Development of Organocatalytic Darzens Reactions Exploiting the Cyclopropenimine Superbase

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SUPPLEMENTARY MATERIALS

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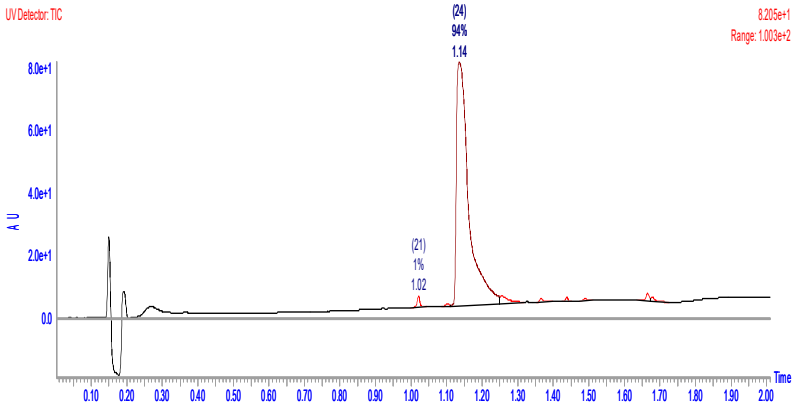
Analytical and spectroscopic data of catalyst **I·HCl**

^{1}H NMR (400 M MHz, $CDCl_3$): δ 7.78 (d, *J* = 9.5 Hz, 1H, N*H*), 7.25-7.12 (m, 5H, Ar*H*), 5.2 (bs, 1H, -O*H*), 4.05-3.78 (m, 3H, NC*H*BnC*H*$_2$OH), 3.27 (ddd, *J* = 11.9, 8.4, 3.8 Hz, 4H, NCy*H*), 3.16-3.00 (m, 2H, -C*H*$_2$Ph), 1.98-1.00 (m, 40H, Cy*H*).

^{13}C NMR (100 MHz, $CDCl_3$): δ 138.43 (1C, C=N), 129.52 (2C, Ar), 128.24 (2C, Ar), 126.33 (1C, Ar), 117.41 (Cq), 114.83 (Cq), 64.08 (1C, NCHBn*C*H$_2$OH), 61.9 (1C, N*C*HBnCH$_2$OH), 59.43 (4C, -NCy), 38.61 (1C, -*C*H$_2$Ph), 32.41 (4C, Cy), 32.24 (4C, Cy), 25.73 (4C, Cy), 25.67 (4C, Cy), 24.68 (4C, Cy).

MS (ESI, 5600eV): Calcd.:[M+H$^+$]: 546.85; Found: [M+H$^+$]: 546.28.

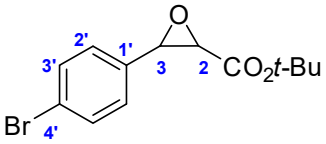
Ultra Performance LC analysis:



Rt (minutes)	Area (%)
1.14	94

Analytical and spectroscopic data for **3aa**

(67% yield, *cis*/*trans*= 1/0.7, white solid):



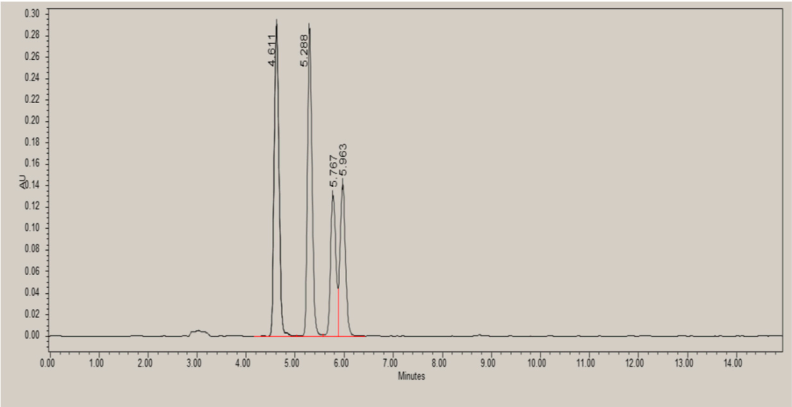
Trans ^{1}H NMR (400 M MHz, $CDCl_3$): δ 7.5 (d, *J* = 8.0 Hz, 2H, H-3'), 7.18 (d, *J* = 8.3 Hz, 2H, H-2'), 3.99 (m, 1H, H-3), 3.36 (d, *J* = 1.5 Hz, 1H, H-2), 1.54 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.86 (1C, C=O), 134.44 (1C, C-1'), 131.78 (2C, C-3′), 127.5 (2C, C-2'), 122.86 (1C, C-4'), 82.9 (1C, *C*H$(CH_3)_3$), 57.39 (1C, C-2), 57.01 (1C, C-3), 28.00 (3C, CH(*C*H$_3)_3$).

Cis ^{1}H NMR (400 M MHz, $CDCl_3$): δ 7.48 (d, *J* = 8.0 Hz, 2H, H-3'), 7.31 (d, *J* = 8.5 Hz, 2H, H-2'), 4.17 (d, *J* = 4.5 Hz, 1H, H-3), 3.72 (d, *J* = 4.5 Hz, 1H, H-2), 1.23 (s, 9H).[1] ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.45 (1C, C=O), 132.32 (1C, C-1'), 131.04 (2C, C-3′), 128.5 (2C, C-2'), 122.3 (1C, C-4'), 82.63 (1C, *C*H$(CH_3)_3$), 56.56 (1C, C-3), 55.89 (1C, C-2), 27.74 (3C, CH(*C*H$_3)_3$).

MS (ESI, 5600eV): Calcd:[M+H$^+$]: 258.08; Found: [M+H$^+$]: 258.8

R$_f$: 0.35 (18/2 Cyclohexane/EtOAc).

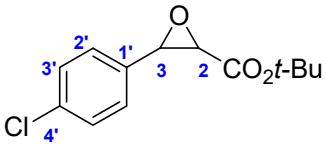
Chiral HPLC: Chiralpak IA (25 × 0.46 cm), 5 µm, *n*-hexane/EtOH = 85/15, 1 ml/min, 220 nm.



Rt (minutes)	Area (%)
4.6	33.8
5.2	31.2
5.7	16.7
5.9	18.3

Analytical and spectroscopic data for **3ab**

(65% yield, *cis*/*trans* = 1/0.7, white solid):



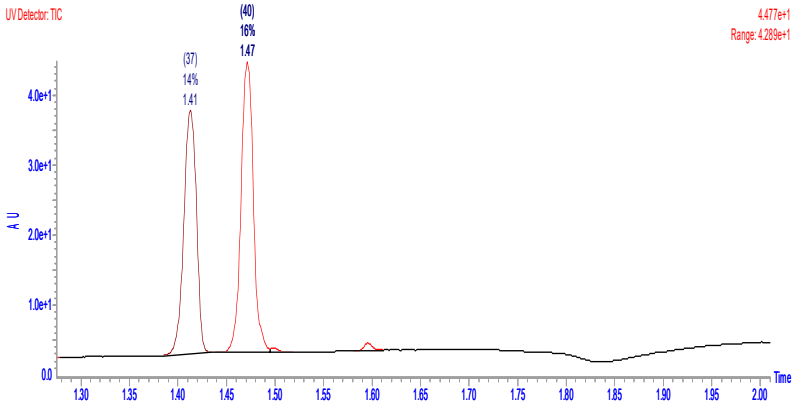
Trans ^{1}H NMR (400 M MHz, $CDCl_3$): δ 7.43-7.2 (m, 4H), 4.02 (d, *J* = 1.5 Hz, 1H, H-3), 3.38 (d, *J* = 1.8 Hz, 1H, H-2), 1.57 (s, 9H, *t*-Bu).[2] ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.91 (1C, C=O), 134.75 (1C, Cq), 133.9 (1C, Cq) 128.84 (2C, C-3′), 127.22 (2C, C-2'), 82.9 (1C, $C(CH_3)_3$), 57.44 (1C, C-2), 56.97 (1C, C-3), 28.00 (3C, $CH(CH_3)_3$).

Cis ^{1}H NMR (400 M MHz, $CDCl_3$): δ 7.43-7.2 (m, 4H), 4.21 (d, *J* = 4.8 Hz, 1H, H-3), 3.74 (d, *J* = 4.8 Hz, 1H, H-2), 1.24 (s, 9H, *t*-Bu).[2] ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.48 (1C, C=O), 134.17 (1C, Cq), 131.78 (1C, Cq) 128.19 (2C, C-3′), 128.1 (2C, C-2'), 82.61 (1C, $C(CH_3)_3$), 56.51 (1C, C-2), 55.96 (1C, C-3), 27.73 (3C, $CH(CH_3)_3$).

MS (ESI, 5600eV): Calcd.: $[M+H^+]$: 255.71; Found: $[M+H^+]$: 255.02.

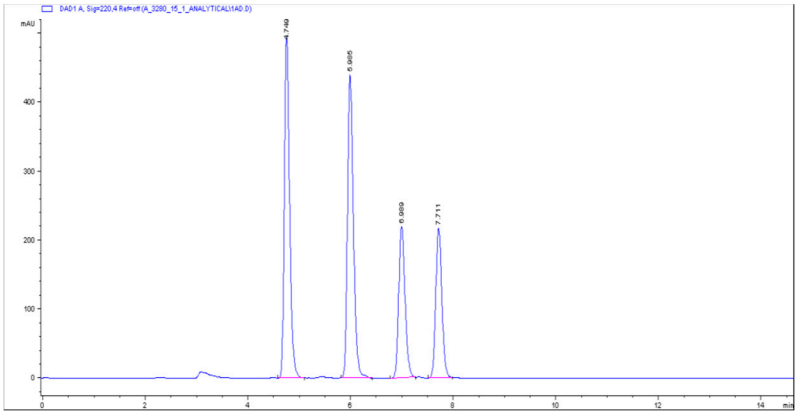
R_f: 0.36 (18/2 Cyclohexane/EtOAc).

Ultra Performance LC analysis:



Rt (minutes)	Area (%)
1.41	14
1.47	16

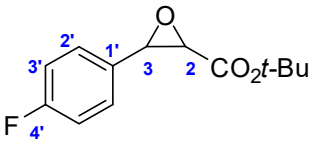
Chiral HPLC: Chiralpak IA (25 × 0.46 cm), 5 µm, *n*-hexane/EtOH = 90/10, 1 ml/min, 220 nm.



Rt (minutes)	Area (%)
4.7	32.9
5.9	32.7
7.0	17.6
7.7	16.8

Analytical and spectroscopic data for **3ac**

(32% yield, *cis*/*trans* = 1/0.9, white solid):



Trans ^{1}H NMR (400 M MHz, $CDCl_3$): δ 7.31–7.22 (m, 2H, H-2'), 7.09-7,01 (m, 2H, H-3'), 4.01 (d, *J* = 1.3 Hz, 1H, H-3), 3.37 (d, *J* = 1.5 Hz, 1H, H-2), 1.52 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 167.03 (1C, C=O), 163.08 (d, *J* = 245 Hz, C-4'), 131.1 (d, *J* = 2 Hz, C-1'), 127.6 (d, *J* = 8 Hz, C-2'), 115.65 (d, *J* = 21 Hz, C-3'), 82.82 (1C, *C*(CH_3)$_3$), 57.41 (1C, C-2), 57.05 (1C, C-3), 28.00 (3C, CH(*C*H_3)$_3$).**Error! Bookmark not defined.**

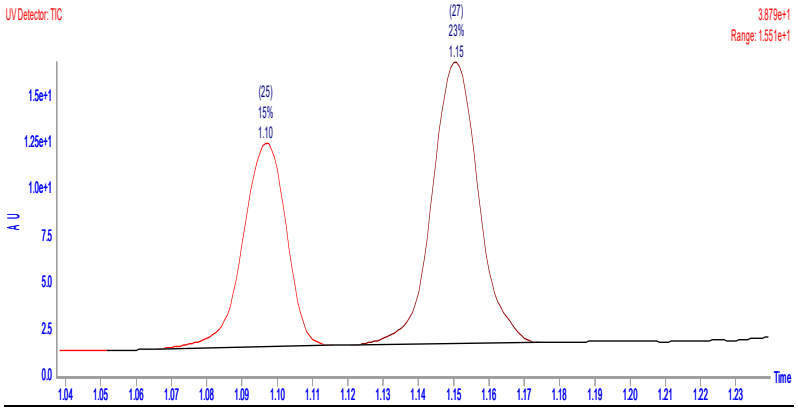
Cis ^{1}H NMR (400 M MHz, $CDCl_3$): δ 7.44–7.36 (m, 2H, H-2'), 7.09-7,01 (m, 2H, H-3'), 4.2 (d, *J* = 4.5 Hz, 1H, H-3), 3.7 (d, *J* = 4.5 Hz, 1H, H-2), 1.22 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.6 (1C, C=O), 162.7 (d, *J* = 245 Hz, C-4'), 129.01 (d, *J* = 3 Hz, C-1'), 128.5 (d, *J*

= 8 Hz, C-2'), 114.89 (d, J = 22 Hz, C-3'), 82.51 (1C, $C(CH_3)_3$), 56.53 (1C, C-2), 55.98 (1C, C-3), 27.71 (3C, CH(CH_3)$_3$).

MS (ESI, 5600eV): Calcd.:[M+H$^+$]: 239.25; Found: [M+H$^+$]: 238.95

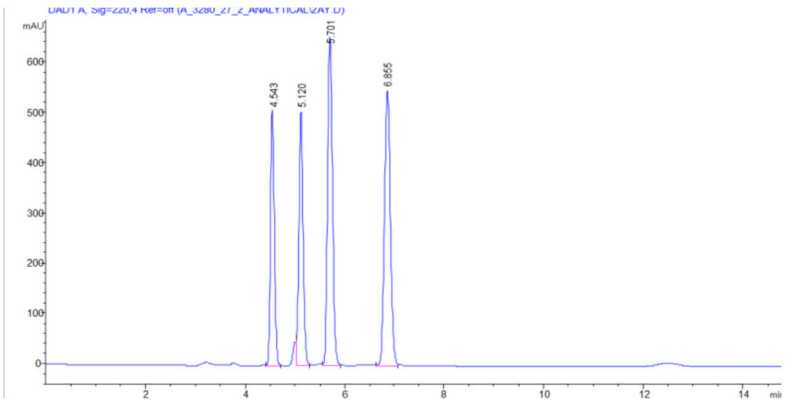
R_f: 0.32 (18/2 Cyclohexane/EtOAc).

Ultra Performance LC analysis:



Rt (min)	Area (%)
1.1	15
1.15	23

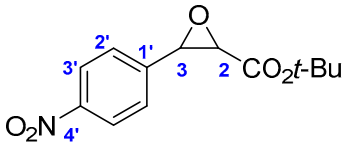
Chiral HPLC: Chiralpak AY-H (25 × 0.46 cm), 5 µm, *n*-hexane/EtOH = 85/15, 1 ml/min, 220 nm.



Rt (minutes)	Area (%)
4.5	18.6
5.1	20.5
5.7	29.9
6.8	31.0

Analytical and spectroscopic data for **3ad**

(47% yield, *cis*/*trans* = 1/0.7, white solid):



Trans ^{1}H NMR (400 M MHz, $CDCl_3$): δ 8.27–8.17 (m, 2H, H-3'), 7.50 (d, *J* = 8.5 Hz, 2H, H-2'), 4.13 (d, *J* = 1.3 Hz, 1H, H-3), 3.39 (d, *J* = 1.3 Hz, 1H, H-2), 1.54 (s, 9H).

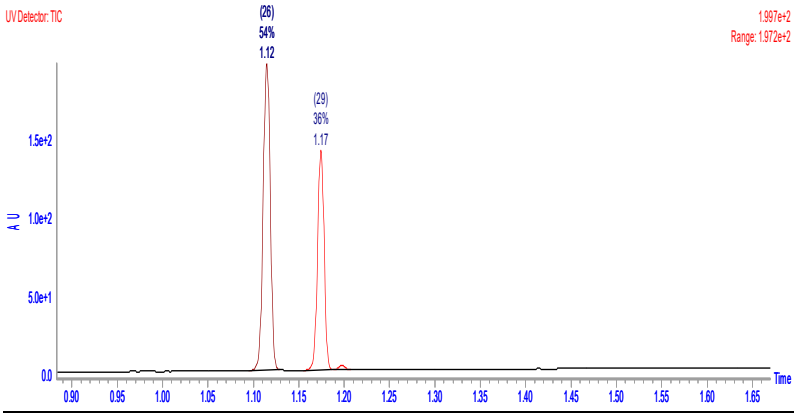
Cis ^{1}H NMR (400 M MHz, $CDCl_3$): δ 8.27–8.17 (m, 2H, H-3'), 7.62 (d, *J* = 8.5 Hz, 2H, H-2'), 4.3 (d, *J* = 4.5 Hz, 1H, H-3), 3.8 (d, *J* = 4.5 Hz, 1H, H-2), 1.22 (s, 9H).[3]

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.28 (1C, C=O), 164.91 (1C, C=O), 142.64 (1C), 140.48 (1C), 130.47 (1C), 127.87 (1C, C-2', *cis*), 126.7 (1C, C-2', *trans*), 124.31 (1C), 123.89 (1C, C-3', *trans*), 123.11 (1C, C-3', *cis*), 83.36 (1C), 83.04 (1C), 57.7 (1C, *trans*), 56.42 (1C, *trans*), 56.25 (1C, *cis*), 55.96 (1C, *cis*), 27.98 (3C, $CH(CH_3)_3$, *trans*), 27.75 (3C, $CH(CH_3)_3$, *cis*).[3]

MS (ESI, 5600eV): Calcd.: $[M+H^+]$: 266.26; Found: $[M+H^+]$: 266.04.

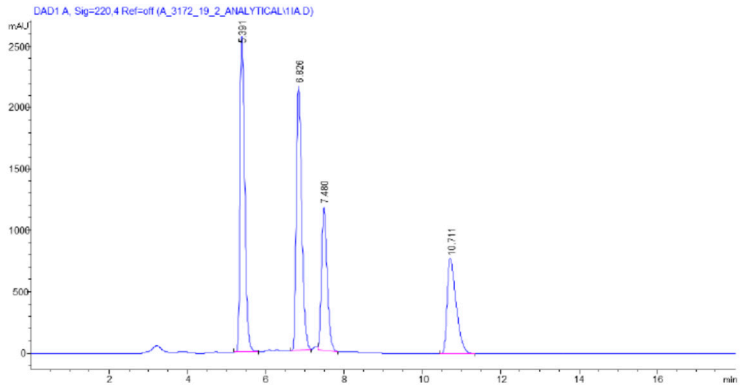
R_f: 0.29 (18/2 Cyclohexane/EtOAc).

Ultra Performance LC analysis:



Rt (min)	Area (%)
1.12	54
1.17	36

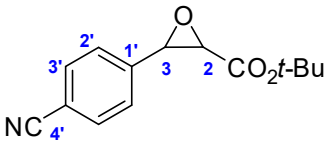
Chiral HPLC: Chiralpak IA (25 × 0.46 cm), 5 μm, *n*-hexane/EtOH = 70/30, 1 ml/min, 220 nm.



Rt (minutes)	Area (%)
5.3	32
6.8	32.3
7.4	17.2
10.7	18.5

Analytical and spectroscopic data for **3ae**

(78% yield, *cis*/*trans* = 1/0.7, white solid):



Trans ^{1}H NMR (400 M MHz, $CDCl_3$): δ 7.71–7.63 (m, 2H, H-3'), 7.42 (d, J = 8.0 Hz, 2H, H-2'), 4.09 (d, J = 1.3 Hz, 1H, H-3), 3.37 (d, J = 1.5 Hz, 1H, H-2), 1.56 (s, 9H).[2]

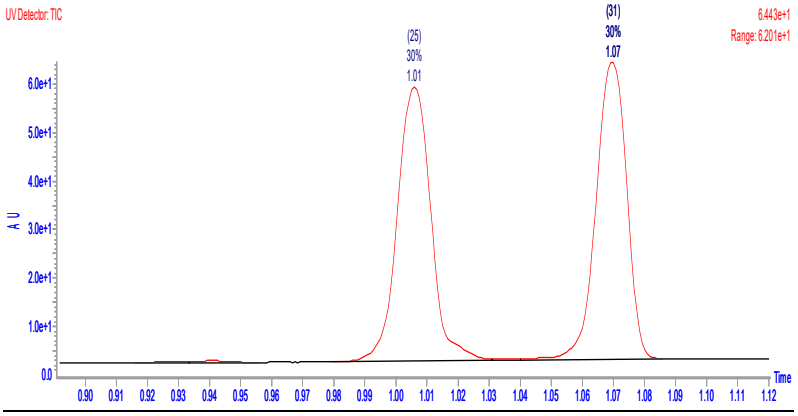
Cis ^{1}H NMR (400 M MHz, $CDCl_3$): δ 7.71–7.63 (m, 2H, H-3'), 7.56 (d, J = 8.0 Hz, 2H, H-2'), 4.25 (d, J = 4.8 Hz, 1H, H-3), 3.78 (d, J = 4.8 Hz, 1H, H-2), 1.21 (s, 9H).[2]

^{13}C NMR (100 MHz, $CDCl_3$): δ 166.38 (1C, C=O), 165.00 (1C, C=O), 140.74 (1C), 138.58 (1C), 132.43 (2C), 131.69 (2C), 127.65 (2C, C-2', *cis*), 126.53 (2C, C-2', *trans*), 118.52 (1C), 118.36 (1C), 112.71 (1C), 112.19 (1C), 83.28 (1C), 82.96 (1C), 57.65 (1C, C-3, *trans*), 56.61 (1C, C-2, *trans*), 56.34 (1C, C-3, *cis*), 55.93 (1C, C-2, *cis*), 27.98 (3C, CH(CH$_3$)$_3$, *trans*), 27.71 (3C, CH(CH$_3$)$_3$, *cis*).

MS (ESI, 5600eV): Calcd.: [M+H$^+$]: 246.27; Found: [M+H$^+$]: 245.99

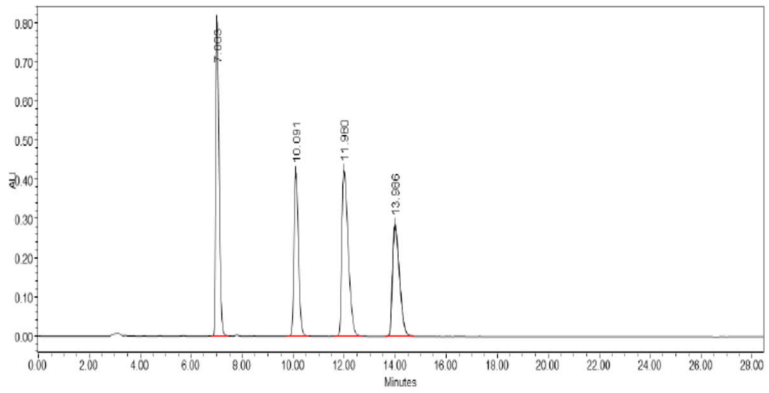
R_f: 0.35 (18/2 Cyclohexane/EtOAc).

Ultra Performance LC analysis:



Rt (minutes)	Area (%)
1.01	30
1.07	30

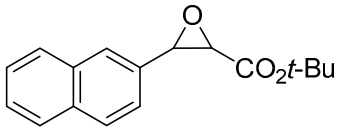
Chiral HPLC: Chiralpak IA (25 × 0.46 cm), 5 µm, *n*-hexane/EtOH = 85/15, 1 ml/min, 220 nm.



Rt (minutes)	Area (%)
7.0	29.4
11.9	28.8
10.1	20.5
13.9	21.3

Analytical and spectroscopic data for **3af**

(41% yield, *cis*/*trans* = 1/0.6, white solid):



Trans ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.32 (m, 7H, Ar), 4.2 (d, J = 1.3 Hz, 1H), 3.54 (d, J = 1.3 Hz, 1H), 1.54 (s, 9H).

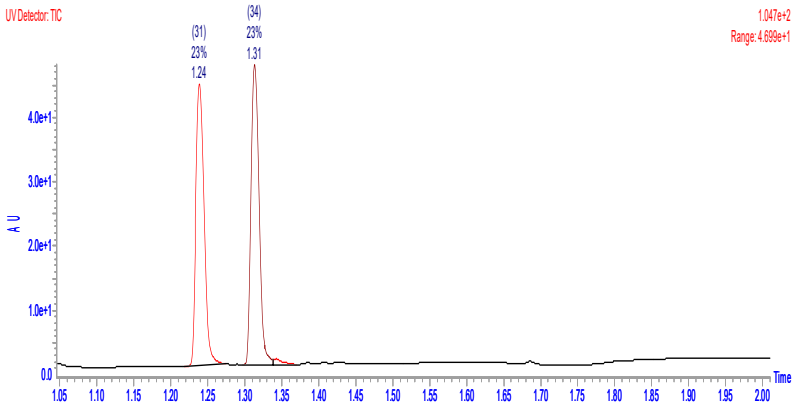
Cis ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.65-7.32 (m, 7H, Ar), 4.39 (d, J = 4.5 Hz, 1H), 3.8 (d, J = 4.8 Hz, 1H), 1.12 (s, 9H).

^{13}C NMR (100 MHz, $CDCl_3$): δ 167.23 (1C, C=O, trans), 165.84 (1C, C=O, cis), 133.57 (1C), 133.2 (1C), 133.04 (1C), 132.73 (1C), 130.72 (1C), 128.57 (1C), 127.96 (1C), 127.85 (1C), 127.8 (1C), 127.73 (1C), 127.64 (1C), 126.56 (1C), 126.47 (1C), 126.28 (1C), 126.17 (1C), 126.08 (1C), 125.96 (1C), 124.24 (1C), 122.59 (1C), 82.77 (1C, *C*H(CH_3)$_3$, *trans*), 82.43 (1C, *C*H(CH_3)$_3$, *cis*), 57.92 (1C, *trans*), 57.51 (1C, *trans*), 57.31 (1C, *cis*), 56.24 (1C, *cis*), 28.03 (1C, CH(*C*H_3)$_3$, *trans*), 27.64 1C, (CH(*C*H_3)$_3$, *cis*).

MS (ESI, 5600eV): Calcd.: [M+H$^+$]: 271.32; Found: [M+H$^+$]: 271.04.

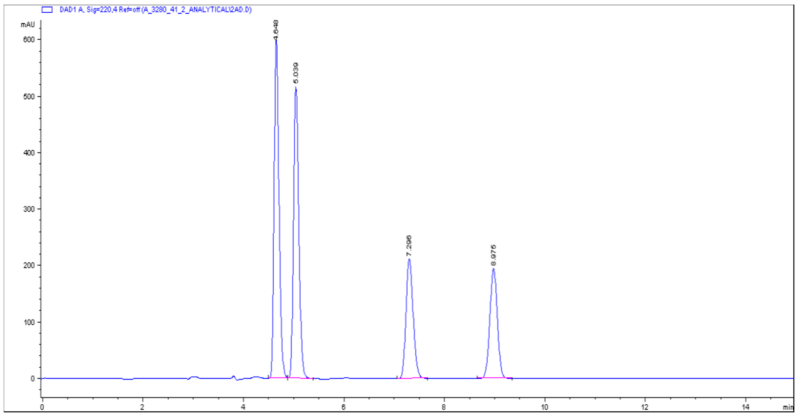
R_f: 0.25 (18/2 Cyclohexane/EtOAc).

Ultra Performance LC analysis:



Rt (minutes)	Area (%)
1.24	23
1.31	23

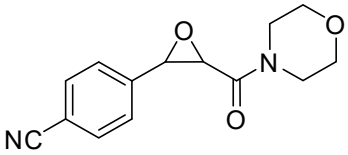
Chiral HPLC: Chiralpak AD-H (25 x 0.46 cm) 5 µm, *n*-hexane/EtOH = 80/20, 1 ml/min, 220 nm.



Rt (minutes)	Area (%)
4.6	34
5.0	31.5
7.3	17.5
8.9	17

Analytical and spectroscopic data for **3ce**

(32% yield, *cis*/*trans* = 1/0.9, white solid):



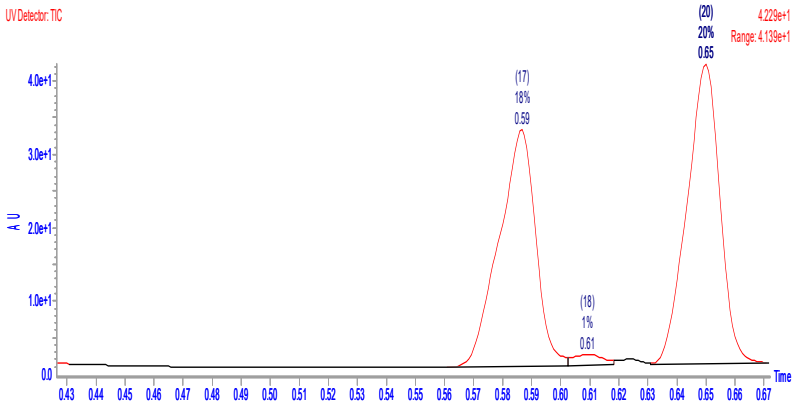
Trans ^{1}H NMR (400 MHz, DMSO-*d6*): 7.87 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 8.3 Hz, 2H), 4.47 (d, *J* = 4.8 Hz, 1H), 4.24 (d, *J* = 4.8 Hz, 1H), 3.67-2.68 (m, 8H). *Cis* ^{1}H NMR (400 MHz, DMSO-*d6*): 7.84 (d, *J* = 8.5 Hz, 2H), 7.57 (d, *J* = 8.3 Hz, 2H), 4.21 (d, *J* = 1.8 Hz, 1H), 4.17 (d, *J* = 1.8 Hz, 1 H), 3.67-2.68 (m, 8H).

^{13}C NMR (100 MHz, DMSO-*d6*): δ 164.85 (1C, C=O), 163.16 (1C, C=O), 142.02 (1C), 140.62 (1C), 132.89 (2C), 132.5 (2C), 127.71 (2C), 127.65 (2C), 119.1 (1C), 119.08 (1C), 111.7 (1C), 111.42 (1C), 66.53 (1C), 66.5 (1C), 66.39 (1C), 66.37 (1C), 58.32 (1C, *cis*), 56.8 (1C, *trans*), 56.58 (1C, *cis*), 56.31 (1C, *trans*), 45.4 (1C), 44.88 (1C), 42.44 (1C), 41.62 (1C).

MS (ESI, 5600eV): Calcd.: [M+H^{+}]: 259.27; Found:[M+H^{+}]: 259.08.

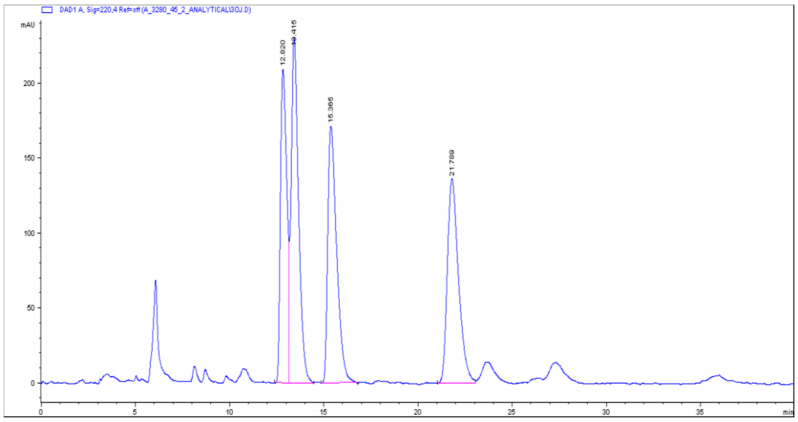
R$_f$: 0.15 (18/2 Cyclohexane/EtOAc).

Ultra Performance LC analysis:



Rt (minutes)	Area (%)
0.59	18
0.65	20

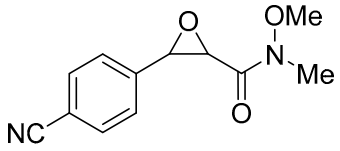
Chiral HPLC: Chiralcel OJ-H (25 x 0.46 cm) 5 µm *n*-hexane/ethanol 60/40, 1 ml/min, 220 nm.



Rt (minutes)	Area (%)
12.8	22
13.4	28
15.3	25
21.7	25

Analytical and spectroscopic data for **3de**

(86% yield, *cis*/*trans* = 1/0.75, white solid):



Trans ^{1}H NMR (400 MHz, DMSO-*d6*): δ 7.87 (d, *J* = 8.3 Hz, 2H), 7.6 (d, *J* = 8.3 Hz, 2H), 4.22 (d, *J* = 1.3 Hz, 1H), 4.11 (d, *J* = 1.5 Hz, 1H), 3.69 (s, 3H, Me), 3.18 (s, 3H, Me).

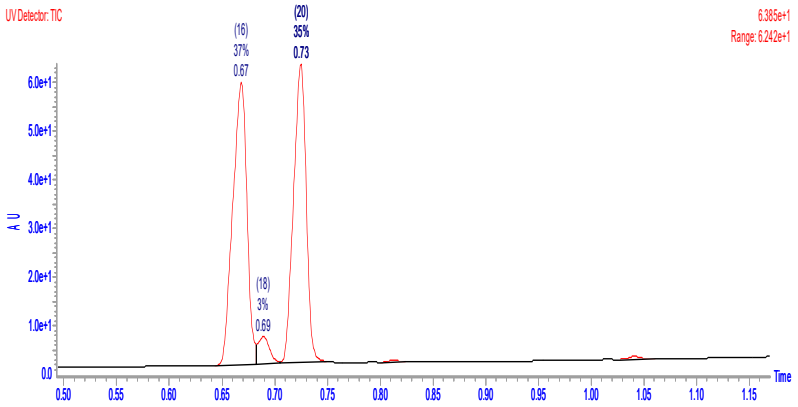
Cis ^{1}H NMR (400 MHz, DMSO-*d6*): δ 7.81 (d, *J* = 8.3 Hz, 2H), 7.55 (d, *J* = 8.3 Hz, 2H), 4.52 (d, *J* = 5 Hz, 1H), 4.35 (bs, 1H), 3.57 (bs, 3H, Me), 2.91 (bs, 3H, Me).

^{13}C NMR (100 MHz, DMSO-*d6*): δ 166.53 (1C, C=O), 165.83 (1C, C=O), 141.91 (1C), 140.34 (1C), 132.97 (2C, *trans*), 132.39 (2C, *cis*), 128.11 (2C, *cis*), 127.59 (2C, *trans*), 119.08 (1C), 119.06 (1C), 111.8 (1C), 111.37 (1C), 62.36 (1C), 62.11 (1C), 57.72 (1C, *cis*), 56.47 (1C, *cis*), 56.27 (1C, *trans*), 56.13 (1C, *trans*), 32.58 (1C), 32.35 (1C).

MS (ESI, 5600eV): Calcd.: [M+H^{+}]: 233.23; Found: [M+H^{+}]: 232.96.

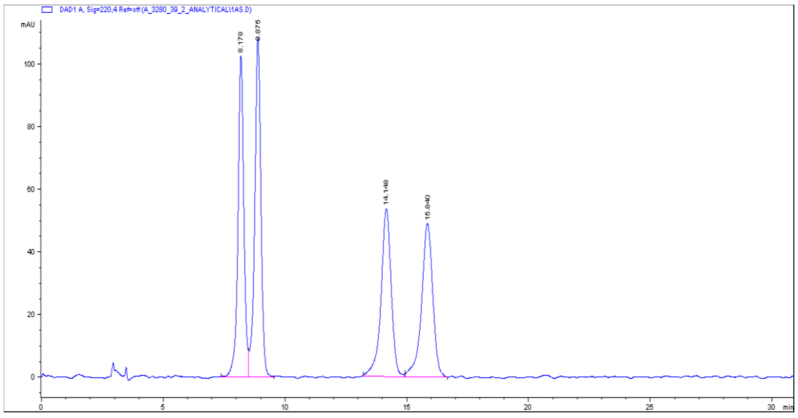
R$_f$: 0.23 (18/2 Cyclohexane/EtOAc).

Ultra Performance LC analysis:



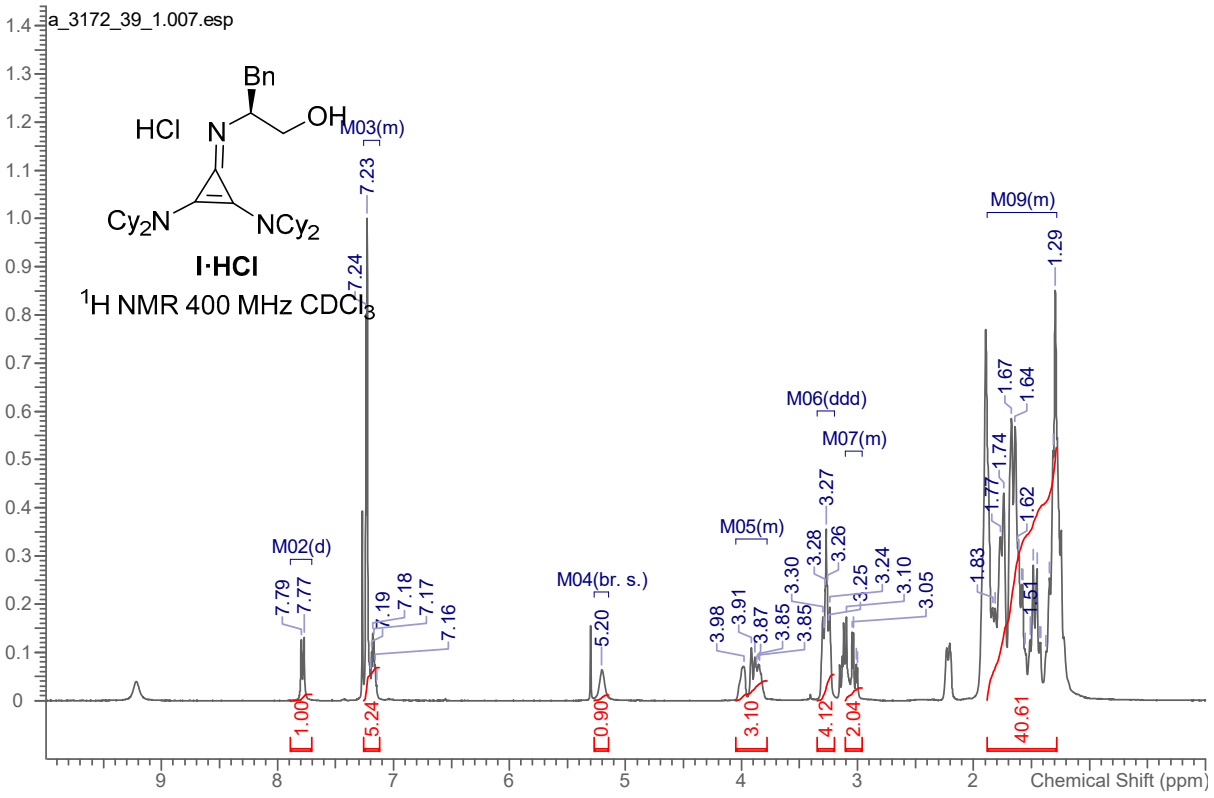
Rt (minutes)	Area (%)
0.67	37
0.73	35

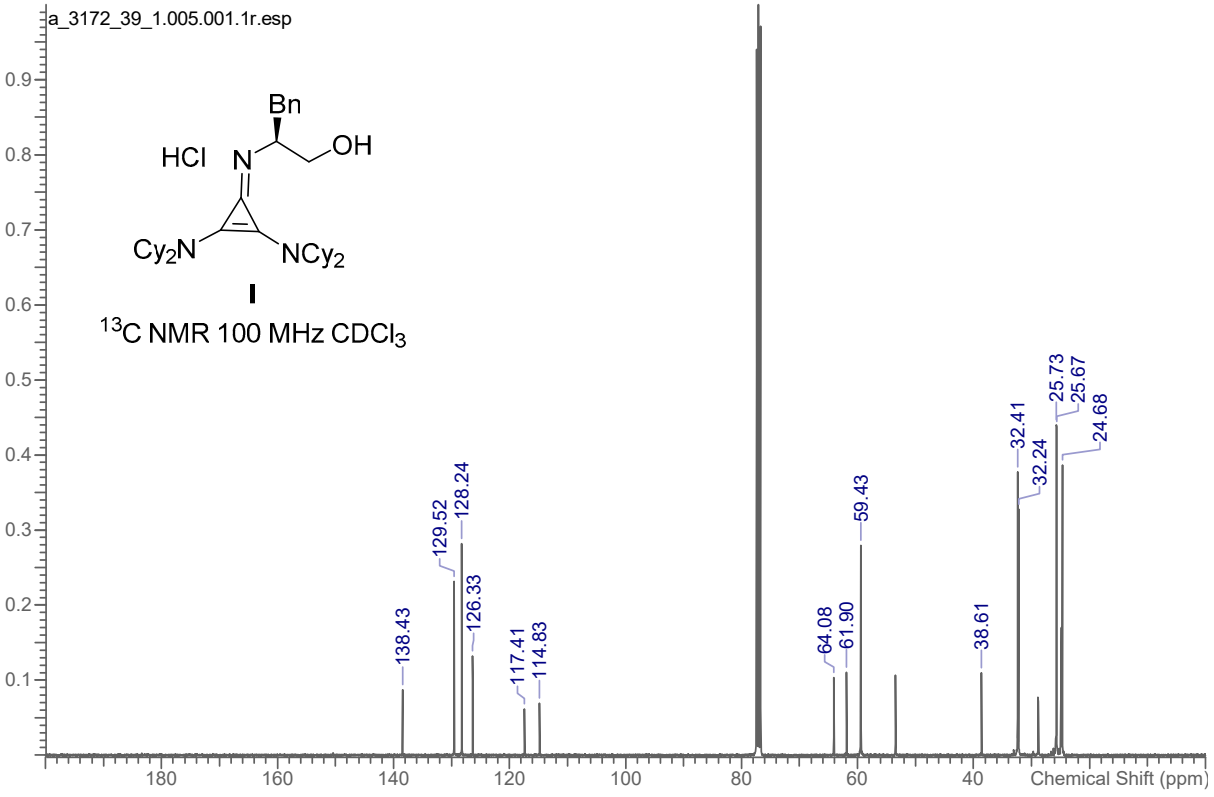
Chiral HPLC: Chiralpak AS-H (25 x 0.46 cm) 5 µm, *n*-hexane/ethanol 70/30, 1 ml/min, 220 nm.

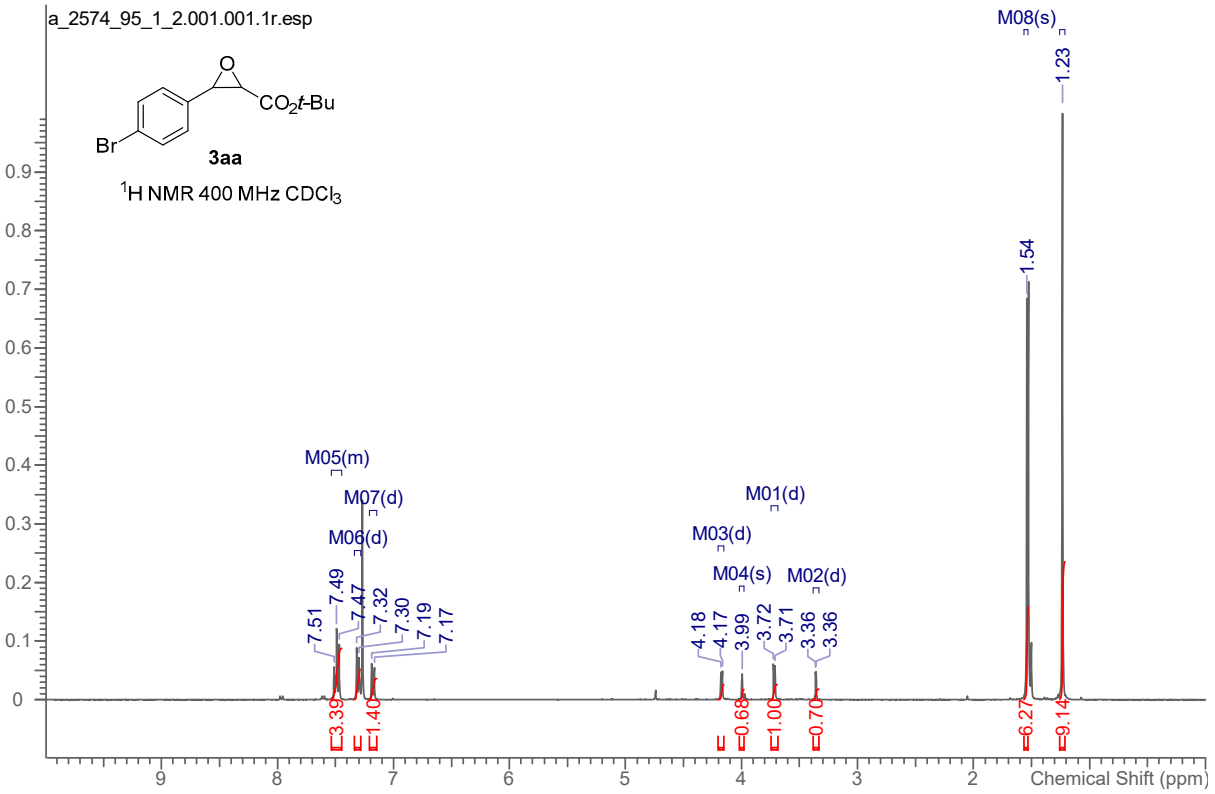


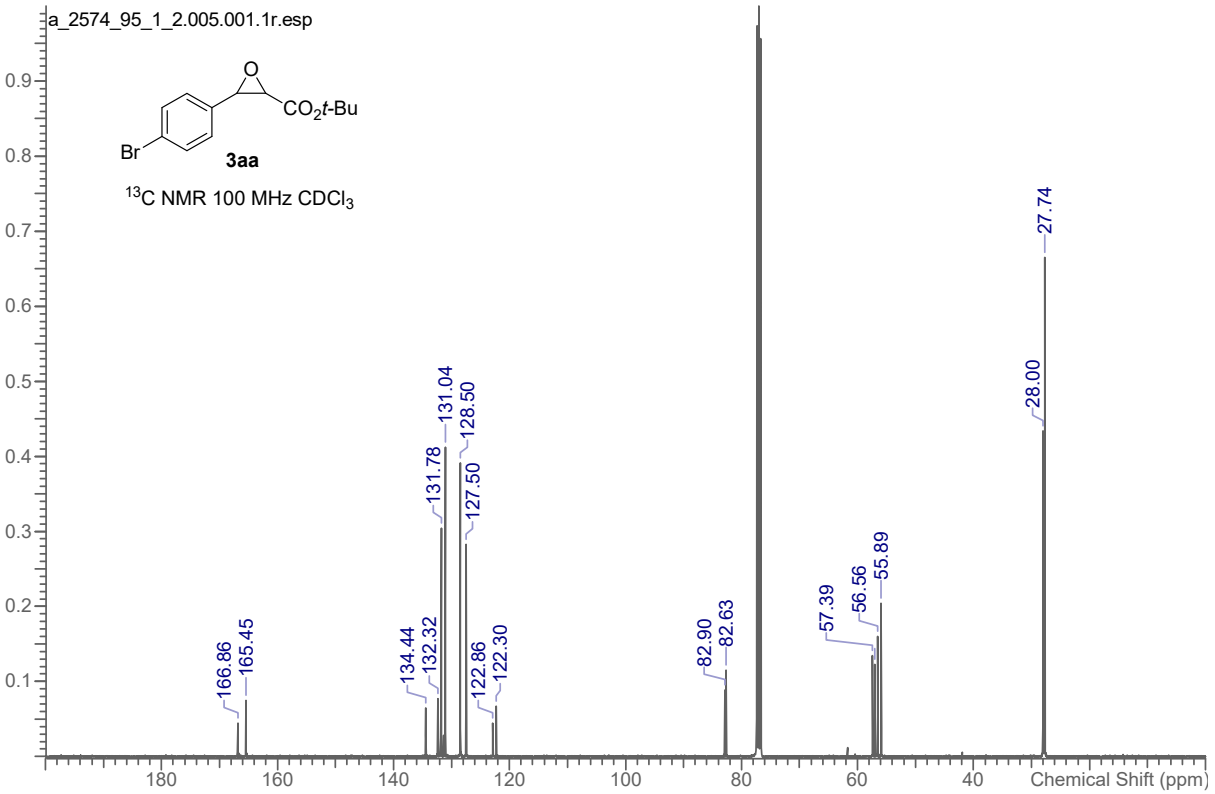
Rt (minutes)	Area (%)
8.1	25.6
8.8	28.1
14.1	23.2
15.8	23.1

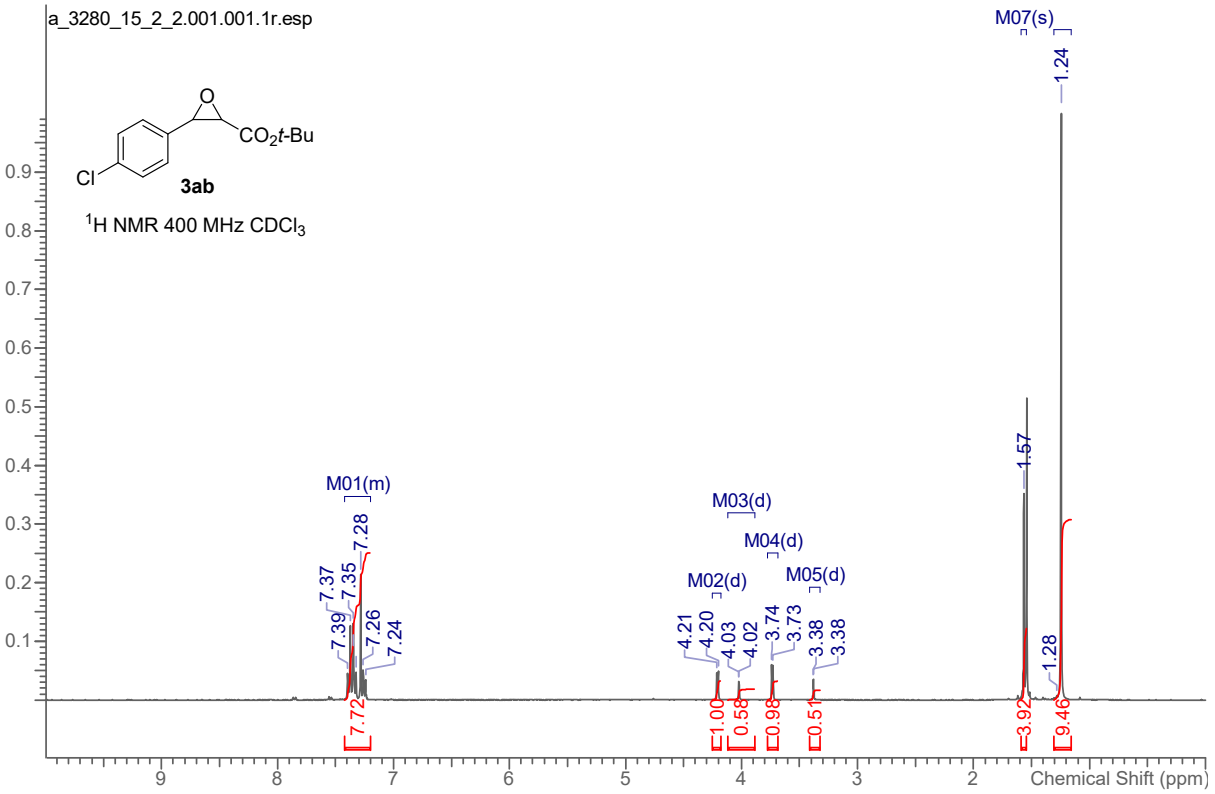
^{1}H NMR and ^{13}C NMR Spectra






a_2574_95_1_2.001.001.1r.esp
O
CO2t-Bu
Br
3aa
1H NMR 400 MHz CDCl3
M08(s)
1.23
1.54
M05(m)
M07(d)
M06(d)
M01(d)
M03(d)
M04(s)
M02(d)
7.51
7.49
7.47
7.32
7.30
7.19
7.17
4.18
4.17
3.99
3.72
3.71
3.36
3.36
3.39
1.40
0.68
1.00
0.70
6.27
9.14
Chemical Shift (ppm)


a_2574_95_1_2.005.001.1r.esp
O
CO2t-Bu
Br
3aa
13C NMR 100 MHz CDCl3
27.74
28.00
131.04
128.50
131.78
127.50
166.86
165.45
134.44
132.32
122.86
122.30
82.90
82.63
57.39
56.56
55.89
Chemical Shift (ppm)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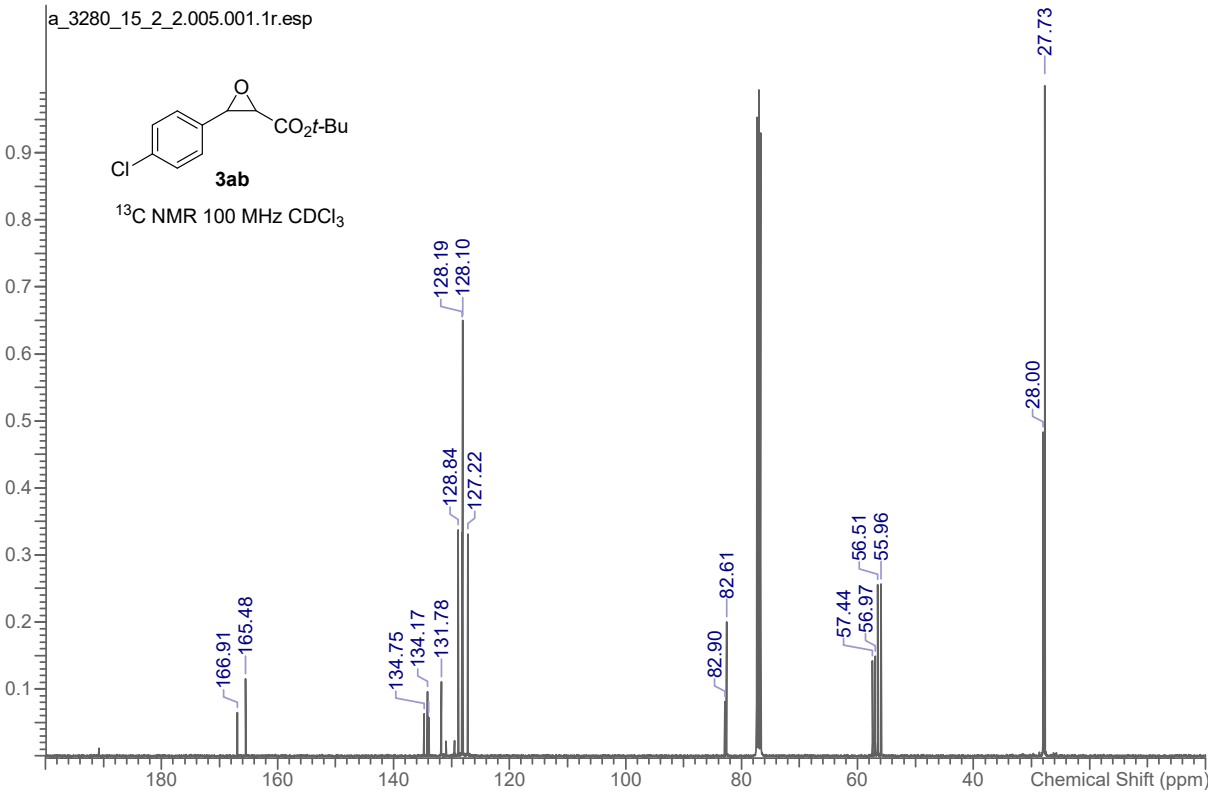
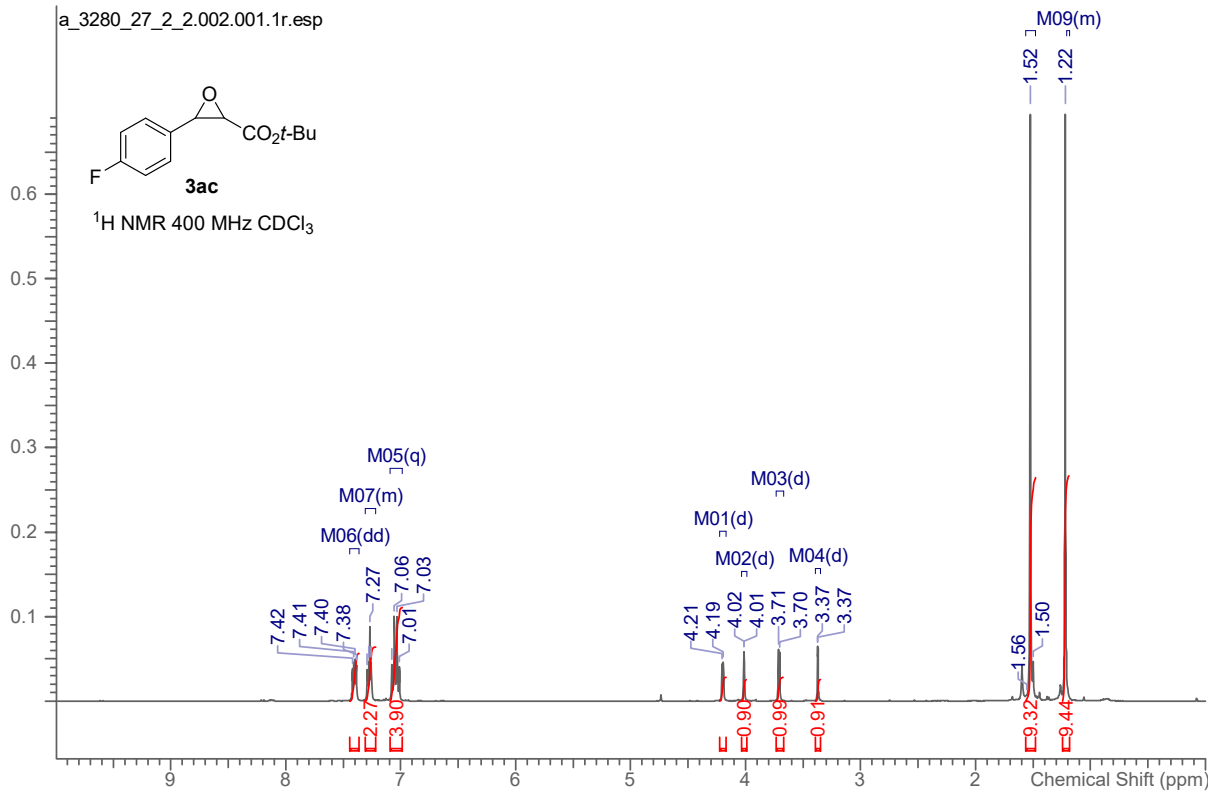
O
CO2t-Bu
Cl
3ab
1H NMR 400 MHz CDCl3
M07(s)
1.24
M01(m)
7.28
7.37
7.35
7.39
7.26
7.24
M03(d)
M04(d)
M02(d)
M05(d)
4.21
4.20
4.03
4.02
3.74
3.73
3.38
3.38
1.57
1.28
7.72
1.00
0.58
0.98
0.51
3.92
9.46
Chemical Shift (ppm)


a_3280_15_2_2.005.001.1r.esp
O
CO2t-Bu
Cl
3ab
13C NMR 100 MHz CDCl3
27.73
128.19
128.10
28.00
128.84
127.22
56.51
55.96
82.61
57.44
56.97
166.91
165.48
134.75
134.17
131.78
82.90
Chemical Shift (ppm)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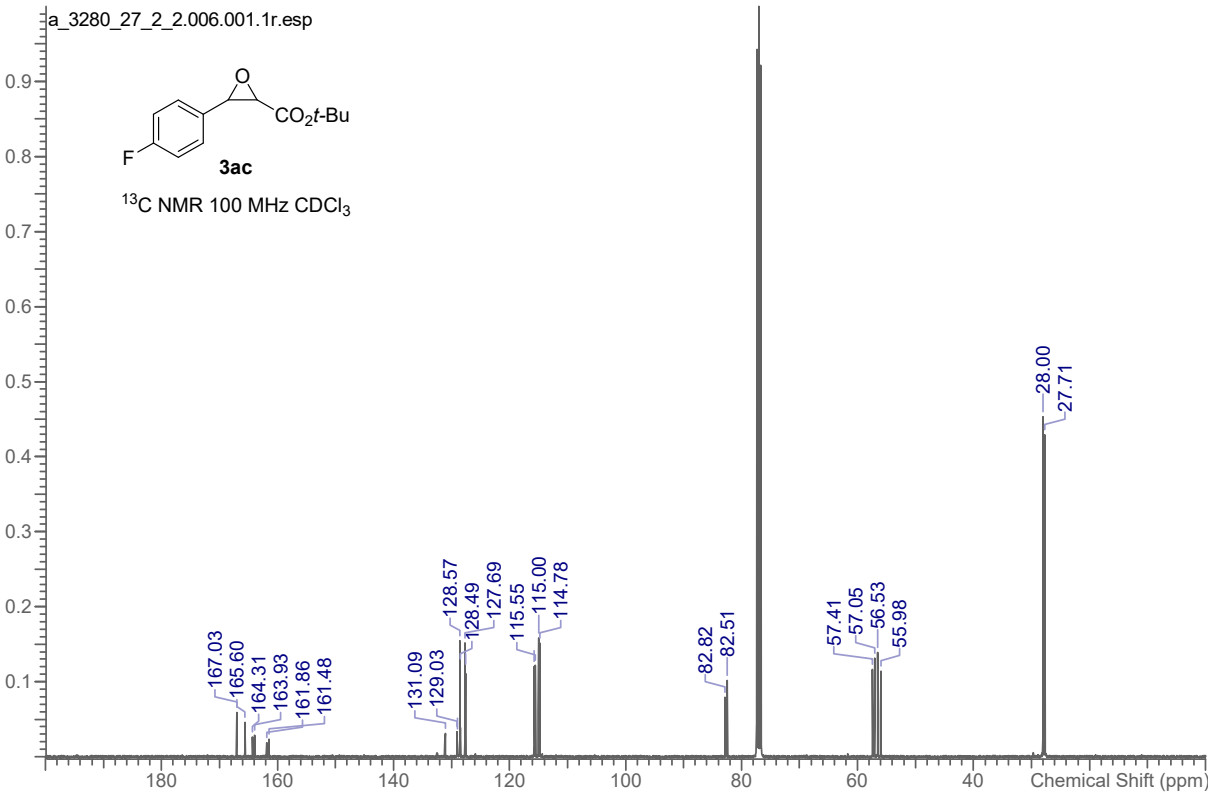
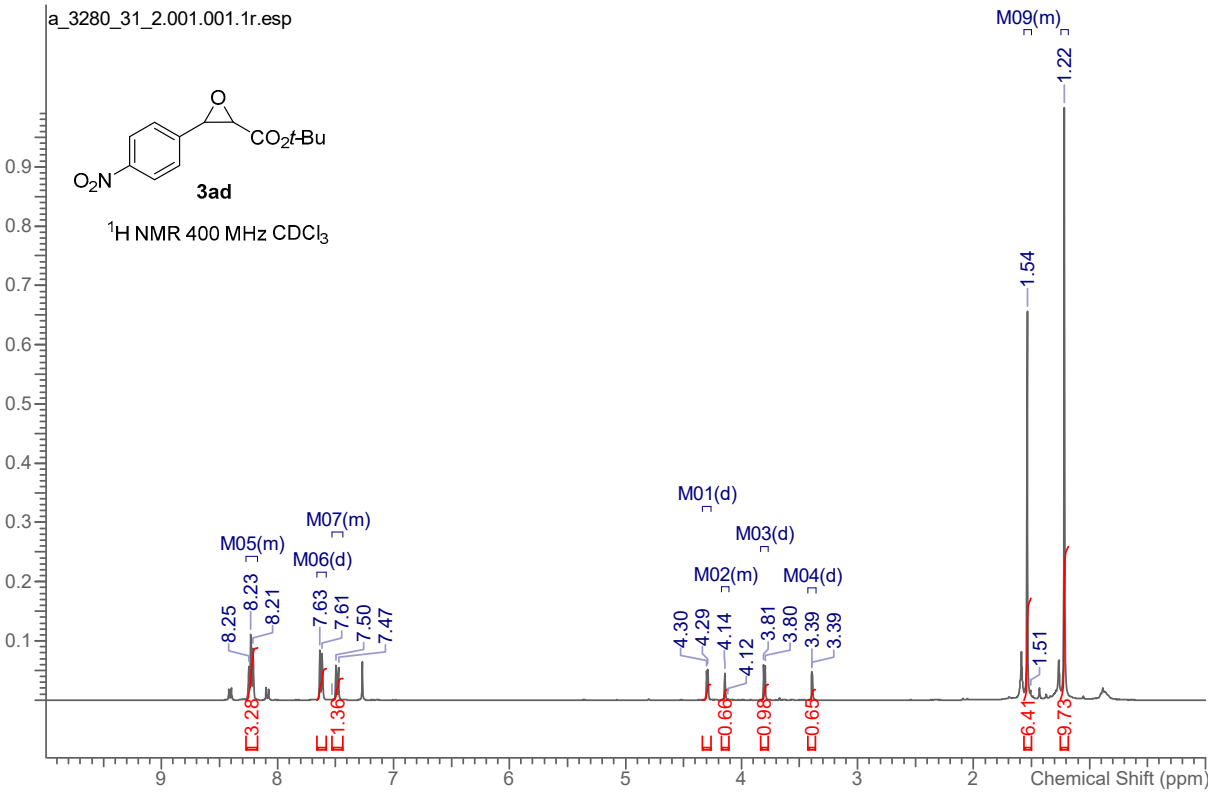
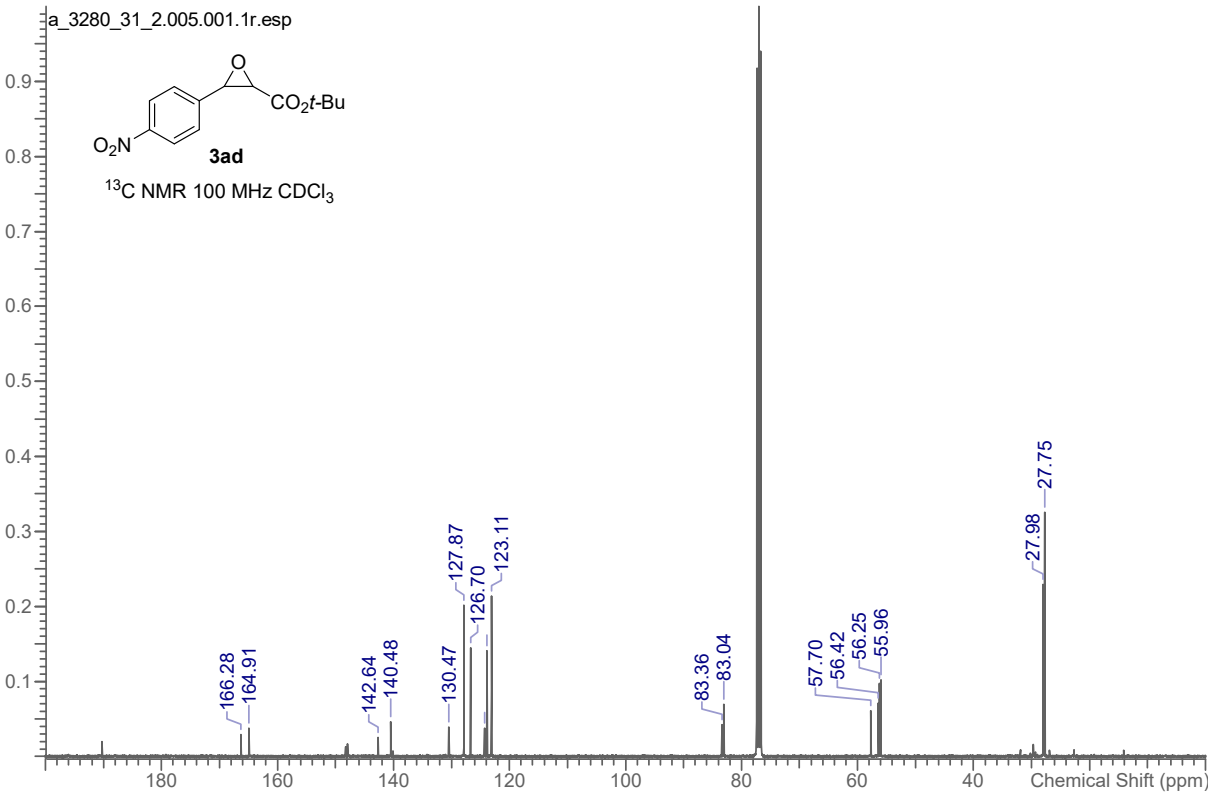
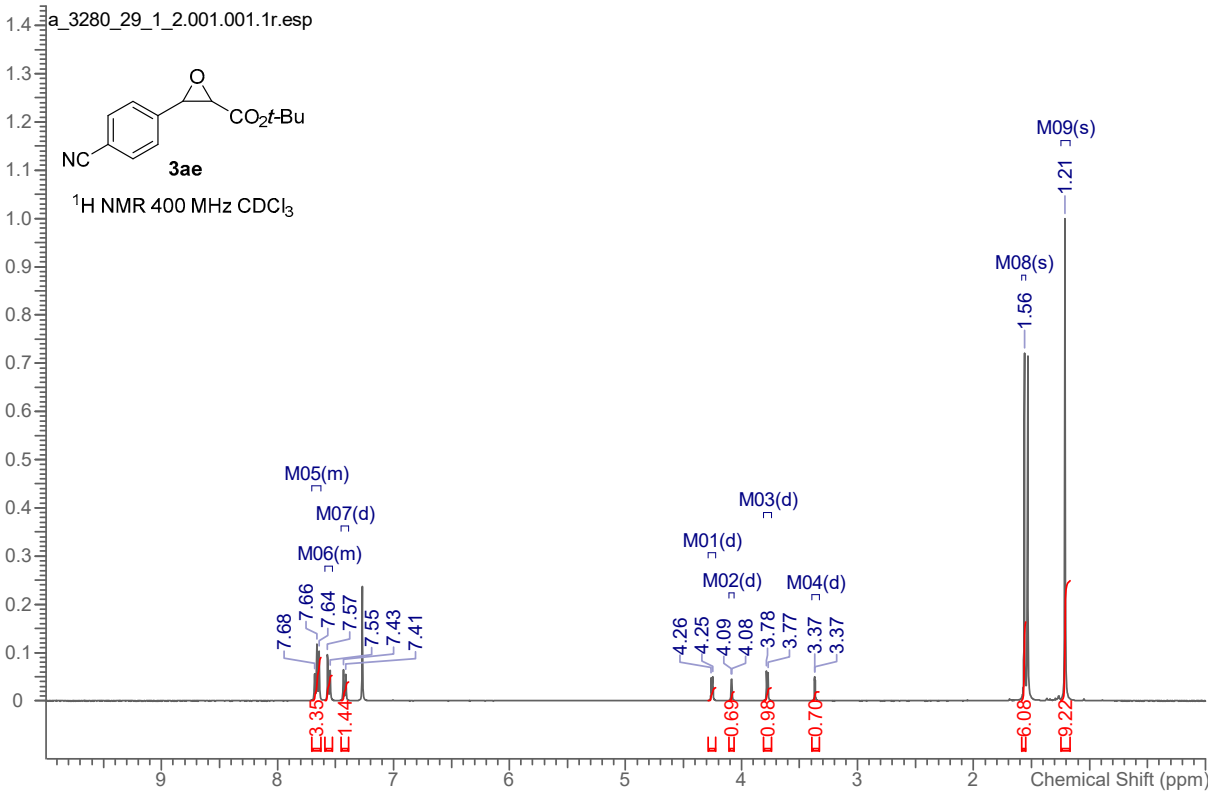
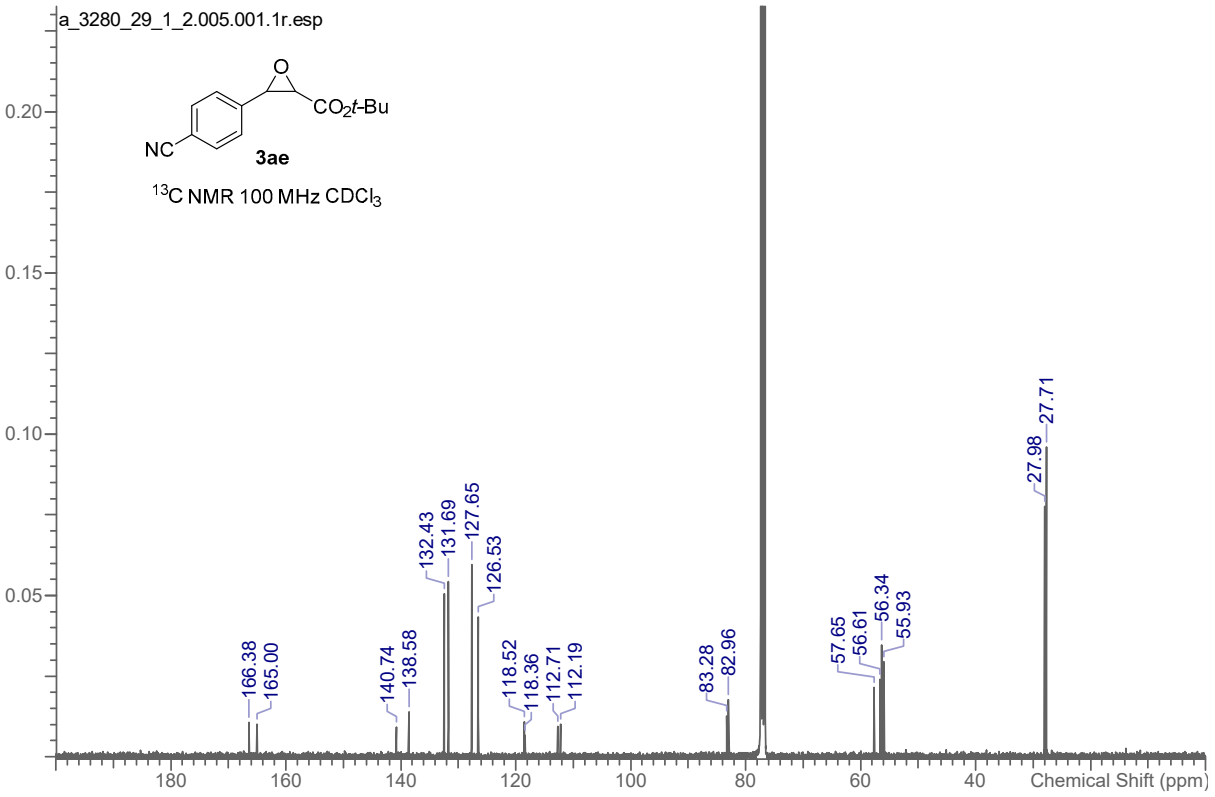
O
CO2t-Bu
F
3ac
1H NMR 400 MHz CDCl3
M09(m)
1.52
1.22
M05(q)
M07(m)
M06(dd)
M03(d)
M01(d)
M02(d)
M04(d)
7.42
7.41
7.40
7.38
7.27
7.06
7.03
7.01
4.21
4.19
4.02
4.01
3.71
3.70
3.37
3.37
1.56
1.50
2.27
3.90
0.90
0.99
0.91
9.32
9.44
Chemical Shift (ppm)

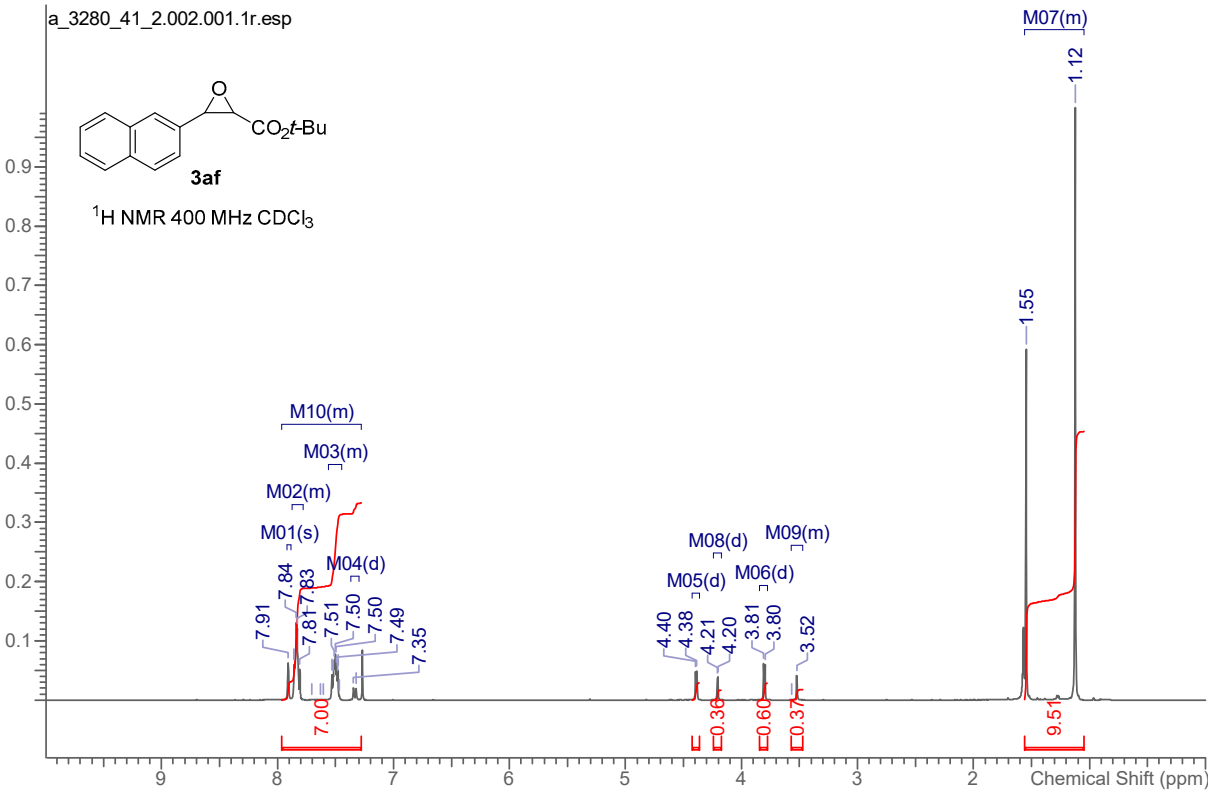

a_3280_27_2_2.006.001.1r.esp
O
CO2t-Bu
F
3ac
13C NMR 100 MHz CDCl3
167.03
165.60
164.31
163.93
161.86
161.48
131.09
129.03
128.57
128.49
127.69
115.55
115.00
114.78
82.82
82.51
57.41
57.05
56.53
55.98
28.00
27.71
Chemical Shift (ppm)


a_3280_31_2.001.001.1r.esp
O
CO2t-Bu
O2N
3ad
1H NMR 400 MHz CDCl3
M09(m)
1.22
1.54
M01(d)
M03(d)
M07(m)
M05(m)
M06(d)
M02(m)
M04(d)
8.25
8.23
8.21
7.63
7.61
7.50
7.47
4.30
4.29
4.14
4.12
3.81
3.80
3.39
3.39
1.51
3.28
1.36
0.66
0.98
0.65
6.41
9.73
Chemical Shift (ppm)


a_3280_31_2.005.001.1r.esp
O
CO2t-Bu
O2N
3ad
13C NMR 100 MHz CDCl3
27.75
27.98
127.87
126.70
123.11
166.28
164.91
142.64
140.48
130.47
83.36
83.04
57.70
56.42
56.25
55.96
Chemical Shift (ppm)


a_3280_29_1_2.001.001.1r.esp
CO2t-Bu
NC
3ae
1H NMR 400 MHz CDCl3
M09(s)
1.21
M08(s)
1.56
M05(m)
M07(d)
M06(m)
M03(d)
M01(d)
M02(d)
M04(d)
7.68
7.66
7.64
7.57
7.55
7.43
7.41
4.26
4.25
4.09
4.08
3.78
3.77
3.37
3.37
3.35
1.44
0.69
0.98
0.70
6.08
9.22
Chemical Shift (ppm)


a_3280_29_1_2.005.001.1r.esp
CO2t-Bu
NC
3ae
13C NMR 100 MHz CDCl3
166.38
165.00
140.74
138.58
132.43
131.69
127.65
126.53
118.52
118.36
112.71
112.19
83.28
82.96
57.65
56.61
56.34
55.93
27.98
27.71
Chemical Shift (ppm)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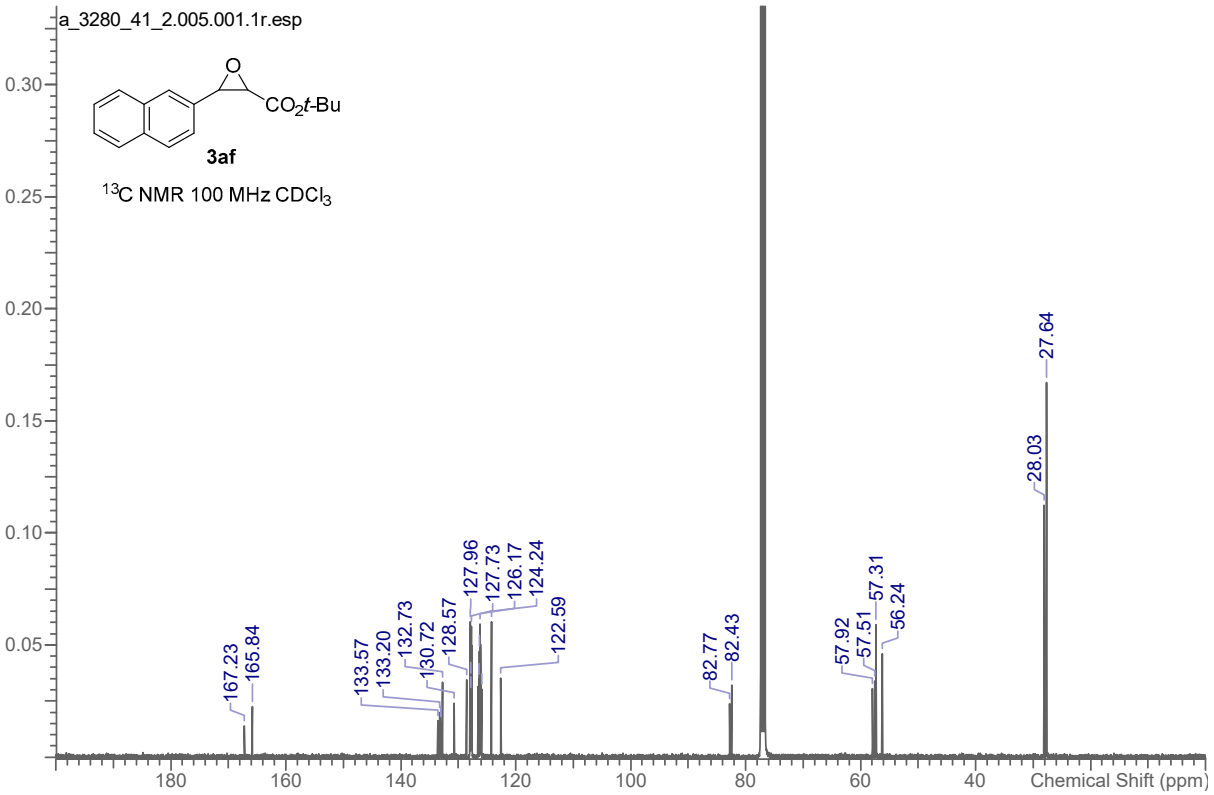
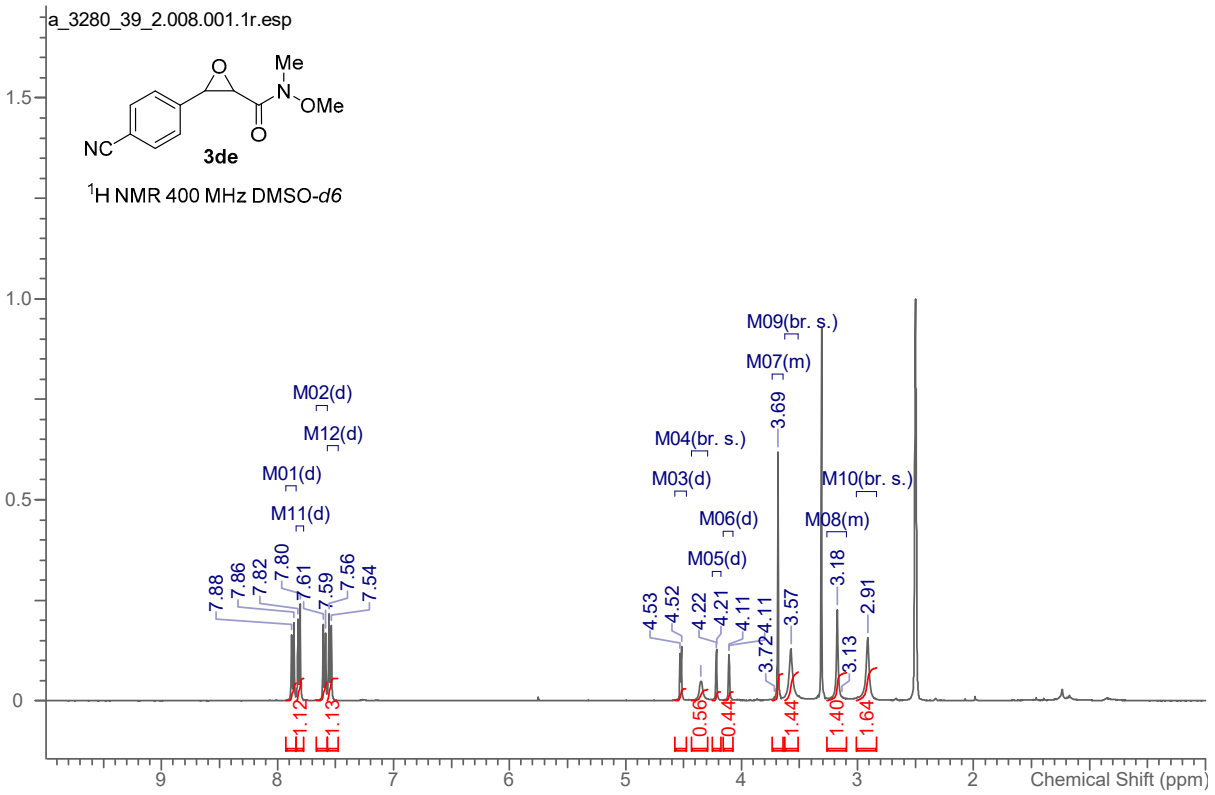
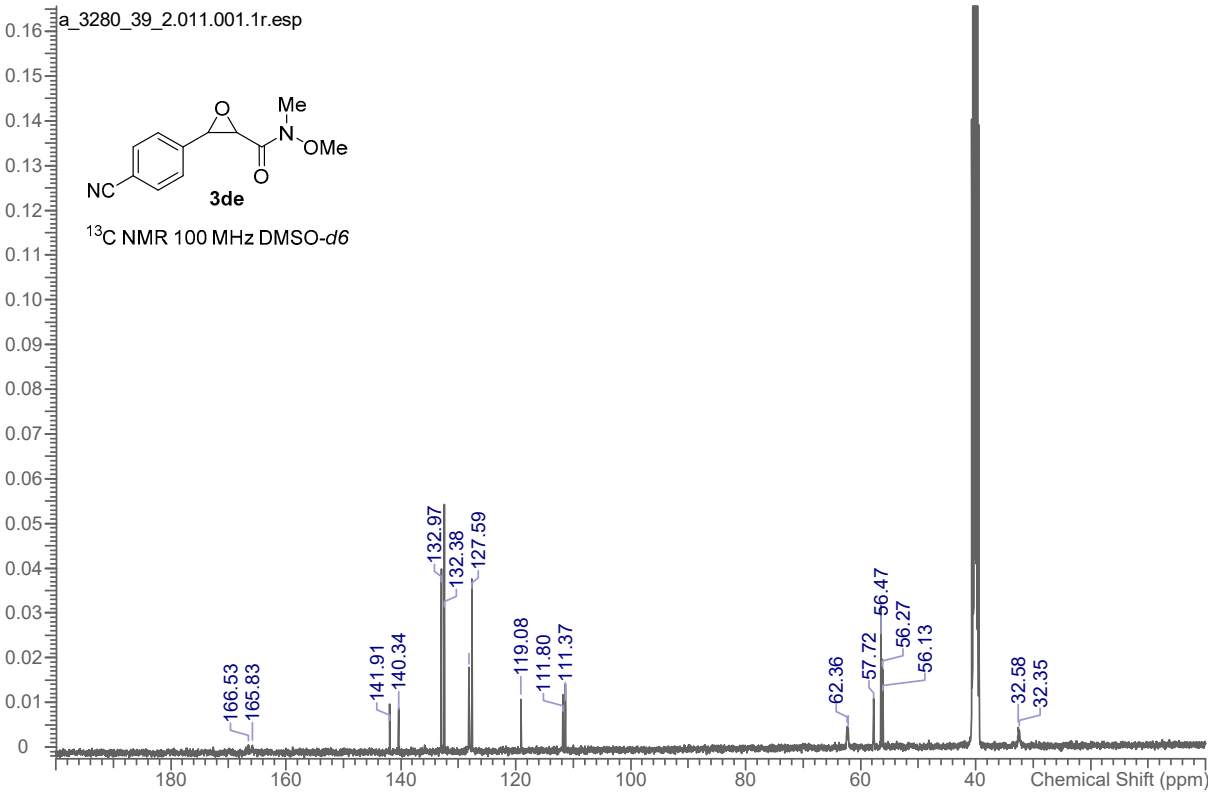
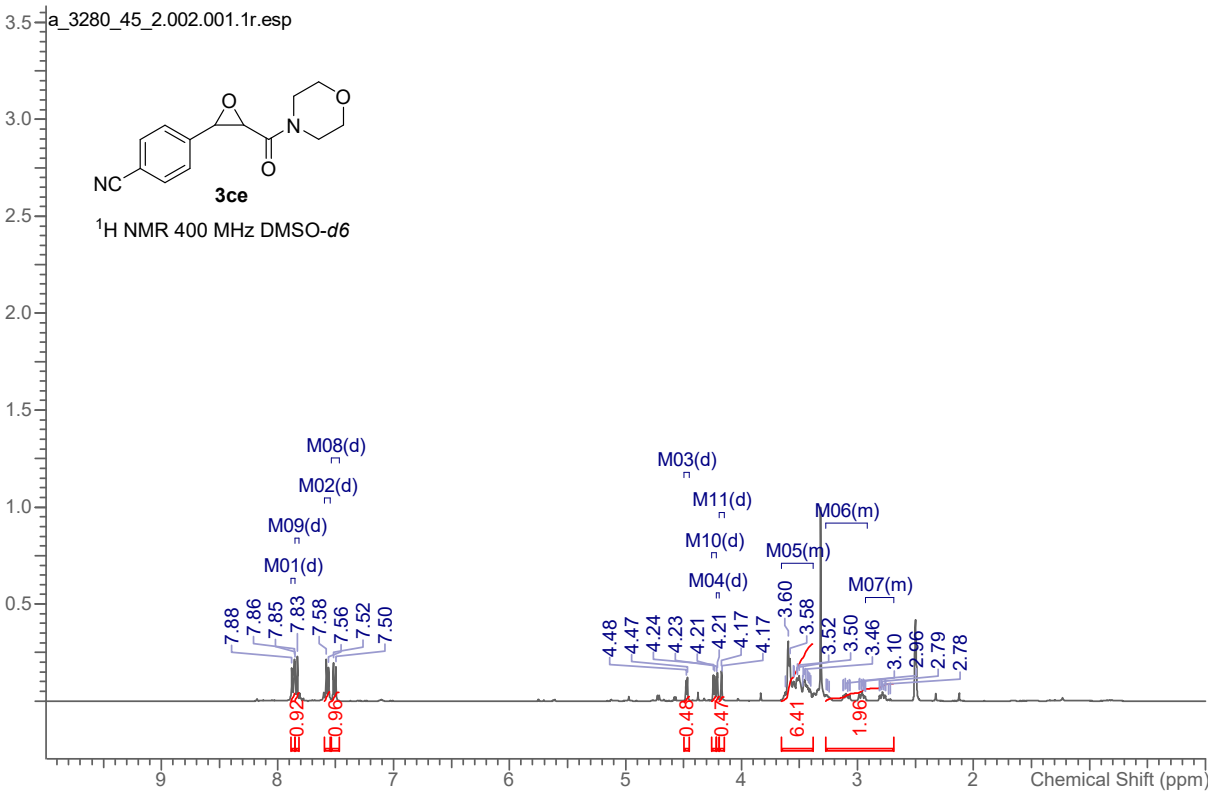
3af
1H NMR 400 MHz CDCl3
M07(m)
1.12
1.55
M10(m)
M03(m)
M02(m)
M01(s)
M04(d)
M08(d)
M09(m)
M05(d)
M06(d)
7.91
7.84
7.83
7.81
7.51
7.50
7.50
7.49
7.35
4.40
4.38
4.21
4.20
3.81
3.80
3.52
7.00
0.36
0.60
0.37
9.51
Chemical Shift (ppm)


a_3280_41_2.005.001.1r.esp
3af
13C NMR 100 MHz CDCl3
27.64
28.03
167.23
165.84
133.57
133.20
132.73
130.72
128.57
127.96
127.73
126.17
124.24
122.59
82.77
82.43
57.92
57.51
57.31
56.24
Chemical Shift (ppm)


a_3280_39_2.008.001.1r.esp
Me
N
OMe
O
NC
3de
1H NMR 400 MHz DMSO-d6
M09(br. s.)
M07(m)
M02(d)
M12(d)
M04(br. s.)
M01(d)
M03(d)
M10(br. s.)
M11(d)
M06(d)
M08(m)
M05(d)
7.88
7.86
7.82
7.80
7.61
7.59
7.56
7.54
4.53
4.52
4.22
4.21
4.11
3.72
4.11
3.57
3.69
3.18
3.13
2.91
1.12
1.13
0.56
0.44
1.44
1.40
1.64
Chemical Shift (ppm)


a_3280_39_2.011.001.1r.esp
Me
N
OMe
O
NC
3de
13C NMR 100 MHz DMSO-d6
166.53
165.83
141.91
140.34
132.97
132.38
127.59
119.08
111.80
111.37
62.36
57.72
56.47
56.27
56.13
32.58
32.35
Chemical Shift (ppm)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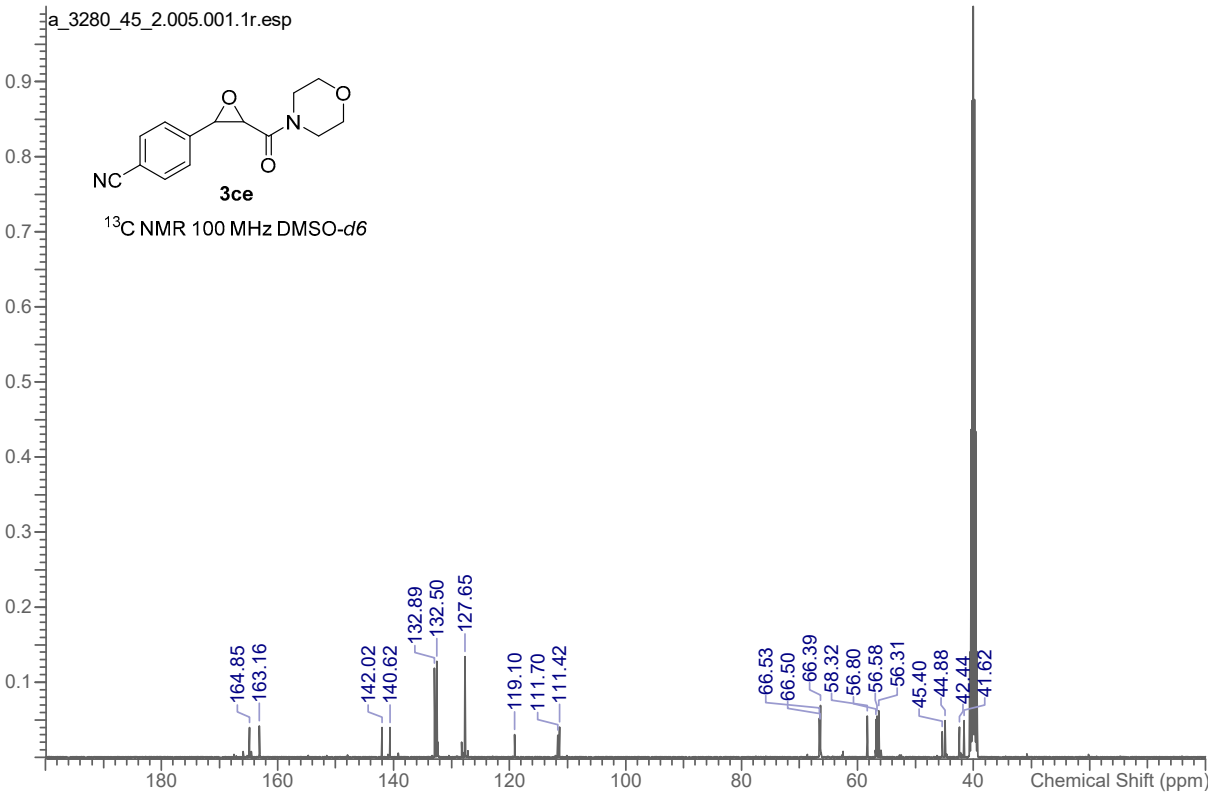
NC
3ce
1H NMR 400 MHz DMSO-d6
M08(d)
M02(d)
M09(d)
M01(d)
M03(d)
M11(d)
M10(d)
M04(d)
M06(m)
M05(m)
M07(m)
7.88
7.86
7.85
7.83
7.58
7.56
7.52
7.50
4.48
4.47
4.24
4.23
4.21
4.21
4.17
4.17
3.60
3.58
3.52
3.50
3.46
3.10
2.96
2.79
2.78
0.92
0.96
0.48
0.47
6.41
1.96
Chemical Shift (ppm)


a_3280_45_2.005.001.1r.esp
NC
3ce
13C NMR 100 MHz DMSO-d6
164.85
163.16
142.02
140.62
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132.50
127.65
119.10
111.70
111.42
66.53
66.50
66.39
58.32
56.80
56.58
56.31
45.40
44.88
42.44
41.62
Chemical Shift (ppm)

References

[1] Sharifi, A.; Abaee, M. S.; Mirzaei, M.; Salimi, R. Ionic Liquid-Mediated Darzens Condensation: An Environmentally-Friendly Procedure for the Room-Temperature Synthesis of α,β-Epoxy Ketones. *J. Iran. Chem. Soc.* **2008**, *5*, 135-139 (doi.org/10.1007/BF03245826).

[2] Kowalkowska, A.; Jończyk, A. Effect of Phase-Transfer Catalyst on Stereochemistry of tert-Butyl-3-aryl(alkyl)-Substituted Glycidates. *Org. Process Res. Dev*. **2010**, *14*, 728-731. (doi.org/10.1021/op1000379)

[3] Arai, S.; Suzuki, Y.; Tokumaru, K.; Shioiri, T. Diastereoselective Darzens reactions of α-chloroesters, amides and nitriles with aromatic aldehydes under phase-transfer catalyzed conditions. *Tetrahedron Lett.* **2002**, *43*, 833-836.