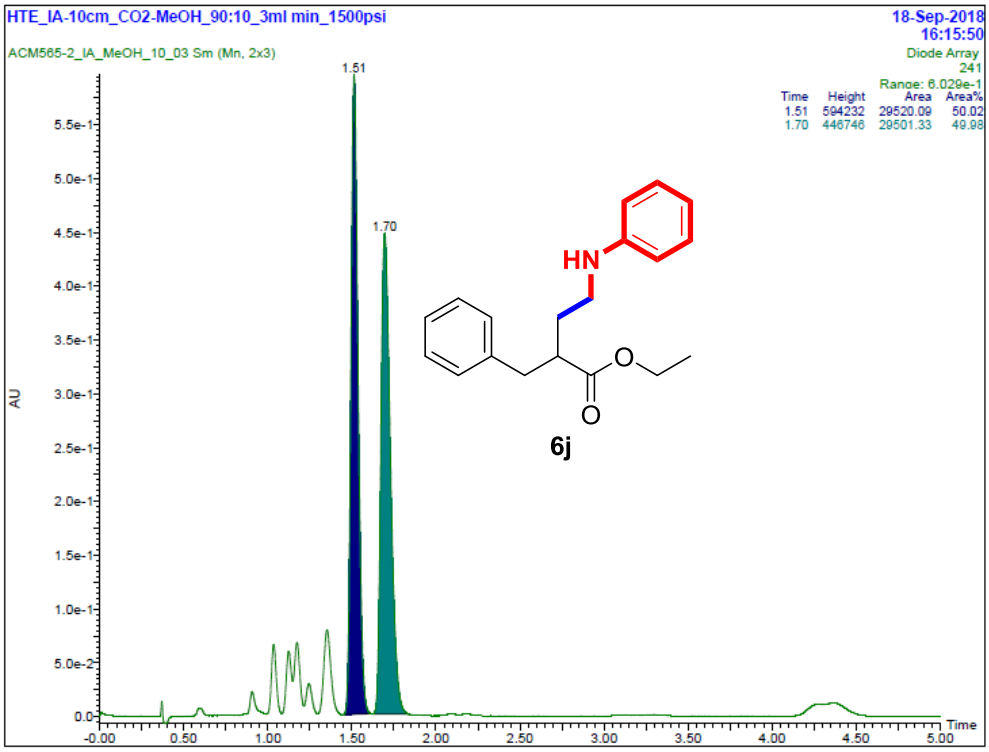

CTAE IG CO2-IPA-DEA 95:5:0.1_2mL/min 2000psi
ACM540-1_IG_IPA-DEA_5_03 Sm (Mn, 2x3)
Diode Array
210
Range: 7.663e-1
Time Height Area Area%
3.92 504047 48104.50 87.27
4.71 65780 7017.38 12.73
3.92
4.71
AU
Time
6f

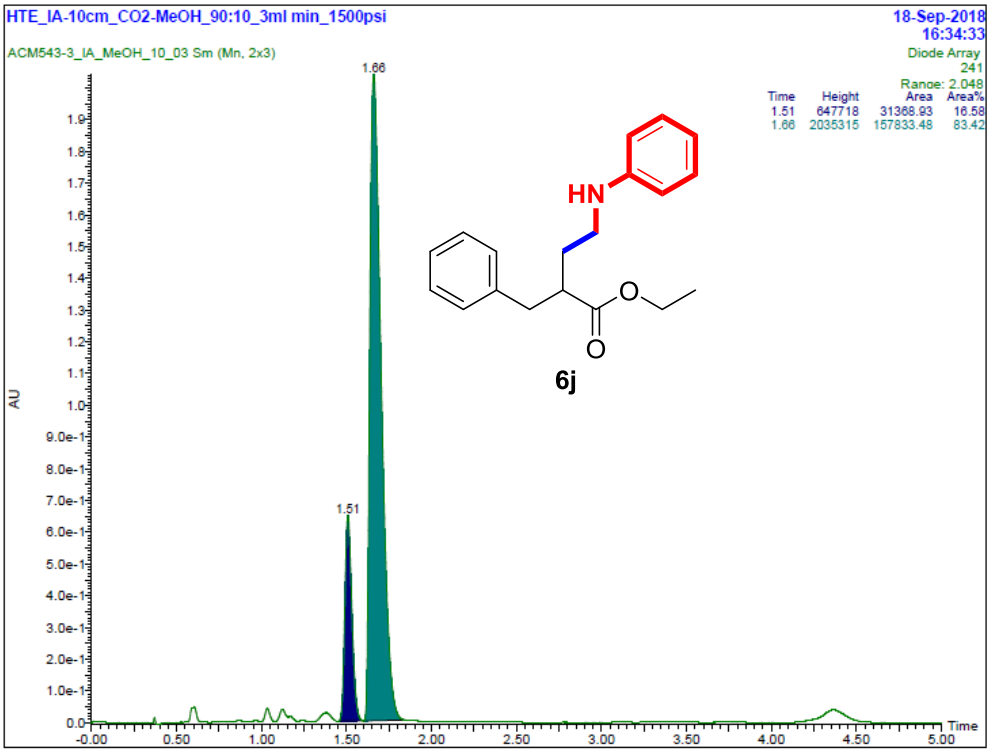

CTAE CEL2 CO2-MeOH-DEA 98:2:0.1_2mL/min 2000psi
25-Jun-2018
ACM527-4_CEL2_MeOH-DEA_2_03 Sm (Mn, 2x3)
Diode Array
210
Range: 1.599e-1
Time Height Area Area%
5.03 138268 29031.90 48.59
5.62 122644 30710.78 51.41
5.03
5.62
6g
AU
Time

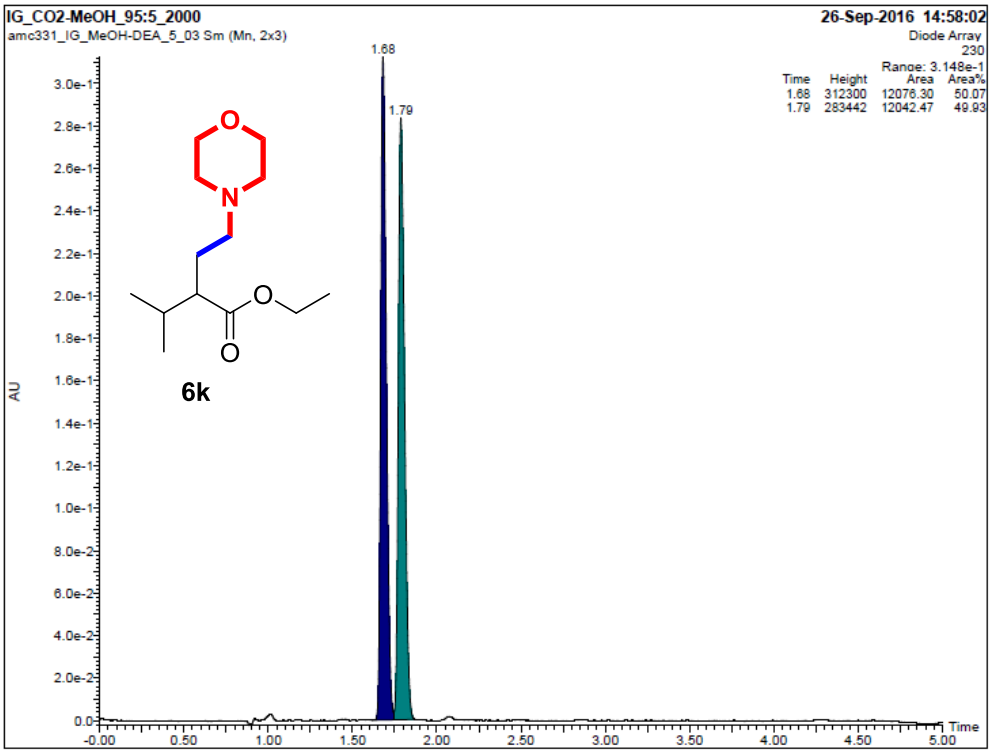

CTAE CEL2 CO2-MeOH-DEA 98:2:0.1_2mL/min 2000psi
25-Jun-2018
ACM542-2_CEL2_MeOH-DEA_2_03 Sm (Mn, 2x3)
Diode Array
210
Range: 4.162e-1
Time Height Area Area%
4.95 395308 92662.63 88.08
5.66 50613 12543.85 11.92
4.95
5.66
6g
AU
Time

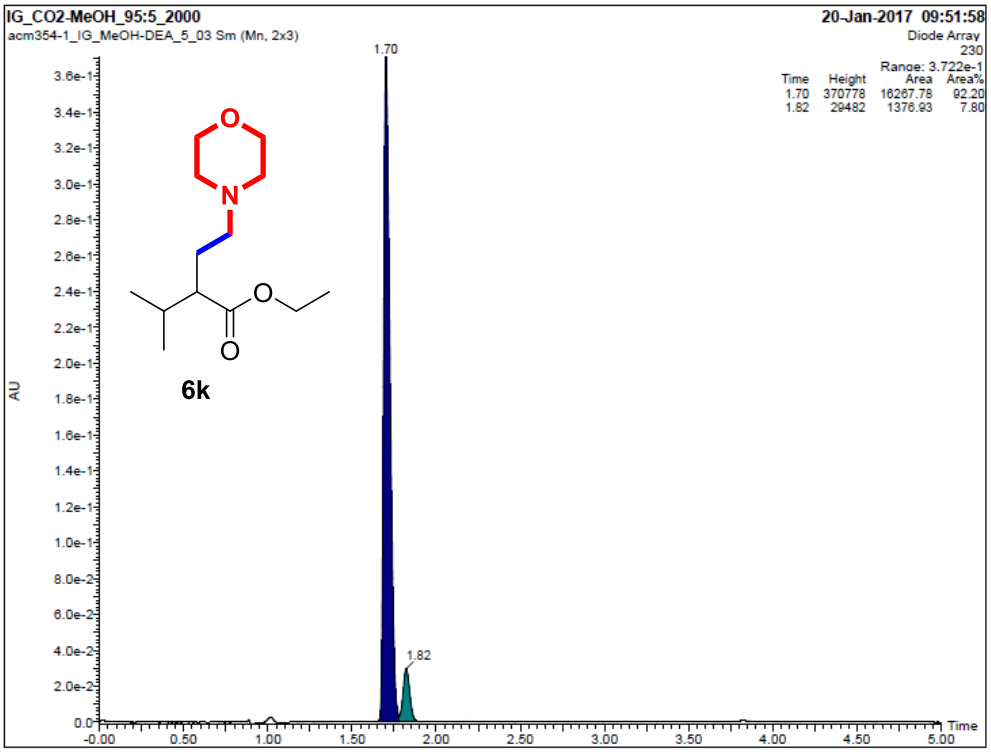

CTAE IG CO2-MeOH 85:15_2mL/min 2000psi
ACM527-5_IG_MeOH_15_03 Sm (Mn, 2x3)
Diode Array
205
Range: 5.536e-1
Time Height Area Area%
2.49 549886 37013.77 50.46
2.74 464034 36337.49 49.54
2.49
2.74
Boc
N
N
O
O
6h
AU
Time

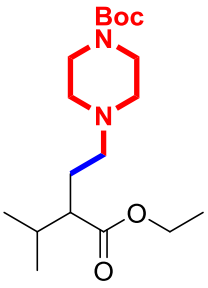

CTAE IG CO2-MeOH 85:15_2mL/min 2000psi
ACM540-3_IG_MeOH_15_03 Sm (Mn, 2x3)
Diode Array
205
Range: 3.399e-1
Time Height Area Area%
2.52 67210 4383.83 14.28
2.74 337187 26305.15 85.72
2.74
2.52
Boc
N
N
O
O
6h
AU
Time


HTE_IA-10cm_CO2-MeOH_90:10_3ml min_1500psi
18-Sep-2018
16:15:50
ACM565-2_IA_MeOH_10_03 Sm (Mn, 2x3)
Diode Array
241
Range: 6.029e-1
Time Height Area Area%
1.51 564232 29520.09 50.02
1.70 446746 29501.33 49.98
1.51
1.70
AU
Time
HN
O
O
6j

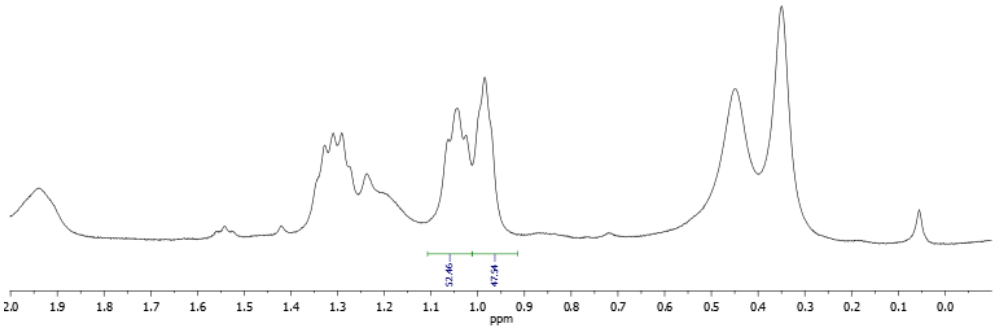

HTE_IA-10cm_CO2-MeOH_90:10_3ml min_1500psi
18-Sep-2018
16:34:33
ACM543-3_IA_MeOH_10_03 Sm (Mn, 2x3)
Diode Array
241
Range: 2.048
Time Height Area Area%
1.51 647718 31368.93 16.58
1.66 2035315 157833.48 83.42
1.66
1.51
AU
Time
HN
O
O
6j

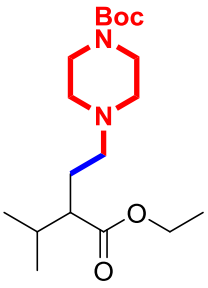

IG_CO2-MeOH_95:5_2000
amc331_IG_MeOH-DEA_5_03 Sm (Mn, 2x3)
26-Sep-2016 14:58:02
Diode Array
230
Range: 3.148e-1
Time Height Area Area%
1.68 312300 12076.30 50.07
1.79 283442 12042.47 49.93
1.68
1.79
6k
AU
Time


IG_CO2-MeOH_95:5_2000
acm354-1_IG_MeOH-DEA_5_03 Sm (Mn, 2x3)
20-Jan-2017 09:51:58
Diode Array
230
Range: 3.722e-1
Time Height Area Area%
1.70 370778 16267.78 92.20
1.82 29482 1376.93 7.80
1.70
1.82
6k
AU
Time


Boc
N
N
O
O

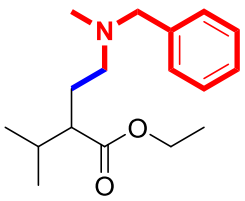
6m


52.46
47.54
2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0
ppm

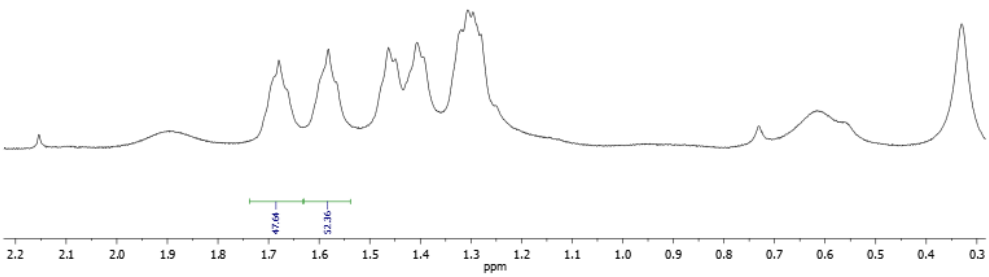

Boc
N
N
O
O

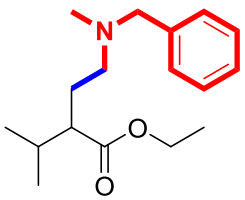
6m

8.65
91.35
2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3 0.2 0.1 0.0
ppm



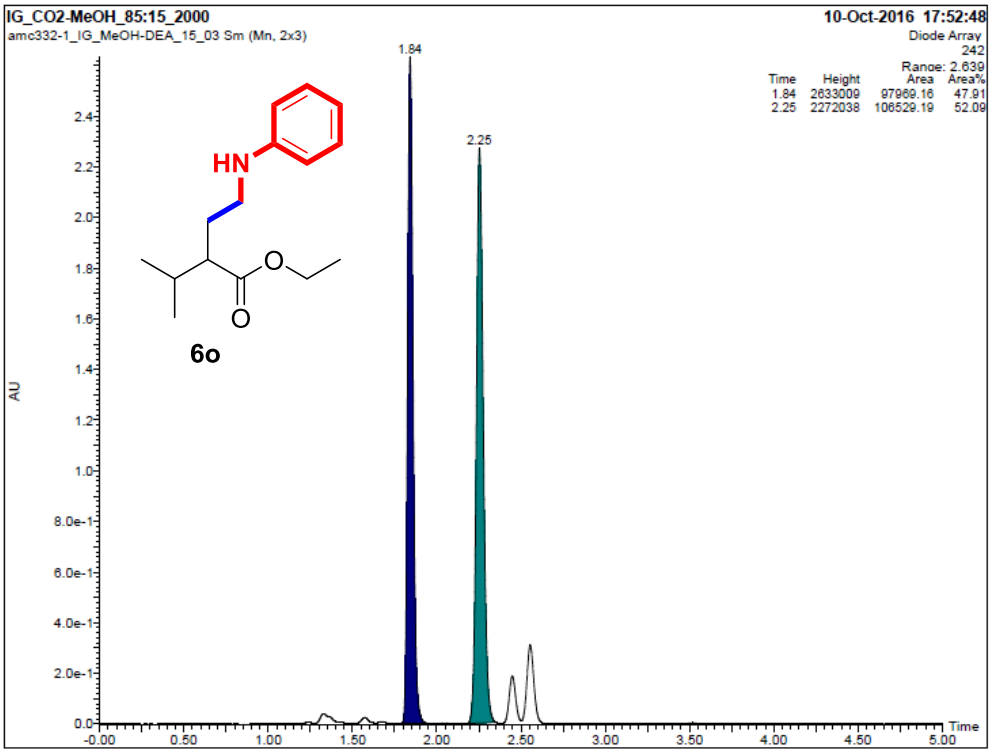
6l

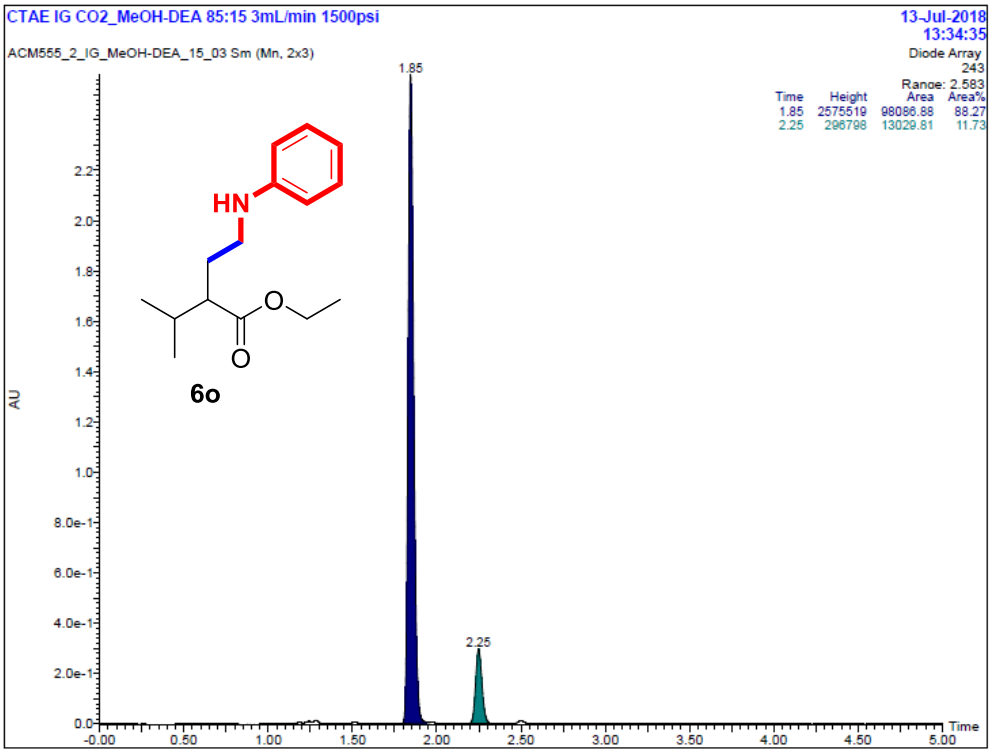

47.64
52.36
2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4 0.3
ppm

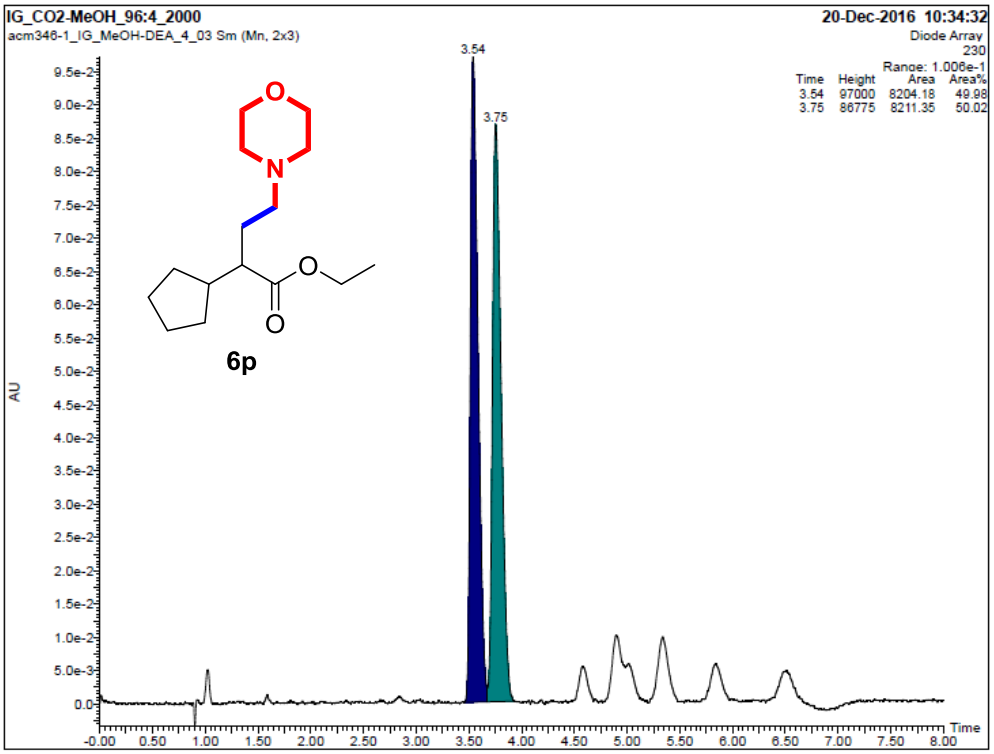


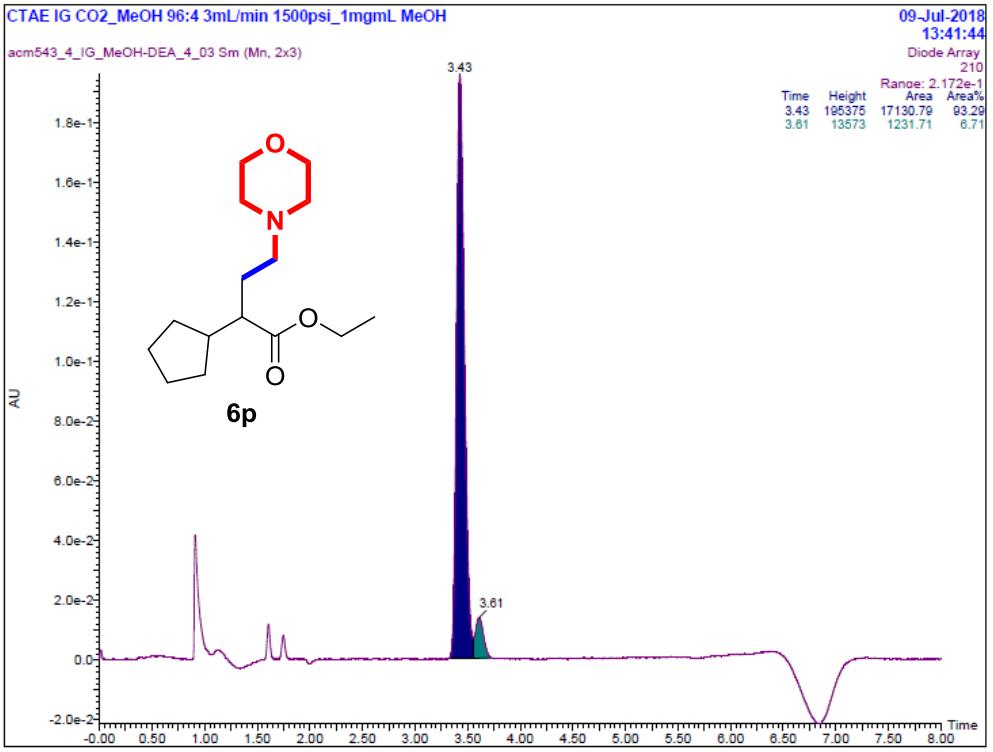
6l

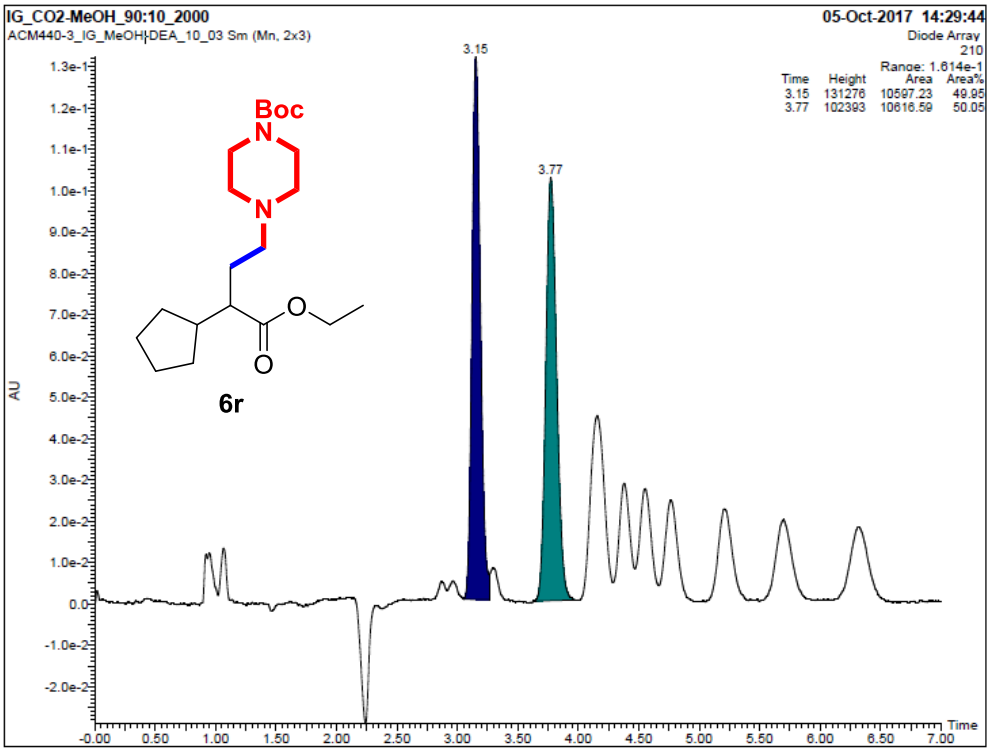
9.14
90.86
2.2 2.1 2.0 1.9 1.8 1.7 1.6 1.5 1.4 1.3 1.2 1.1 1.0 0.9 0.8 0.7 0.6 0.5 0.4
ppm

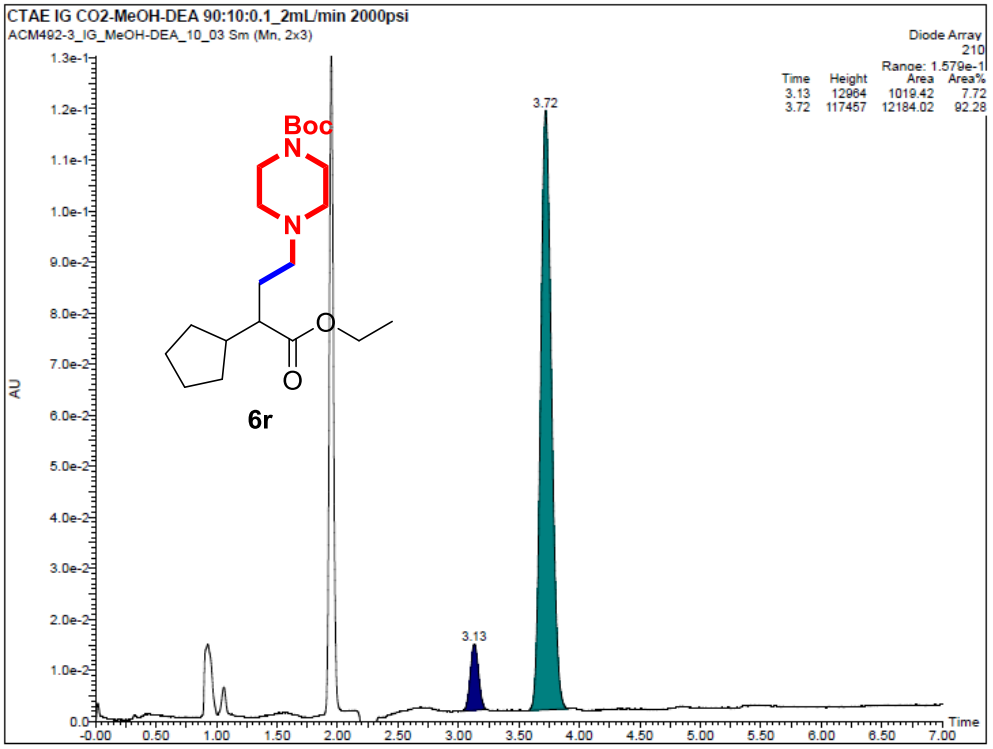

IG_CO2-MeOH_85:15_2000
10-Oct-2016 17:52:48
amc332-1_IG_MeOH-DEA_15_03 Sm (Mn, 2x3)
Diode Array
242
Range: 2.639
Time Height Area Area%
1.84 2633009 97969.16 47.91
2.25 2272038 106529.19 52.09
1.84
2.25
HN
O
O
6o
AU
Time

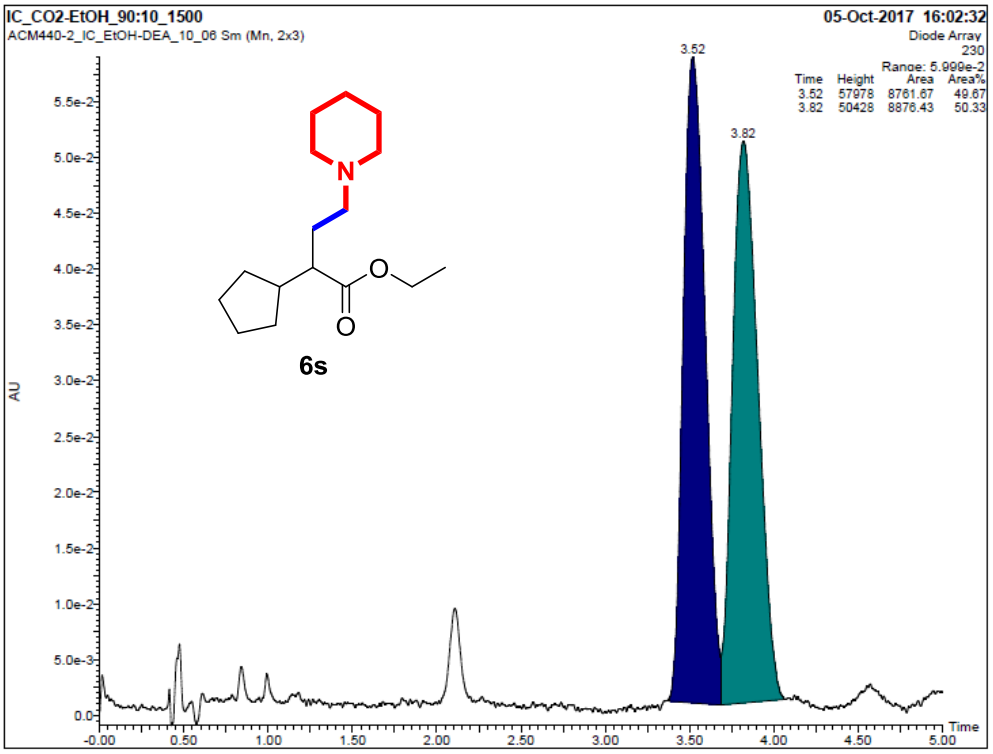

CTAE IG CO2_MeOH-DEA 85:15 3mL/min 1500psi
13-Jul-2018
13:34:35
ACM555_2_IG_MeOH-DEA_15_03 Sm (Mn, 2x3)
Diode Array
243
Range: 2.583
Time Height Area Area%
1.85 2575519 98086.88 88.27
2.25 296798 13029.81 11.73
1.85
2.25
HN
O
O
6o
AU
Time

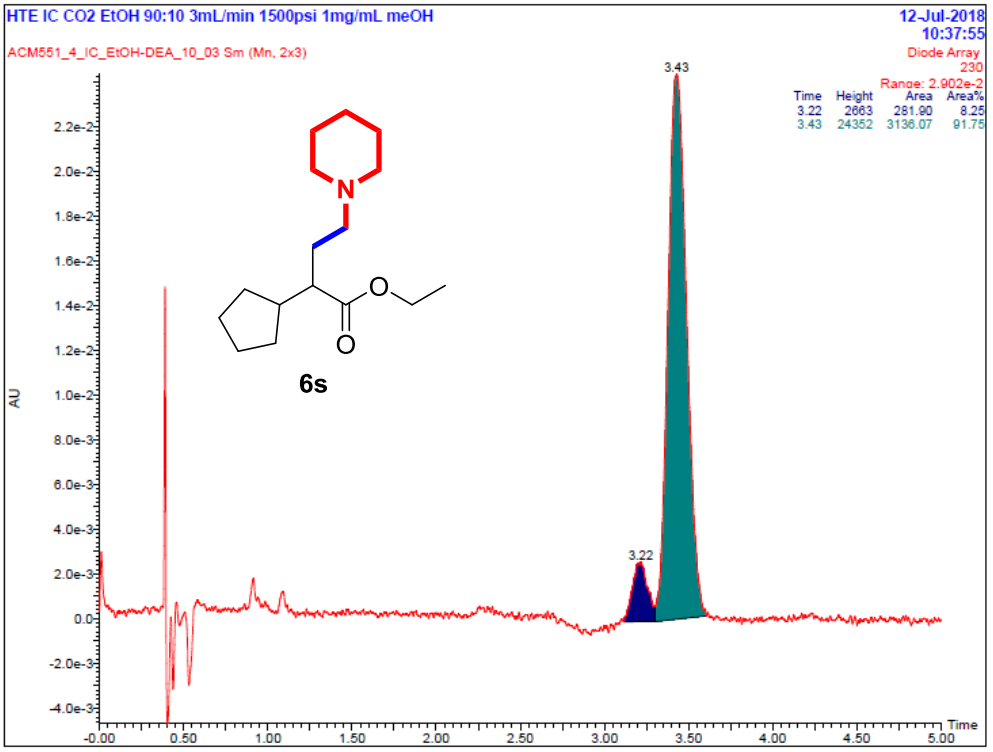

IG_CO2-MeOH_96:4_2000
20-Dec-2016 10:34:32
acm346-1_IG_MeOH-DEA_4_03 Sm (Mn, 2x3)
Diode Array
230
Range: 1.008e-1
Time Height Area Area%
3.54 97000 8204.18 49.98
3.75 86775 8211.35 50.02
3.54
3.75
AU
Time
6p

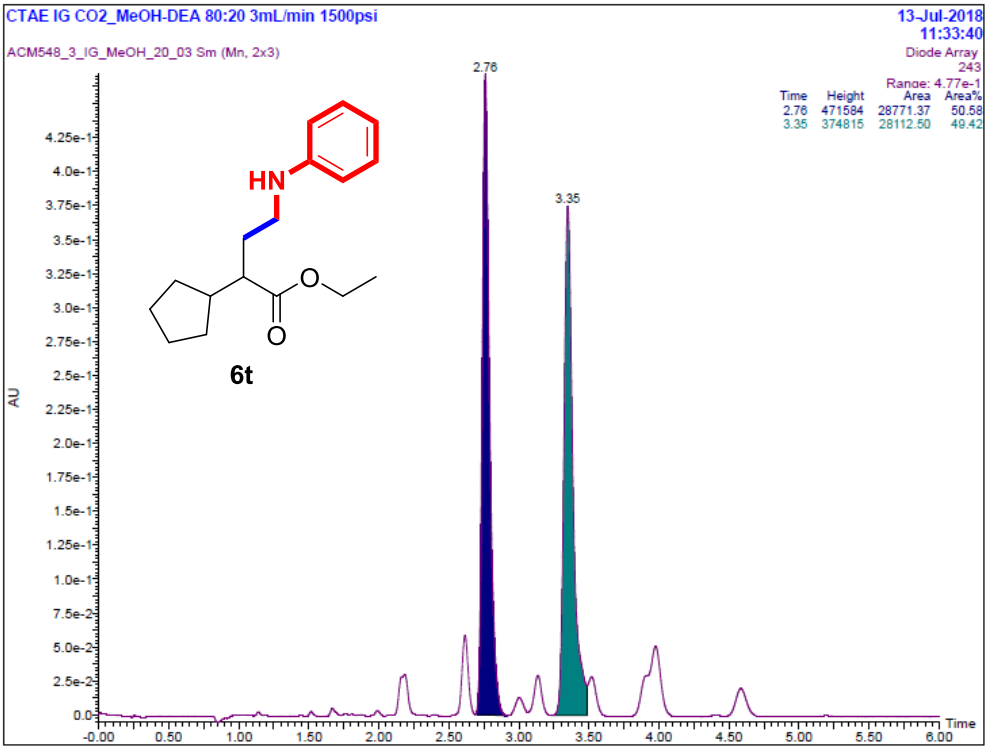

CTAE IG CO2_MeOH 96:4 3mL/min 1500psi_1mgmL MeOH
09-Jul-2018
13:41:44
acm543_4_IG_MeOH-DEA_4_03 Sm (Mn, 2x3)
Diode Array
210
Range: 2.172e-1
Time Height Area Area%
3.43 195375 17130.79 93.29
3.61 13573 1231.71 6.71
3.43
3.61
AU
Time
6p

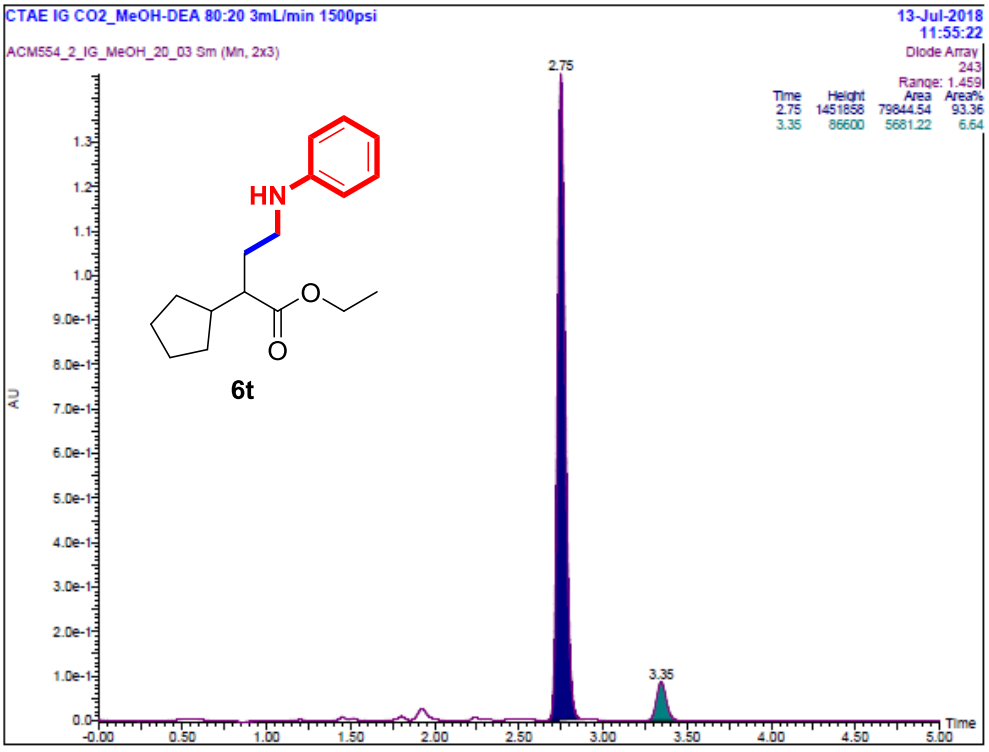

IG_CO2-MeOH_90:10_2000
05-Oct-2017 14:29:44
ACM440-3_IG_MeOH-DEA_10_03 Sm (Mn, 2x3)
Diode Array
210
Range: 1.614e-1
Time Height Area Area%
3.15 131276 10597.23 49.95
3.77 102393 10616.59 50.05
3.15
3.77
Boc
N
N
O
O
6r
AU
Time

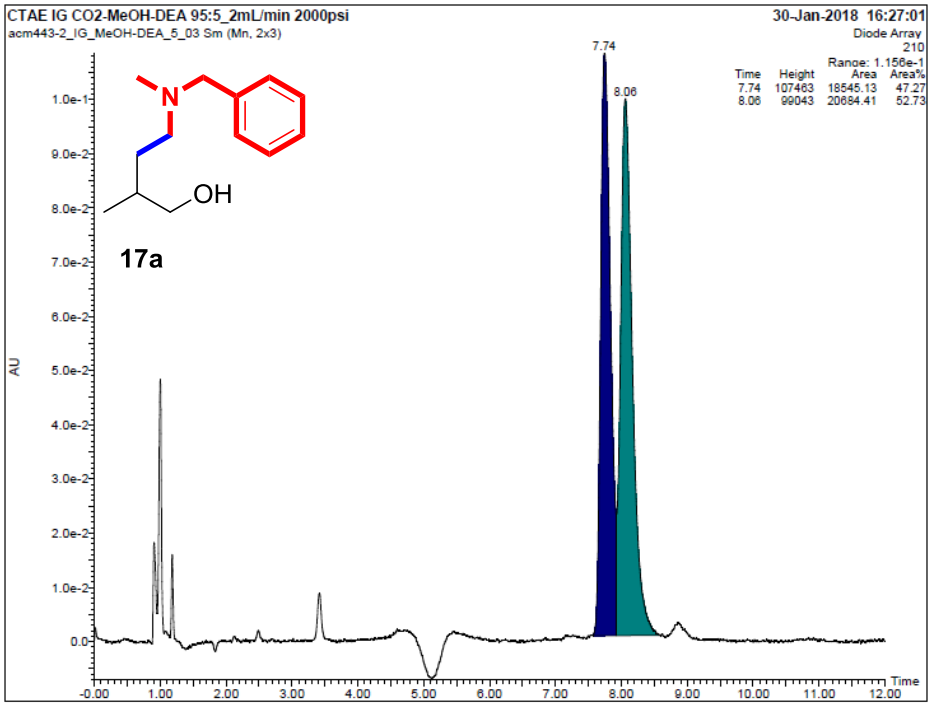

CTAE IG CO2-MeOH-DEA 90:10:0.1_2mL/min 2000psi
ACM492-3_IG_MeOH-DEA_10_03 Sm (Mn, 2x3)
Diode Array
210
Range: 1.579e-1
Time Height Area Area%
3.13 12964 1019.42 7.72
3.72 117457 12184.02 92.28
3.72
3.13
Boc
N
N
O
O
6r
AU
Time

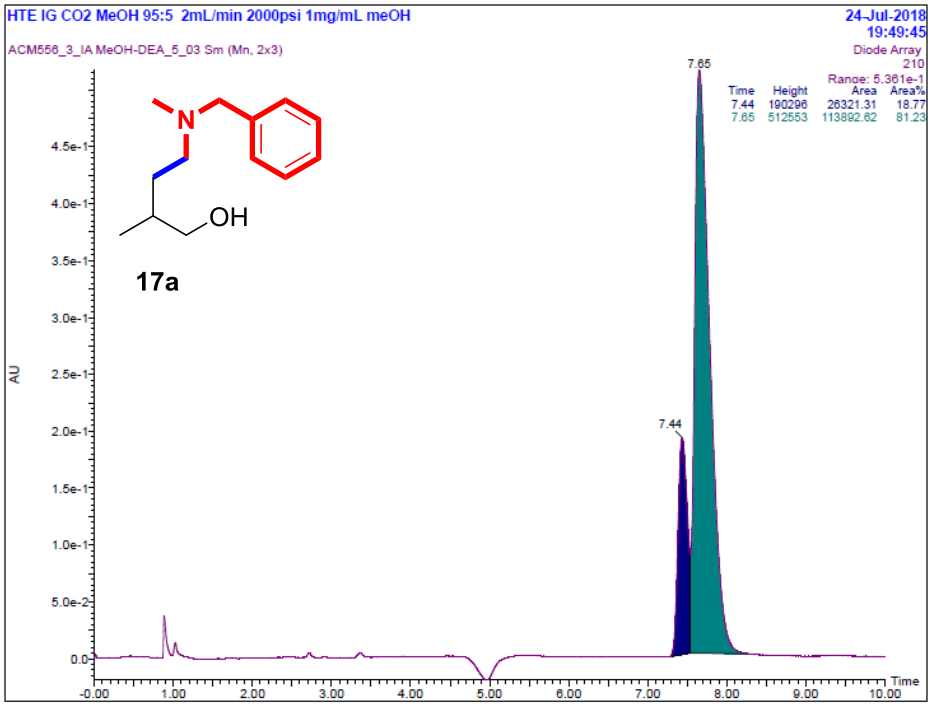

IC_CO2-EtOH_90:10_1500
05-Oct-2017 16:02:32
ACM440-2_IC_EtOH-DEA_10_06 Sm (Mn, 2x3)
Diode Array
230
Range: 5.999e-2
Time Height Area Area%
3.52 57978 8761.67 49.67
3.82 50428 8876.43 50.33
3.52
3.82
6s
AU
Time


HTE IC CO2 EtOH 90:10 3mL/min 1500psi 1mg/mL meOH
12-Jul-2018
10:37:55
ACM551_4_IC_EtOH-DEA_10_03 Sm (Mn, 2x3)
Diode Array
230
Range: 2.902e-2
Time Height Area Area%
3.22 2663 281.90 8.25
3.43 24352 3136.07 91.75
3.43
3.22
6s
AU
Time


CTAE IG CO2_MeOH-DEA 80:20 3mL/min 1500psi
13-Jul-2018
11:33:40
ACM548_3_IG_MeOH_20_03 Sm (Mn, 2x3)
Diode Array
243
Range: 4.77e-1
Time Height Area Area%
2.76 471584 28771.37 50.58
3.35 374815 28112.50 49.42
2.76
3.35
HN
O
O
6t
AU
Time


CTAE IG CO2_MeOH-DEA 80:20 3mL/min 1500psi
13-Jul-2018
11:55:22
ACM554_2_IG_MeOH_20_03 Sm (Mn, 2x3)
Diode Array
243
Range: 1.459
Time Height Area Area%
2.75 1451858 79844.54 93.36
3.35 86600 5681.22 6.64
2.75
3.35
HN
O
O
6t
AU
Time


CTAE IG CO2-MeOH-DEA 95:5_2mL/min 2000psi
30-Jan-2018 16:27:01
acm443-2_IG_MeOH-DEA_5_03 Sm (Mn, 2x3)
Diode Array
210
Range: 1.156e-1
Time Height Area Area%
7.74 107463 18545.13 47.27
8.06 99043 20684.41 52.73
7.74
8.06
N
OH
17a
AU
Time


HTE IG CO2 MeOH 95:5 2mL/min 2000psi 1mg/mL meOH
24-Jul-2018
19:49:45
ACM556_3_IA MeOH-DEA_5_03 Sm (Mn, 2x3)
Diode Array
210
Range: 5.361e-1
Time Height Area Area%
7.44 190296 26321.31 18.77
7.65 512553 113892.62 81.23
7.65
7.44
N
OH
17a
AU
Time