Intramolecular Asymmetric Reductive Amination: Synthesis of Enantioenriched Dibenz[*c*,*e*]azepines

Supporting Information

Tao Yang,[a] Xiaochong Guo,[a] Qin Yin,*[,a,b] and Xumu Zhang*[,a]

[a]Department of Chemistry and Shenzhen Grubbs Institute, Southern University of Science and Technology, Shenzhen, Guangdong 518055, People's Republic of China

zhangxm@sustc.edu.cn

[b]Academy for Advanced Interdisciplinary Studies, Southern University of Science and Technology, Shenzhen, Guangdong 518000, People's Republic of China

yinq@sustc.edu.cn

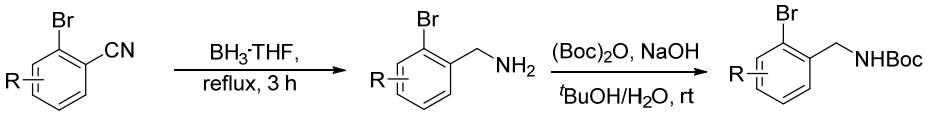
Contents

1. General information

Unless otherwise mentioned, all experiments were carried out under an atmosphere of argon in a glovebox or using standard Schlenk techniques. Solvents were dried with standard procedures and degassed with N_2. Flash column chromatography was performed using Tsingdao silica gel (60, particle size 300-400 mesh). NMR spectra were recorded on a Bruker DPX 400 spectrometer at 400 MHz for ^{1}H NMR, 101 MHz for ^{13}C NMR or a Bruker DPX 500 spectrometer at 500 MHz for ^{1}H NMR, 126 MHz for ^{13}C NMR. Chemical shifts (δ) are reported in ppm and respectively referenced to internal standard Me_4Si and solvent signals (Me_4Si, 0 ppm for ^{1}H NMR in $CDCl_3$; 77.0 ppm in $CDCl_3$ for ^{13}C NMR). HPLC and UPLC analysis was carried out on Angilent 1200 Series instrument using chiral columns.

2. Substrates preparation

S-2 were synthesized according to a literature's method.[1]



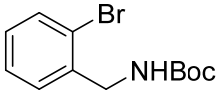
S-1 **S-2**

Step 1:

To a solution of the aryl cyanides **S-1** (5 mmol) in dry THF (5 mL) was added slowly 1 M BH_3-THF complex (20 mL) at 0 ^{o}C. The reaction mixture was then heated to reflux for 3 h, followed by dropwise addition of 2 *N* hydrochloric acid (20 mL) at 0 ^{o}C. The aqueous phase was separated and neutralized with 2 *N* sodium hydroxide solution (20 mL), and the organic phase was extracted with ethyl acetate (15 mL×2). The combined organic phases were dried over Na_2SO_4 and concentrated under reduced pressure. The crude product was used for the next step without further purification.

Step 2:

The crude product obtained above was dissolved in ^{t}BuOH/H_2O (5/5 mL). NaOH (2.0 equiv) and di-*tert*-butyl dicarbonate (1.2 equiv) were successively added. The mixture was stirred for 3 h at room temperature. The reaction was quenched with H_2O (5 mL) and extracted with EtOAc (5 mL×2). The combined organic layers were washed with brine, dried over Na_2SO_4, filtered and then concentrated under reduced pressure. The residue was purified by flash chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 30/1).

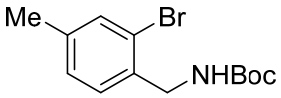


Chemical Formula: $C_{12}H_{16}BrNO_2$

***tert*-butyl (2-bromobenzyl)carbamate** (**S-2a**):[2] 1.33 g, 93% yield for the second step (starting from commercial available (2-bromophenyl)methanamine, 5 mmol scale).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (d, *J* = 7.7 Hz, 1H), 7.40 (d, *J* = 7.7 Hz, 1H), 7.30 (t, *J* = 7.7 Hz, 1H), 7.15 (t, *J* = 7.7 Hz, 1H), 5.09 (s, 1H), 4.40 (d, *J* = 6.3 Hz, 2H), 1.47 (s, 9H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.8, 138.0, 132.7, 129.7, 129.0, 127.7, 123.5, 79.7, 44.9, 28.4 ppm.

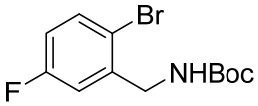


Chemical Formula: $C_{13}H_{18}BrNO_2$

***tert*-butyl (2-bromo-4-methylbenzyl)carbamate** (**S-2b**):[2] 930 mg, 62 % yield for 2 steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (s, 1H), 7.26 (d, *J* = 5.8 Hz, 1H), 7.09 – 7.07 (m, 1H), 4.99 (s, 1H), 4.34 (d, *J* = 6.2 Hz, 2H), 2.31 (s, 3H), 1.45 (s, 9H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 155.7, 139.2, 134.9, 133.2, 129.7, 128.4, 123.3, 79.6, 44.6, 28.4, 20.7 ppm.

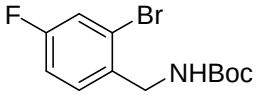


Chemical Formula: $C_{12}H_{15}BrFNO_2$

***tert*-butyl (2-bromo-5-fluorobenzyl)carbamate** (**S-2c**):[3] 1.43 g, 94% yield for the second step (starting from commercial available (2-bromo-5-fluoro-phenyl)methanamine, 5 mmol scale).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.48 (dd, *J* = 8.8, 5.2 Hz, 1H), 7.11 (dd, *J* = 9.2, 3.1 Hz, 1H), 6.87 (td, *J* = 8.4, 3.2 Hz, 1H), 5.05 (s, 1H), 4.35 (d, *J* = 6.4 Hz, 2H), 1.46 (s, 9H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 162.1 (d, *J* = 247.7 Hz), 155.7, 140.2 (d, *J* = 7.4 Hz), 133.8 (d, *J* = 8.0 Hz), 117.1 (d, *J* = 3.2 Hz), 116.3 (d, *J* = 23.7 Hz), 115.9 (d, *J* = 22.6 Hz), 80.0, 44.7, 28.4 ppm.

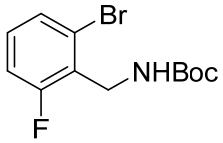


Chemical Formula: $C_{12}H_{15}BrFNO_2$

***tert*-butyl (2-bromo-4-fluorobenzyl)carbamate** (**S-2d**):[2] 791 mg, 52 % yield for 2 steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37 (dd, *J* = 8.4, 6.0 Hz, 1H), 7.29 (dd, *J* = 8.0, 2.4 Hz, 1H), 7.01 (td, *J* = 8.4, 2.4 Hz, 1H), 5.03 (s, 1H), 4.35 (d, *J* = 6.3 Hz, 2H), 1.45 (s, 9H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.6 (d, *J* = 250.3 Hz), 155.7, 134.0 (d, *J* = 2.4 Hz), 130.8 (d, *J* = 8.7 Hz), 123.4 (d, *J* = 9.4 Hz), 120.0 (d, *J* = 24.5 Hz), 114.7 (d, *J* = 20.6 Hz), 79.8, 44.2, 28.4 ppm.



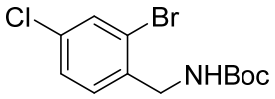
Chemical Formula: $C_{12}H_{15}BrFNO_2$
Exact Mass: 303.0270

tert-butyl (2-bromo-6-fluorobenzyl)carbamate (**S-2e**)：1.06 g, 70 % yield for 2 steps.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.38 (d, *J* = 8.0 Hz, 1H), 7.18 – 7.14 (m, 1H), 7.06 (t, *J* = 8.8 Hz, 1H), 4.95 (s, 1H), 4.53 (d, *J* = 5.9 Hz, 2H), 1.46 (s, 9H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.3 (d, *J* = 251.7 Hz), 155.3, 130.0 (d, *J* = 9.3 Hz), 128.6 (d, *J* = 3.6 Hz), 126.1 (d, *J* = 17.2 Hz), 125.3, 115.0 (d, *J* = 23.0 Hz), 79.7, 38.3, 28.4 ppm.

HRMS (ESI) Calculated for $C_{12}H_{16}NBrO_2F$ $[M+H]^+$ 304.0343; found 304.0334.



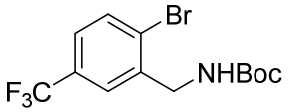
Chemical Formula: $C_{12}H_{15}BrClNO_2$
Exact Mass: 318.9975

***tert*-butyl (2-bromo-4-chlorobenzyl)carbamate (S-2f)**：816 mg, 51 % yield for 2 steps.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.56 (s, 1H), 7.33 (d, *J* = 8.4 Hz, 1H), 7.28 (d, *J* = 8.4 Hz, 1H), 5.08 (s, 1H), 4.35 (d, *J* = 6.5 Hz, 2H), 1.46 (s, 9H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.7, 136.6, 133.8, 132.3, 130.4, 127.8, 123.6, 79.9, 44.3, 28.4 ppm.

HRMS (ESI) Calculated for $C_{12}H_{16}NBrO_2Cl$ $[M+H]^+$ 320.0047; found 320.0039.

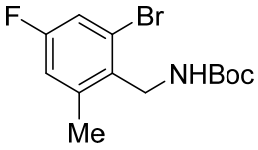


Chemical Formula: $C_{13}H_{15}BrF_3NO_2$

***tert*-butyl (2-bromo-5-(trifluoromethyl)benzyl)carbamate (S-2g)**:[4] 814 mg, 46 % yield for 2 steps.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 8.0 Hz, 1H), 7.62 (s, 1H), 7.41 (d, *J* = 8.0 Hz, 1H), 5.13 (s, 1H), 4.44 (d, *J* = 6.3 Hz, 2H), 1.48 (s, 9H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.8, 139.2, 133.3, 130.1 (q, *J* = 33.2 Hz), 127.0, 125.7, 125.4 (q, *J* = 3.3 Hz), 123.7 (q, *J* = 272.4 Hz), 80.1, 44.6, 28.3 ppm.



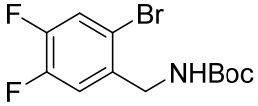
Chemical Formula: $C_{13}H_{17}BrFNO_2$
Exact Mass: 317.0427

***tert*-butyl (2-bromo-4-fluoro-6-methylbenzyl)carbamate (S-2h)**：1.03 g, 65 % yield for 2 steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.15 (dd, *J* = 7.9, 2.7 Hz, 1H), 6.87 (dd, *J* = 9.1, 2.6 Hz, 1H), 4.81 (s, 1H), 4.45 (d, *J* = 5.8 Hz, 2H), 2.48 (s, 3H), 1.44 (s, 9H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 161.3 (d, *J* = 250.5 Hz), 155.5, 141.4 (d, *J* = 8.9 Hz), 132.2 (d, *J* = 2.7 Hz), 125.6 (d, *J* = 10.2 Hz), 117.7 (d, *J* = 24.5 Hz), 116.8 (d, *J* = 20.6 Hz), 79.6, 41.2, 28.4, 20.8 ppm.

HRMS (ESI) Calculated for $C_{13}H_{18}NBrO_2F$ $[M+H]^+$ 318.0499; found 318.0487.



Chemical Formula: $C_{12}H_{14}BrF_2NO_2$
Exact Mass: 321.0176

***tert*-butyl (2-bromo-4,5-difluorobenzyl)carbamate (S-2i)**：934 mg, 58 % yield for 2 steps.

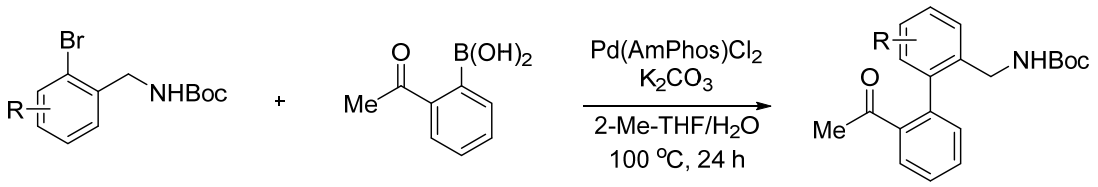
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 (t, *J* = 8.4 Hz, 1H), 7.26 – 7.22 (m, 1H), 5.12 (s, 1H), 4.31 (d, *J* = 6.4 Hz, 2H), 1.47 (s, 9H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 155.7, 149.6 (dd, *J* = 249.4, 12.3 Hz), 149.2 (dd, *J* = 252.1, 13.5

Hz), 135.2 – 135.1 (m), 121.5 (d, J = 20.0 Hz), 117.8 (d, J = 19.1 Hz), 116.2 (dd, J = 7.4, 3.6 Hz), 80.1, 44.1, 28.4 ppm.

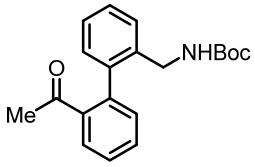
HRMS (ESI) Calculated for $C_{12}H_{15}NBrO_2F_2$ $[M+H]^+$ 322.0249; found 322.0238.

1a-1i were synthesized according to a literature's method.[5]



S-2 **1**

To a solution of **S-2** (2 mmol) and arylboronic acid (1.2 equiv) in 2-methyltetrahydrofuran (8 mL) and water (8 mL) was added K_2CO_3 (3 equiv). The mixture was degassed by bubbling with nitrogen for 20 min. The catalyst Pd(amphos)Cl_2 (0.05 equiv) was then added and the reaction was allowed to stir at 100 °C for 24 h. The reaction mixture was cooled to room temperature and the organic layer was separated. The aqueous layer was extracted with ethyl acetate (2 x 10 mL). The combined organic layers were washed with brine and dried over Na_2SO_4. The solvent was removed under reduced pressure and the crude product was subjected to column chromatography (eluent: petroleum ether/ethyl acetate = 9/1 to 4/1).

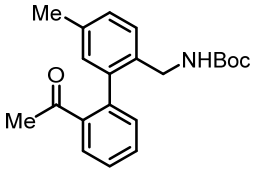


Chemical Formula: $C_{20}H_{23}NO_3$

***tert*-butyl ((2'-acetyl-[1,1'-biphenyl]-2-yl)methyl)carbamate (1a):**[5] an oil, 552 mg, 85% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71 (dd, J = 7.8, 1.4 Hz, 1H), 7.55 – 7.49 (m, 1H), 7.47 – 7.42 (m, 2H), 7.38 – 7.35 (m, 1H), 7.39 – 7.24 (m, 2H), 7.05 (d, J = 7.5 Hz, 1H), 4.96 (s, 1H), 4.20 (dd, J = 14.8, 6.4 Hz, 1H), 4.06 (dd, J = 14.6, 5.0 Hz, 1H), 2.20 (s, 3H), 1.39 (s, 9H);

^{13}C{^{1}H} NMR (126 MHz, $CDCl_3$) δ 202.6, 155.8, 140.4, 139.4, 139.4, 136.4, 131.1, 130.8, 129.3, 128.5, 128.4, 128.2, 127.7, 127.2, 79.2, 42.7, 29.8, 28.4 ppm.



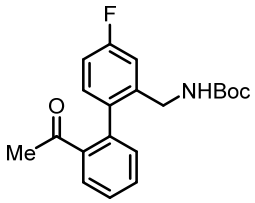
Chemical Formula: $C_{21}H_{25}NO_3$
Exact Mass: 339.1834

***tert*-butyl ((2'-acetyl-5-methyl-[1,1'-biphenyl]-2-yl)methyl)carbamate (1b)**: an oil, 472 mg, 70% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, J = 8.0 Hz, 1H), 7.52 (t, J = 7.0 Hz, 1H), 7.45 (t, J = 7.5, Hz, 1H), 7.34 (d, J = 7.8 Hz, 1H), 7.25 (dd, J = 7.5, 1.3 Hz, 1H), 7.19 (d, J = 7.5 Hz, 1H), 6.89 (s, 1H), 4.93 (s, 1H), 4.16 (dd, J = 14.5, 5.0 Hz, 1H), 4.05 (dd, J = 14.5, 5.0 Hz, 1H), 2.35 (s, 3H), 2.22 (s, 3H), 1.40 (s, 9H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 202.7, 155.7, 140.3, 139.6, 139.4, 136.8, 133.4, 131.0, 130.9, 130.0, 128.9, 128.6, 128.3, 127.6, 79.1, 42.4, 29.8, 28.4, 21.0 ppm.

HRMS (ESI) Calculated for $C_{21}H_{26}NO_3$ $[M+H]^+$ 340.1907; found 340.1896.



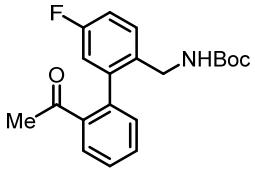
Chemical Formula: $C_{20}H_{22}FNO_3$
Exact Mass: 343.1584

***tert*-butyl ((2'-acetyl-4-fluoro-[1,1'-biphenyl]-2-yl)methyl)carbamate (1c):** an oil, 316 mg, 46% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.52 (td, *J* = 7.2, 1.6 Hz, 1H), 7.46 (td, *J* = 7.6, 1.6 Hz, 1H), 7.22 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.16 (dd, *J* = 9.6, 2.4 Hz, 1H), 7.03 – 6.94 (m, 2H), 4.97 (s, 1H), 4.19 (dd, *J* = 15.6, 6.8 Hz, 1H), 3.97 (dd, *J* = 15.6, 5.2 Hz, 1H), 2.25 (s, 3H), 1.40 (s, 9H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.3, 162.5 (d, *J* = 246.8 Hz), 155.8, 139.3, 139.2 (d, *J* = 7.2 Hz), 138.5, 136.0 (d, *J* = 3.1 Hz), 131.2, 131.2, 130.6 (d, *J* = 7.6 Hz), 128.5, 127.9, 114.8 (d, *J* = 22.2 Hz), 113.9 (d, *J* = 21.3 Hz), 79.5, 42.5, 29.8, 28.4 ppm.

HRMS (ESI) Calculated for $C_{20}H_{23}NFO_3$ $[M+H]^+$ 344.1656; found 344.1644.



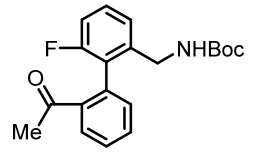
Chemical Formula: $C_{20}H_{22}FNO_3$
Exact Mass: 343.1584

***tert*-butyl ((2'-acetyl-5-fluoro-[1,1'-biphenyl]-2-yl)methyl)carbamate (1d)**: an oil, 391 mg, 57% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 1H), 7.54 (td, *J* = 7.5, 1.5 Hz, 1H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H), 7.41 (dd, *J* = 8.5, 5.5 Hz, 1H), 7.24 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.06 (td, *J* = 8.5, 2.5 Hz, 1H), 6.78 (dd, *J* = 9.0, 2.5 Hz, 1H), 4.98 (s, 1H), 4.15 (dd, *J* = 14.5, 6.5 Hz, 1H), 3.98 (dd, *J* = 14.5, 5.0 Hz, 1H), 2.34 (s, 3H), 1.40 (s, 9H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.8, 161.4 (d, *J* = 246.9 Hz), 155.7, 142.4 (d, *J* = 7.9 Hz), 138.7, 138.4, 132.4 (d, *J* = 3.3 Hz), 131.4, 130.8, 130.2 (d, *J* = 8.4 Hz), 128.6, 128.1, 115.9 (d, *J* = 21.8 Hz), 114.7 (d, *J* = 20.8 Hz), 79.2, 42.1, 29.6, 28.4 ppm.

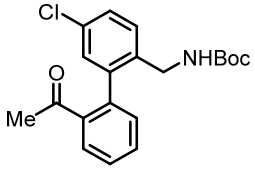
HRMS (ESI) Calculated for $C_{20}H_{23}NFO_3$ $[M+H]^+$ 344.1656; found 344.1645.



Chemical Formula: $C_{20}H_{22}FNO_3$
Exact Mass: 343.1584

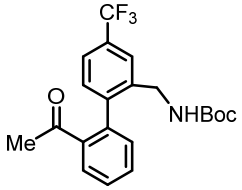
***tert*-butyl ((2'-acetyl-6-fluoro-[1,1'-biphenyl]-2-yl)methyl)carbamate (1e):** an oil, 179 mg, 52% yield (1 mmol scale).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.56 – 7.47 (m, 2H), 7.29 – 7.23 (m, 2H), 7.10 (t, *J* = 9.2 Hz, 1H), 6.86 (d, *J* = 7.6 Hz, 1H), 4.97 (s, 1H), 4.34 (dd, *J* = 14.0, 6.0 Hz, 1H), 4.09 (dd, *J* = 14.0, 4.8 Hz, 1H), 2.34 (s, 3H), 1.37 (s, 9H);
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.8, 161.6 (d, *J* = 247.5 Hz), 155.2, 143.6 (d, *J* = 3.8 Hz), 138.8, 138.4 (d, *J* = 2.7 Hz), 131.2, 131.0, 128.7, 128.6, 128.0, 125.0 (d, *J* = 1.6 Hz), 123.5 (d, *J* = 15.3 Hz), 114.8 (d, *J* = 22.5 Hz), 79.0, 36.4, 29.5, 28.4 ppm.
HRMS (ESI) Calculated for $C_{20}H_{23}NFO_3$ $[M+H]^+$ 344.1656; found 344.1647.



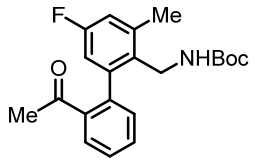
Chemical Formula: $C_{20}H_{22}ClNO_3$
Exact Mass: 359.1288

***tert*-butyl ((2'-acetyl-5-chloro-[1,1'-biphenyl]-2-yl)methyl)carbamate (1f):** an oil, 278 mg, 39% yield.
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.77 (d, *J* = 8.0 Hz, 1H), 7.55 (td, *J* = 7.5, 1.5 Hz, 1H), 7.49 (td, *J* = 7.5, 1.5 Hz, 1H), 7.39 (d, *J* = 8.0 Hz, 1H), 7.34 (dd, *J* = 8.5, 2.5 Hz, 1H), 7.24 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.05 (d, *J* = 2.5 Hz, 1H), 4.99 (s, 1H), 4.16 (dd, *J* = 15.0, 6.5 Hz, 1H), 3.97 (dd, *J* = 15.0, 5.0 Hz, 1H), 2.36 (s, 3H), 1.40 (s, 9H);
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.6, 155.7, 142.2, 138.5, 138.3, 135.3, 132.7, 131.4, 130.9, 129.7, 128.8, 128.7, 128.1, 128.0, 79.3, 42.1, 29.6, 28.4 ppm.
HRMS (ESI) Calculated for $C_{20}H_{21}NClO_3$ $[M-H]^-$ 358.1215; found 358.1218.



Chemical Formula: $C_{21}H_{22}F_3NO_3$
Exact Mass: 393.1552

***tert*-butyl ((2'-acetyl-4-(trifluoromethyl)-[1,1'-biphenyl]-2-yl)methyl)carbamate (1g):** an oil, 185 mg, 47% yield (1 mmol scale).
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.6 Hz, 1H), 7.70 (s, 1H), 7.60 – 7.50 (m, 3 H), 7.23 (dd, *J* = 7.2, 1.6 Hz, 1H), 7.16 (d, *J* = 7.6 Hz, 1H), 5.03 (s, 1H), 4.25 (dd, *J* = 15.2, 6.8 Hz, 1H), 4.04 (dd, *J* = 15.2, 4.8 Hz, 1H), 2.39 (s, 3H), 1.42 (s, 9H);
^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.2, 155.8, 144.4, 138.5, 138.1, 137.6, 131.6, 130.8, 130.0 (q, *J* = 32.5 Hz). 129.3, 129.0, 128.2, 124.7 (q, *J* = 2.5 Hz), 124.0 (q, *J* = 272.2 Hz) 123.8 (q, *J* = 3.8 Hz), 79.5, 42.5, 29.4, 28.3 ppm.
HRMS (ESI) Calculated for $C_{21}H_{23}NF_3O_3$ $[M+H]^+$ 394.1624; found 394.1611.



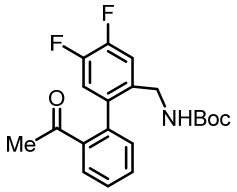
Chemical Formula: $C_{21}H_{24}FNO_3$
Exact Mass: 357.1740

***tert*-butyl ((2'-acetyl-5-fluoro-3-methyl-[1,1'-biphenyl]-2-yl)methyl)carbamate (1h):** an oil, 193 mg, 54% yield (1 mmol scale).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.76 (d, *J* = 7.5 Hz, 1H), 7.53 (t, *J* = 7.0 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.21 (dd, *J* = 7.5, 1.5 Hz, 1H), 6.93 (dd, *J* = 9.5, 2.5 Hz, 1H), 6.59 (dd, *J* = 8.5, 2.5 Hz, 1H), 5.01 (s, 1H), 4.27 (d, *J* = 13.5 Hz, 1H), 3.89 (d, *J* = 13.5 Hz, 1H), 2.44 (s, 3H), 2.43 (s, 3H), 1.40 (s, 9H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 202.1, 161.0 (d, *J* = 246.7 Hz), 155.4, 143.8 (d, *J* = 8.2 Hz), 140.4 (d, *J* = 8.2 Hz), 139.3 (d, *J* = 1.4 Hz), 138.6, 131.2, 131.0, 130.1, 128.5, 127.9, 116.6 (d, *J* = 20.5 Hz), 113.1 (d, *J* = 21.1 Hz), 79.0, 39.2 (d, *J* = 14.6 Hz), 29.7, 28.4, 19.7 ppm.

HRMS (ESI) Calculated for $C_{21}H_{25}NFO_3$ $[M+H]^+$ 358.1813; found 358.1801.



Chemical Formula: $C_{20}H_{21}F_2NO_3$
Exact Mass: 361.1489

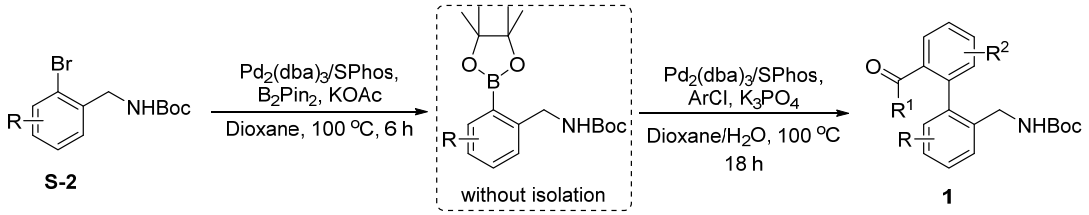
***tert*-butyl ((2'-acetyl-4,5-difluoro-[1,1'-biphenyl]-2-yl)methyl)carbamate (1i):** an oil, 184 mg, 51% yield (1 mmol scale).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77 (d, *J* = 7.6 Hz, 1H), 7.57 – 7.48 (m, 2H), 7.27 – 7.22 (m, 2H), 6.89 – 6.85 (m, 1H), 5.00 (s, 1H), 4.13 (dd, *J* = 15.2, 6.4 Hz, 1H), 3.90 (dd, *J* = 15.2, 5.0 Hz, 1H), 2.38 (s, 3H), 1.42 (s, 9H),

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 201.5, 155.8, 149.7 (dd, *J* = 249.5, 12.6 Hz), 148.8 (dd, *J* = 249.5, 12.6 Hz), 138.5, 137.5, 136.7 (dd, *J* = 5.0, 3.8 Hz), 133.9 (t, *J* = 3.9 Hz), 131.5, 131.1, 128.8, 128.3, 117.7 (d, *J* = 17.3 Hz), 116.9 (d, *J* = 17.7 Hz), 79.5, 41.9, 29.6, 28.3 ppm.

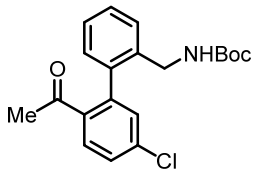
HRMS (ESI) Calculated for $C_{20}H_{22}NF_2O_3$ $[M+H]^+$ 362.1562; found 362.1551.

1j-1t were synthesized by a modified known procedure.[6]



An oven-dried 25-mL Schlenk tube was charged with Pd_2dba_3 (9.2 mg, 0.01 mmol), SPhos (16.4 mg, 0.04 mmol), bis(pinacolato)diboron (304 mg, 1.2 mmol), aryl bromide **S-2**(1.2 mmol) and KOAc (196 mg, 2.00 mmol). The Schlenk tube was capped with a rubber stopper and then evacuated and backfilled with argon (this sequence was carried out two times). 1,4-Dioxane (5.00 mL) was added via syringe and the reaction mixture was heated to 100 °C for 6 h. At this point a mixture of Pd_2dba_3 (9.2 mg, 0.01 mmol)/SPhos (16.4 mg, 0.04 mmol), aryl chloride (1 mmol) in dioxane (1 mL) and 5 M K_3PO_4 (aq.) (1 mL) were successively added into the reaction tube under N_2 atmosphere. The reaction mixture remained heating at 100 °C for 18 h. The reaction mixture was then cool to room temperature and filtered through a thin pad of celite (eluted with ethyl acetate). The filtrate was washed with brine, dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by flash

chromatography on silica gel (eluent: petroleum ether/ethyl acetate = 9/1 to 4/1).



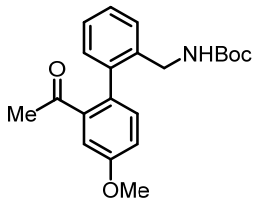
Chemical Formula: $C_{20}H_{22}ClNO_3$
Exact Mass: 359.1288

***tert*-butyl ((2'-acetyl-5'-chloro-[1,1'-biphenyl]-2-yl)methyl)carbamate (1j):** an oil, 214 mg, 58% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 8.4 Hz, 1H), 7.47 – 7.39 (m, 3H), 7.33 – 7.28 (m, 2H), 7.07 (d, *J* = 7.2 Hz, 1H), 4.91 (s, 1H), 4.22 (dd, *J* = 14.8, 6.4 Hz, 1H), 4.06 (dd, *J* = 14.8, 5.2 Hz, 1H), 2.19 (s, 3H), 1.42 (s, 9H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 201.1, 155.7, 141.4, 139.1, 137.5, 137.2, 136.3, 130.9, 130.0, 129.2, 128.6, 128.5, 127.9, 127.3, 79.4, 42.6, 29.7, 28.4 ppm.

HRMS (ESI) Calculated for $C_{20}H_{21}NClO_3$ $[M-H]^-$ 358.1215; found 358.1217.



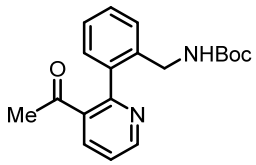
Chemical Formula: $C_{21}H_{25}NO_4$
Exact Mass: 355.1784

***tert*-butyl ((2'-acetyl-4'-methoxy-[1,1'-biphenyl]-2-yl)methyl)carbamate (1k):** an oil, 198 mg, 56% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.45 (d, *J* = 7.6 Hz, 1H), 7.37 (t, *J* = 7.2 Hz, 1H), 7.30 – 7.27 (m, 1H), 7.23 (d, *J* = 2.4 Hz, 1H), 7.18 (d, *J* = 8.4 Hz, 1H), 7.08 – 7.05 (m, 2H), 4.94 (s, 1H), 4.21 (dd, *J* = 14.8, 6.4 Hz, 1H), 4.10 (dd, *J* = 14.8, 5.2 Hz, 1H), 3.90 (s, 3H), 2.16 (s, 3H), 1.41 (s, 9H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.5, 158.8, 155.8, 140.5, 140.0, 136.8, 131.9, 131.6, 129.9, 128.4, 128.1, 127.2, 116.7, 113.4, 79.2, 55.6, 42.7, 29.9, 28.4 ppm.

HRMS (ESI) Calculated for $C_{21}H_{26}NO_4$ $[M+H]^+$ 356.1856; found 356.1846.



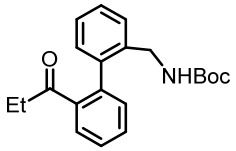
Chemical Formula: $C_{19}H_{22}N_2O_3$
Exact Mass: 326.1630

***tert*-butyl (2-(3-acetylpyridin-2-yl)benzyl)carbamate (1l):** an oil, 156 mg, 48% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.76 (dd, *J* = 4.8, 1.8 Hz, 1H), 7.99 (dd, *J* = 7.9, 1.8 Hz, 1H), 7.58 (d, *J* = 7.7 Hz, 1H), 7.44 (td, *J* = 7.6, 1.4 Hz, 1H), 7.40 (dd, *J* = 7.9, 4.8 Hz, 1H), 7.32 (td, *J* = 7.5, 1.3 Hz, 1H), 7.08 (dd, *J* = 7.6, 1.3 Hz, 1H), 5.55 (s, 1H), 4.27 (d, *J* = 6.1 Hz, 2H), 2.02 (s, 3H), 1.42 (s, 9H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 202.1, 157.6, 155.7, 150.6, 139.0, 137.3, 136.6, 136.5, 130.2, 130.2, 129.7, 127.6, 122.3, 79.2, 42.8, 29.8, 28.4 ppm.

HRMS (ESI) Calculated for $C_{19}H_{23}N_2O_3$ $[M+H]^+$ 327.1703; found 327.1693.



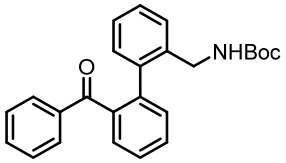
Chemical Formula: $C_{21}H_{25}NO_3$
Exact Mass: 339.1834

***tert*-butyl ((2'-propionyl-[1,1'-biphenyl]-2-yl)methyl)carbamate (1m):** an oil, 160 mg, 47% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 7.1, 1.0 Hz, 1H), 7.51 (t, *J* = 7.5 Hz, 1H), 7.48 – 7.43 (m, 2H), 7.37 (td, *J* = 7.5, 1.5 Hz, 1H), 7.28 – 7.26 (m, 2H), 7.05 (d, *J* = 7.5 Hz, 1H), 5.03 (s, 1H), 4.23 (dd, *J* = 15.0, 6.5 Hz, 1H), 4.07 (dd, *J* = 15.0, 5.0 Hz, 1H), 2.64 – 2.49 (m, 2H), 1.41 (s, 9H), 0.98 (t, *J* = 7.5 Hz, 3H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 206.0, 155.8, 140.4, 139.6, 139.2, 136.5, 130.8, 130.7, 129.2, 128.6, 128.1, 127.8, 127.6, 127.1, 79.1, 42.7, 35.3, 28.4, 8.3 ppm.

HRMS (ESI) Calculated for $C_{21}H_{26}NO_3$ $[M+H]^+$ 340.1907; found 340.1895.



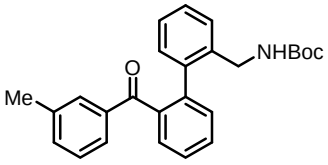
Chemical Formula: $C_{25}H_{25}NO_3$
Exact Mass: 387.1834

***tert*-butyl ((2'-benzoyl-[1,1'-biphenyl]-2-yl)methyl)carbamate (1n):** an oil, 182 mg, 47% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.6 Hz, 2H), 7.59 – 7.45 (m, 4H), 7.41 – 7.36 (m, 4H), 7.24 (td, *J* = 7.6, 1.4 Hz, 1H), 7.10 (t, *J* = 7.6 Hz, 1H), 6.99 (d, *J* = 7.6 Hz, 1H), 5.36 (s, 1H), 4.34 (dd, *J* = 14.4, 7.2 Hz, 1H), 4.11 (dd, *J* = 14.4, 4.2 Hz, 1H), 1.43 (s, 9H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.1, 155.9, 140.1, 139.4, 138.7, 137.6, 136.7, 133.1, 130.7, 130.1, 130.0, 129.5, 128.6, 128.5, 128.3, 128.1, 126.9, 126.9, 79.0, 42.7, 28.4 ppm.

HRMS (ESI) Calculated for $C_{25}H_{26}NO_3$ $[M+H]^+$ 388.1907; found 388.1893.



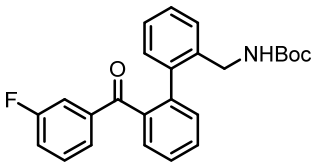
Chemical Formula: $C_{26}H_{27}NO_3$
Exact Mass: 401.1991

***tert*-butyl ((2'-(3-methylbenzoyl)-[1,1'-biphenyl]-2-yl)methyl)carbamate (1o):** an oil, 212 mg, 52% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.58 – 7.44 (m, 5H), 7.38 – 7.34 (m, 3H), 7.30 – 7.23 (m, 2H), 7.11 (t, *J* = 7.6 Hz, 1H), 6.98 (d, *J* = 7.6 Hz, 1H), 5.37 (s, 1H), 4.34 (dd, *J* = 14.4, 7.2 Hz, 1H), 4.10 (dd, *J* = 14.4, 3.8 Hz, 1H), 2.37 (s, 3H), 1.42 (s, 9H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.2, 155.9, 140.1, 139.5, 138.8, 138.1, 137.6, 136.7, 133.9, 130.6, 130.3, 130.0, 129.4, 128.7, 128.6, 128.1, 128.1, 127.5, 126.8, 79.0, 42.7, 28.4, 21.3 ppm.

HRMS (ESI) Calculated for $C_{26}H_{28}NO_3$ $[M+H]^+$ 402.2063; found 402.2048.



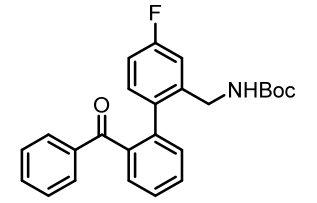
Chemical Formula: $C_{25}H_{24}FNO_3$
Exact Mass: 405.1740

***tert*-butyl ((2'-(3-fluorobenzoyl)-[1,1'-biphenyl]-2-yl)methyl)carbamate (1p):** an oil, 206 mg, 51% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 – 7.57 (m, 1H), 7.52 – 7.47 (m, 3H), 7.40 – 7.34 (m, 4H), 7.28 – 7.20 (m, 2H), 7.12 (t, *J* = 7.6 Hz, 1H), 6.97 (d, *J* = 7.6 Hz, 1H), 5.25 (s, 1H), 4.34 (dd, *J* = 14.4, 6.8 Hz, 1H), 4.10 (dd, *J* = 14.5, 4.2 Hz, 1H), 1.43 (s, 9H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 196.7, 162.4 (d, *J* = 249.5 Hz), 155.9, 140.2, 139.6 (d, *J* = 6.3 Hz), 139.1, 138.2, 136.7, 130.8, 130.5, 129.9 (d, *J* = 7.7 Hz), 129.5, 128.6, 128.6, 128.2, 127.1, 126.9, 125.8 (d, *J* = 2.2 Hz), 120.1 (d, *J* = 21.6 Hz), 116.3 (d, *J* = 22.3 Hz), 79.1, 42.6, 28.4 ppm.

HRMS (ESI) Calculated for $C_{25}H_{25}NFO_3$ $[M+H]^+$ 406.1813; found 406.1798.



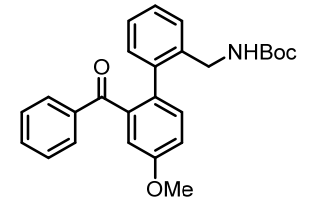
Chemical Formula: $C_{25}H_{24}FNO_3$
Exact Mass: 405.1740

***tert*-butyl ((2'-benzoyl-4-fluoro-[1,1'-biphenyl]-2-yl)methyl)carbamate (1q):** an oil, 158 mg, 39% yield.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.6 Hz, 2H), 7.59 – 7.52 (m, 2H), 7.51 – 7.46 (m, 2H), 7.40 (t, *J* = 7.8 Hz, 2H), 7.34 (d, *J* = 7.6 Hz, 1H), 7.07 (dd, *J* = 9.6, 2.0 Hz, 1H), 6.95 (dd, *J* = 8.4, 5.6 Hz, 1H), 6.79 (td, *J* = 8.4, 2.8 Hz, 1H), 5.27 (s, 1H), 4.33 (dd, *J* = 15.0, 7.2 Hz, 1H), 4.03 (dd, *J* = 15.0, 4.4 Hz, 1H), 1.44 (s, 9H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 198.0, 162.3 (d, *J* = 247.0 Hz), 155.9, 139.5 (d, *J* = 7.2 Hz), 139.0, 138.9 (d, *J* = 3.5 Hz), 137.5, 134.9 (d, *J* = 3.6 Hz), 133.2, 131.0, 130.9, 130.2, 130.0, 128.6, 128.3, 127.2, 114.9 (d, *J* = 22.6 Hz), 113.6 (d, *J* = 21.3 Hz), 79.3, 42.4, 28.4 ppm.

HRMS (ESI) Calculated for $C_{25}H_{25}NFO_3$ $[M+H]^+$ 406.1813; found 406.1799.



Chemical Formula: $C_{26}H_{27}NO_4$
Exact Mass: 417.1940

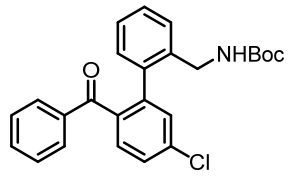
***tert*-butyl ((2'-benzoyl-4'-methoxy-[1,1'-biphenyl]-2-yl)methyl)carbamate (1r):** an oil, 179 mg, 43% yield.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.72 (d, *J* = 7.5 Hz, 2H), 7.52 (t, *J* = 7.5 Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 7.33 (d, *J* = 7.5 Hz, 1H), 7.27 (d, *J* = 9.5 Hz, 1H), 7.21 (td, *J* = 7.5, 1.5 Hz, 1H), 7.08 (m, 2H), 7.02 (d, *J* = 2.5 Hz, 1H), 6.97 (d, *J* = 7.5 Hz, 1H), 5.29 (s, 1H), 4.32 (dd, *J* = 14.5, 7.0 Hz,

1H), 4.26 – 3.94 (m, 1H), 3.88 (s, 3H), 1.43 (s, 9H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 197.9, 158.2, 155.9, 139.8, 139.0, 137.4, 137.0, 133.2, 132.1, 131.7, 130.0, 130.0, 128.6, 128.3, 127.9, 126.8, 115.6, 113.9, 79.0, 55.5, 42.7, 28.4 ppm.

HRMS (ESI) Calculated for $C_{26}H_{28}NO_4$ $[M+H]^+$ 418.2012; found 418.1998.



Chemical Formula: $C_{25}H_{24}ClNO_3$
Exact Mass: 421.1445

***tert*-butyl ((2'-benzoyl-5'-chloro-[1,1'-biphenyl]-2-yl)methyl)carbamate (1s):** an oil, 210mg, 50% yield.

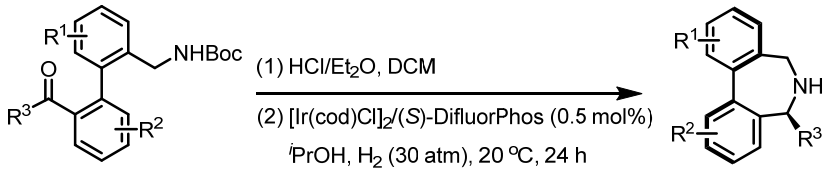
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.69 (d, J = 7.5 Hz, 2H), 7.54 (t, J = 7.5 Hz, 1H), 7.45 (s, 2H), 7.43 – 7.34 (m, 4H), 7.26 (td, J = 7.5, 1.5 Hz, 1H), 7.12 (t, J = 7.5 Hz, 1H), 6.97 (d, J = 7.5 Hz, 1H), 5.26 (s, 1H), 4.36 (dd, J = 14.5, 7.0 Hz, 1H), 4.08 (dd, J = 14.5, 4.0 Hz, 1H), 1.44 (s, 9H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 196.9, 155.8, 142.0, 138.0, 137.3, 137.1, 136.6, 136.2, 133.3, 130.8, 130.0, 130.0, 129.3, 128.7, 128.5, 128.4, 127.2, 127.0, 79.2, 42.6, 28.4 ppm.

HRMS (ESI) Calculated for $C_{25}H_{25}NClO_3$ $[M+H]^+$ 422.1517; found 422.1503.

3. General procedure for the synthesis of enantioenriched dibenz[*c*,*e*]azepines

Part 1: General procedure for the synthesis of 5-alkyl-substituted dibenz[*c*,*e*]azepines

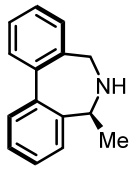


1 **2**

In a glovebox, to a 2.5 mL vial was added the catalyst precursor $[Ir(cod)Cl]_2$ (3.4 mg, 0.005 mmol), (*S*)-DifluorPhos (7.5 mg, 0.011 mmol) and anhydrous CH_2Cl_2 (0.3 mL) under argon atmosphere. The mixture was stirred for 0.5 h at room temperature to give a clear solution.

To a 5 mL vial was added substrate **1** (0.1 mmol) and CH_2Cl_2 (0.6 mL), followed by addition of HCl (2 M in Et_2O) (4 equiv). The resulting mixture was stirred at room temperature for 6 h. All volatiles were then removed, and the crude intermediate was transferred to an argon-filled glovebox. An aliquot of the above *in situ* prepared catalyst solution (30 μL, 0.0005mmol) was transferred to the vial containing crude intermediate via a syringe, followed by addition of 0.6 mL ^{i}PrOH and $Ti(O^{i}Pr)_4$ (1.0 equiv). The vial was placed in an autoclave which was then charged with 30 atm of H_2. The reaction was stirred at 20 ^{o}C for 24 h. After carefully releasing the hydrogen, the solution was neutralized with aqueous sodium bicarbonate solution (5 mL), and then extracted with DCM (5 mL×2). The combined organic phases were concentrated and passed through a short column of silica gel with ethyl acetate/petroleum ether (1/2) as eluents to give the chiral products. The obtained products were pure enough for NMR analysis.

For those secondary amine products, direct determination of their *ee* values was difficult. To facilitate the measurement, the obtained chiral amines were all derived into their benzamides with BzCl.



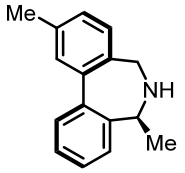
Chemical Formula: $C_{15}H_{15}N$
Molecular Weight: 209.29

(*S*)-5-methyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2a):[5] an oil, 18.7 mg, 89% yield, 96% *ee*; $[\alpha]^{25}_{D}$ = + 34.6 (*c* = 1.0, $CHCl_3$). Scale-up synthesis of **2a** following the same procedure, 1.5 mmol scale: 88% yield, 96% *ee*.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 – 7.33 (m, 8H), 3.72 (d, *J* = 12.6 Hz, 1H), 3.71 (q, *J* = 6.6 Hz, 1H), 3.49 (d, *J* = 12.6 Hz, 1H), 2.01 (brs, 1H), 1.47 (d, *J* = 6.6 Hz, 3H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.2, 141.2, 139.3, 137.0, 128.3, 128.1, 128.1, 128.0, 128.0, 127.7, 127.5, 124.9, 50.1, 49.4, 18.9 ppm.

Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 80/20, 0.80 mL/min, 254 nm): t_1 = 7.9 min (minor), t_2 = 13.4 min (major).



Chemical Formula: $C_{16}H_{17}N$
Exact Mass: 223.1361

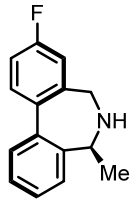
(*S*)-2,7-dimethyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2b): an oil, 19.2 mg, 86% yield, 91% *ee*; $[\alpha]^{25}_{D}$ = + 19.1 (*c* = 0.4, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.42 (m, 4H), 7.31 (s, 1H), 7.26 (d, *J* = 7.5 Hz, 1H), 7.21 (d, *J* = 7.5 Hz, 1H), 3.76 – 3.72 (m, 2H), 3.48 (d, *J* = 12.6 Hz, 1H), 2.46 (s, 3H), 2.37 (brs, 1H), 1.50 (d, *J* = 6.5 Hz, 3H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.3, 141.1, 139.3, 137.5, 134.1, 128.7, 128.5, 128.3, 128.0, 127.9, 127.6, 124.9, 50.2, 48.9, 21.3, 18.9 ppm.

Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 80/20, 0.80 mL/min, 254 nm): t_1 = 7.1 min (minor), t_2 = 11.6 min (major).

HRMS (ESI) Calculated for $C_{16}H_{18}N$ $[M+H]^+$ 224.1434; found 224.1437.



Chemical Formula: $C_{15}H_{14}FN$
Exact Mass: 227.1110

(*S*)-3-fluoro-7-methyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2c): an oil, 20.6 mg, 91% yield, 97% *ee*; $[\alpha]^{25}_{D}$ = + 16.3 (*c* = 0.57, $CHCl_3$).

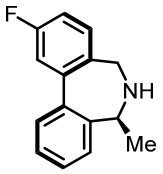
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 5H), 7.14 (td, *J* = 8.5, 2.5 Hz, 1H), 7.08 (dd, *J* = 9.0, 2.5 Hz, 1H), 3.74 – 3.70 (m, 2H), 3.48 (d, *J* = 12.8 Hz, 1H), 2.42 (brs, 1H), 1.50 (d, *J* = 6.5 Hz, 3H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.5 (d, *J* = 247.0 Hz), 140.2, 139.0, 138.9 (d, *J* = 6.9 Hz),

137.1 (d, *J* = 3.1 Hz), 129.2 (d, *J* = 8.2 Hz), 128.2, 127.9, 127.6, 125.0, 115.1 (d, *J* = 21.3 Hz), 114.6 (d, *J* = 21.2 Hz), 50.2, 49.2, 18.9 ppm.

Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 80/20, 0.80 mL/min, 254 nm): t_1 = 7.4 min (minor), t_2 = 14.1 min (major).

HRMS (ESI) Calculated for $C_{15}H_{15}NF$ $[M+H]^+$ 228.1183; found 228.1176.



Chemical Formula: $C_{15}H_{14}FN$
Exact Mass: 227.1110

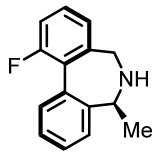
(*S*)-2-fluoro-7-methyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2d): an oil, 20.9 mg, 92% yield, 96% *ee*; $[\alpha]^{25}_D$ = + 42.1 (*c* = 0.69, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.50 – 7.43 (m, 4H), 7.32 (dd, *J* = 8.5, 5.5 Hz, 1H), 7.19 (dd, *J* = 9.5, 2.5 Hz, 1H), 7.07 (td, *J* = 8.5, 2.5 Hz, 1H), 3.74 – 3.70 (m, 2H), 3.44 (d, *J* = 12.5 Hz, 1H), 2.13 (brs, 1H), 1.50 (d, *J* = 6.5 Hz, 3H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.4 (d, *J* = 245.3 Hz), 143.2 (d, *J* = 7.8 Hz), 140.1 (d, *J* = 2.2 Hz), 139.3, 132.7 (d, *J* = 3.1 Hz), 129.8 (d, *J* = 8.4 Hz), 128.6, 127.9, 127.6, 125.1, 114.6 (d, *J* = 7.8 Hz), 114.4 (d, *J* = 8.6 Hz), 50.1, 48.5, 18.8 ppm.

Enantiomeric excess was determined by HPLC for the corresponding benzamide (OD-3 column, hexane/*i*PrOH 85/15, 0.40 mL/min, 254 nm): t_1 = 15.5 min (major), t_2 = 17.2 min (minor).

HRMS (ESI) Calculated for $C_{15}H_{15}NF$ $[M+H]^+$ 228.1183; found 228.1176.



Chemical Formula: $C_{15}H_{14}FN$
Exact Mass: 227.1110

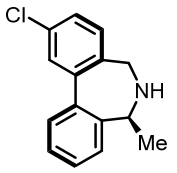
(*S*)-1-fluoro-7-methyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2e): an oil, 20.9 mg, 92% yield, 96% *ee*; $[\alpha]^{25}_D$ = + 43.4 (*c* = 0.80, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.41 (m, 4H), 7.38 – 7.34 (m, 1H), 7.25 (d, *J* = 6.8 Hz, 1H), 7.11 (t, *J* = 8.6 Hz, 1H), 4.21 (d, *J* = 13.5 Hz, 1H), 3.70 (q, *J* = 6.5 Hz, 1H), 3.18 (dd, *J* = 13.5, 3.5 Hz, 1H), 2.11 (brs, 1H), 1.47 (d, *J* = 6.6 Hz, 3H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.8 (d, *J* = 245.0 Hz), 143.8 (d, *J* = 4.4 Hz), 140.2 (d, *J* = 2.6 Hz), 139.1, 128.6, 128.6, 127.9, 127.6, 125.2, 123.7 (d, *J* = 17.1 Hz), 123.3 (d, *J* = 3.1 Hz), 114.6 (d, *J* = 23.3 Hz), 50.2, 40.4 (d, *J* = 3.9 Hz), 18.9 ppm.

Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 80/20, 0.80 mL/min, 254 nm): t_1 = 8.5 min (minor), t_2 = 17.1 min (major).

HRMS (ESI) Calculated for $C_{15}H_{15}NF$ $[M+H]^+$ 228.1183; found 228.1175.



Chemical Formula: $C_{15}H_{14}ClN$
Exact Mass: 243.0815

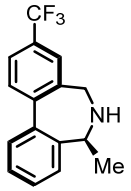
(*S*)-2-chloro-7-methyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2f): an oil, 21.1 mg, 87% yield, 91% *ee*; $[\alpha]^{25}_D$ = + 8.9 (*c* = 0.52, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.44 (m, 5H), 7.36 (d, *J* = 8.2 Hz, 1H), 7.29 (d, *J* = 6.8 Hz, 1H), 3.76 – 3.69 (m, 2H), 3.45 (d, *J* = 12.6 Hz, 1H), 2.07 (brs, 1H), 1.50 (d, *J* = 6.6 Hz, 3H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 142.9, 139.9, 139.3, 135.4, 133.5, 129.7, 128.7, 128.0, 128.0, 127.9, 127.7, 125.0, 50.1, 48.7, 18.8 ppm.

Enantiomeric excess was determined by HPLC for the corresponding benzamide (IG-3 column, hexane/*i*PrOH 70/30, 1 mL/min, 254 nm): t_1 = 10.4 min (minor), t_2 = 15.3 min (major).

HRMS (ESI) Calculated for $C_{15}H_{15}NCl$ $[M+H]^+$ 244.0888; found 244.0879.



Chemical Formula: $C_{16}H_{14}F_3N$
Exact Mass: 277.1078

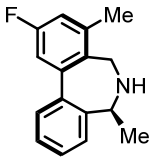
(*S*)-7-methyl-3-(trifluoromethyl)-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2g): an oil, 24.6 mg, 89% yield, 89% *ee*; $[\alpha]^{25}_D$ = + 20.8 (*c* = 0.65, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.9 Hz, 1H), 7.60 (s, 1H), 7.57 (d, *J* = 7.9 Hz, 1H), 7.49 – 7.48 (m, 2H), 7.45 – 7.44 (m, 2H), 3.78 (d, *J* = 12.8 Hz, 1H), 3.67 (q, *J* = 6.6 Hz, 1H), 3.50 (d, *J* = 12.8 Hz, 1H), 2.13 (brs, 1H), 1.48 (d, *J* = 6.6 Hz, 3H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 144.9, 139.8, 139.4, 137.6, 130.9, 130.0 (q, *J* = 32.3 Hz), 128.9, 128.0, 127.7, 125.3 (q, *J* = 273.4 Hz), 125.2 (q, *J* = 4.2, 3.7 Hz), 125.1, 124.7 (q, *J* = 3.8 Hz), 50.1, 49.2, 18.8 ppm.

Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 80/20, 0.80 mL/min, 254 nm): t_1 = 6.9 min (minor), t_2 = 10.3 min (major).

HRMS (ESI) Calculated for $C_{16}H_{15}NF_3$ $[M+H]^+$ 278.1151; found 278.1142.



Chemical Formula: $C_{16}H_{16}FN$
Exact Mass: 241.1267

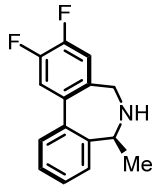
(*S*)-2-fluoro-4,7-dimethyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2h): an oil, 22.6 mg, 94% yield, 96% *ee*; $[\alpha]^{25}_D$ = + 15.3 (*c* = 0.50, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.48 – 7.46 (m, 2H), 7.44 – 7.43 (m, 2H), 7.02 (dd, *J* = 9.5, 2.5 Hz, 1H), 6.97 (dd, *J* = 9.5, 2.5 Hz, 1H), 3.96 (d, *J* = 13.0 Hz, 1H), 3.65 (q, *J* = 6.6 Hz, 1H), 3.22 (d, *J* = 13.0 Hz, 1H), 2.48 (s, 3H), 2.22 (brs, 1H), 1.51 (d, *J* = 6.6 Hz, 3H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 161.5 (d, *J* = 244.8 Hz), 143.6 (d, *J* = 8.2 Hz), 140.8 (d, *J* = 2.4 Hz), 139.1, 137.5 (d, *J* = 8.0 Hz), 130.8 (d, *J* = 3.1 Hz), 128.5, 127.8, 127.5, 124.8, 116.3 (d, *J* = 20.8 Hz), 112.3 (d, *J* = 21.3 Hz), 50.2, 43.8, 19.8 (d, *J* = 1.7 Hz), 18.6 ppm.

Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 80/20, 0.80 mL/min, 254 nm): t_1 = 7.7 min (minor), t_2 = 12.8 min (major).

HRMS (ESI) Calculated for $C_{16}H_{17}NF$ $[M+H]^+$ 242.1340; found 242.1331.



Chemical Formula: $C_{15}H_{13}F_2N$
Exact Mass: 245.1016

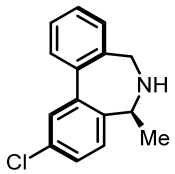
(*S*)-2,3-difluoro-7-methyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2i): an oil, 21.6 mg, 88% yield, 97% *ee*; $[\alpha]^{25}_D$ = + 29.1 (*c* = 0.61, $CHCl_3$) .

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.49 – 7.43 (m, 3H), 7.40 – 7.38 (m, 1H), 7.31 – 7.28 (m, 1H), 7.18 (dd, *J* = 10.5, 8.0 Hz, 1H), 3.72 (q, *J* = 6.6 Hz, 1H), 3.69 (d, *J* = 12.8 Hz, 1H), 3.43 (d, *J* = 12.8 Hz, 1H), 2.41 (brs, 1H), 1.51 (d, *J* = 6.6 Hz, 3H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 149.8 (dd, *J* = 252.0, 10.0 Hz), 149.7 (dd, *J* = 252.0, 8.8 Hz), 139.3, 139.0, 137.8 (dd, *J* = 6.0, 3.7 Hz), 133.6 – 133.1 (m), 128.7, 127.8, 127.8, 125.2, 117.2 (d, *J* = 16.6 Hz), 116.5 (d, *J* = 17.2 Hz), 50.2, 48.5, 18.8 ppm.

Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 80/20, 0.80 mL/min, 254 nm): t_1 = 7.6 min (minor), t_2 = 16.2 min (major).

HRMS (ESI) Calculated for $C_{15}H_{14}NF_2$ $[M+H]^+$ 246.1089; found 246.1082.



Chemical Formula: $C_{15}H_{14}ClN$
Exact Mass: 243.0815

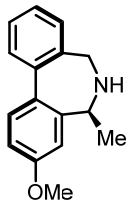
(*S*)-2-chloro-5-methyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2j): an oil, 22.1 mg, 91% yield, 96% *ee*; $[\alpha]^{25}_D$ = + 7.4 (*c* = 0.72, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.41 (m, 6H), 7.36 (d, *J* = 7.5 Hz, 1H), 3.76 (d, *J* = 12.5 Hz, 1H), 3.68 (q, *J* = 6.5 Hz, 1H), 3.50 (d, *J* = 12.5 Hz, 1H), 1.96 (brs, 1H), 1.48 (d, *J* = 6.5 Hz, 3H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 142.9, 139.9, 137.6, 136.8, 133.2, 128.7, 128.5, 128.1, 127.9, 127.8, 127.6, 126.5, 49.7, 49.2, 18.8 ppm.

Enantiomeric excess was determined by HPLC for the corresponding benzamide (OD-3 column, hexane/*i*PrOH 85/15, 0.40 mL/min, 254 nm): t_1 = 15.4 min (major), t_2 = 18.1 min (minor).

HRMS (ESI) Calculated for $C_{15}H_{15}NCl$ $[M+H]^+$ 244.0888; found 244.0880.



Chemical Formula: $C_{16}H_{17}NO$
Exact Mass: 239.1310

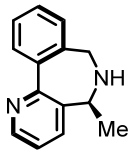
(*S*)-3-methoxy-5-methyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2k): an oil, 22.4 mg, 94% yield, 97% *ee*; $[\alpha]^{25}_{D}$ = + 65.2 (*c* = 0.61, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46 – 7.44 (m, 2H), 7.40 (d, *J* = 8.5 Hz, 1H), 7.37 – 7.34 (m, 2H), 7.03 (s, 1H), 6.98 (dd, *J* = 8.5, 2.5 Hz, 1H), 3.90 (s, 3H), 3.78 – 3.67 (m, 2H), 3.52 (d, *J* = 12.5 Hz, 1H), 2.18 (brs, 1H), 1.49 (d, *J* = 6.5 Hz, 3H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.7, 141.0, 140.7, 136.6, 133.7, 129.0, 128.4, 127.9, 127.6, 127.5, 112.3, 111.2, 55.4, 50.3, 49.4, 18.9 ppm.

Enantiomeric excess was determined by HPLC for the corresponding benzamide (OD-3 column, hexane/*i*PrOH 85/15, 0.40 mL/min, 254 nm): t_1 = 19.0 min (minor), t_2 = 20.4 min (major).

HRMS (ESI) Calculated for $C_{16}H_{18}NO$ $[M+H]^+$ 240.1383; found 240.1374.



Chemical Formula: $C_{14}H_{14}N_2$
Exact Mass: 210.1157

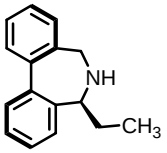
(*S*)-5-methyl-6,7-dihydro-5H-benzo[*c*]pyrido[2,3-*e*]azepine (2l): an oil, 18.6 mg, 89% yield, 84% *ee*; $[\alpha]^{25}_{D}$ = – 84.2 (*c* = 0.41, $CHCl_3$). Following the general procedure using 2 equivalent of $Ti(O^iPr)_4$.

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.68 (dd, *J* = 4.8, 1.6 Hz, 1H), 7.83 (dd, *J* = 7.5, 1.4 Hz, 1H), 7.79 (dd, *J* = 7.9, 1.6 Hz, 1H), 7.50 (td, *J* = 7.5, 1.5 Hz, 1H), 7.44 (td, J = 7.4, 1.5 Hz, 1H), 7.35 – 7.32 (m, 2H), 3.80 (d, *J* = 13.1 Hz, 1H), 3.74 (q, *J* = 6.6 Hz, 1H), 3.53 (d, *J* = 13.1 Hz, 1H), 2.30 (brs, 1H), 1.49 (d, *J* = 6.6 Hz, 3H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 158.5, 148.4, 140.1, 136.8, 134.7, 134.6, 133.4, 129.5, 128.3, 128.2, 122.6, 49.6, 49.2, 18.4 ppm.

Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 80/20, 0.80 mL/min, 254 nm): t_1 = 9.0 min (minor), t_2 = 10.4 min (major).

HRMS (ESI) Calculated for $C_{14}H_{15}N_2$ $[M+H]^+$ 211.1230; found 211.1223.



Chemical Formula: $C_{16}H_{17}N$
Exact Mass: 223.1361

(*S*)-5-ethyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2m): an oil, 18.1 mg, 81% yield, 60% *ee*; $[\alpha]^{25}_{D}$ = +15.4 (*c* = 0.31, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.38 (m, 7H), 7.37 – 7.32 (m, 1H), 3.75 (d, *J* = 12.8 Hz, 1H), 3.47 (d, *J* = 12.8 Hz, 1H), 3.43 (t, *J* = 7.2 Hz, 1H), 2.03 (brs, 1H), 1.98 – 1.92 (m, 1H), 1.84 – 1.77

(m, 1H), 0.89 (t, J = 7.4 Hz, 3H);

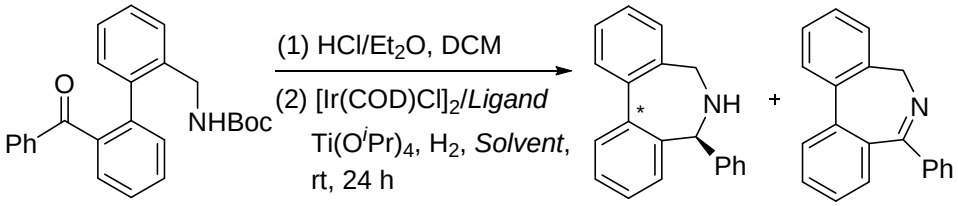
^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 141.6, 141.2, 138.1, 137.0, 128.2, 128.2, 128.1, 128.0, 128.0, 127.6, 127.4, 125.7, 57.1, 49.2, 26.1, 11.5 ppm.

Enantiomeric excess was determined by HPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 80/20, 0.80 mL/min, 254 nm): t_1 = 7.2 min (minor), t_2 = 13.0 min (major).

HRMS (ESI) Calculated for $C_{16}H_{18}NCl$ $[M+H]^+$ 224.1434; found 224.1426.

Part 2:

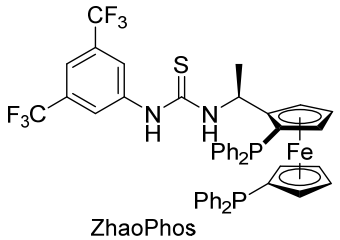
Table S1. Optimization of reaction conditions for the synthesis of diaryl-substituted dibenz[c,e]azepines.[a-c]



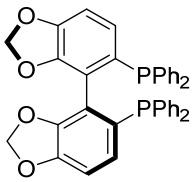
1n **2n** **2n'**

Entry	*Ligand*	*Solvent*	Conv.(%)[b]	**2n**/**2n'**[b]	**2n**: *ee* (%)[c]
1	ZhaoPhos	DCM	>99	65/35	-36
2	(*S*)-Segphos	DCM	>99	36/64	89
3	(*S*)-MeO-BiPhep	DCM	>99	53/47	86
4	(*S*)-DifluorPhos	DCM	>99	43/57	75
5	(*S*)-Segphos	^{i}PrOH	>99	47/53	89
6	(*S*)-Segphos	THF	>99	42/58	76
7	(*S*)-Segphos	EtOAc	>99	32/68	84
8	(*S*)-Segphos	Toluene	>99	35/65	89
9[d]	(*S*)-Segphos	^{i}PrOH	>99	61/39	80
10[e]	(*S*)-Segphos	^{i}PrOH	>99	70/30	89
11[e,f]	(*S*)-Segphos	^{i}PrOH	>99	85/15(72)	89

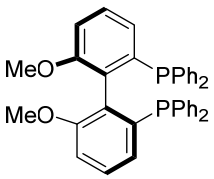
[a]Reaction conditions: **1n** (0.1 mmol), $[Ir(COD)Cl]_2$ (0.5 mol%), ligand (1.1 mol%), HCl/Et_2O (4.0 equiv), Ti($O^{i}Pr$)$_4$ (1 equiv), solvent (0.6 mL); [b]Determined by ^{1}H NMR; isolated yield of **2n** in parentheses; [c]Determined by UPLC; [d]The reaction was conducted at 50 °C; [e]60 atm H_2 was used for 36 h; [f]2 mol% loading of $[Ir(COD)Cl]_2$ was used for 48 h.



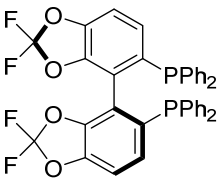
ZhaoPhos



(*S*)-SegPhos

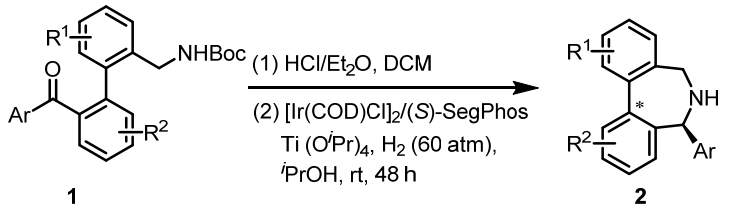


(*S*)-MeO-BiPhep



(*S*)-DifluorPhos

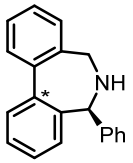
General procedure for the synthesis of 5-aryl-substituted dibenz[*c*,*e*]azepines



1 **2**

In a glovebox, to a 2.5 mL vial was added the catalyst precursor $[Ir(cod)Cl]_2$ (13.4 mg, 0.02 mmol), (*S*)-SegPhos (26.8 mg, 0.044 mmol) and anhydrous CH_2Cl_2 (0.5 mL) under argon atmosphere. The mixture was stirred for 0.5 h at room temperature to give a clear solution.

To a 5 mL vial was added substrate **1** (0.1 mmol) and CH_2Cl_2 (0.6 mL), followed by addition of HCl (2 M in Et_2O) (4 equiv). The resulting mixture was stirred at room temperature for 6 h. All volatiles were then removed, and the crude intermediate was transferred to an argon-filled glovebox. An aliquot of the above *in situ* prepared catalyst solution (50 μL, 0.002 mmol) was transferred to the vial containing crude intermediate via a syringe, followed by addition of 0.6 mL ^{i}PrOH and $Ti(O^{i}Pr)_4$ (1.0 equiv). The vial was placed in an autoclave which was then charged with 60 atm of H_2. The reaction was stirred at rt for 48 h. After carefully releasing the hydrogen, the solution was neutralized with aqueous sodium bicarbonate solution (5 mL), and then extracted with DCM (5 mL×2). The combined organic phases were concentrated and passed through a short column of silica gel with ethyl acetate/petroleum ether (1/3) as eluents to give the chiral products. The obtained products were pure enough for NMR analysis. The enantiomeric excesses were determined by UPLC analysis. (The absolute configuration of the axial chirality is not indicated at this stage, due to the lack of sufficient evidence and support from literature)



Chemical Formula: $C_{20}H_{17}N$
Exact Mass: 271.1361

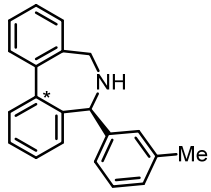
(*S*)-5-phenyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2n): an oil, 19.5 mg, 72% yield, 89% *ee*; $[\alpha]^{25}_{D}$ = + 3.5 (*c* = 0.25, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.49 – 7.38 (m, 5H), 7.38 – 7.32 (m, 4H), 7.30 – 7.26 (m, 1H), 7.22 (td, *J* = 7.6, 1.4 Hz, 1H), 6.78 (dd, *J* = 7.7, 1.2 Hz, 1H), 4.83 (s, 1H), 3.87 (d, *J* = 13.6 Hz, 1H), 3.63 (d, *J* = 13.6 Hz, 1H), 2.32 (brs, 1H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.8, 141.0, 141.0, 139.4, 137.3, 128.5, 128.3, 128.2, 128.2, 128.0, 127.9, 127.9, 127.8, 127.7, 127.5, 127.3, 60.1, 49.6 ppm.

Enantiomeric excess was determined by UPLC (OD-3 column, hexane/*i*PrOH 80/20, 0.50 mL/min, 254 nm): t_1 = 2.0 min (major), t_2 = 2.9 min (minor).

HRMS (ESI) Calculated for $C_{20}H_{18}N$ $[M+H]^+$ 272.1434; found 272.1423.



Chemical Formula: $C_{21}H_{19}N$
Exact Mass: 285.1517

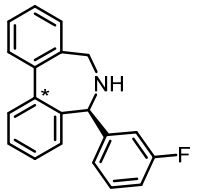
(*S*)-5-(*o*-tolyl)-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2o): an oil, 19.4 mg, 68% yield, 88% *ee*; $[\alpha]^{25}_{D} = -2.8$ (*c* = 0.26, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.49 – 7.42 (m, 2H), 7.41 (td, *J* = 7.4, 1.4 Hz, 1H), 7.37 – 7.32 (m, 2H), 7.27 (s, 1H), 7.22 – 7.21 (m, 3H), 7.10 (d, *J* = 6.9 Hz, 1H), 6.81 (dd, *J* = 7.7, 1.2 Hz, 1H), 4.80 (s, 1H), 3.86 (d, *J* = 13.6 Hz, 1H), 3.62 (d, *J* = 13.6 Hz, 1H), 2.33 (s, 3H), 2.28 (brs, 1H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 141.6, 141.0, 140.9, 139.5, 137.8, 137.3, 129.2, 128.3, 128.2, 128.1, 128.0, 128.0, 127.9, 127.8, 127.8, 127.7, 127.5, 125.6, 60.0, 49.6, 21.5 ppm.

Enantiomeric excess was determined by UPLC (OD-3 column, hexane/*i*PrOH 80/20, 0.50 mL/min, 254 nm): t_1 = 1.8 min (major), t_2 = 2.9 min (minor).

HRMS (ESI) Calculated for $C_{21}H_{20}N$ $[M+H]^+$ 286.1590; found 286.1579.



Chemical Formula: $C_{20}H_{16}FN$
Exact Mass: 289.1267

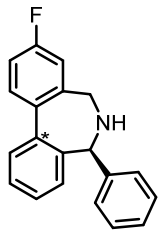
(*S*)-5-(3-fluorophenyl)-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2p): an oil, 22.8 mg, 79% yield, 87% *ee*; $[\alpha]^{25}_{D} = +4.5$ (*c* = 0.51, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.5, 1.5 Hz, 1H), 7.49 – 7.37 (m, 4H), 7.34 (td, *J* = 7.5, 1.4 Hz, 1H), 7.28 – 7.21 (m, 3H), 7.14 (d, *J* = 7.7 Hz, 1H), 6.96 (td, *J* = 8.3, 2.1 Hz, 1H), 6.78 (dd, *J* = 7.8, 1.2 Hz, 1H), 4.84 (s, 1H), 3.86 (d, *J* = 13.6 Hz, 1H), 3.61 (d, *J* = 13.6 Hz, 1H), 2.01 (brs, 1H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.9 (d, *J* = 245.2 Hz), 144.8 (d, *J* = 6.9 Hz), 140.9, 140.8, 138.9, 137.2, 129.5 (d, *J* = 8.1 Hz), 128.4, 128.1, 128.1, 128.0, 127.9, 127.9, 127.8, 127.7, 124.0 (d, *J* = 2.8 Hz), 115.4 (d, *J* = 22.0 Hz), 114.0 (d, *J* = 21.2 Hz), 59.7 (d, *J* = 1.8 Hz), 49.5 ppm.

Enantiomeric excess was determined by UPLC (OD-3 column, hexane/*i*PrOH 80/20, 0.50 mL/min, 254 nm): t_1 = 2.0 min (major), t_2 = 2.3 min (minor).

HRMS (ESI) Calculated for $C_{20}H_{17}NF$ $[M+H]^+$ 290.1340; found 290.1329.



Chemical Formula: $C_{20}H_{16}FN$
Exact Mass: 289.1267

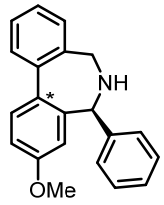
(*S*)-3-fluoro-7-phenyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2q): an oil, 20.5 mg, 74% yield, 91% *ee*; $[\alpha]^{25}_{D}$ = + 1.71 (*c* = 0.59, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 8.5, 5.5 Hz, 1H), 7.45 (t, *J* = 7.9 Hz, 3H), 7.41 – 7.36 (m, 3H), 7.33 – 7.30 (m, 1H), 7.26 (td, *J* = 7.5, 1.5 Hz, 1H), 7.19 (td, *J* = 8.5, 2.7 Hz, 1H), 7.09 (dd, *J* = 8.8, 2.7 Hz, 1H), 6.82 (d, *J* = 7.7 Hz, 1H), 4.85 (s, 1H), 3.86 (d, *J* = 13.7 Hz, 1H), 3.64 (d, *J* = 13.6 Hz, 1H), 2.36 (brs, 1H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 162.7 (d, *J* = 247.1 Hz), 141.6, 140.0, 139.3 (d, *J* = 6.7 Hz), 139.2, 136.9 (d, *J* = 3.2 Hz), 129.3 (d, *J* = 8.1 Hz), 128.5, 128.3, 128.2, 127.9, 127.7, 127.6, 127.4, 114.8 (d, *J* = 21.0 Hz), 114.6 (d, *J* = 21.3 Hz), 60.2, 49.4 ppm.

Enantiomeric excess was determined by UPLC (OD-3 column, hexane/*i*PrOH 80/20, 0.50 mL/min, 254 nm): t_1 = 2.0 min (major), t_2 = 2.5 min (minor).

HRMS (ESI) Calculated for $C_{20}H_{17}NF$ $[M+H]^+$ 290.1340; found 290.1329.



Chemical Formula: $C_{21}H_{19}NO$
Exact Mass: 301.1467

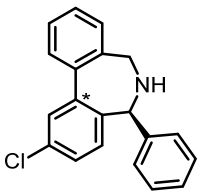
(*S*)-3-fluoro-7-phenyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2r): an oil, 19.5 mg, 65% yield, 81% *ee*; $[\alpha]^{25}_{D}$ = + 37.0 (*c* = 0.46, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.6, 1.3 Hz, 1H), 7.50 – 7.45 (m, 3H), 7.42 – 7.34 (m, 5H), 7.31 (d, *J* = 7.2 Hz, 1H), 6.93 (dd, *J* = 8.4, 2.7 Hz, 1H), 6.38 (d, *J* = 2.7 Hz, 1H), 4.86 (s, 1H), 3.90 (d, *J* = 13.5 Hz, 1H), 3.70 (s, 3H), 3.67 (d, *J* = 13.5 Hz, 1H), 2.29 (brs, 1H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 159.4, 141.4, 140.9, 140.8, 137.0, 133.6, 128.8, 128.5, 128.3, 128.1, 127.9, 127.8, 127.6, 127.4, 114.5, 112.4, 60.2, 55.2, 49.6 ppm.

Enantiomeric excess was determined by UPLC (OD-3 column, hexane/*i*PrOH 80/20, 0.50 mL/min, 254 nm): t_1 = 2.1 min (major), t_2 = 3.4 min (minor).

HRMS (ESI) Calculated for $C_{21}H_{20}NO$ $[M+H]^+$ 302.1539; found 302.1532.



Chemical Formula: $C_{20}H_{16}ClN$
Exact Mass: 305.0971

(*S*)-2-chloro-5-phenyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (2s): 24.7 mg, 81% yield, 84% *ee*; $[\alpha]^{25}_{D}$ = - 4.3 (*c* = 0.51, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.5, 1.7 Hz, 1H), 7.50 – 7.45 (m, 1H), 7.45 – 7.37 (m, 4H), 7.37 – 7.27 (m, 4H), 7.17 (dd, *J* = 8.4, 2.3 Hz, 1H), 6.70 (d, *J* = 8.3 Hz, 1H), 4.77 (s, 1H), 3.87 (d, *J* = 13.7 Hz, 1H), 3.61 (d, *J* = 13.7 Hz, 1H), 2.16 (brs, 1H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 142.6, 141.3, 139.7, 138.0, 137.3, 133.3, 129.8, 128.9, 128.4, 128.3, 128.2, 128.1, 127.7, 127.7, 127.6, 127.5, 59.6, 49.4 ppm.

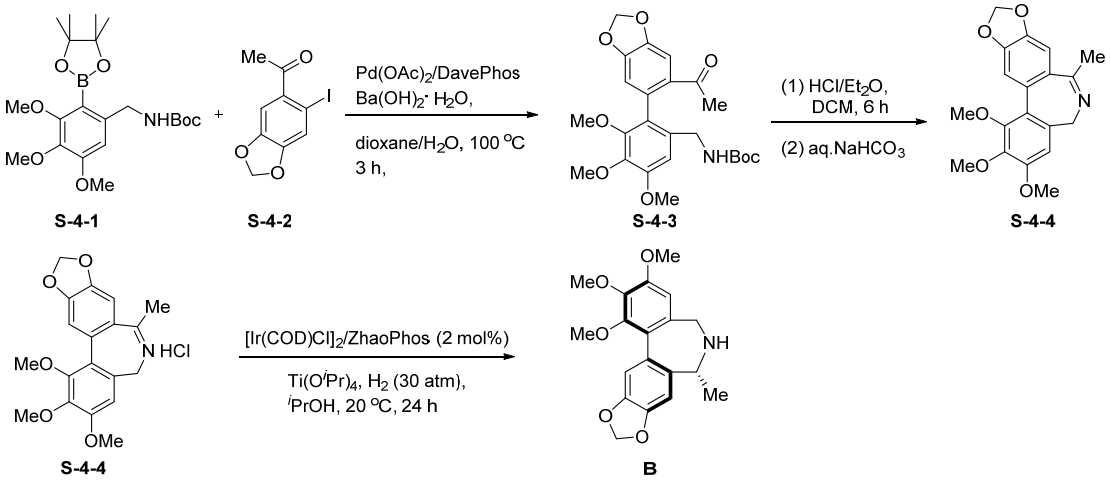
Enantiomeric excess was determined by UPLC (OD-3 column, hexane/*i*PrOH 80/20, 0.50 mL/min,

254 nm): t_1 = 2.0 min (major), t_2 = 2.6 min (minor).

HRMS (ESI) Calculated for $C_{20}H_{17}NCl$ $[M+H]^+$ 306.1044; found 306.1035.

4. Synthetic applications.

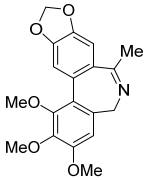
4.1. The synthesis route towards bioactive compound of B



S-4-1 and **S-4-2** were synthesized according to a known procedure.[7]

A sealed tube was charged with the aryl iodide **S-4-2** (0.2 mmol, 1 equiv), the arylboronate **S-4-1** (0.3 mmol, 1.5 equiv), $Pd(OAc)_2$ (0.05 equiv), DavePhos (0.1 equiv), $Ba(OH)_2{\cdot}8\ H_2O$ (1.1 equiv) and a 9/1 mixture of dioxane and water ([**S-4-2**] = 0.5 M). The tube was sealed, placed in an oil bath and then to heated at 100°C for 3 h. After cooling down to room temperature, the mixture was filtered through celite and $MgSO_4$. The filtrate was concentrated and then purified by flash chromatography on silica gel (petroleum ether/ethyl acetate = 3/1) to give an inseparable mixture of the expected product and a by-product of the reaction (the protodeiodination product or pinacol). The product **S-4-3** was subjected to HCl/Et_2O (2M, 4 equiv) in DCM (0.5 mL) for 6 h, then neutralized with 1N $NaHCO_3$, the organic phase was concentrated and purified by flash chromatography on silica gel with ethyl acetate/petroleum ether (1/1) as eluents to afford the imine **S-4-4** 26% yield for 2 steps, 17.5 mg.

Asymmetric hydrogenation of the imine hydrochlorides salts **S-4-4** (15 mg) follows the general procedure for the synthesis of 5-alkyl-substituted dibenz[*c,e*]azepines with a slightly revised conditions: using 2 mol% of $[Ir(COD)Cl]_2$, 4.4 mol% of ZhaoPhos and 3 equiv of $Ti(O^iPr)_4$.



Chemical Formula: $C_{19}H_{19}NO_5$
Exact Mass: 341.1263

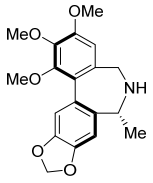
1,2,3-trimethoxy-7-methyl-5H-[1,3]dioxolo[4',5':4,5]benzo[1,2-*c*]benzo[*e*]azepine (S-4-4): 17.5 mg, 26% yield for 2 steps.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 (s, 1H), 7.03 (s, 1H), 6.77 (s, 1H), 6.09 (d, *J* = 1.4 Hz, 1H), 6.05 (d, *J* = 1.4 Hz, 1H), 4.49 (d, *J* = 10.7 Hz, 1H), 3.91 (s, 3H), 3.89 (s, 3H), 3.66-3.63 (m, 4H), 2.33 (s, 3H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.0, 151.7, 147.6, 146.1, 141.7, 137.2, 130.9, 130.4, 129.9,

123.1, 110.6, 106.4, 106.3, 101.6, 61.1, 60.9, 56.0, 54.9, 26.1 ppm.

HRMS (ESI) Calculated for $C_{19}H_{20}NO_5$ $[M+H]^+$ 342.1336; found 342.1327.



Chemical Formula: $C_{19}H_{21}NO_5$
Exact Mass: 343.1420

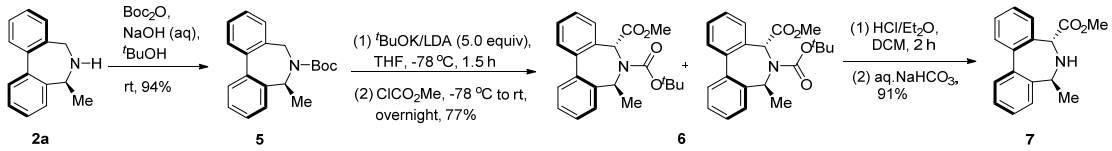
(7*R*,12*bR*)-1,2,3-trimethoxy-7-methyl-6,7-dihydro-5H-[1,3]dioxolo[4',5':4,5]benzo[1,2-c]benzo[e]azepine (B):[7] 12.3 mg, 81% yield, 75% *ee*. $[\alpha]^{25}_D = -13.8$ ($c = 0.67$, $CHCl_3$). (lit.[7] $[\alpha]^{25}_D = -47$ ($c = 0.87$, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.05 (s, 1H), 6.97 (s, 1H), 6.73 (s, 1H), 6.03 (d, $J = 1.5$ Hz, 1H), 6.00 (d, $J = 1.5$ Hz, 1H), 3.92 (s, 3H), 3.91 (s, 3H), 3.70 (s, 3H), 3.73 – 3.62 (m, 2H), 3.38 (d, $J = 12.5$ Hz, 1H), 2.88 (brs, 1H), 1.55 (d, $J = 6.6$ Hz, 3H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.0, 150.6, 147.2, 146.5, 142.1, 131.8, 131.4, 130.2, 125.9, 110.0, 108.0, 105.2, 101.2, 61.1, 60.9, 56.1, 49.9, 48.8, 18.2 ppm.

Enantiomeric excess was determined by UPLC for the corresponding benzamide (AD-3 column, hexane/*i*PrOH 80/20, 0.50 mL/min, 254 nm): $t_1 = 4.4$ min (major), $t_2 = 9.2$ min (minor).

4.2. Synthesis towards 7-member cyclic amino acid derivative 7



Step 1

To a solution of **2a** (105 mg, 0.5 mmol) in ^{t}BuOH (2 mL) was added 1N NaOH (aq) (1 mL) followed by addition of $(Boc)_2O$ (130 mg, 0.6 mmol). The resulting mixture was stirred at rt for 3 h. The solution was concentrated and purified by flash chromatography on silica gel with ethyl acetate/petroleum ether (1/30) as eluents to afford **5 (**145 mg, 94% yield, 95% *ee*).

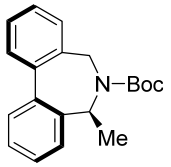
Step 2

A solution of **5** (31 mg, 0.1 mmol) in dry THF (1 mL) was cooled to -78 ^{o}C under N_2 atmosphere. To the solution was slowly added ^{t}BuOK (1 M in THF, 0.5 mmol), followed by addition of 1 M LDA (0.5 mL). The solution was stirred at -78 ^{o}C for 1.5 h. Methyl chloroformate (0.3 mmol) was then added and the mixture was stirred at -78 ^{o}C for 1.5 h and then allowed warm to room temperature for overnight. The mixture was quenched by addition of saturated aqueous ammonium chloride (5 mL) and the organic layer was extracted with ethyl acetate (3 x 5 mL). The combined organic phases were concentrated under reduced pressure and the residue was purified by flash chromatography (ethyl acetate/petroleum ether 1:6) to give **6** as a mixture of two rotamers (28.2 mg, 77% yield, 95% *ee*).

Step 3

To the solution of **6** (36.7 mg, 0.1 mmol) in DCM (1 mL) was added 2 M HCl/Et_2O (0.3 mL), and the solution was stirred for 2 h before quench with 1 N $NaHCO_3$ (2 mL). The organic phase was extracted with DCM (2 x 3 mL), and the combined organic phases were concentrated under

reduced pressure. The residue was purified by flash chromatography (ethyl acetate/petroleum ether = 1/3) to give **7** (24.3 mg, 91% yield).



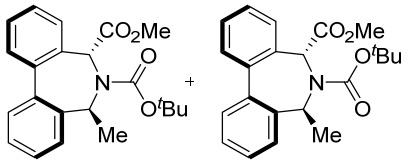
Chemical Formula: $C_{20}H_{23}NO_2$

***tert*-butyl (S)-5-methyl-5,7-dihydro-6H-dibenzo[*c*,*e*]azepine-6-carboxylate (5):**[8] 145 mg, 94% yield, 95% *ee*. $[\alpha]^{25}_D = -305.7$ (*c* = 0.77, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 – 7.34 (m, 8H), 5.10 (s, 2H), 3.71 (d, *J* = 13.7 Hz, 1H), 1.53 (s, 9H), 0.86 (d, *J* = 6.9 Hz, 3H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 153.7, 141.0, 139.2, 139.2, 135.3, 130.2, 129.6, 129.2, 128.6, 128.3, 128.2, 128.2, 127.6, 79.8, 57.6, 53.5, 28.6, 21.4 ppm.

Enantiomeric excess was determined by UPLC (AD-3 column, hexane/*i*PrOH 98/2, 0.30 mL/min, 254 nm): t_1 = 3.5 min (major), t_2 = 3.9 min (minor).



Chemical Formula: $C_{22}H_{25}NO_4$
Exact Mass: 367.1784

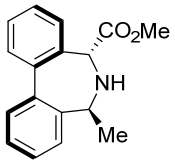
6-(*tert*-butyl) 5-methyl(5*R*,7*S*)-7-methyl-5,7-dihydro-6H-dibenzo[*c*,*e*]azepine-5,6-dicarboxylate (6): 28.2 mg, 77% yield, 95 % *ee*. $[\alpha]^{25}_D = -217.5$ (*c* = 0.67, $CHCl_3$). *Product was isolated as a 1.3:1 mixture of rotamers. ^{1}H NMR and ^{13}C NMR data listed is for the mixture of rotamers.*

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 – 7.29 (m, 8 x 2.3H), 6.04 (s, 1.3H), 5.76 (s, 1H), 5.46 (d, *J* = 7.0 Hz, 1H), 5.22 (q, *J* = 6.9 Hz, 1.3H), 3.15 (s, 3H), 3.14 (s, 3.9H), 1.56 (s, 9 x 1.3H), 1.51 (s, 9H), 0.90 (d, *J* = 7.1 Hz, 3 x 1.3H), 0.87 (d, *J* = 7.1 Hz, 3H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 171.4, 171.2, 154.3, 153.6, 140.2, 139.9, 139.0, 138.9, 138.4, 138.2, 134.5, 134.0, 130.9, 130.9, 130.7, 130.5, 129.7, 129.4, 129.3, 129.2, 128.5, 128.5, 128.4, 128.4, 128.3, 128.3, 128.2, 128.1, 80.6, 80.6, 61.5, 60.0, 57.3, 56.2, 52.0, 52.0, 28.6, 28.5, 21.4, 20.9 ppm.

Enantiomeric excess was determined by UPLC (OD-3 column, hexane/*i*PrOH 95/5, 0.30 mL/min, 254 nm): t_1 = 4.7 min (major), t_2 = 5.6 min (minor).

HRMS (ESI) Calculated for $C_{22}H_{26}NO_4$ $[M+H]^+$ 368.1856; found 368.1847.



Chemical Formula: $C_{17}H_{17}NO_2$
Exact Mass: 267.1259

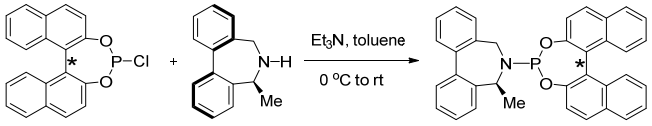
methyl (*5R,7S*)-7-methyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine-5-carboxylate (7): 24.3 mg, 91% yield. $[\alpha]^{25}_D = +16.8$ (*c* =0.47, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.37 (m, 7H), 7.10 (d, *J* = 7.5 Hz, 1H), 4.35 (s, 1H), 3.77 (s, 3H), 3.66 (q, *J* = 6.5 Hz, 1H), 1.49 (d, *J* = 6.5 Hz, 3H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 173.0, 140.8, 140.3, 138.8, 134.9, 128.5, 128.4, 128.4, 128.1, 128.0, 127.8, 125.1, 125.0, 60.6, 52.2, 49.4, 18.7 ppm.

HRMS (ESI) Calculated for $C_{17}H_{18}NO_2$ $[M+H]^+$ 268.1332; found 268.1321.

4.3. Synthesis of Ligand 1, 2 and their application in asymmetric hydrogenation of α-dehydroamino acid derivatives

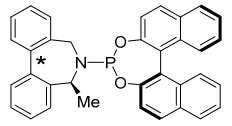


R-binoP-Cl
S-binoP-Cl

2a

L1: 36% yield
L2: 52% yield

To a solution of (*R*)-binoP-Cl or (*S*)-binoP-Cl (0.2 mmol) in dry toluene (2 mL) was added dry diisopropylethylamine (1.1 equiv), followed by addition of **2a** (1.1 equiv) in dry toluene (0.3 mL) at 0 °C. The mixture was stirred for 3 h at room temperature. The solvent was removed in vacuo and the residue was purified by flash chromatography (ethyl acetate/petroleum ether = 1/20) to afford the product **L1** or **L2** as a white solid.



Chemical Formula: $C_{35}H_{26}NO_2P$
Exact Mass: 523.1701

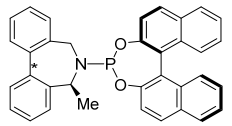
(5*S*)-6-((11*bR*)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)-5-methyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (L1): 37.6 mg, 36% yield. $[\alpha]^{25}_D$ = – 244.9 (*c* = 0.49, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 8.03 (d, *J* = 8.8 Hz, 1H), 7.96 (d, *J* = 8.2 Hz, 1H), 7.81 (d, *J* = 8.1 Hz, 1H), 7.68 (d, *J* = 8.8 Hz, 1H), 7.62 (d, *J* = 8.7 Hz, 1H), 7.57 – 7.48 (m, 4H), 7.48 – 7.42 (m, 3H), 7.42 – 7.34 (m, 3H), 7.32 – 7.26 (m, 2H), 7.26 – 7.21 (m, 1H), 7.10 (dd, *J* = 7.5, 1.3 Hz, 1H), 7.07 (d, *J* = 8.8 Hz, 1H), 4.94 (dq, *J* = 14.3, 7.1 Hz, 1H), 4.00 (d, *J* = 12.9 Hz, 1H), 3.18 (dd, *J* = 12.9, 3.1 Hz, 1H), 0.99 (d, *J* = 7.0 Hz, 3H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 150.2 (d, *J* = 4.9 Hz), 149.6, 141.4, 139.6, 139.6 (d, *J* = 6.7 Hz), 139.5, 136.3 (d, *J* = 2.6 Hz), 132.8, 132.5, 131.4, 130.7, 130.3, 130.1, 129.3, 129.3, 129.1, 128.3, 128.3, 128.2, 128.16, 128.0, 127.5, 127.1, 126.9, 126.1, 126.0, 124.8, 124.5, 124.0 (d, *J* = 5.0 Hz), 122.7 (d, *J* = 2.2 Hz), 122.1 (d, *J* = 1.8 Hz), 121.9, 57.0 (d, *J* = 44.0 Hz), 45.4 (d, *J* = 3.9 Hz), 24.5 (d, *J* = 5.5 Hz) ppm.

^{31}P NMR (202 MHz, $CDCl_3$) δ 143.63 ppm.

HRMS (ESI) Calculated for $C_{35}H_{27}NO_2P$ $[M+H]^+$ 524.1774; found 524.1765.



Chemical Formula: $C_{35}H_{26}NO_2P$
Exact Mass: 523.1701

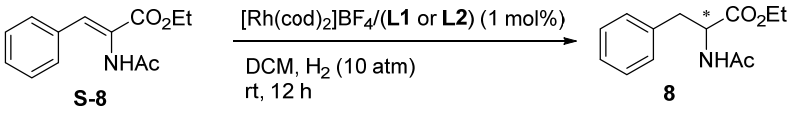
(5*S*)-6-((11*bS*)-dinaphtho[2,1-d:1',2'-f][1,3,2]dioxaphosphepin-4-yl)-5-methyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine (L2): 54.4 mg, 52% yield. $[\alpha]^{25}_D$ = + 153.9 (*c* = 0.40, $CHCl_3$).

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 – 7.97 (m, 3H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.54 (d, *J* = 8.7 Hz, 1H), 7.49 – 7.24 (m, 14H), 6.94 (d, *J* = 7.5 Hz, 1H), 4.75 – 4.42 (m, 1H), 4.00 (dd, *J* = 13.4, 6.7 Hz, 1H), 3.74 (dd, *J* = 13.3, 2.1 Hz, 1H), 0.96 (d, *J* = 7.0 Hz, 3H);

^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$) δ 149.8 (d, *J* = 4.6 Hz), 149.6, 141.5, 139.4, 139.4, 136.0 (d, *J* = 7.2 Hz), 132.8 (d, *J* = 1.7 Hz), 132.8, 131.4, 130.8, 130.3, 130.1, 129.5, 129.2, 129.1, 128.3, 128.2 (d, *J* = 1.8 Hz), 128.0, 128.0, 127.8, 127.6, 127.1 (d, *J* = 1.6 Hz), 126.1 (d, *J* = 1.6 Hz), 124.8, 124.7, 124.0 (d, *J* = 5.0 Hz), 122.6, 122.6, 122.0 (d, *J* = 1.9 Hz), 57.1 (d, *J* = 23.5 Hz), 47.3 (d, *J* = 19.6 Hz), 24.4 (d, *J* = 5.2 Hz) ppm.

^{31}P NMR (162 MHz, $CDCl_3$) δ 146.52 ppm.

HRMS (ESI) Calculated for $C_{35}H_{27}NO_2P$ $[M+H]^+$ 524.1774; found 524.1763.

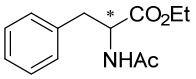


S-8 **8**

L1: 96% yield, 98% *ee*
L2: 97% yield, 97% *ee*

In a glovebox, to a solution of $[Rh(COD)_2]BF_4$ (2.0 mg, 0.005mmol) in CH_2Cl_2 (0.5 mL) was added ligand **L1** or **L2**(5.75 mg, 2.2 equiv.), The resulting mixture was stirred for 30 min.

To a 2.5 mL vial was added substrate **S-8** (0.1 mmol) and dry DCM (0.5 mL), then an aliquot of the above *in situ* prepared catalyst solution (100 μL, 0.001mmol) was transferred to the vial via a syringe. The vial was placed in an autoclave which was then charged with 10 atm of H_2. The reaction was stirred at rt for 12 h. After carefully releasing the hydrogen, the solution was concentrated and passed through a short column of silica gel with ethyl acetate/petroleum ether (1/2) as eluents to give the chiral products. The obtained products were pure enough for NMR analysis. The enantiomeric excesses were determined by HPLC analysis.



Chemical Formula:

L1: ethyl acetyl-*L*-phenylalaninate(8): 22.6 mg, 96% yield, 98% *ee*; $[\alpha]^{25}_D$ = + 71.9 (*c* = 0.61, $CHCl_3$).

L2: ethyl acetyl-*D*-phenylalaninate(8):[9] 22.7 mg, 97% yield, 97% *ee*. $[\alpha]^{25}_D$ = – 77.3 (*c* = 0.41, $CHCl_3$).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.32 – 7.25 (m, 3H), 7.13 – 7.12 (m, 2H), 6.03 (d, *J* = 7.8 Hz, 1H), 4.88 (dt, *J* = 7.7, 5.9 Hz, 1H), 4.19 (qt, *J* = 7.2, 1.3 Hz, 2H), 3.13 (t, *J* = 6.2 Hz, 2H), 2.00 (s, 3H), 1.26 (t, *J* = 7.1 Hz, 3H);

^{13}C {^{1}H} NMR (126 MHz, $CDCl_3$) δ 171.7, 169.6, 135.9, 129.3, 128.5, 127.1, 61.5, 53.2, 37.9, 23.2, 14.1 ppm.

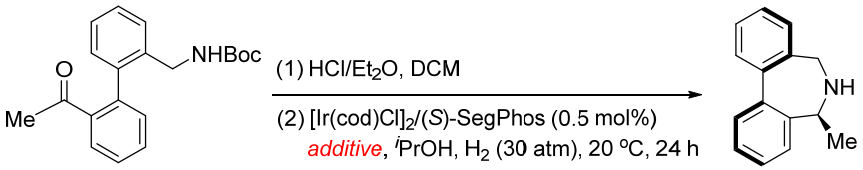
Enantiomeric excess was determined by HPLC (OD-H column, hexane/*i*PrOH 90/10, 1 mL/min, 220 nm): t_1 = 7.7 min (minor), t_2 = 9.8 min (major) using **L1**.

Enantiomeric excess was determined by HPLC (OD-H column, hexane/*i*PrOH 90/10, 1 mL/min, 220 nm): t_1 = 7.6 min (major), t_2 = 9.9 min (minor) using **L2**.

5. Mechanistic study

5.1 Evaluation of Lewis acid additives[a]

The procedure follows General procedure for the synthesis of 5-alkyl-substituted dibenz[*c*,*e*]azepines using the corresponding Lewis acids in place of $Ti(O^iPr)_4$.



1a **2a**

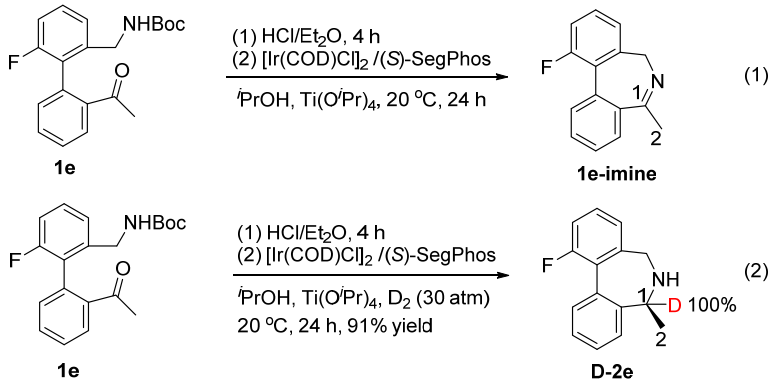
entry	*additive*	yield (%)[b]	*ee* (%)[c]
1	$Ti(O^iPr)_4$	91%	92%
2	$AlCl_3$	<2	-
3	$InCl_3$	<2	-
4	$FeCl_3$	<2	-
5	$Zn(OTf)_2$	<2	-
6	$BF_3•Et_2O$	<2	-
7	$Ti(OEt)_4$	92%	90%

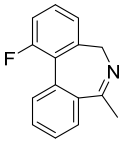
[a] Reaction conditions: **1a** (0.1 mmol), $[Ir(COD)Cl]_2$ (0.5 mol%), (*S*)-SegPhos (1.1 mol%), HCl/Et_2O (4.0 equiv), *additive* (1 equiv), ^iPrOH (0.6 mL). [b] Determined by ^1H NMR. [c] Determined by HPLC for the corresponding benzamides.

We tested some other Lewis acids including $AlCl_3$, $InCl_3$, $FeCl_3$, $Zn(OTf)_2$, $BF_3•Et_2O$ and $Ti(OEt)_4$, and the results disclosed that only titanium Lewis acid could efficiently accelerate the transformation. The success of titanium Lewis acid is partly due to its excellent solubility, compared to other metal salts ($AlCl_3$, $InCl_3$, $FeCl_3$) in ^iPrOH. Although $Zn(OTf)_2$ and $BF_3•Et_2O$ were soluble, very low conversion of imines were observed in both cases. We tentatively proposed that the titanium Lewis acid could activate the in situ formed imine intermediate. However, when we mixed the independently prepared imine with 1.0 equiv of $Ti(OiPr)_4$, no obvious complexation was detected from ^1H NMR and ^{13}C NMR study (see 5.3).

5.2 Control experiments and deuterium labeling experiments

The procedure follows General procedure for the synthesis of 5-alkyl-substituted dibenz[*c*,*e*]azepines. In experiment (1), the reaction was conducted in ^iPrOH in the absence of H_2 gas. The reduction process was completely shut down, and only **1e-imine** was obtained. In experiment (2), the reaction was conducted in ^iPrOH or THF as solvent in the presence of D_2 gas. Completely deuterium-labeled products at C1 position were obtained in both cases, which demonstrated D_2 gas was the real reducing reagent. Meanwhile, no deuterium incorporation at C2 position was observed, which excluded the possibility of hydrogenating enamine intermediates.



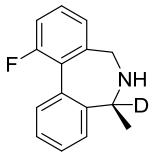


Chemical Formula: $C_{15}H_{12}FN$
Exact Mass: 225.0954

1-fluoro-7-methyl-5H-dibenzo[*c*,*e*]azepine (1e-imine): 21.4 mg, 95% yield (0.1 mmol scale). **^{1}H NMR** (600 MHz, CD_3OD) δ 7.79 (d, *J* = 7.8 Hz, 1H), 7.75 (d, *J* = 7.8 Hz, 1H), 7.62 (t, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.6 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.42 – 7.37 (m, 1H), 7.19 (t, *J* = 8.8 Hz, 1H), 5.00 (s, 1H), 3.45 (s, 1H), 2.34 (d, *J* = 6.3 Hz, 3H);

^{13}C {^{1}H} NMR (151 MHz, CD_3OD) δ 170.4, 158.7 (d, *J* = 244.5 Hz), 140.5 (d, *J* = 4.2 Hz), 137.7 (d, *J* = 2.2 Hz), 134.9, 130.1, 128.9, 128.6 (d, *J* = 8.8 Hz), 127.8, 127.7, 127.0 (d, *J* = 17.3 Hz), 123.9 (d, *J* = 3.2 Hz), 114.1 (d, *J* = 22.7 Hz), 44.2, 24.4 ppm.

HRMS (ESI) Calculated for $C_{15}H_{13}NF$ $[M+H]^+$ 226.1027; found 226.1023.



Chemical Formula: $C_{15}H_{13}DFN$
Exact Mass: 228.1173

(7*S*)-1-fluoro-7-methyl-6,7-dihydro-5H-dibenzo[*c*,*e*]azepine-7-*d*: 20.7 mg, 91% yield (0.1 mmol scale). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.03 – 6.68 (m, 7H), 4.21 (d, *J* = 13.2 Hz, 1H), 3.18 (dd, *J* = 13.2, 3.1 Hz, 1H), 1.99 (s, 1H), 1.47 (s, 1H).

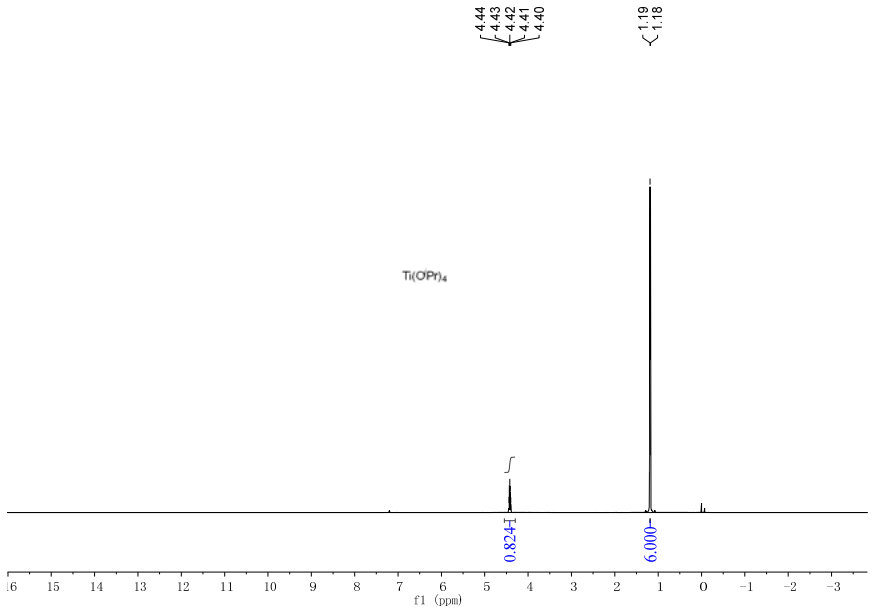
5.3 NMR experiments to study the interaction of 1e-imine with Ti(O^{i}Pr)$_4$

In an oven-dried NMR tube, **1e-imine** (15 mg) was dissolved in 0.6 mL CD_3OD, and Ti(O^{i}Pr)$_4$ (1.0 or 2.0 equivs) was then added. The resulting mixture was sonicated for 5 min, the NMR data was then collected.

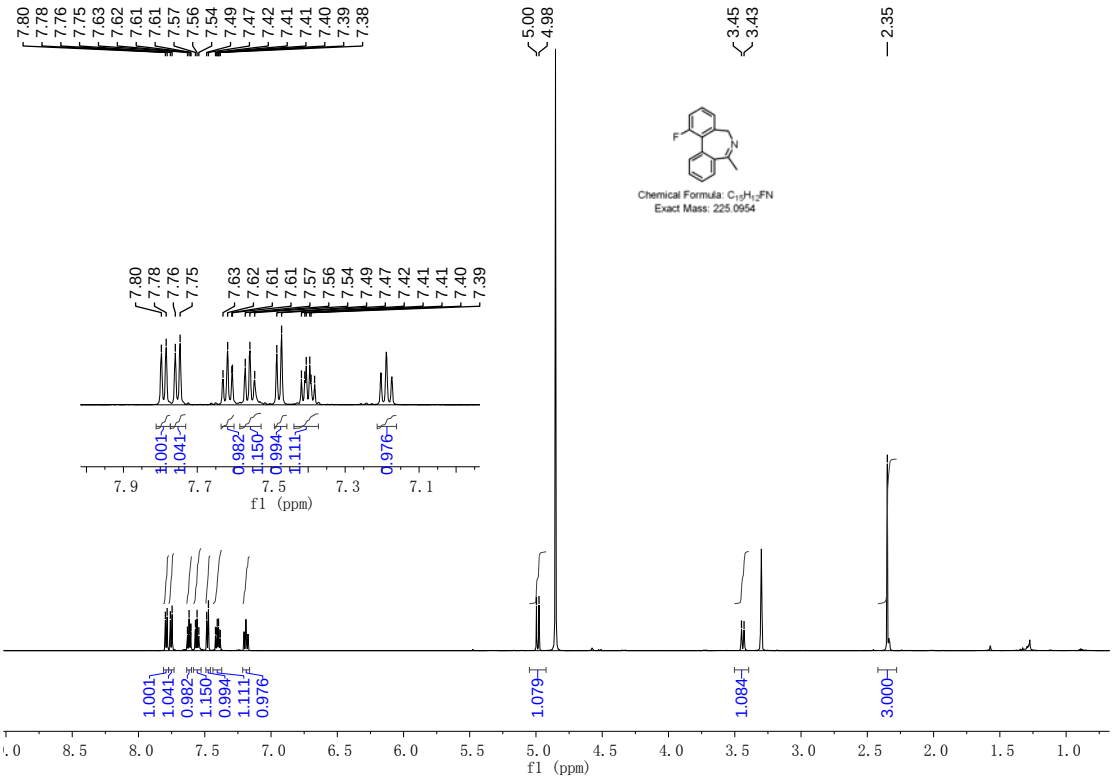
With 1 equiv of Ti(O^{i}Pr)$_4$, no obvious complexation was observed from ^{1}H NMR and ^{13}C NMR specta. With 2 equivalents of Ti(O^{i}Pr)$_4$, the ^{1}H NMR chemical shift of **1e-imine** did not change, however, the integration of Me group decreased a lot.

NMR experiments in $CDCl_3$ were also conducted, again no obvious complexation was observed (not shown).

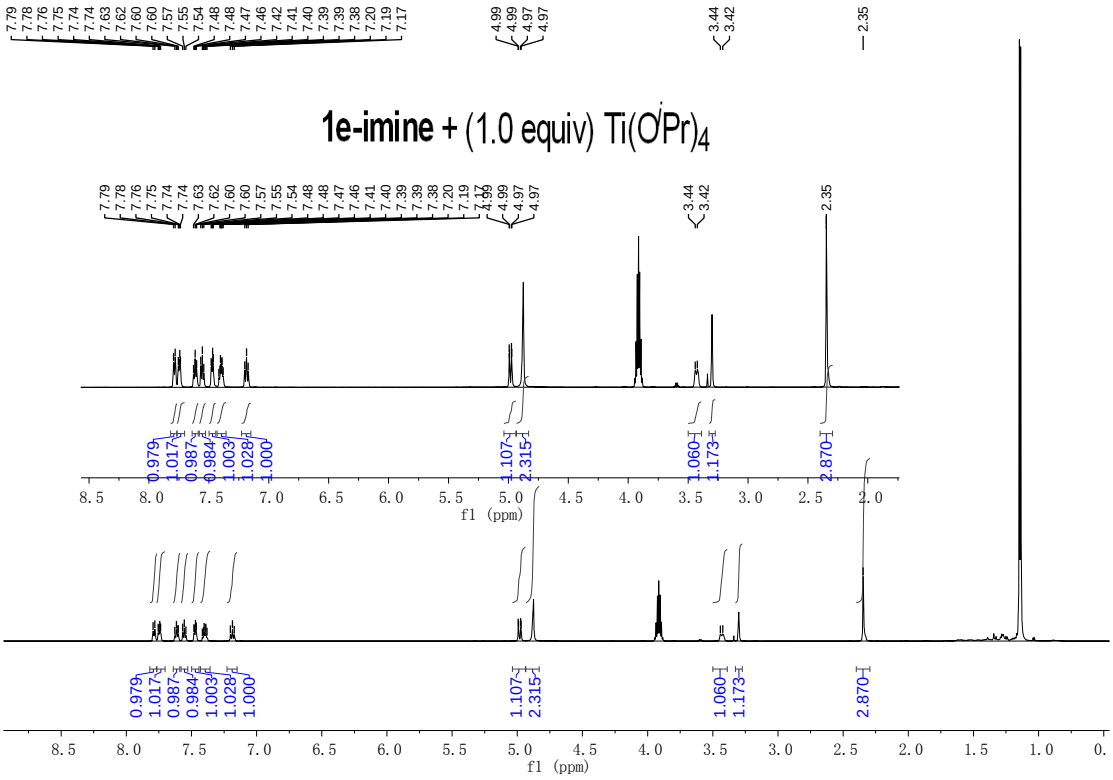
^{1}H NMR for Ti(O^{i}Pr)$_4$ in $CDCl_3$ (400 M).



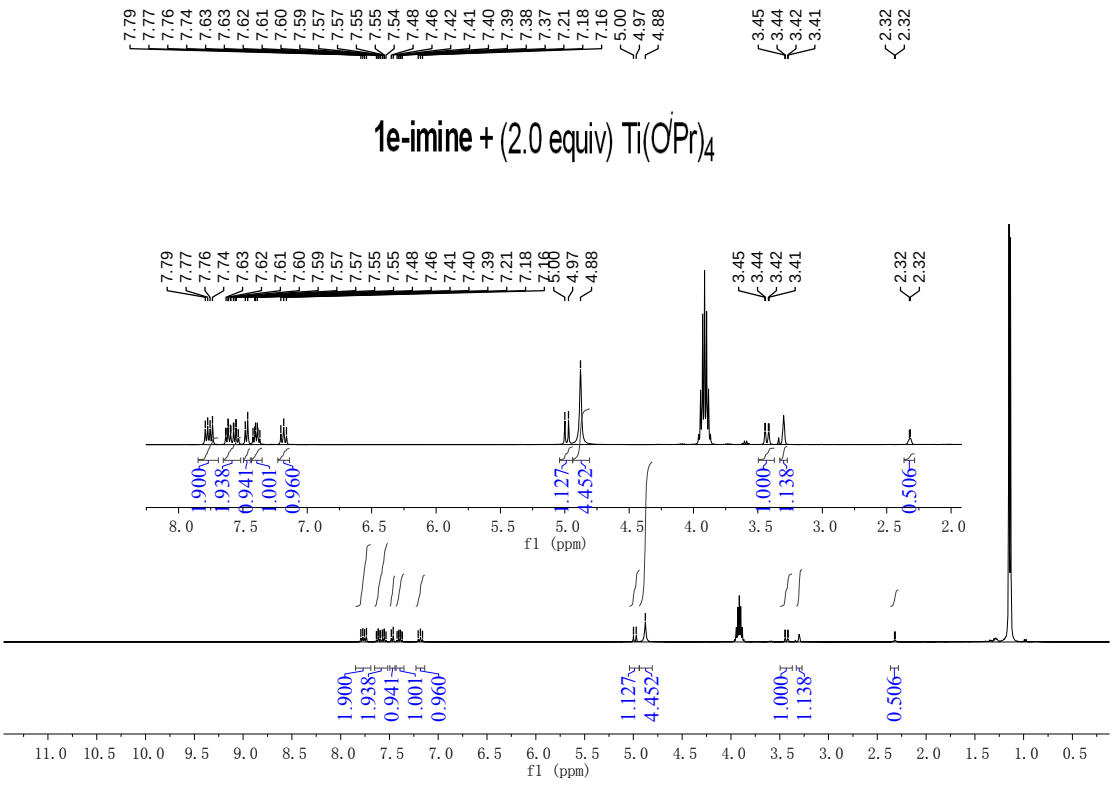
^{1}H NMR for **1e-imine** (in CD_3OD, 400 M)



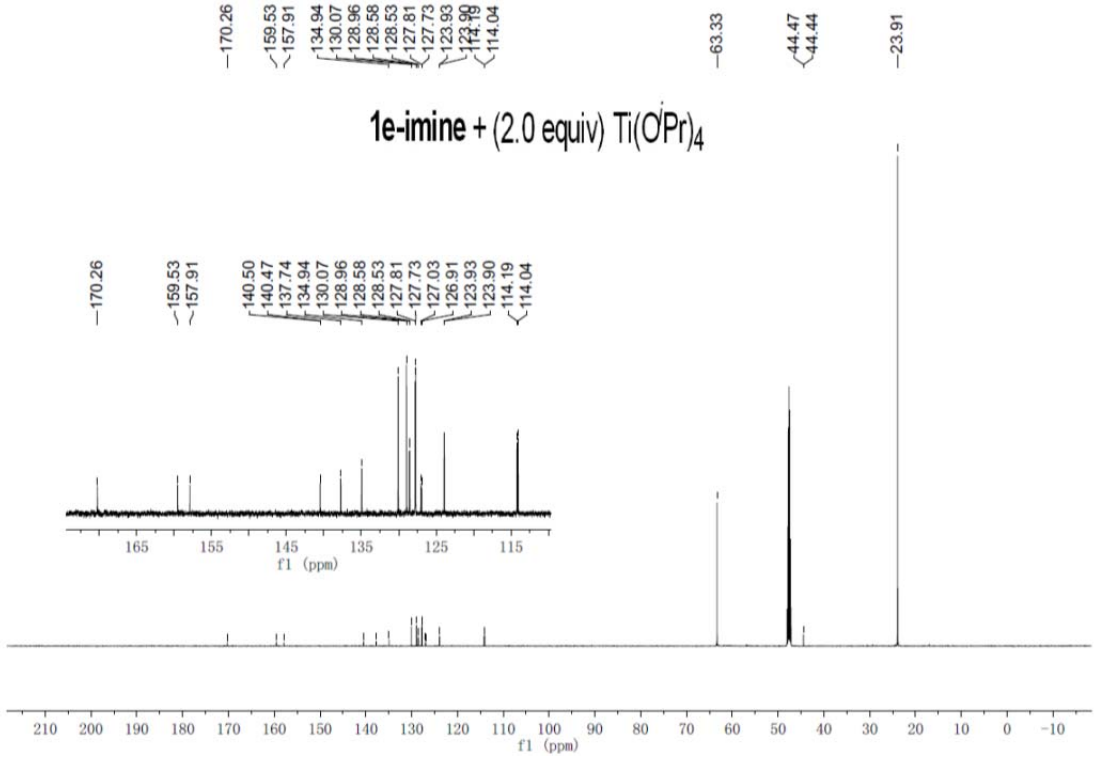
^{1}H NMR for **1e-imine**+Ti(O^{i}Pr)$_4$ (1:1) (in CD_3OD, 400 M)



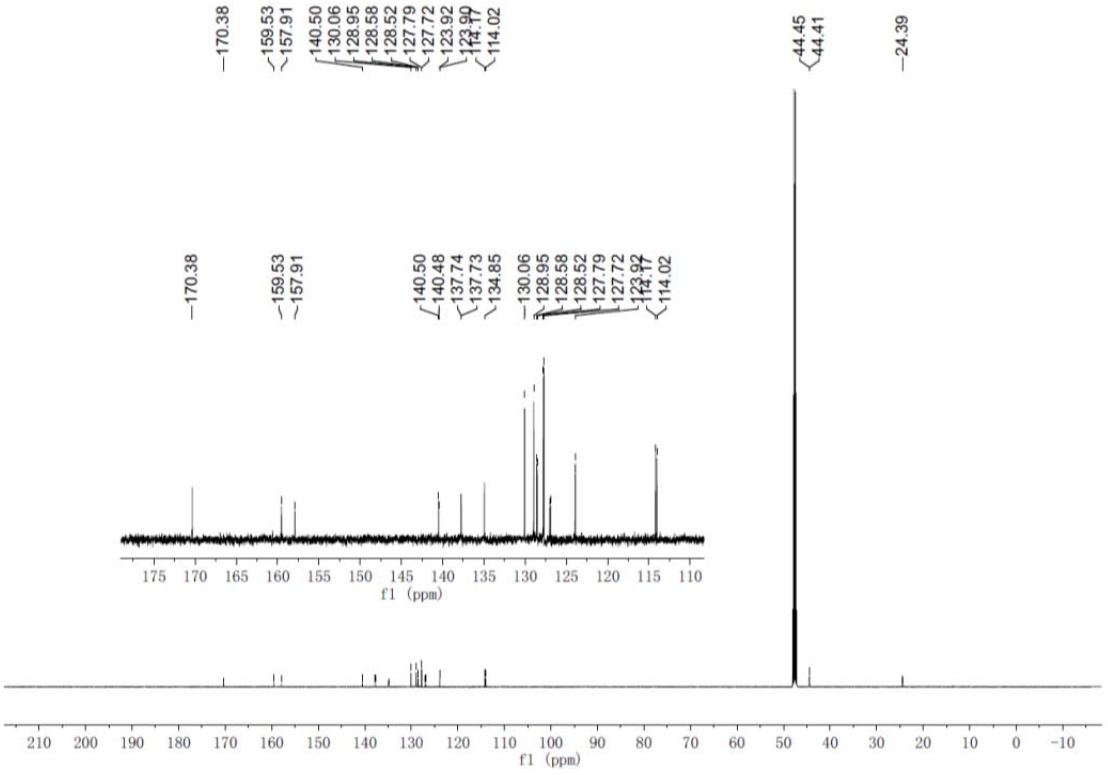
^{1}H NMR for **1e-imine**+Ti(O^{i}Pr)$_4$ (1:2) (in CD_3OD, 400 M)



^{13}C NMR for **1e-imine**+Ti(O^{i}Pr)$_4$ (1:2) (in CD_3OD, 600 M)



^{13}C NMR for **1e-imine** (in CD_3OD, 600 M)



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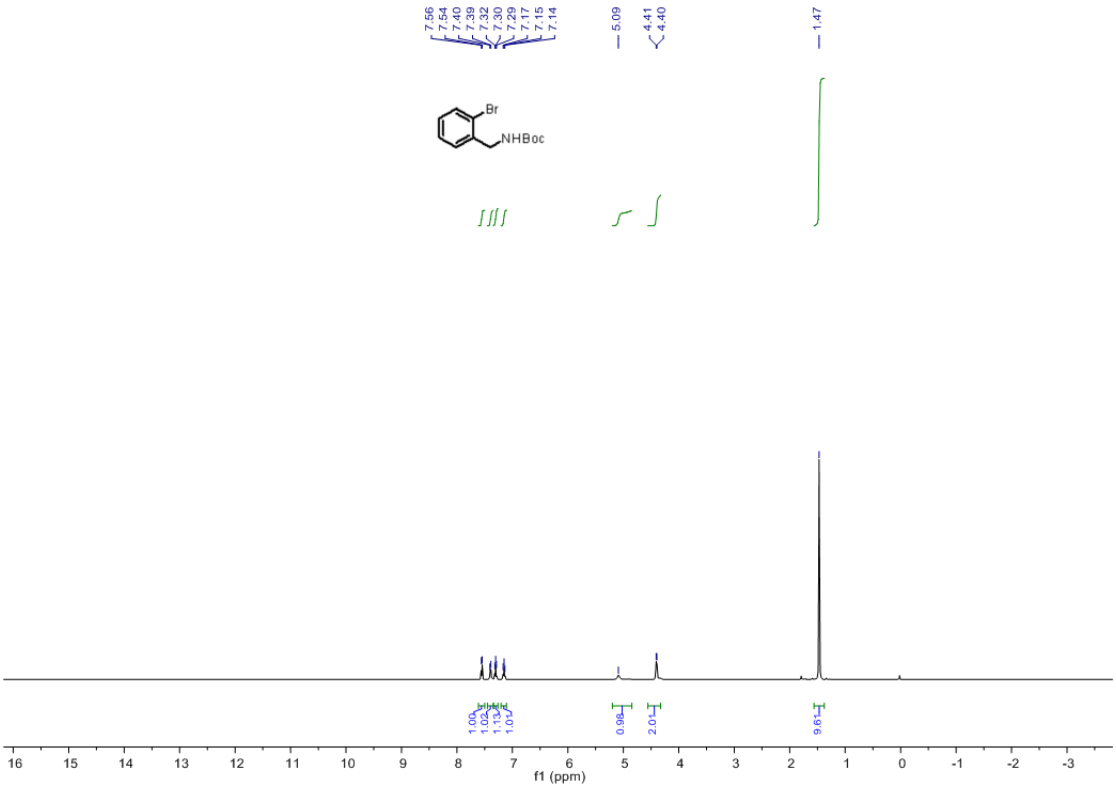
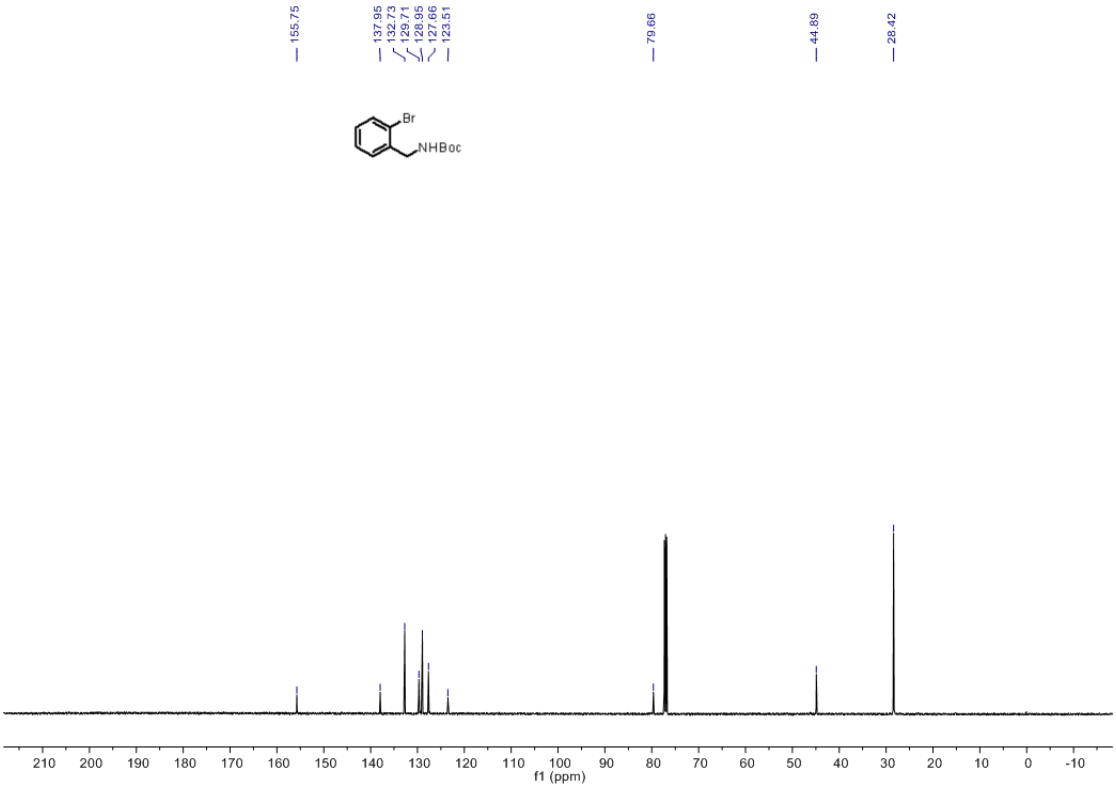
7. NMR Spectra

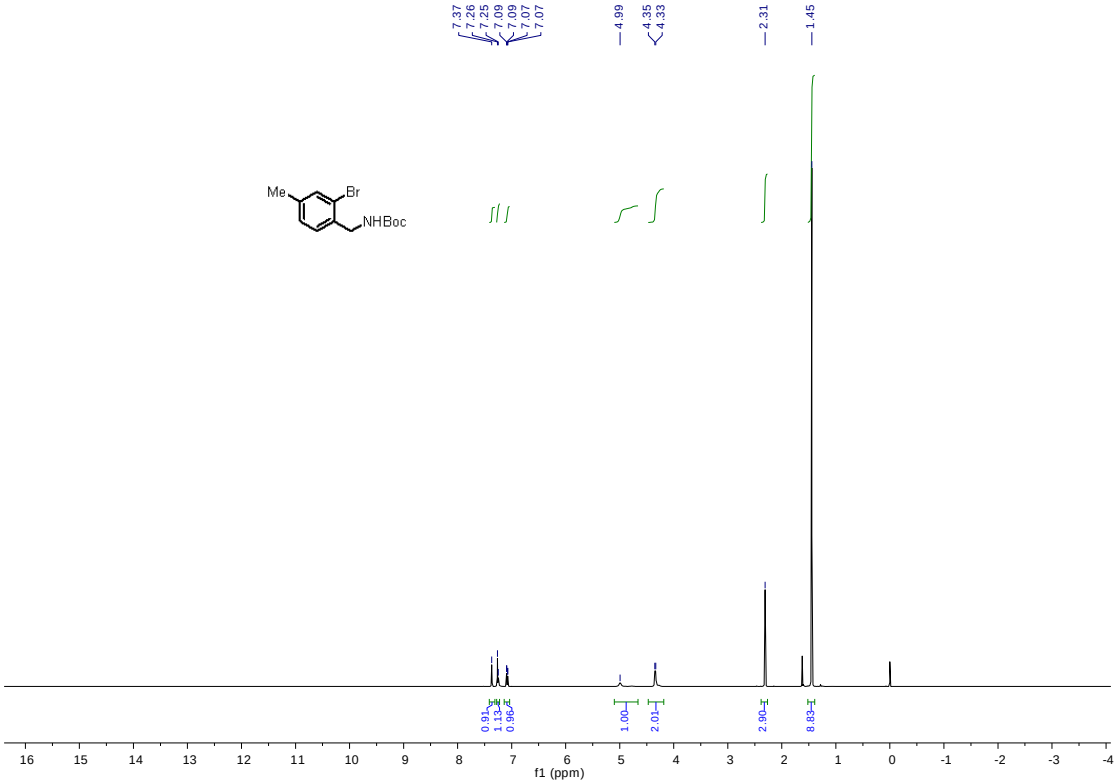
^{1}H NMR for **S-2a** (500 MHz, $CDCl_3$)



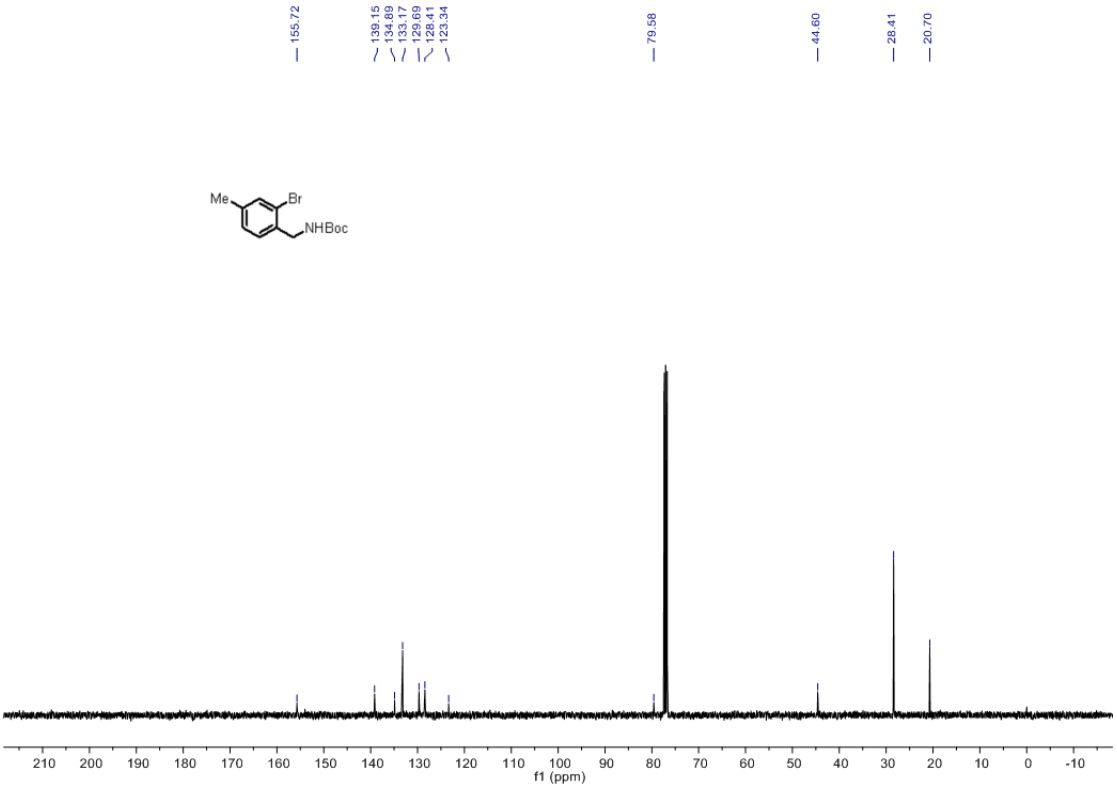
^{13}C NMR for **S-2a** (126 MHz, $CDCl_3$)



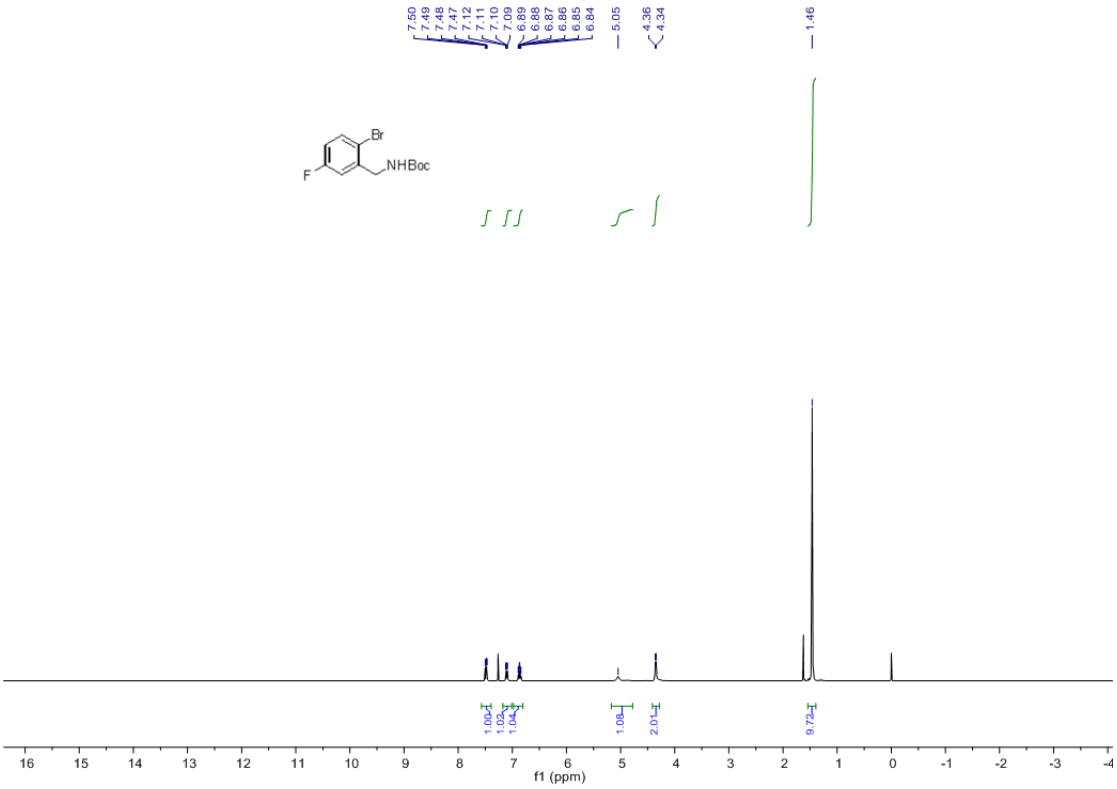
^{1}H NMR for **S-2b** (400 MHz, $CDCl_3$)



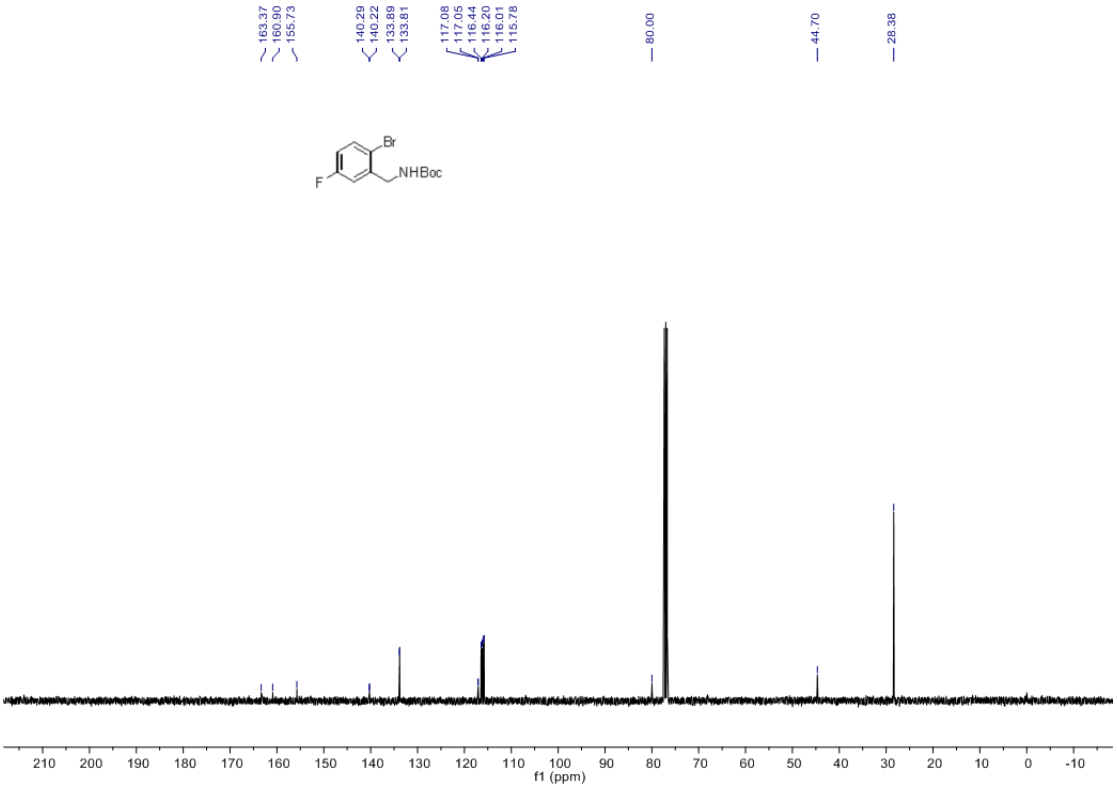
^{13}C NMR for **S-2b** (101 MHz, $CDCl_3$)



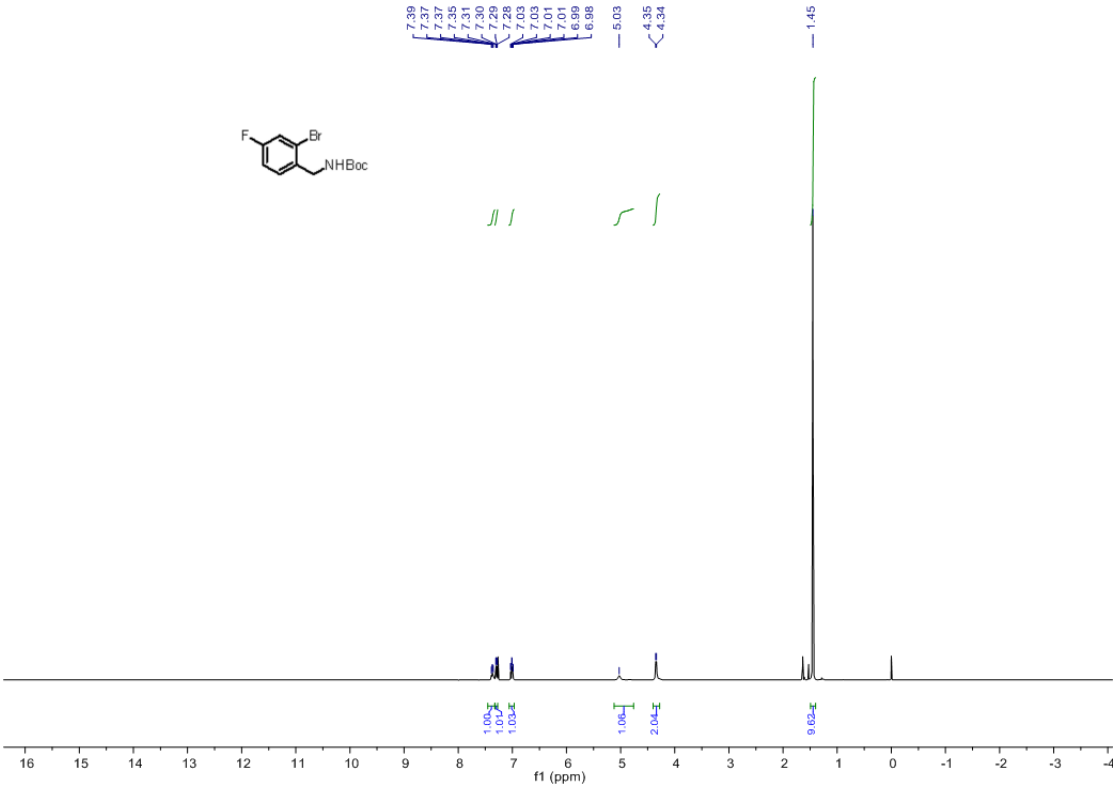
^{1}H NMR for **S-2c** (400 MHz, $CDCl_3$)



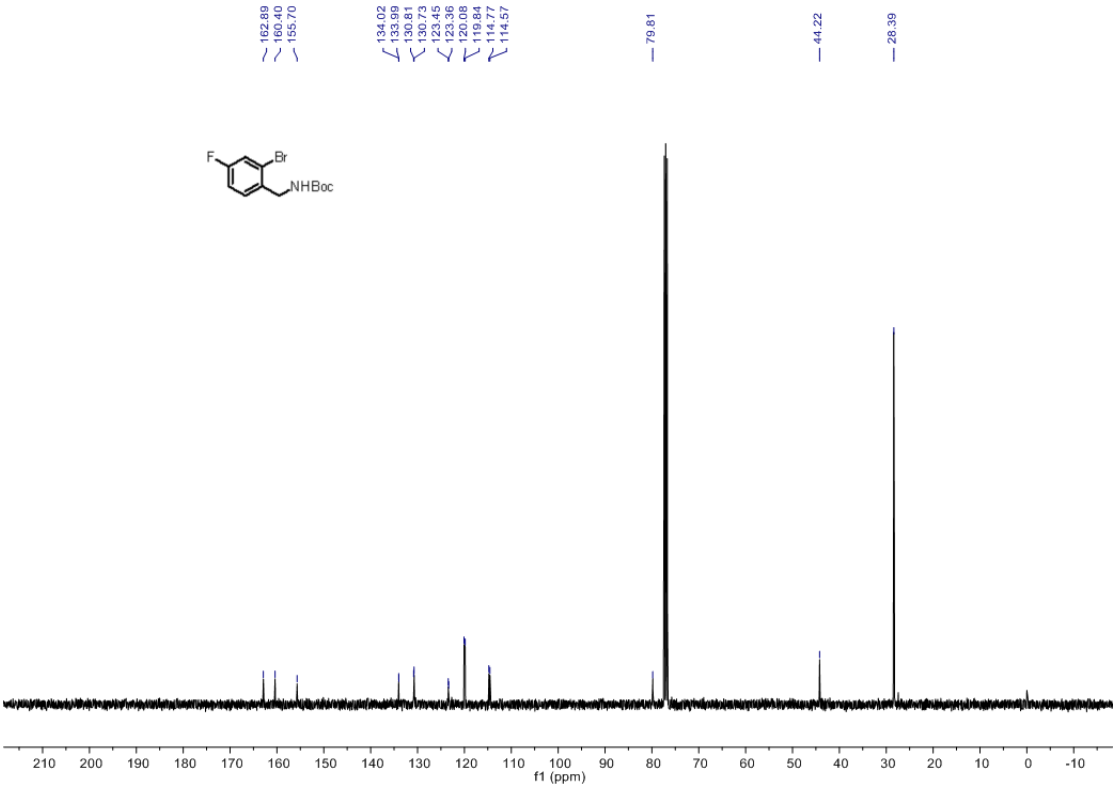
^{13}C NMR for **S-2c** (101 MHz, $CDCl_3$)



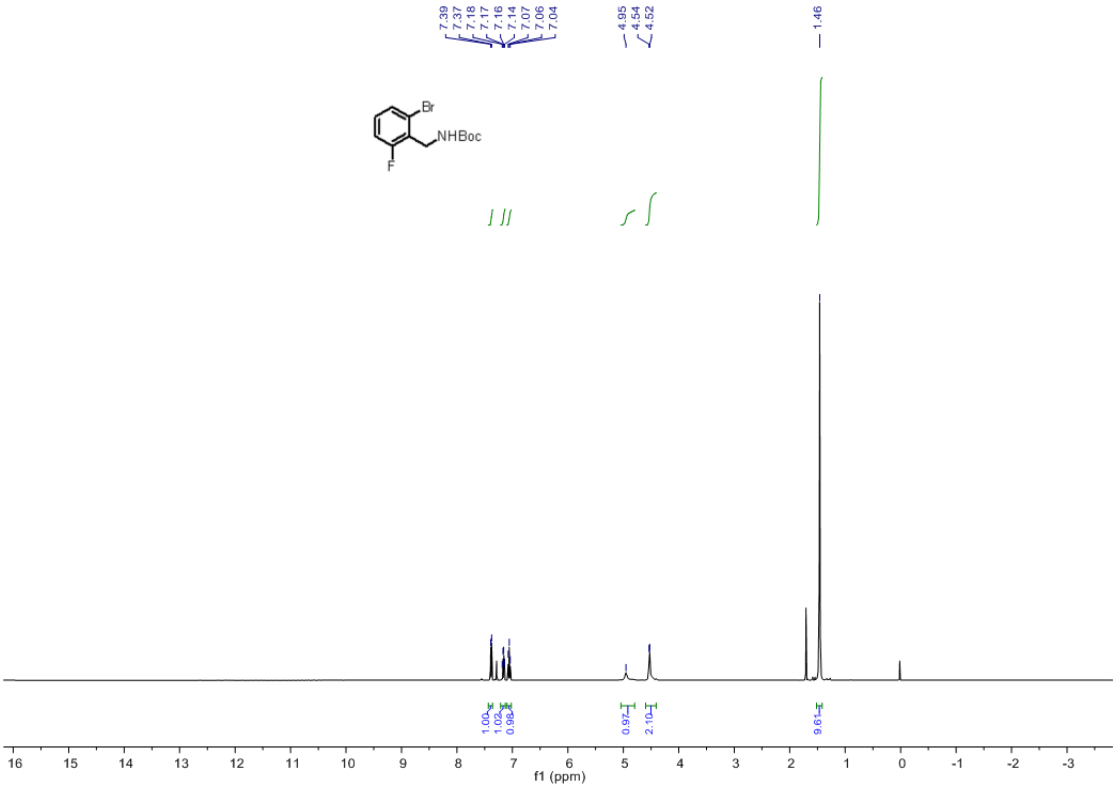
^{1}H NMR for **S-2d** (400 MHz, $CDCl_3$)



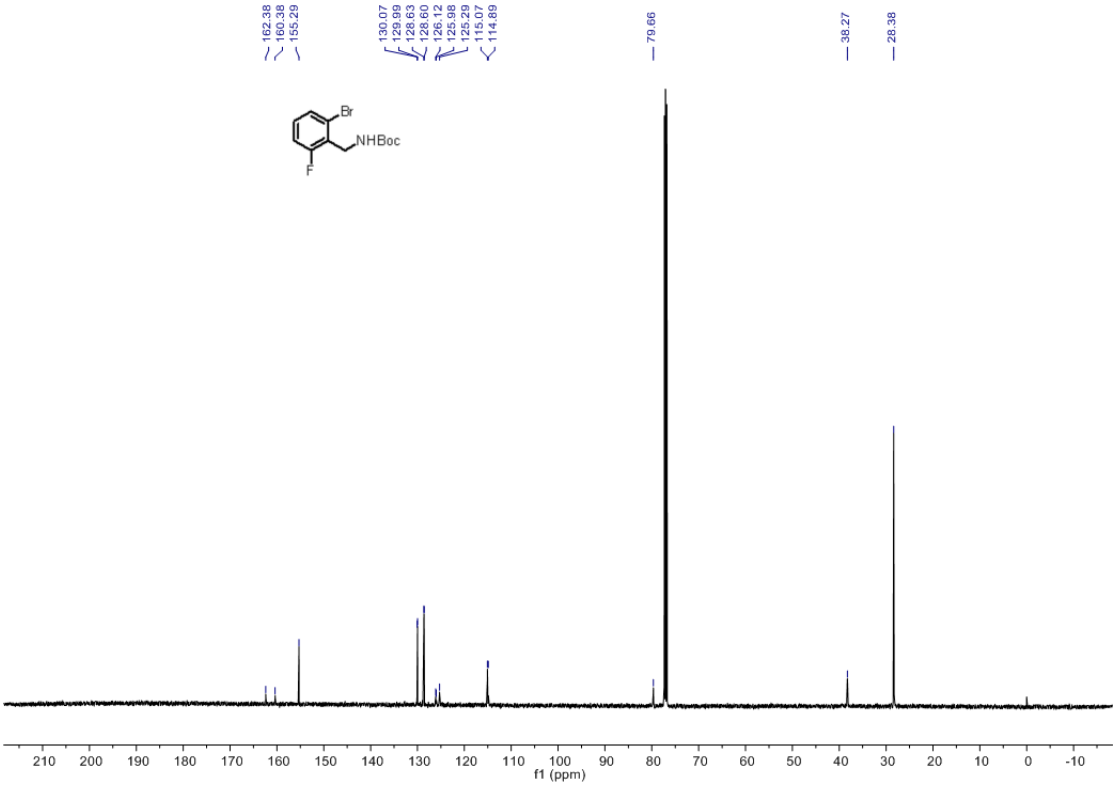
^{13}C NMR for **S-2d** (101 MHz, $CDCl_3$)



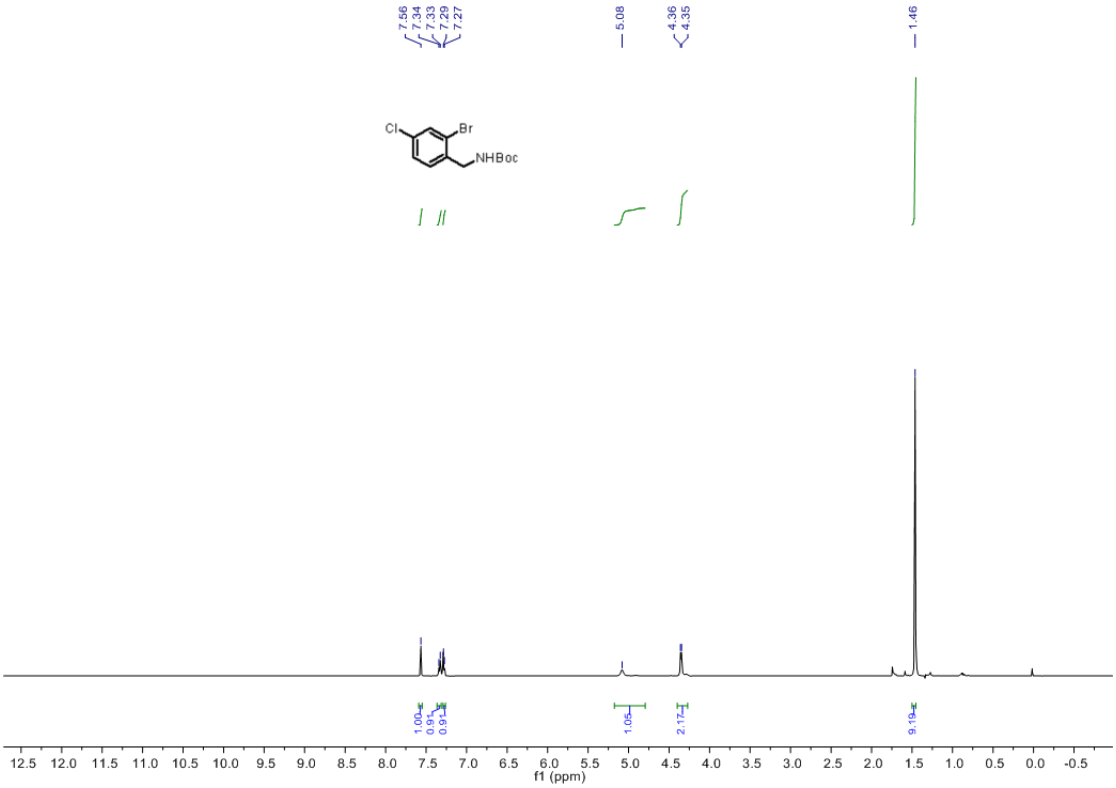
^{1}H NMR for **S-2e** (500 MHz, $CDCl_3$)



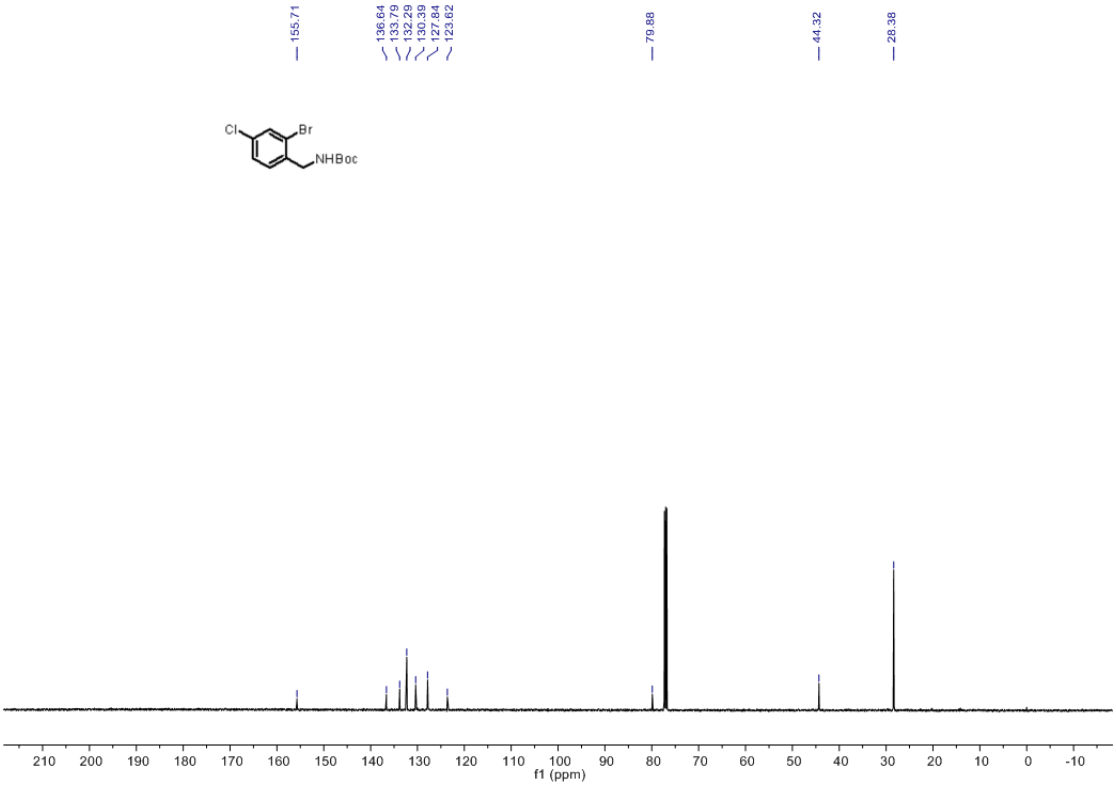
^{13}C NMR for **S-2e** (126 MHz, $CDCl_3$)



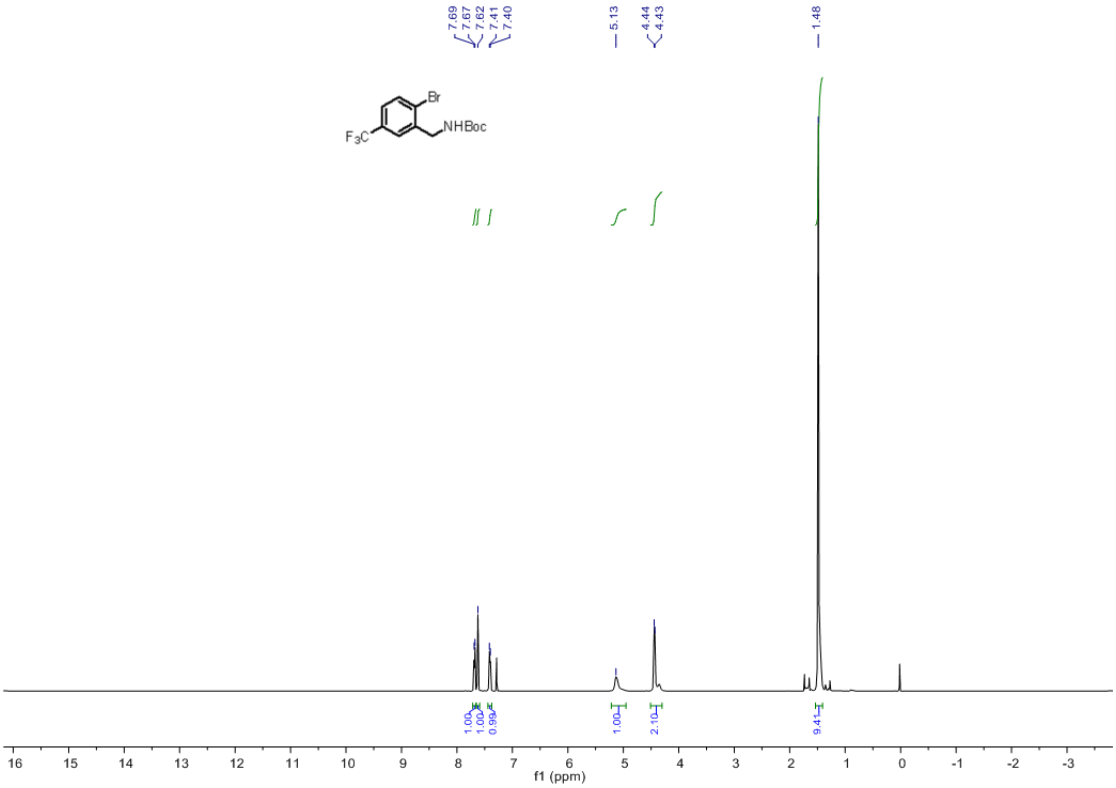
^{1}H NMR for **S-2f** (500 MHz, $CDCl_3$)



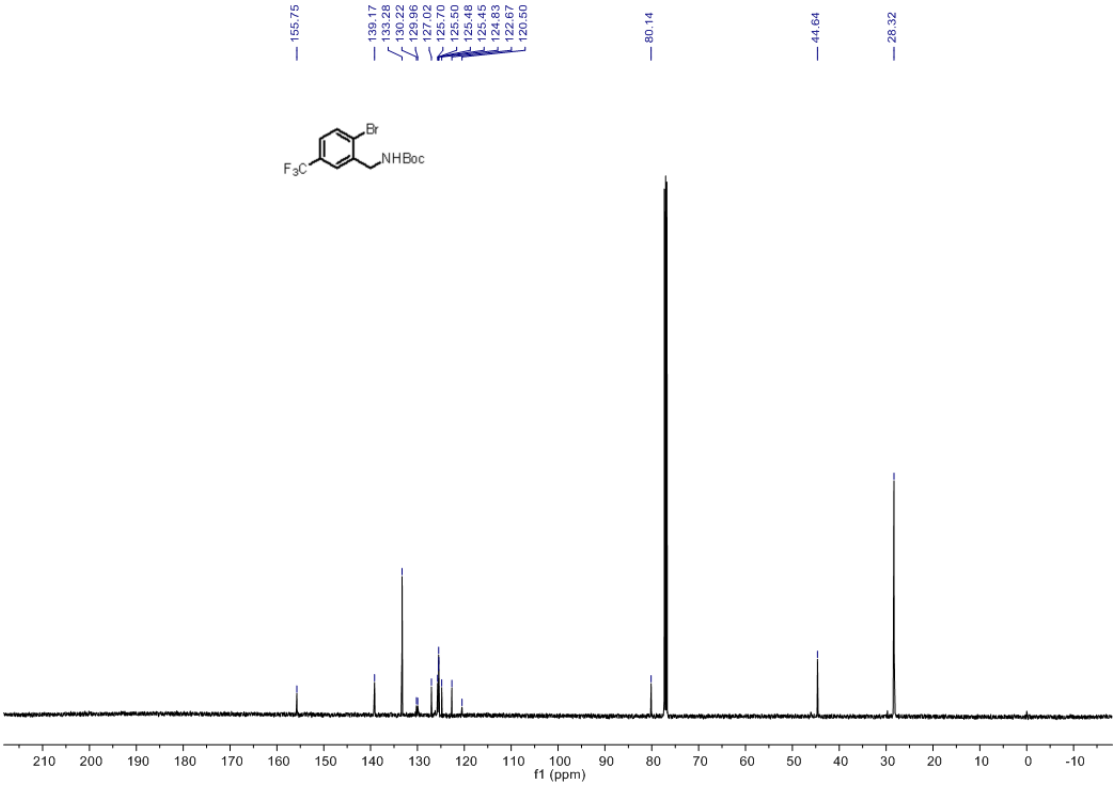
^{13}C NMR for **S-2f** (126 MHz, $CDCl_3$)



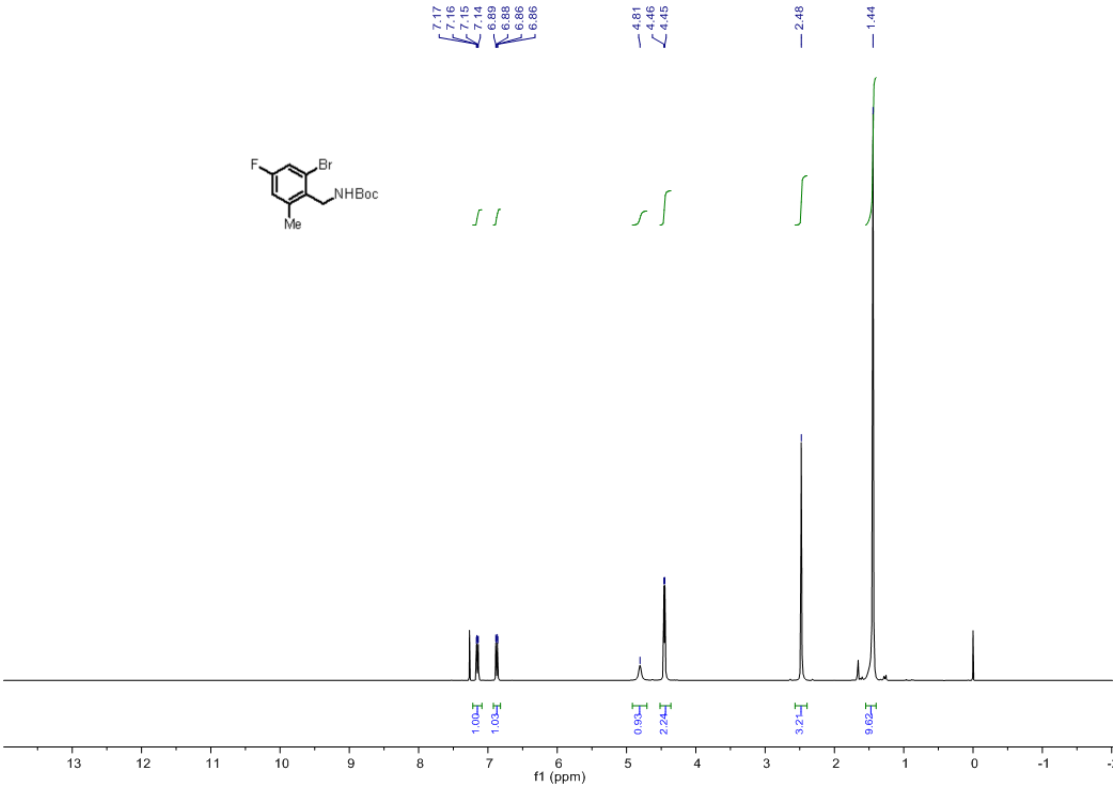
^{1}H NMR for **S-2g** (500 MHz, $CDCl_3$)



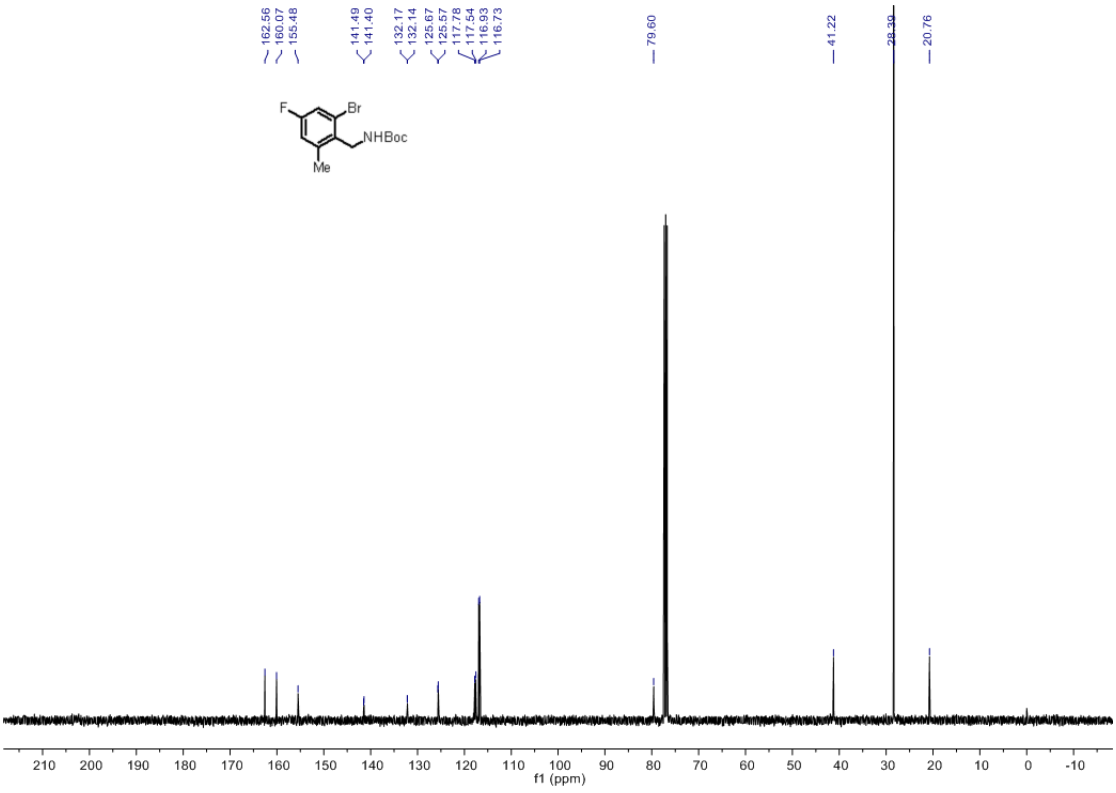
^{13}C NMR for **S-2g** (126 MHz, $CDCl_3$)



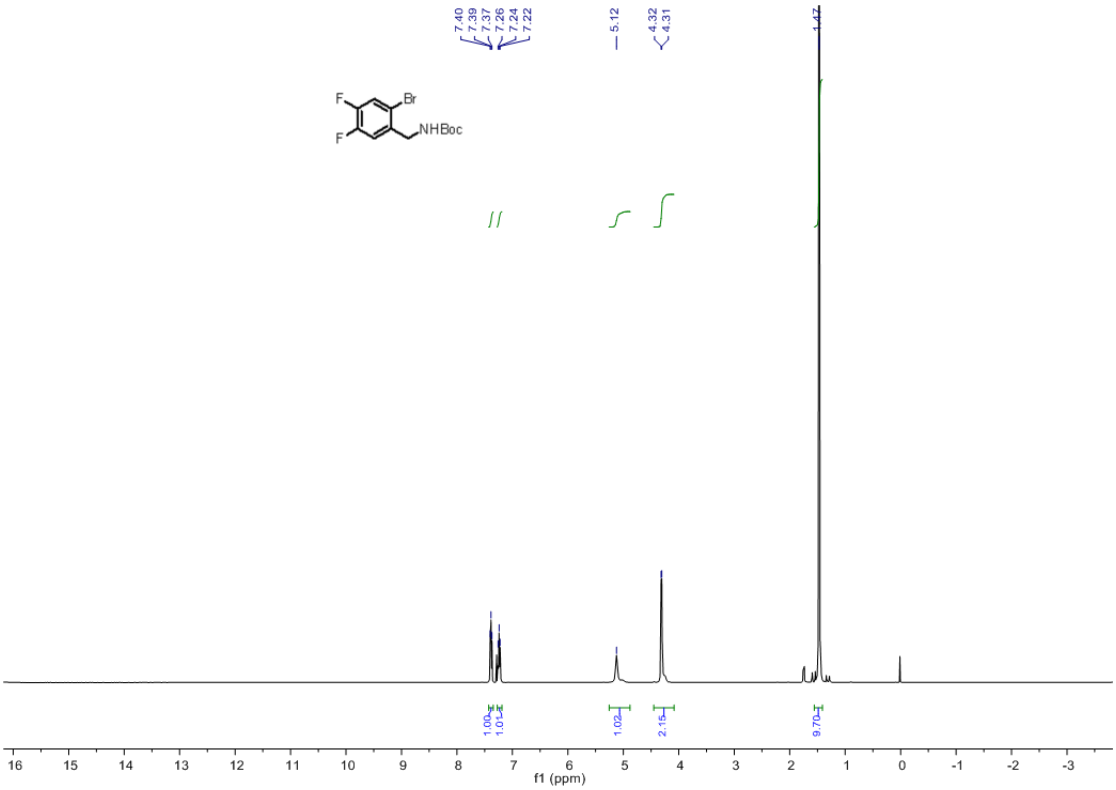
^{1}H NMR for **S-2h** (400 MHz, $CDCl_3$)



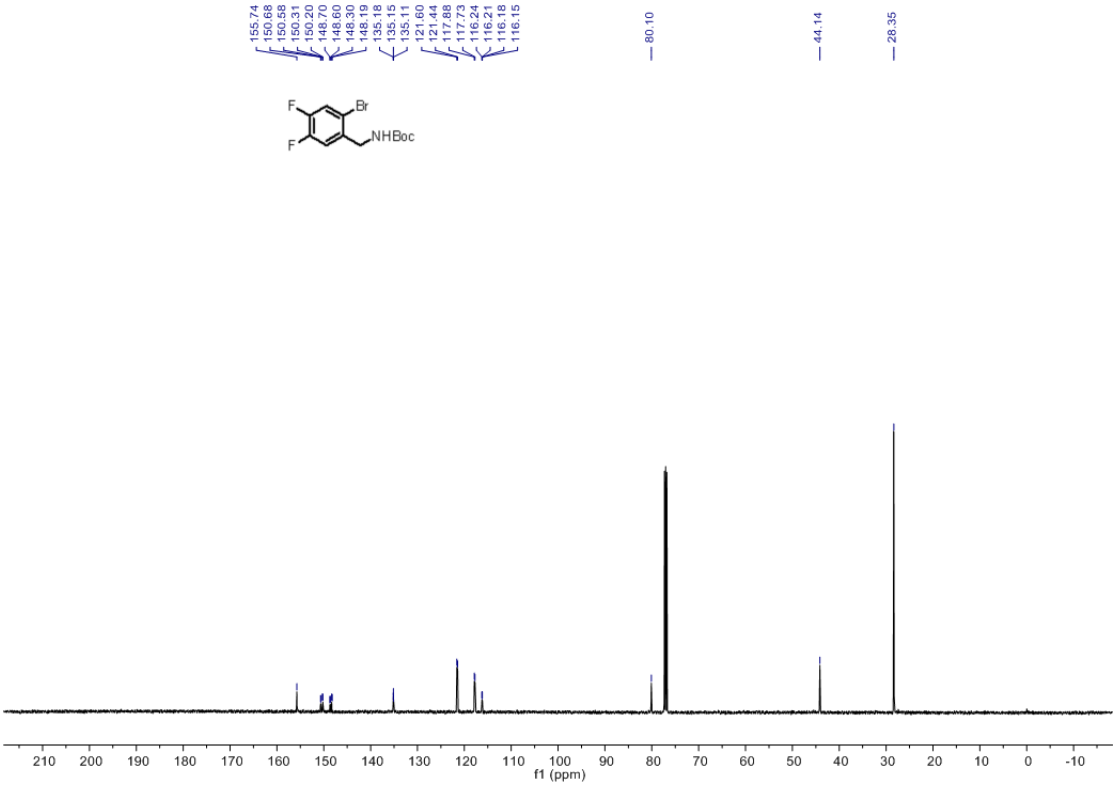
^{13}C NMR for **S-2h** (101 MHz, $CDCl_3$)



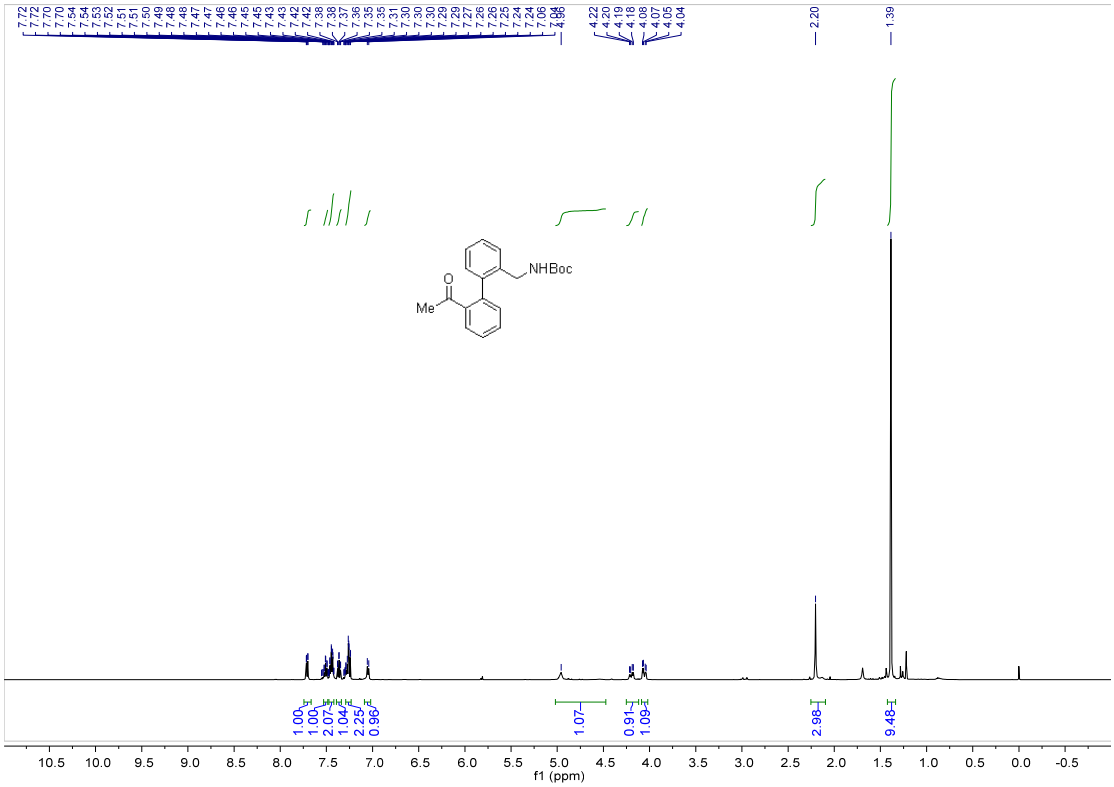
^{1}H NMR for **S-2i** (500 MHz, $CDCl_3$)



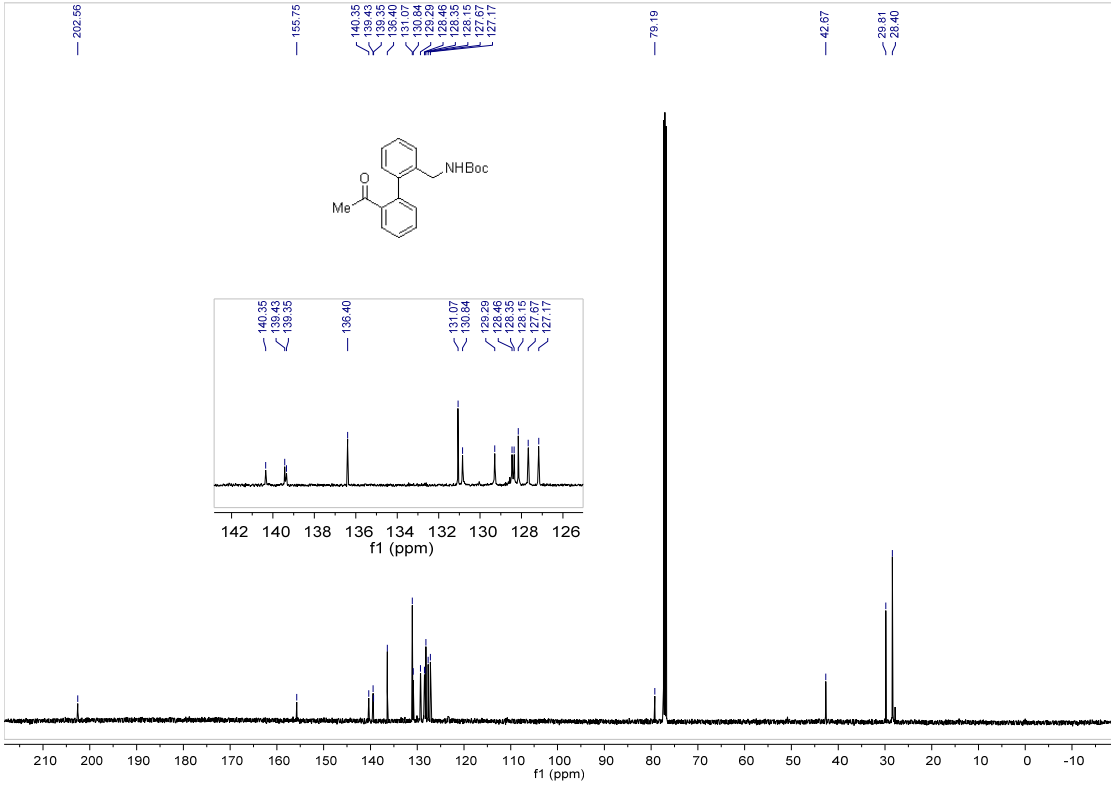
^{13}C NMR for **S-2i** (126 MHz, $CDCl_3$)



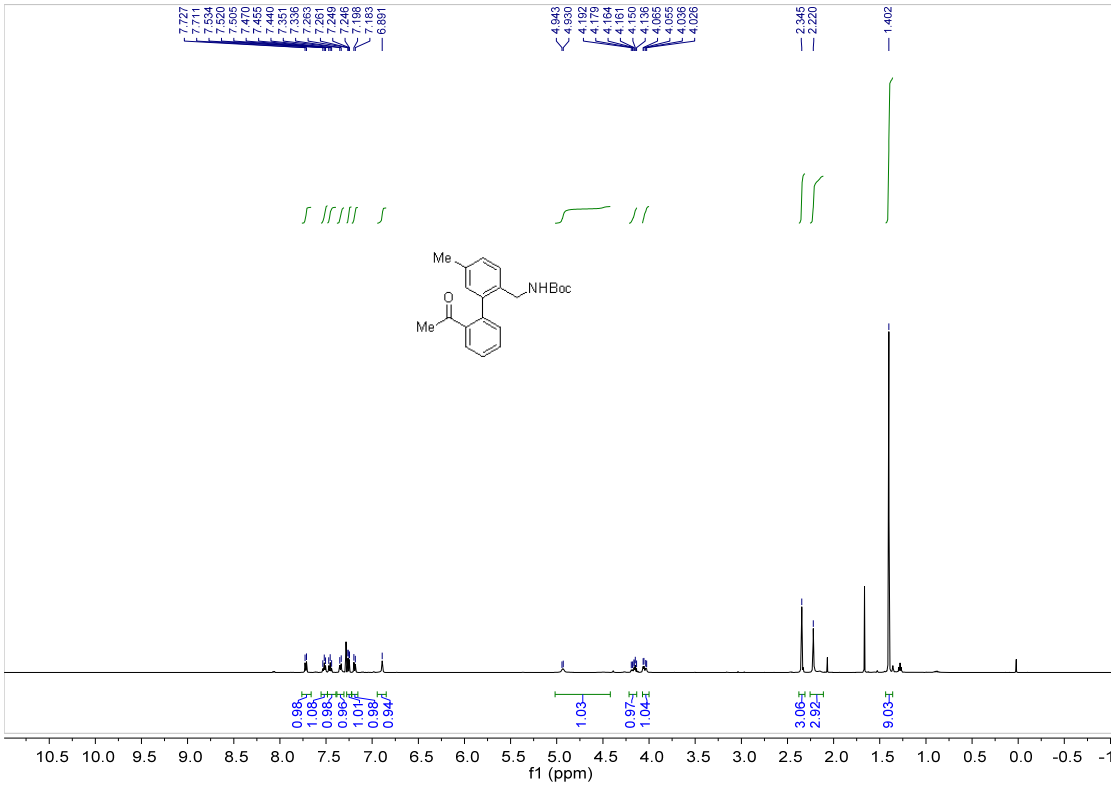
^{1}H NMR for **1a** (500 MHz, $CDCl_3$)



^{13}C NMR for **1a** (126 MHz, $CDCl_3$)



^{1}H NMR for **1b** (500 MHz, $CDCl_3$)



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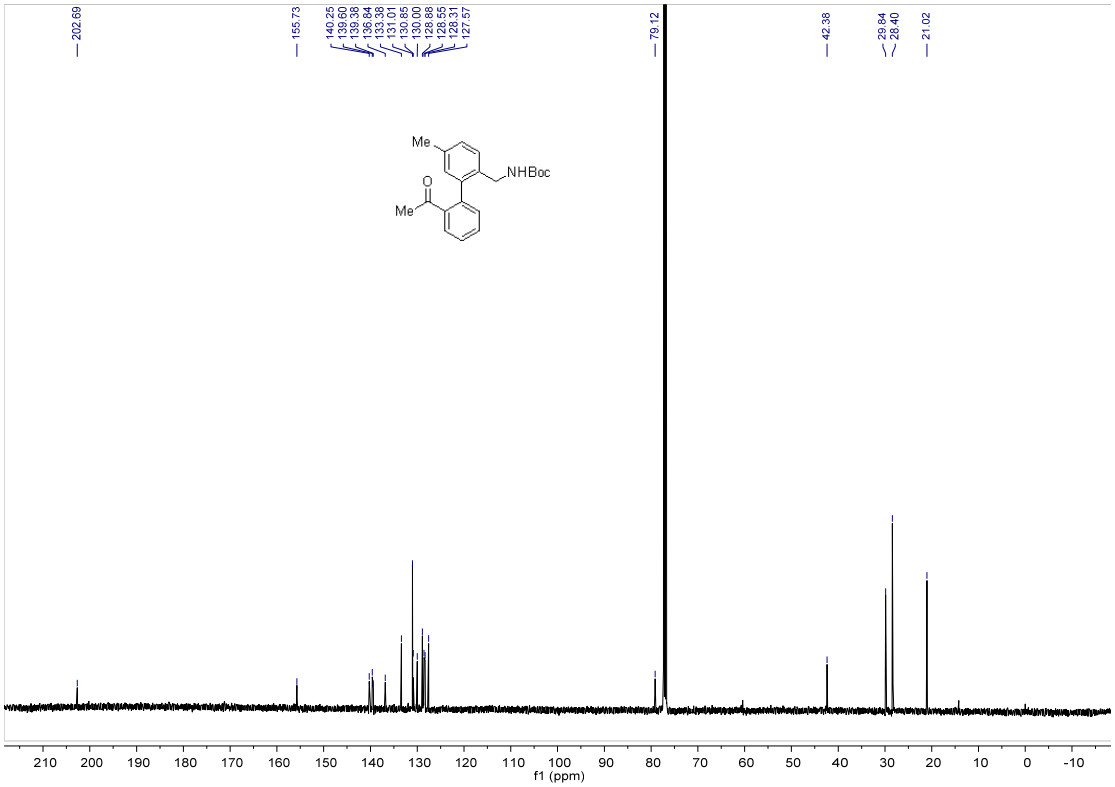

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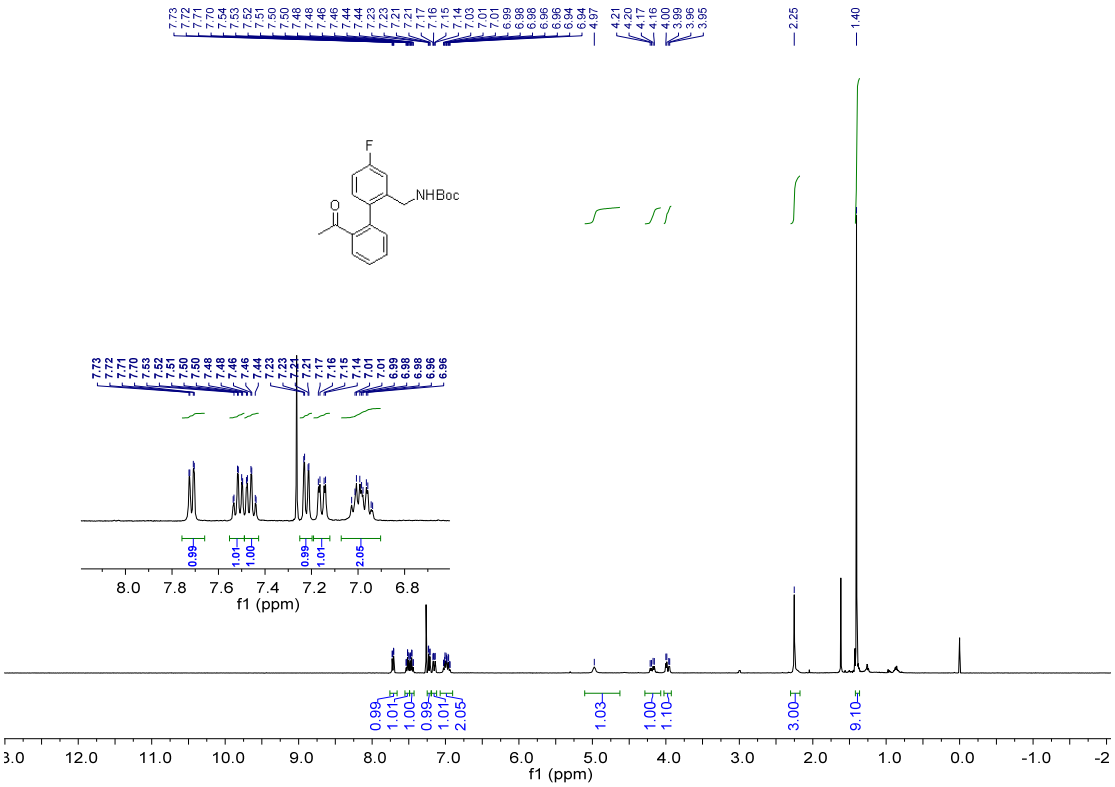

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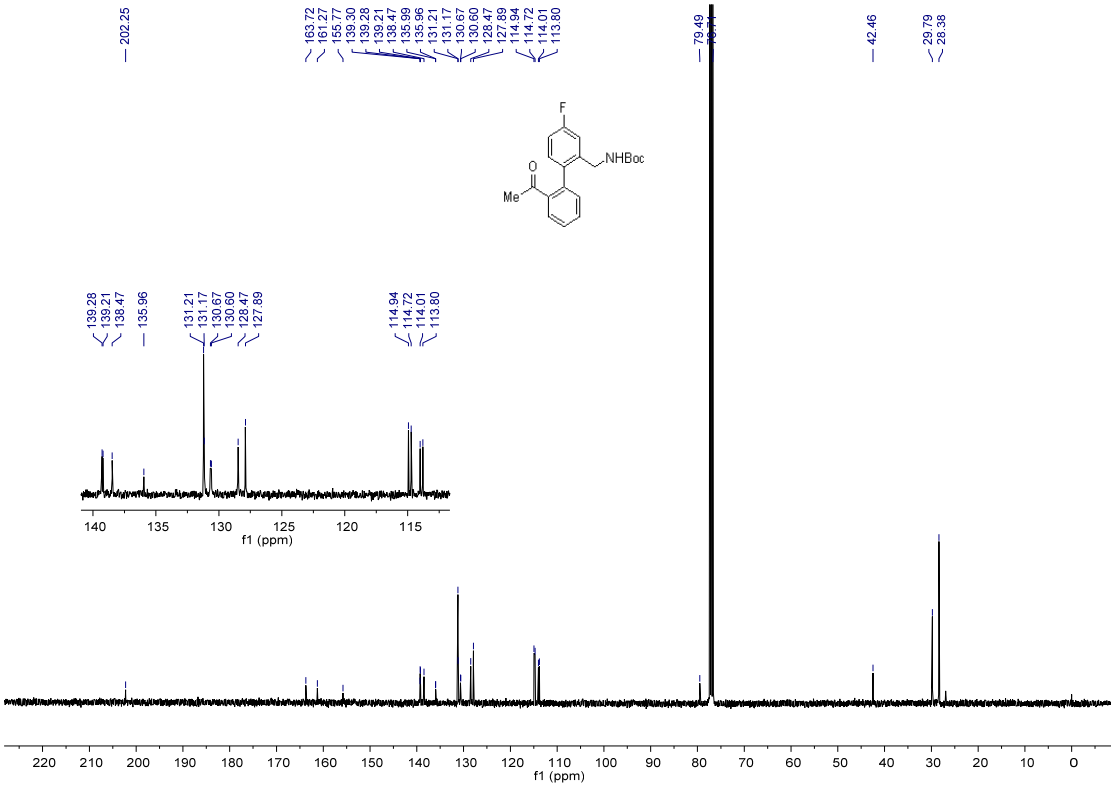

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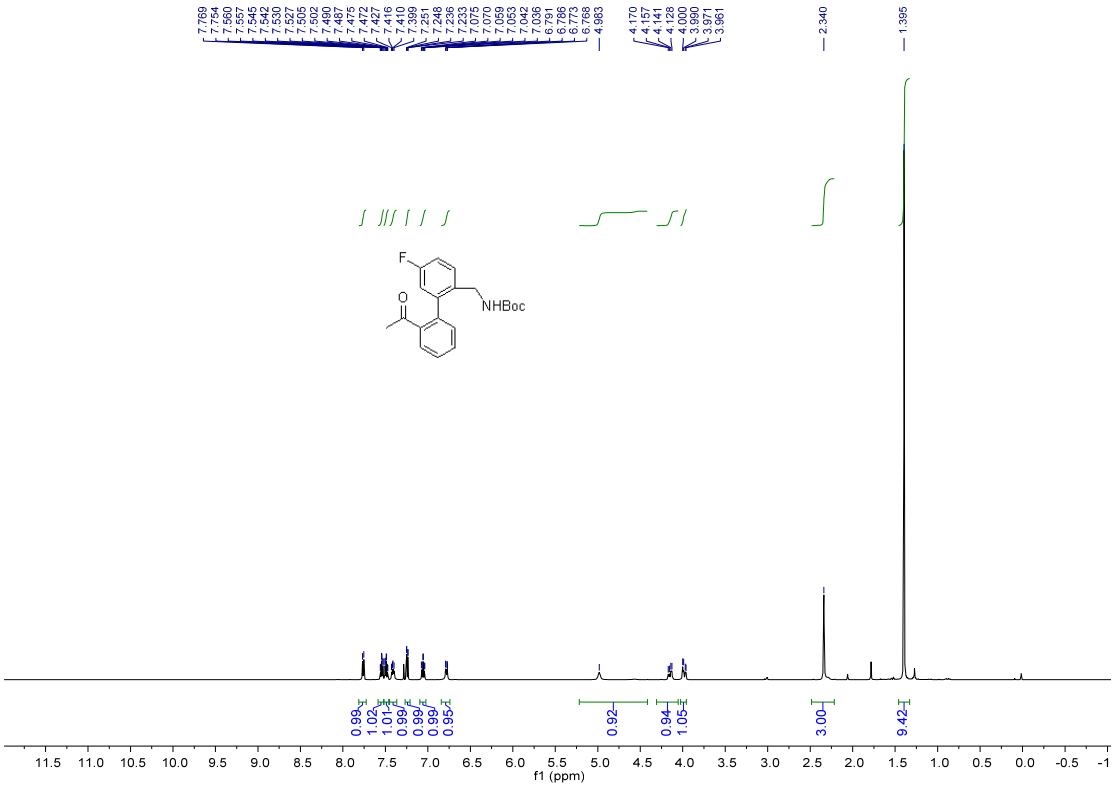

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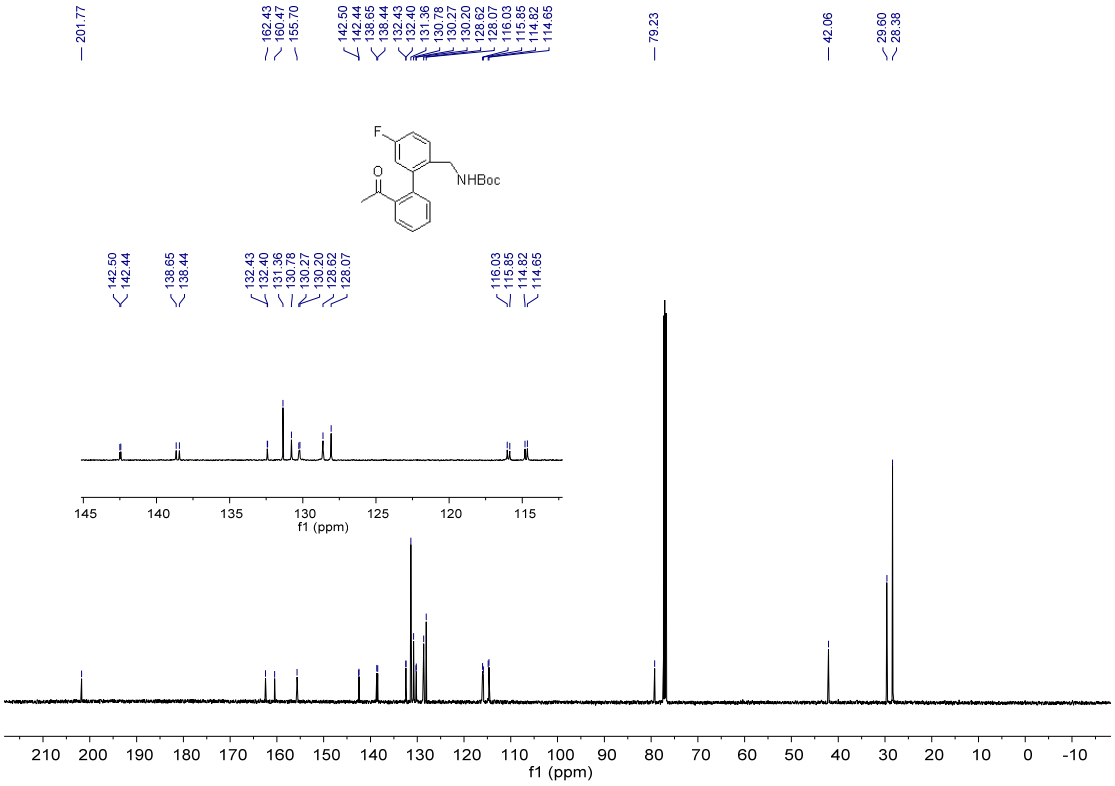

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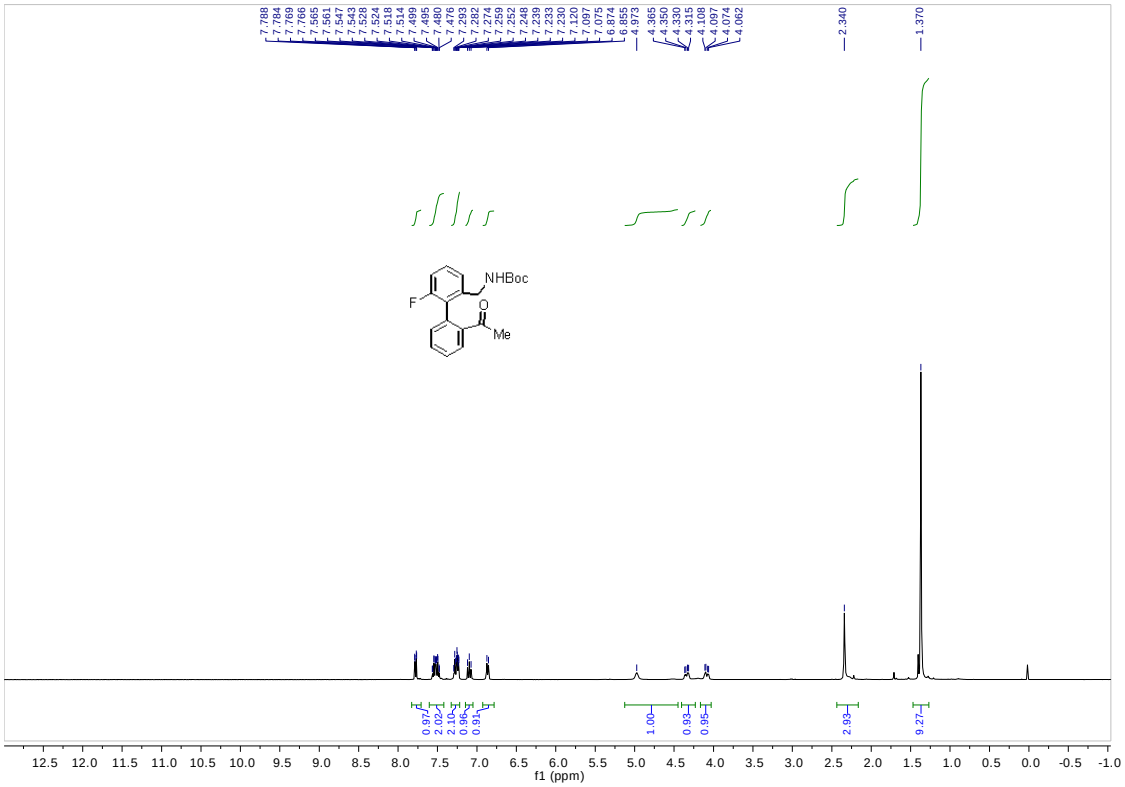
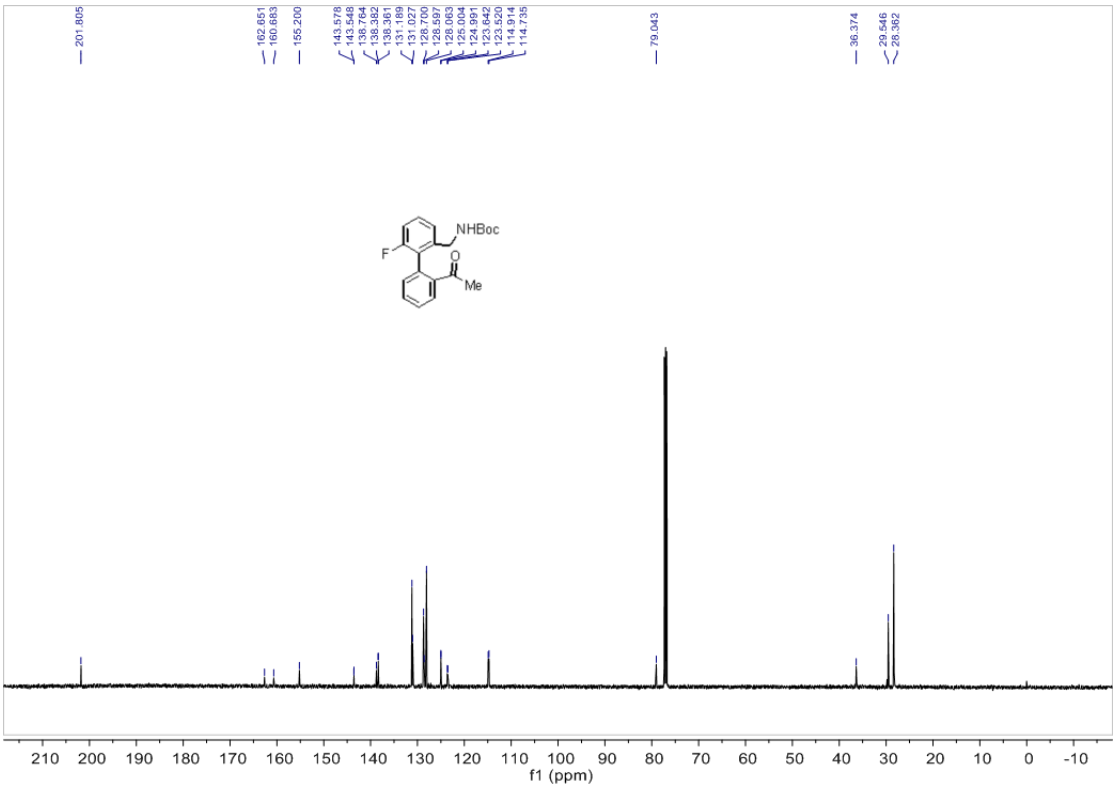
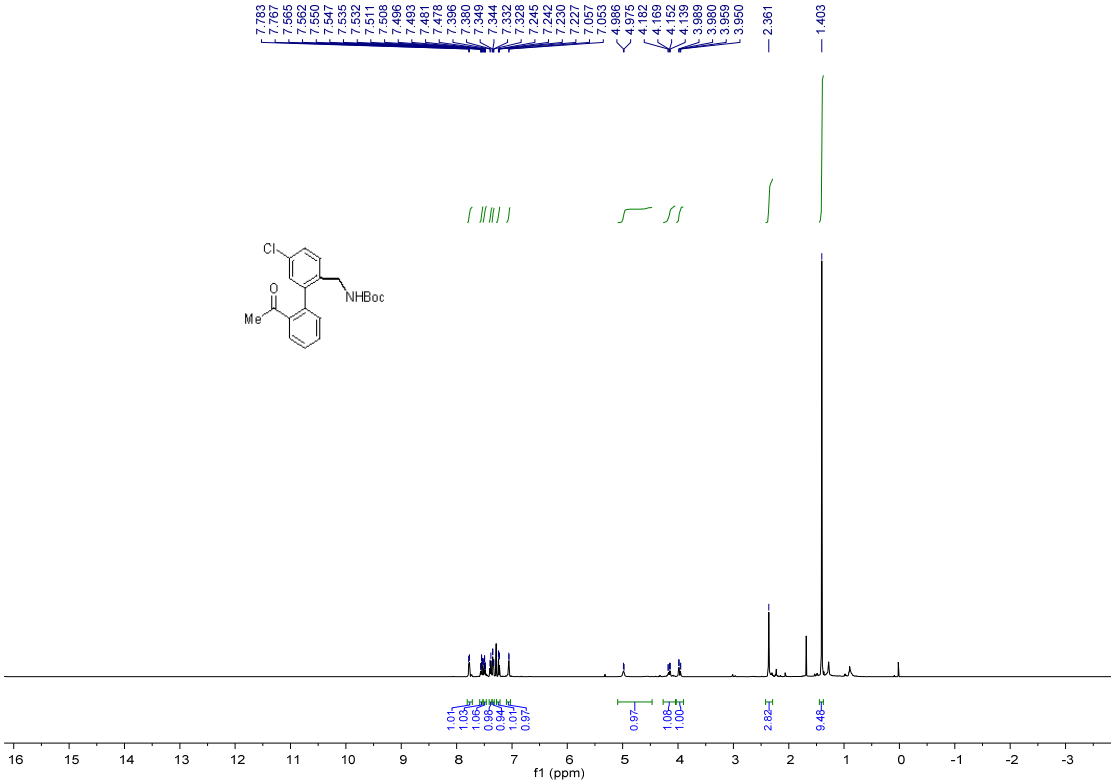


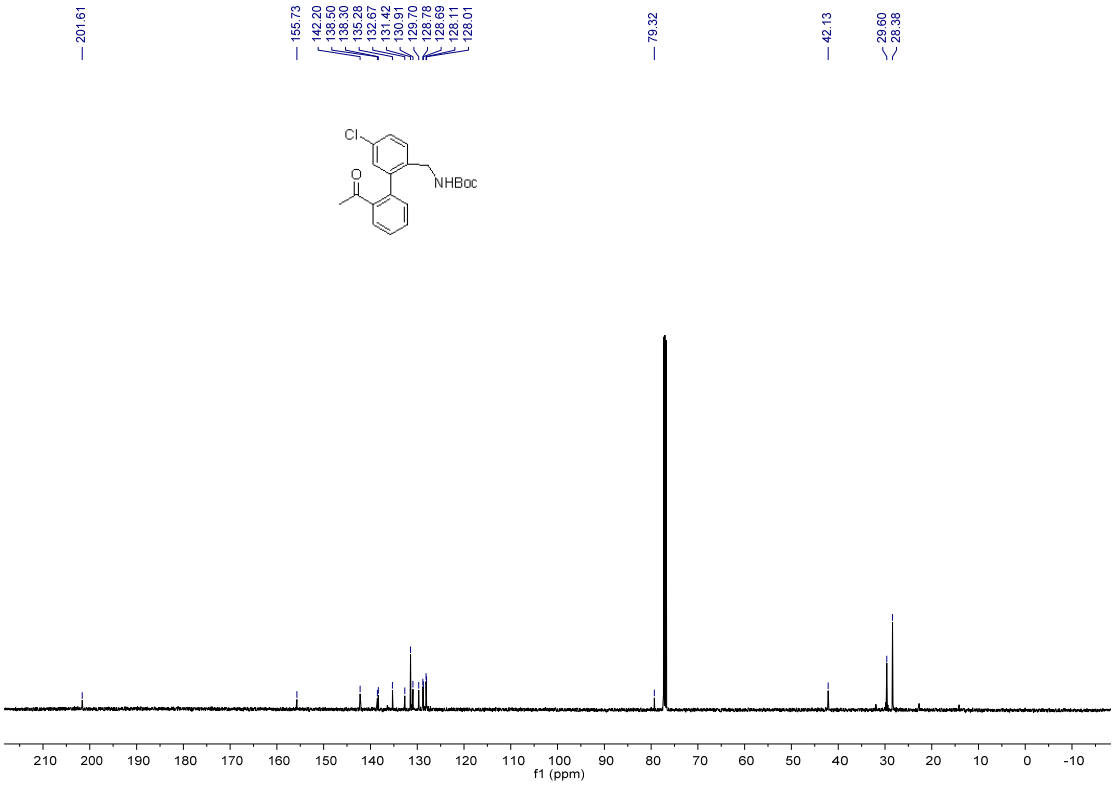
^{13}C NMR for **1e** (126 MHz, $CDCl_3$)



^{1}H NMR for **1f** (500 MHz, $CDCl_3$)



^{13}C NMR for **1f** (126 MHz, $CDCl_3$)



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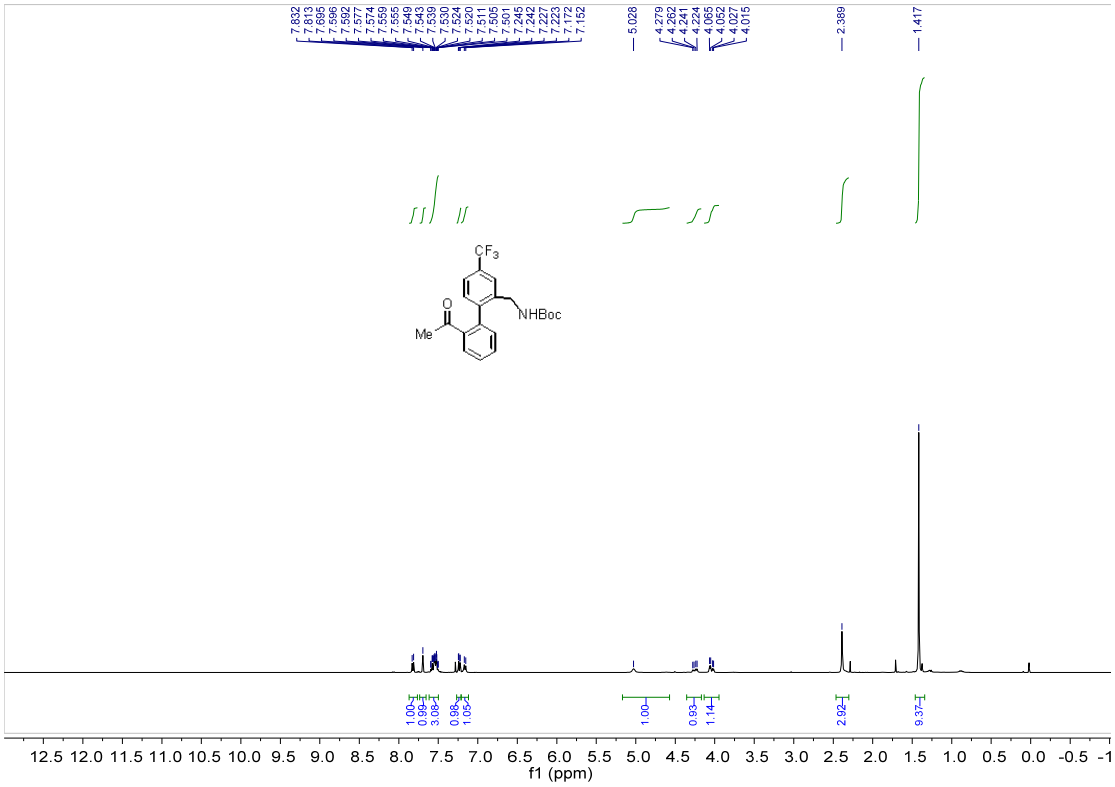
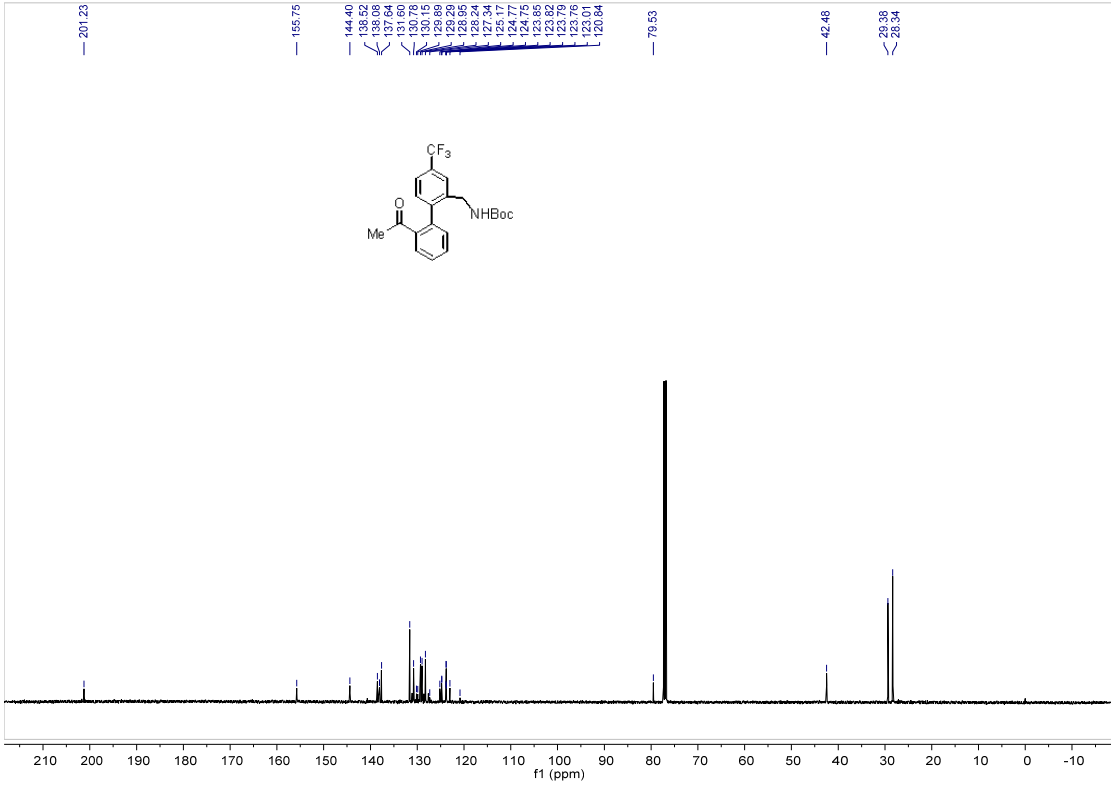


^{13}C NMR for **1g** (126 MHz, $CDCl_3$)



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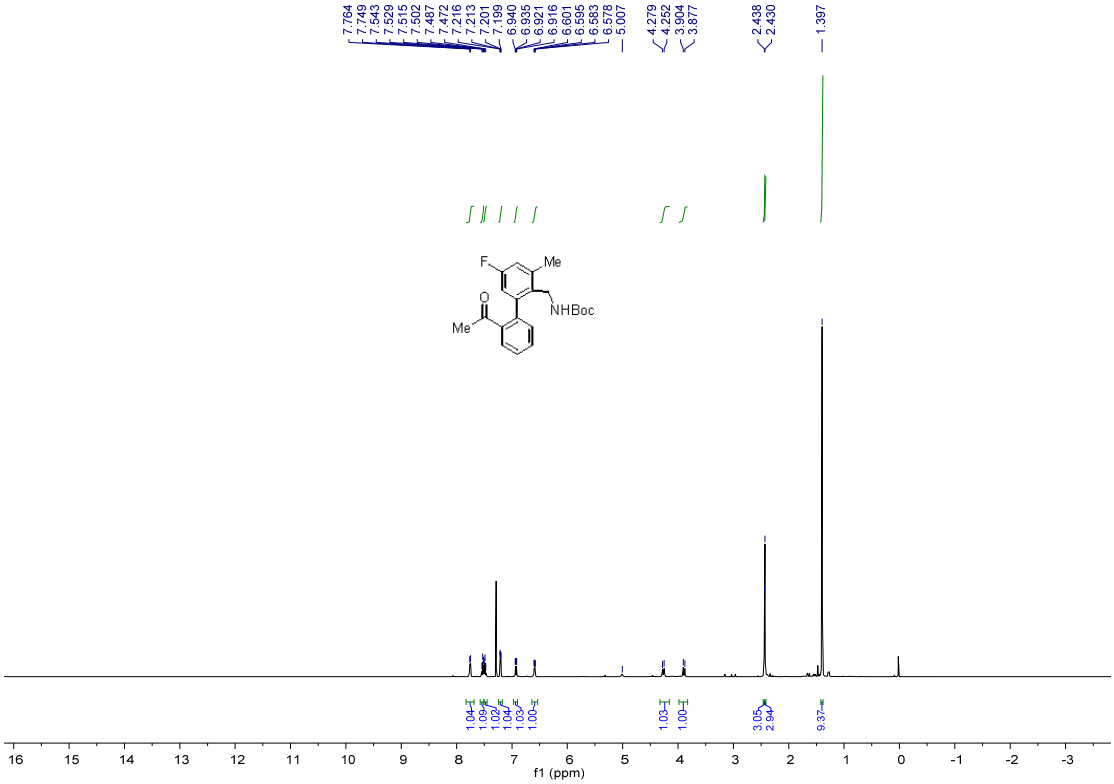

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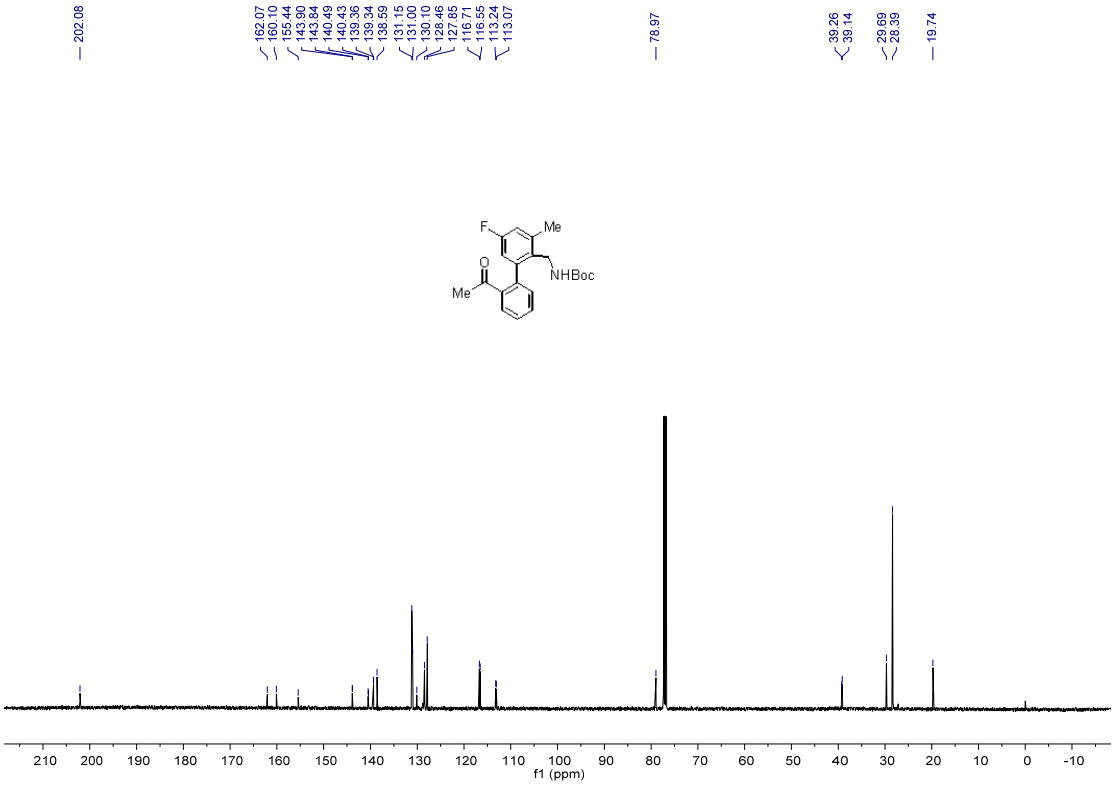

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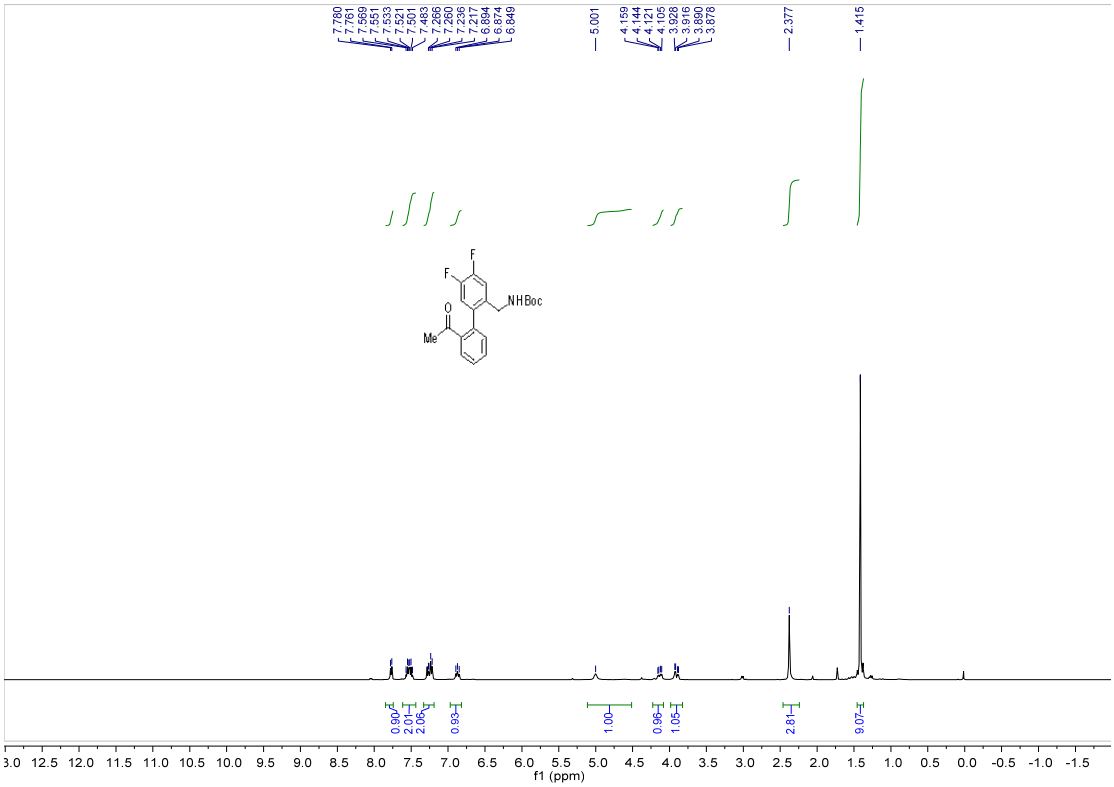

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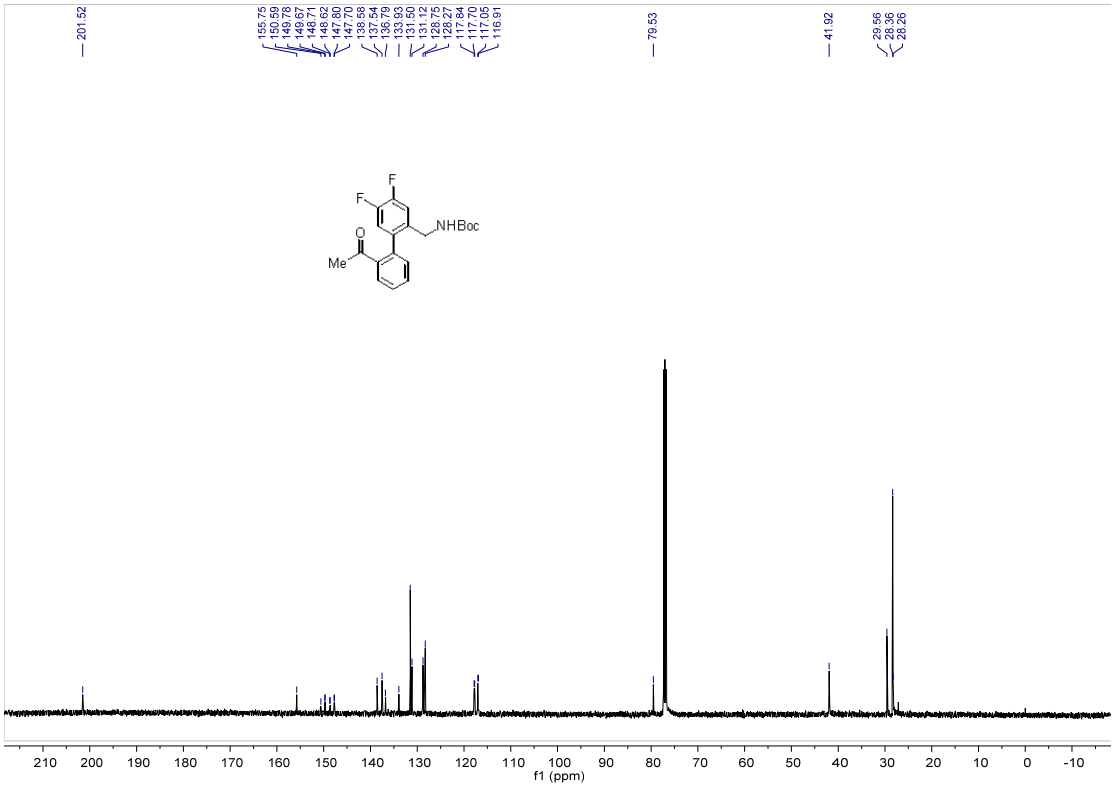

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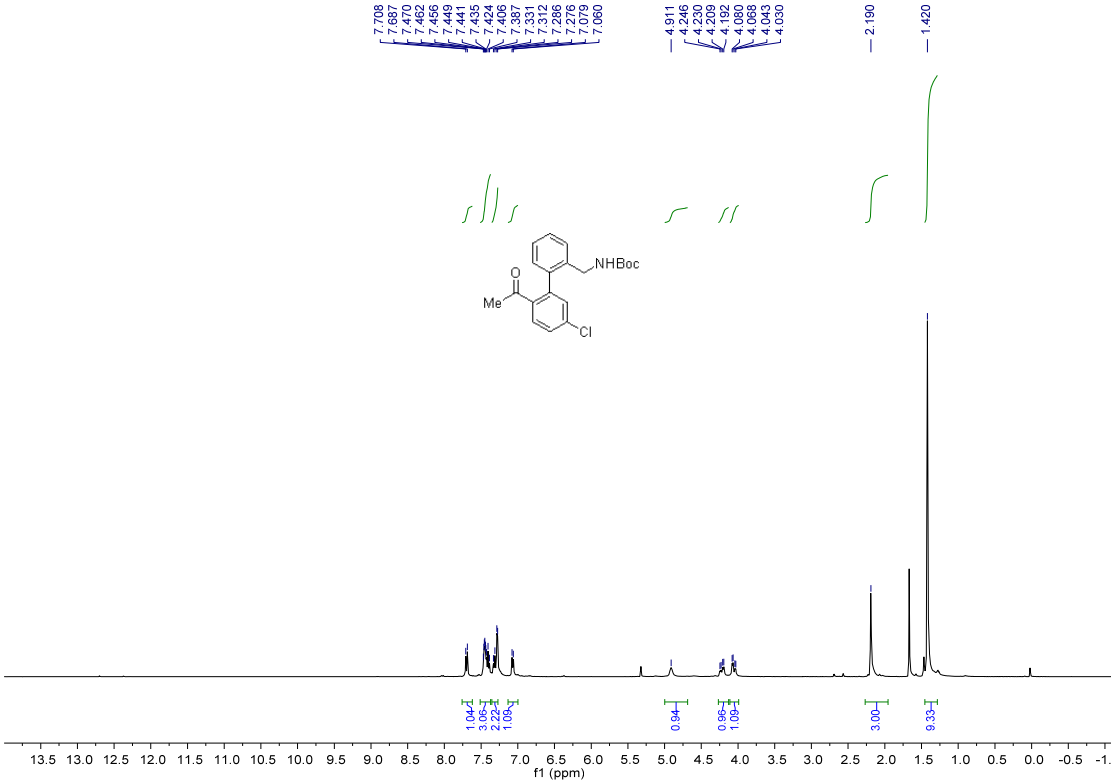

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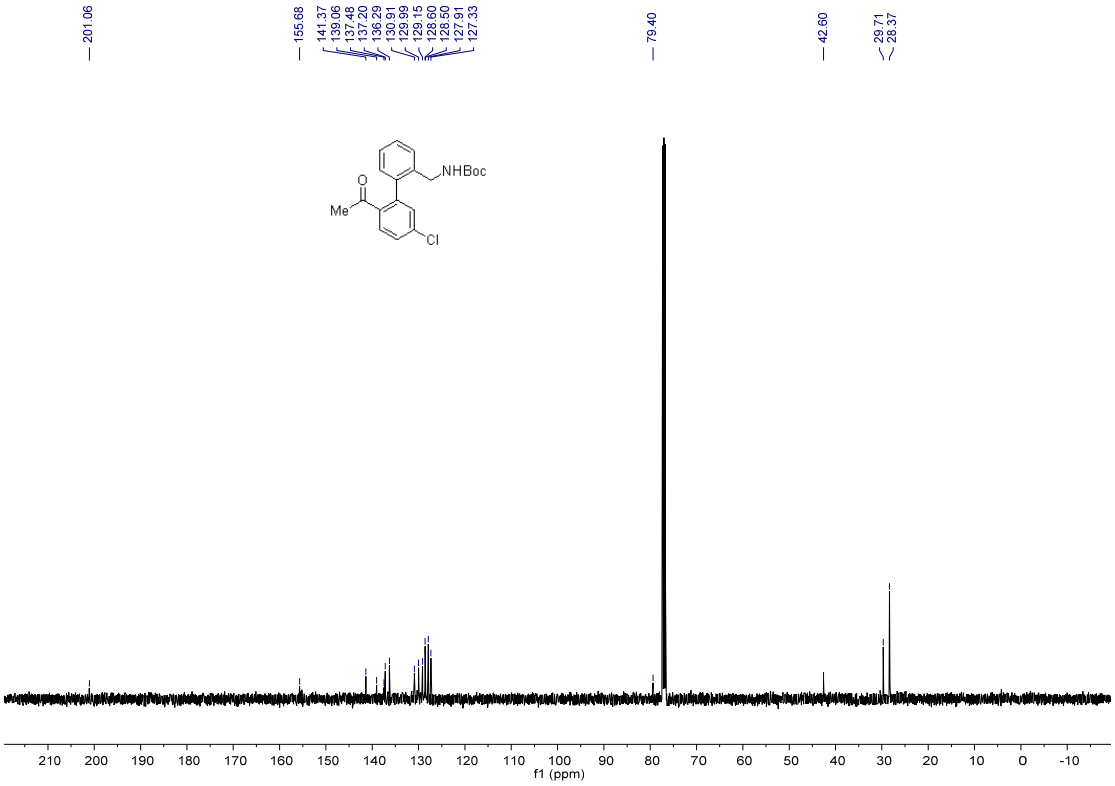

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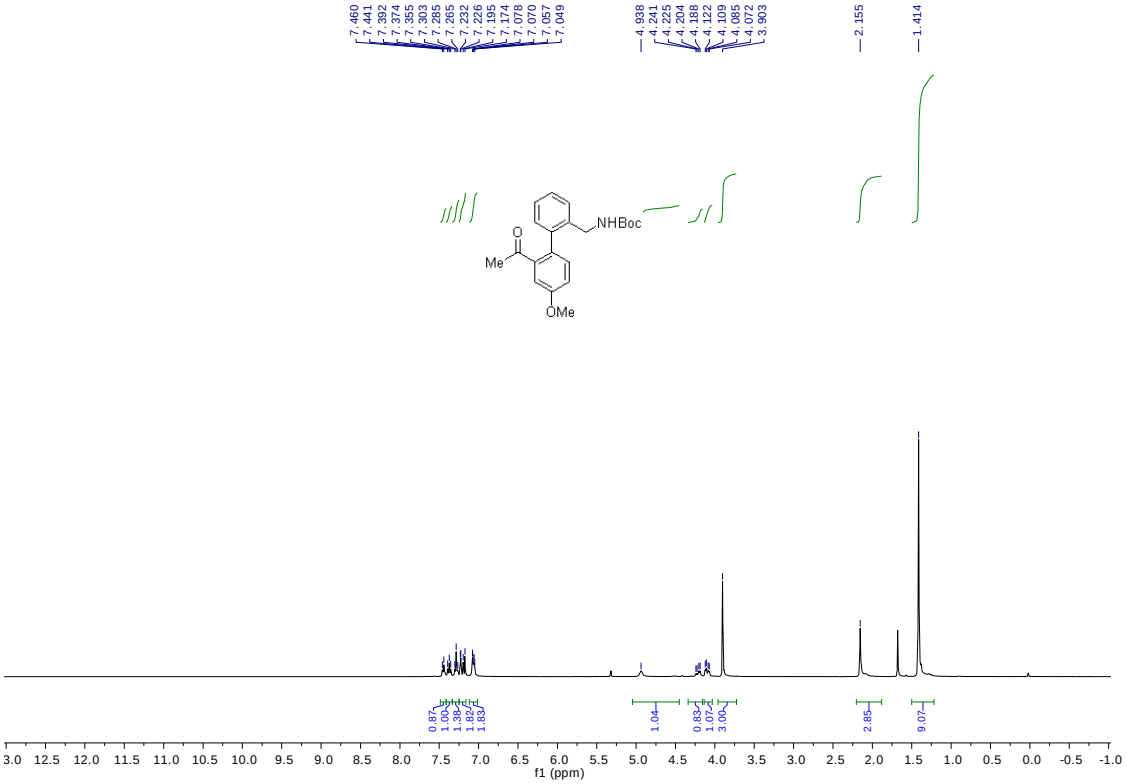
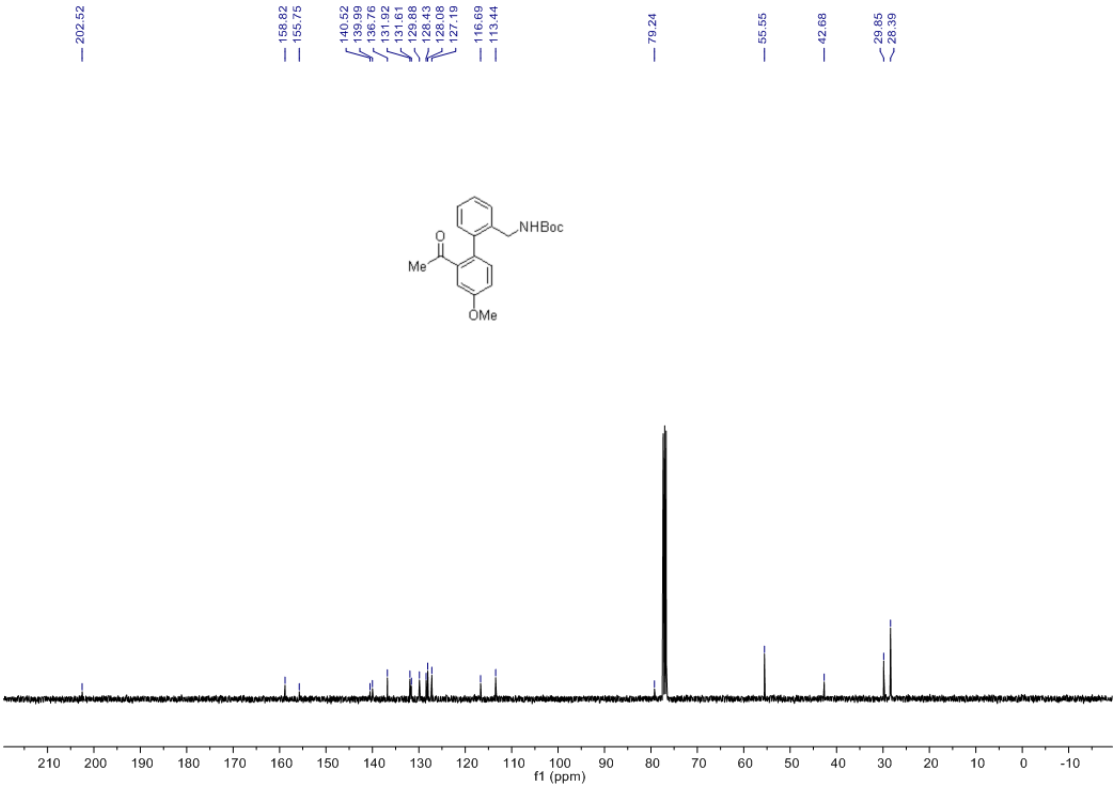


^{13}C NMR for **1k** (101 MHz, $CDCl_3$)



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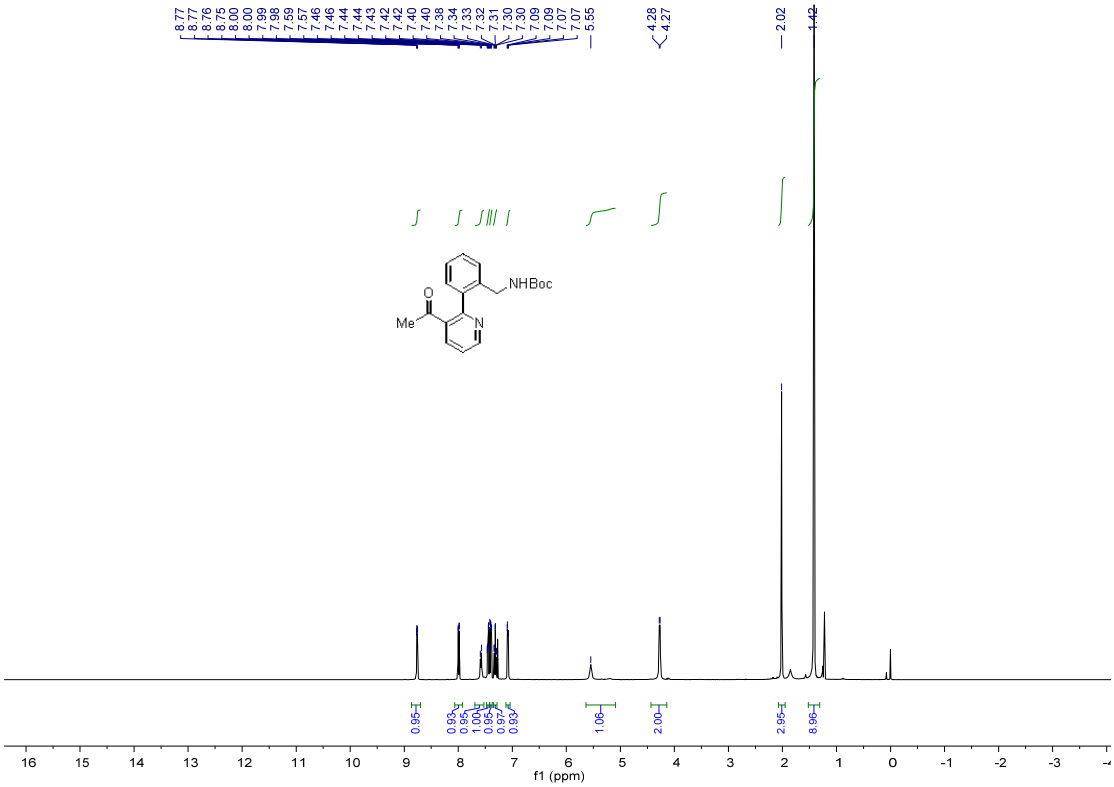

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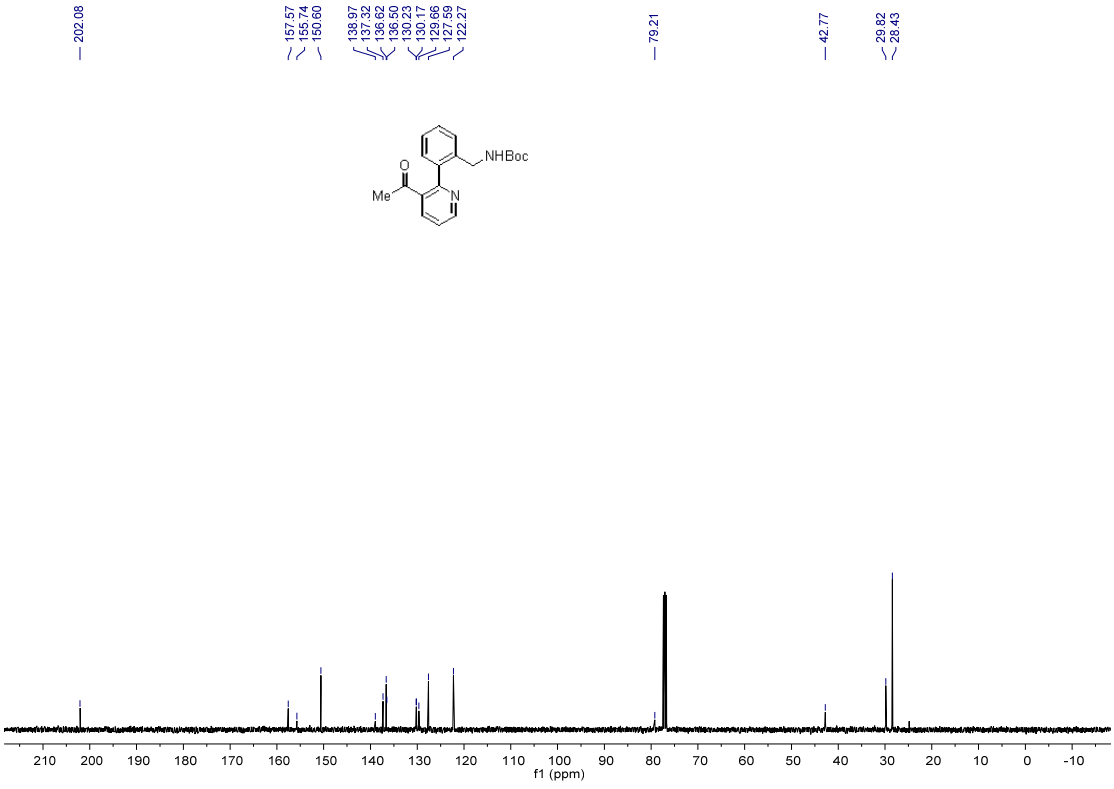

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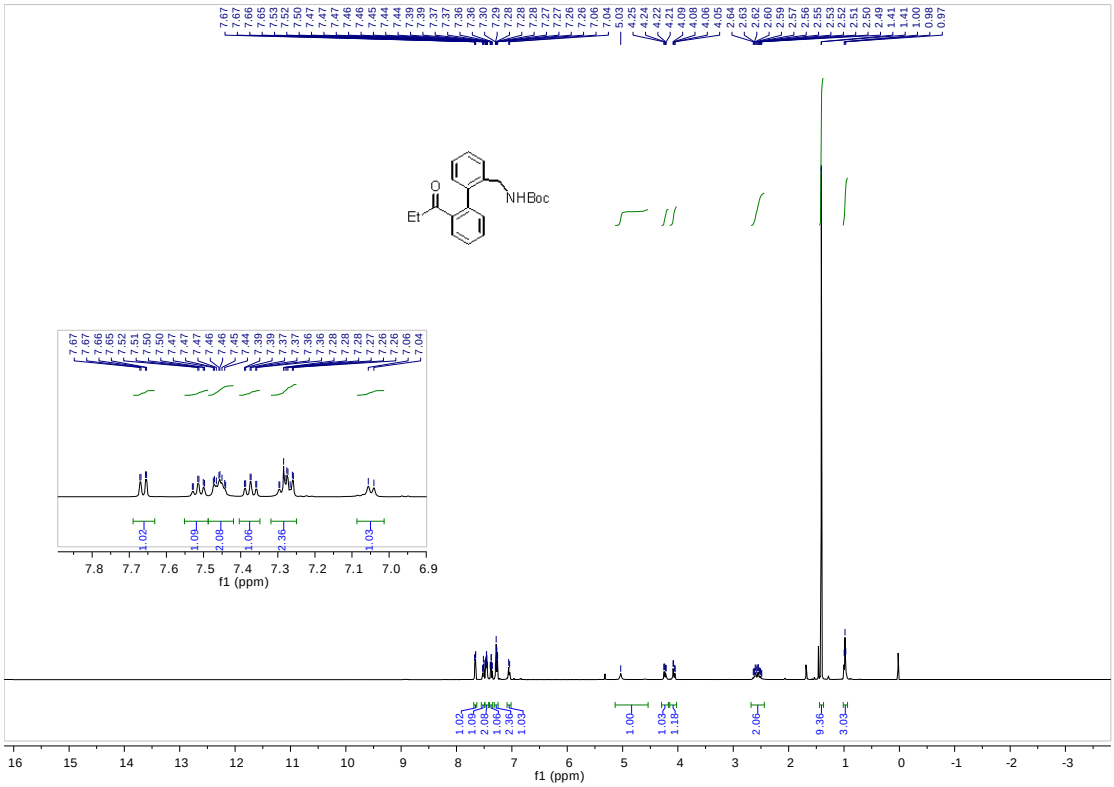
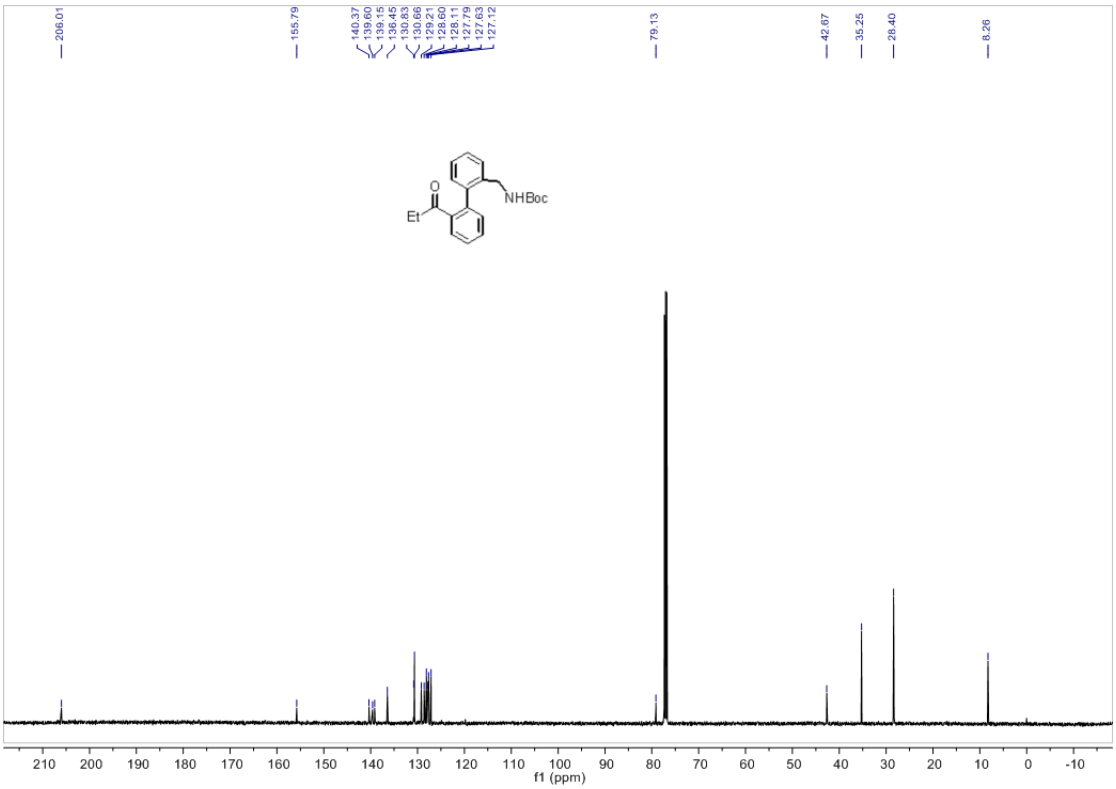
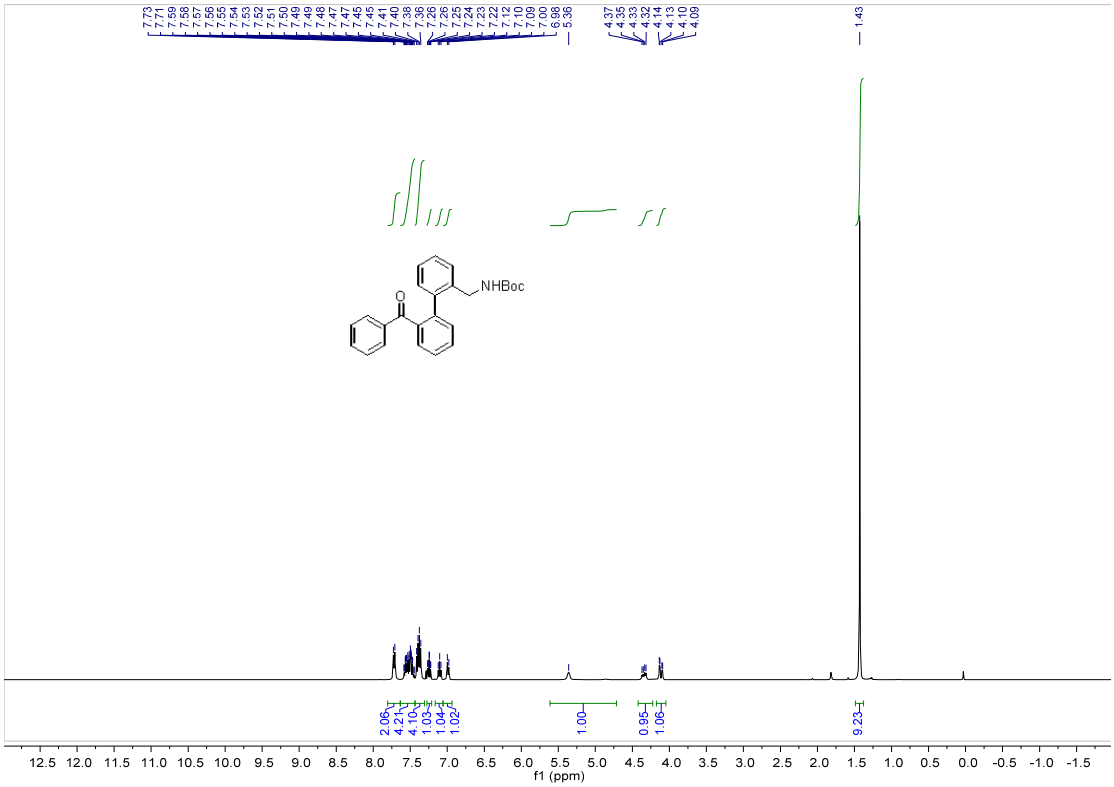


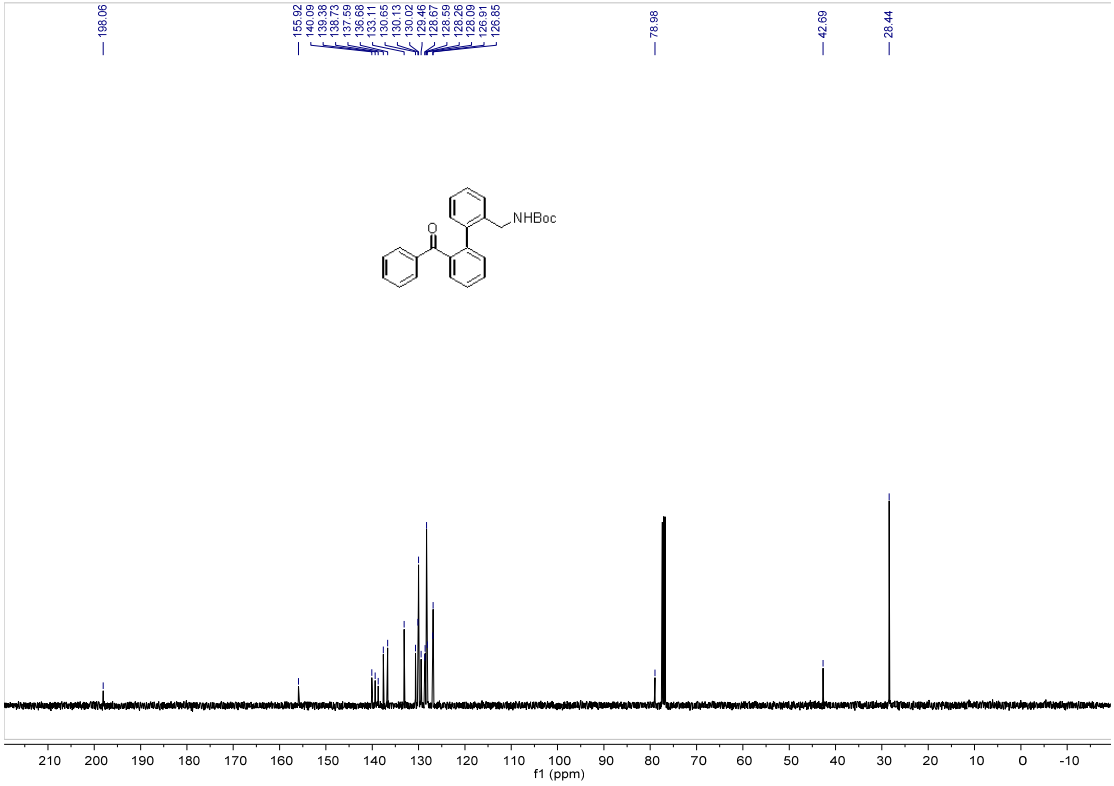
^{13}C NMR for **1m** (126 MHz, $CDCl_3$)



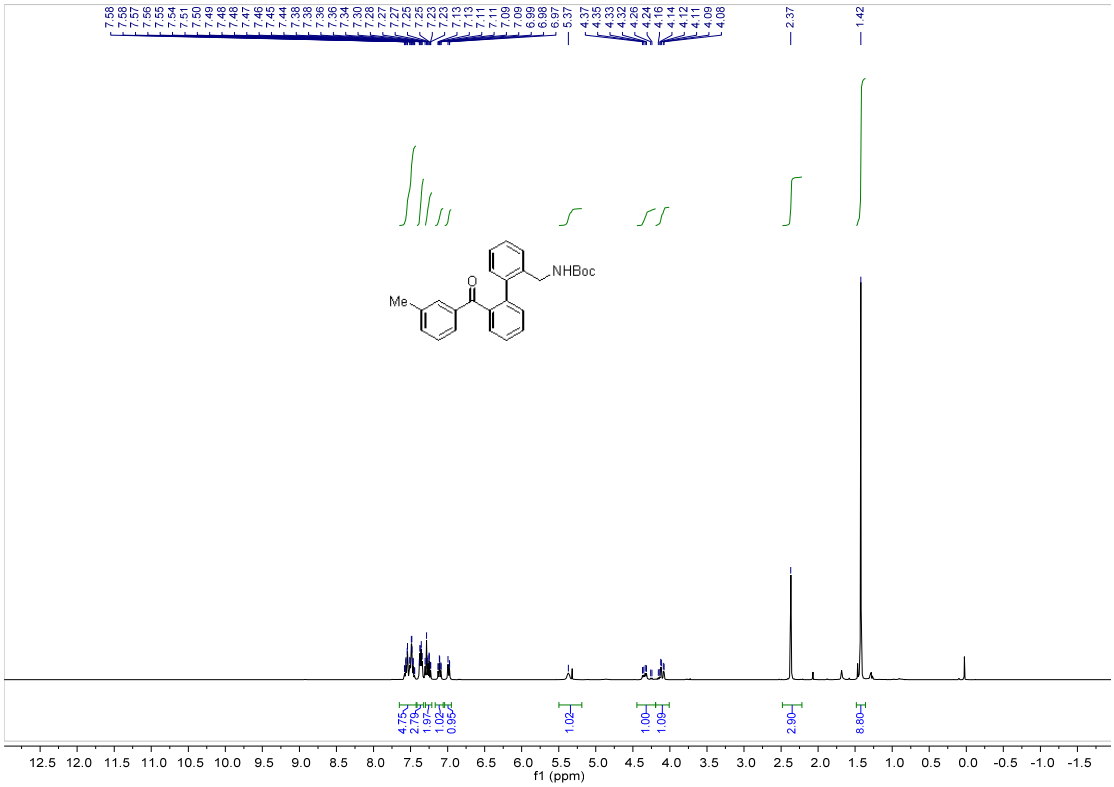
^{1}H NMR for **1n** (400 MHz, $CDCl_3$)



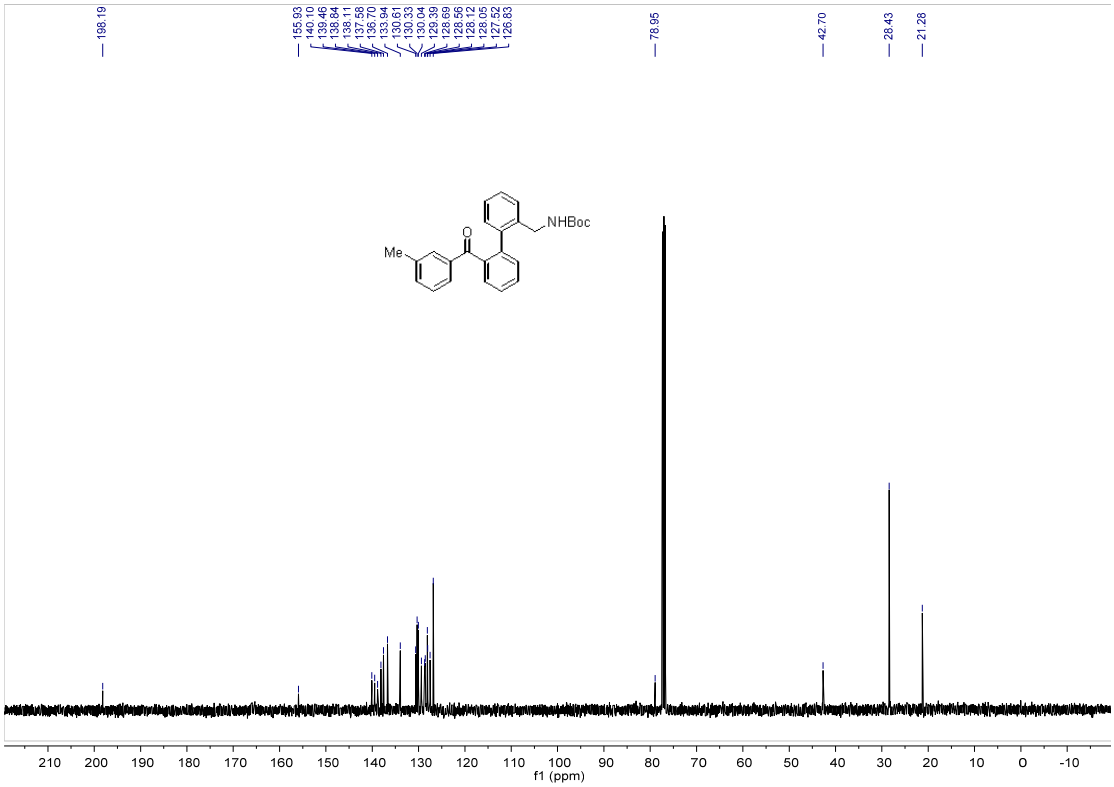
^{13}C NMR for **1n** (101 MHz, $CDCl_3$)



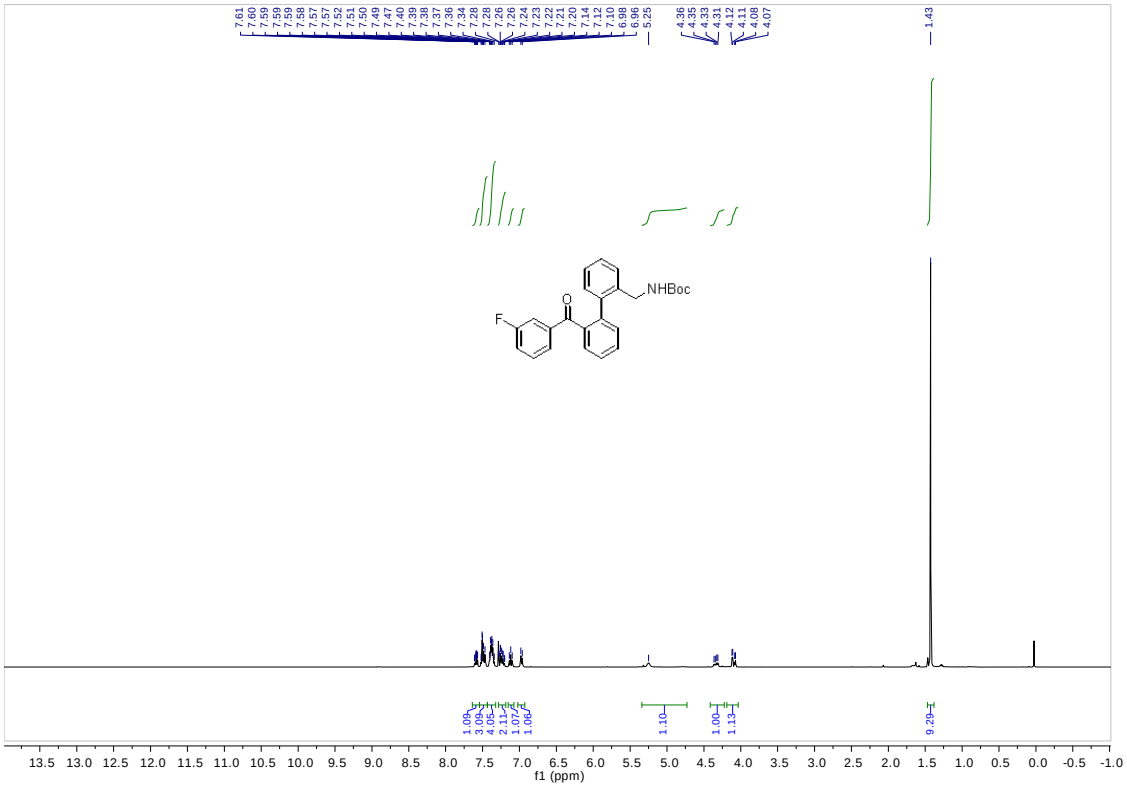
^{1}H NMR for **1o** (400 MHz, $CDCl_3$)



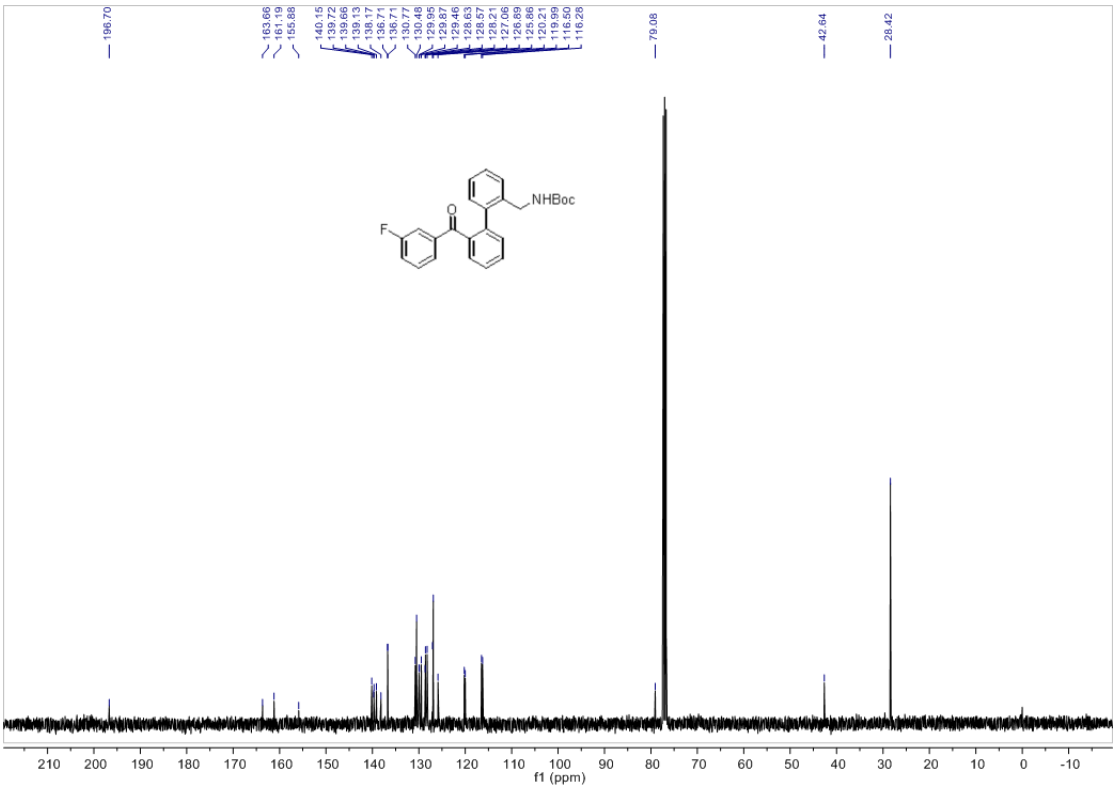
^{13}C NMR for **1o** (101 MHz, $CDCl_3$)



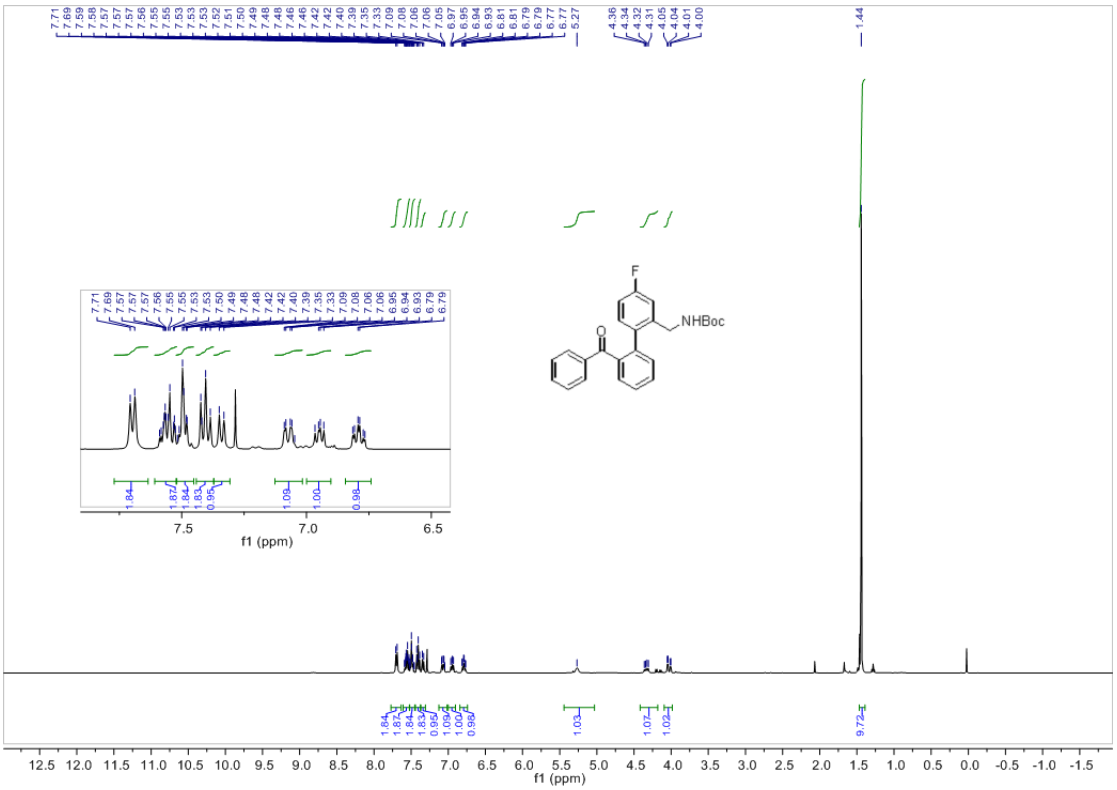
^{1}H NMR for **1p** (400 MHz, $CDCl_3$)



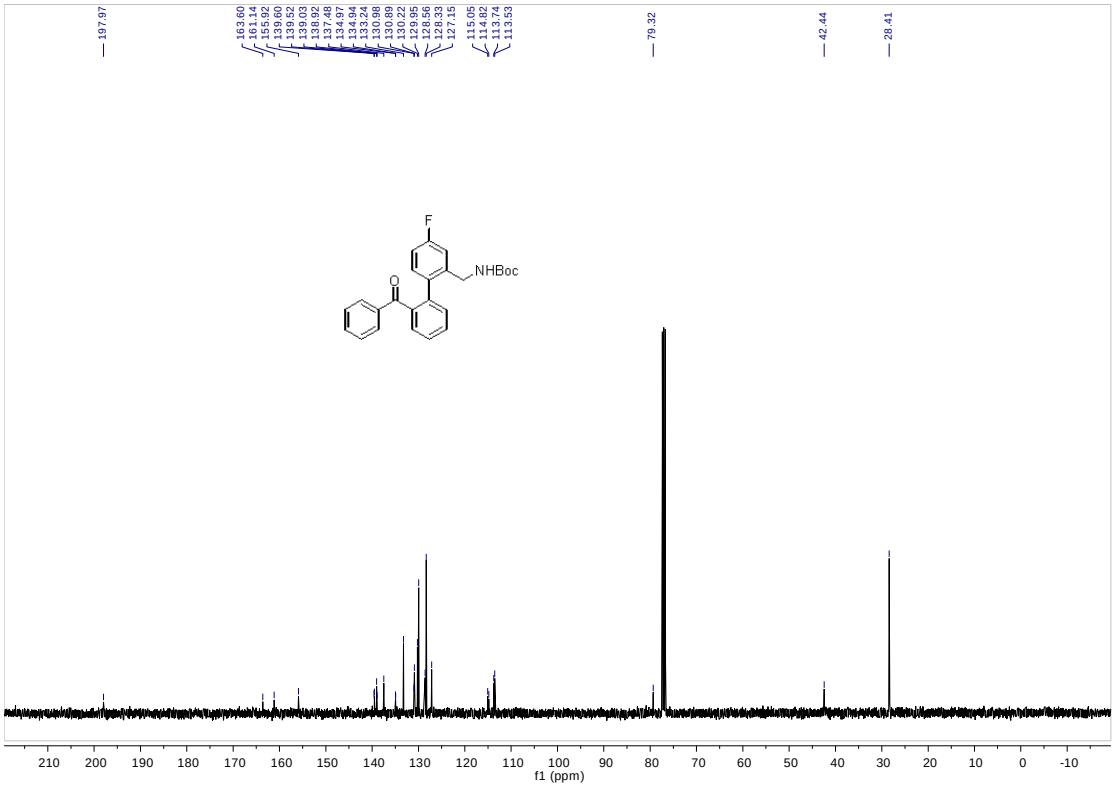
^{13}C NMR for **1p** (101 MHz, $CDCl_3$)



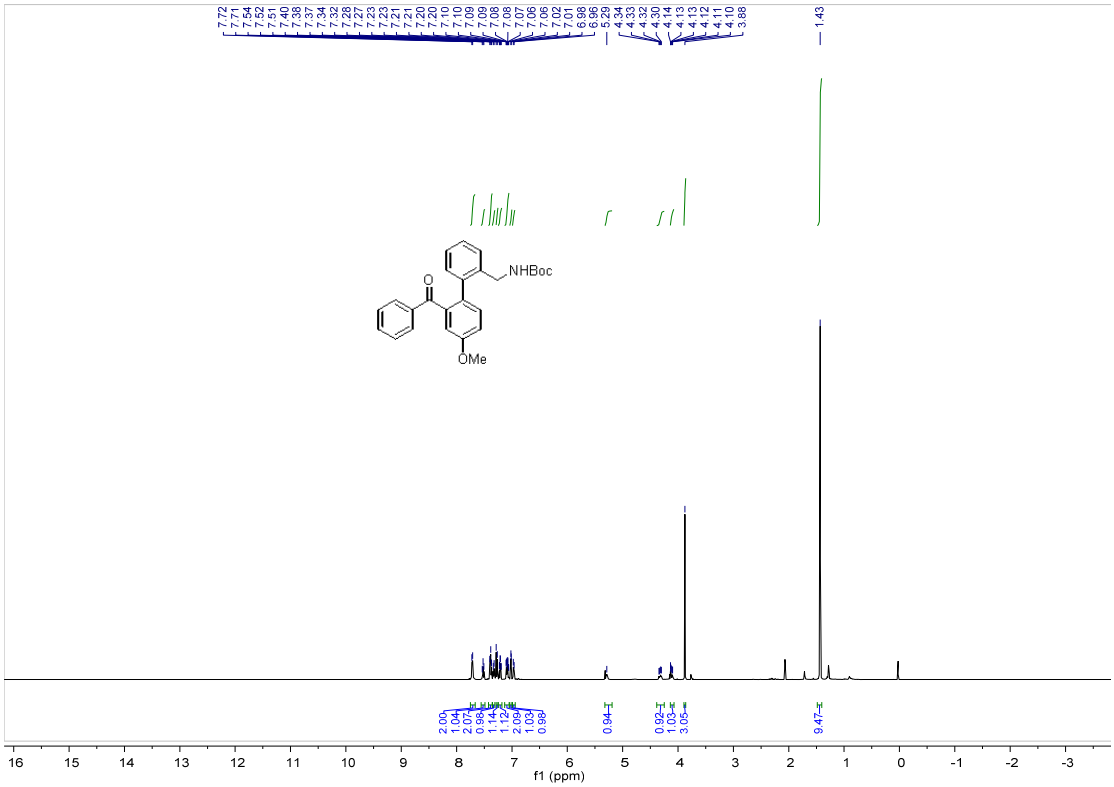
^{1}H NMR for **1q** (400 MHz, $CDCl_3$)



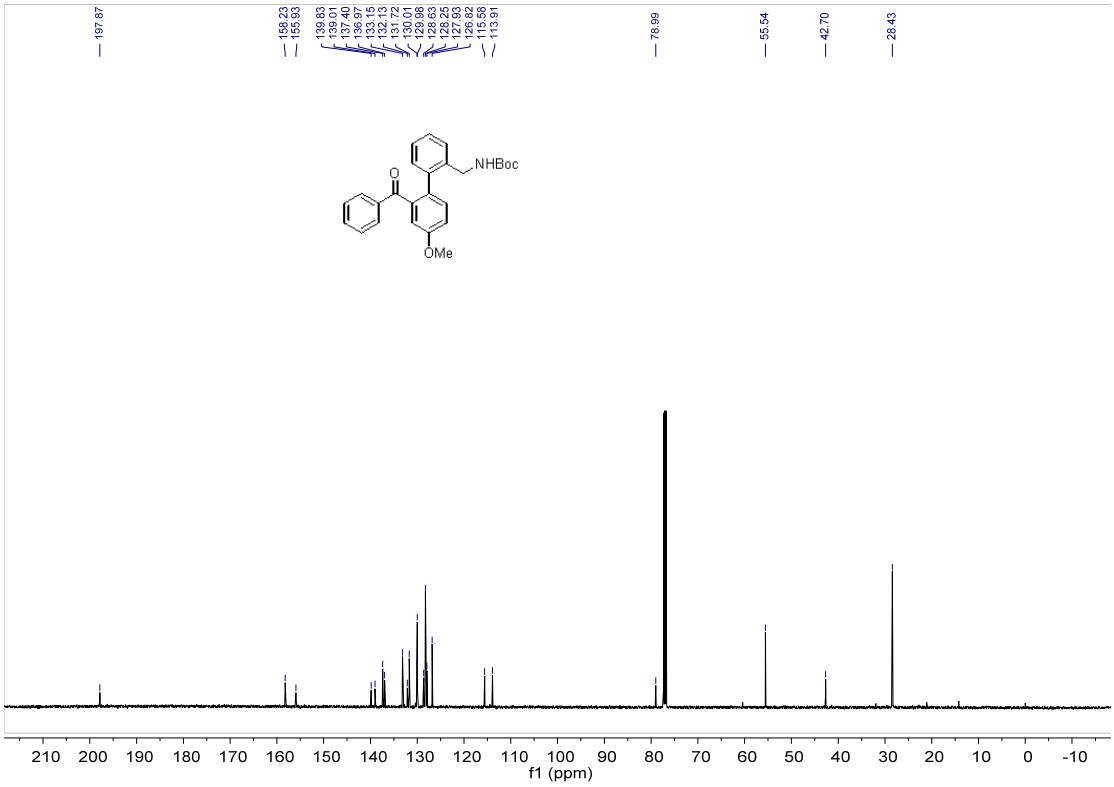
^{13}C NMR for **1q** (101 MHz, $CDCl_3$)



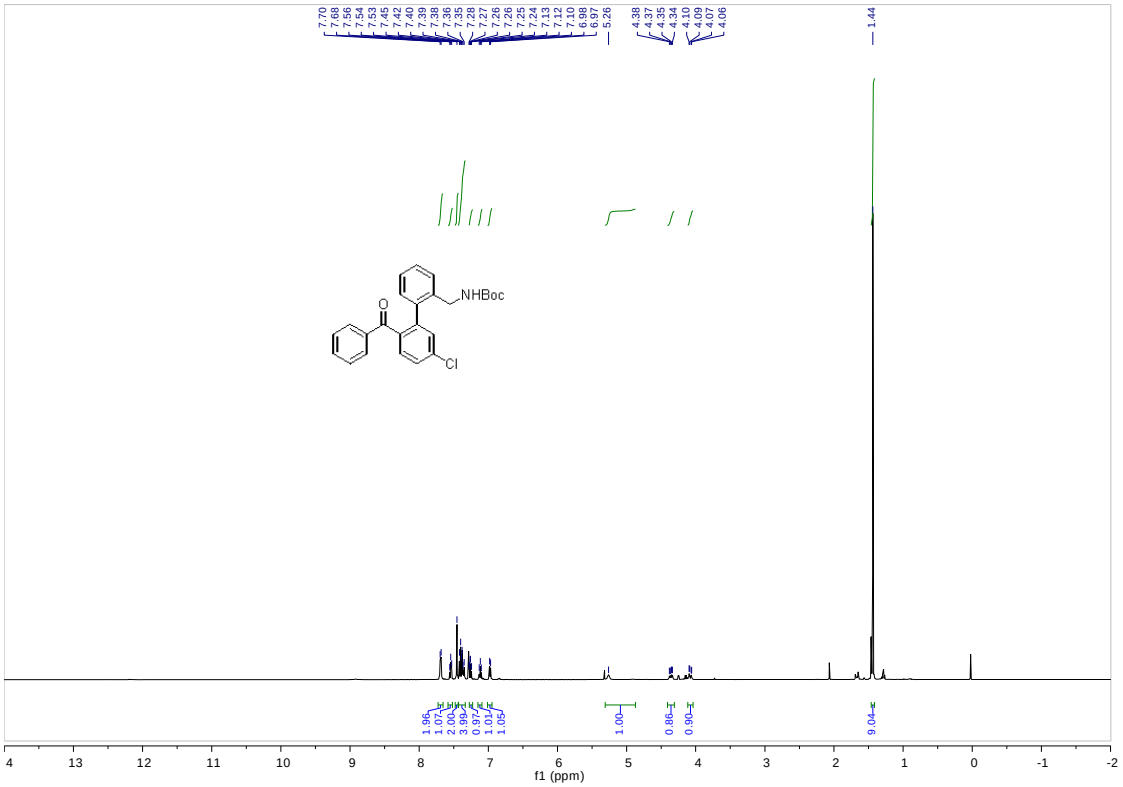
^{1}H NMR for **1r** (500 MHz, $CDCl_3$)



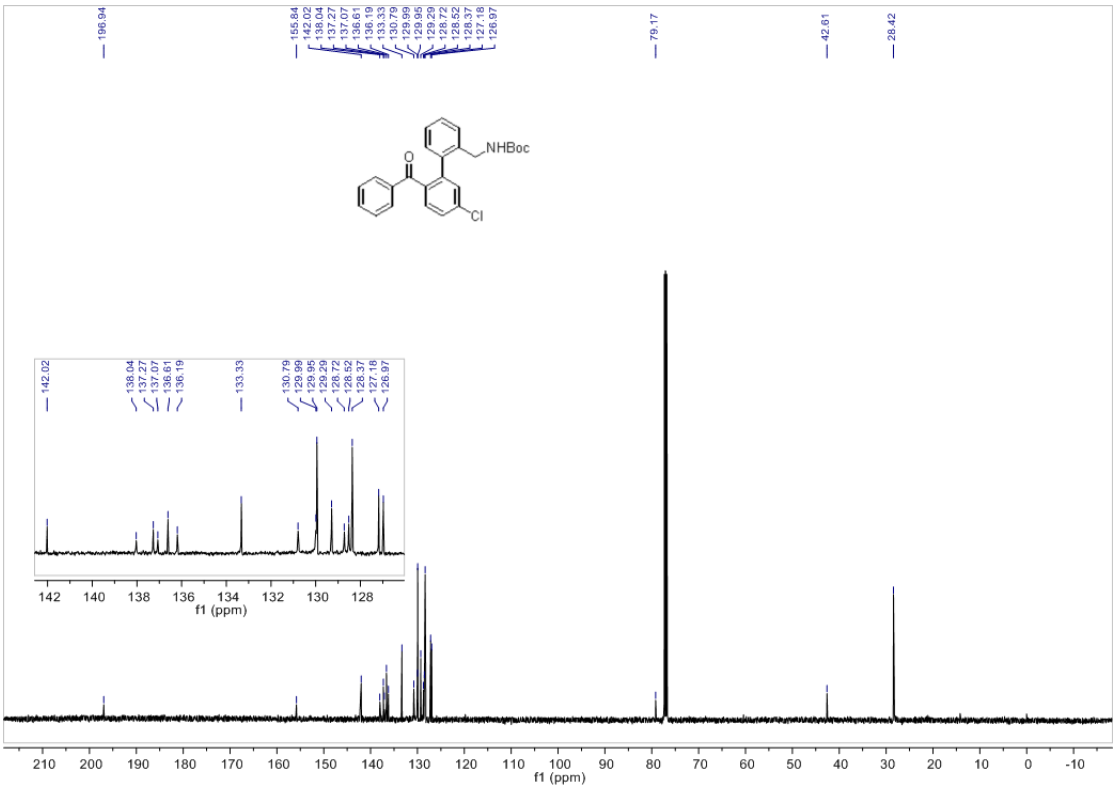
^{13}C NMR for **1r** (126 MHz, $CDCl_3$)



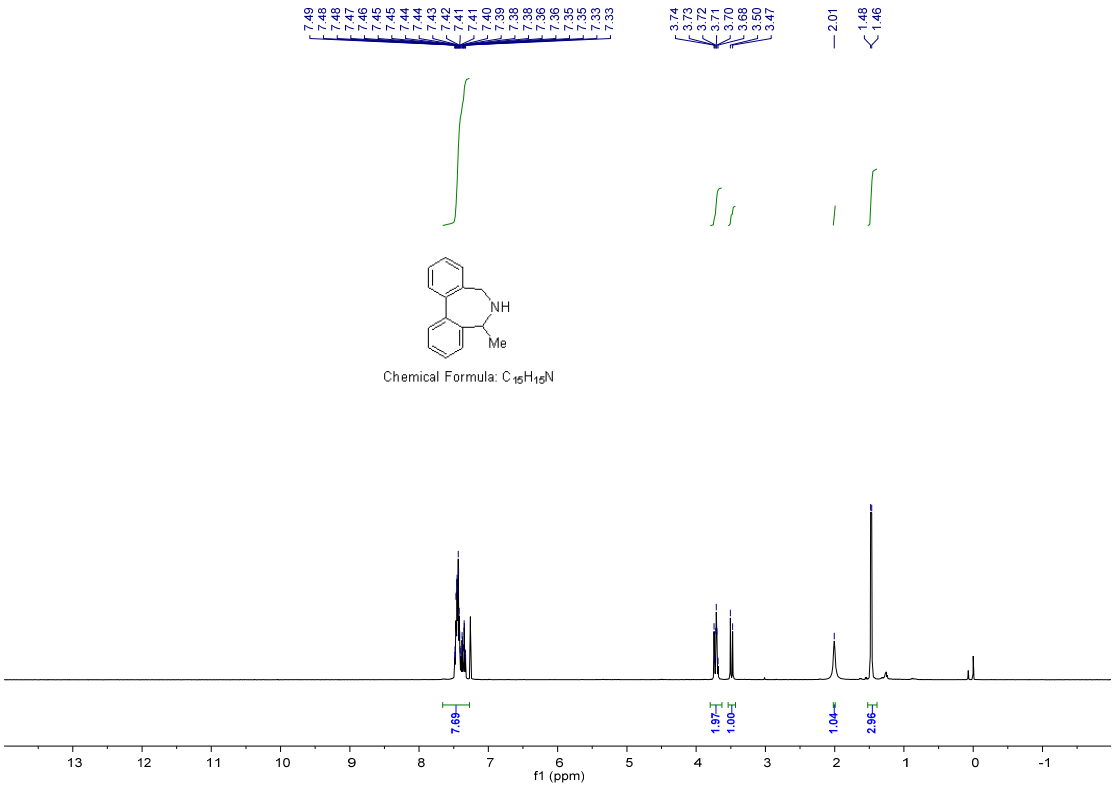
^{1}H NMR for **1s** (500 MHz, $CDCl_3$)



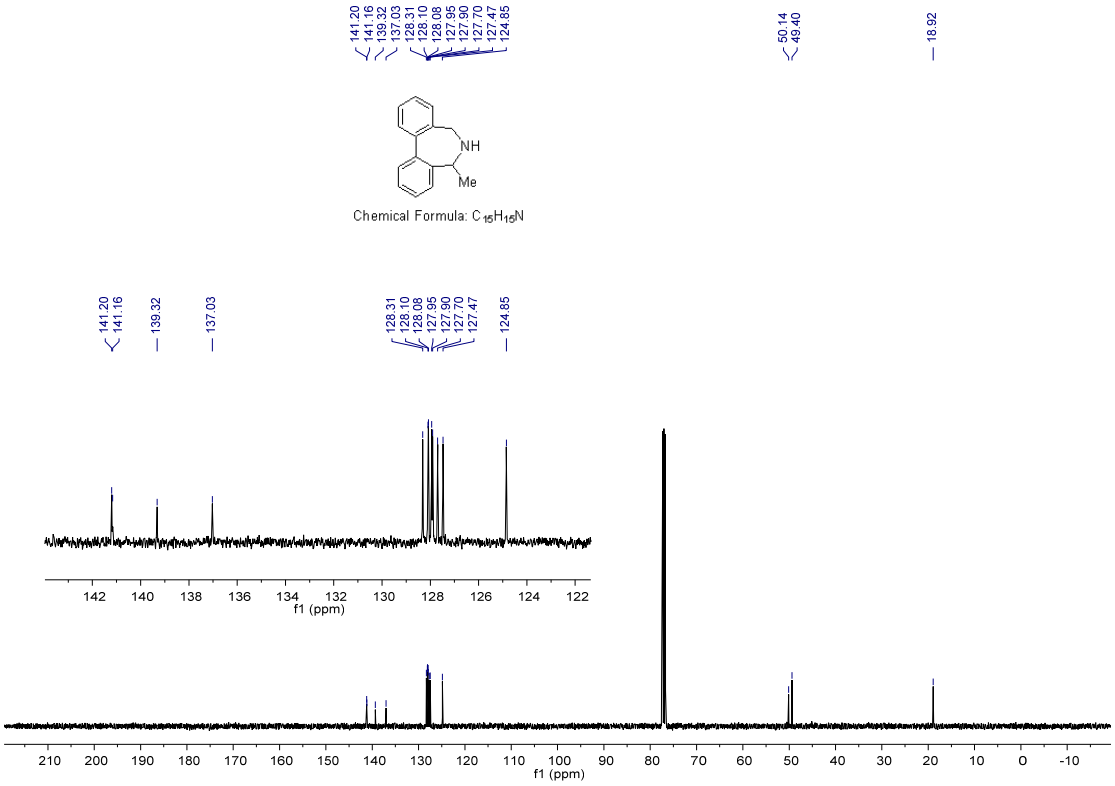
^{13}C NMR for **1s** (126 MHz, $CDCl_3$)



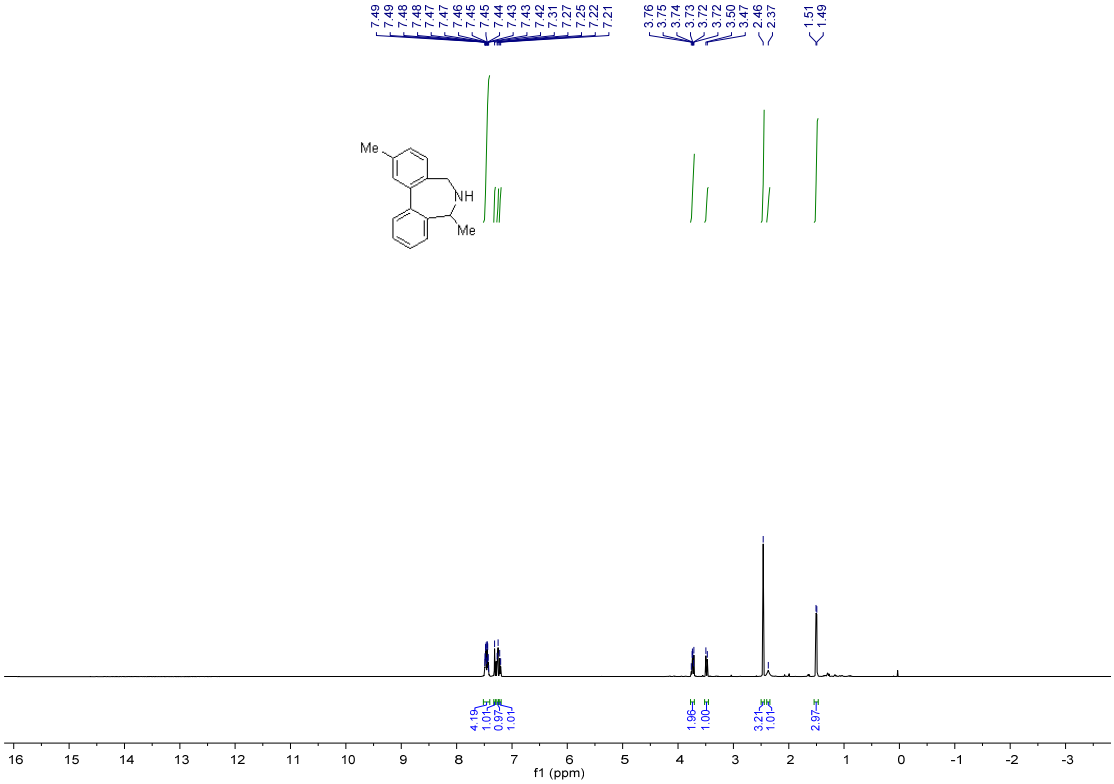
^{1}H NMR for **2a** (400 MHz, $CDCl_3$)



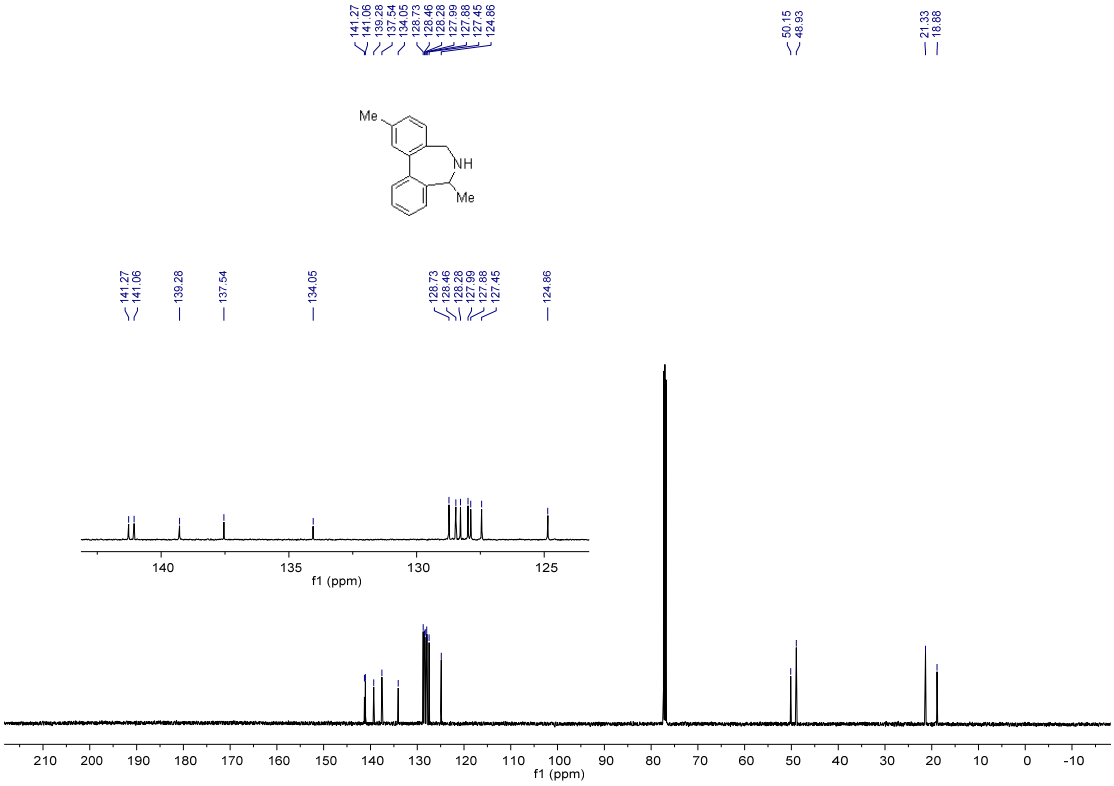
^{13}C NMR for **2a** (101 MHz, $CDCl_3$)



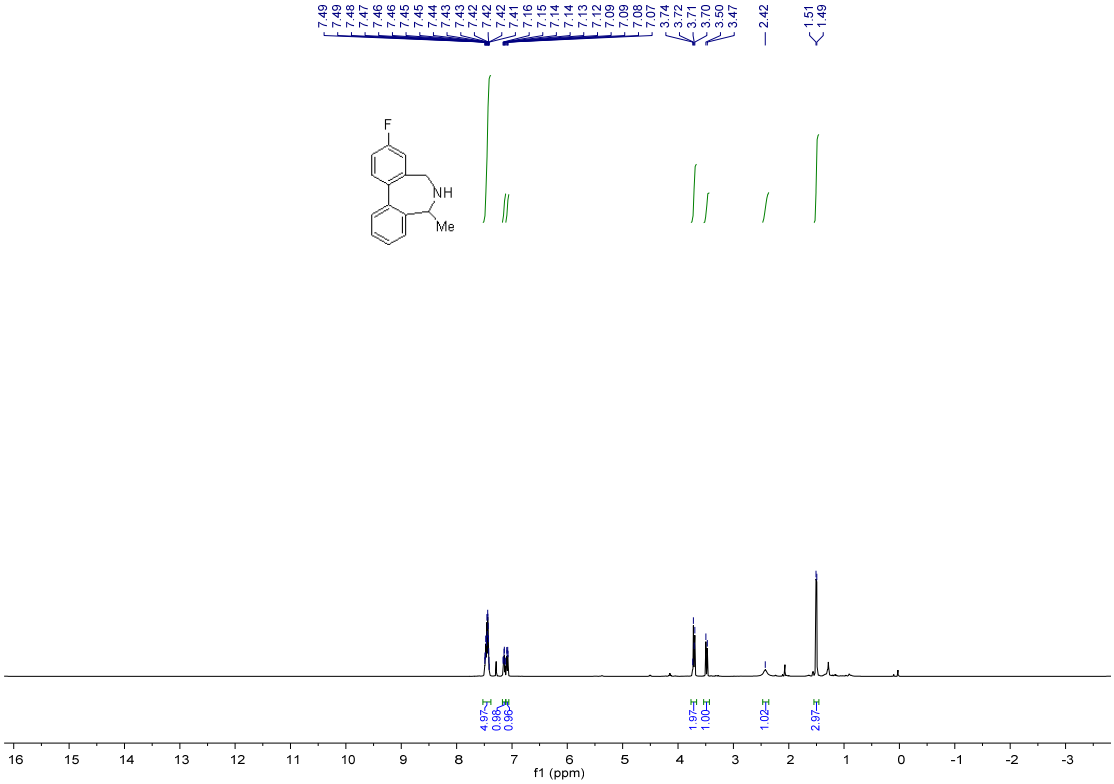
^{1}H NMR for **2b** (500 MHz, $CDCl_3$)



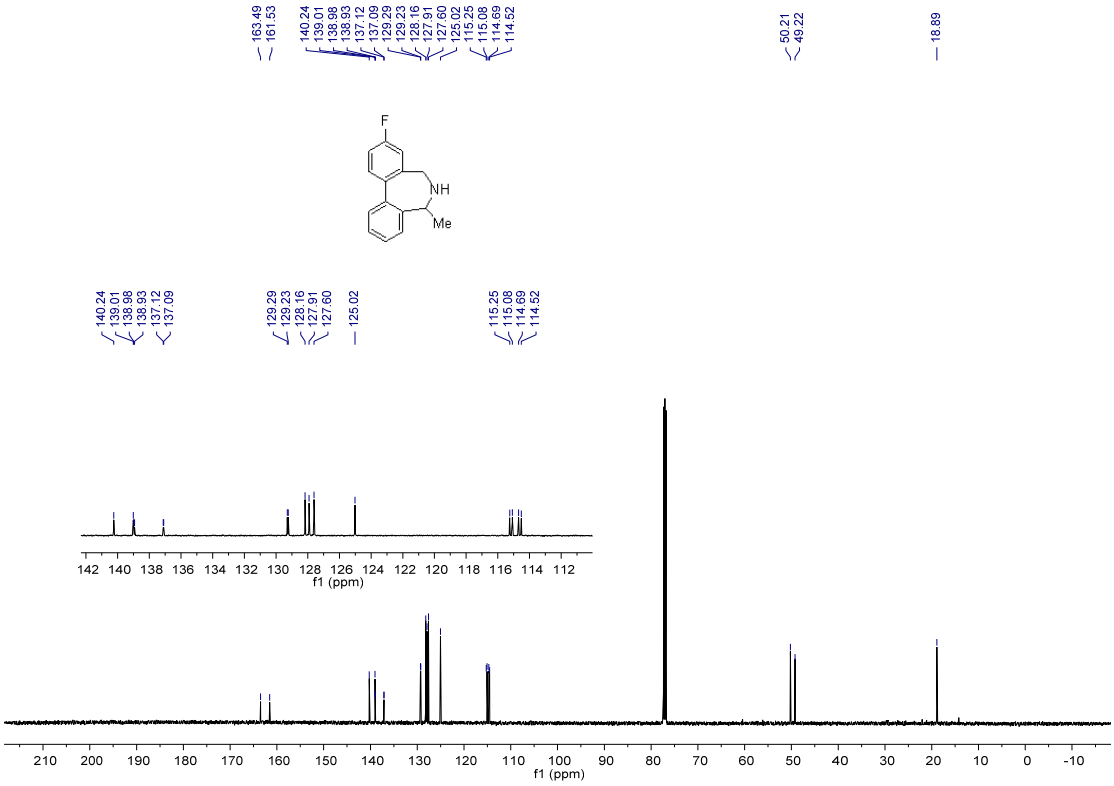
^{13}C NMR for **2b** (126 MHz, $CDCl_3$)



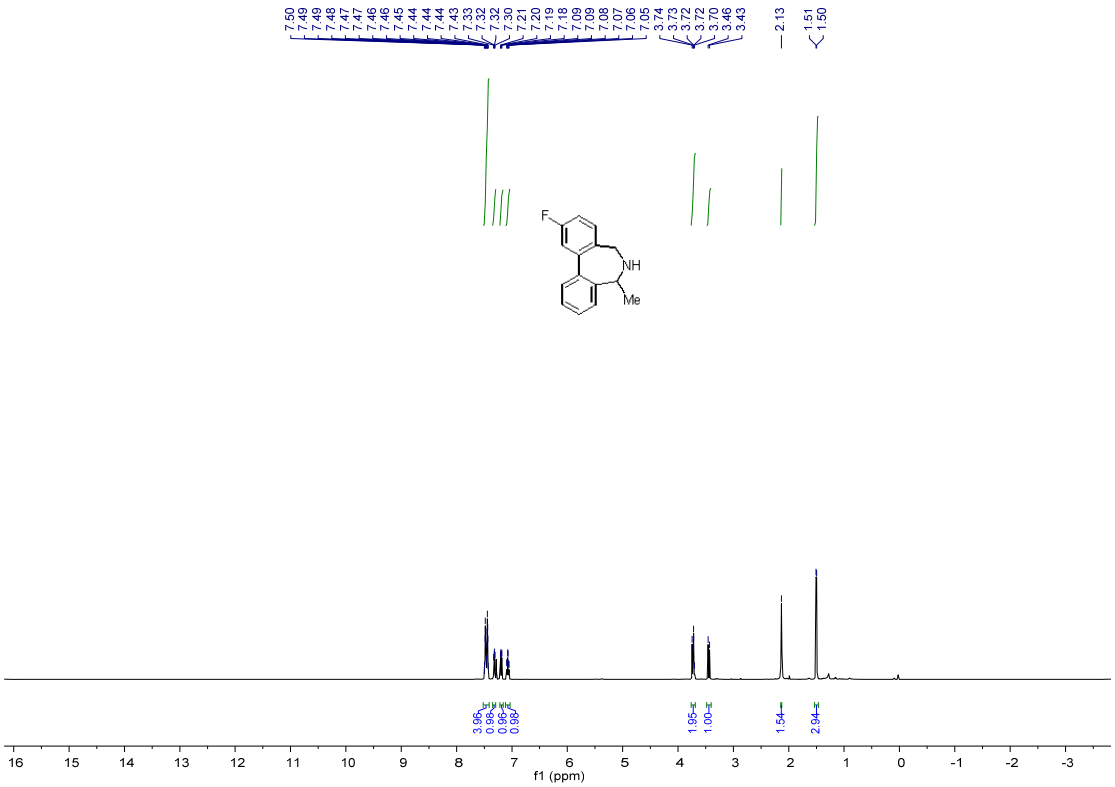
^{1}H NMR for **2c** (500 MHz, $CDCl_3$)



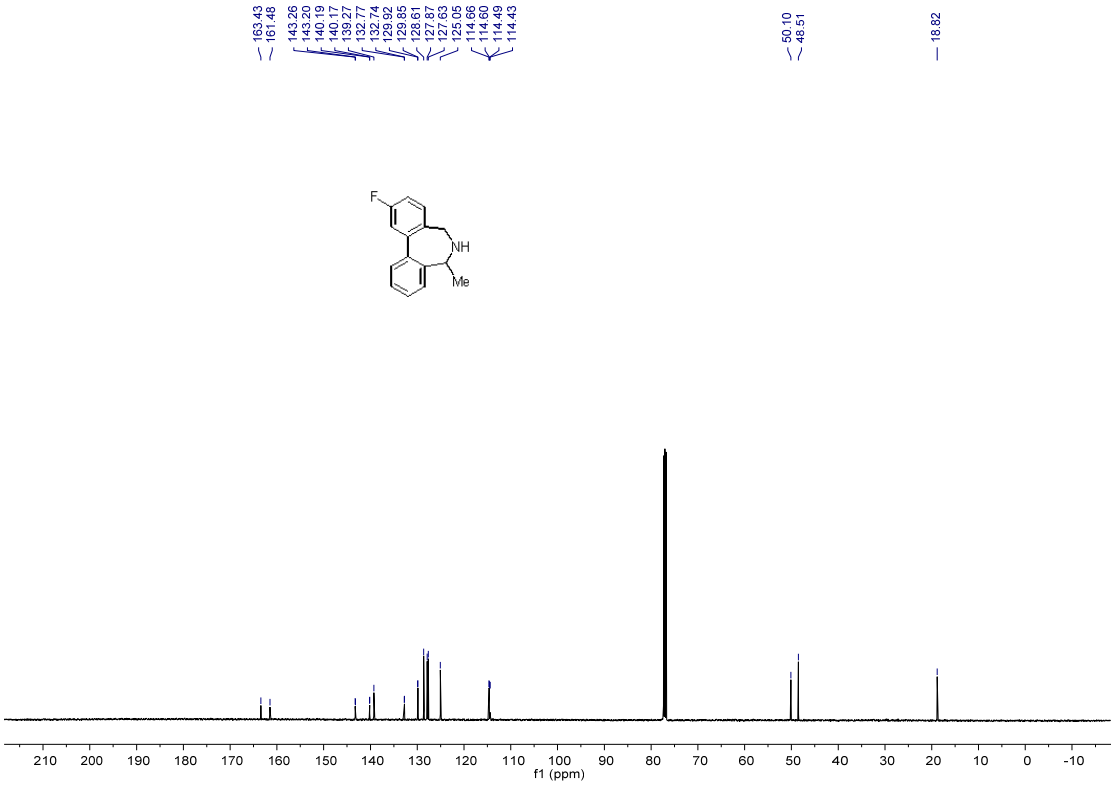
^{13}C NMR for **2c** (126 MHz, $CDCl_3$)



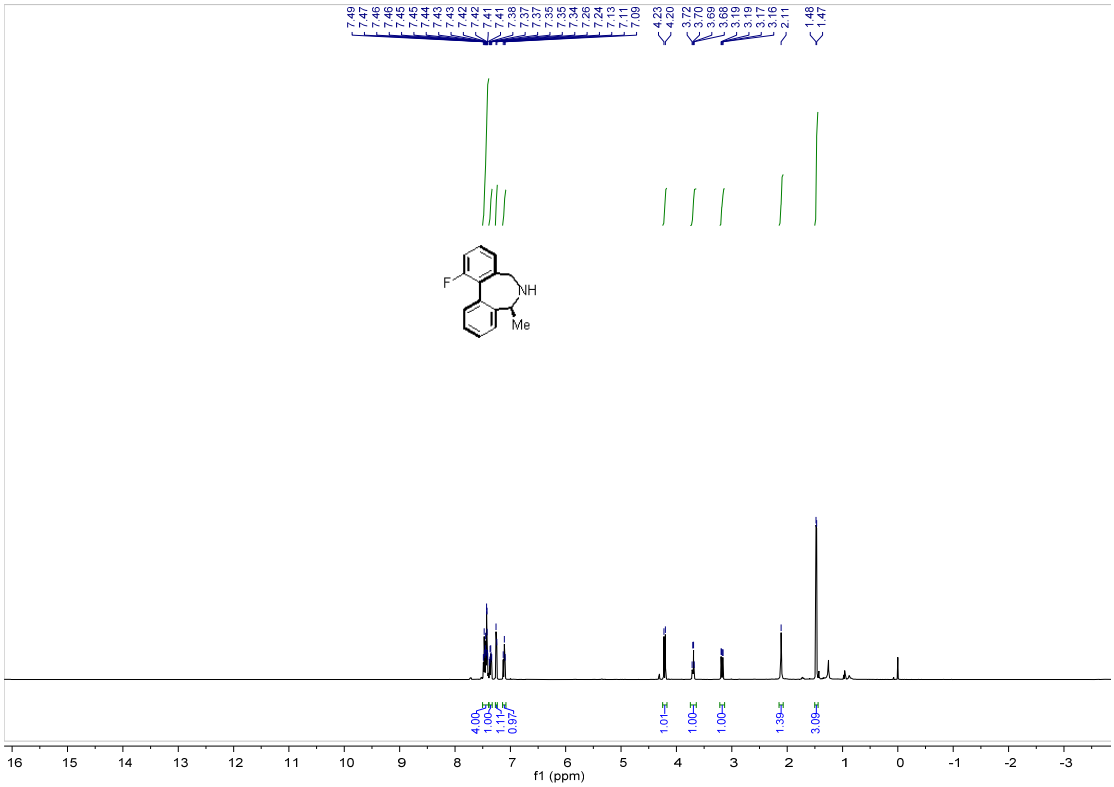
^{1}H NMR for **2d** (500 MHz, $CDCl_3$)



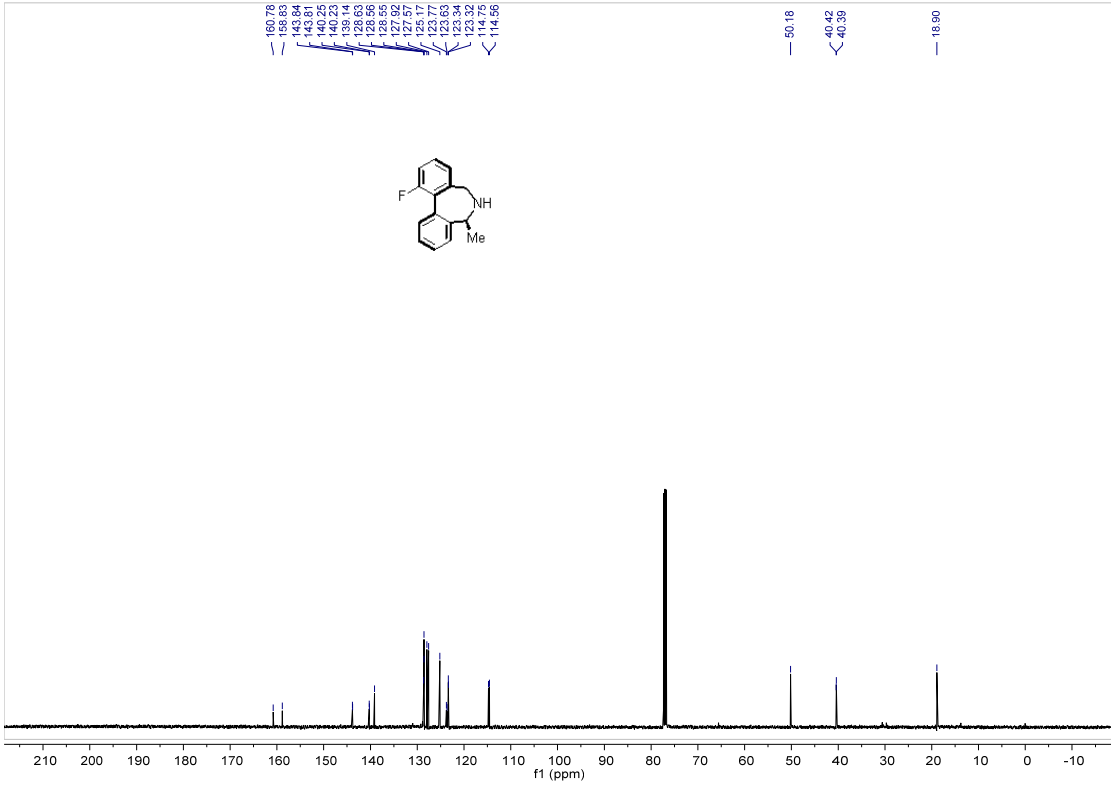
^{13}C NMR for **2d** (126 MHz, $CDCl_3$)



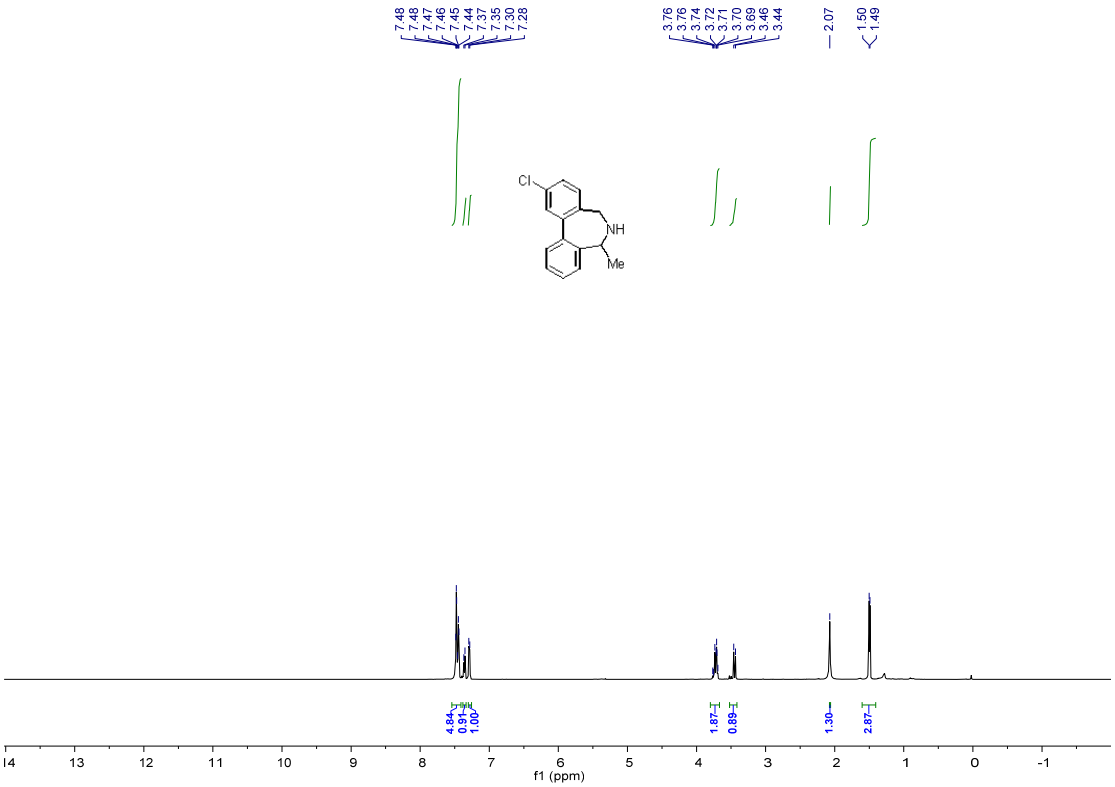
^{1}H NMR for **2e** (500 MHz, $CDCl_3$)



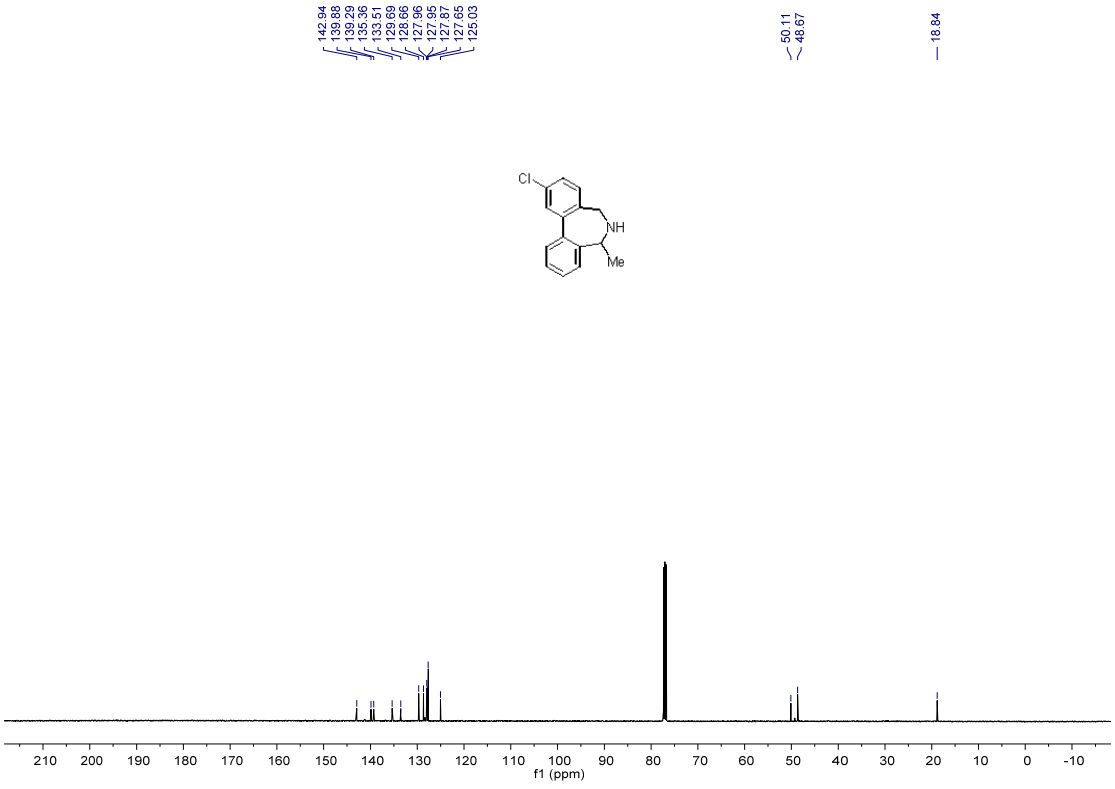
^{13}C NMR for **2e** (126 MHz, $CDCl_3$)



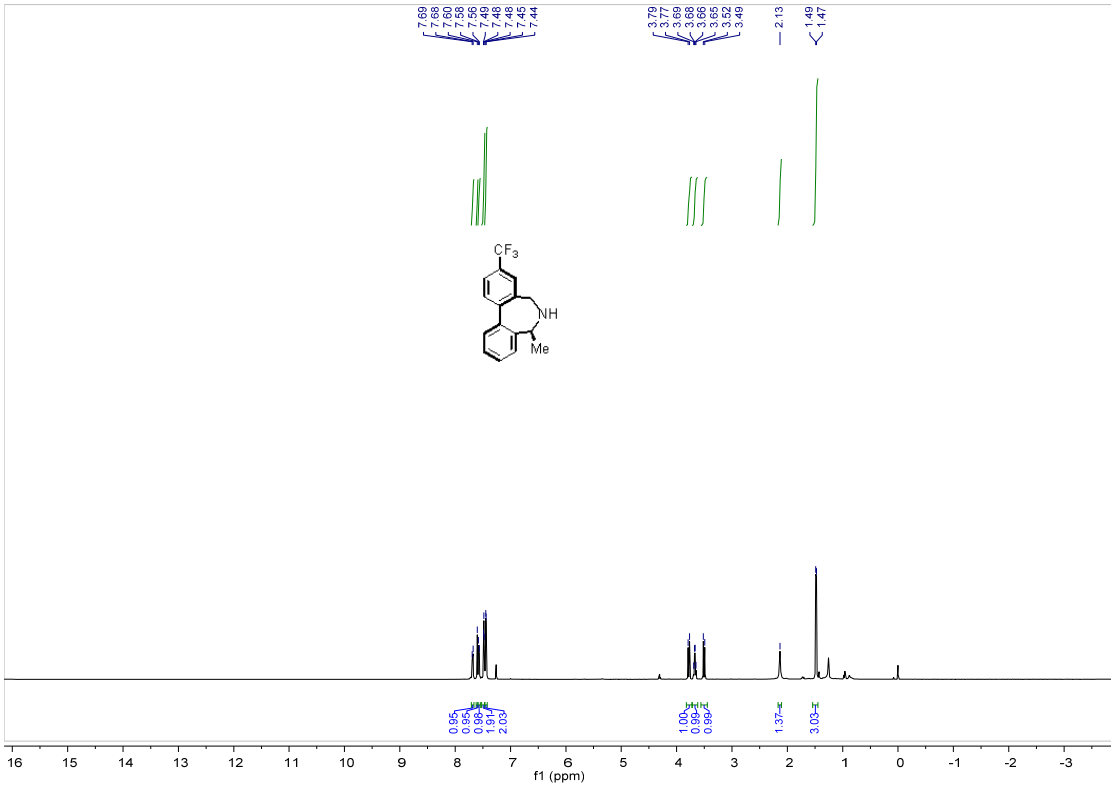
^{1}H NMR for **2f** (500 MHz, $CDCl_3$)



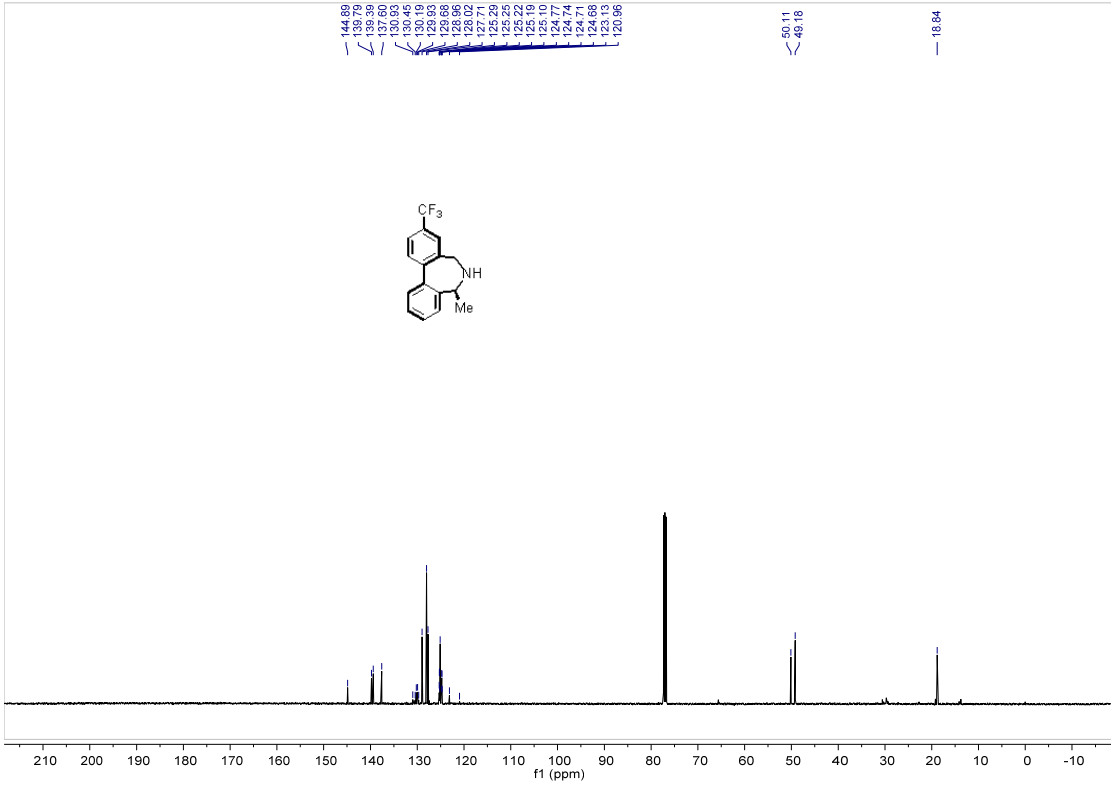
^{13}C NMR for **2f** (126 MHz, $CDCl_3$)



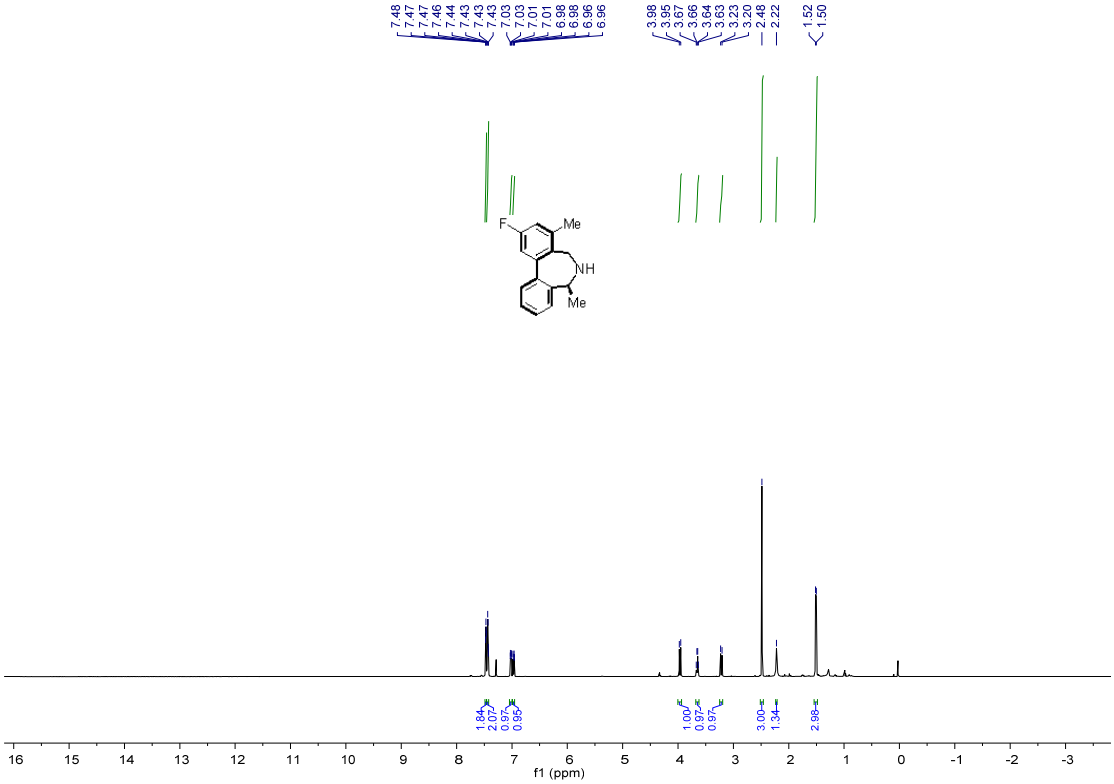
^{1}H NMR for **2g** (500 MHz, $CDCl_3$)



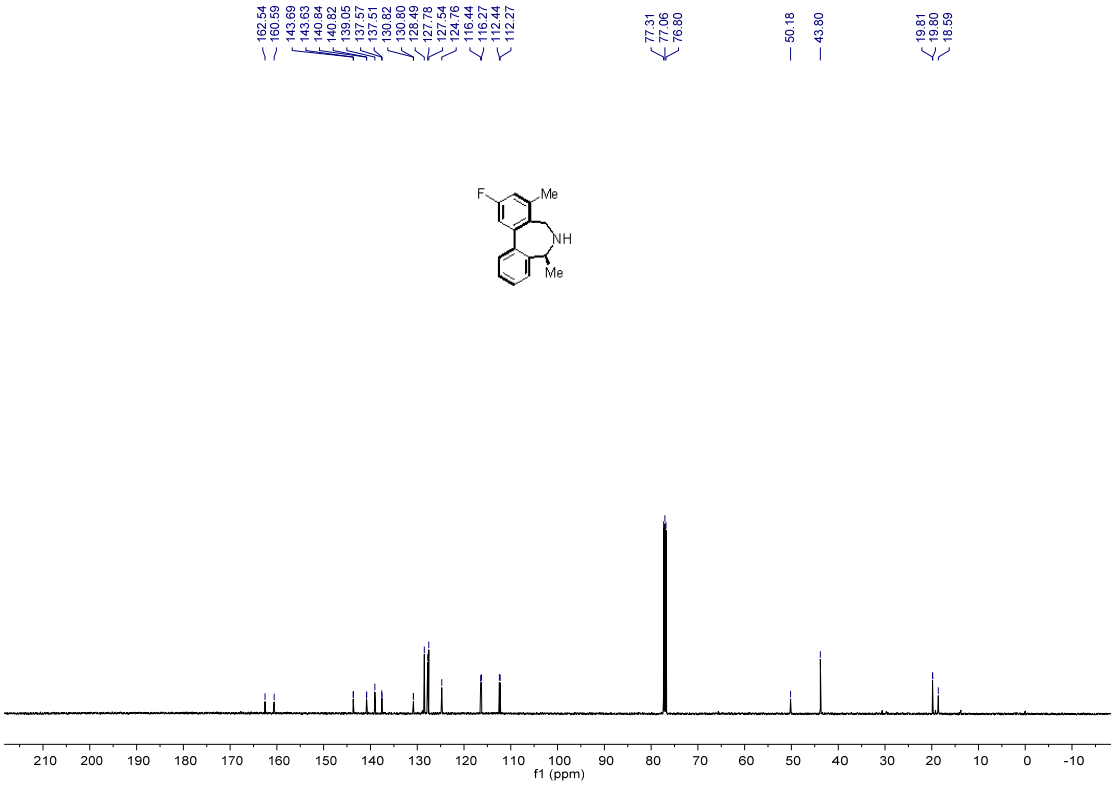
^{13}C NMR for **2g** (126 MHz, $CDCl_3$)



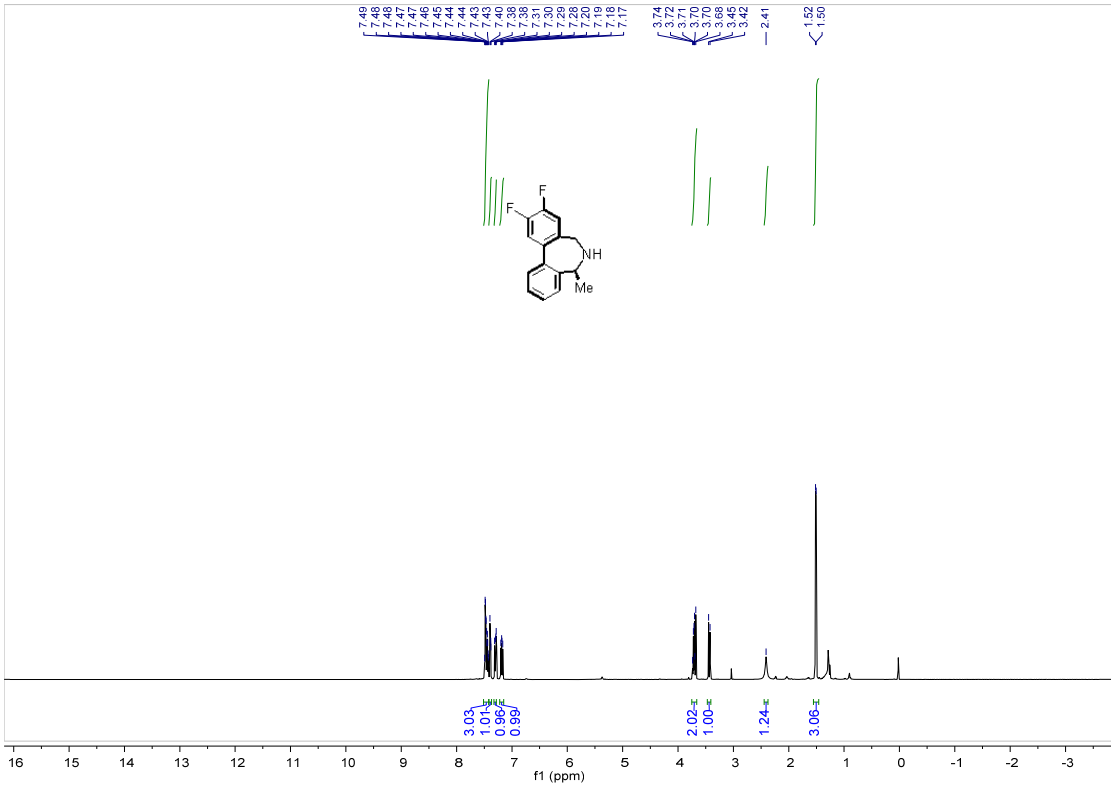
^{1}H NMR for **2h** (500 MHz, $CDCl_3$)



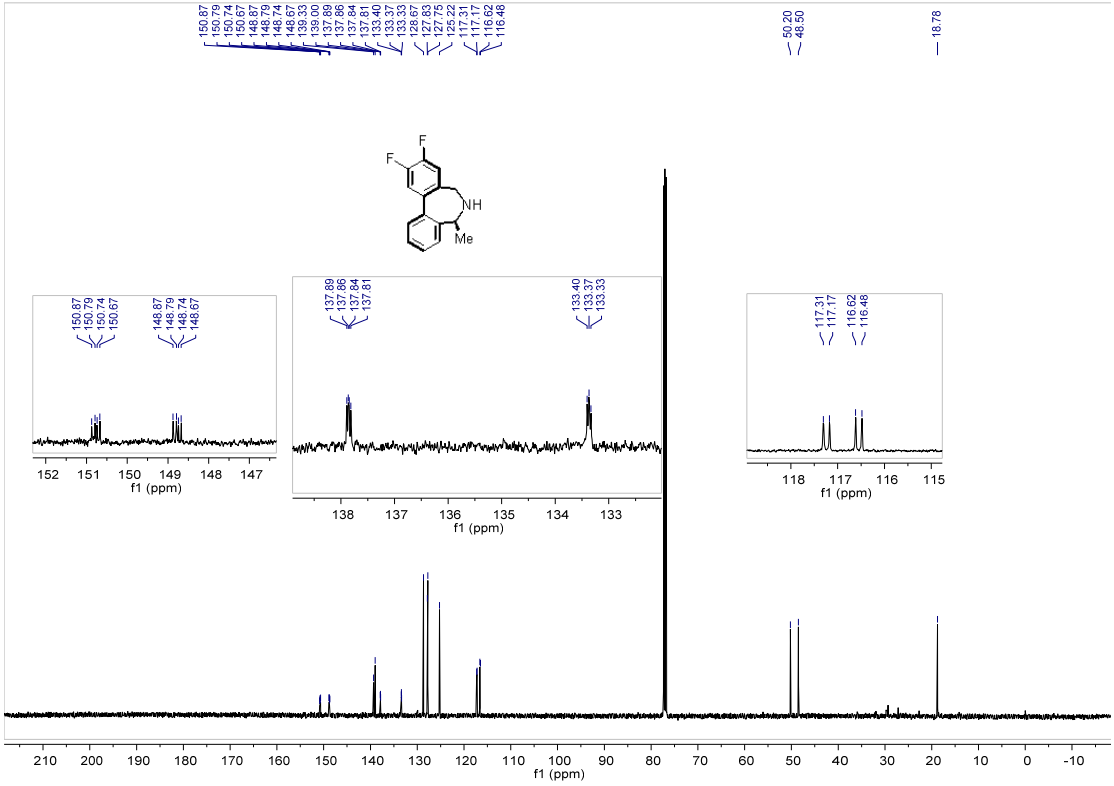
^{13}C NMR for **2h** (126 MHz, $CDCl_3$)



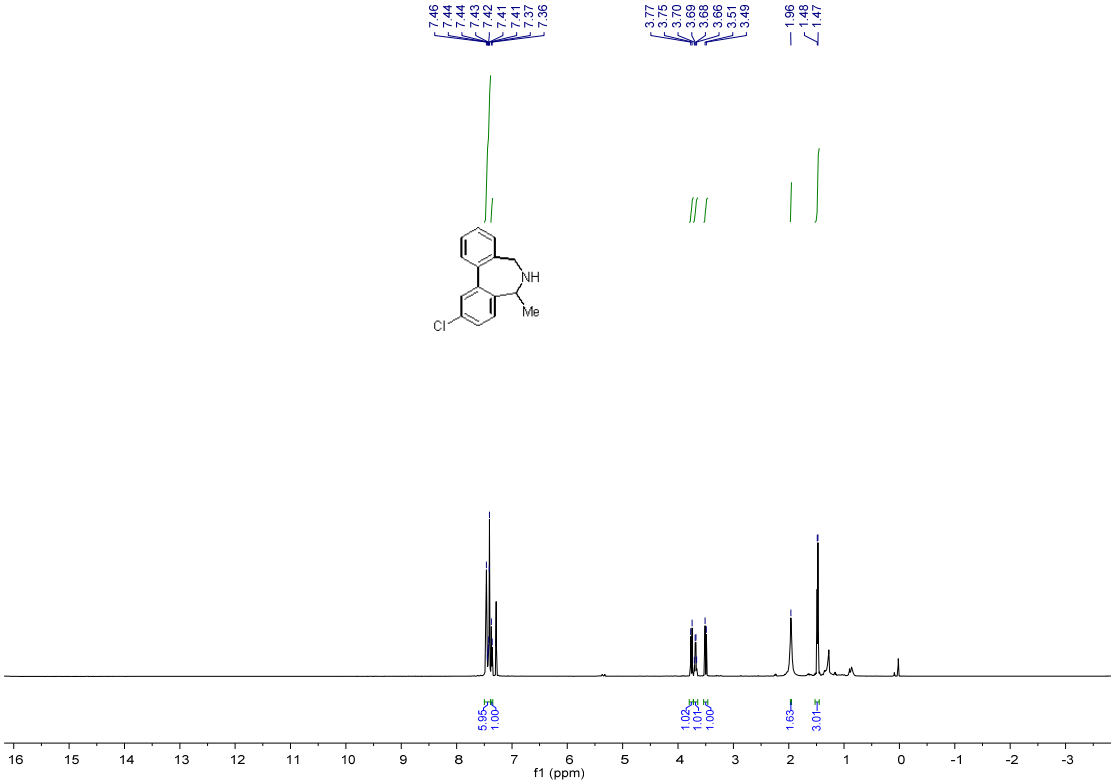
^{1}H NMR for **2i** (500 MHz, $CDCl_3$)



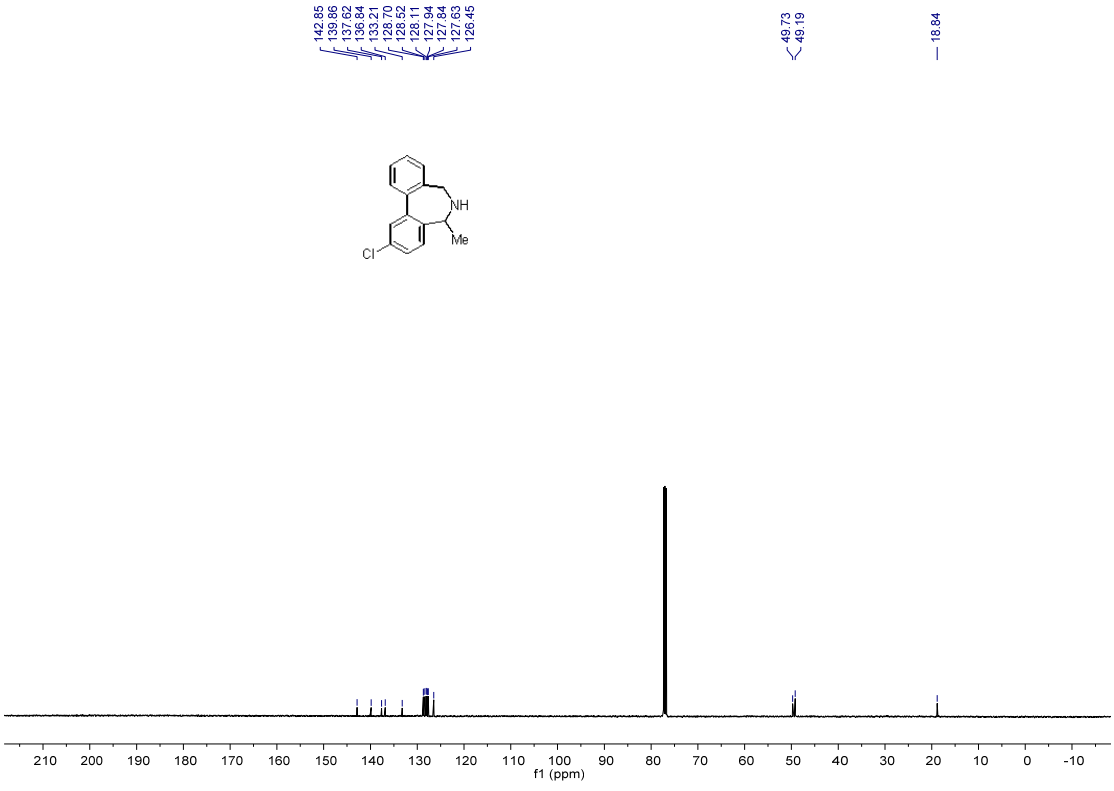
^{13}C NMR for **2i** (126 MHz, $CDCl_3$)



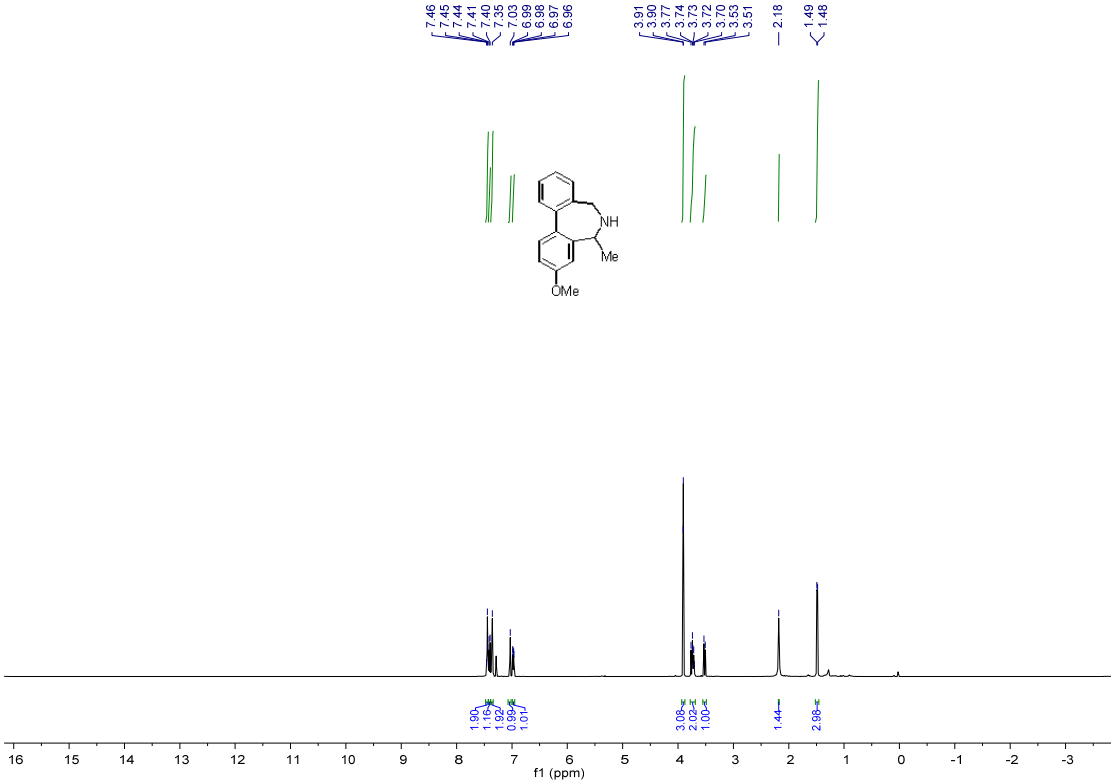
^{1}H NMR for **2j** (500 MHz, $CDCl_3$)



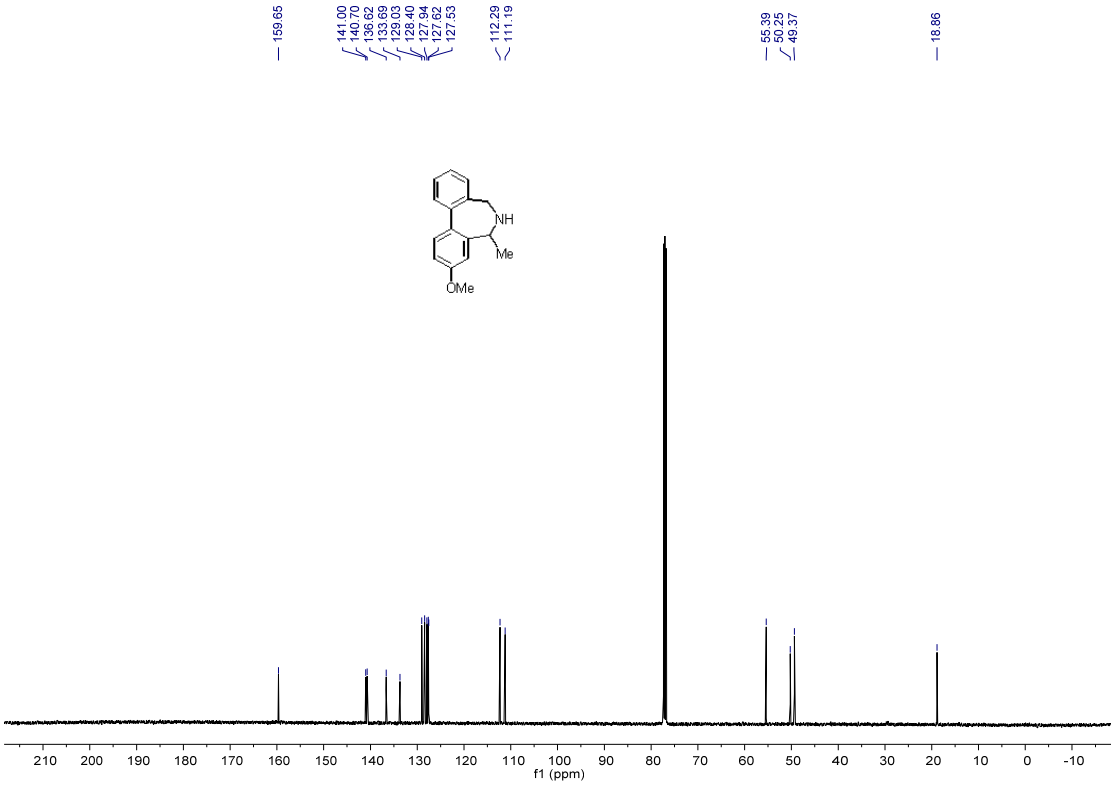
^{13}C NMR for **2j** (126 MHz, $CDCl_3$)



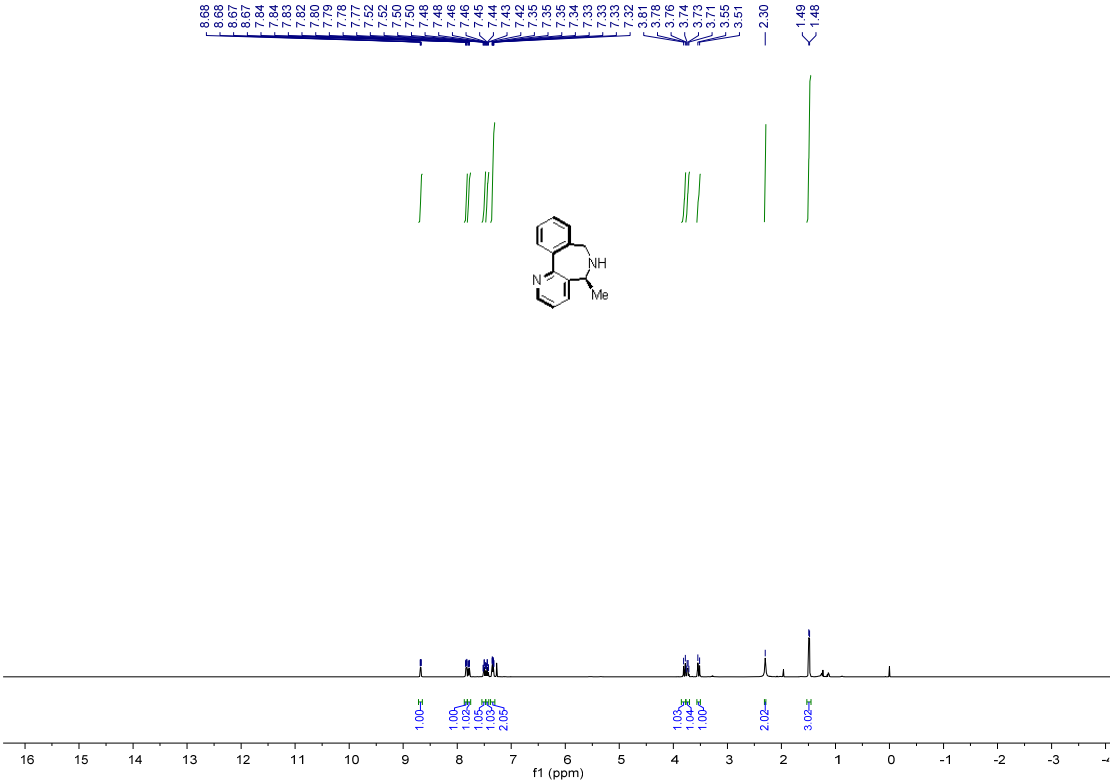
^{1}H NMR for **2k** (500 MHz, $CDCl_3$)



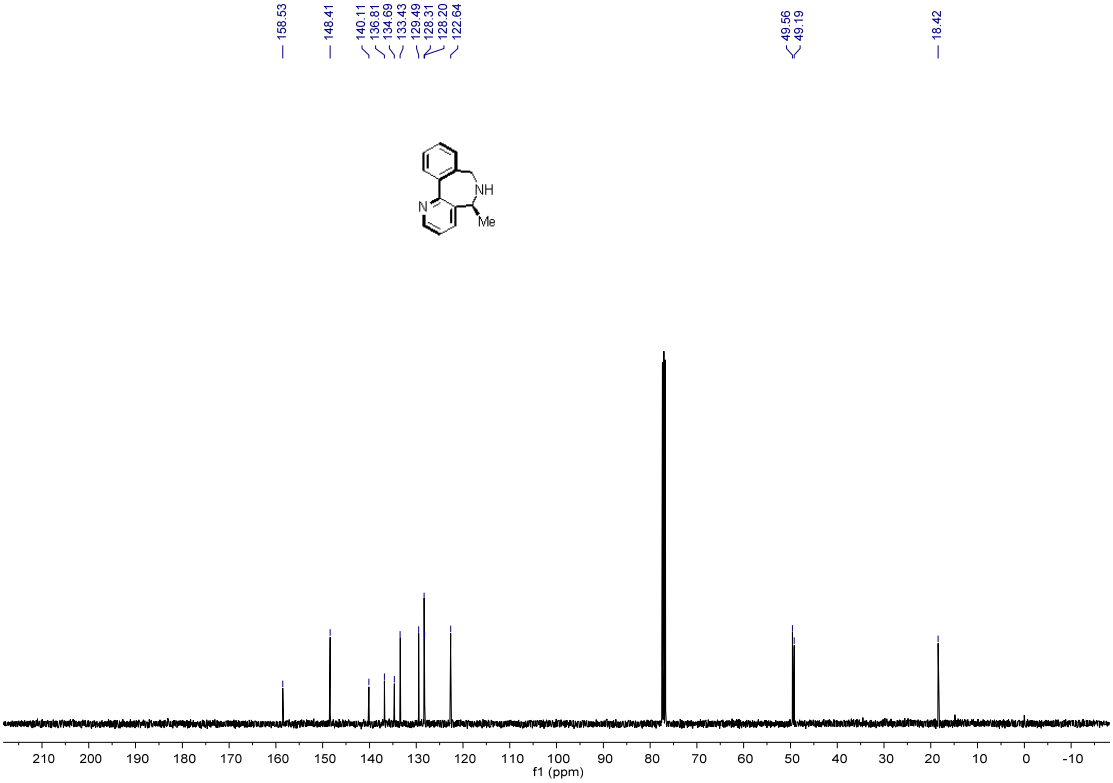
^{13}C NMR for **2k** (126 MHz, $CDCl_3$)



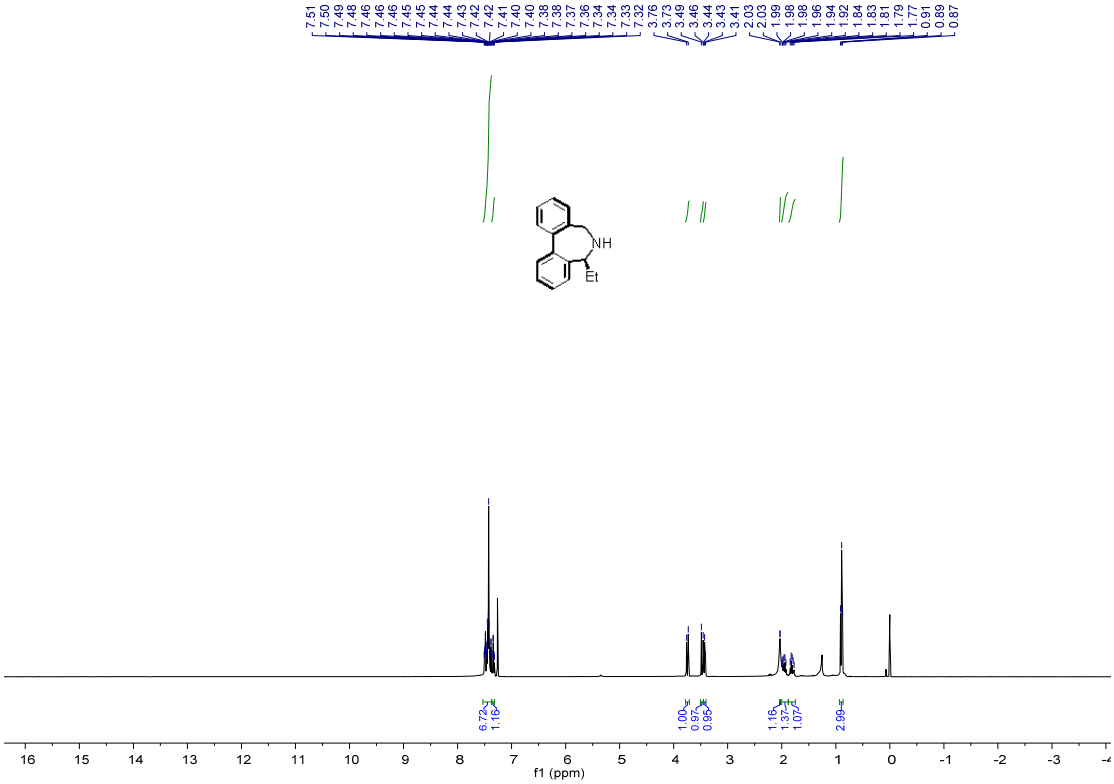
^{1}H NMR for **2l** (400 MHz, $CDCl_3$)



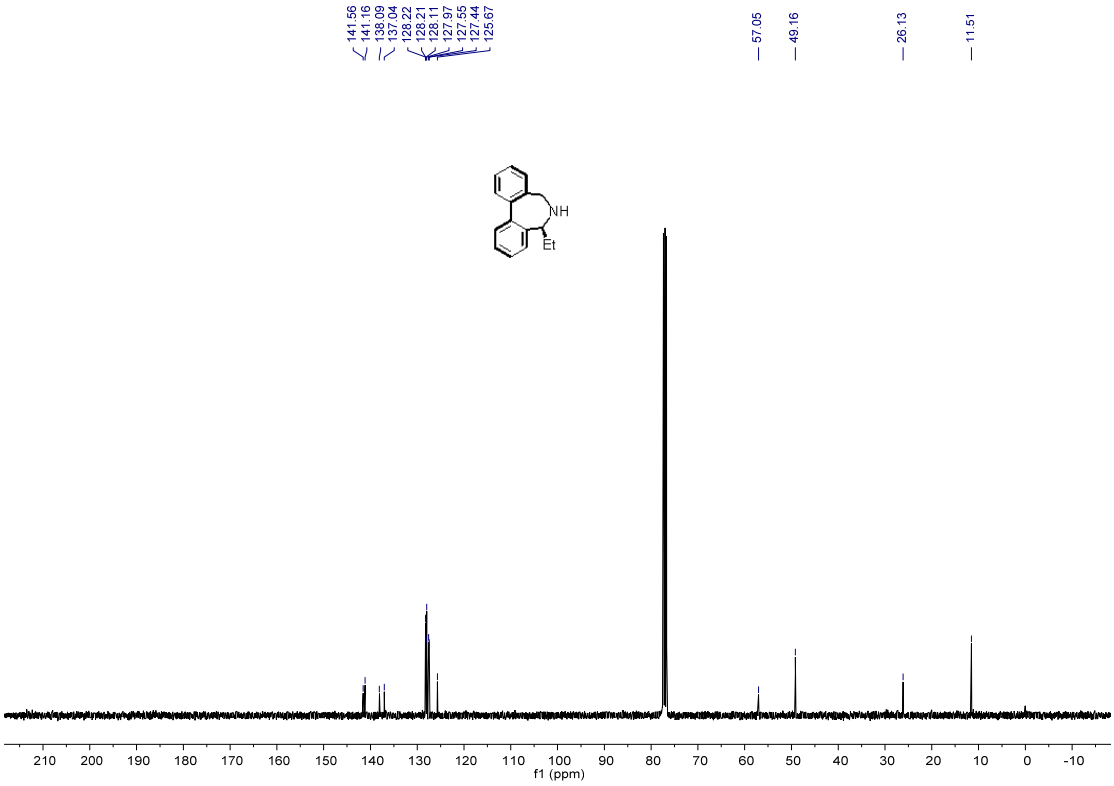
^{13}C NMR for **2l** (101 MHz, $CDCl_3$)



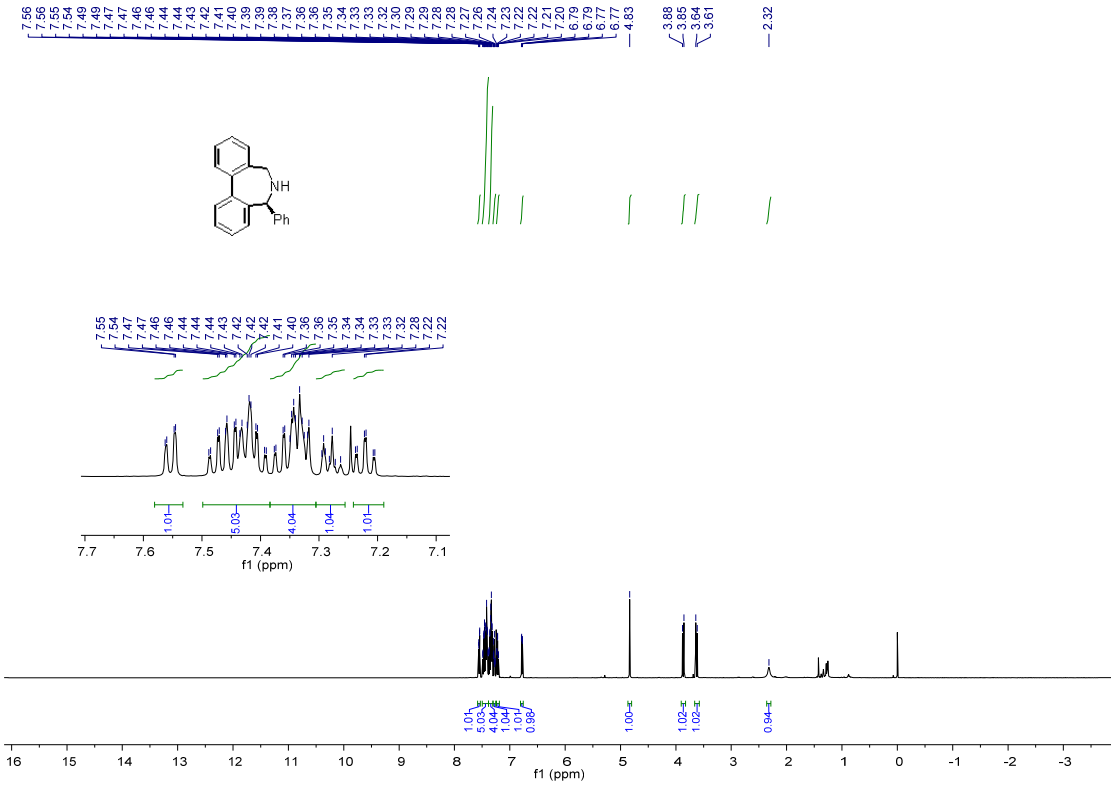
^{1}H NMR for **2m** (400 MHz, $CDCl_3$)



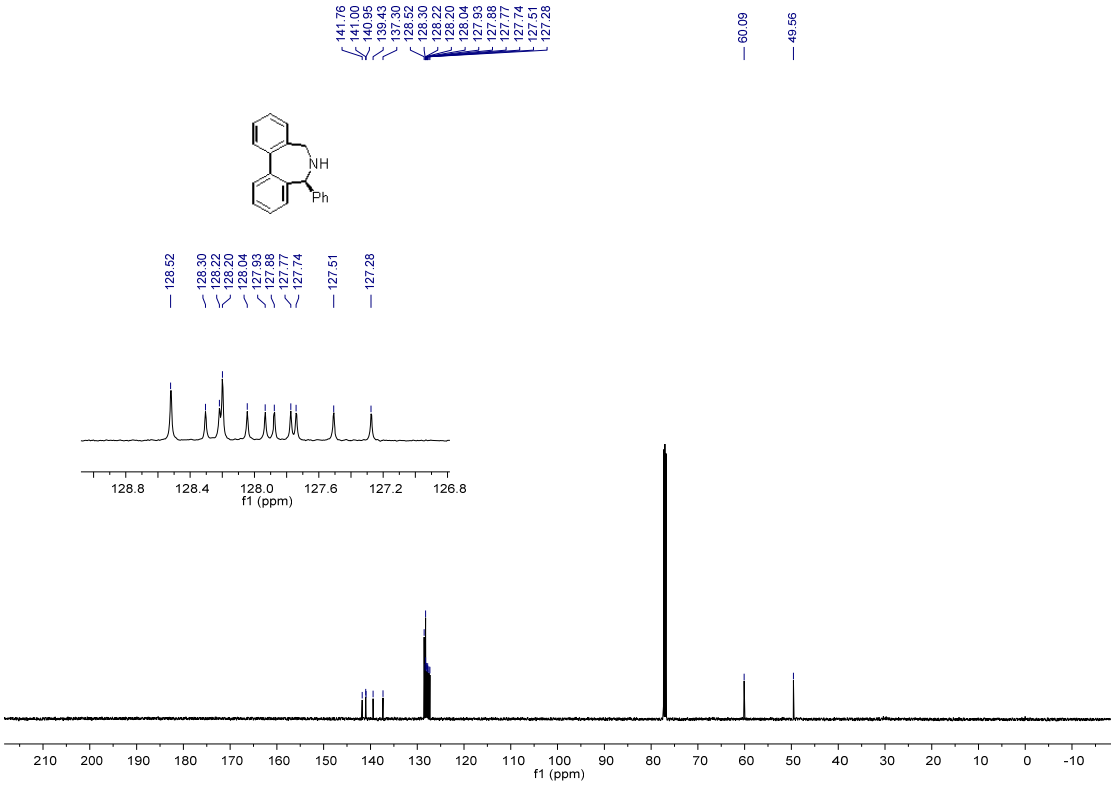
^{13}C NMR for **2m** (101 MHz, $CDCl_3$)



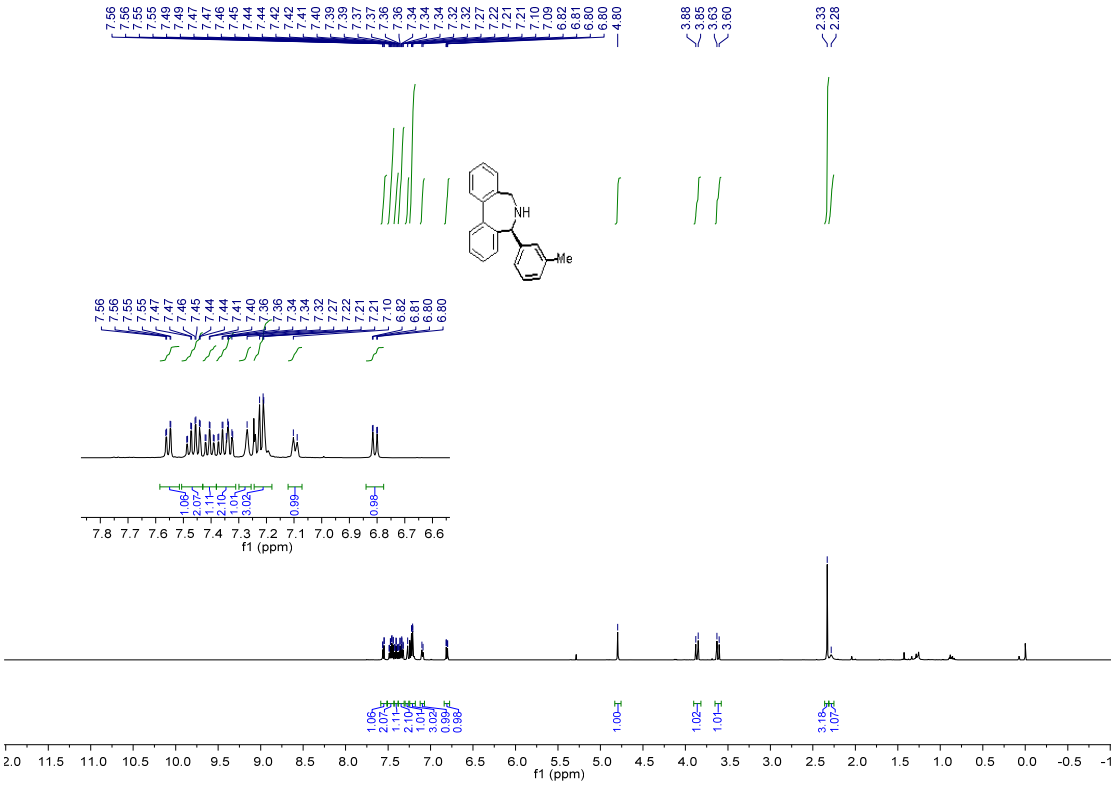
^{1}H NMR for **2n** (500 MHz, $CDCl_3$)



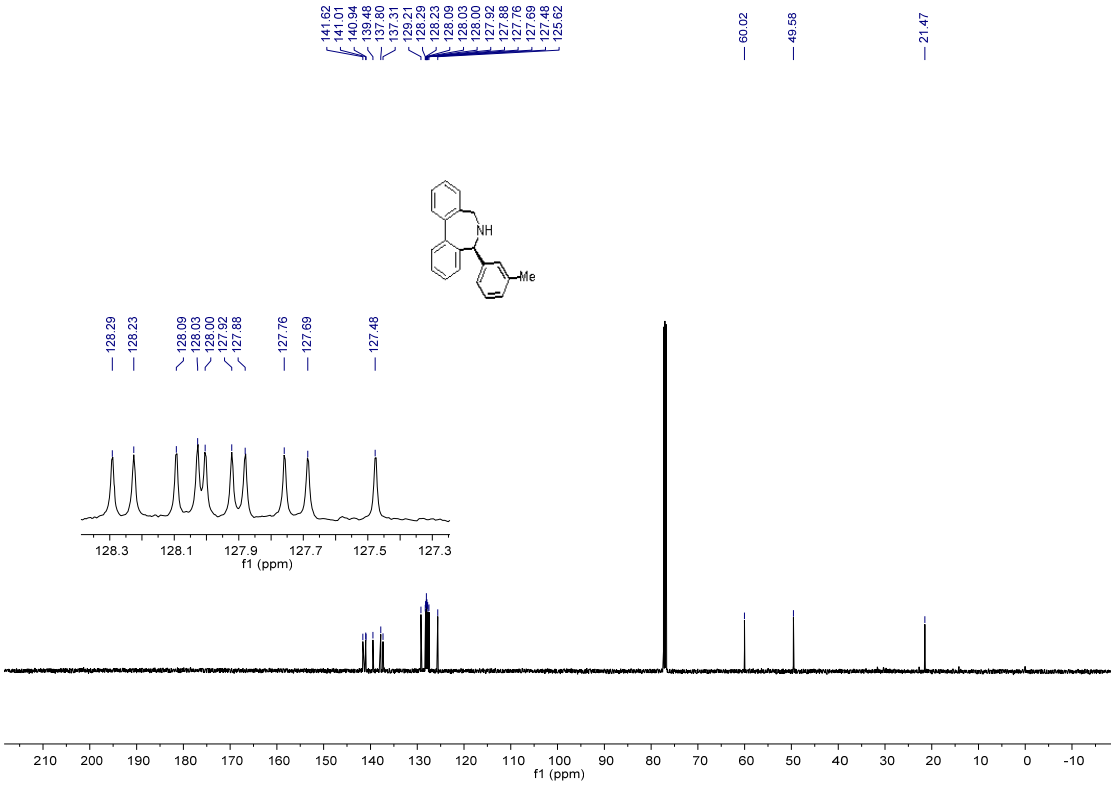
^{13}C NMR for **2n** (126 MHz, $CDCl_3$)



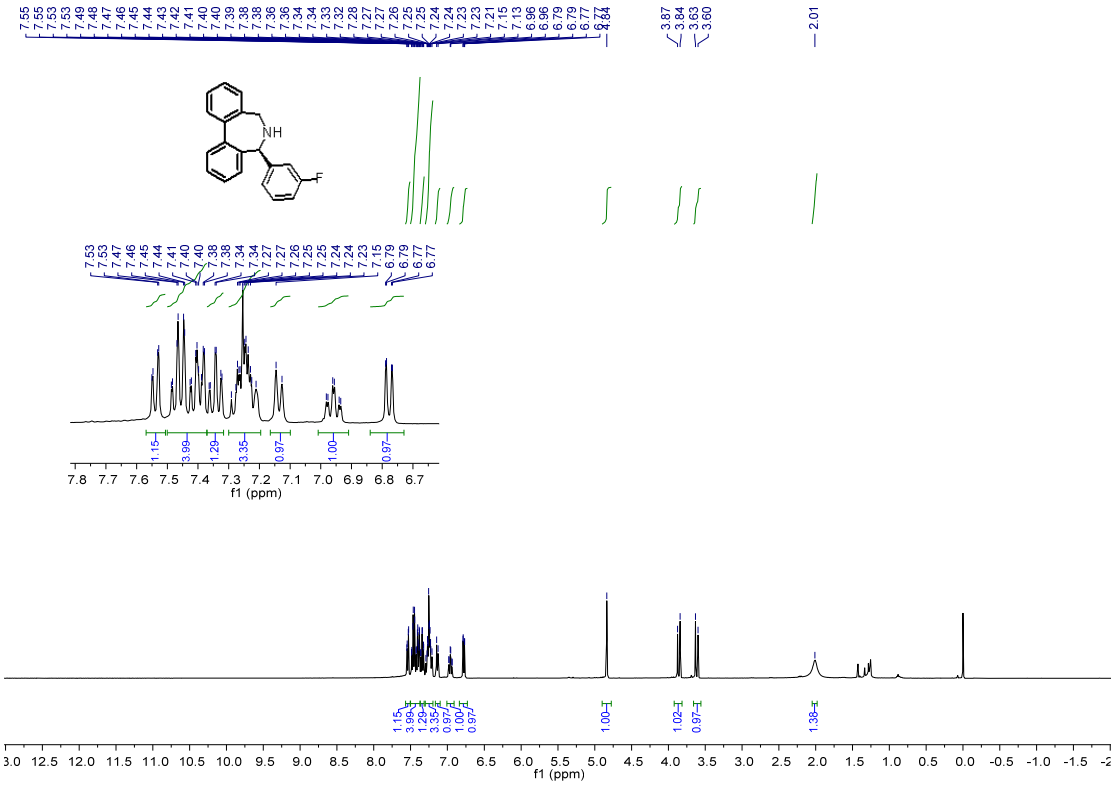
^{1}H NMR for **2o** (500 MHz, $CDCl_3$)



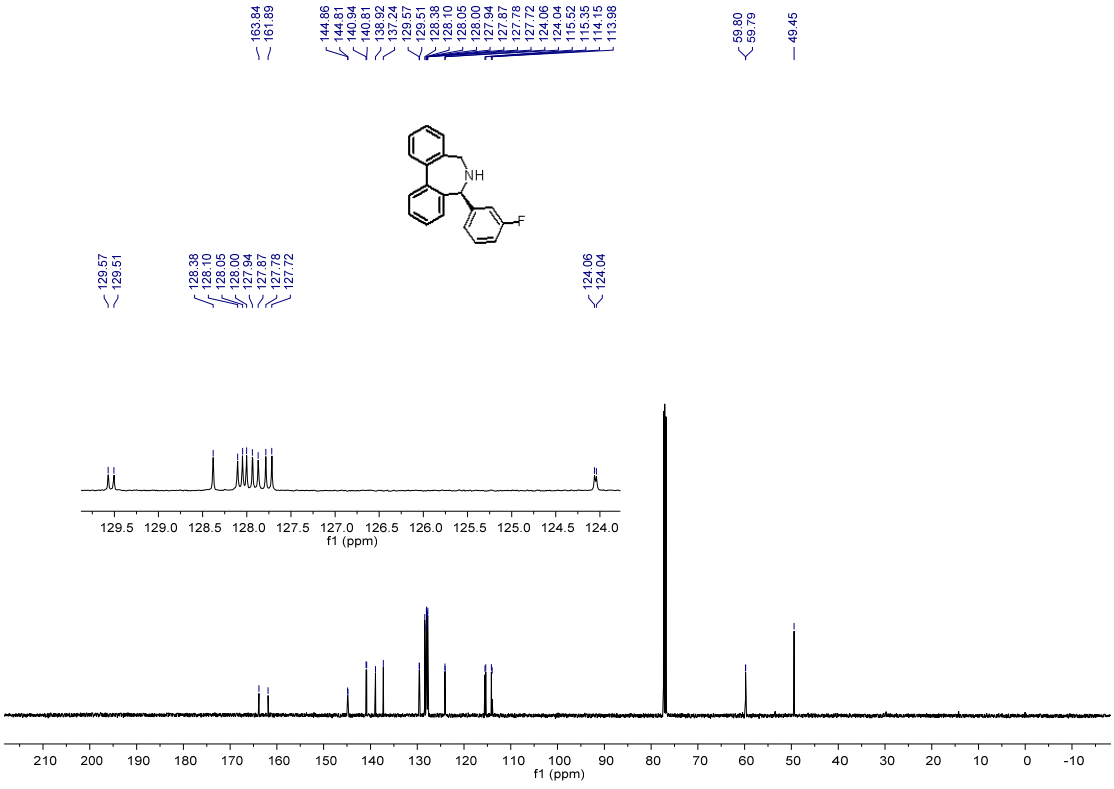
^{13}C NMR for **2o** (126 MHz, $CDCl_3$)



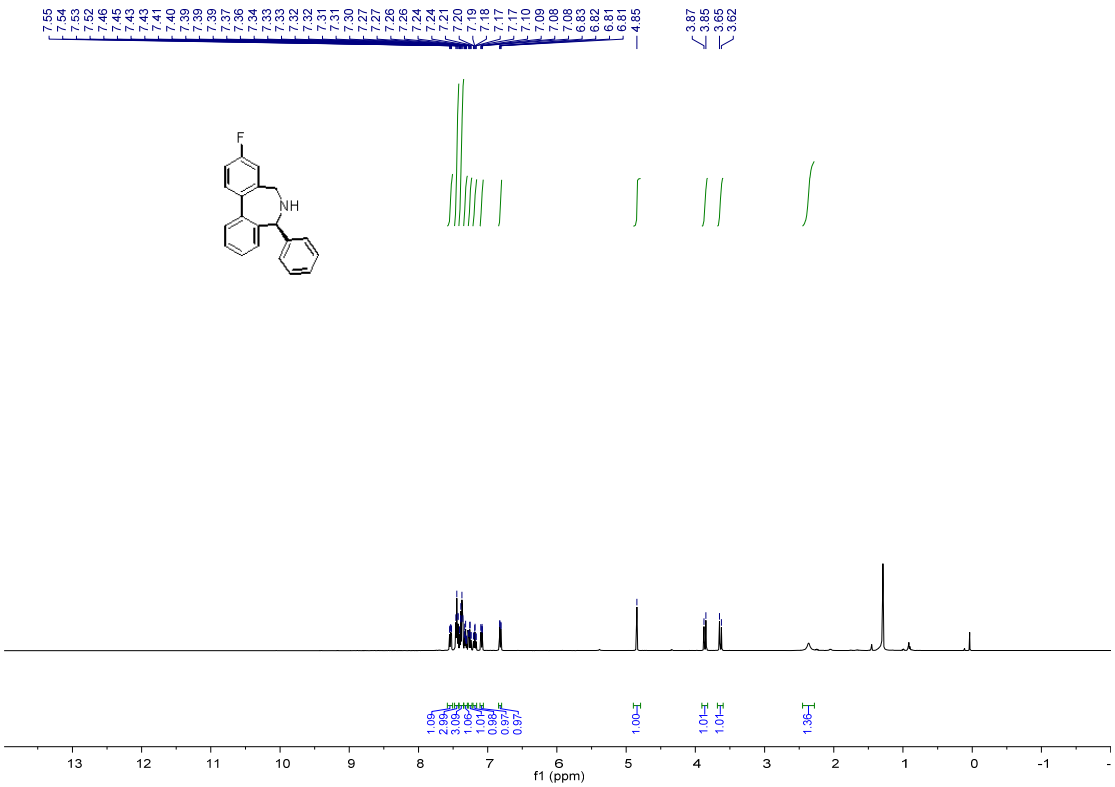
^{1}H NMR for **2p** (500 MHz, $CDCl_3$)



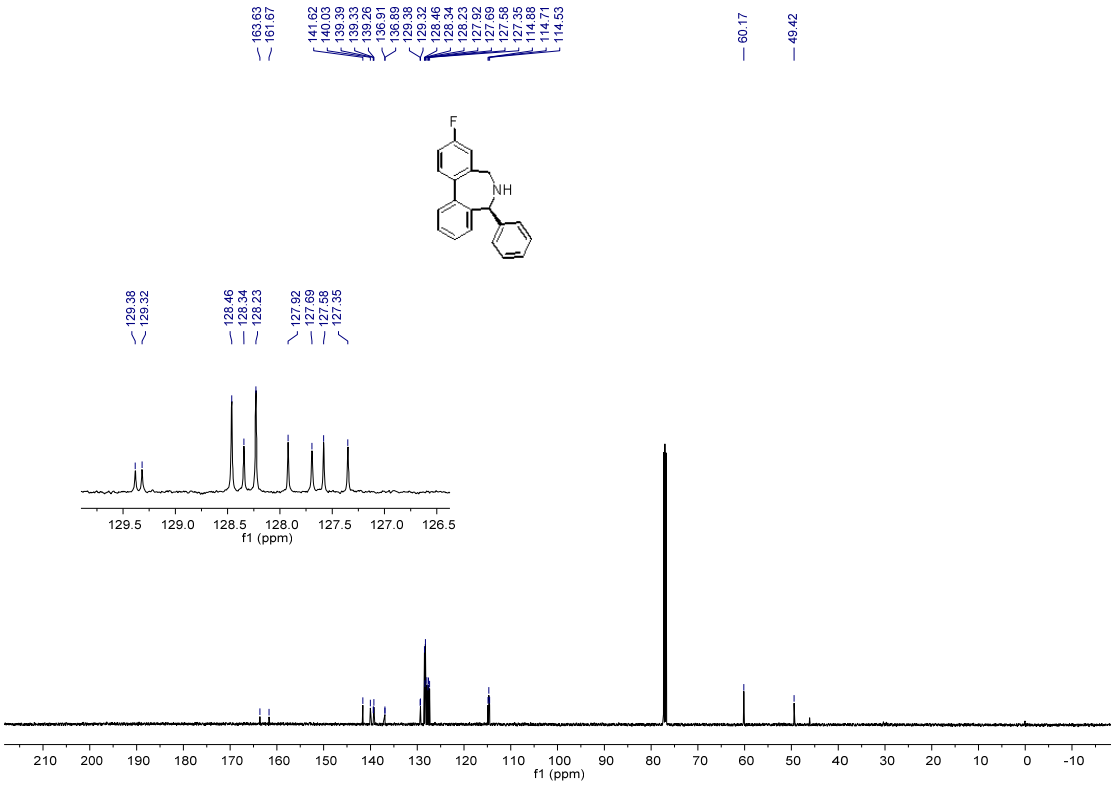
^{13}C NMR for **2p** (126 MHz, $CDCl_3$)



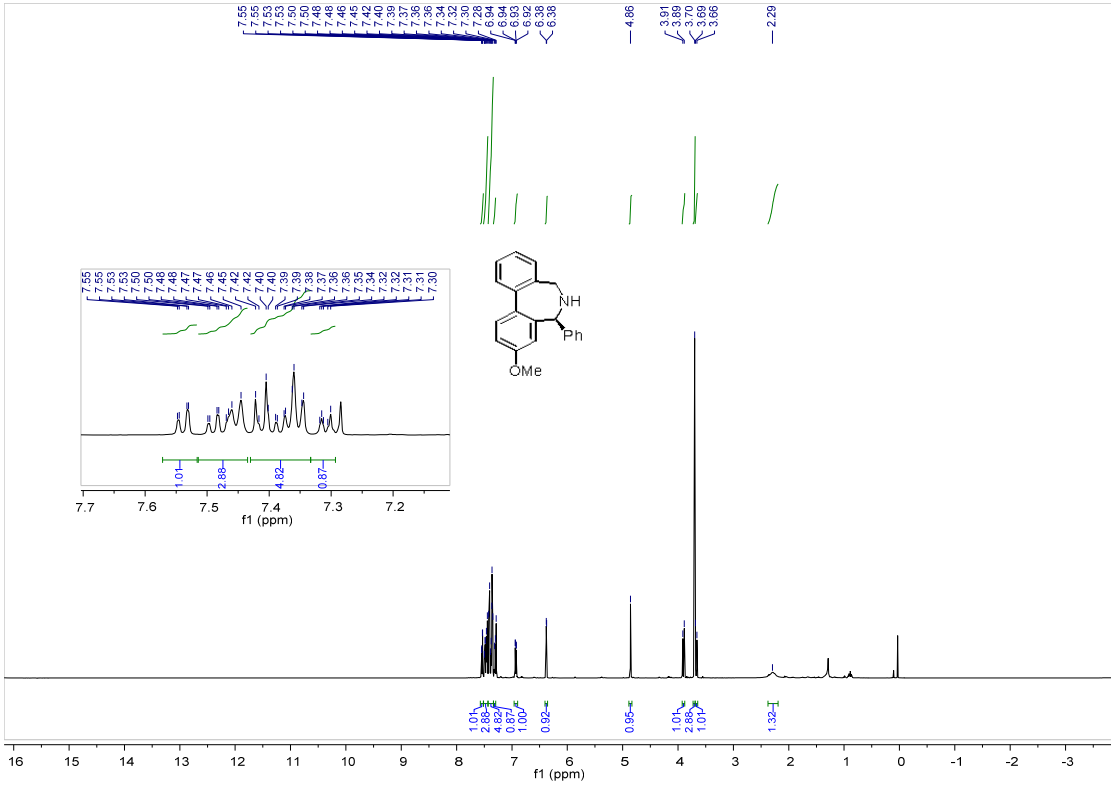
^{1}H NMR for **2q** (500 MHz, $CDCl_3$)



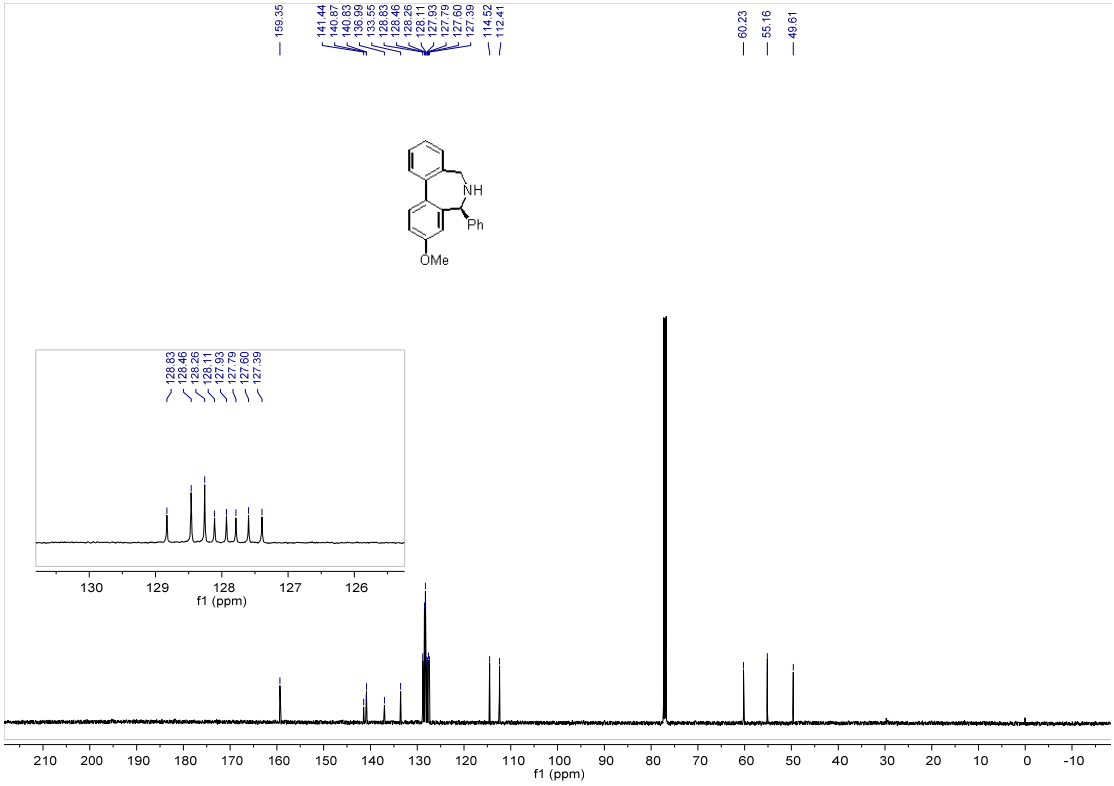
^{13}C NMR for **2q** (126 MHz, $CDCl_3$)



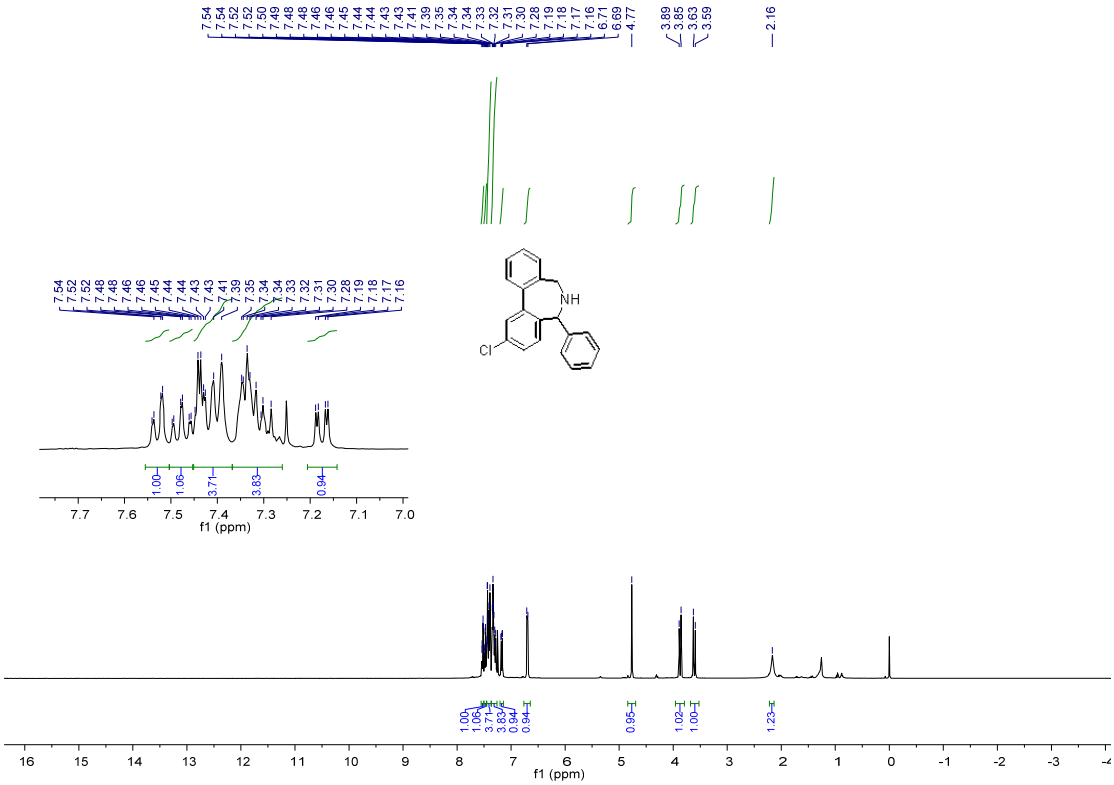
^{1}H NMR for **2r** (500 MHz, $CDCl_3$)



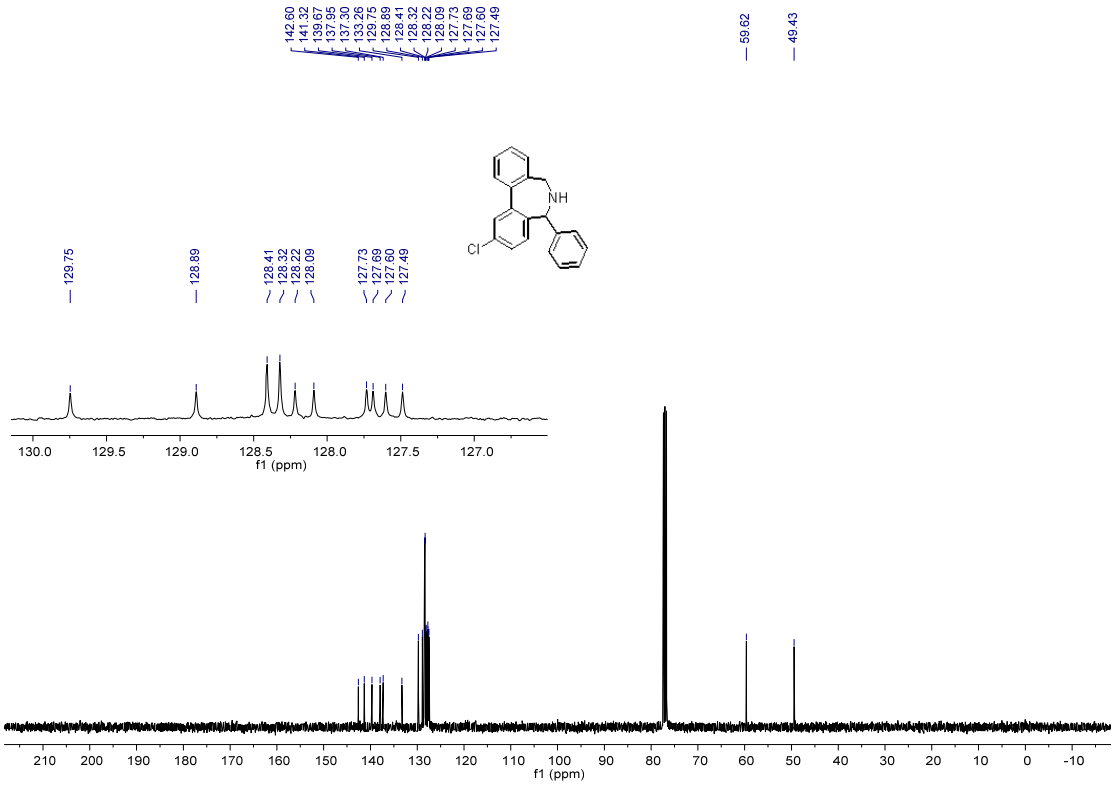
^{13}C NMR for **2r** (126 MHz, $CDCl_3$)



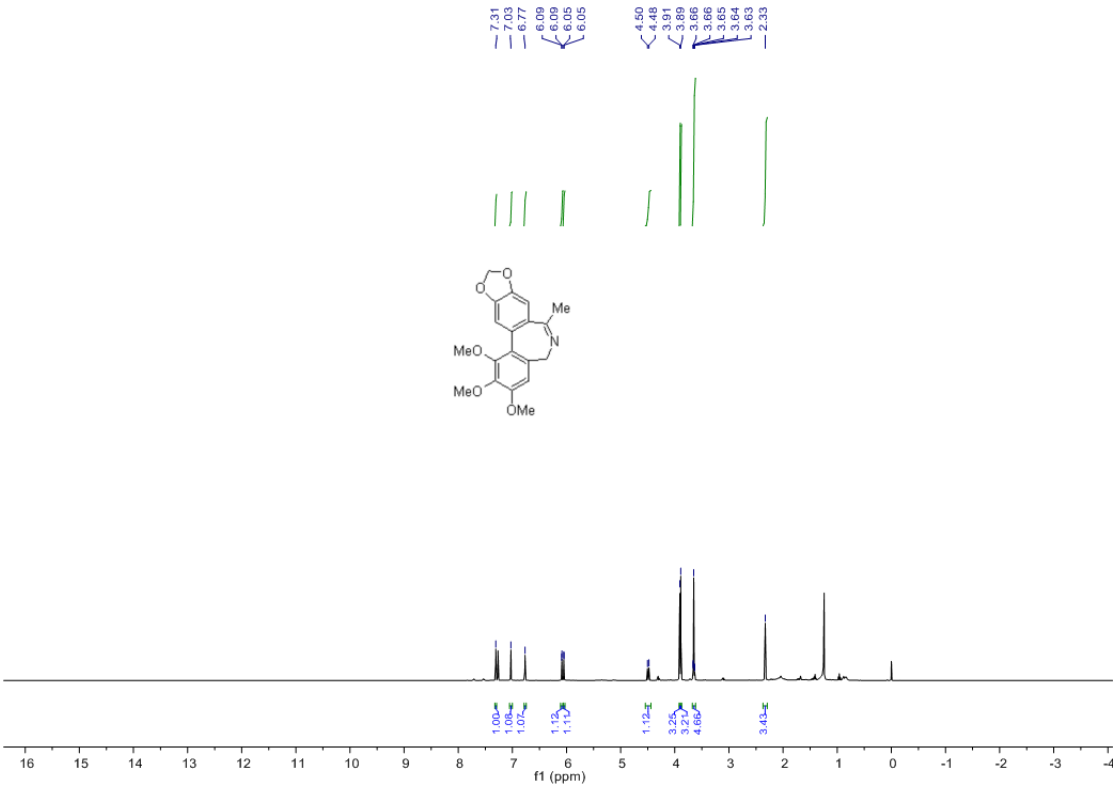
^{1}H NMR for **2s** (500 MHz, $CDCl_3$)



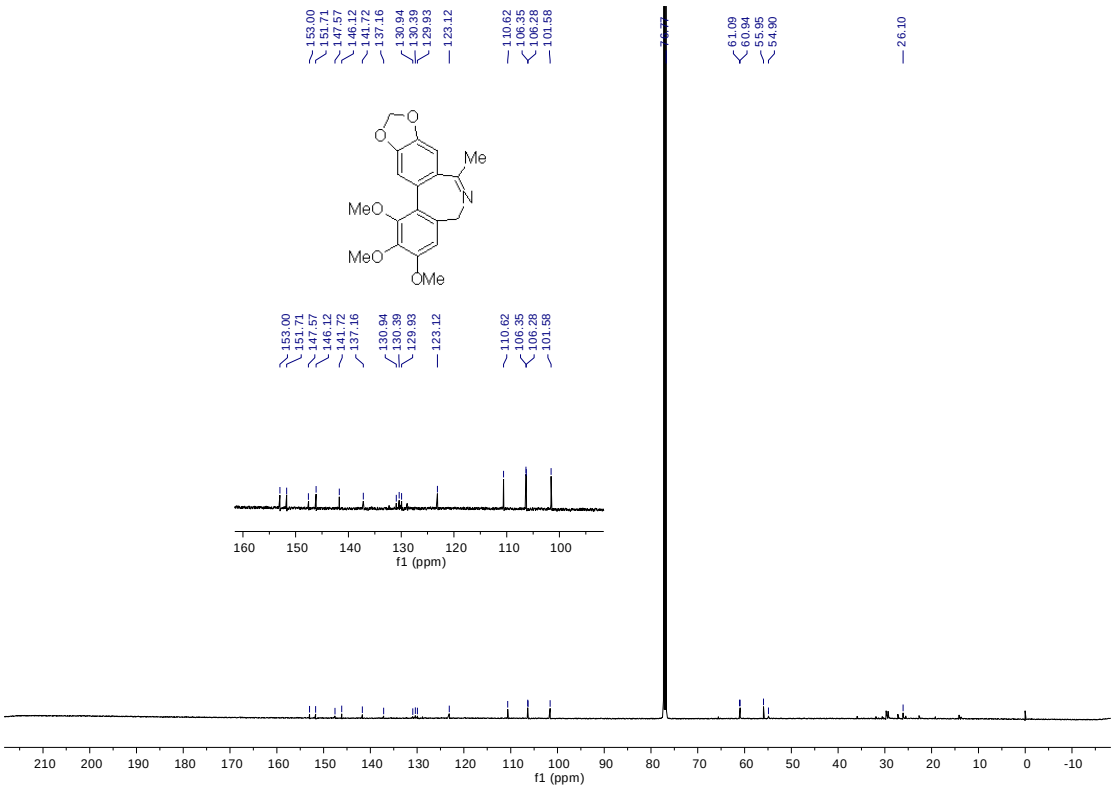
^{13}C NMR for **2s** (101 MHz, $CDCl_3$)



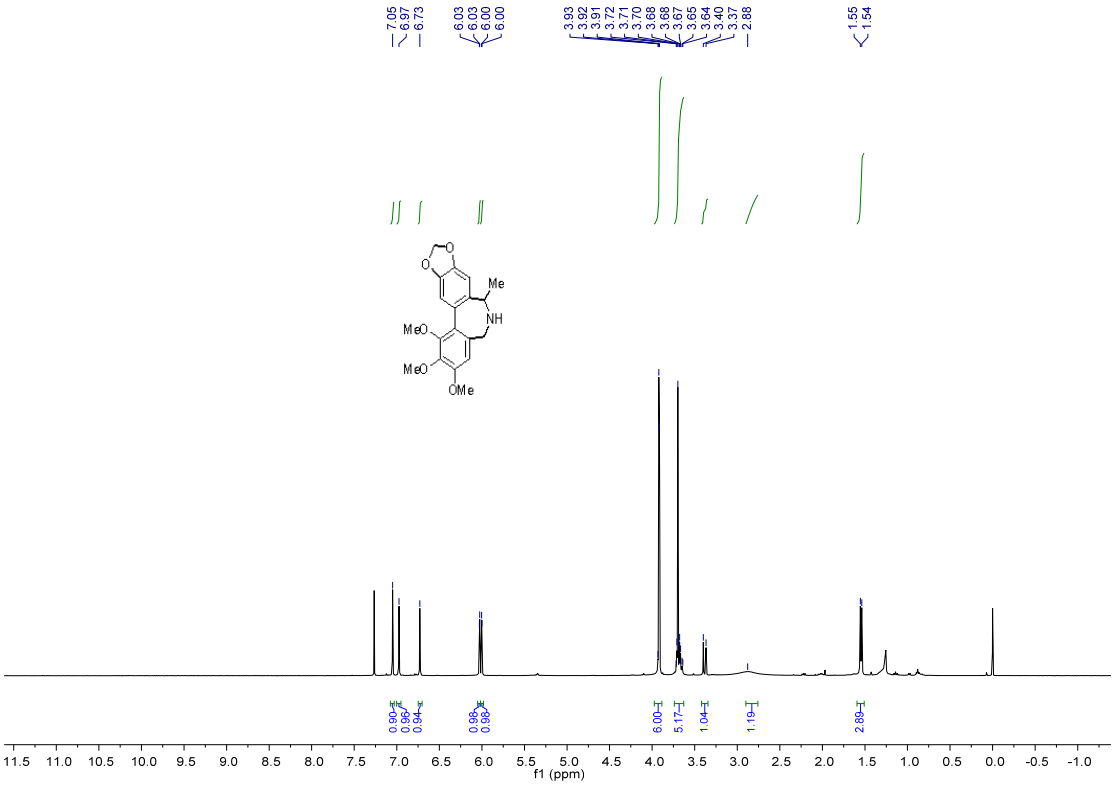
^{1}H NMR for **S-4-4** (400 MHz, $CDCl_3$)



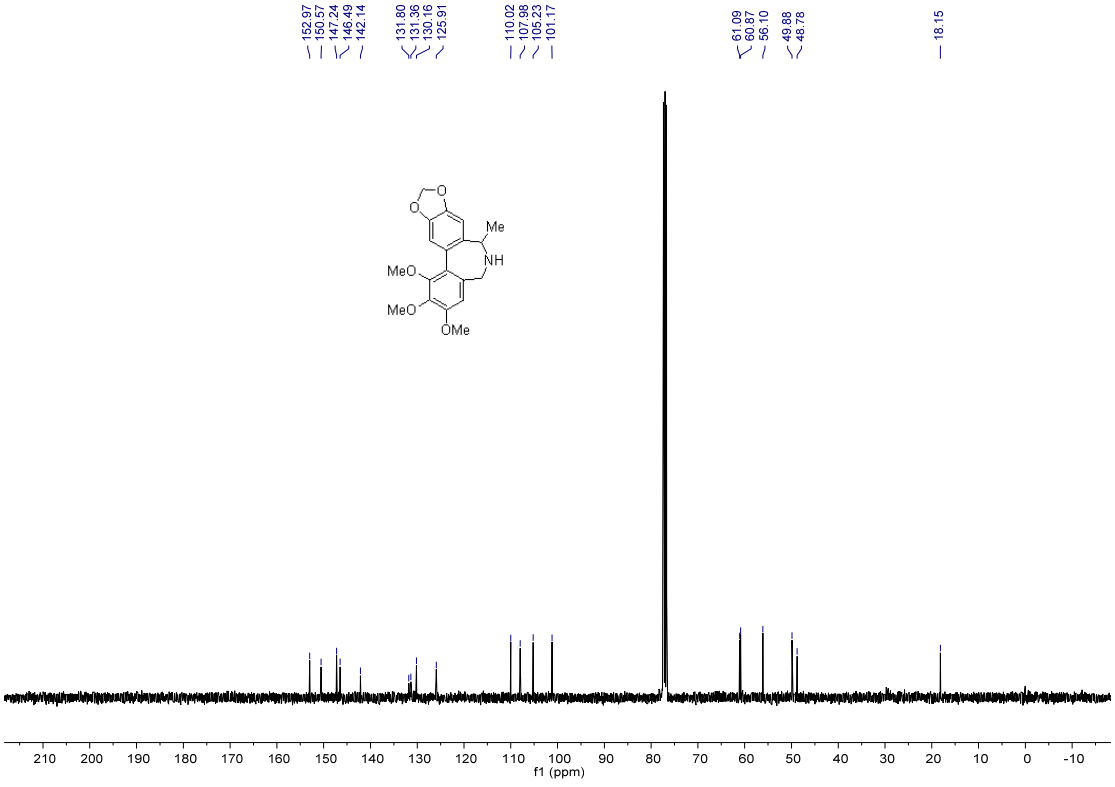
^{13}C NMR for **S-4-4** (126 MHz, $CDCl_3$)



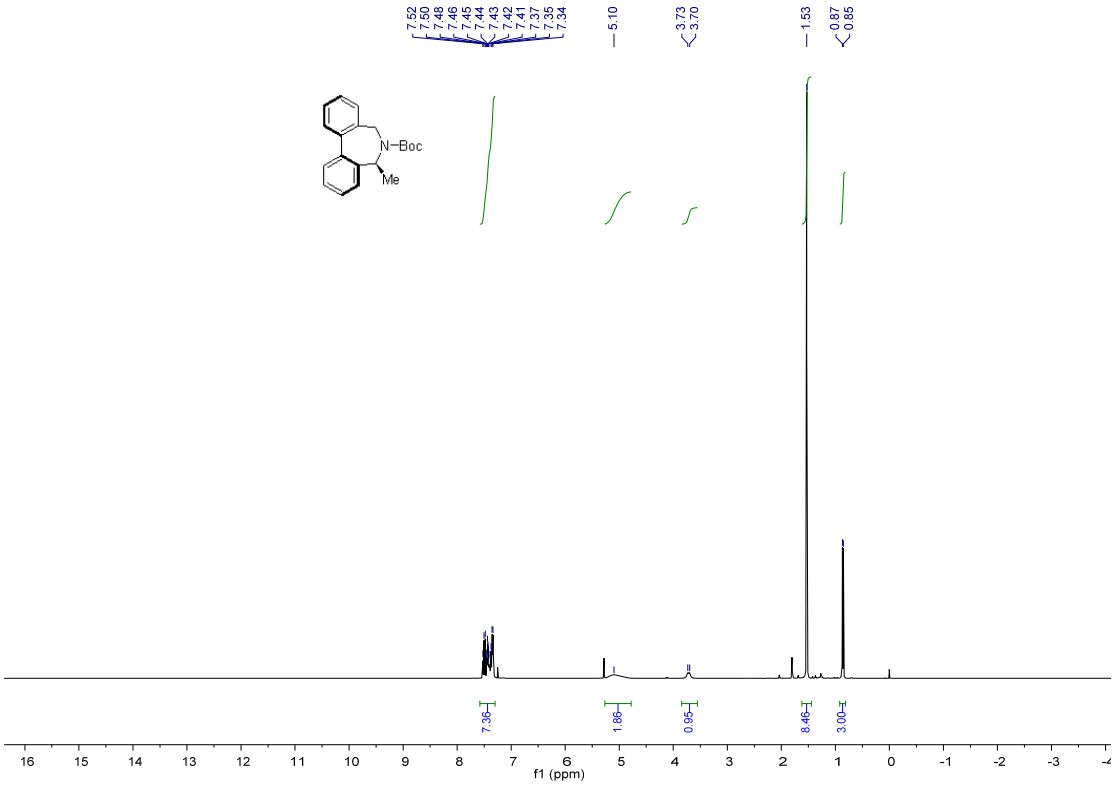
^{1}H NMR for **B** (500 MHz, $CDCl_3$)



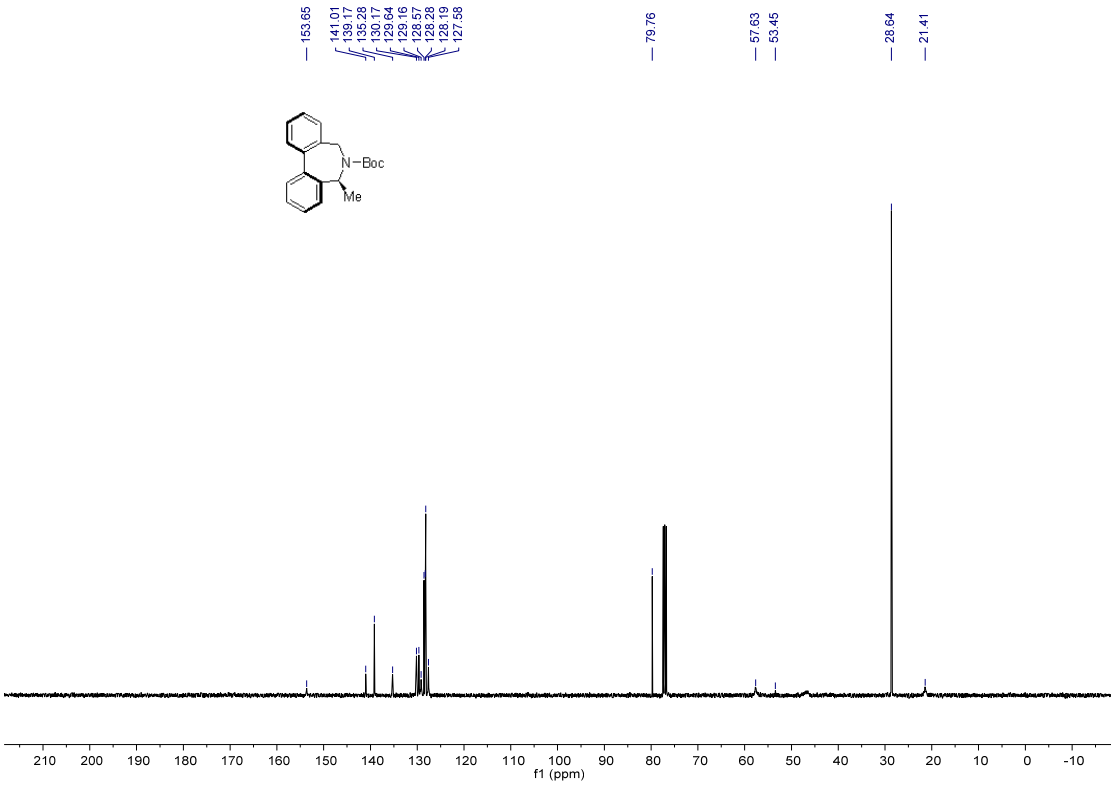
^{13}C NMR for **B** (101 MHz, $CDCl_3$)



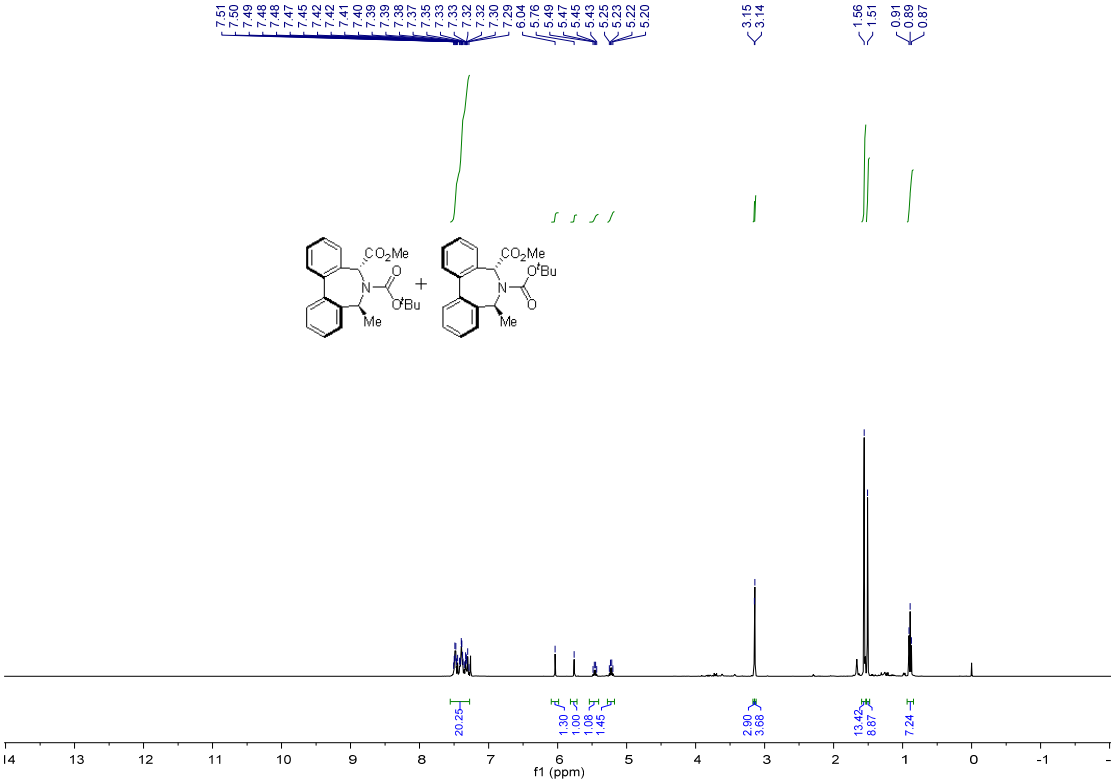
^{1}H NMR for **5** (400 MHz, $CDCl_3$)



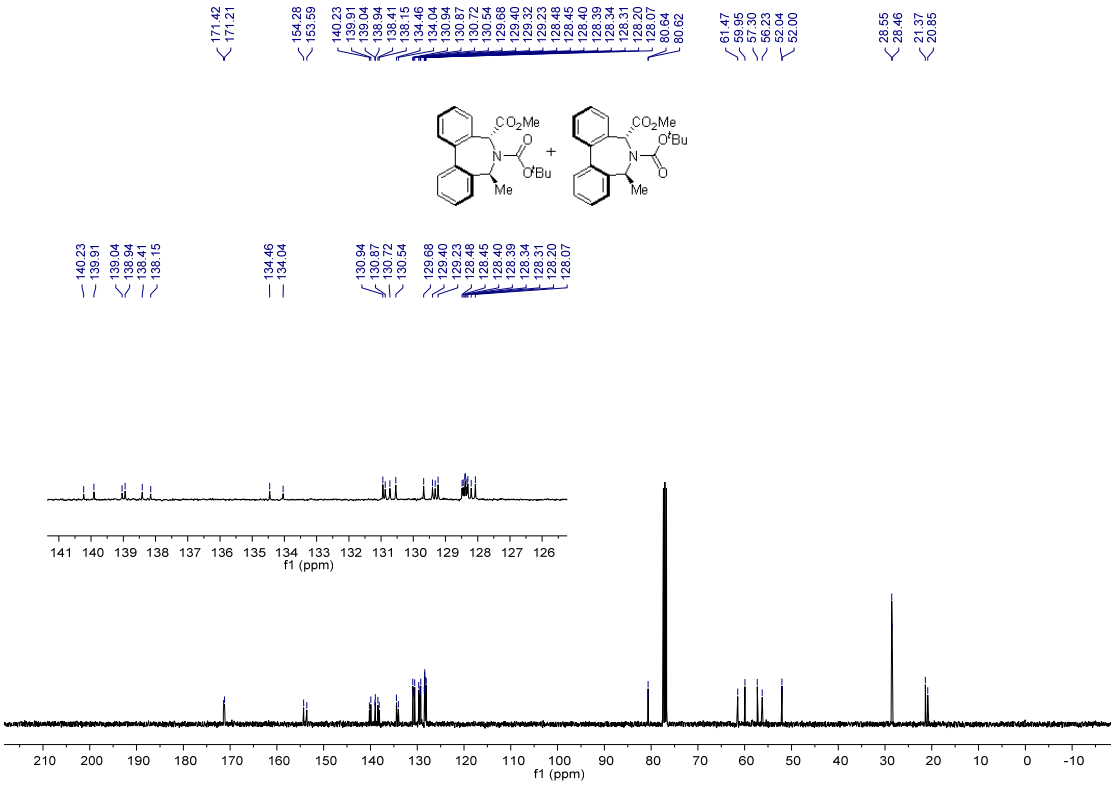
^{13}C NMR for **5** (101 MHz, $CDCl_3$)



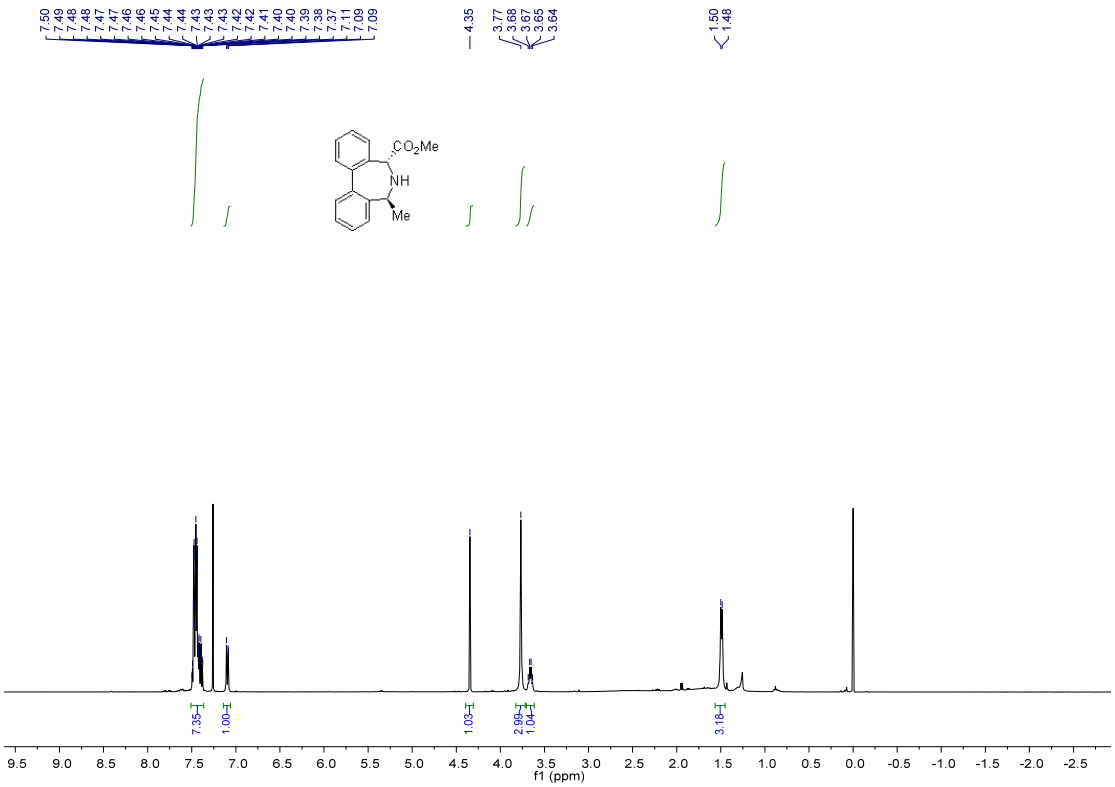
^{1}H NMR for **6** (400 MHz, $CDCl_3$)



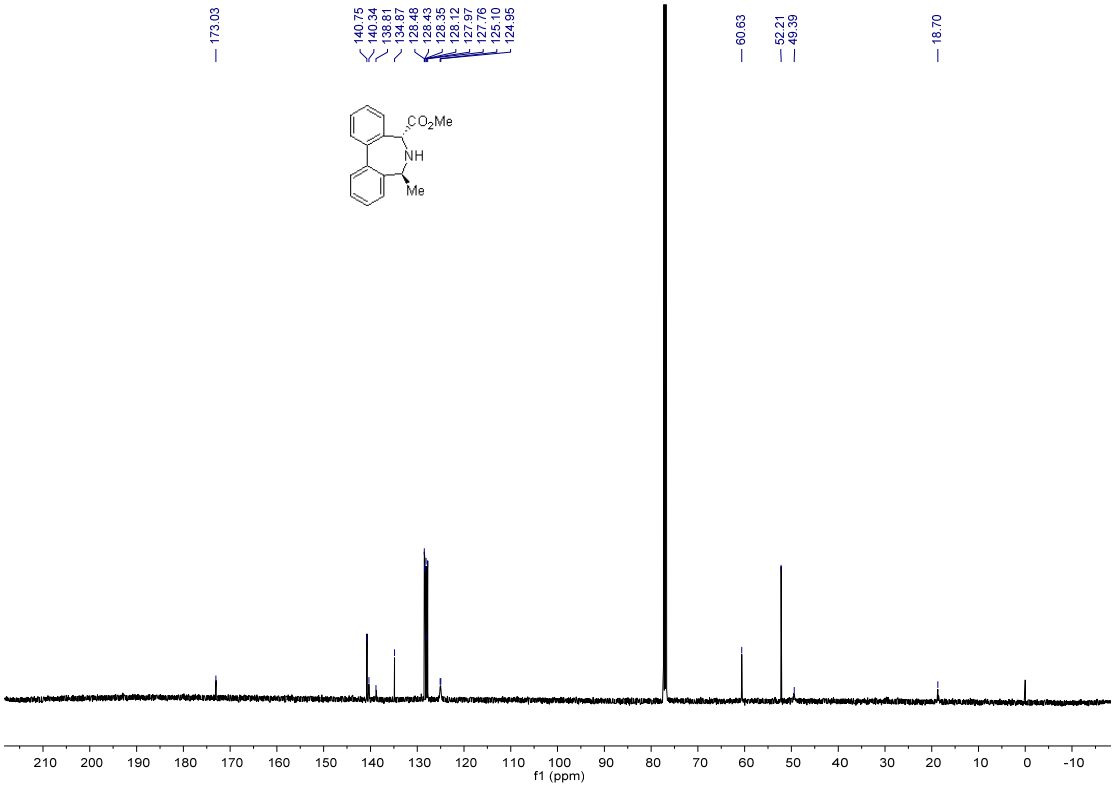
^{13}C NMR for **6** (101 MHz, $CDCl_3$)



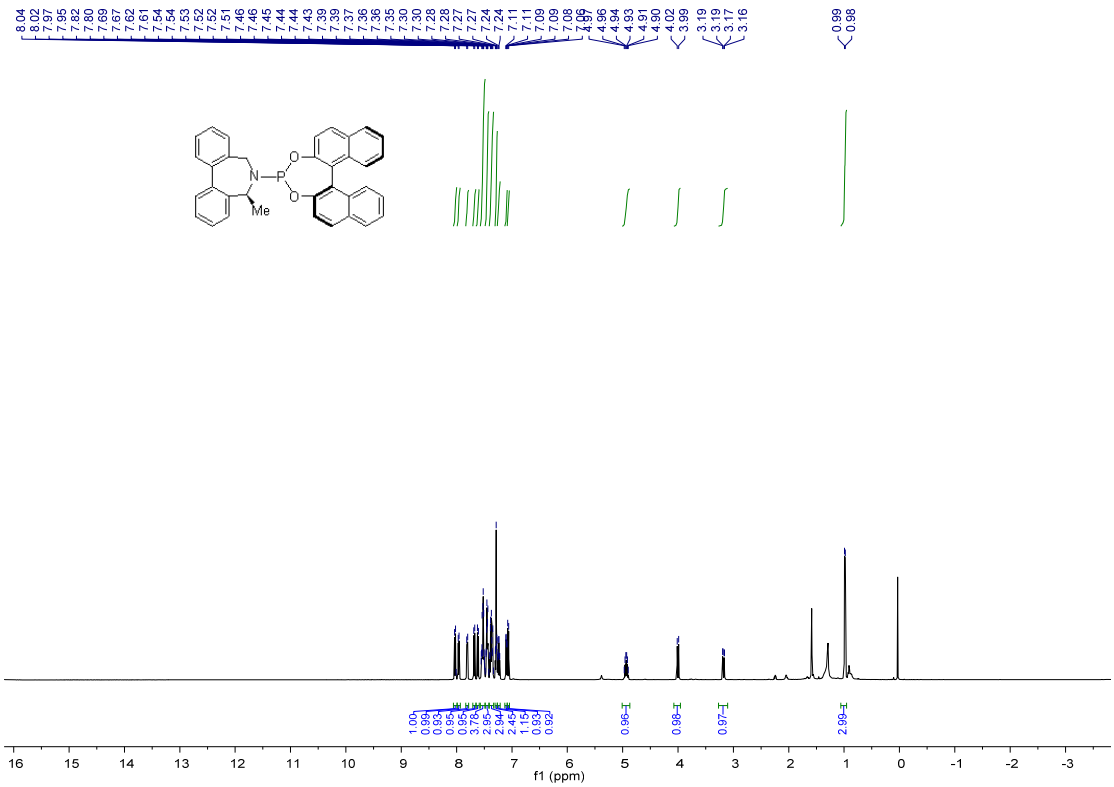
^{1}H NMR for **7** (400 MHz, $CDCl_3$)



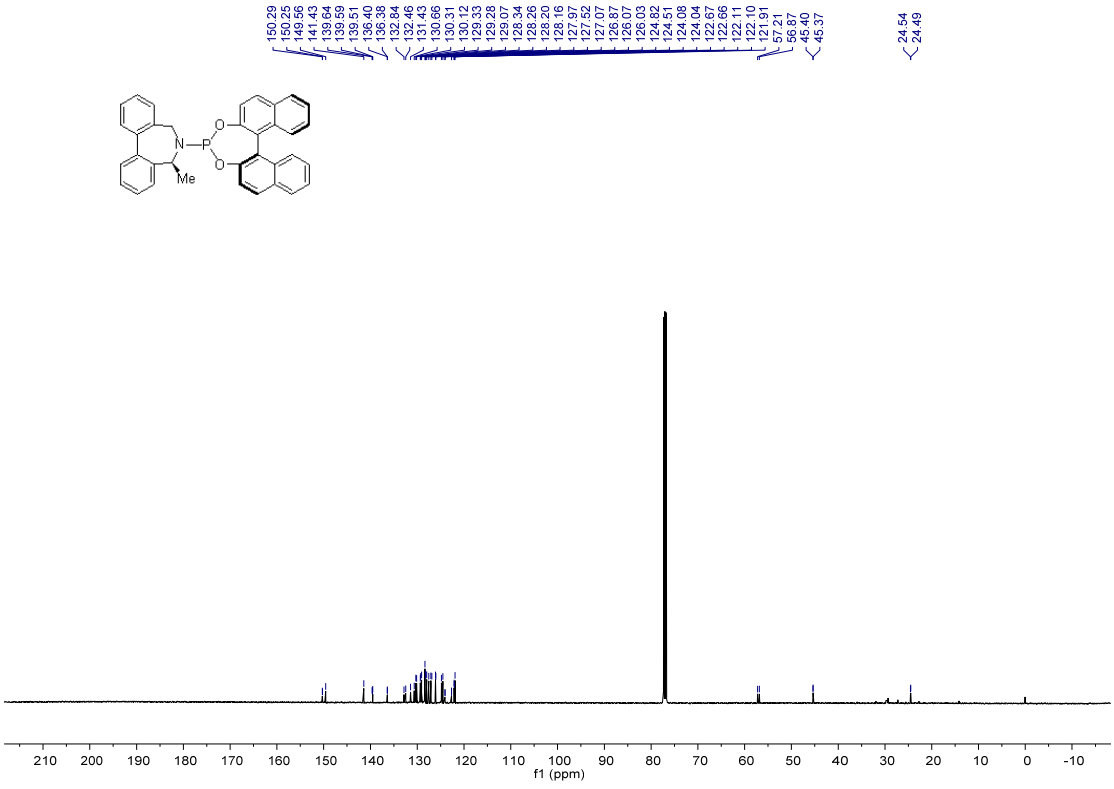
^{13}C NMR for **7** (126 MHz, $CDCl_3$)



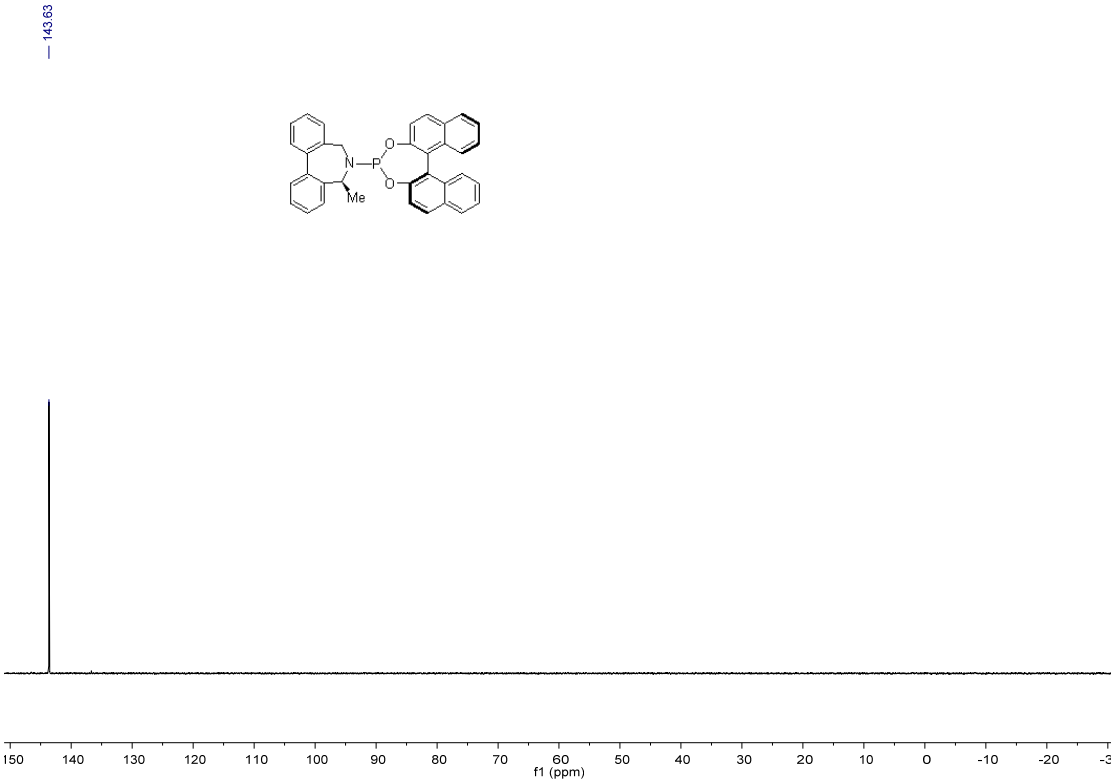
^{1}H NMR for **L1** (500 MHz, $CDCl_3$)



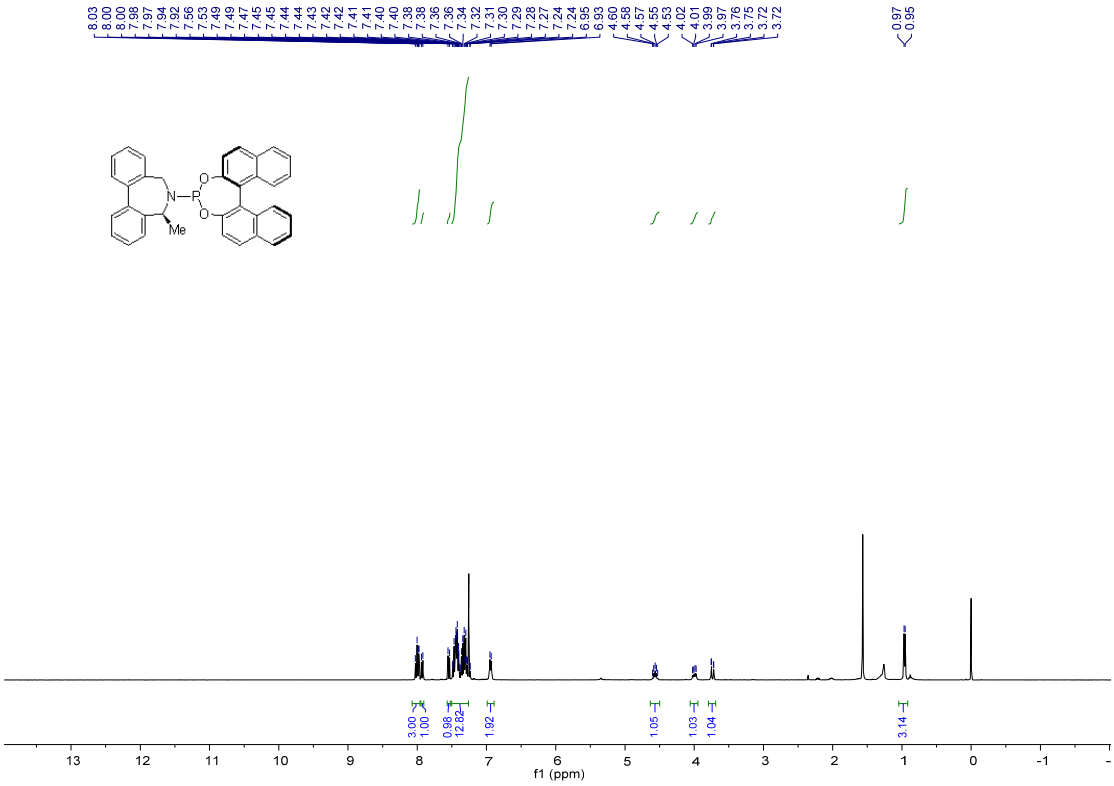
^{13}C NMR for **L1** (126 MHz, $CDCl_3$)



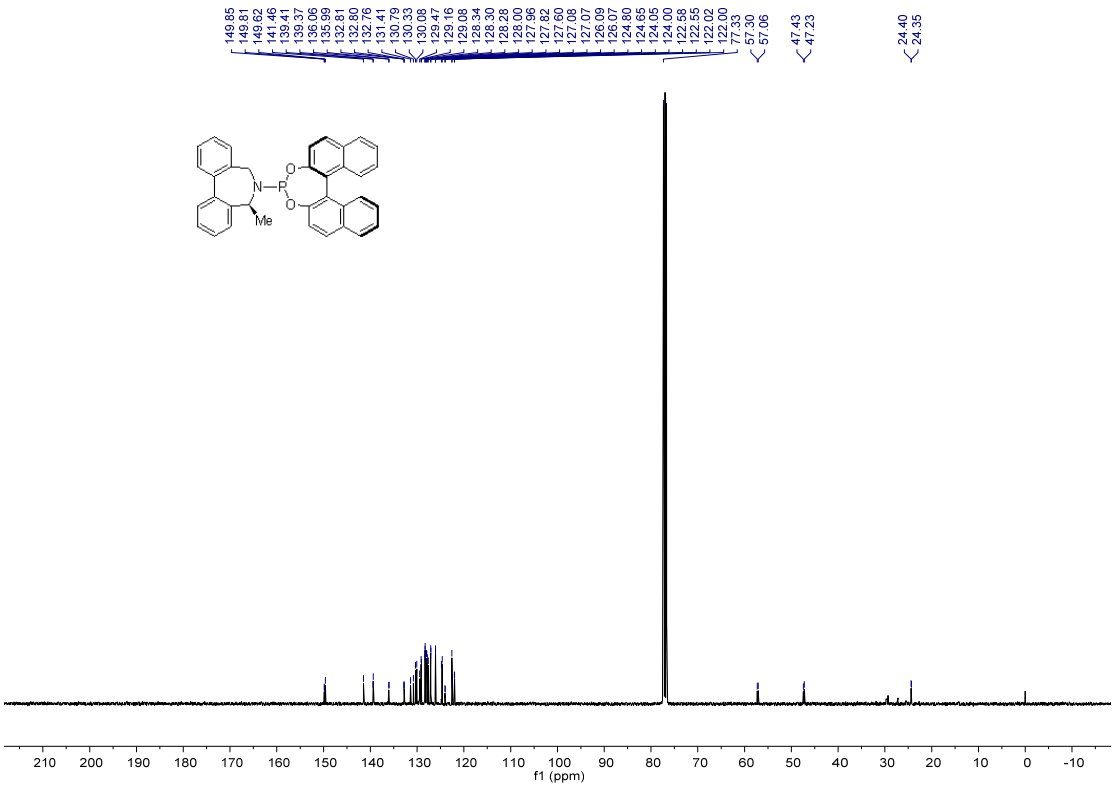
^{31}P NMR for **L1** (202 MHz, $CDCl_3$)



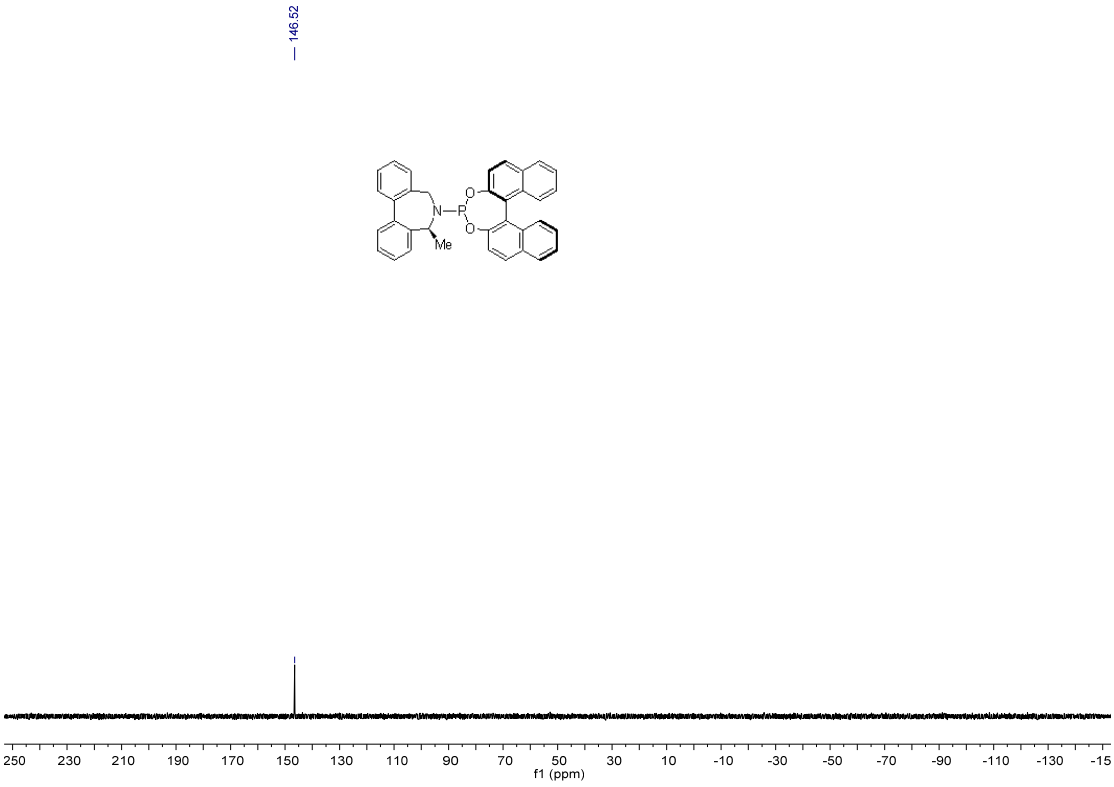
^{1}H NMR for **L2** (500 MHz, $CDCl_3$)



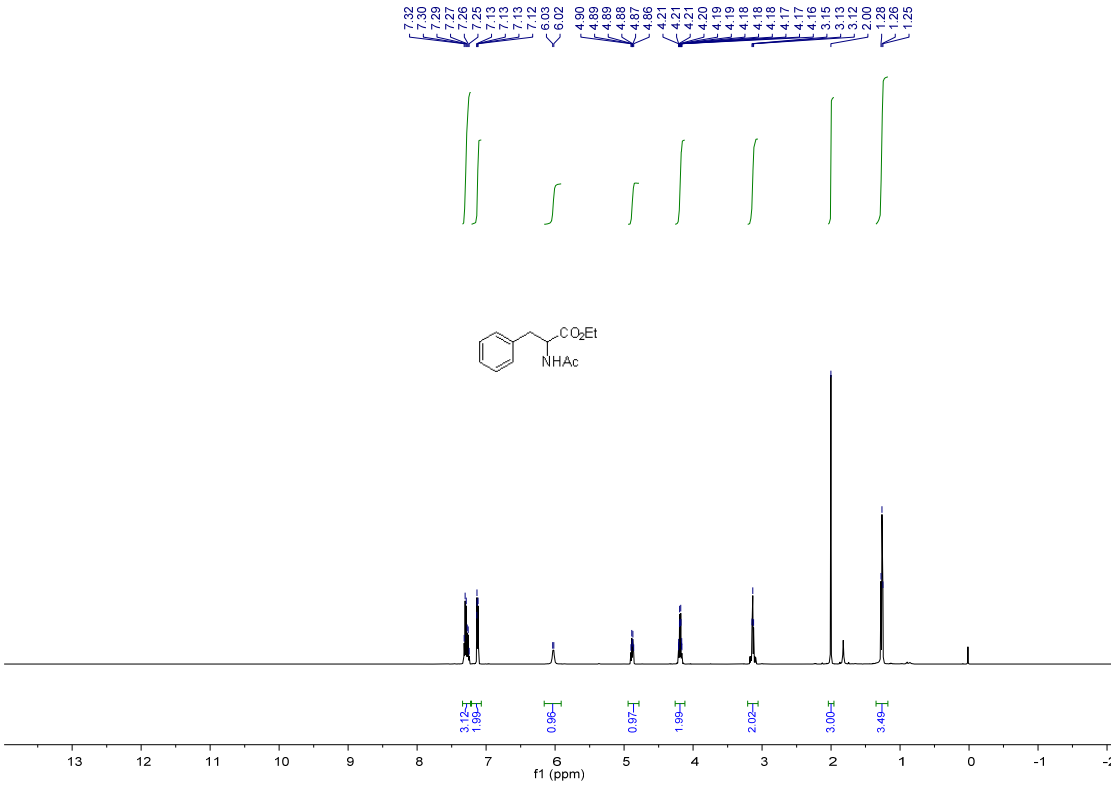
^{13}C NMR for **L2** (126 MHz, $CDCl_3$)



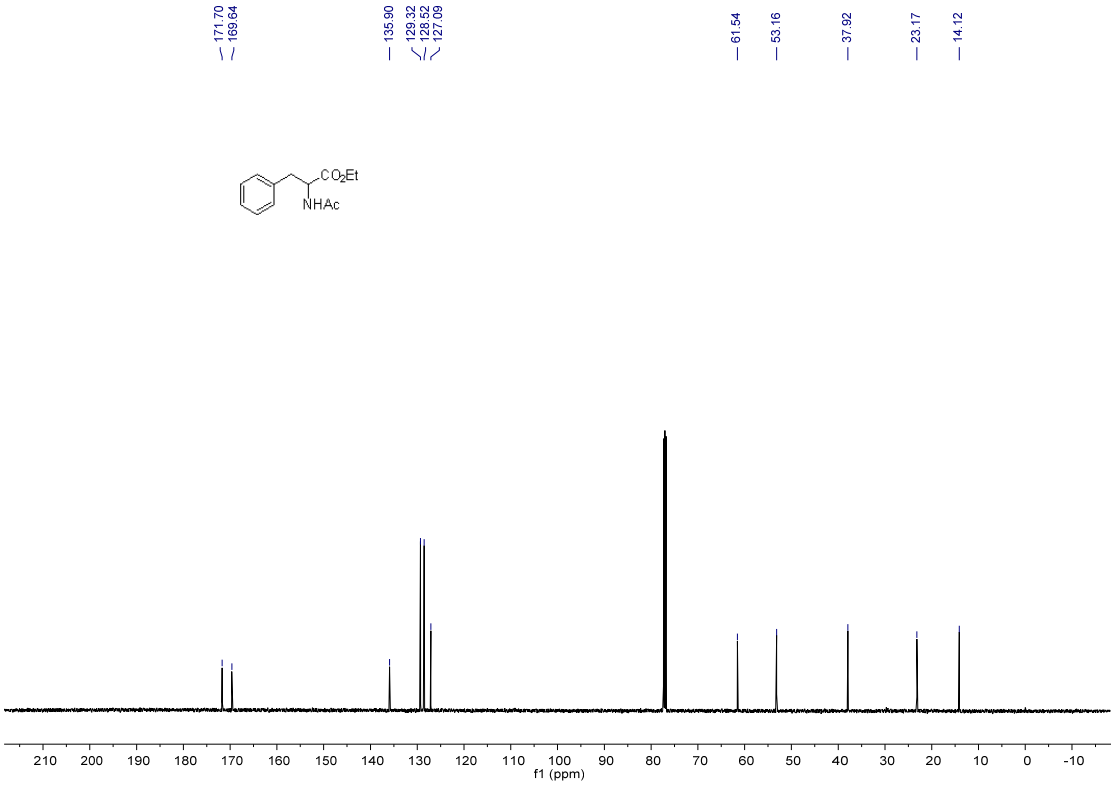
^{31}P NMR for **L2** (202 MHz, $CDCl_3$)



^{1}H NMR for **8** (500 MHz, $CDCl_3$)

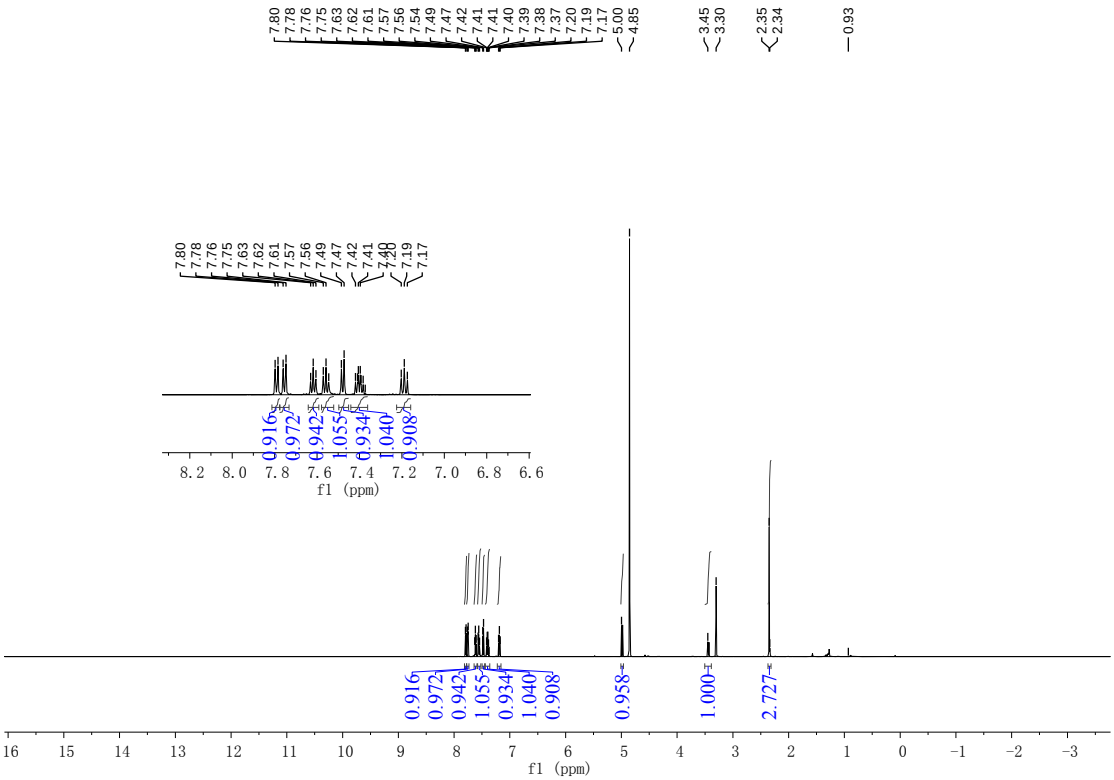


^{13}C NMR for **8** (126 MHz, $CDCl_3$)

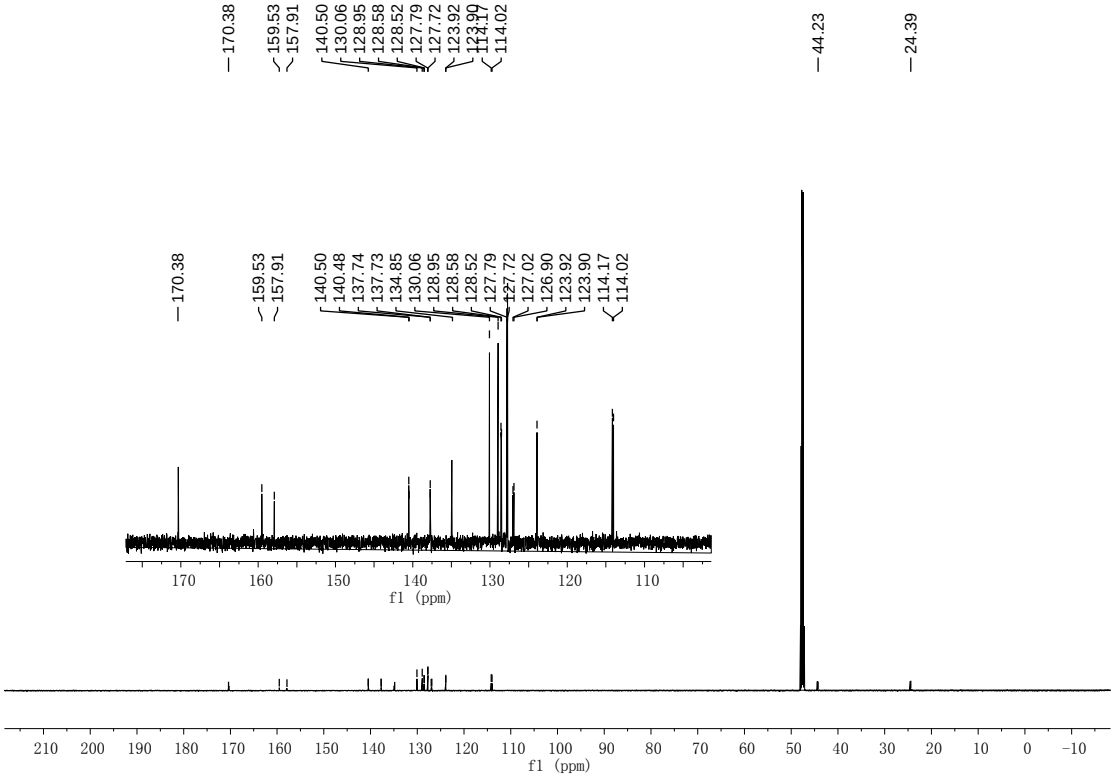


^{1}H NMR for **1e-imine** (600 MHz, CD_3OD)

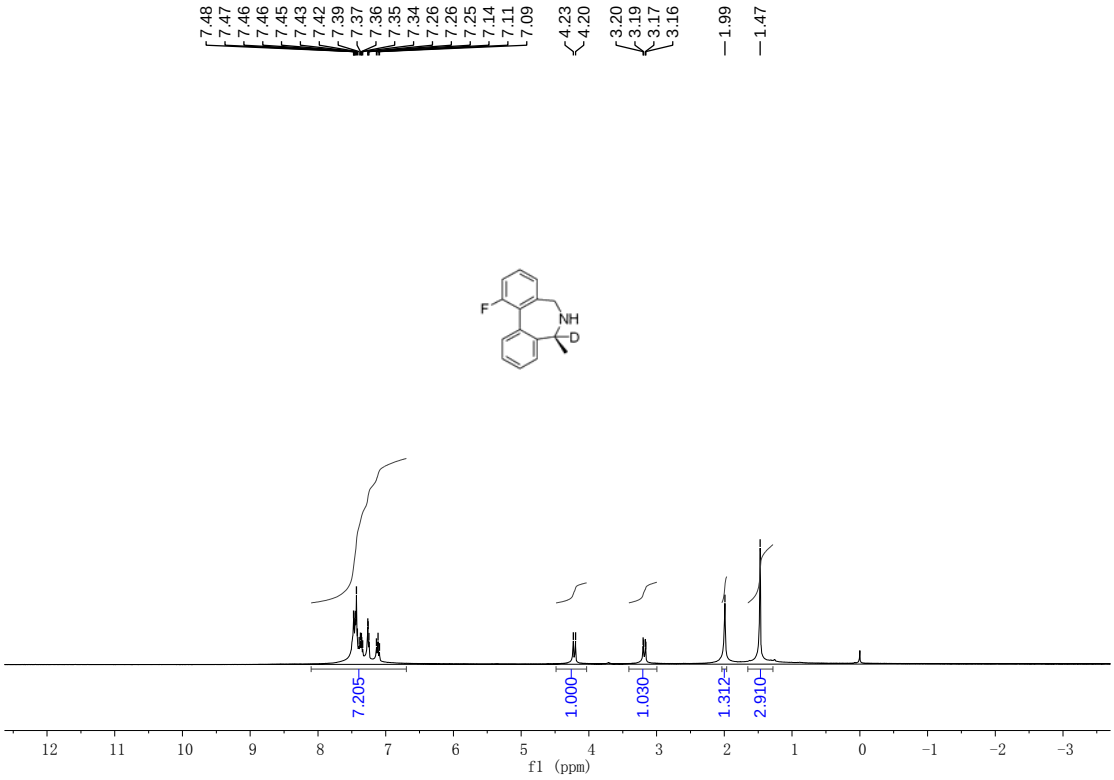
^{1}H NMR for **1e-imine** (600 MHz, CD_3OD)



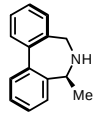
^{13}C NMR for **1e-imine** (151 MHz, CD_3OD)



^{1}H NMR for **d-2e** (400 MHz, $CDCl_3$)



8. HPLC spectra

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Acq. Instrument : 1260-DAD                      Location :   P1-A-01
Injection Date  : 3/30/2018 16:16:59               Inj :   2
                                              Inj Volume : 1.000 µl
Acq. Method     : d:\Chem32\1\Data\YANGTAO\YT-3-81A-2 2018-03-30 15-55-14\YANGT-AD-3-80-20-0.
                  8-20MIN .M
Last changed    : 3/30/2018 16:31:44 by SYSTEM
                  (modified after loading)
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-81A-2 2018-03-30 15-55-14\YANGT-AD-3-80-20-0.
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Last changed    : 3/31/2018 16:01:05 by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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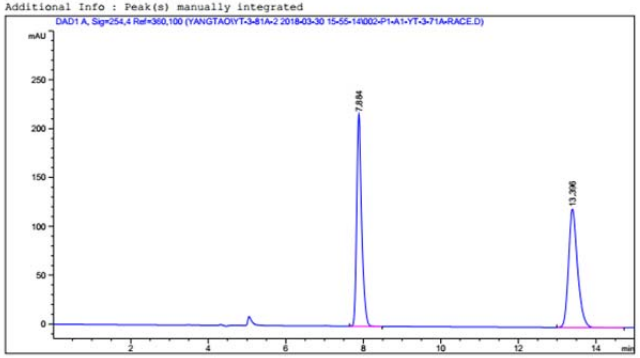


```
---------------------------------------------------------------------
                      Area Percent Report
---------------------------------------------------------------------

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|-------|
   1   7.884 BB    0.1352 1955.29980  216.78224  49.9376
   2  13.396 BBA   0.2448 1960.18323  121.12246  50.0624

Totals :                  3915.48303  337.90470
```

```
Acq. Operator   : SYSTEM                        Seq. Line :   3
Acq. Instrument : 1260-DAD                      Location :   P1-A-02
Injection Date  : 3/30/2018 16:32:51               Inj :   1
                                              Inj Volume : 1.000 µl
Acq. Method     : d:\Chem32\1\Data\YANGTAO\YT-3-81A-2 2018-03-30 15-55-14\YANGT-AD-3-80-20-0.
                  8-20MIN .M
Last changed    : 3/30/2018 16:33:20 by SYSTEM
                  (modified after loading)
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-81A-2 2018-03-30 15-55-14\YANGT-AD-3-80-20-0.
                  8-20MIN .M (Sequence Method)
Last changed    : 3/31/2018 16:02:44 by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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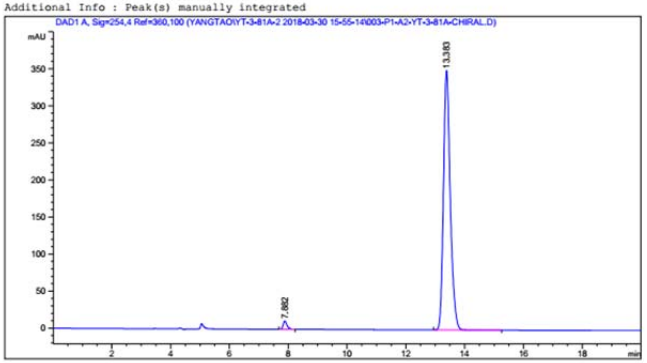


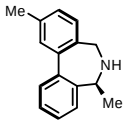

```
---------------------------------------------------------------------
                      Area Percent Report
---------------------------------------------------------------------

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|-------|
   1   7.882 BB    0.1349  101.75381   11.31420   1.7724
   2  13.383 BB    0.2441 5639.10791  349.70294  98.2276

Totals :                  5740.86172  361.01714
```




```
Acq. Operator   : SYSTEM                      Seq. Line :   4
Acq. Instrument : 1260-DAD                     Location :   P1-A-03
Injection Date  : 3/30/2018 16:53:41              Inj :   1
                                            Inj Volume : 1.000 µl
Acq. Method     : d:\Chem32\1\Data\YANGTAO\YT-3-81A-2 2018-03-30 15-55-14\YANGT-AD-3-80-20-0.
                  8-20MIN .M
Last changed    : 3/30/2018 16:33:20 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-81A-2 2018-03-30 15-55-14\YANGT-AD-3-80-20-0.
                  8-20MIN .M (Sequence Method)
Last changed    : 3/31/2018 16:02:44 by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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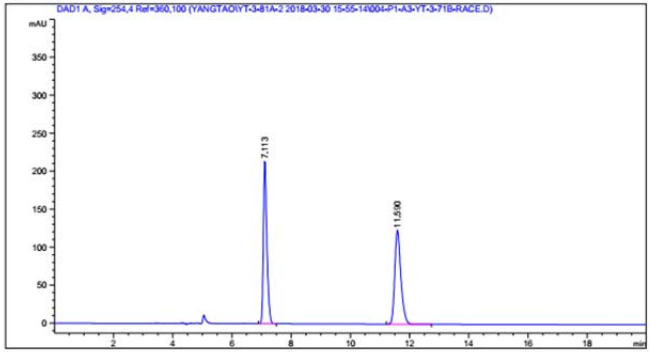


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=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.113 BB    0.1243 1764.18530  213.66061  49.9443
   2  11.590 BB    0.2148 1768.12170  123.64839  50.0557

Totals :                  3532.30701  337.30901
```

```
Acq. Operator   : SYSTEM                      Seq. Line :   5
Acq. Instrument : 1260-DAD                     Location :   P1-A-04
Injection Date  : 3/30/2018 17:14:44              Inj :   1
                                            Inj Volume : 1.000 µl
Acq. Method     : d:\Chem32\1\Data\YANGTAO\YT-3-81A-2 2018-03-30 15-55-14\YANGT-AD-3-80-20-0.
                  8-20MIN .M
Last changed    : 3/30/2018 16:33:20 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-81A-2 2018-03-30 15-55-14\YANGT-AD-3-80-20-0.
                  8-20MIN .M (Sequence Method)
Last changed    : 3/31/2018 16:04:29 by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
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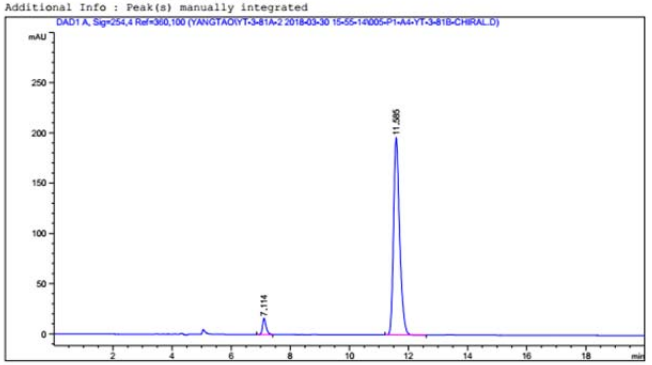
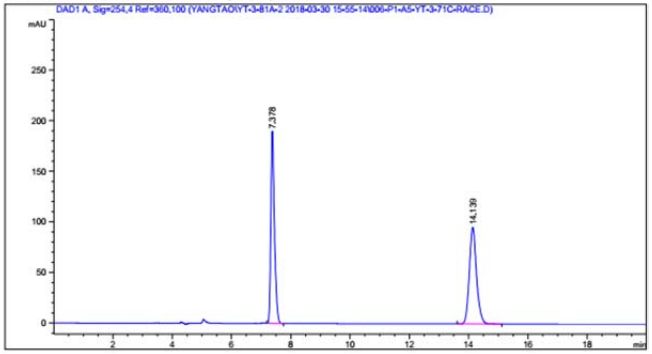



```
=====================================================================
                        Area Percent Report
=====================================================================

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.114 BB    0.1244  133.63428   16.16743   4.5386
   2  11.585 BB    0.2172 2810.73218  196.10164  95.4614

Totals :                  2944.36646  212.26907
```

Acq. Operator : SYSTEM Seq. Line : 6
Acq. Instrument : 1260-DAD Location : P1-A-05
Injection Date : 3/30/2018 17:35:34 Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-81A-2 2018-03-30 15-55-14\YANGT-AD-3-80-20-0.8-20MIN .M
Last changed : 3/30/2018 16:33:20 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-81A-2 2018-03-30 15-55-14\YANGT-AD-3-80-20-0.8-20MIN .M (Sequence Method)
Last changed : 3/31/2018 16:04:29 by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



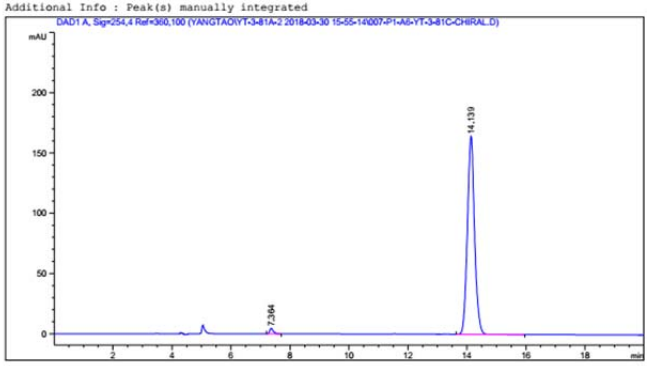
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.378	BB	0.1267	1608.20178	190.10049	49.8974
2	14.139	BB	0.2554	1614.81384	95.43284	50.1026
Totals :				3223.01563	285.53333	

Acq. Operator : SYSTEM Seq. Line : 7
Acq. Instrument : 1260-DAD Location : P1-A-06
Injection Date : 3/30/2018 17:56:24 Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-81A-2 2018-03-30 15-55-14\YANGT-AD-3-80-20-0.8-20MIN .M
Last changed : 3/30/2018 16:33:20 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-81A-2 2018-03-30 15-55-14\YANGT-AD-3-80-20-0.8-20MIN .M (Sequence Method)
Last changed : 3/31/2018 16:05:31 by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated

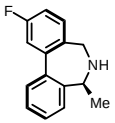


Area Percent Report

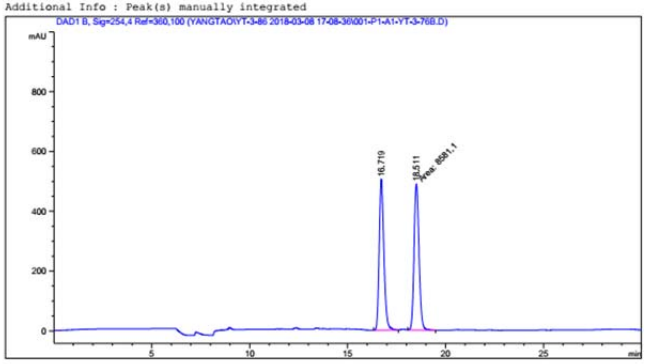
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.364	BB	0.1271	38.68418	4.55564	1.3771
2	14.139	BB	0.2567	2770.35010	164.29024	98.6229
Totals :				2809.03428	168.84588	



Acq. Operator : SYSTEM Seq. Line : 1
Acq. Instrument : 1260-DAD Location : P1-A-01
Injection Date : 3/8/2018 17:09:30 Inj : 1
Inj Volume : 2.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-86 2018-03-08 17-08-36\YANGT-DD-3-85-15-0.4-40MIN .M
Last changed : 3/8/2018 17:08:34 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-86 2018-03-08 17-08-36\YANGT-DD-3-85-15-0.4-40MIN .M (Sequence Method)
Last changed : 3/31/2018 16:08:49 by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



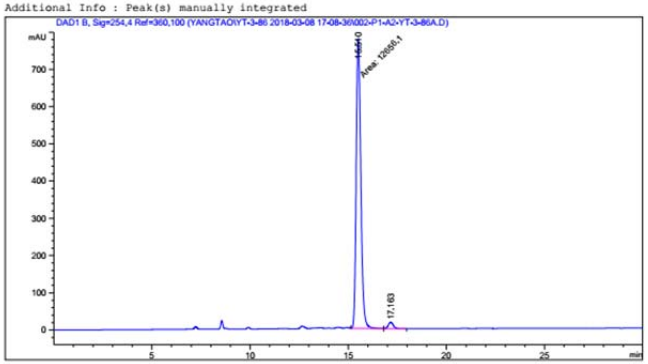
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.719	BB	0.2569	8423.99902	504.25610	49.5381
2	18.511	FM	0.2929	8581.10059	488.30594	50.4619
Totals :				1.70051e4	992.56204	

Acq. Operator : SYSTEM Seq. Line : 2
Acq. Instrument : 1260-DAD Location : P1-A-02
Injection Date : 3/8/2018 17:41:48 Inj : 1
Inj Volume : 2.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-86 2018-03-08 17-08-36\YANGT-DD-3-85-15-0.4-40MIN .M
Last changed : 3/8/2018 17:08:34 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-86 2018-03-08 17-08-36\YANGT-DD-3-85-15-0.4-40MIN .M (Sequence Method)
Last changed : 3/31/2018 16:13:40 by SYSTEM
Additional Info : Peak(s) manually integrated



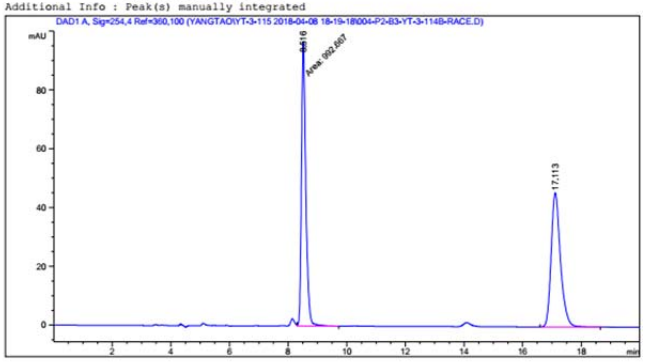
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.510	FM	0.2715	1.26561e4	777.01373	97.7772
2	17.163	BB	0.2668	287.71439	16.88693	2.2228
Totals :				1.29438e4	793.90066	

Acq. Operator : SYSTEM Seq. Line : 4
Acq. Instrument : 1260-DAD Location : P2-B-03
Injection Date : 4/8/2018 19:17:32 Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-115 2018-04-08 18-19-18\YANGT-AD-3-80-20-0.8-20MIN .M
Last changed : 4/8/2018 19:30:05 by SYSTEM
(modified after loading)
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-115 2018-04-08 18-19-18\YANGT-AD-3-80-20-0.8-20MIN .M (Sequence Method)
Last changed : 4/9/2018 10:34:57 by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



Area Percent Report

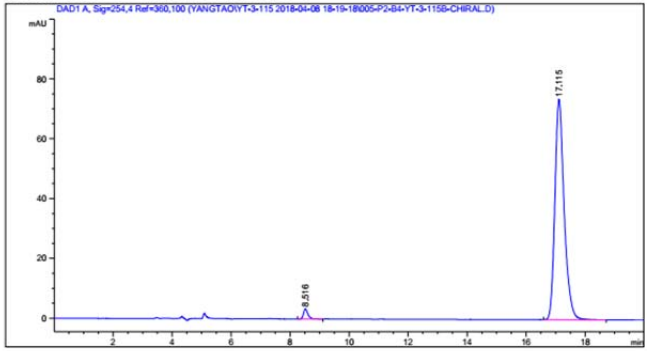
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.516	FM	0.1707	992.66748	96.94692	49.8423
2	17.113	BB	0.3295	998.94812	45.61114	50.1577

Totals : 1991.61560 142.55806

Acq. Operator : SYSTEM Seq. Line : 5
Acq. Instrument : 1260-DAD Location : P2-B-04
Injection Date : 4/8/2018 19:38:21 Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-115 2018-04-08 18-19-18\YANGT-AD-3-80-20-0.8-20MIN .M
Last changed : 4/8/2018 19:30:05 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-115 2018-04-08 18-19-18\YANGT-AD-3-80-20-0.8-20MIN .M (Sequence Method)
Last changed : 4/9/2018 10:34:57 by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



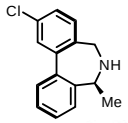
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

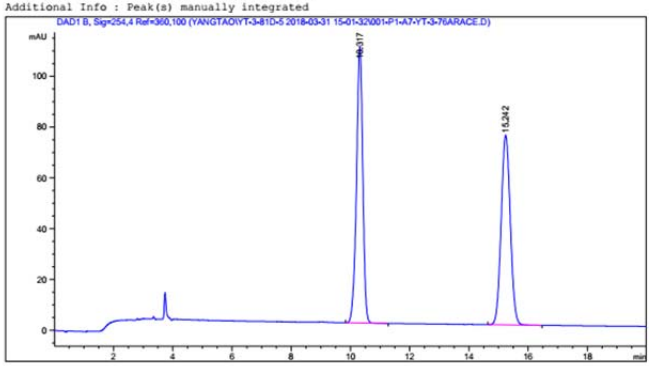
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.516	BB	0.1527	34.83677	3.42526	2.1149
2	17.115	BB	0.3294	1612.40649	73.65868	97.8851

Totals : 1647.24326 77.08394



Acq. Operator : SYSTEM Seq. Line : 1
Acq. Instrument : 1260-DAD Location : P1-A-07
Injection Date : 3/31/2018 15:02:20 Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-81D-5 2018-03-31 15-01-32\YANGT-IG-3-70-30-1-15MIN .M
Last changed : 3/31/2018 15:01:50 by SYSTEM
(modified after loading)
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-81D-5 2018-03-31 15-01-32\YANGT-IG-3-70-30-1-15MIN .M (Sequence Method)
Last changed : 3/31/2018 15:22:23 by SYSTEM
Additional Info : Peak(s) manually integrated



Area Percent Report

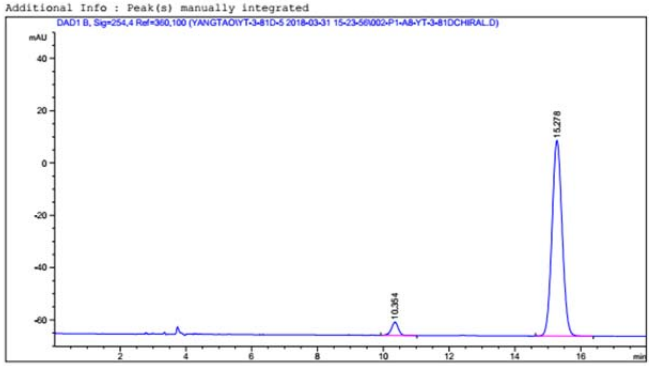
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.317	BB	0.2232	1599.68030	108.98331	50.0470
2	15.242	BB	0.3333	1596.67688	74.72705	49.9530

Totals : 3196.35718 183.71037

Acq. Operator : SYSTEM Seq. Line : 2
Acq. Instrument : 1260-DAD Location : P1-A-08
Injection Date : 3/31/2018 15:41:23 Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-81D-5 2018-03-31 15-23-56\YANGT-IG-3-70-30-1-15MIN .M
Last changed : 3/31/2018 15:53:33 by SYSTEM
(modified after loading)
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-81D-5 2018-03-31 15-23-56\YANGT-IG-3-70-30-1-15MIN .M (Sequence Method)
Last changed : 3/31/2018 16:07:04 by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



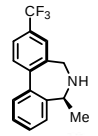
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

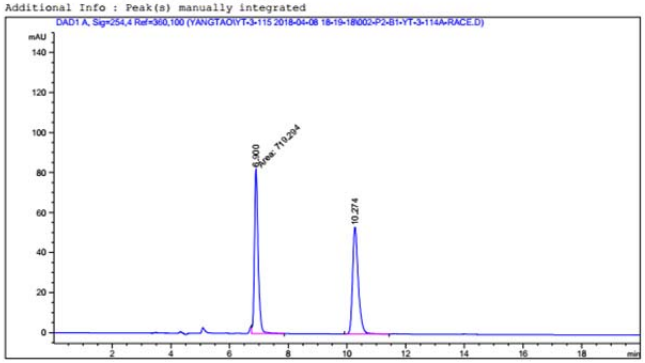
Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.354	BB	0.2238	73.48118	5.05016	4.3876
2	15.278	BB	0.3359	1601.26318	74.75245	95.6124

Totals : 1674.74436 79.80261



Acq. Operator : SYSTEM Seq. Line : 2
Acq. Instrument : 1260-DAD Location : P2-B-01
Injection Date : 4/8/2018 18:40:56 Inj : 2
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-115 2018-04-08 18-19-18\YANGT-AD-3-80-20-0.8-20MIN .M
Last changed : 3/30/2018 15:53:48 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-115 2018-04-08 18-19-18\YANGT-AD-3-80-20-0.8-20MIN .M (Sequence Method)
Last changed : 4/9/2018 10:32:45 by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



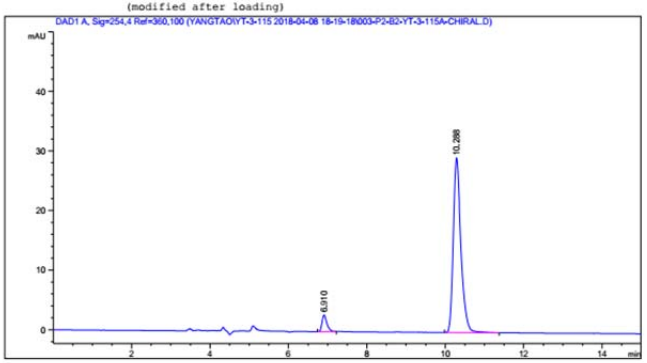
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.900	FM	0.1459	719.29407	82.15416	50.1441
2	10.274	BB	0.2004	715.16101	53.33185	49.8559
Totals :				1434.45508	135.48601	

Acq. Operator : SYSTEM Seq. Line : 3
Acq. Instrument : 1260-DAD Location : P2-B-02
Injection Date : 4/8/2018 19:01:45 Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-115 2018-04-08 18-19-18\YANGT-AD-3-80-20-0.8-20MIN .M
Last changed : 4/8/2018 19:14:16 by SYSTEM
(modified after loading)
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-115 2018-04-08 18-19-18\YANGT-AD-3-80-20-0.8-20MIN .M (Sequence Method)
Last changed : 4/9/2018 10:34:21 by SYSTEM
(modified after loading)



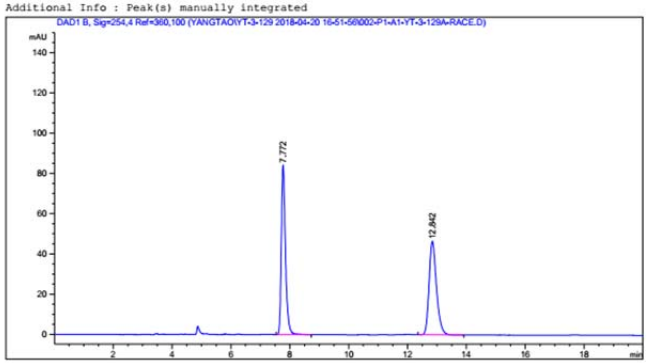
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.910	BB	0.1273	23.68740	2.78324	5.6750
2	10.288	BB	0.2011	393.71396	29.23816	94.3250
Totals :				417.40135	32.02141	

Acq. Operator : SYSTEM Seq. Line : 2
Acq. Instrument : 1260-DAD Location : P1-A-01
Injection Date : 4/20/2018 17:13:41 Inj : 2
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-129 2018-04-20 16-51-56\yt-AD3-80-20-0.8 mL-20Min.M
Last changed : 4/20/2018 16:48:12 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-129 2018-04-20 16-51-56\yt-AD3-80-20-0.8 mL-20Min.M (Sequence Method)
Last changed : 4/20/2018 19:48:04 by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



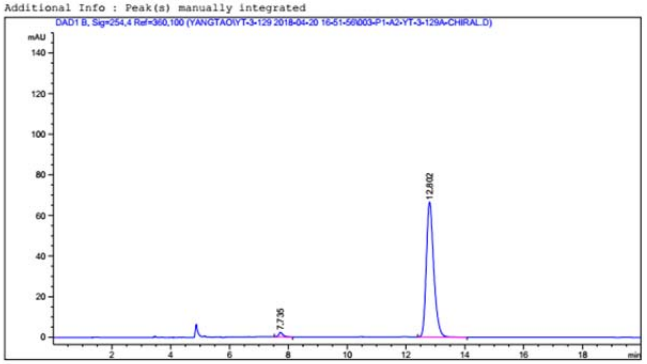
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.772	BB	0.1471	816.27844	84.23363	50.0715
2	12.842	BB	0.2665	813.94635	46.42828	49.9285
Totals :				1630.22479	130.66190	

Acq. Operator : SYSTEM Seq. Line : 3
Acq. Instrument : 1260-DAD Location : P1-A-02
Injection Date : 4/20/2018 17:34:32 Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-129 2018-04-20 16-51-56\yt-AD3-80-20-0.8 mL-20Min.M
Last changed : 4/20/2018 16:48:12 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-129 2018-04-20 16-51-56\yt-AD3-80-20-0.8 mL-20Min.M (Sequence Method)
Last changed : 4/20/2018 19:48:04 by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



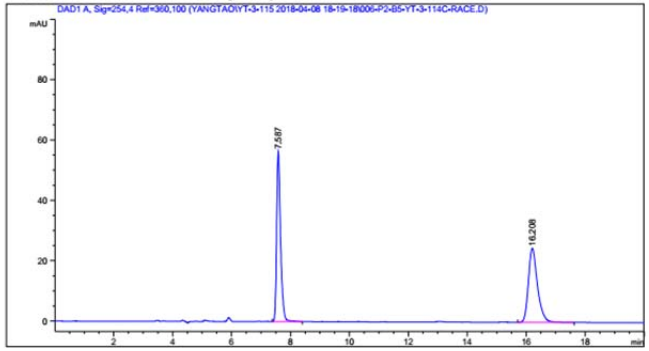
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.735	BB	0.1424	20.32127	2.14704	1.7139
2	12.802	BB	0.2664	1165.34558	66.51070	98.2861
Totals :				1185.66685	68.65774	

Acq. Operator : SYSTEM Seq. Line : 6
Acq. Instrument : 1260-DAD Location : P2-B-05
Injection Date : 4/8/2018 19:59:09 Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-115 2018-04-08 18-19-18\YANGT-AD-3-80-20-0.8-20MIN .M
Last changed : 4/8/2018 19:30:05 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-115 2018-04-08 18-19-18\YANGT-AD-3-80-20-0.8-20MIN .M (Sequence Method)
Last changed : 4/9/2018 10:34:57 by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



Area Percent Report

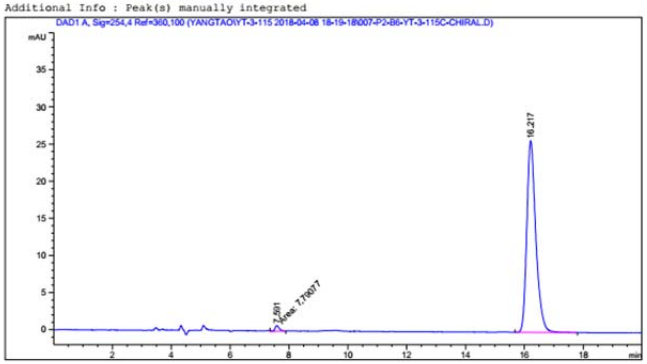
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.587	BB	0.1375	519.78247	56.39363	49.6847
2	16.208	BB	0.3221	526.37976	24.55159	50.3153

Totals : 1046.16223 80.94522

Acq. Operator : SYSTEM Seq. Line : 7
Acq. Instrument : 1260-DAD Location : P2-B-06
Injection Date : 4/8/2018 20:19:58 Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-115 2018-04-08 18-19-18\YANGT-AD-3-80-20-0.8-20MIN .M
Last changed : 4/8/2018 19:30:05 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-115 2018-04-08 18-19-18\YANGT-AD-3-80-20-0.8-20MIN .M (Sequence Method)
Last changed : 4/9/2018 10:36:58 by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



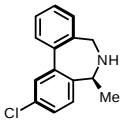
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

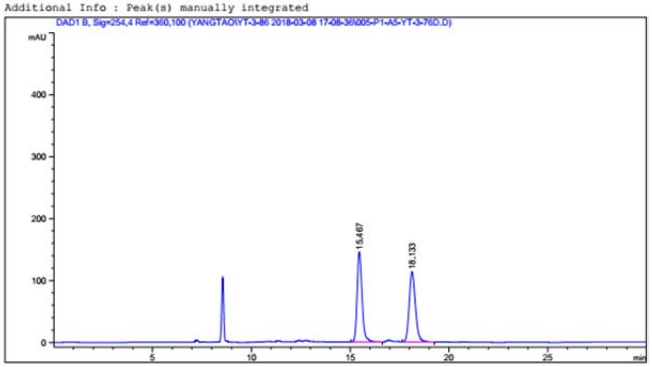
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.591	MM	0.1661	7.79077	7.81500e-1	1.3930
2	16.217	BB	0.3215	551.50739	25.78564	98.6070

Totals : 559.29816 26.56714



Acq. Operator : SYSTEM Seq. Line : 5
Acq. Instrument : 1260-DAD Location : P1-A-05
Injection Date : 3/8/2018 19:14:19 Inj : 1
Inj Volume : 2.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-86 2018-03-08 17-08-36\YANGT-DD-3-85-15-0.4-40MIN .M
Last changed : 3/8/2018 17:08:34 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-86 2018-03-08 17-08-36\YANGT-DD-3-85-15-0.4-40MIN .M (Sequence Method)
Last changed : 3/31/2018 16:10:49 by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



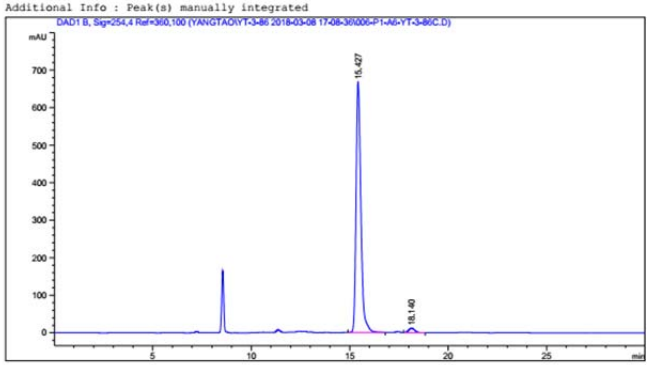
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.467	BB	0.2661	2514.19067	145.16817	50.3002
2	18.133	BB	0.3375	2484.17651	113.45380	49.6998
Totals :				4998.36719	258.62196	

Acq. Operator : SYSTEM Seq. Line : 6
Acq. Instrument : 1260-DAD Location : P1-A-06
Injection Date : 3/8/2018 19:45:08 Inj : 1
Inj Volume : 2.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-86 2018-03-08 17-08-36\YANGT-DD-3-85-15-0.4-40MIN .M
Last changed : 3/8/2018 17:08:34 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-86 2018-03-08 17-08-36\YANGT-DD-3-85-15-0.4-40MIN .M (Sequence Method)
Last changed : 3/31/2018 16:11:41 by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated

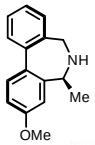


Area Percent Report

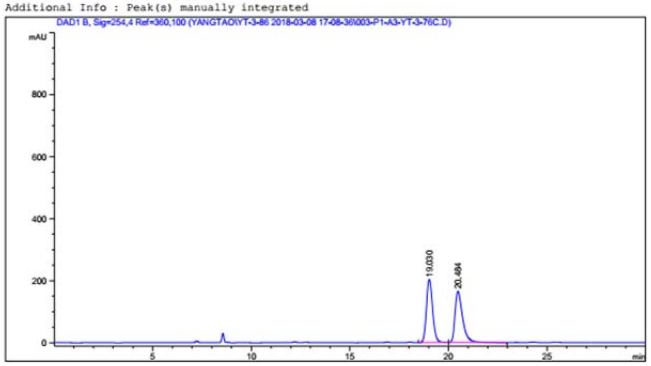
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.427	BB	0.2598	1.13096e4	667.18707	97.7980
2	18.140	BB	0.3276	254.64725	12.00050	2.2020
Totals :				1.15642e4	679.18757	



Acq. Operator : SYSTEM Seq. Line : 3
Acq. Instrument : 1260-DAD Location : P1-A-03
Injection Date : 3/8/2018 18:12:39 Inj : 1
Inj Volume : 2.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-86 2018-03-08 17-08-36\YANGT-DD-3-85-15-0.4-40MIN .M
Last changed : 3/8/2018 17:08:34 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-86 2018-03-08 17-08-36\YANGT-DD-3-85-15-0.4-40MIN .M (Sequence Method)
Last changed : 3/31/2018 16:08:49 by SYSTEM (modified after loading)
Additional Info : Peak(s) manually integrated



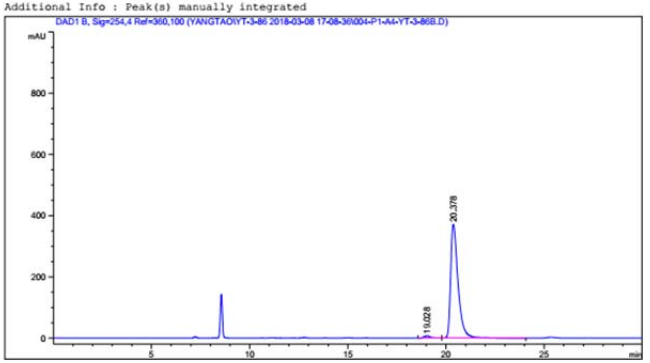
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.030	BB	0.3343	4404.45801	203.67908	50.1889
2	20.484	BB	0.3998	4371.30518	164.62981	49.8111
Totals :				8775.76318	368.30888	

Acq. Operator : SYSTEM Seq. Line : 4
Acq. Instrument : 1260-DAD Location : P1-A-04
Injection Date : 3/8/2018 18:43:30 Inj : 1
Inj Volume : 2.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-86 2018-03-08 17-08-36\YANGT-DD-3-85-15-0.4-40MIN .M
Last changed : 3/8/2018 17:08:34 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-86 2018-03-08 17-08-36\YANGT-DD-3-85-15-0.4-40MIN .M (Sequence Method)
Last changed : 3/31/2018 16:08:49 by SYSTEM (modified after loading)
Additional Info : Peak(s) manually integrated

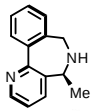


Area Percent Report

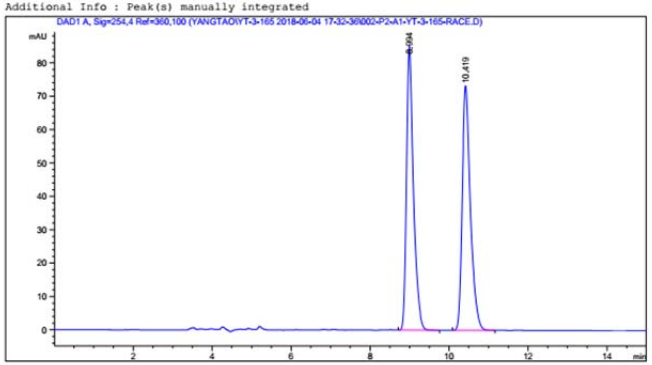
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	19.028	BB	0.3594	161.44896	6.79088	1.6337
2	20.378	BB	0.3957	9721.15332	371.04114	98.3663
Totals :				9882.60228	377.83202	



Acq. Operator : SYSTEM Seq. Line : 2
Acq. Instrument : 1260-DAD Location : P2-A-01
Injection Date : 6/4/2018 17:49:17 Inj : 2
Inj Volume : 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 2.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-165 2018-06-04 17-32-36\YANGT-AD-3-80-20-0.8-20MIN .M
Last changed : 6/4/2018 17:48:27 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-165 2018-06-04 17-32-36\YANGT-AD-3-80-20-0.8-20MIN .M (Sequence Method)
Last changed : 6/4/2018 17:48:30 by SYSTEM
Additional Info : Peak(s) manually integrated



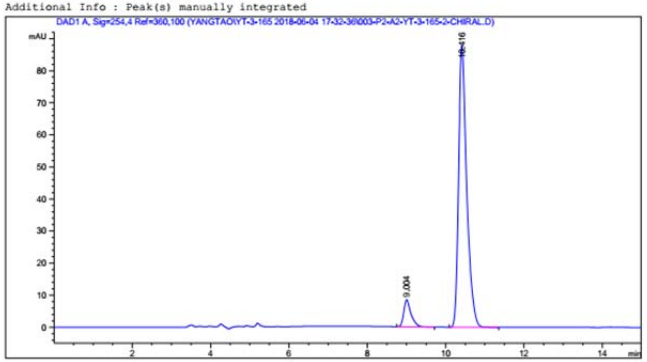
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.994	BB	0.1840	1051.44958	85.17190	49.9631
2	10.419	BB	0.2137	1053.00195	73.25212	50.0369
Totals :				2104.45154	158.42402	

Acq. Operator : SYSTEM Seq. Line : 3
Acq. Instrument : 1260-DAD Location : P2-A-02
Injection Date : 6/4/2018 18:05:06 Inj : 1
Inj Volume : 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 2.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-165 2018-06-04 17-32-36\YANGT-AD-3-80-20-0.8-20MIN .M
Last changed : 6/4/2018 17:48:27 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-165 2018-06-04 17-32-36\YANGT-AD-3-80-20-0.8-20MIN .M (Sequence Method)
Last changed : 6/4/2018 17:48:30 by SYSTEM
Additional Info : Peak(s) manually integrated



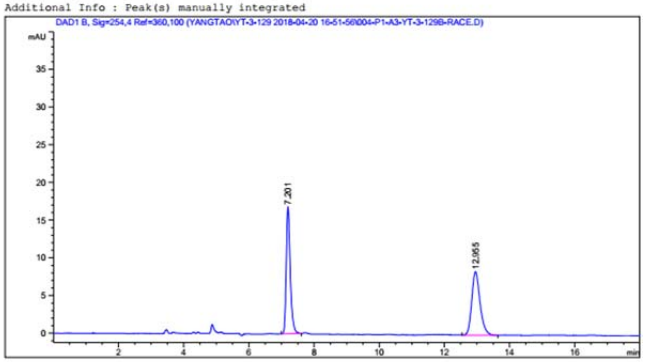
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.004	BB	0.1909	109.96561	8.50301	7.9627
2	10.416	BB	0.2171	1271.03992	87.71360	92.0373
Totals :				1381.00552	96.21661	

```
Acq. Operator   : SYSTEM                      Seq. Line :   4
Acq. Instrument : 1260-DAD                    Location :   P1-A-03
Injection Date  : 4/20/2018 17:55:21              Inj :   1
                                            Inj Volume : 1.000 µl
Acq. Method     : d:\Chem32\1\Data\YANGTAO\YT-3-129 2018-04-20 16-51-56\yt-AD3-80-20-0.8 mL-
                  20Min.M
Last changed    : 4/20/2018 18:13:16 by SYSTEM
                  (modified after loading)
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-129 2018-04-20 16-51-56\yt-AD3-80-20-0.8 mL-
                  20Min.M (Sequence Method)
Last changed    : 4/20/2018 19:49:37 by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

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                        Area Percent Report
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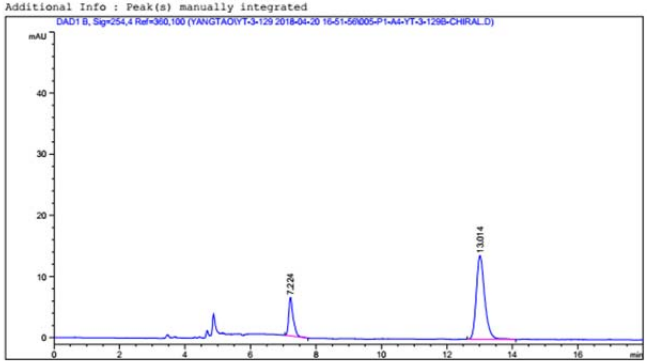
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.201 BB    0.1279  144.45171   16.86463  49.2853
   2  12.955 BB    0.2677  148.64120    8.43151  50.7147

Totals :                   293.09291   25.29614
```

```
Acq. Operator   : SYSTEM                      Seq. Line :   5
Acq. Instrument : 1260-DAD                    Location :   P1-A-04
Injection Date  : 4/20/2018 18:14:11              Inj :   1
                                            Inj Volume : 1.000 µl
Acq. Method     : d:\Chem32\1\Data\YANGTAO\YT-3-129 2018-04-20 16-51-56\yt-AD3-80-20-0.8 mL-
                  20Min.M
Last changed    : 4/20/2018 18:13:16 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-129 2018-04-20 16-51-56\yt-AD3-80-20-0.8 mL-
                  20Min.M (Sequence Method)
Last changed    : 4/20/2018 19:53:05 by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]       [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.224 BB    0.1391   59.93843    6.29694  19.6812
   2  13.014 BB    0.2726  244.60773   13.67805  80.3188

Totals :                   304.54616   19.97499
```
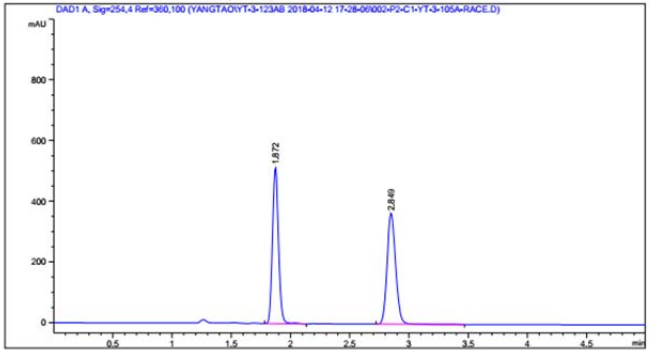

Acq. Operator : SYSTEM Seq. Line : 2
Acq. Instrument : 1290-DAD Location : P2-C-01
Injection Date : 4/12/2018 5:34:27 PM Inj : 2
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-123AB 2018-04-12 17-28-06\YT-OD-3-80-20-0.5-5MIN.M
Last changed : 4/4/2018 5:59:36 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-123AB 2018-04-12 17-28-06\YT-OD-3-80-20-0.5-5MIN.M (Sequence Method)
Last changed : 4/12/2018 6:23:38 PM by SYSTEM
Additional Info : Peak(s) manually integrated



Area Percent Report

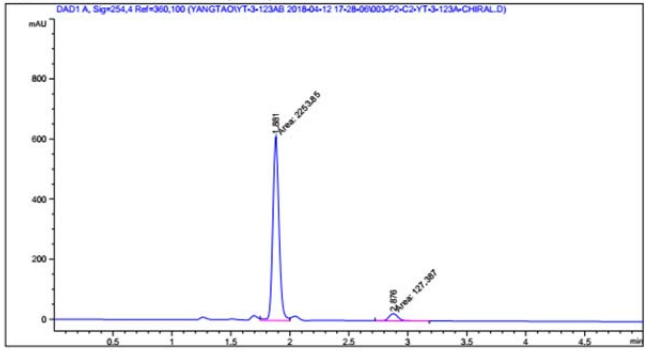
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.872	BV R	0.0554	1839.96179	515.41150	50.0585
2	2.849	BB	0.0766	1835.66064	365.24612	49.9415

Totals : 3675.62244 880.65762

Acq. Operator : SYSTEM Seq. Line : 3
Acq. Instrument : 1290-DAD Location : P2-C-02
Injection Date : 4/12/2018 5:39:53 PM Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-123AB 2018-04-12 17-28-06\YT-OD-3-80-20-0.5-5MIN.M
Last changed : 4/4/2018 5:59:36 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-123AB 2018-04-12 17-28-06\YT-OD-3-80-20-0.5-5MIN.M (Sequence Method)
Last changed : 4/12/2018 6:23:38 PM by SYSTEM
Additional Info : Peak(s) manually integrated



Area Percent Report

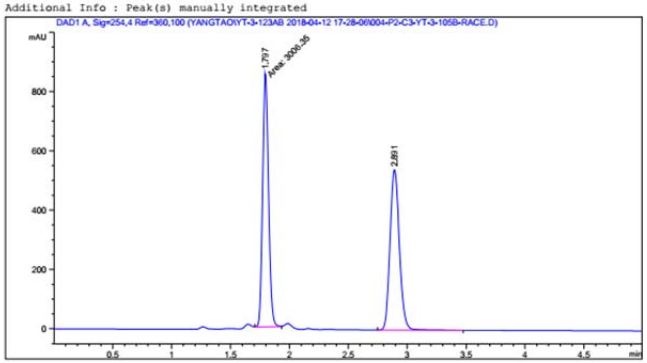
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.881	MF	0.0613	2253.84766	613.16290	94.6504
2	2.876	FM	0.0885	127.38746	24.00337	5.3496

Totals : 2381.23512 637.16627

Acq. Operator : SYSTEM Seq. Line : 4
Acq. Instrument : 1290-DAD Location : P2-C-03
Injection Date : 4/12/2018 5:45:19 PM Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-123AB 2018-04-12 17-28-06\YT-OD-3-80-20-0.5-5MIN.M
Last changed : 4/4/2018 5:59:36 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-123AB 2018-04-12 17-28-06\YT-OD-3-80-20-0.5-5MIN.M (Sequence Method)
Last changed : 4/12/2018 6:23:38 PM by SYSTEM
Additional Info : Peak(s) manually integrated



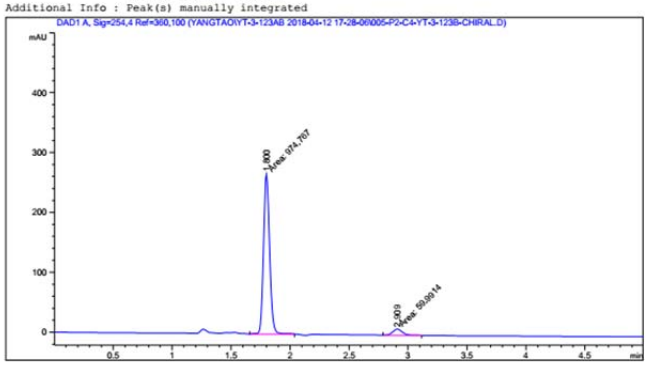
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.797	MM	0.0583	3006.35132	859.52960	50.2231
2	2.891	BB	0.0841	2979.63794	541.92139	49.7769
Totals :				5985.98926	1401.45099	

Acq. Operator : SYSTEM Seq. Line : 5
Acq. Instrument : 1290-DAD Location : P2-C-04
Injection Date : 4/12/2018 5:50:46 PM Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-123AB 2018-04-12 17-28-06\YT-OD-3-80-20-0.5-5MIN.M
Last changed : 4/4/2018 5:59:36 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-123AB 2018-04-12 17-28-06\YT-OD-3-80-20-0.5-5MIN.M (Sequence Method)
Last changed : 4/12/2018 10:29:12 PM by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



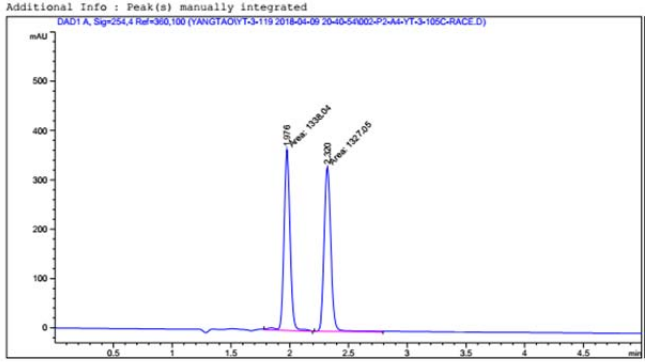
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.800	MM	0.0607	974.76721	267.77173	94.2024
2	2.909	MF	0.0973	59.99144	10.27125	5.7976
Totals :				1034.75865	278.04298	

```
Acq. Operator   : SYSTEM                      Seq. Line :   2
Acq. Instrument : 1290-DAD                    Location :   P2-A-04
Injection Date  : 4/9/2018 8:47:12 PM              Inj :   2
                                             Inj Volume : 1.000 µl
Acq. Method     : d:\Chem32\1\Data\YANGTAO\YT-3-119 2018-04-09 20-40-54\YT-OD-3-80-20-0.5-
                  5MIN.M
Last changed    : 4/4/2018 5:59:36 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-119 2018-04-09 20-40-54\YT-OD-3-80-20-0.5-
                  5MIN.M (Sequence Method)
Last changed    : 4/12/2018 10:30:32 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

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                        Area Percent Report
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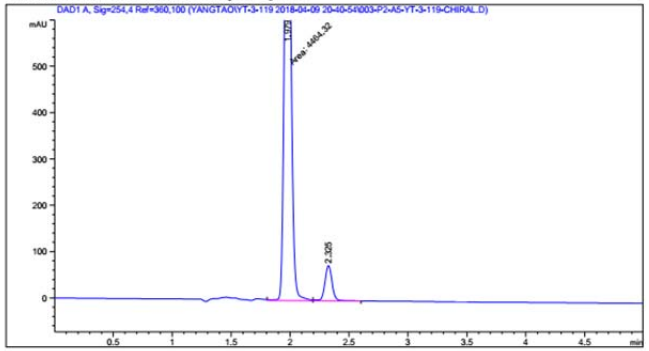
Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   1.976 MM    0.0607 1338.03650  367.37585  50.2062
   2   2.320 MF    0.0661 1327.04578  334.67859  49.7938

Totals :                  2665.08228  702.05444
```

```
Acq. Operator   : SYSTEM                      Seq. Line :   3
Acq. Instrument : 1290-DAD                    Location :   P2-A-05
Injection Date  : 4/9/2018 8:52:38 PM              Inj :   1
                                             Inj Volume : 1.000 µl
Acq. Method     : d:\Chem32\1\Data\YANGTAO\YT-3-119 2018-04-09 20-40-54\YT-OD-3-80-20-0.5-
                  5MIN.M
Last changed    : 4/4/2018 5:59:36 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-119 2018-04-09 20-40-54\YT-OD-3-80-20-0.5-
                  5MIN.M (Sequence Method)
Last changed    : 4/12/2018 10:30:32 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   1.979 FM    0.0604 4464.31592 1232.04358  93.4102
   2   2.325 VB    0.0643  314.94308   76.08009   6.5898

Totals :                  4779.25900 1308.12366
```
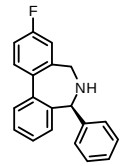
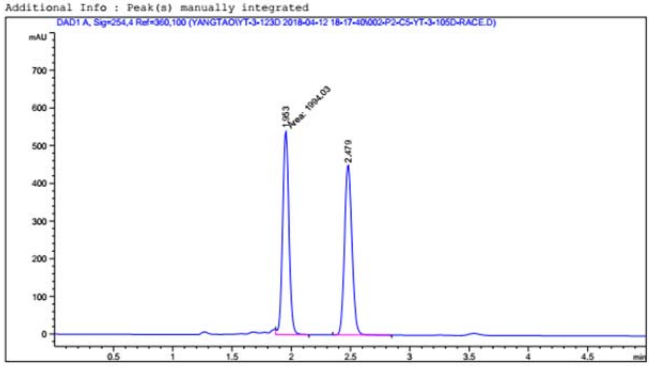



Acq. Operator : SYSTEM Seq. Line : 2
Acq. Instrument : 1290-DAD Location : P2-C-05
Injection Date : 4/12/2018 6:23:58 PM Inj : 2
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-123D 2018-04-12 18-17-40\YT-OD-3-80-20-0.5-5MIN.M
Last changed : 4/4/2018 5:59:36 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-123D 2018-04-12 18-17-40\YT-OD-3-80-20-0.5-5MIN.M (Sequence Method)
Last changed : 4/12/2018 10:33:00 PM by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



Area Percent Report

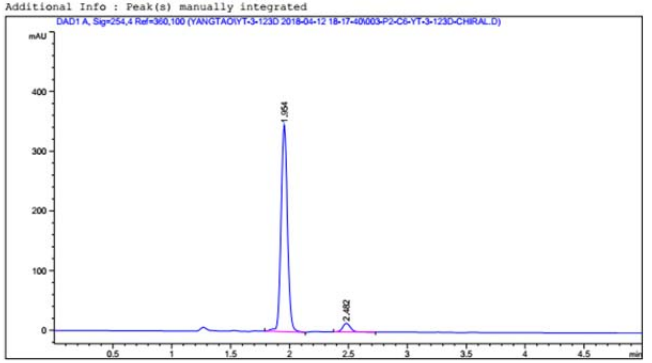
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.953	FM	0.0614	1994.02698	541.01489	50.1480
2	2.479	BB	0.0672	1982.25500	451.44815	49.8520

Totals : 3976.28198 992.46304

Acq. Operator : SYSTEM Seq. Line : 3
Acq. Instrument : 1290-DAD Location : P2-C-06
Injection Date : 4/12/2018 6:29:25 PM Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-123D 2018-04-12 18-17-40\YT-OD-3-80-20-0.5-5MIN.M
Last changed : 4/4/2018 5:59:36 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-123D 2018-04-12 18-17-40\YT-OD-3-80-20-0.5-5MIN.M (Sequence Method)
Last changed : 4/12/2018 10:33:51 PM by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



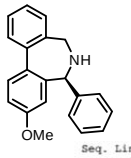
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

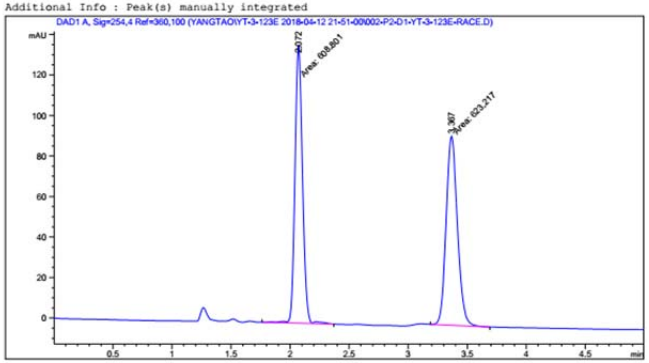
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.954	VB R	0.0578	1309.30640	345.34579	95.3534
2	2.482	BB	0.0702	63.80222	14.25882	4.6466

Totals : 1373.10862 359.60461




```
Acq. Operator   : SYSTEM                        Seq. Line :   2
Acq. Instrument : 1290-DAD                     Location :   P2-D-01
Injection Date  : 4/12/2018 9:57:22 PM              Inj :   2
                                              Inj Volume : 1.000 µl
Method          : d:\Chem32\1\Data\YANGTAO\YT-3-123E 2018-04-12 21-51-00\YT-OD-3-80-20-0.5-
                  5MIN.M (Sequence Method)
Last changed    : 4/4/2018 5:59:36 PM by SYSTEM
Additional Info : Peak(s) manually integrated
```

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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|-------|
   1   2.072 MM    0.0734  608.80127  138.16801  49.4150
   2   3.367 MM    0.1111  623.21680   93.45047  50.5850

Totals :                  1232.01807  231.61848

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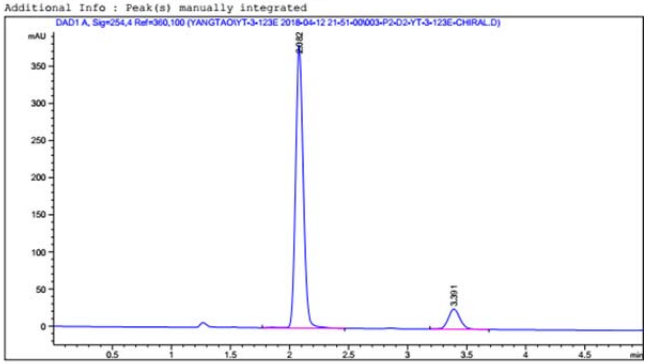
                        *** End of Report ***
```

```
Acq. Operator   : SYSTEM                        Seq. Line :   3
Acq. Instrument : 1290-DAD                     Location :   P2-D-02
Injection Date  : 4/12/2018 10:02:49 PM             Inj :   1
                                              Inj Volume : 1.000 µl
Method          : d:\Chem32\1\Data\YANGTAO\YT-3-123E 2018-04-12 21-51-00\YT-OD-3-80-20-0.5-
                  5MIN.M (Sequence Method)
Last changed    : 4/4/2018 5:59:36 PM by SYSTEM
Additional Info : Peak(s) manually integrated
```

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                        Area Percent Report
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Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|-------|
   1   2.082 BB    0.0709 1721.33044  379.72549  90.2873
   2   3.391 BB    0.1057  185.17363   27.09702   9.7127

Totals :                  1906.50407  406.82252
```
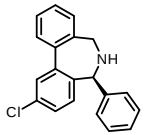
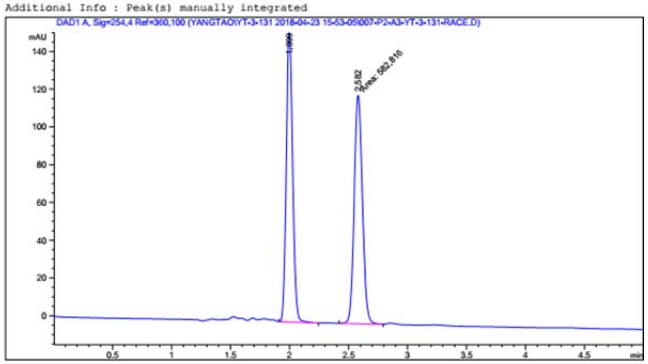



Acq. Operator : SYSTEM Seq. Line : 7
Acq. Instrument : 1290-DAD Location : P2-A-03
Injection Date : 4/23/2018 4:33:37 PM Inj : 2
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-131 2018-04-23 15-53-05\YT-OD-3-80-20-0.5-5MIN.M
Last changed : 4/4/2018 5:59:36 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-131 2018-04-23 15-53-05\YT-OD-3-80-20-0.5-5MIN.M (Sequence Method)
Last changed : 4/23/2018 4:52:45 PM by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



Area Percent Report

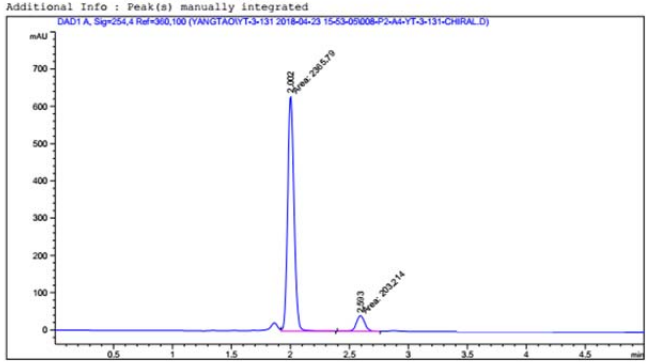
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	1.999	BB	0.0576	580.95111	155.51361	49.9199
2	2.582	MF	0.0798	582.81567	121.65110	50.0801

Totals : 1163.76678 277.16471

Acq. Operator : SYSTEM Seq. Line : 8
Acq. Instrument : 1290-DAD Location : P2-A-04
Injection Date : 4/23/2018 4:39:31 PM Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-3-131 2018-04-23 15-53-05\YT-OD-3-80-20-0.5-5MIN.M
Last changed : 4/4/2018 5:59:36 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-131 2018-04-23 15-53-05\YT-OD-3-80-20-0.5-5MIN.M (Sequence Method)
Last changed : 4/23/2018 4:51:44 PM by SYSTEM
(modified after loading)
Additional Info : Peak(s) manually integrated



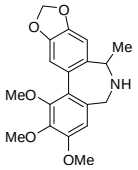
Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

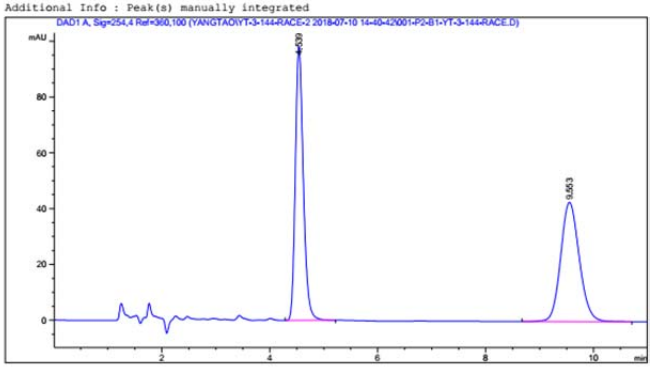
Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	2.002	FM	0.0623	2365.78784	633.11407	92.0898
2	2.593	MF	0.0816	203.21356	41.52388	7.9102

Totals : 2569.00140 674.63795

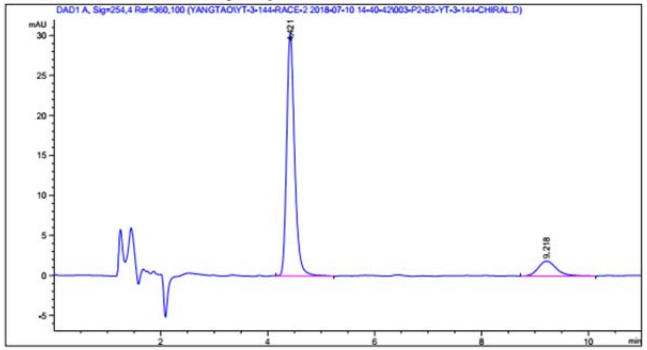



```
Acq. Operator   : SYSTEM                        Seq. Line :   1
Acq. Instrument : 1290-DAD                      Location :   P2-B-01
Injection Date  : 7/10/2018 2:42:09 PM             Inj :   1
                                               Inj Volume : 2.000 µl
Acq. Method     : d:\Chem32\1\Data\YANGTAO\YT-3-144-RACE-2 2018-07-10 14-40-42\YT-AD-3-80-20-
                  0.5-5MIN.M
Last changed    : 7/10/2018 2:42:06 PM by SYSTEM
                  (modified after loading)
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-144-RACE-2 2018-07-10 14-40-42\YT-AD-3-80-20-
                  0.5-5MIN.M (Sequence Method)
Last changed    : 7/10/2018 2:53:12 PM by SYSTEM
Additional Info : Peak(s) manually integrated
```

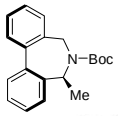



```
---------------------------------------------------------------------
                        Area Percent Report
---------------------------------------------------------------------

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.539 BB    0.1586 1012.91516   98.00934  49.6820
   2   9.553 BB    0.3701 1025.88159   42.72975  50.3180

Totals :                  2038.79675  140.73909
```

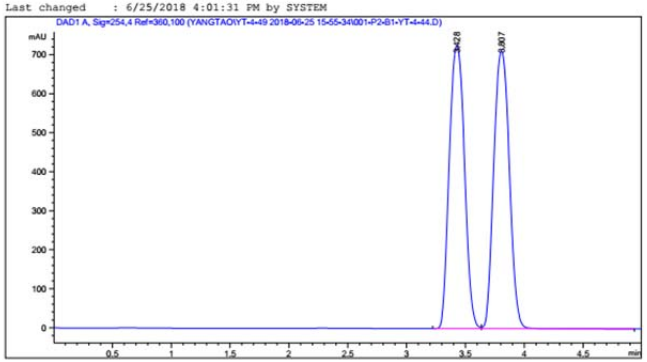
```
Acq. Operator   : SYSTEM                        Seq. Line :   3
Acq. Instrument : 1290-DAD                      Location :   P2-B-02
Injection Date  : 7/10/2018 3:05:02 PM             Inj :   1
                                               Inj Volume : 2.000 µl
Acq. Method     : d:\Chem32\1\Data\YANGTAO\YT-3-144-RACE-2 2018-07-10 14-40-42\YT-AD-3-80-20-
                  0.5-5MIN.M
Last changed    : 7/10/2018 2:42:06 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-3-144-RACE-2 2018-07-10 14-40-42\YT-AD-3-80-20-
                  0.5-5MIN.M (Sequence Method)
Last changed    : 7/10/2018 2:53:12 PM by SYSTEM
Additional Info : Peak(s) manually integrated
```




```
---------------------------------------------------------------------
                        Area Percent Report
---------------------------------------------------------------------

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   4.421 BB    0.1559  311.17883   30.28291  87.4999
   2   9.218 BB    0.3628   44.45462    1.87343  12.5001

Totals :                   355.63346   32.15634
```



Acq. Operator : SYSTEM Seq. Line : 1
Acq. Instrument : 1290-DAD Location : P2-B-01
Injection Date : 6/25/2018 3:56:28 PM Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-4-49 2018-06-25 15-55-34\YT-AD-3-98-2-0.3-5MIN.M
Last changed : 6/25/2018 4:01:01 PM by SYSTEM (modified after loading)
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-4-49 2018-06-25 15-55-34\YT-AD-3-98-2-0.3-5MIN.M (Sequence Method)
Last changed : 6/25/2018 4:01:31 PM by SYSTEM



Area Percent Report

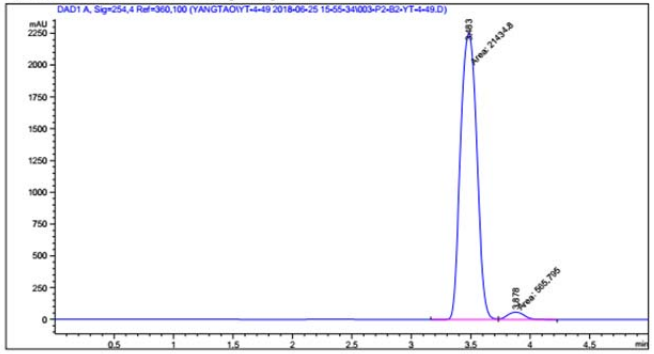
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.428	BV	0.1471	6528.99219	724.80731	49.9169
2	3.807	VBA	0.1494	6550.73926	711.88379	50.0831

Totals : 1.30797e4 1436.69110

Acq. Operator : SYSTEM Seq. Line : 3
Acq. Instrument : 1290-DAD Location : P2-B-02
Injection Date : 6/25/2018 4:07:22 PM Inj : 1
Inj Volume : 1.000 µl
Acq. Method : d:\Chem32\1\Data\YANGTAO\YT-4-49 2018-06-25 15-55-34\YT-AD-3-98-2-0.3-5MIN.M
Last changed : 6/25/2018 4:01:01 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-4-49 2018-06-25 15-55-34\YT-AD-3-98-2-0.3-5MIN.M (Sequence Method)
Last changed : 6/25/2018 4:01:31 PM by SYSTEM
Additional Info : Peak(s) manually integrated



Area Percent Report

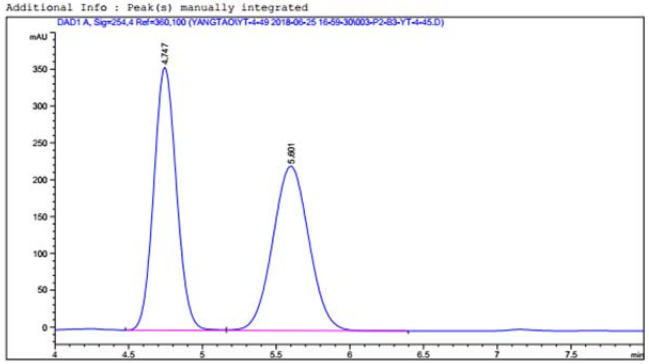
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	3.483	MF	0.1586	2.14348e4	2251.88159	97.4283
2	3.878	FM	0.1642	565.79474	57.41494	2.5717

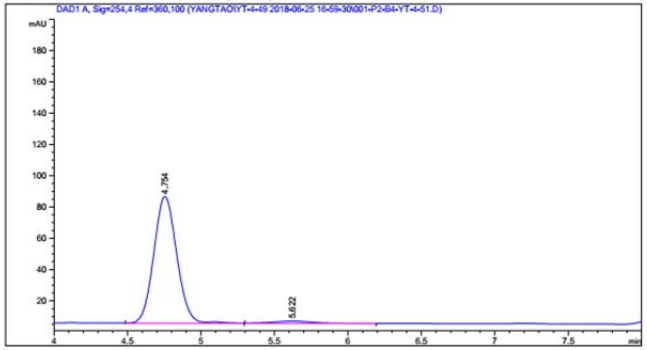
Totals : 2.20006e4 2309.29654

```
Acq. Operator   : SYSTEM                        Seq. Line :   3
Acq. Instrument : 1290-DAD                       Location :   P2-B-03
Injection Date  : 6/25/2018 5:18:05 PM              Inj :   1
                                                Inj Volume : 1.000 µl
Acq. Method     : d:\Chem32\1\Data\YANGTAO\YT-4-49 2018-06-25 16-59-30\YT-AD-3-95-5-0.3-5MIN.
                  M
Last changed    : 6/25/2018 3:20:04 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-4-49 2018-06-25 16-59-30\YT-AD-3-95-5-0.3-5MIN.
                  M (Sequence Method)
Last changed    : 8/24/2018 5:09:45 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

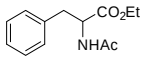



```
-----------------------------------------------------------------------
                      Area Percent Report
-----------------------------------------------------------------------

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|-------|
   1   4.747 BV    0.1669 3817.83228  356.68829  50.0402
   2   5.601 VB    0.2673 3811.69238  223.14366  49.9598

Totals :                  7629.52466  579.83195
```

```
Acq. Operator   : SYSTEM                        Seq. Line :   1
Acq. Instrument : 1290-DAD                       Location :   P2-B-04
Injection Date  : 6/25/2018 5:01:11 PM              Inj :   1
                                                Inj Volume : 1.000 µl
Acq. Method     : d:\Chem32\1\Data\YANGTAO\YT-4-49 2018-06-25 16-59-30\YT-AD-3-95-5-0.3-5MIN.
                  M
Last changed    : 6/25/2018 3:20:04 PM by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-4-49 2018-06-25 16-59-30\YT-AD-3-95-5-0.3-5MIN.
                  M (Sequence Method)
Last changed    : 8/24/2018 4:50:49 PM by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

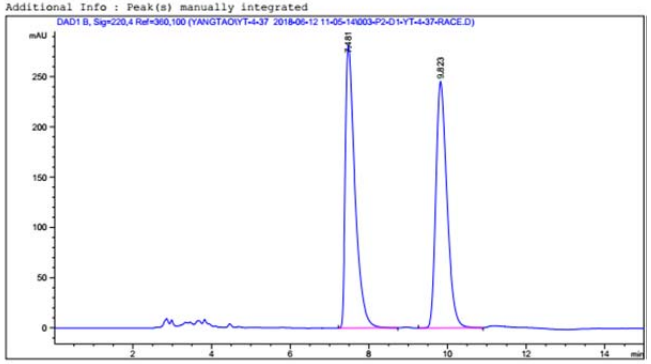



```
-----------------------------------------------------------------------
                      Area Percent Report
-----------------------------------------------------------------------

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 A, Sig=254,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|-------|
   1   4.754 BV R  0.1687  879.54651   81.01995  97.2534
   2   5.622 BB    0.2732   24.83981    1.39883   2.7466

Totals :                   904.38631   82.41878
```



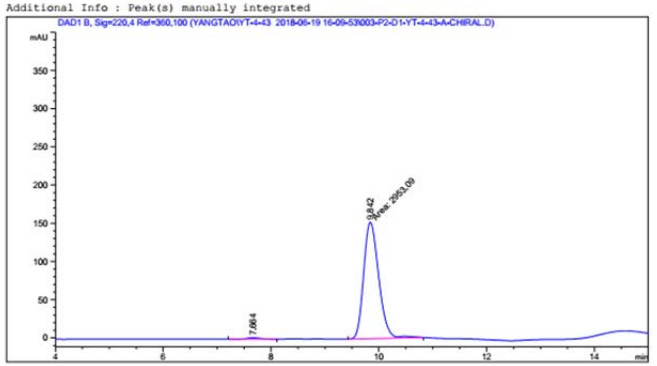
Using L1

```
Acq. Operator   : SYSTEM                       Seq. Line :   3
Acq. Instrument : 1260-DAD                     Location :   P2-D-01
Injection Date  : 6/12/2018 11:37:47               Inj :   1
                                              Inj Volume : 1.000 µl
Method          : d:\Chem32\1\Data\YANGTAO\YT-4-37  2018-06-12 11-05-14\YT-OD-H-90-10-1ML-
                  15MIN.M (Sequence Method)
Last changed    : 6/12/2018 11:03:35 by SYSTEM
Additional Info : Peak(s) manually integrated
```

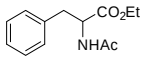



```
------------------------------------------------------------------------
                        Area Percent Report
------------------------------------------------------------------------

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.481 BB    0.2546 4788.84961  281.24911  49.8812
   2   9.823 BB    0.3030 4811.65527  245.13409  50.1188

Totals :                  9600.50488  526.38321
```

```
Acq. Operator   : SYSTEM                       Seq. Line :   3
Acq. Instrument : 1260-DAD                     Location :   P2-D-01
Injection Date  : 6/19/2018 16:42:27               Inj :   1
                                              Inj Volume : 1.000 µl
Different Inj Volume from Sample Entry!  Actual Inj Volume : 3.000 µl
Acq. Method     : d:\Chem32\1\Data\YANGTAO\YT-4-43  2018-06-19 16-09-53\YT-OD-H-90-10-1ML-
                  15MIN.M
Last changed    : 6/12/2018 11:03:35 by SYSTEM
Analysis Method : d:\Chem32\1\Data\YANGTAO\YT-4-43  2018-06-19 16-09-53\YT-OD-H-90-10-1ML-
                  15MIN.M (Sequence Method)
Last changed    : 8/24/2018 16:59:28 by SYSTEM
                  (modified after loading)
Additional Info : Peak(s) manually integrated
```

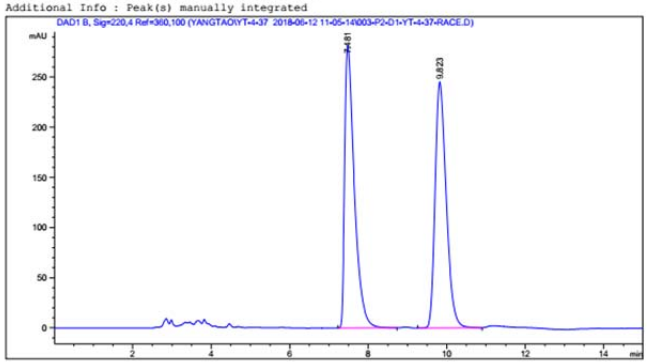



```
------------------------------------------------------------------------
                        Area Percent Report
------------------------------------------------------------------------

Sorted By             :      Signal
Multiplier            :      1.0000
Dilution              :      1.0000
Use Multiplier & Dilution Factor with ISTDs


Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak RetTime Type  Width     Area      Height     Area
  #   [min]        [min]   [mAU*s]     [mAU]       %
----|-------|----|-------|----------|----------|--------|
   1   7.664 BB    0.2703   32.52962   1.83953   1.0895
   2   9.842 MM    0.3233 2953.09302  152.21458  98.9105

Totals :                  2985.62264  154.05412
```



Using L2

Acq. Operator : SYSTEM Seq. Line : 3
Acq. Instrument : 1260-DAD Location : P2-D-01
Injection Date : 6/12/2018 11:37:47 Inj : 1
Inj Volume : 1.000 µl
Method : d:\Chem32\1\Data\YANGTAO\YT-4-37 2018-06-12 11-05-14\YT-OD-H-90-10-1ML-15MIN.M (Sequence Method)
Last changed : 6/12/2018 11:03:35 by SYSTEM
Additional Info : Peak(s) manually integrated



Area Percent Report

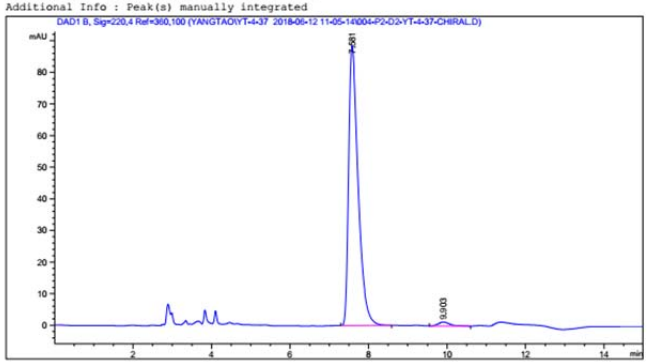
Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.481	BB	0.2546	4788.84961	281.24911	49.8812
2	9.823	BB	0.3030	4811.65527	245.13409	50.1188

Totals : 9600.50488 526.38321

Acq. Operator : SYSTEM Seq. Line : 4
Acq. Instrument : 1260-DAD Location : P2-D-02
Injection Date : 6/12/2018 11:53:37 Inj : 1
Inj Volume : 1.000 µl
Different Inj Volume from Sample Entry! Actual Inj Volume : 2.000 µl
Method : d:\Chem32\1\Data\YANGTAO\YT-4-37 2018-06-12 11-05-14\YT-OD-H-90-10-1ML-15MIN.M (Sequence Method)
Last changed : 6/12/2018 11:03:35 by SYSTEM
Additional Info : Peak(s) manually integrated



Area Percent Report

Sorted By : Signal
Multiplier : 1.0000
Dilution : 1.0000
Use Multiplier & Dilution Factor with ISTDs

Signal 1: DAD1 B, Sig=220,4 Ref=360,100

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.581	BB	0.2520	1486.61377	88.49747	98.2737
2	9.903	BB	0.2948	26.11446	1.25463	1.7263

Totals : 1512.72823 89.75211