

Supporting Information for

Enantioselective Synthesis of Tunable Chiral Pyridine–Aminophosphine Ligands and Their Application in Asymmetric Hydrogenation

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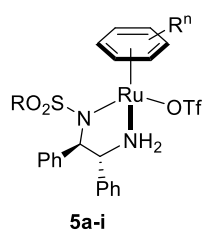
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1. General information

Unless otherwise noted, all experiments were carried out under an atmosphere of nitrogen using standard Schlenk techniques or in a nitrogen-filled glovebox. ^1H NMR and ^{13}C NMR spectras were recorded on Bruker Model Avance DMX 300 Spectrometer (^1H 300 MHz and ^{13}C 75 MHz, respectively), Bruker Model Avance DMX 400 Spectrometer (^1H 400 MHz and ^{13}C 100 MHz, respectively) and Bruker Model Avance DMX 500 Spectrometer (^1H 500 MHz and ^{13}C 125 MHz, respectively). Chemical shifts (δ) were given in ppm and were referenced to residual solvent or TMS peaks. Optical rotations were measured with Rudolph Autopl VI polarimeter. High resolution mass spectras (P-ESI HRMS) were obtained on Thermo Fisher Q Exactive Mass Spectrometer. HPLC analyses were performed on a Varian Prostar 210 liquid chromatograph. The single crystal X-ray analyses were measured with MM007HF Saturn724+ and XtaLAB Synergy-R. All organic solvents were dried using standard, published methods and were distilled before use. All other chemicals were used as received from Aldrich or Acros without further purification. The Ru-catalysts,¹ 2-(pyridin-2-yl) quinolines,² P,N-ligands and Ir-catalysts,³ benzoazepines and benzodiazepines⁶ were synthesized according to the modified literature methods.

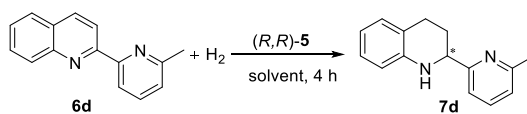
2. Optimization of conditions for asymmetric hydrogenation

All ruthenium catalysts used for this study were prepared according to the reported methods.¹



- (*R,R*)-**5a**: $\text{R}^n\text{-Ar}$ = *p*-cymene; R = 4- $\text{CH}_3\text{C}_6\text{H}_4$;
(*R,R*)-**5b**: $\text{R}^n\text{-Ar}$ = *p*-cymene; R = CH_3 ;
(*R,R*)-**5c**: $\text{R}^n\text{-Ar}$ = *p*-cymene; R = C_6H_5 ;
(*R,R*)-**5d**: $\text{R}^n\text{-Ar}$ = *p*-cymene; R = 2,4,6-triisopropylphenyl;
(*R,R*)-**5e**: $\text{R}^n\text{-Ar}$ = *p*-cymene; R = CF_3 ;
(*R,R*)-**5f**: $\text{R}^n\text{-Ar}$ = *p*-cymene; R = 4- $\text{CF}_3\text{C}_6\text{H}_4$;
(*R,R*)-**5g**: $\text{R}^n\text{-Ar}$ = benzene; R^1 = 4- $\text{CH}_3\text{C}_6\text{H}_4$;
(*R,R*)-**5h**: $\text{R}^n\text{-Ar}$ = hexamethylbenzene; R = 4- $\text{CH}_3\text{C}_6\text{H}_4$;
(*R,R*)-**5i**: $\text{R}^n\text{-Ar}$ = hexamethylbenzene; R = CH_3 ;

Table S1. Optimization of the reaction conditions for asymmetric hydrogenation of **6d**^a



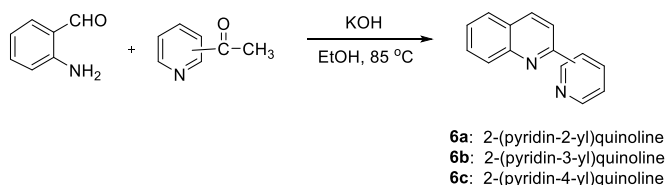
entry	catalyst	solvent	temp (°C)	H ₂ (atm)	conv. (%) ^b	ee. (%) ^c
1	(<i>R,R</i>)- 5a	toulene	25	50	70	52
2	(<i>R,R</i>)- 5a	DCM	25	50	90	72
3	(<i>R,R</i>)- 5a	THF	25	50	8	68
4	(<i>R,R</i>)- 5a	MeOH	25	50	72	79
5	(<i>R,R</i>)- 5a	EtOH	25	50	77	86
6	(<i>R,R</i>)- 5a	<i>i</i> -PrOH	25	50	>99	87
7	(<i>R,R</i>)- 5a	<i>n</i> -BuOH	25	50	65	87
8	(<i>R,R</i>)- 5h	<i>i</i> -PrOH	25	30	86	97
9	(<i>R,R</i>)- 5h	<i>i</i> -PrOH	25	10	50	95
10	(<i>R,R</i>)- 5h	<i>i</i> -PrOH	50	50	>99	93

^aReaction conditions: substrate **6d** (0.2 mmol) in solvent (2.0 mL), Ru-catalyst **5** (2.0 mol %), H₂ (50 atm), stirred at 25 °C for 4 h. ^bThe conversions were determined by ¹H NMR spectroscopy of the crude reaction mixtures. ^cThe enantiomeric excesses were determined by HPLC with a chiral OB-H column.

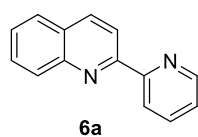
3. General procedure for the synthesis of 2-(pyridin-2-yl)quinolines

(1) Compounds: **6a-c**

The corresponding quinolines **6a-c** were synthesized according to the previously reported procedures.^{2a-b}

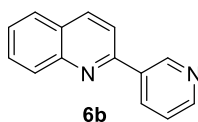


To a stirred solution of 2-aminobenzaldehyde (4.2 g, 0.035 mol) in EtOH (100 mL) at 25 °C was added acetylpyridine (5.0 g, 0.042 mol) and KOH (0.4 g, 0.007 mol). The reaction mixture was stirred at 85 °C for 3 h. After cooling to room temperature, the mixture was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum=1/8, v/v) to give yellow solids **2a-c**. The analytical data of the products are summarized below.



2-(pyridin-2-yl)quinoline (6a): (Known compound, see: R. Wang, H. Fan, W. Zhao and F. Li, *Org. Lett.* 2016, **18**, 3558); yellow solid, m.p. 98-100 °C, 72% yield; ¹H NMR (500 MHz, CDCl₃): δ (ppm)

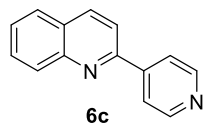
8.75 (d, *J* = 3.0 Hz, 1H), 8.67 (d, *J* = 8.0 Hz, 1H), 8.57 (d, *J* = 8.5 Hz, 1H), 8.29 (d, *J* = 8.5 Hz, 1H), 8.19 (d, *J* = 8.0 Hz, 1H), 7.90-7.85 (m, 2H), 7.74 (t, *J* = 7.5 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.37 (t, *J* = 5.5 Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 156.5, 156.3, 149.3, 148.0, 137.1, 136.9, 129.9, 129.7, 128.4, 127.7, 126.9, 124.2, 122.0, 119.1.



2-(pyridin-3-yl)quinoline (6b): (Known compound, see: L.-Y. Xi, R.-Y. Zhang, L. Zhang, S.-Y. Chen and X.-Q. Yu, *Org. Biomol. Chem.* 2015, **13**, 3942); yellow solid, m.p. 65-67 °C, 65% yield; ¹H

NMR (400 MHz, CDCl₃): δ (ppm) 9.36 (d, *J* = 1.6 Hz, 1H), 8.70 (dd, *J*₁ = 4.4 Hz, *J*₂ = 1.2 Hz, 1H), 8.52-8.49 (m, 1H), 8.25 (d, *J* = 8.8 Hz, 1H), 8.17 (d, *J* = 8.4 Hz, 1H), 7.88-7.83 (m, 2H), 7.77-7.73 (m, 1H), 7.57-7.53 (m, 1H), 7.45 (dd, *J*₁ = 8.0 Hz, *J*₂ =

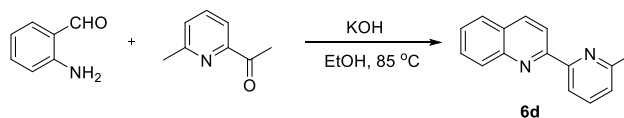
4.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 154.7, 150.3, 148.9, 148.5, 137.3, 135.2, 135.1, 130.1, 129.9, 127.7, 127.5, 126.9, 123.8, 118.6.



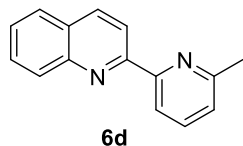
2-(pyridin-4-yl)quinoline (6c): (Known compound, see: L.-Y. Xi, R.-Y. Zhang, L. Zhang, S.-Y. Chen and X.-Q. Yu, *Org. Biomol. Chem.* 2015, **13**, 3942); yellow solid, m.p. 96-98 °C, 82% yield; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.78 (d, $J = 5.2$ Hz, 2H), 8.28 (d, $J = 8.4$ Hz, 1H), 8.19 (d, $J = 8.8$ Hz, 1H), 8.06 (dd, $J_1 = 4.4$ Hz, $J_2 = 1.6$ Hz, 2H), 7.91-7.85 (m, 2H), 7.79-7.75 (m, 1H), 7.60-7.56 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 154.5, 150.6, 148.4, 146.7, 137.3, 130.2, 130.1, 127.9, 127.6, 127.3, 121.7, 118.5.

(2) Compound: **6d**

The corresponding 2-(pyridin-2-yl)quinoline **6d** was synthesized according to the previously reported procedure.^{2c}



To a stirred solution of 2-aminobenzaldehyde (0.7 g, 0.006 mol) in EtOH (50 mL) at 25 °C was added acetylpyridine (1.2 eq, 0.007 mol) and KOH (0.2 eq, 0.001 mol). The reaction mixture was stirred at 85 °C for 3 h. After cooling to room temperature, the mixture was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum=1/8, v/v) to give the yellow solid **6d**. The analytical data of the product are summarized below.



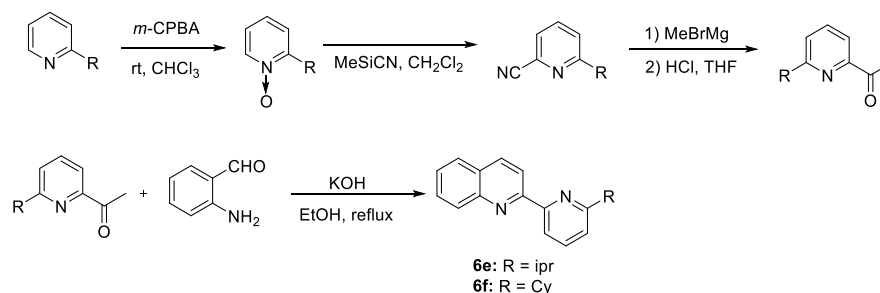
2-(6-methylpyridin-2-yl)quinoline (6d): (Known compound, see: J. Uenishi, T. Tanaka, K. Nishiwaki, W. Wakabayashi, S. Oae and H. Tsukube, *J. Org. Chem.* 1993, **58**, 4382); yellow

solid, m.p. 97-99 °C, 57% yield; ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.61 (d, $J = 8.7$ Hz, 1H), 8.46 (d, $J = 7.8$ Hz, 1H), 8.27 (d, $J = 8.7$ Hz, 1H), 8.19 (d, $J = 8.4$ Hz, 1H), 7.85 (d, $J = 8.1$ Hz, 1H), 7.79-7.70 (m, 2H), 7.57-7.52 (m, 1H), 7.23 (d, $J = 7.5$ Hz, 1H), 2.68 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3): δ (ppm) 158.1, 156.6, 155.8, 148.0,

137.3, 136.9, 129.9, 129.6, 128.4, 127.7, 126.8, 123.7, 119.3, 119.0, 24.8.

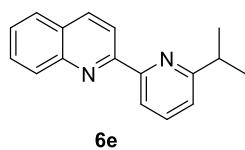
(3) Compounds: **6e-f**

The corresponding intermediates were synthesized according to the previously reported procedures.^{2d-e}

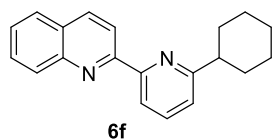


To a stirred solution of 2-substitued-pyridine in CHCl_3 (0.5 M) at 0°C was added a solution of 3-chloroperoxybenzoic acid in CHCl_3 (1.5 eq). The resultant yellow solution was stirred at 0°C for 10 min and stirred at room temperature for 3 h. Then, an aqueous solution of saturated sodium sulfite (50 mL) was added to quench the reaction, and then an aqueous solution of saturated sodium hydrogencarbonat (100 mL) was added to neutralize the reaction. The organic layer was removed, and the aqueous layer was extracted with EtOAc (3×20 mL). The extracts were combined, dried over Na_2SO_4 , and evaporated under reduced pressure to yield the pyridine-1-oxide. And then to a stirred solution of pyridine-1-oxide in CH_2Cl_2 (0.5 M) at 25°C , trimethylsilyl cyanide (1.3 eq) and dimethylcarbamyyl chloride (1.3 eq) were added. The reaction was stirred at 25°C for 12 h. Then, an aqueous solution of saturated sodium hydrogencarbonat (100 mL) was added to neutralize the reaction. The orgnic layer was removed, and the aqueous layer was extracted with EtOAc (3×20 mL). The extracts were combined, dried over Na_2SO_4 , and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum) to yield the corresponding cyanopyridine. And then to a stirred solution of cyanopyridine in dry THF (1.0 M) at -25°C under nitrogen, a solution of 3.0 M methylmagnesium bromidein in diethyl ether (1.5 eq) were added. The reaction was stirred at -25°C for 1 h and stirred at room temperature overnight until all of the cyanopyridine was consumed as indicated by TLC. Then, an aqueous

solution of hydrochloric acid (37%, 20 mL) at 0 °C was added to the reaction. The reaction mixture was stirred at 0 °C for 10 min and stirred at room temperature for 4 h, and then washed with aqueous solution of saturated sodium hydrogencarbonat. The organic layer was removed, and the aqueous layer was extracted with EtOAc (3 × 20 mL). The extracts were combined, dried over Na₂SO₄, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum) to yield the corresponding 2-acetylpyridine. And then to a stirred solution of 2-aminobenzyl aldehyde in EtOH (1.0 M) at 25 °C, 2-acetylpyridine (1.2 eq) and KOH (0.2 eq) were added. The reaction mixture was stirred at 85 °C for 3 h. After cooling to room temperature, the mixture was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum) to give yellow solids **6e-f**. The analytical data of the products are summarized below.



2-(6-isopropylpyridin-2-yl)quinoline (6e): (New compound); yellow solid, m.p. 49-50 °C, 65% yield; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.69 (d, *J* = 8.5 Hz, 1H), 8.48 (d, *J* = 8.0 Hz, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 8.19 (d, *J* = 8.5 Hz, 1H), 7.85 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.73 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.24 (d, *J* = 7.5 Hz, 1H), 3.19 (sep, *J* = 6.8 Hz, 1H), 1.41 (d, *J* = 7.0 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 166.8, 157.0, 155.4, 148.0, 137.3, 136.7, 129.9, 129.5, 128.4, 127.7, 126.7, 121.2, 119.4, 119.1, 36.5, 22.8. HRMS-ESI exact mass calcd. for C₁₇H₁₇N₂⁺ ([M+H]⁺) requires m/z 249.13863, found m/z 249.13850.

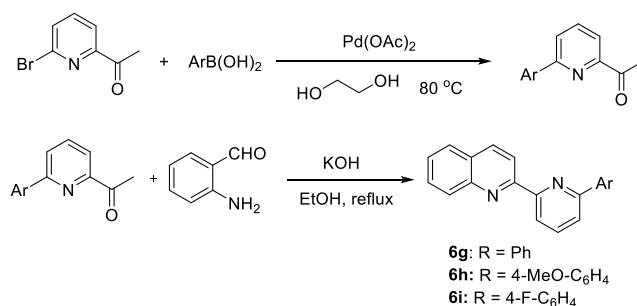


2-(6-cyclohexylpyridin-2-yl)quinoline (6f): (New compound); white solid, m.p. 37-38 °C, 53% yield; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.67 (d, *J* = 8.5 Hz, 1H), 8.46 (d, *J* = 7.5 Hz, 1H), 8.26 (d, *J* = 8.5 Hz, 1H), 8.17 (d, *J* = 8.5 Hz, 1H), 7.84 (d, *J* = 8.0 Hz, 1H), 7.78 (t, *J* = 7.8 Hz, 1H), 7.72 (t, *J* = 7.5 Hz, 1H), 7.54 (t, *J* = 7.3 Hz, 1H), 7.21 (d, *J* = 8.0 Hz, 1H), 2.85-2.80 (m, 1H), 2.08-2.05 (m, 2H), 1.92-1.89 (m, 2H), 1.81-1.79 (m, 1H),

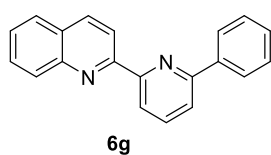
1.70-1.62 (m, 2H), 1.52-1.44 (m, 2H), 1.38-1.37 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 166.0, 157.0, 155.5, 148.1, 137.2, 136.7, 129.9, 129.5, 128.4, 127.7, 126.6, 121.5, 119.5, 119.1, 46.6, 33.1, 26.8, 26.4. HRMS-ESI exact mass calcd. for $\text{C}_{20}\text{H}_{21}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 289.16993, found m/z 289.16952.

(4) Compounds: **6g-j**

The corresponding intermediates were synthesized according to the previously reported procedures.^{2f}

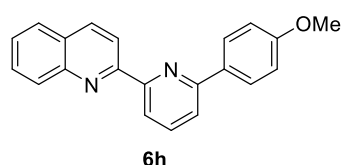


To a stirred solution of 2-acetyl-6-bromopyridine in ethylene glycol (0.5 M) at 25 °C was added corresponding boric acid (1.5 eq), palladium diacetate (0.5% eq) and tripotassium phosphate (2.0 eq). The reaction was stirred at 80 °C for 12 h. After cooling to room temperature, the organic layer was extracted with EtOAc (10 × 50 mL). The extracts were combined, and evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum) to yield the corresponding 2-acetylpyridine. And to a stirred solution of 2-aminobenzyl aldehyde in EtOH (1.0 M) at 25 °C, 2-acetylpyridine (1.2 eq) and KOH (0.2 eq) were added. The reaction mixture was stirred at 85 °C for 3 h. After cooling to room temperature, the mixture was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum) to give yellow solids **6g-i**. The analytical data of the products are summarized below.



2-(6-phenylpyridin-2-yl)quinoline (6g): (Known compound, see: C. T. Carver and P. L. Diaconescu, *J. Am. Chem. Soc.* 2008, **130**, 7558); white solid, m.p. 121-123 °C, 40% yield; ^1H NMR (500 MHz, CDCl_3): δ (ppm) 8.82 (d, J = 8.5 Hz, 1H), 8.65 (d, J = 7.5 Hz, 1H),

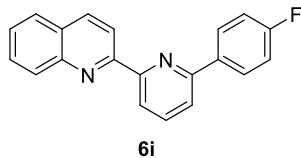
8.31 (d, $J = 8.5$ Hz, 1H), 8.21 (d, $J = 7.5$ Hz, 3H), 7.95 (t, $J = 7.8$ Hz, 1H), 7.85 (dd, $J_1 = 22.0$ Hz, $J_2 = 8.0$ Hz, 2H), 7.75 (t, $J = 7.5$ Hz, 1H), 7.58-7.53 (m, 3H), 7.48-7.45 (m, 1H), ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 156.6, 156.4, 155.8, 147.8, 139.4, 137.9, 137.0, 129.8, 129.7, 129.2, 128.9, 128.5, 127.8, 127.1, 126.9, 120.8, 120.3, 119.4.



2-(6-(4-methoxyphenyl)pyridin-2-yl)quinoline (6h):

(New compound); yellow solid, m.p. 122-123 °C, 72% yield; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.80 (d, $J =$

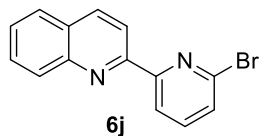
8.4 Hz, 1H), 8.59 (d, $J = 7.6$ Hz, 1H), 8.30 (d, $J = 8.8$ Hz, 1H), 8.21-8.15 (m, 3H), 7.92-7.86 (m, 2H), 7.77-7.72 (m, 2H), 7.58-7.54 (m, 1H), 7.06 (d, $J = 8.8$ Hz, 2H), 3.90 (s, 3H), ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 160.7, 156.6, 156.3, 155.9, 148.1, 137.8, 136.7, 132.2, 130.0, 129.6, 128.5, 128.4, 127.8, 126.8, 120.0, 119.5, 119.4, 114.3, 55.5. HRMS-ESI exact mass calcd. for $\text{C}_{21}\text{H}_{17}\text{ON}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 313.13354, found m/z 313.13348.



2-(6-(4-fluorophenyl)pyridin-2-yl)quinoline (6i): (New

compound); yellow solid, m.p. 135-137 °C, 78% yield; ^1H NMR (500 MHz, CDCl_3): δ (ppm) 8.77 (d, $J = 9.0$ Hz, 1H),

8.64 (d, $J = 8.0$ Hz, 1H), 8.30 (d, $J = 8.5$ Hz, 1H), 8.21-8.17 (m, 3H), 7.93 (t, $J = 7.8$ Hz, 1H), 7.87 (d, $J = 8.0$ Hz, 1H), 7.77-7.73 (m, 2H), 7.57 (t, $J = 7.5$ Hz, 1H), 7.21 (t, $J = 8.5$ Hz, 2H), ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 163.7 (d, $^1J_{\text{FC}} = 246.3$ Hz), 156.4, 156.1, 155.5, 148.1, 137.9, 136.8, 135.6 (d, $^4J_{\text{FC}} = 2.5$ Hz), 130.0, 129.7, 128.9 (d, $^3J_{\text{FC}} = 8.8$ Hz), 128.5, 127.8, 126.9, 120.4, 120.1, 119.2, 115.8 (d, $^2J_{\text{FC}} = 22.5$ Hz). HRMS-ESI exact mass calcd. for $\text{C}_{20}\text{H}_{14}\text{FN}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 301.11355, found m/z 301.11362.



2-(6-bromopyridin-2-yl)quinoline (6j): (New compound); **6j**

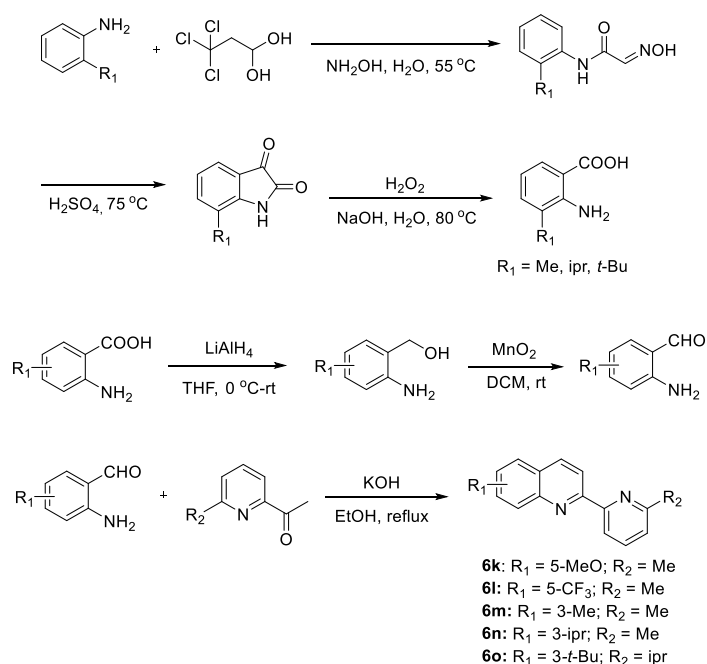
was synthesized according to the procedures as compound

6d.^{2c} yellow solid, m.p. 52-53 °C, 80% yield; ^1H NMR (300 MHz, CDCl_3): δ (ppm) 8.65 (dd, $J_1 = 7.8$ Hz, $J_2 = 0.9$ Hz, 1H), 8.56 (d, $J = 8.7$ Hz, 1H), 8.28 (d, $J = 8.7$ Hz,

1H), 8.15 (d, $J = 8.4$ Hz, 1H), 7.86 (d, $J = 8.1$ Hz, 1H), 7.77-7.70 (m, 2H), 7.59-7.53 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 157.5, 154.6, 147.8, 141.7, 139.3, 137.2, 129.9, 129.9, 128.6, 128.5, 127.8, 127.3, 120.7, 119.2. HRMS-ESI exact mass calcd. for $\text{C}_{14}\text{H}_{10}\text{BrN}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 285.00219, found m/z 285.00235.

(5) Compounds: **6k-o**

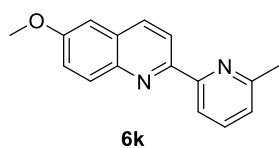
First, the corresponding 2-aminobenzoic acids were synthesized according to the previously reported procedures.^{2g-h}



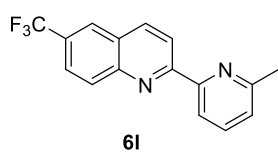
To a stirred solution of aniline in H_2O (0.1 M) at 25 °C, chloral hydrate solution (1.2 eq), hydroxylamine hydrochloride (3.6 eq), sodium sulfate (1.0 eq) and hydrochloric acid (12.5 mL) were added. The reaction was stirred at 55 °C for 12 h. After cooling to room temperature, the reaction mixture was filtered, and the filter cake was washed with water (3×50 mL) to yield yellow solid. To the solid at 55 °C was added H_2SO_4 (45.0 mL, 18.4 M) dropwise during 0.5 h. Then, the reaction was stirred at 80 °C for 10 min. After cooling to room temperature and pouring into ice water for 30 min, the mixture was filtered. The obtained filter cake was washed with water (3×50 mL) to yield brown solid. To a stirred solution of brown solid in saturated sodium hydroxide at 80 °C was added H_2O_2 (33.0 mL, 15%) dropwise during 0.5 h. The reaction was stirred at 80 °C for 5 h. After cooling to room temperature and adding

activated carbon, the reaction mixture was washed with aqueous solution of hydrochloric acid, filtered, and washed with EtOH. The organic layers were combined, and evaporated under reduced pressure to yield the corresponding 2-aminobenzoic acid.

To a stirred suspension of lithium aluminium hydride in dry THF (0.5 M, 1.5 eq) at 0 °C under nitrogen was added a solution of 2-aminobenzoic acid (1.0 eq) in dry THF (1.0 M). The reaction was then stirred at 25 °C for another 12 h. Then, sodium sulfate decahydrate (1.0 M) was added to quench the reaction, filtered with celite, and the filtrate was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum) to yield the corresponding 2-aminobenzyl alcohol. And to a stirred solution of 2-aminobenzyl alcohol in DCM (1.0 M) at 25 °C was added manganese dioxide (5.0 eq). The reaction was stirred at 25 °C for 12 h, filtered with celite, and the filtrate was evaporated under reduced pressure (< 25 °C) to yield the corresponding 2-aminobenzyl aldehyde. And to a stirred solution of 2-aminobenzyl aldehyde in EtOH (1.0 M) at 25 °C was added 2-acetylpyridine (1.2 eq) and KOH (0.2 eq). The reaction mixture was stirred at 85 °C for 3 h. After cooling to room temperature, the mixture was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum) to give yellow solids **6k-o**. The analytical data of the products are summarized below.



6-methoxy-2-(6-methylpyridin-2-yl)quinoline (6k): (New compound); white solid, m.p. 163-164 °C, 58% yield; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 8.63 (d, *J* = 9.0 Hz, 1H), 8.55 (d, *J* = 8.0 Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H), 7.57 (d, *J* = 7.0 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 2.92 (s, 3H), 2.68 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 157.9, 156.3, 155.1, 147.0, 137.8, 137.1, 137.0, 129.6, 128.3, 126.5, 125.7, 123.5, 118.9, 118.7, 24.8, 18.0. HRMS-ESI exact mass calcd. for C₁₆H₁₅ON₂⁺ ([M+H]⁺) requires *m/z* 251.11789, found *m/z* 251.11751.



2-(6-methylpyridin-2-yl)-6-(trifluoromethyl)quinoline (6l):

(New compound); white solid, m.p. 153-154 °C, 54% yield; ¹H

NMR (500 MHz, CDCl₃): δ (ppm) 8.74 (d, *J* = 8.5 Hz, 1H),

8.48 (d, *J* = 8.0 Hz, 1H), 8.36 (d, *J* = 8.5 Hz, 1H), 8.28 (d, *J* = 9.0 Hz, 1H), 8.17 (s,

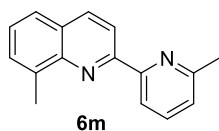
1H), 7.89 (dd, *J*₁ = 9.0 Hz, *J*₂ = 1.5 Hz, 1H), 7.79 (t, *J* = 7.8 Hz, 1H), 7.28-7.26 (m,

1H), 2.70 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 158.4, 158.2, 155.0, 149.0,

137.6, 131.0, 128.5 (q, ²*J*_{FC} = 32.5 Hz), 127.3, 125.7 (q, ³*J*_{FC} = 4.6 Hz), 125.3, 125.3,

124.4, 124.2 (q, ¹*J*_{FC} = 270.9 Hz), 120.6, 119.4, 24.7. HRMS-ESI exact mass calcd.

for C₁₆H₁₂F₃N₂⁺ ([M+H]⁺) requires m/z 289.09471, found m/z 289.09460.



8-methyl-2-(6-methylpyridin-2-yl)quinoline (6m): (New

compound); yellow solid, m.p. 64-66 °C, 48% yield; ¹H NMR (500

MHz, CDCl₃): δ (ppm) 8.63 (d, *J* = 9.0 Hz, 1H), 8.55 (d, *J* = 8.0

Hz, 1H), 8.23 (d, *J* = 8.5 Hz, 1H), 7.75 (t, *J* = 7.8 Hz, 1H), 7.68 (d, *J* = 8.0 Hz, 1H),

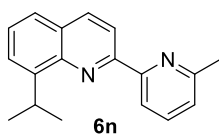
7.58 (d, *J* = 7.0 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 2.92 (s,

3H), 2.68 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ(ppm) 157.9, 156.3, 155.1, 147.0,

137.8, 137.1, 137.0, 129.6, 128.3, 126.5, 125.7, 123.5, 118.9, 118.7, 24.8, 18.0.

HRMS-ESI exact mass calcd. for C₁₆H₁₅N₂⁺ ([M+H]⁺) requires m/z 235.12298, found

m/z 235.12282.



8-isopropyl-2-(6-methylpyridin-2-yl)quinoline (6n): (New

compound); yellow oil, 32% yield; ¹H NMR (500 MHz, CDCl₃): δ

(ppm) 8.61 (d, *J* = 8.5 Hz, 1H), 8.52 (d, *J* = 8.0 Hz, 1H), 8.18 (d, *J*

= 8.5 Hz, 1H), 7.69 (t, *J* = 7.5 Hz, 1H), 7.62 (d, *J* = 7.5 Hz, 1H), 7.57 (d, *J* = 7.0 Hz,

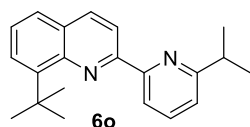
1H), 7.45 (t, *J* = 7.5 Hz, 1H), 7.13 (d, *J* = 7.5 Hz, 1H), 4.51-4.46 (m, 1H), 2.64 (s, 3H),

1.45 (d, *J* = 7.0 Hz, 6H); ¹³C NMR (125 MHz, CDCl₃): δ(ppm) 157.7, 156.3, 154.8,

147.7, 145.7, 137.0, 128.4, 126.7, 125.4, 125.2, 123.4, 118.8, 118.5, 27.8, 24.8, 23.7.

HRMS-ESI exact mass calcd. for C₁₈H₁₉N₂⁺ ([M+H]⁺) requires m/z 263.15428, found

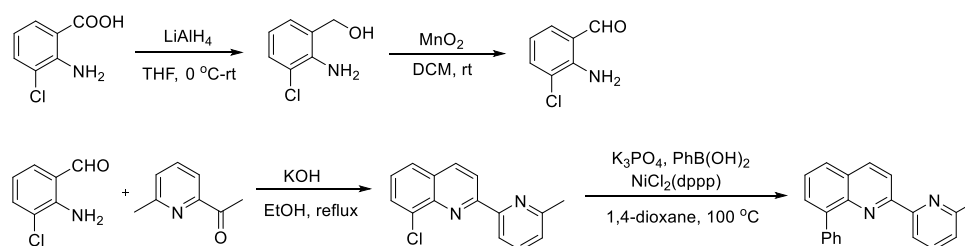
m/z 263.15404.



8-(*t*-butyl)-2-(6-isopropylpyridin-2-yl)quinoline (6o): (New compound); oil, 42% yield; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.72 (d, $J = 8.8$ Hz, 1H), 8.51 (dd, $J_1 = 8.0$ Hz, $J_2 = 0.8$ Hz, 1H), 8.24 (d, $J = 8.8$ Hz, 1H), 7.82 (t, $J = 7.8$ Hz, 1H), 7.72-7.69 (m, 2H), 7.46 (t, $J = 7.8$ Hz, 1H), 7.24 (d, $J = 7.6$ Hz, 1H), 3.25-3.16 (m, 1H), 1.80 (s, 9H), 1.44 (d, $J = 7.2$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 166.6, 156.0, 153.9, 148.3, 146.7, 137.4, 137.3, 129.3, 126.7, 126.2, 126.2, 120.9, 119.0, 118.1, 36.8, 36.5, 31.5, 22.9. HRMS-ESI exact mass calcd. for $\text{C}_{21}\text{H}_{25}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 305.20123, found m/z 305.20084.

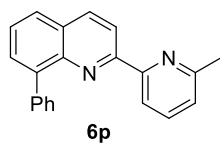
(6) Compound: **6p**

The corresponding intermediates were synthesized according to the previously reported procedures.²ⁱ



To a stirred suspension of lithium aluminium hydride in dry THF (0.5 M, 1.5 eq) at 0 °C under nitrogen was added a solution of 2-aminobenzoic acid (1.0 eq) in dry THF (1.0 M). The reaction was stirred at 25 °C for 12 h. Then, sodium sulfate decahydrate (1.0 M) was added to quench the reaction, filtered with celite, and the filtrate was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum) to yield the corresponding 2-aminobenzyl alcohol. And to a stirred solution of 2-aminobenzyl alcohol in DCM (1.0 M) at 25 °C was added manganese dioxide (5.0 eq). The reaction was stirred at 25 °C for 12 h, filtered with celite, and the filtrate was evaporated under reduced pressure (< 25 °C) to yield the corresponding 2-aminobenzyl aldehyde. And to a stirred solution of 2-aminobenzyl aldehyde in EtOH (1.0 M) at 25 °C was added

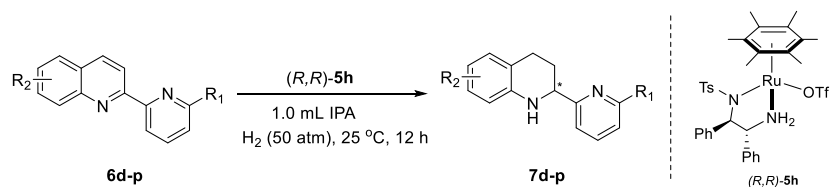
2-acetylpyridine (1.2 eq) and KOH (0.2 eq). The reaction mixture was stirred at 85 °C for 3 h. After cooling to room temperature, the mixture was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum) to give a yellow solid. To a stirred solution of yellow solid in 1,4-dioxane (0.1 M) at 25 °C was added phenylboronic acid (2.0 eq), K₃PO₄ (3.0 eq) and NiCl₂(dppp) (1% eq). The reaction was stirred at 100 °C for 12 h. After cooling to room temperature, the organic layer was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: ethyl acetate/petroleum = 1:50, v/v) to yield the white solid.



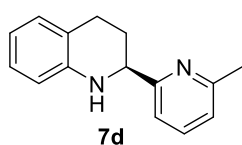
2-(6-methylpyridin-2-yl)-8-phenylquinoline (6p): (New compound); white solid, m.p. 105-107 °C, 40% yield; ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.70 (d, *J* = 8.8 Hz, 1H), 8.33-8.27 (m, 2H),

7.89-7.80 (m, 4H), 7.68-7.54 (m, 4H), 7.49-7.45 (m, 1H), 7.17 (d, *J* = 7.6 Hz, 1H), 2.67 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 157.7, 155.9, 155.8, 145.4, 140.9, 139.7, 137.2, 137.1, 131.3, 130.3, 128.8, 127.8, 127.4, 127.3, 126.6, 123.6, 119.1, 118.7, 24.8. HRMS-ESI exact mass calcd. for C₂₁H₁₇N₂⁺ ([M+H]⁺) requires *m/z* 297.13863, found *m/z* 297.13858.

4. General procedure for asymmetric hydrogenation



Typical procedure: A 30 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with substrates **6** (0.2 mmol) and catalyst (*R,R*)-**5h** (0.004 mmol) in 2.0 mL IPA under N₂ atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The mixture was stirred at room temperature for 12 h. Then the hydrogen gas was carefully released and the conversions were determined by ¹H NMR. The reaction mixture was filtered through a short pad of silica eluted with EA and PE to give the isolated pure product. The enantiomeric excesses of the product were determined by HPLC with a chiral column.

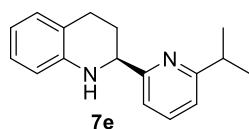


(S)-2-(6-methylpyridin-2-yl)-1,2,3,4-tetrahydroquinoline (7d):

(New compound); pale yellow oil, 92% yield, 98% ee; $[\alpha]_D^{20} = -104.0$ ($c = 0.25$, CHCl₃); ¹H NMR (400 MHz, CDCl₃): δ (ppm)

7.57 (t, $J = 7.8$ Hz, 1H), 7.24 (d, $J = 8.0$ Hz, 1H), 7.06-6.98 (m, 3H), 6.66-6.61 (m, 2H), 4.57 (dd, $J_1 = 8.8$ Hz, $J_2 = 3.6$ Hz, 1H), 2.95-2.87 (m, 1H), 2.72-2.65 (m, 1H), 2.58 (s, 3H), 2.29-2.23 (m, 1H), 2.05-1.95 (m, 1H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 162.5, 157.8, 144.3, 137.3, 129.3, 127.1, 121.9, 121.2, 117.6, 117.3, 114.6, 56.9, 28.9, 26.1, 24.5. HRMS-ESI exact mass calcd. for C₁₅H₁₇N₂⁺ ($[M+H]^+$) requires m/z 225.13863, found m/z 225.13826.

The enantiomeric excess was determined by HPLC on Chiralcel OB-H column (hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{R1} = 10.6$ min (minor), $t_{R2} = 12.8$ min (major).

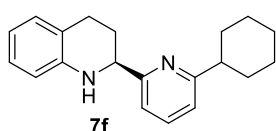


(S)-2-(6-isopropylpyridin-2-yl)-1,2,3,4-tetrahydroquinoline

(7e): (New compound); pale yellow oil, 90% yield, 97% ee;

$[\alpha]_D^{20} = -165.0$ ($c = 0.25$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.59 (t, $J = 7.8$ Hz, 1H), 7.21 (d, $J = 8.0$ Hz, 1H), 7.07-6.98 (m, 3H), 6.65-6.62 (m, 2H), 4.55 (dd, $J_1 = 9.0$ Hz, $J_2 = 3.0$ Hz, 1H), 3.09-3.06 (m, 1H), 2.96-2.89 (m, 1H), 2.73-2.68 (m, 1H), 2.29-2.25 (m, 1H), 2.00-1.95 (m, 1H), 1.31 (d, $J = 7.0$ Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 166.8, 161.9, 144.5, 137.2, 129.3, 127.0, 121.3, 118.8, 117.8, 117.2, 114.6, 56.8, 36.4, 28.9, 26.4, 22.8. HRMS-ESI exact mass calcd. for $\text{C}_{17}\text{H}_{21}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 253.16993, found m/z 253.16977.

The enantiomeric excess was determined by HPLC on Chiralcel OB-H column (hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{R1} = 6.5$ min (minor), $t_{R2} = 7.5$ min (major).



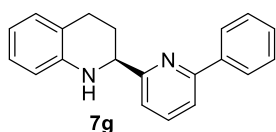
(S)-2-(6-cyclohexylpyridin-2-yl)-1,2,3,4-tetrahydroquinoline

(7f): (New compound); pale yellow oil, 91% yield, 96% ee;

$[\alpha]_D^{20} = -124.8$ ($c = 0.25$, CHCl_3); ^1H NMR (500 MHz, CDCl_3):

δ (ppm) 7.59 (t, $J = 7.8$ Hz, 1H), 7.21 (d, $J = 7.5$ Hz, 1H), 7.05-6.98 (m, 3H), 6.66-6.62 (m, 2H), 4.65 (s, 1H), 4.56-4.54 (m, 1H), 2.95-2.89 (m, 1H), 2.73-2.68 (m, 2H), 2.29-2.24 (m, 1H), 2.01-1.94 (m, 3H), 1.87-1.84 (m, 2H), 1.77-1.75 (m, 1H), 1.54-1.39 (m, 4H), 1.32-1.25 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 166.0, 162.0, 144.5, 137.1, 129.3, 127.0, 121.3, 119.2, 117.8, 117.2, 114.6, 56.9, 46.6, 33.2, 33.1, 28.9, 26.7, 26.3. HRMS-ESI exact mass calcd. for $\text{C}_{20}\text{H}_{25}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 293.20123, found m/z 293.20093.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column (hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{R1} = 6.5$ min (minor), $t_{R2} = 7.1$ min (major).



(S)-2-(6-phenylpyridin-2-yl)-1,2,3,4-tetrahydroquinoline

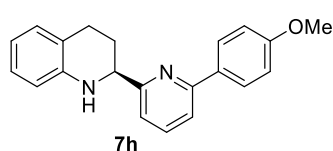
(7g): (New compound); yellow oil, 90% yield, 96% ee; $[\alpha]_D^{20}$

$= -159.0$ ($c = 0.25$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ

(ppm) 8.02 (d, $J = 7.5$ Hz, 2H), 7.72 (t, $J = 7.8$ Hz, 1H), 7.62 (d, $J = 8.0$ Hz, 1H), 7.49-7.40 (m, 3H), 7.34 (d, $J = 8.0$ Hz, 1H), 7.05-7.00 (m, 2H), 6.67-6.64 (m, 2H),

4.72 (s, 1H), 4.66 (dd, $J_1 = 9.0$ Hz, $J_2 = 3.5$ Hz, 1H), 2.96-2.90 (m, 1H), 2.75-2.70 (m, 1H), 2.35-2.29 (m, 1H), 2.13-2.05 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 162.9, 156.7, 144.3, 139.5, 137.5, 129.4, 129.1, 128.9, 127.1, 121.3, 119.0, 118.9, 117.3, 114.6, 56.9, 28.7, 26.2. HRMS-ESI exact mass calcd. for $\text{C}_{20}\text{H}_{19}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 287.15428, found m/z 287.15387.

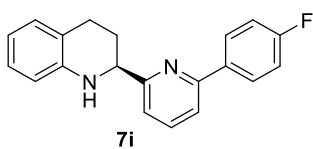
The enantiomeric excess was determined by HPLC on Chiralcel AD-H column (hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 23.7$ min (minor), $t_{\text{R}2} = 30.6$ min (major).



(S)-2-(6-(4-methoxyphenyl)pyridin-2-yl)-1,2,3,4-tetrahydroquinoline (7h): (New compound); colorless oil, 83% yield, 96% ee; $[\alpha]_{\text{D}}^{20} = -104.8$ ($c = 0.25$, CHCl_3); ^1H

NMR (500 MHz, CDCl_3): δ (ppm) 7.99 (d, $J = 9.0$ Hz, 2H), 7.69 (t, $J = 7.8$ Hz, 1H), 7.56 (d, $J = 7.5$ Hz, 1H), 7.29 (d, $J = 7.5$ Hz, 1H), 7.05-6.99 (m, 4H), 6.67-6.64 (m, 2H), 4.64 (dd, $J_1 = 9.0$ Hz, $J_2 = 3.5$ Hz, 1H), 3.87 (s, 3H), 2.95-2.90 (m, 1H), 2.76-2.70 (m, 1H), 2.33-2.29 (m, 1H), 2.12-2.06 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 162.6, 160.6, 156.4, 144.4, 137.5, 132.1, 129.4, 128.4, 127.1, 121.4, 118.3, 118.2, 117.3, 114.6, 114.3, 56.9, 55.5, 28.7, 26.2. HRMS-ESI exact mass calcd. for $\text{C}_{21}\text{H}_{21}\text{ON}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 317.16484, found m/z 317.16479.

The enantiomeric excess was determined by HPLC on Chiralcel OB-H column (hexane : isopropanol = 80 : 20, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 52.2$ min (minor), $t_{\text{R}2} = 91.4$ min (major).

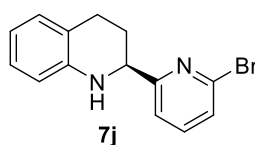


(S)-2-(6-(4-fluorophenyl)pyridin-2-yl)-1,2,3,4-tetrahydroquinoline (7i): (New compound); colorless oil, 93% yield, 97% ee; $[\alpha]_{\text{D}}^{20} = -127.0$ ($c = 0.25$, CHCl_3); ^1H NMR (400 MHz,

CDCl_3): δ (ppm) 8.03-7.99 (m, 2H), 7.73 (t, $J = 7.8$ Hz, 1H), 7.57 (d, $J = 7.6$ Hz, 1H), 7.35 (d, $J = 7.6$ Hz, 1H), 7.15 (t, $J = 8.6$ Hz, 2H), 7.06-6.99 (m, 2H), 6.68-6.65 (m, 2H), 4.66 (dd, $J_1 = 8.8$ Hz, $J_2 = 3.6$ Hz, 1H), 2.97-2.87 (m, 1H), 2.75-2.68 (m, 1H), 2.35-2.28 (m, 1H), 2.16-2.04 (m, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 163.7 (d,

$^1J_{\text{FC}} = 247.0$ Hz), 162.9, 155.7, 144.2, 137.7, 135.6, 129.4, 128.9 (d, $^3J_{\text{FC}} = 8.0$ Hz), 127.1, 121.4, 119.1, 118.7, 117.5, 115.8 (d, $^2J_{\text{FC}} = 21.0$ Hz), 114.7, 56.9, 28.7, 26.1. HRMS-ESI exact mass calcd. for $\text{C}_{20}\text{H}_{18}\text{FN}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 305.14485, found m/z 305.14474.

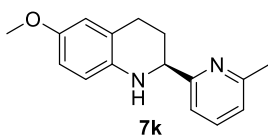
The enantiomeric excess was determined by HPLC on Chiralcel AD-H column (hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 25.2$ min (major), $t_{\text{R}2} = 43.9$ min (minor).



(S)-2-(6-bromopyridin-2-yl)-1,2,3,4-tetrahydroquinoline (7j):

(New compound); pale yellow oil, 52% yield, 95% ee; $[\alpha]_{\text{D}}^{20} = -108.5$ ($c = 0.25$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.53 (t, $J = 7.8$ Hz, 1H), 7.41-7.37 (m, 2H), 7.04 (t, $J = 7.5$ Hz, 1H), 6.99 (d, $J = 7.0$ Hz, 1H), 6.69 (t, $J = 7.5$ Hz, 1H), 6.65 (d, $J = 8.0$ Hz, 1H), 4.60 (dd, $J_1 = 8.0$ Hz, $J_2 = 4.0$ Hz, 1H), 2.90-2.84 (m, 1H), 2.67-2.61 (m, 1H), 2.28-2.22 (m, 1H), 2.10-2.03 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 165.3, 143.7, 141.7, 139.2, 129.4, 127.2, 126.6, 121.2, 119.5, 117.7, 114.6, 56.5, 28.5, 25.5. HRMS-ESI exact mass calcd. for $\text{C}_{14}\text{H}_{14}\text{BrN}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 289.03349, found m/z 289.03323.

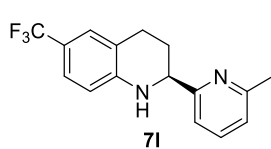
The enantiomeric excess was determined by HPLC on Chiralcel OB-H column (hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 23.4$ min (minor), $t_{\text{R}2} = 28.2$ min (major).



(S)-6-methoxy-2-(6-methylpyridin-2-yl)-1,2,3,4-tetrahydroquinoline (7k):

(New compound); pale yellow oil, 80% yield, 95% ee; $[\alpha]_{\text{D}}^{20} = -82.0$ ($c = 0.25$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.56 (t, $J = 7.8$ Hz, 1H), 7.24 (t, $J = 7.5$ Hz, 1H), 7.04 (d, $J = 7.5$ Hz, 1H), 6.66-6.58 (m, 3H), 4.48 (dd, $J_1 = 9.3$ Hz, $J_2 = 2.8$ Hz, 1H), 3.74 (s, 3H), 2.97-2.90 (m, 1H), 2.72-2.67 (m, 1H), 2.56 (s, 3H), 2.27-2.22 (m, 1H), 2.01-1.97 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 162.7, 157.8, 152.1, 138.5, 137.1, 122.6, 121.9, 117.5, 115.9, 114.7, 113.2, 57.4, 56.0, 29.3, 26.7, 24.6. HRMS-ESI exact mass calcd. for $\text{C}_{16}\text{H}_{19}\text{ON}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 255.14919, found m/z 255.14882.

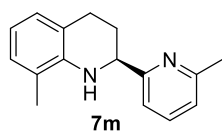
The enantiomeric excess was determined by HPLC on Chiralcel AD-H column (hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 15.8 min (minor), t_{R2} = 18.2 min (major).



(S)-2-(6-methylpyridin-2-yl)-6-trifluoromethyl-1,2,3,4-tetra

hydroquinoline (7l): (New compound); colorless oil, 65% yield, 89% ee; $[\alpha]_D^{20}$ = -69.2 (c = 0.25, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.49 (t, J = 7.6 Hz, 1H), 7.18-7.14 (m, 2H), 7.08 (d, J = 8.0 Hz, 1H), 6.98 (d, J = 7.6 Hz, 1H), 6.54 (d, J = 8.0 Hz, 1H), 4.93 (s, 1H), 4.50 (d, J = 6.0 Hz, 1H), 2.87-2.79 (m, 1H), 2.67-2.61 (m, 1H), 2.49 (s, 3H), 2.24-2.15 (m, 1H), 1.96-1.87 (m, 1H), ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 161.4, 158.1, 147.0, 137.1, 126.4 (q, $^3J_{\text{FC}}$ = 3.7 Hz), 125.2 (q, $^1J_{\text{FC}}$ = 268.0 Hz), 124.3 (q, $^3J_{\text{FC}}$ = 4.0 Hz), 122.0, 121.8, 120.6, 118.5 (q, $^2J_{\text{FC}}$ = 32.3 Hz), 117.4, 113.6, 56.5, 28.1, 26.0, 24.6. HRMS-ESI exact mass calcd. for $\text{C}_{16}\text{H}_{16}\text{N}_2\text{F}_3^+$ ($[\text{M}+\text{H}]^+$) requires m/z 293.12601, found m/z 293.12570.

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 9.9 min (major), t_{R2} = 11.4 min (minor).

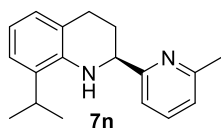


(S)-8-methyl-2-(6-methylpyridin-2-yl)-1,2,3,4-tetrahydroquinol

-ine (7m): (New compound); pale yellow oil, 79% yield, 98% ee; $[\alpha]_D^{20}$ = -93.0 (c = 0.25, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.57 (t, J = 7.8 Hz, 1H), 7.25 (d, J = 7.0 Hz, 1H), 7.05 (d, J = 7.5 Hz, 1H), 6.94 (d, J = 7.0 Hz, 1H), 6.89 (d, J = 7.0 Hz, 1H), 6.60 (t, J_1 = 7.3 Hz, 1H), 4.60 (d, J = 7.0 Hz, 1H), 4.42 (s, 1H), 2.98-2.92 (m, 1H), 2.74-2.69 (m, 1H), 2.57 (s, 3H), 2.30-2.25 (m, 1H), 2.17 (s, 3H), 2.01-1.95 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 162.8, 157.8, 142.3, 137.2, 128.2, 127.2, 121.9, 121.6, 120.7, 117.5, 116.7, 57.3, 29.0, 26.5, 24.6, 17.4. HRMS-ESI exact mass calcd. for $\text{C}_{16}\text{H}_{19}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 239.15428, found m/z 239.15413.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column

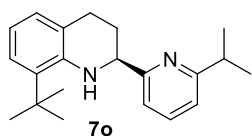
(hexane : isopropanol = 99 : 1, flowing rate = 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 10.1 min (minor), t_{R2} = 11.1 min (major).



(S)-8-isopropyl-2-(6-methylpyridin-2-yl)-1,2,3,4-tetrahydroquinoline (7n): (New compound); pale yellow oil, 83% yield, 86% ee; $[\alpha]_D^{20}$ = -190.0 (c = 0.25, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ

(ppm) 7.57 (t, J = 7.5 Hz, 1H), 7.24-7.22 (m, 1H), 7.04 (t, J = 8.0 Hz, 2H), 6.88 (d, J = 7.0 Hz, 1H), 6.67 (t, J = 7.3 Hz, 1H), 4.68 (s, 1H), 4.60-4.59 (m, 1H), 3.00-2.90 (m, 2H), 2.75-2.70 (m, 1H), 2.57 (s, 3H), 2.28-2.25 (m, 1H), 1.98-1.90 (m, 1H), 1.30 (t, J = 7.3 Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 162.8, 157.7, 141.0, 137.1, 131.8, 127.0, 123.1, 121.8, 121.1, 117.5, 116.9, 57.2, 28.9, 27.3, 26.9, 24.6, 22.4. HRMS-ESI exact mass calcd. for $\text{C}_{18}\text{H}_{23}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 267.18558, found m/z 267.18528.

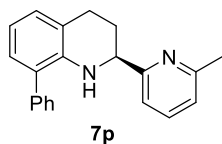
The enantiomeric excess was determined by HPLC on Chiralcel AD-H column (hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 4.5 min (major), t_{R2} = 5.0 min (minor).



(S)-8-(*t*-butyl)-2-(6-isopropylpyridin-2-yl)-1,2,3,4-tetrahydroquinoline (7o): (New compound); pale yellow oil, 88% yield, 77% ee; $[\alpha]_D^{20}$ = -150.0 (c = 0.25, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.60 (t, J = 7.8 Hz, 1H), 7.19 (d, J = 7.6 Hz, 1H), 7.13 (d, J = 7.2 Hz, 1H), 7.06 (d, J = 7.6 Hz, 1H), 6.91 (d, J = 7.2 Hz, 1H), 6.60 (t, J = 7.6 Hz, 1H), 5.62 (s, 1H), 4.57 (d, J = 8.8 Hz, 1H), 3.11-3.03 (m, 2H), 2.87-2.81 (m, 1H), 2.37-2.31 (m, 1H), 1.91-1.82 (m, 1H), 1.50 (s, 9H), 1.32 (dd, J_1 = 7.0 Hz, J_2 = 1.8 Hz, 6H); ^{13}C

NMR (100 MHz, CDCl_3): δ (ppm) 166.4, 161.1, 142.6, 137.1, 132.9, 127.7, 124.4, 121.3, 119.0, 117.7, 116.1, 56.4, 36.5, 34.4, 30.0, 28.4, 22.8, 22.7. HRMS-ESI exact mass calcd. for $\text{C}_{21}\text{H}_{29}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 309.23253, found m/z 309.23193.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column (hexane : isopropanol = 99.5 : 0.5, flowing rate = 1.0 mL/min, 25 °C, UV detection at λ = 254 nm), t_{R1} = 17.6 min (major), t_{R2} = 18.9 min (minor).



(S)-2-(6-methylpyridin-2-yl)-8-phenyl-1,2,3,4-tetrahydroquinol

-ine (7p): (New compound); pale yellow oil, 90% yield, 80% ee;

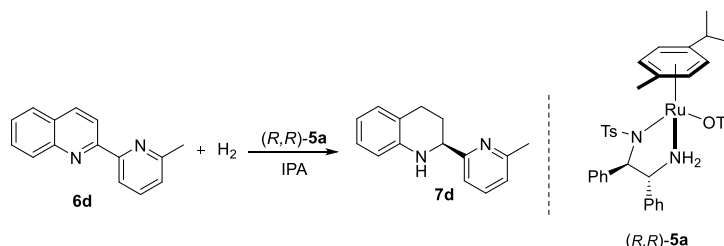
$[\alpha]_D^{20} = -137.0$ ($c = 0.25$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.54-7.50 (m, 3H), 7.43 (t, $J = 7.8$ Hz, 2H), 7.31 (t, $J = 7.5$ Hz, 1H), 7.16 (d, $J = 7.5$ Hz, 1H), 7.01-6.99 (m, 3H), 6.71 (t, $J = 7.3$ Hz, 1H), 4.81 (s, 1H), 4.53 (d, $J = 4.5$ Hz, 1H), 2.98-2.92 (m, 1H), 2.76-2.71 (m, 1H), 2.51 (s, 3H), 2.30-2.24 (m, 1H), 2.06-1.99 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 162.9, 157.8, 141.1, 139.7, 137.1, 129.5, 128.9, 128.7, 128.4, 127.2, 126.8, 121.7, 121.1, 117.3, 116.6, 57.0, 28.7, 26.3, 24.5. HRMS-ESI exact mass calcd. for $\text{C}_{21}\text{H}_{21}\text{N}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 301.16993, found m/z 301.17010.

The enantiomeric excess was determined by HPLC on Chiralcel AD-H column (hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{R1} = 5.5$ min (major), $t_{R2} = 6.1$ min (minor).

5. General procedure for the synthesis of P,N-ligands

(1) Gram-scale asymmetric hydrogenation

Table S2. Optimization of the reaction conditions for gram-scale asymmetric hydrogenation of **6d**^a

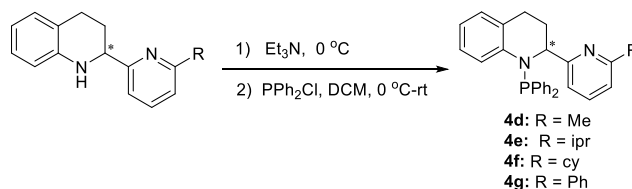


entry	6d (mg/mmol)	solvent (mL)	time (h)	conv. (%) ^b	ee (%) ^c
1	11.5/0.05	0.5	4	96	89
2	110/0.5	5.0	4	96	88
3	110/0.5	2.5	4	>99	89
4	220/1.0	5.0	4	>99	89
5	330/1.5	5.0	4	>99	89
6	1100/5.0	5.0	12	>99	89
7	1320/6.0	5.0	12	>99	89
8	2200/10	6.0	24	>99	88
9	3300/15	6.0	48	>99	88

^aReaction conditions: substrate **6d** in IPA, Ru-catalyst **5a** (2.0 mol %), H₂ (50 atm), stirred at 25 °C. ^bThe conversions were determined by ¹H NMR spectroscopy of the crude reaction mixtures.

^cThe enantiomeric excesses were determined by HPLC with a chiral OB-H column.

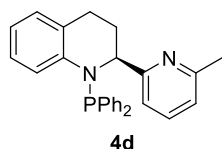
(2) The synthesis of P,N-ligands **4**



To a stirred solution of tetrahydroquinoline (1.0 eq) in anhydrous DCM (0.5 M) at 0 °C under nitrogen was added anhydrous triethylamine (3.0 eq). After the reaction mixture was stirred at 0 °C for 1 h, chlorodiphenylphosphine (1.0 eq) was added. The

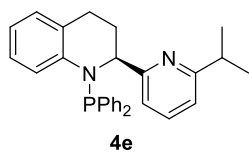
reaction mixture was stirred at 0 °C for 1 h and stirred at room temperature overnight. Then, anhydrous basic aluminum oxide was added to the solution, and the solvent was evaporated under reduced pressure to provide the powder. The powder was eluted by anhydrous petroleum quickly to give the spummy solid. Then, recrystallization from anhydrous methanol yielded the corresponding white solid. The analytical data of the products **4d-g** are summarized below.

Determination of enantiomeric excess: The synthesized ligands were dissolved in DCM and hydrolyzed by adding dilute hydrochloric acid, affording chiral 1,2,3,4-tetrahydroquinolines which were used for the determination of enantiomeric excess.



(S)-1-(diphenylphosphanyl)-2-(6-methylpyridin-2-yl)-1,2,3,4-tetrahydroquinoline (4d): (New compound); white solid, m.p. 110-111 °C, 60% yield, 99% ee; $[\alpha]_D^{20} = -72.4$ ($c = 0.25$, CHCl_3);

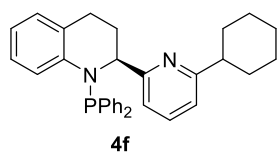
^1H NMR (500 MHz, CDCl_3): δ (ppm) 8.08-8.05 (m, 1H), 7.44-7.31 (m, 7H), 7.17 (t, $J = 7.8$ Hz, 1H), 7.10-7.01 (m, 4H), 6.97 (d, $J = 7.5$ Hz, 1H), 6.78 (t, $J = 7.5$ Hz, 1H), 6.69 (d, $J = 7.5$ Hz, 1H), 6.61 (d, $J = 7.0$ Hz, 1H), 4.95 (s, 1H), 2.59-2.56 (m, 1H), 2.34 (s, 3H), 2.31-2.25 (m, 2H), 2.10-2.04 (m, 1H); ^{31}P NMR (202 MHz, CDCl_3): δ (ppm) 50.7 (s); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 161.9, 156.9, 145.8 (d, $J_{\text{C-P}} = 22.5$ Hz), 137.5 (d, $J_{\text{C-P}} = 16.3$ Hz), 135.8, 135.6 (d, $J_{\text{C-P}} = 11.3$ Hz), 134.4 (d, $J_{\text{C-P}} = 23.8$ Hz), 131.2 (d, $J_{\text{C-P}} = 18.8$ Hz), 130.0, 129.4, 128.6 (d, $J_{\text{C-P}} = 5.0$ Hz), 127.9 (d, $J_{\text{C-P}} = 7.5$ Hz), 127.0, 124.8 (d, $J_{\text{C-P}} = 3.8$ Hz), 120.4, 118.9, 118.8, 117.5, 117.2, 61.0 (d, $J_{\text{C-P}} = 7.5$ Hz), 27.3, 24.3, 23.5. HRMS-ESI exact mass calcd. for $\text{C}_{27}\text{H}_{26}\text{N}_2\text{P}^+$ ($[\text{M}+\text{H}]^+$) requires m/z 409.18281, found m/z 409.18286.



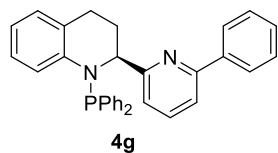
(S)-1-(diphenylphosphanyl)-2-(6-isopropylpyridin-2-yl)-1,2,3,4-tetrahydroquinoline (4e): (New compound); white solid, m.p. 85-87 °C, 58% yield, 99% ee; $[\alpha]_D^{20} = -116.8$ ($c = 0.25$, CHCl_3);

^1H NMR (500 MHz, CDCl_3): δ (ppm) 8.06 (t, $J = 7.8$ Hz, 1H), 7.44-7.31 (m, 7H), 7.15 (t, $J = 7.8$ Hz, 1H), 7.11-7.05 (m, 2H), 7.00 (t, $J = 7.0$ Hz, 2H), 6.96 (d, $J = 7.5$

Hz, 1H), 6.77 (t, $J = 7.5$ Hz, 1H), 6.70 (d, $J = 7.5$ Hz, 1H), 6.59 (d, $J = 7.5$ Hz, 1H), 4.95 (s, 1H), 2.83 (sept, $J = 6.8$ Hz, 1H), 2.58-2.54 (m, 1H), 2.29-2.22 (m, 2H), 2.11-2.03 (m, 1H), 1.16 (d, $J = 7.0$ Hz, 3H), 1.15 (d, $J = 7.0$ Hz, 3H); ^{31}P NMR (202 MHz, CDCl_3): δ (ppm) 50.4 (s); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 166.1, 161.5, 145.9 (d, $J_{\text{C-P}} = 22.5$ Hz), 137.7 (d, $J_{\text{C-P}} = 16.3$ Hz), 135.8, 135.6 (d, $J_{\text{C-P}} = 12.5$ Hz), 134.4 (d, $J_{\text{C-P}} = 25.0$ Hz), 131.2 (d, $J_{\text{C-P}} = 18.8$ Hz), 130.0, 129.5, 128.6 (d, $J_{\text{C-P}} = 5.0$ Hz), 127.9 (d, $J_{\text{C-P}} = 8.8$ Hz), 126.9, 126.9, 124.9 (d, $J_{\text{C-P}} = 3.8$ Hz), 119.0, 118.8, 117.4, 117.1, 61.0 (d, $J_{\text{C-P}} = 6.3$ Hz), 36.4, 27.4, 23.6, 22.7. HRMS-ESI exact mass calcd. for $\text{C}_{27}\text{H}_{30}\text{N}_2\text{P}^+$ ($[\text{M}+\text{H}]^+$) requires m/z 437.21411, found m/z 437.21396.

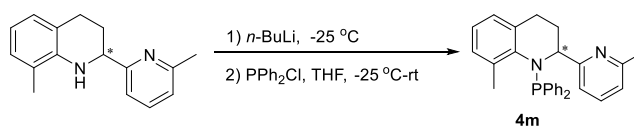


(S)-2-(6-cyclohexylpyridin-2-yl)-1-(diphenylphosphanyl)-1,2,3,4-tetrahydroquinoline (4f): (New compound); white solid, m.p. 92-93 °C, 63% yield, 99% ee; $[\alpha]_{\text{D}}^{20} = -60.0$ ($c = 0.25$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.99 (t, $J = 7.6$ Hz, 1H), 7.34-7.25 (m, 7H), 7.07 (t, $J = 7.4$ Hz, 1H), 7.01-6.86 (m, 5H), 6.68 (t, $J = 7.0$ Hz, 1H), 6.60 (d, $J = 7.6$ Hz, 1H), 6.50 (d, $J = 7.2$ Hz, 1H), 4.88 (s, 1H), 2.49-2.40 (m, 2H), 2.20-2.13 (m, 2H), 2.02-1.99 (m, 1H), 1.71-1.61 (m, 5H), 1.27-1.12 (m, 5H); ^{31}P NMR (162 MHz, CDCl_3): δ (ppm) 50.3 (s); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 165.3, 161.5, 145.9 (d, $J_{\text{C-P}} = 22.5$ Hz), 137.7 (d, $J_{\text{C-P}} = 16.3$ Hz), 135.8, 135.6 (d, $J_{\text{C-P}} = 11.3$ Hz), 134.4 (d, $J_{\text{C-P}} = 23.8$ Hz), 131.2 (d, $J_{\text{C-P}} = 18.8$ Hz), 130.0, 129.5, 128.6 (d, $J_{\text{C-P}} = 5.0$ Hz), 127.9 (d, $J_{\text{C-P}} = 7.5$ Hz), 126.9, 124.9 (d, $J_{\text{C-P}} = 3.8$ Hz), 119.1, 118.8, 117.5, 117.4, 117.1, 61.0 (d, $J_{\text{C-P}} = 6.3$ Hz), 46.6, 33.1, 27.4, 26.7, 26.2, 23.6. HRMS-ESI exact mass calcd. for $\text{C}_{32}\text{H}_{34}\text{N}_2\text{P}^+$ ($[\text{M}+\text{H}]^+$) requires m/z 477.24541, found m/z 477.24521.

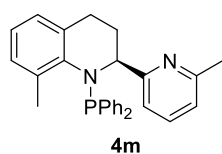


(S)-1-(diphenylphosphanyl)-2-(6-phenylpyridin-2-yl)-1,2,3,4-tetrahydroquinoline (4g): (New compound); white solid, m.p. 93-94 °C, 65% yield, 99% ee; $[\alpha]_{\text{D}}^{20} = -99.2$ ($c = 0.25$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 8.05 (t, $J = 7.4$ Hz, 1H), 7.82-7.80 (m, 2H), 7.46-7.35 (m, 10H), 7.29-7.16 (m, 3H), 7.05-6.96 (m, 4H), 6.81-6.74 (m, 2H), 5.05 (s, 1H), 2.61-2.56 (m, 1H), 2.43-2.28 (m, 2H), 2.10-2.02 (m, 1H); ^{31}P NMR (162

MHz, CDCl₃): δ (ppm) 51.8 (s); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 162.4, 156.2, 145.9 (d, J_{C-P} = 22.0 Hz), 139.8, 137.7 (d, J_{C-P} = 17.0 Hz), 136.2, 135.9 (d, J_{C-P} = 12.0 Hz), 134.1 (d, J_{C-P} = 23.0 Hz), 131.5 (d, J_{C-P} = 18.0 Hz), 130.0, 129.5, 128.7, 128.7, 128.6 (d, J_{C-P} = 5.0 Hz), 128.0 (d, J_{C-P} = 7.0 Hz), 127.0, 126.9, 125.1 (d, J_{C-P} = 4.0 Hz), 120.2, 119.1, 117.9, 117.7, 117.6, 61.1 (d, J_{C-P} = 6.0 Hz), 27.3, 23.6. HRMS-ESI exact mass calcd. for C₃₂H₂₈N₂P⁺ ([M+H]⁺) requires m/z 471.19846, found m/z 471.19861.



To a stirred solution of tetrahydroquinoline (1.0 eq) in anhydrous THF (0.5 M) at -25 °C under nitrogen was added *n*-BuLi (1.2 eq). After the reaction mixture was stirred at -25 °C for 1 h, chlorodiphenylphosphine (1.0 eq) was added. The reaction mixture was stirred at -25 °C for 1 h and stirred at room temperature overnight. Then, anhydrous basic aluminum oxide was added to the solution and the solvent was evaporated under reduced pressure to provide the powder. The powder was eluted by anhydrous petroleum quickly to give the spummy solid. Then, recrystallization from anhydrous methanol yielded **4m** as a white solid. The analytical data of the product are summarized below.



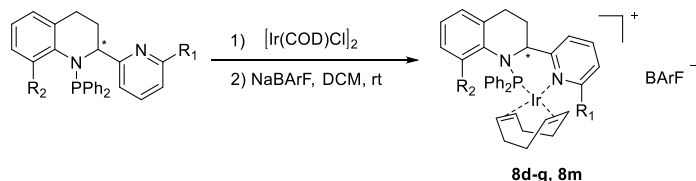
(S)-1-(diphenylphosphanyl)-8-methyl-2-(6-methylpyridin-2-yl)-1,2,3,4-tetrahydroquinoline (4m): (New compound); white solid,

m.p. 100-101 °C, 43% yield, 99% ee; $[\alpha]_D^{20}$ = -113.5 (*c* = 0.25, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.50 (t, *J* = 7.0 Hz, 2H), 7.45-7.33 (m, 6H), 7.24-7.19 (m, 3H), 7.12 (d, *J* = 7.5 Hz, 1H), 6.94 (d, *J* = 7.5 Hz, 1H), 6.90-6.86 (m, 2H), 6.74 (d, *J* = 7.0 Hz, 1H), 4.77 (s, 1H), 2.62 (s, 3H), 2.45 (s, 3H), 2.33-2.28 (m, 1H), 2.08-2.01 (m, 1H), 1.94-1.89 (m, 1H), 1.18-1.12 (m, 1H); ³¹P NMR (202 MHz, CDCl₃): δ (ppm) 63.0 (s); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 163.0, 157.5,

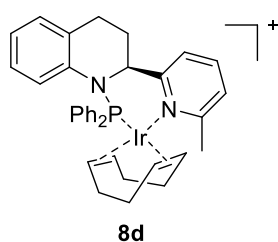
144.5 (d, J_{C-P} = 20.0 Hz), 138.1 (d, J_{C-P} = 18.8 Hz), 137.9 (d, J_{C-P} = 5.0 Hz), 136.7, 134.8 (d, J_{C-P} = 23.8 Hz), 131.2 (d, J_{C-P} = 5.0 Hz), 131.0 (d, J_{C-P} = 5.0 Hz), 130.8 (d,

$J_{C-P} = 18.8$ Hz), 130.1, 129.7, 128.7 (d, $J_{C-P} = 6.3$ Hz), 128.2 (d, $J_{C-P} = 5.0$ Hz), 127.9, 126.8, 120.0 (d, $J_{C-P} = 2.5$ Hz), 120.8, 118.4, 60.8 (d, $J_{C-P} = 8.8$ Hz), 26.6, 24.7, 23.8, 20.5 (d, $J_{C-P} = 18.8$ Hz). HRMS-ESI exact mass calcd. for $C_{28}H_{28}N_2P^+$ ($[M+H]^+$) requires m/z 423.19846, found m/z 423.19785.

6. General procedure for the synthesis of Ir-P,N-catalysts

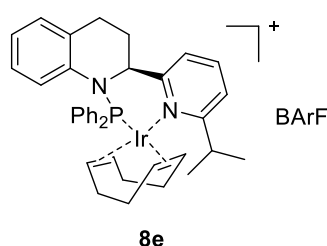


General procedure:³ To a stirred solution of P,N-ligands (1.0 eq) in anhydrous DCM (0.5 M) at 25 °C under nitrogen was added $[Ir(COD)Cl]_2$ (0.5 eq). After the reaction mixture was stirred at 25 °C for 2 h, sodium tetrakis[3,5-bis(trifluoromethyl)phenyl]borate (1.5 eq) was added. The reaction mixture was stirred at room temperature for another 2 h. Then, the solvent was evaporated under reduced pressure. The residue was purified by silica gel column chromatography (eluent: DCM) to yield the red solid. The analytical data of the products are summarized below.

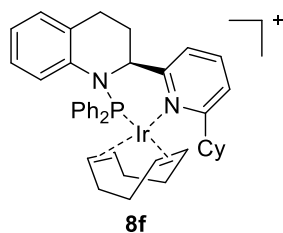


(S)-8d: (New compound); red solid, m.p. 185-187 °C, 83% yield; $[\alpha]_D^{20} = -56.0$ ($c = 0.25$, $CHCl_3$); 1H NMR (500 MHz, CD_2Cl_2): δ (ppm) 7.73 (s, 8H), 7.56 (s, 4H), 7.49-7.43 (m, 2H), 7.39-7.29 (m, 7H), 7.22-7.18 (m, 2H), 7.10-7.05 (m, 2H), 6.92-6.87 (m, 1H), 6.67 (t, $J = 7.5$ Hz, 1H), 6.48 (t, $J = 7.8$ Hz, 1H), 6.21 (d, $J = 8.0$ Hz, 1H), 5.02 (m, 1H), 4.13-4.07 (m, 2H), 3.36-3.35 (m, 1H), 3.07-2.99 (m, 2H), 2.86-2.84 (m, 1H), 2.60-2.42 (m, 4H), 2.37-2.27 (m, 5H), 2.20-2.04 (m, 2H), 1.73-1.55 (m, 2H); ^{31}P NMR (162 MHz, CD_2Cl_2): δ (ppm) 59.6 (s); ^{13}C NMR (125 MHz, CD_2Cl_2): δ (ppm) 162.2 (q, $^1J_{C-B} = 49.2$ Hz, 4C; BARF quat. C *ipso* to B), 161.1, 160.1, 140.3, 139.1 (d, $J_{C-P} = 5.0$ Hz), 135.2 (br, $^2J_{C-B}$, $^3J_{C-F}$, 8C; BARF *ortho* CH), 132.3, 132.2 (d, $J_{C-P} = 2.5$ Hz), 132.1 (d, $J_{C-P} = 11.3$ Hz), 132.0 (d, $J_{C-P} = 2.5$ Hz), 131.8, 131.4 (d, $J_{C-P} = 2.5$ Hz), 130.5 (d, J_{C-P}

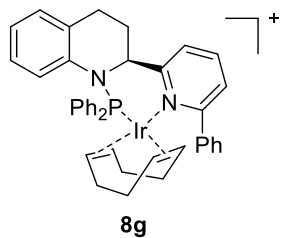
= 12.5 Hz), 129.3 (qq, $^3J_{C-B}$, $^2J_{C-F}$, 8C; BArF C *ipso* to CF₃), 128.3, 127.9, 126.6, 125.0 (q, $^1J_{C-F}$ = 270.8 Hz, 8C; BArF CF₃), 122.7, 122.6, 122.2, 120.9 (d, J_{C-P} = 3.8 Hz), 119.6, 117.9 (sept, $^3J_{C-F}$ = 3.8 Hz, 4C; BArF *para* CH), 98.0 (d, J_{C-P} = 10.0 Hz), 89.5 (d, J_{C-P} = 13.8 Hz), 67.8 (d, J_{C-P} = 13.8 Hz), 66.7, 64.4, 37.1 (d, J_{C-P} = 2.5 Hz), 34.1, 31.0, 29.1, 28.0 (d, J_{C-P} = 7.5 Hz), 27.7, 26.0 (d, J_{C-P} = 18.8 Hz). FTMS-ESI exact mass calcd. for C₃₅H₃₇IrN₂P⁺ ([M-BArF]⁺) requires m/z 709.23181, found m/z 709.23151.



(S)-8e: (New compound); red solid, m.p. 150-152 °C, 85% yield; $[\alpha]_D^{20}$ = -35.2 (*c* = 0.25, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.59 (t, *J* = 7.8 Hz, 1H), 7.52 (s, 8H), 7.33 (s, 4H), 7.26 (d, *J* = 8.0 Hz, 1H), 7.22-7.17 (m, 3H), 7.14-7.07 (m, 4H), 7.00 (t, *J* = 8.0 Hz, 3H), 6.81 (d, *J* = 7.5 Hz, 1H), 6.69 (qui, *J* = 6.0 Hz, 1H), 6.46 (t, *J* = 7.5 Hz, 1H), 6.25 (t, *J* = 7.8 Hz, 1H), 5.91 (d, *J* = 8.0 Hz, 1H), 4.90 (m, 1H), 4.09 (m, 1H), 3.85-3.83 (m, 1H), 3.66 (qui, *J* = 6.7 Hz, 1H), 3.08 (m, 1H), 2.85-2.76 (m, 2H), 2.57-2.55 (m, 1H), 2.42-2.35 (m, 1H), 2.28-2.18 (m, 2H), 2.12-2.07 (m, 2H), 1.92-1.78 (m, 2H), 1.46-1.32 (m, 3H), 1.14-1.07 (m, 6H); ³¹P NMR (202 MHz, CDCl₃): δ (ppm) 59.0 (s); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 171.0, 161.8 (q, $^1J_{C-B}$ = 49.6 Hz, 4C; BArF quat. C *ipso* to B), 159.0, 140.7, 138.9 (d, J_{C-P} = 5.0 Hz), 134.9 (br, $^2J_{C-B}$, $^3J_{C-F}$, 8C; BArF *ortho* CH), 132.0 (d, J_{C-P} = 2.5 Hz), 131.8 (d, J_{C-P} = 10.0 Hz), 131.5 (d, J_{C-P} = 2.5 Hz), 131.2, 130.9 (d, J_{C-P} = 2.5 Hz), 130.8, 130.1 (d, J_{C-P} = 12.5 Hz), 129.7 (d, J_{C-P} = 10.0 Hz), 129.0 (qq, $^3J_{C-B}$, $^2J_{C-F}$, 8C; BArF C *ipso* to CF₃), 128.2, 126.6, 124.7 (q, $^1J_{C-F}$ = 270.8 Hz, 8C; BArF CF₃), 124.4, 123.0, 122.6, 120.8 (d, J_{C-P} = 3.8 Hz), 119.5, 117.6 (sept, $^3J_{C-F}$ = 3.8 Hz, 4C; BArF *para* CH), 97.1 (d, J_{C-P} = 8.8 Hz), 86.4 (d, J_{C-P} = 16.3 Hz), 67.3, 66.8 (d, J_{C-P} = 13.8 Hz), 65.1, 39.9, 37.7 (d, J_{C-P} = 2.5 Hz), 34.9, 28.2, 27.9 (d, J_{C-P} = 7.5 Hz), 27.7, 25.0 (d, J_{C-P} = 2.5 Hz), 23.7, 22.4. FTMS-ESI exact mass calcd. for C₃₇H₄₁IrN₂P⁺ ([M-BArF]⁺) requires m/z 737.26311, found m/z 737.26355.

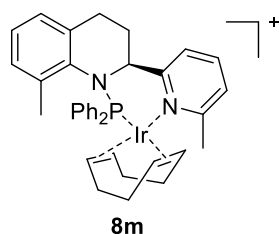


(S)-8f: (New compound); red solid, m.p. 180-182 °C, 75% yield; $[\alpha]_D^{20} = -33.2$ ($c = 0.25$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.77-7.71 (m, 9H), 7.51 (m, 4H), 7.43 (t, $J = 6.8$ Hz, 1H), 7.38-7.37 (m, 3H), 7.31-7.24 (m, 4H), 7.22-7.18 (m, 2H), 7.13 (t, $J = 7.0$ Hz, 1H), 6.98 (t, $J = 6.3$ Hz, 1H), 6.87-6.82 (m, 1H), 6.66-6.61 (m, 1H), 6.45-6.41 (m, 1H), 6.11 (t, $J = 7.0$ Hz, 1H), 5.09 (m, 1H), 4.36 (m, 1H), 3.94-3.93 (m, 1H), 3.65-3.63 (m, 1H), 3.24 (m, 1H), 3.03-3.00 (m, 1H), 2.72 (m, 1H), 2.60-2.30 (m, 5H), 2.08-2.01 (m, 2H), 1.91 (m, 2H), 1.72-1.43 (m, 7H), 1.26-1.16 (m, 3H), 0.96-0.93 (m, 1H), 0.56-0.54 (m, 1H); ^{31}P NMR (162 MHz, CDCl_3): δ (ppm) 58.3 (s); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 169.4, 161.9 (q, $^1J_{\text{C-B}} = 49.2$ Hz, 4C; BArF quat. C *ipso* to B), 159.2, 140.6, 138.9 (d, $J_{\text{C-P}} = 3.8$ Hz), 135.0 (br, $^2J_{\text{C-B}}$, $^3J_{\text{C-F}}$, 8C; BArF *ortho* CH), 132.0, 131.8 (d, $J_{\text{C-P}} = 10.0$ Hz), 131.4, 131.3, 131.0, 130.9, 130.1 (d, $J_{\text{C-P}} = 12.5$ Hz), 129.6 (d, $J_{\text{C-P}} = 10.0$ Hz), 128.9 (qq, $^3J_{\text{C-B}}$, $^2J_{\text{C-F}}$, 8C; BArF C *ipso* to CF_3), 128.2, 126.6, 125.0, 124.8 (q, $^1J_{\text{C-F}} = 282.1$ Hz, 8C; BArF CF_3), 123.1, 122.6, 120.8, 119.4, 117.6 (sept, $^3J_{\text{C-F}}$, 4C; BArF *para* CH), 97.1 (d, $J_{\text{C-P}} = 8.8$ Hz), 86.0 (d, $J_{\text{C-P}} = 15.0$ Hz), 67.6, 66.7 (d, $J_{\text{C-P}} = 13.8$ Hz), 65.4, 53.6, 51.1, 38.3, 35.4, 34.0, 33.1, 29.9, 27.9 (d, $J_{\text{C-P}} = 12.5$ Hz), 27.7 (d, $J_{\text{C-P}} = 16.3$ Hz), 26.5, 25.5, 25.2. FTMS-ESI exact mass calcd. for $\text{C}_{40}\text{H}_{45}\text{IrN}_2\text{P}^+$ ($[\text{M-BArF}]^+$) requires m/z 777.29441, found m/z 777.29352.



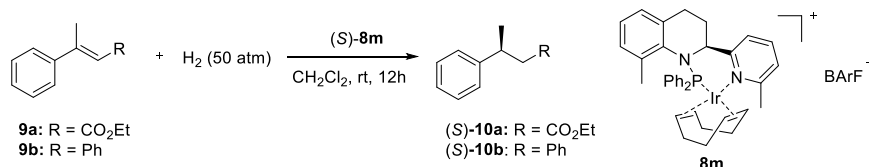
(S)-8g: (New compound); red solid, m.p. 188-189 °C, 87% yield; $[\alpha]_D^{20} = -68.8$ ($c = 0.25$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.97-7.93 (m, 1H), 7.73-7.68 (m, 9H), 7.55-7.47 (m, 10H), 7.39-7.29 (m, 7H), 7.06 (d, $J = 7.5$ Hz, 2H), 6.99 (d, $J = 7.5$ Hz, 1H), 6.86-6.81 (m, 1H), 6.67 (t, $J = 7.3$ Hz, 1H), 6.51 (t, $J = 7.8$ Hz, 1H), 6.31 (d, $J = 8.0$ Hz, 1H), 4.63 (m, 1H), 4.16 (m, 1H), 3.41 (m, 1H), 3.06-2.98 (m, 2H), 2.79-2.62 (m, 3H), 2.39-2.26 (m, 2H), 2.10-1.89 (m, 4H), 1.26-1.25 (m, 1H), 1.12-1.11 (m, 1H), 0.97-0.93 (m, 1H); ^{31}P NMR (202 MHz, CDCl_3): δ (ppm) 58.8 (s); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 162.3, 161.9 (q, $^1J_{\text{C-B}} = 49.6$ Hz, 4C; BArF quat. C *ipso* to B), 160.5, 140.4, 139.0 (d,

$J_{C-P} = 5.0$ Hz), 138.6, 135.0 (br, $^2J_{C-B}$, $^3J_{C-F}$, 8C; BArF *ortho* CH), 133.9, 133.5, 132.1, 131.9 (d, $J_{C-P} = 10.0$ Hz), 131.6, 131.4, 131.1, 129.9 (d, $J_{C-P} = 12.5$ Hz), 129.7 (d, $J_{C-P} = 10.0$ Hz), 129.0 (qq, $^3J_{C-B}$, $^2J_{C-F}$, 8C; BArF C *ipso* to CF₃), 128.2, 128.0, 127.3, 126.7, 124.7 (q, $^1J_{C-F} = 270.8$ Hz, 8C; BArF CF₃), 123.1, 122.8, 122.7, 121.0, 120.2, 117.6 (sept, $^3J_{C-F}$, 4C; BArF *para* CH), 94.0 (d, $J_{C-P} = 8.8$ Hz), 85.7 (d, $J_{C-P} = 15.0$ Hz), 67.3 (d, $J_{C-P} = 15.0$ Hz), 66.8, 65.6, 36.2, 34.7, 29.9, 28.2 (d, $J_{C-P} = 8.8$ Hz), 27.6, 24.5. FTMS-ESI exact mass calcd. for C₄₀H₃₉IrN₂P⁺ ([M-BArF]⁺) requires m/z 771.24746, found m/z 771.24725.

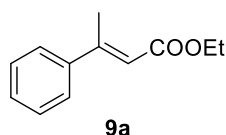


(S)-8m: (New compound); red solid, m.p. 192-193 °C, 84% yield; $[\alpha]_D^{20} = -44.8$ ($c = 0.25$, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.72 (s, 8H), 7.52 (s, 4H), 7.35-7.25 (m, 8H), 7.14-6.97 (m, 6H), 6.84-6.81 (m, 1H), 6.48 (d, $J = 7.0$ Hz, 1H), 5.05 (m, 1H), 4.68-4.54 (m, 2H), 4.12 (m, 1H), 3.97-3.96 (m, 1H), 3.68-3.63 (m, 1H), 3.41-3.36 (m, 1H), 3.27 (m, 1H), 2.99-2.87 (m, 1H), 2.44-2.16 (m, 8H), 2.01-1.95 (m, 1H), 1.56 (m, 5H); ³¹P NMR (202 MHz, CDCl₃): δ (ppm) 58.9 (s); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 162.0, 161.8 (q, $^1J_{C-B} = 49.6$ Hz, 4C; BArF quat. C *ipso* to B), 159.8, 142.4, 139.2, 135.0 (br, $^2J_{C-B}$, $^3J_{C-F}$, 8C; BArF *ortho* CH), 133.8, 133.2 (d, $J_{C-P} = 11.3$ Hz), 132.8, 132.5, 132.2, 132.0, 131.0, 129.9 (d, $J_{C-P} = 12.5$ Hz), 128.9 (qq, $^3J_{C-B}$, $^2J_{C-F}$, 8C; BArF C *ipso* to CF₃), 128.0 (d, $J_{C-P} = 11.3$ Hz), 127.4 (d, $J_{C-P} = 20.0$ Hz), 125.9, 125.1, 123.6 (q, $^1J_{C-F} = 270.6$ Hz, 8C; BArF CF₃), 120.6, 120.2, 117.6 (sept, $^3J_{C-F}$, 4C; BArF *para* CH), 95.4 (d, $J_{C-P} = 10.0$ Hz), 92.1 (d, $J_{C-P} = 13.8$ Hz), 69.9 (d, $J_{C-P} = 7.5$ Hz), 65.8, 59.2, 37.2 (d, $J_{C-P} = 32.5$ Hz), 34.0, 29.9, 28.6, 28.3, 27.2, 24.8, 20.8. FTMS-ESI exact mass calcd. for C₃₆H₃₉IrN₂P⁺ ([M-BArF]⁺) requires m/z 723.24746, found m/z 723.24579.

7. General procedure for asymmetric hydrogenation of olefins

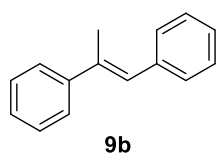


A 30 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with Ir-catalyst (*S*)-**8m** (3.4 mg, 2.0 mol %) and substrate **6** (0.1 mmol) in DCM (1.0 mL) under nitrogen atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 25 °C for 12 h. Then the hydrogen gas was carefully released and the conversion was determined by ^1H NMR. The reaction mixture was filtered through a short pad of silica (petroleum/DCM, 2/1, v/v) to give the pure product. The enantiomeric excess of the product was determined by HPLC with a chiral column. The analytical data of the products are summarized below.



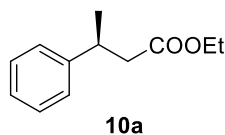
Ethyl *trans*-beta-methylcinnamate (9a): (Known compound, see: A. Lightfoot, P. Schnider and A. Pfaltz, *Angew. Chem., Int. Ed.* 1998, **37**, 2897); colourless oil; ^1H NMR (300 MHz, CDCl_3):

δ (ppm) 7.49-7.45 (m, 2H), 7.38-7.34 (m, 3H), 6.13 (m, 1H), 4.21 (q, $J = 7.1$ Hz, 2H), 2.57 (s, 3H), 1.31 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 166.9, 155.5, 142.3, 129.0, 128.5, 126.4, 117.3, 59.9, 18.0, 14.4.



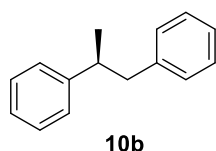
***E*-1,2-diphenylpropene (9b):** (Known compound, see: A. Lightfoot, P. Schnider and A. Pfaltz, *Angew. Chem., Int. Ed.* 1998, **37**, 2897); colourless oil; ^1H NMR (300 MHz, CDCl_3): δ (ppm)

7.54-7.52 (m, 2H), 7.40-7.35 (m, 6H), 7.31-7.21 (m, 2H), 6.84 (m, 1H), 2.29 (s, 3 H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 144.1, 138.5, 137.6, 129.3, 128.5, 128.3, 127.8, 127.3, 126.6, 126.1, 17.6.



Ethyl (*S*)-3-phenylbutanoate (10a): (Known compound, see: A. Lightfoot, P. Schnider and A. Pfaltz, *Angew. Chem., Int. Ed.* 1998, **37**, 2897); colourless oil, 94% yield, 99% ee; $[\alpha]_{\text{D}}^{20} = +40$ ($c = 0.25$, CHCl_3), [Lit.⁴ $[\alpha]_{\text{D}}^{20} = +9.3$ ($c = 1.43$, CHCl_3), 82% ee for (*S*) enantiomer]; ^1H NMR (300 MHz, CDCl_3): δ (ppm) 7.31-7.20 (m, 5H), 4.06 (q, $J = 7.2$ Hz, 2H), 3.27 (q, $J = 7.1$ Hz, 1H), 2.64-2.48 (m, 2H), 1.29 (d, $J = 6.9$ Hz, 3H), 1.16 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 172.4, 145.8, 128.5, 126.8, 126.4, 60.2, 43.0, 36.6, 21.8, 14.2.

The enantiomeric excess was determined by HPLC on Chiralcel OB-H column (hexane : isopropanol = 99.5 : 0.5, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 7.4$ min (minor), $t_{\text{R}2} = 9.3$ min (major).



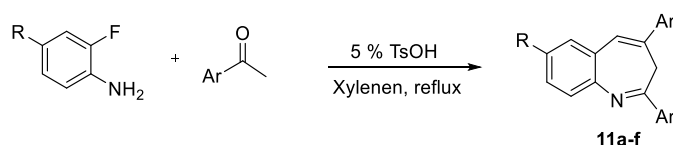
(*S*)-1,2-Diphenylpropane (10b): (Known compound, see: A. Lightfoot, P. Schnider and A. Pfaltz, *Angew. Chem., Int. Ed.* 1998, **37**, 2897); colourless oil, 95% yield, 99% ee; $[\alpha]_{\text{D}}^{20} = +37$ ($c = 0.25$, CHCl_3), [Lit.⁵ $[\alpha]_{\text{D}}^{23.5} = -80.5$ ($c = 2.07$, CHCl_3), >99% ee for (*R*) enantiomer]; ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.27-7.13 (m, 7H), 7.07-7.06 (m, 2H), 3.01-2.91 (m, 2H), 2.77-2.73 (m, 1H), 1.23 (d, $J = 6.5$ Hz, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 147.1, 140.9, 129.3, 128.4, 128.2, 127.2, 126.1, 126.0, 45.2, 42.0, 21.3.

The enantiomeric excess was determined by HPLC on Chiralcel OJ-H column (hexane : isopropanol = 95 : 5, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 5.5$ min (minor), $t_{\text{R}2} = 8.5$ min (major).

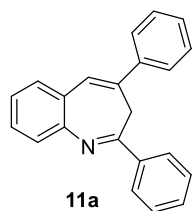
8. General procedure for the synthesis of benzoazepines and benzodiazepines

(1) The procedure for the synthesis of 2,4-diaryl-3*H*-benzo[*b*]azepines

The corresponding substrates were synthesized according to the previously reported procedures.^{6a}



A solution of 2-fluoroaniline (6.0 mmol, 1.0 equiv), aryl methyl ketone (6.0 mmol, 1.0 equiv) and *p*-toluenesulfonic acid (0.05 g, 0.3 mmol, 0.05 equiv) in 30 mL of xylene was heated to reflux for 24 h. After cooling to room temperature, the solution was washed with saturated NaHCO₃ solution, and dried over Na₂SO₄. Removal of the solvent under reduced pressure gave dark oil or solid, which was purified by crystallization using EtOH as solvent. The analytical data of the products are summarized below.



2,4-diphenyl-3*H*-benzo[*b*]azepine (11a): (Known compound, see: K.

Ramig, S. Alli, M. Cheng, M. Leung, R. Razi, M. Washington and L.

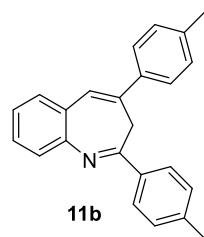
Kudzma, *Synlett* 2007, **18**, 2868); ¹H NMR (500 MHz, CDCl₃): δ

(ppm) 7.89-7.87 (m, 2H), 7.60-7.59 (m, 1H), 7.55-7.54 (m, 2H), 7.48

(d, *J* = 8.0 Hz, 1H), 7.40-7.32 (m, 7H), 7.23-7.20 (m, 1H), 7.08 (s, 1H), 3.40 (s, 2H);

¹³C NMR (125 MHz, CDCl₃): δ (ppm) 157.6, 146.8, 140.0, 138.2, 135.0, 130.7, 130.4,

129.7, 128.9, 128.7, 128.2, 128.1, 128.0, 127.1, 127.0, 126.9, 124.2, 34.0.



2,4-di-*p*-tolyl-3*H*-benzo[*b*]azepine (11b): (Known compound, see:

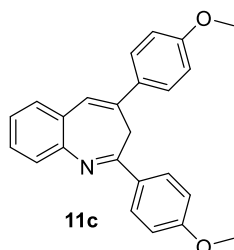
K. Ramig, S. Alli, M. Cheng, M. Leung, R. Razi, M. Washington

and L. Kudzma, *Synlett* 2007, **18**, 2868); ¹H NMR (500 MHz,

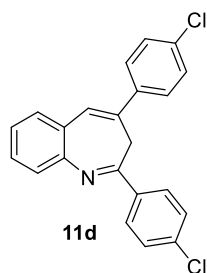
CDCl₃): δ (ppm) 7.81-7.78 (m, 2H), 7.61-7.57 (m, 1H), 7.47-7.43

(m, 3H), 7.38-7.35 (m, 1H), 7.23-7.04 (m, 5H), 7.04 (s, 1H), 3.36 (s, 2H), 2.36 (s, 3H),

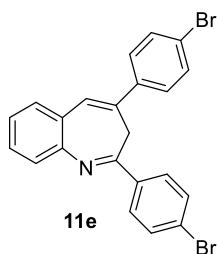
2.32 (s, 3H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 157.7, 146.5, 140.8, 137.9, 137.1, 135.0, 130.6, 129.9, 129.6, 129.4, 128.3, 128.2, 128.0, 127.0, 126.8, 126.2, 124.1, 33.8, 21.5, 21.3.



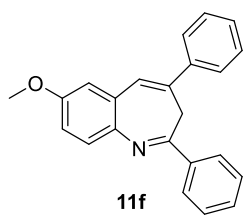
2,4-bis(4-methoxyphenyl)-3H-benzo[*b*]azepine (11c): (Known compound, see: K. Ramig, S. Alli, M. Cheng, M. Leung, R. Razi, M. Washington and L. Kudzma, *Synlett* 2007, **18**, 2868); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.87-7.85 (m, 2H), 7.56-7.55 (m, 1H), 7.51-7.45 (m, 3H), 7.38-7.34 (m, 1H), 7.20-7.17 (m, 1H), 6.99 (s, 1H), 6.93-6.90 (m, 2H), 6.86-6.83 (m, 2H), 3.83 (s, 3H), 3.79 (s, 3H), 3.33 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 161.4, 159.5, 156.5, 146.9, 134.5, 132.7, 130.9, 130.6, 129.9, 128.2, 128.0, 126.8, 125.4, 123.7, 114.2, 114.0, 55.5, 33.8.



2,4-bis(4-chlorophenyl)-3H-benzo[*b*]azepine (11d): (Known compound, see: K. Ramig, S. Alli, M. Cheng, M. Leung, R. Razi, M. Washington and L. Kudzma, *Synlett* 2007, **18**, 2868); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.86-7.85 (m, 2H), 7.74 (s, 1H), 7.61-7.26 (m, 9H), 7.10 (s, 1H), 3.40 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 142.5, 140.1, 137.7, 134.5, 133.5, 130.7, 130.1, 129.3, 128.8, 128.2, 127.9, 127.8, 127.7, 126.1, 33.9.



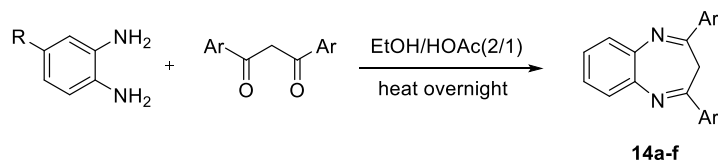
2,4-bis(4-bromophenyl)-3H-benzo[*b*]azepine (11e): (Known compound, see: Z.-S. Yang, Z.-Y. Ding, F. Chen, Y.-M. He, N.-F. Yang and Q.-H. Fan, *Eur. J. Org. Chem.*, 2017, 1973); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.74-7.72 (m, 2H), 7.59-7.48 (m, 6H), 7.43-7.38 (m, 3H), 7.26-7.23 (m, 1H), 7.06-7.05 (m, 1H), 3.32 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 156.0, 146.5, 138.7, 136.7, 133.4, 132.2, 132.0, 130.7, 129.7, 129.4, 128.5, 128.1, 127.5, 127.5, 125.3, 124.5, 122.4, 33.6.



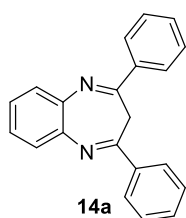
7-methoxy-2,4-diphenyl-3H-benzo[b]azepine (11f): (Known compound, see: Z.-S. Yang, Z.-Y. Ding, F. Chen, Y.-M. He, N.-F. Yang and Q.-H. Fan, *Eur. J. Org. Chem.*, 2017, 1973); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.86-7.85 (m, 2H), 7.53-7.52 (m, 3H), 7.37-7.28 (m, 6H), 7.02-7.00 (m, 2H), 6.91 (s, 1H), 3.83 (s, 3H), 3.39 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 155.9, 141.3, 139.9, 138.5, 134.8, 130.7, 130.0, 129.9, 128.8, 128.6, 128.0, 127.9, 126.9, 126.7, 115.6, 112.5, 55.5, 33.8.

(2) The procedure for the synthesis of 2,4-diaryl-3H-benzodiazepines

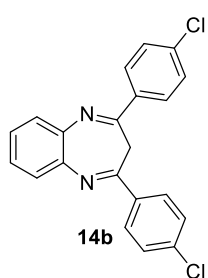
The corresponding substrates were synthesized according to the previously reported procedures.^{6b}



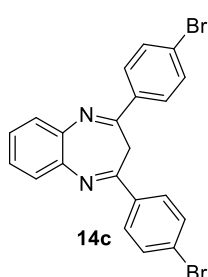
2,4-Diaryl-substituted-3H-1,5-benzodiazepines **14a-f** were prepared according to the method previously reported in the literature. o-Phenylenediamine (5 mmol) and 1,3-diarylpentane-1,3-dione (5 mmol) in a mixture of ethanol (5 mL) and acetic acid (2.5 mL) were heated overnight. The mixture was cooled, neutralized by NaOH and then recrystallized from ethanol. The analytical data of the products are summarized below.



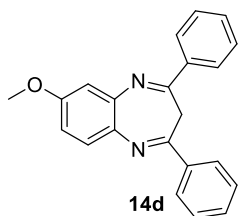
2,4-diphenyl-3H-1,5-benzodiazepine (14a): (Known compound, see: I. L. Finar, *J. Chem. Soc.*, 1958, 4904); white solid, m.p. 156-159 °C, 65% yield; ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.98-7.96 (m, 4H), 7.64-7.60 (m, 2H), 7.44-7.39 (m, 6H), 7.37-7.33 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 154.3, 140.8, 137.4, 130.7, 128.9, 128.8, 128.2, 125.6, 35.1.



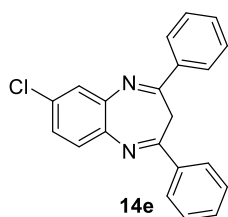
2,4-bis(4-chlorophenyl)-3H-1,5-benzozepine (14b): (Known compound, see: Z.-Y. Ding, F. Chen, J. Qin, Y.-M. He and Q.-H. Fan, *Angew. Chem., Int. Ed.* 2012, **51**, 5706); white solid, m.p. 220-222 °C, 63% yield; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.89-7.87 (m, 4H), 7.59-7.57 (m, 2H), 7.39-7.33 (m, 6H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 152.5, 140.6, 137.2, 135.6, 129.5, 129.1, 128.9, 125.9, 34.7.



2,4-bis(4-bromophenyl)-3H-1,5-benzozepine (14c): (Known compound, see: Z.-Y. Ding, F. Chen, J. Qin, Y.-M. He and Q.-H. Fan, *Angew. Chem., Int. Ed.* 2012, **51**, 5706); white solid, m.p. 223-225 °C, 84% yield; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.83-7.81 (m, 4H), 7.59-7.55 (m, 6H), 7.37-7.35 (m, 2H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 152.6, 140.6, 136.1, 132.2, 129.8, 128.9, 126.0, 125.8, 34.6.

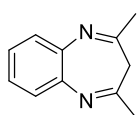


7-methoxy-2,4-diphenyl-3H-1,5-benzodiazepine (14d): (Known compound, see: Z.-Y. Ding, F. Chen, J. Qin, Y.-M. He and Q.-H. Fan, *Angew. Chem., Int. Ed.* 2012, **51**, 5706); yellow solid, m.p. 169-172 °C, 78% yield; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.97-7.96 (m, 4H), 7.55-7.53 (m, 1H), 7.43-7.40 (m, 6H), 7.09-7.07 (m, 1H), 7.00-6.97 (m, 1H); 3.90 (s, 3H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 157.1, 153.7, 151.8, 141.8, 137.6, 137.4, 135.1, 130.8, 130.5, 130.3, 128.9, 128.8, 128.3, 128.1, 115.1, 110.1, 55.7, 35.3.



7-chloro-2,4-Diphenyl-3H-1,5-benzodiazepine (14e): (Known compound, see: M. Takahashi, T. Takada and T. Sakagami, *J. Heterocyclic Chem.* 1987, **24**, 797); white solid, m.p. 178-180 °C, 69% yield; ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.97-7.96 (m,

4H), 7.61 (d, $J = 2.0$ Hz, 1H), 7.53 (d, $J = 8.5$ Hz, 1H), 7.45-7.40 (m, 6H), 7.31-7.28 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 155.1, 154.5, 141.6, 139.4, 137.2, 137.0, 131.1, 131.0, 130.6, 130.2, 128.9, 128.4, 128.3, 128.2, 125.9, 35.3.

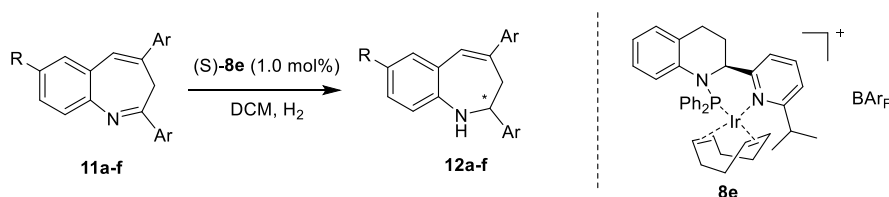


14f

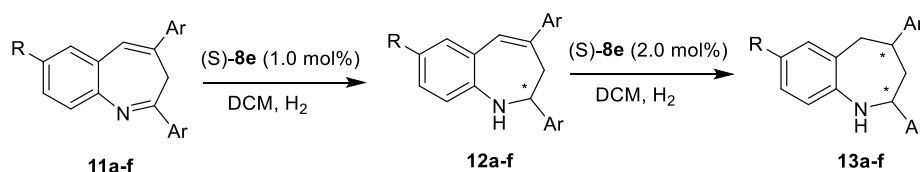
2,4-dimethyl-3H-1,5-benzodiazepine (14f): (Known compound, see: I. L. Finar, *J. Chem. Soc.*, 1958, 4904); white solid, m.p. 146-147 °C, 79% yield; ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.36-7.35 (m, 2H), 7.22-7.20 (m, 2H), 2.81 (s, 2H), 2.34 (s, 6H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 157.8, 140.4, 127.6, 125.0, 43.3, 27.8.

9. General procedure for asymmetric hydrogenation of cyclic imines

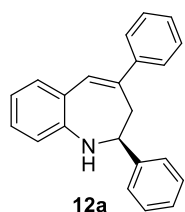
(1) Asymmetric hydrogenation of 2,4-diaryl-3H-benzo[*b*]azepines



For 12 a-f: A 30 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with Ir-catalyst (*S*)-**8e** (3.4 mg, 1.0 mol %) and substrate **11** (0.2 mmol) in DCM (2 mL) under nitrogen atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 25 °C for 12 h. Then, the hydrogen gas was carefully released and the conversion was determined by ^1H NMR. The reaction mixture was filtered through a short pad of silica (petroleum/DCM, 2/1, v/v) to give the pure products. The enantiomeric excess of the product was determined by HPLC with a chiral column. The analytical data of the products are summarized below.

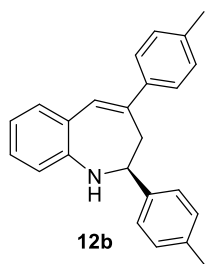


For 13a-f (one-pot and two-step): A 30 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with Ir-catalyst (*S*)-**8e** (3.4 mg, 1.0 mol %) and substrate **11** (0.2 mmol) in DCM (2 mL) under nitrogen atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 25 °C for 12 h. Then, the hydrogen gas was carefully released, and another Ir-catalyst (*S*)-**8e** (6.8 mg, 2.0 mol %) in DCM (2 mL) was added. The final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 25 °C for 12 h. Then, the hydrogen gas was carefully released and the conversion was determined by ¹H NMR. The reaction mixture was filtered through a short pad of silica (petroleum/acetone, 45/1, v/v) to give the pure products. The enantiomeric excess of the product was determined by HPLC with a chiral column. The analytical data of the products are summarized below.



(*S*)-2,4-diphenyl-2,3-dihydro-1*H*-benzo[*b*]azepine (12a): (Known compound, see: Z.-S. Yang, Z.-Y. Ding, F. Chen, Y.-M. He, N.-F. Yang and Q.-H. Fan, *Eur. J. Org. Chem.*, 2017, 1973); white solid, 94% yield, 87% ee; $[\alpha]_{\text{D}}^{20} = -260.2$ ($c = 0.25$, CHCl₃); ¹H NMR (500 MHz, CDCl₃): δ (ppm) 7.44-7.42 (m, 2H), 7.39-7.38 (m, 4H), 7.34-7.29 (m, 3H), 7.24-7.21 (m, 2H), 7.04-7.00 (m, 1H), 6.83-6.80 (m, 1H), 6.76 (d, $J = 2.5$ Hz, 1H), 6.61 (d, $J = 7.5$ Hz, 1H), 4.40 (dd, $J_1 = 9.5$ Hz, $J_2 = 1.5$ Hz, 1H), 3.33-3.27 (m, 1H), 3.02 (dd, $J_1 = 17.5$ Hz, $J_2 = 1.5$ Hz, 1H); ¹³C NMR (125 MHz, CDCl₃): δ (ppm) 147.2, 144.7, 144.6, 139.0, 134.1, 129.2, 128.4, 128.0, 127.9, 127.0, 126.9, 126.2, 123.2, 119.6, 117.9, 59.7, 44.8.

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 85 : 15, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 6.9$ min (major), $t_{\text{R}2} = 9.6$ min (minor).

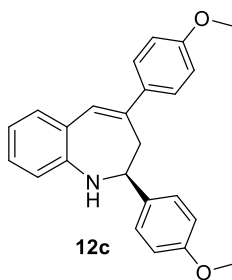


(S)-2,4-di-p-tolyl-2,3-dihydro-1H-benzo[b]azepine (12b):

(Known compound, see: Z.-S. Yang, Z.-Y. Ding, F. Chen, Y.-M. He, N.-F. Yang and Q.-H. Fan, *Eur. J. Org. Chem.*, 2017, 1973); white solid, 91% yield, 90% ee; $[\alpha]_{\text{D}}^{20} = -213.0$ ($c = 1.0$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.33 (d, $J = 8.5$ Hz, 2H), 7.27 (d, $J = 7.5$ Hz, 2H), 7.21-7.16 (m, 3H), 7.11 (d, $J = 7.5$ Hz, 2H), 6.99 (t, $J = 7.3$ Hz, 1H), 6.79 (t, $J = 7.3$ Hz, 1H), 6.74 (d, $J = 1.5$ Hz, 1H), 6.57 (d, $J = 8.0$ Hz, 1H), 4.34 (d, $J = 9.5$ Hz, 1H), 3.29-3.23 (m, 1H), 3.00 (d, $J = 17.5$ Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H);

^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 147.3, 141.9, 141.8, 138.9, 137.6, 136.7, 134.0, 129.8, 129.1, 128.5, 127.7, 126.7, 126.0, 123.3, 119.5, 117.8, 59.3, 44.9, 21.2, 21.2.

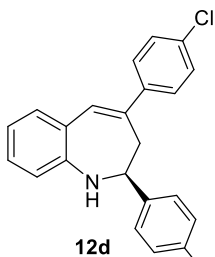
The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 85 : 15, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 6.1$ min (major), $t_{\text{R}2} = 12.3$ min (minor).



(S)-2,4-bis(4-methoxyphenyl)-2,3-dihydro-1H-benzo[b]azepine (12c):

(Known compound, see: Z.-S. Yang, Z.-Y. Ding, F. Chen, Y.-M. He, N.-F. Yang and Q.-H. Fan, *Eur. J. Org. Chem.*, 2017, 1973); white solid, 90% yield, 95% ee; $[\alpha]_{\text{D}}^{20} = -237.6$ ($c = 0.25$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.39-7.37 (m, 2H), 7.33-7.30 (m, 2H), 7.25-7.21 (m, 2H), 7.03-7.00 (m, 1H), 6.93-6.91 (m, 2H), 6.87-6.81 (m, 3H), 6.70 (d, $J = 2.0$ Hz, 1H), 6.63 (d, $J = 6.0$ Hz, 1H), 4.37 (d, $J = 9.0$ Hz, 1H), 3.85-3.76 (m, 5H), 3.28-3.22 (m, 1H), 2.98 (d, $J = 17.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 159.3, 158.8, 147.0, 138.6, 137.2, 137.0, 133.9, 128.0, 127.8, 127.6, 127.3, 123.6, 119.7, 118.0, 114.5, 113.8, 59.2, 55.5, 44.9, 29.9.

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 85 : 15, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 12.1$ min (major), $t_{\text{R}2} = 40.1$ min (minor).

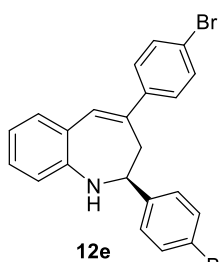


(S)-2,4-bis(4-chlorophenyl)-2,3-dihydro-1H-benzo[b]azepine

(12d): (Known compound, see: Z.-S. Yang, Z.-Y. Ding, F. Chen, Y.-M. He, N.-F. Yang and Q.-H. Fan, *Eur. J. Org. Chem.*, 2017, 1973); yellow solid, 89% yield, 92% ee; $[\alpha]_{\text{D}}^{20} = -210.6$ ($c = 0.25$, CHCl_3), [Lit.⁷ $[\alpha]_{\text{D}}^{20} = -218.4$ ($c = 1.0$, CHCl_3), 89% ee for

(*S*) enantiomer]; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.37-7.21 (m, 9H), 7.06 (t, $J = 7.6$ Hz, 1H), 6.84 (t, $J = 7.6$ Hz, 1H), 6.73 (s, 1H), 6.65 (d, $J = 7.6$ Hz, 1H), 4.42 (d, $J = 8.8$ Hz, 1H), 3.27-3.20 (m, 1H), 2.94 (d, $J = 16.8$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 147.1, 142.9, 137.3, 134.2, 133.8, 132.8, 129.7, 129.4, 129.2, 128.8, 128.5, 128.2, 128.2, 127.4, 122.9, 119.8, 118.0, 59.1, 44.4.

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 85 : 15, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 8.5$ min (major), $t_{\text{R}2} = 13.2$ min (minor).

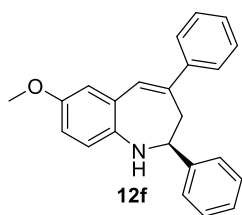


(S)-2,4-bis(4-bromophenyl)-2,3-dihydro-1H-benzo[b]azepine

(12e): (Known compound, see: Z.-S. Yang, Z.-Y. Ding, F. Chen, Y.-M. He, N.-F. Yang and Q.-H. Fan, *Eur. J. Org. Chem.*, 2017, 1973); yellow solid, 55% yield, 88% ee; $[\alpha]_{\text{D}}^{20} = -207.6$ ($c = 0.25$, CHCl_3); ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.47 (d, $J =$

8.4 Hz, 2H), 7.41-7.38 (m, 2H), 7.24-7.18 (m, 5H), 7.05-7.00 (m, 1H), 6.81 (t, $J = 7.4$ Hz, 1H), 6.71 (d, $J = 1.6$ Hz, 1H), 6.60 (d, $J = 8.0$ Hz, 1H), 4.35 (d, $J = 8.0$ Hz, 1H), 3.22-3.15 (m, 1H), 2.90 (dd, $J_1 = 17.0$ Hz, $J_2 = 1.4$ Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 146.9, 143.3, 143.2, 137.2, 134.2, 132.2, 131.4, 129.7, 128.5, 128.2, 127.7, 122.8, 121.8, 120.9, 119.8, 118.0, 59.0, 44.1.

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 85 : 15, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 9.4$ min (major), $t_{\text{R}2} = 14.9$ min (minor).



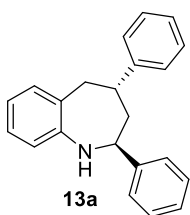
(S)-7-methoxy-2,4-diphenyl-2,3-dihydro-1H-benzo[b]azepine

(12f): (Known compound, see: Z.-S. Yang, Z.-Y. Ding, F. Chen, Y.-M. He, N.-F. Yang and Q.-H. Fan, *Eur. J. Org. Chem.*, 2017,

1973); white solid, 65% yield, 90% ee; $[\alpha]_{\text{D}}^{20} = -278.0$ ($c = 0.25$,

CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.44-7.43 (m, 2H), 7.38-7.37 (m, 4H), 7.32-7.29 (m, 3H), 7.22 (d, $J = 7.5$ Hz, 1H), 6.78 (d, $J = 3.0$ Hz, 1H), 6.71 (s, 1H), 6.66-6.63 (m, 1H), 6.55 (d, $J = 8.5$ Hz, 1H), 4.34 (d, $J = 9.0$ Hz, 1H), 3.75 (s, 3H), 3.31-3.25 (m, 1H), 2.99 (d, $J = 17.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 153.4, 144.8, 144.5, 141.6, 140.0, 129.1, 128.8, 128.4, 127.9, 127.1, 126.8, 126.2, 124.6, 119.1, 117.8, 114.5, 60.4, 55.8, 45.0.

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 85 : 15, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 7.7$ min (major), $t_{\text{R}2} = 8.5$ min (minor).



(2S,4S)-2,4-diphenyl-2,3,4,5-tetrahydro-1H-benzo[b]azepine (13a):

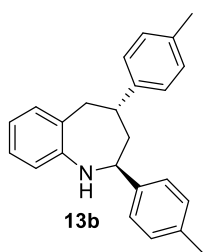
(New compound); white solid, m.p. 107-108 °C, 90% yield, dr = 11:1,

88% ee; $[\alpha]_{\text{D}}^{20} = +25.2$ ($c = 0.25$, CHCl_3); ^1H NMR (500 MHz,

CDCl_3): δ (ppm) 7.45-7.44 (m, 2H), 7.37-7.32 (m, 2H), 7.30-7.27 (m,

5H), 7.21-7.18 (m, 1H), 7.15 (d, $J = 7.5$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 2H), 6.90 (t, $J = 7.3$ Hz, 1H), 6.77 (d, $J = 7.5$ Hz, 1H), 3.94 (d, $J = 11.0$ Hz, 1H), 3.78 (s, 1H), 3.29 (t, $J = 12.5$ Hz, 1H), 2.95 (d, $J = 13.5$ Hz, 1H), 2.80 (t, $J = 11.5$ Hz, 1H), 2.26-2.10 (m, 2H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 149.4, 148.0, 145.7, 132.9, 131.1, 129.0, 128.7, 127.8, 127.3, 126.8, 126.6, 125.3, 121.9, 120.4, 63.7, 49.1, 44.7, 43.2. HRMS-ESI exact mass calcd. for $\text{C}_{22}\text{H}_{22}\text{N}^+$ ($[\text{M}+\text{H}]^+$) requires m/z 300.17468, found m/z 300.17505.

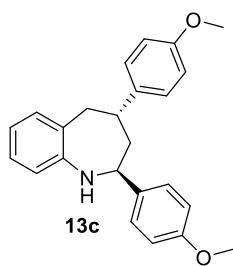
The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 5.3$ min (major), $t_{\text{R}2} = 6.3$ min (minor).



(2*S*,4*S*)-2,4-di-*p*-tolyl-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine

(13b): (New compound); white solid, m.p. 127-129 °C, 93% yield, dr = 12:1, 90% ee; $[\alpha]_{\text{D}}^{20} = +31.6$ ($c = 0.25$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.32 (d, $J = 8.0$ Hz, 2H), 7.18-7.06 (m, 8H), 6.88 (t, $J = 7.0$ Hz, 1H), 6.74 (d, $J = 7.0$ Hz, 1H), 3.89 (d, $J = 10.5$ Hz, 1H), 3.72 (s, 1H), 3.25 (t, $J = 12.5$ Hz, 1H), 2.91 (d, $J = 13.5$ Hz, 1H), 2.76 (t, $J = 11.5$ Hz, 1H), 2.33 (s, 3H), 2.31 (s, 3H), 2.22-2.15 (m, 1H), 2.07 (d, $J = 13.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 149.4, 145.1, 142.8, 137.4, 135.7, 133.0, 131.1, 129.5, 129.3, 127.2, 126.7, 126.5, 121.8, 120.4, 63.4, 49.0, 44.2, 43.4, 21.2, 21.1. HRMS-ESI exact mass calcd. for $\text{C}_{24}\text{H}_{26}\text{N}^+$ ($[\text{M}+\text{H}]^+$) requires m/z 328.20598, found m/z 328.20609.

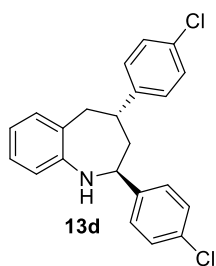
The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 4.6$ min (major), $t_{\text{R}2} = 5.8$ min (minor).



(2*S*,4*S*)-2,4-bis(4-methoxyphenyl)-2,3,4,5-tetrahydro-1*H*-benzo[*b*]azepine (13c): (New compound); white solid, m.p. 134-135 °C,

87% yield, dr = 16:1, 99% ee; $[\alpha]_{\text{D}}^{20} = +11.6$ ($c = 0.25$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.36 (d, $J = 8.5$ Hz, 2H), 7.23-7.20 (m, 2H), 7.13 (d, $J = 7.5$ Hz, 1H), 7.09 (t, $J = 7.5$ Hz, 1H), 6.88-6.84 (m, 5H), 6.77 (s, 1H), 3.89 (d, $J = 11.0$ Hz, 1H), 3.79 (s, 3H), 3.78 (s, 1H), 3.24 (s, 1H), 2.91 (d, $J = 14.0$ Hz, 1H), 2.75 (t, $J = 11.5$ Hz, 1H), 2.19 (d, $J = 9.5$ Hz, 1H), 2.07-2.04 (m, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 159.1, 158.0, 149.4, 140.3, 138.1, 132.9, 131.1, 128.4, 127.7, 127.2, 121.8, 120.4, 114.2, 114.0, 63.1, 55.4, 55.4, 49.1, 43.8, 43.5. HRMS-ESI exact mass calcd. for $\text{C}_{24}\text{H}_{26}\text{NO}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 360.19581, found m/z 360.19580.

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 90 : 10, flowing rate = 0.5 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 38.8$ min (major), $t_{\text{R}2} = 66.6$ min (minor).



(2*S*,4*S*)-2,4-bis(4-chlorophenyl)-2,3,4,5-tetrahydro-1*H*-benzo[*b*]

azepine (13d): (New compound); white solid, m.p. 203-204 °C, 95%

yield, dr = 20:1, 96% ee; $[\alpha]_D^{20} = +27.6$ ($c = 0.25$, CHCl_3); ^1H

NMR (400 MHz, CDCl_3): δ (ppm) 7.38-7.36 (m, 2H), 7.32-7.30

(m, 2H), 7.27-7.25 (m, 2H), 7.23-7.21 (m, 2H), 7.18-7.08 (m, 2H),

6.92 (t, $J = 7.0$ Hz, 1H), 6.78 (s, 1H), 3.90 (d, $J = 11.6$ Hz, 1H), 3.23 (t, $J = 11.6$ Hz,

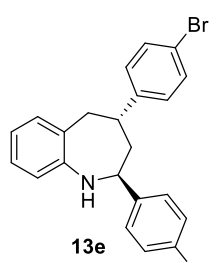
1H), 2.88 (d, $J = 14.0$ Hz, 1H), 2.76 (t, $J = 11.6$ Hz, 1H), 2.16-2.13 (m, 1H), 2.02 (d, J

= 12.8 Hz, 1H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 149.0, 146.2, 143.9, 133.5,

132.5, 132.0, 131.2, 129.0, 128.8, 128.1, 127.9, 127.5, 122.1, 120.5, 62.9, 48.8, 44.0,

43.0. HRMS-ESI exact mass calcd. for $\text{C}_{22}\text{H}_{20}\text{NCl}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 368.09673, found m/z 368.09700.

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{R1} = 6.9$ min (major), $t_{R2} = 9.6$ min (minor).



(2*S*,4*S*)-2,4-bis(4-bromophenyl)-2,3,4,5-tetrahydro-1*H*-benzo[*b*]

azepine (13e): (New compound); white solid, m.p. 204-205 °C, 92%

yield, dr = 5:1, 90% ee; $[\alpha]_D^{20} = +25.6$ ($c = 0.25$, CHCl_3); ^1H NMR

(500 MHz, CDCl_3): δ (ppm) 7.46-7.45 (m, 2H), 7.35-7.26 (m, 8H),

7.21-7.11 (m, 3H), 6.92 (s, 1H), 6.79 (s, 1H), 3.96 (d, $J = 10.0$ Hz,

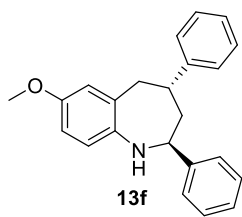
1H), 3.80 (s, 1H), 3.30 (s, 1H), 2.95 (d, $J = 13.5$ Hz, 1H), 2.84-2.79 (m, 1H), 2.23 (s,

1H), 2.12 (d, $J = 13.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 149.0, 146.7,

144.4, 132.1, 131.8, 131.2, 129.1, 128.6, 128.3, 127.5, 122.1, 121.7, 120.6, 120.1,

63.0, 48.7, 44.0, 42.9. HRMS-ESI exact mass calcd. for $\text{C}_{22}\text{H}_{19}\text{NBr}_2^+$ ($[\text{M}+\text{H}]^+$) requires m/z 455.99570, found m/z 455.99600.

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 90 : 10, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{R1} = 7.4$ min (major), $t_{R2} = 10.0$ min (minor).



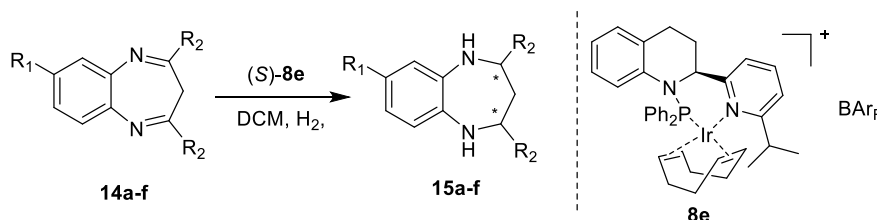
**(2*S*,4*S*)-7-methoxy-2,4-diphenyl-2,3,4,5-tetrahydro-1*H*-benzo-
[b]azepi-ne (13f):** (New compound); yellow solid, m.p. 119-120

°C, 60% yield, dr = 11:1, 83% ee; $[\alpha]_D^{20} = +17.6$ ($c = 0.25$, CHCl_3); ^1H NMR (500 MHz, CDCl_3): δ (ppm) 7.44-7.42 (m, 2H),

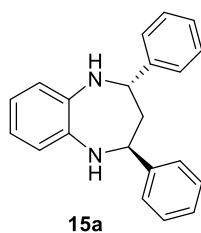
7.39-7.25 (m, 7H), 7.20-7.17 (m, 1H), 6.73-6.70 (m, 2H), 6.65-6.63 (m, 1H), 3.87 (d, $J = 11.0$ Hz, 1H), 3.74 (s, 3H), 3.33 (t, $J = 12.0$ Hz, 1H), 2.86 (d, $J = 13.5$ Hz, 1H), 2.79 (t, $J = 10.5$ Hz, 1H), 2.24-2.17 (m, 1H), 2.09 (d, $J = 13.0$ Hz, 1H); ^{13}C NMR (125 MHz, CDCl_3): δ (ppm) 154.8, 148.0, 145.7, 142.8, 134.6, 128.9, 128.7, 127.7, 126.8, 126.5, 126.3, 121.3, 116.5, 112.0, 64.1, 55.6, 49.3, 44.7, 43.0. HRMS-ESI exact mass calcd. for $\text{C}_{23}\text{H}_{24}\text{NO}^+$ ($[\text{M}+\text{H}]^+$) requires m/z 330.18524, found m/z 330.18550.

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 90 : 10, flowing rate = 0.5 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 25.0$ min (major), $t_{\text{R}2} = 28.2$ min (minor).

(2) Asymmetric hydrogenation of 2,4-diaryl-3*H*-benzodiazepines



A 30 mL glass-lined stainless-steel reactor equipped with a magnetic stirrer bar was charged with Ir-catalyst (*S*)-**8e** (13.6 mg, 4.0 mol %) and substrate **14** (0.2 mmol) in DCM (2 mL) under nitrogen atmosphere in a glove box. The autoclave was closed, and the final pressure of the hydrogen gas was adjusted to 50 atm after purging the autoclave with hydrogen gas several times. The reaction mixture was stirred at 25 °C for 12 h. Then the hydrogen gas was carefully released and the conversion was determined by ^1H NMR. The reaction mixture was filtered through a short pad of silica (petroleum/DCM, 2/1, v/v) to give the pure products. The enantiomeric excess of the product was determined by HPLC with a chiral column. The analytical data of the product are summarized below.

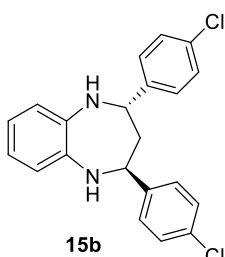


(2*S*,4*S*)-2,4-diphenyl-2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepine

(15a): (Known compound, see: Z.-Y. Ding, F. Chen, J. Qin, Y.-M. He and Q.-H. Fan, *Angew. Chem., Int. Ed.* 2012, **51**, 5706); yellow solid, m.p. 137-141 °C, 95% yield, dr = 16:1, 99% ee; $[\alpha]_{\text{D}}^{20} = -127.6$ ($c = 0.25$, CHCl_3), [Lit.⁸ $[\alpha]_{\text{D}}^{20} = -136.5$ ($c = 1.0$, CHCl_3), 99%

ee for (*S,S*) enantiomer]; ¹H NMR (500 MHz, CDCl_3): δ (ppm) 7.42 (d, $J = 7.0$ Hz, 4H), 7.33 (t, $J = 7.5$ Hz, 4H), 7.28-7.25 (m, 2H), 6.68-6.65 (m, 2H), 6.55-6.52 (m, 2H), 5.06 (t, $J = 7.3$ Hz, 2H), 3.44 (s, 2H), 2.29 (t, $J = 7.5$ Hz, 2H); ¹³C NMR (125 MHz, CDCl_3): δ (ppm) 144.1, 138.2, 128.9, 127.7, 126.9, 120.7, 118.8, 59.1, 45.6.

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 75 : 25, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 6.5$ min (major), $t_{\text{R}2} = 15.2$ min (minor).

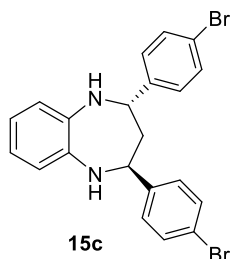


(2*S*,4*S*)-2,4-bis(4-chlorophenyl)-2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepine (15b): (Known compound, see: Z.-Y. Ding, F. Chen, J.

Qin, Y.-M. He and Q.-H. Fan, *Angew. Chem., Int. Ed.* 2012, **51**, 5706); yellow solid, m.p. 172-176 °C, 92% yield, dr = 10:1, 97% ee; $[\alpha]_{\text{D}}^{20} = -105.0$ ($c = 0.25$, CHCl_3), [Lit.⁸ $[\alpha]_{\text{D}}^{20} = -109.8$ ($c =$

1.0, CHCl_3), >99% ee for (*S,S*) enantiomer]; ¹H NMR (400 MHz, CDCl_3): δ (ppm) 7.36-7.29 (m, 8H), 6.71-6.68 (m, 2H), 6.59-6.56 (m, 2H), 4.96 (t, $J = 7.2$ Hz, 2H), 3.40 (s, 2H), 2.22 (t, $J = 7.4$ Hz, 2H); ¹³C NMR (100 MHz, CDCl_3): δ (ppm) 142.5, 137.8, 133.4, 129.0, 128.3, 121.1, 119.1, 58.1, 45.2.

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 75 : 25, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 8.6$ min (major), $t_{\text{R}2} = 28.3$ min (minor).

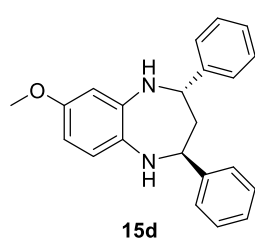


(2*S*,4*S*)-2,4-bis(4-bromophenyl)-2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepine (15c): (Known compound, see: Z.-Y. Ding, F. Chen,

J. Qin, Y.-M. He and Q.-H. Fan, *Angew. Chem., Int. Ed.* 2012, **51**,

5706); yellow solid, m.p. 140-143 °C, 95% yield, dr > 20:1, 99% ee; $[\alpha]_{\text{D}}^{20} = -115.2$ ($c = 0.25$, CHCl_3), [Lit.⁸ $[\alpha]_{\text{D}}^{20} = -106.2$ ($c = 1.0$, CHCl_3), 99% ee for (*S,S*) enantiomer]; ¹H NMR (400 MHz, CDCl_3): δ (ppm) 7.46 (d, $J = 8.4$ Hz, 4H), 7.29 (d, $J = 8.4$ Hz, 4H), 6.72-6.70 (m, 2H), 6.58-6.56 (m, 2H), 4.94 (t, $J = 7.2$ Hz, 2H), 3.41 (s, 2H), 2.22 (t, $J = 7.2$ Hz, 2H); ¹³C NMR (100 MHz, CDCl_3): δ (ppm) 143.0, 137.8, 132.2, 128.7, 121.5, 121.1, 119.2, 58.2, 45.1.

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 60 : 40, flowing rate = 0.9 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 9.8$ min (major), $t_{\text{R}2} = 35.2$ min (minor).



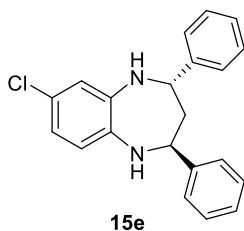
(2*S*,4*S*)-7-methoxy-2,4-diphenyl-2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepine (15d): (Known compound, see: Z.-Y. Ding, F.

Chen, J. Qin, Y.-M. He and Q.-H. Fan, *Angew. Chem., Int. Ed.* 2012, **51**, 5706); yellow solid, m.p. 102-104 °C, 90% yield, dr >

20:1, 99% ee; $[\alpha]_{\text{D}}^{20} = -63.1$ ($c = 0.25$, CHCl_3), [Lit.⁸ $[\alpha]_{\text{D}}^{20} =$

-76.1 ($c = 1.0$, CHCl_3), 97% ee for (*S,S*) enantiomer]; ¹H NMR (400 MHz, CDCl_3): δ (ppm) 7.41 (d, $J = 7.2$ Hz, 4H), 7.33 (t, $J = 7.2$ Hz, 4H), 7.27-7.24 (m, 2H), 6.48 (d, $J = 8.4$ Hz, 1H), 6.26-6.24 (m, 1H), 6.15 (d, $J = 2.0$ Hz, 1H), 5.06 (dd, $J_1 = 10.0$ Hz, $J_2 = 4.4$ Hz, 1H), 4.88 (dd, $J_1 = 9.2$ Hz, $J_2 = 4.8$ Hz, 1H), 3.67 (s, 3H), 3.35 (s, 2H), 2.36-2.22 (m, 2H); ¹³C NMR (100 MHz, CDCl_3): δ (ppm) 154.6, 144.4, 144.2, 139.5, 131.7, 128.9, 128.9, 127.7, 127.6, 126.9, 126.9, 119.9, 105.3, 104.7, 59.5, 58.5, 55.6, 45.6.

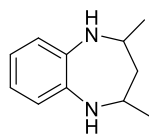
The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 60 : 40, flowing rate = 0.9 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 8.5$ min (major), $t_{\text{R}2} = 24.8$ min (minor).



(2*S*,4*S*)-7-chloro-2,4-diphenyl-2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepine (15e): (Known compound, see: Z.-Y. Ding, F. Chen, J. Qin, Y.-M. He and Q.-H. Fan, *Angew. Chem., Int. Ed.* 2012, **51**,

5706); yellow solid, m.p. 118-120 °C, 93% yield, dr > 20:1, 99% ee; $[\alpha]_{\text{D}}^{20} = -75.2$ ($c = 0.25$, CHCl_3), [Lit.⁸ $[\alpha]_{\text{D}}^{20} = -79.8$ ($c = 1.0$, CHCl_3), 99% ee for (*S,S*) enantiomer]; ^1H NMR (400 MHz, CDCl_3): δ (ppm) 7.39-7.26 (m, 11H), 6.59 (d, $J = 8.0$ Hz, 1H), 6.48 (d, $J = 1.6$ Hz, 1H), 6.41 (d, $J = 8.4$ Hz, 1H), 5.04-4.95 (m, 2H), 3.41 (s, 2H), 2.29-2.26 (m, 2H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 143.8, 143.7, 139.4, 136.8, 129.0, 129.0, 127.9, 127.9, 126.9, 125.1, 120.1, 119.7, 118.3, 59.0, 58.8, 45.2.

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 85 : 15, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 7.7$ min (major), $t_{\text{R}2} = 15.9$ min (minor).



2,4-dimethyl-2,3,4,5-tetrahydro-1*H*-1,5-benzodiazepine (15f):

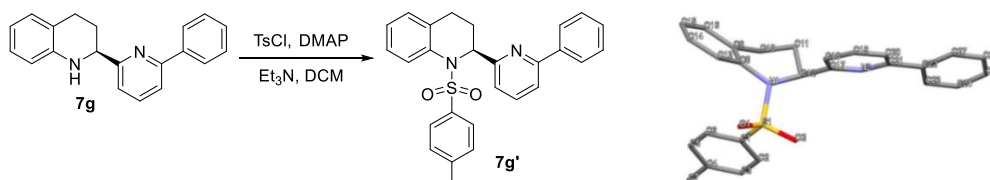
(Known compound, see: Z.-Y. Ding, F. Chen, J. Qin, Y.-M. He and Q.-H. Fan, *Angew. Chem., Int. Ed.* 2012, **51**, 5706); yellow oil, 94% yield, dr =

2:1 (*cis* : *trans*), 10% ee; $[\alpha]_{\text{D}}^{20} = -9.1$ ($c = 0.25$, CHCl_3), [Lit.⁸ $[\alpha]_{\text{D}}^{20} = -32.4$ ($c = 0.25$, CHCl_3), 99% ee for (*R,R*) enantiomer]; ^1H NMR (500 MHz, CDCl_3): δ (ppm) 6.78-6.72 (m, 4H), 6.67-6.65 (m, 1H), 6.57-6.55 (m, 1H), 3.79-3.75 (m, 1H), 3.34 (s, 3H), 2.85-2.79 (m, 2H), 1.71-1.64 (m, 2H), 1.46-1.39 (m, 1H), 1.29 (d, $J = 6.5$ Hz, 6H), 1.17 (d, $J = 6.5$ Hz, 4H); ^{13}C NMR (100 MHz, CDCl_3): δ (ppm) 140.3, 138.5, 121.5, 120.6, 120.5, 119.1, 52.8, 49.0, 48.2, 46.0, 24.1, 22.1.

The enantiomeric excess was determined by HPLC on Chiralcel OD-H column (hexane : isopropanol = 75 : 25, flowing rate = 1.0 mL/min, 25 °C, UV detection at $\lambda = 254$ nm), $t_{\text{R}1} = 6.9$ min (minor), $t_{\text{R}2} = 10.7$ min (major).

10. Determination of absolute configuration

The absolute configuration of **7g** was determined to be (*S*) based on single crystal X-ray analysis (*Scheme S1*). The configuration of the other chiral products are assigned by analogy.



Scheme S1: Single crystal structure of **7g'**

The absolute configuration of **8f-g** and **8m** were determined to be (*S*) based on single crystal X-ray analysis (*Figure S1*). The configuration of the other chiral products (**8d**, **8e**) are assigned by analogy.

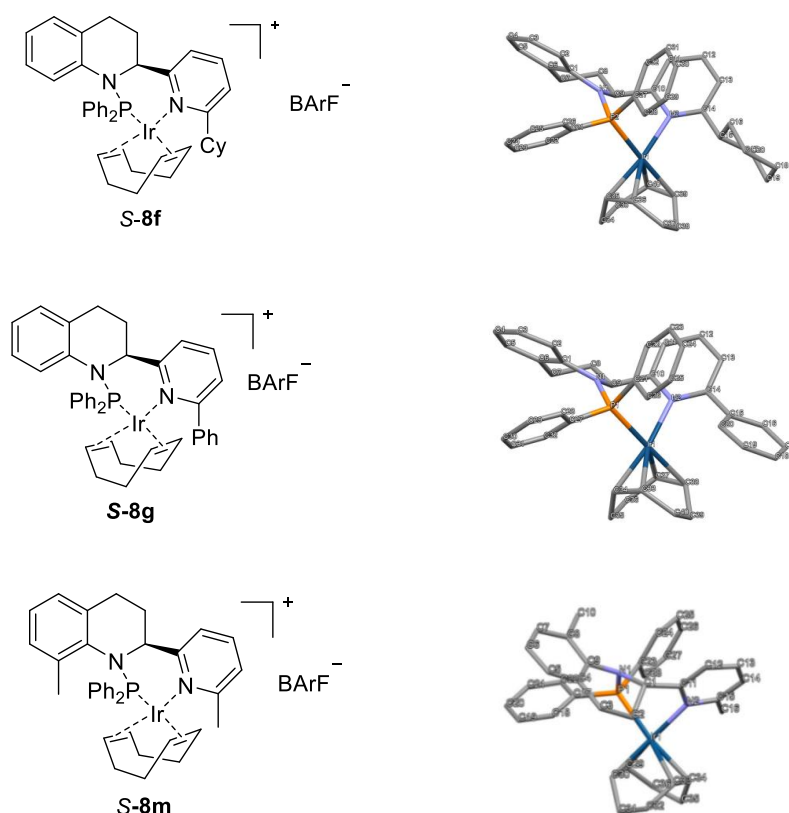


Figure S1. Single crystal structure of **8f-g** and **8m**

The absolute configuration of **12c** was determined to be (2*S*) based on single crystal X-ray analysis (*Figure S2*). The configuration of the other chiral products (**12a**, **12b**, **12d**, **12e**, **12f**) are assigned by analogy.

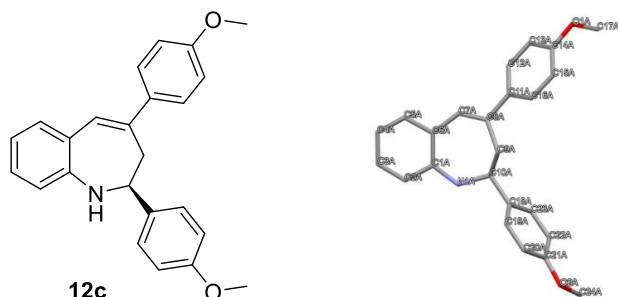
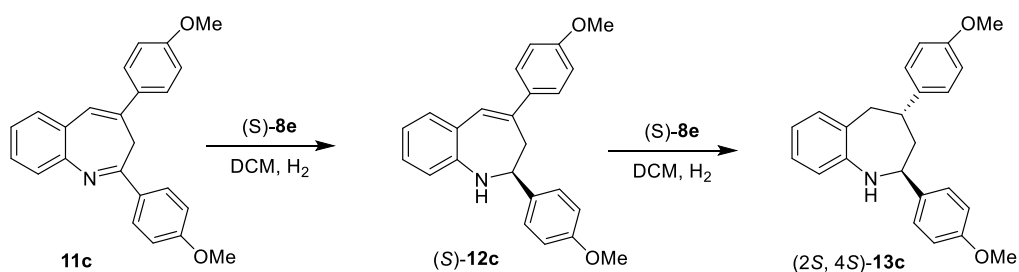
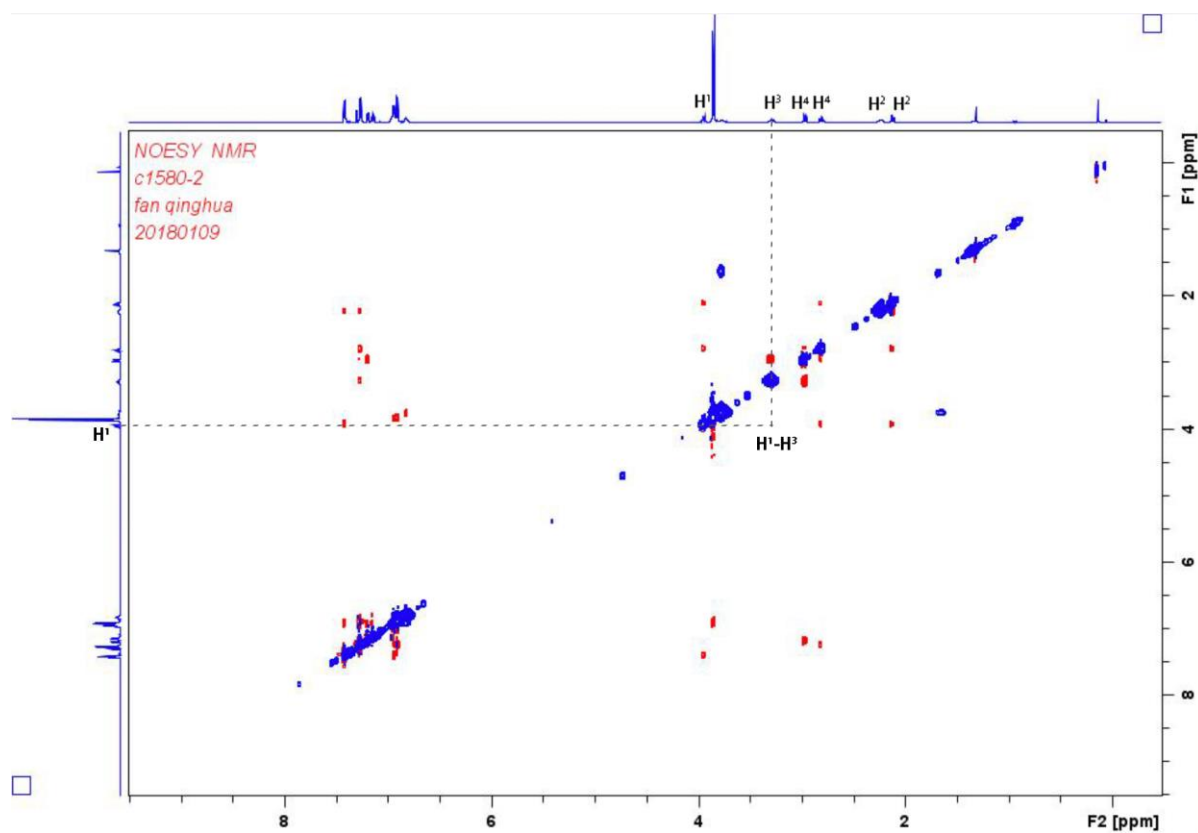
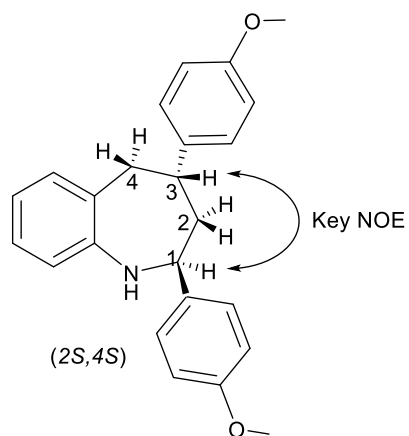


Figure S2. Single crystal structure of **12c**

The absolute configuration of **13c** was determined to be (2*S*,4*S*) based on the absolute configuration of **12c** in combination with 2D-NOESY spectrum (*Scheme S2*). The configuration of the other chiral products (**13a**, **13b**, **13d**, **13e**, **13f**) are assigned by analogy.



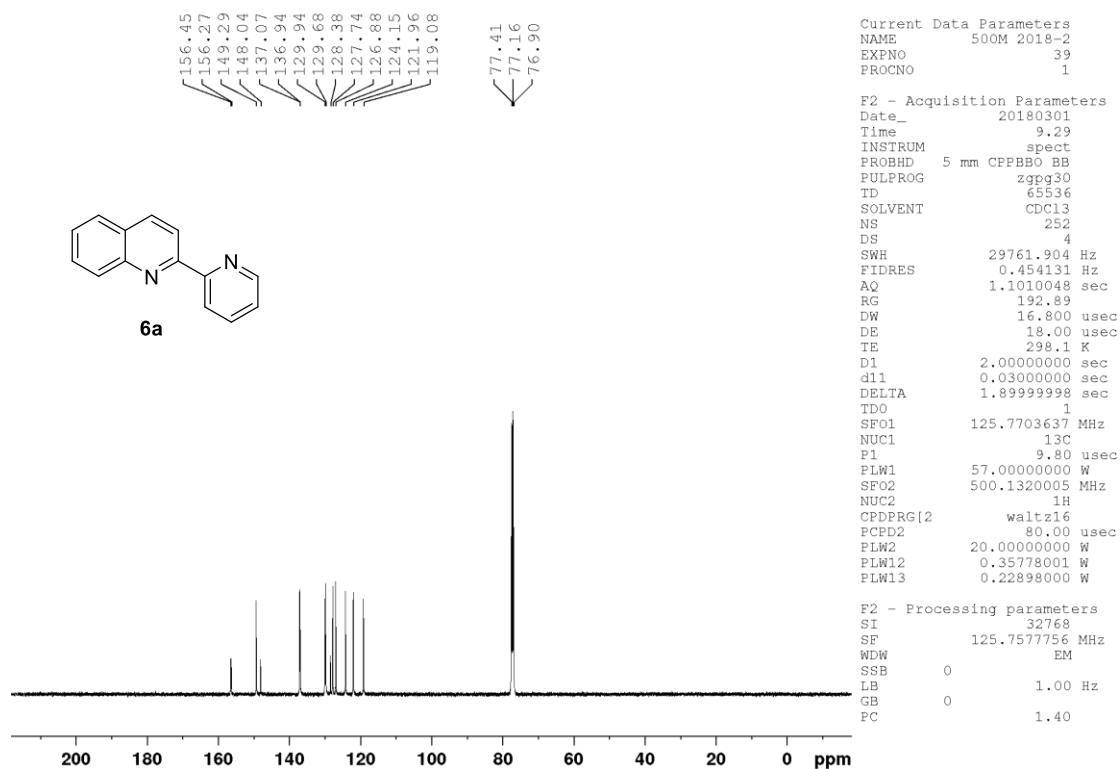
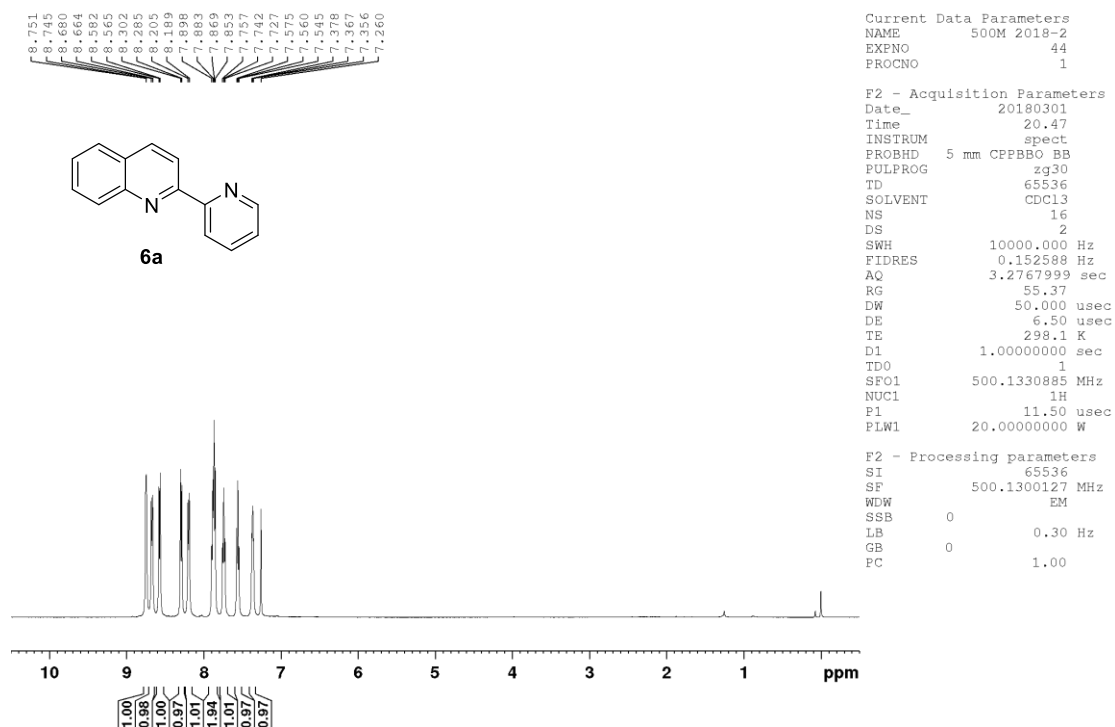


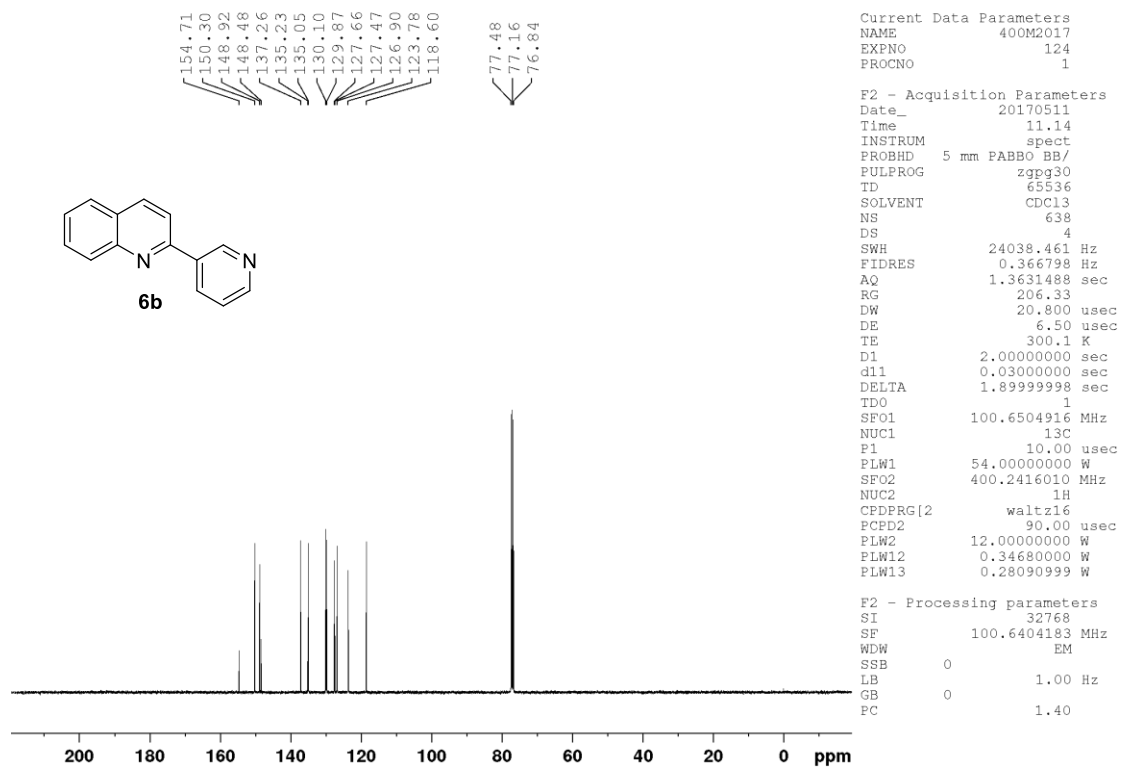
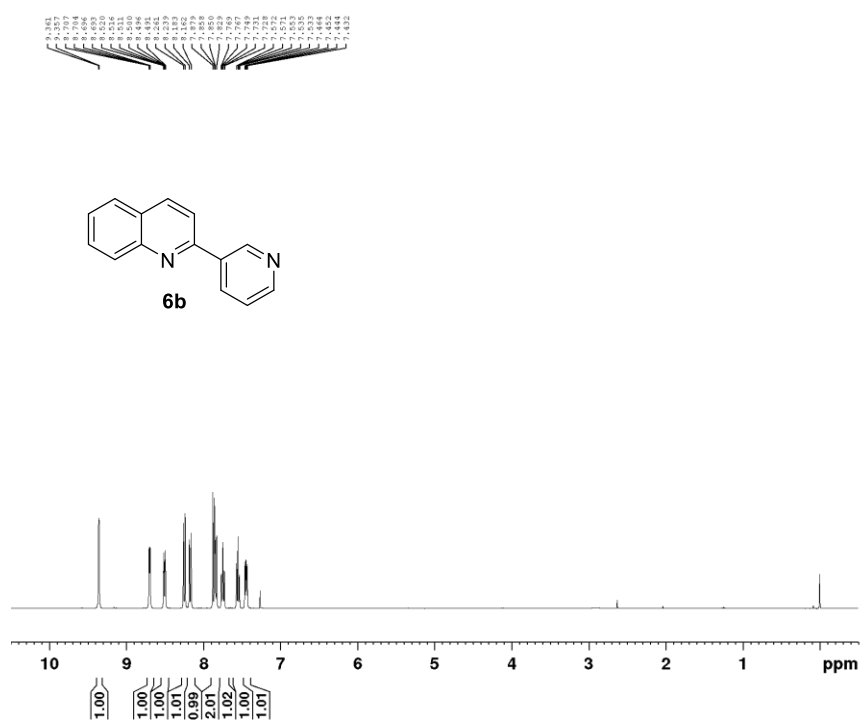
Scheme S2. The 2D-NOESY Spectrum of **13c**

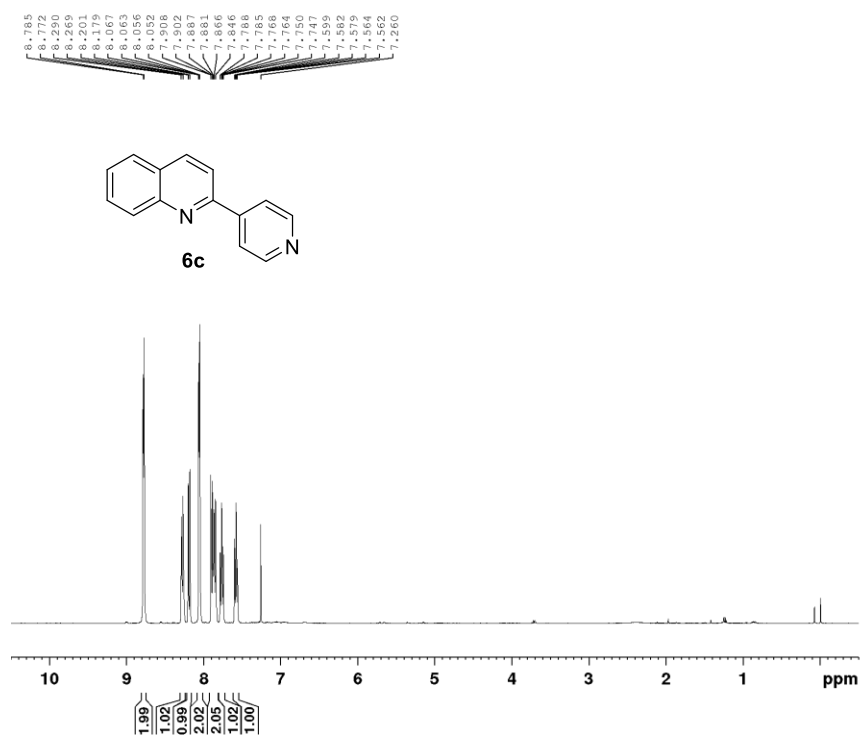
11. References

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12. Copy of NMR spectra



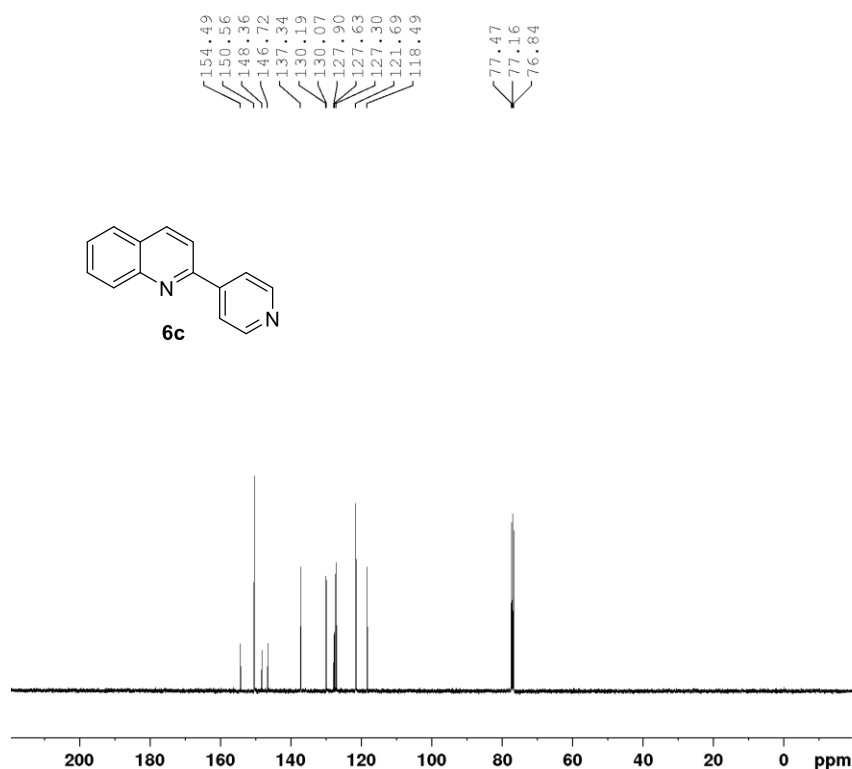




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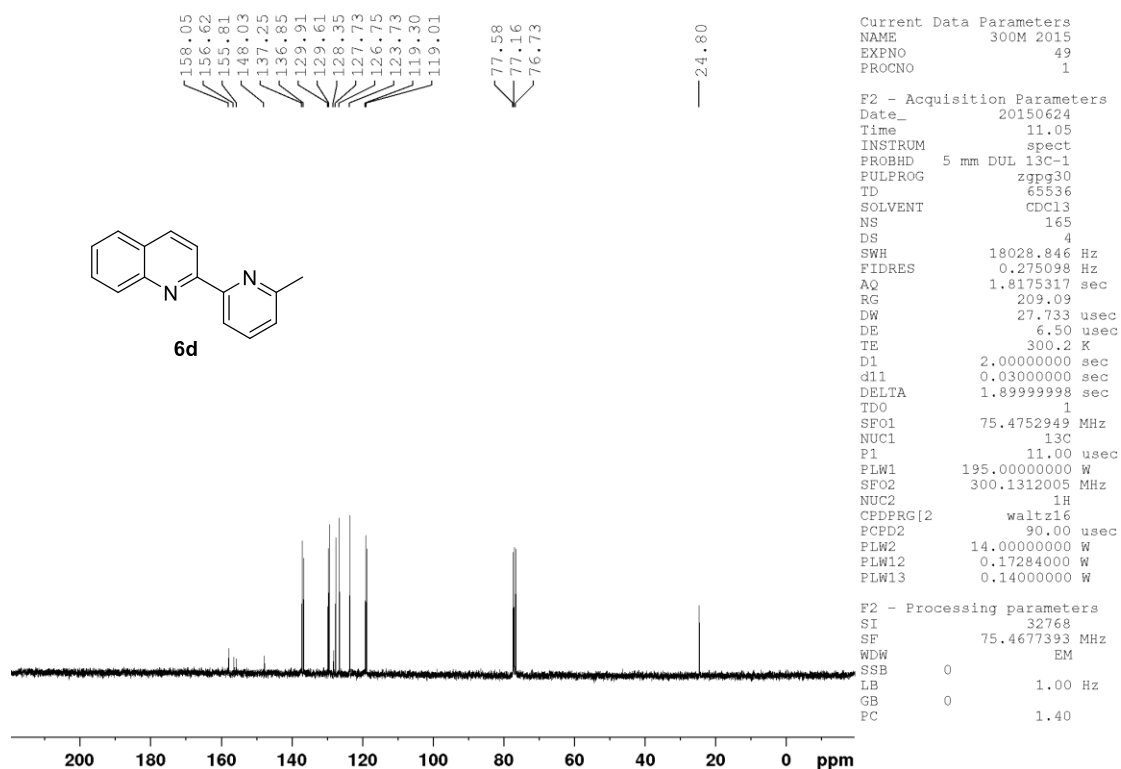
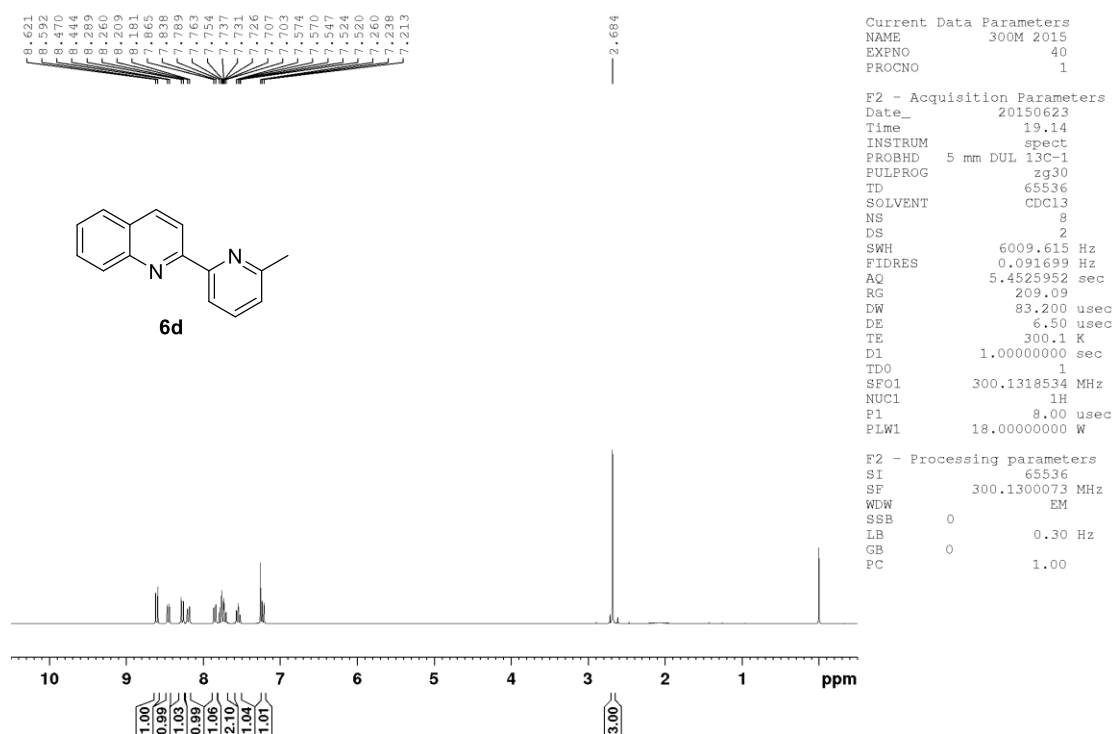
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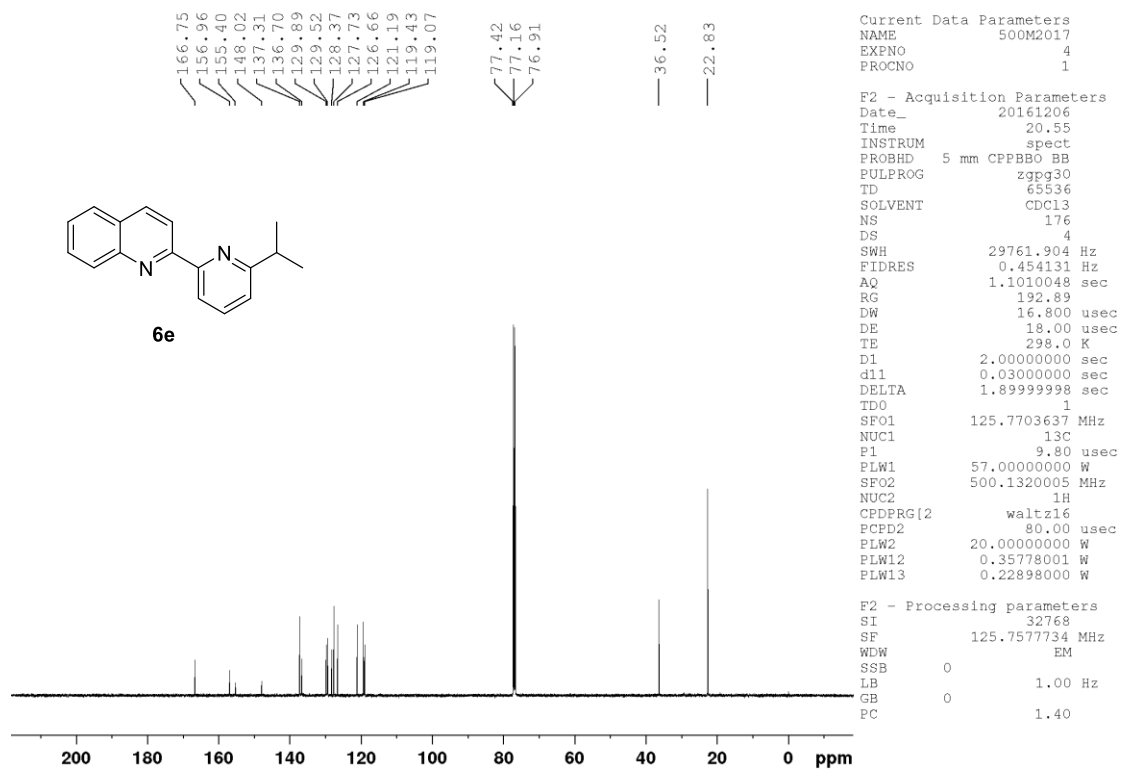
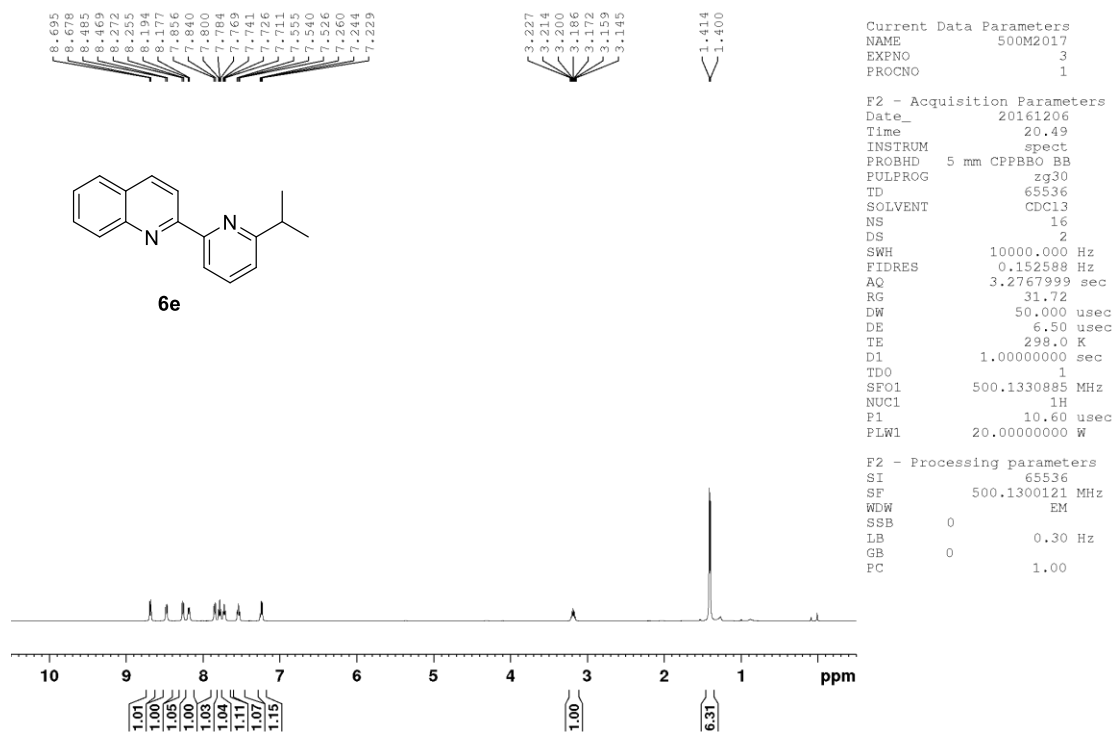


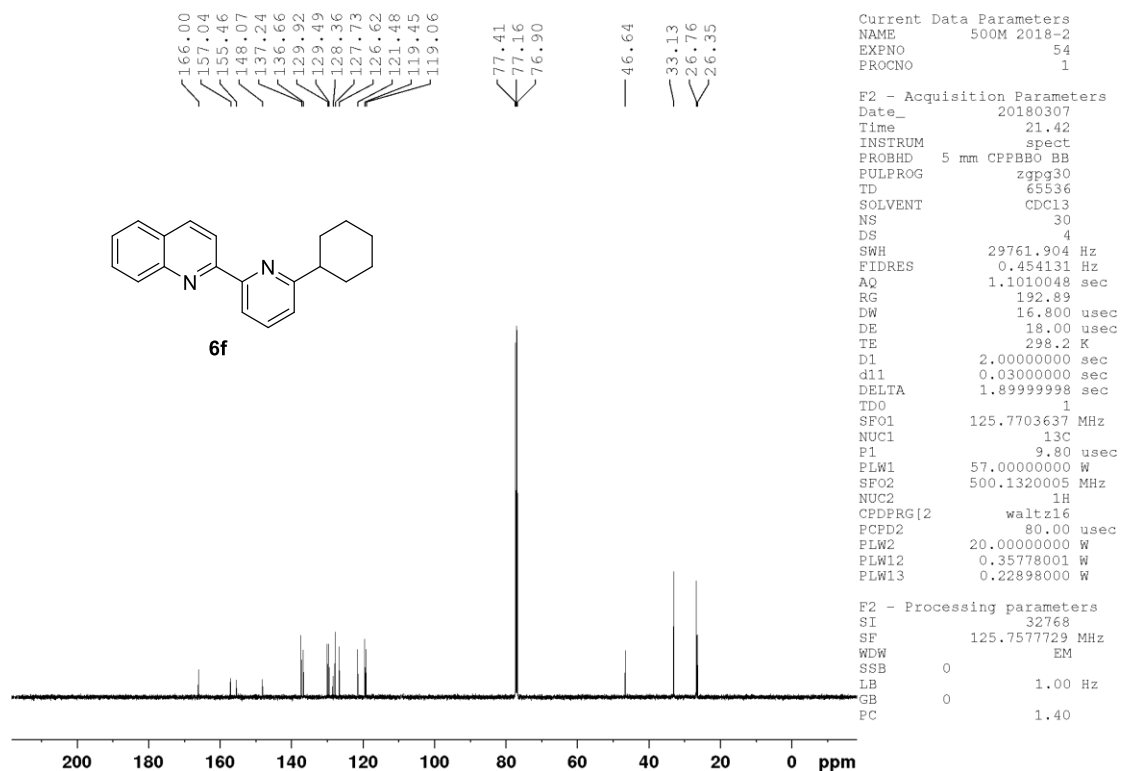
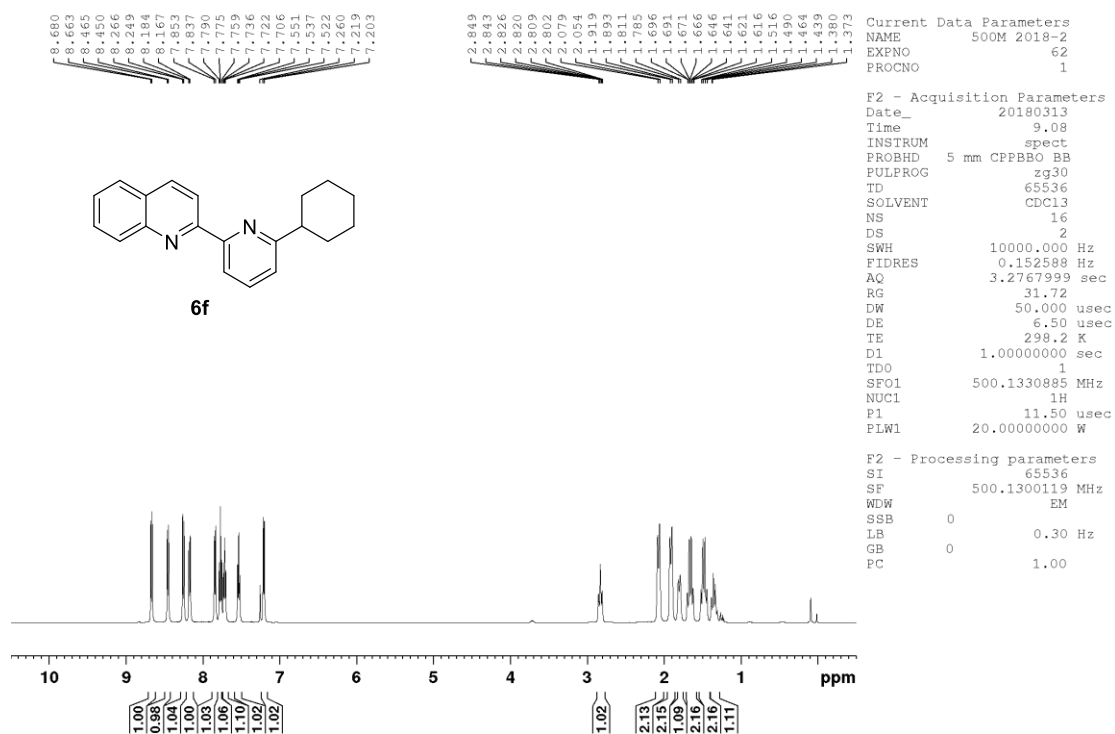
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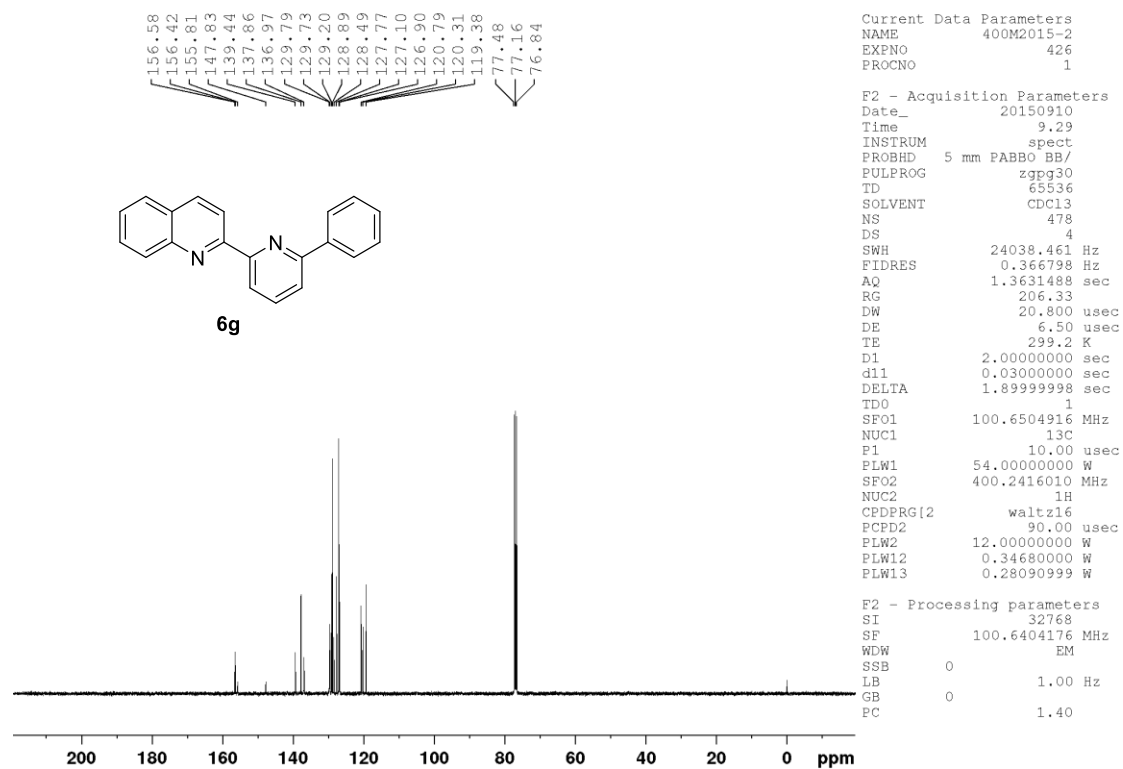
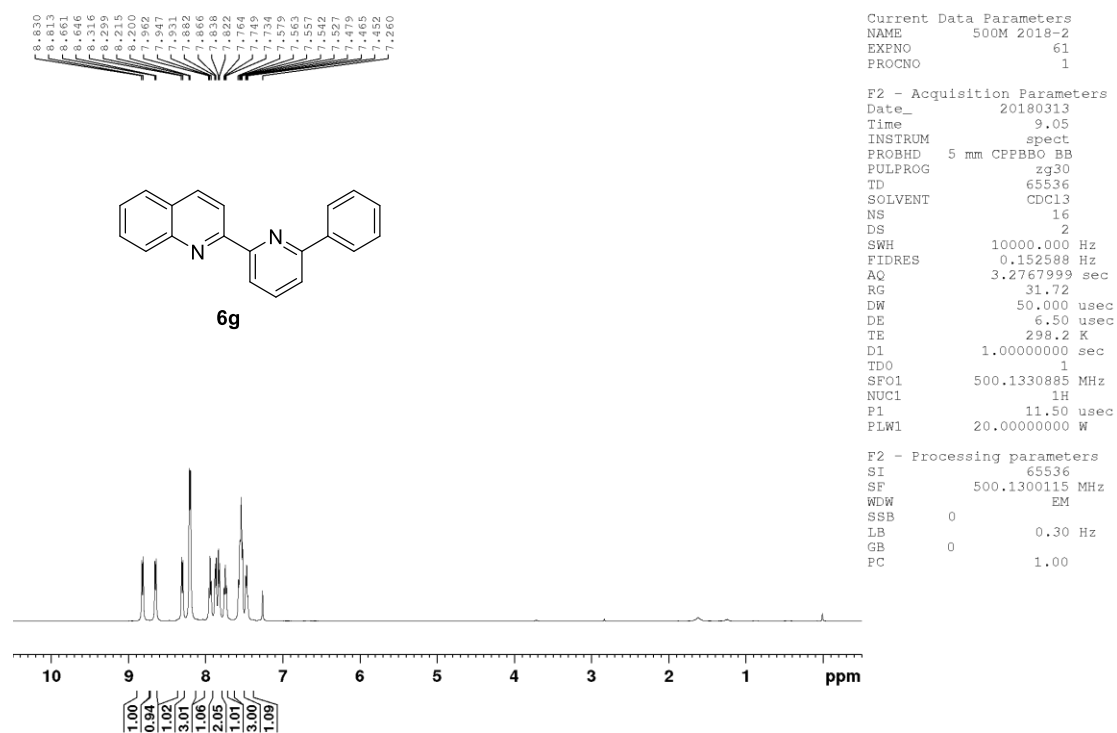
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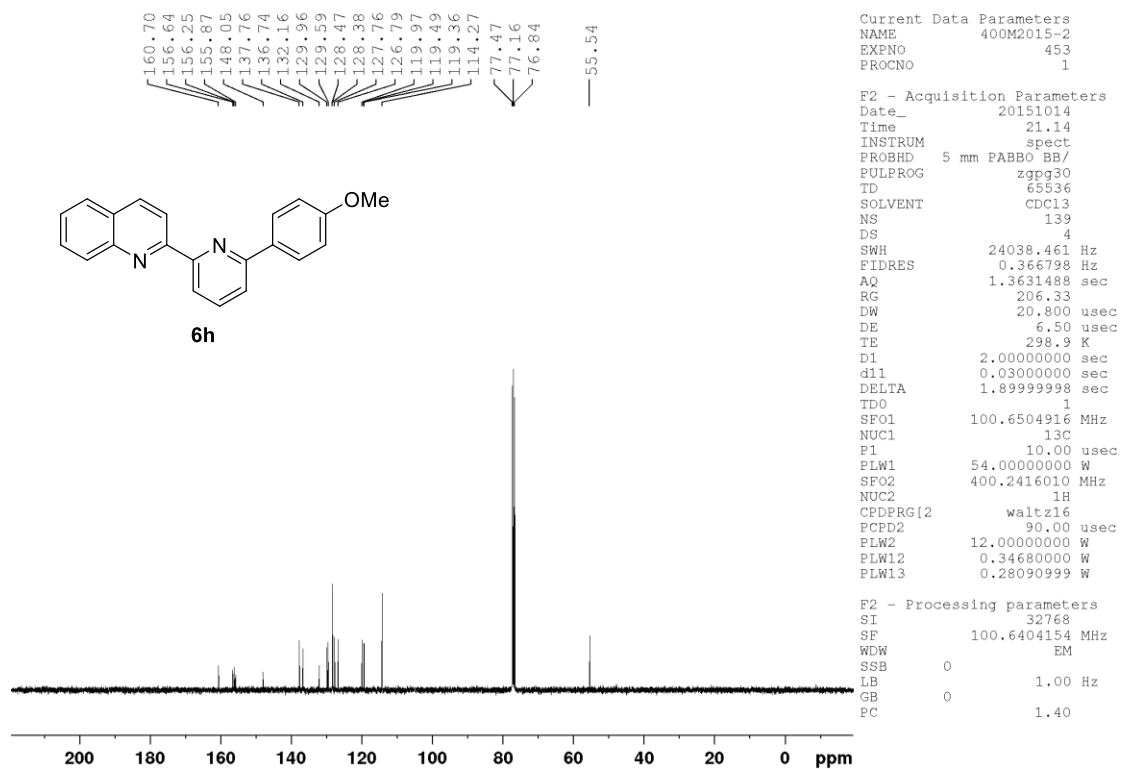
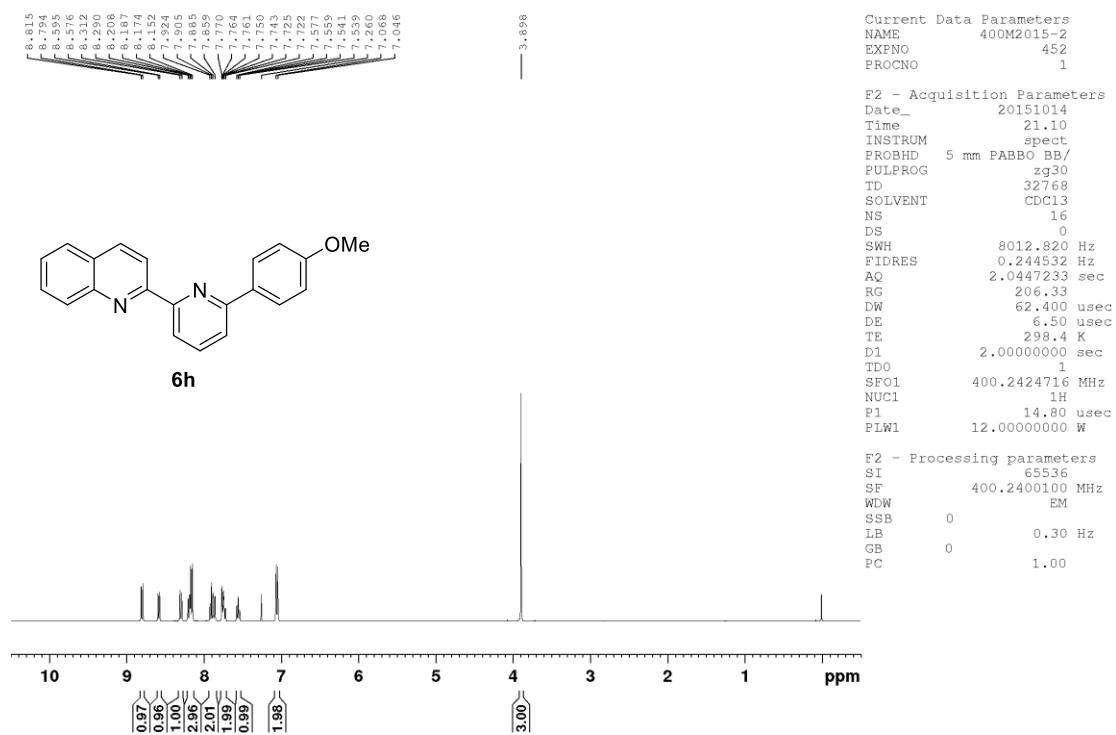
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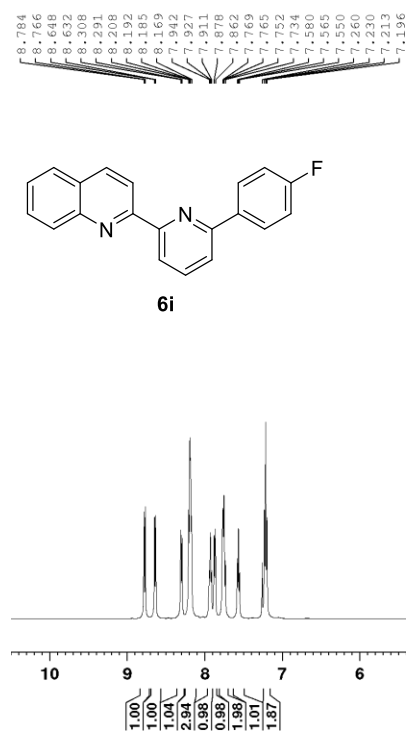












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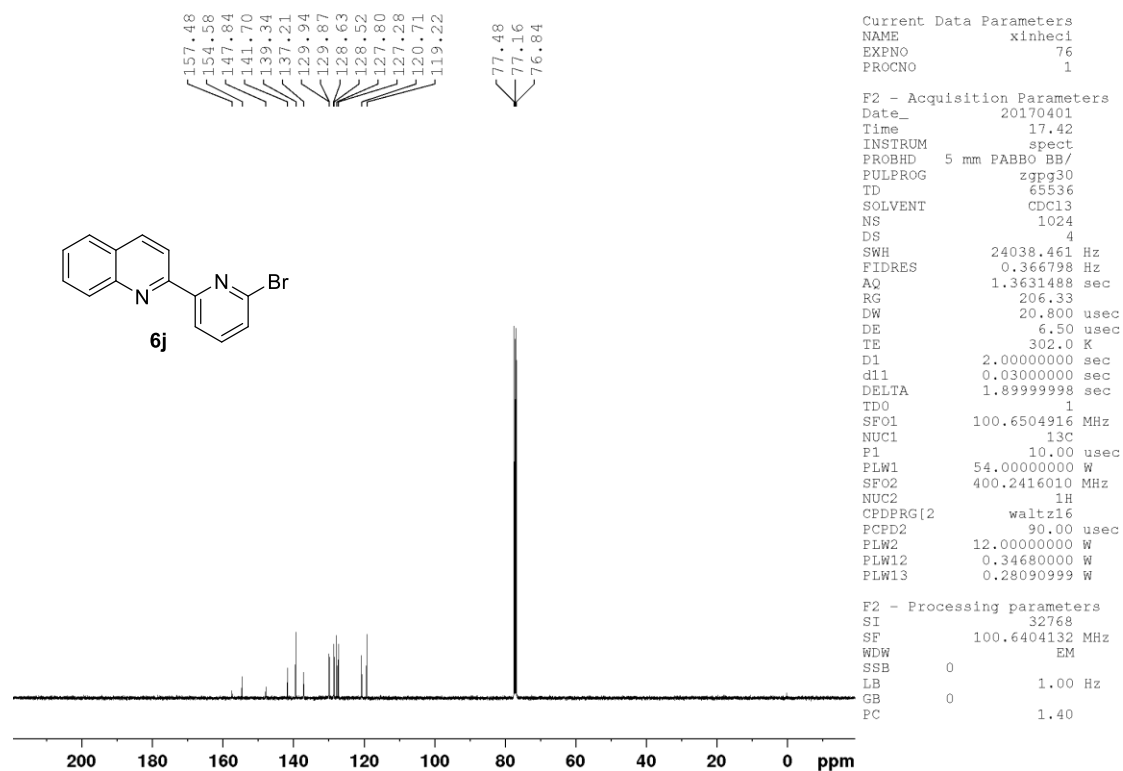
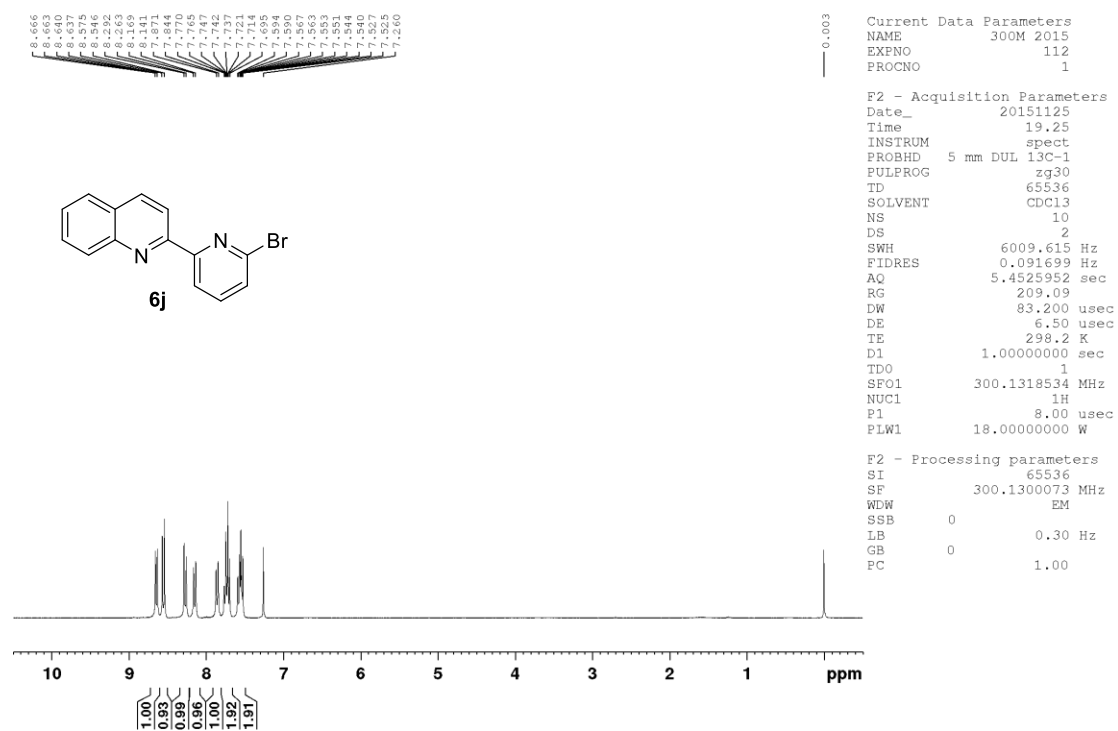
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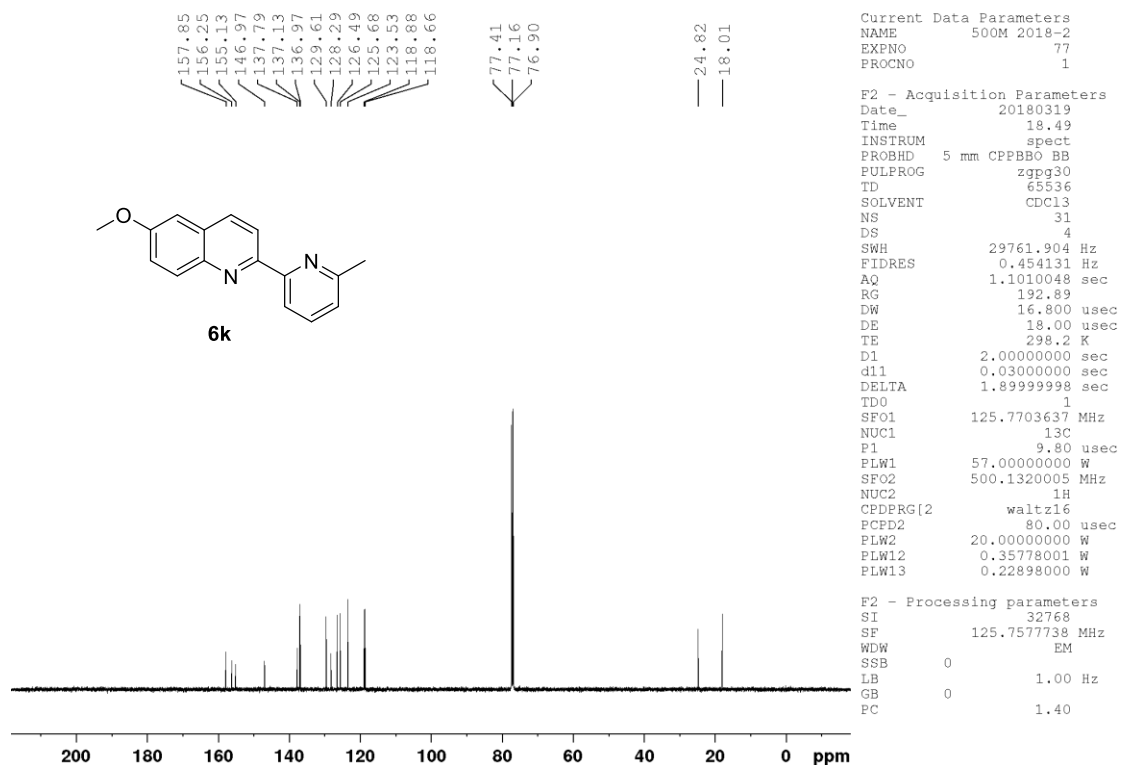
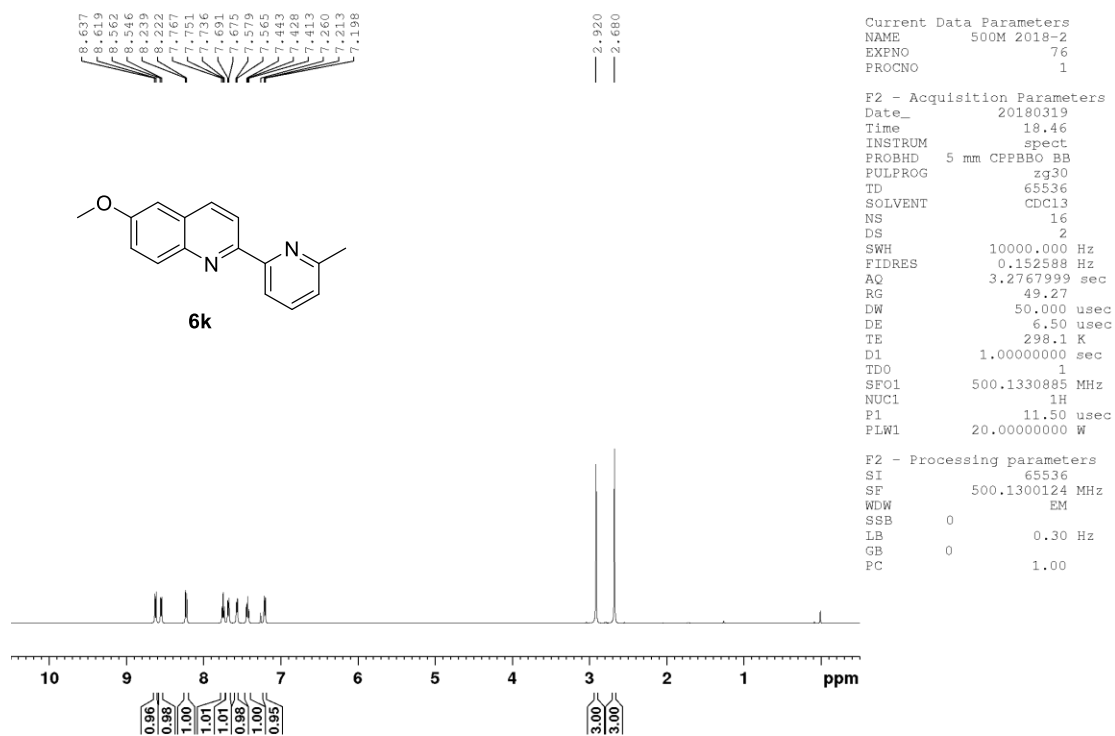


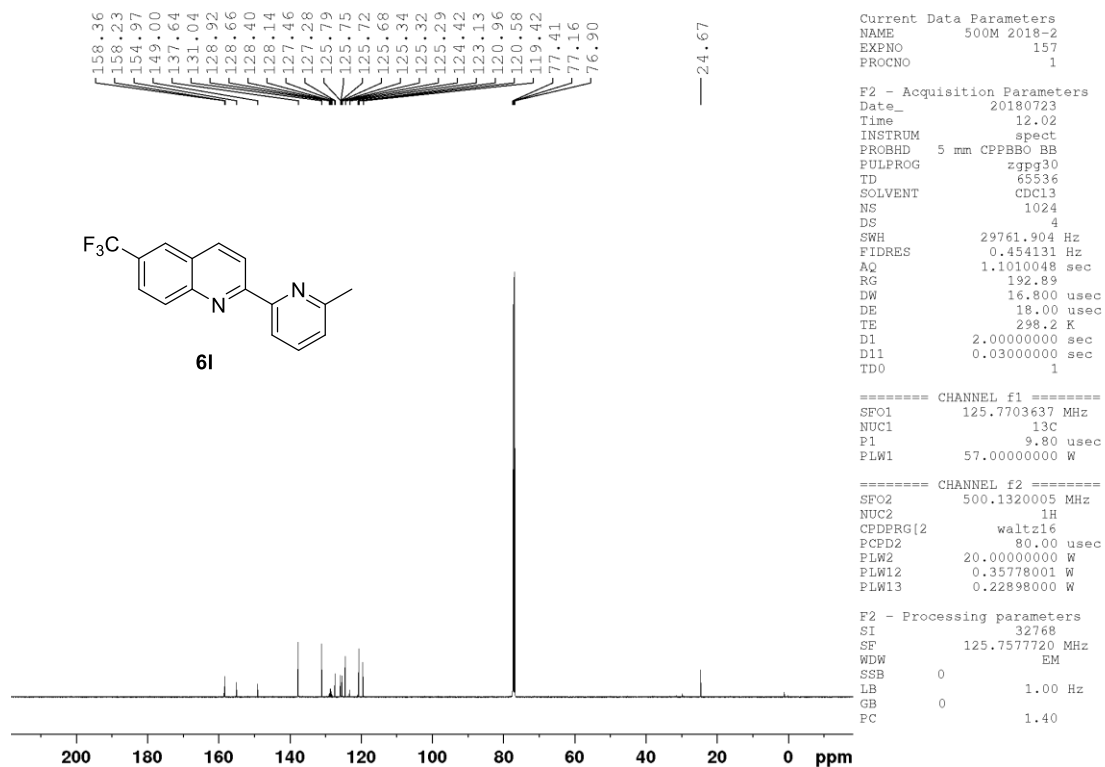
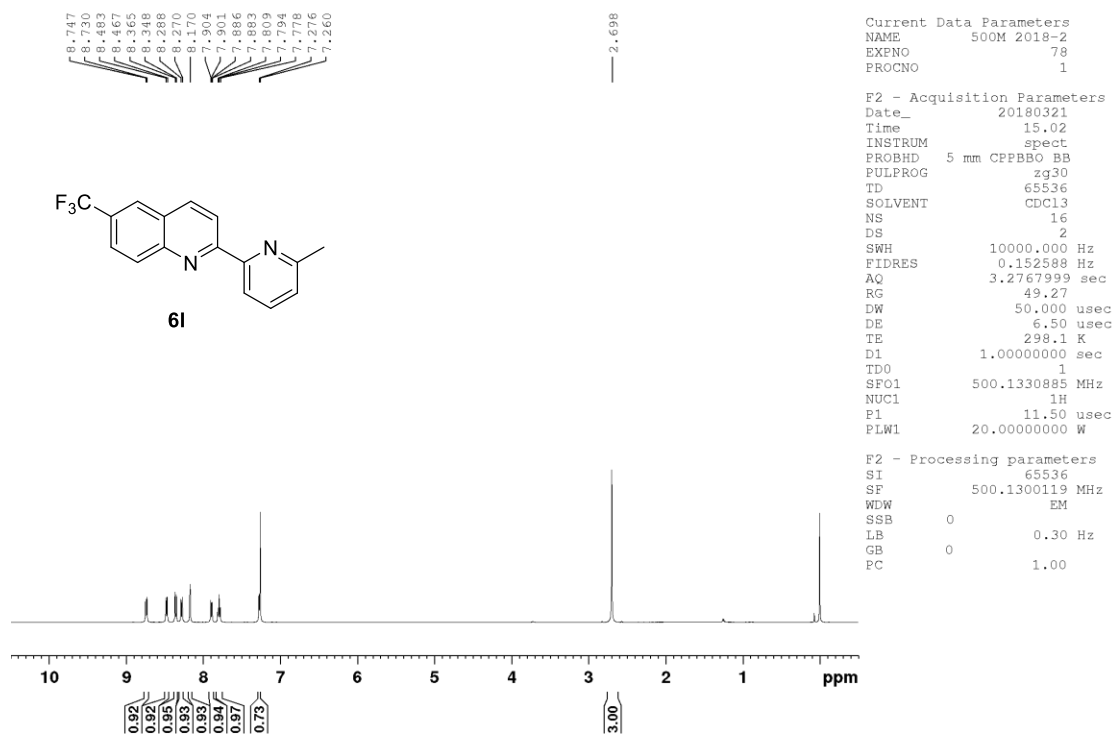
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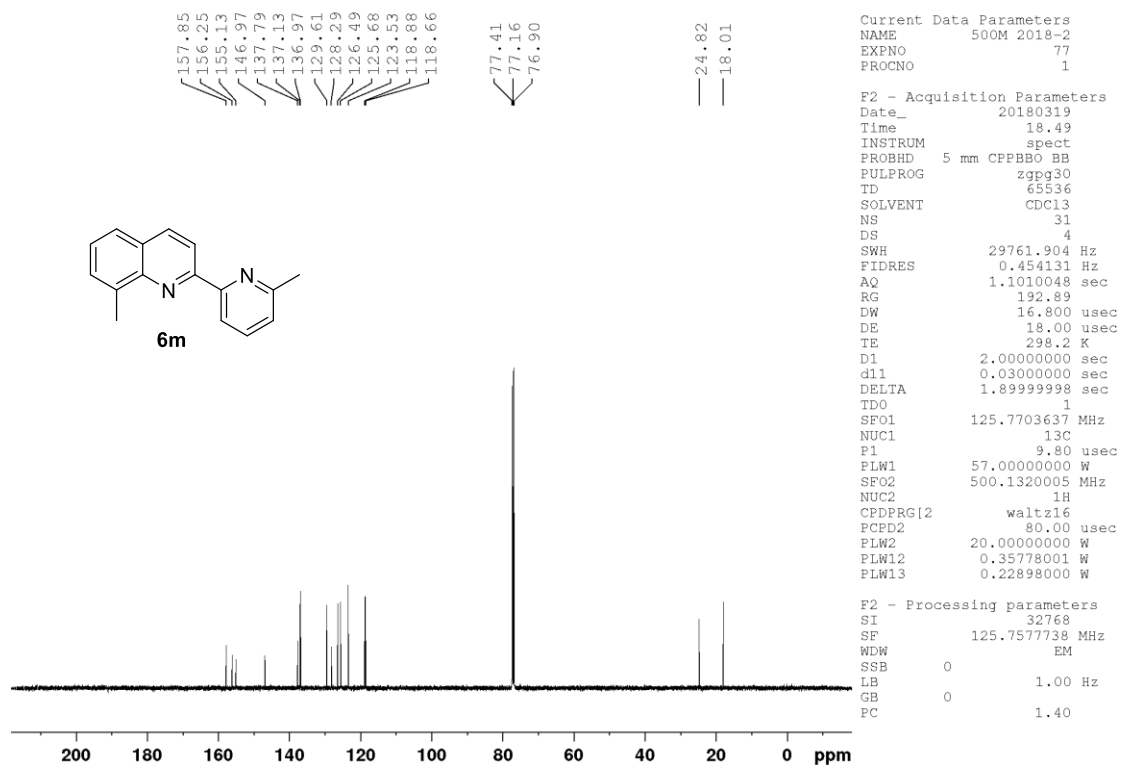
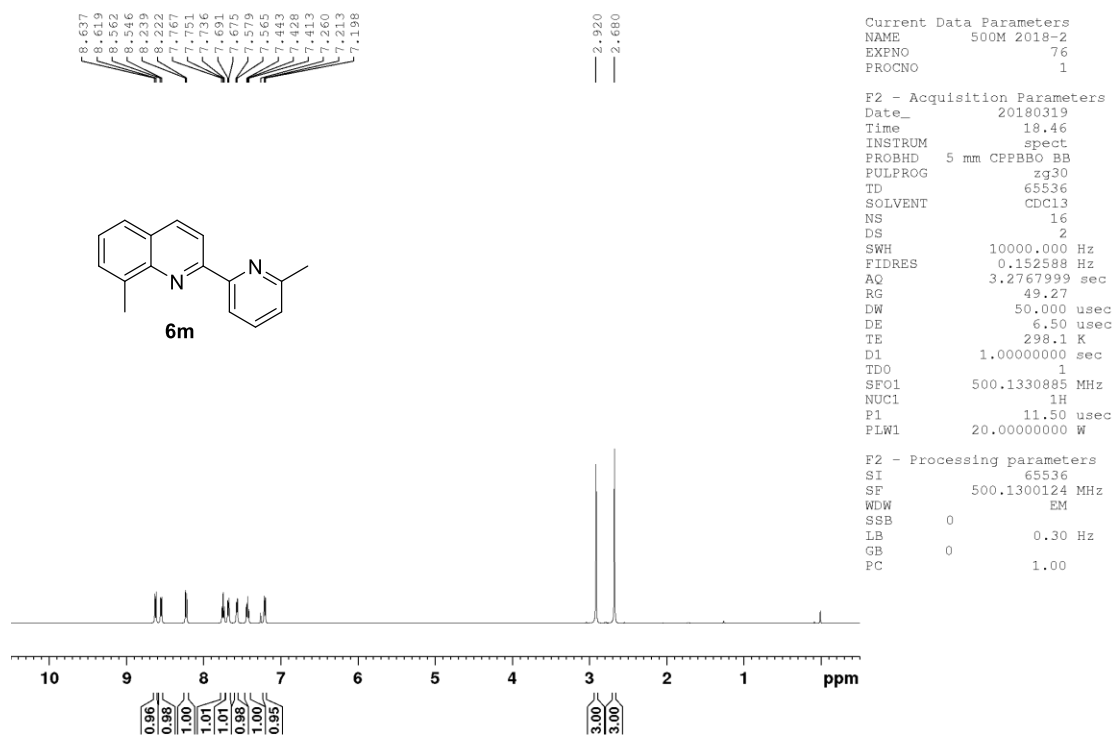
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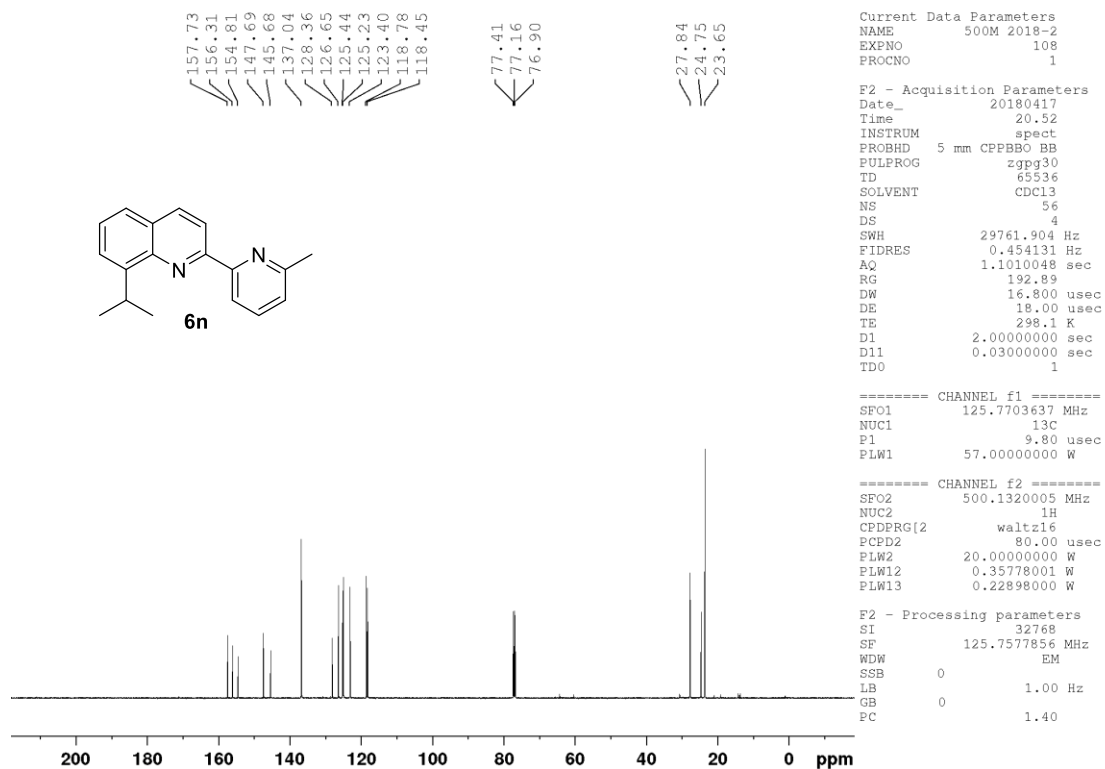
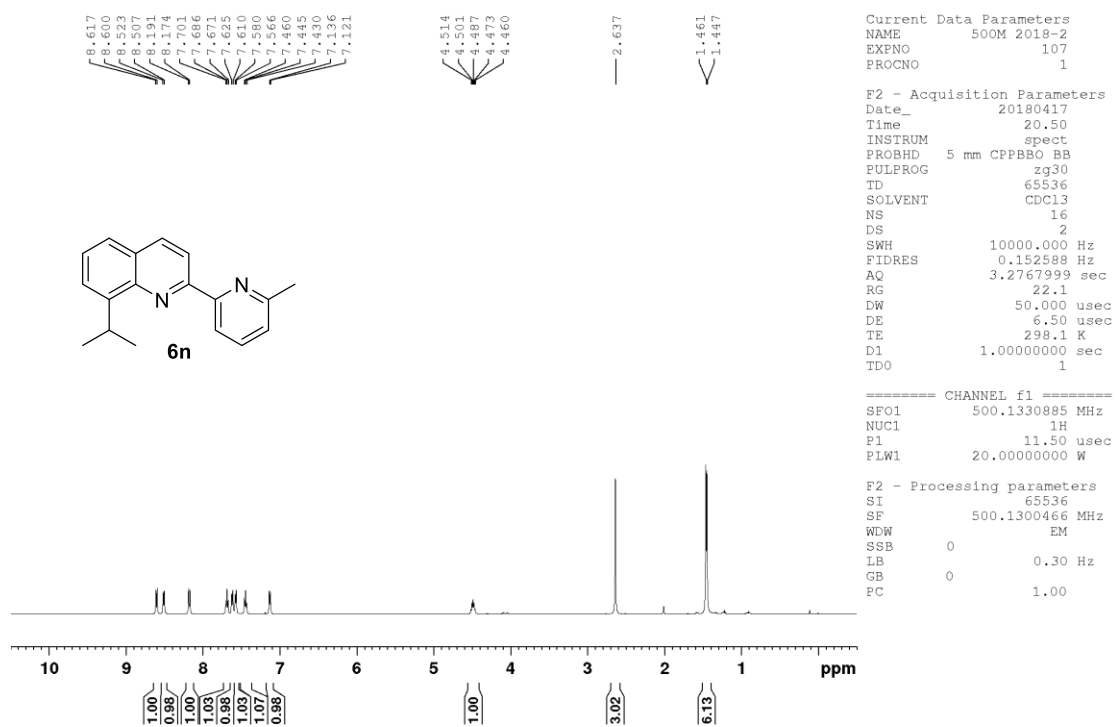
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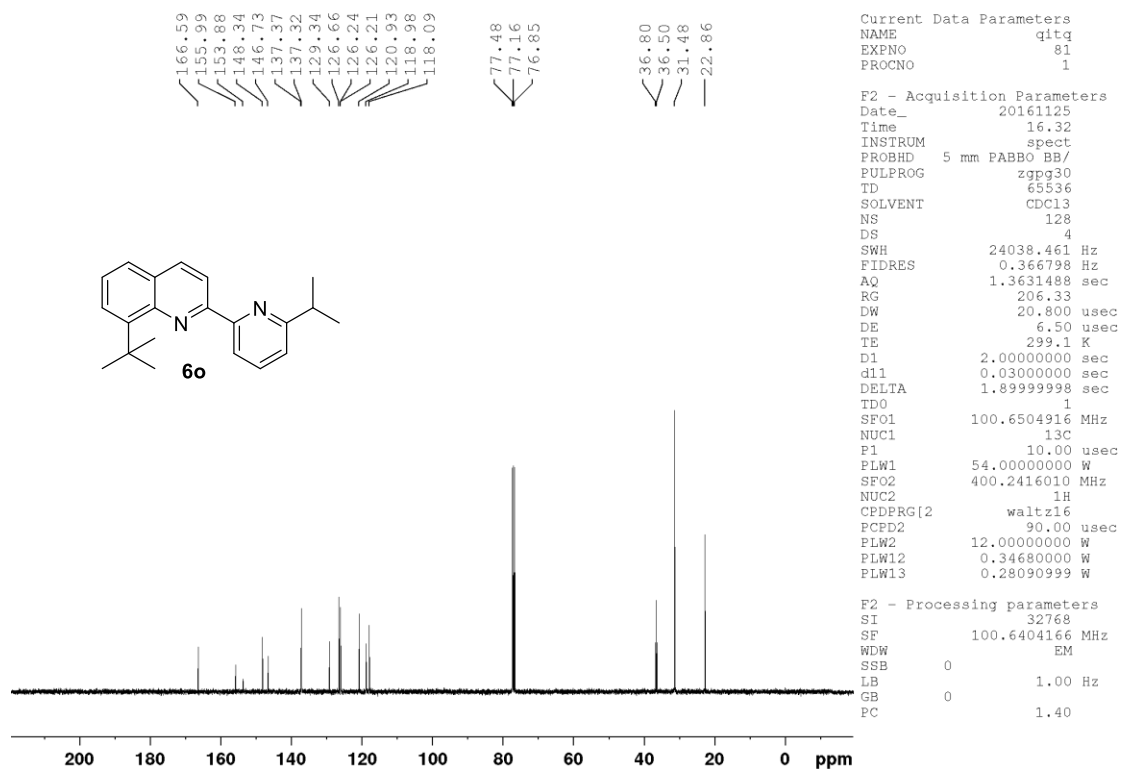
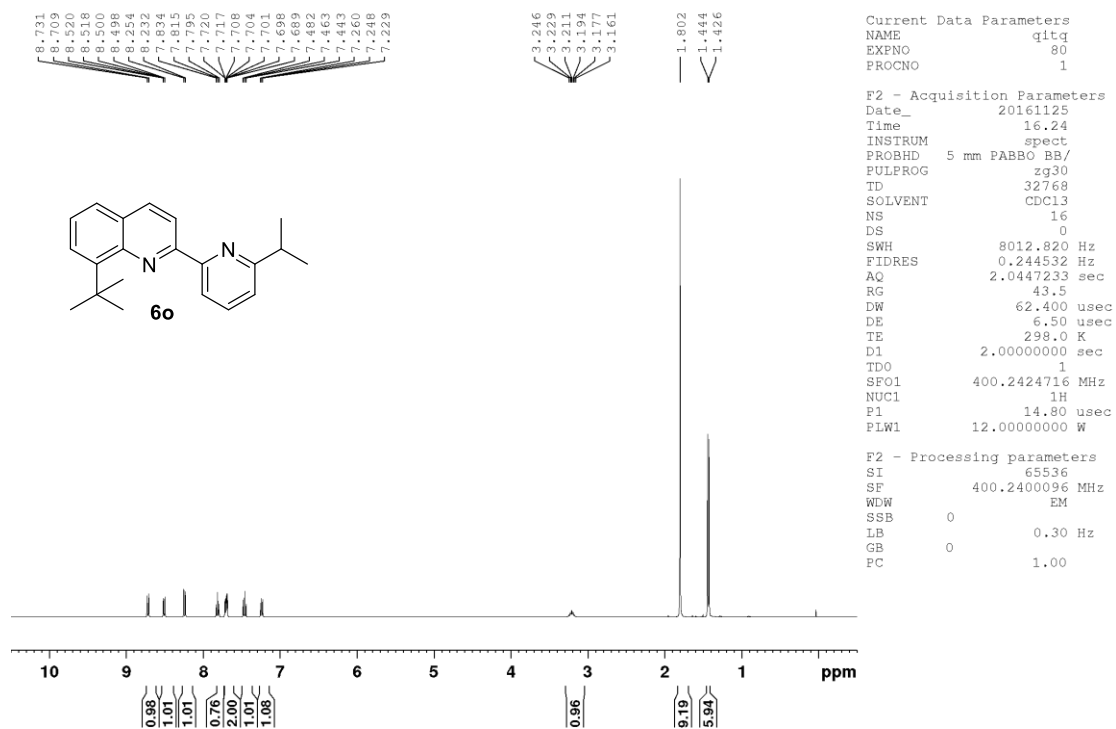


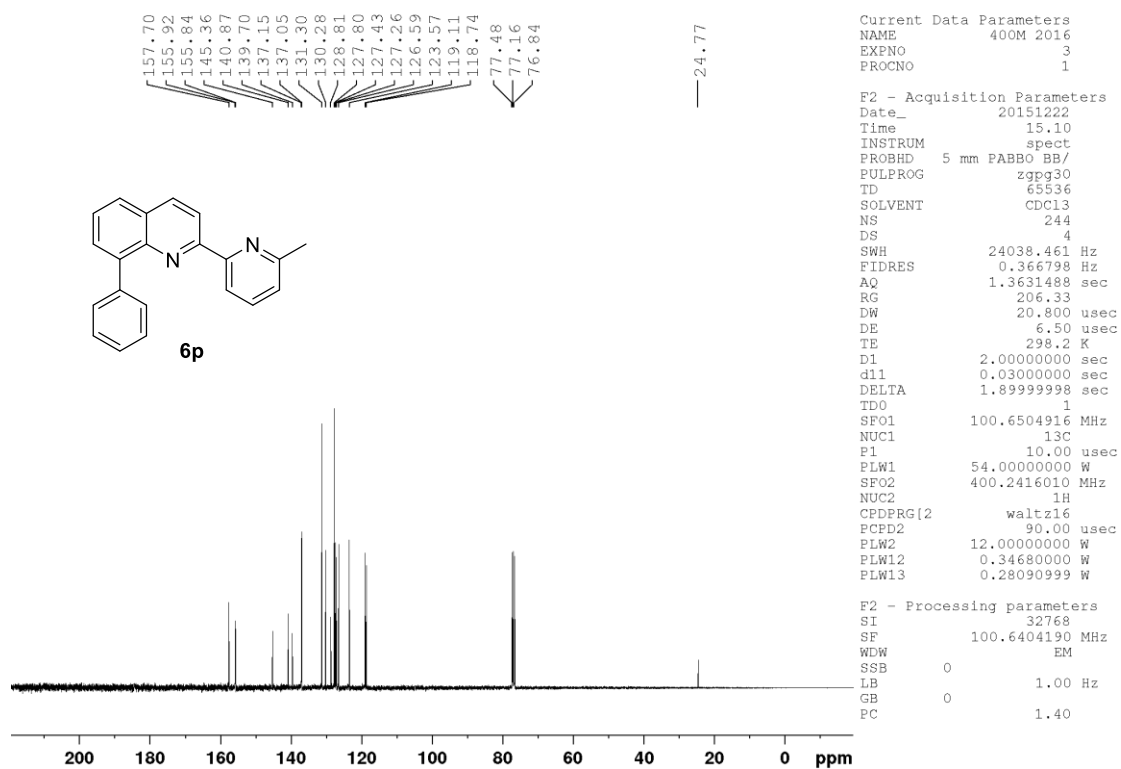
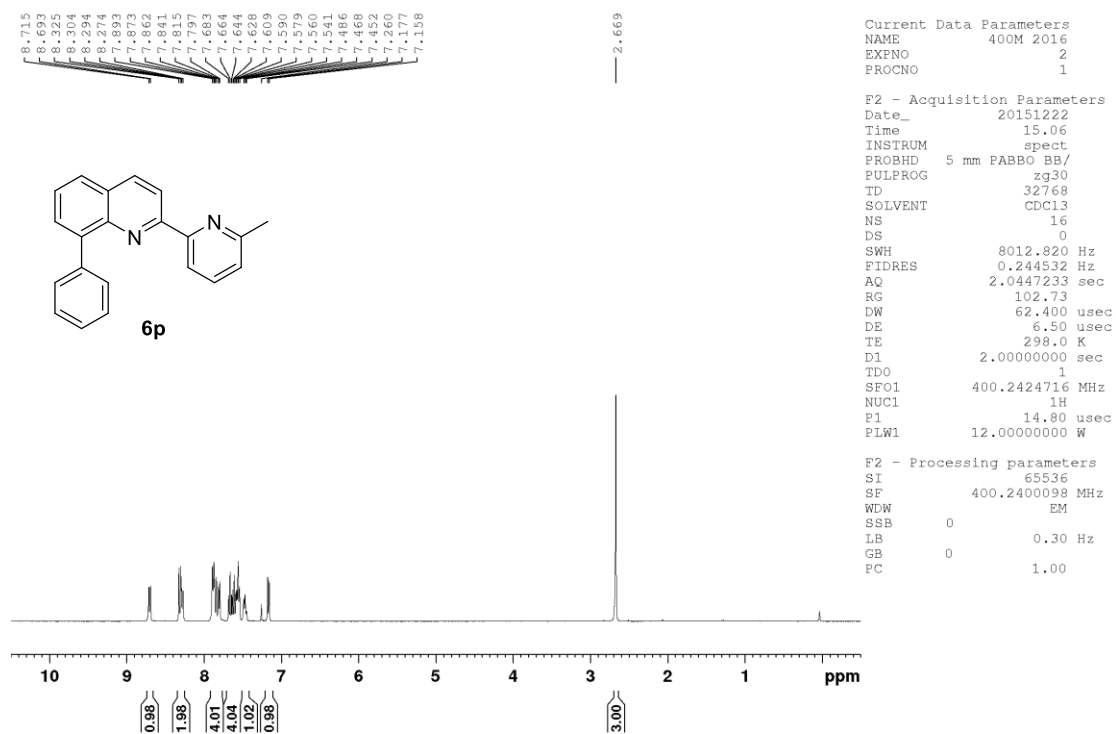


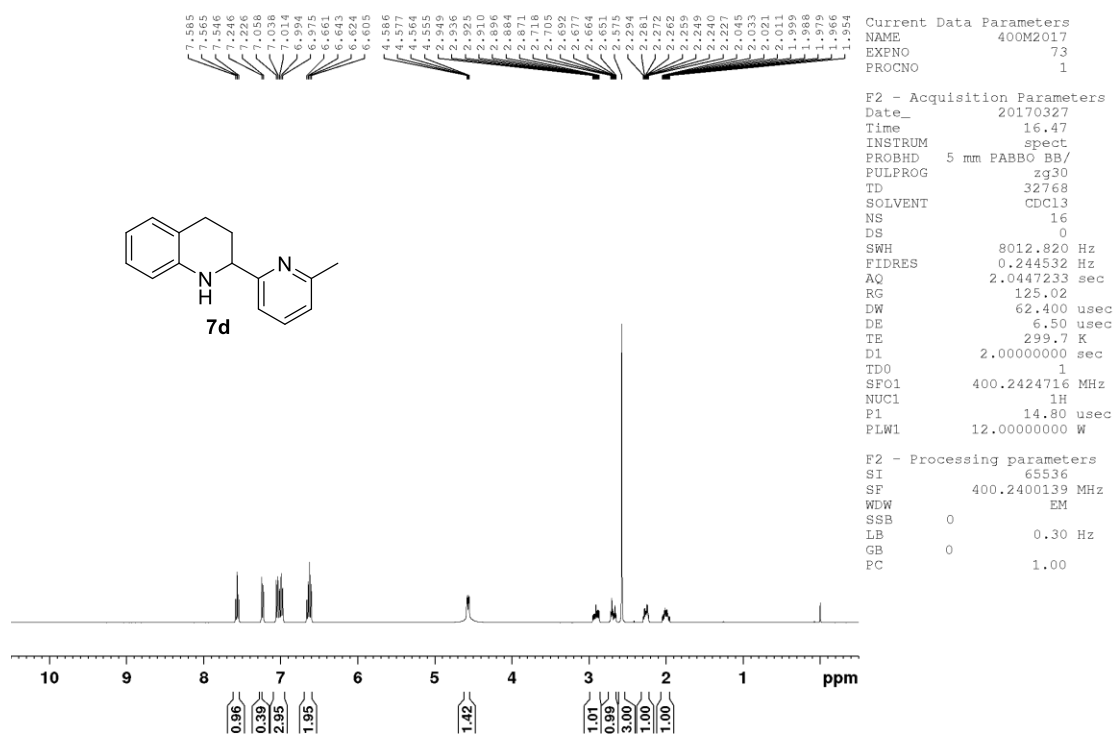


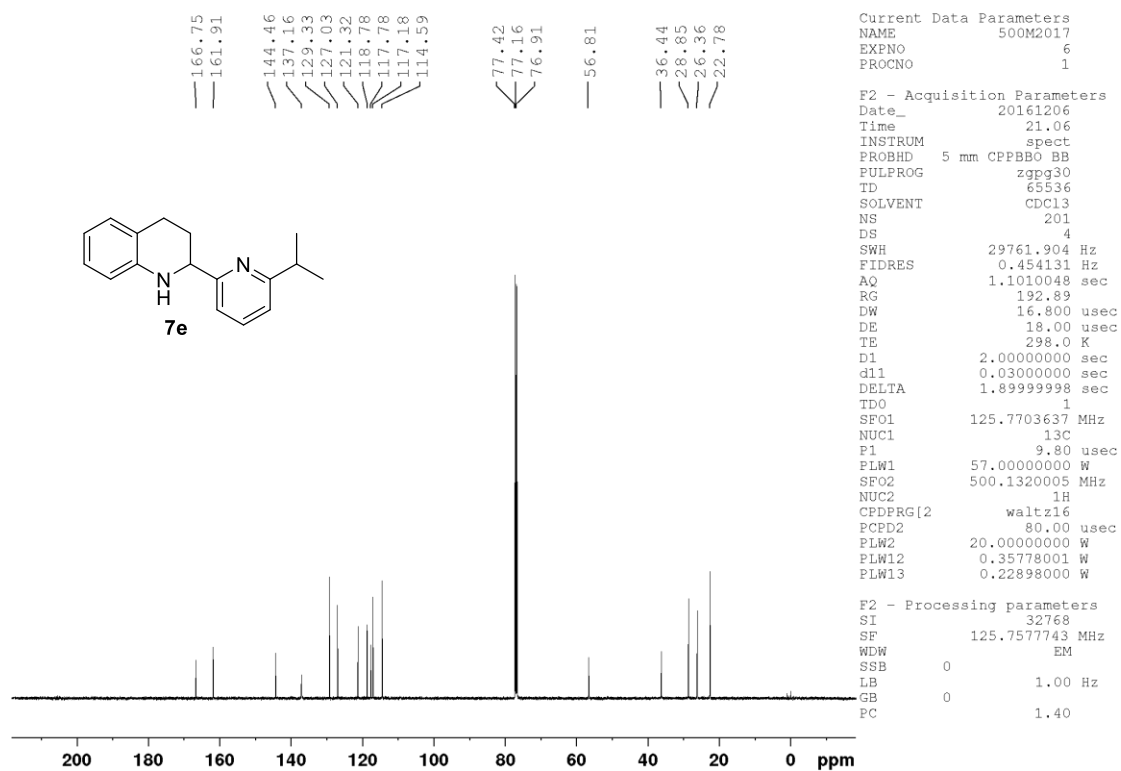
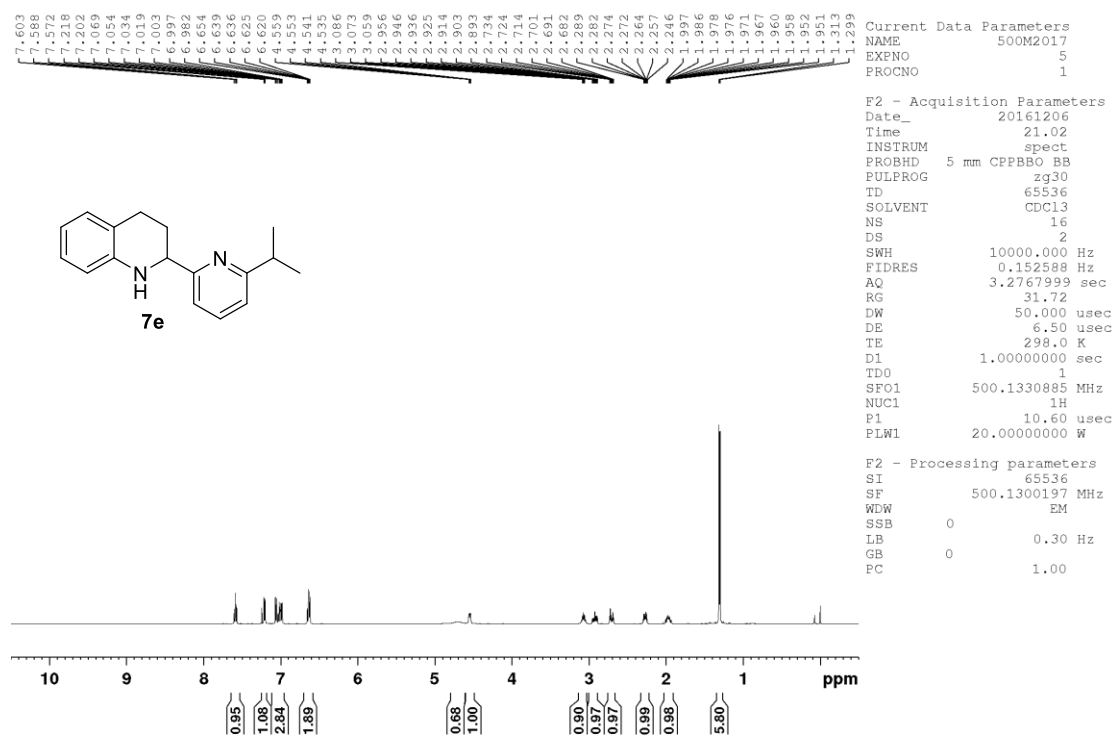


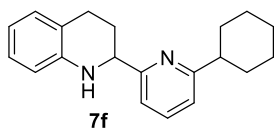
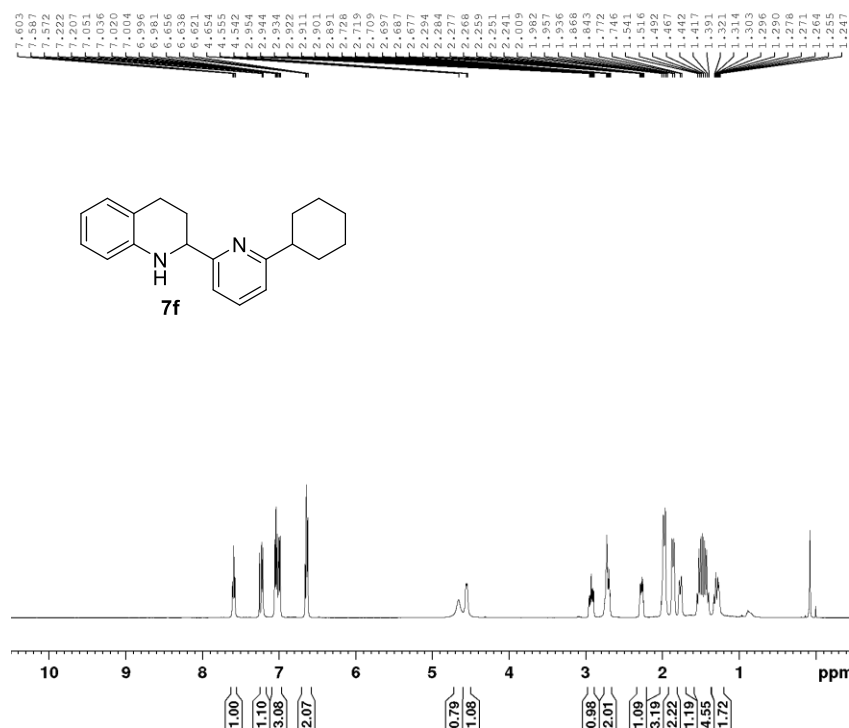








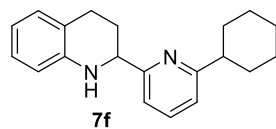
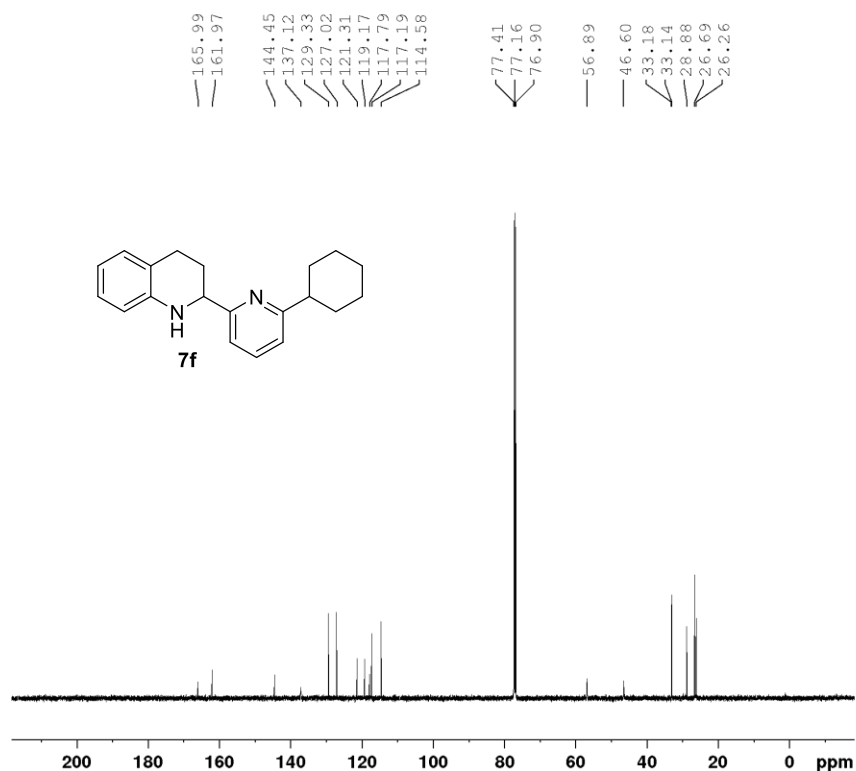




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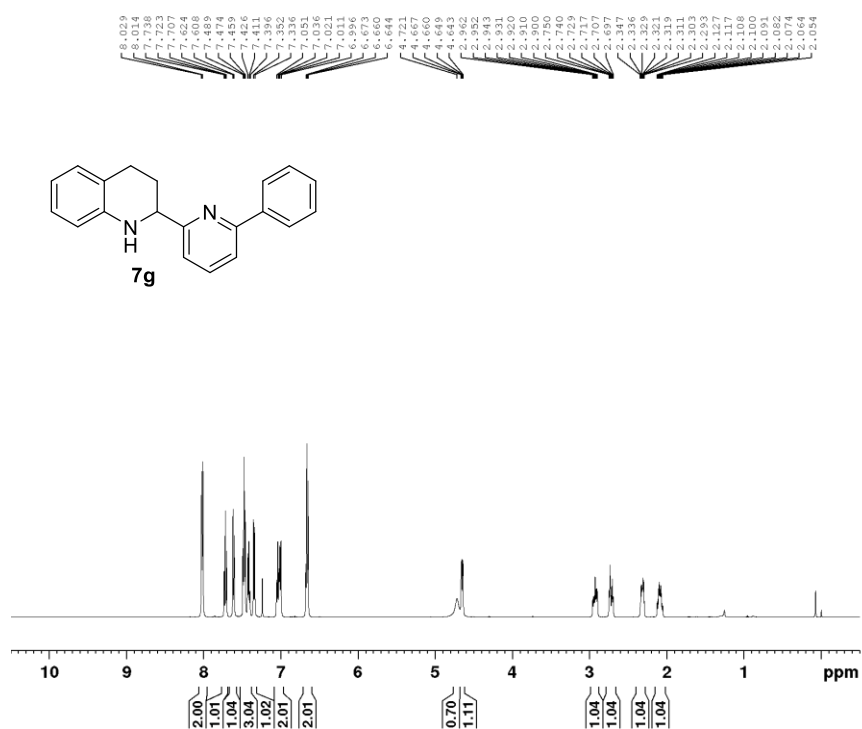
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SFO2 500.1320005 MHz
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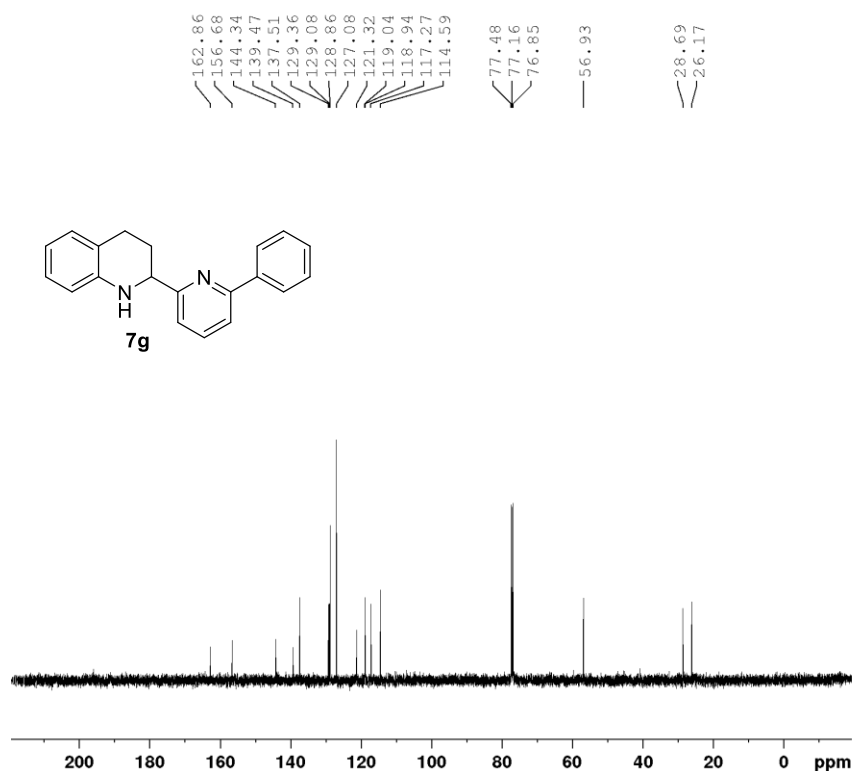
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PROCNO 1

F2 - Acquisition Parameters
Date_ 20180307
Time 21.50
INSTRUM spect
PROBHD 5 mm CFPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 31.72
DW 50.000 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TD0 1
SF01 500.1330885 MHz
NUC1 1H
P1 11.50 usec
PLW1 20.00000000 W

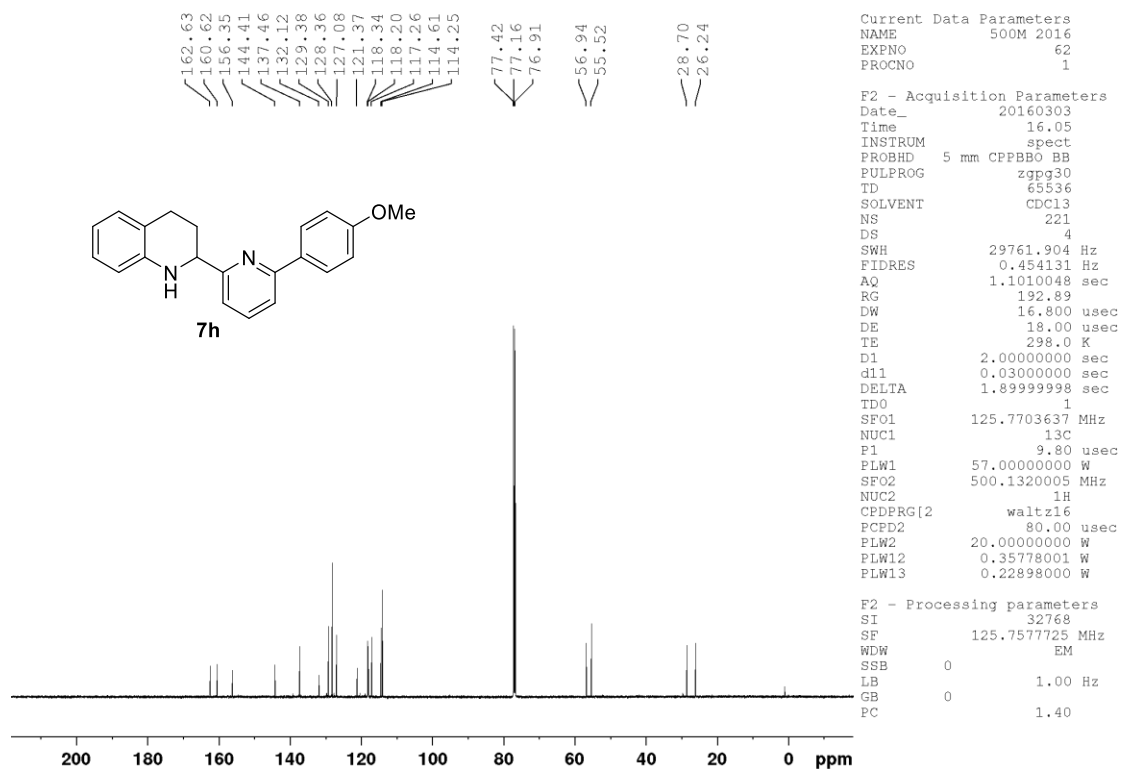
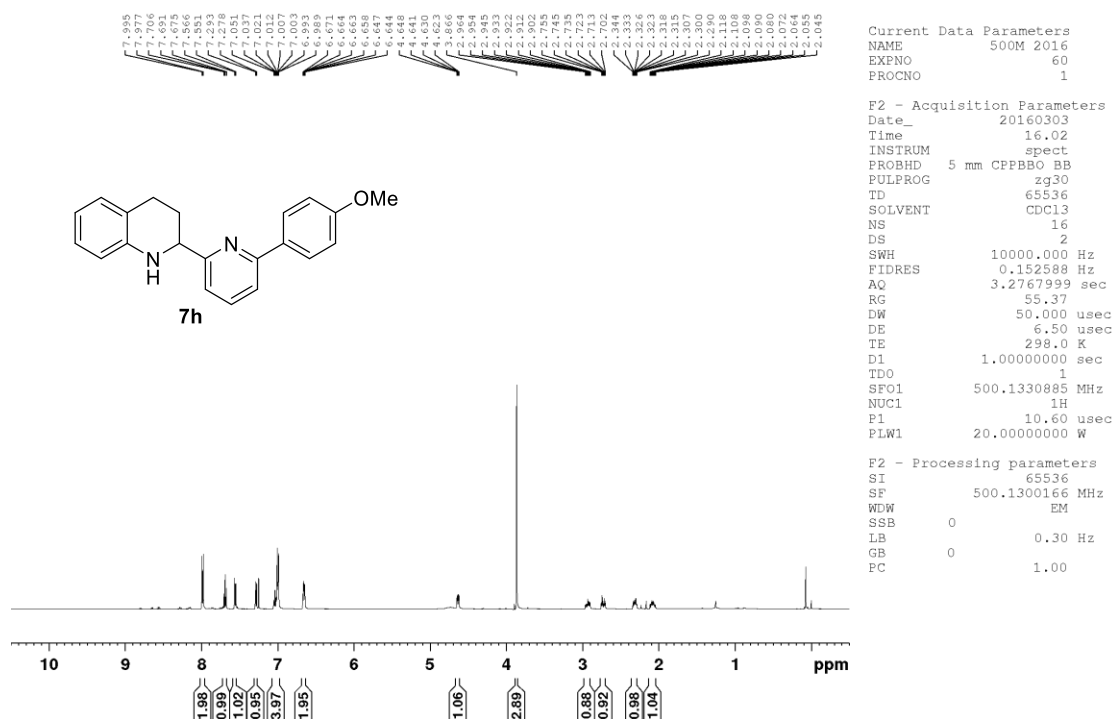
F2 - Processing parameters
SI 65536
SF 500.1300235 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

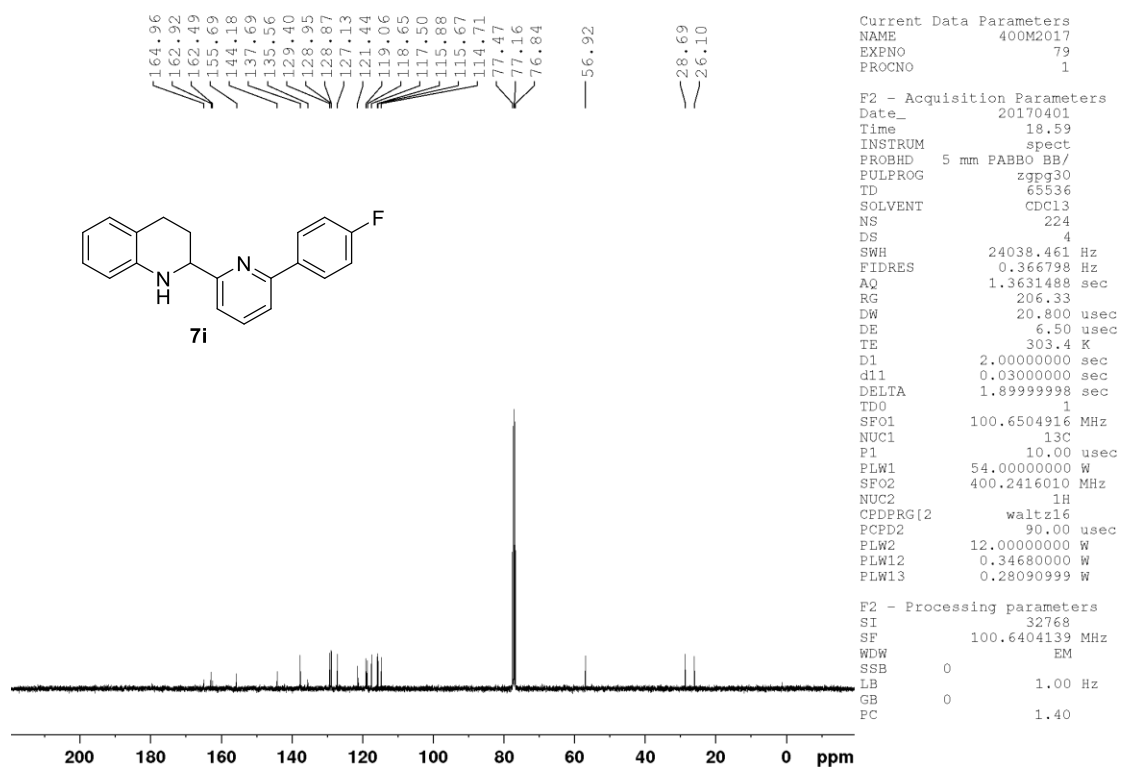
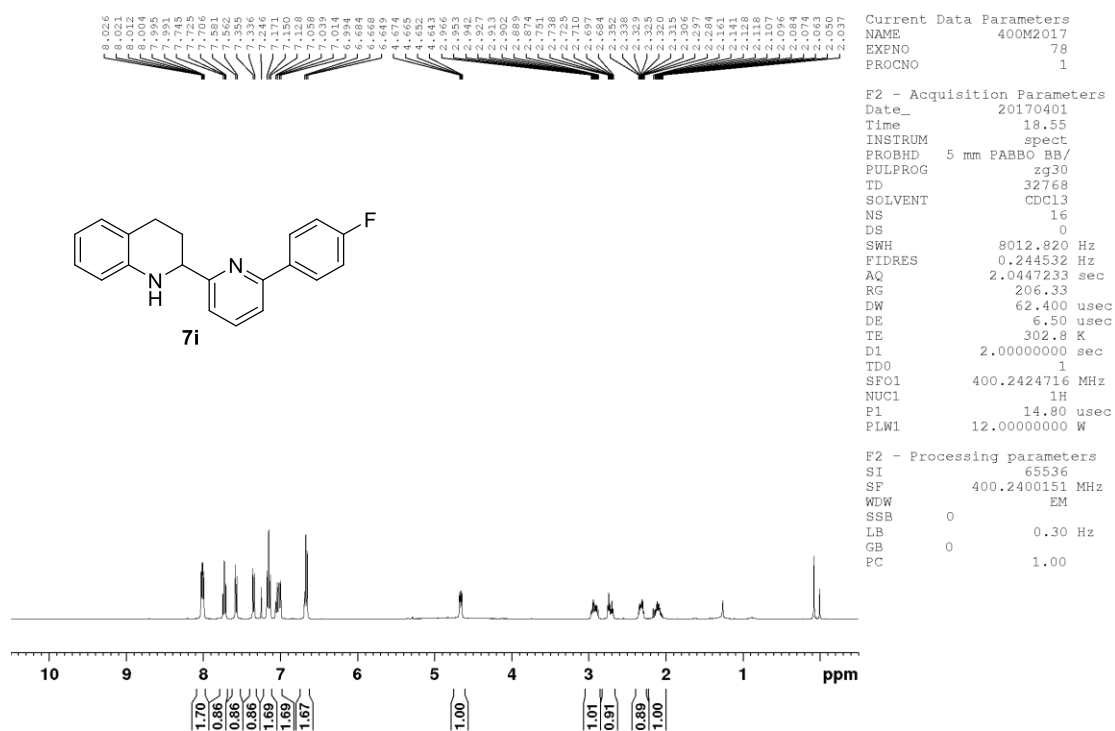


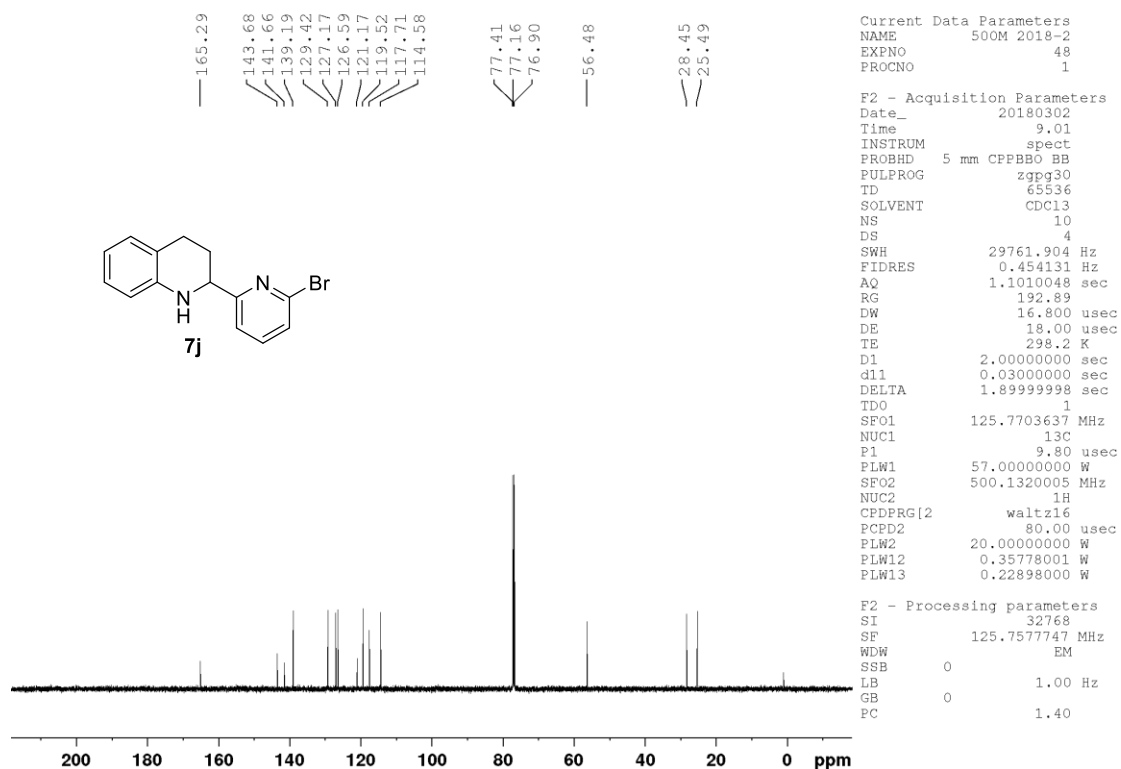
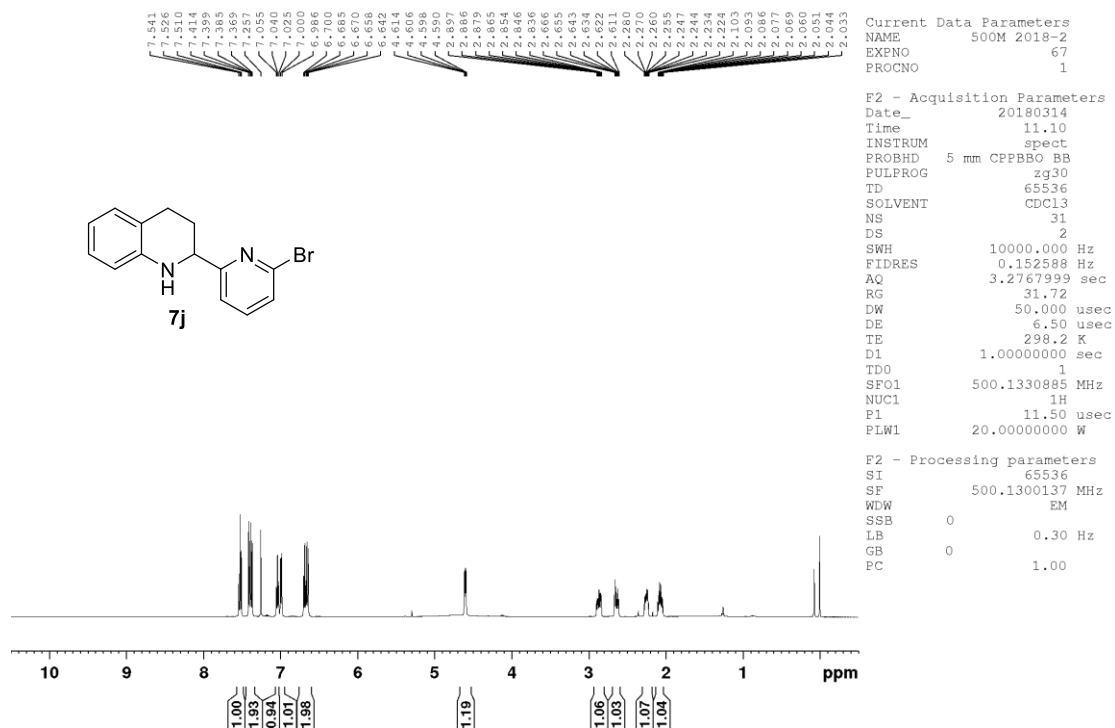
Current Data Parameters
NAME 400M 2018
EXPNO 325
PROCNO 1

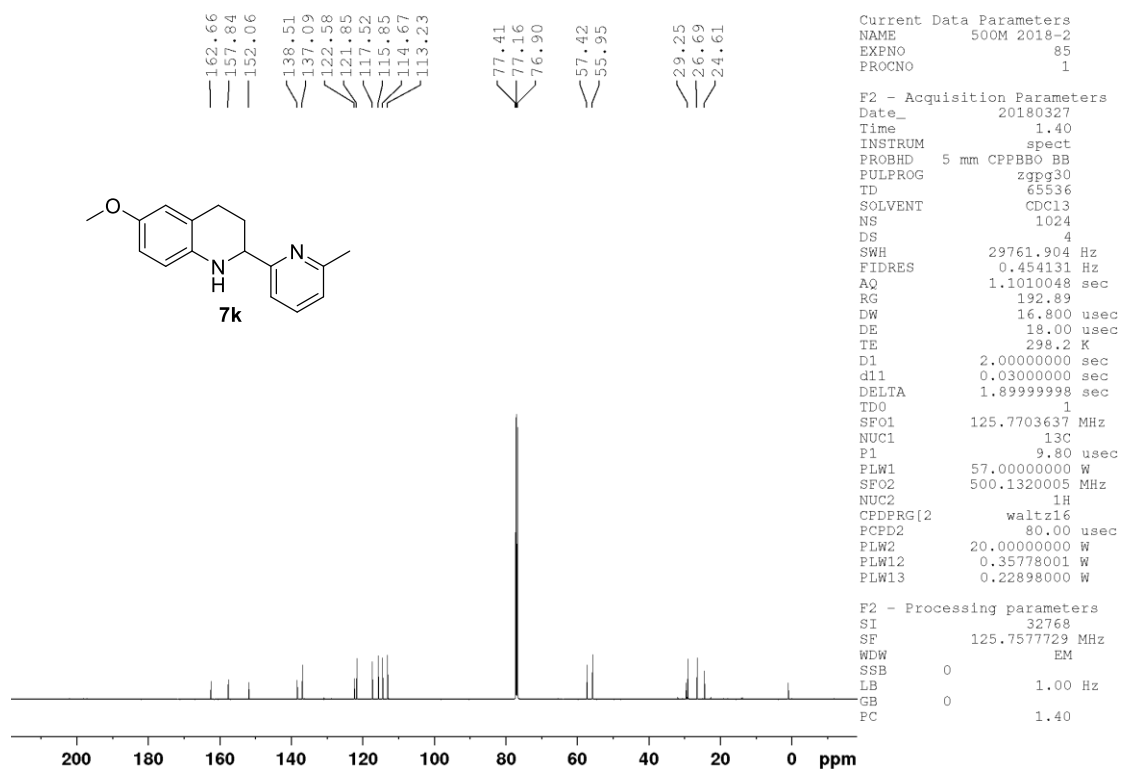
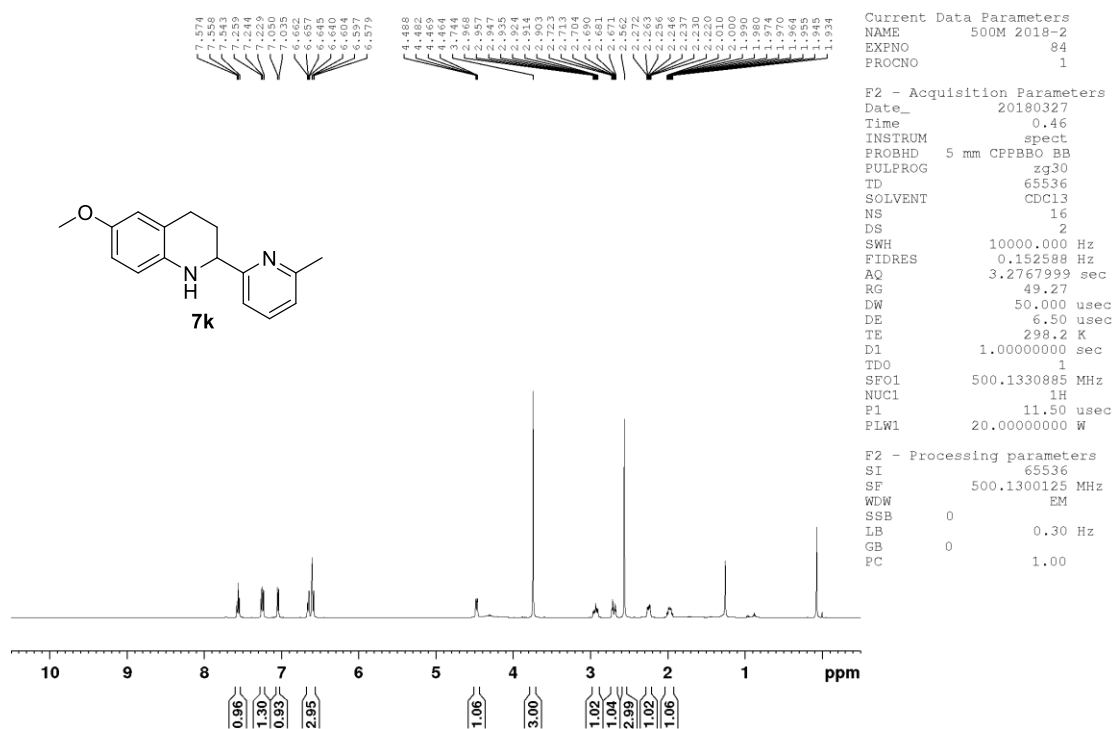
F2 - Acquisition Parameters
Date_ 20180305
Time 15.05
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 9
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 206.33
DW 20.800 usec
DE 6.50 usec
TE 298.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999999 sec
TD0 1
SF01 100.6504916 MHz
NUC1 13C
P1 10.00 usec
PLW1 54.00000000 W
SF02 400.2416010 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.34680000 W
PLW13 0.28090999 W

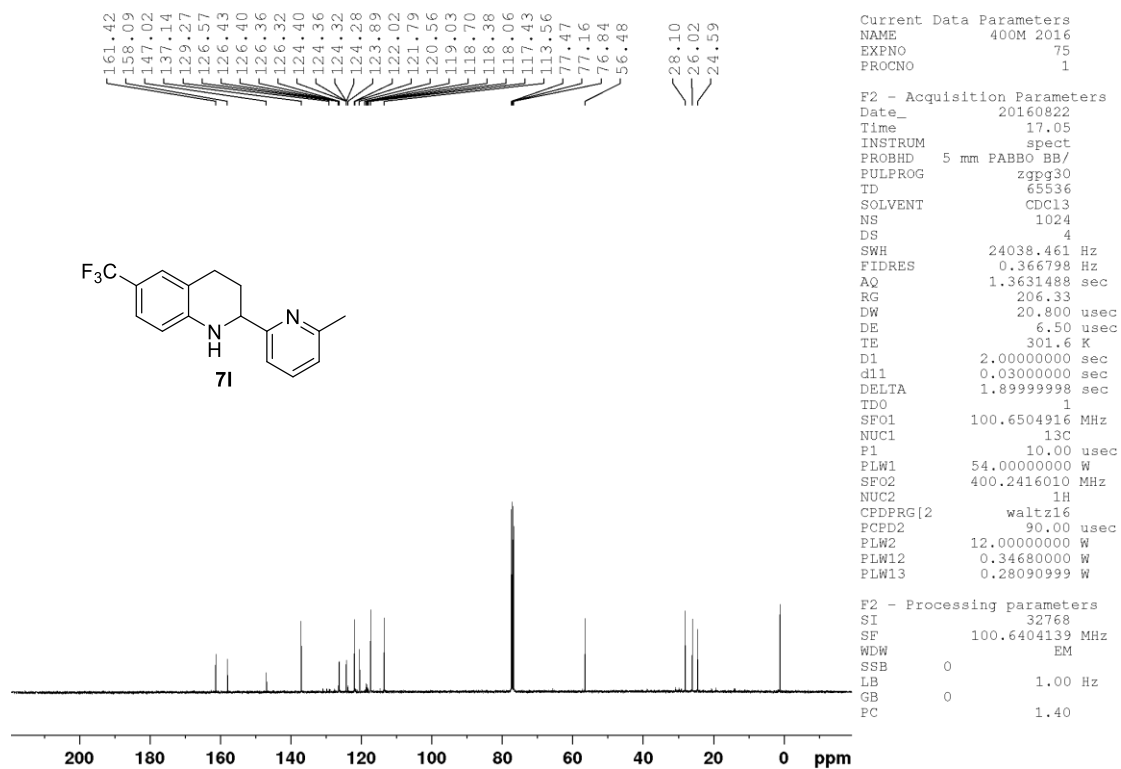
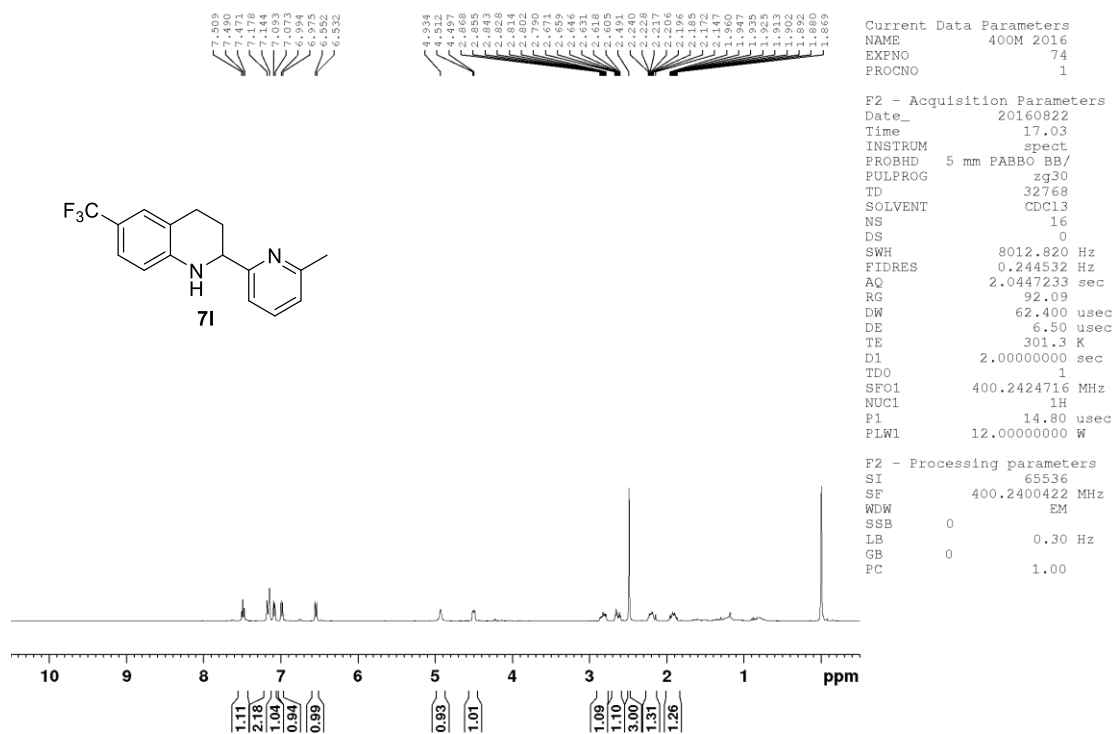
F2 - Processing parameters
SI 32768
SF 100.6404202 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

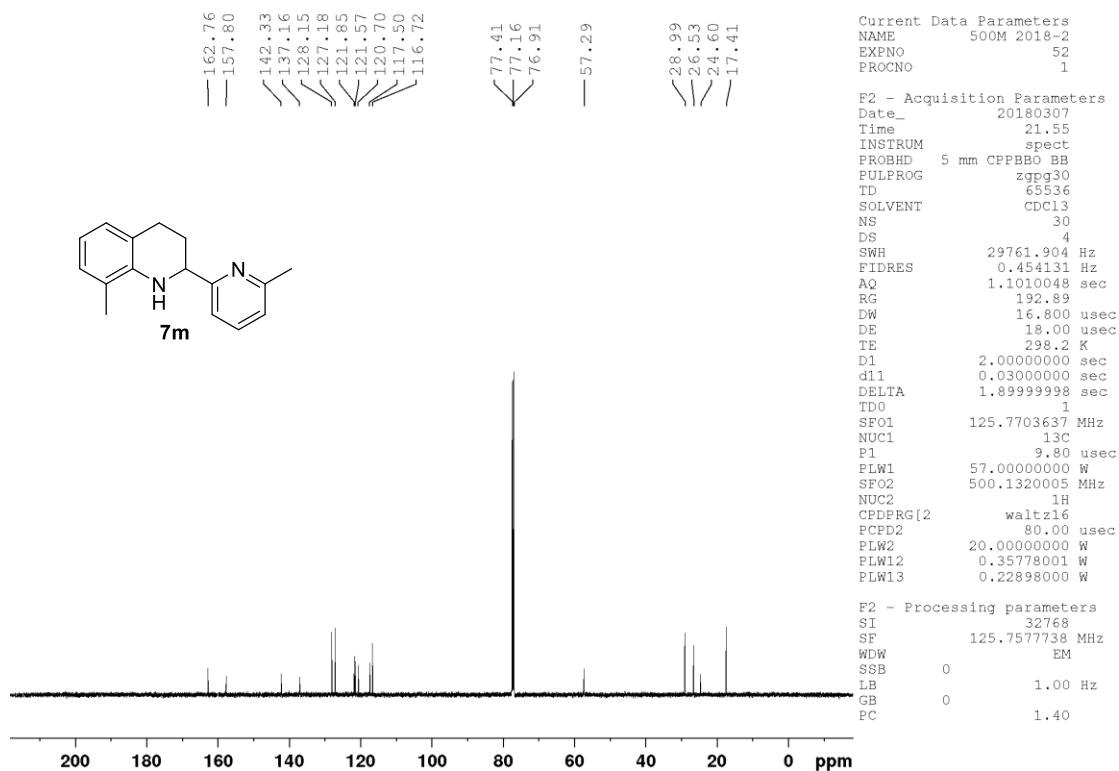
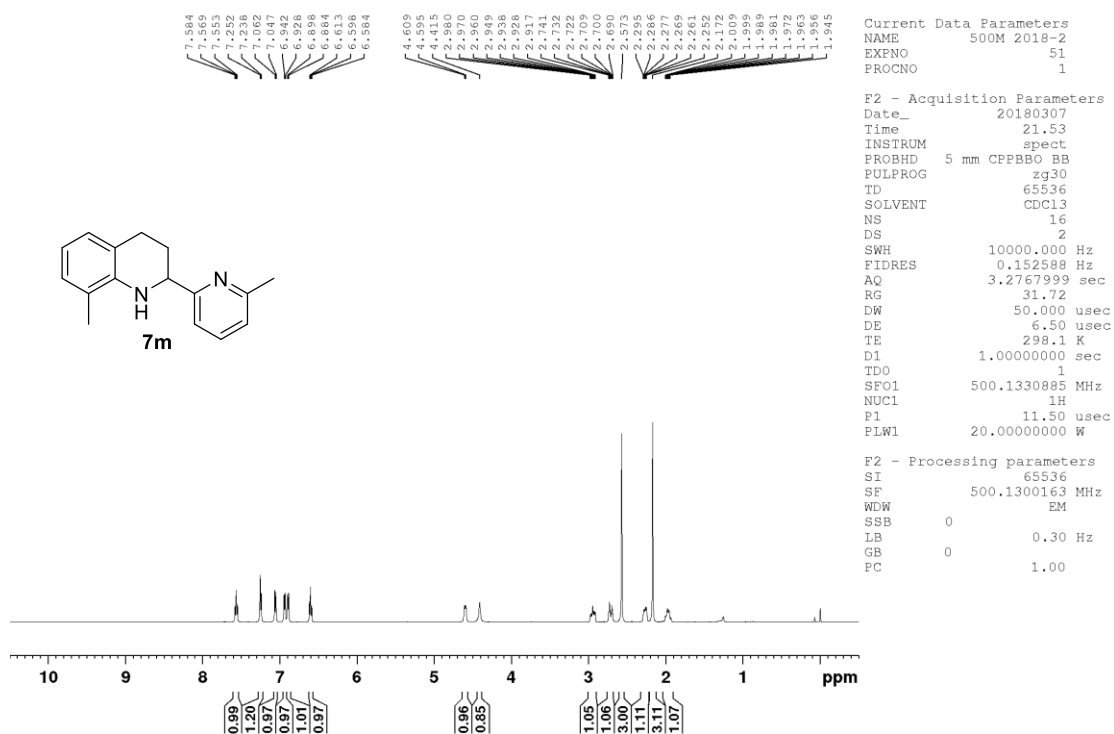


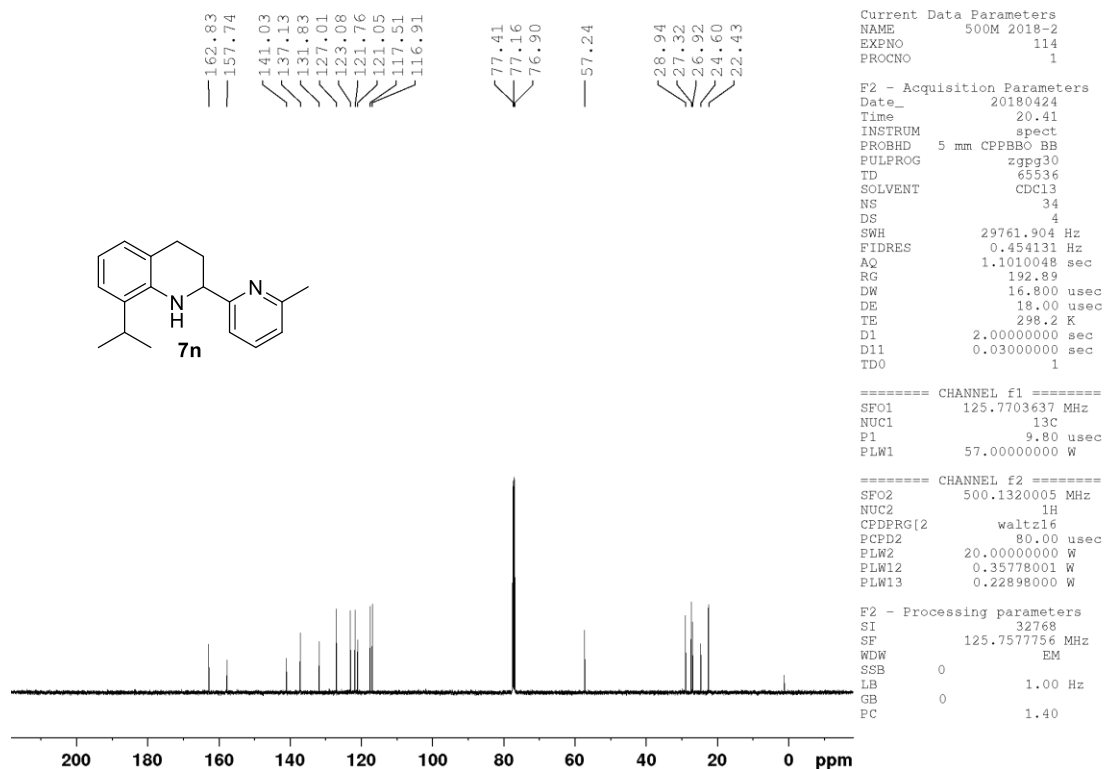
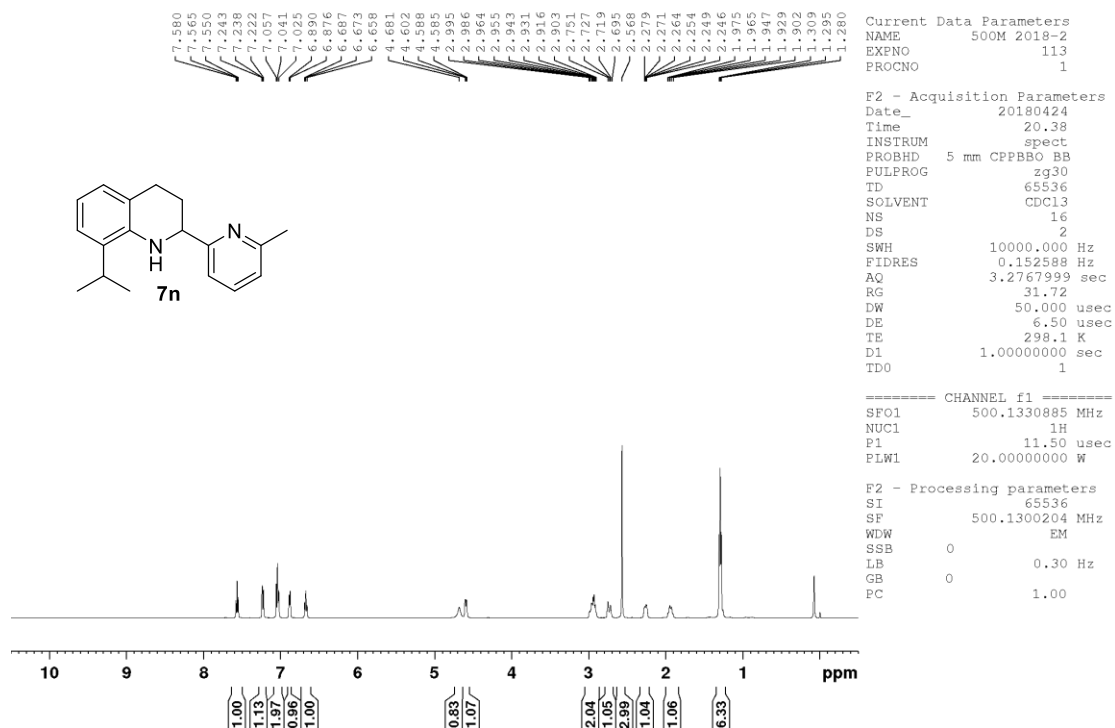


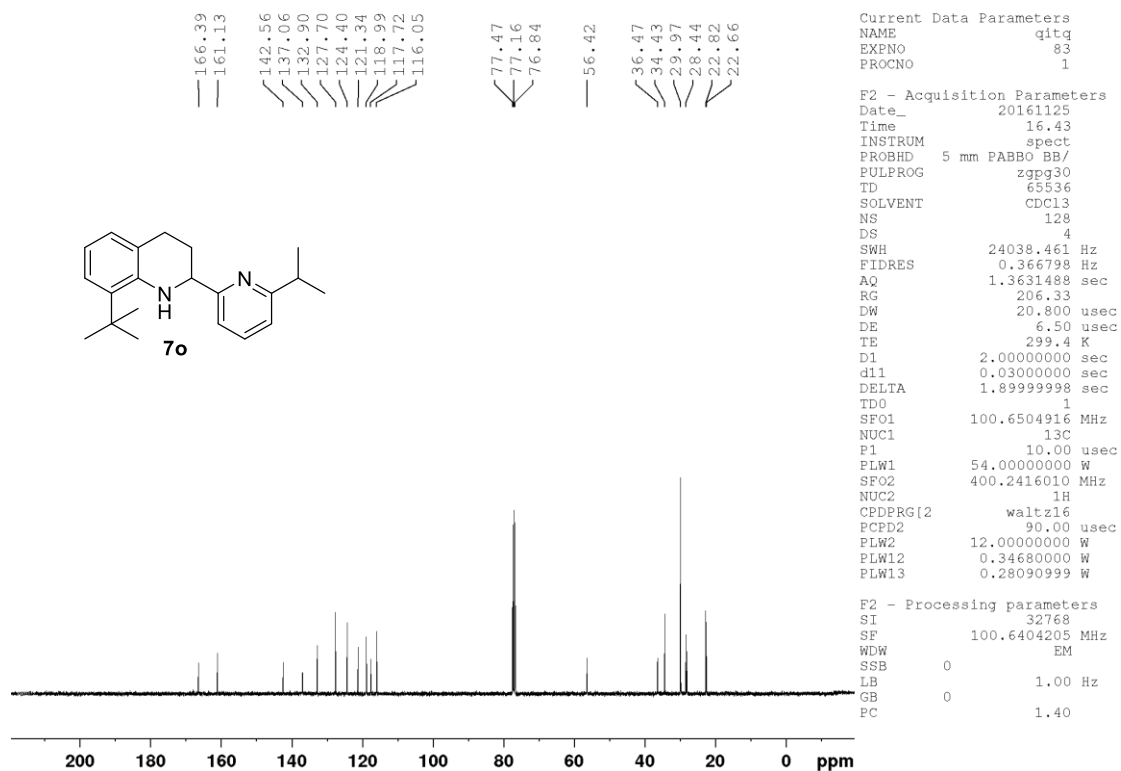
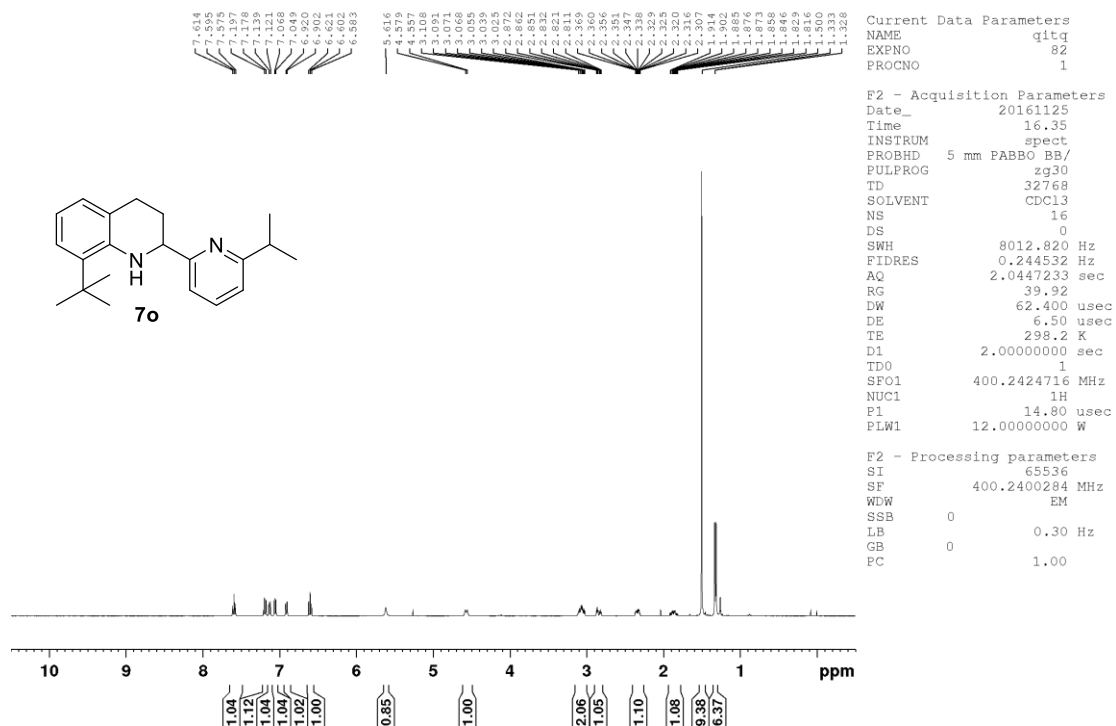


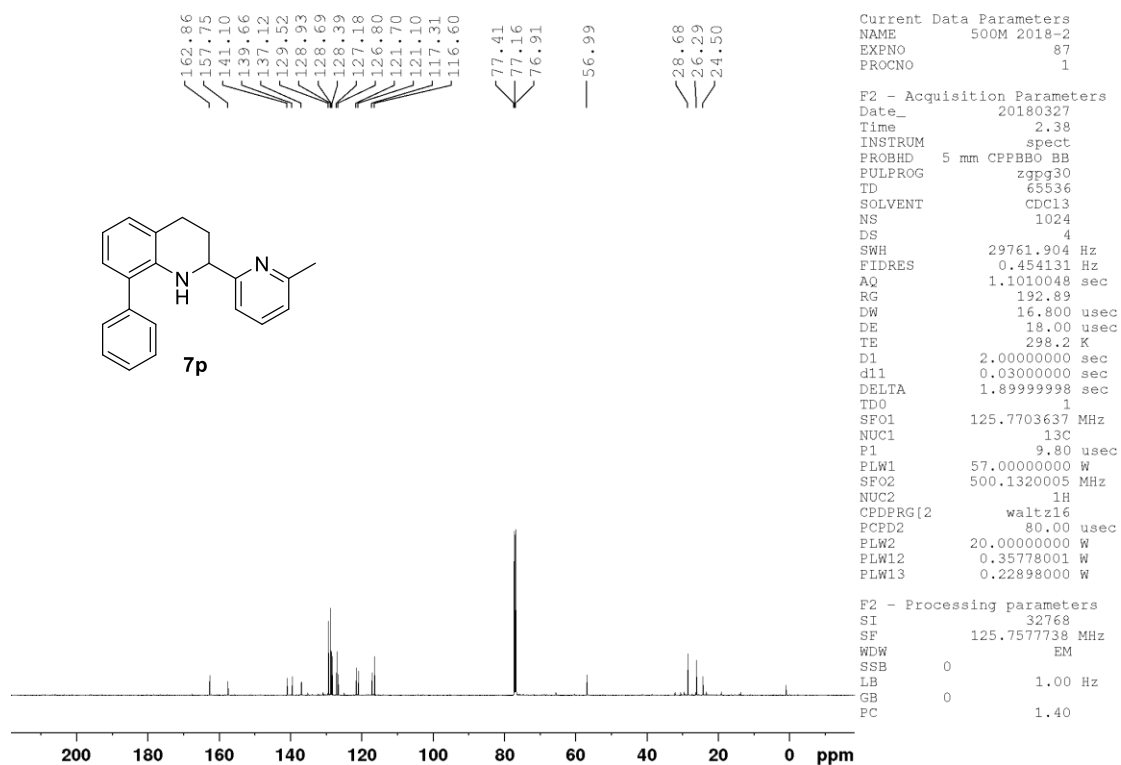
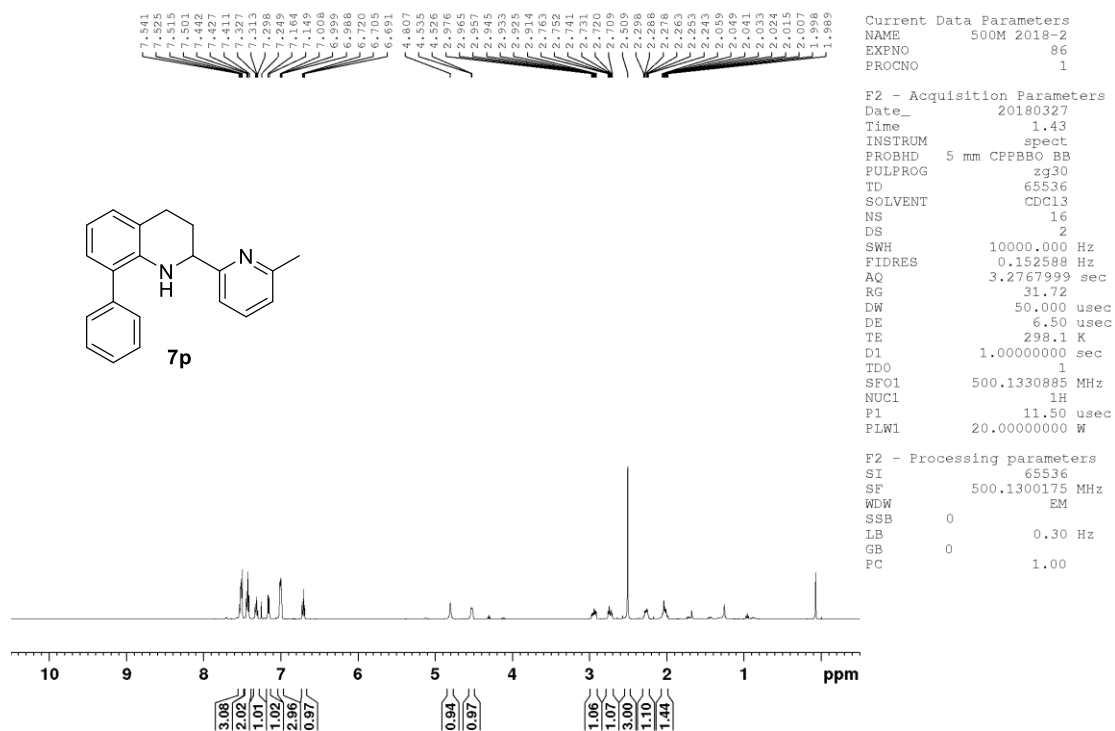


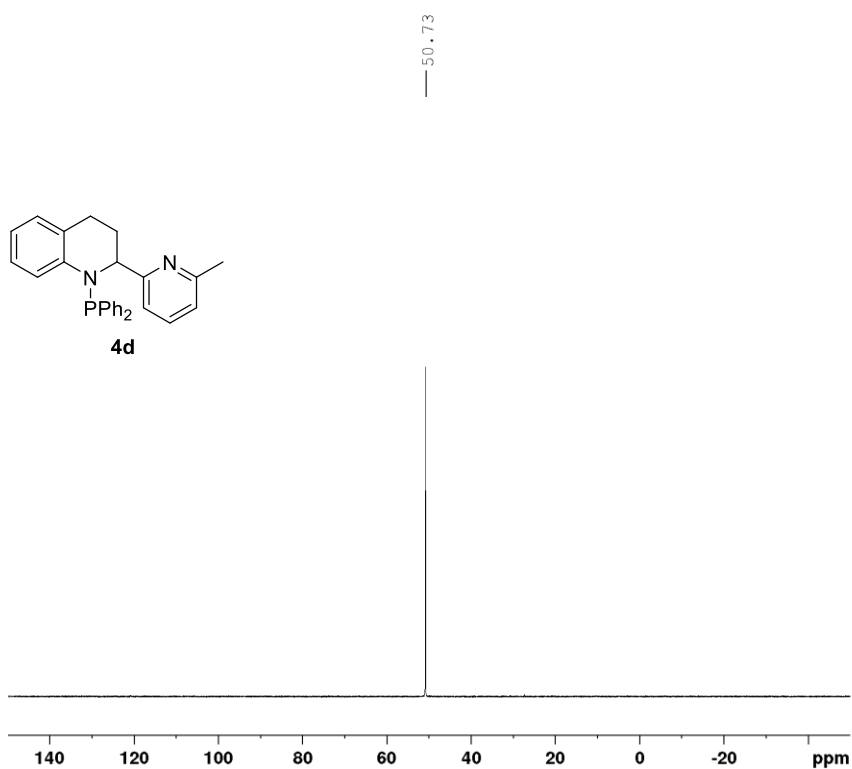












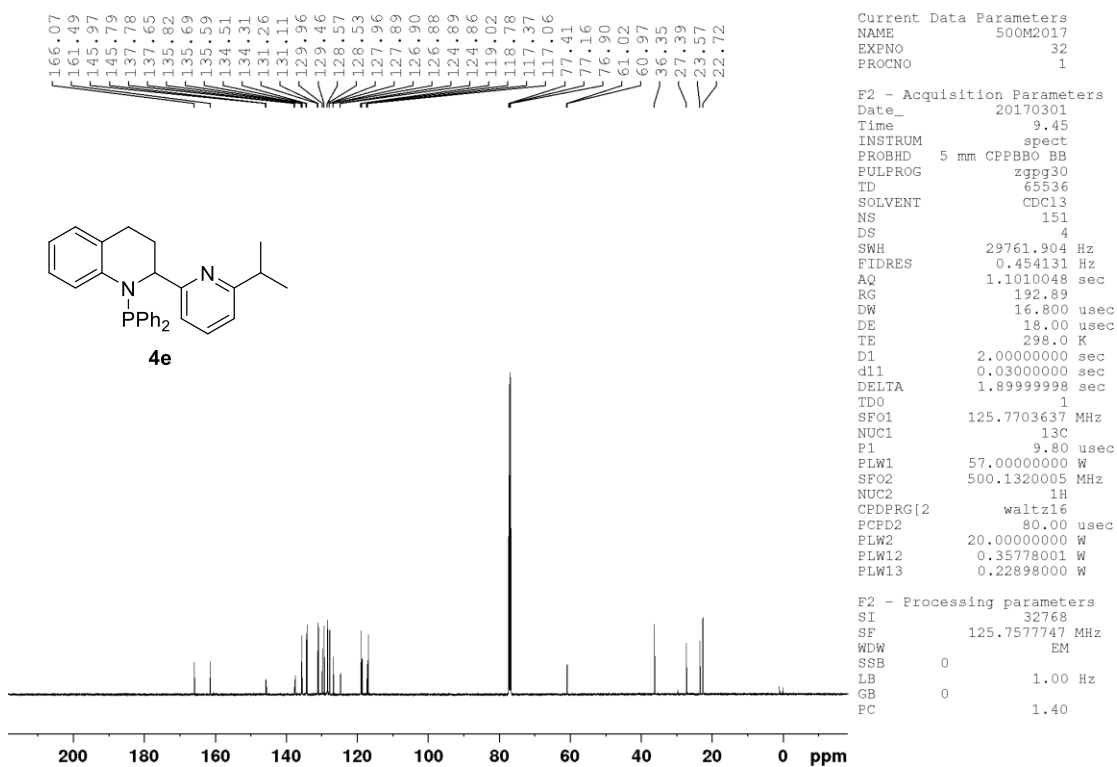
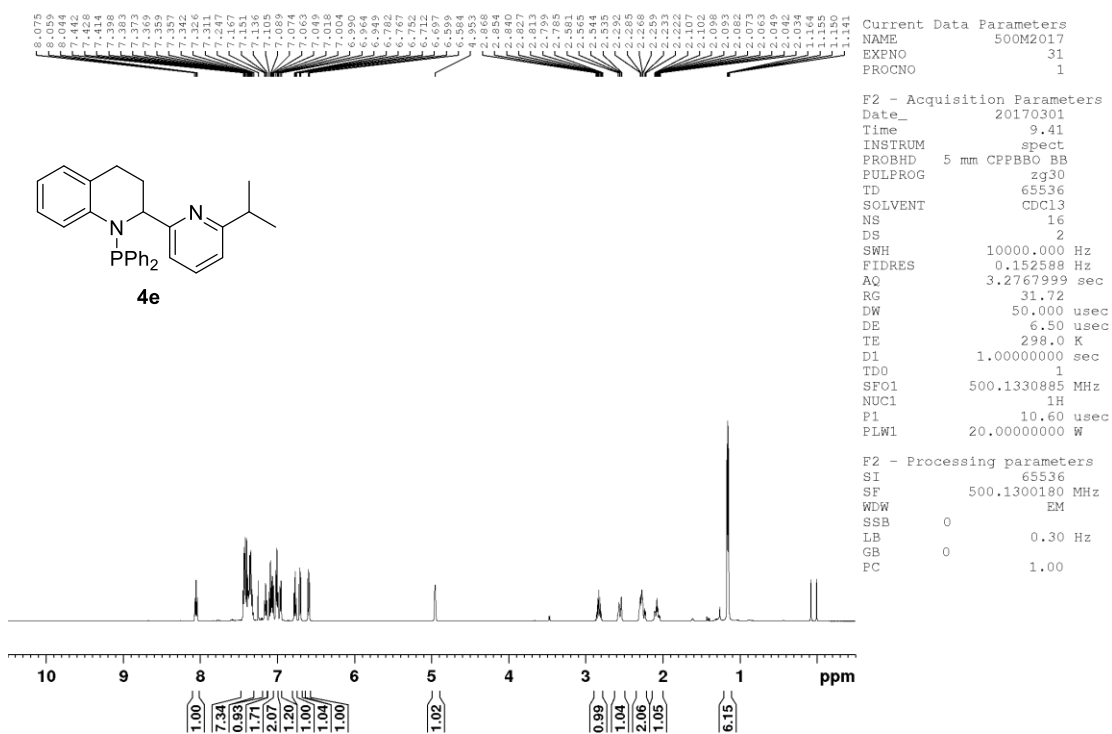
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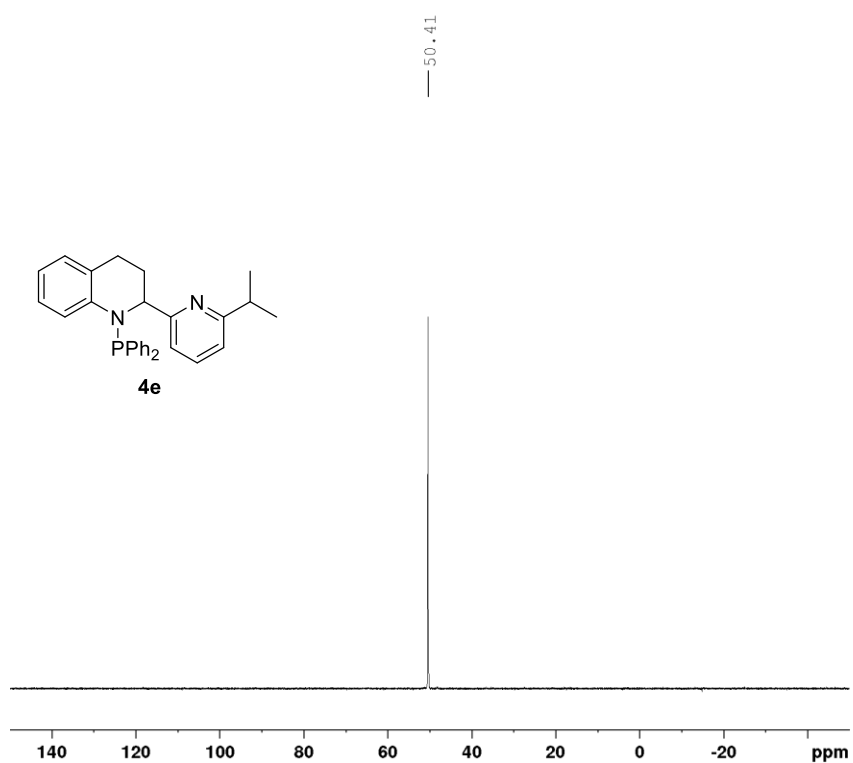
Current Data Parameters
NAME          500M P31
EXPNO         7
PROCNO        1

F2 - Acquisition Parameters
Date_         20161213
Time          16.34
INSTRUM       spect
PROBHD        5 mm CPPBBO BB
PULPROG       zgpgg
TD            65536
SOLVENT       CDCl3
NS            16
DS            4
SWH           100000.000 Hz
FIDRES        1.525879 Hz
AQ            0.3276800 sec
RG            192.89
DW            5.000 usec
DE            18.00 usec
TE            298.0 K
D1            2.00000000 sec
d11           0.03000000 sec
DELTA         1.89999998 sec
TD0           1
SF01          202.4664578 MHz
NUC1          31P
P1            11.50 usec
PLW1          52.96599960 W
SF02          500.1320005 MHz
NUC2          1H
CPDPRG[2]     waltz16
PCPD2         80.00 usec
PLW2          20.00000000 W
PLW12         0.35778001 W
PLW13         0.22898000 W

F2 - Processing parameters
SI            32768
SF            202.4563350 MHz
WDW           EM
SSB           0
LB            1.00 Hz
GB            0
PC            1.40

```

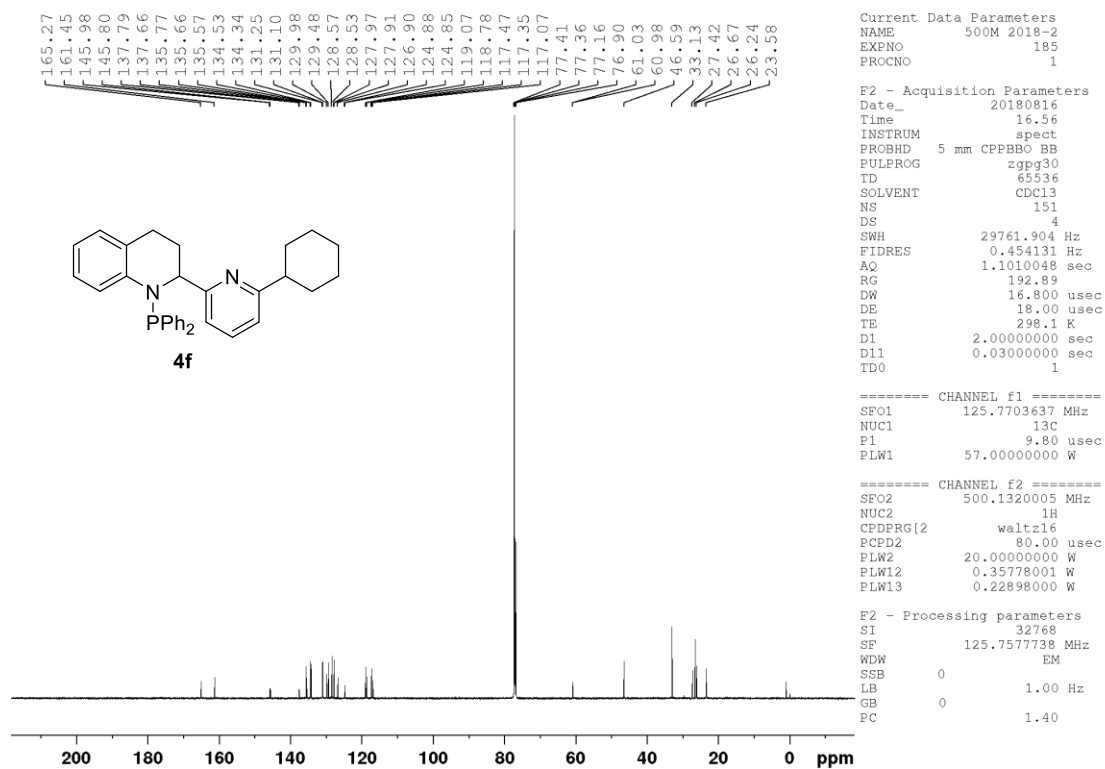
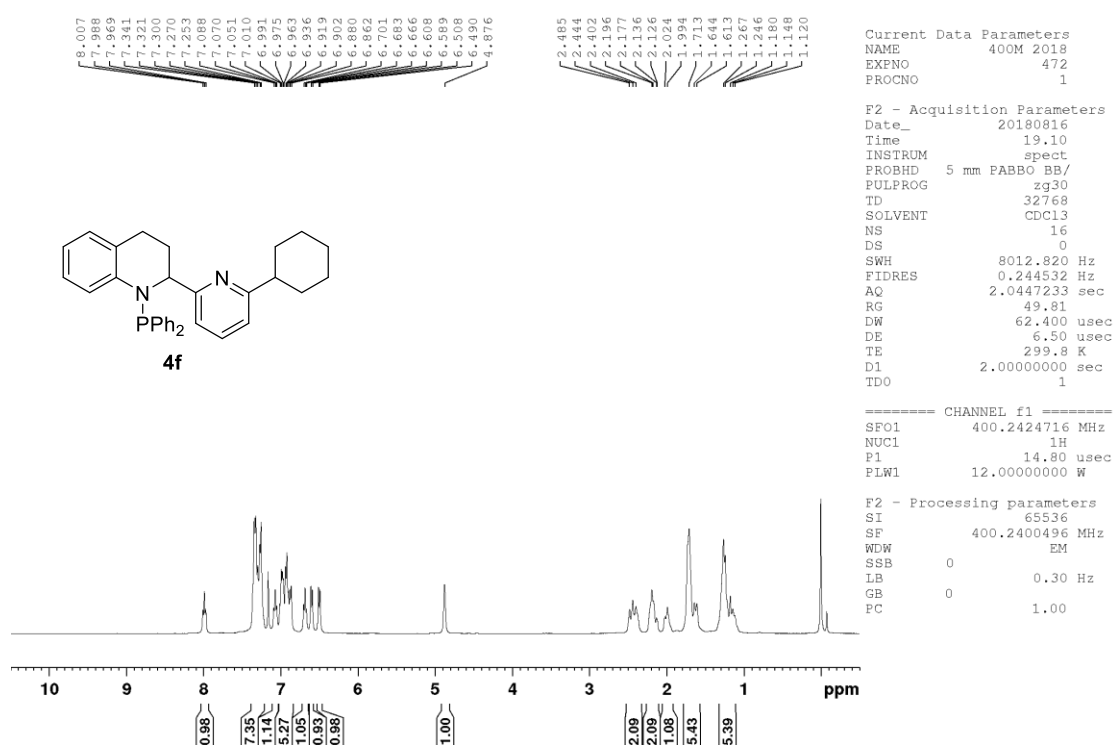


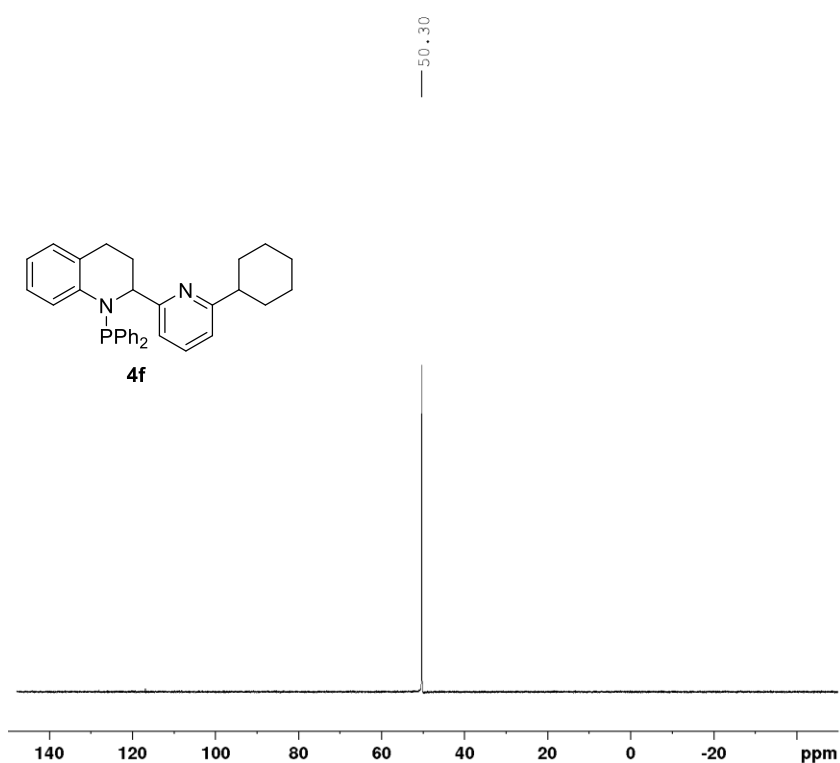


Current Data Parameters
NAME 500M P31
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170301
Time 9.36
INSTRUM spect
PROBHD 5 mm CFPBBO BB
PULPROG zgpgg
TD 65536
SOLVENT CDCl3
NS 16
DS 4
SWH 100000.000 Hz
FIDRES 1.525879 Hz
AQ 0.3276800 sec
RG 192.89
DW 5.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SF01 202.4664578 MHz
NUC1 31P
P1 11.50 usec
PLW1 52.96599960 W
SF02 500.1320005 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 80.00 usec
PLW2 20.00000000 W
PLW12 0.35778001 W
PLW13 0.22898000 W

F2 - Processing parameters
SI 32768
SF 202.4563350 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

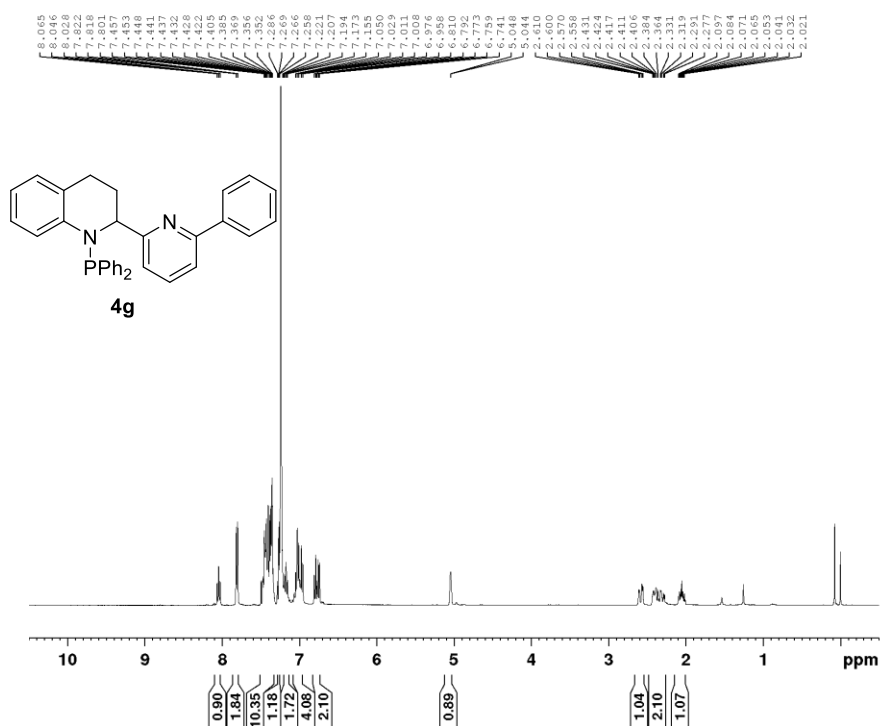




Current Data Parameters
 NAME 400 M P31
 EXPNO 4
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20171211
 Time 17.15
 INSTRUM spect
 PROBHD 5 mm PABBO BB/
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 4
 SWH 64102.563 Hz
 FIDRES 0.978127 Hz
 AQ 0.5111808 sec
 RG 206.33
 DW 7.800 usec
 DE 6.50 usec
 TE 298.6 K
 D1 2.0000000 sec
 d11 0.0300000 sec
 DELTA 1.8999999 sec
 TD0 1
 SF01 162.0120208 MHz
 NUC1 31P
 P1 14.60 usec
 PLW1 13.0000000 W
 SF02 400.2416010 MHz
 NUC2 1H
 CPDPRG(2) waltz16
 PCPD2 90.00 usec
 PLW2 12.0000000 W
 PLW12 0.3468000 W
 PLW13 0.2809099 W

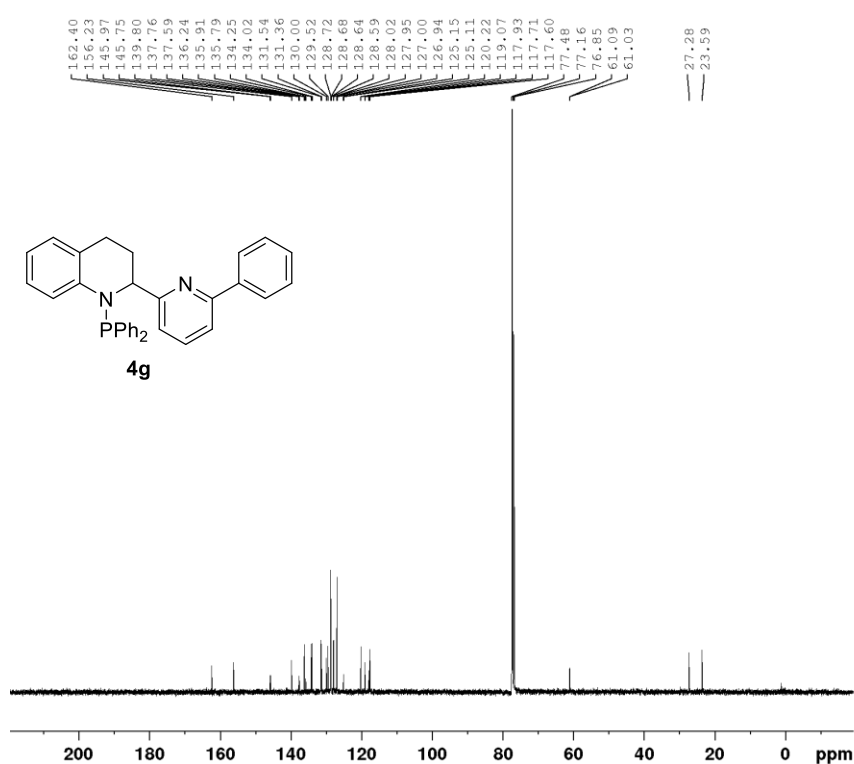
F2 - Processing parameters
 SI 32768
 SF 162.0201218 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40



Current Data Parameters
NAME 400M2017
EXPNO 290
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171211
Time 15.43
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447233 sec
RG 49.81
DW 62.400 usec
DE 6.50 usec
TE 298.6 K
D1 2.00000000 sec
TD0 1
SF01 400.2424716 MHz
NUC1 1H
P1 14.80 usec
PLW1 12.00000000 W

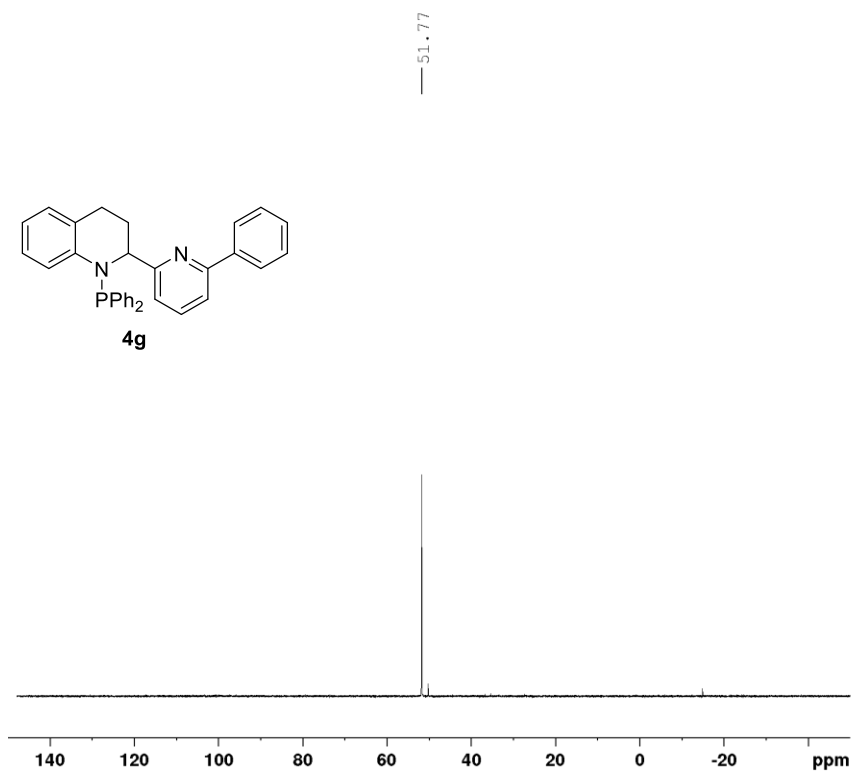
F2 - Processing parameters
SI 65536
SF 400.2400178 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME 400M2017
EXPNO 291
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171211
Time 15.46
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 470
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 206.33
DW 20.800 usec
DE 6.50 usec
TE 298.8 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999999 sec
TD0 1
SF01 100.6504916 MHz
NUC1 13C
P1 10.00 usec
PLW1 54.00000000 W
SFO2 400.2416010 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.34680000 W
PLW13 0.28090999 W

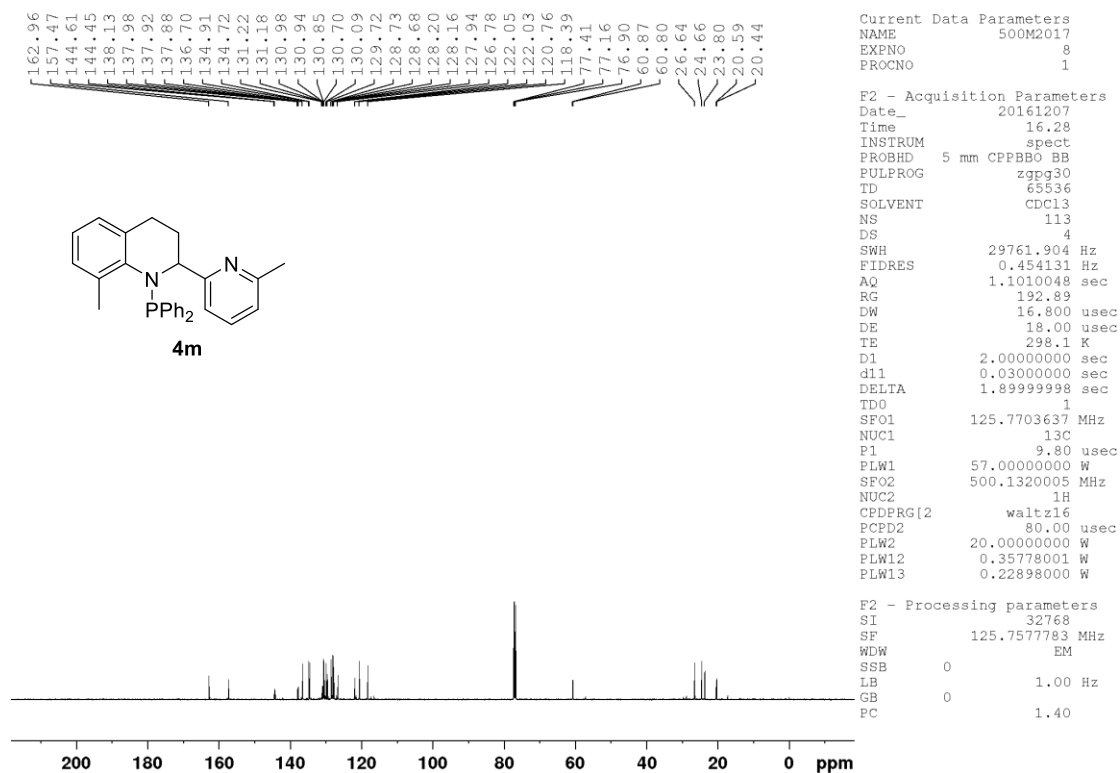
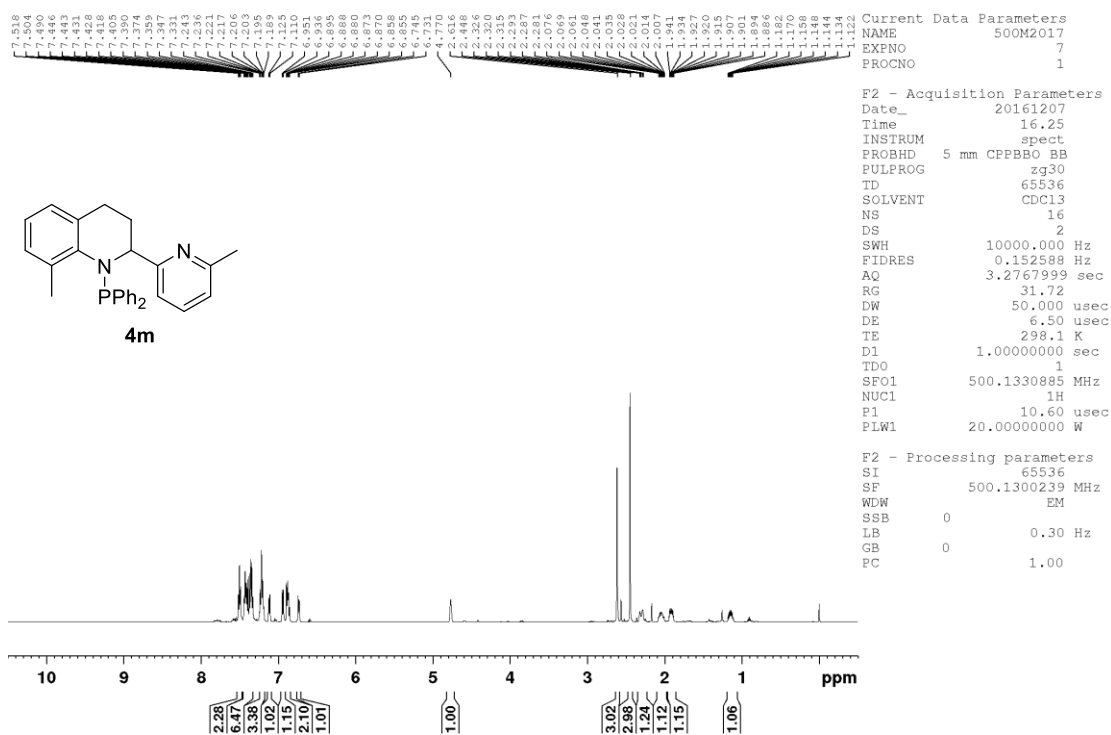
F2 - Processing parameters
SI 32768
SF 100.6404151 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

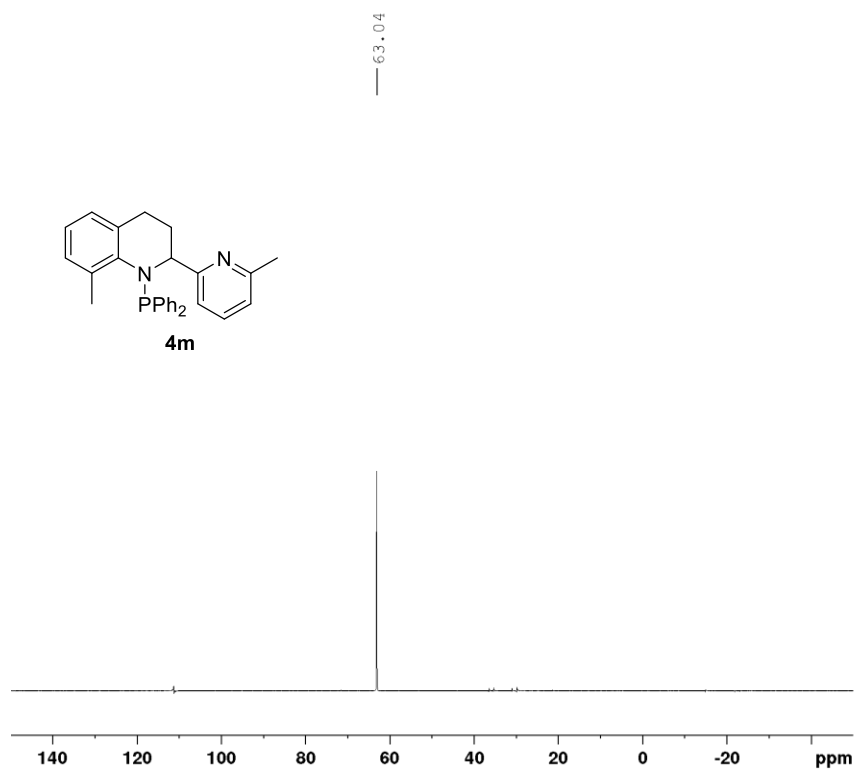


Current Data Parameters
NAME 400 M P31
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171211
Time 17.18
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 16
DS 4
SWH 64102.563 Hz
FIDRES 0.978127 Hz
AQ 0.5111808 sec
RG 206.33
DW 7.800 usec
DE 6.50 usec
TE 298.7 K
D1 2.0000000 sec
d11 0.0300000 sec
DELTA 1.89999998 sec
TD0 1
SF01 162.0120208 MHz
NUC1 31P
P1 14.60 usec
PLW1 13.00000000 W
SF02 400.2416010 MHz
NUC2 1H
CPDPRG12 waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.34680000 W
PLW13 0.28090999 W

F2 - Processing parameters
SI 32768
SF 162.0201218 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

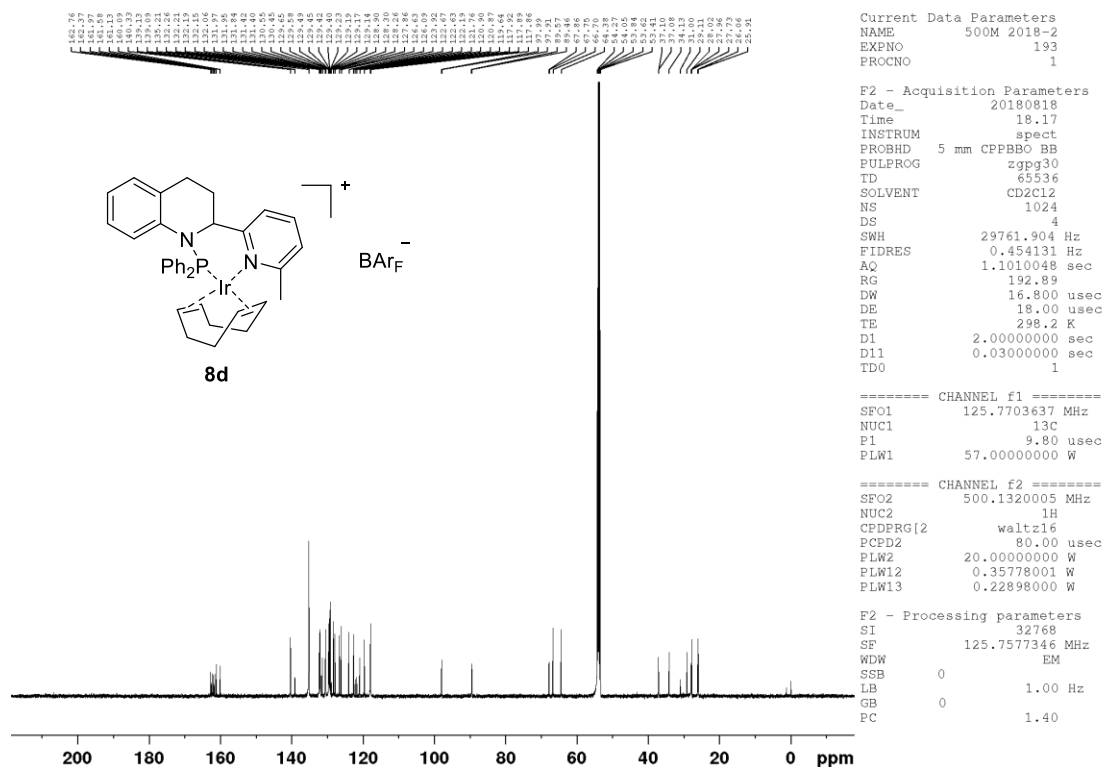
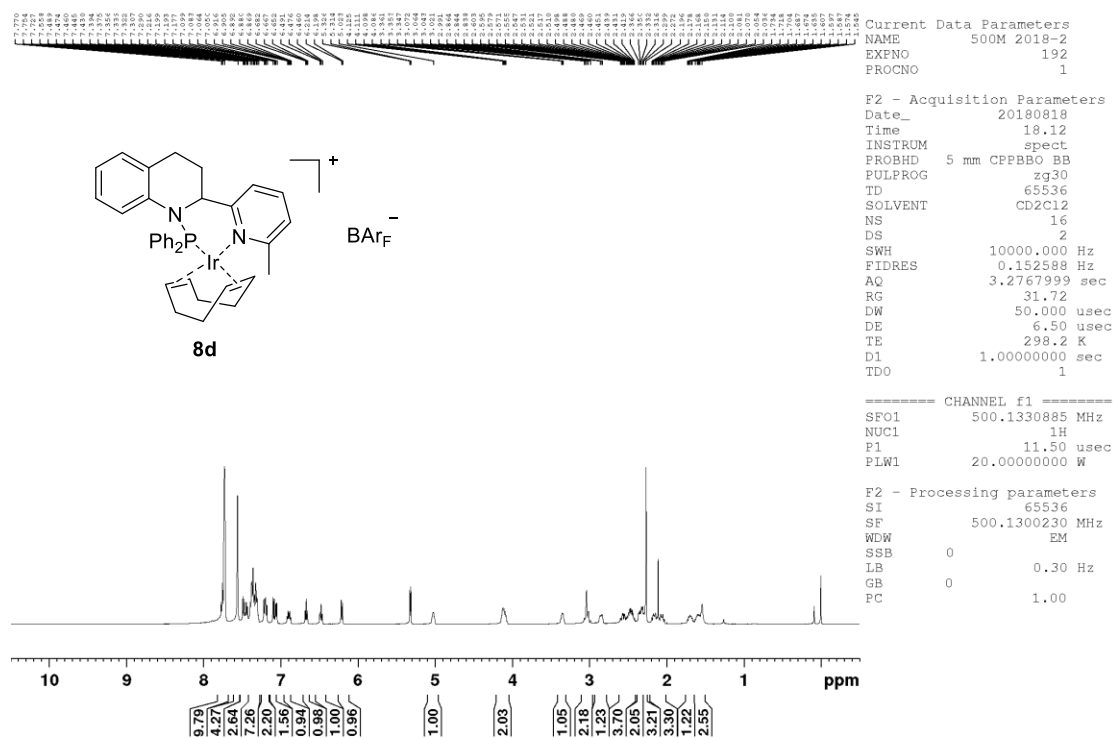


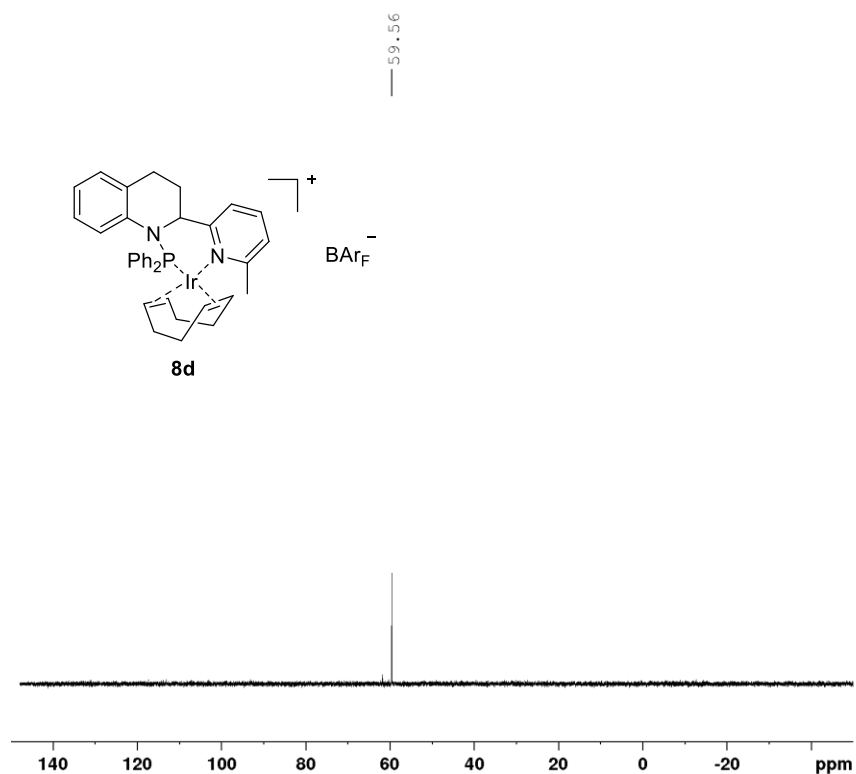


Current Data Parameters
NAME 500M P31
EXPNO 5
PROCNO 1

F2 - Acquisition Parameters
Date_ 20161207
Time 16.13
INSTRUM spect
PROBHD 5 mm CPBBO BB
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 16
DS 4
SWH 100000.000 Hz
FIDRES 1.525879 Hz
AQ 0.3276800 sec
RG 192.89
DW 5.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SF01 202.4664578 MHz
NUC1 31P
P1 11.50 usec
PLW1 52.96599960 W
SF02 500.1320005 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 80.00 usec
PLW2 20.00000000 W
PLW12 0.35778001 W
PLW13 0.22898000 W

F2 - Processing parameters
SI 32768
SF 202.4563350 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40





Current Data Parameters

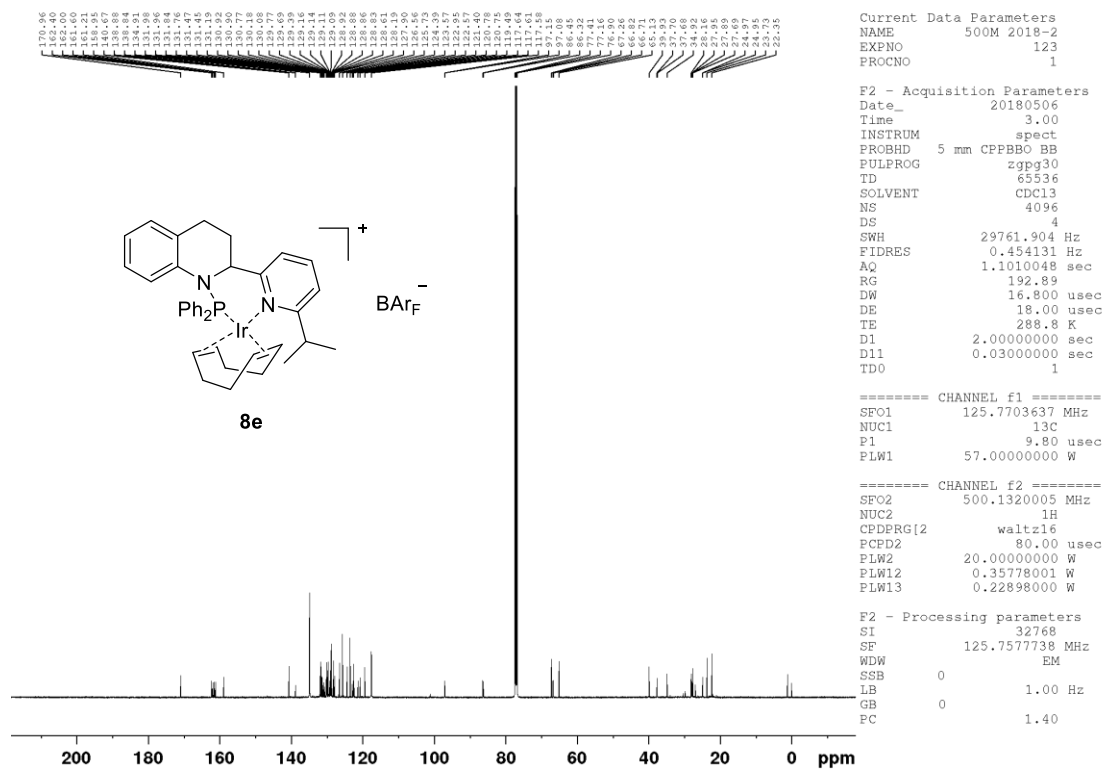
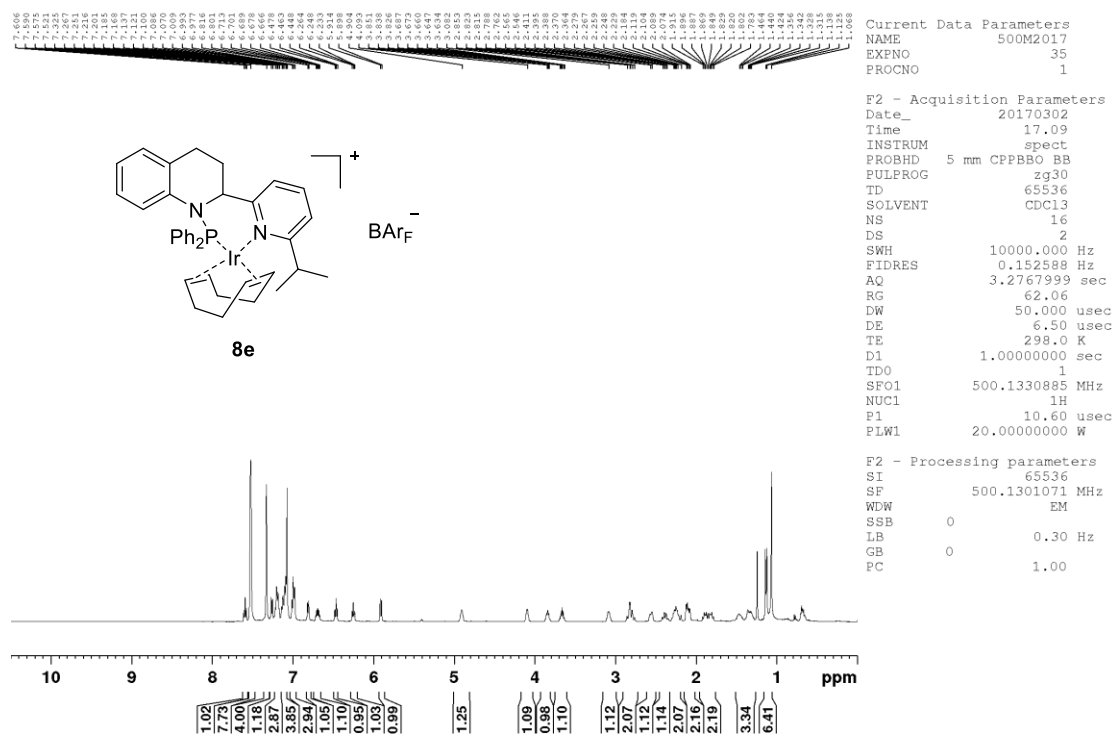
NAME	400 M P31
EXPNO	11
PROCNO	1

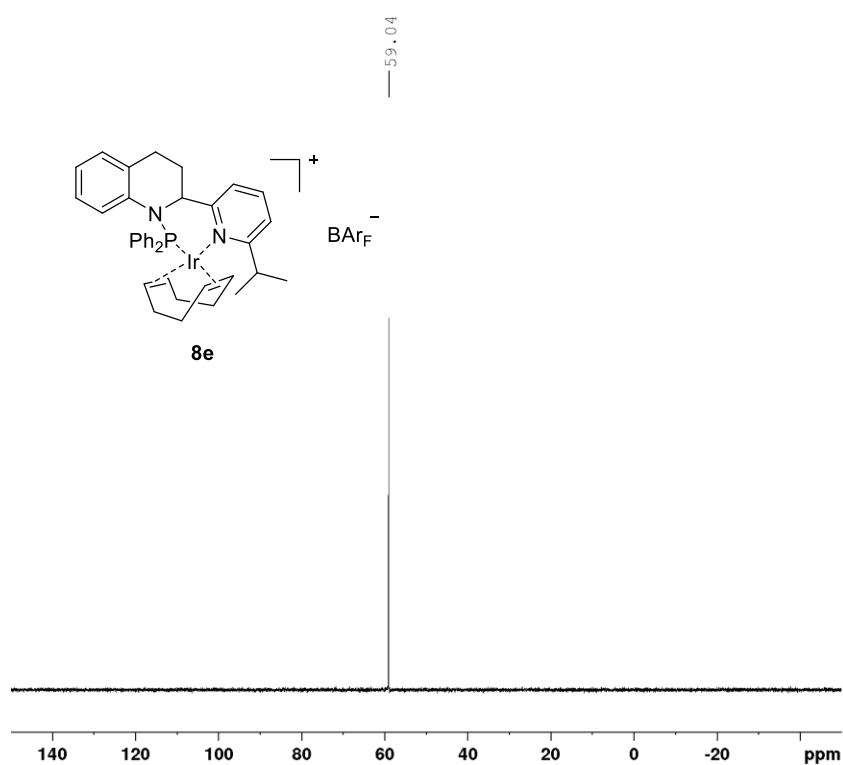
F2 - Acquisition Parameters

Date_	20171211
Time	21.08
INSTRUM	spect
PROBHD	5 mm PABBO BB/
PULPROG	zgpg30
TD	65536
SOLVENT	Acetone
NS	16
DS	4
SWH	64102.563 Hz
FIDRES	0.978127 Hz
AQ	0.5111808 sec
RG	206.33
DW	7.800 usec
DE	6.50 usec
TE	298.3 K
D1	2.00000000 sec
d11	0.03000000 sec
DELTA	1.89999998 sec
TD0	1
SFO1	162.0120208 MHz
NUC1	31P
P1	14.60 usec
PLW1	13.00000000 W
SFO2	400.2416010 MHz
NUC2	1H
CPDPRG[2]	waltz16
PCPD2	90.00 usec
PLW2	12.00000000 W
PLW12	0.34680000 W
PLW13	0.28090999 W

F2 - Processing parameters

SI	32768
SF	162.0201218 MHz
WDW	EM
SSB	0
LB	1.00 Hz
GB	0
PC	1.40

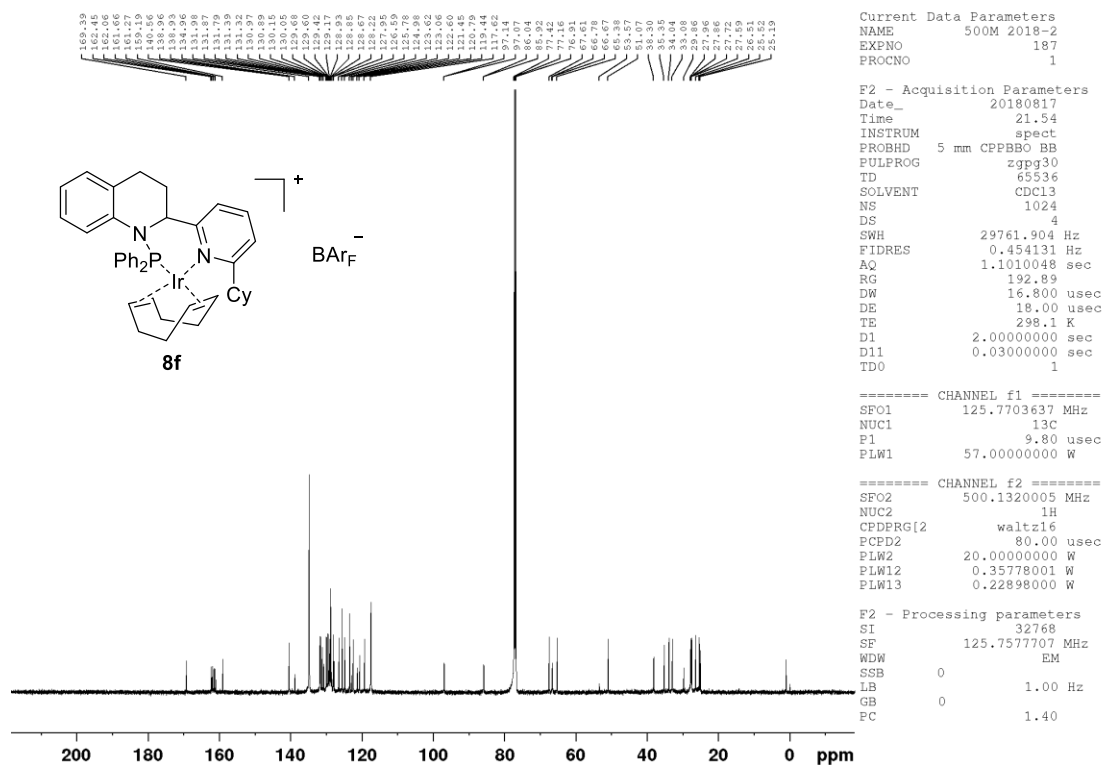
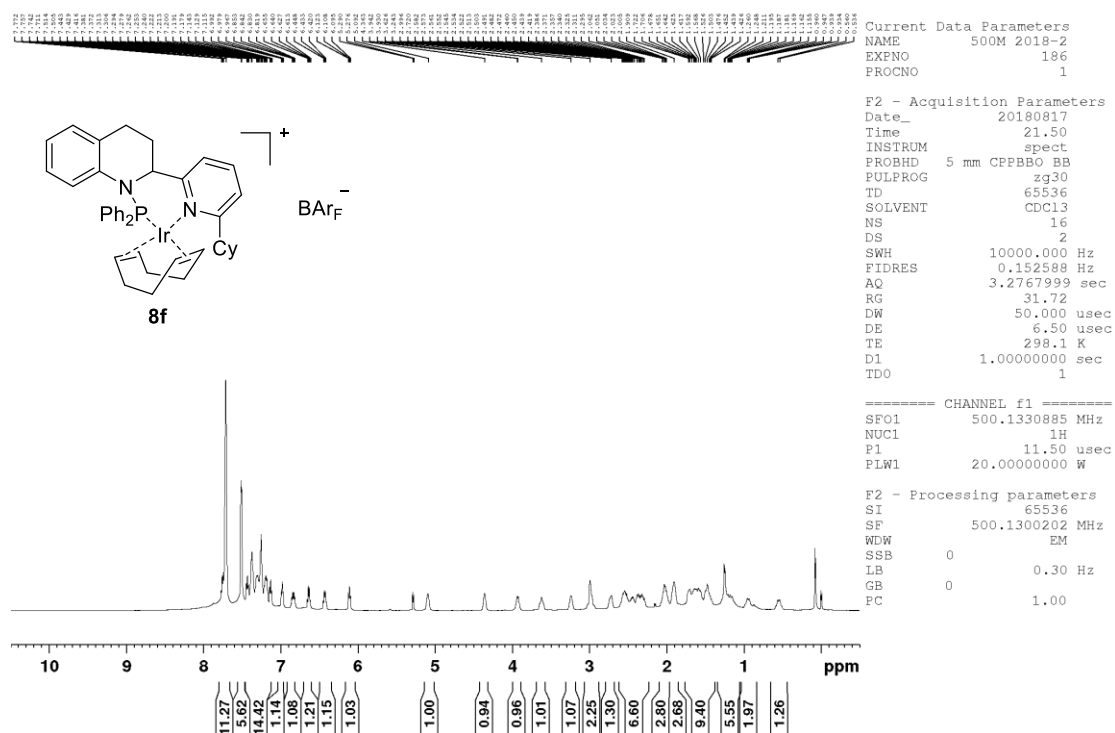


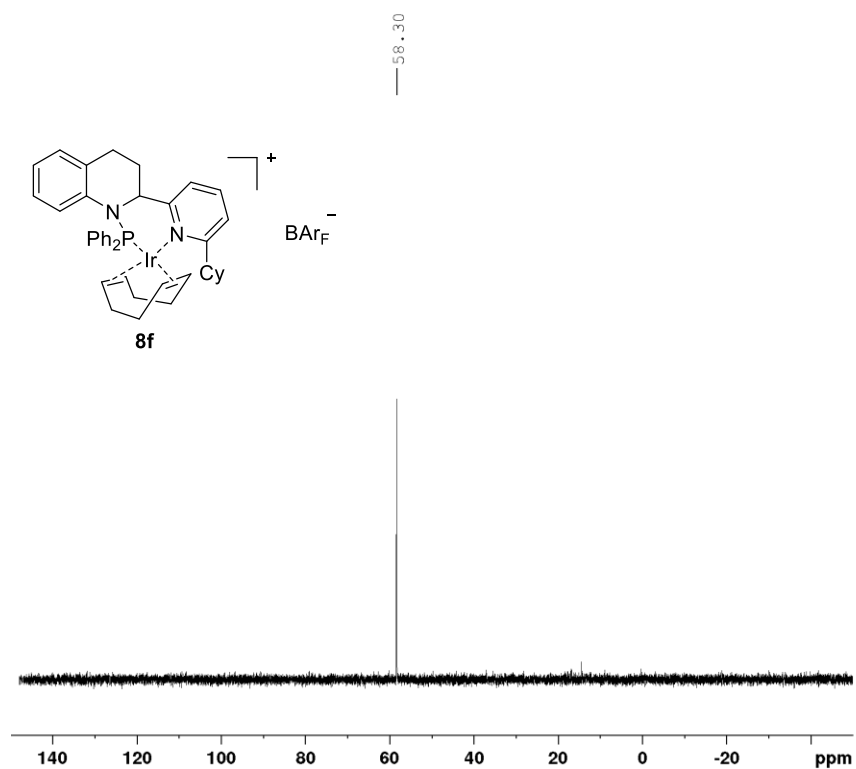


Current Data Parameters
NAME 500M P31
EXPNO 17
PROCNO 1

F2 - Acquisition Parameters
Date_ 20170302
Time 17.05
INSTRUM spect
PROBHD 5 mm CFPBBO BB
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 16
DS 4
SWH 100000.000 Hz
FIDRES 1.525879 Hz
AQ 0.3276800 sec
RG 192.89
DW 5.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 202.4664578 MHz
NUC1 31P
P1 11.50 usec
PLW1 52.96599960 W
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 80.00 usec
PLW2 20.00000000 W
PLW12 0.35778001 W
PLW13 0.22898000 W

F2 - Processing parameters
SI 32768
SF 202.4563350 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

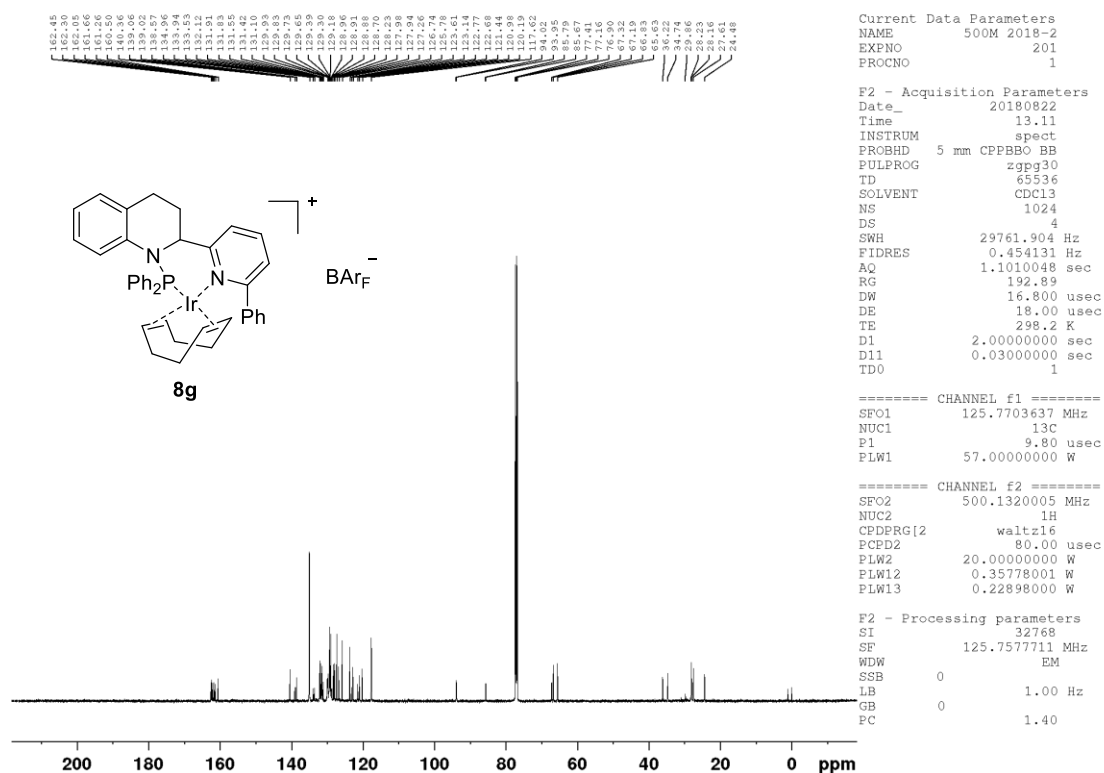
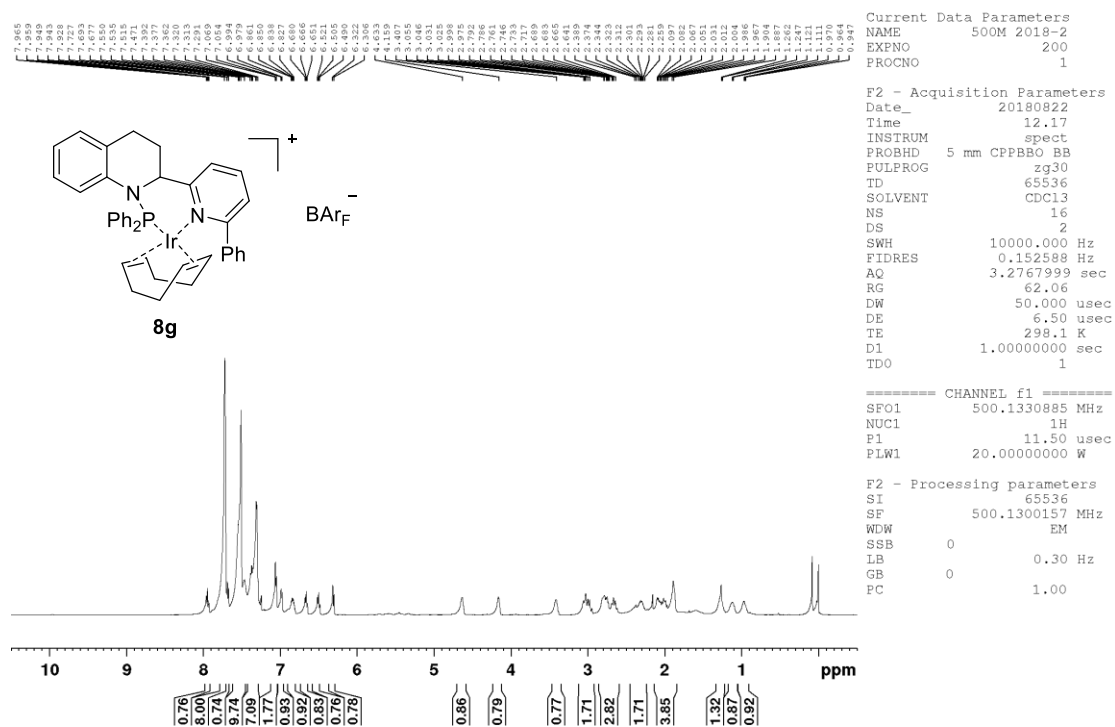


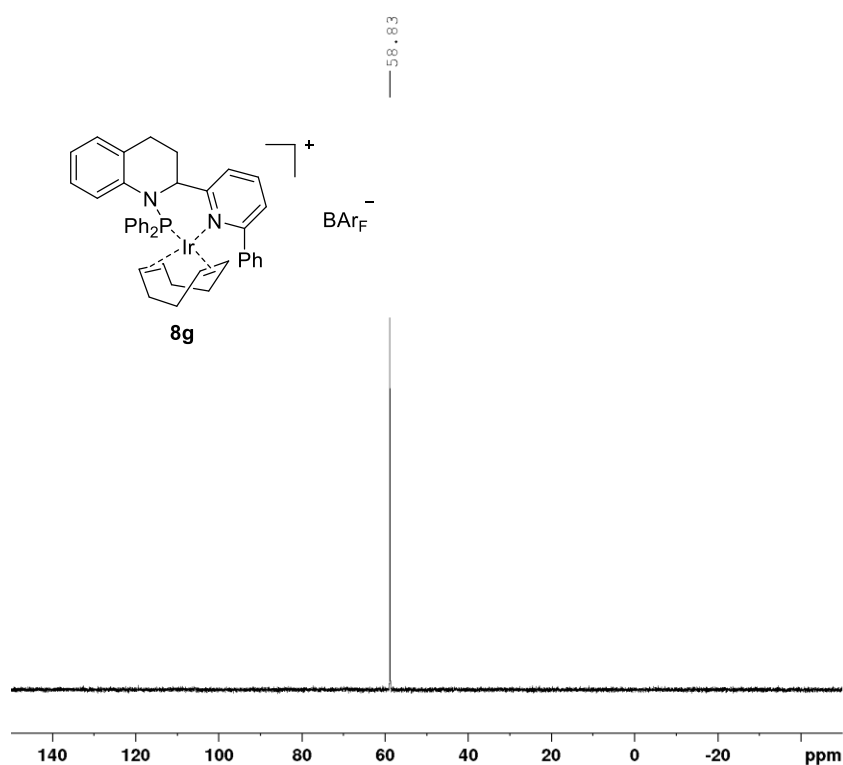


Current Data Parameters
NAME 400 M P31
EXPNO 12
PROCNO 1

F2 - Acquisition Parameters
Date_ 20171211
Time 21.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT Acetone
NS 16
DS 4
SWH 64102.563 Hz
FIDRES 0.978127 Hz
AQ 0.5111808 sec
RG 206.33
DW 7.800 usec
DE 6.50 usec
TE 298.5 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 162.0120208 MHz
NUC1 31P
P1 14.60 usec
PLW1 13.00000000 W
SFO2 400.2416010 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.34680000 W
PLW13 0.28090999 W

F2 - Processing parameters
SI 32768
SF 162.0201218 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

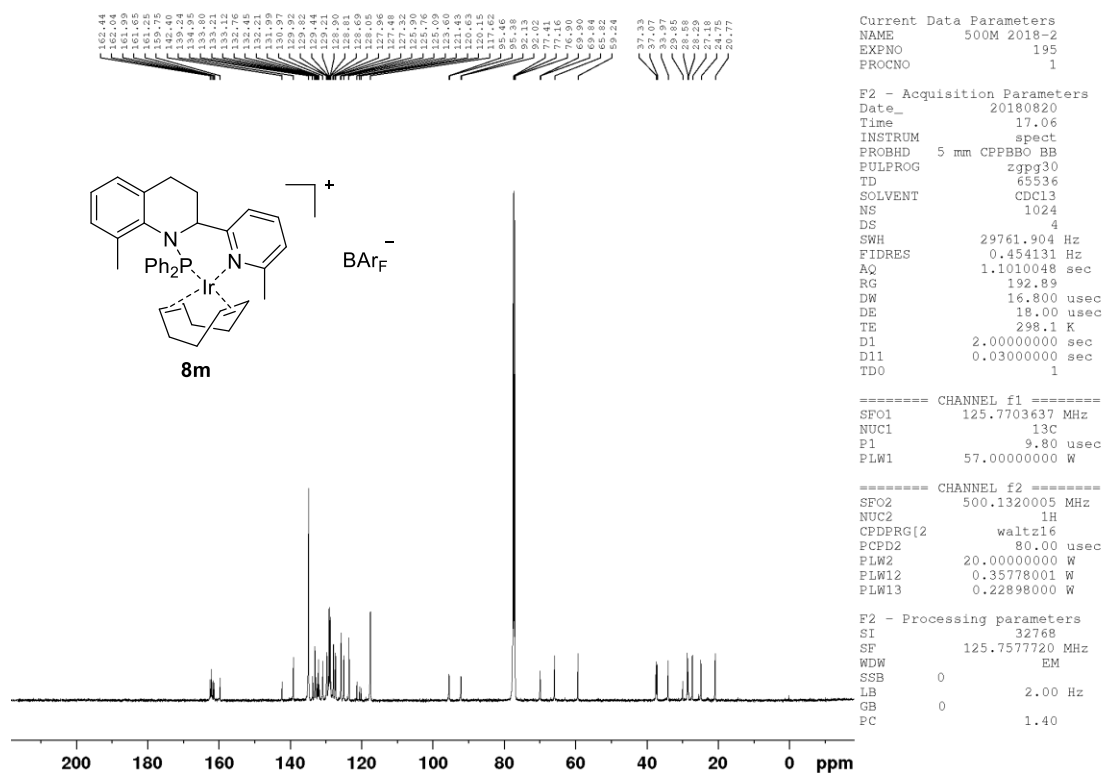
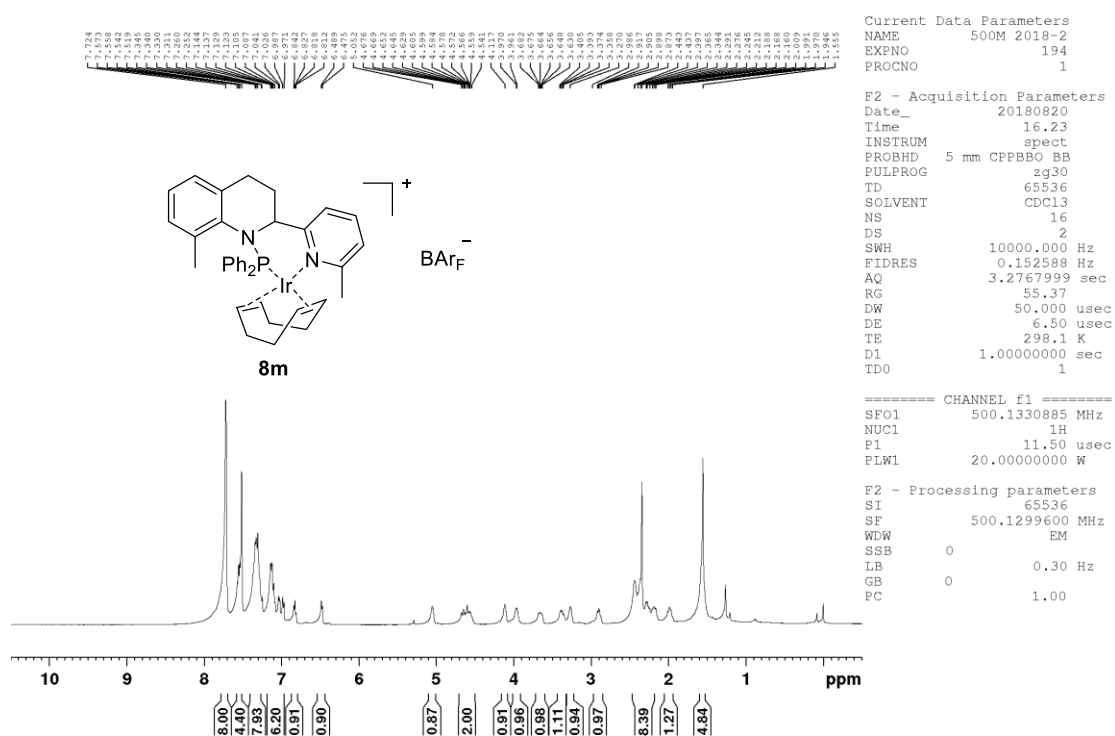


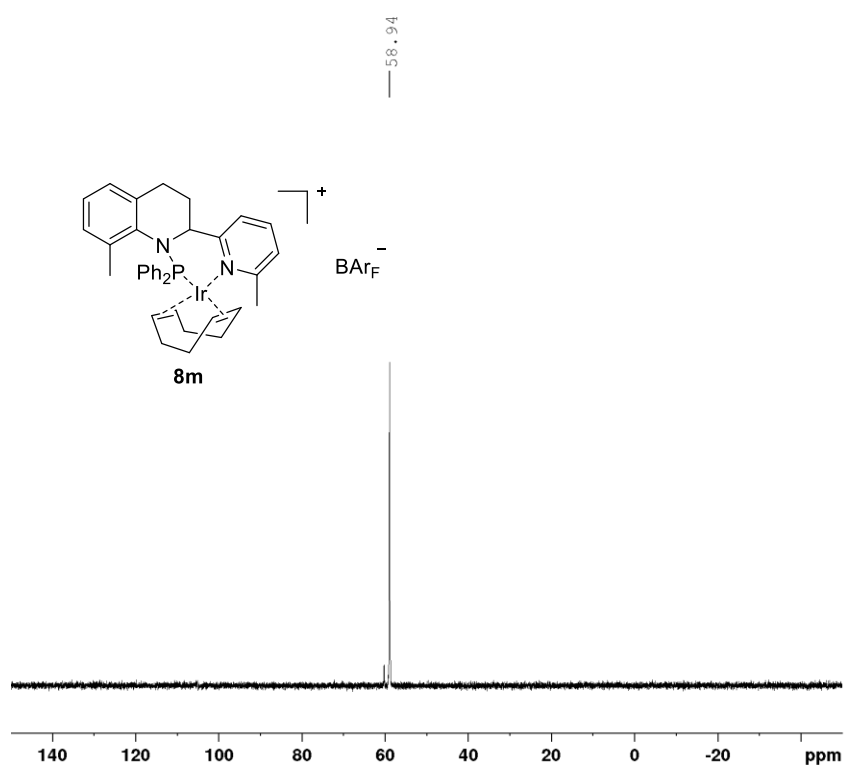


Current Data Parameters
NAME 500M P31
EXPNO 11
PROCNO 1

F2 - Acquisition Parameters
Date_ 20161228
Time 9.38
INSTRUM spect
PROBHD 5 mm CFPBBO BB
PULPROG zgpg
TD 65536
SOLVENT CDCl3
NS 16
DS 4
SWH 100000.000 Hz
FIDRES 1.525879 Hz
AQ 0.3276800 sec
RG 192.89
DW 5.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SF01 202.4664578 MHz
NUC1 31P
P1 11.50 usec
PLW1 52.96599960 W
SF02 500.1320005 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 80.00 usec
PLW2 20.00000000 W
PLW12 0.35778001 W
PLW13 0.22898000 W

F2 - Processing parameters
SI 32768
SF 202.4563350 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

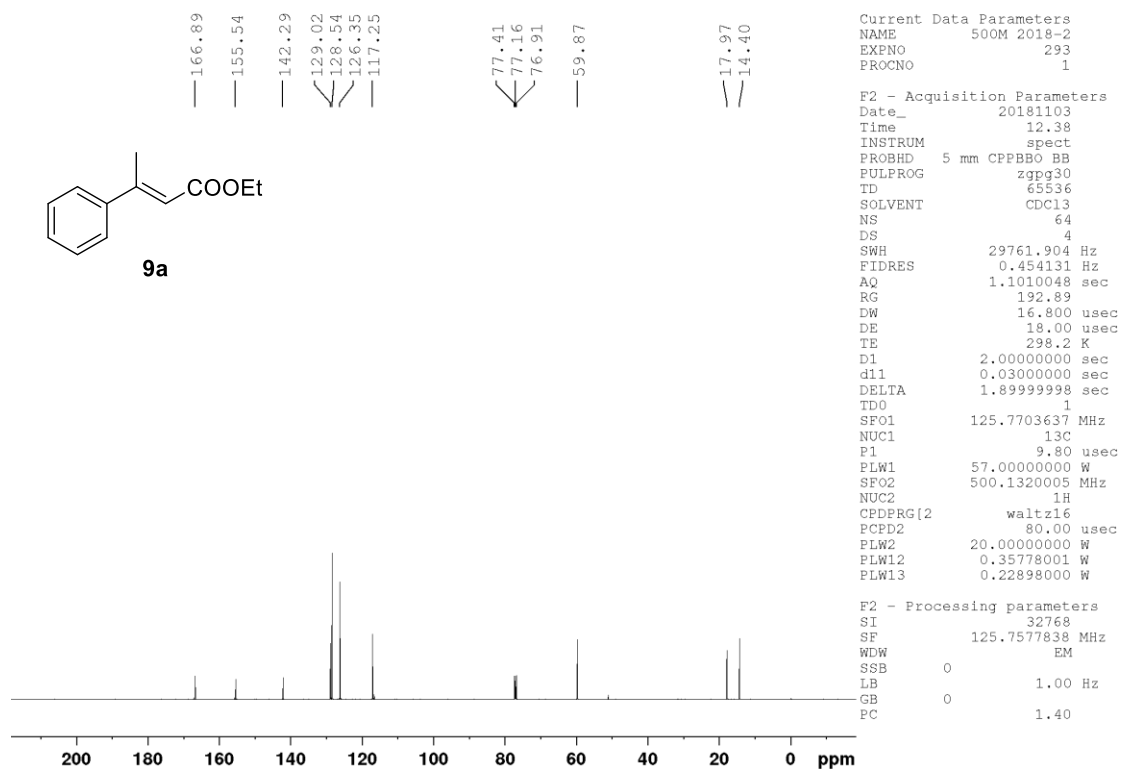
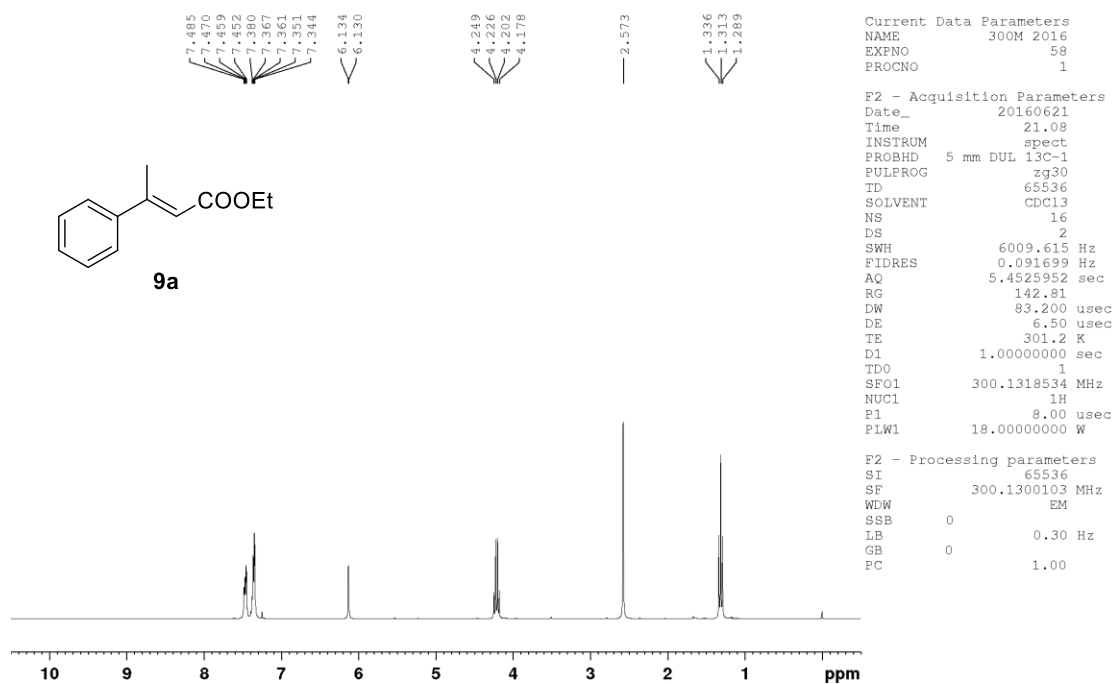


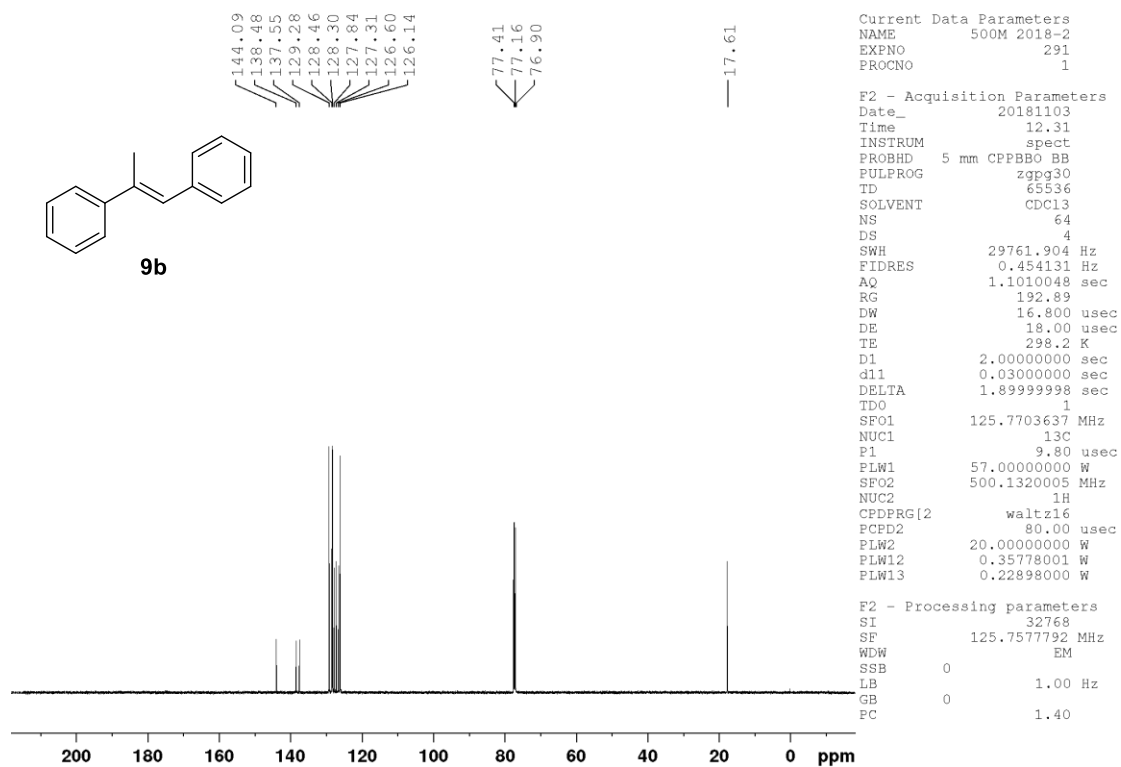
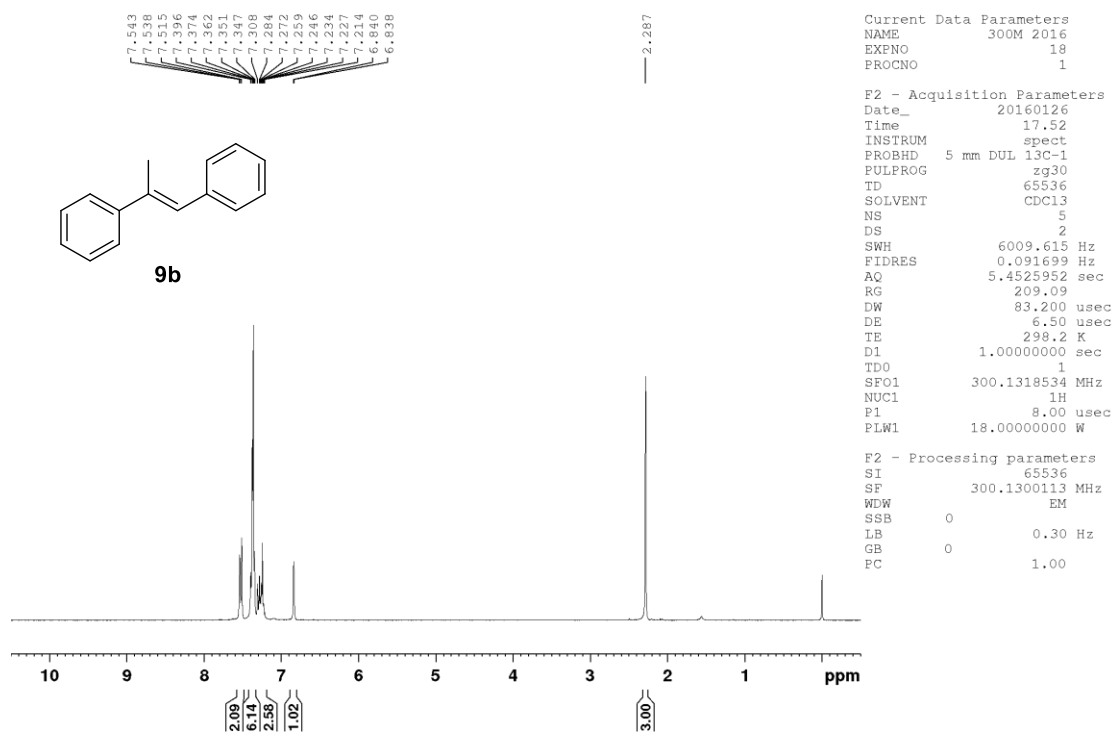


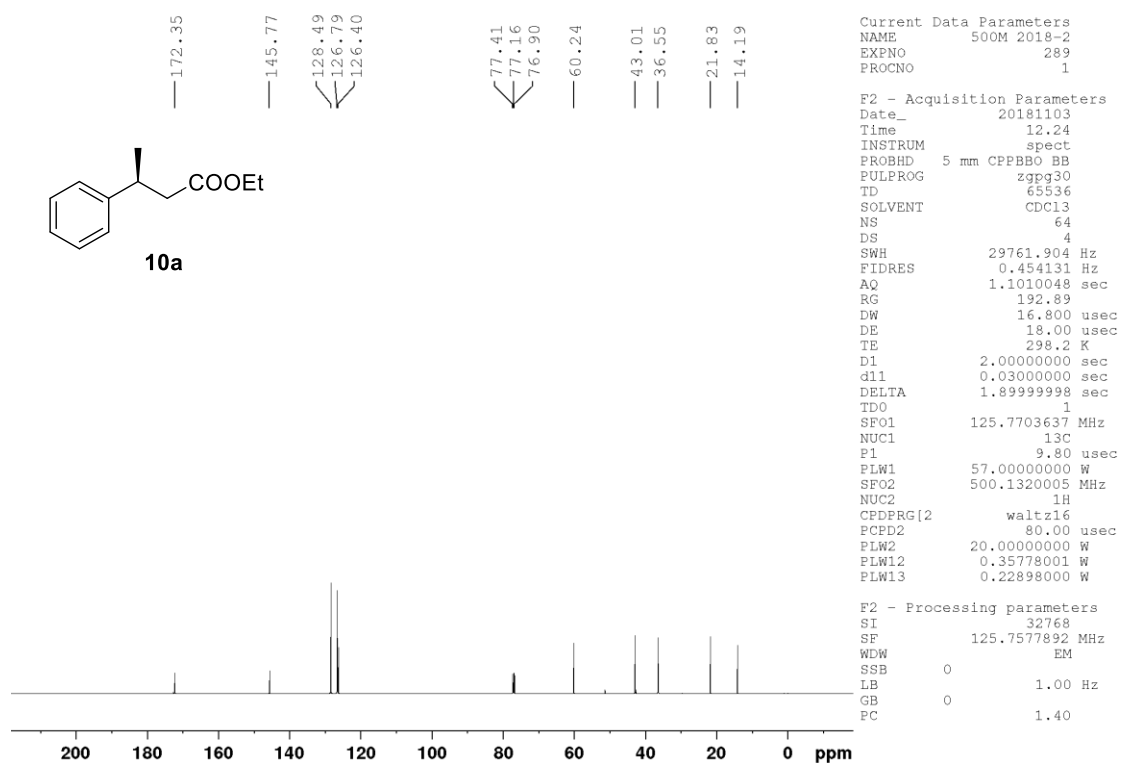
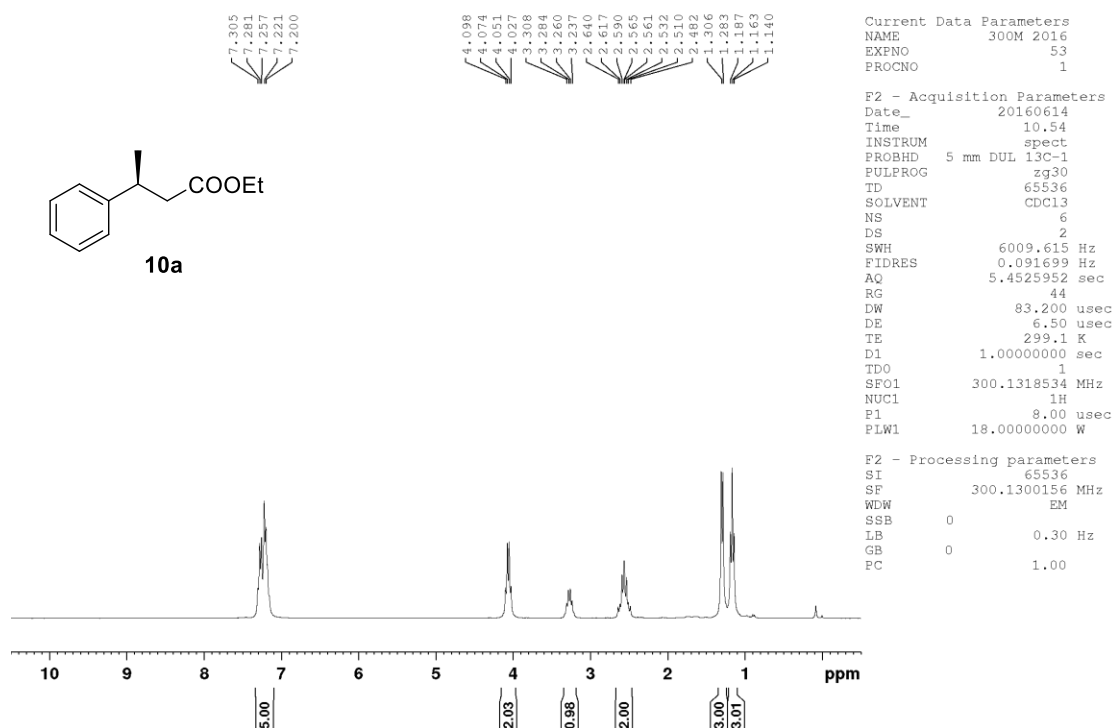
Current Data Parameters
NAME 500M P31
EXPNO 6
PROCNO 1

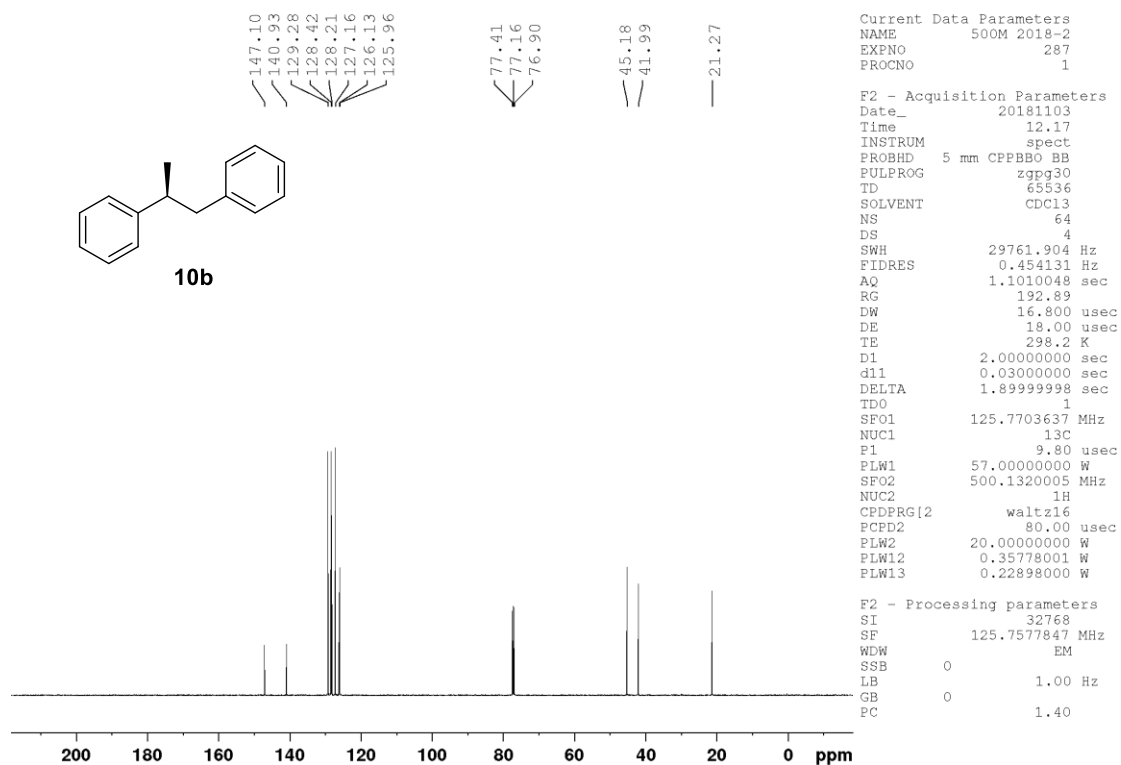
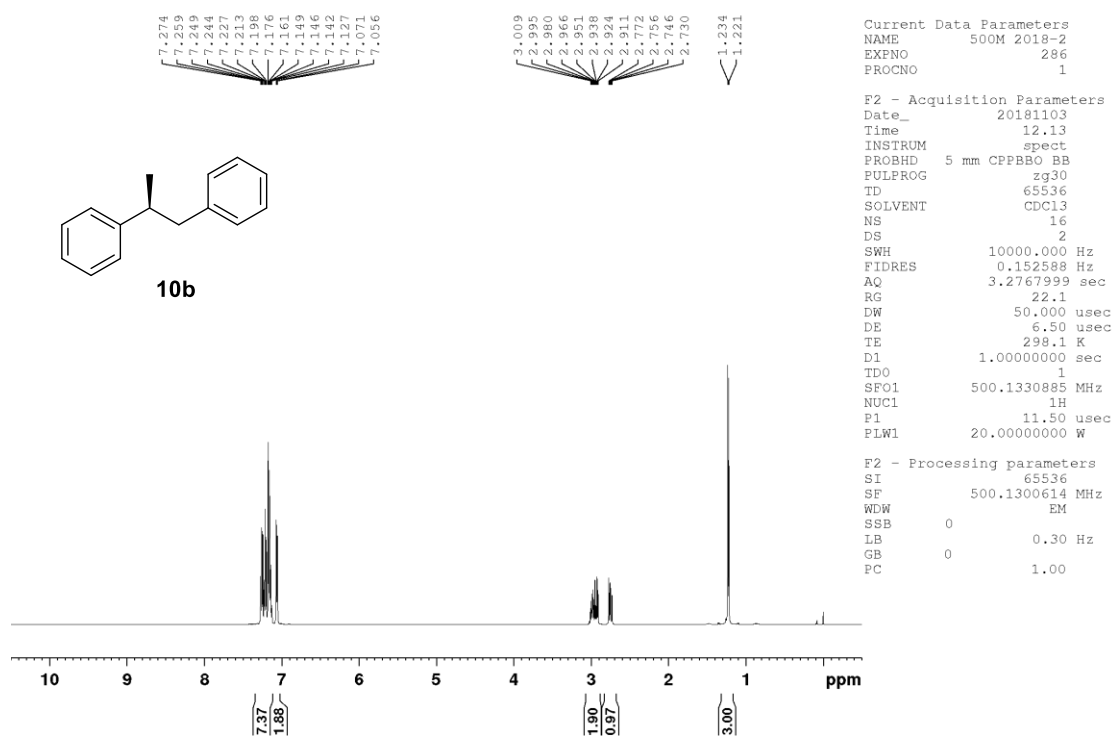
F2 - Acquisition Parameters
Date_ 20161207
Time 16.15
INSTRUM spect
PROBHD 5 mm CFPBBO BB
PULPROG zgpg
TD 65536
SOLVENT CDCl₃
NS 16
DS 4
SWH 100000.000 Hz
FIDRES 1.525879 Hz
AQ 0.3276800 sec
RG 192.89
DW 5.000 usec
DE 18.00 usec
TE 298.0 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SF01 202.4664578 MHz
NUC1 31P
P1 11.50 usec
PLW1 52.96599960 W
SF02 500.1320005 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 80.00 usec
PLW2 20.00000000 W
PLW12 0.35778001 W
PLW13 0.22898000 W

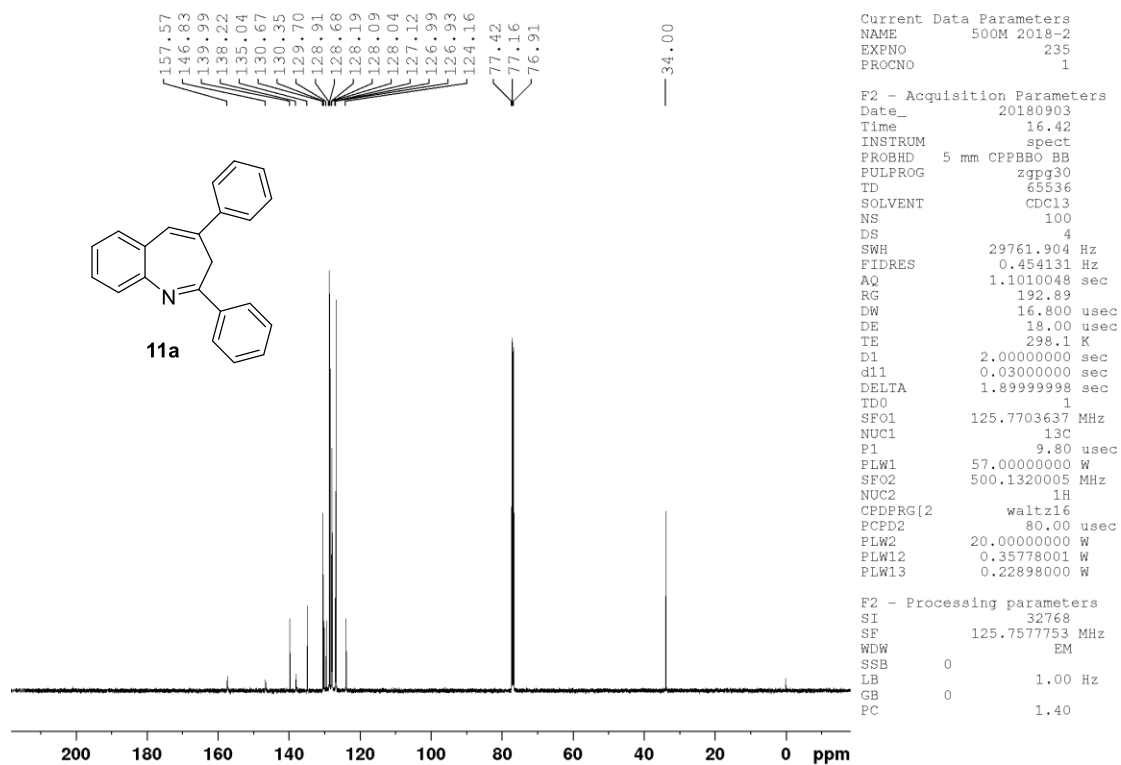
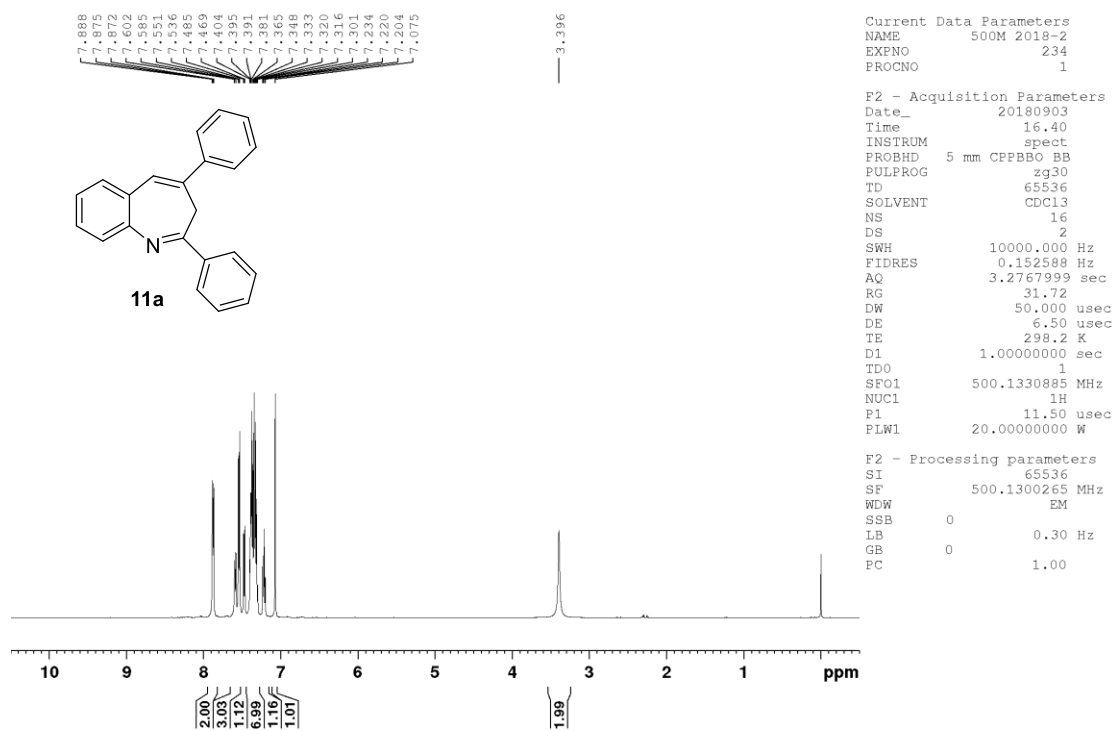
F2 - Processing parameters
SI 32768
SF 202.4563350 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

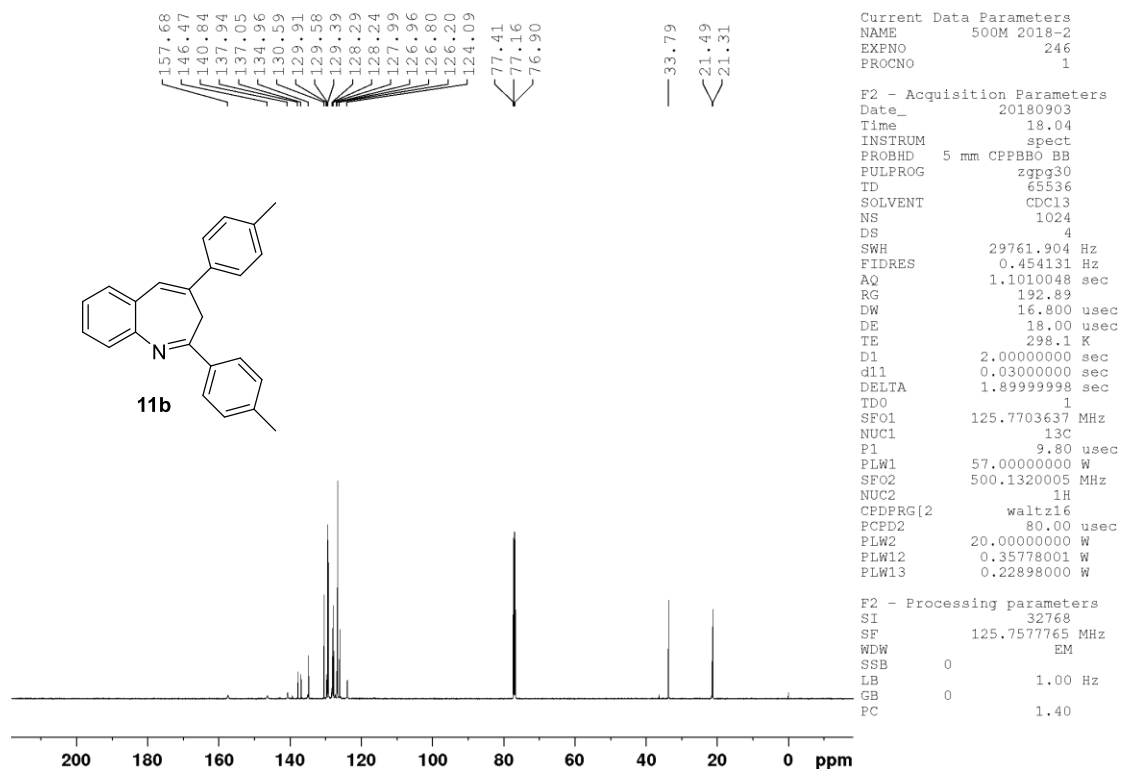
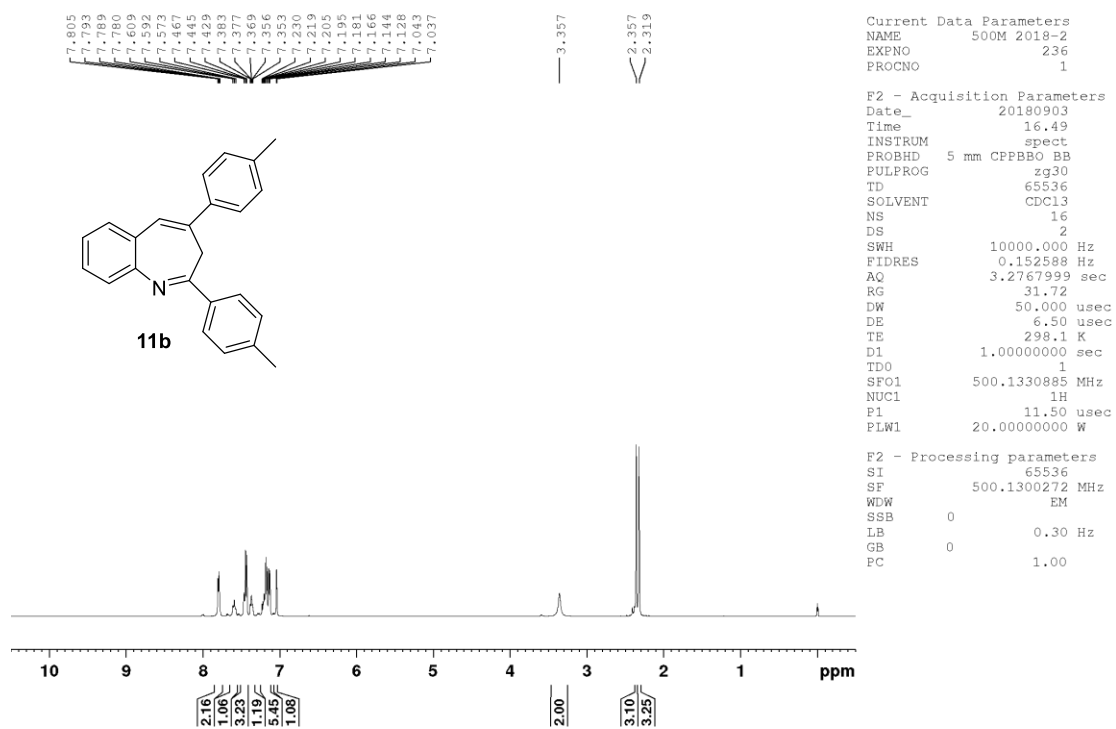


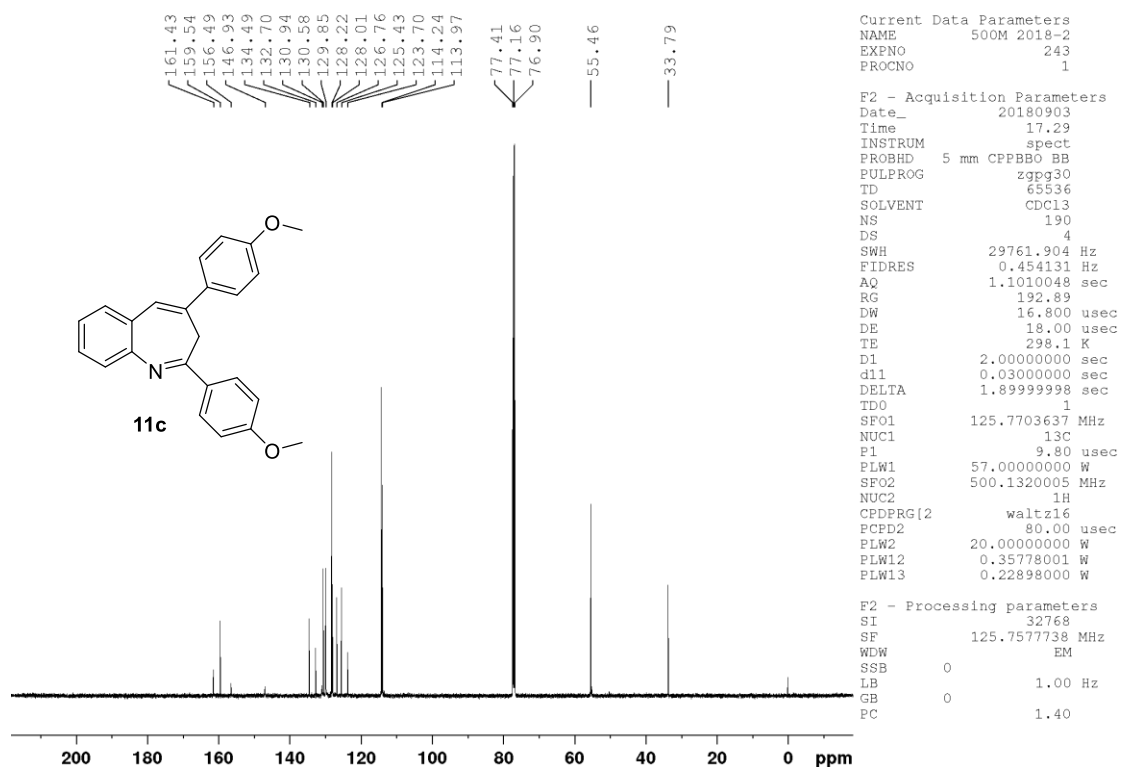
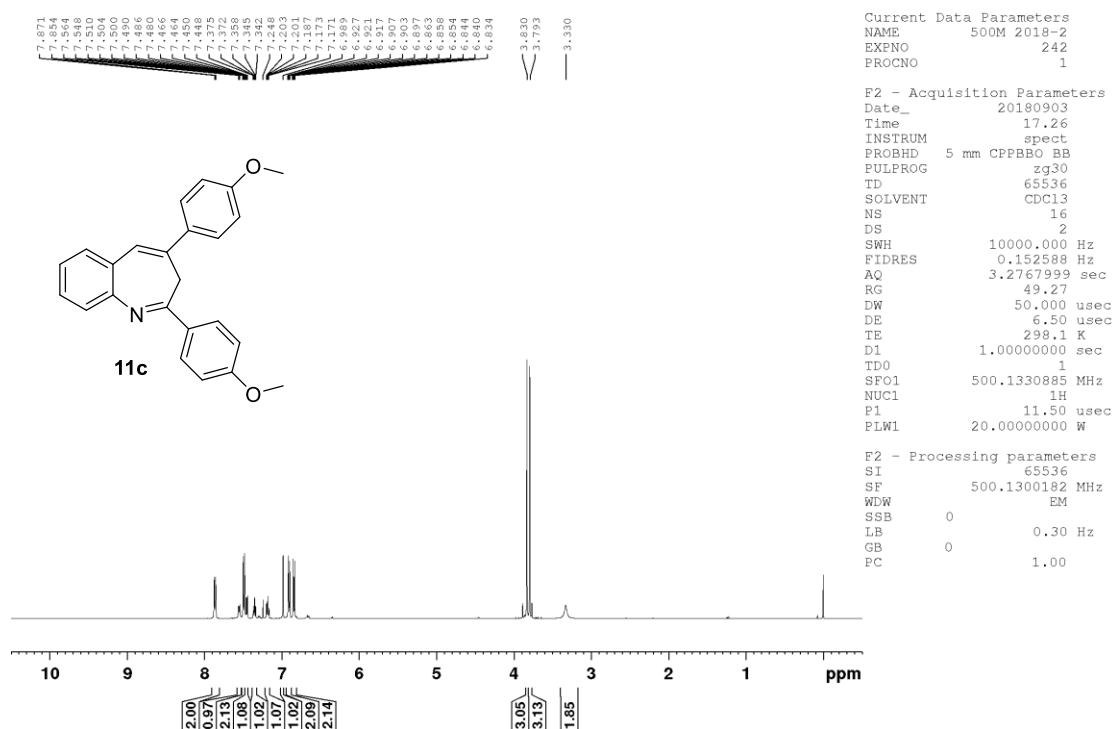


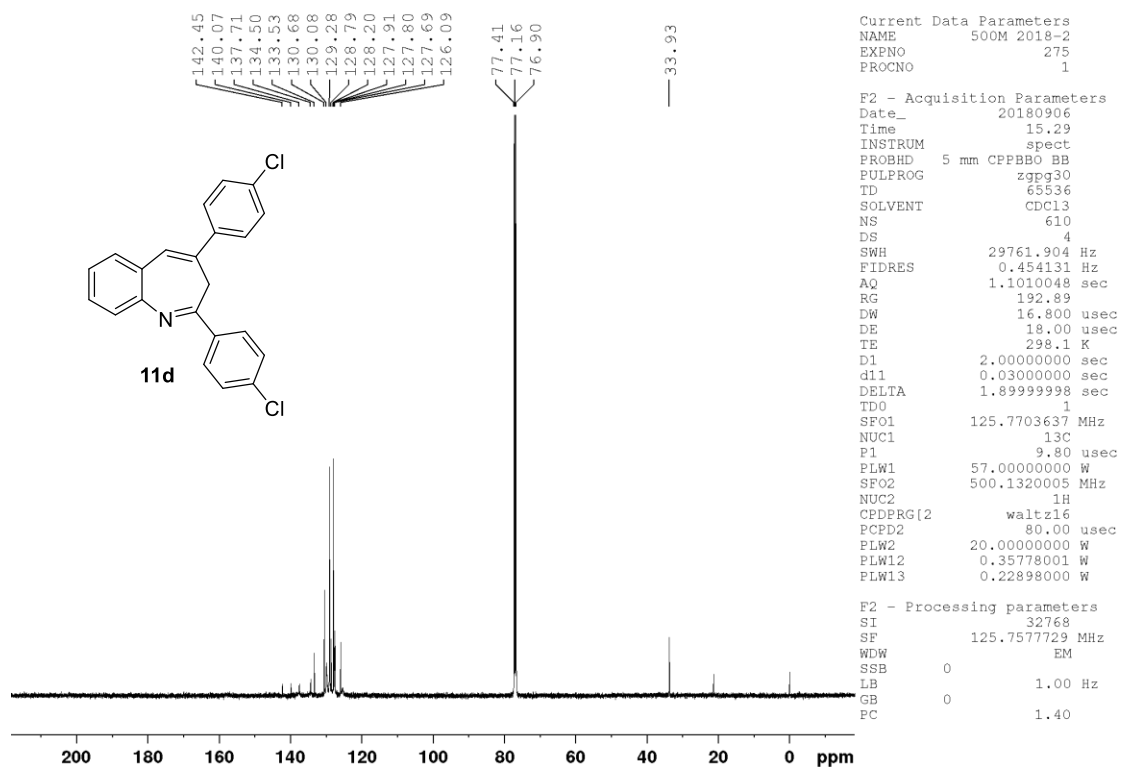
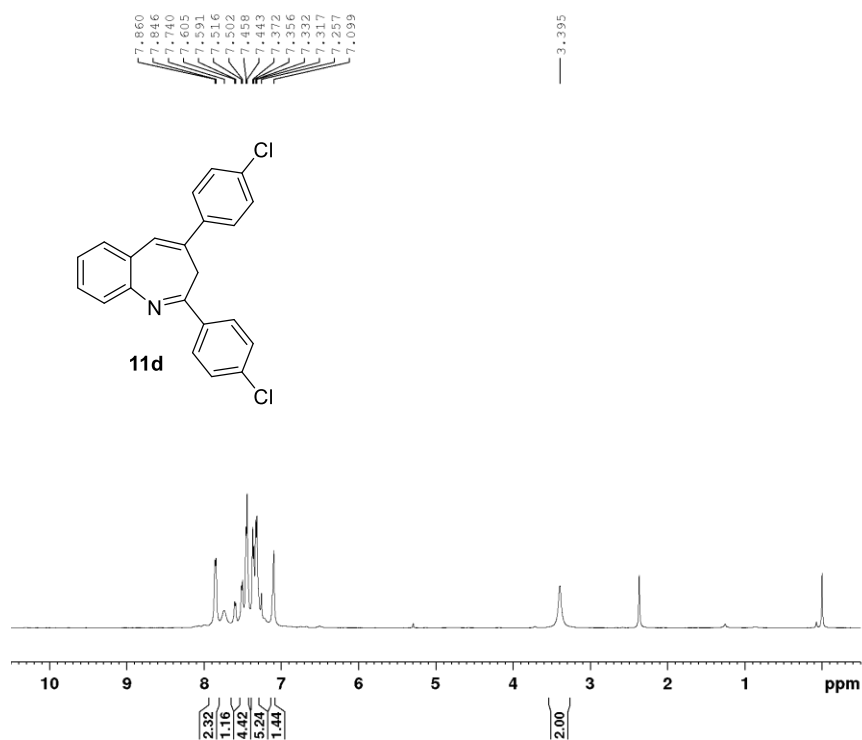


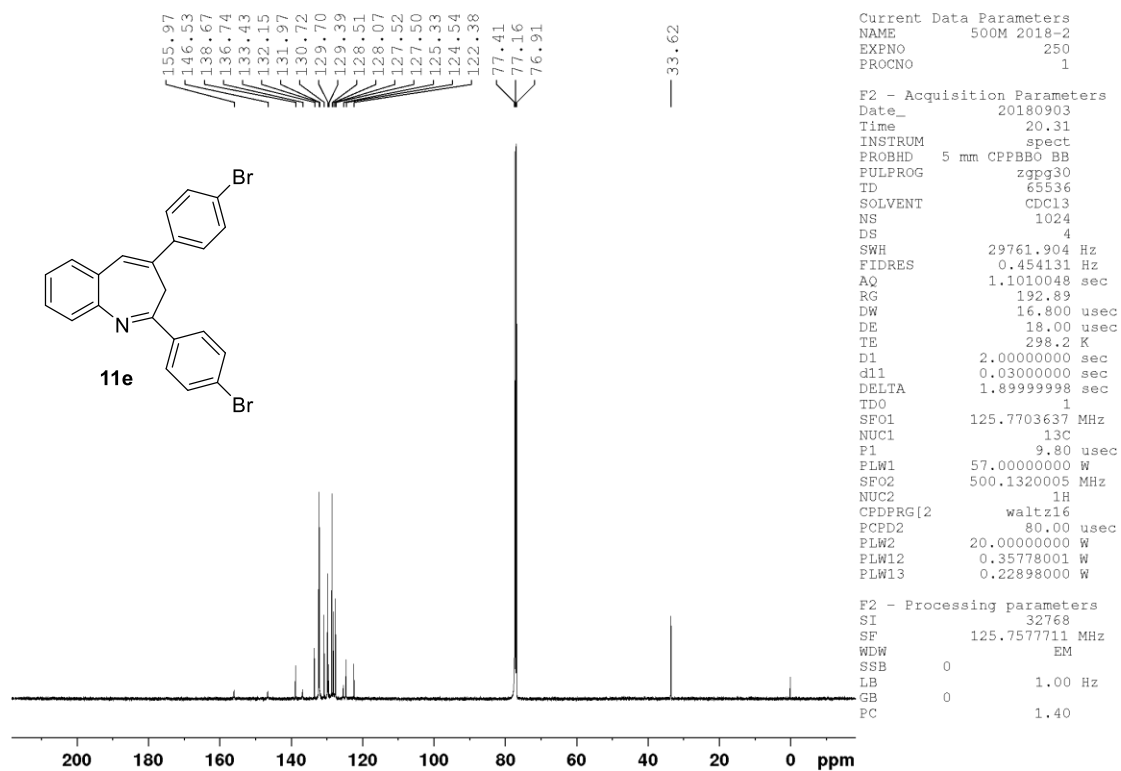
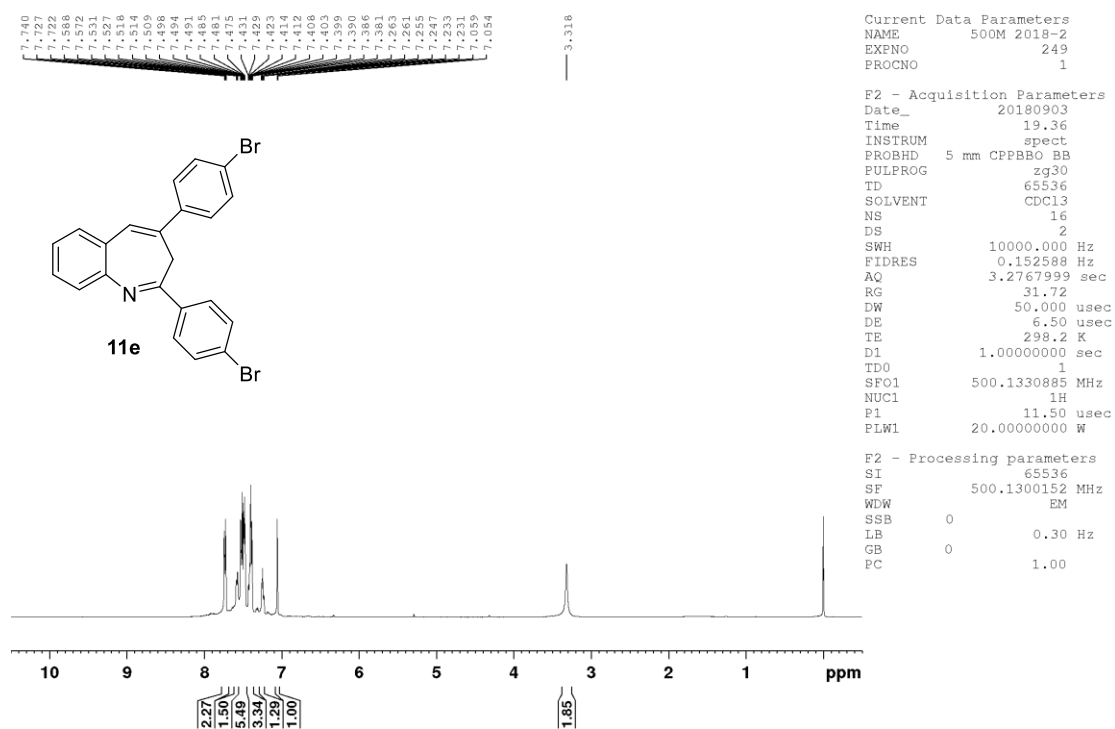


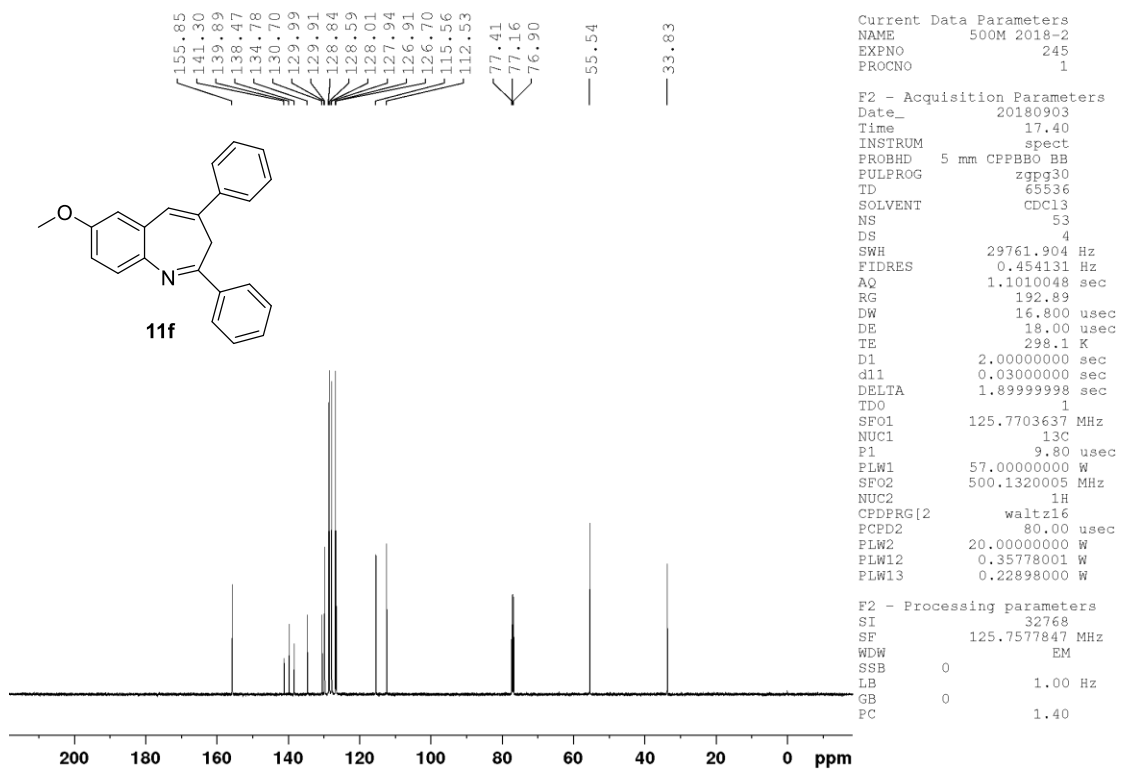
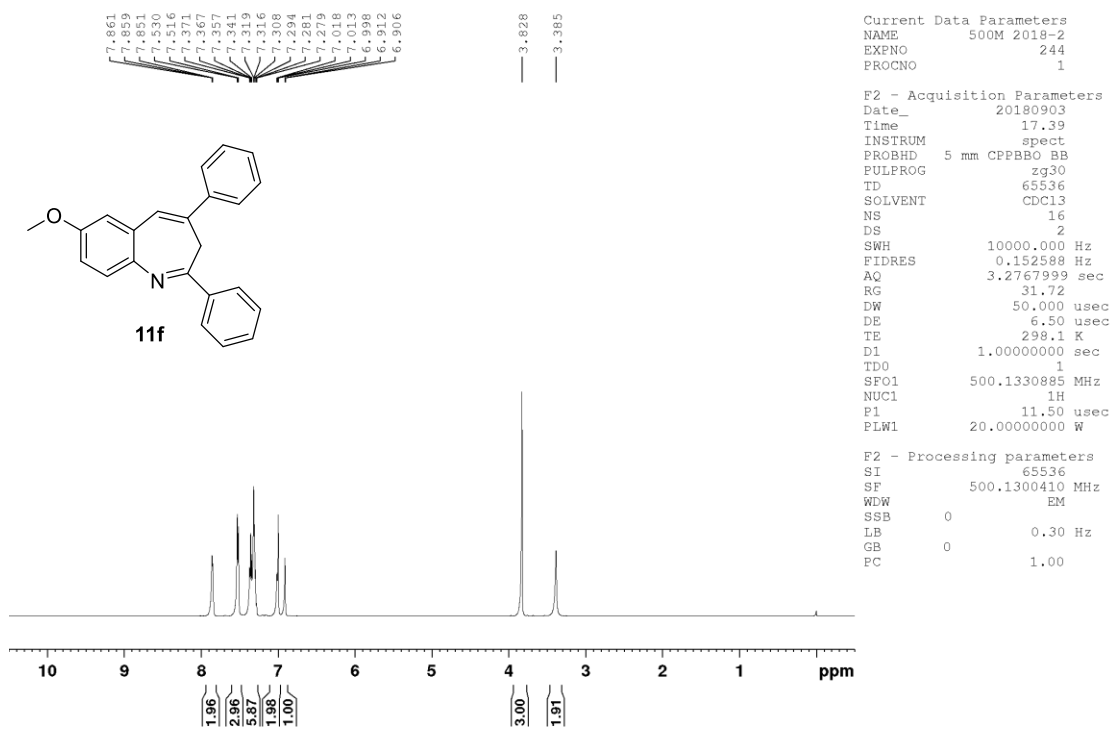


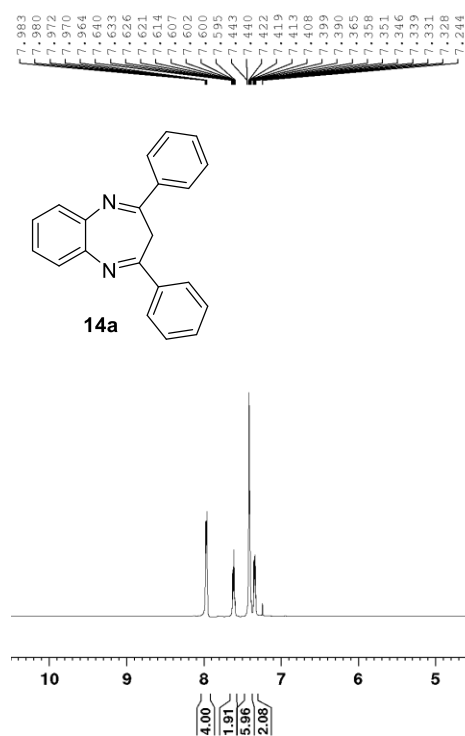








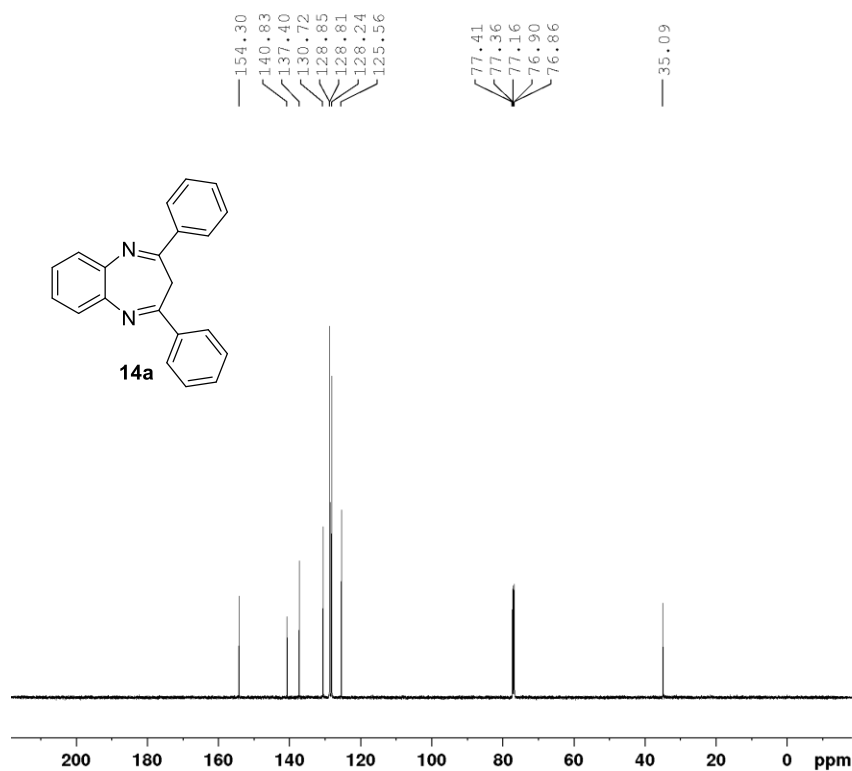




Current Data Parameters
NAME 500M 2018-2
EXPNO 257
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180904
Time 9.58
INSTRUM spect
PROBHD 5 mm CFPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 31.72
DW 50.000 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TDO 1
SFO1 500.1330885 MHz
NUC1 1H
P1 11.50 usec
PLW1 20.00000000 W

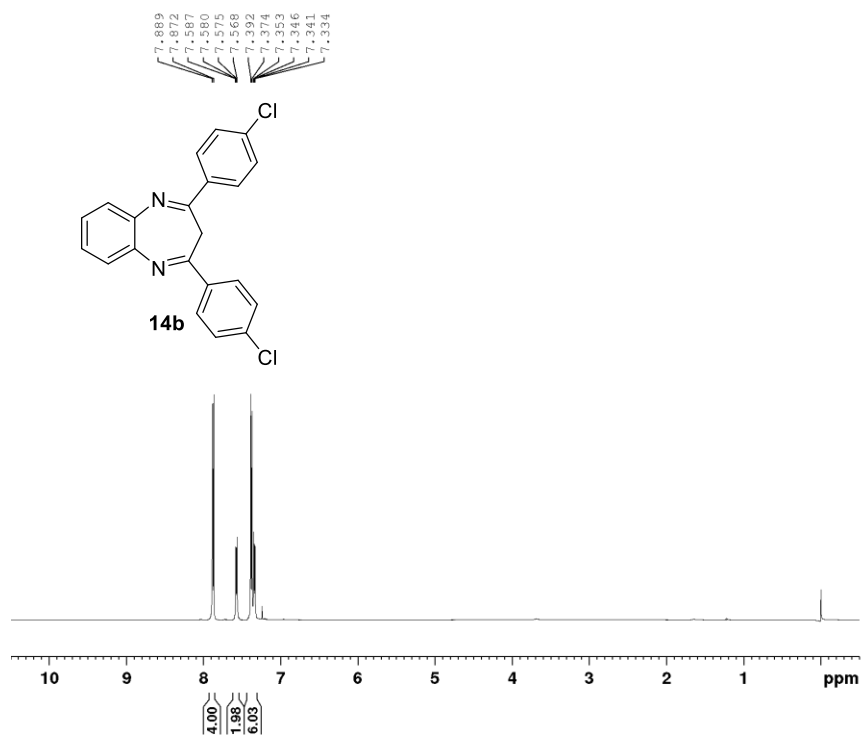
F2 - Processing parameters
SI 65536
SF 500.1300199 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME 500M 2018-2
EXPNO 258
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180904
Time 10.00
INSTRUM spect
PROBHD 5 mm CFPBBO BB
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 37
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 192.89
DW 16.800 usec
DE 18.00 usec
TE 298.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TDO 1
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
PLW1 57.00000000 W
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG[2] waltz16
PCPD2 80.00 usec
PLW2 20.00000000 W
PLW12 0.35778001 W
PLW13 0.22898000 W

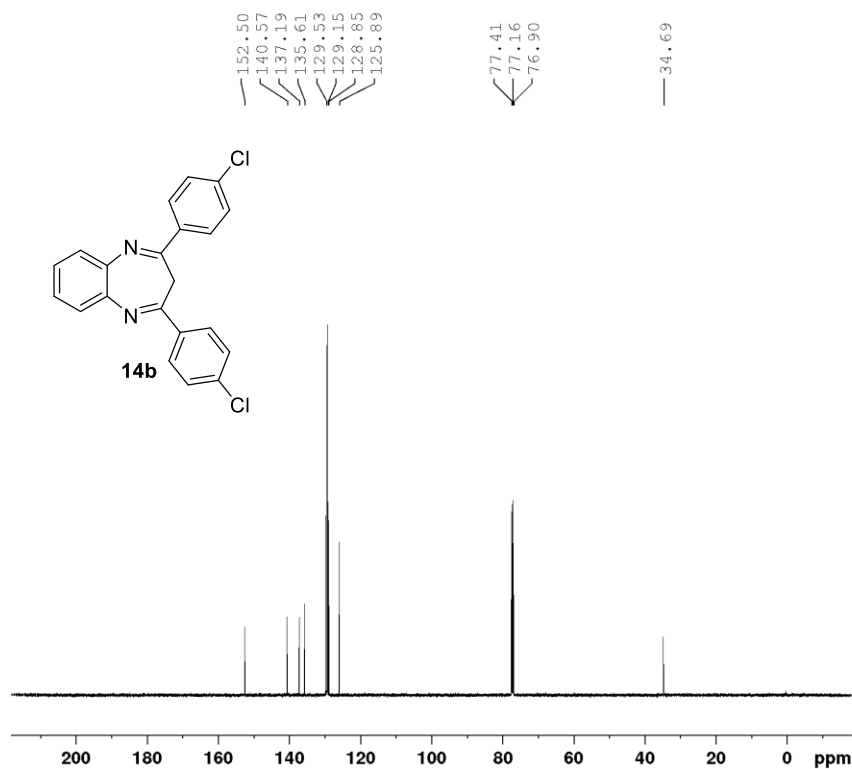
F2 - Processing parameters
SI 32768
SF 125.7577820 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



Current Data Parameters
 NAME 500M 2018-2
 EXPNO 259
 PROCNO 1

F2 - Acquisition Parameters
 Date_ 20180904
 Time 10.05
 INSTRUM spect
 PROBHD 5 mm CFPBBO BB
 PULPROG zg30
 TD 65536
 SOLVENT CDCl3
 NS 16
 DS 2
 SWH 10000.000 Hz
 FIDRES 0.152588 Hz
 AQ 3.2767999 sec
 RG 31.72
 DW 50.000 usec
 DE 6.50 usec
 TE 298.2 K
 D1 1.00000000 sec
 TD0 1
 SFO1 500.1330885 MHz
 NUC1 1H
 P1 11.50 usec
 PLW1 20.00000000 W

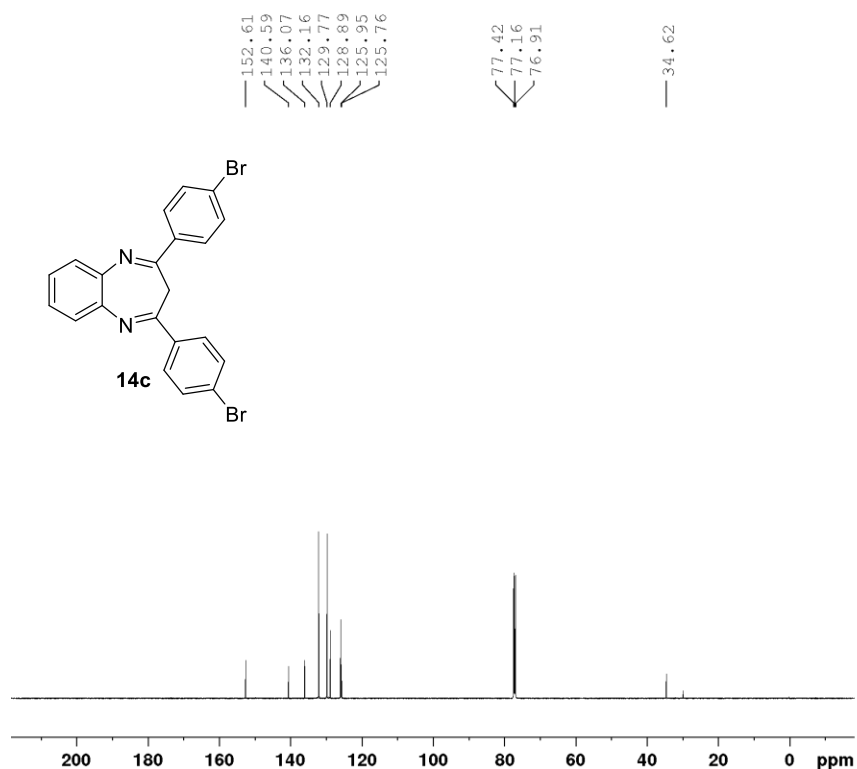
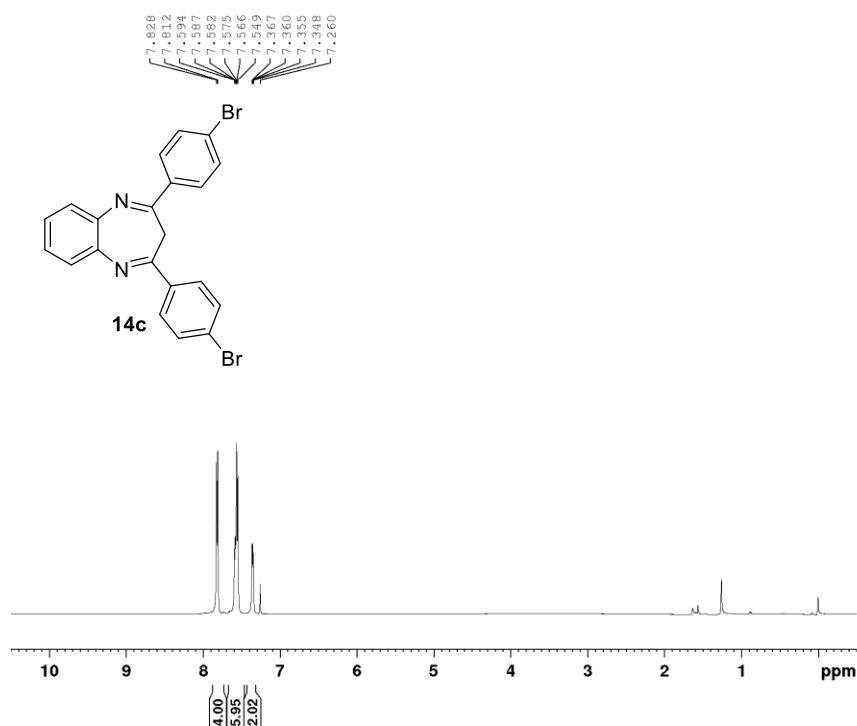
F2 - Processing parameters
 SI 65536
 SF 500.1300190 MHz
 WDW EM
 SSB 0
 LB 0.30 Hz
 GB 0
 PC 1.00

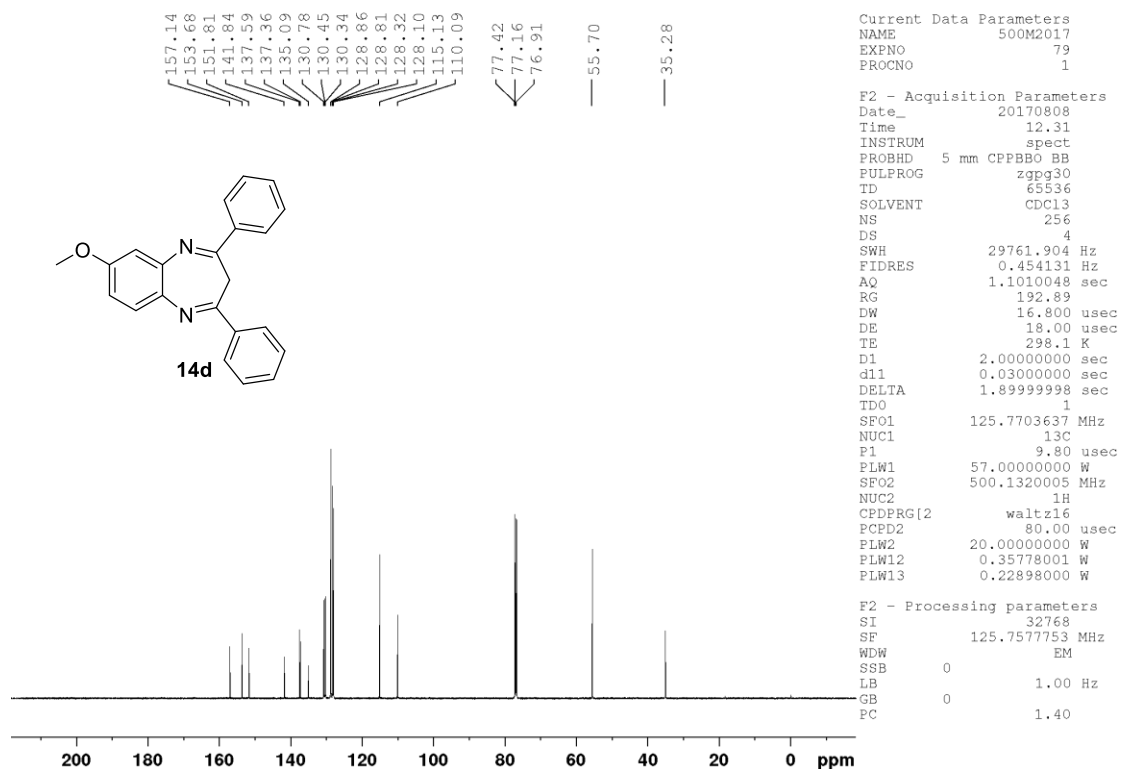
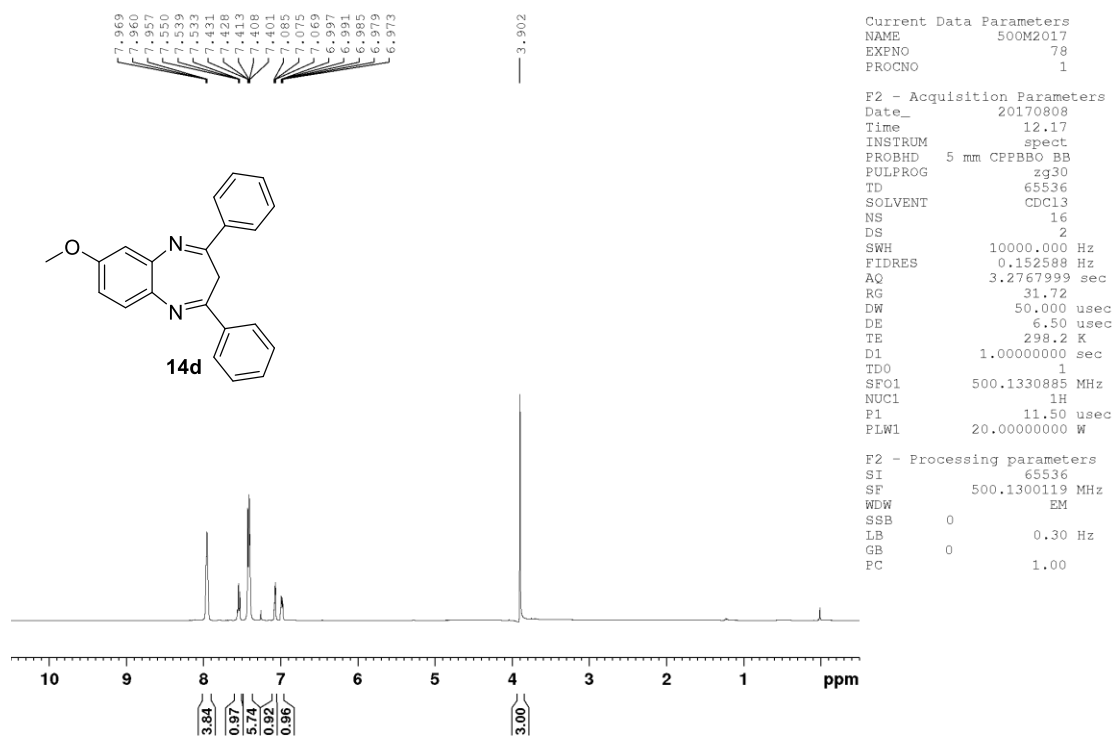


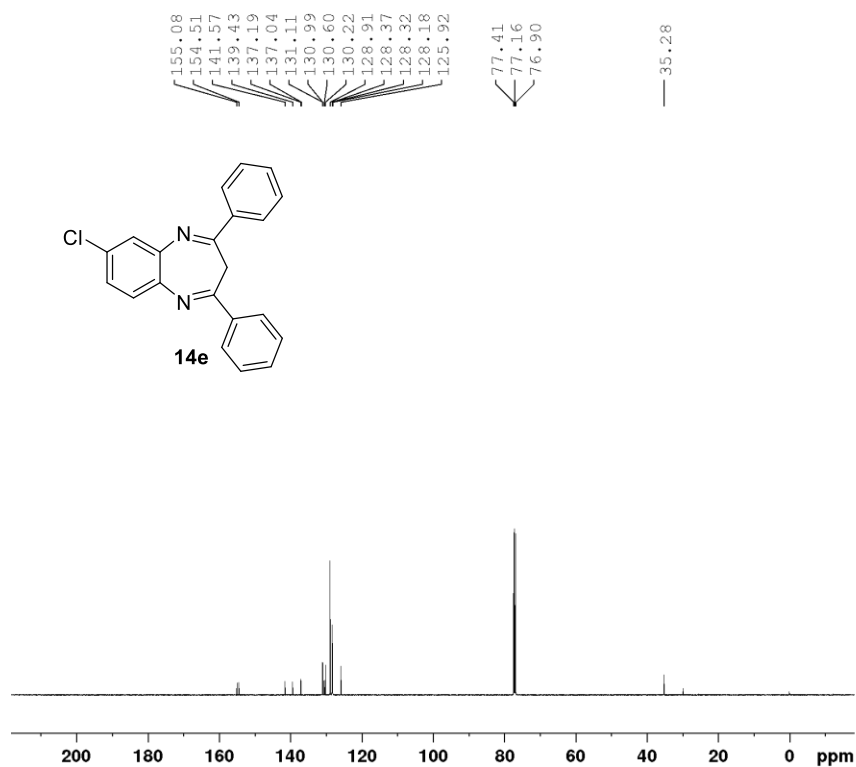
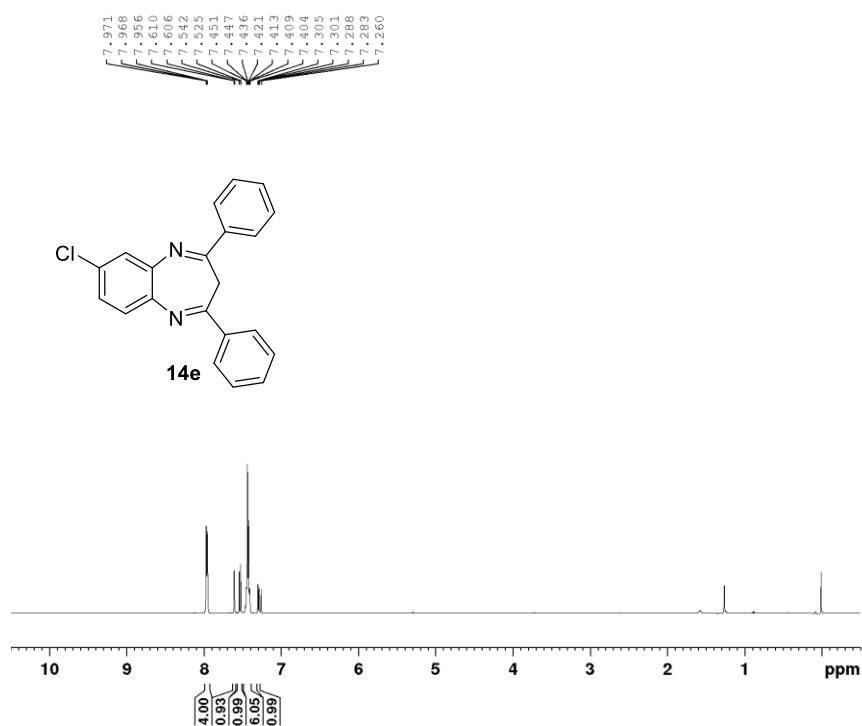
Current Data Parameters
 NAME 500M 2018-2
 EXPNO 260
 PROCNO 1

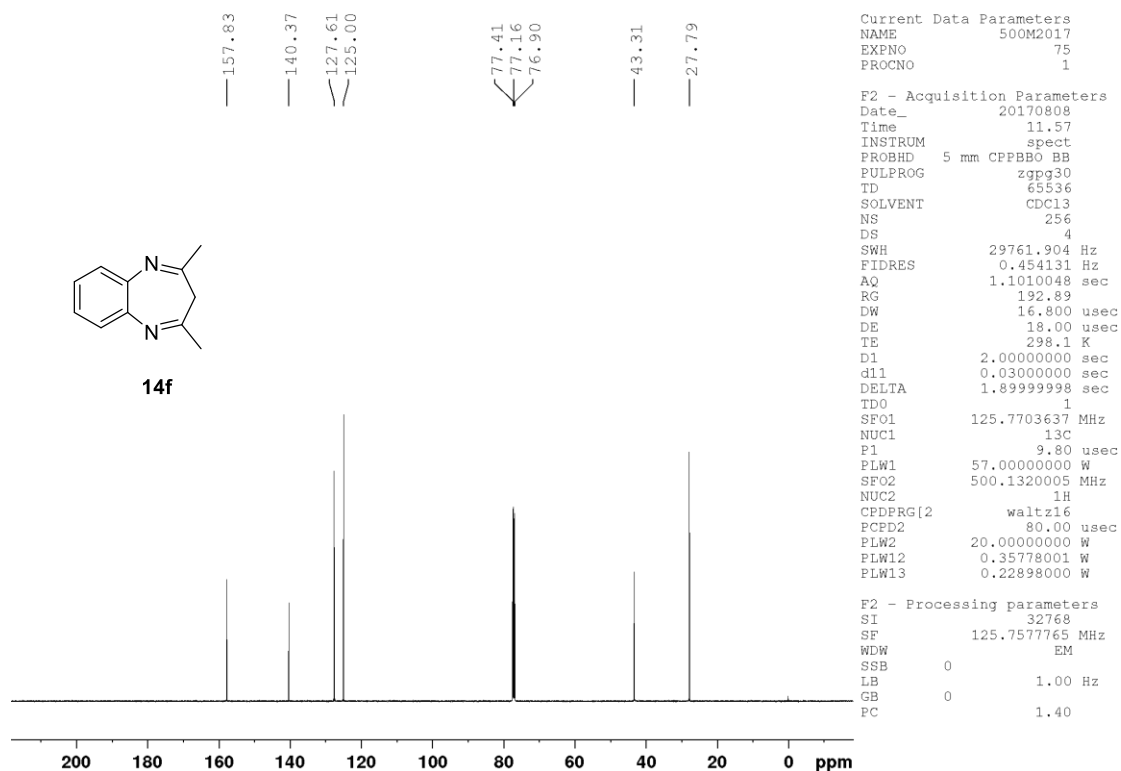
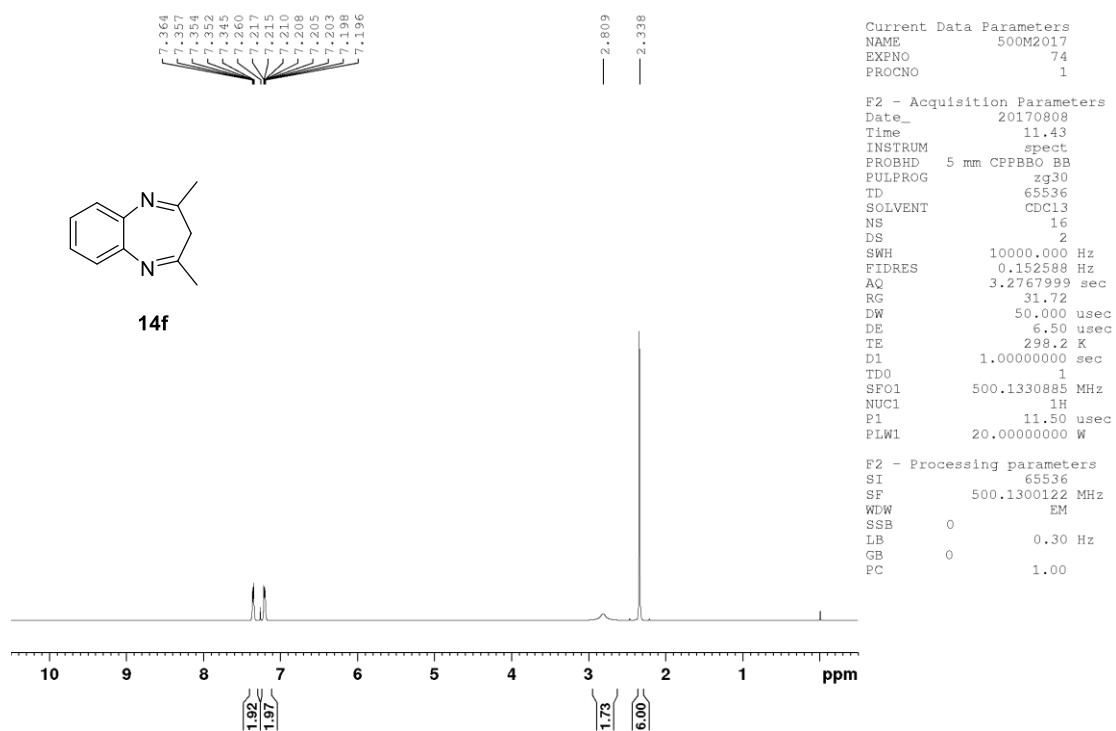
F2 - Acquisition Parameters
 Date_ 20180904
 Time 10.06
 INSTRUM spect
 PROBHD 5 mm CFPBBO BB
 PULPROG zgpg30
 TD 65536
 SOLVENT CDCl3
 NS 20
 DS 4
 SWH 29761.904 Hz
 FIDRES 0.454131 Hz
 AQ 1.1010048 sec
 RG 192.89
 DW 16.800 usec
 DE 18.00 usec
 TE 298.1 K
 D1 2.00000000 sec
 d11 0.03000000 sec
 DELTA 1.89999998 sec
 TD0 1
 SFO1 125.7703637 MHz
 NUC1 13C
 P1 9.80 usec
 PLW1 57.00000000 W
 SFO2 500.1320005 MHz
 NUC2 1H
 CPDPRG2 waltz16
 PCPD2 80.00 usec
 PLW2 20.00000000 W
 PLW12 0.35778001 W
 PLW13 0.22898000 W

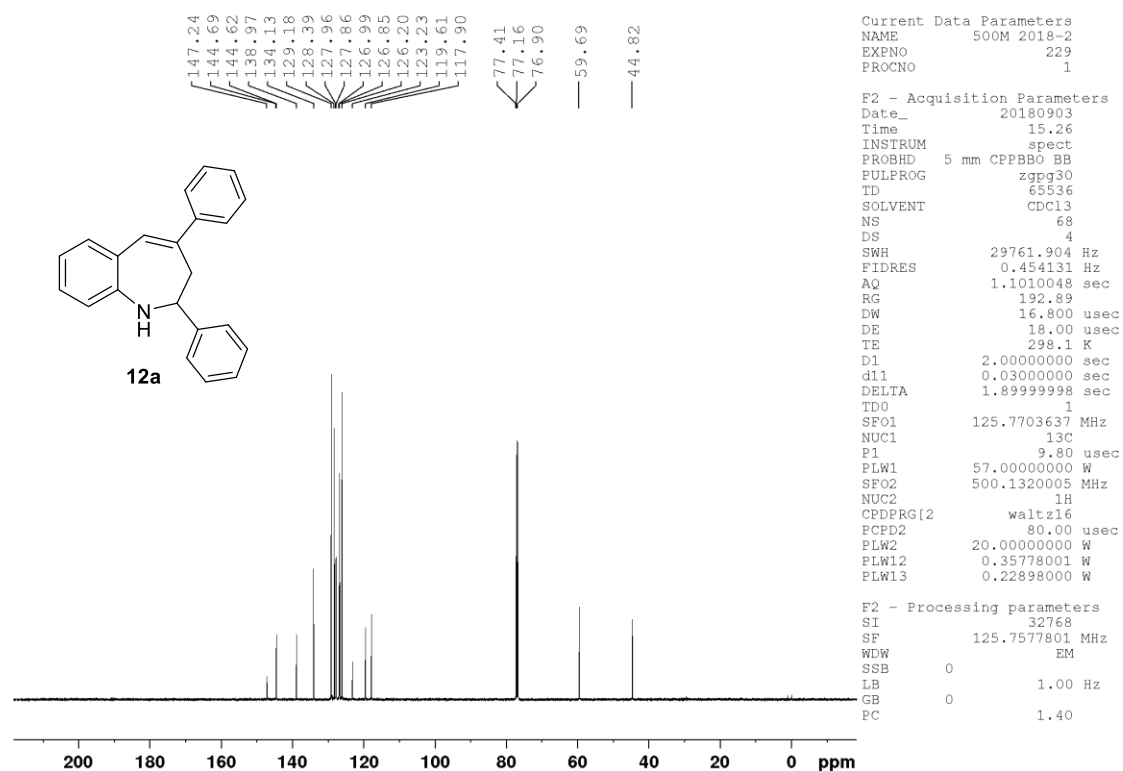
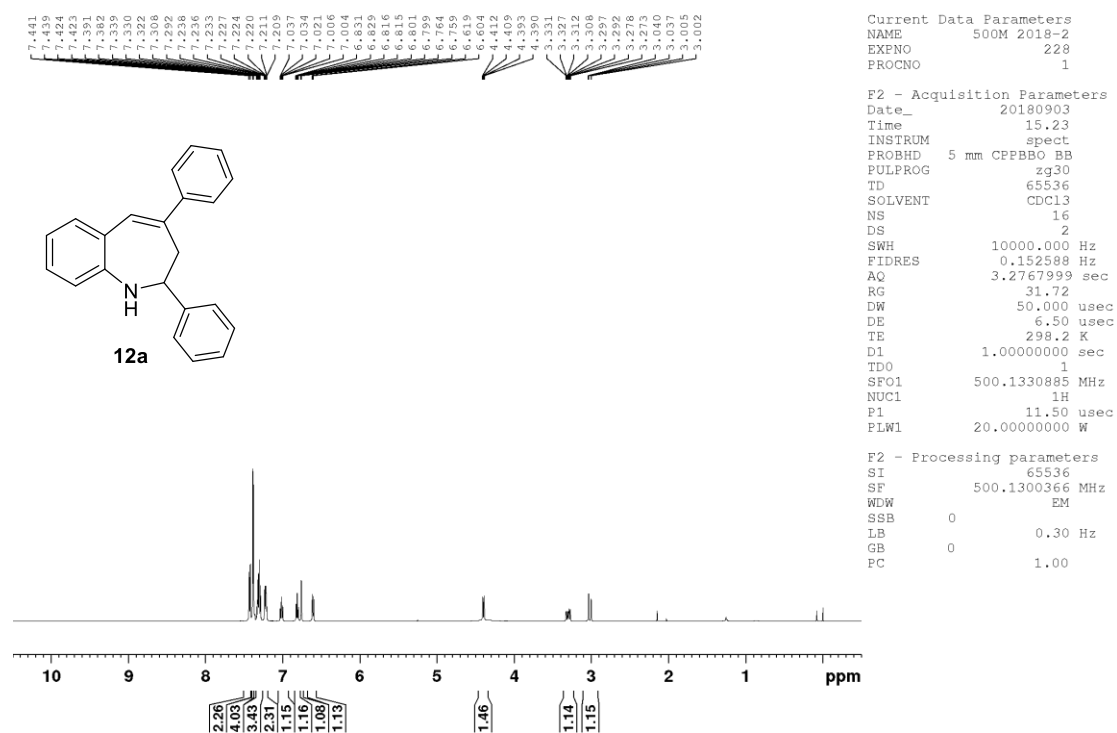
F2 - Processing parameters
 SI 32768
 SF 125.757765 MHz
 WDW EM
 SSB 0
 LB 1.00 Hz
 GB 0
 PC 1.40

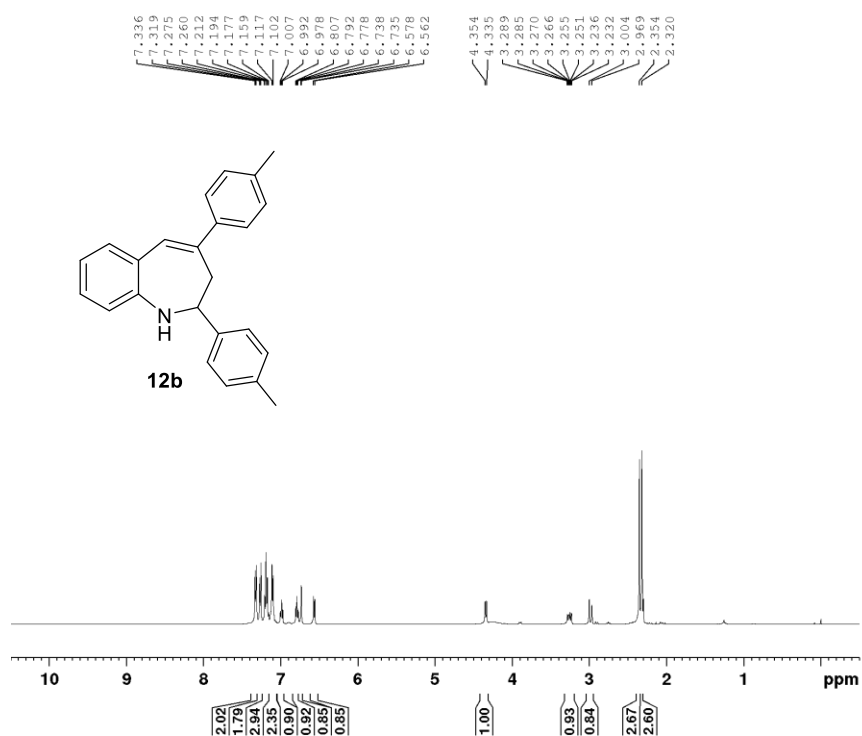








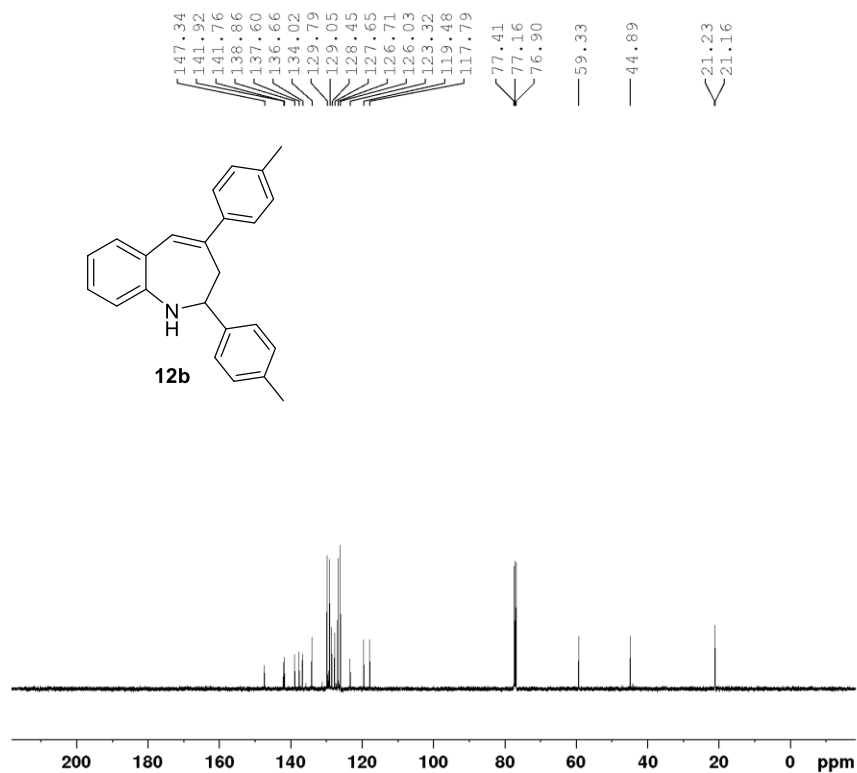




Current Data Parameters
NAME 500M 2018-2
EXPNO 204
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180827
Time 20.30
INSTRUM spect
PROBHD 5 mm CFPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 25.06
DW 50.000 usec
DE 6.50 usec
TE 298.1 K
D1 1.00000000 sec
TD0 1
SFO1 500.1330885 MHz
NUC1 1H
P1 11.50 usec
PLW1 20.00000000 W

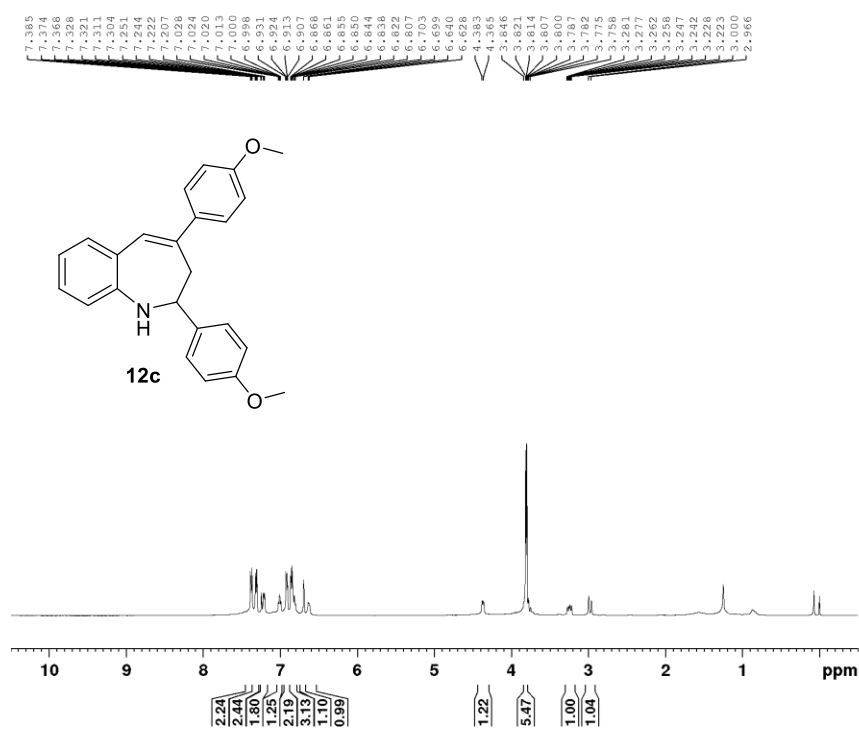
F2 - Processing parameters
SI 65536
SF 500.1300549 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



Current Data Parameters
NAME 500M 2018-2
EXPNO 209
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180827
Time 20.44
INSTRUM spect
PROBHD 5 mm CFPBBO BB
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 5
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 192.89
DW 16.800 usec
DE 18.00 usec
TE 298.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999998 sec
TD0 1
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
PLW1 57.00000000 W
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 80.00 usec
PLW2 20.00000000 W
PLW12 0.35778001 W
PLW13 0.22898000 W

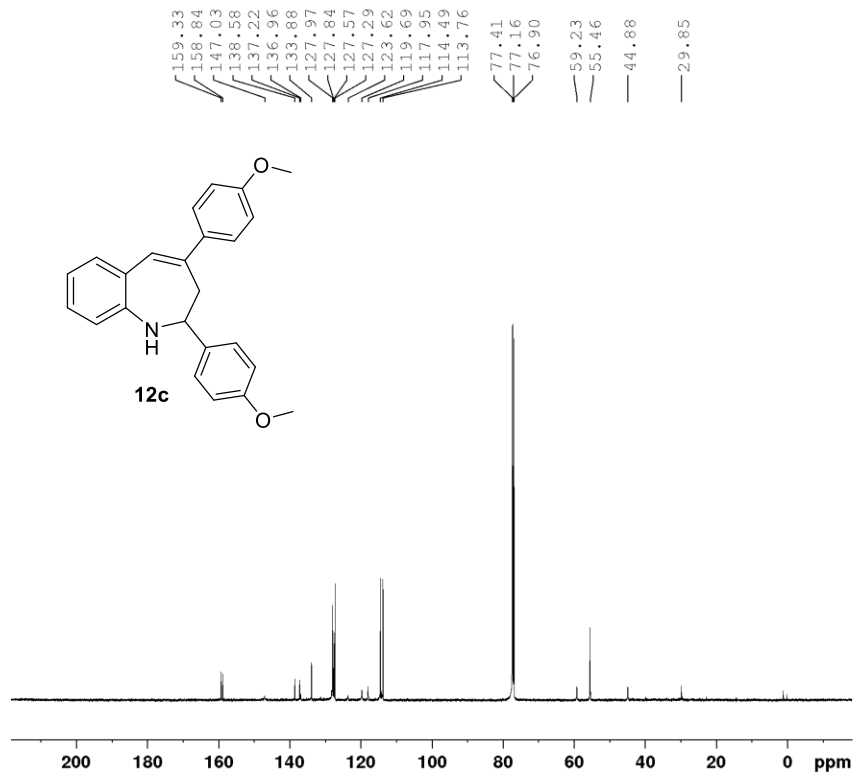
F2 - Processing parameters
SI 32768
SF 125.7577865 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



Current Data Parameters
NAME 500M 2018-2
EXPNO 263
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180904
Time 11.11
INSTRUM spect
PROBHD 5 mm CFPBBO BB
PULPROG zg30
TD 65536
SOLVENT CDCl3
NS 16
DS 2
SWH 10000.000 Hz
FIDRES 0.152588 Hz
AQ 3.2767999 sec
RG 31.72
DW 50.000 usec
DE 6.50 usec
TE 298.2 K
D1 1.00000000 sec
TDO 1
SFO1 500.130885 MHz
NUC1 1H
P1 11.50 usec
PLW1 20.00000000 W

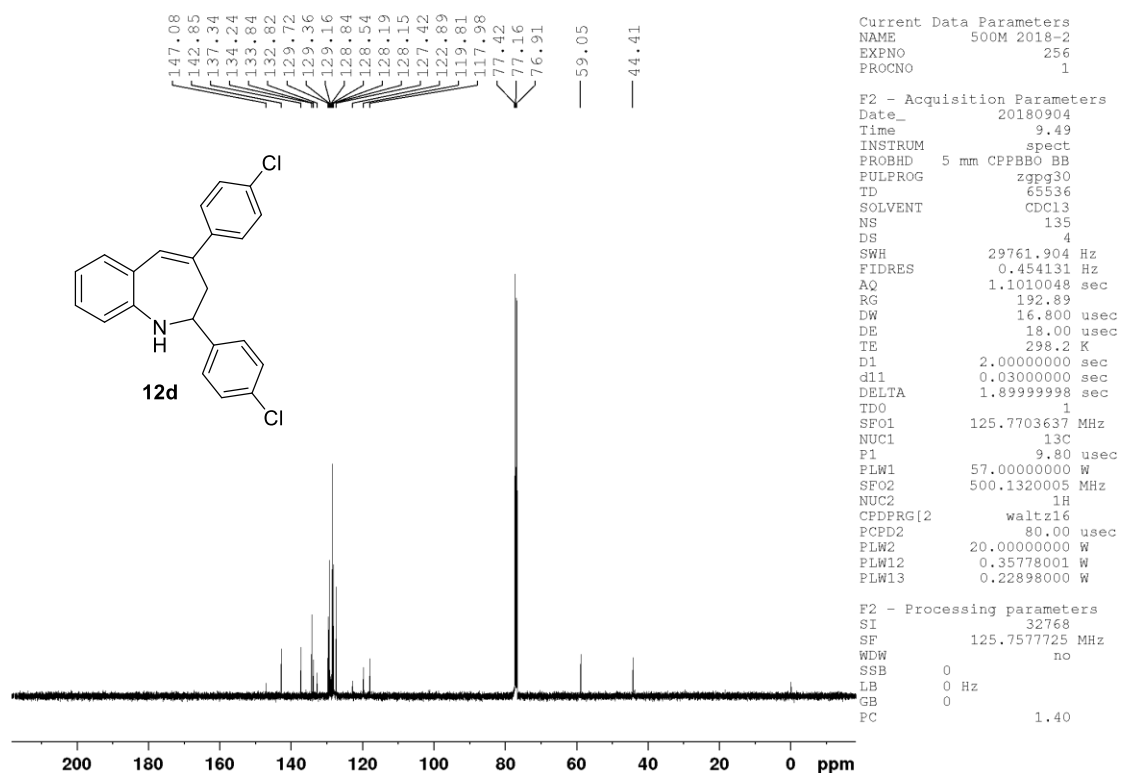
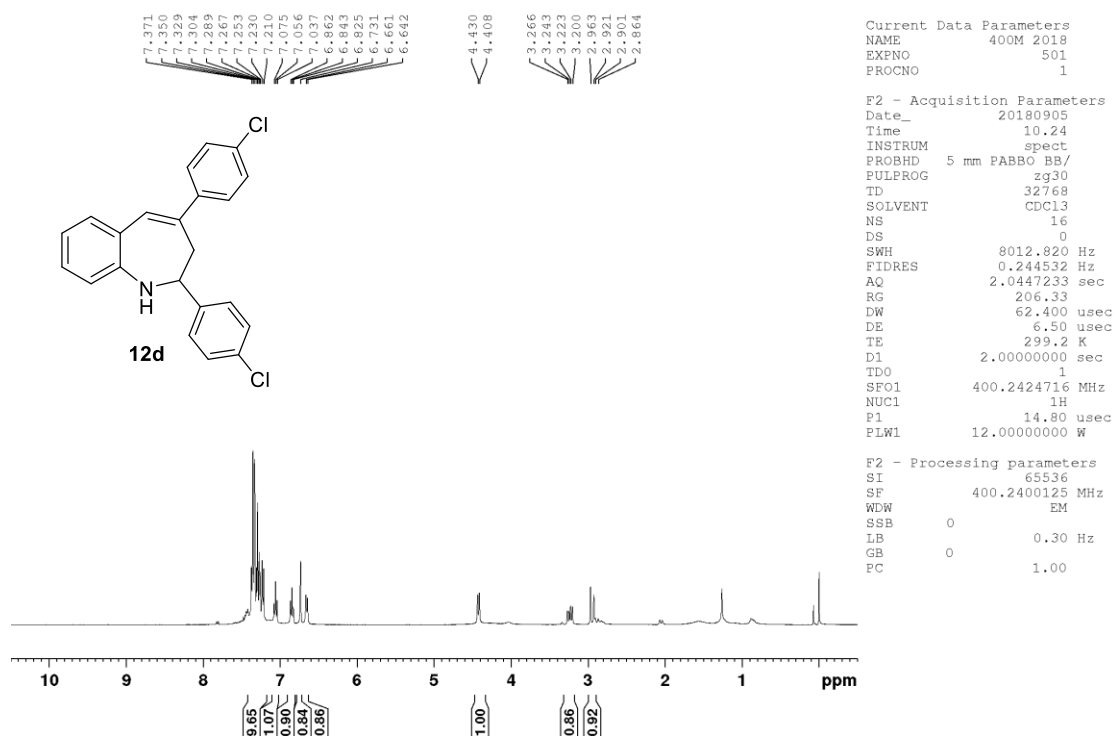
F2 - Processing parameters
SI 65536
SF 500.1300186 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00

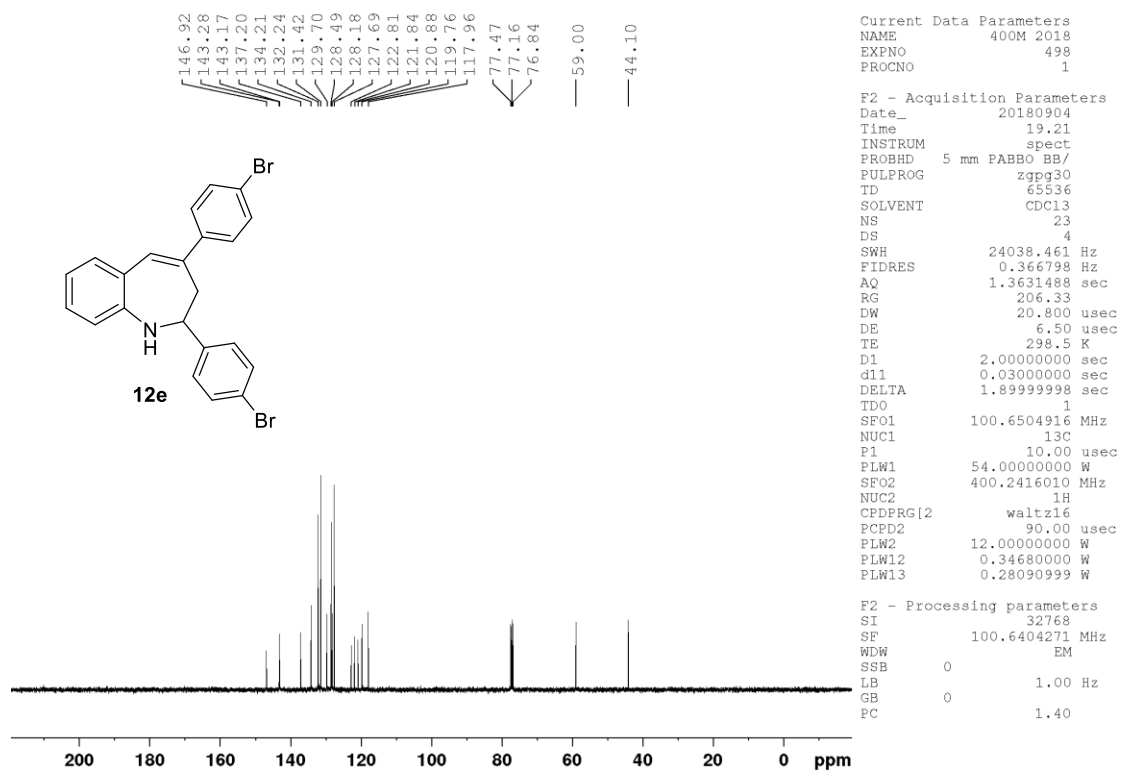
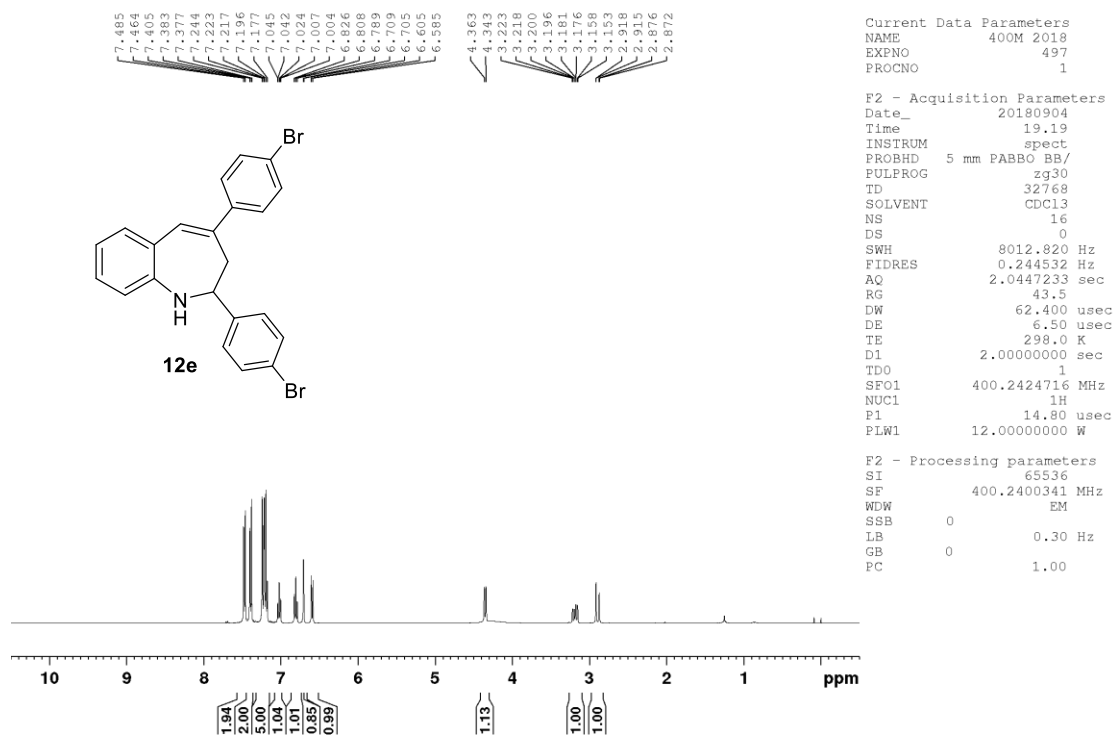


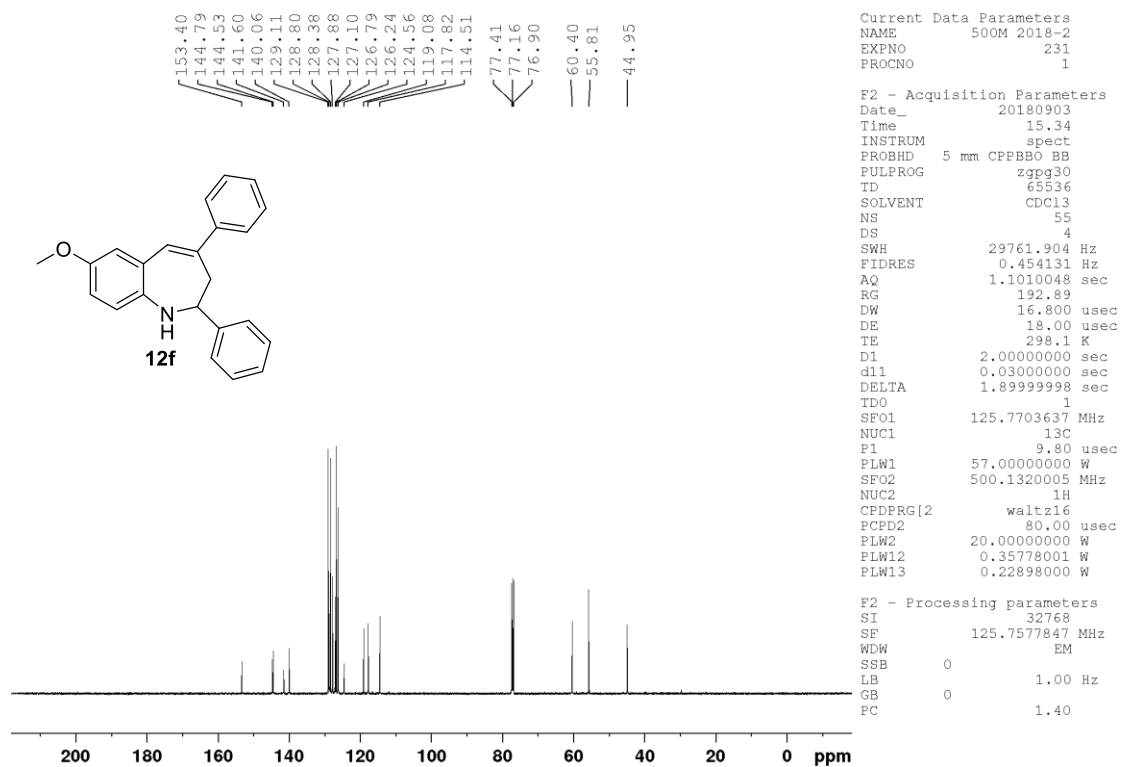
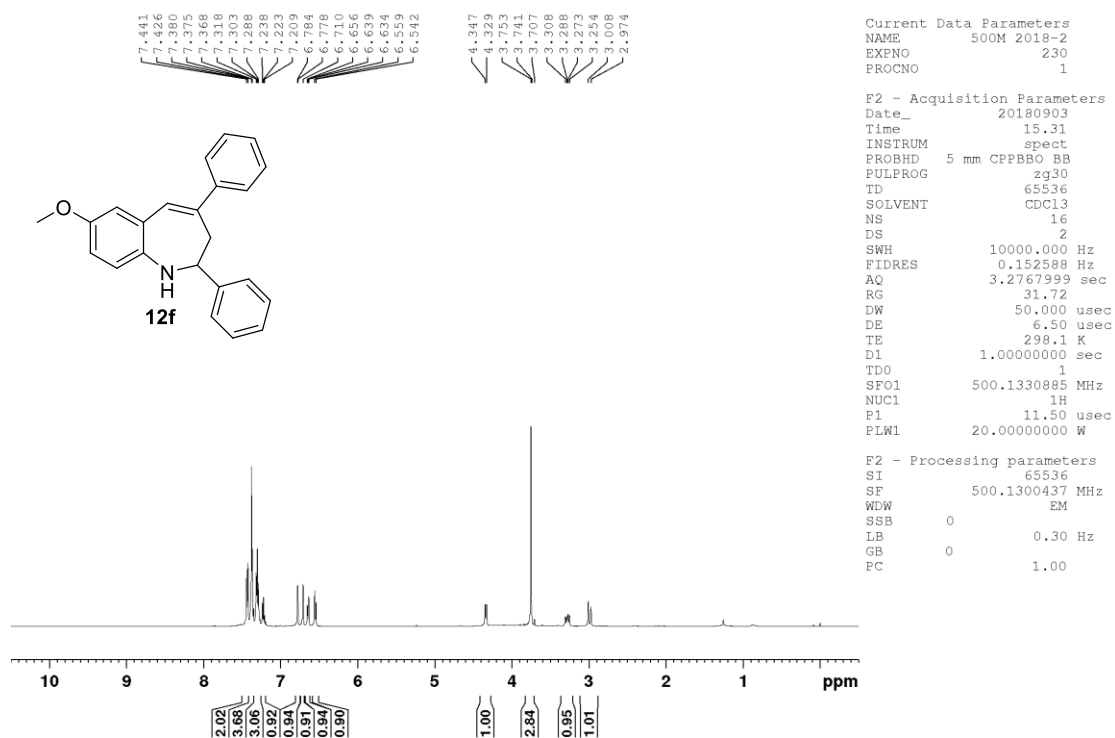
Current Data Parameters
NAME 500M 2018-2
EXPNO 265
PROCNO 1

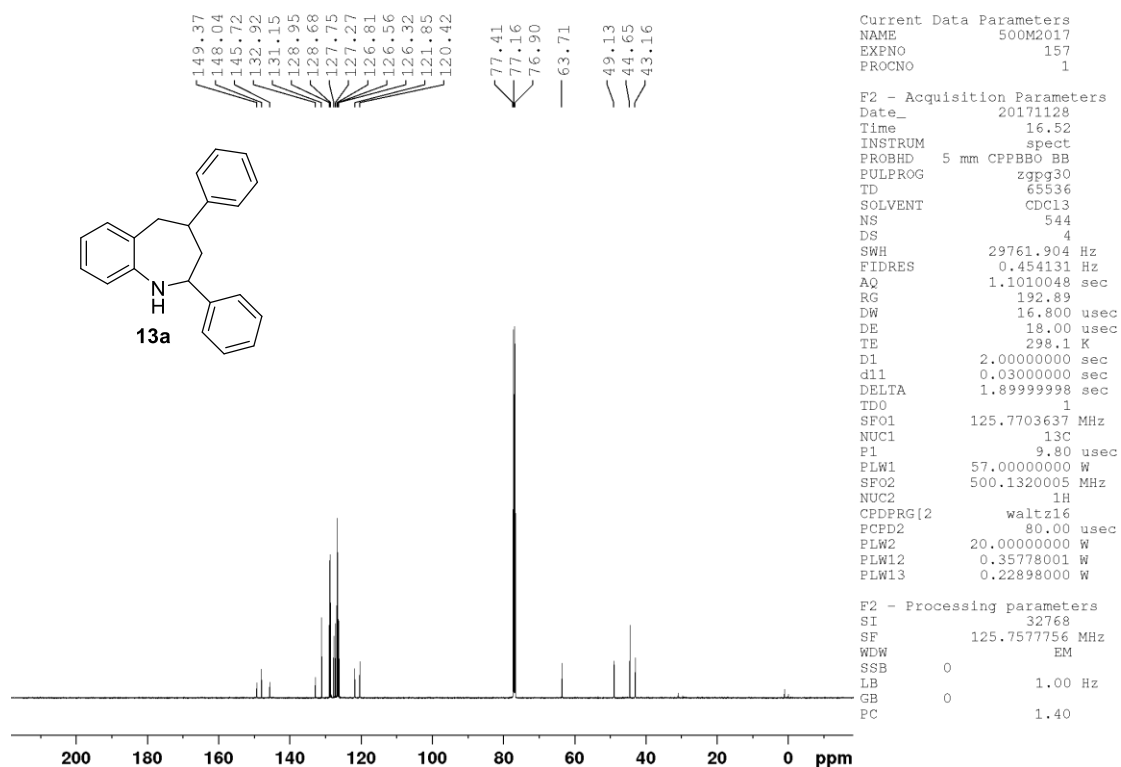
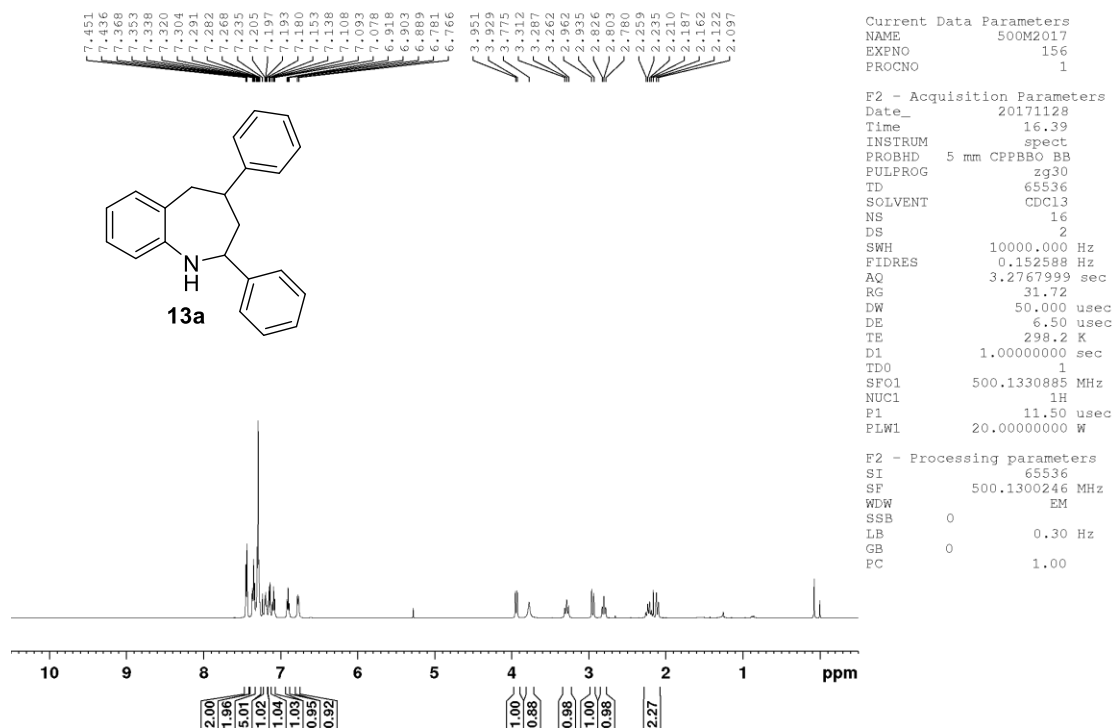
F2 - Acquisition Parameters
Date_ 20180904
Time 11.25
INSTRUM spect
PROBHD 5 mm CFPBBO BB
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 1024
DS 4
SWH 29761.904 Hz
FIDRES 0.454131 Hz
AQ 1.1010048 sec
RG 192.89
DW 16.800 usec
DE 18.00 usec
TE 298.1 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999999 sec
TDO 1
SFO1 125.7703637 MHz
NUC1 13C
P1 9.80 usec
PLW1 57.00000000 W
SFO2 500.1320005 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 80.00 usec
PLW2 20.00000000 W
PLW12 0.35778001 W
PLW13 0.22898000 W

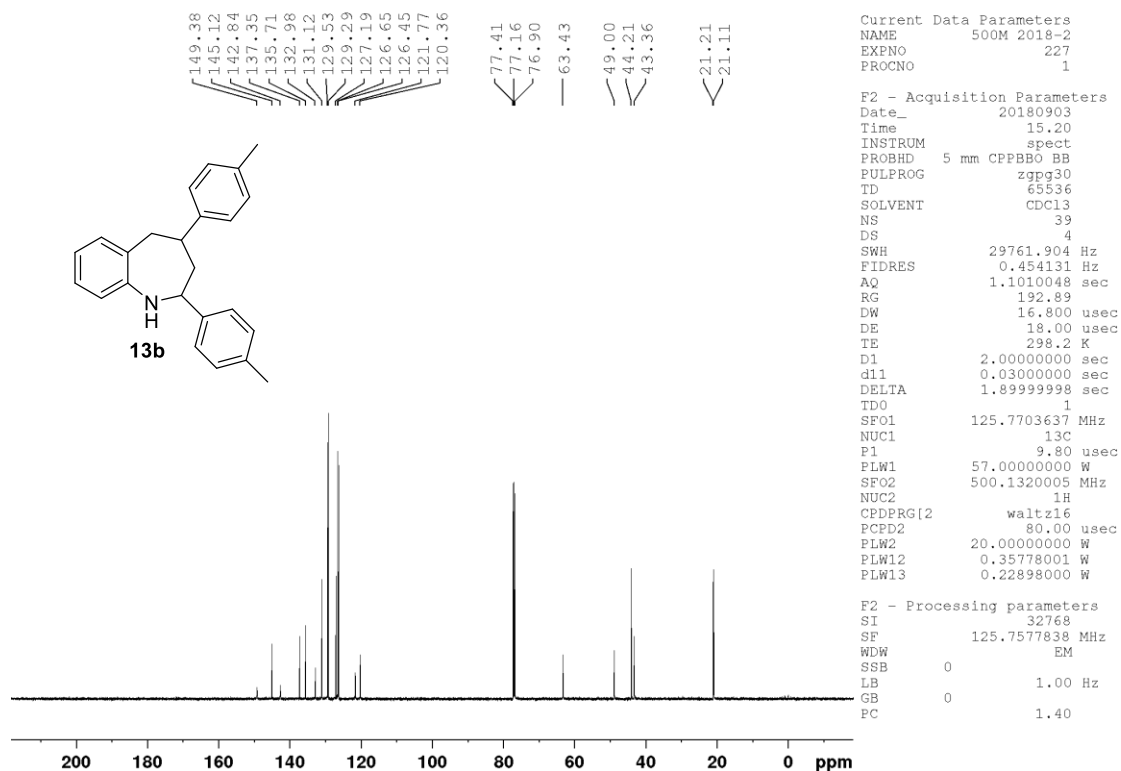
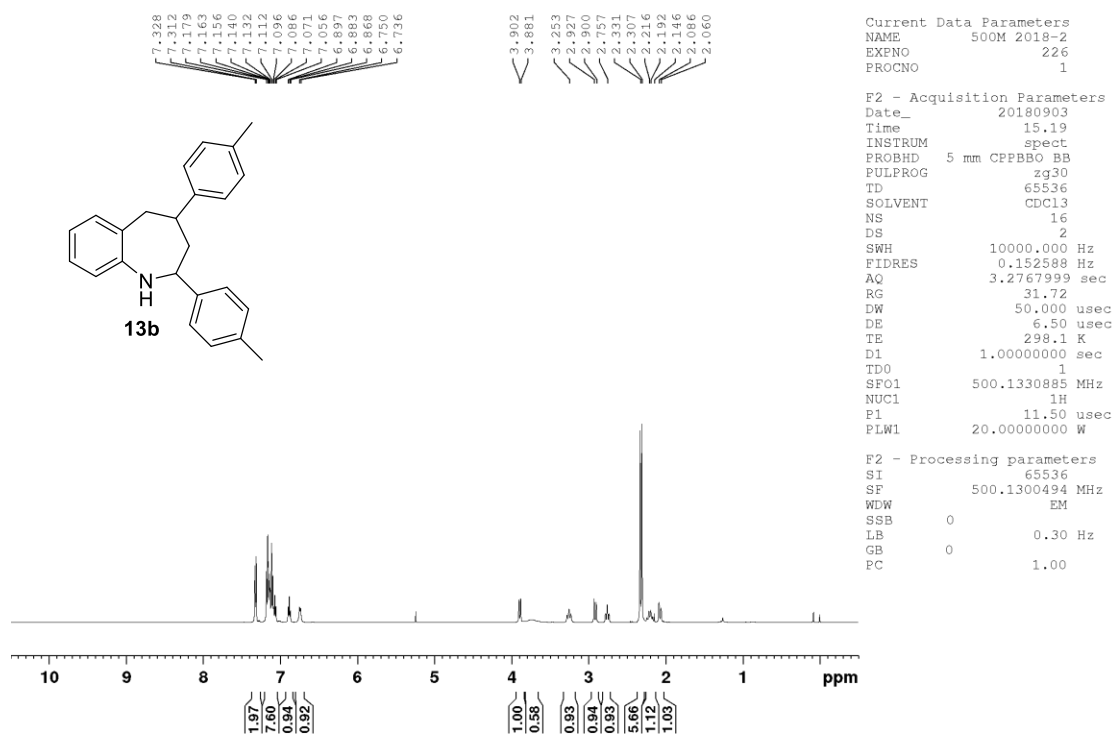
F2 - Processing parameters
SI 32768
SF 125.7577729 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40

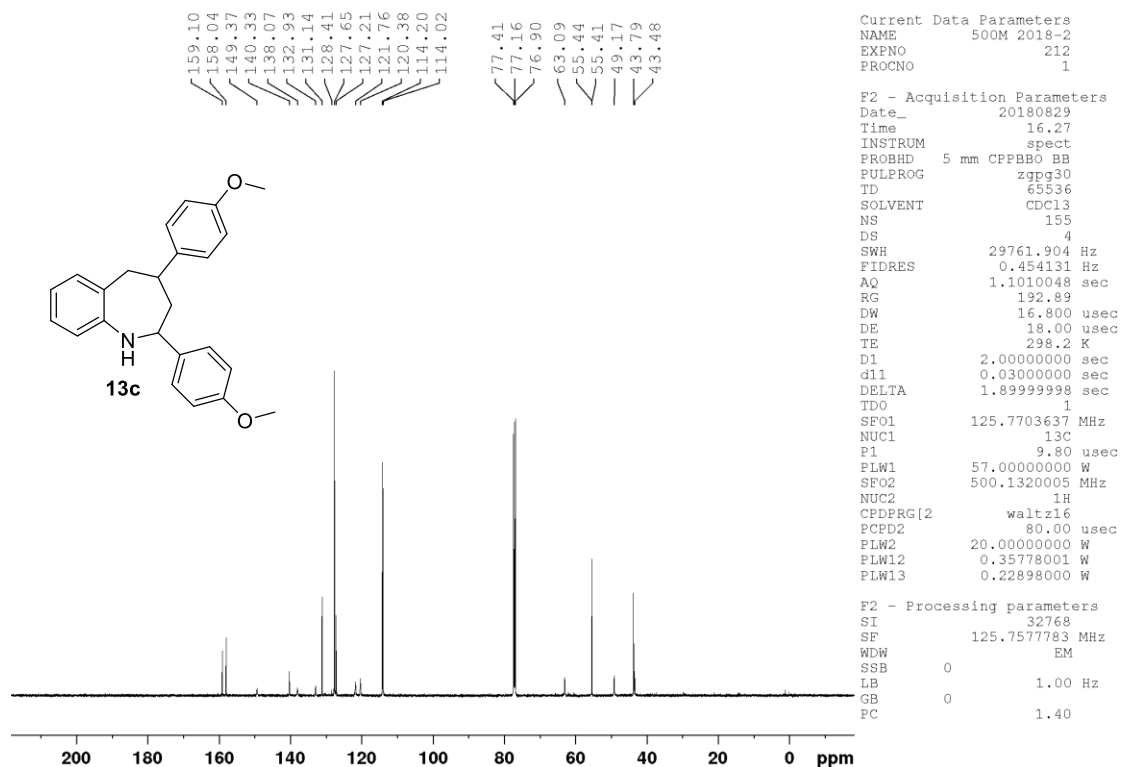
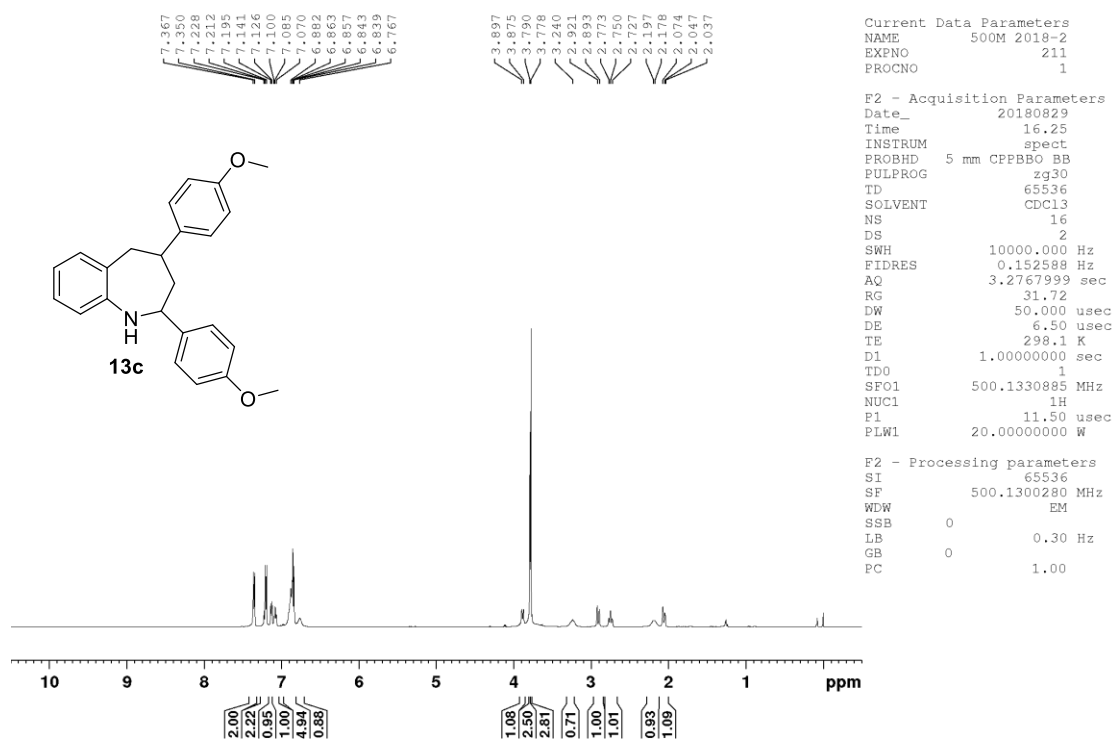


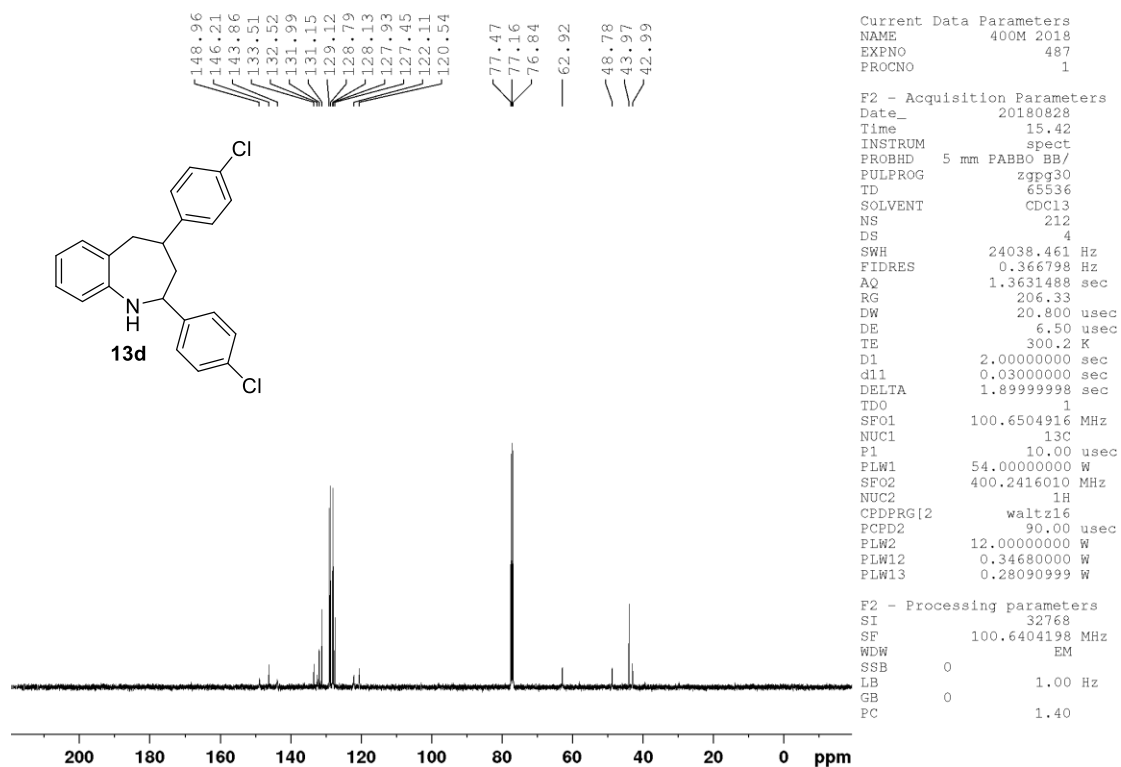
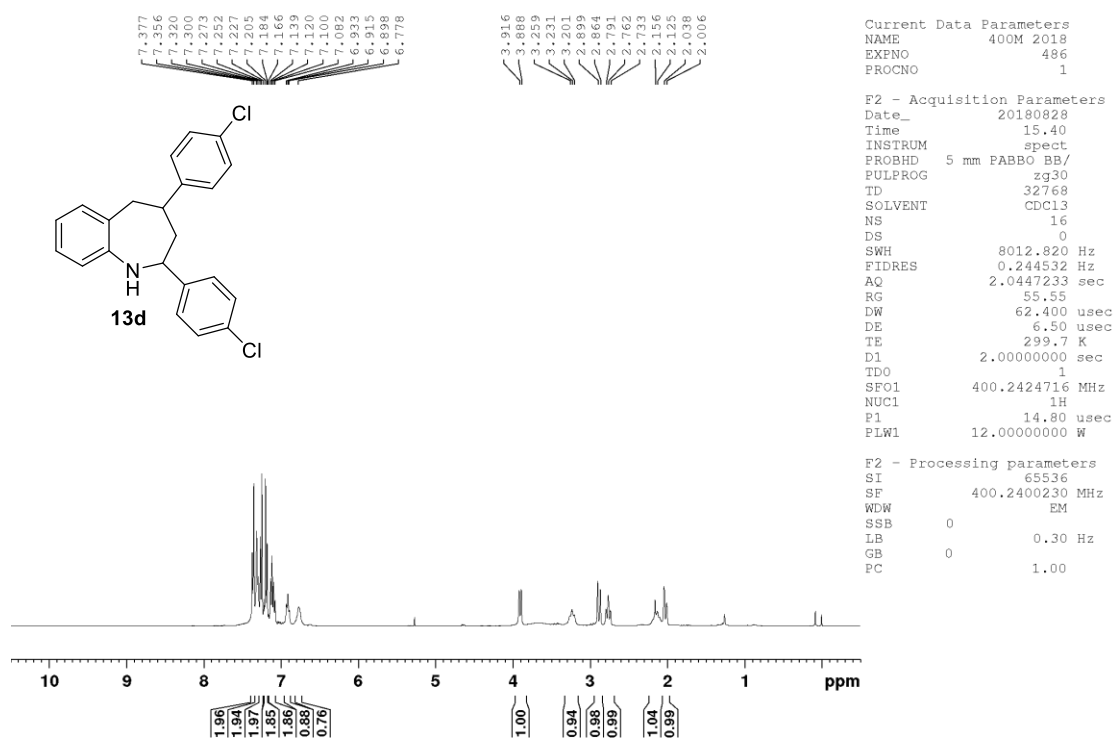


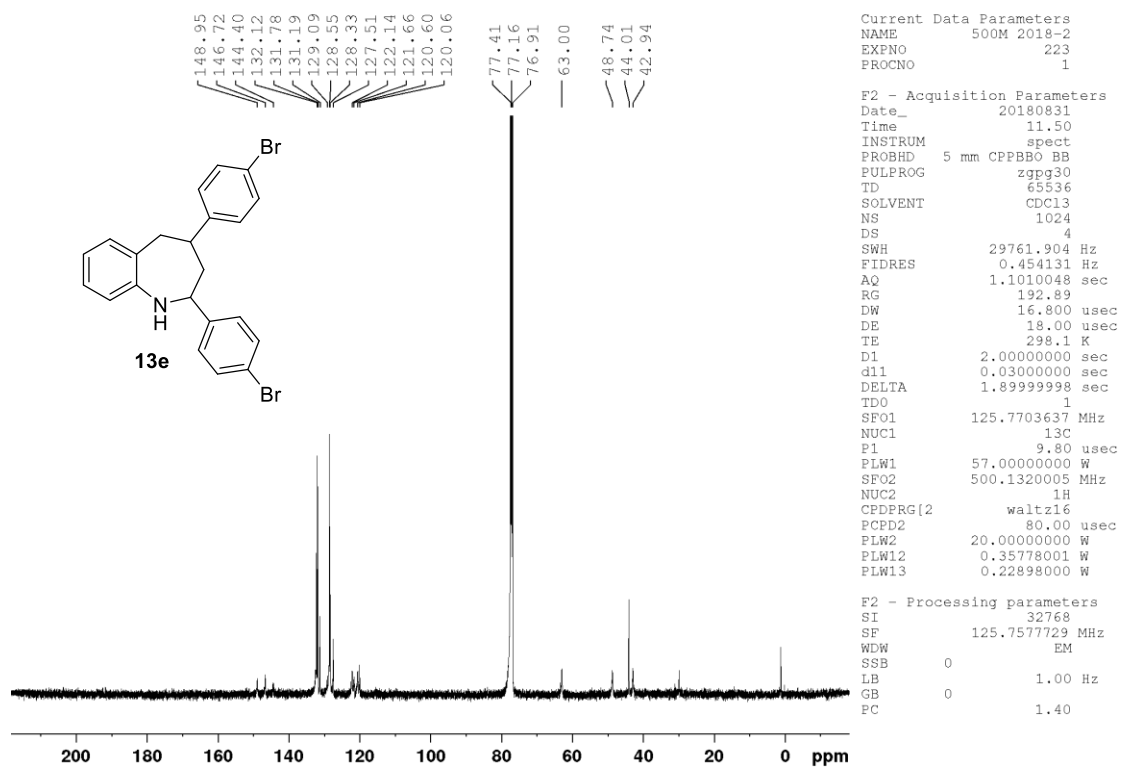
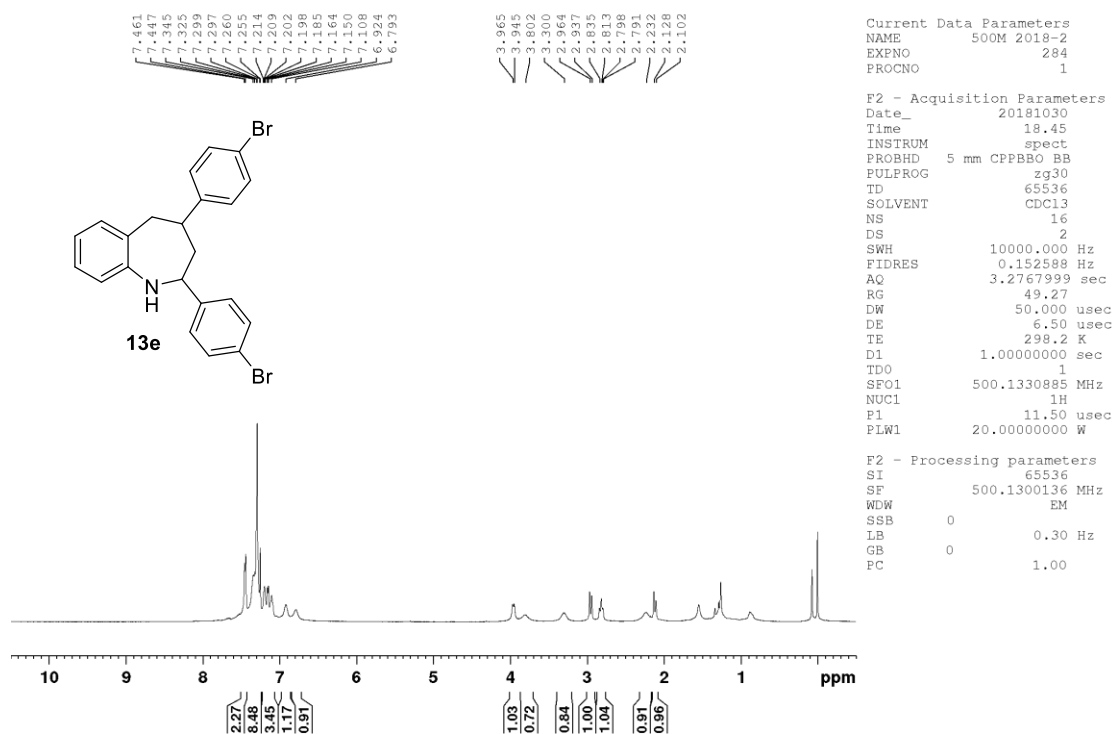


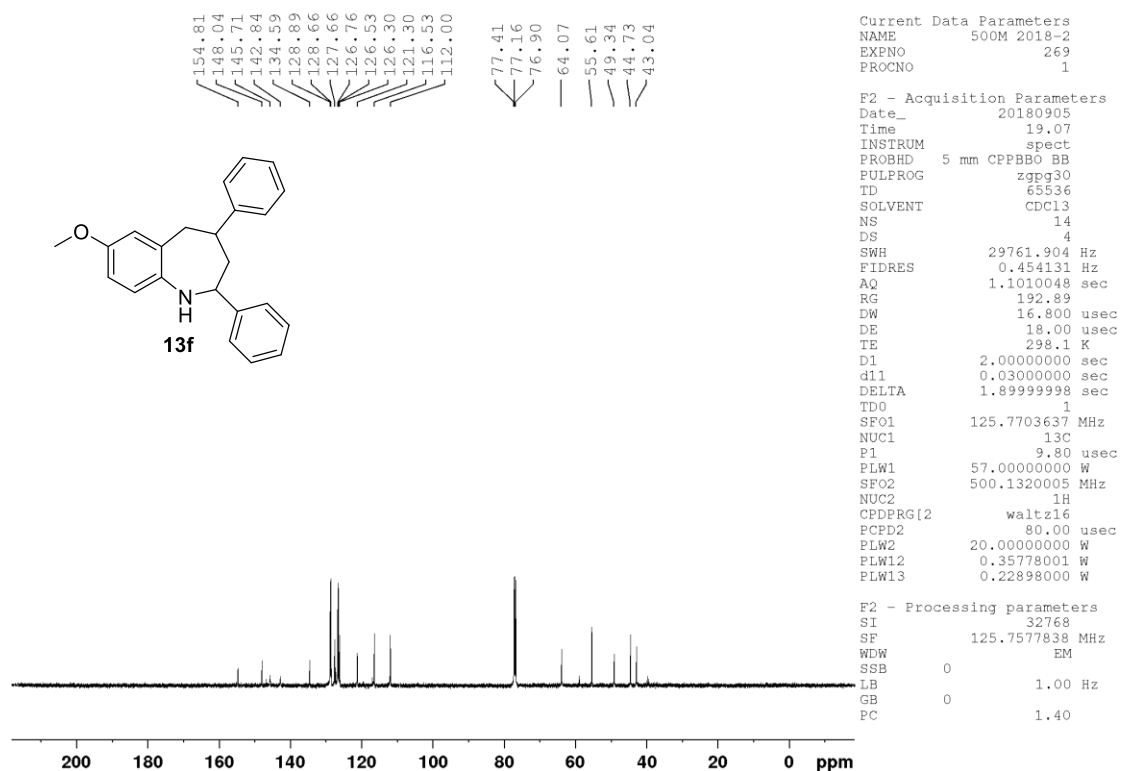
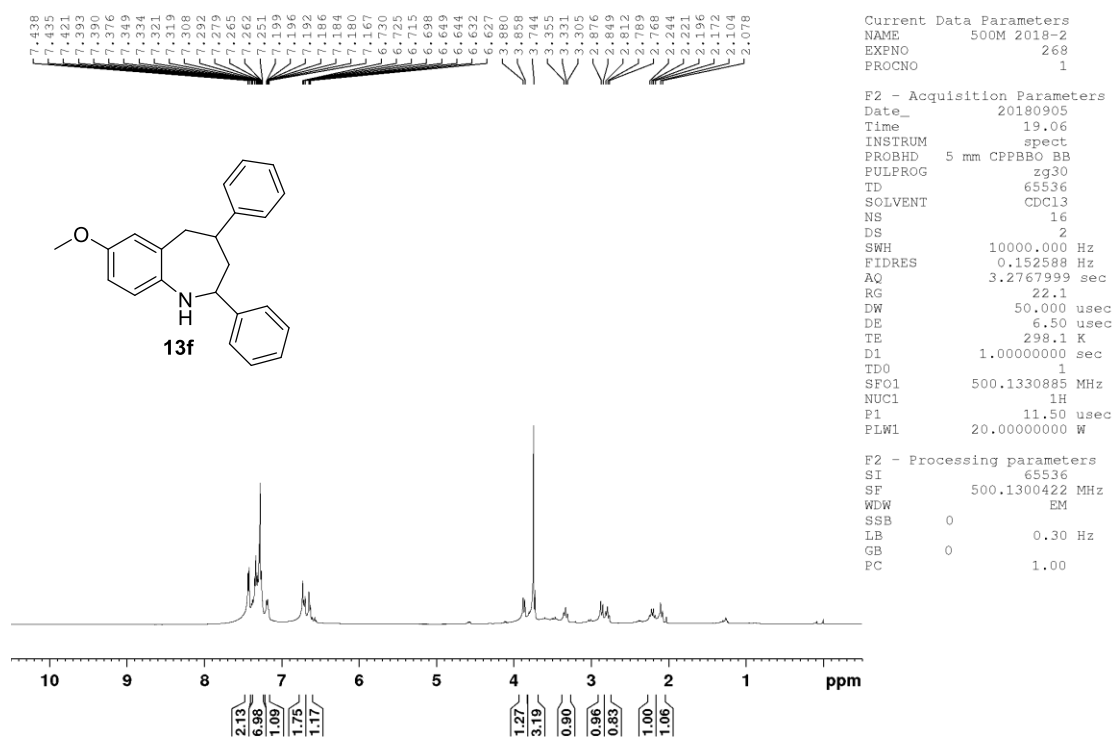


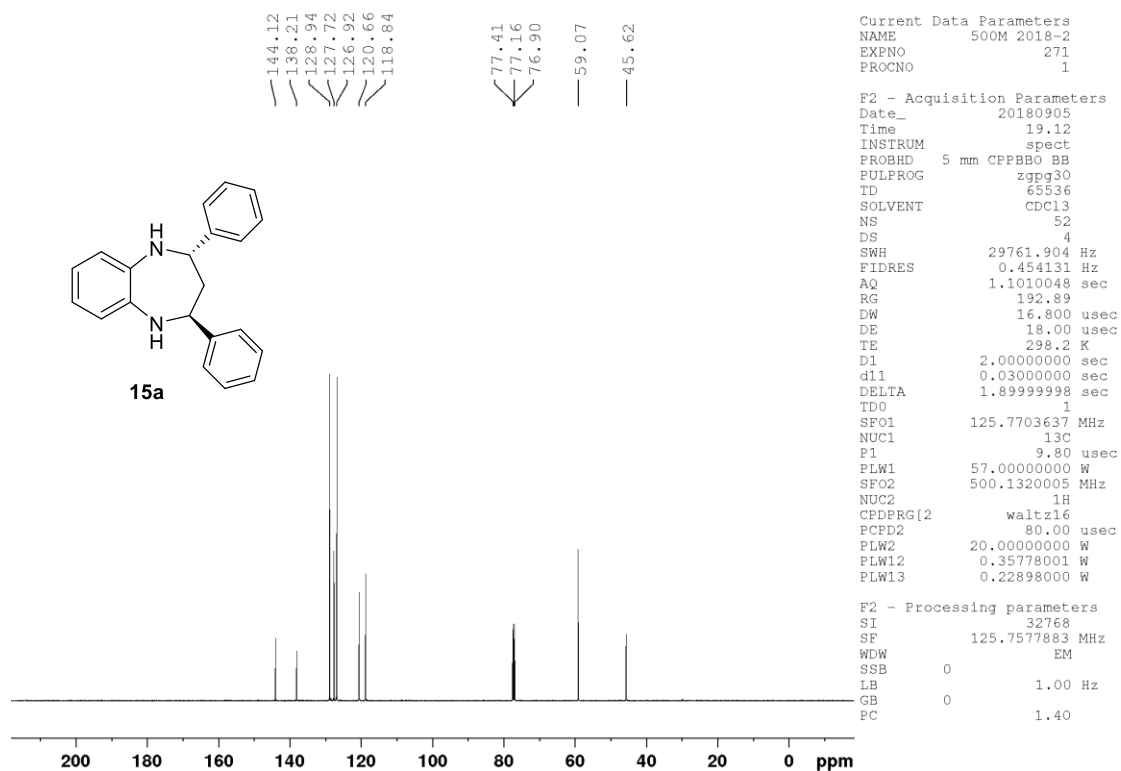
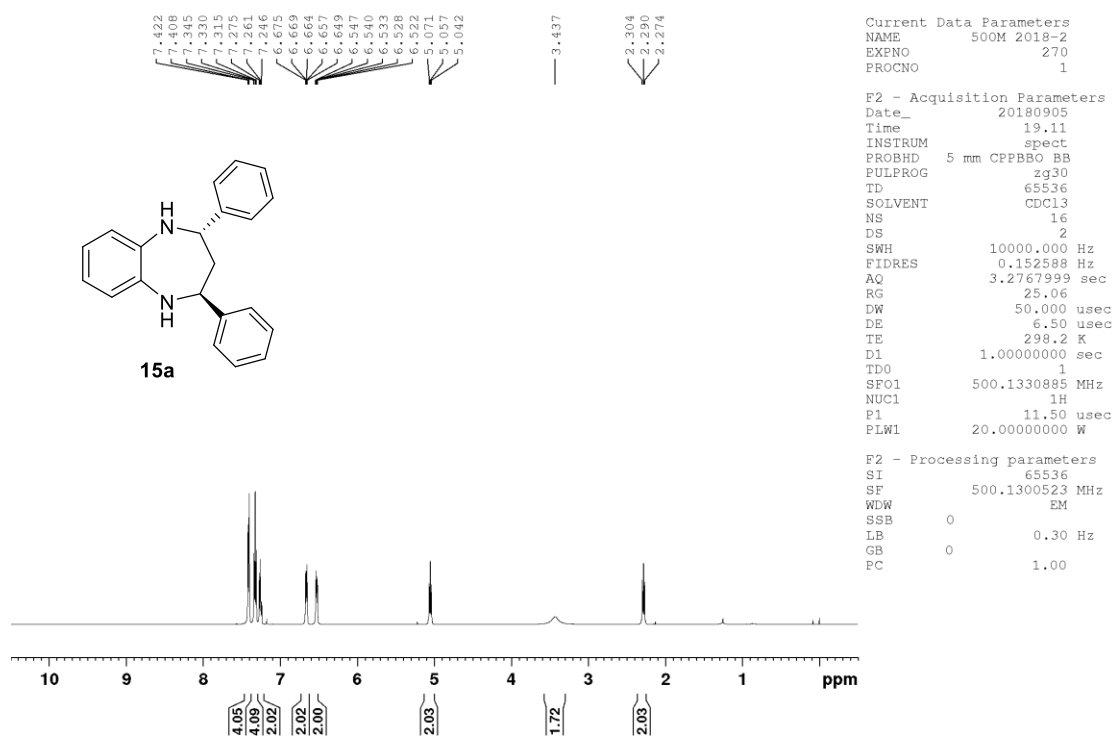


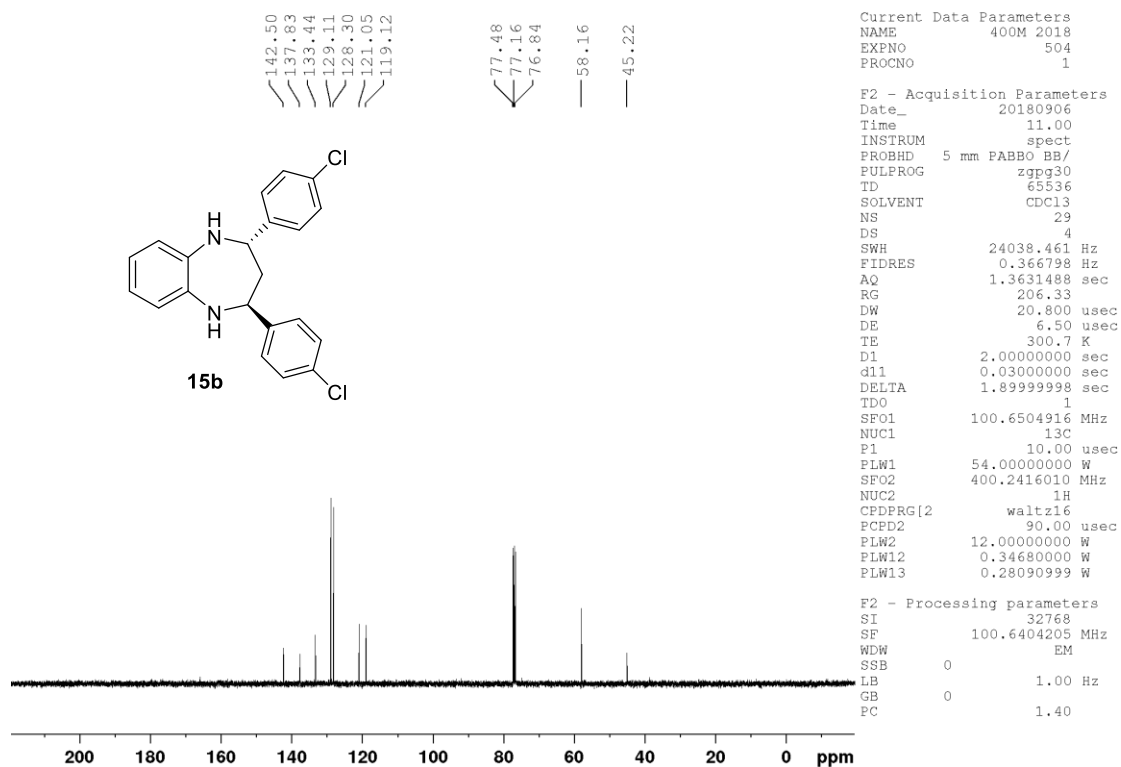
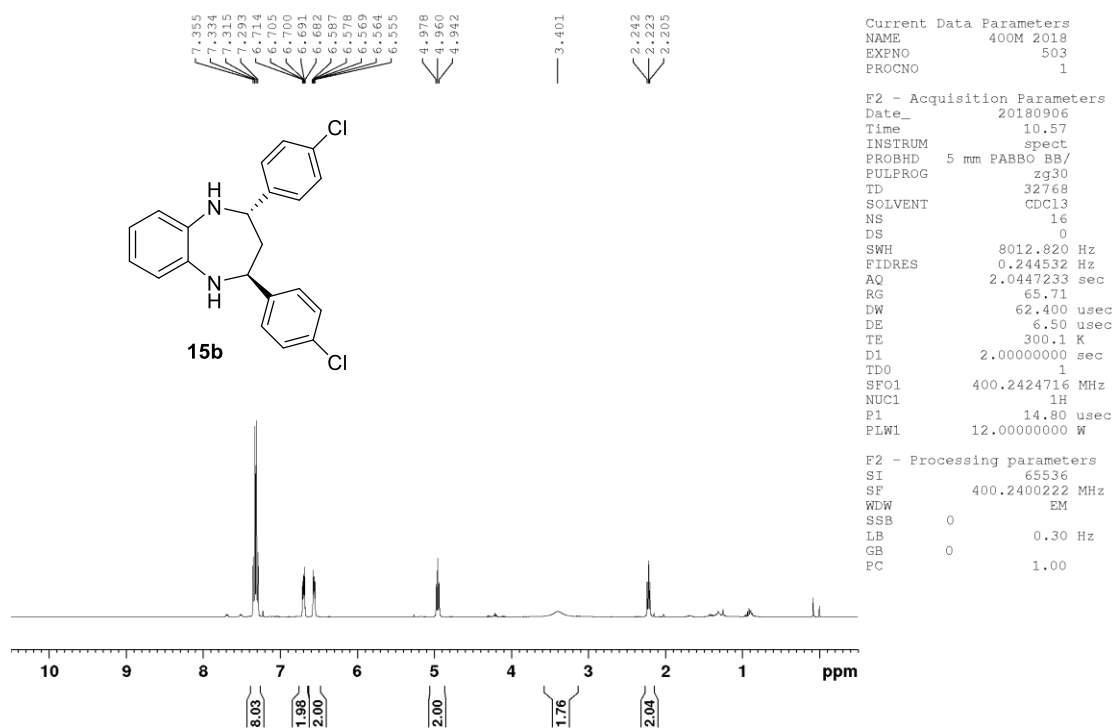


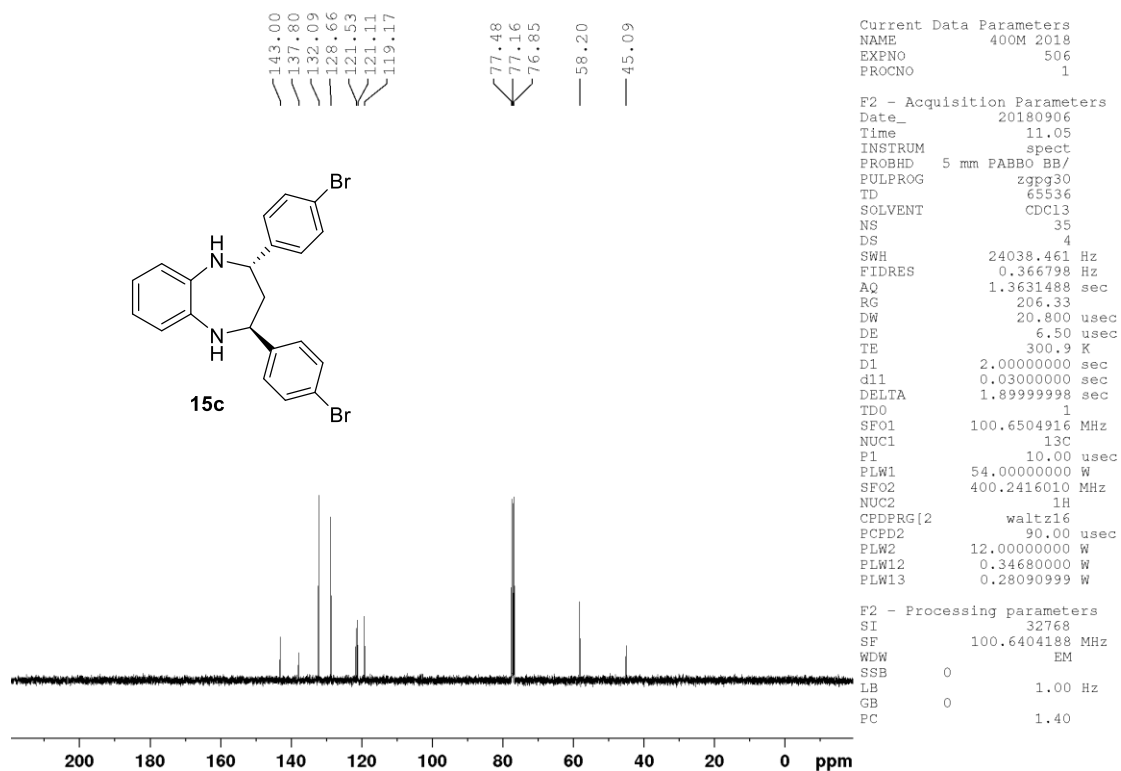
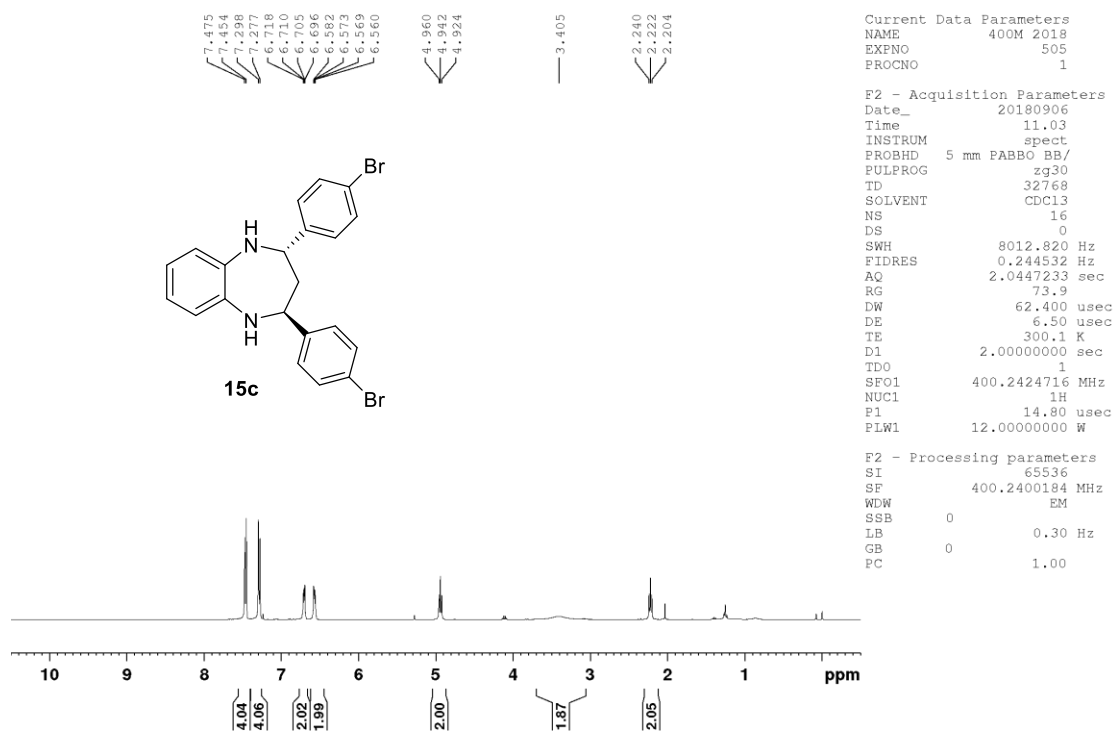


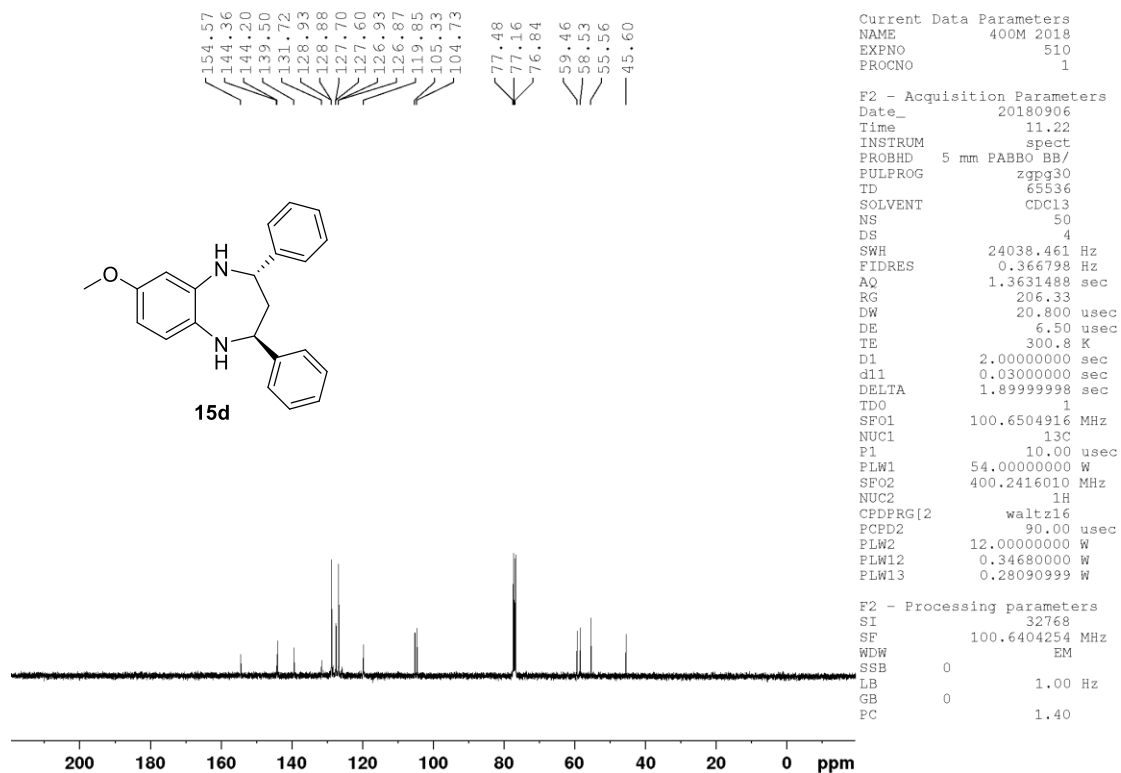
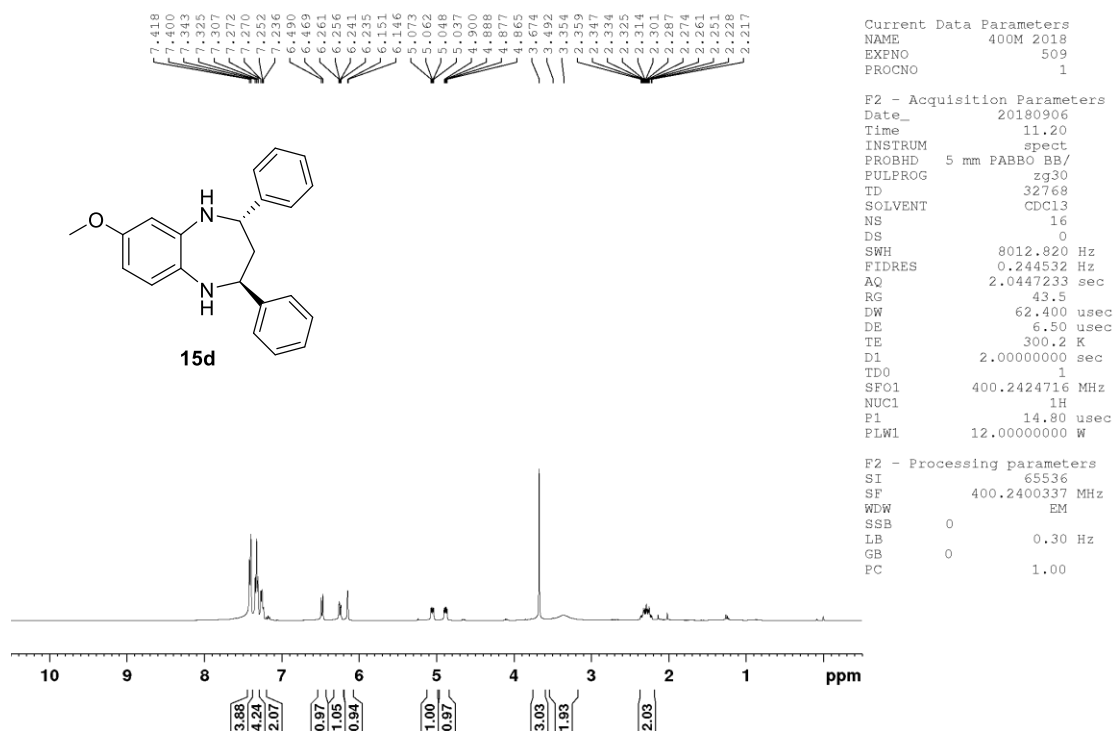


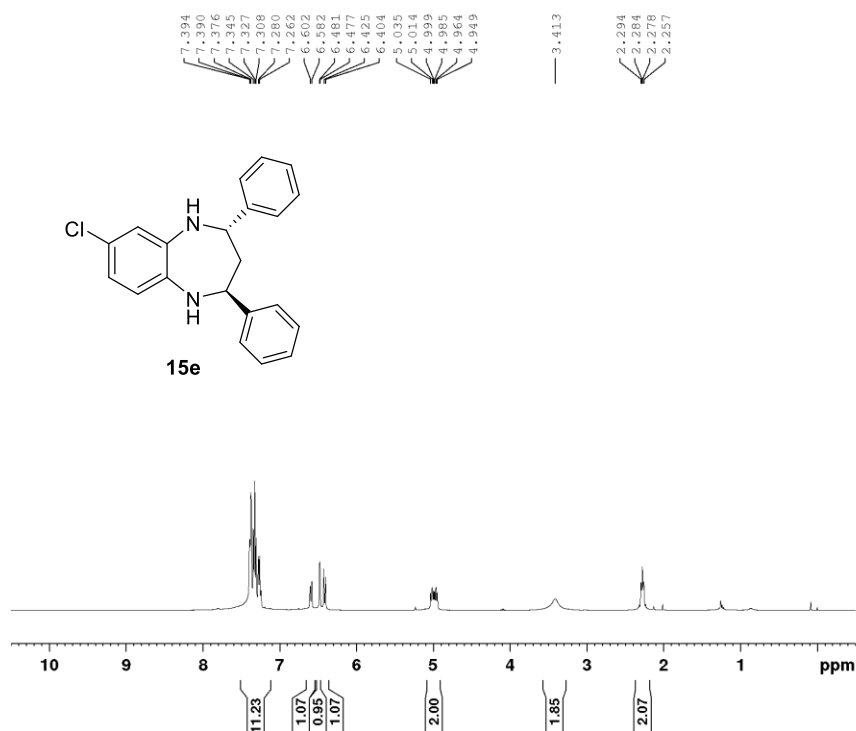








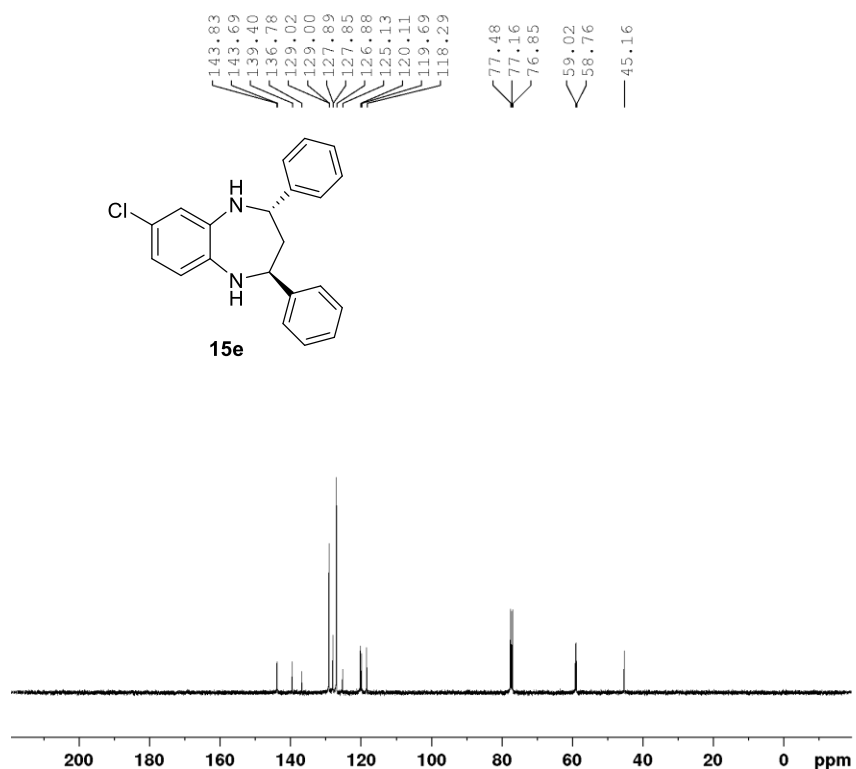




Current Data Parameters
NAME 400M 2018
EXPNO 507
PROCNO 1

F2 - Acquisition Parameters
Date_ 20180906
Time 11.10
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zg30
TD 32768
SOLVENT CDCl3
NS 16
DS 0
SWH 8012.820 Hz
FIDRES 0.244532 Hz
AQ 2.0447233 sec
RG 43.5
DW 62.400 usec
DE 6.50 usec
TE 300.1 K
D1 2.00000000 sec
TD0 1
SFO1 400.2424716 MHz
NUC1 1H
P1 14.80 usec
PLW1 12.00000000 W

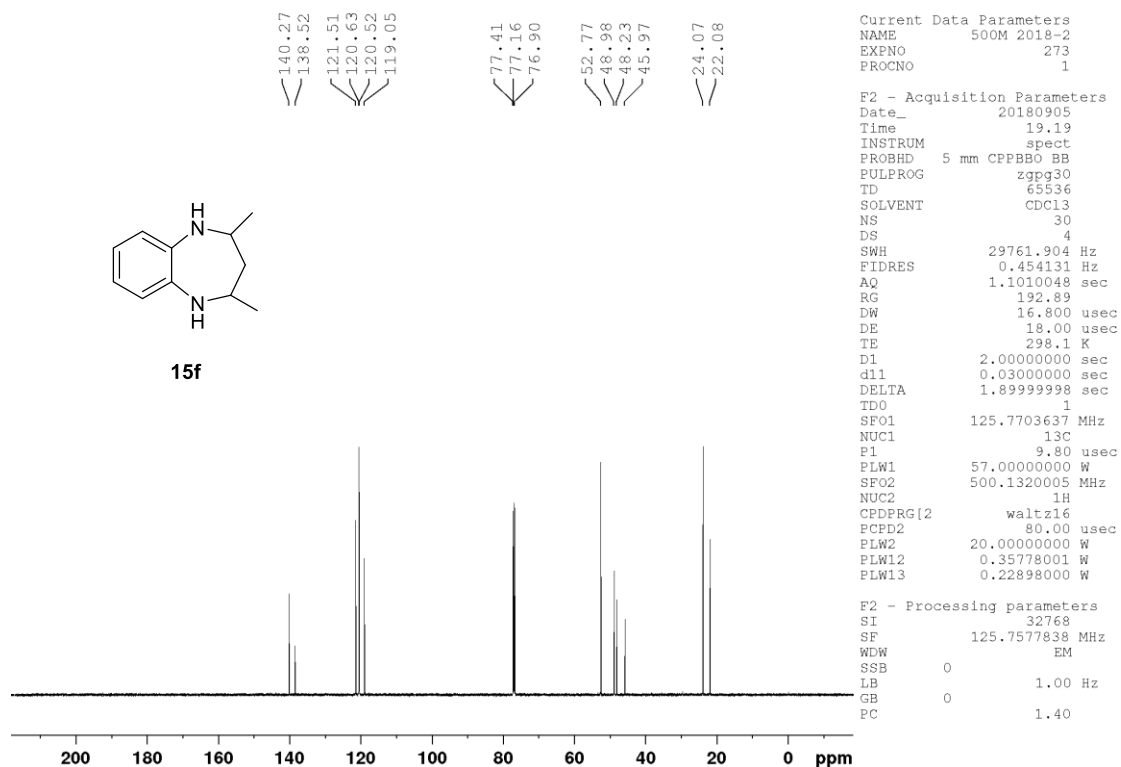
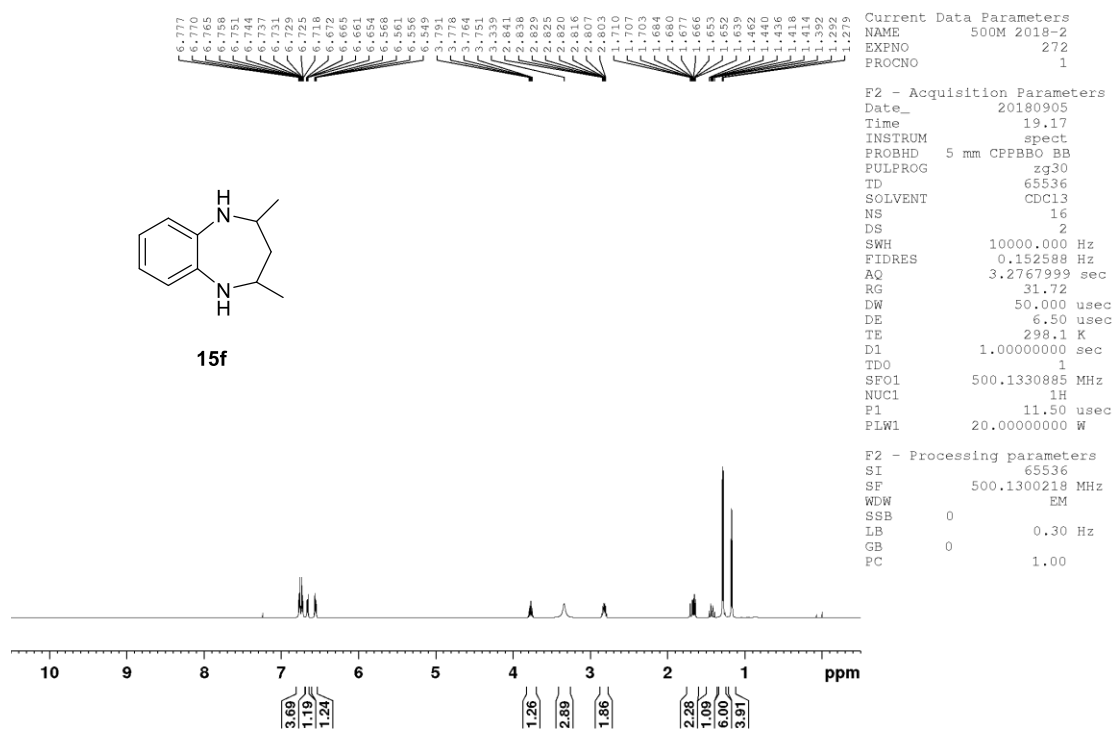
F2 - Processing parameters
SI 65536
SF 400.2400358 MHz
WDW EM
SSB 0
LB 0.30 Hz
GB 0
PC 1.00



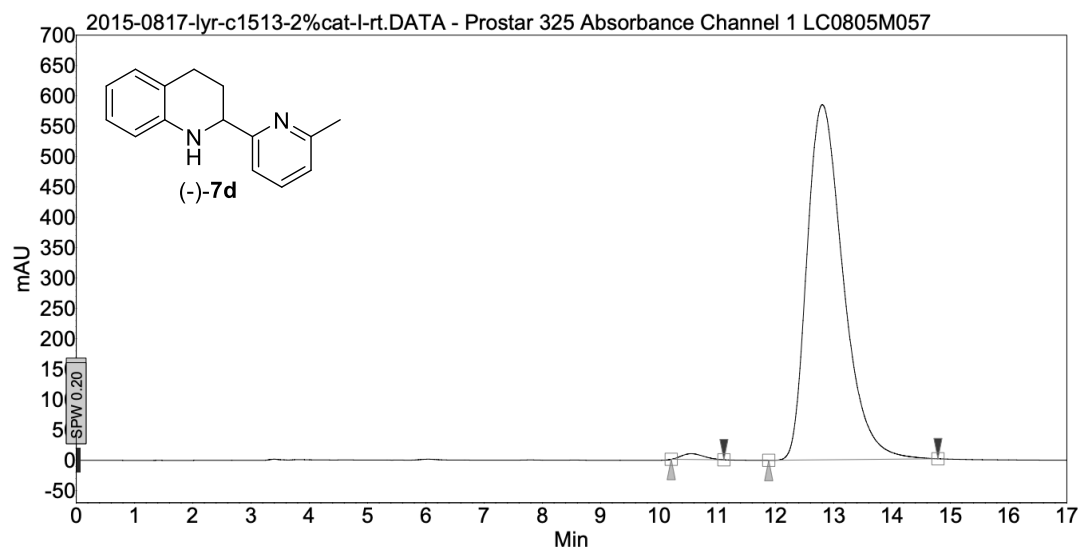
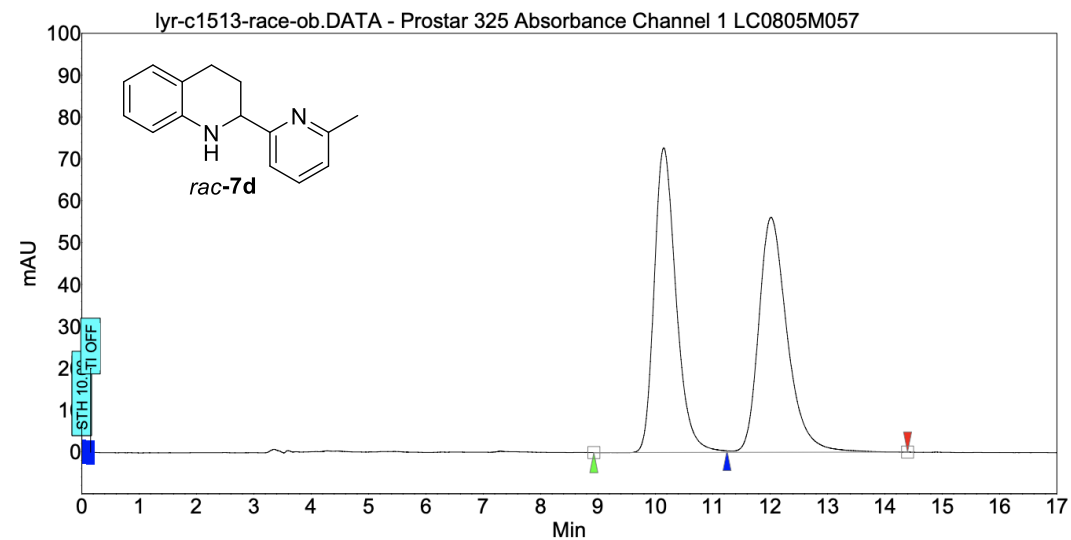
Current Data Parameters
NAME 400M 2018
EXPNO 508
PROCNO 1

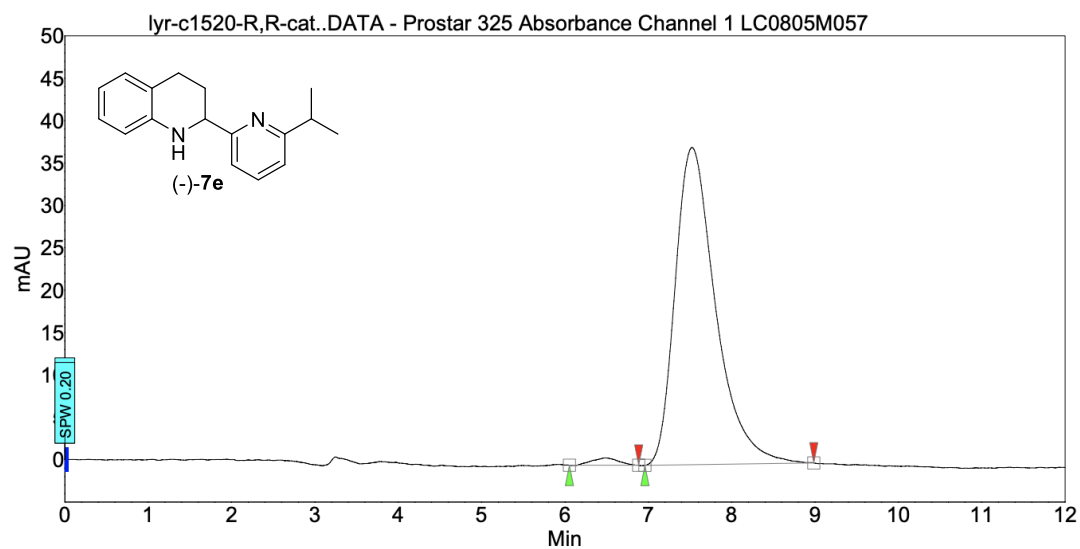
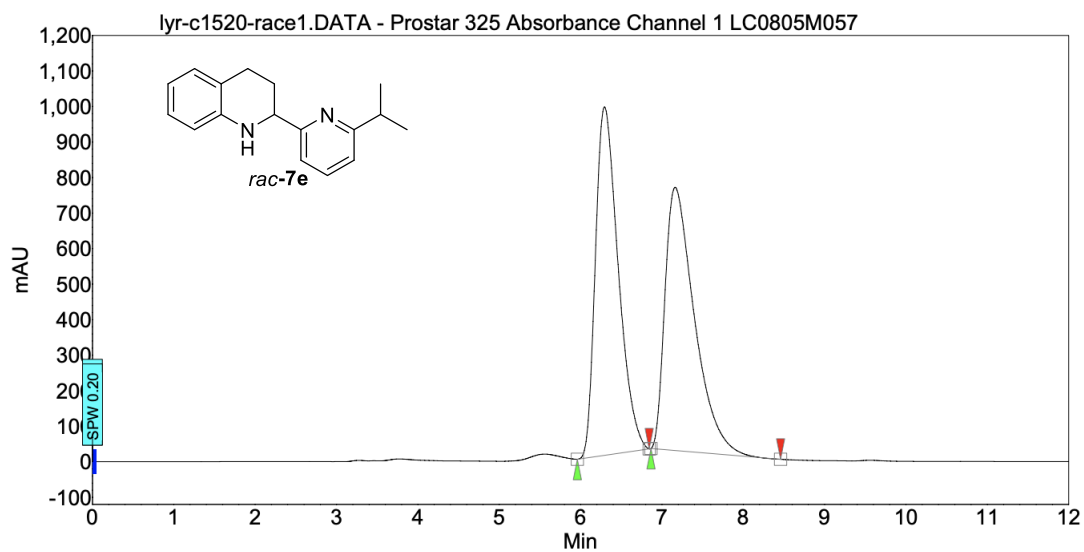
F2 - Acquisition Parameters
Date_ 20180906
Time 11.12
INSTRUM spect
PROBHD 5 mm PABBO BB/
PULPROG zgpg30
TD 65536
SOLVENT CDCl3
NS 126
DS 4
SWH 24038.461 Hz
FIDRES 0.366798 Hz
AQ 1.3631488 sec
RG 206.33
DW 20.800 usec
DE 6.50 usec
TE 300.8 K
D1 2.00000000 sec
d11 0.03000000 sec
DELTA 1.89999999 sec
TD0 1
SFO1 100.6504916 MHz
NUC1 13C
P1 10.00 usec
PLW1 54.00000000 W
SFO2 400.2416010 MHz
NUC2 1H
CPDPRG2 waltz16
PCPD2 90.00 usec
PLW2 12.00000000 W
PLW12 0.34680000 W
PLW13 0.28090999 W

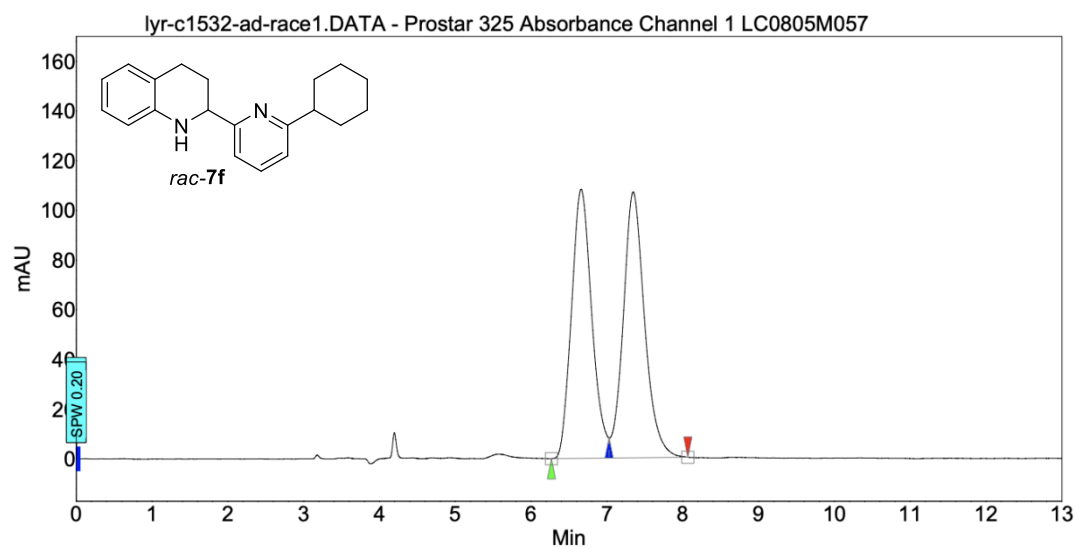
F2 - Processing parameters
SI 32768
SF 100.6404239 MHz
WDW EM
SSB 0
LB 1.00 Hz
GB 0
PC 1.40



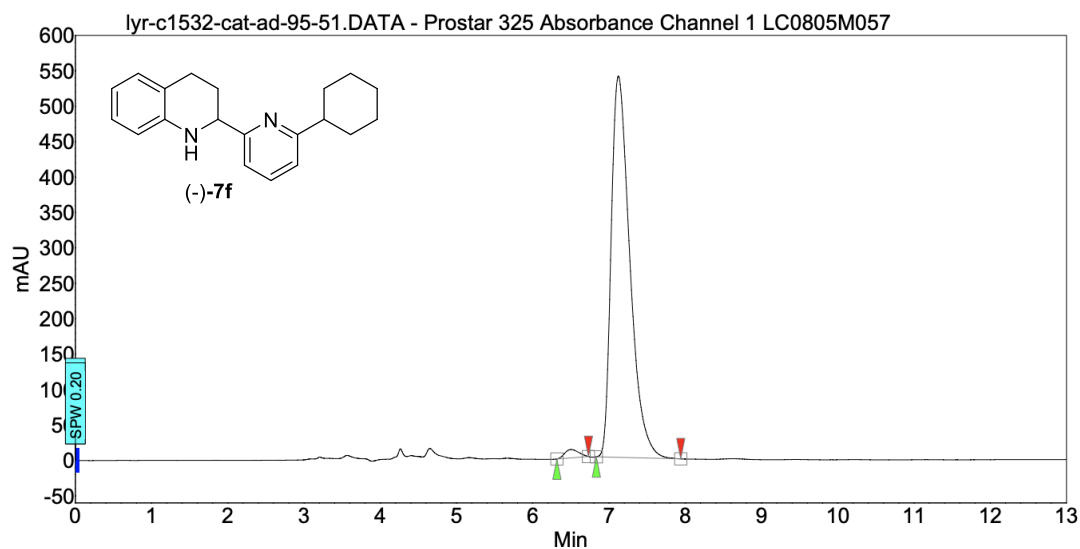
13. Copy of HPLC spectra



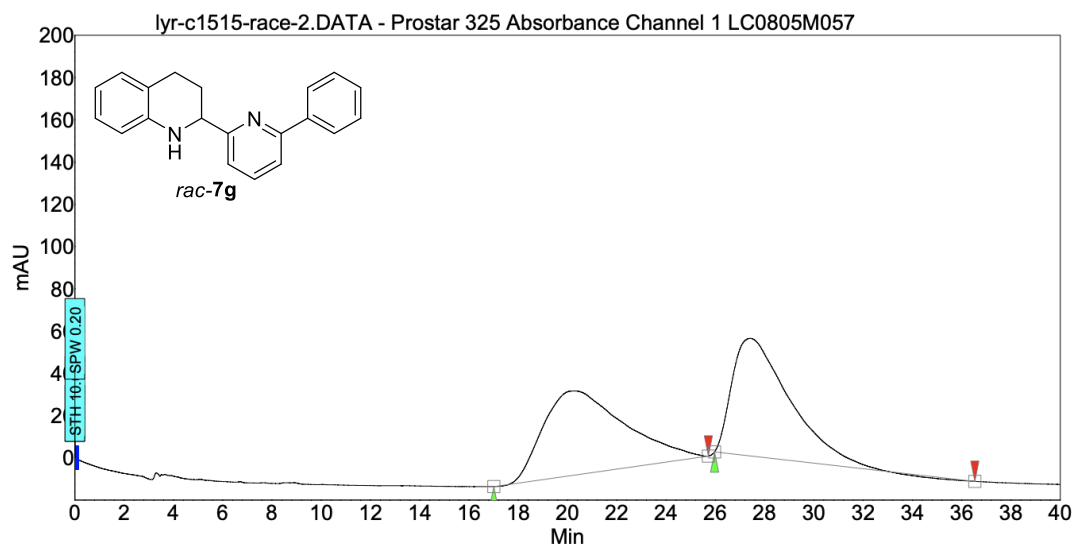




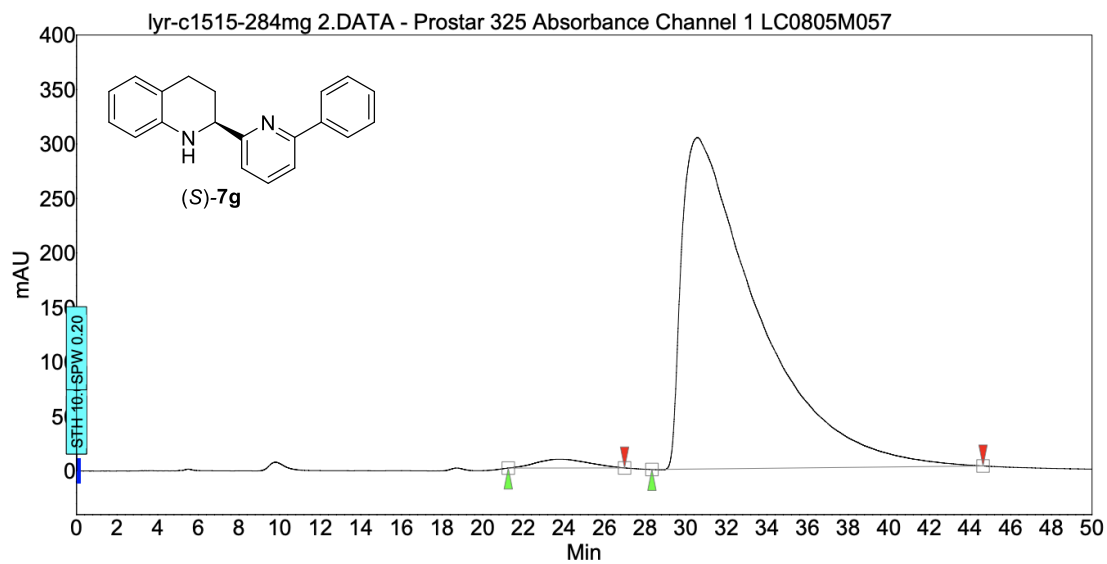
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	6.66	49.02	108.3	33.6	49.018
2	未知	7.35	50.98	107.0	35.0	50.982
Total			100.00	215.3	68.6	100.000



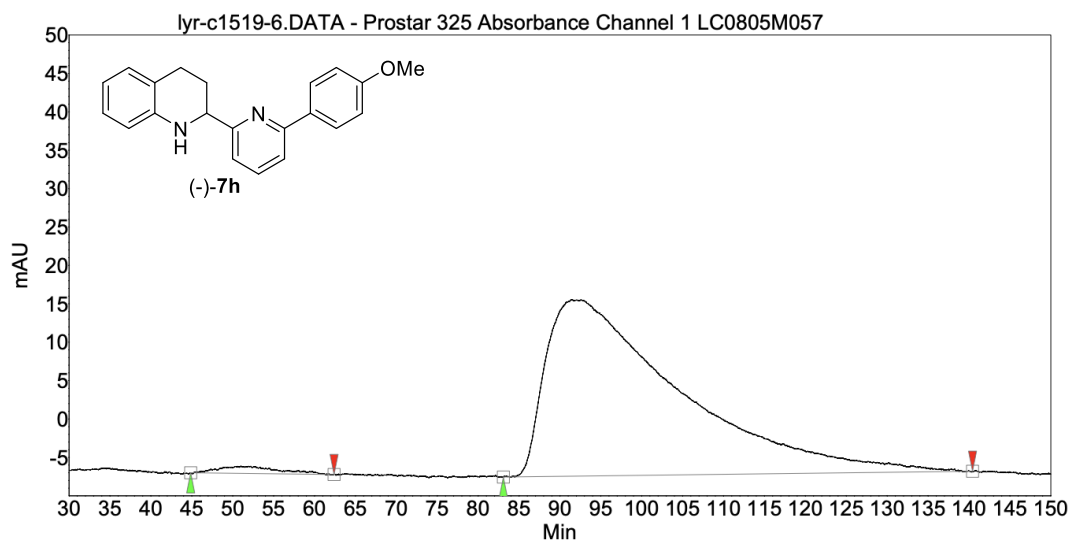
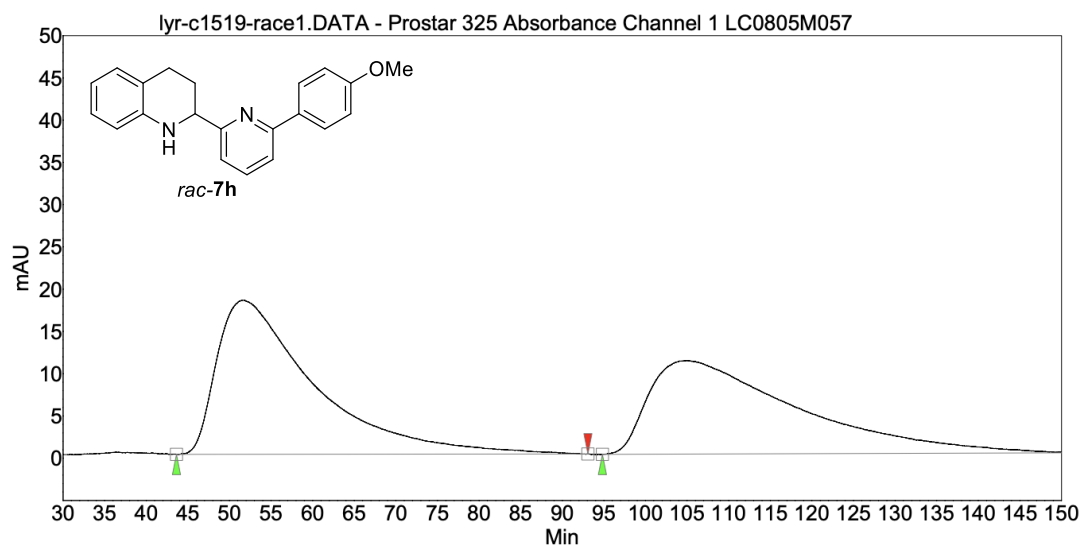
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	6.49	1.63	11.9	2.5	1.631
2	未知	7.12	98.37	538.3	152.5	98.369
Total			100.00	550.1	155.0	100.000

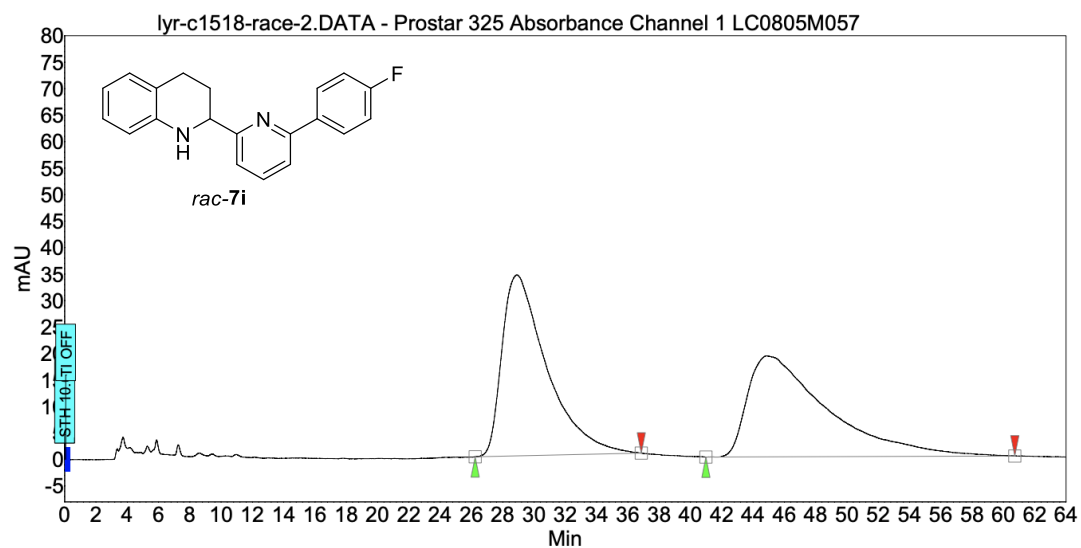


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	20.10	50.21	40.0	151.9	50.213
2	未知	27.43	49.79	55.7	150.7	49.787
Total			100.00	95.7	302.6	100.000

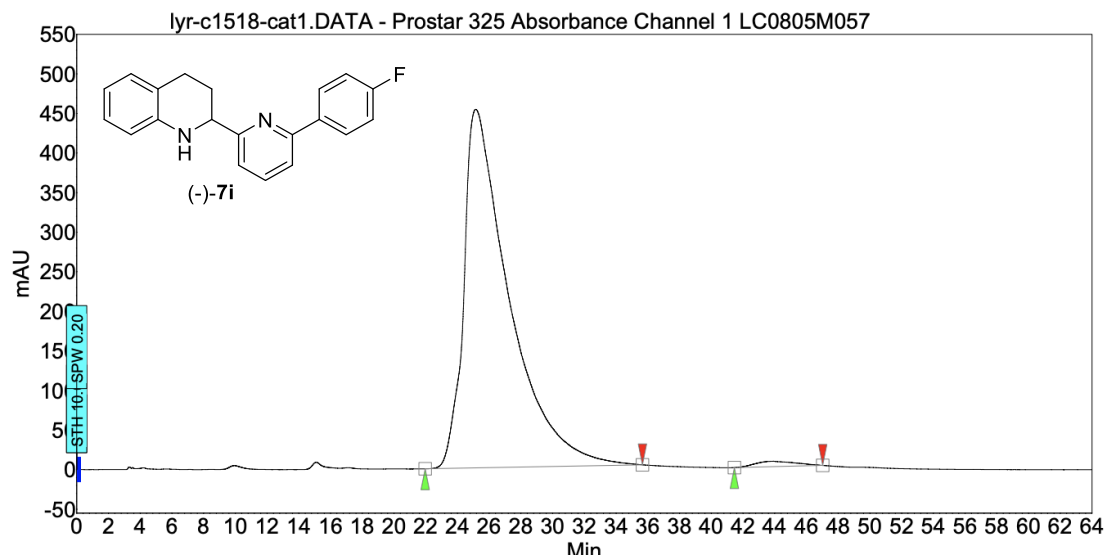


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	23.66	1.78	8.0	23.9	1.777
2	未知	30.57	98.22	304.1	1321.2	98.223
Total			100.00	312.0	1345.1	100.000

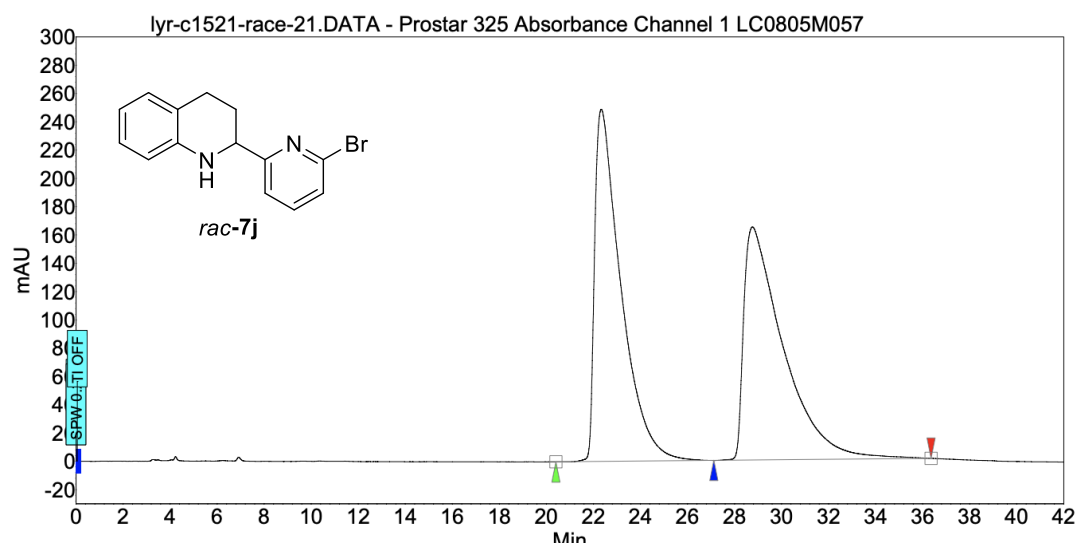




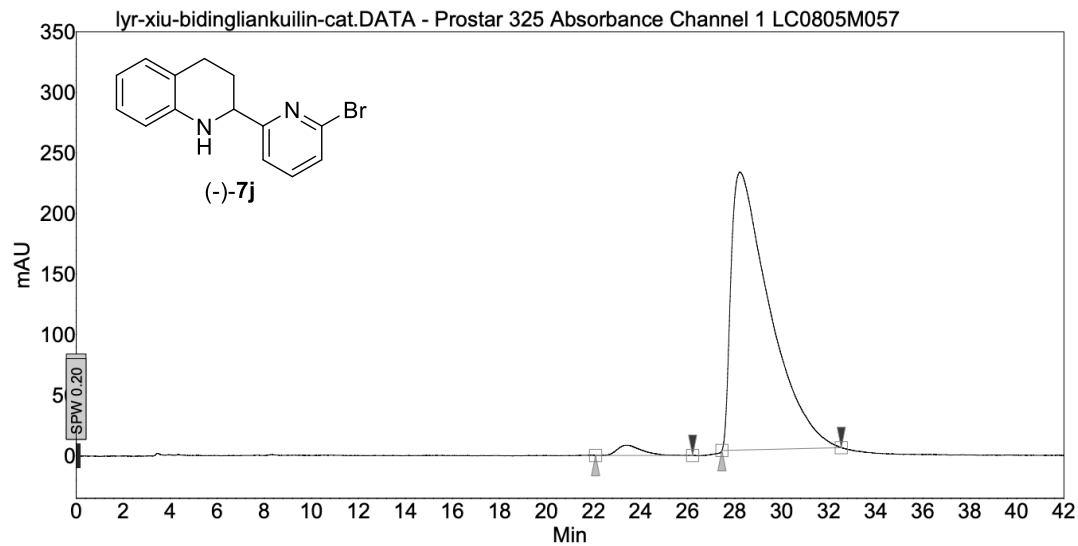
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	28.91	50.21	34.2	113.4	50.209
2	未知	44.86	49.79	19.1	112.4	49.791
Total			100.00	53.2	225.8	100.000



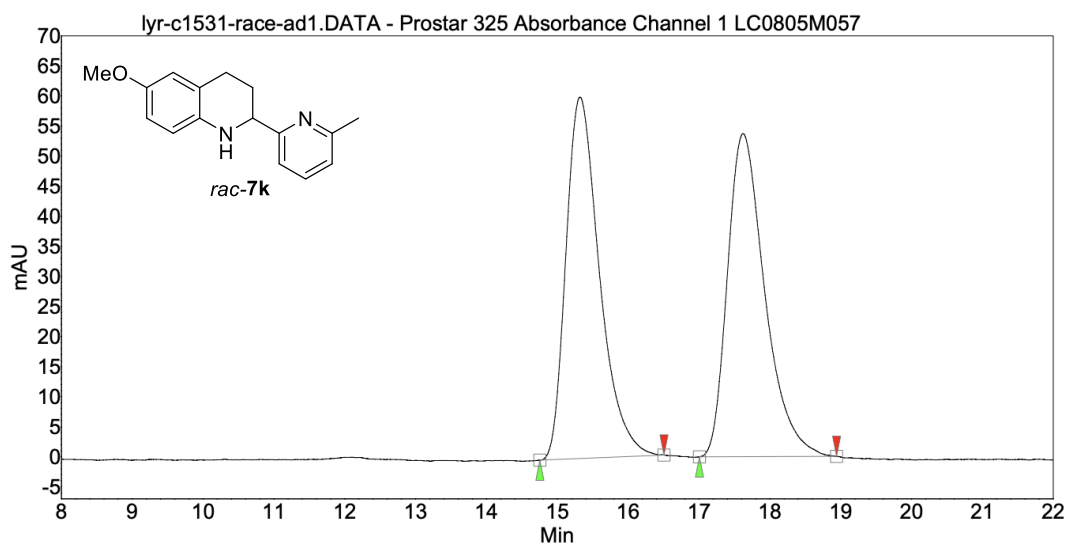
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	25.15	98.69	453.1	1498.5	98.693
2	未知	43.85	1.31	6.8	19.8	1.307
Total			100.00	459.9	1518.3	100.000



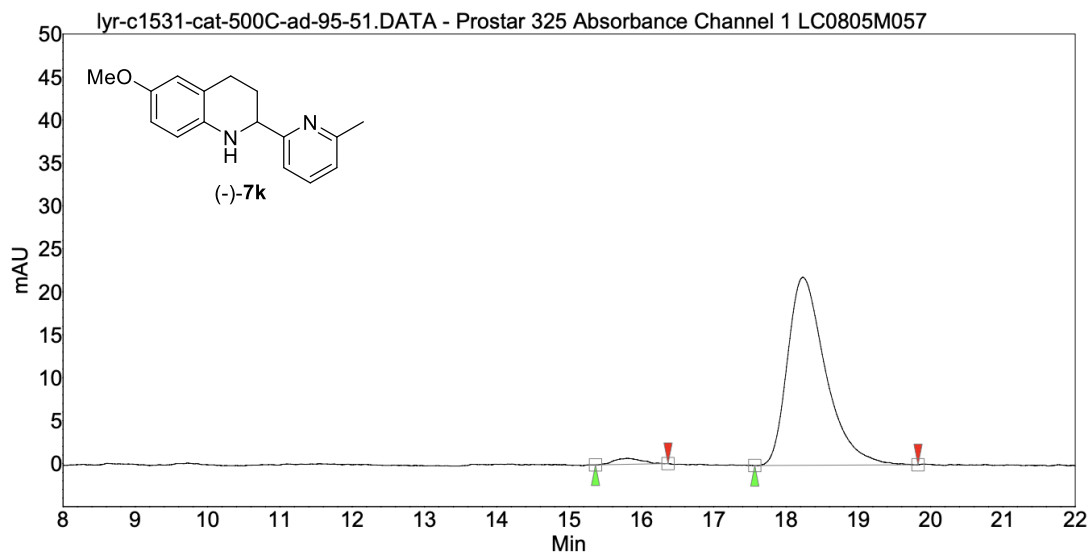
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	22.33	50.11	248.9	321.5	50.113
2	未知	28.77	49.89	164.7	320.0	49.887
Total			100.00	413.6	641.5	100.000



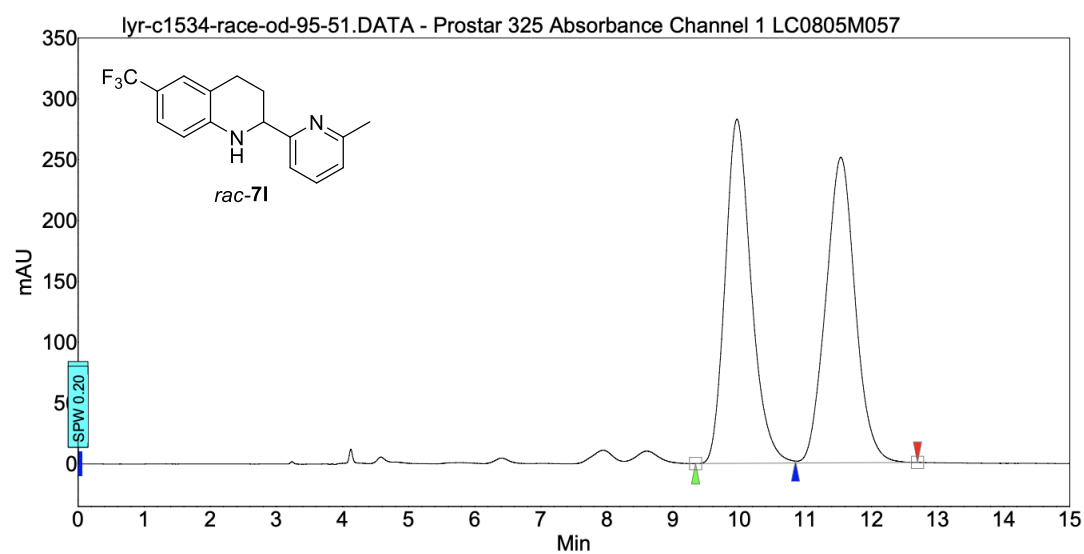
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	23.37	2.34	8.4	10.4	2.336
1	未知	28.23	97.66	229.4	436.8	97.664
Total			100.00	237.8	447.2	100.000



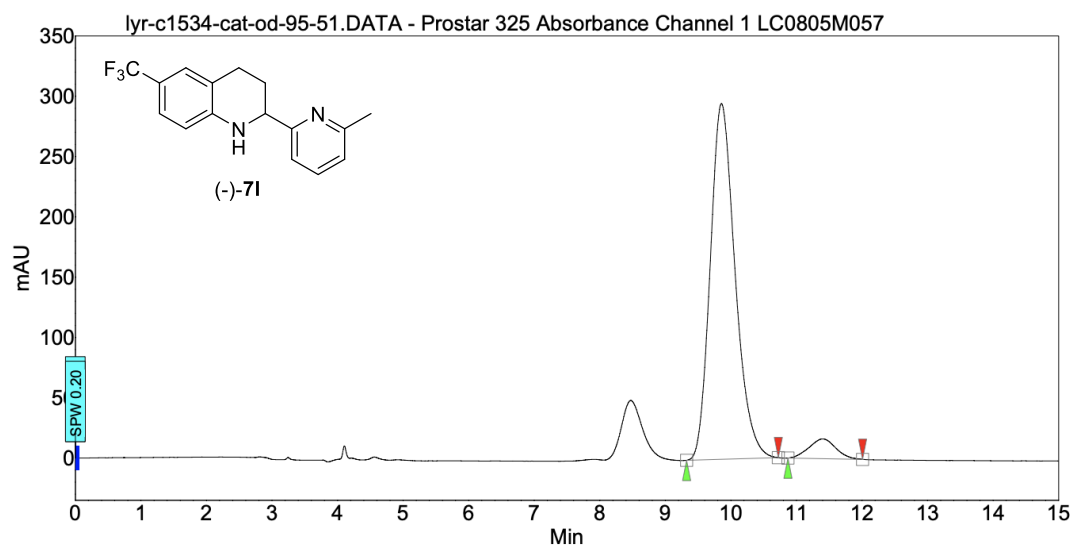
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	15.32	50.11	60.1	32.9	50.109
1	未知	17.62	49.89	53.7	32.8	49.891
Total			100.00	113.8	65.7	100.000



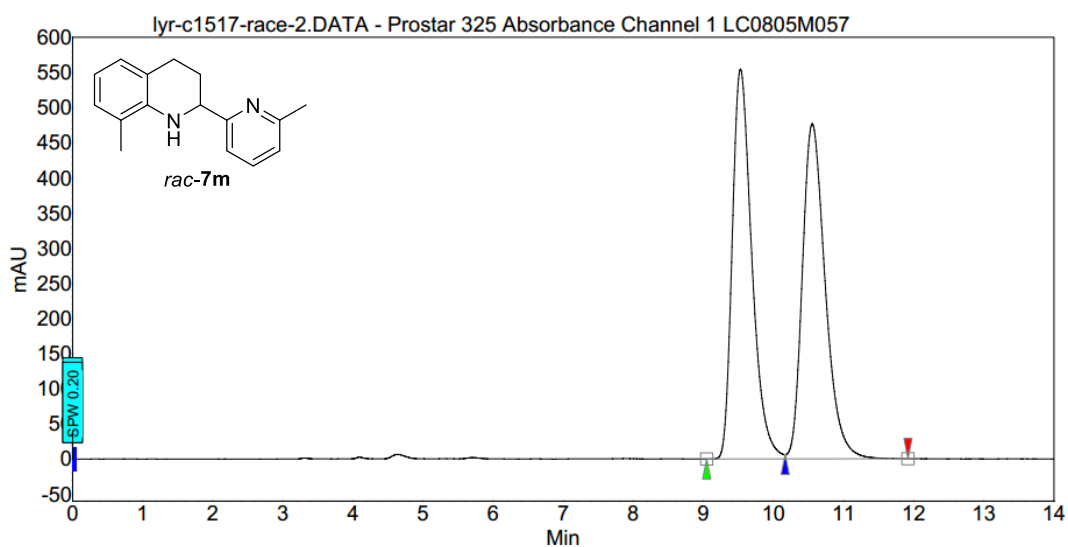
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	15.80	2.28	0.7	0.3	2.283
2	未知	18.23	97.72	21.9	13.4	97.717
Total			100.00	22.6	13.7	100.000



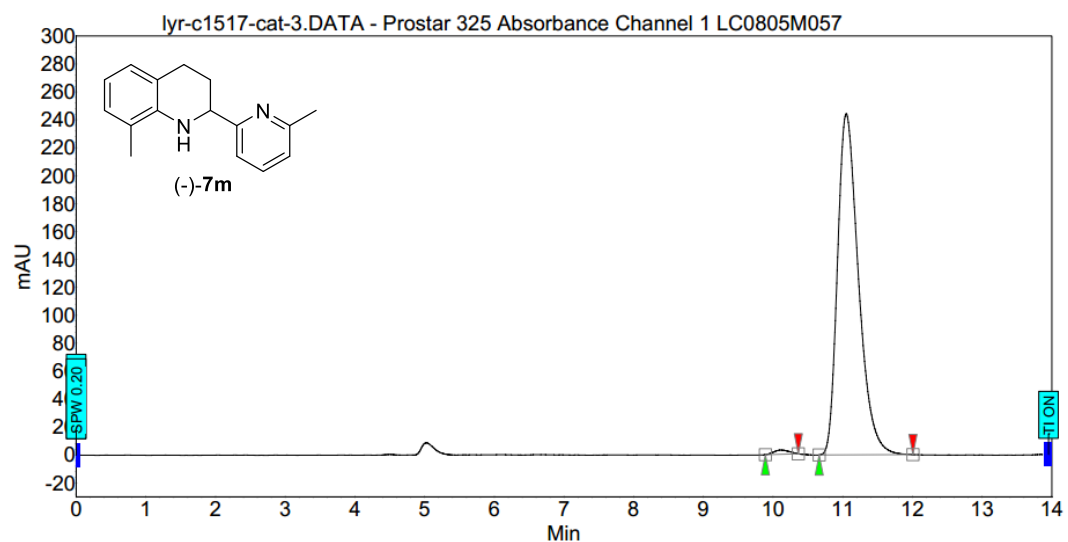
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	9.97	49.90	283.0	129.1	49.902
2	未知	11.54	50.10	251.1	129.6	50.098
Total			100.00	534.1	258.6	100.000



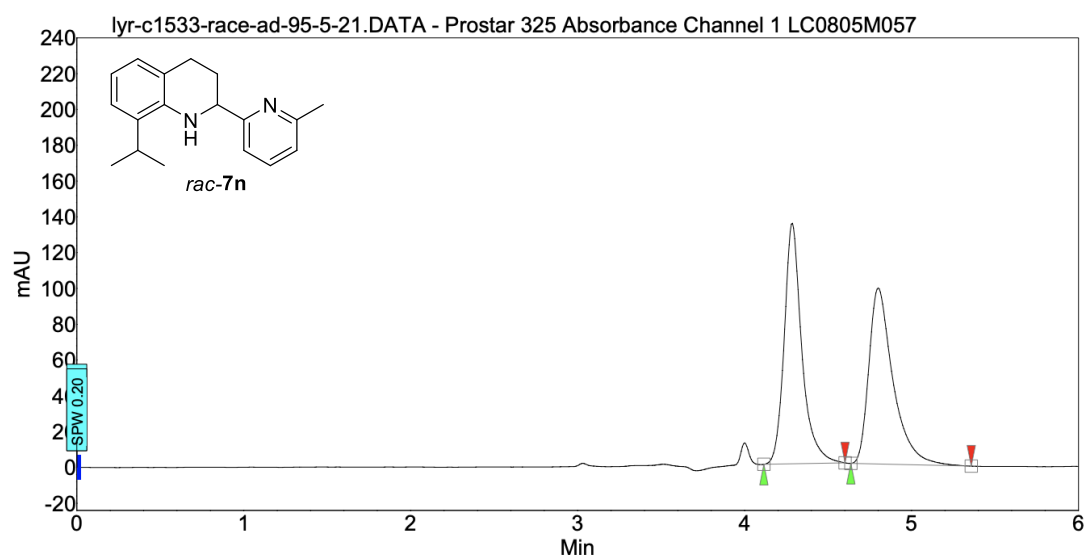
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	9.85	94.37	294.9	129.6	94.367
2	未知	11.40	5.63	16.3	7.7	5.633
Total			100.00	311.2	137.4	100.000



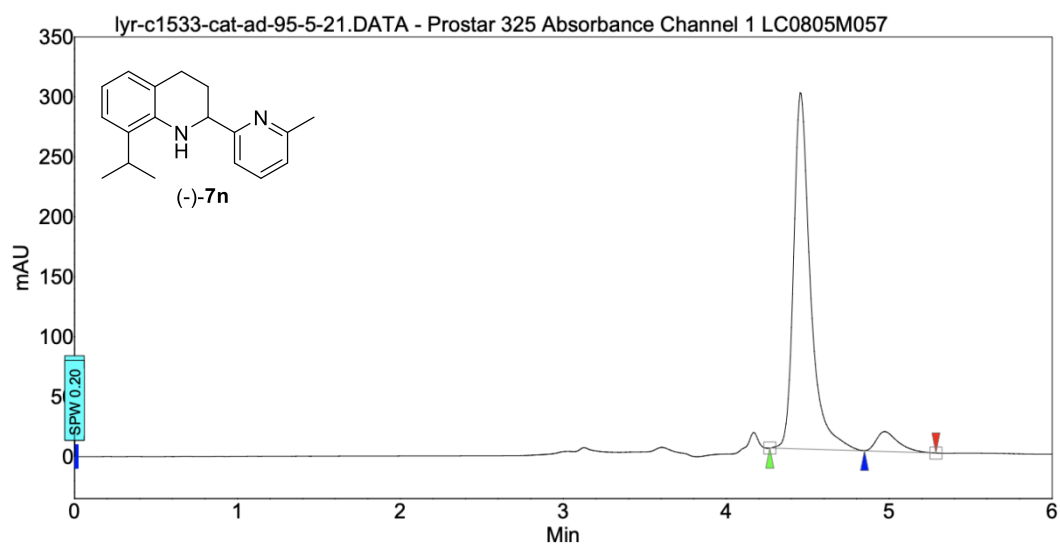
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	9.53	49.86	554.6	179.4	49.860
2	未知	10.55	50.14	476.8	180.4	50.140
Total			100.00	1031.4	359.8	100.000



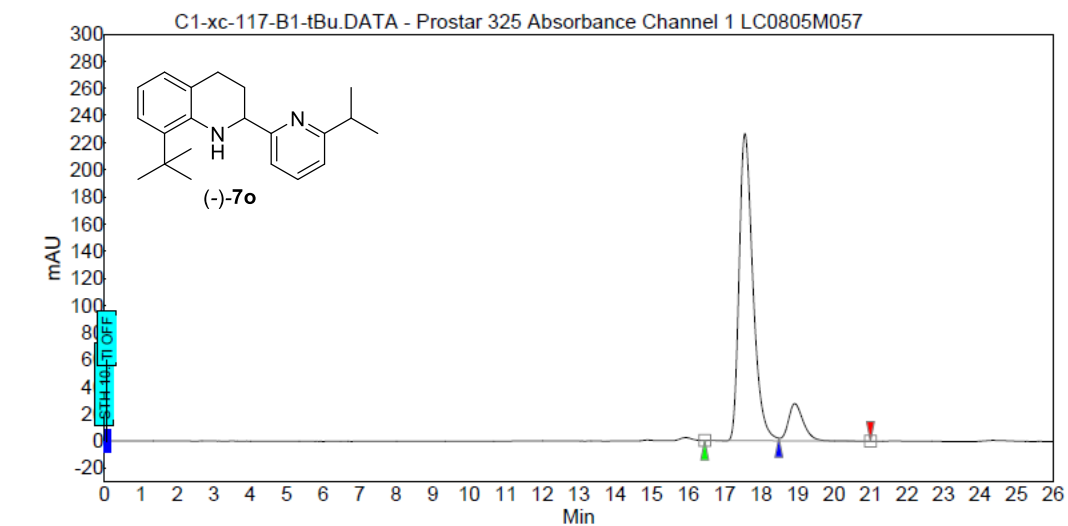
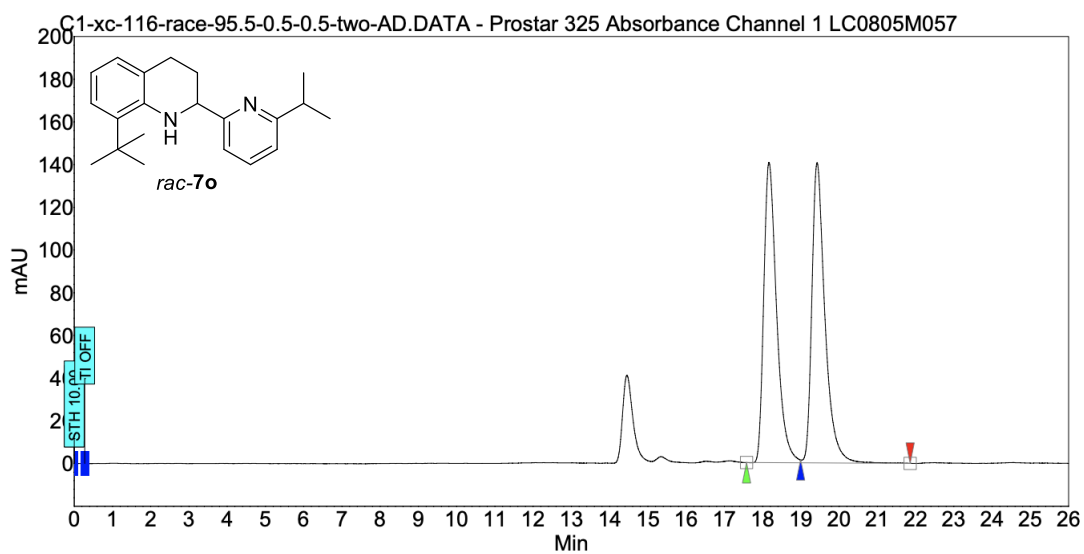
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	10.11	0.90	3.0	0.8	0.899
2	未知	11.05	99.10	244.2	85.1	99.101
Total			100.00	247.2	85.9	100.000

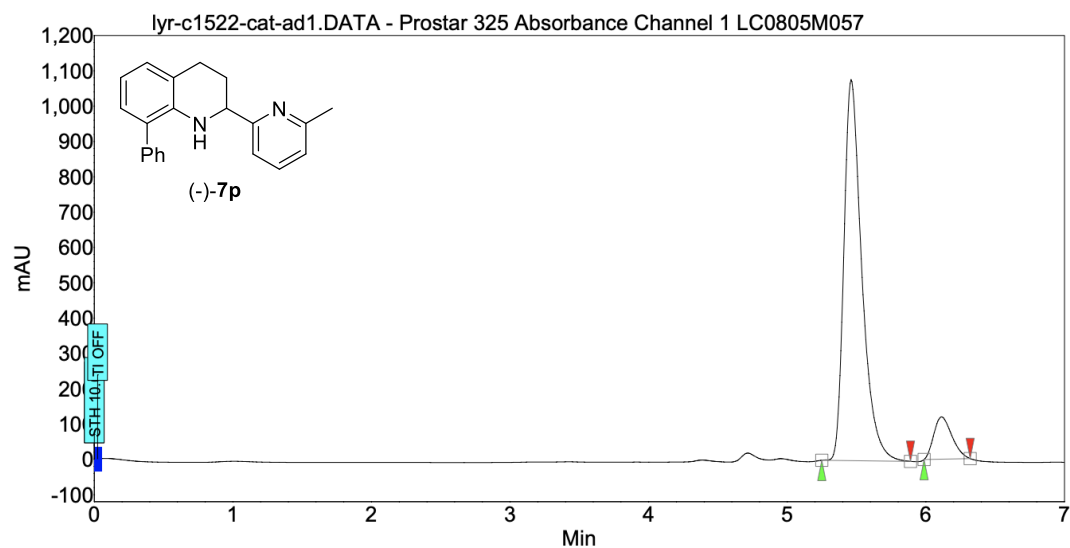
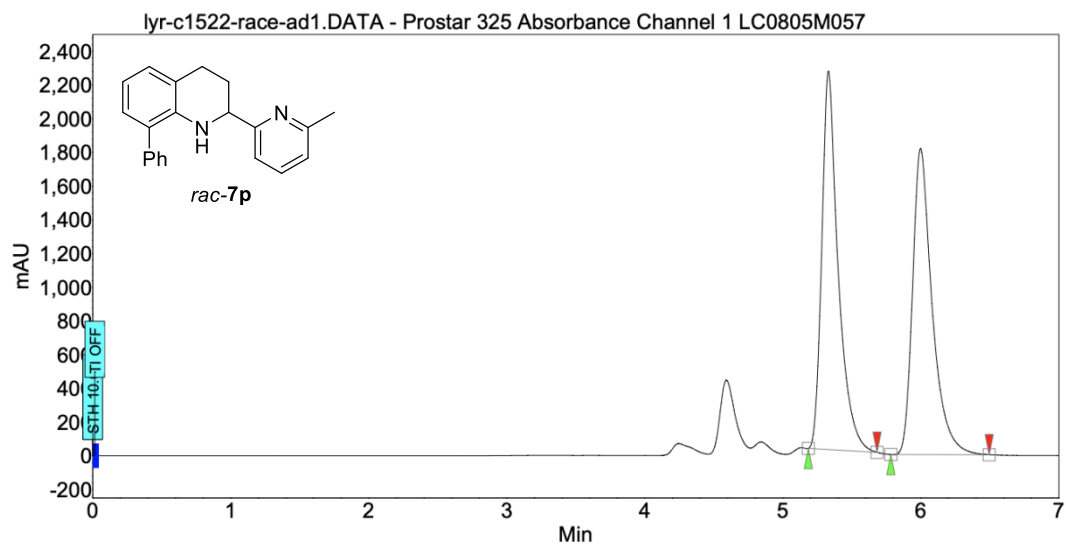


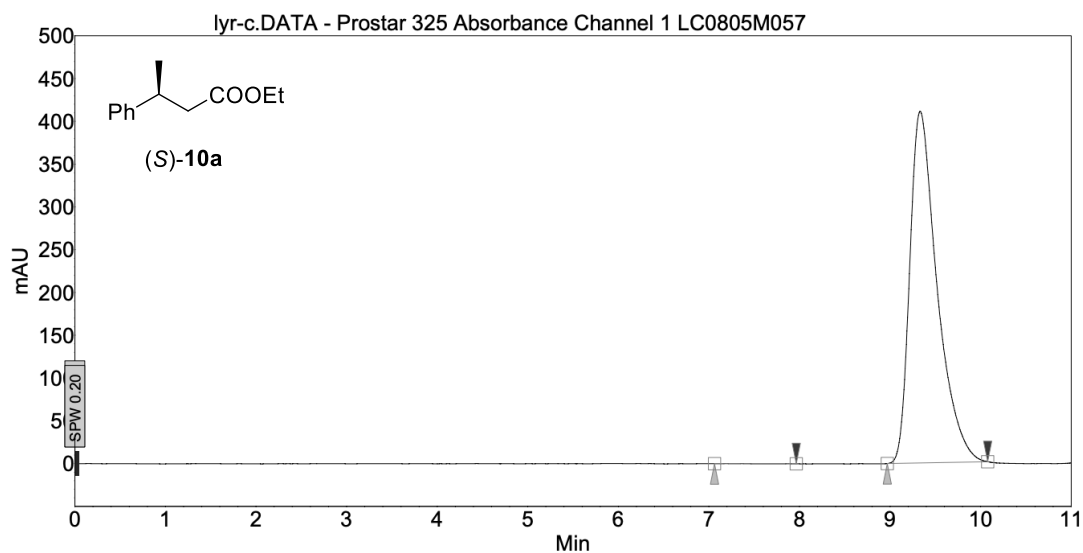
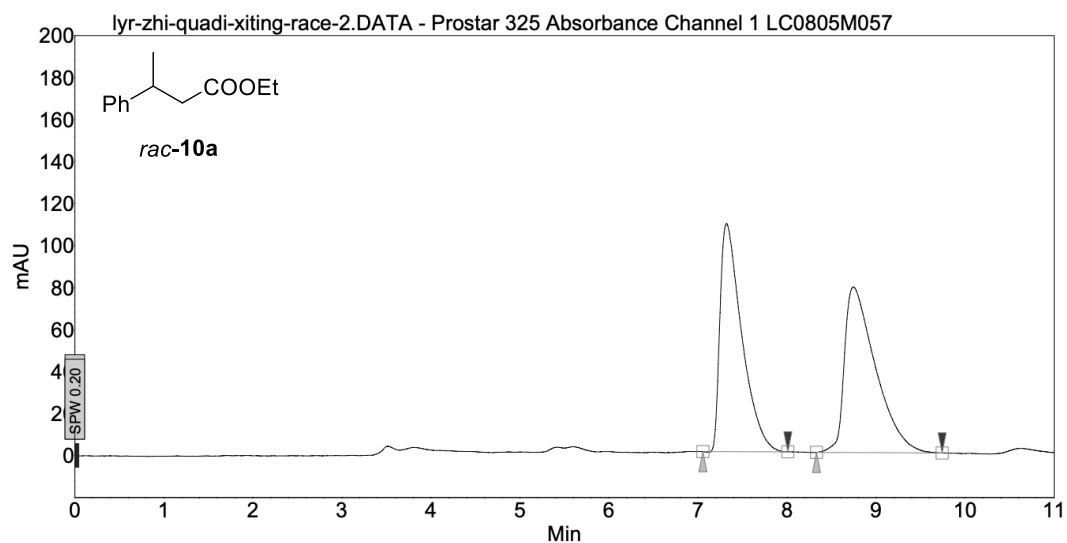
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	4.29	49.89	134.5	16.4	49.892
2	未知	4.80	50.11	98.4	16.5	50.108
Total			100.00	232.9	32.9	100.000

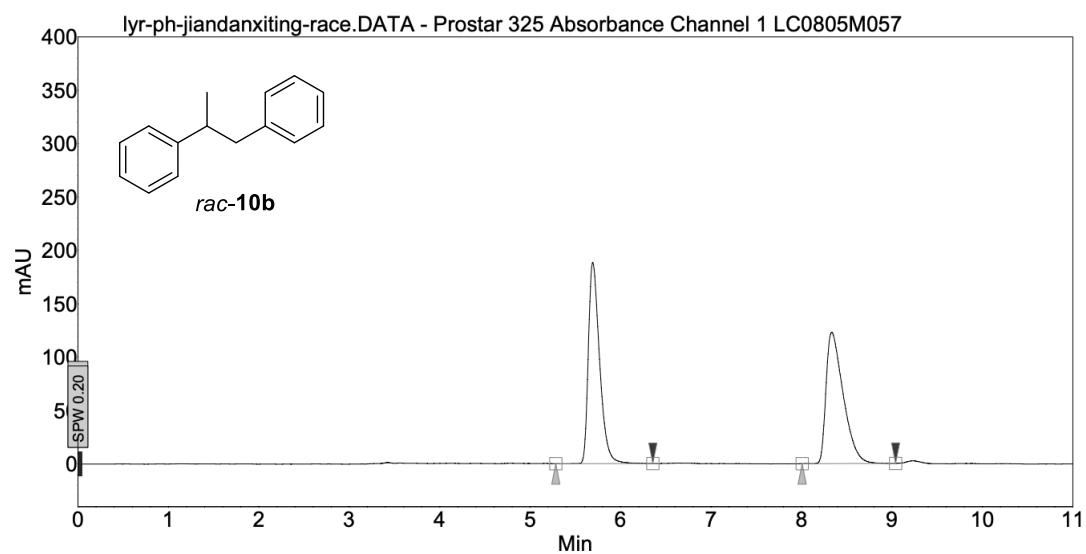


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	4.45	93.25	297.1	35.6	93.250
2	未知	4.97	6.75	16.6	2.6	6.750
Total			100.00	313.7	38.1	100.000

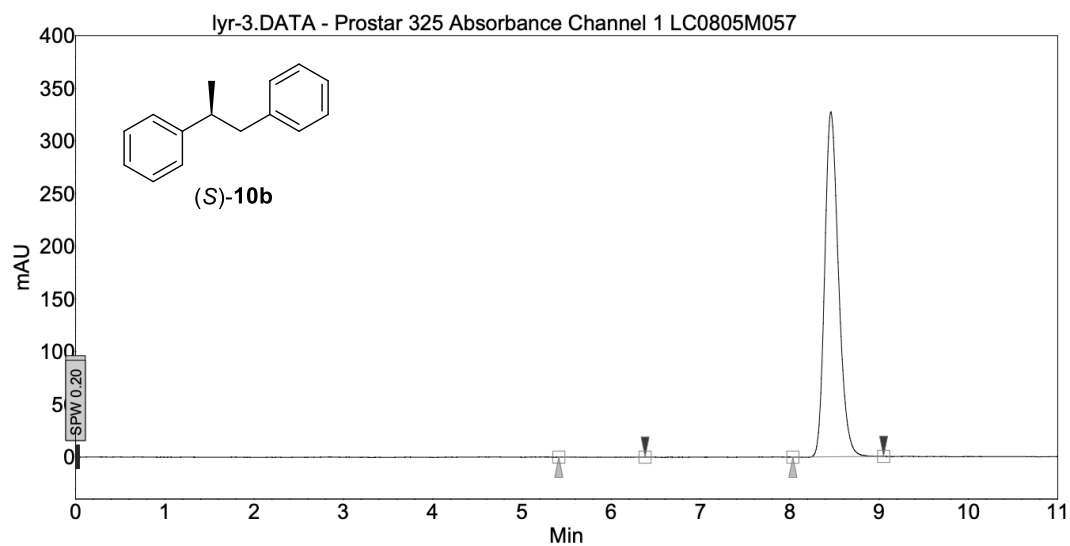




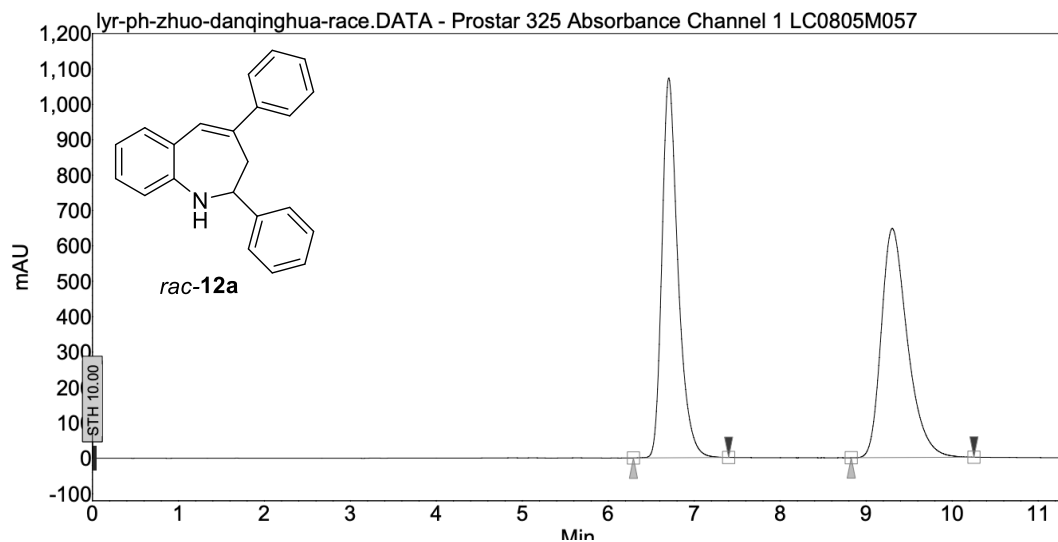




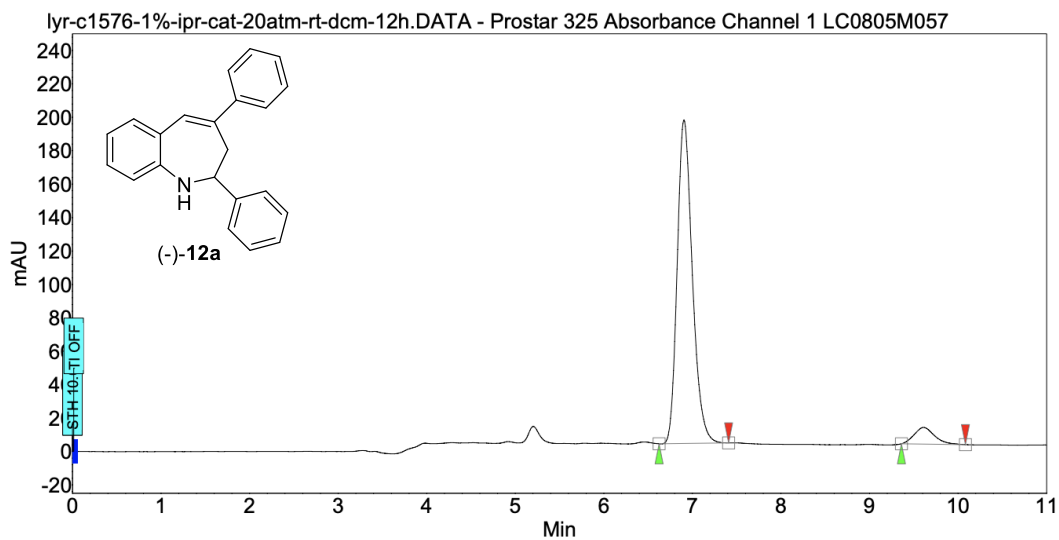
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	5.69	50.09	188.6	27.1	50.095
2	未知	8.33	49.91	123.1	27.0	49.905
Total			100.00	311.7	54.1	100.000



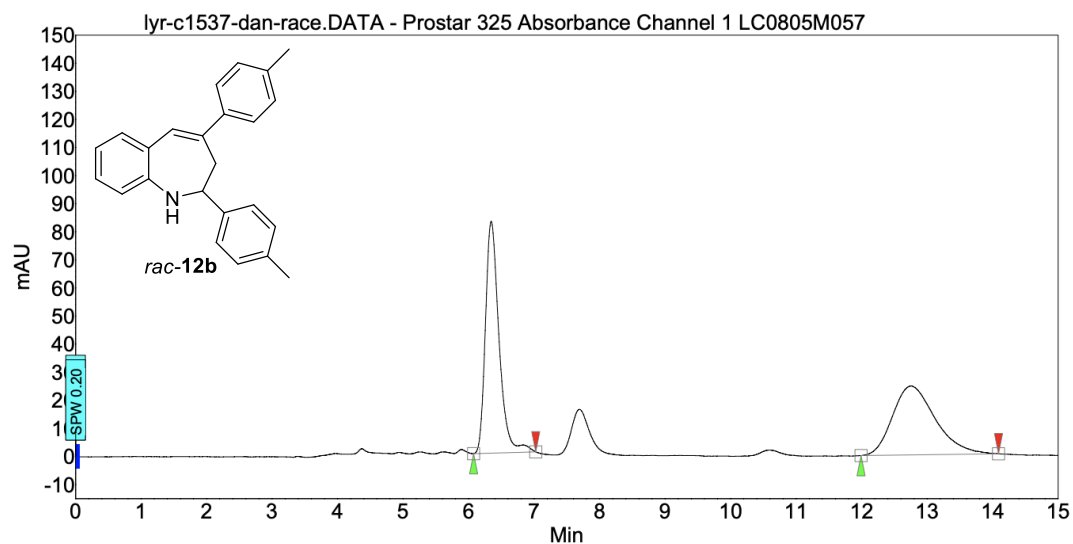
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	5.49	0.03	0.2	0.0	0.032
1	未知	8.46	99.97	327.5	58.6	99.968
Total			100.00	327.7	58.6	100.000



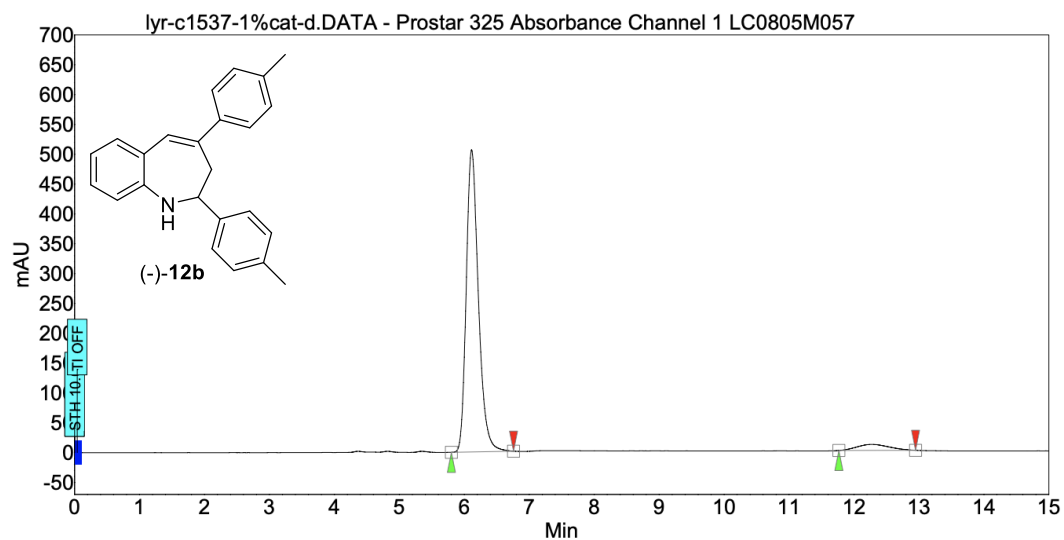
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	6.71	50.38	1073.3	231.7	50.382
2	未知	9.31	49.62	647.1	228.2	49.618
Total			100.00	1720.4	459.9	100.000



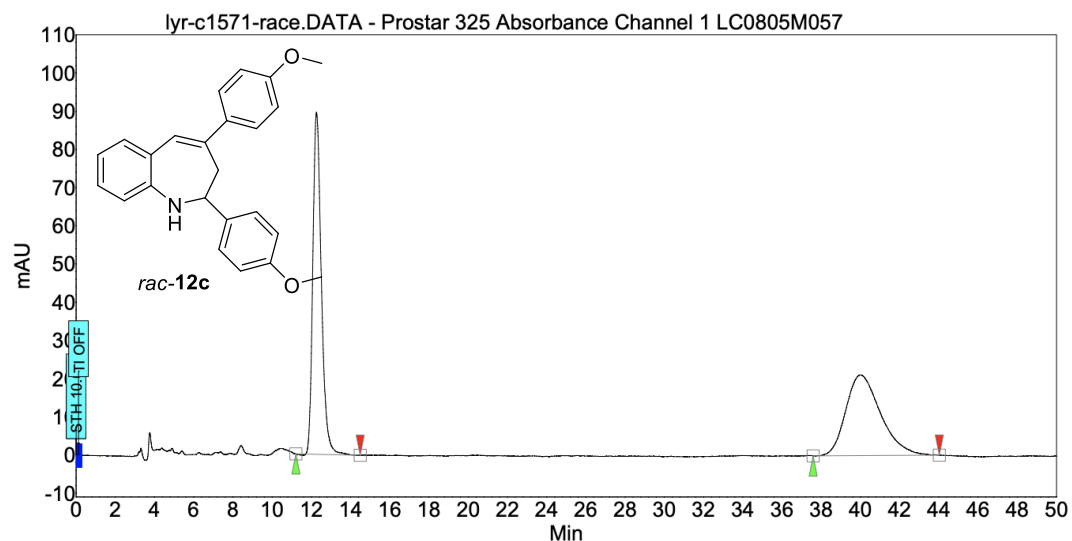
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	6.91	93.54	193.7	38.4	93.539
2	未知	9.61	6.46	9.9	2.6	6.461
Total			100.00	203.6	41.0	100.000



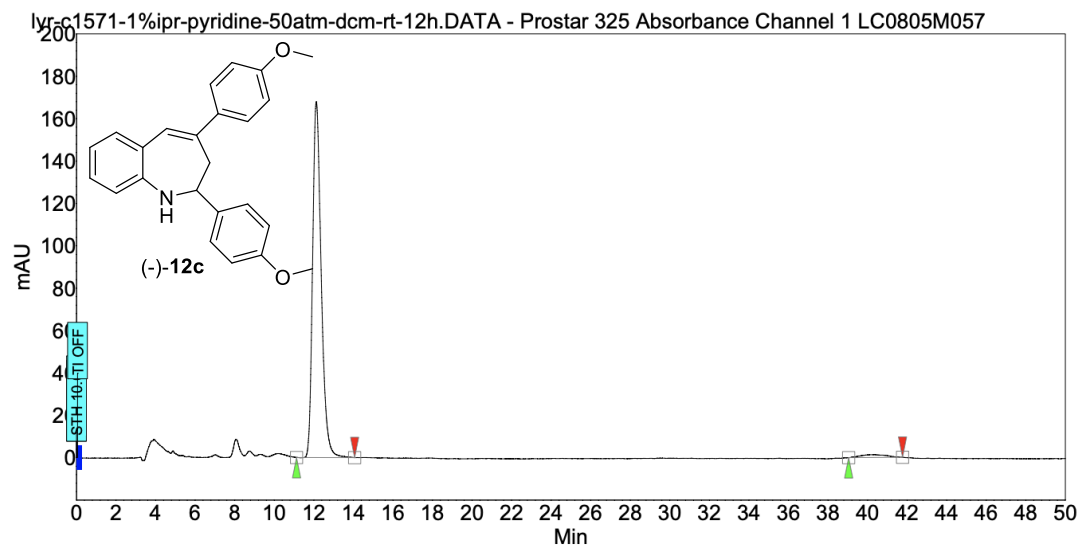
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	6.35	51.83	82.5	19.9	51.831
1	未知	12.75	48.17	24.5	18.5	48.169
Total			100.00	107.0	38.4	100.000



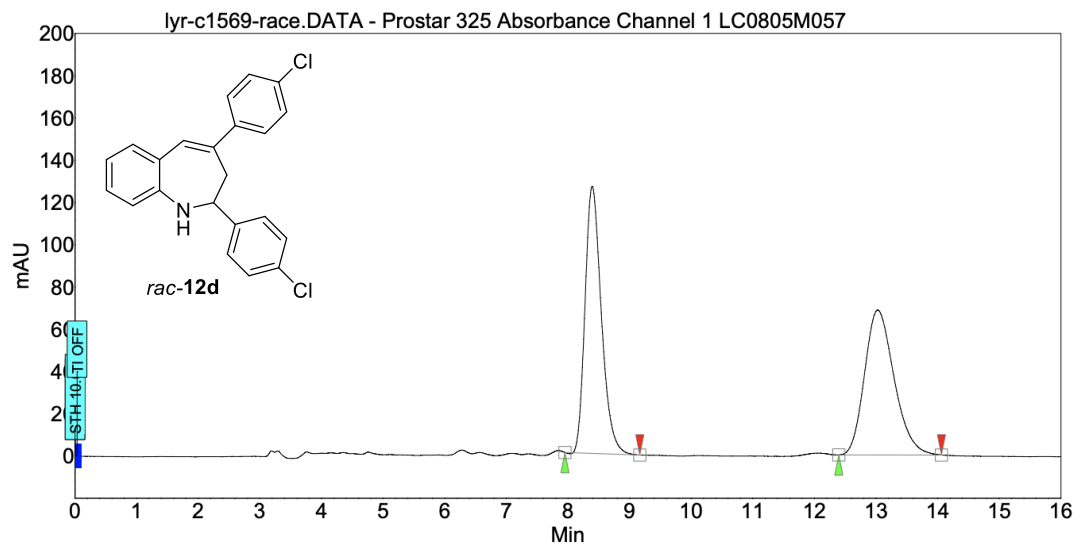
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	6.11	95.03	506.4	109.5	95.027
2	未知	12.27	4.97	10.0	5.7	4.973
Total			100.00	516.5	115.2	100.000



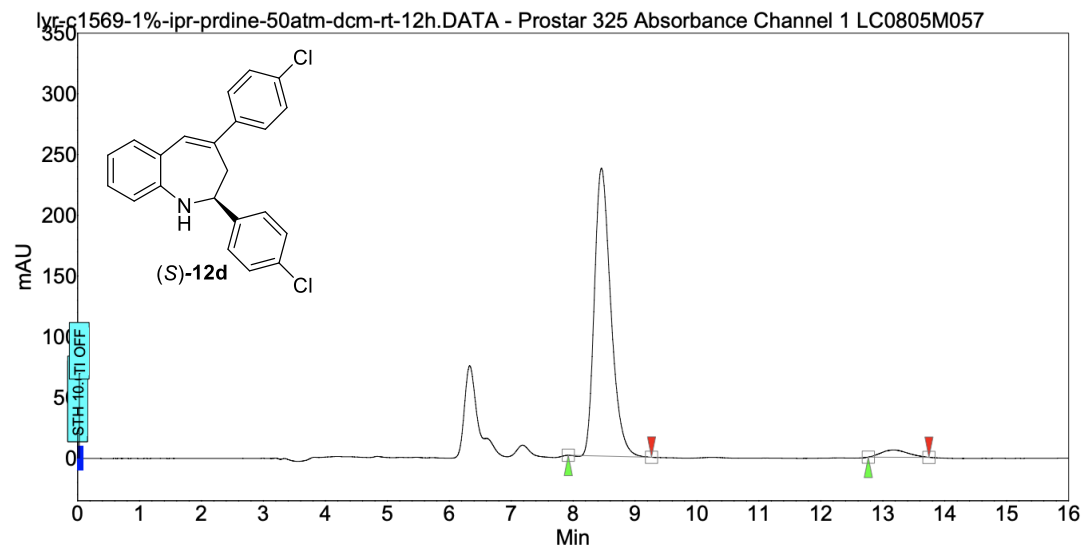
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	12.26	50.95	89.5	45.0	50.953
1	未知	39.99	49.05	21.1	43.3	49.047
Total			100.00	110.6	88.4	100.000



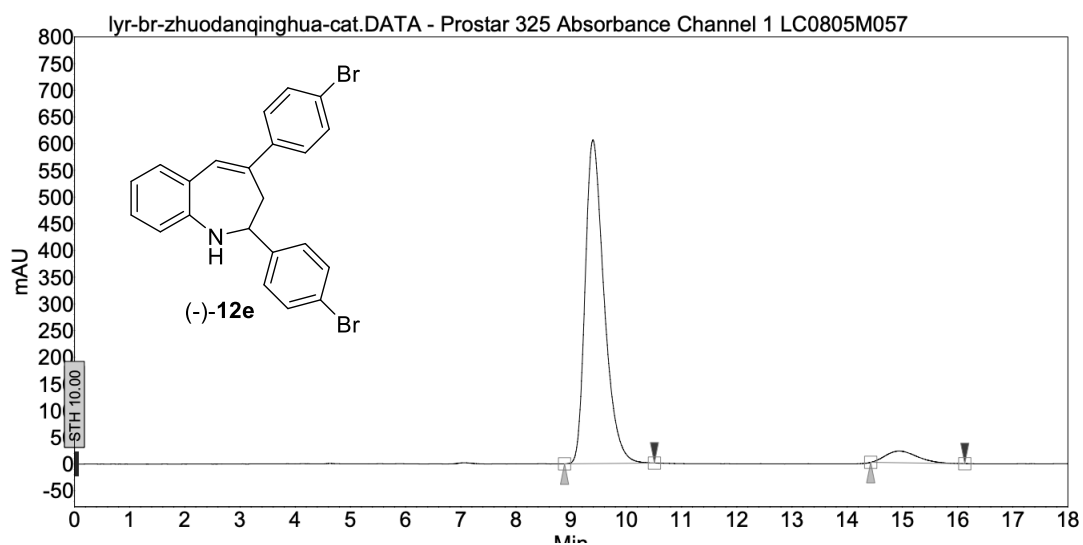
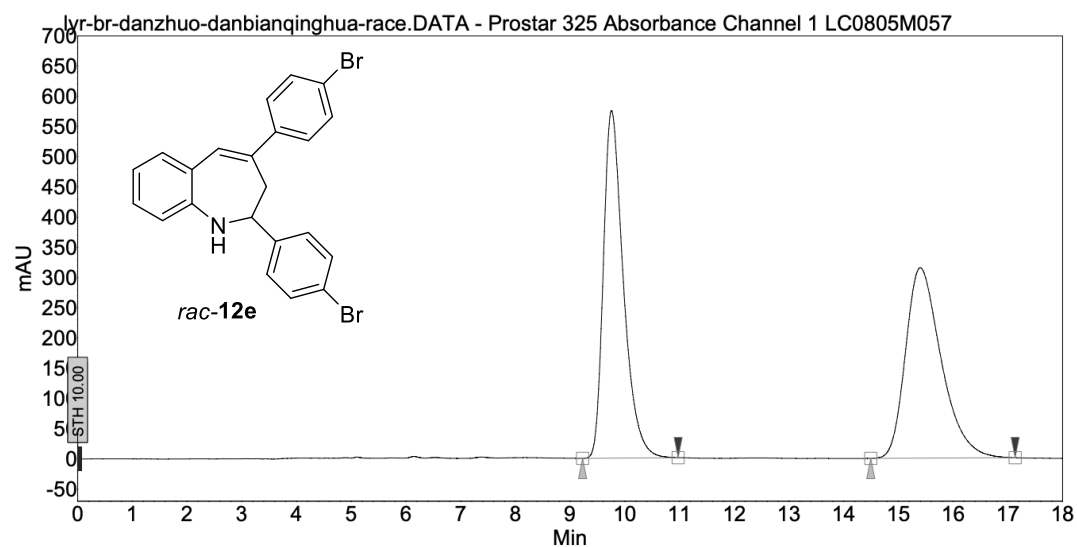
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	12.13	97.71	167.9	84.6	97.713
2	未知	40.13	2.29	1.3	2.0	2.287
Total			100.00	169.2	86.6	100.000

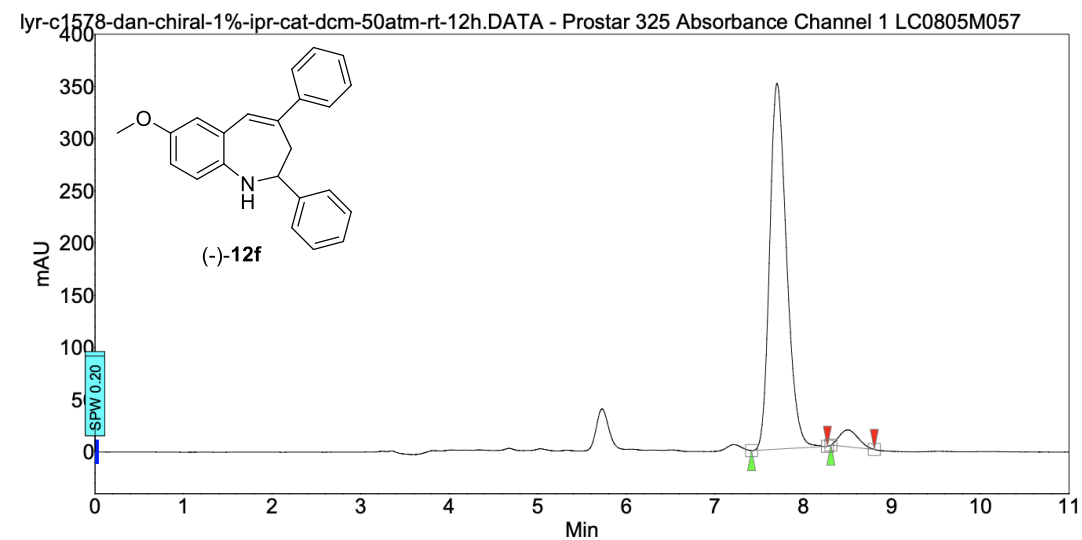
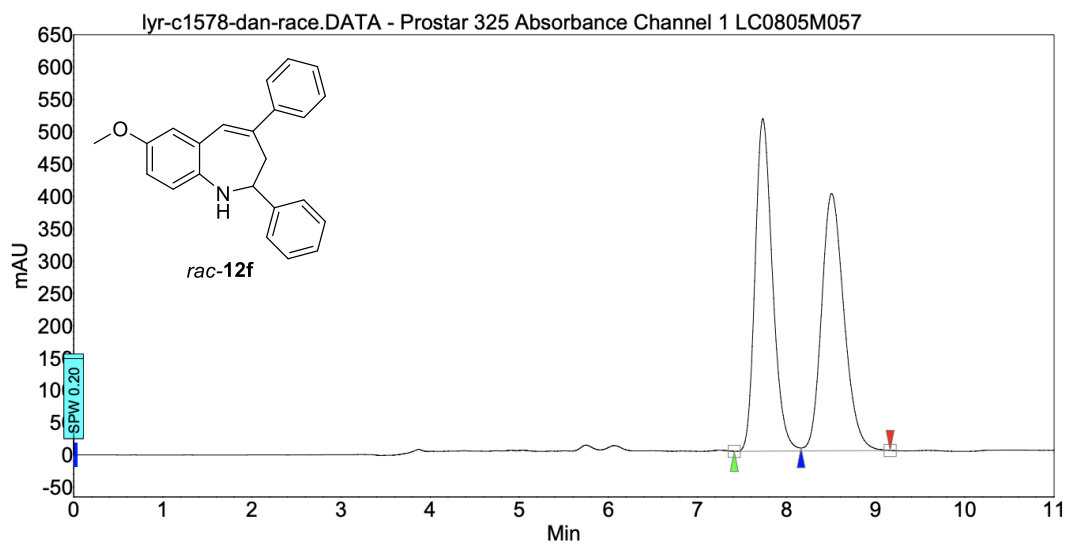


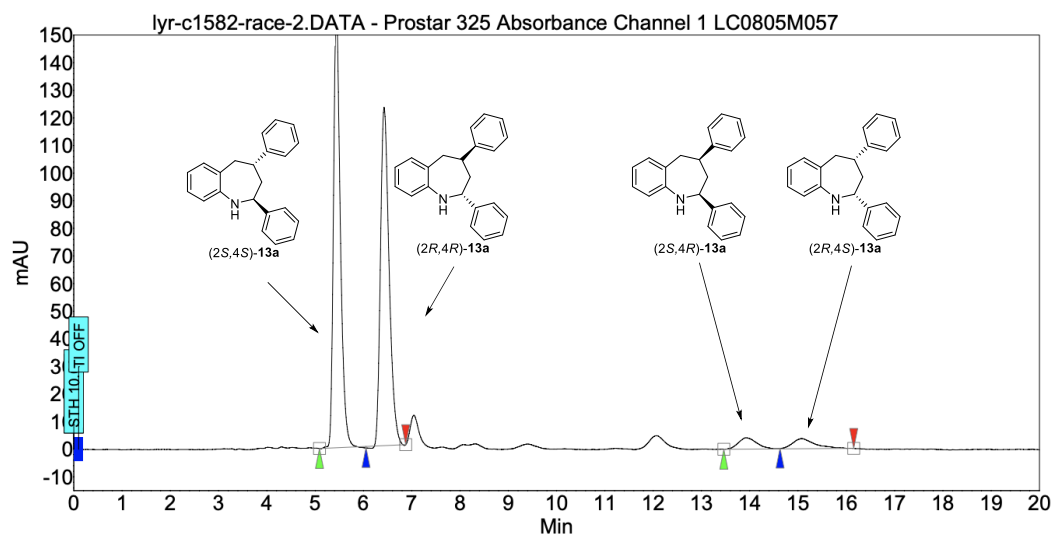
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	8.39	50.49	126.5	38.8	50.493
2	未知	13.03	49.51	68.6	38.1	49.507
Total			100.00	195.1	76.9	100.000



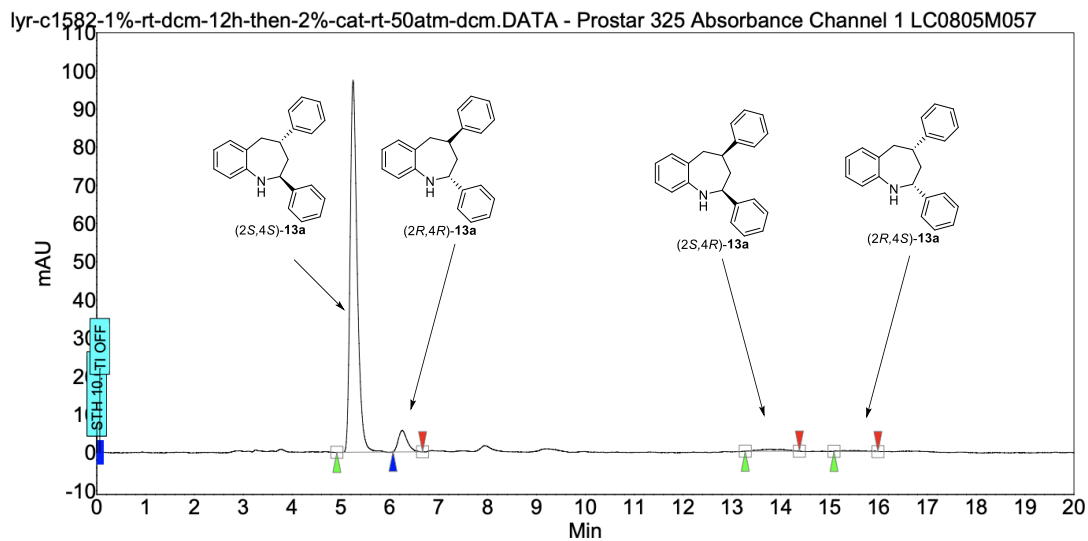
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	8.46	96.05	237.0	72.7	96.052
1	未知	13.17	3.95	6.0	3.0	3.948
Total			100.00	243.0	75.7	100.000



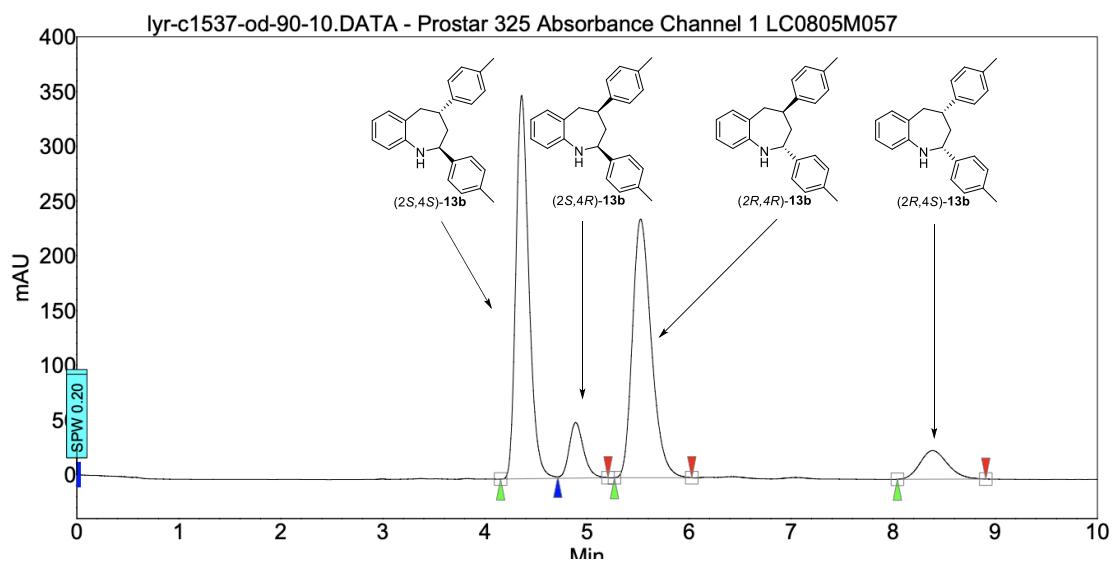




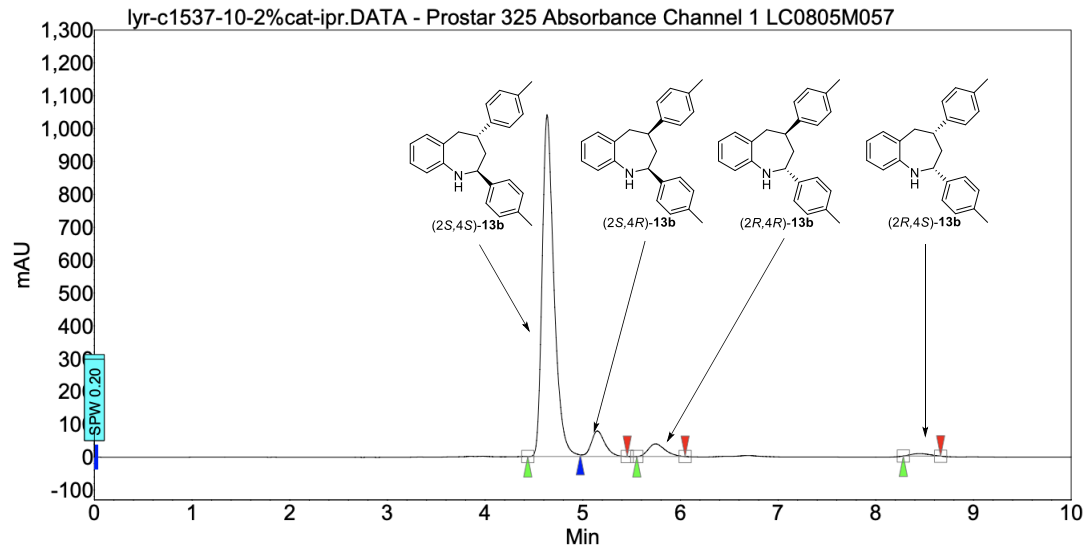
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	5.44	47.30	159.0	26.1	47.296
2	未知	6.43	45.86	122.5	25.3	45.861
3	未知	13.93	3.26	4.1	1.8	3.256
4	未知	15.07	3.59	3.7	2.0	3.587
Total			100.00	289.3	55.2	100.000



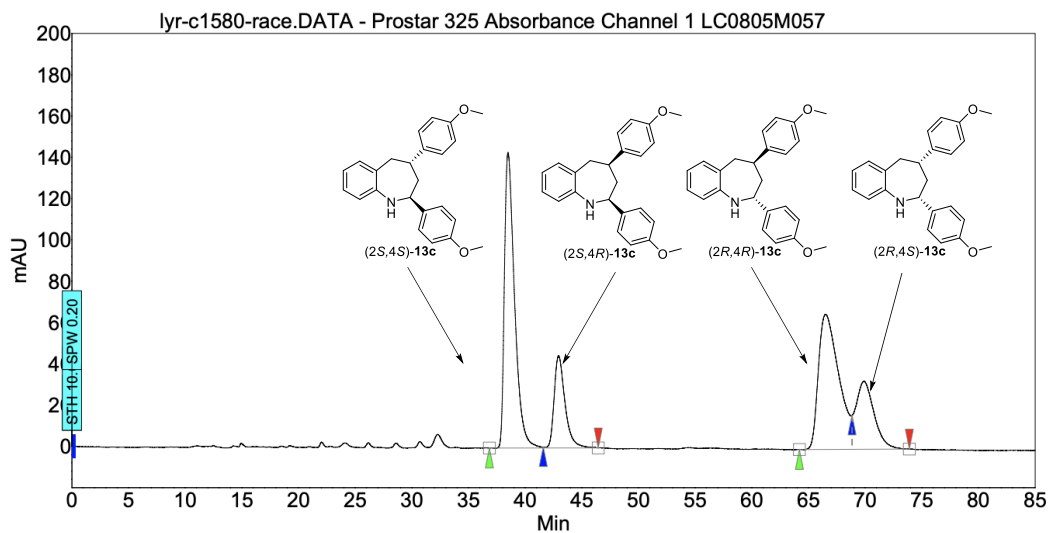
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	5.25	90.82	97.5	16.4	90.818
2	未知	6.25	6.71	5.6	1.2	6.710
3	未知	13.79	1.80	0.5	0.3	1.798
4	未知	15.50	0.67	0.2	0.1	0.674
Total			100.00	103.9	18.0	100.000



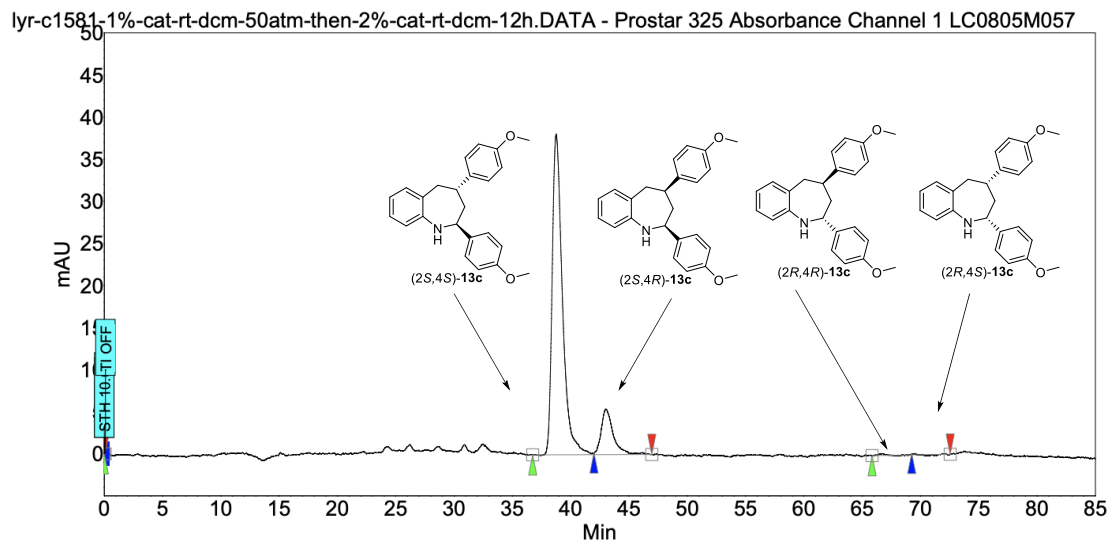
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	4.36	43.51	350.3	51.8	43.508
4	未知	4.89	6.95	50.9	8.3	6.953
2	未知	5.53	42.64	236.2	50.8	42.642
3	未知	8.39	6.90	26.1	8.2	6.897
Total			100.00	663.5	119.1	100.000



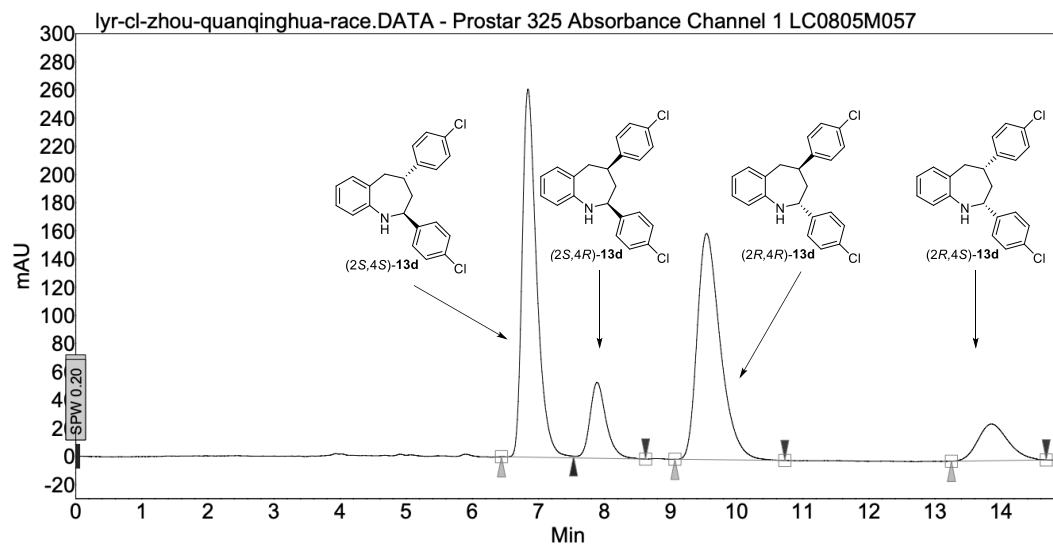
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	4.63	86.80	1040.3	145.1	86.800
4	未知	5.15	7.60	77.9	12.7	7.602
2	未知	5.75	4.61	38.6	7.7	4.612
3	未知	8.45	0.99	7.5	1.6	0.986
Total			100.00	1164.3	167.1	100.000



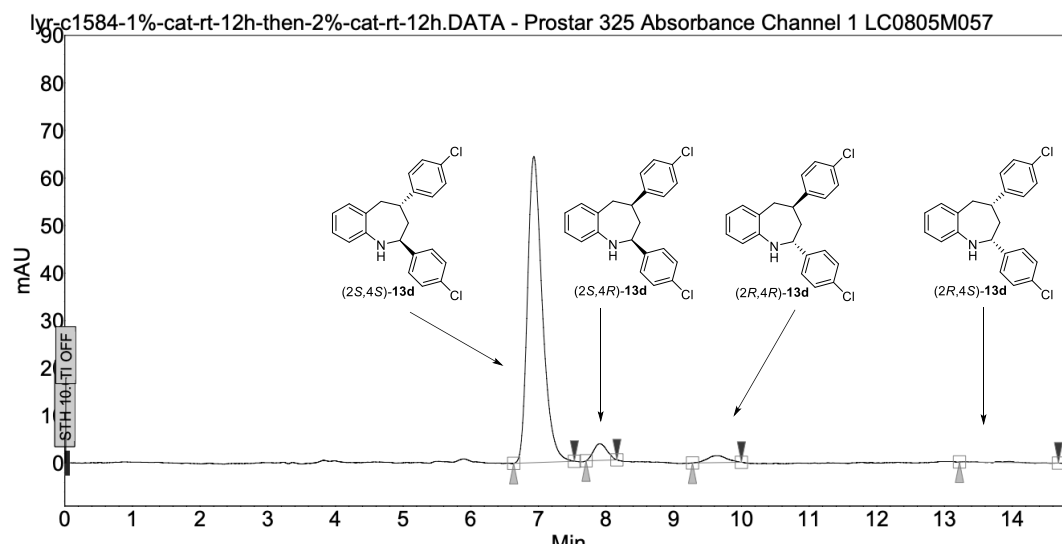
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	38.48	37.54	143.1	148.4	37.536
2	未知	42.95	12.55	44.6	49.6	12.550
3	未知	66.51	34.44	65.4	136.1	34.438
4	未知	69.91	15.48	32.9	61.2	15.476
Total			100.00	286.0	395.3	100.000



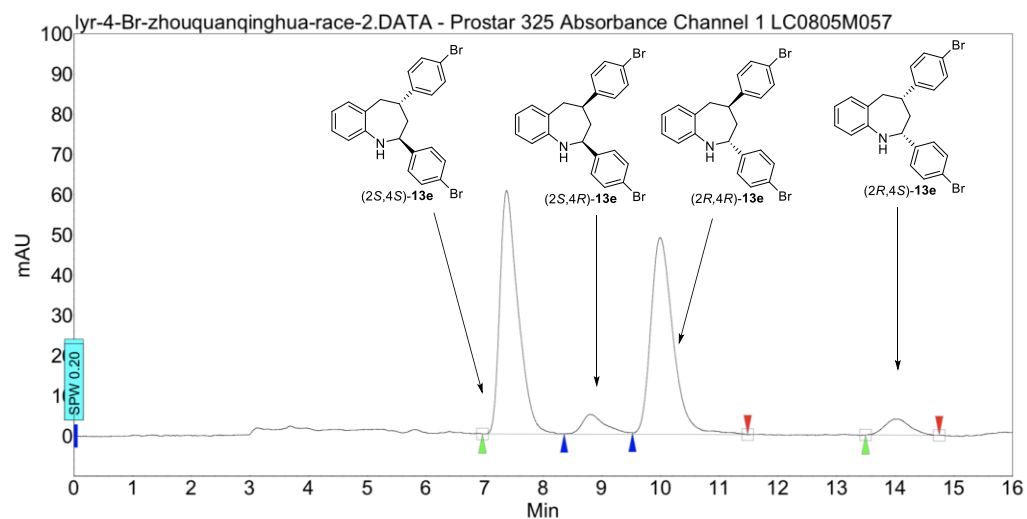
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	38.75	85.29	38.1	38.8	85.293
2	未知	43.03	14.40	5.4	6.5	14.395
3	未知	66.64	0.18	0.2	0.1	0.179
4	未知	70.78	0.13	0.2	0.1	0.133
Total			100.00	43.9	45.5	100.000



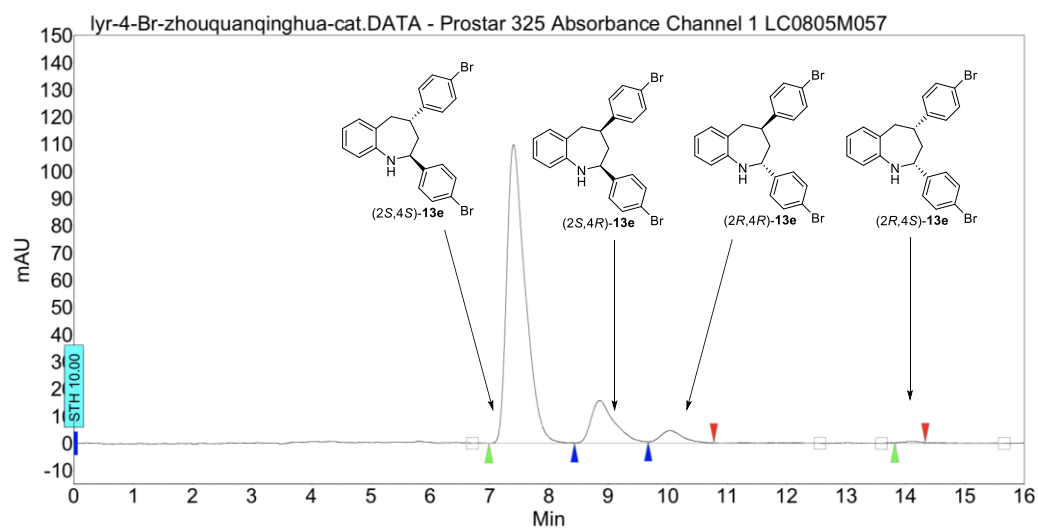
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	6.84	41.23	261.3	66.2	41.229
3	未知	7.89	9.56	53.9	15.3	9.559
1	未知	9.54	40.59	160.4	65.1	40.591
4	未知	13.85	8.62	26.0	13.8	8.621
Total			100.00	501.7	160.5	100.000



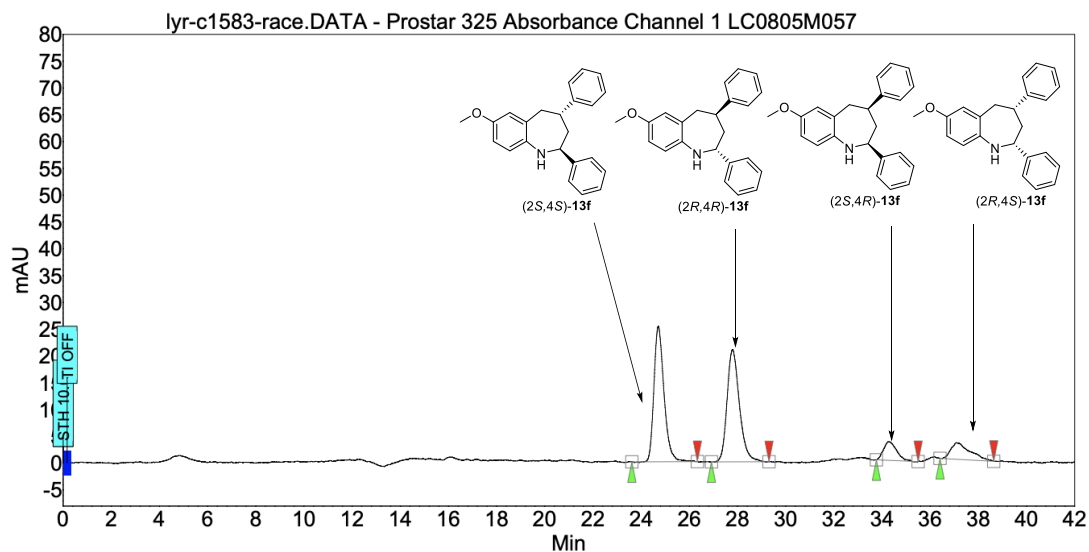
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	6.93	92.39	64.4	16.3	92.394
2	未知	7.91	4.56	3.5	0.8	4.563
3	未知	9.62	2.79	1.4	0.5	2.790
4	未知	13.96	0.25	0.2	0.0	0.253
Total			100.00	69.6	17.7	100.000



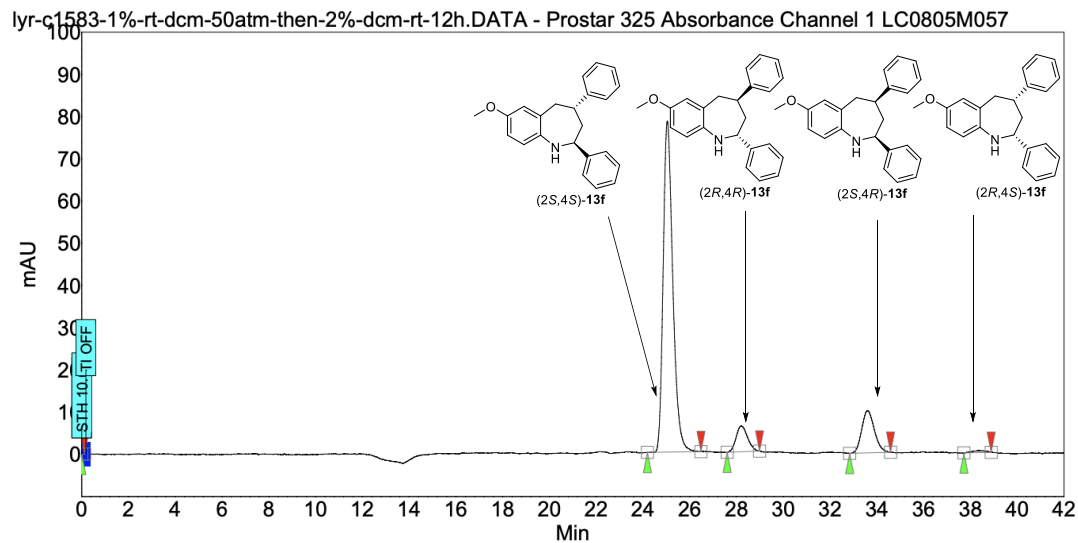
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
2	未知	7.37	45.72	60.6	21.8	45.717
3	未知	8.80	4.78	4.9	2.3	4.784
4	未知	9.99	45.21	49.0	21.6	45.212
1	未知	14.05	4.29	4.0	2.0	4.287
Total			100.00	118.5	47.7	100.000



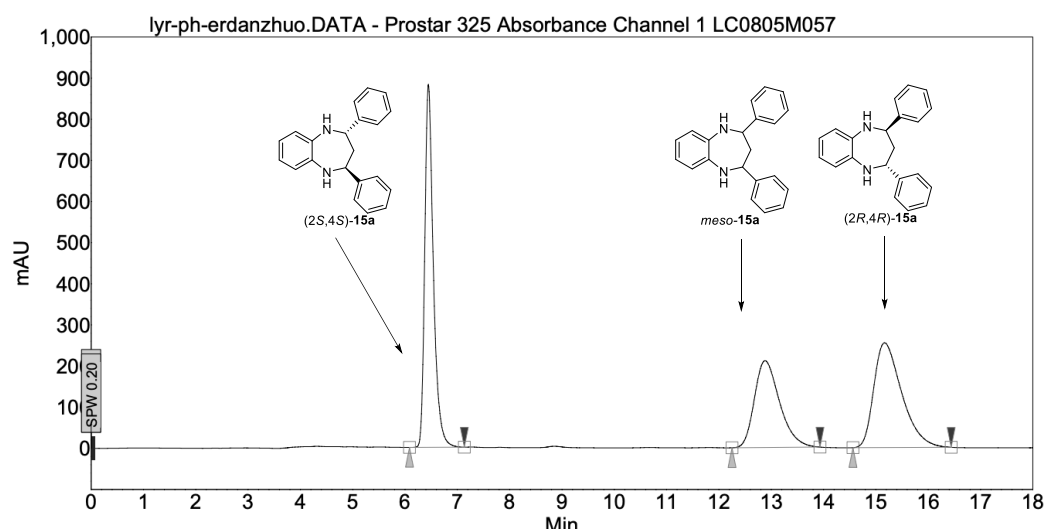
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	7.40	80.49	109.9	39.7	80.487
2	未知	8.85	14.63	15.8	7.2	14.629
3	未知	10.03	4.32	4.7	2.1	4.318
4	未知	14.11	0.57	0.7	0.3	0.565
Total			100.00	131.1	49.3	100.000



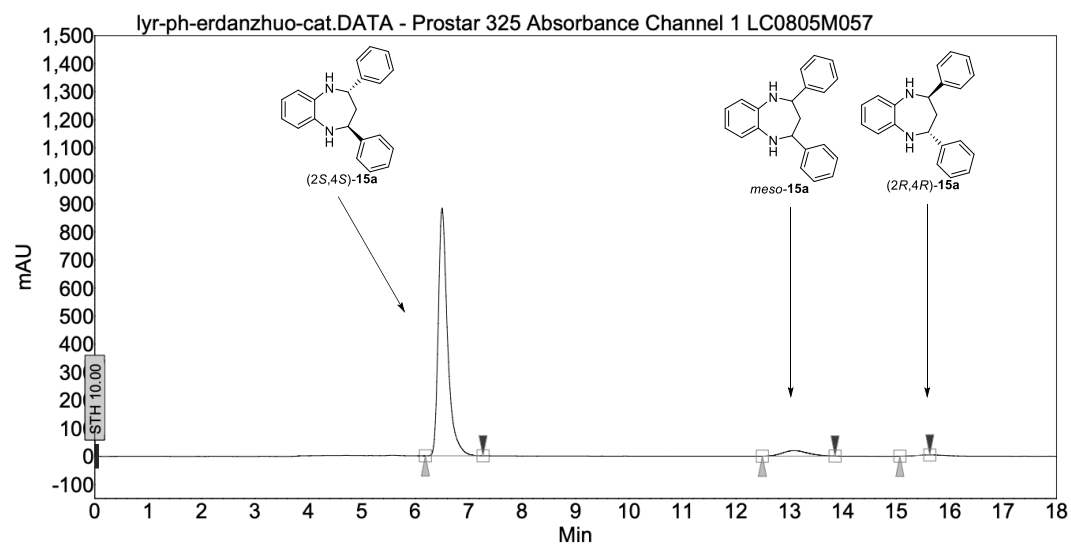
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	24.71	41.14	25.3	12.2	41.141
2	未知	27.79	41.85	20.9	12.4	41.847
3	未知	34.27	7.30	3.5	2.2	7.299
4	未知	37.09	9.71	3.1	2.9	9.713
Total			100.00	52.8	29.7	100.000



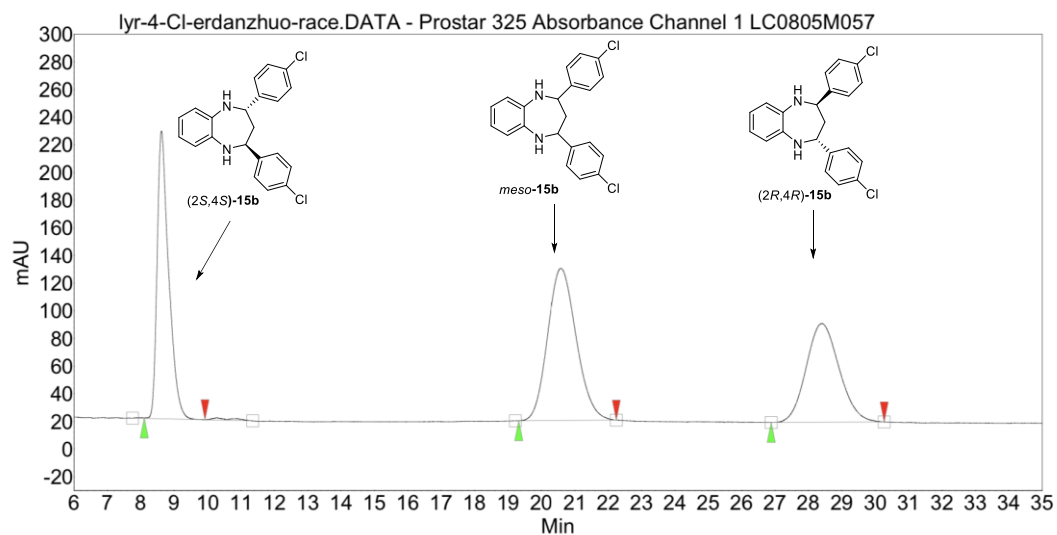
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	25.03	78.85	78.4	37.3	78.852
2	未知	28.20	7.28	6.1	3.4	7.278
3	未知	33.60	13.20	10.0	6.2	13.199
4	未知	38.31	0.67	0.5	0.3	0.671
Total			100.00	95.0	47.3	100.000



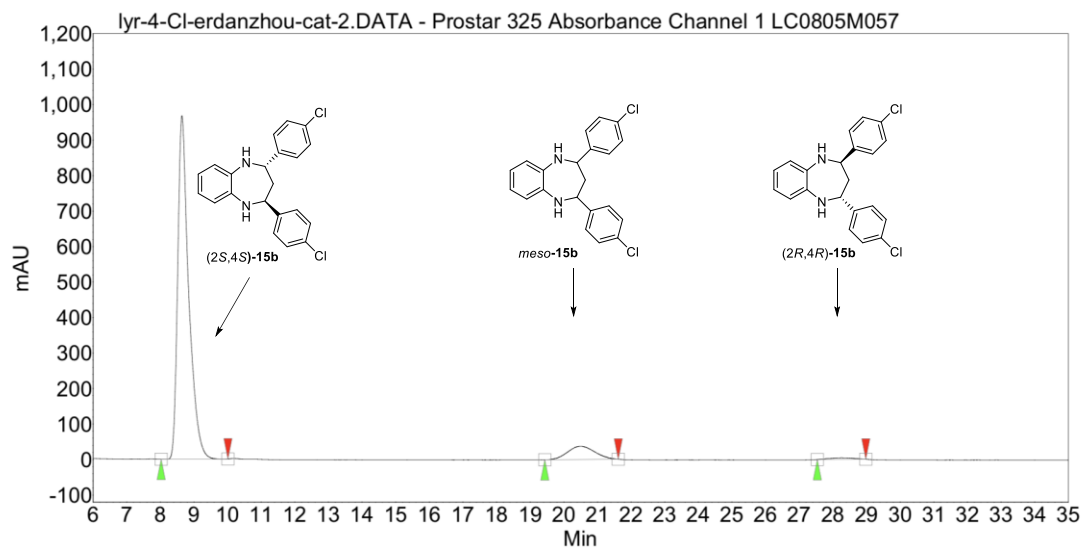
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	6.45	37.89	882.6	168.0	37.890
2	未知	12.88	26.54	211.1	117.7	26.541
3	未知	15.17	35.57	254.7	157.8	35.570
Total			100.00	1348.4	443.5	100.000



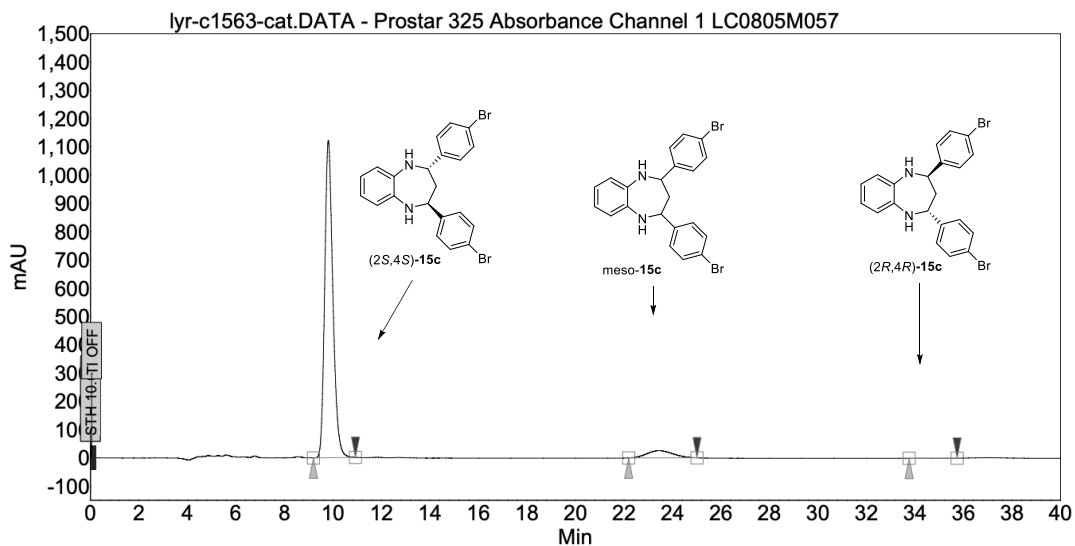
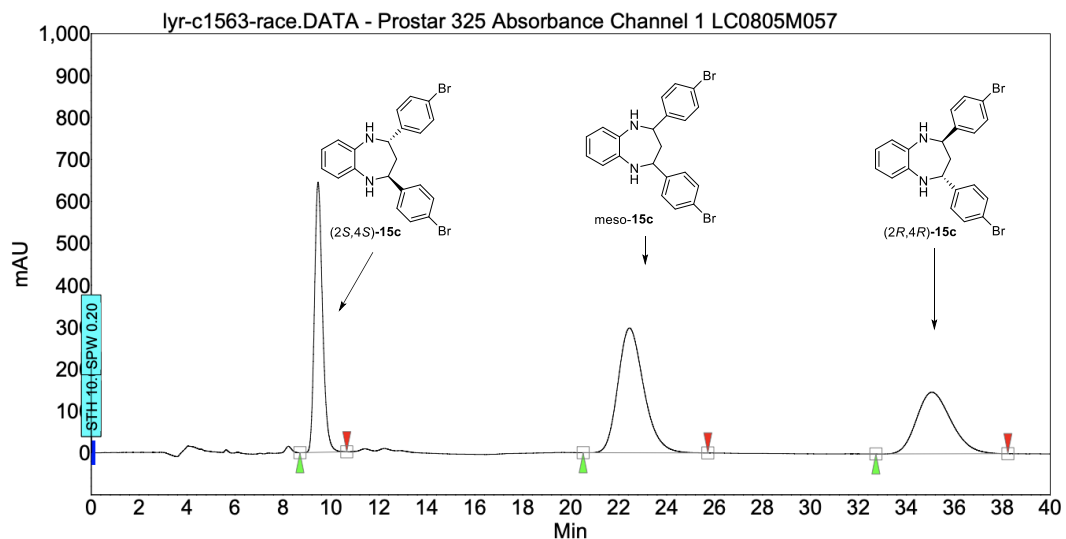
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	6.50	94.13	883.0	177.7	94.133
2	未知	13.08	5.81	19.8	11.0	5.812
3	未知	15.24	0.05	0.7	0.1	0.055
Total			100.00	903.5	188.8	100.000

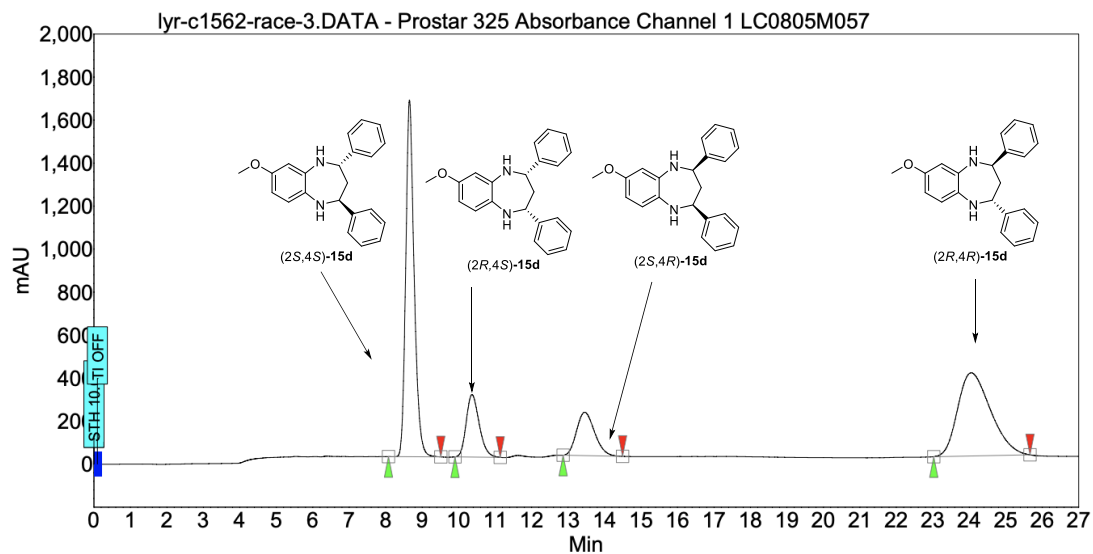


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	8.61	30.41	208.1	83.4	30.406
2	未知	20.58	39.83	109.9	109.3	39.832
3	未知	28.40	29.76	71.3	81.6	29.762
Total			100.00	389.3	274.3	100.000

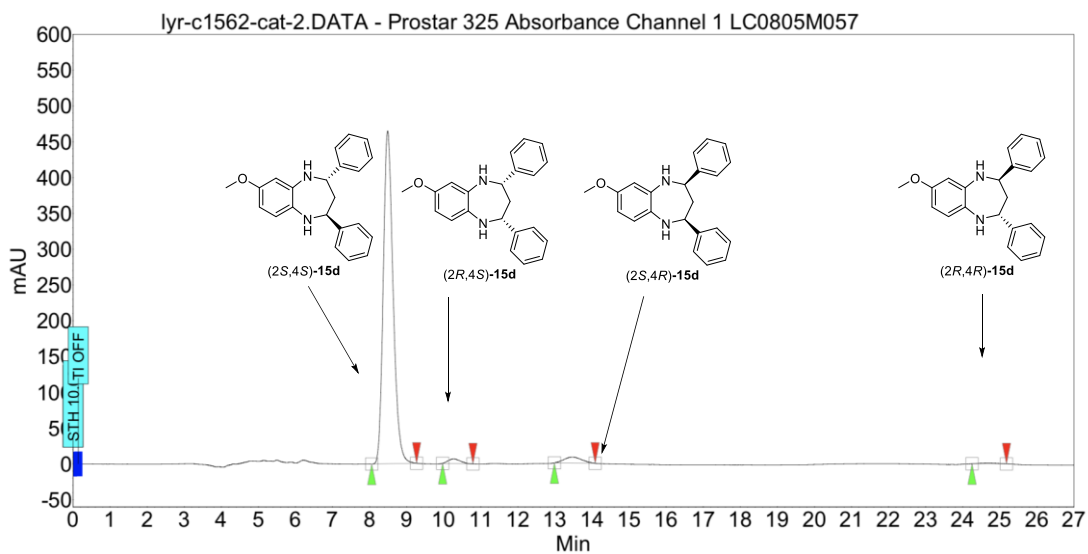


Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	8.64	90.42	967.9	366.2	90.417
2	未知	20.49	8.65	37.4	35.0	8.647
3	未知	28.26	0.94	4.6	3.8	0.936
Total			100.00	1010.0	405.0	100.000

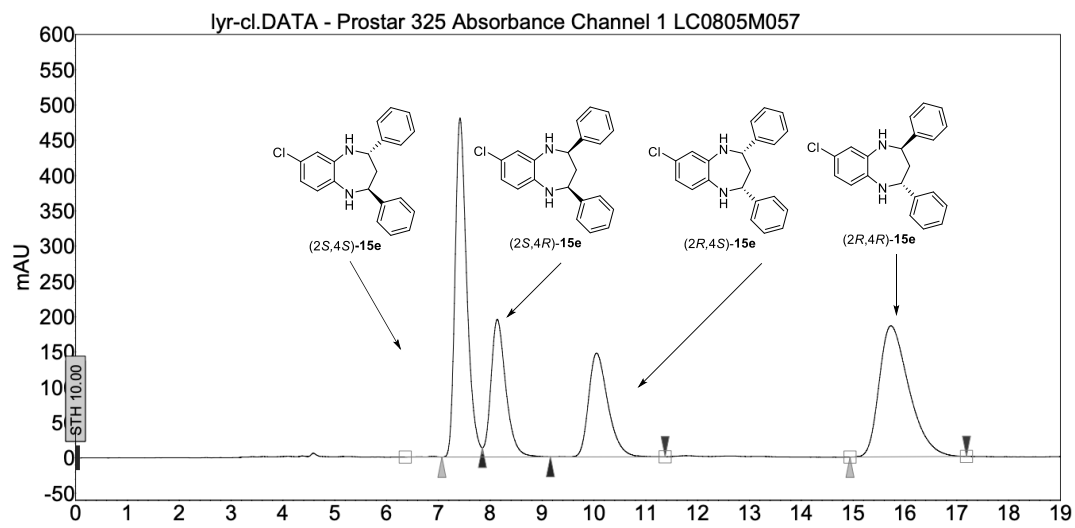




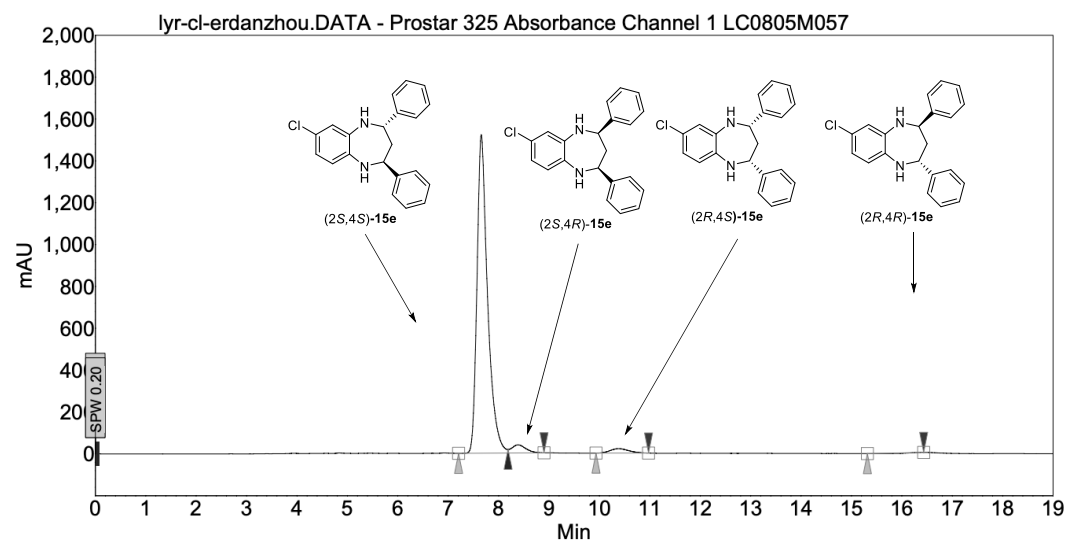
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	8.65	40.84	1658.6	441.9	40.841
3	未知	10.37	11.10	290.5	120.1	11.096
4	未知	13.45	10.70	201.8	115.7	10.696
2	未知	24.05	37.37	386.9	404.3	37.368
Total			100.00	2537.9	1082.0	100.000



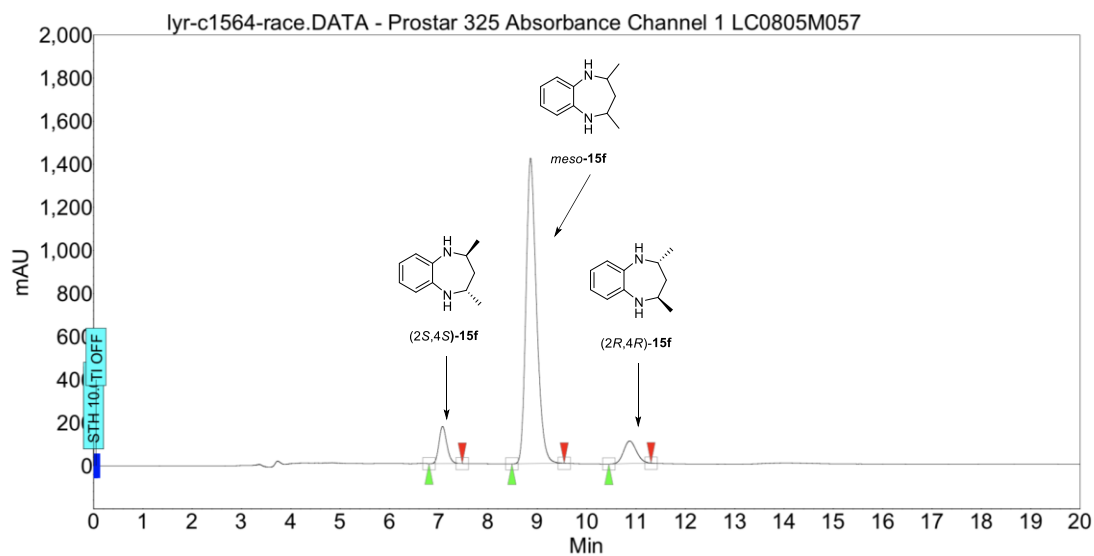
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	8.49	94.85	464.9	142.4	94.850
2	未知	10.27	1.64	6.4	2.5	1.638
3	未知	13.48	3.08	8.3	4.6	3.077
4	未知	24.68	0.43	1.1	0.7	0.435
Total			100.00	480.7	150.2	100.000



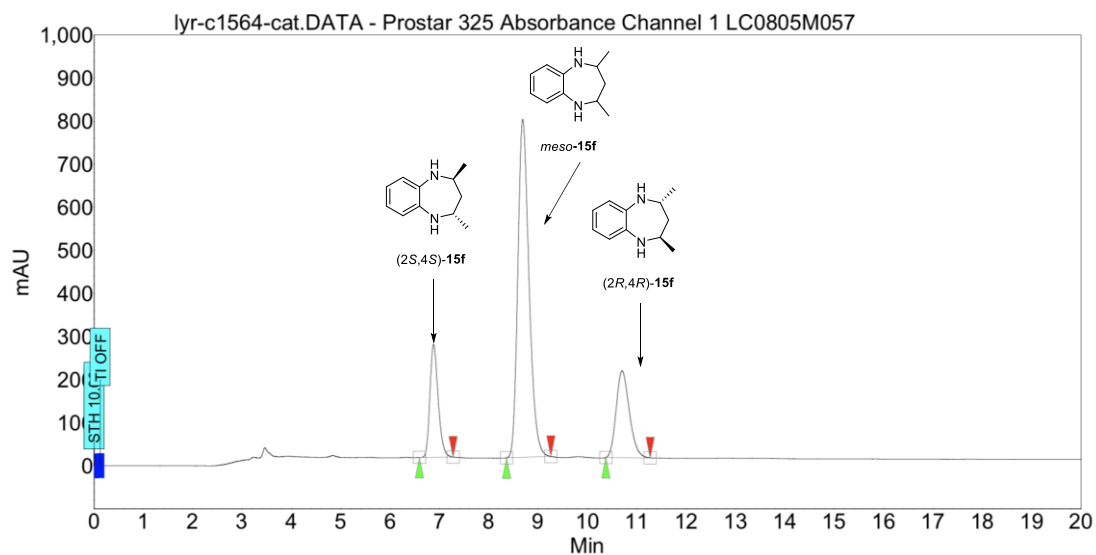
Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	7.41	33.28	480.2	125.7	33.275
2	未知	8.13	17.19	195.0	64.9	17.187
3	未知	10.05	16.81	147.0	63.5	16.812
4	未知	15.73	32.73	185.7	123.7	32.725
Total			100.00	1007.9	377.9	100.000



Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	7.65	94.12	1521.8	370.7	94.119
2	未知	8.39	3.19	38.8	12.6	3.193
3	未知	10.38	2.34	21.3	9.2	2.336
4	未知	15.90	0.35	2.5	1.4	0.352
Total			100.00	1584.4	393.9	100.000



Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	7.07	7.80	173.3	32.3	7.798
2	未知	8.86	84.59	1419.2	349.9	84.589
3	未知	10.87	7.61	104.9	31.5	7.614
Total			100.00	1697.3	413.7	100.000



Index	文件名	时间 [Min]	数量 [% 面积]	高度 [mAU]	Area [mAU.Min]	Area % [%]
1	未知	6.88	15.89	262.4	50.6	15.889
2	未知	8.69	64.57	784.9	205.7	64.567
3	未知	10.70	19.54	201.4	62.3	19.544
Total			100.00	1248.7	318.6	100.000