Supporting Information for

$B_2(OH)_4$-mediated one-pot synthesis of tetrahydroquinoxalines from 2-amino(nitro)anilines and 1, 2-dicarbonyl compounds in water

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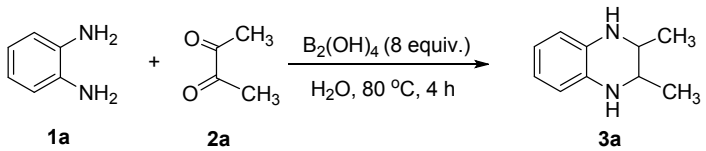
1. General Information

Unless otherwise noted, all reagents, catalysts and solvents were purchased from commercial suppliers and used without further purification. Column Chromatography was performed with silica gel (200-300 mesh). NMR spectra were recorded on Bruker ADVANCE III (400 MHz) spectrometers. $CDCl_3$ was the solvent used for the NMR analysis with tetramethylsilane as the internal standard. Chemical shifts were reported up field to TMS (0.00 ppm) for ^1H NMR and relative to $CDCl_3$ (77.0 ppm) for ^{13}C NMR.

2. General Procedure for the Synthesis of Tetrahydroquinoxalines

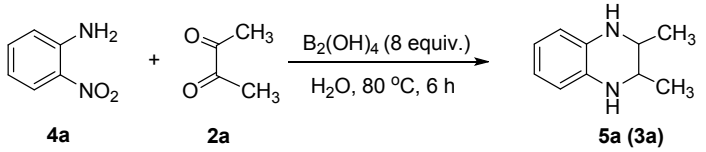
2.1 Start from 2-Aminoanilines and 1,2-Dicarbonyl Compounds



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

A flask was charged with 2-aminoaniline (**1a**; 1 mmol, 108 mg), 2,3-butanedione (**2a**; 1 mmol, 86 mg), $B_2(OH)_4$ (8 mmol, 720 mg, 8 eq.) and water (3 mL) under N_2. The reaction was stirred at 80 °C for 4 h. When the reaction was complete monitored by TLC, the mixture was cooled to room temperature, extracted with ethyl acetate (3×20 mL). The combined organic phase was washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude product. After determination of the diastereomeric excess by ^1H NMR, the crude product was purified by silica gel column chromatography to give the product **3a** as white solid.

2.2 Start from 2-Nitroanilines and 1,2-Dicarbonyl Compounds



4a **2a** **5a (3a)**

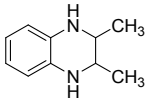
A flask was charged with 2-nitroaniline (**4a**; 1 mmol, 138 mg), 2,3-butanedione (**2a**; 1 mmol, 86 mg), $B_2(OH)_4$ (8 mmol, 720 mg, 8 eq.) and water (3 mL) under N_2. The reaction was stirred at 80 °C for 6 h. When the reaction was complete monitored by TLC, the mixture was cooled to room temperature, extracted with ethyl acetate (3×20 mL). The combined organic phase was

washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure to give a crude product. After determination of the diastereomeric excess by ^1H NMR, the crude product was purified by silica gel column chromatography to give the product **5a** as white solid.

2.3 Determination of *cis/trans* Ratio of the Products

The *cis/trans* ratio of the product was determined by ^1H NMR of the crude reaction mixture. For example, the reaction mixture of **3a** was extracted with ethyl acetate, and the combined organic phase was washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated to give a crude product. The diastereomeric excess (*cis*/*trans* of **3a** = 70/30) was determined by ^1H NMR spectroscopy of the crude product according to the corresponding signals.

3. Analytical Data of the Products



2, 3-Dimethyl-1,2,3,4-tetrahydroquinoxaline (3a)

Purified by flash column chromatography (PE: EA = 3:1), 96% yield (155 mg), white solid.

cis/trans = 70/30 (separable).

2, 3-Dimethyl-1,2,3,4-tetrahydroquinoxaline (5a)

Purified by flash column chromatography (PE: EA = 3:1), 82% yield (132mg), white solid.

cis/trans = 83/17 (separable).

2, 3-Dimethyl-1,2,3,4-tetrahydroquinoxaline (6)

Purified by flash column chromatography (PE: EA = 3:1), 23% yield (37 mg), white solid.

cis/trans = 68/32 (separable).

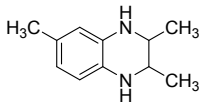
***cis* isomer (CAS: 7739-04-0)** [1, 2]

^1H NMR (400 MHz, $CDCl_3$): δ = 6.62 (dd, J_1 = 3.6 Hz, J_2 = 3.2 Hz, 2H), 6.53 (dd, J_1 = 3.6 Hz, J_2 = 3.2 Hz, 2H), 3.54-3.52 (m, 2H), 1.17-1.16 (d, J = 6.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 132.66, 118.56, 114.42, 49.04, 17.28.

***trans* isomer (CAS: 7739-05-1)** [1, 2]

^1H NMR (400 MHz, $CDCl_3$): δ = 6.62 (dd, J_1 = 3.6 Hz, J_2 = 3.2 Hz, 2H), 6.54 (dd, J_1 = 3.2 Hz, J_2 = 3.6 Hz, 2H), 3.06 (q, J = 2.0 Hz, 2H), 1.21 (d, J = 6.0 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ

= 133.50, 118.59, 113.93, 52.05, 19.04.



2,3,6-Trimethyl-1,2,3,4-tetrahydroquinoxaline (3b)

Purified by flash column chromatography (PE: EA = 3:1), 95% yield (167 mg), white solid. *cis/trans* = 65/35 (separable).

2,3,6-Trimethyl-1,2,3,4-tetrahydroquinoxaline (5b)

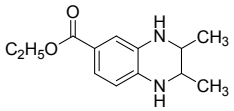
Purified by flash column chromatography (PE: EA = 3:1), 85% yield (149 mg), white solid. *cis/trans* = 67/33 (separable).

***cis* isomer (CAS: 1350827-80-3)** [2]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.45 (t, J = 3.6 Hz, 2H), 6.38 (d, J = 1.6 Hz, 1H), 3.52-3.49 (m, 4H), 2.22 (s, 3H), 1.16 (d, J = 6.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 132.70, 130.12, 128.17, 118.96, 115.15, 114.69, 49.18, 49.15, 20.75, 17.24, 17.21.

***trans* isomer (CAS: 1350827-88-1)** [2]

^{1}H NMR (400 MHz, $CDCl_3$): δ =6.45 (t, J = 8.0 Hz, 2H), 6.37 (d, J = 2.0 Hz, 1H), 3.09 (s, 2H), 2.21 (s, 3H), 1.19 (dd, J_1 = 2.0 Hz, J_2 = 1.6 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 133.55, 130.94, 128.20, 118.92, 114.66, 114.21, 52.21, 20.71, 19.08.

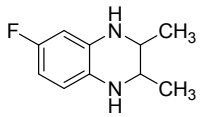


Ethyl 2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline-6-carboxylate (3c)

Purified by flash column chromatography (PE: EA = 5:1), 93% yield (217 mg), white solid. *cis/trans* = 69/31 (inseparable).

Mixture of *cis* and *trans* isomer of 3c (inseparable)

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.36 (dd, J_1 = 1.6 Hz, J_2 = 2.0 Hz, 1H), 7.23 (dd, J_1 = 2.0 Hz, J_2 = 2.0 Hz, 1H), 6.46 (dd, J_1 = 3.6 Hz, J_2 = 4.0 Hz, 1H), 4.33 (dd, J_1 = 7.6 Hz, J_2 = 7.6 Hz, 2H), 3.63-3.48 (m, 2H, *cis*), 3.16-2.99 (m, 1H, *trans*), 1.38 (dd, J_1 = 6.4 Hz, J_2 = 8.0Hz, 3H), 1.22 (d, J = 6.0 Hz, 2H, *trans*), 1.17 (t, J = 6.4 Hz, 4H, *cis*); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 167.09, 138.05 (*trans*), 137.44 (*cis*), 132.21 (*trans*), 131.43 (*cis*), 121.61 (*trans*), 121.53 (*cis*), 119.49 (*trans*), 119.45 (*cis*), 115.19 (*trans*), 114.76 (*cis*), 112.42 (*trans*), 112.02 (*cis*), 60.14, 52.24 (*trans*), 51.40 (*trans*), 49.22 (*cis*), 48.49 (*cis*), 19.06 (*trans*), 18.89 (*trans*), 17.35 (cis), 17.09 (*cis*), 14.49.



6-Fluoro-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline (3d) [2]

Purified by flash column chromatography (PE: EA = 5:1), 90% yield (162 mg), white solid.

cis/trans = 56/44 (inseparable).

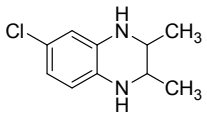
6-Fluoro-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline (5c)[2]

Purified by flash column chromatography (PE: EA = 5:1), 76% yield (137 mg), white solid.

cis/trans = 67/33 (inseparable).

Mixture of *cis* and *trans* isomer of 3d (inseparable)[2]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.40-6.37 (m, 1H), 6.27-6.19 (m, 2H), 3.48-3.41 (m, 2H, *cis*), 3.04-2.92 (m, 1H, *trans*), 1.16 (dd, J_1 = 1.6 Hz, J_2 = 1.6 Hz, 3H, *trans*), 1.11 (dd, J_1 = 1.6 Hz, J_2 = 1.2 Hz, 6H, *cis*); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 157.41 (d, J = 300 Hz, 1C), 134.59 (d, J = 11.0 Hz, 1C, *trans*), 133.82 (d, J = 11.0 Hz, 1C, *cis*), 129.15 (*trans*), 128.26 (*cis*), 114.80 (d, J = 9.2 Hz, 1C, *cis*), 114.30 (d, J = 9.2 Hz, 1C, *trans*), 103.86 (d, J = 5.4 Hz, 1C, *cis*), 103.64 (d, J = 5.4 Hz, 1C, *trans*), 101.00 (d, J = 25.9 Hz, 1C, *cis*), 100.55 (d, J = 25.9 Hz, 1C, *trans*), 52.14 (*trans*), 51.87 (*trans*), 49.07(*cis*), 48.91(*cis*), 18.99 (*trans*), 18.88 (*trans*), 17.11(*cis*).



6-Chloro-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline (3e)[2]

Purified by flash column chromatography (PE: EA = 5:1), 92% yield (180 mg), white solid.

cis/trans = 66/34 (separable).

6-Chloro-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline (5d)[2]

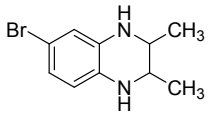
Purified by flash column chromatography (PE: EA = 5:1), 81% yield (159 mg), white solid.

cis/trans = 63/37 (separable).

***cis* isomer**: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.67 (dd, J_1 = 2.4 Hz, J_2 = 2.0 Hz, 1H), 6.62 (d, J = 2.4 Hz, 1H), 6.37 (d, J = 8.4 Hz, 1H) 3.63 (s, 2H), 3.53-3.48 (m, 2H), 1.14 (d, J = 6.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 134.12,131.62, 120.69, 116.39, 115.28, 109.99, 48.85, 48.80, 17.23, 17.16.

***trans* isomer**: **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.54 (dd, J_1 = 2.4 Hz, J_2 = 2.0 Hz, 1H), 6.49 (d, J = 2.0 Hz, 1H), 6.43 (d, J = 8.4 Hz, 1H), 3.05-2.99 (m, 2H), 1.19 (dd, J_1 = 1.2 Hz, J_2 = 1.2 Hz, 6H),

^{13}C NMR (100 MHz, $CDCl_3$): δ = 134.51, 131.85, 123.03, 117.79, 114.46, 113.26, 51.90, 18.95, 18.92.



6-Bromo-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline (3f)[2]

Purified by flash column chromatography (PE: EA = 5:1), 89% yield (213 mg), white solid.

cis/trans = 62/38(separable).

6-Bromo-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline (5e)[2]

Purified by flash column chromatography (PE: EA = 5:1), 65% yield (156 mg), white solid.

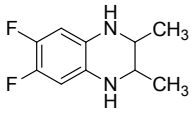
cis/trans = 64/36(separable).

***cis* isomer (CAS: 2095787-12-3)** [1, 2]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.54 (dd, J_1 = 3.2 Hz, J_2 = 2.8 Hz, 1H), 6.48 (d, J = 2.4 Hz, 1H), 6.42 (d, J = 8.4 Hz, 1H), 3.71 (s, 2H), 3.54-3.49 (m, 2H), 1.15 (d, J = 3.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 133.76, 131.13, 122.93, 117.77, 114.88, 113.65, 48.89, 48.84, 17.21, 17.16.

***trans* isomer (CAS: 2095787-26-9)** [1, 2]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.68 (dd, J_1 = 2.0 Hz, J_2 = 2.0 Hz, 1H), 6.63 (d, J = 3.6 Hz, 1H), 6.39 (d, J = 8.4 Hz, 1H), 3.07-3.00 (m, 2H), 1.21 (d, J = 4.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 134.85, 132.35, 120.72, 116.00, 114.84, 110.03, 51.84, 51.79, 29.70, 18.94.



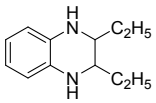
6,7-Difluoro-2,3-dimethyl-1,2,3,4-tetrahydroquinoxaline (3g)

Purified by flash column chromatography (PE: EA = 5:1), 78% yield (154 mg), white solid.

cis/trans = 79/21 (separable).

***cis* isomer: ^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.46 (dd, J_1 = 5.2 Hz, J_2 = 5.2 Hz, 1H), 6.30-6.24 (m, 1H), 3.54-3.47 (m, 2H), 1.16 (d, J = 6.4 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 157.28 (d, J = 233 Hz, 1C), 133.90 (d, J = 10 Hz, 1C), 127.76, 115.11 (d, J = 9.2 Hz, 1C), 103.86 (d, J = 22.3 Hz, 1C), 101.01 (d, J = 25.9 Hz, 1C), 49.03, 48.87, 17.07, 16.86.

***trans* isomer: ^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.33 (t, J = 8.4 Hz, 2H), 3.00 (s, 2H), 1.19 (d, J = 6.0 Hz, 6H), **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 144.22 (d, J = 15 Hz, 1C), 141.90 (d, J = 16 Hz, 1C), 129.18, 102.39 (d, J = 8.4 Hz, 1C), 102.29 (d, J = 8.4 Hz, 1C), 51.87, 18.87.



2,3-Diethyl-1,2,3,4-tetrahydroquinoxaline (3h)

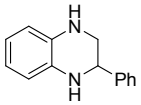
Purified by flash column chromatography (PE: EA = 5:1), 76% yield (144 mg), yellow solid. *cis/trans* = 0/100 (*cis* isomer was not detected).

2,3-Diethyl-1,2,3,4-tetrahydroquinoxaline (5f)

Purified by flash column chromatography (PE: EA = 5:1), 74% yield (141 mg), yellow solid. *cis/trans* = 0/100 (*cis* isomer was not detected).

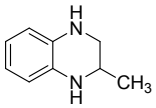
***trans*-2,3-Diethyl-1,2,3,4-tetrahydroquinoxaline (CAS: 2095787-23-6)** [3]

^{1}H NMR (400 MHz, $CDCl_3$): δ = 6.62 (dd, J = 3.2 Hz, 2H), 6.54 (dd, J = 3.2 Hz, 2H), 3.78 (s, 2H), 3.30 (dd, J_1 = 6.4 Hz, J_2 = 2.4 Hz, 2H), 1.50 (t, J = 7.2 Hz, 4H), 1.02 (t, J = 7.2 Hz, 6H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 132.90, 118.45, 114.31, 54.61, 23.01, 10.50 .



2-Phenyl-1,2,3,4-tetrahydroquinoxaline (3i)[1, 2]

Purified by flash column chromatography (PE: EA = 10:1), 75% yield (157 mg), yellow solid. CAS: 5021-47-6. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 7.45-7.34 (m, 5H), 6.70-6.67 (m, 2H), 6.65-6.61 (m, 2H), 4.53 (dd, J_1 = 3.2 Hz, J_2 = 2.8 H, 1H), 3.39 (s, 1H), 3.50 (dd, J = 3.2 Hz, 1H), 3.37 (dd, J_1 = 8.0 Hz, J_2 = 8.4 H, 1H); **^{13}C NMR** (100 MHz, $CDCl_3$): δ =141.84, 134.18, 132.70, 128.67, 127.94, 127.92, 127.03, 127.00,119.03, 118.81, 114.81, 114.48, 54.76, 49.16.



2-Methyl-1,2,3,4-tetrahydroquinoxaline (3j) [1, 2]

Purified by flash column chromatography (PE: EA = 5:1), 81% yield (119 mg), yellow solid. CAS: 6640-55-7. **^{1}H NMR** (400 MHz, $CDCl_3$): δ = 6.65 (dd, J_1 = 3.2 Hz, J_2 = 3.6 Hz, 2H), 6.56 (dd, J_1 = 2.8 Hz, J_2 = 2.8 Hz, 2H), 3.58-3.34 (m, 4H), 3.08 (dd, J_1 = 2.8 Hz, J_2 = 2.8 Hz, 1H), 1.23 (d, J = 7.2 Hz, 3H), **^{13}C NMR** (100 MHz, $CDCl_3$): δ = 133.62, 133.25, 118.71, 114.53, 114.48, 48.28, 45.74, 19.96.

References

[1] Qin, J.; Chen, F.; Ding, Z.; He, Y. M.; Xu, L.; Fan, Q. H., *Org. Lett.,* **2011**, *13*, 6568.

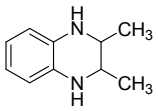
[2] Murata, S.; Sugimoto, T.; Matsuura, S. *Heterocycles*, **1987**, *26*, 763

[3] Shi, F.; Tan, W.; Zhang, H. H.; Li, M.; Q. Ye, G.; Ma, H.; Tu, S. J.; Li, G., *Adv. Synth. Catal.,* **2013**, *355*, 3715.

[4] George, H. F.; Harry, P. S. *J. Org. Chem.*, **1974**, *39,* 635.

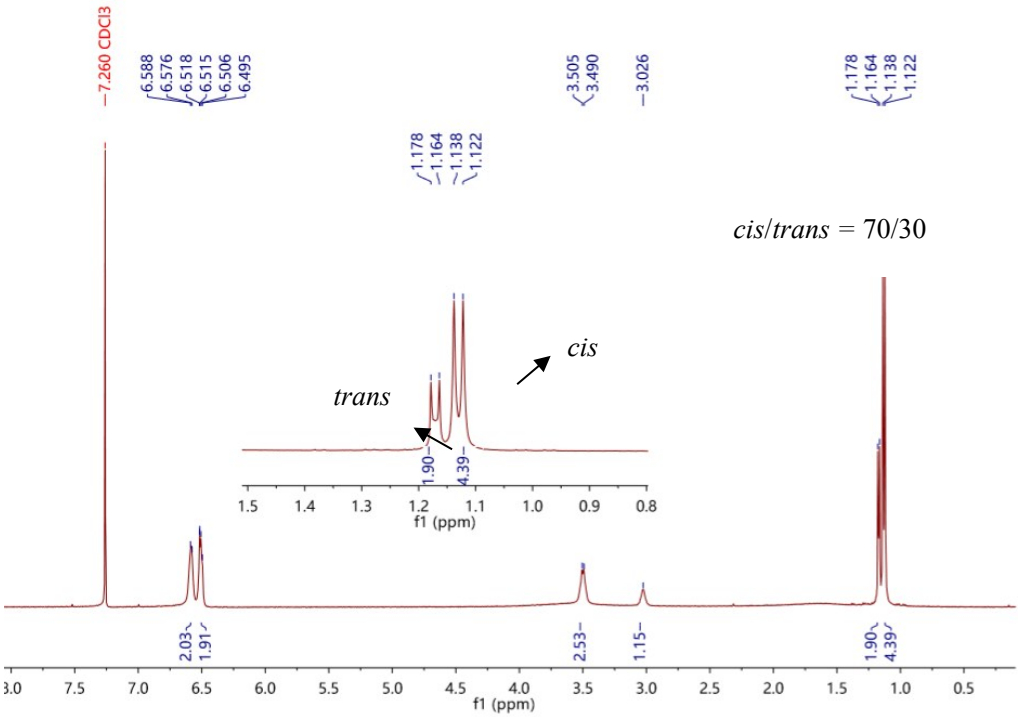
[5] Li, S. L; Meng, W.; Du, H.F., Org. Lett., **2017**, *19*, 2604.

4. ^{1}H NMR & ^{13}C NMR Spectra of the Products

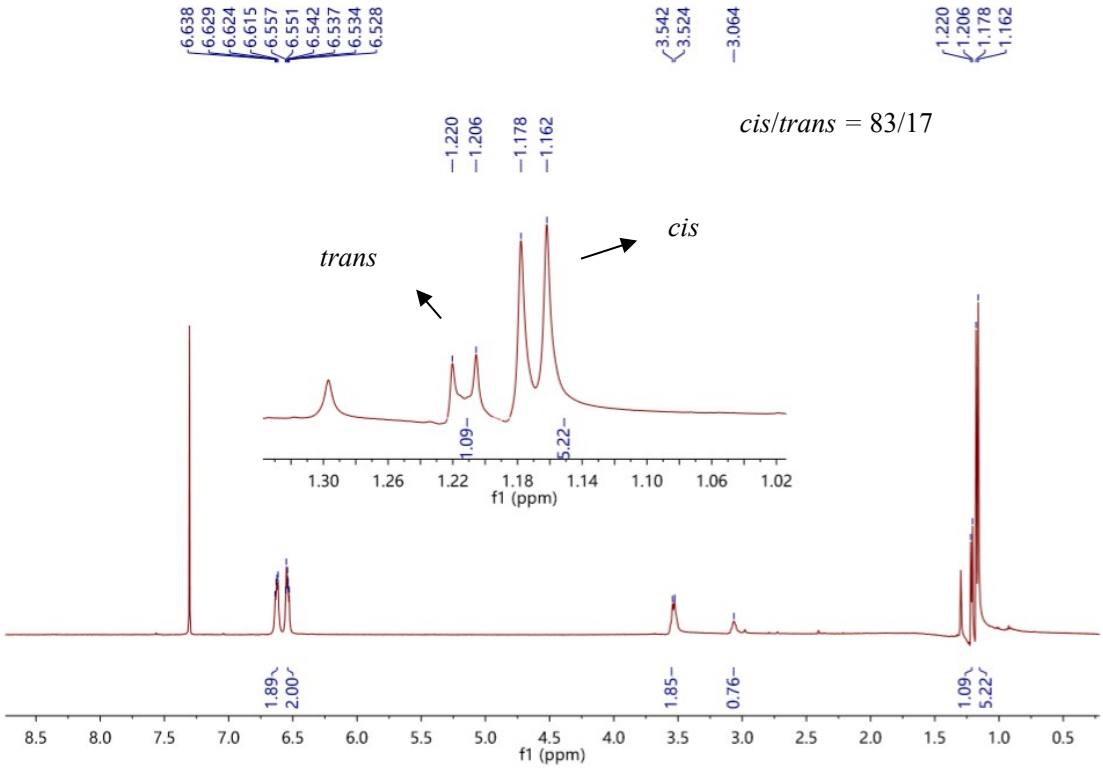


3a or 5a or 6

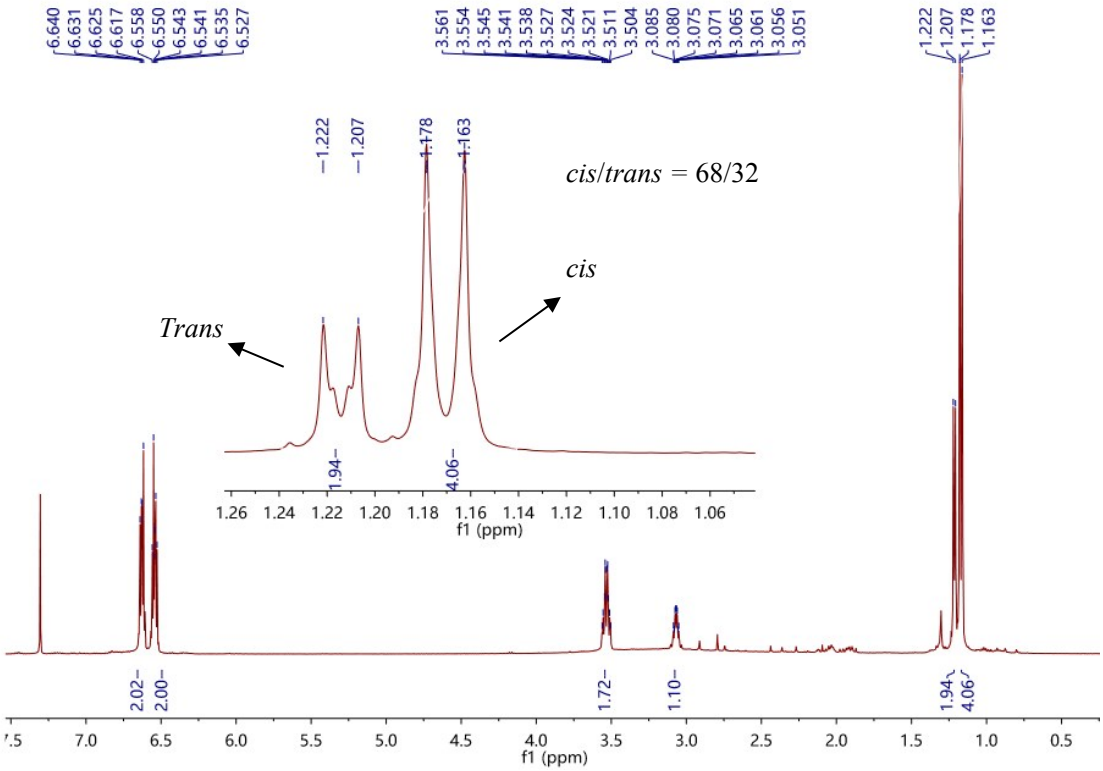
cis/*trans* of **3a** = 70/30 determined by ^{1}H NMR of the crude product

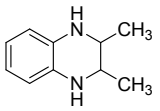


cis/*trans* of **5a** = 83/17 determined by ^{1}H NMR of the crude product

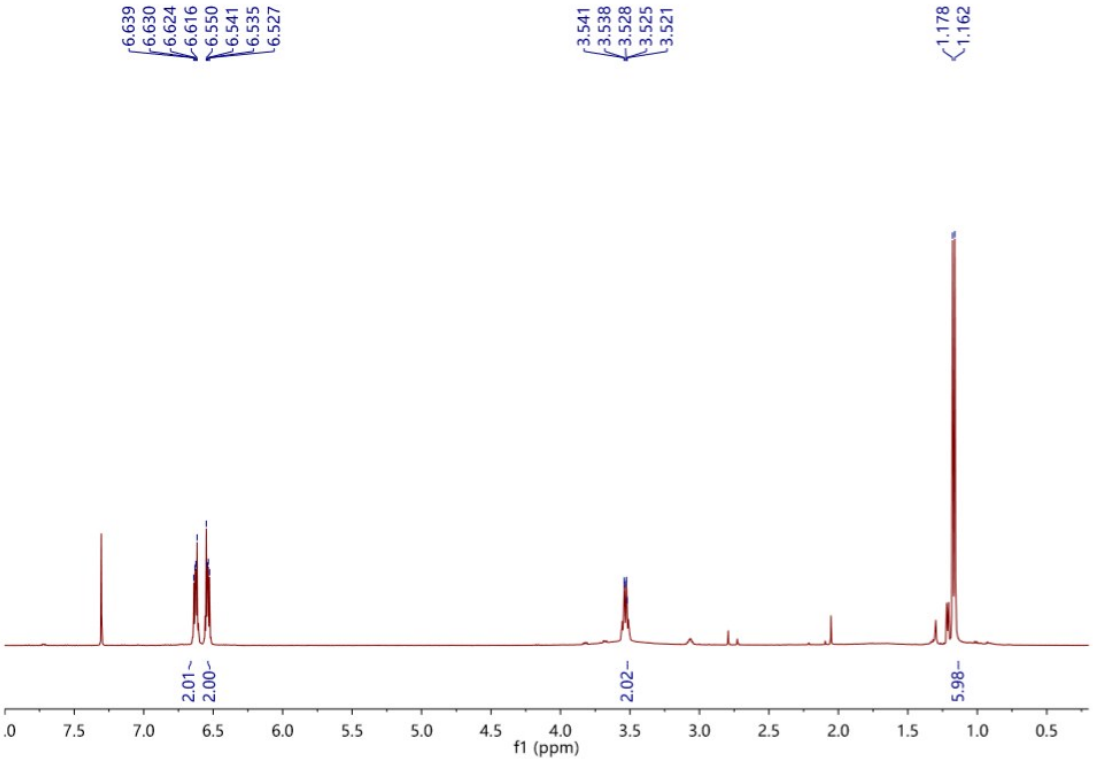


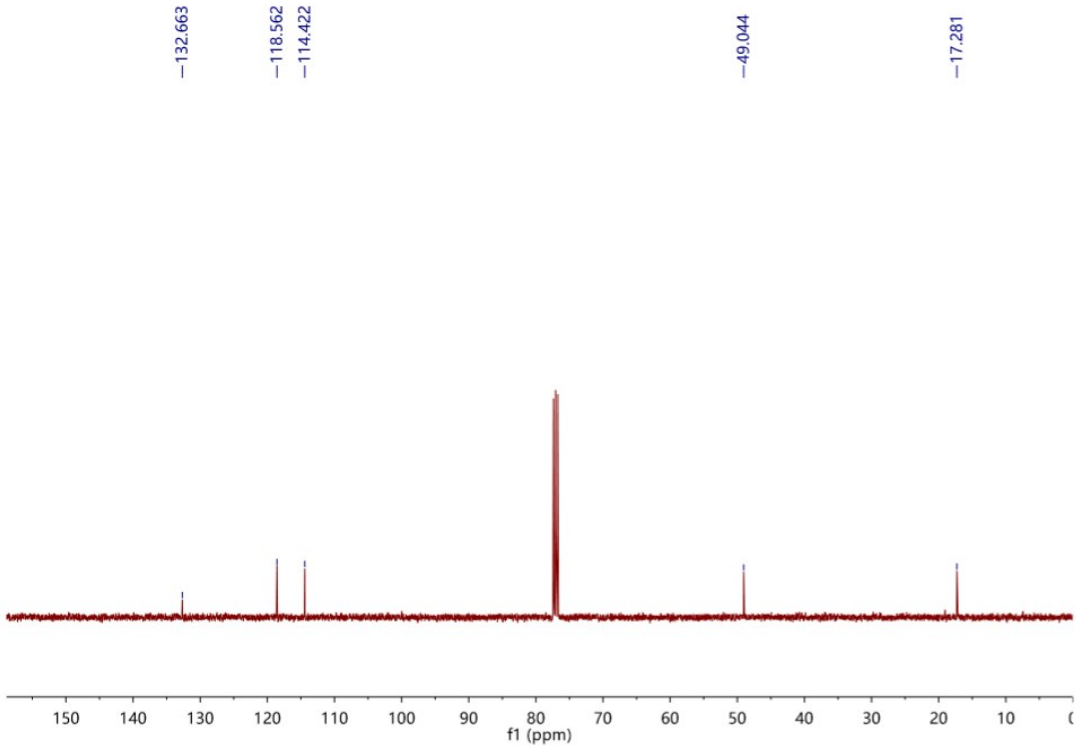
cis/*trans* of **6** = 68/32 determined by ^{1}H NMR of the crude product

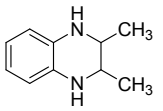




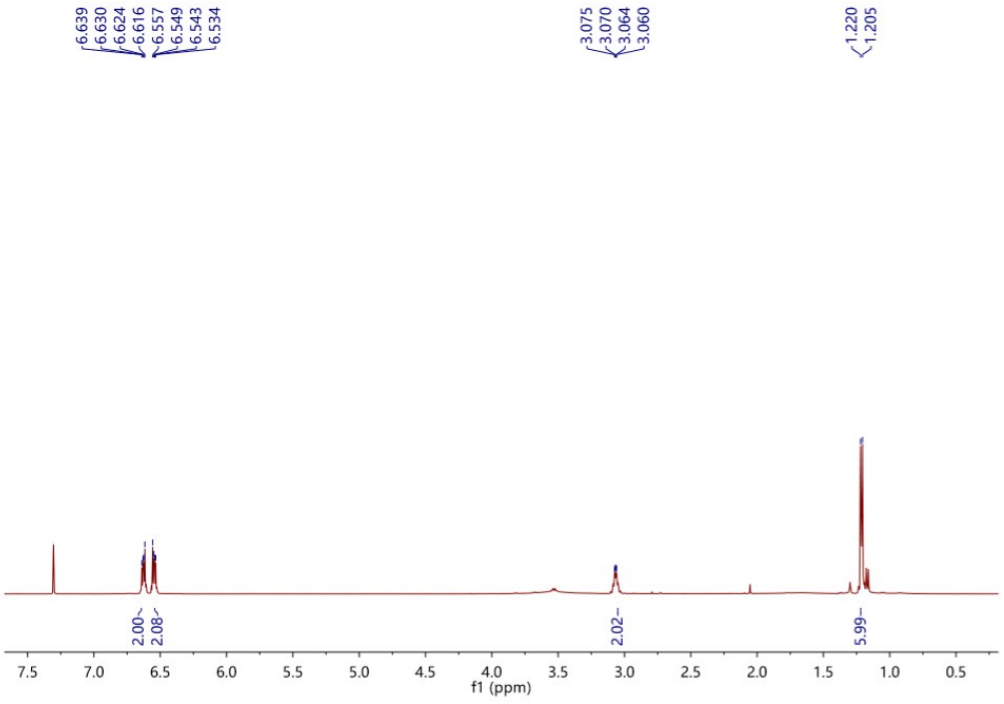
cis-**3a**

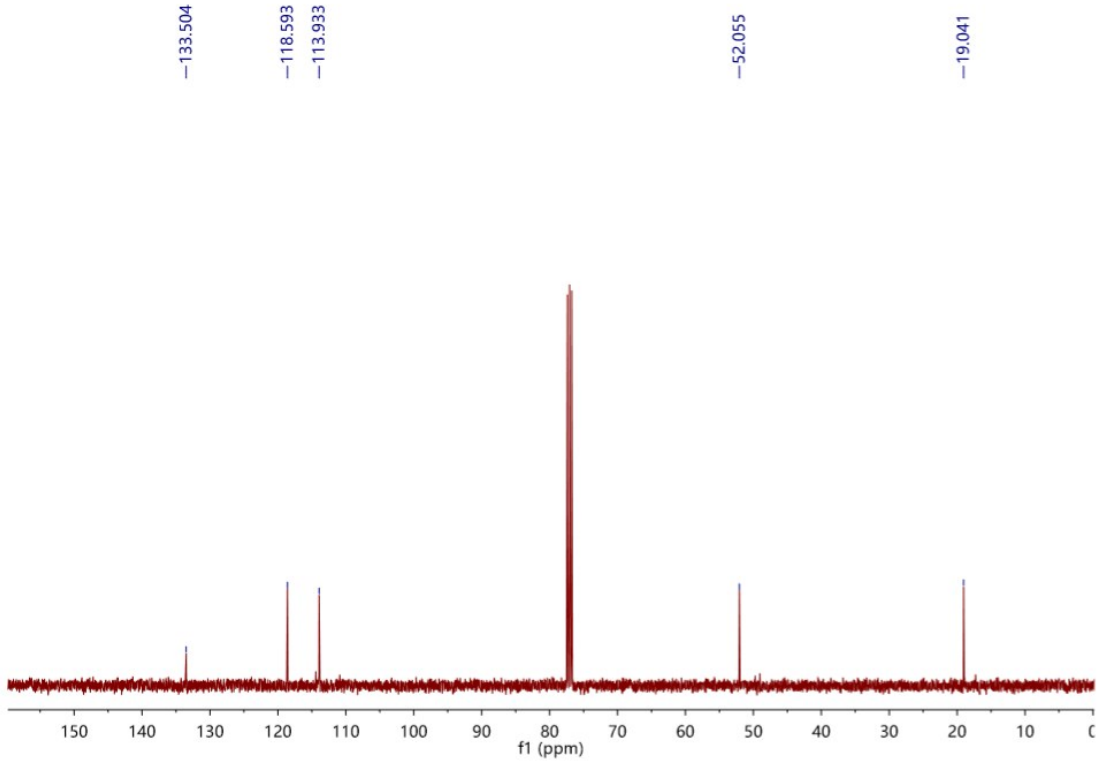

6.639
6.630
6.624
6.616
6.550
6.541
6.535
6.527
3.541
3.538
3.528
3.525
3.521
1.178
1.162
2.01
2.00
2.02
5.98
f1 (ppm)

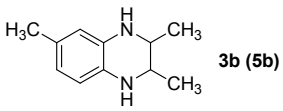

132.663
118.562
114.422
49.044
17.281
f1 (ppm)


H
N
CH3
N
H
CH3

trans-**3a**

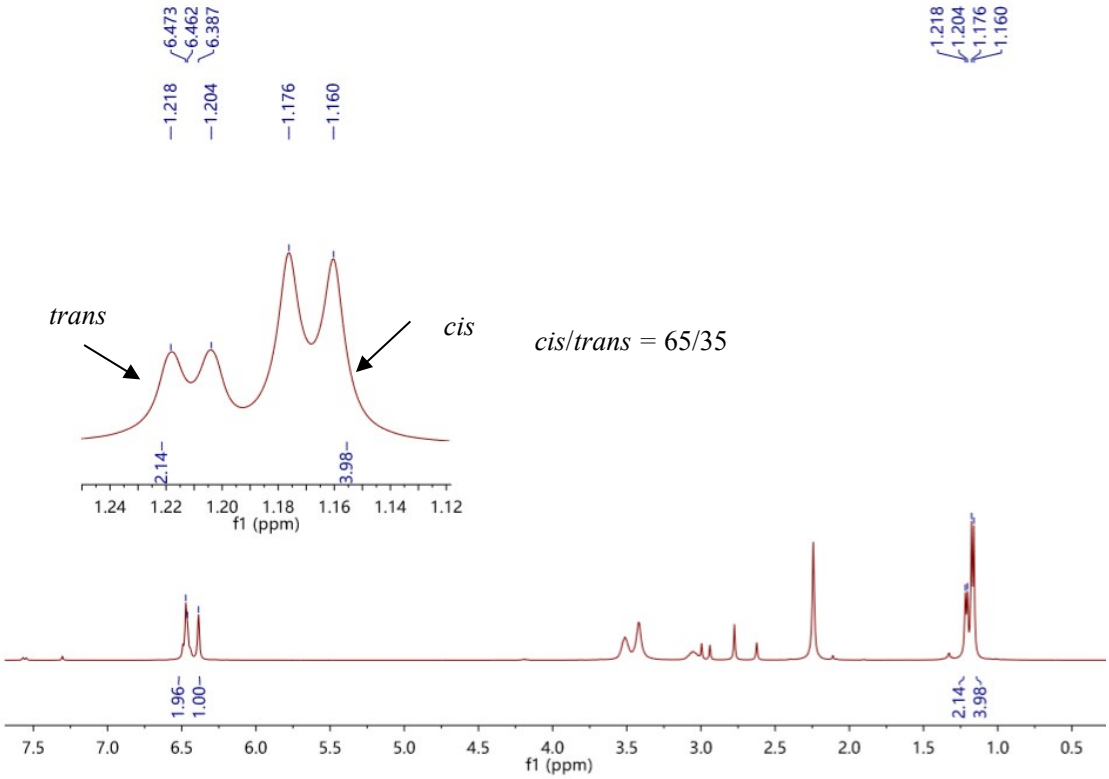

6.639
6.630
6.624
6.616
6.557
6.549
6.543
6.534
3.075
3.070
3.064
3.060
1.220
1.205
2.00
2.08
2.02
5.99
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


133.504
118.593
113.933
52.055
19.041
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

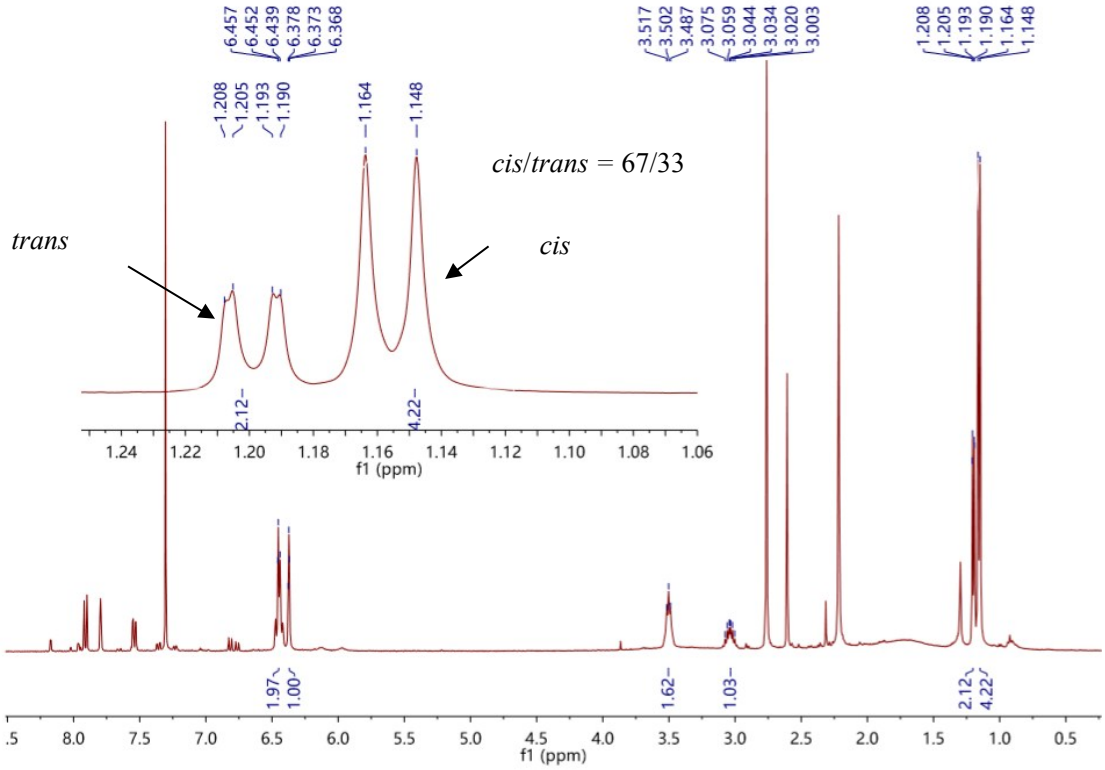


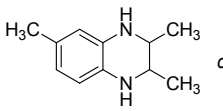
3b (5b)

cis/*trans* of **3b** = 65/35 determined by ^{1}H NMR of the crude product.

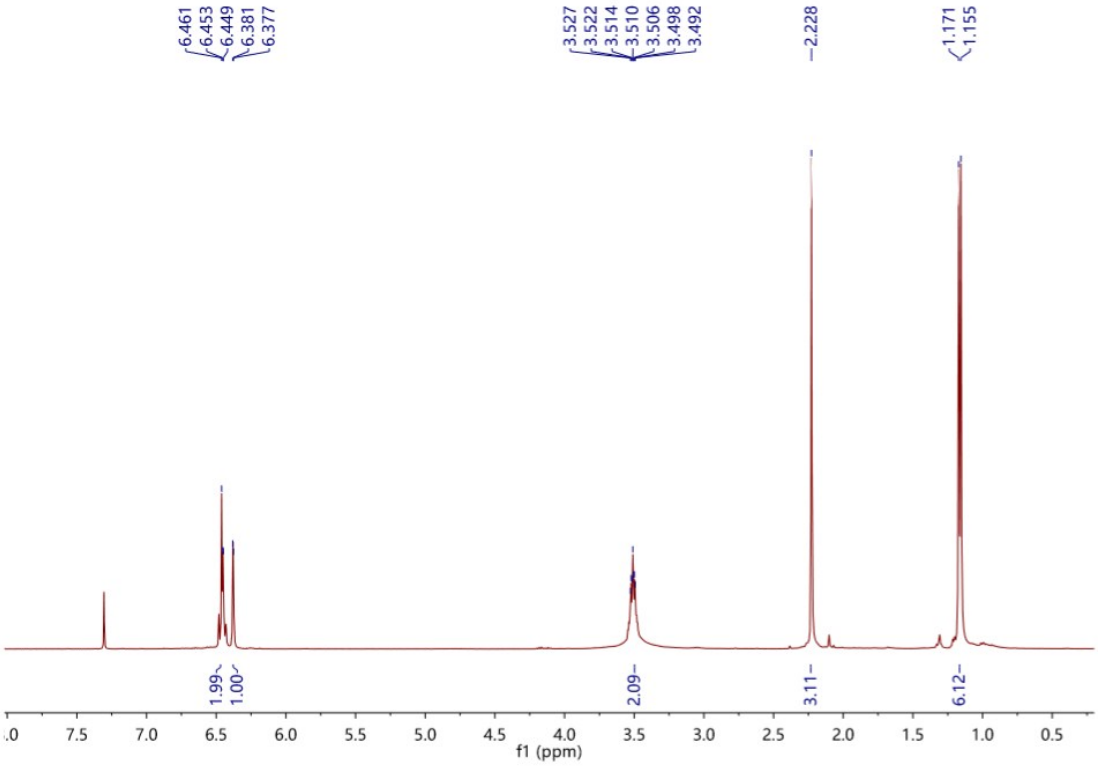


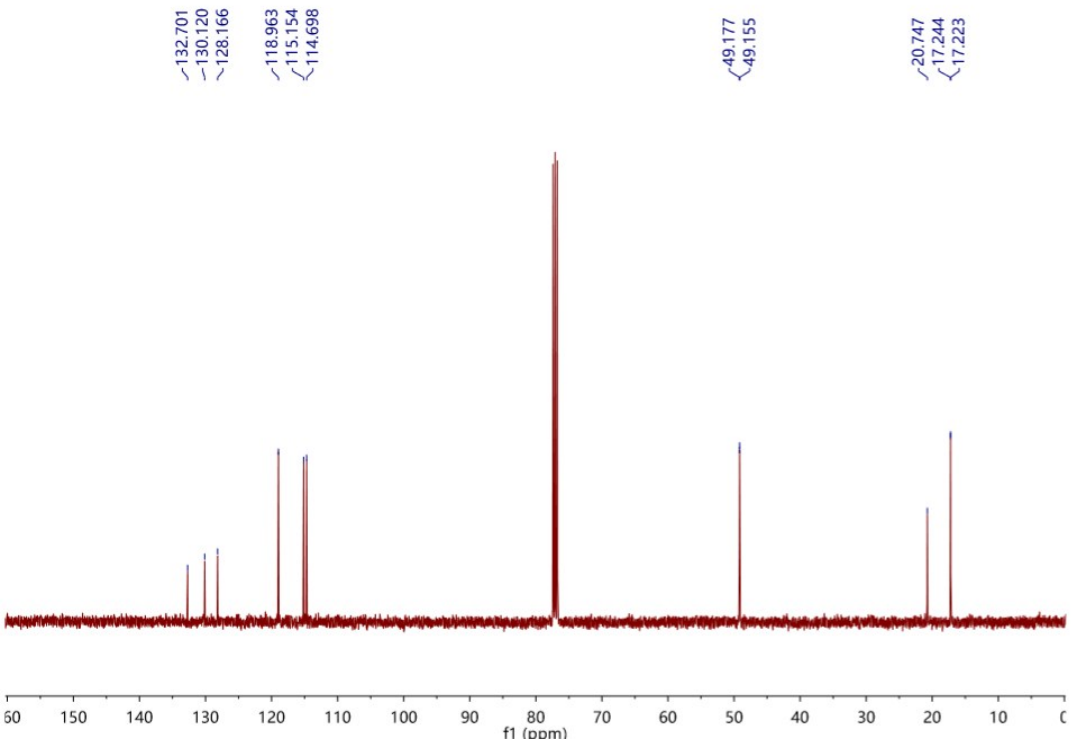
cis/*trans* of **5b** = 67/33 determined by ^{1}H NMR of the crude product.

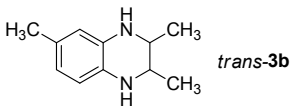



H3C
CH3
N
H
N
H
CH3

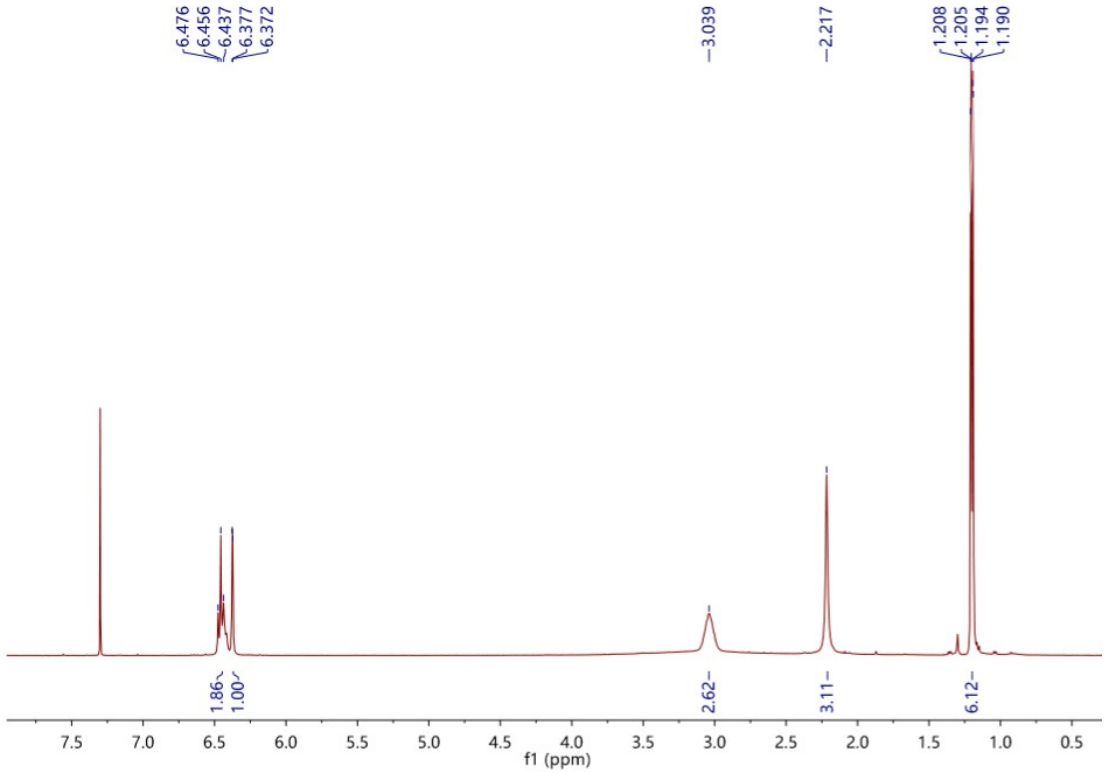
cis-**3b**

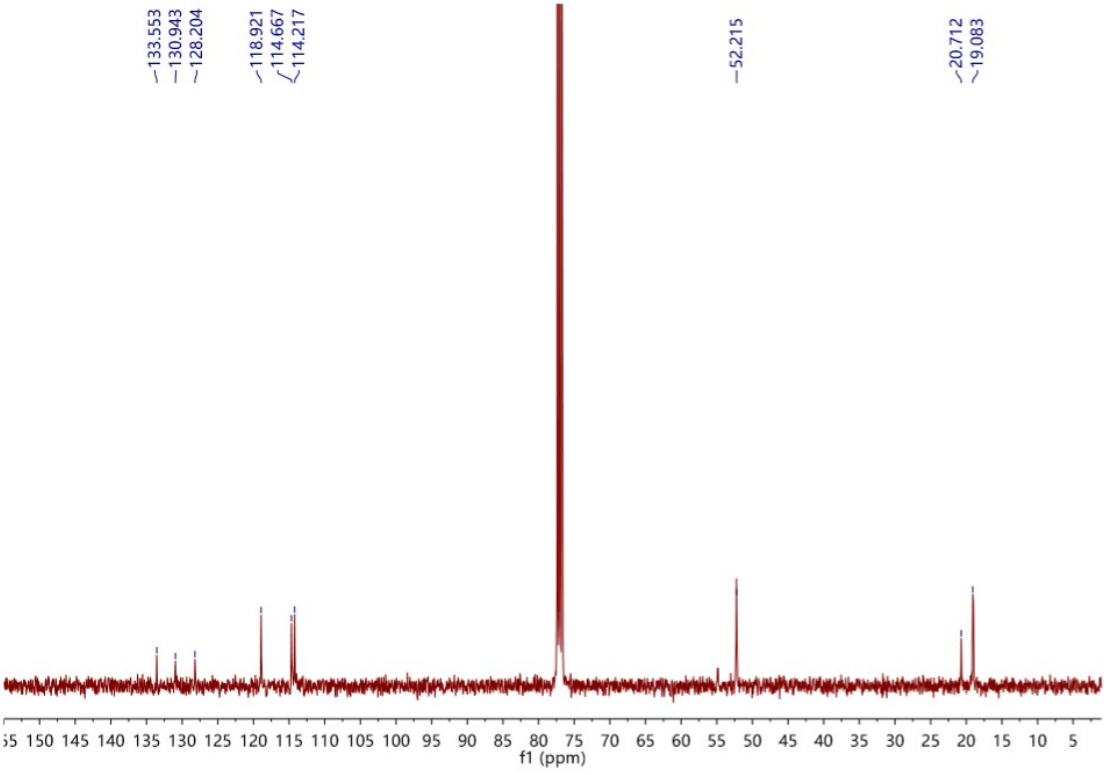

6.461
6.453
6.449
6.381
6.377
3.527
3.522
3.514
3.510
3.506
3.498
3.492
2.228
1.171
1.155
1.99
1.00
2.09
3.11
6.12
f1 (ppm)

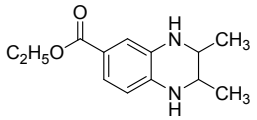

132.701
130.120
128.166
118.963
115.154
114.698
49.177
49.155
20.747
17.244
17.223
f1 (ppm)


H3C
CH3
N
H
N
H
CH3

trans-**3b**

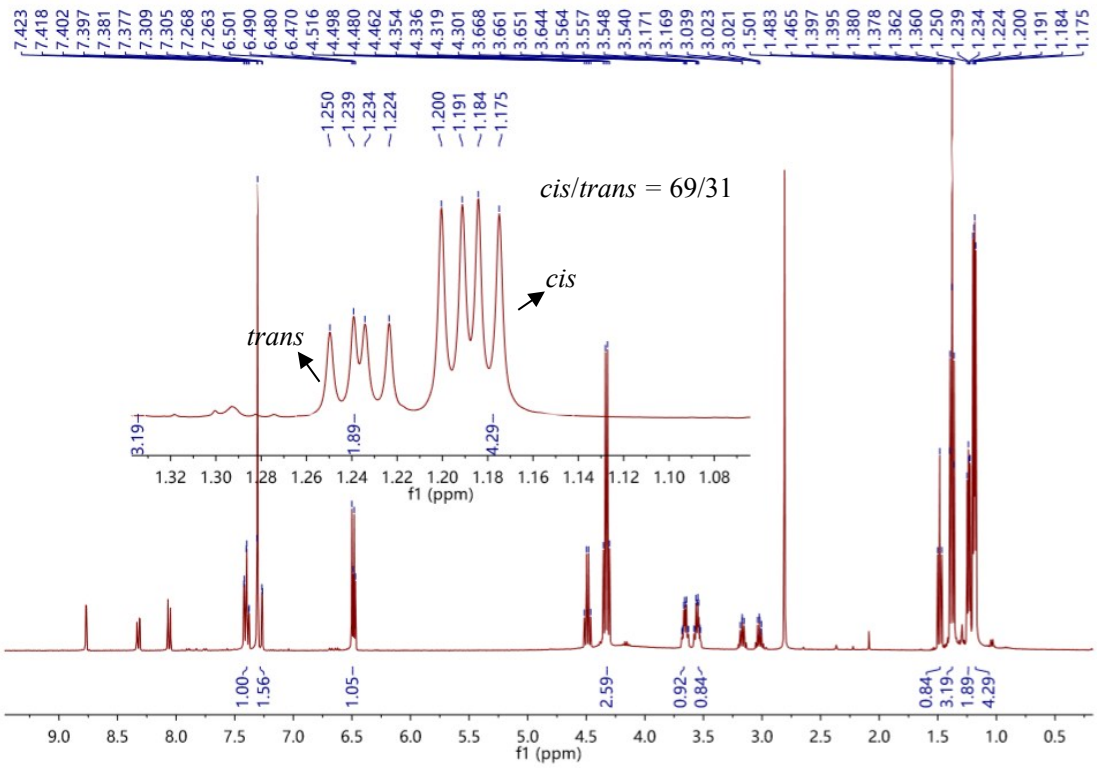

6.476
6.456
6.437
6.377
6.372
3.039
2.217
1.208
1.205
1.194
1.190
1.86
1.00
2.62
3.11
6.12
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

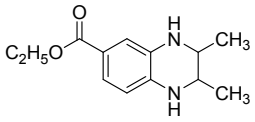

133.553
130.943
128.204
118.921
114.667
114.217
52.215
20.712
19.083
f1 (ppm)



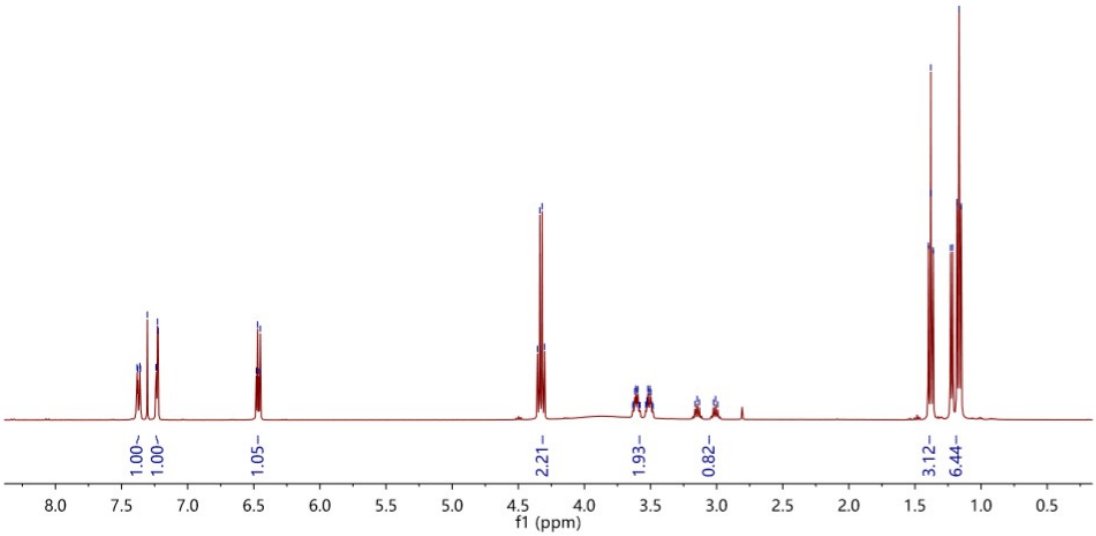
3c

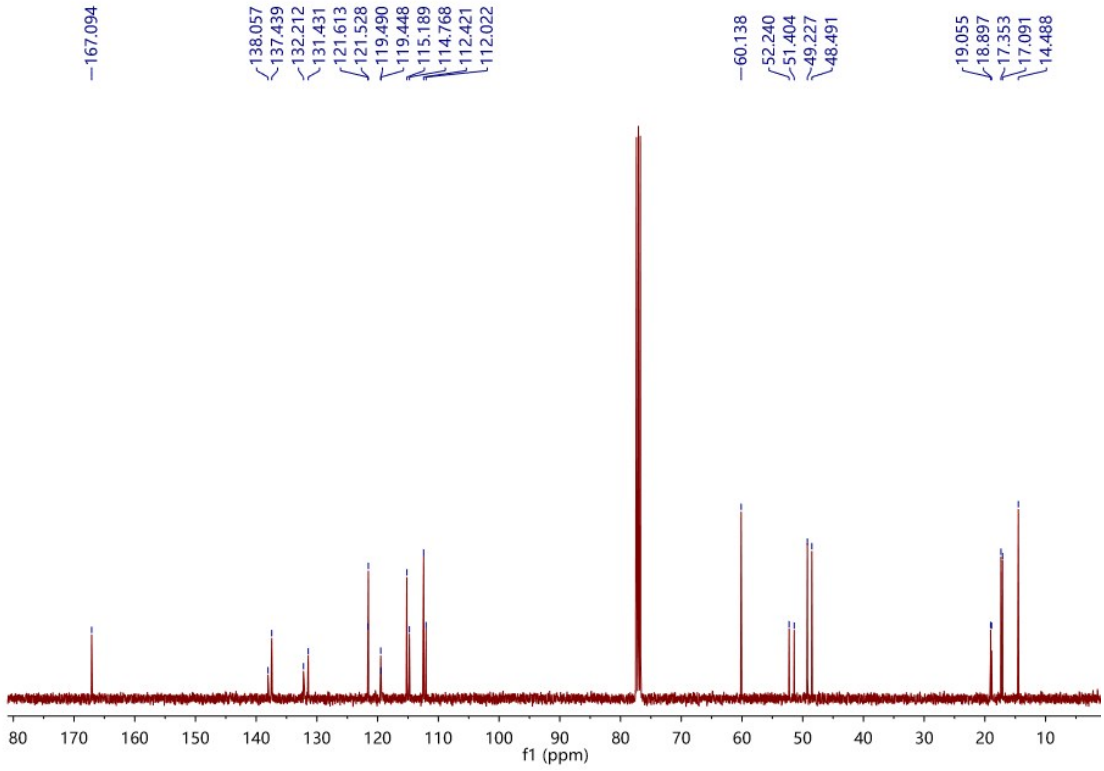
cis/*trans* of **3c** = 69/31 determined by ^{1}H NMR of the crude product.

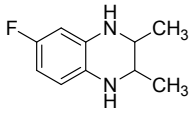




3c *(cis/trans)* inseparable

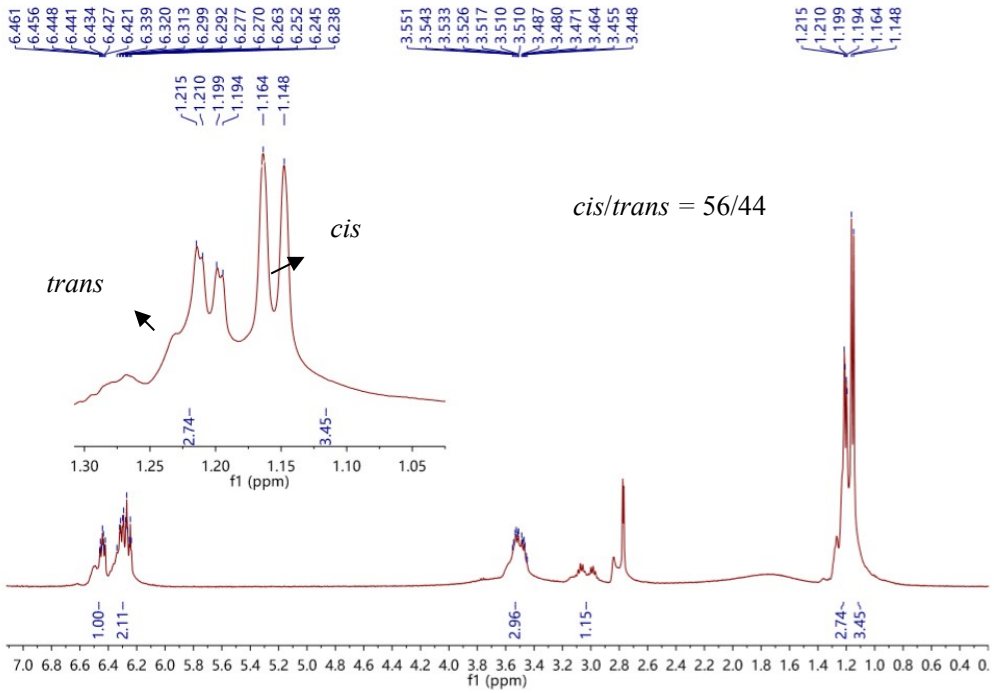




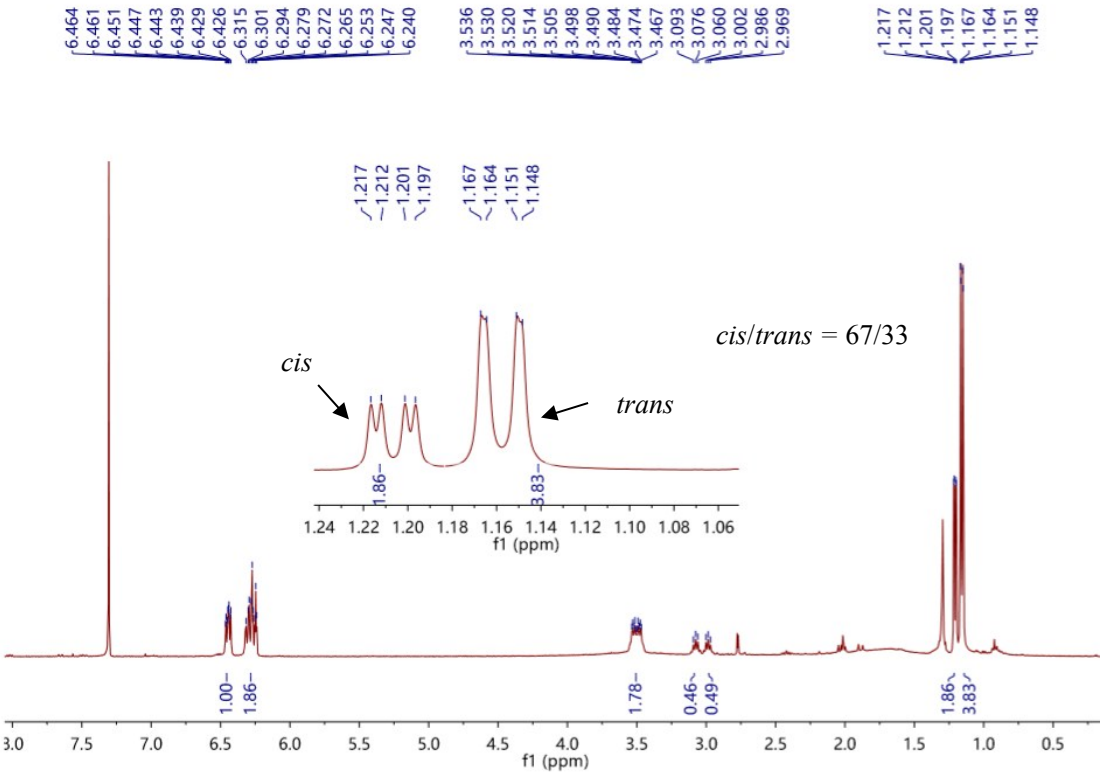


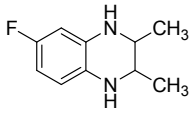
3d (5c)

cis/*trans* of **3d** = 56/44 determined by ^{1}H NMR of the crude product.

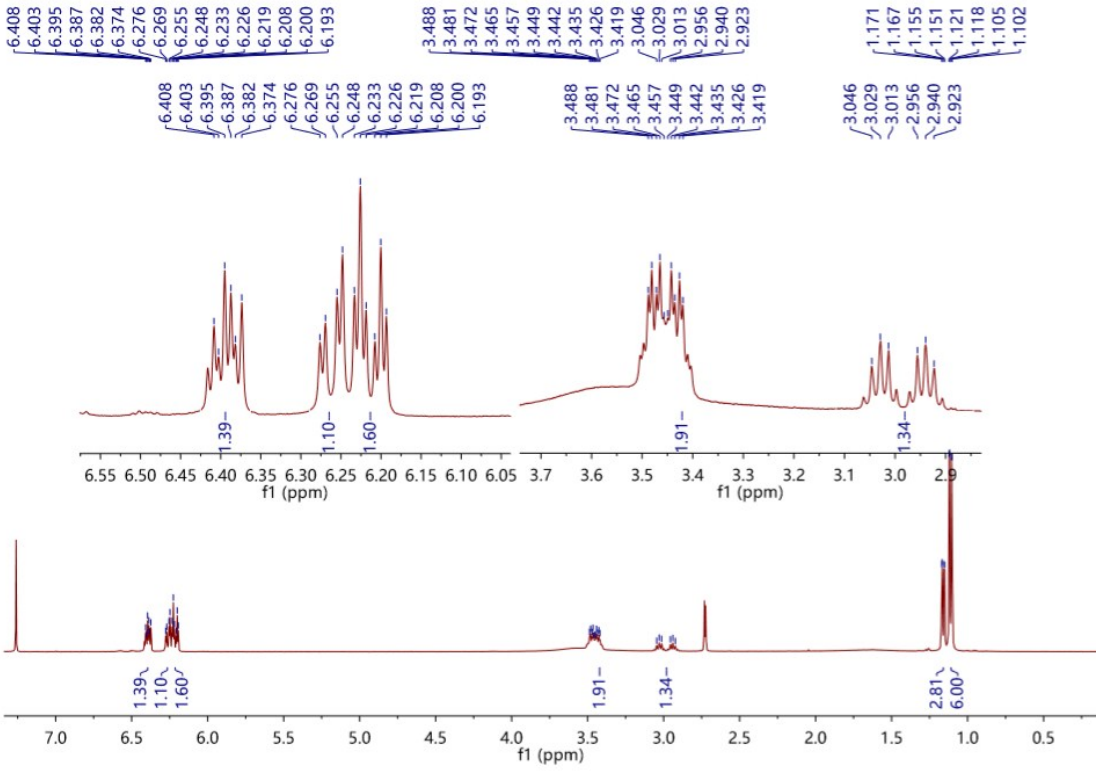


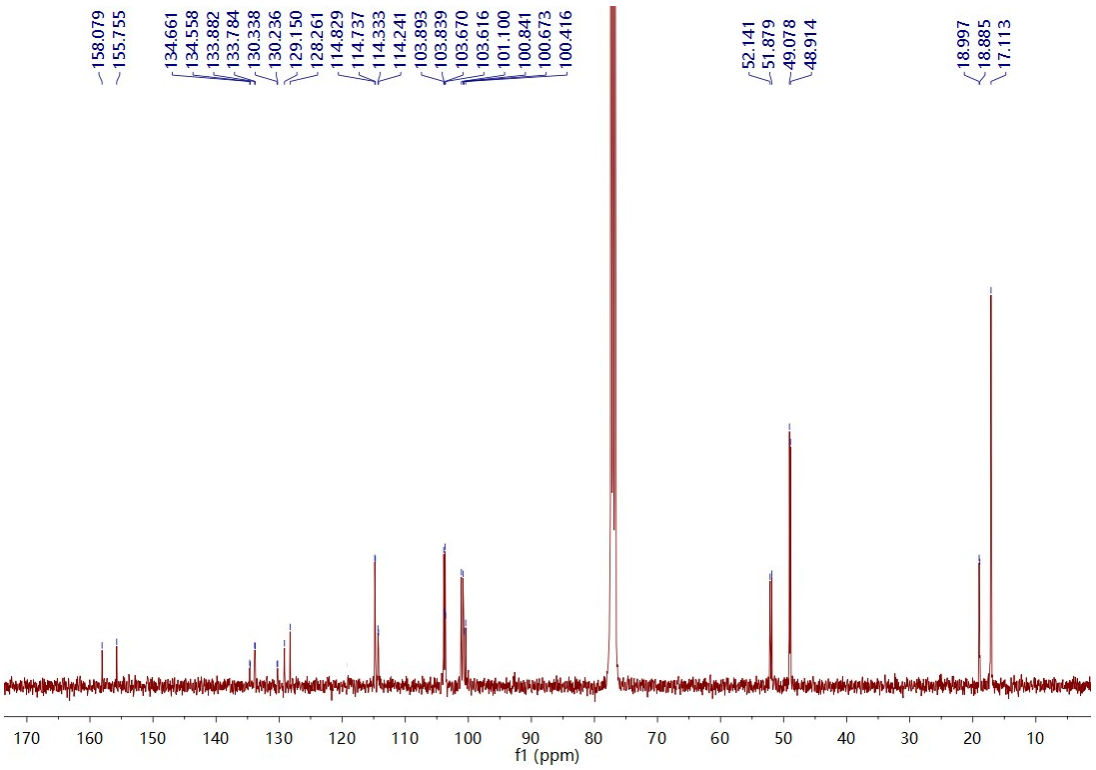
cis/*trans* of **5c**= 67/33 determined by ^{1}H NMR of the crude product.

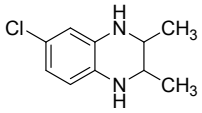




3d (*cis/trans*) inseparable

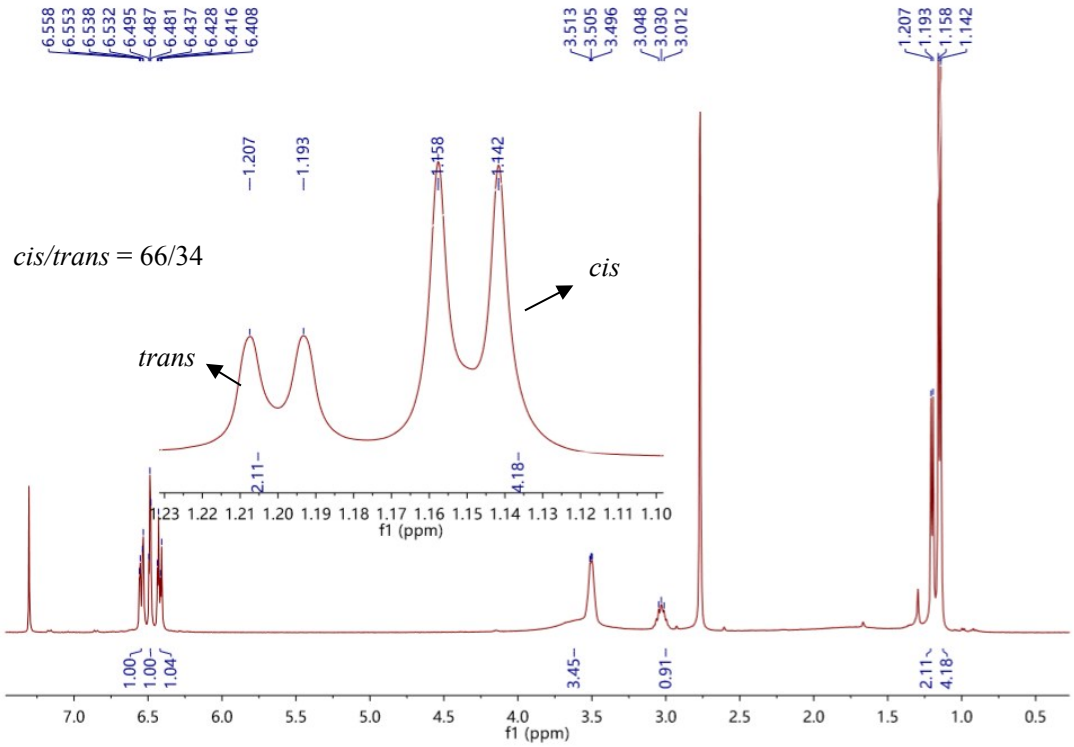




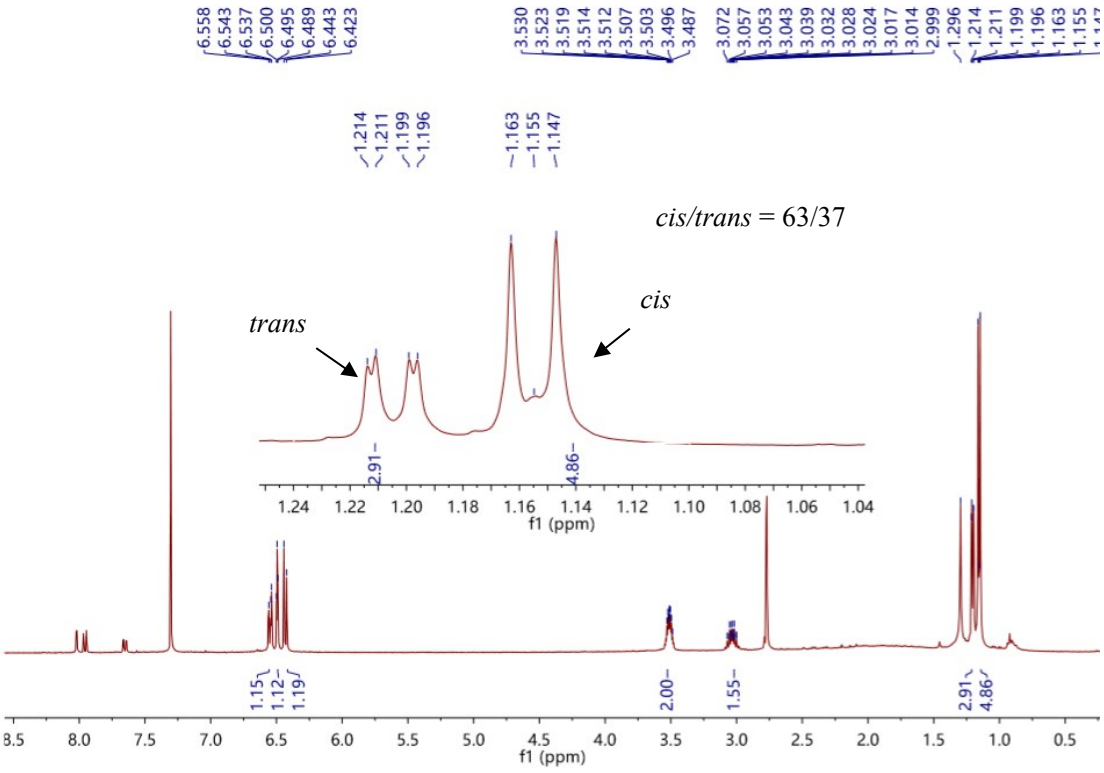


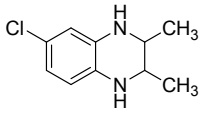
3e (5d)

cis/*trans* of **3e** = 66/34 determined by ^{1}H NMR of the crude product.

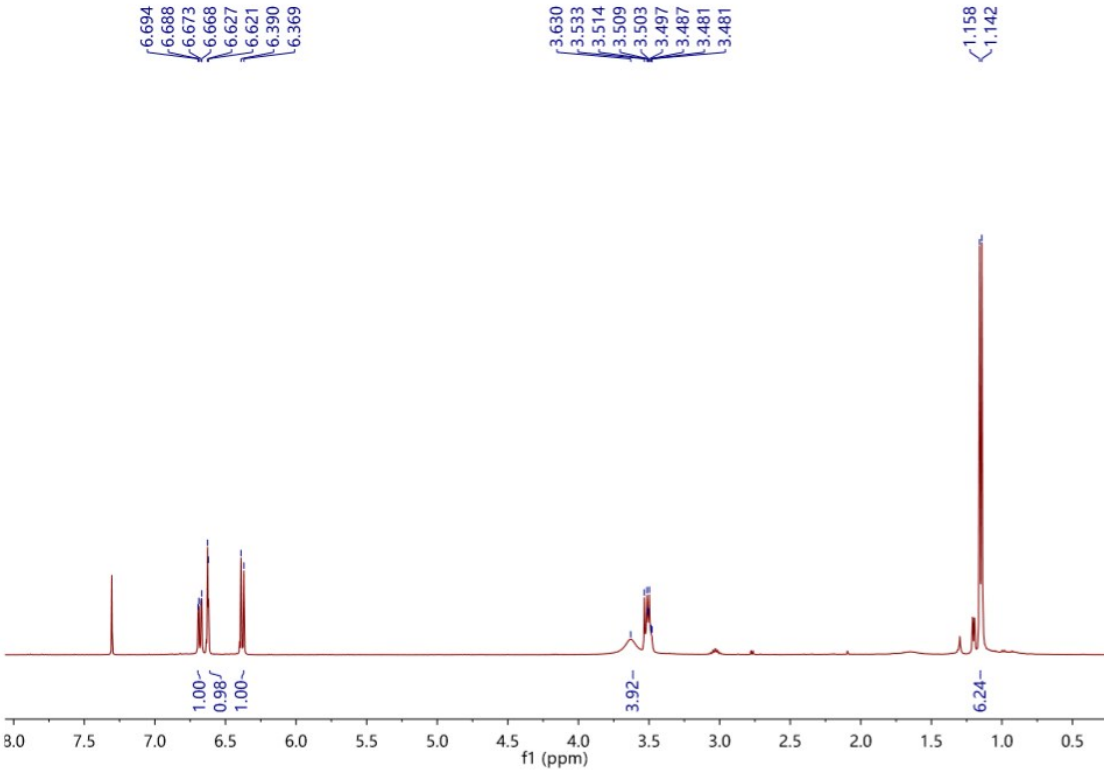


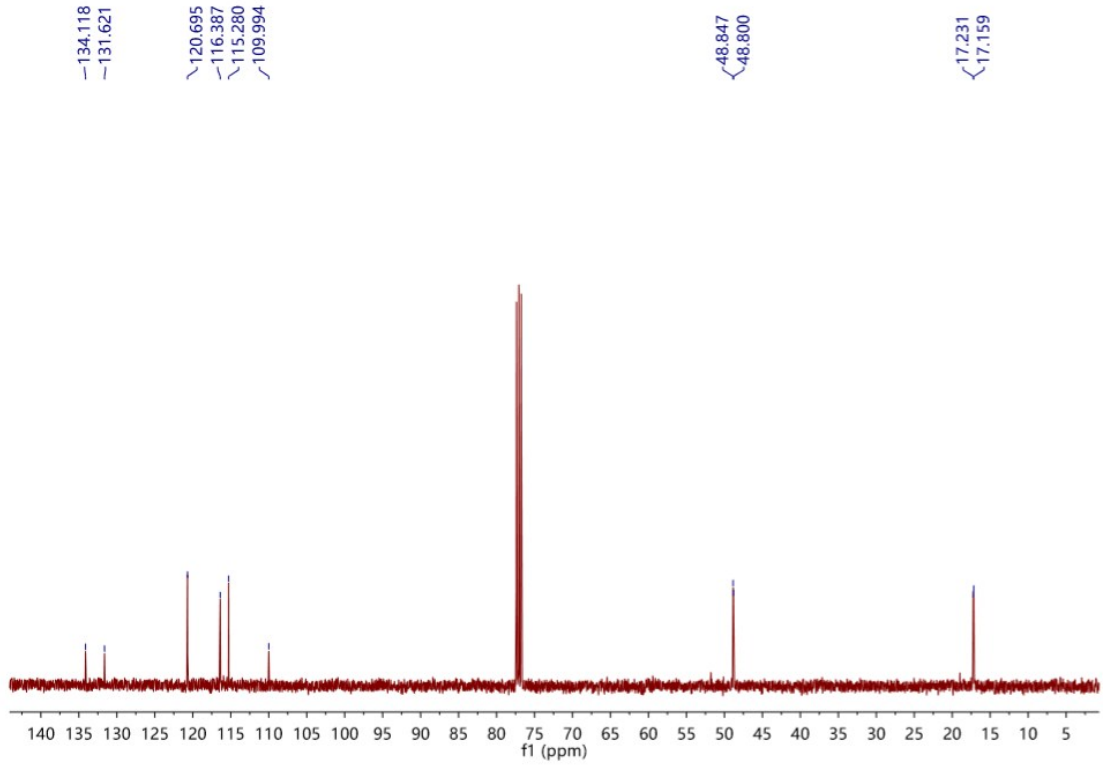
cis/*trans* of **5d** = 63/37 determined by ^{1}H NMR of the crude product.

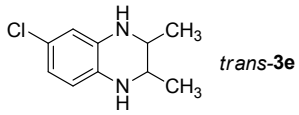



Cl
H
N
CH3
N
H
CH3

cis-**3e**


6.694
6.688
6.673
6.668
6.627
6.621
6.390
6.369
3.630
3.533
3.514
3.509
3.503
3.497
3.487
3.481
3.481
1.158
1.142
1.00
0.98
1.00
3.92
6.24
f1 (ppm)


134.118
131.621
120.695
116.387
115.280
109.994
48.847
48.800
17.231
17.159
f1 (ppm)

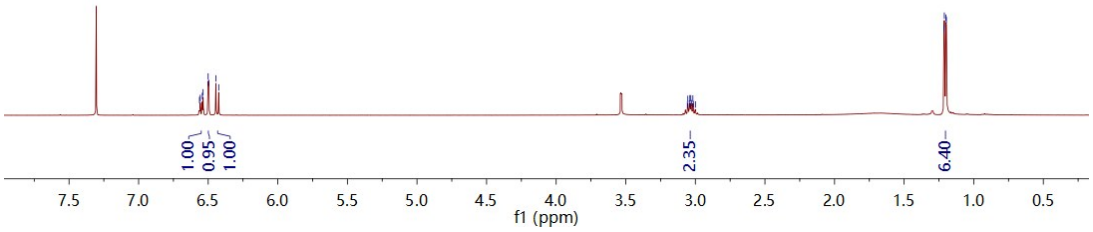

Cl
H
N
CH3
N
H
CH3

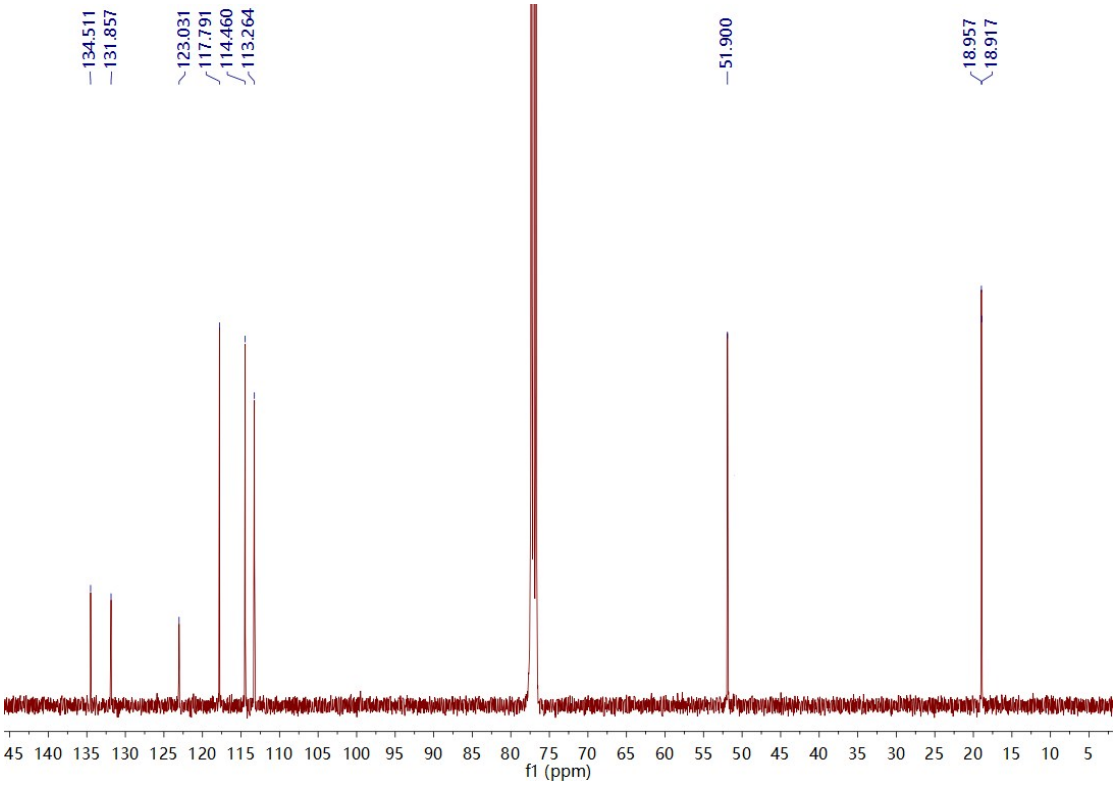
trans-**3e**

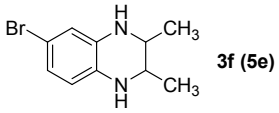

6.563
6.557
6.542
6.537
6.500
6.495
6.445
6.424


3.057
3.054
3.043
3.039
3.032
3.028
3.018
3.014
2.999


1.214
1.211
1.199
1.196

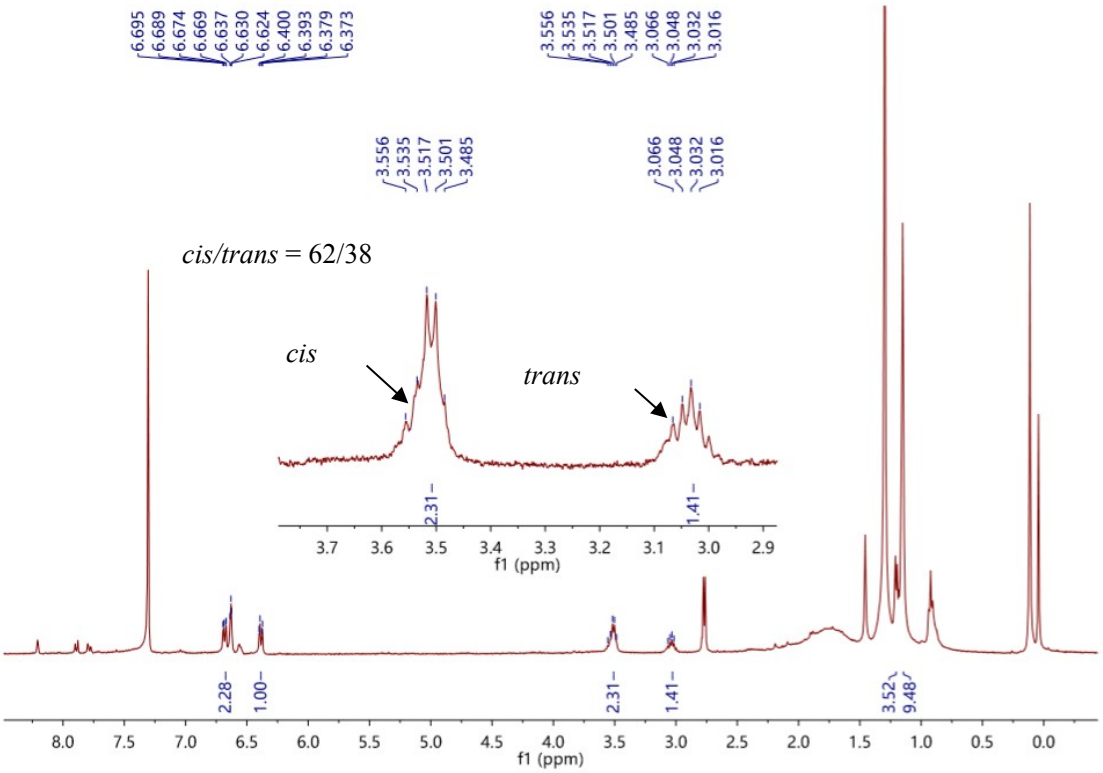

1.00
0.95
1.00
2.35
6.40
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


134.511
131.857
123.031
117.791
114.460
113.264
51.900
18.957
18.917
45 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5
f1 (ppm)

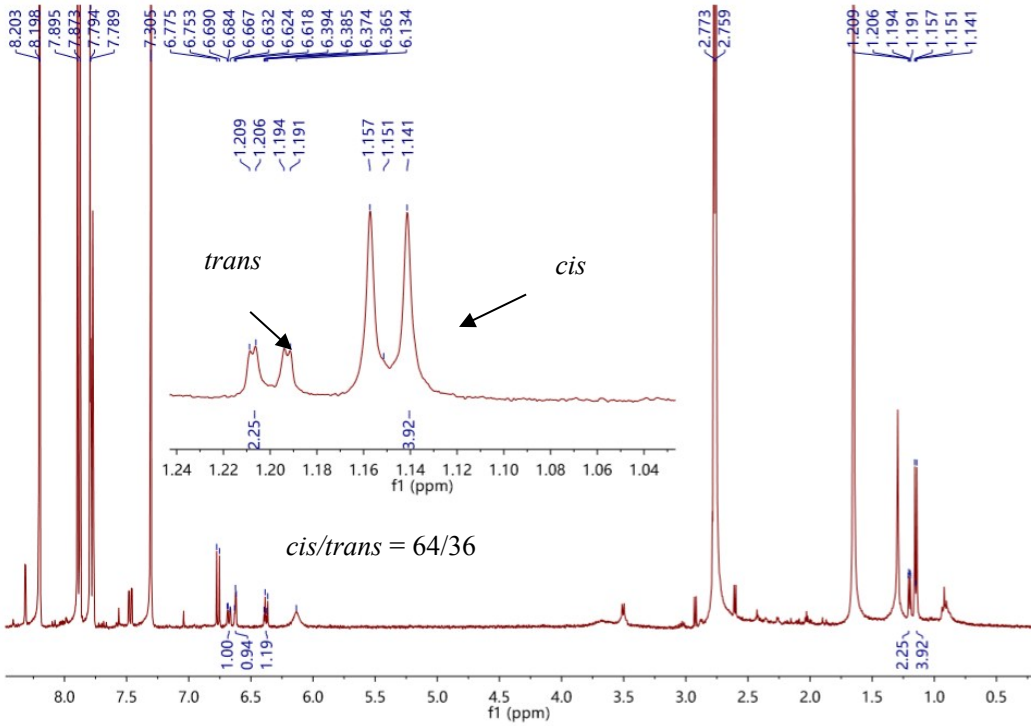


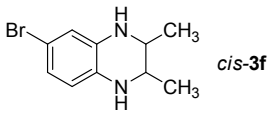
3f (5e)

cis/*trans* of **3f** = 62/38determined by ^{1}H NMR of the crude product.

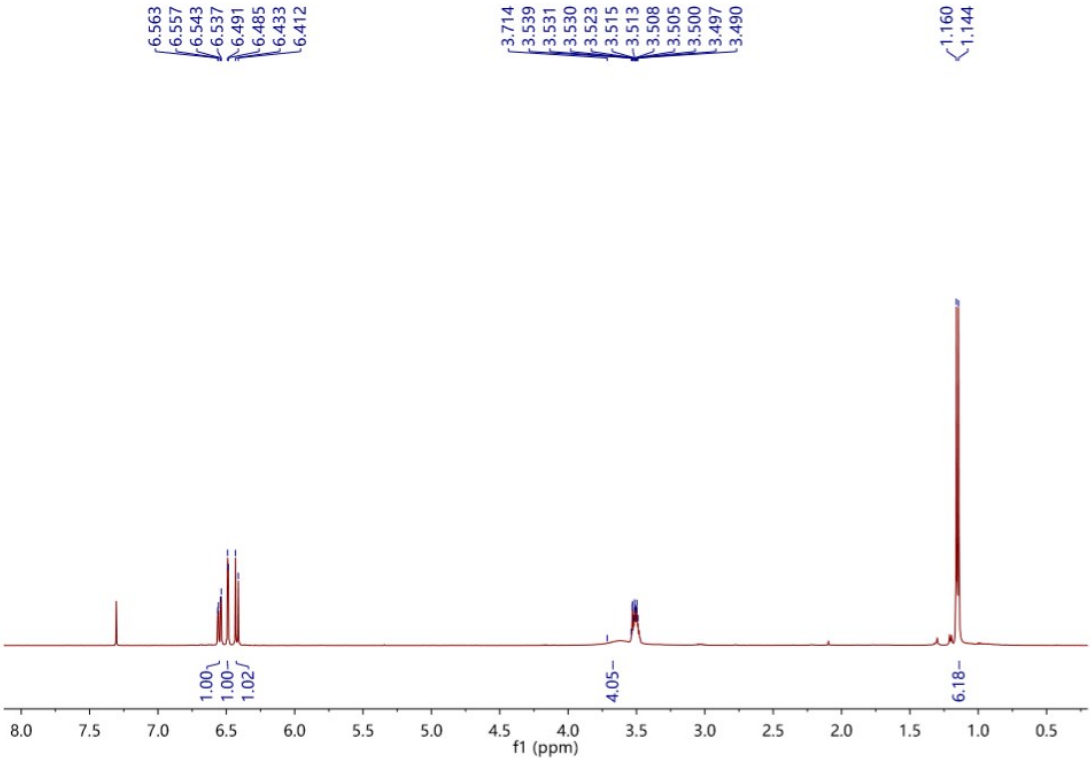


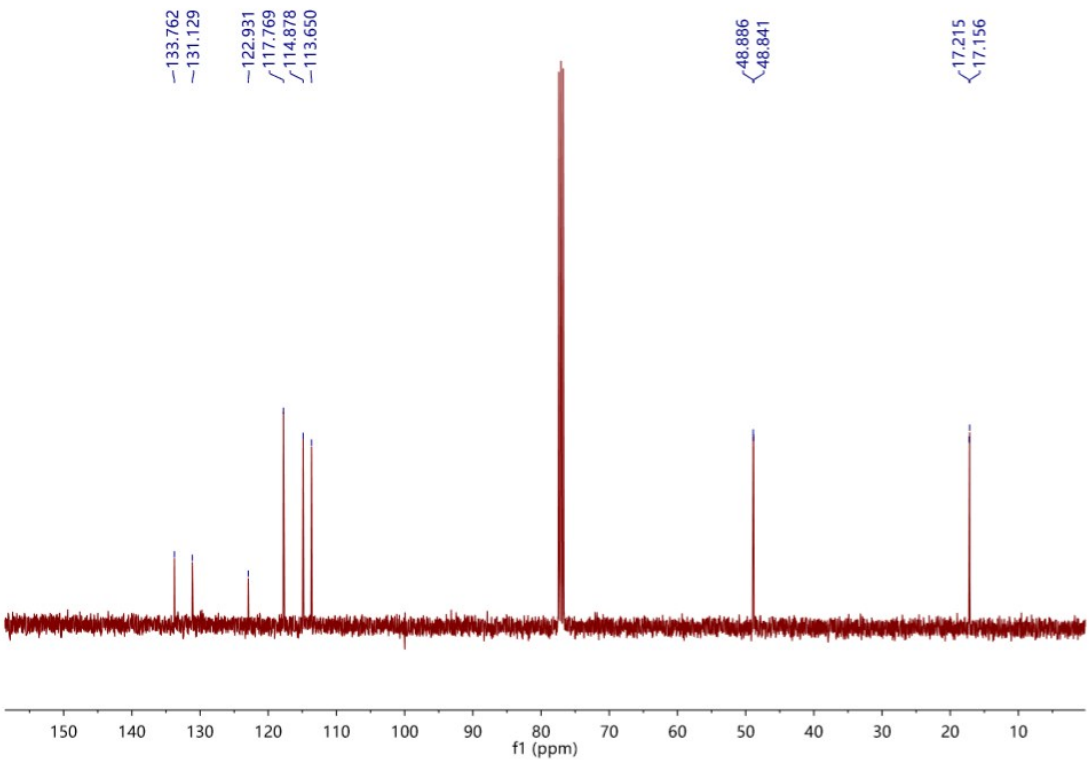
cis/*trans* of **5e** = 64/36determined by ^{1}H NMR of the crude product.

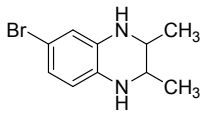



Br
H
N
CH3
N
H
CH3

cis-**3f**


6.563
6.557
6.543
6.537
6.491
6.485
6.433
6.412
3.714
3.539
3.531
3.530
3.523
3.515
3.513
3.508
3.505
3.500
3.497
3.490
1.160
1.144
1.00
1.00
1.02
4.05
6.18
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


133.762
131.129
122.931
117.769
114.878
113.650
48.886
48.841
17.215
17.156
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

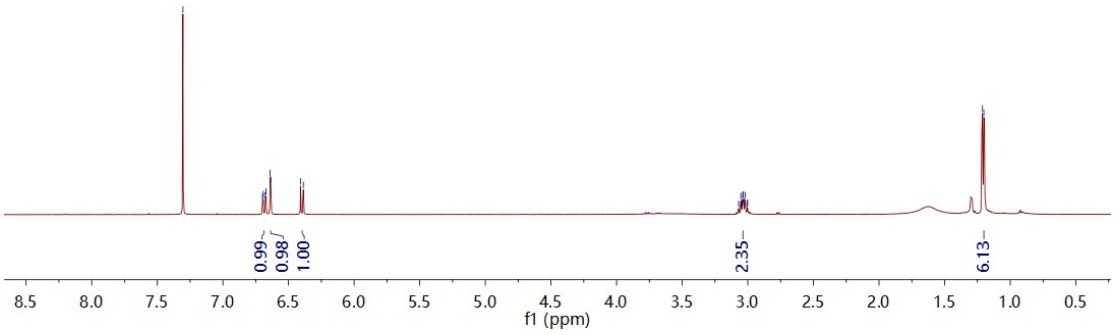

Br
H
N
CH3
N
H
CH3

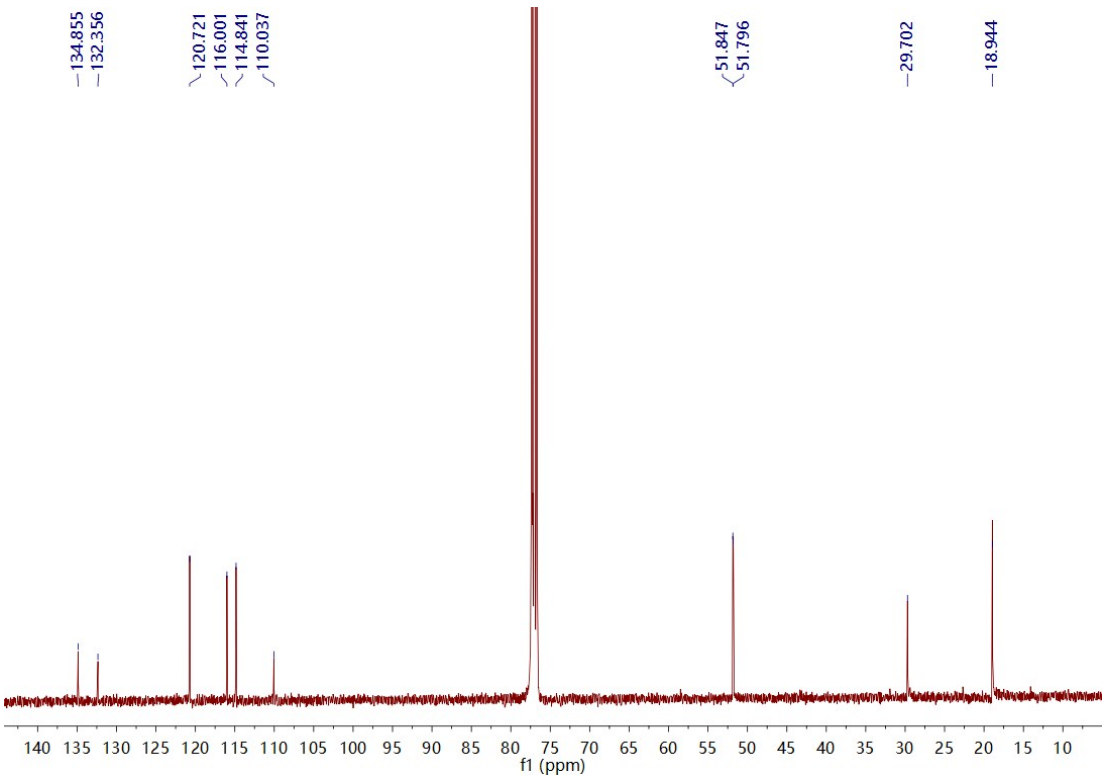
trans-**3f**

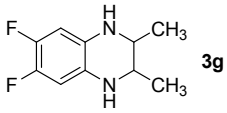

7.305
6.698
6.693
6.677
6.672
6.641
6.635
6.408
6.387


3.070
3.053
3.048
3.044
3.039
3.034
3.029
3.019
3.005
3.001


1.211
1.201

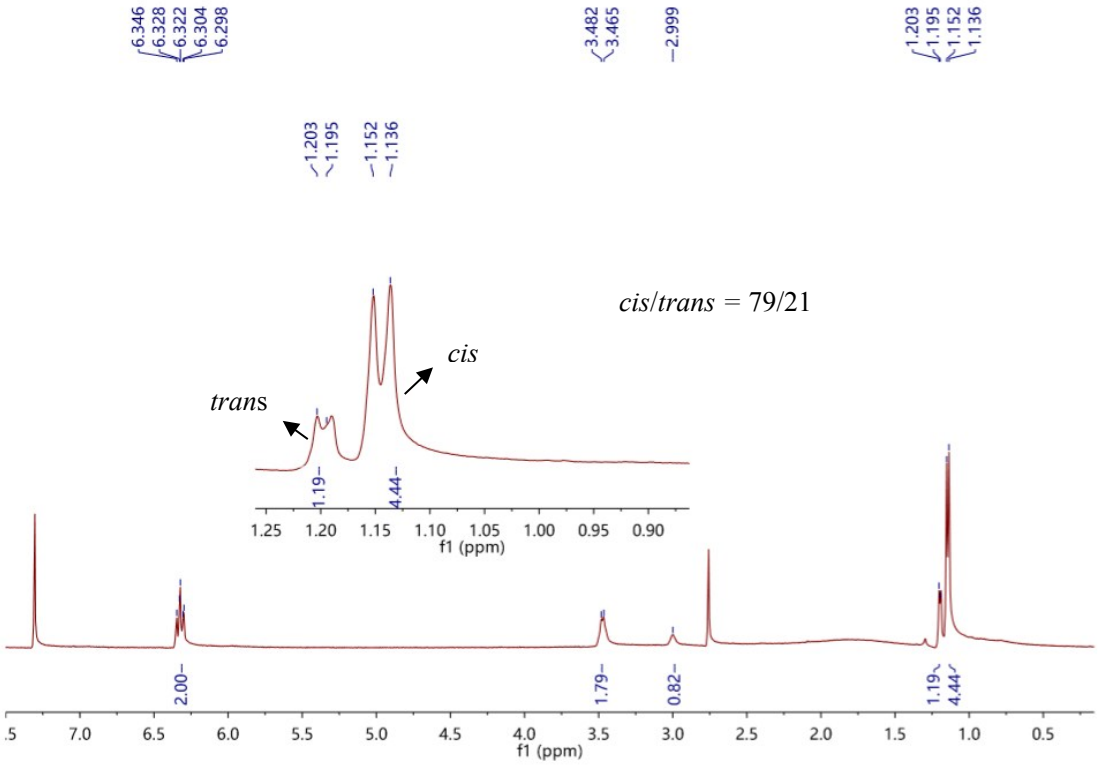

0.99
0.98
1.00
2.35
6.13
8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)

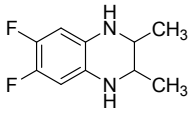

134.855
132.356
120.721
116.001
114.841
110.037
51.847
51.796
29.702
18.944
140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10
f1 (ppm)



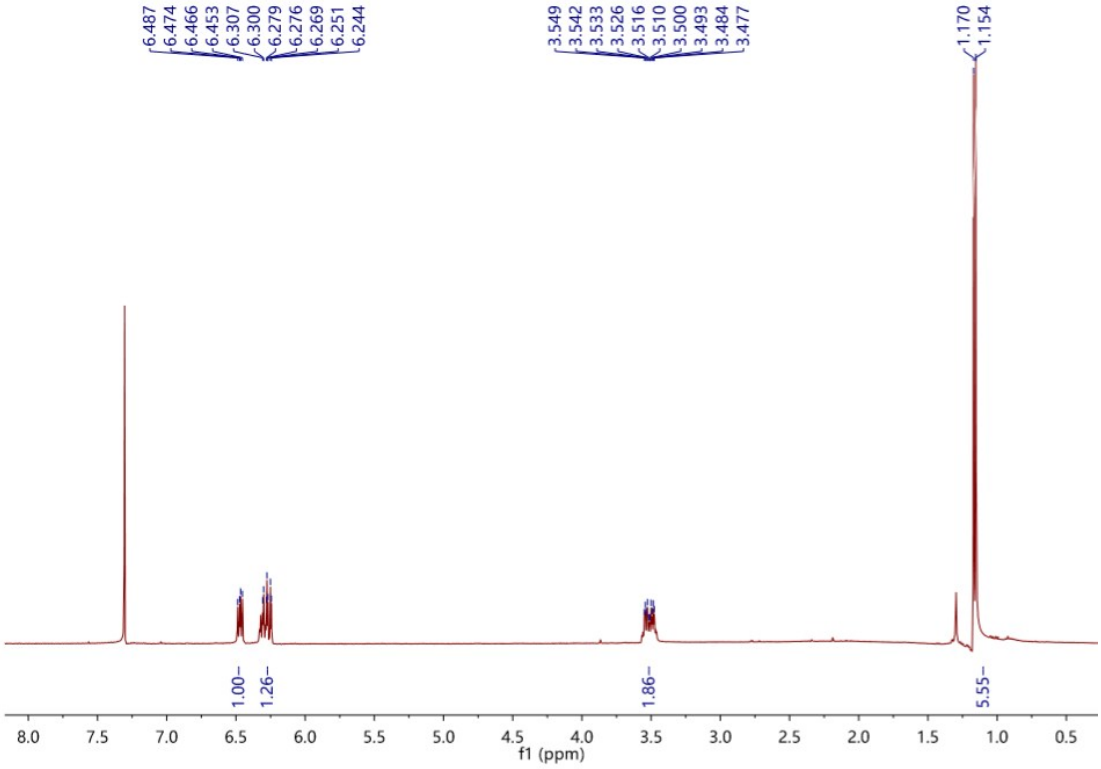
3g

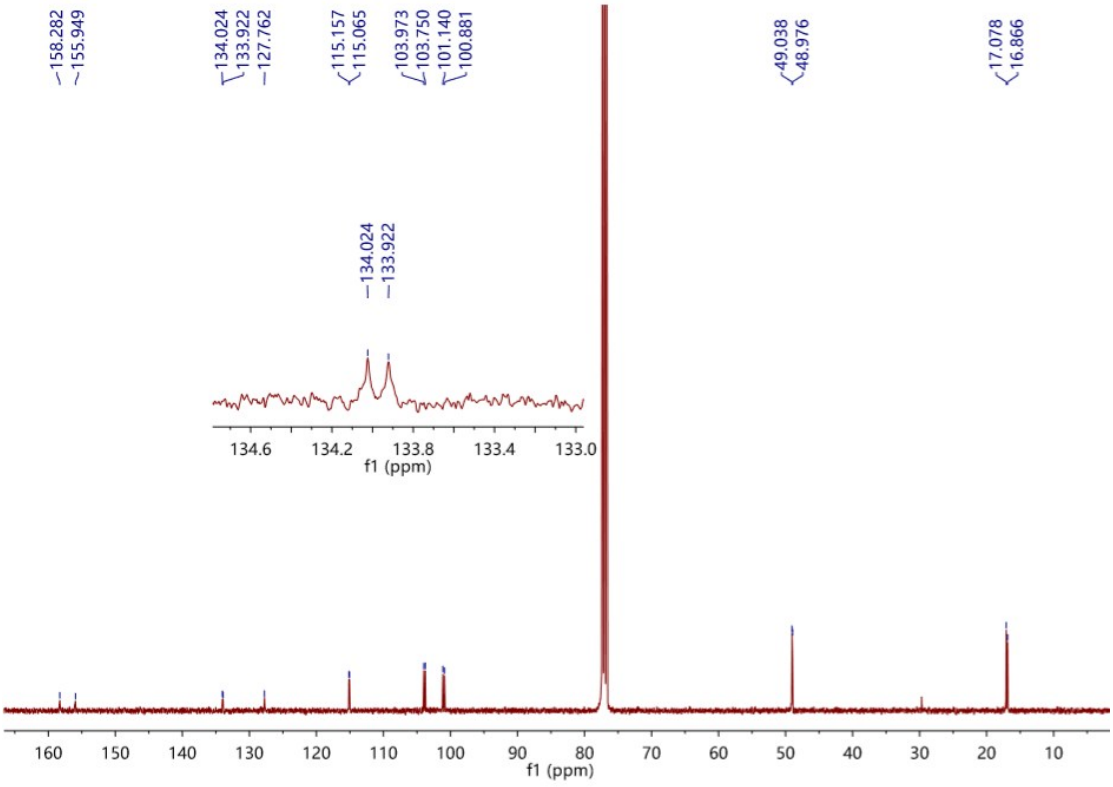
cis/*trans* of **3g** = 79/21 determined by ^{1}H NMR of the crude product.

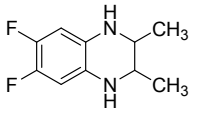



F
F
H
N
CH3
CH3
H
N

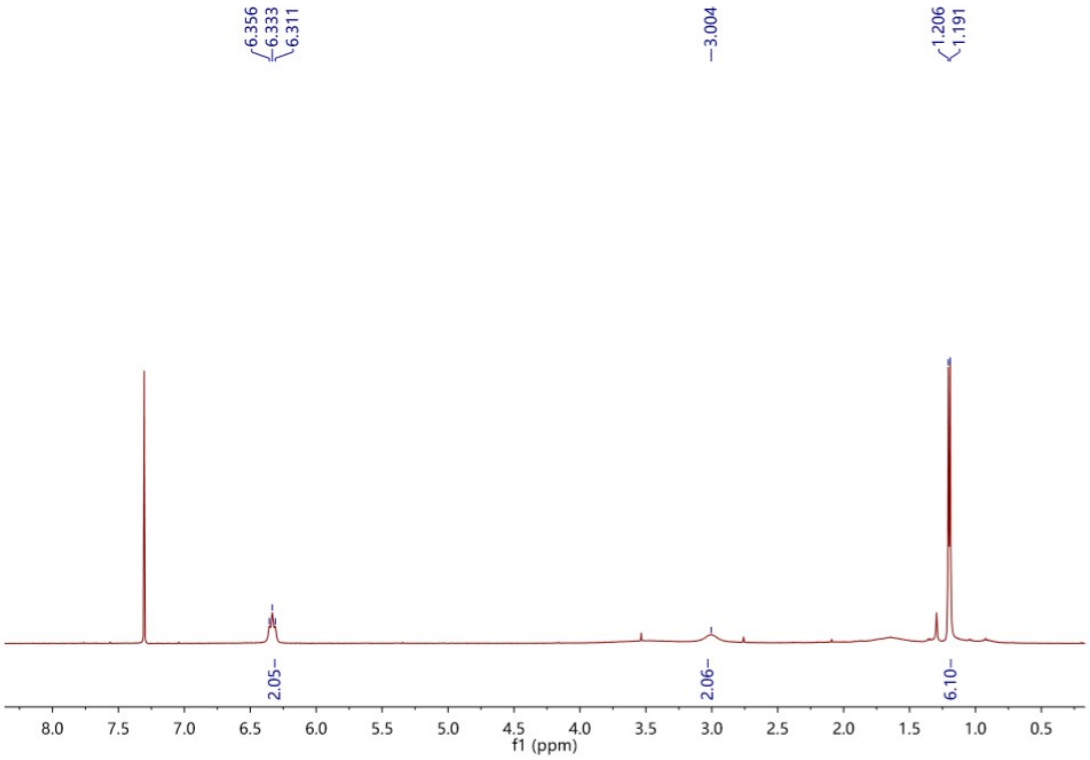
cis-**3g**

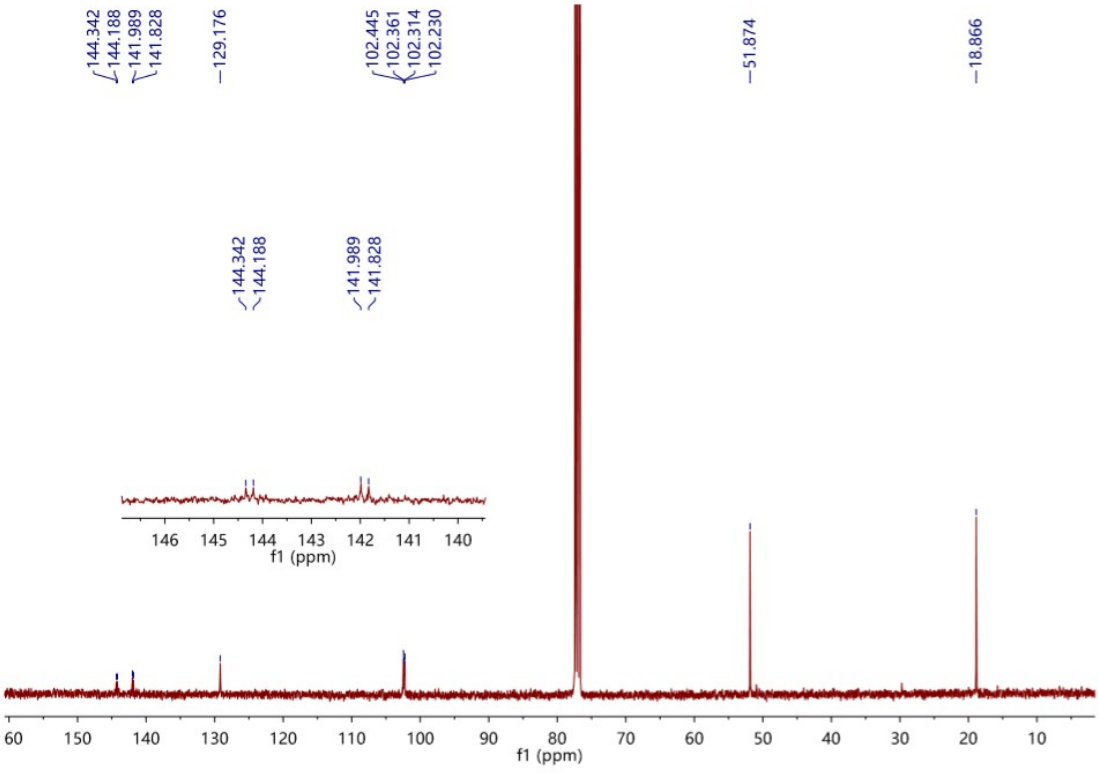

6.487
6.474
6.466
6.453
6.307
6.300
6.279
6.276
6.269
6.251
6.244
3.549
3.542
3.533
3.526
3.516
3.510
3.500
3.493
3.484
3.477
1.170
1.154
1.00
1.26
1.86
5.55
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

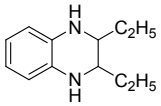

158.282
155.949
134.024
133.922
127.762
115.157
115.065
103.973
103.750
101.140
100.881
49.038
48.976
17.078
16.866
134.024
133.922
134.6
134.2
133.8
133.4
133.0
f1 (ppm)
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


F
F
H
N
CH3
H
N
CH3

trans-**3g**

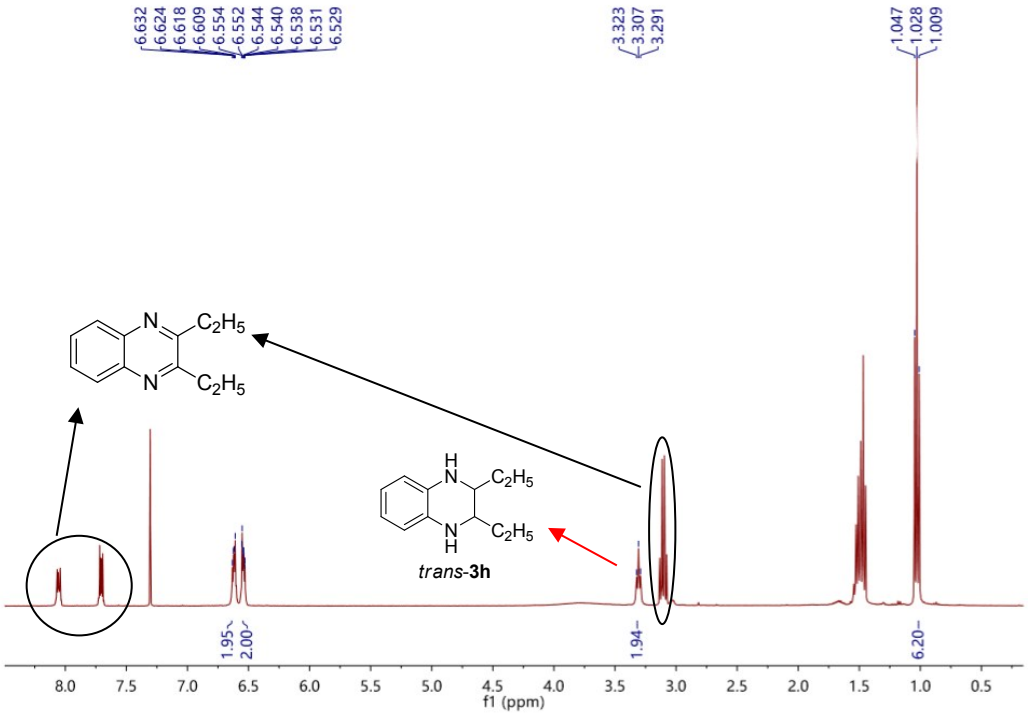

6.356
6.333
6.311
3.004
1.206
1.191
2.05
2.06
6.10
8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5
f1 (ppm)


144.342
144.188
141.989
141.828
129.176
102.445
102.361
102.314
102.230
51.874
18.866
144.342
144.188
141.989
141.828
146 145 144 143 142 141 140
f1 (ppm)
60 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)

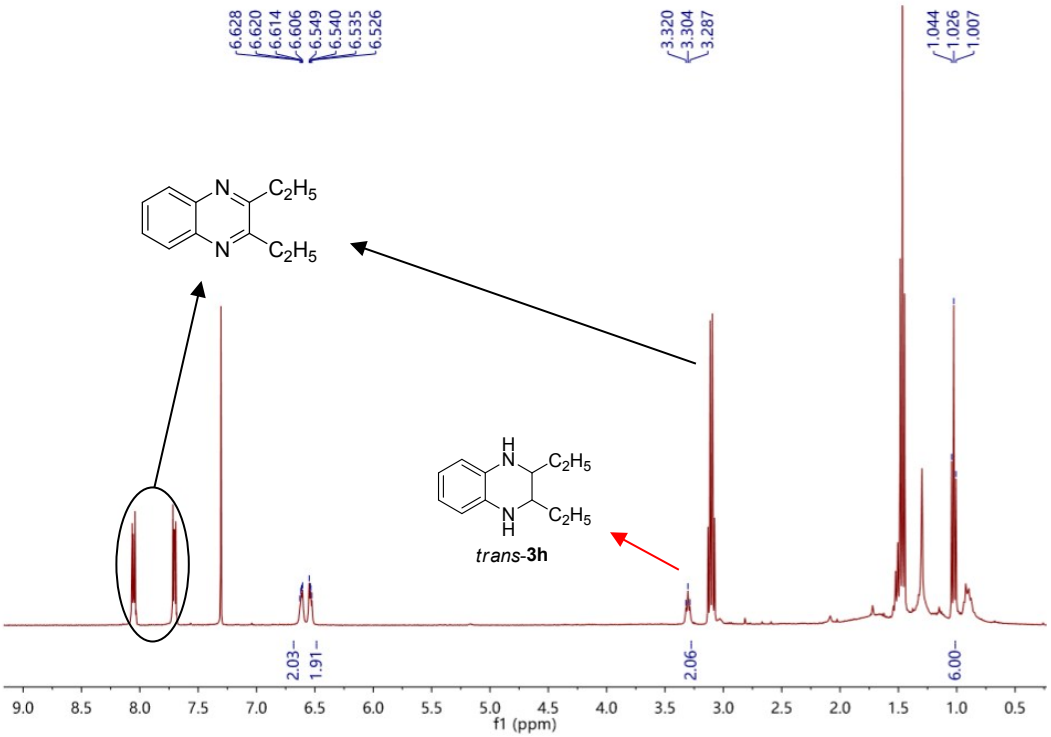


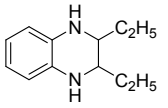
3h (5f)

cis/*trans* of **3h** = 0/100 determined by ^{1}H NMR of the crude product (*cis* isomer was not detected).

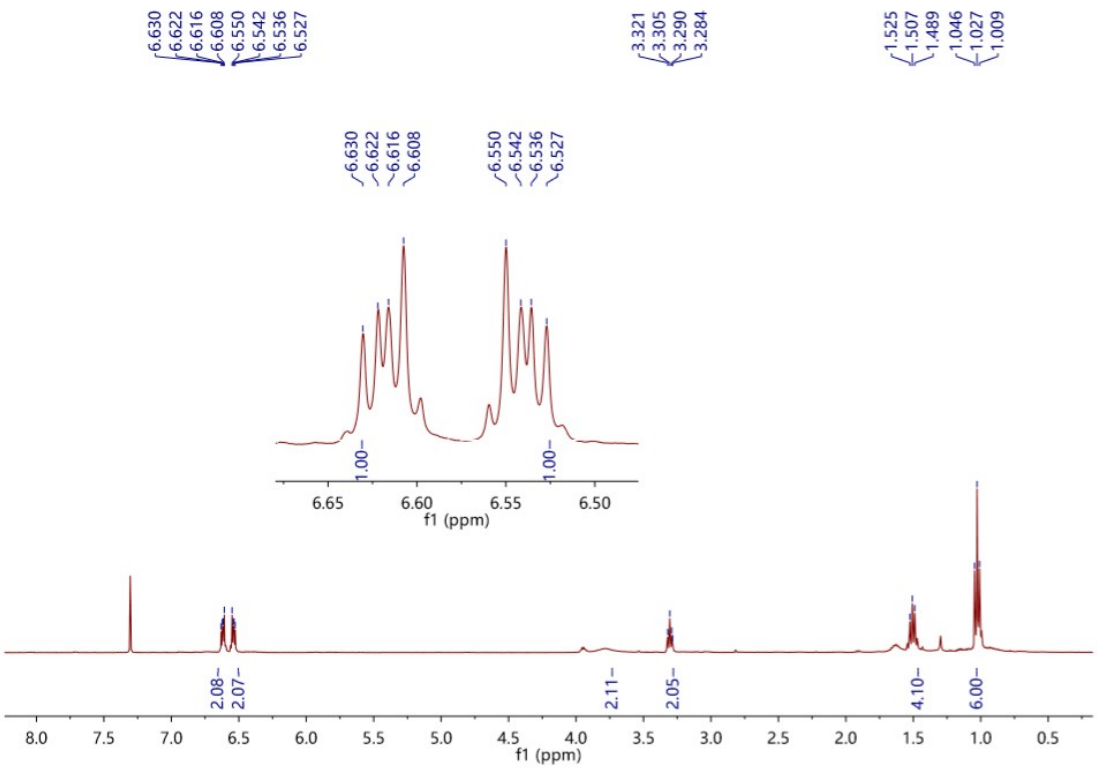


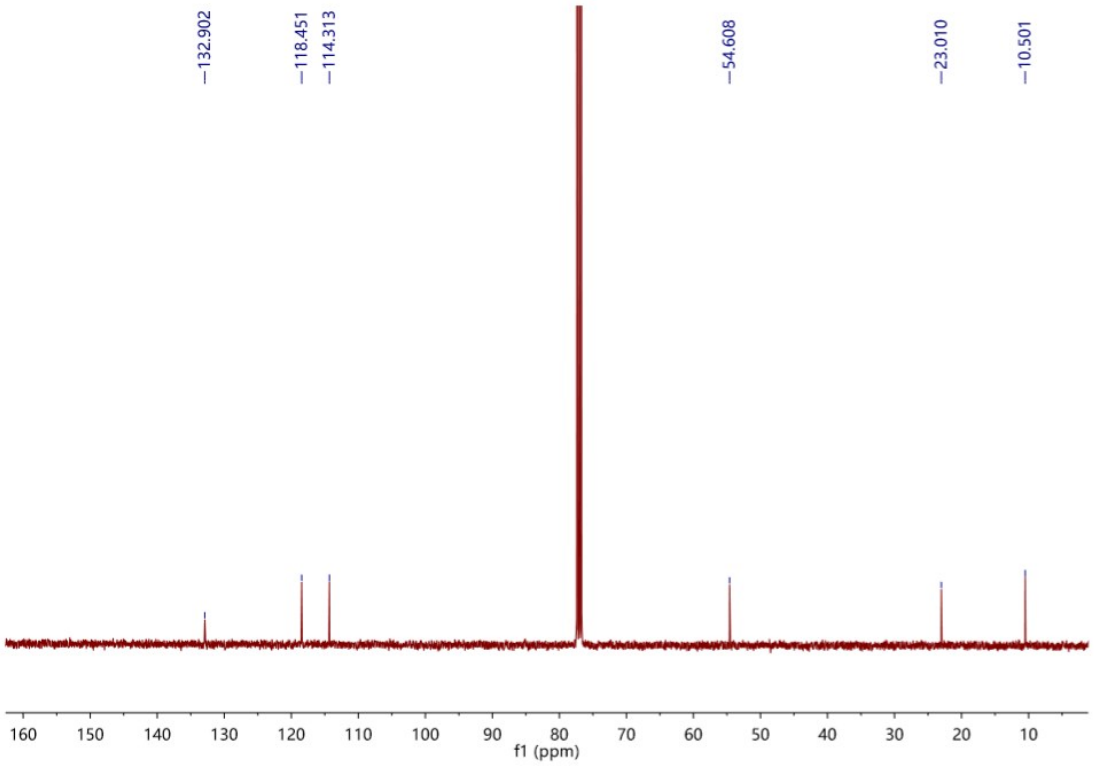
cis/*trans* of **5f** = 0/100 determined by ^{1}H NMR of the crude product (*cis* isomer was not detected).

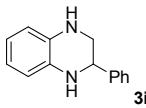




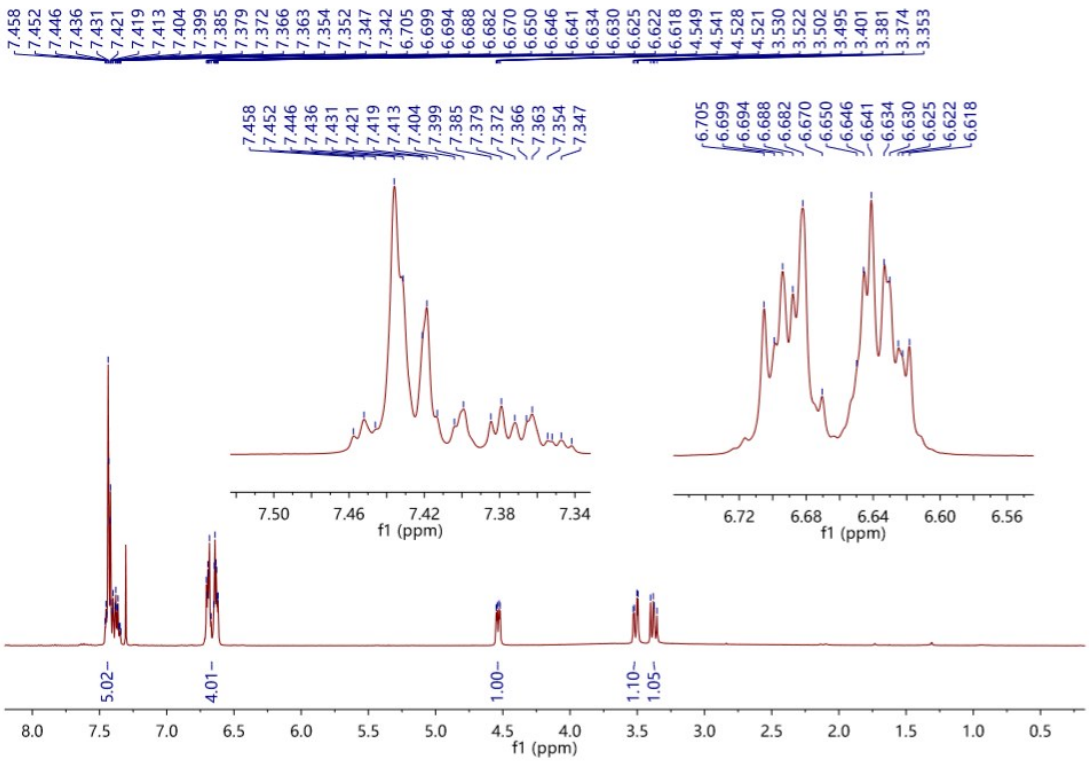
trans-**3h**

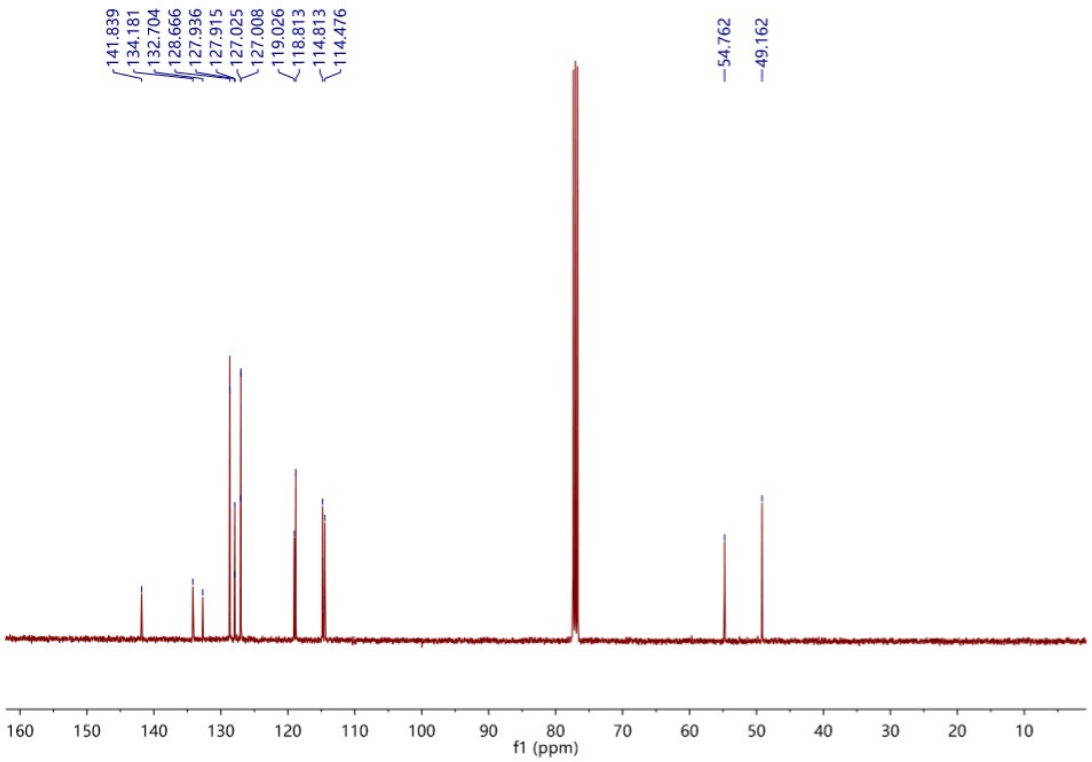

6.630
6.622
6.616
6.608
6.550
6.542
6.536
6.527
3.321
3.305
3.290
3.284
1.525
1.507
1.489
1.046
1.027
1.009
1.00
1.00
6.65
6.60
6.55
6.50
f1 (ppm)
2.08
2.07
2.11
2.05
4.10
6.00
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)

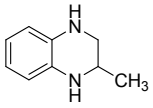

132.902
118.451
114.313
54.608
23.010
10.501
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)


H
N
N
H
Ph

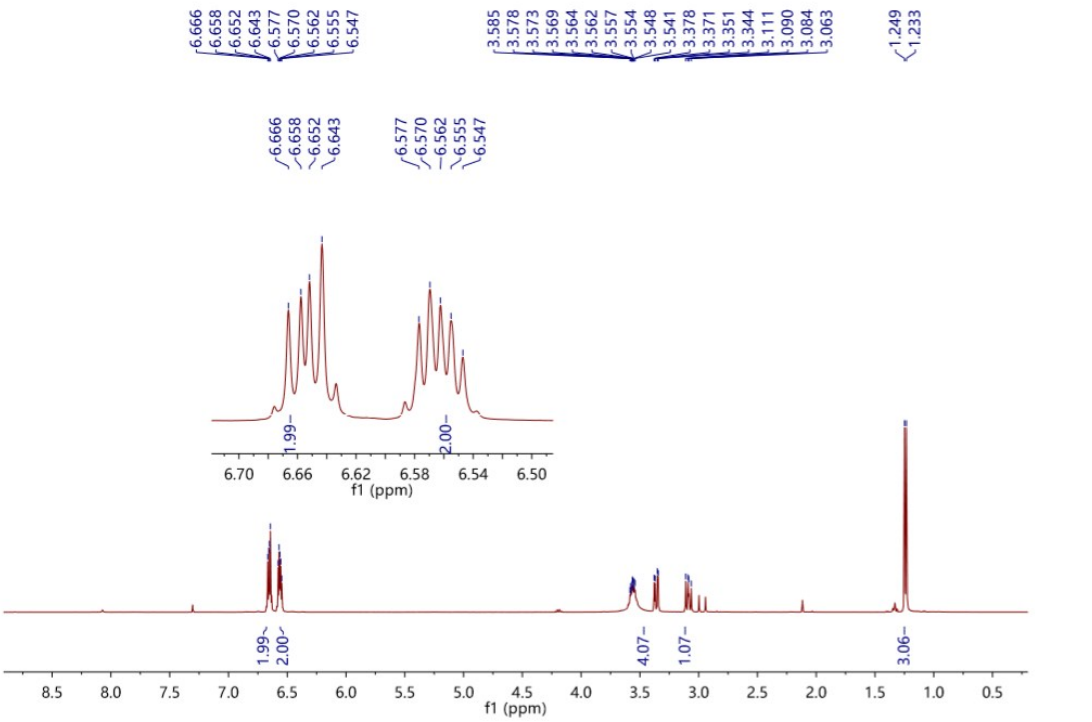
3i (5g)

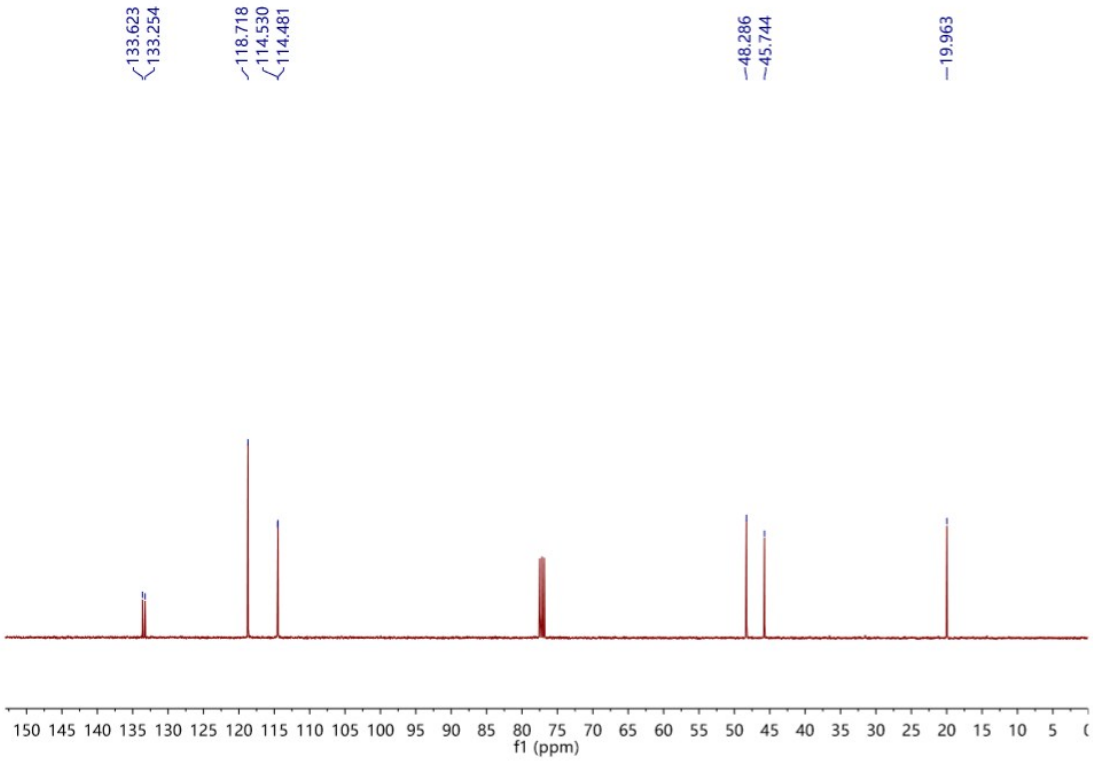

7.458
7.452
7.446
7.436
7.431
7.421
7.419
7.413
7.404
7.399
7.385
7.379
7.372
7.366
7.363
7.354
7.352
7.347
7.342
6.705
6.699
6.694
6.688
6.682
6.670
6.650
6.646
6.641
6.634
6.630
6.625
6.622
6.618
4.549
4.541
4.528
4.521
3.530
3.522
3.502
3.495
3.401
3.381
3.374
3.353
7.50
7.46
7.42
7.38
7.34
f1 (ppm)
6.72
6.68
6.64
6.60
6.56
f1 (ppm)
5.02
4.01
1.00
1.10
1.05
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
f1 (ppm)


141.839
134.181
132.704
128.666
127.936
127.915
127.025
127.008
119.026
118.813
114.813
114.476
54.762
49.162
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
f1 (ppm)

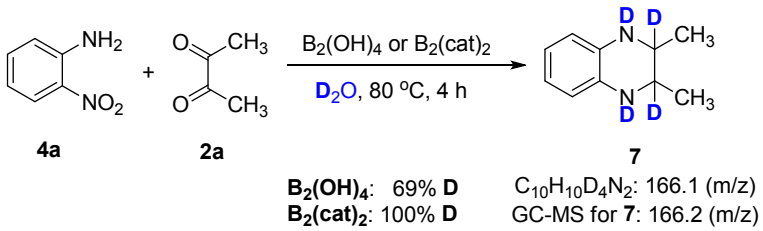


3j (5h)


6.666
6.658
6.652
6.643
6.577
6.570
6.562
6.555
6.547
3.585
3.578
3.573
3.569
3.564
3.562
3.557
3.554
3.548
3.541
3.378
3.371
3.351
3.344
3.111
3.090
3.084
3.063
1.249
1.233
1.99
2.00
f1 (ppm)
4.07
1.07
3.06

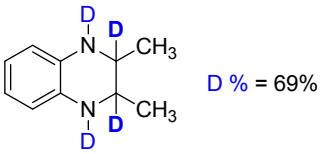

133.623
133.254
118.718
114.530
114.481
48.286
45.744
19.963
f1 (ppm)

5. The Deuterium Labeling Experiment

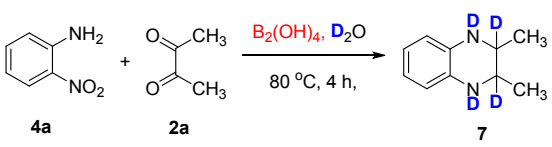


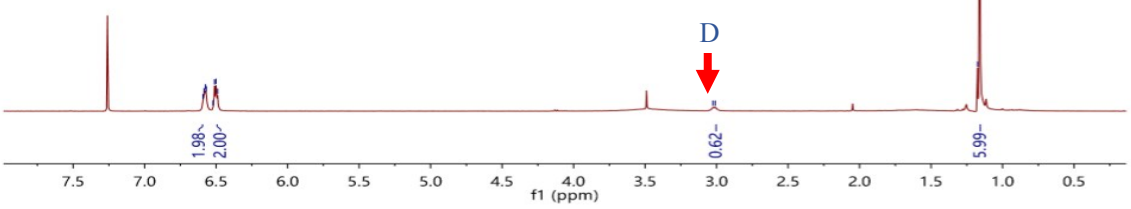
A flask was charged with 2-nitroaniline (**4a**, 1 mmol, 138 mg), 2,3-butanedione (**2a**, 1 mmol, 86 mg), $B_2(OH)_4$ or $B_2(cat)_2$(8 mmol) and D_2O (3 mL) under N_2. The reaction was stirred at 80 °C for 4 h. When the reaction was complete monitored by TLC, the mixture was cooled to room temperature, extracted with ethyl acetate (3×20 mL). The combined organic phase was washed with water, dried over anhydrous Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to give the product **7**. The products were determined by ^1H NMR and GC-MS.

$B_2(OH)_4$:

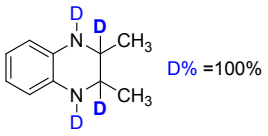


D % = 69%

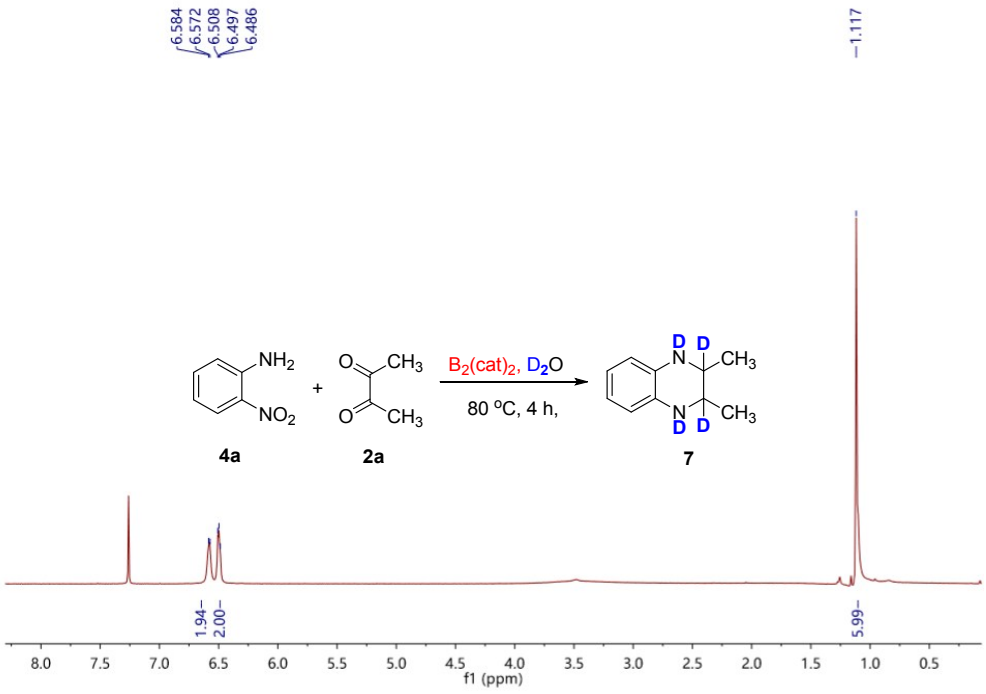




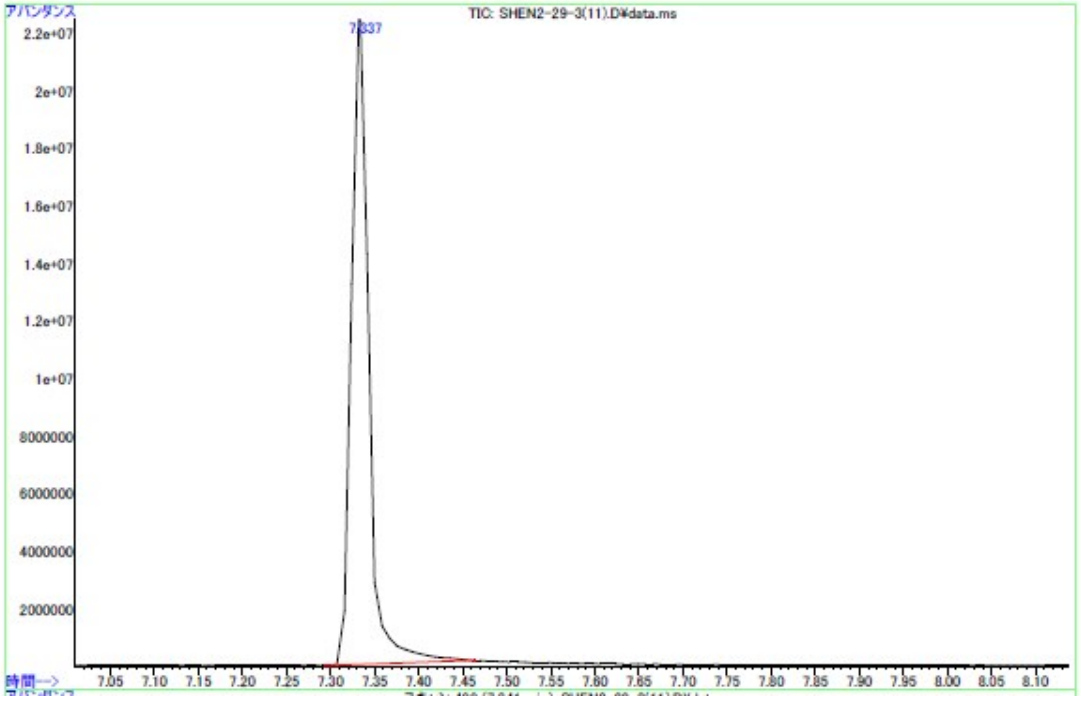
$B_2(cat)_2$:

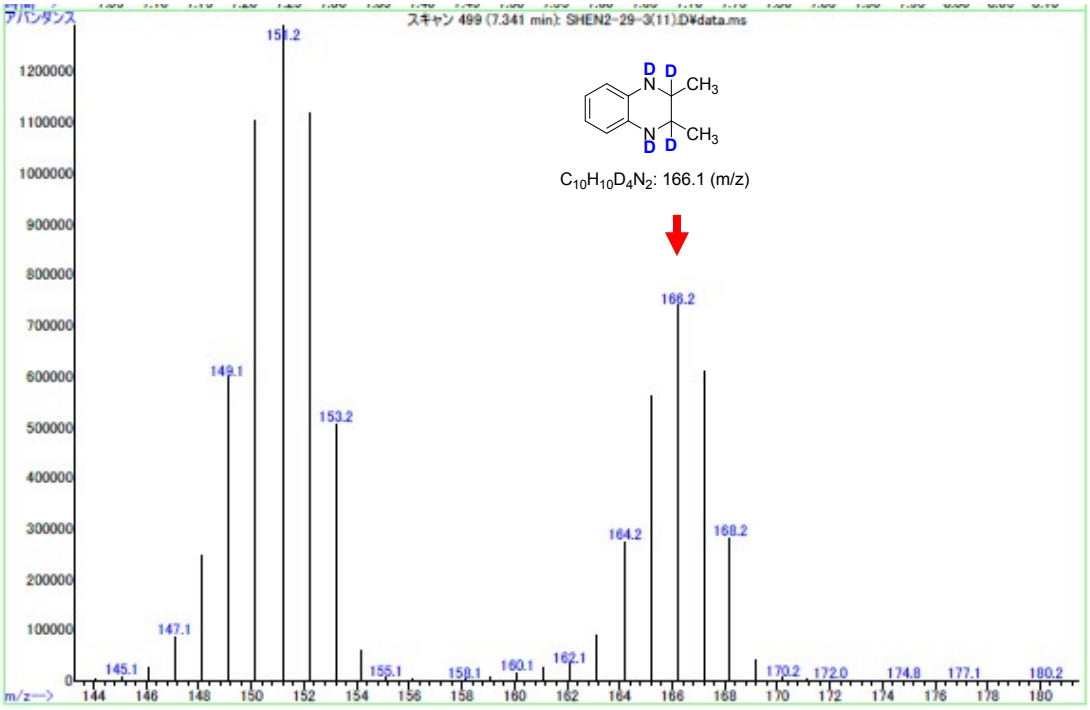


D% =100%



GC-MS:




アバンダンス
スキャン 499 (7.341 min): SHEN2-29-3(11).D¥data.ms
D D
N
CH3
N
CH3
D D
C10H10D4N2: 166.1 (m/z)
151.2
149.1
153.2
166.2
164.2
168.2
147.1
145.1
155.1
158.1
160.1
162.1
170.2
172.0
174.8
177.1
180.2
m/z-->