

Supplementary Information

Towards *trans*-Dual Deuterated Cyclopropanes via Photoredox

Synergistic Deuteration with D₂O

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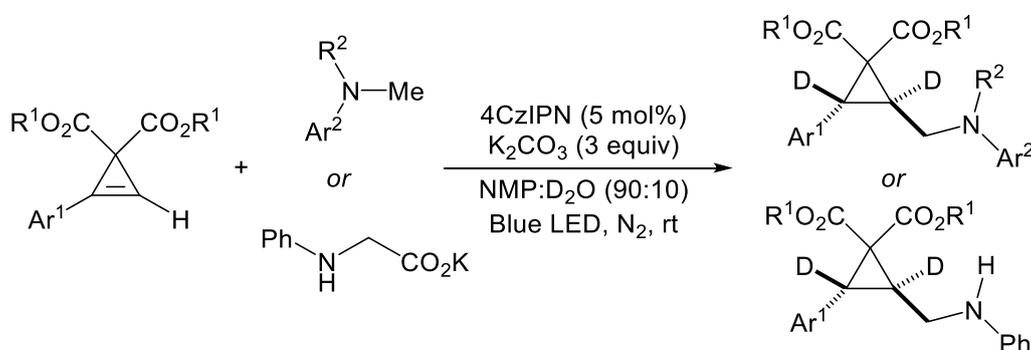
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1. General Information.

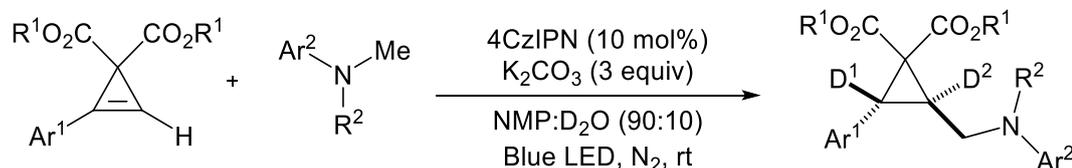
All the temperatures are referred to the preheated oil baths used. ^1H NMR spectra were recorded on a Bruker AVANCE III 500 or JNM-ECZ400S/L1 spectrometer in CDCl_3 (tetramethylsilane as an internal standard). The data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublets, dt = doublet of triplets, td = triplet of doublets, tt = triplet of triplets), coupling constant(s) in Hz, integration. ^{13}C NMR spectra was recorded on a Bruker AVANCE III 500 or JNM-ECZ400S/L1 spectrometer and data are reported in terms of chemical shift relative to CDCl_3 (77.00 ppm). In a typical experiment, blue LEDs (450-465 nm) with a cooling fan were used as a visible light source. Commercially available reagents and solvents were purchased from Adamas, Sinopharm, and Sigma-Aldrich. Cyclopropenes were synthesized according to literatures.¹⁻⁶

2. Synthesis of *trans*-Dual Deuterated Cyclopropanes.

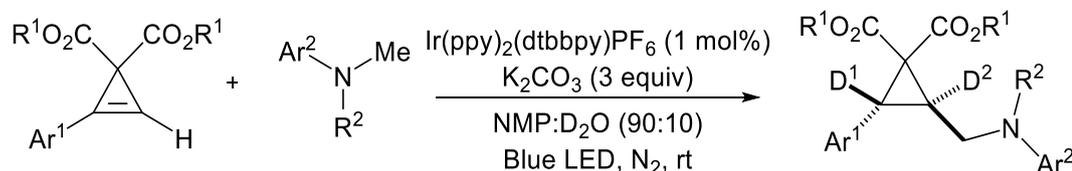


General Procedure I: Under nitrogen atmosphere, to a 10 mL Schlenk tube equipped with a stirring bar is added 4CzIPN (5 mol%), K_2CO_3 (0.3 mmol), cyclopropene (0.1 mmol), tertiary methylamine or potassium *N*-phenyl glycinate (0.3 mmol), *N*-methyl pyrrolidinone (0.9 mL), and D_2O (0.1 mL) successively, and the tube was sealed with a septum. The mixture was stirred at room temperature irradiated with a blue LED (6 W) overnight. The reaction was complete as monitored by TLC, and quenched with H_2O (2.5 mL). The aqueous layer was extracted with ethyl acetate (5

mL × 3) and the combined organic layer was washed with brine (5 mL), dried over anhydrous MgSO₄, filtered and concentrated in vacuo to afford corresponding product via chromatography on silica gel.

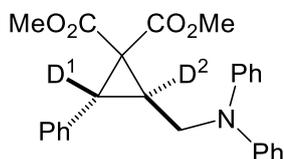


General Procedure II: Under nitrogen atmosphere, to a 10 mL Schlenk tube equipped with a stirring bar is added 4CzIPN (10 mol%), K₂CO₃ (0.3 mmol), cyclopropene (0.1 mmol), methylamine (0.3 mmol), *N*-methyl pyrrolidinone (0.9 mL), and D₂O (0.1 mL) successively, and the tube was sealed with a septum. The mixture was stirred at room temperature irradiated with a blue LED (6 W) overnight. The reaction was complete as monitored by TLC, and quenched with H₂O (2.5 mL). The aqueous layer was extracted with ethyl acetate (5 mL × 3) and the combined organic layer was washed with brine (5 mL), dried over anhydrous MgSO₄, filtered and concentrated in vacuo to afford corresponding product via chromatography on silica gel.



General Procedure III: Under nitrogen atmosphere, to a 10 mL Schlenk tube equipped with a stirring bar is added Ir(ppy)₂(dtbbpy)PF₆ (1 mol%), K₂CO₃ (0.3 mmol), cyclopropene (0.1 mmol), methylamine (0.3 mmol), *N*-methyl pyrrolidinone (0.9 mL), and D₂O (0.1 mL) successively, and the tube was sealed with a septum. The mixture was stirred at room temperature irradiated with a blue LED (6 W) overnight. The reaction was complete as monitored by TLC, and quenched with H₂O (2.5 mL). The aqueous layer was extracted with ethyl acetate (5 mL × 3) and the combined organic layer was washed with brine (5 mL), dried over anhydrous MgSO₄, filtered and concentrated in vacuo to afford corresponding product via chromatography on silica gel.

(1) Dimethyl (2*S,3*R**)-2-((diphenylamino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (1) (wyq-3-34, wyq-5-43).**



1

trans:cis = 11:1, D¹, D² = 94%, 95%

Following General Procedure I, **1** was afforded as a colorless oil (31.5 mg, 77%, D¹/D² = 94%/95%, *trans:cis* = 11:1), eluent (0-9% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.23 (m, 4 H), 7.20 (d, *J* = 7.4 Hz, 3 H), 7.05 (dd, *J* = 8.0, 1.4 Hz, 2 H), 7.02 (d, *J* = 7.4 Hz, 4 H), 6.96 (t, *J* = 7.3 Hz, 2 H), 3.98 (d, *J* = 15.3 Hz, 1 H), 3.88 (d, *J* = 15.2 Hz, 1 H), 3.61 (s, 3 H), 3.33 (s, 3 H), 3.17 (s, 0.06 H), 2.90 (t, *J* = 6.5 Hz, 0.05 H); ¹³C NMR (126 MHz, CDCl₃) δ 168.23, 166.84, 147.65, 134.25, 129.40, 128.37, 128.12, 127.32, 121.76, 121.29, 52.76, 52.21, 49.20, 42.08, 36.35, 36.05 (t, *J*_{C-D} = 23.9 Hz), 29.21, 28.91 (t, *J*_{C-D} = 24.6 Hz); HRMS calcd for C₂₆H₂₄D₂NO₄ ([M+H]⁺): 418.1982; found: 418.1988.

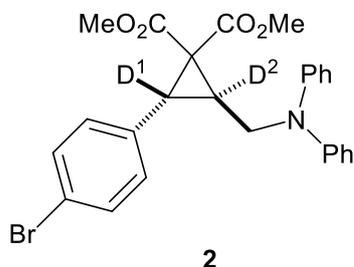
The following signals are discernible for the *cis*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 3.75 (s, 3 H), 3.54 (s, 3 H), 4.36 (d, *J* = 15.2 Hz, 1 H); ¹³C NMR (126 MHz, CDCl₃) δ 129.26, 121.51.

Gram-scale synthesis of 1 (wyq-9-28).

Under nitrogen atmosphere, to a 25 mL Schlenk tube equipped with a stirring bar is added 4CzIPN (126.8 mg, 0.15 mmol, 5 mol%), K₂CO₃ (1.2490 g, 9 mmol, 3 equiv), **S1** (696.5 mg, 3 mmol, 1 equiv), **S2** (1.6550 g, 9 mmol, 3 equiv), *N*-methyl pyrrolidinone (9 mL), and D₂O (1 mL) successively, and the tube was sealed with a septum. The mixture was stirred at room temperature irradiated with a blue LED for 48 h. The aqueous layer was extracted with ethyl acetate (10 mL × 3) and the combined organic layer was washed with brine, dried over anhydrous MgSO₄, filtered and concentrated in vacuo to afford corresponding product via chromatography on silica

gel, **1** was afforded as a colorless oil (959.8 mg, 77%, $D^1/D^2 = 94\%/95\%$, *trans:cis* = 11:1), eluent (0-9% of ethyl acetate in petroleum ether).

(2) Dimethyl (2R*,3S*)-2-(4-bromophenyl)-3-((diphenylamino)methyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (2) (wyq-4-11).



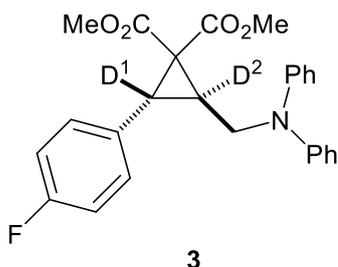
trans:cis = 13:1, D^1 , D^2 = 94%, 96%

Following General Procedure I, **2** was afforded as a colorless oil (31.1 mg, 63%, $D^1/D^2 = 94\%/96\%$, *trans:cis* = 13:1), eluent (0-11% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.32 (d, $J = 8.4$ Hz, 2 H), 7.29 – 7.22 (m, 4 H), 7.03 – 6.93 (m, 6 H), 6.90 (d, $J = 8.4$ Hz, 2 H), 3.99 (d, $J = 15.1$ Hz, 1 H), 3.82 (d, $J = 15.2$ Hz, 1 H), 3.63 (s, 3 H), 3.38 (s, 3 H), 3.33 (s, 0.06 H), 2.83 (t, $J = 6.5$ Hz, 0.04 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.00, 166.66, 147.63, 133.40, 131.27, 130.12, 129.44, 121.89, 121.55, 121.33, 52.84, 52.41, 49.25, 41.99, 35.82, 35.52 (t, $J_{\text{C-D}} = 24.6$ Hz), 29.25, 28.96 (t, $J_{\text{C-D}} = 23.2$ Hz); HRMS calcd for $\text{C}_{26}\text{H}_{23}\text{D}_2\text{BrNO}_4$ ($[\text{M}+\text{H}]^+$): 496.1087; found: 496.1094.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 4.31 (d, $J = 15.2$ Hz, 2 H), 3.76 (s, 3 H), 3.56 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 131.34, 131.00, 129.35, 121.39, 53.03, 52.27.

(3) Dimethyl (2S*,3R*)-2-((diphenylamino)methyl)-3-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (3) (wyq-4-16).



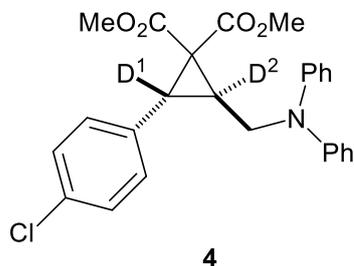
trans:cis = 10:1, D^1 , D^2 = 94%, 96%

Following General Procedure I, **3** was afforded as a colorless oil (28.8 mg, 65%, $D^1/D^2 = 94\%/96\%$, *trans:cis* = 10:1), eluent (0-10% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.26 (m, $J = 8.6, 7.2$ Hz, 4 H), 7.04 – 6.97 (m, 6 H), 6.98 – 6.85 (m, 4 H), 3.99 (d, $J = 15.2$ Hz, 1 H), 3.83 (d, $J = 15.2$ Hz, 1 H), 3.63 (s, 3 H), 3.36 (s, 3 H), 3.12 (s, 0.06 H), 2.84 (t, $J = 6.5$ Hz, 0.04 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.12, 166.76, 162.08 (d, $J_{\text{C-F}} = 246.1$ Hz), 147.67, 130.07 (d, $J_{\text{C-F}} = 8.2$ Hz), 129.44, 121.87, 121.33, 115.05 (d, $J_{\text{C-F}} = 21.4$ Hz), 52.80, 52.30, 49.27, 41.95, 35.73, 35.43 (t, $J_{\text{C-D}} = 24.6$ Hz), 29.39, 29.10 (t, $J_{\text{C-D}} = 25.2$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -114.79; HRMS calcd for $\text{C}_{26}\text{H}_{23}\text{D}_2\text{FNO}_4$ ($[\text{M}+\text{H}]^+$): 436.1888; found: 436.1897.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 4.31 (d, $J = 15.2$ Hz, 1 H), 3.76 (s, 3 H), 3.55 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 129.34, 121.94, 121.59, 52.99, 52.19.

(4) Dimethyl (2*R,3*S**)-2-(4-chlorophenyl)-3-((diphenylamino)methyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (4) (wyq-4-24).**



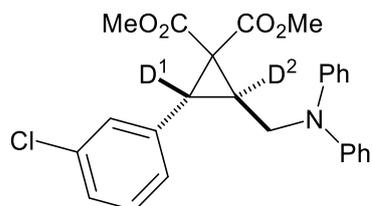
trans:cis = 14:1, $D^1, D^2 = 94\%, 95\%$

Following General Procedure I, **4** was afforded as a colorless oil (33.9 mg, 75%, $D^1/D^2 = 94\%/95\%$, *trans:cis* = 14:1), eluent (0-10% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.23 (m, 4 H), 7.20 – 7.15 (m, 2 H), 7.04 – 6.98 (m, 4 H), 7.00 – 6.94 (m, 4 H), 4.00 (d, $J = 15.1$ Hz, 1 H), 3.83 (d, $J = 15.2$ Hz, 1 H), 3.63 (s, 3 H), 3.38 (s, 3 H), 3.10 (s, 0.06 H), 2.84 (t, $J = 6.5$ Hz, 0.05 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.02, 166.67, 147.58, 133.25, 132.83, 129.76, 129.45, 128.32, 121.89, 121.30, 52.86, 52.41, 49.22, 42.00, 35.73, 35.43 (t, $J_{\text{C-D}} = 24.6$ Hz), 29.24, 28.95 (t, $J_{\text{C-D}} = 24.6$ Hz); HRMS calcd for $\text{C}_{26}\text{H}_{23}\text{D}_2\text{ClNO}_4$ ($[\text{M}+\text{H}]^+$): 452.1592; found: 452.1599.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 4.31 (d, $J = 15.1$ Hz, 1 H), 3.76 (s, 3 H), 3.56 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 130.65, 129.35, 121.54.

(5) Dimethyl (2*R,3*S**)-2-(3-chlorophenyl)-3-((diphenylamino)methyl) cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (5) (wyq-9-21).**



5

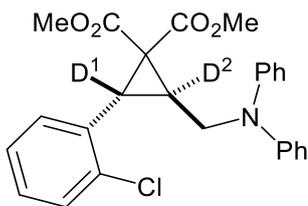
trans:*cis* = 13:1, D¹, D² = 97%, 93%

Following General Procedure III, **5** was afforded as a colorless oil (31.7 mg, 70%, D¹/D² = 97%/93%, *trans*:*cis* = 13:1), eluent (0-10% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.23 (m, 4 H), 7.14 (dt, $J = 15.4, 8.1$ Hz, 2 H), 7.04 – 6.99 (m, 5 H), 6.98 (t, $J = 7.3$ Hz, 2 H), 6.91 (d, $J = 7.6$ Hz, 1 H), 3.99 (d, $J = 15.2$ Hz, 1 H), 3.84 (d, $J = 15.3$ Hz, 1 H), 3.63 (s, 3 H), 3.40 (s, 3 H), 3.25 (s, 0.03 H), 2.83 (t, $J = 6.5$ Hz, 0.07 H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.96, 166.61, 147.60, 136.46, 134.01, 129.46, 129.35, 128.71, 127.58, 126.47, 121.91, 121.34, 52.89, 52.40, 49.17, 41.99, 35.83, 35.52 (t, $J_{\text{C-D}} = 24.6$ Hz), 29.33, 29.04 (t, $J_{\text{C-D}} = 24.6$ Hz); HRMS calcd for $\text{C}_{26}\text{H}_{23}\text{D}_2\text{ClNO}_4$ ($[\text{M}+\text{H}]^+$): 452.1592; found: 452.1600.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 4.34 (d, $J = 15.2$ Hz, 1 H), 3.77 (s, 3 H), 3.58 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 121.52.

(6) Dimethyl (2*S,3*S**)-2-(2-chlorophenyl)-3-((diphenylamino)methyl) cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (6) (wyq-4-29).**



6

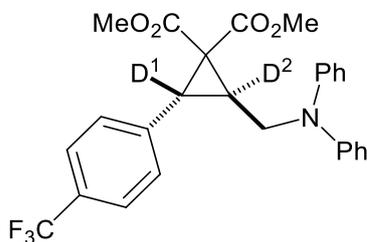
trans:cis = 13:1, D¹, D² = 96%, 95%

Following General Procedure I, **6** was afforded as a colorless oil (31.6 mg, 71%, D¹/D² = 96%/95%, *trans:cis* = 13:1), eluent (0-10% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.32 – 7.24 (m, 5 H), 7.15 (td, *J* = 7.7, 1.7 Hz, 1 H), 7.09 (td, *J* = 7.6, 1.4 Hz, 1 H), 7.04 – 7.01 (m, 4 H), 6.97 (t, *J* = 7.2 Hz, 2 H), 6.91 (dd, *J* = 7.7, 1.8 Hz, 1 H), 4.03 (d, *J* = 15.2 Hz, 1 H), 3.89 (d, *J* = 15.3 Hz, 1 H), 3.64 (s, 3 H), 3.35 (s, 3 H), 3.30 (s, 0.04 H), 2.94 (t, *J* = 6.5 Hz, 0.05 H); ¹³C NMR (126 MHz, CDCl₃) δ 167.85, 166.82, 147.64, 136.00, 132.38, 129.44, 129.34, 129.30, 129.12, 128.69, 126.34, 122.05, 121.86, 121.74, 121.30, 52.79, 52.28, 49.37, 41.37, 35.24, 34.94 (t, *J*_{C-D} = 24.6 Hz), 29.28, 29.00 (t, *J*_{C-D} = 24.6 Hz); HRMS calcd for C₂₆H₂₃D₂ClNO₄ ([M+H]⁺): 452.1592; found: 452.1601.

The following signals are discernible for the *cis*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 4.18 (d, *J* = 14.8 Hz, 1 H), 4.11 (d, *J* = 14.8 Hz, 1 H), 3.76 (s, 3 H), 3.42 (s, 3 H); ¹³C NMR (126 MHz, CDCl₃) δ 129.38, 122.08, 121.77.

(7) Dimethyl (2*S,3*R**)-2-((diphenylamino)methyl)-3-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (7) (wyq-7-37).**



7

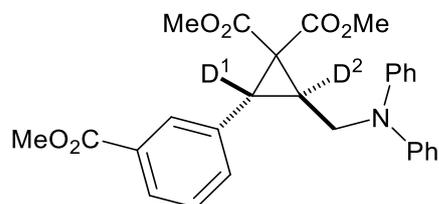
trans:cis = 13:1, D¹, D² = 95%, 95%

Following General Procedure II, **7** was afforded as a colorless oil (33.2 mg, 67%, D¹/D² = 95%/95%, *trans:cis* = 13:1), eluent (0-10% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.46 (d, $J = 8.1$ Hz, 2 H), 7.30 – 7.19 (m, 5 H), 7.14 (d, $J = 8.0$ Hz, 2 H), 7.03 – 6.98 (m, 3 H), 6.98 – 6.88 (m, 2 H), 4.02 (d, $J = 15.2$ Hz, 1 H), 3.84 (d, $J = 15.2$ Hz, 1 H), 3.65 (s, 3 H), 3.37 (s, 3 H), 3.17 (s, 0.05 H), 2.89 (t, $J = 6.5$ Hz, 0.05 H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.87, 166.54, 147.57, 138.51, 129.57 (q, $J_{\text{C-F}} = 32.5$ Hz), 129.47, 128.77, 125.06 (q, $J_{\text{C-F}} = 3.7$ Hz), 124.01 (q, $J_{\text{C-F}} = 272.4$ Hz) 121.94, 121.30, 52.95, 52.45, 49.18, 42.16, 35.85, 35.54 (t, $J_{\text{C-D}} = 24.6$ Hz), 29.28, 28.99 (t, $J_{\text{C-D}} = 24.6$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -62.57; HRMS calcd for $\text{C}_{27}\text{H}_{23}\text{D}_2\text{F}_3\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 486.1856; found: 486.1864.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 4.34 (d, $J = 15.3$ Hz, 1 H), 3.78 (s, 3 H), 3.58 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 129.36, 129.25, 121.52, 121.47.

(8) Dimethyl (2*S,3*R**)-2-((diphenylamino)methyl)-3-(3-(methoxycarbonyl)phenyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (8) (wyq-4-26).**



8

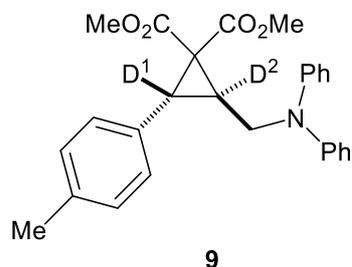
trans:cis = 12:1, D^1 , D^2 = 92%, 93%

Following General Procedure I, **8** was afforded as a colorless oil (28.8 mg, 58%, $\text{D}^1/\text{D}^2 = 92\%/93\%$, *trans:cis* = 12:1), eluent (0-10% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.87 (d, $J = 7.6$ Hz, 1 H), 7.77 (s, 1 H), 7.30 – 7.27 (m, 2 H), 7.26 – 7.19 (m, 3 H), 7.03 (d, $J = 8.0$ Hz, 4 H), 6.99 – 6.87 (m, 3 H), 4.01 (d, $J = 15.2$ Hz, 1 H), 3.90 – 3.84 (m, 4 H), 3.63 (s, 3 H), 3.36 (s, 3 H), 3.19 (s, 0.08 H), 2.90 (t, $J = 6.4$ Hz, 0.07 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.00, 166.68, 147.61, 134.82, 132.71, 130.14, 129.76, 129.43, 128.60, 128.23, 121.87, 121.52, 121.34, 52.86, 52.34, 52.08, 49.20, 41.99, 35.99, 35.69 (t, $J_{\text{C-D}} = 23.9$ Hz), 29.35, 29.04 (t, $J_{\text{C-D}} = 24.6$ Hz); HRMS calcd for $\text{C}_{28}\text{H}_{26}\text{D}_2\text{NO}_6$ ($[\text{M}+\text{H}]^+$): 476.2037; found: 476.2046.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 3.77 (s, 3 H), 3.59 (s, 3 H), 3.37 (s, 3 H).

(9) Dimethyl (2*S,3*R**)-2-((diphenylamino)methyl)-3-(*p*-tolyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (9) (wyq-4-20).**



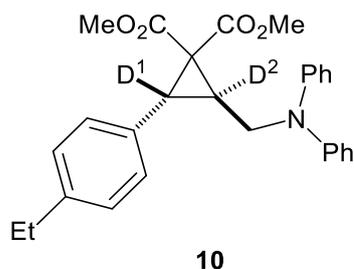
trans:cis = 9:1, D^1 , D^2 = 93%, 93%

Following General Procedure I, **9** was afforded as a colorless oil (30.8 mg, 66%, D^1/D^2 = 93%/93%, *trans:cis* = 9:1), eluent (0-11% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.29 – 7.19 (m, 4 H), 7.01 (t, J = 6.2 Hz, 6 H), 6.96 (q, J = 7.6 Hz, 4 H), 3.97 (d, J = 15.0 Hz, 1 H), 3.87 (d, J = 15.2 Hz, 1 H), 3.60 (s, 3 H), 3.35 (s, 3 H), 3.13 (s, 0.07 H), 2.87 (t, J = 6.7 Hz, 0.07 H), 2.27 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.32, 166.94, 147.67, 136.95, 131.14, 129.39, 128.84, 128.24, 121.73, 121.29, 52.71, 52.22, 49.24, 46.15, 42.01, 36.20, 35.89 (t, $J_{\text{C-D}}$ = 23.9 Hz), 29.29, 29.00 (t, $J_{\text{C-D}}$ = 23.9 Hz), 21.04; HRMS calcd for $\text{C}_{27}\text{H}_{26}\text{D}_2\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 432.2138; found: 432.2147.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 4.34 (d, J = 15.2 Hz, 1 H), 3.75 (s, 3 H), 3.54 (s, 3 H), 2.29 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 129.25, 129.09, 128.95, 121.52, 52.91, 52.12, 46.15.

(10) Dimethyl (2*S,3*R**)-2-((diphenylamino)methyl)-3-(4-ethylphenyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (10) (wyq-7-40).**



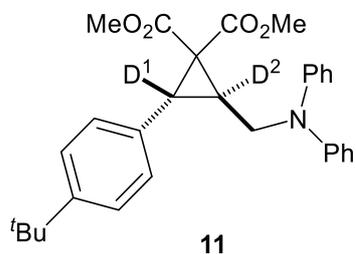
trans:cis = 14:1, D^1 , D^2 = 93%, 92%

Following General Procedure II, **10** was afforded as a colorless oil (36.7 mg, 77%, $D^1/D^2 = 93\%/92\%$, *trans:cis* = 14:1), eluent (0-9% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.25 (m, 2 H), 7.27 – 7.22 (m, 2 H), 7.06 – 6.99 (m, 6 H), 7.00 – 6.91 (m, 4 H), 3.97 (d, $J = 15.3$ Hz, 1 H), 3.87 (d, $J = 15.2$ Hz, 1 H), 3.60 (s, 3 H), 3.34 (s, 3 H), 3.14 (s, 0.07 H), 2.88 (t, $J = 6.5$ Hz, 0.08 H), 2.57 (q, $J = 7.6$ Hz, 2 H), 1.18 (t, $J = 7.6$ Hz, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.34, 166.96, 147.69, 143.36, 131.41, 129.41, 128.33, 127.63, 121.75, 121.31, 52.72, 52.21, 49.23, 42.07, 36.19, 35.88 (t, $J_{\text{C-D}} = 24.6$ Hz), 29.36, 29.07 (t, $J_{\text{C-D}} = 24.6$ Hz), 28.43, 15.41; HRMS calcd for $\text{C}_{28}\text{H}_{28}\text{D}_2\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 446.2295; found: 446.2297.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 4.36 (d, $J = 15.2$ Hz, 1 H), 3.75 (s, 3 H), 3.56 (s, 3 H), 1.22 (t, $J = 7.6$ Hz, 3 H).

(11) Dimethyl (2*S,3*R**)-2-(4-(tert-butyl)phenyl)-3-((diphenylamino)methyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (11) (wyq-4-10).**



trans:cis = 13:1, D^1 , D^2 = 95%, 94%

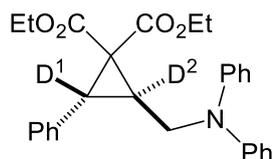
Following General Procedure I, **11** was afforded as a colorless oil (32.9 mg, 70%, $D^1/D^2 = 95\%/94\%$, *trans:cis* = 13:1), eluent (0-11% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.30 – 7.25 (m, 2 H), 7.27 – 7.20 (m, 4 H), 7.05 – 6.98 (m, 5 H), 7.00 – 6.93 (m, 3 H), 3.96 (d, $J = 15.3$ Hz, 1 H), 3.88 (d, $J = 15.3$ Hz, 1 H), 3.59 (s, 3 H), 3.32 (s, 3 H), 3.15 (s, 0.05 H), 2.89 (t, $J = 6.4$ Hz, 0.06 H), 1.26 (s, 9 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.36, 166.99, 150.29, 147.67, 131.19, 129.42, 128.06, 125.04, 121.78, 121.32, 52.74, 52.17, 49.20, 42.13, 35.97, 35.81, 35.69 (t, $J_{\text{C-D}} = 15.1$ Hz), 35.57, 34.44,

31.25, 29.30, 29.00 (t, $J_{C-D} = 14.5$ Hz); HRMS calcd for $C_{30}H_{32}D_2NO_4$ ($[M+H]^+$): 474.2608; found: 474.2616.

The following signals are discernible for the *cis*-isomer: 1H NMR (500 MHz, $CDCl_3$) δ 4.39 (d, $J = 15.3$ Hz, 2 H), 3.75 (s, 3 H), 3.58 (s, 3 H), 1.28 (s, 9 H).

(12) Diethyl (2*S,3*R**)-2-((diphenylamino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (12) (wyq-4-17).**



12

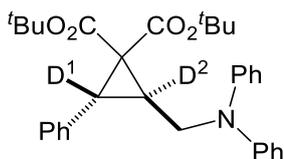
trans:cis = 10:1, $D^1, D^2 = 94\%, 95\%$

Following General Procedure I, **12** was afforded as a colorless oil (27.6 mg, 62%, $D^1/D^2 = 94\%/95\%$, *trans:cis* = 10:1), eluent (0-10% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: 1H NMR (500 MHz, $CDCl_3$) δ 7.29 – 7.22 (m, 4 H), 7.22 – 7.14 (m, 3 H), 7.08 – 7.00 (m, 6 H), 6.99 – 6.91 (m, 2 H), 4.23 – 4.16 (m, 1 H), 4.06 – 3.96 (m, 2 H), 3.86 – 3.78 (m, 3 H), 3.15 (s, 0.06 H), 2.86 (t, $J = 6.5$ Hz, 0.05 H), 1.22 (t, $J = 7.2$ Hz, 3 H), 0.84 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 167.87, 166.42, 147.77, 134.37, 129.38, 128.55, 128.04, 127.21, 121.75, 121.36, 61.75, 61.13, 49.33, 42.24, 42.24, 36.31, 36.00 (t, $J_{C-D} = 24.6$ Hz), 35.81, 28.76, 28.47 (t, $J_{C-D} = 24.6$ Hz), 14.05, 13.66; HRMS calcd for $C_{28}H_{28}D_2NO_4$ ($[M+H]^+$): 446.2295; found: 446.2297.

The following signals are discernible for the *cis*-isomer: 1H NMR (500 MHz, $CDCl_3$) δ 1.27 – 1.25 (m, 3 H), 1.08 (t, $J = 7.1$ Hz, 3 H); ^{13}C NMR (126 MHz, $CDCl_3$) δ 129.26, 121.57.

(13) Di-*tert*-butyl (2*S,3*R**)-2-((diphenylamino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (13) (wyq-4-33).**



13

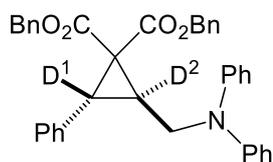
trans:cis = 18:1, D¹, D² = 95%, 88%

Following General Procedure I, **13** was afforded as a colorless oil (33.5 mg, 68%, D¹/D² = 95%/88%, *trans:cis* = 18:1), eluent (0-6% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.30 – 7.20 (m, 4 H), 7.20 – 7.07 (m, 3 H), 7.05 – 7.03 (m, 6 H), 6.95 (t, *J* = 7.3 Hz, 2 H), 4.06 (d, *J* = 14.8 Hz, 1 H), 3.70 (d, *J* = 14.8 Hz, 1 H), 3.05 (s, 0.05 H), 2.71 (dd, *J* = 8.5, 4.8 Hz, 0.12 H), 1.46 (s, 9 H), 1.10 (s, 9 H); ¹³C NMR (126 MHz, CDCl₃) δ 167.17, 165.59, 147.81, 134.61, 129.38, 128.83, 127.84, 126.93, 121.74, 121.40, 82.06, 81.10, 49.39, 43.88, 35.78, 35.47 (t, *J*_{C-D} = 24.6 Hz), 30.20, 29.69 (t, *J*_{C-D} = 24.6 Hz), 28.04, 27.51; HRMS calcd for C₃₂H₃₆D₂NO₄ ([M+H]⁺): 502.2921; found: 502.2925.

The following signals are discernible for the *cis*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 1.48 (s, 9 H), 1.34 (s, 9 H); ¹³C NMR (126 MHz, CDCl₃) δ 118.41, 27.87.

(14) Dibenzyl (2*S,3*R**)-2-((diphenylamino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (14) (wyq-9-17).**



14

trans:cis = 10:1, D¹, D² = 93%, 96%

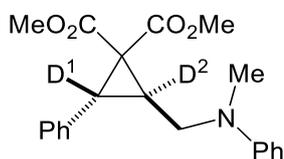
Following General Procedure III, **14** was afforded as a colorless oil (27.4 mg, 50%, D¹/D² = 93%/96%, *trans:cis* = 10:1), eluent (0-10% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.31 – 7.25 (m, 3 H), 7.23 (t, *J* = 7.8 Hz, 6 H), 7.17 (p, *J* = 7.9 Hz, 6 H), 7.05 – 7.00 (m, 2 H), 6.99 (d, *J* = 8.1 Hz, 4 H), 6.95 (t, *J* = 7.2 Hz, 2 H), 6.88 (d, *J* = 7.2 Hz,

2 H), 5.15 (d, $J = 12.3$ Hz, 1 H), 4.89 (d, $J = 12.3$ Hz, 1 H), 4.72 (q, $J = 12.3$ Hz, 2 H), 4.00 (d, $J = 15.0$ Hz, 1 H), 3.82 (d, $J = 15.0$ Hz, 1 H), 3.20 (s, 0.07 H), 2.92 (t, $J = 6.7$ Hz, 0.04 H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.63, 166.24, 147.66, 135.35, 135.16, 134.04, 129.41, 128.49, 128.29, 128.16, 128.09, 128.05, 128.00, 127.36, 121.80, 121.36, 67.51, 67.18, 49.09, 42.23, 36.75, 36.45 (t, $J_{\text{C-D}} = 24.6$ Hz), 29.68, 28.99 (t, $J_{\text{C-D}} = 24.6$ Hz); HRMS calcd for $\text{C}_{38}\text{H}_{32}\text{D}_2\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 570.2608; found: 570.2612.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 4.92 (s, 2 H), 4.36 (d, $J = 15.2$ Hz, 1 H).

(15) Dimethyl (2*S,3*R**)-2-((methyl(phenyl)amino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (15) (wyq-3-37).**



15

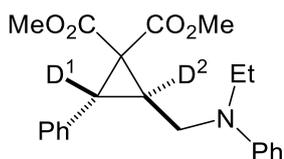
trans:cis = 23:1, $\text{D}^1, \text{D}^2 = 96\%, 94\%$

Following General Procedure I, **15** was afforded as a colorless oil (27.5 mg, 77%, $\text{D}^1/\text{D}^2 = 96\%/94\%$, *trans:cis* = 23:1), eluent (0-10% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.29 – 7.18 (m, 5 H), 7.12 (d, $J = 6.6$ Hz, 2 H), 6.84 (d, $J = 8.1$ Hz, 2 H), 6.75 (t, $J = 7.3$ Hz, 1 H), 3.77 (s, 3 H), 3.65 (d, $J = 14.8$ Hz, 1 H), 3.42 (d, $J = 15.0$ Hz, 1 H), 3.37 (s, 3 H), 3.30 (s, 0.04 H), 2.97 (s, 3 H), 2.79 (t, $J = 6.7$ Hz, 0.06 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.38, 167.01, 149.43, 134.24, 129.23, 128.47, 128.20, 127.39, 117.31, 113.36, 52.84, 52.29, 50.23, 41.43, 37.94, 36.52, 36.21 (t, $J_{\text{C-D}} = 24.6$ Hz), 28.51, 28.23 (t, $J_{\text{C-D}} = 24.6$ Hz); HRMS calcd for $\text{C}_{21}\text{H}_{22}\text{D}_2\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 356.1825; found: 356.1837.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 2.81 (s, 3 H).

(16) Dimethyl (2*S,3*R**)-2-((ethyl(phenyl)amino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (16) (wyq-9-3).**



16

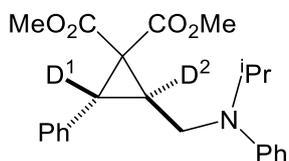
trans:cis = 17:1, D¹, D² = 92%, 97%

Following General Procedure III, **16** was afforded as a colorless oil (28.6 mg, 77%, D¹/D² = 92%/97%, *trans:cis* = 17:1), eluent (0-10% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.29 – 7.17 (m, 5 H), 7.14 (dd, *J* = 7.7, 1.9 Hz, 2 H), 6.81 (d, *J* = 7.7 Hz, 2 H), 6.72 (t, *J* = 7.2 Hz, 1 H), 3.79 (s, 3 H), 3.59 (d, *J* = 15.2 Hz, 1 H), 3.48 – 3.35 (m, 3 H), 3.37 (s, 3 H), 3.31 (s, 0.08 H), 2.81 (t, *J* = 6.4 Hz, 0.03 H) 1.15 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (126 MHz, CDCl₃) δ 168.42, 167.00, 147.96, 134.31, 129.34, 128.49, 128.20, 127.39, 116.72, 113.06, 52.84, 52.28, 47.89, 44.75, 41.82, 36.78, 36.47 (t, *J*_{C-D} = 24.6 Hz), 29.67, 28.83 (t, *J*_{C-D} = 24.6 Hz), 12.13; HRMS calcd for C₂₂H₂₄D₂NO₄ ([M+H]⁺): 370.1982; found: 370.1991.

The following signals are discernible for the *cis*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 3.77 (s, 3 H), 3.67 (s, 3 H), 1.03 (t, *J* = 7.0 Hz, 3 H); ¹³C NMR (126 MHz, CDCl₃) δ 129.08.

(17) Dimethyl (2*S,3*R**)-2-((isopropyl(phenyl)amino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (17) (wyq-9-19).**



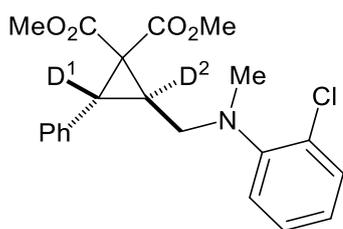
17

trans:cis > 20:1, D¹, D² = 99%, 96%

Following General Procedure I, **17** was afforded as a colorless oil (31.4 mg, 80%, D¹/D² = 99%/96%, *trans:cis* > 20:1), eluent (0-11% of ethyl acetate in petroleum ether); ¹H NMR (400 MHz, CDCl₃) δ 7.30 – 7.25 (m, 2 H), 7.22 – 7.17 (m, 3 H), 7.10 (dd, *J* = 7.4, 2.2 Hz, 2 H), 6.91 (d, *J* = 8.2 Hz, 2 H), 6.76 (t, *J* = 7.2 Hz, 1 H), 4.05 (hept, *J* = 6.7 Hz, 1 H), 3.84 (s, 3 H), 3.43 (d, *J* = 15.4 Hz, 1 H), 3.35 (s, 3 H), 3.25 (d, *J* = 15.4 Hz, 1

H), 3.16 (s, 0.01 H), 2.72 (dd, $J = 7.2, 3.8$ Hz, 0.04 H), 1.18 (t, $J = 6.7$ Hz, 6 H); ^{13}C NMR (126 MHz, CDCl_3) δ 68.53, 166.95, 148.49, 134.41, 129.31, 128.47, 128.15, 127.32, 117.24, 114.36, 52.81, 52.26, 48.85, 42.64, 42.11, 38.02, 37.70 (t, $J_{\text{C-D}} = 30.2$ Hz), 30.19, 29.89 (t, $J_{\text{C-D}} = 30.7$ Hz), 20.84, 19.77; HRMS calcd for $\text{C}_{23}\text{H}_{26}\text{D}_2\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 384.2138; found: 384.2136.

(18) Dimethyl (2*S,3*R**)-2-(((2-chlorophenyl)(methyl)amino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (18) (wyq-3-49).**



18

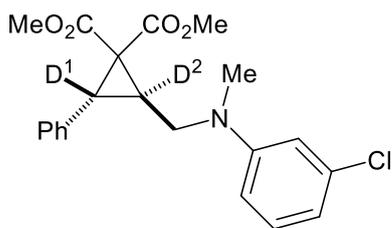
trans:cis = 8:1, $\text{D}^1, \text{D}^2 = 98\%, 85\%$

Following General Procedure I, **18** was afforded as a colorless oil (35.7 mg, 90%, $\text{D}^1/\text{D}^2 = 98\%/85\%$, *trans:cis* = 8:1), eluent (0-11% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.36 – 7.33 (m, 1 H), 7.26 – 7.18 (m, 4 H), 7.16 – 7.10 (m, 3 H), 6.97 – 6.93 (m, 1 H), 3.72 (s, 3 H), 3.42 – 3.34 (m, 4 H), 3.29 (d, $J = 13.9$ Hz, 1 H), 3.22 (s, 0.02 H), 2.89 (s, 3 H), 2.79 (t, $J = 6.7$ Hz, 0.15 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.17, 167.09, 149.04, 134.35, 130.66, 128.90, 128.37, 128.16, 128.13, 127.32, 123.68, 121.82, 52.74, 52.59, 52.27, 41.66, 40.47, 36.19, 35.88 (t, $J_{\text{C-D}} = 23.9$ Hz), 28.57, 28.28 (t, $J_{\text{C-D}} = 23.9$ Hz); HRMS calcd for $\text{C}_{21}\text{H}_{21}\text{D}_2\text{ClNO}_4$ ($[\text{M}+\text{H}]^+$): 390.1436; found: 390.1442.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 3.78 (s, 3 H), 3.61 (s, 3 H), 2.76 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 129.54, 127.03, 125.77, 123.86, 122.16, 120.27, 119.36, 110.55, 52.96, 52.11, 41.32.

(19) Dimethyl (2*S,3*R**)-2-(((3-chlorophenyl)(methyl)amino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (19) (wyq-4-4-2).**



19

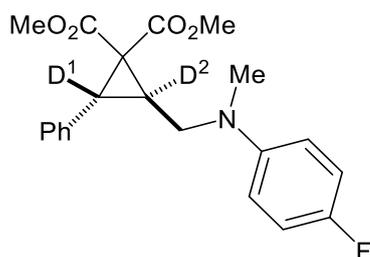
trans:cis = 14:1, D¹, D² = 96%, 92%

Following General Procedure I, **19** was afforded as a colorless oil (27.1 mg, 67%, D¹/D² = 96%/92%, *trans:cis* = 14:1), eluent (0-12% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.34 – 7.19 (m, 3 H), 7.18 – 7.10 (m, 3 H), 6.76 (s, 1 H), 6.73 – 6.64 (m, 2 H), 3.77 (s, 3 H), 3.63 (d, *J* = 15.0 Hz, 1 H), 3.43 (d, *J* = 15.1 Hz, 1 H), 3.38 (s, 3 H), 3.29 (s, 0.04 H), 2.96 (s, 3 H), 2.76 (t, *J* = 6.7 Hz, 0.08 H); ¹³C NMR (126 MHz, CDCl₃) δ 168.33, 166.88, 150.46, 135.19, 134.10, 130.15, 128.44, 128.28, 127.50, 117.03, 113.00, 111.22, 52.89, 52.34, 49.90, 41.53, 37.87, 36.43, 36.12 (t, *J*_{C-D} = 24.6 Hz), 28.47, 28.18 (t, *J*_{C-D} = 24.6 Hz); HRMS calcd for C₂₁H₂₁D₂ClNO₄ ([M+H]⁺): 390.1436; found: 390.1441.

The following signals are discernible for the *cis*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 4.02 (d, *J* = 15.4 Hz, 1 H), 3.78 (s, 3 H), 3.67 (s, 3 H), 2.81 (s, 3 H).

(20) Dimethyl (2*S,3*R**)-2-(((4-fluorophenyl)(methyl)amino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (20) (wyq-8-50).**



20

trans:cis = 14:1, D¹, D² = 95%, 94%

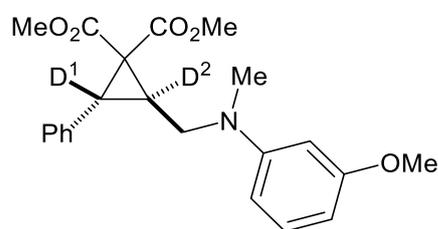
Following General Procedure III, **20** was afforded as a colorless oil (30.7 mg, 79%, D¹/D² = 95%/94%, *trans:cis* = 14:1), eluent (0-12% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.29 – 7.18 (m, 3 H), 7.11 (d, *J* = 6.2 Hz, 2 H), 6.95 (t, *J* = 8.7 Hz, 2 H), 6.81 – 6.75 (m, 2 H), 3.76 (s, 3 H), 3.57 (d, *J* = 14.7 Hz, 1 H), 3.39 – 3.35 (m, 4 H), 3.27 (s,

0.05 H), 2.94 – 2.90 (m, 3 H), 2.75 (t, $J = 6.8$ Hz, 0.06 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.36, 167.00, 156.06 (d, $J_{\text{C-F}} = 236.4$ Hz), 146.36, 134.23, 128.42, 128.24, 127.44, 115.58 (d, $J_{\text{C-F}} = 22.1$ Hz), 115.24 (d, $J_{\text{C-F}} = 7.4$ Hz), 52.81, 52.30, 51.22, 41.51, 38.56, 36.57, 36.27 (t, $J_{\text{C-D}} = 24.6$ Hz), 29.67, 28.13 (t, $J_{\text{C-D}} = 24.6$ Hz); ^{19}F NMR (471 MHz, CDCl_3) δ -127.68; HRMS calcd for $\text{C}_{21}\text{H}_{21}\text{D}_2\text{FNO}_4$ ($[\text{M}+\text{H}]^+$): 374.1731; found: 374.1737.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 3.77 (s, 3 H), 3.65 (s, 3 H), 2.78 (s, 3 H).

(21) Dimethyl (2*S,3*R**)-2-(((3-methoxyphenyl)(methyl)amino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (21) (wyq-9-4).**



21

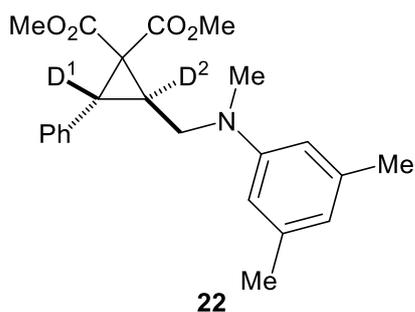
trans:cis = 16:1, D^1 , D^2 = 96%, 95%

Following General Procedure III, **21** was afforded as a colorless oil (17.1 mg, 65%, $\text{D}^1/\text{D}^2 = 96\%/95\%$, *trans:cis* = 16:1), eluent (0-12% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.19 (m, 2 H), 7.24 – 7.09 (m, 4 H), 6.46 (dd, $J = 8.3, 2.1$ Hz, 1 H), 6.36 (t, $J = 2.4$ Hz, 1 H), 6.33 (dd, $J = 8.1, 1.9$ Hz, 1 H), 3.80 (s, 3 H), 3.78 (s, 3 H), 3.65 (d, $J = 15.1$ Hz, 1 H), 3.40 (d, $J = 15.0$ Hz, 1 H), 3.37 (s, 3 H), 3.31 (s, 0.04 H), 2.96 (s, 3 H), 2.39 (t, $J = 7.5$ Hz, 0.05 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.38, 166.98, 160.79, 150.79, 134.22, 129.91, 128.49, 128.21, 127.40, 106.31, 102.13, 99.84, 55.11, 52.85, 52.29, 50.19, 41.43, 38.01, 36.49, 36.18 (t, $J_{\text{C-D}} = 25.2$ Hz), 28.52, 28.23 (t, $J_{\text{C-D}} = 25.2$ Hz); HRMS calcd for $\text{C}_{22}\text{H}_{24}\text{D}_2\text{NO}_5$ ($[\text{M}+\text{H}]^+$): 386.1931; found: 386.1940.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 3.77 (s, 3 H), 3.76 (s, 3 H), 3.67 (s, 3 H), 2.80 (s, 3 H).

(22) Dimethyl (2*S,3*R**)-2-(((3,5-dimethylphenyl)(methyl)amino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (22) (wyq-4-9).**



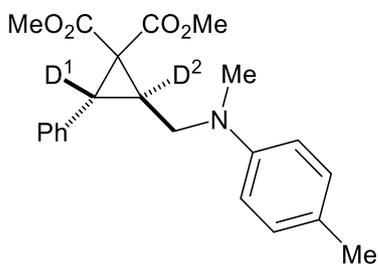
trans:cis = 14:1, D¹, D² = 96%, 93%

Following General Procedure I, **22** was afforded as a colorless oil (29.9 mg, 77%, D¹/D² = 96%/93%, *trans:cis* = 14:1), eluent (0-11% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.27 – 7.18 (m, 3 H), 7.14 (d, *J* = 6.7 Hz, 2 H), 6.47 (s, 2 H), 6.43 (s, 1 H), 3.78 (s, 3 H), 3.63 (d, *J* = 14.9 Hz, 1 H), 3.37 (s, 3 H), 3.36 (d, 1 H), 3.29 (s, 0.04 H), 2.94 (s, 3 H), 2.77 (t, *J* = 6.3 Hz, 0.07 H), 2.28 (s, 6 H); ¹³C NMR (126 MHz, CDCl₃) δ 168.36, 167.04, 149.65, 138.70, 134.30, 128.50, 128.18, 127.35, 119.42, 111.46, 52.80, 52.26, 50.43, 41.49, 38.07, 36.53, 36.22 (t, *J*_{C-D} = 25.2 Hz), 31.23, 28.63, 28.35 (t, *J*_{C-D} = 23.9 Hz), 21.73; HRMS calcd for C₂₃H₂₆D₂NO₄ ([M+H]⁺): 384.2138; found: 384.2147.

The following signals are discernible for the *cis*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 3.76 (s, 3 H), 3.67 (s, 3 H), 2.81 (s, 3 H), 2.24 (s, 6 H). ¹³C NMR (126 MHz, CDCl₃) δ 129.10, 125.08.

(23) Dimethyl (2*S,3*R**)-2-((methyl(*p*-tolyl)amino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (23) (wyq-9-2).**



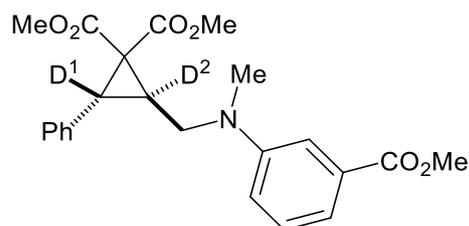
trans:cis = 15:1, D¹, D² = 95%, 96%

Following General Procedure III, **23** was afforded as a colorless oil (23.8 mg, 65%, D¹/D² = 95%/96%, *trans:cis* = 15:1), eluent (0-10% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.27 – 7.17 (m, 3 H), 7.15 – 7.10 (m, 2 H), 7.06 (d, $J = 8.3$ Hz, 2 H), 6.76 (d, $J = 8.2$ Hz, 2 H), 3.76 (s, 3 H), 3.60 (d, $J = 14.8$ Hz, 1 H), 3.39 – 3.31 (m, 4 H), 3.28 (s, 0.05 H), 2.93 (s, 3 H), 2.76 (t, $J = 6.8$ Hz, 0.04 H), 2.26 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.38, 167.05, 147.56, 134.36, 129.75, 129.21, 128.51, 128.19, 127.36, 114.03, 52.79, 52.24, 50.83, 41.49, 38.22, 36.59, 36.28 (t, $J_{\text{C-D}} = 24.6$ Hz), 28.62, 28.21 (t, $J_{\text{C-D}} = 24.6$ Hz), 20.24; HRMS calcd for $\text{C}_{22}\text{H}_{24}\text{D}_2\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 370.1982; found: 370.1988.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 3.65 (s, 3 H), 2.79 (s, 3H), 2.24 (s, 3 H).

(24) Dimethyl (2*S,3*R**)-2-(((3-(methoxycarbonyl)phenyl)(methyl)amino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (24) (wyq-7-45).**

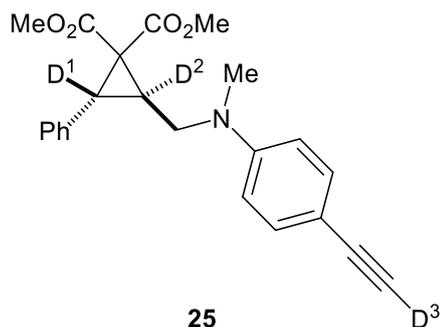


24

trans:cis > 20:1, D^1 , $\text{D}^2 = 94\%$, 94%

Following General Procedure II, **24** was afforded as a colorless oil (23.3 mg, 56%, $\text{D}^1/\text{D}^2 = 94\%/94\%$, *trans:cis* > 20:1), eluent (0-12% of ethyl acetate in petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 7.49 (s, 1 H), 7.42 (d, $J = 8.0$ Hz, 1 H), 7.31 (t, $J = 7.9$ Hz, 1 H), 7.25 – 7.18 (m, 3 H), 7.12 (dd, $J = 8.0, 1.7$ Hz, 2 H), 7.02 (dd, $J = 8.3, 2.8$ Hz, 1 H), 3.90 (s, 3 H), 3.77 (s, 3 H), 3.68 (d, $J = 15.0$ Hz, 1 H), 3.50 (d, $J = 15.1$ Hz, 1 H), 3.37 (s, 3 H), 3.31 (s, 0.06 H), 3.01 (s, 3 H), 2.78 (t, $J = 6.7$ Hz, 0.06 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.31, 167.57, 166.89, 149.30, 134.07, 131.03, 129.19, 128.41, 128.23, 127.44, 118.34, 117.52, 113.93, 52.87, 52.32, 52.00, 49.96, 41.45, 37.98, 36.41, 36.10 (t, $J_{\text{C-D}} = 24.6$ Hz), 28.42, 28.13 (t, $J_{\text{C-D}} = 24.6$ Hz); HRMS calcd for $\text{C}_{23}\text{H}_{24}\text{D}_2\text{NO}_6$ ($[\text{M}+\text{H}]^+$): 414.1880; found: 414.1887.

(25) Dimethyl (2*S,3*R**)-2-(((4-ethynylphenyl)(methyl)amino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (25) (wyq-4-14-2).**

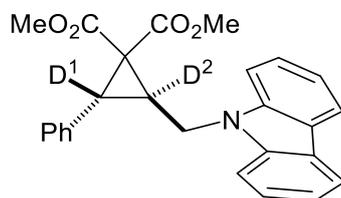


trans:cis > 20:1, D¹, D², D³ = 89%, 94%, 62%

Following General Procedure I and without the aqueous work-up procedure, the crude mixture was directly subjected to flash chromatography eluent (0-10% of ethyl acetate in petroleum ether) to afford **25** as a colorless oil (21.1 mg, 53%, D¹/D²/D³ = 89%/94%/62%, *trans:cis* > 20:1).

The following signals are discernible for the *trans*-isomer: ¹H NMR (400 MHz, CDCl₃) δ 7.39 (d, *J* = 8.7 Hz, 2 H), 7.25 – 7.18 (m, 3 H), 7.14 – 7.06 (m, 2 H), 6.73 (d, *J* = 8.8 Hz, 2 H), 3.77 (s, 3 H), 3.68 (d, *J* = 15.1 Hz, 1 H), 3.46 (d, *J* = 15.1 Hz, 1 H), 3.37 (s, 3 H), 3.31 (s, 0.11 H), 3.00 (s, 3 H), 2.99 (s, 0.38 H), 2.77 (t, *J* = 6.7 Hz, 0.06 H); ¹³C NMR (126 MHz, CDCl₃) δ 168.34, 166.88, 149.29, 134.02, 133.40, 128.41, 128.28, 127.51, 112.34, 109.63, 75.00, 52.93, 52.36, 49.56, 41.43, 39.97 (t, *J*_{C-D} = 25.2 Hz), 37.80, 29.67, 29.31 (t, *J*_{C-D} = 23.9 Hz); HRMS calcd for C₂₃H₂₂D₃NO₄ ([M+H]⁺): 381.1888; found: 381.1890.

(26) Dimethyl (2*S,3*R**)-2-((9*H*-carbazol-9-yl)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (26) (wyq-4-27).**



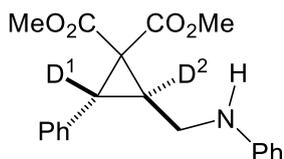
trans:cis > 20:1, D¹, D² = 91%, 91%

Following General Procedure I, **26** was afforded as a colorless oil (28.0 mg, 66%, D¹/D² = 91%/91%, *trans:cis* > 20:1), eluent (0-11% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 8.10 (d, $J = 7.8$ Hz, 2 H), 7.57 – 7.43 (m, 4 H), 7.30 – 7.20 (m, 2 H), 7.16 – 7.08 (m, 3 H), 6.97 – 6.88 (m, 2 H), 4.65 (d, $J = 15.3$ Hz, 1 H), 4.46 (d, $J = 15.4$ Hz, 1 H), 3.84 (s, 3 H), 3.52 (s, 0.09 H), 3.34 (s, 3 H), 3.16 – 3.10 (m, 0.09 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.45, 166.58, 140.28, 133.71, 128.43, 128.16, 127.47, 123.16, 120.40, 119.25, 108.73, 53.11, 52.36, 41.72, 40.55, 36.64, 36.34 (t, $J_{\text{C-D}} = 24.6$ Hz), 29.46, 29.16 (t, $J_{\text{C-D}} = 24.6$ Hz); HRMS calcd for $\text{C}_{26}\text{H}_{22}\text{D}_2\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 416.1825; found: 416.1831.

The following signals are discernible for the *cis*-isomer: ^{13}C NMR (126 MHz, CDCl_3) δ 128.71, 125.61, 120.16, 119.05, 109.05.

(27) Dimethyl (2*S,3*R**)-2-phenyl-3-((phenylamino)methyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (27) (wyq-5-29).**



27

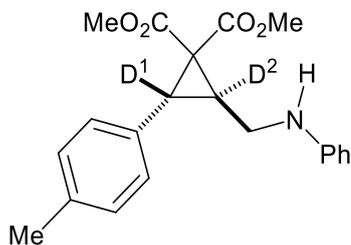
trans:cis = 14:1, $\text{D}^1, \text{D}^2 = 92\%, 90\%$

Following General Procedure I, **27** was afforded as a white solid (31.6 mg, 91%, $\text{D}^1/\text{D}^2 = 92\%/90\%$, *trans:cis* = 14:1), eluent (0-11% of ethyl acetate in petroleum ether): m.p. 72.9-73.4 °C.

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.26 (q, $J = 7.2, 6.1$ Hz, 3 H), 7.21 – 7.15 (m, 4 H), 6.73 (t, $J = 7.2$ Hz, 1 H), 6.64 (d, $J = 8.0$ Hz, 2 H), 3.76 (s, 3 H), 3.48 (d, $J = 13.2$ Hz, 1 H), 3.40 (s, 3 H), 3.27 (s, 0.08 H), 3.23 (d, $J = 13.2$ Hz, 1 H), 2.86 (t, $J = 7.0$ Hz, 0.01 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.15, 167.03, 147.75, 134.12, 129.28, 128.48, 128.22, 127.45, 117.90, 113.05, 52.95, 52.38, 42.27, 41.91, 35.87, 35.57 (t, $J_{\text{C-D}} = 24.6$ Hz), 30.15, 29.84 (t, $J_{\text{C-D}} = 24.6$ Hz); HRMS calcd for $\text{C}_{20}\text{H}_{20}\text{D}_2\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 342.1669; found: 342.1672.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 3.78 (s, 3 H), 3.66 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 129.62, 113.43.

(28) Dimethyl (2*S,3*R**)-2-((phenylamino)methyl)-3-(*p*-tolyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (28) (wyq-5-36).**



28

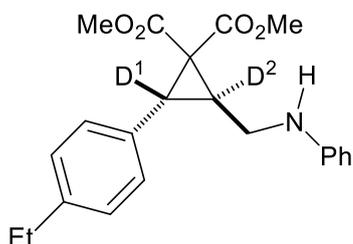
trans:cis = 10:1, D¹, D² = 93%, 86%

Following General Procedure I, **28** was afforded as a colorless oil (29.3 mg, 80%, D¹/D² = 93%/86%, *trans:cis* = 10:1), eluent (0-8% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.18 (t, *J* = 7.7 Hz, 2 H), 7.07 (s, 4 H), 6.72 (t, *J* = 7.2 Hz, 1 H), 6.64 (d, *J* = 7.9 Hz, 2 H), 3.75 (s, 3 H), 3.47 (d, *J* = 13.1 Hz, 1 H), 3.43 (s, 3 H), 3.34 (s, 0.07 H), 3.22 (d, *J* = 13.1 Hz, 1 H), 2.83 (t, *J* = 7.1 Hz, 0.14 H), 2.29 (s, 3 H); ¹³C NMR (126 MHz, CDCl₃) δ 168.23, 167.12, 147.80, 137.11, 131.00, 129.26, 128.94, 128.34, 117.84, 113.03, 52.91, 52.39, 42.29, 41.83, 35.69, 35.38 (t, *J*_{C-D} = 24.6 Hz), 30.22, 29.92 (t, *J*_{C-D} = 24.6 Hz), 21.06; HRMS calcd for C₂₁H₂₂D₂NO₄ ([M+H]⁺): 356.1825; found: 356.1834.

The following signals are discernible for the *cis*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 3.77 (s, 3 H), 3.66 (s, 3 H), 2.31 (s, 3 H); ¹³C NMR (126 MHz, CDCl₃) δ 129.48, 129.08, 113.37.

(29) Dimethyl (2*R,3*S**)-2-(4-ethylphenyl)-3-((phenylamino)methyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (29) (wyq-5-34).**



29

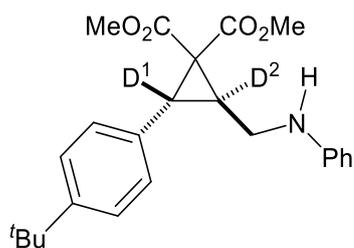
trans:cis = 12:1, D¹, D² = 95%, 84%

Following General Procedure I, **29** was afforded as a colorless oil (27.3 mg, 69%, D¹/D² = 95%/84%, *trans:cis* = 12:1), eluent (0-8% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.18 (t, $J = 7.8$ Hz, 2 H), 7.09 (s, 4 H), 6.73 (t, $J = 7.2$ Hz, 1 H), 6.64 (d, $J = 7.8$ Hz, 2 H), 3.75 (s, 3 H), 3.46 (d, $J = 13.1$ Hz, 1 H), 3.42 (s, 3 H), 3.32 (s, 0.05 H), 3.22 (d, $J = 13.0$ Hz, 1 H), 2.84 (t, $J = 7.0$ Hz, 0.16 H), 2.60 (q, $J = 7.7$ Hz, 2 H), 1.19 (t, $J = 7.6$ Hz, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.22, 167.12, 147.80, 143.49, 131.23, 129.26, 128.40, 127.71, 117.83, 113.02, 52.91, 52.37, 42.27, 41.88, 35.71, 35.41 (t, $J_{\text{C-D}} = 24.6$ Hz), 30.23, 29.93 (t, $J_{\text{C-D}} = 24.6$ Hz), 28.43, 15.40; HRMS calcd for $\text{C}_{22}\text{H}_{24}\text{D}_2\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 370.1982; found: 370.1988.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 3.77 (s, 3 H), 3.67 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 129.53, 113.34.

(30) Dimethyl (2*R,3*S**)-2-(4-(*tert*-butyl)phenyl)-3-((phenylamino)methyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (30) (wyq-5-35).**



30

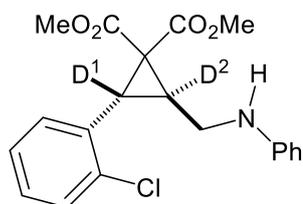
trans:cis = 10:1, $\text{D}^1, \text{D}^2 = 94\%, 80\%$

Following General Procedure I, **30** was afforded as a white solid (33.4 mg, 85%, $\text{D}^1/\text{D}^2 = 94\%/80\%$, *trans:cis* = 10:1), eluent (0-11% of ethyl acetate in petroleum ether): m.p. 87.5-89.0 °C.

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.28 (d, $J = 7.9$ Hz, 2 H), 7.18 (t, $J = 7.6$ Hz, 2 H), 7.11 (d, $J = 7.9$ Hz, 2 H), 6.73 (t, $J = 7.5$ Hz, 1 H), 6.64 (d, $J = 8.0$ Hz, 2 H), 3.75 (s, 3 H), 3.45 (d, $J = 13.1$ Hz, 1 H), 3.40 (s, 3 H), 3.32 (s, 0.06 H), 3.23 (d, $J = 13.2$ Hz, 1 H), 2.85 (t, $J = 7.1$ Hz, 0.20 H), 1.28 (s, 9 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.21, 167.13, 150.41, 147.77, 130.98, 129.27, 128.12, 125.12, 117.86, 113.04, 52.92, 52.33, 42.26, 41.94, 35.60, 35.30 (t, $J_{\text{C-D}} = 24.6$ Hz), 34.44, 31.25, 30.21, 29.90 (t, $J_{\text{C-D}} = 24.6$ Hz); HRMS calcd for $\text{C}_{24}\text{H}_{28}\text{D}_2\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 398.2295; found: 398.2300.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 3.77 (s, 3 H), 3.68 (s, 3 H), 1.29 (s, 9 H); ^{13}C NMR (126 MHz, CDCl_3) δ 125.29, 113.51.

(31) Dimethyl (2*S,3*S**)-2-(2-chlorophenyl)-3-((phenylamino)methyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (31) (wyq-5-31).**



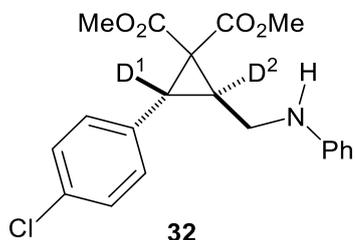
31

trans:cis = 10:1, D^1 , D^2 = 94%, 94%

Following General Procedure I, **31** was afforded as a colorless oil (20.4 mg, 54%, D^1/D^2 = 94%/94%, *trans:cis* = 10:1), eluent (0-9% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.35 (dd, J = 7.2, 2.0 Hz, 1 H), 7.22 – 7.15 (m, 4 H), 7.13 – 7.07 (m, 1 H), 6.74 (t, J = 7.3 Hz, 1 H), 6.66 (d, J = 7.4 Hz, 2 H), 3.79 (s, 3 H), 3.53 (d, J = 13.3 Hz, 1 H), 3.44 (s, 3 H), 3.34 (s, 0.06 H), 3.24 (d, J = 13.3 Hz, 1 H), 2.89 (t, J = 7.1 Hz, 0.06 H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.84, 167.10, 147.68, 135.88, 132.31, 129.63, 129.31, 129.31, 128.82, 126.42, 117.99, 113.09, 52.98, 52.47, 42.41, 41.18, 34.58, 34.29 (t, $J_{\text{C-D}}$ = 25.2 Hz), 30.51, 30.21 (t, $J_{\text{C-D}}$ = 24.6 Hz); HRMS calcd for $\text{C}_{20}\text{H}_{19}\text{D}_2\text{ClNO}_4$ ($[\text{M}+\text{H}]^+$): 376.1279; found: 376.1288.

(32) Dimethyl (2*R,3*S**)-2-(4-chlorophenyl)-3-((phenylamino)methyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (32) (wyq-5-33).**



32

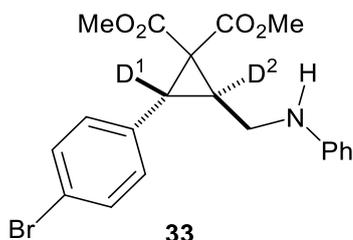
trans:cis = 10:1, D^1 , D^2 = 95%, 92%

Following General Procedure I, **32** was afforded as a colorless oil (30.0 mg, 79%, D^1/D^2 = 95%/92%, *trans:cis* = 10:1), eluent (0-9% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.23 (d, $J = 8.5$ Hz, 2 H), 7.18 (t, $J = 7.8$ Hz, 2 H), 7.11 (d, $J = 8.3$ Hz, 2 H), 6.73 (t, $J = 7.3$ Hz, 1 H), 6.64 (d, $J = 8.0$ Hz, 2 H), 3.76 (s, 3 H), 3.44 (m, 4 H), 3.28 (s, 0.05 H), 3.23 (d, $J = 13.4$ Hz, 1 H), 2.81 (t, $J = 6.9$ Hz, 0.08 H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.94, 166.84, 147.65, 133.36, 132.69, 129.88, 129.30, 128.41, 118.00, 113.06, 53.03, 52.54, 42.18, 41.86, 35.13, 34.83 (t, $J_{\text{C-D}} = 25.2$ Hz), 30.26, 29.96 (t, $J_{\text{C-D}} = 25.2$ Hz); HRMS calcd for $\text{C}_{20}\text{H}_{19}\text{D}_2\text{ClNO}_4$ ($[\text{M}+\text{H}]^+$): 376.1279; found: 376.1287.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 3.78 (s, 3 H), 3.66 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 131.12.

(33) Dimethyl (2*R,3*S**)-2-(4-bromophenyl)-3-((phenylamino)methyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (33) (wyq-5-38).**



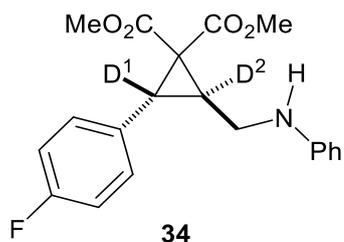
trans:cis = 12:1, D^1 , D^2 = 93%, 89%

Following General Procedure I, **33** was afforded as a colorless oil (34.4 mg, 79%, $\text{D}^1/\text{D}^2 = 93\%/89\%$, *trans:cis* = 12:1), eluent (0-9% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 7.39 (d, $J = 8.5$ Hz, 2 H), 7.19 (t, $J = 7.7$ Hz, 2 H), 7.06 (d, $J = 8.1$ Hz, 2 H), 6.74 (t, $J = 7.2$ Hz, 1 H), 6.65 (d, $J = 7.8$ Hz, 2 H), 3.77 (s, 3 H), 3.50 – 3.42 (m, 4 H), 3.30 (s, 0.07 H), 3.23 (d, $J = 13.3$ Hz, 1 H), 2.81 (t, $J = 7.0$ Hz, 0.11 H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.93, 166.83, 147.59, 133.22, 131.37, 130.23, 129.31, 121.50, 118.07, 113.12, 53.04, 52.57, 42.22, 41.84, 35.19, 34.88 (t, $J_{\text{C-D}} = 24.6$ Hz), 30.20, 29.90 (t, $J_{\text{C-D}} = 24.6$ Hz); HRMS calcd for $\text{C}_{20}\text{H}_{19}\text{D}_2\text{BrNO}_4$ ($[\text{M}+\text{H}]^+$): 420.0774; found: 420.0782.

The following signals are discernible for the *cis*-isomer: ^1H NMR (500 MHz, CDCl_3) δ 3.79 (s, 3 H), 3.67 (s, 3 H).

(34) Dimethyl (2*R,3*S**)-2-(4-fluorophenyl)-3-((phenylamino)methyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (34) (wyq-5-37).**



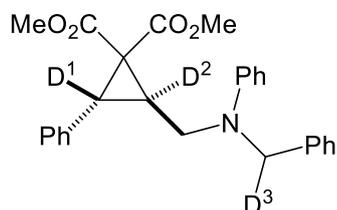
34
trans:cis = 9:1, D¹, D² = 95%, 95%

Following General Procedure I, **34** was afforded as a colorless oil (28.1 mg, 79%, D¹/D² = 95%/95%, *trans:cis* = 9:1), eluent (0-8% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.22 – 7.12 (m, 4 H), 6.95 (t, *J* = 8.5 Hz, 2 H), 6.73 (t, *J* = 7.2 Hz, 1 H), 6.64 (d, *J* = 8.0 Hz, 2 H), 3.76 (s, 3 H), 3.47 (d, *J* = 13.3 Hz, 1 H), 3.43 (s, 3 H), 3.31 (s, 0.05 H), 3.23 (d, *J* = 13.3 Hz, 1 H), 2.81 (t, 0.05 H); ¹³C NMR (126 MHz, CDCl₃) δ 168.03, 166.93, 162.11 (d, *J*_{C-F} = 246.4 Hz), 147.66, 130.17 (d, *J*_{C-F} = 8.2 Hz), 129.86 (d, *J*_{C-F} = 3.3 Hz), 129.30, 118.00, 115.16 (d, *J*_{C-F} = 21.7 Hz), 113.08, 53.00, 52.47, 42.22, 41.78, 35.09, 34.79 (t, *J*_{C-D} = 23.9 Hz), 30.33, 30.03 (t, *J*_{C-D} = 25.2 Hz); ¹⁹F NMR (471 MHz, CDCl₃) δ -114.60; HRMS calcd for C₂₀H₁₉D₂FNO₄ ([M+H]⁺): 360.1575; found: 360.1582.

The following signals are discernible for the *cis*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 3.78 (s, 3 H), 3.66 (s, 3 H); ¹³C NMR (126 MHz, CDCl₃) δ 131.44 (d, *J*_{C-F} = 8.2 Hz).

(35) **Dimethyl** **(2*R**,3*S**)-2-phenyl-3-((phenyl(phenylmethyl)-d)amino)methyl)cyclopropane-1,1-dicarboxylate-2,3-*d*₂ (35) (wyq-9-8).**



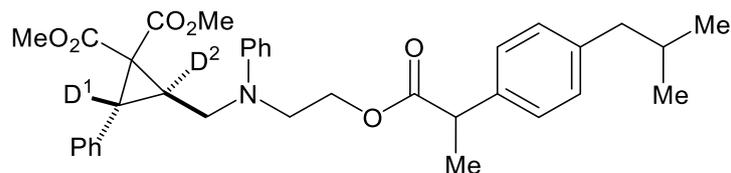
35
trans:cis > 20:1, D¹, D², D³ = 65%, 97%, 43%

Following General Procedure III, **35** was afforded as a colorless oil (37.0 mg, 85%, D¹/D²/D³ = 65%/95%/43%, *trans:cis* > 20:1), eluent (0-10% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.22 (m, 2 H), 7.27 – 7.17 (m, 8 H), 6.82 (d, $J = 8.0$ Hz, 2 H), 6.74 (t, $J = 7.2$ Hz, 1 H), 4.61 (d, $J = 7.4$ Hz, 1.57 H), 3.73 (d, $J = 15.6$ Hz, 1 H), 3.68 (s, 3 H), 3.53 (d, $J = 15.3$ Hz, 1 H), 3.36 (s, 3 H), 3.25 (s, 0.35 H), 2.88 (t, $J = 6.3$ Hz, 0.03 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.27, 166.88, 148.50, 138.36, 134.13, 129.32, 128.51, 128.40, 128.17, 127.38, 126.81, 126.59, 117.16, 113.03, 54.45, 54.12 (t, $J_{\text{C-D}} = 21.4$ Hz), 52.80, 52.29, 48.47, 41.85, 41.80, 36.67, 36.36 (t, $J_{\text{C-D}} = 23.7$ Hz), 28.82, 28.53 (t, $J_{\text{C-D}} = 23.5$ Hz); HRMS calcd for $\text{C}_{27}\text{H}_{26}\text{D}_3\text{NO}_4$ ($[\text{M}+\text{H}]^+$): 433.2201; found: 433.2190.

The following signals are discernible for the *cis*-isomer: ^1H NMR (400 MHz, CDCl_3) δ 3.76 (s, 3 H), 3.59 (s, 3 H).

(36) Dimethyl (2*S,3*R**)-2-(((2-((2-(4-isobutylphenyl)propanoyl)oxy)ethyl)(phenyl)amino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (36) (wyq-4-45).**



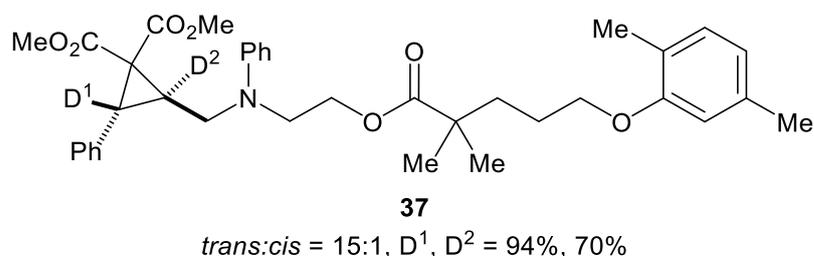
36

trans:cis > 20:1, $\text{D}^1, \text{D}^2 = 94\%, 80\%$

Following General Procedure I, **36** was afforded as a colorless oil (40.1 mg, 70%, $\text{D}^1/\text{D}^2 = 94\%/80\%$, *trans:cis* > 20:1), eluent (0-9% of ethyl acetate in petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 7.27 – 7.18 (m, 5 H), 7.18 – 7.08 (m, 4 H), 7.09 – 7.03 (m, 2 H), 6.81 (dd, $J = 8.5, 2.7$ Hz, 2 H), 6.75 (t, $J = 7.3$ Hz, 1 H), 4.28 – 4.13 (m, 2 H), 3.74 (d, $J = 7.0$ Hz, 3 H), 3.67 – 3.60 (m, 1 H), 3.57 (q, $J = 6.0$ Hz, 2 H), 3.50 (dd, $J = 15.2, 4.7$ Hz, 1 H), 3.45 – 3.38 (m, 1 H), 3.35 (d, $J = 1.8$ Hz, 3 H), 3.27 (s, 0.06 H), 2.78 (q, $J = 6.0$ Hz, 0.2 H), 2.42 (d, $J = 7.2$ Hz, 2 H), 1.83 (dt, $J = 13.4, 6.9$ Hz, 1 H), 1.46 – 1.39 (m, 3 H), 0.89 (dd, $J = 6.5, 1.5$ Hz, 6 H); ^{13}C NMR (126 MHz, CDCl_3) δ 174.61, 168.30, 166.87, 147.69, 140.52, 137.58, 134.16, 129.40, 129.31, 128.41, 128.21, 127.42, 127.13, 117.48, 113.21, 113.18, 61.79, 52.85, 52.28, 48.87, 48.83, 48.40, 48.37, 44.99, 41.85, 36.47, 36.16 (t, $J_{\text{C-D}} = 23.8$ Hz), 30.11, 28.96, 28.89, 28.60 (t, $J_{\text{C-D}} = 23.2$

Hz), 22.35, 18.43, 18.40; HRMS calcd for C₃₅H₄₀D₂NO₆ ([M+H]⁺): 574.3132; found: 574.3137.

(37) Dimethyl (2S*,3R*)-2-(((2-((5-(2,5-dimethylphenoxy)-2,2-dimethylpentanoyl)oxy)ethyl)(phenyl)amino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-d₂ (37) (wyq-4-46).



Following General Procedure I, **37** was afforded as a colorless oil (46.3 mg, 75%, D¹/D² = 94%/70%, *trans:cis* = 15:1), eluent (0-9% of ethyl acetate in petroleum ether).

The following signals are discernible for the *trans*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 7.27 – 7.17 (m, 5 H), 7.11 (d, *J* = 8.0 Hz, 2 H), 6.98 (d, *J* = 7.4 Hz, 1 H), 6.87 (d, *J* = 8.2 Hz, 2 H), 6.75 (t, *J* = 7.3 Hz, 1 H), 6.64 (d, *J* = 7.3 Hz, 1 H), 6.58 (s, 1 H), 4.22 (t, *J* = 6.3 Hz, 2 H), 3.88 – 3.82 (m, 2 H), 3.77 (s, 3 H), 3.66 – 3.59 (m, 3 H), 3.49 (d, *J* = 15.2 Hz, 1 H), 3.36 (s, 3 H), 3.31 (s, 0.06 H), 2.81 (t, *J* = 6.3 Hz, 0.3 H), 2.29 (s, 3 H), 2.16 (s, 3 H), 1.67 (d, *J* = 3.0 Hz, 4 H), 1.18 (s, 6 H); ¹³C NMR (126 MHz, CDCl₃) δ 177.66, 168.27, 166.84, 156.92, 147.81, 136.38, 134.17, 130.25, 129.42, 128.42, 128.20, 127.42, 123.53, 120.68, 117.57, 113.33, 112.01, 67.88, 61.57, 52.84, 52.26, 48.97, 48.46, 42.01, 41.78, 37.06, 36.60, 36.36 (t, *J*_{C-D} = 22.7 Hz), 28.90, 28.60 (t, *J*_{C-D} = 23.3 Hz), 25.06, 21.34, 15.70; HRMS calcd for C₃₇H₄₄D₂NO₇ ([M+H]⁺): 618.3394; found: 618.3399.

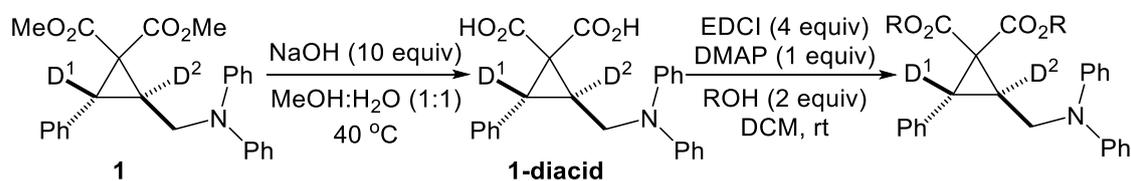
The following signals are discernible for the *cis*-isomer: ¹H NMR (500 MHz, CDCl₃) δ 3.75 (s, 3 H), 3.66 (s, 3 H), 1.14 (s, 6 H).

(38) Dimethyl (2S*,3R*)-2-(((2-(2-(adamantan-1-yl)acetoxy)ethyl)(phenyl)amino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-d₂ (38) (wyq-4-39).

2 H), 6.86 (d, $J = 8.1$ Hz, 2 H), 6.76 (t, $J = 7.2$ Hz, 1 H), 4.72 (tt, $J = 11.3, 4.8$ Hz, 1 H), 4.29 – 4.17 (m, 2 H), 3.79 (s, 3 H), 3.66 – 3.56 (m, 3 H), 3.48 (d, $J = 15.2$ Hz, 1 H), 3.37 (s, 3 H), 3.28 (s, 0.05 H), 2.82 (t, $J = 6.3$ Hz, 0.18 H), 2.30 – 2.24 (m, 1 H), 2.20 – 2.09 (m, 1 H), 2.03 (s, 3 H), 1.95 (d, $J = 12.4$ Hz, 1 H), 1.82 (t, $J = 12.3$ Hz, 4 H), 1.75 – 1.65 (m, 2 H), 1.54 (d, $J = 13.5$ Hz, 3 H), 1.47 – 1.38 (m, 6 H), 1.31 – 1.22 (m, 5 H), 1.13 (t, $J = 12.9$ Hz, 3 H), 1.05 (t, $J = 10.1$ Hz, 3 H), 0.93 (s, 3 H), 0.88 (d, $J = 6.5$ Hz, 3 H), 0.63 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 174.17, 170.65, 168.33, 166.90, 147.84, 134.18, 129.45, 128.46, 128.24, 127.46, 117.53, 113.21, 74.40, 61.31, 56.48, 55.95, 52.91, 52.34, 49.08, 48.55, 42.72, 41.89, 40.41, 40.13, 36.41, 36.12 (t, $J_{\text{C-D}} = 22.7$ Hz), 35.78, 35.31, 35.03, 34.58, 32.25, 31.10, 30.87, 28.87, 28.59 (t, $J_{\text{C-D}} = 23.9$ Hz), 28.17, 27.01, 26.63, 26.31, 24.16, 23.32, 21.46, 20.82, 18.26, 12.03; HRMS calcd for $\text{C}_{48}\text{H}_{64}\text{D}_2\text{NO}_8$ ($[\text{M}+\text{H}]^+$): 786.4908; found: 786.4916.

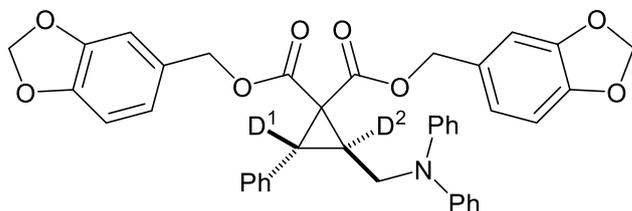
3. Synthetic applications.

3.1 Transformation of 1.



General Procedure IV: To a round bottom flask were added **1** (0.1 mmol), NaOH (1 mmol), MeOH (1.0 ml), and H₂O (1.0 mL). The mixture was stirred at 40 °C overnight until the completion of the reaction as monitored by TLC. The aqueous layer was extracted with dichloromethane (5 mL × 3) and the combined organic layer was washed with brine (5 mL), dried over anhydrous MgSO₄, filtered and concentrated in vacuo to afford corresponding **1-diacid**, which was used directly for the following step. To a round bottom flask were added **1-diacid**, alcohol (0.2 mmol), EDCI (0.4 mmol), DMAP (0.1 mmol), and dichloromethane (1.5 mL). The mixture was stirred at room temperature overnight until the completion of the reaction as monitored by TLC. Then the mixture was concentrated in vacuo to afford corresponding product via chromatography on silica gel.

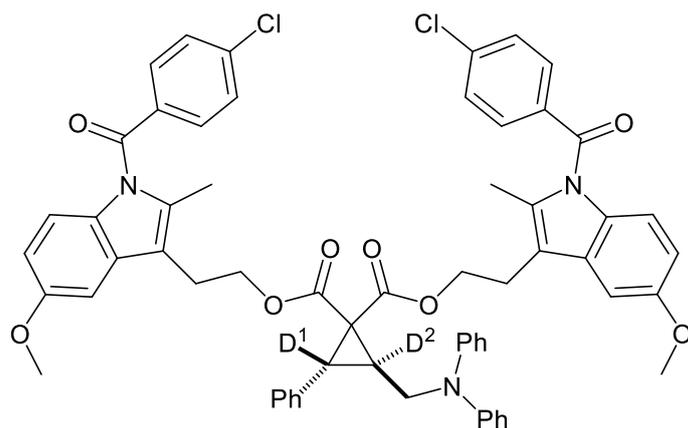
(1) Bis(benzo[d][1,3]dioxol-5-ylmethyl) (2*S,3*R**)-2-((diphenylamino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (40) (wyq-9-34).**



40 ($D^1, D^2 = 94\%, 95\%$)

Following General Procedure IV, **40** was afforded as a colorless oil (34.3 mg, 52% for two steps, $D^1/D^2 = 94\%/95\%$), eluent (0-25% of ethyl acetate in petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 7.24 (t, $J = 7.8$ Hz, 4 H), 7.18 – 7.13 (m, 3 H), 7.03 – 6.90 (m, 8 H), 6.75 – 6.70 (m, 3 H), 6.62 (d, $J = 7.9$ Hz, 1 H), 6.42 (dd, $J = 7.9, 1.7$ Hz, 1 H), 6.34 (d, $J = 1.8$ Hz, 1 H), 5.93 (d, $J = 8.7$ Hz, 4 H), 5.05 (d, $J = 12.0$ Hz, 1 H), 4.77 (d, $J = 12.1$ Hz, 1 H), 4.62 (q, $J = 11.9$ Hz, 2 H), 3.98 (d, $J = 15.1$ Hz, 1 H), 3.80 (d, $J = 15.1$ Hz, 1 H), 3.17 (s, 0.06 H), 2.88 (t, $J = 6.6$ Hz, 0.05 H); ^{13}C NMR (126 MHz, CDCl_3) δ 167.56, 166.20, 147.70, 147.63, 147.46, 133.96, 129.39, 129.04, 128.87, 128.45, 128.10, 127.31, 122.27, 122.16, 121.79, 121.34, 109.03, 108.88, 108.13, 107.91, 101.13, 101.02, 67.45, 67.13, 49.05, 42.15, 37.04, 36.57 (t, $J_{\text{C-D}} = 28.4$ Hz), 29.65, 28.95 (t, $J_{\text{C-D}} = 28.7$ Hz); HRMS calcd for $\text{C}_{40}\text{H}_{31}\text{D}_2\text{NO}_8$ ($[\text{M}+\text{H}]^+$): 658.2404; found: 658.2420.

(2) Bis(2-(1-(4-chlorobenzoyl)-5-methoxy-2-methyl-1*H*-indol-3-yl)ethyl) (2*S,3*R**)-2-((diphenylamino)methyl)-3-phenylcyclopropane-1,1-dicarboxylate-2,3-*d*₂ (41) (wyq-9-37).**

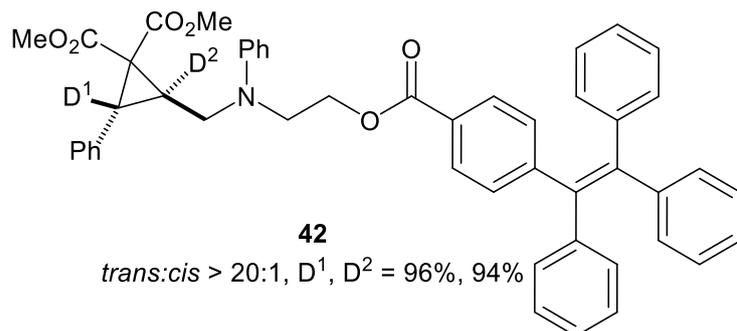


41 ($D^1, D^2 = 94\%, 95\%$)

Following General Procedure IV, **41** was afforded as a pale green oil (44.4 mg, 47% for two steps, $D^1/D^2 = 94\%/95\%$), eluent (0-25% of ethyl acetate in petroleum ether); ^1H NMR (500 MHz, CDCl_3) δ 7.57 (d, $J = 8.2$ Hz, 2 H), 7.53 (d, $J = 8.2$ Hz, 2 H), 7.42 (d, $J = 8.2$ Hz, 2 H), 7.36 (d, $J = 8.2$ Hz, 2 H), 7.27 – 7.17 (m, 5 H), 7.12 – 7.06 (m, 3 H), 7.00 – 6.91 (m, 7 H), 6.90 (d, $J = 2.6$ Hz, 1 H), 6.81 (t, $J = 9.2$ Hz, 2 H), 6.73 (d, $J = 2.6$ Hz, 1 H), 6.63 (d, $J = 9.0$ Hz, 2 H), 4.23 – 4.09 (m, 2 H), 3.89 (d, $J = 15.1$ Hz, 1 H), 3.82 (s, 3 H), 3.82 – 3.77 (m, 4 H), 3.79 – 3.72 (m, 1 H), 3.69 – 3.61 (m, 1 H), 3.16 (s, 0.06 H), 2.98 – 2.76 (m, 2.05 H), 2.36 – 2.21 (m, 5 H), 2.15 (s, 3 H); ^{13}C NMR (126 MHz, CDCl_3) δ 168.14, 168.11, 167.73, 166.21, 156.02, 155.95, 147.65, 139.11, 139.09, 135.35, 135.17, 134.03, 133.91, 133.84, 131.03, 131.02, 130.83, 130.79, 130.64, 129.40, 129.05, 129.03, 128.45, 128.07, 127.38, 121.85, 121.32, 115.05, 114.99, 114.90, 114.74, 111.36, 111.22, 101.16, 64.93, 63.95, 55.70, 55.67, 48.94, 42.24, 36.28, 35.98 (t, $J_{\text{C-D}} = 27.2$ Hz), 29.67, 28.56 (t, $J_{\text{C-D}} = 24.8$ Hz), 23.33, 22.76, 13.21, 12.98; HRMS calcd for $\text{C}_{62}\text{H}_{52}\text{D}_2\text{Cl}_2\text{N}_3\text{O}_8$ ($[\text{M}+\text{H}]^+$): 1040.3408; found: 1040.3410.

3.2 Synthesis and characterization of aggregation-induced emission (AIE) compounds.

(1) Synthesis of Dimethyl ($2R^*,3S^*$)-2-phenyl-3-((phenyl(2-((4-(1,2,2-triphenylvinyl) benzoyl)oxy)ethyl)amino)methyl)cyclopropane-1,1-dicarboxylate-2,3- d_2 (**42**) (wyq-5-8).



Following General Procedure I, **42** was afforded as a colorless oil (57.2 mg, 75%, D¹/D² = 96%/94%, *trans:cis* > 20:1), eluent (0-11% of ethyl acetate in petroleum ether); ¹H NMR (500 MHz, CDCl₃) δ 7.70 (d, *J* = 8.1 Hz, 2 H), 7.27 – 7.21 (m, 3 H), 7.19 (d, *J* = 5.6 Hz, 2 H), 7.12 – 7.05 (m, 12 H), 7.04 – 6.98 (m, 7 H), 6.89 (d, *J* = 8.2 Hz, 2 H), 6.74 (t, *J* = 7.3 Hz, 1 H), 4.42 (t, *J* = 6.3 Hz, 2 H), 3.78 – 3.71 (m, 5 H), 3.63 (d, *J* = 7.7 Hz, 1 H), 3.52 (d, *J* = 15.1 Hz, 1 H), 3.35 (s, 3 H), 3.27 (s, 0.04 H), 2.83 (t, *J* = 6.3 Hz, 0.06 H); ¹³C NMR (126 MHz, CDCl₃) δ 168.28, 166.85, 166.31, 148.90, 147.79, 143.16, 143.06, 143.03, 142.44, 139.86, 134.09, 131.27, 131.21, 131.19, 129.45, 129.03, 128.41, 128.20, 127.82, 127.79, 127.66, 127.59, 127.41, 126.84, 126.67, 117.56, 113.27, 62.04, 52.88, 52.29, 49.07, 48.59, 41.73, 36.69, 36.36 (t, *J*_{C-D} = 23.9 Hz), 28.88, 28.59 (t, *J*_{C-D} = 23.3 Hz); HRMS calcd for C₄₉H₄₂D₂NO₆ ([M+H]⁺): 744.3289; found: 744.3288.

(2) Characterization of aggregation-induced emission (AIE) properties of **S7** and **42**.

Stock solutions of compounds were prepared in THF: **S7** (1 M), **42** (1 M). Samples for fluorescence measurement (8 μM) were prepared by diluting the stock solutions with a mixture of THF and water at different ratios. All fluorescence emission spectra were measured with the exciting wavelength of 450 nm.

TEM images were measured in a mixture of water and THF (95/5) (Figure S1).

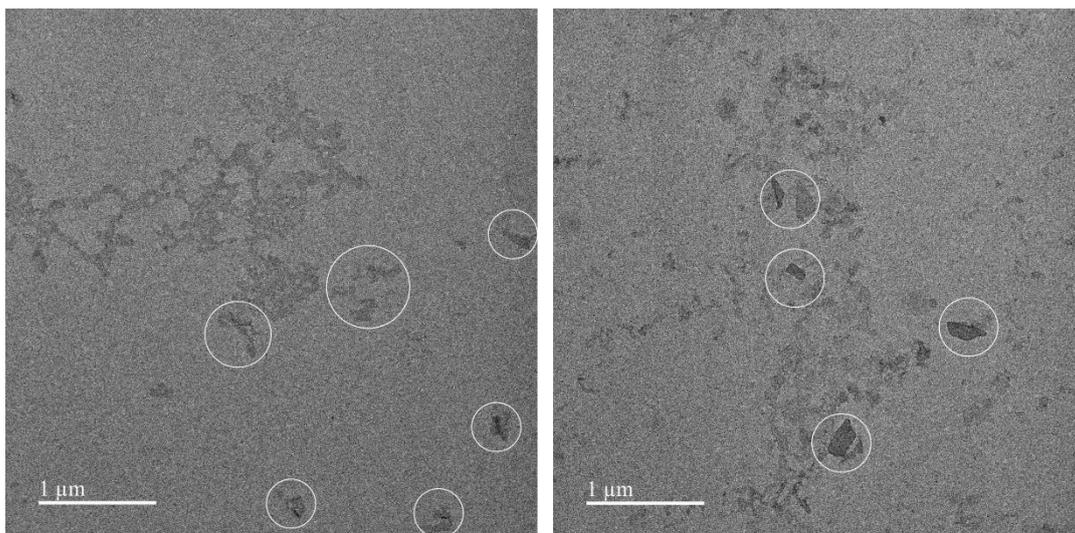
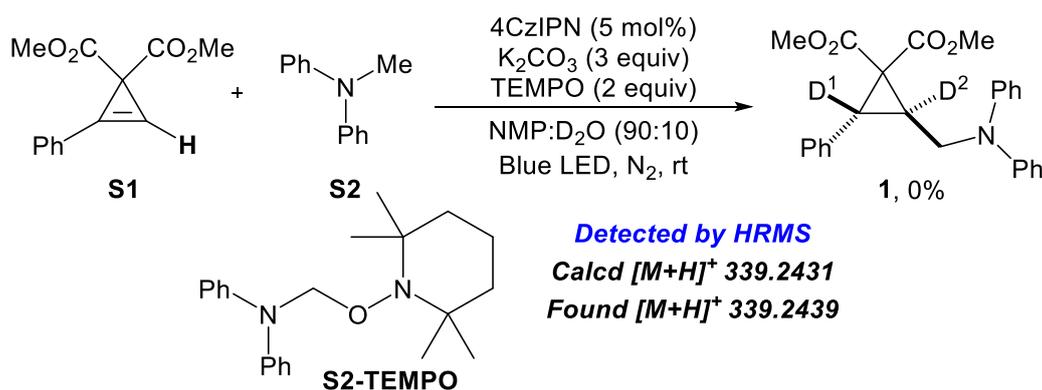


Figure S1. TEM images of **S7** (left) and **42** (right) in water/THF (95/5).

4. Mechanistic investigations.

4.1 Trap of the radical intermediate with TEMPO.



Under nitrogen atmosphere, to a 10 mL Schlenk tube equipped with a stirring bar is added 4CzIPN (5 mol%), K₂CO₃ (0.3 mmol), **S1** (0.1 mmol), **S2** (0.3 mmol), TEMPO (0.2 mmol), *N*-methyl pyrrolidinone (0.9 mL), and D₂O (0.1 mL) successively, and the tube was sealed with a septum. The mixture was stirred at room temperature overnight, and quenched with H₂O (2.5 mL). The aqueous layer was extracted with EtOAc (5 mL × 3) and the combined organic layer was washed with brine (5 mL), dried over anhydrous MgSO₄, filtered and concentrated in vacuo. The crude mixture was analyzed with ¹H NMR and HRMS and no product **1** was formed, instead, the adduct product **S2-TEMPO** was detected by HRMS: C₂₂H₃₁N₂O⁺ ([M+H]⁺) calcd: 339.2431; found: 339.2439 (Figure S2).

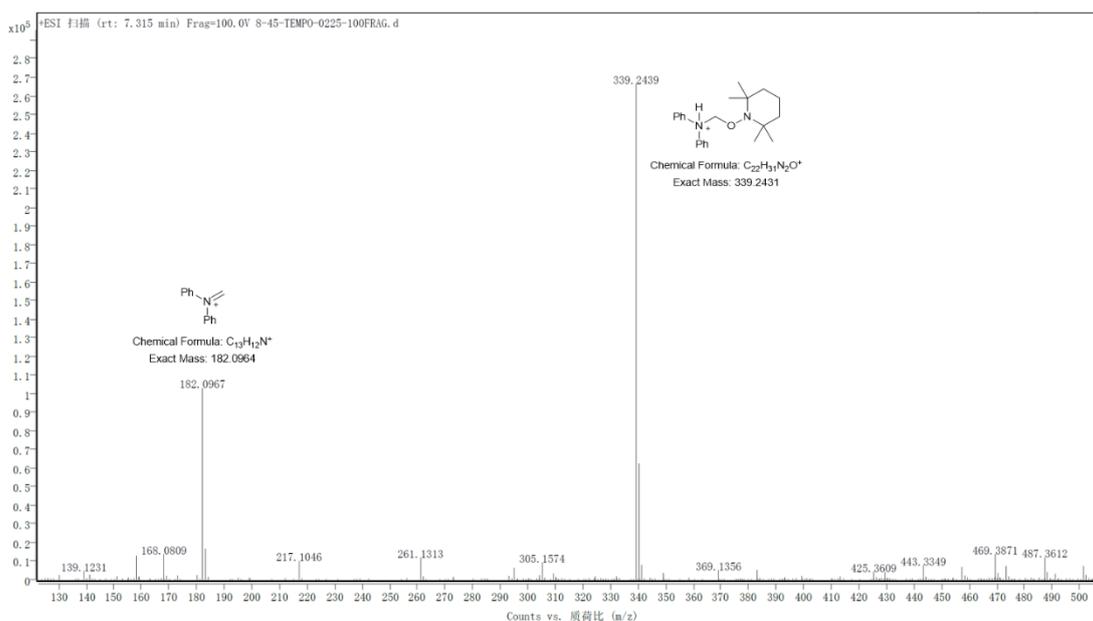
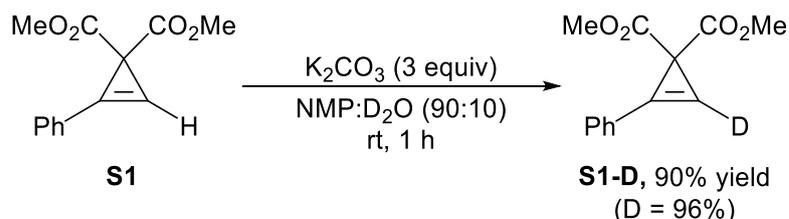


Figure S2. HRMS spectrum of **S2-TEMPO**.

4.2 Deuteration of **S1** in the absence of **S2**.



To a 10 mL Schlenk tube equipped with a stirring bar was added K_2CO_3 (0.3 mmol), **S1** (0.1 mmol), *N*-methyl pyrrolidinone (0.9 mL), and D_2O (0.1 mL) successively, and the tube was sealed with a septum. The mixture was stirred at room temperature for one hour. The residual was directly conducted chromatography on silica gel to afford **S1-D** as a white solid (22.6 mg, 90%, $D = 96\%$) with eluent (0-15% of ethyl acetate in petroleum ether): ^1H NMR (500 MHz, CDCl_3) δ 7.63 (dd, $J = 6.3, 2.9$ Hz, 2 H), 7.47 – 7.41 (m, 3 H), 6.90 (s, 0.04 H), 3.73 (s, 6 H); ^{13}C NMR (126 MHz, CDCl_3) δ 171.12, 130.56, 130.32, 128.87, 123.91, 111.99, 95.23, 94.93 (t, $J_{\text{C-D}} = 35.9$ Hz), 52.37, 32.67; HRMS calcd for $\text{C}_{13}\text{H}_{12}\text{DO}_4$ ($[\text{M}+\text{H}]^+$): 234.0871; found: 234.0876.

4.3 Luminescence quenching studies of 4CzIPN with **S1** and **S2**.

Stock solutions of compounds were prepared in *N*-methyl pyrrolidinone: 4CzIPN (10 μM), **S1** (1 M), and **S2** (1 M). All solutions with different concentrations of compounds were prepared by diluting these stock solutions with *N*-methyl

pyrrolidinone. Fluorescent quenching studies of 4CzIPN (10 μ M) with different concentrations of S1 and S2 were performed with the exciting wavelength of 450 nm.

4.4 Determination of quantum yield:

The quantum yield of this reaction was determined according to a reported procedure.⁷

(1) Preparation of stock solutions:

A 0.15 M solution of potassium ferrioxalate was prepared by dissolving 1.11 g of potassium ferrioxalate hydrate in 15 mL of 0.05 M H₂SO₄. A buffered solution of phenanthroline was prepared by dissolving 10 mg of phenanthroline and 2.25 g of sodium acetate in 15 mL of 0.5 M H₂SO₄. Both solutions were stored in the dark.

(2) Determination of fraction of light absorbed at 456 nm for the ferrioxalate solution:

The absorbance (A) of the above ferrioxalate solution at 456 nm was measured to be 1.69 (Figure S3). The fraction of light absorbed (f) by this solution was calculated:

$$f = 1 - 10^{-A}$$
$$f = 1 - 10^{-1.69} = 0.98$$

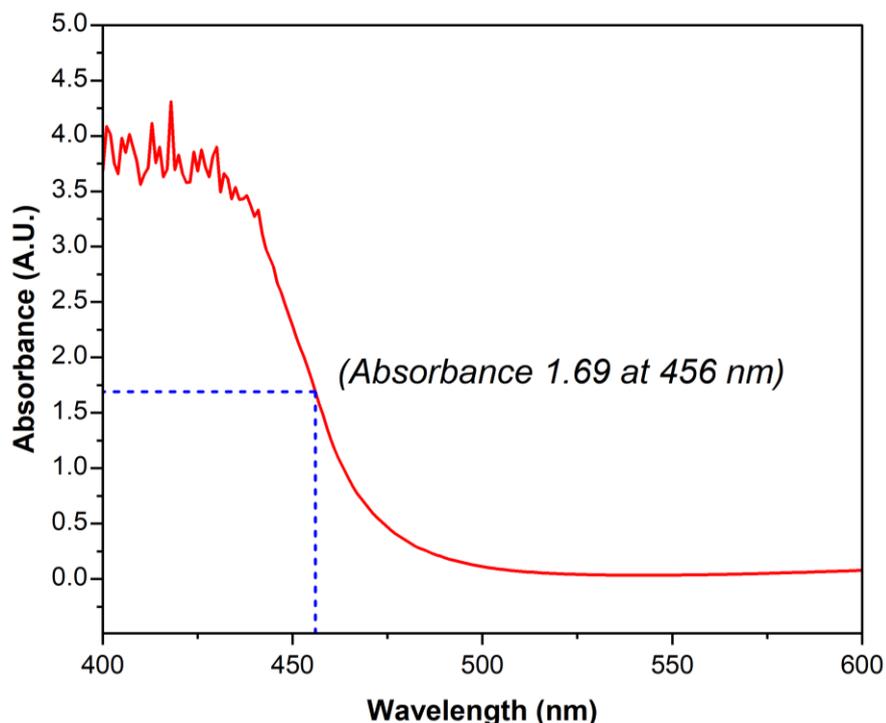


Figure S3. UV-vis spectrum of the potassium ferrioxalate solution.

(3) Determination of light intensity at 456 nm:

The photon flux of the photoreactor was determined by standard ferrioxalate actinometry. To determine the photon flux of the photoreactor, 1.0 mL of 0.15 M potassium ferrioxalate solution was placed in a quartz cuvette and was irradiated with blue LEDs for 10 seconds. After irradiation, 0.175 mL of the phenanthroline solution was added to the cuvette. The solution was then allowed to rest for 1 h, ensuring the complete coordination of phenanthroline to ferrous ions. The absorbance of the above solution was measured with a UV-vis spectrometer (Figure S4). A non-irradiated sample was also prepared and measured (Figure S5).

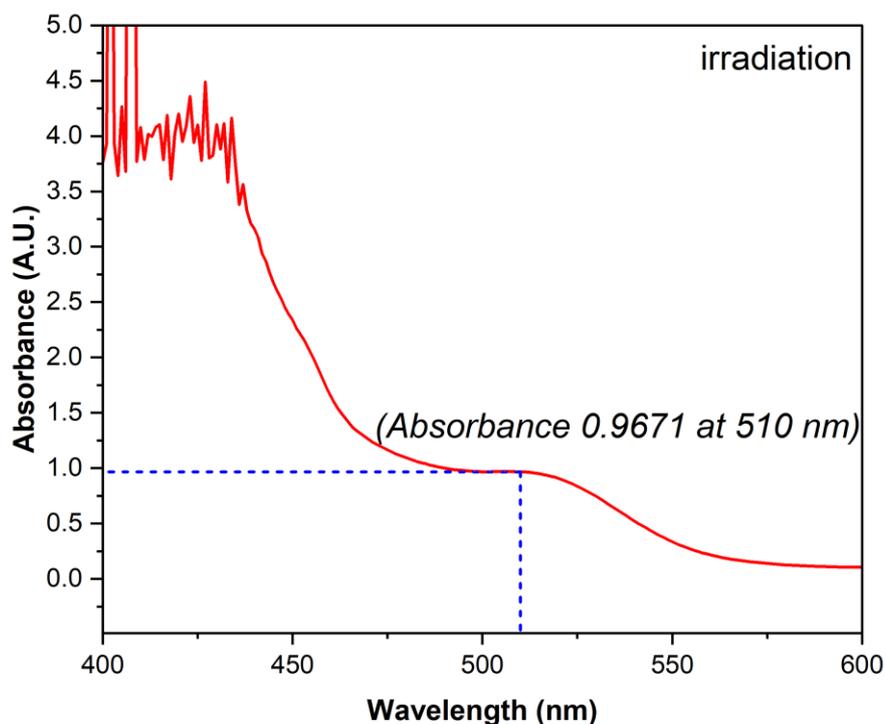


Figure S4. UV-vis spectrum of the potassium ferrioxalate-phenanthroline solution with irradiation.

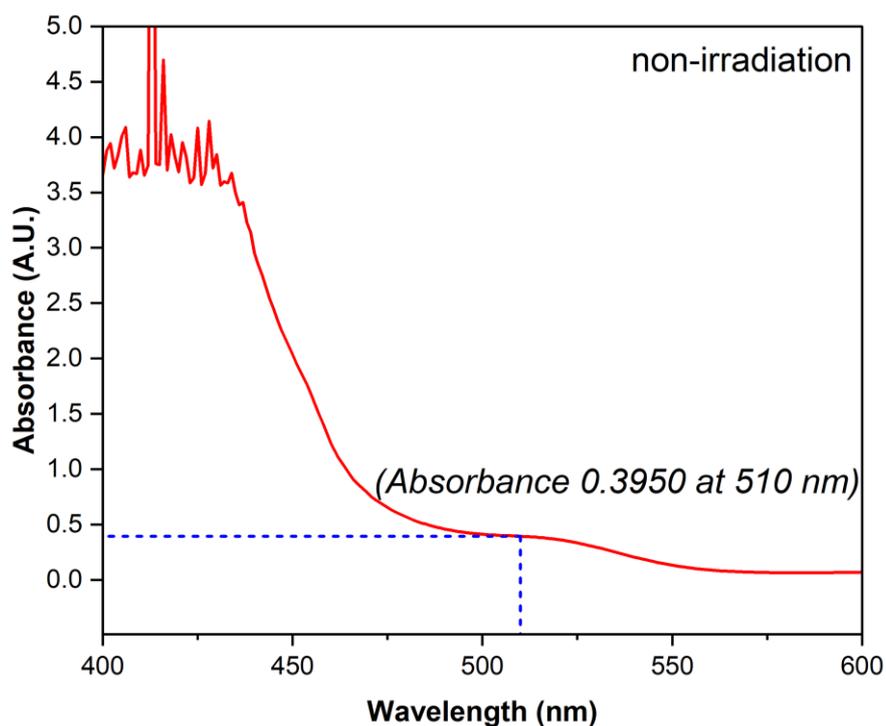


Figure S5. UV-vis spectrum of the potassium ferrioxalate-phenanthroline solution without irradiation.

The amount of Fe^{2+} formed during the irradiation has been calculated using the following equation:

$$\text{mol } Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon}$$

Where V is the total volume (0.001175 L) of the solution after addition of phenanthroline, ΔA is the difference in absorbance at 510 nm between the irradiated and non-irradiated solutions ($A_{\text{irradiation}} = 0.9671$, $A_{\text{non-irradiation}} = 0.3950$, $\Delta A = 0.5721$), l is the path length (1.000 cm), and ε is the molar absorptivity at 510 nm (11,100 L/mol/cm). The photon flux has been calculated using the following equation

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi \cdot t \cdot f}$$

Where Φ is the quantum yield for the ferrioxalate actinometer (0.92 for a 0.15 M solution at $\lambda = 456$ nm), t is the irradiation time (10 s), and f is the fraction of light absorbed at $\lambda = 456$ nm (0.98, *vide supra*). The photon flux of the photoreactor was calculated to be 6.7×10^{-9} einstein/s.

$$\text{mol } Fe^{2+} = \frac{V \cdot \Delta A}{l \cdot \varepsilon} = \frac{0.001175 \text{ L} \times 0.5721}{1.000 \text{ cm} \times 11100 \text{ L mol}^{-1} \cdot \text{cm}^{-1}} = 6.1 \times 10^{-8} \text{ mol}$$

$$\text{photon flux} = \frac{\text{mol } Fe^{2+}}{\Phi \cdot t \cdot f} = \frac{6.1 \times 10^{-8} \text{ mol}}{0.92 \times 10 \text{ s} \times 0.98} = 6.7 \times 10^{-9} \text{ einstein} \cdot \text{s}^{-1}$$

(4) Determination of the quantum yield:

Under nitrogen atmosphere, to a 10 mL Schlenk tube equipped with a stirring bar were added 4CZIPN (4.1 mg, 0.005 mmol, 5 mol%), K₂CO₃ (41.9 mg, 0.3 mmol, 3 equiv), S1 (24.0 mg, 0.1 mmol, 1 equiv), S2 (55.1 mg, 0.3 mmol, 3 equiv), *N*-methyl pyrrolidinone (0.9 mL) and D₂O (0.1 mL) successively, and the tube was sealed with a septum. The mixture was stirred at room temperature irradiated with a blue LED for 1 h. The aqueous layer was extracted with ethyl acetate (5 mL × 3) and the combined organic layer was washed with brine (5 mL), dried over anhydrous MgSO₄, filtered and concentrated in vacuo to afford corresponding product via chromatography on silica gel to afford **1** (3.0 mg, 7%).

The quantum yield (Φ) has been calculated using the equation

$$\Phi = \frac{\text{mol product}}{\text{flux} \cdot t \cdot f}$$

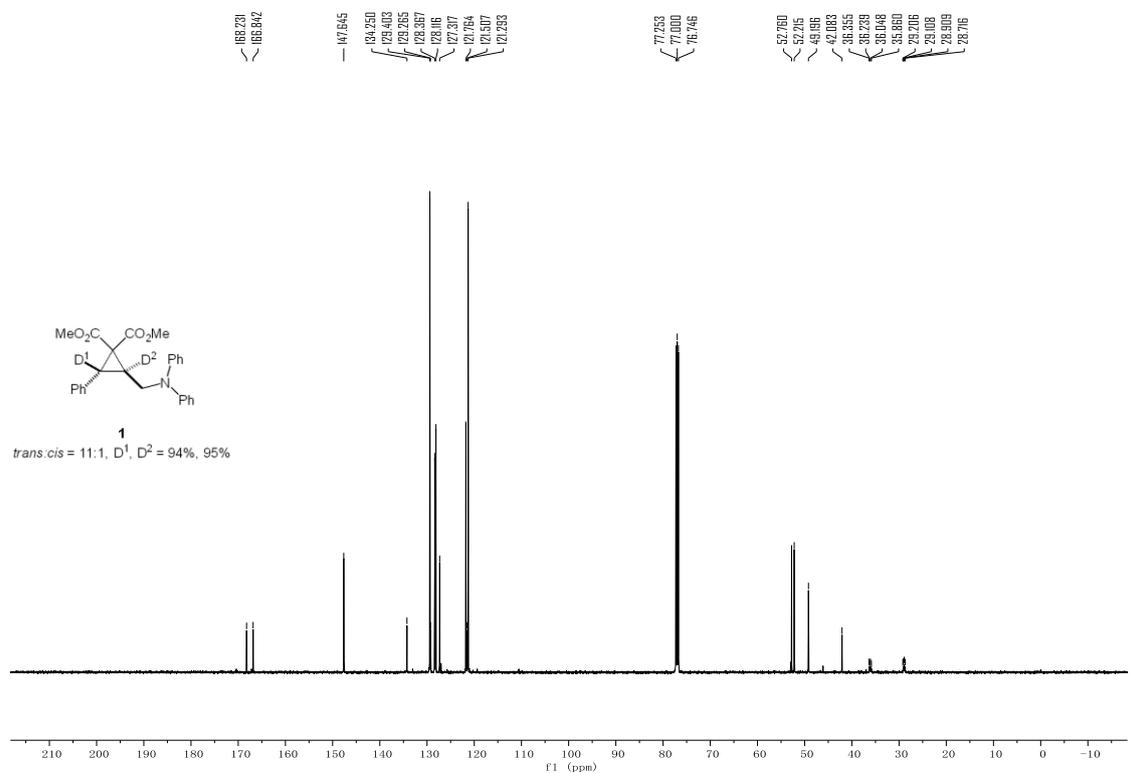
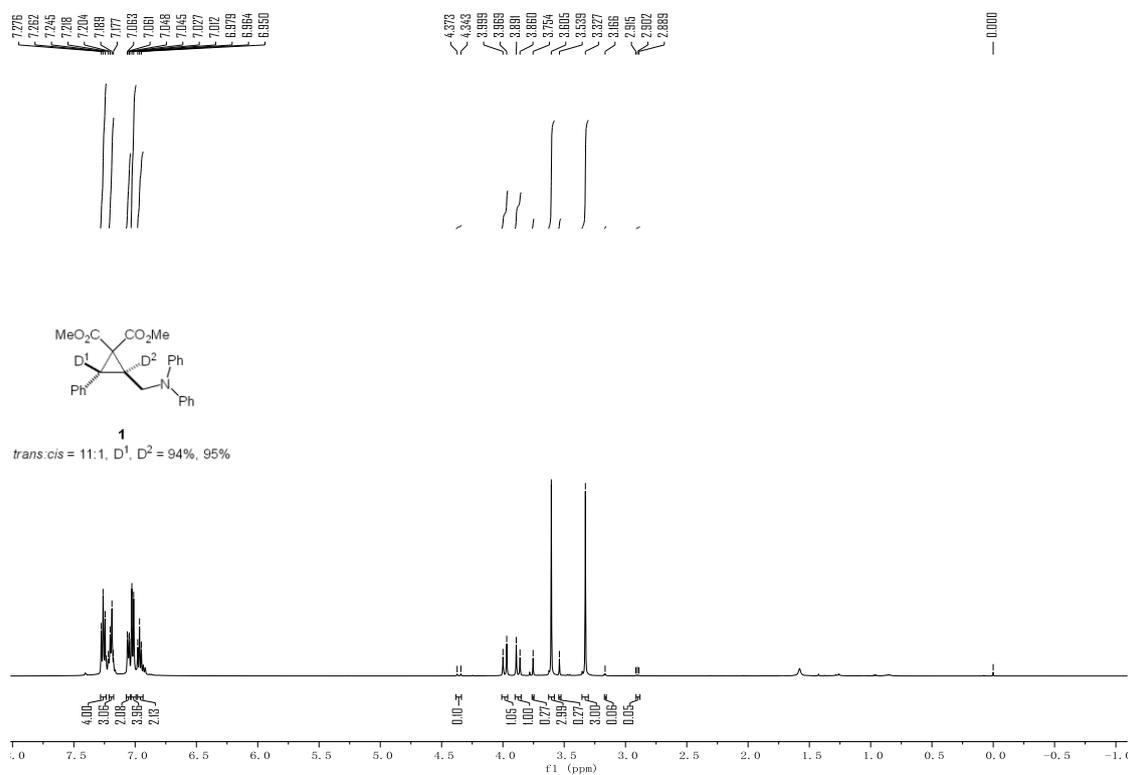
Where t is the reaction time (3600 s), and f is the previously calculated fraction of light absorbed by the solution.

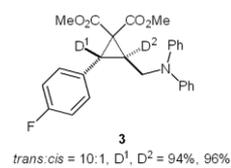
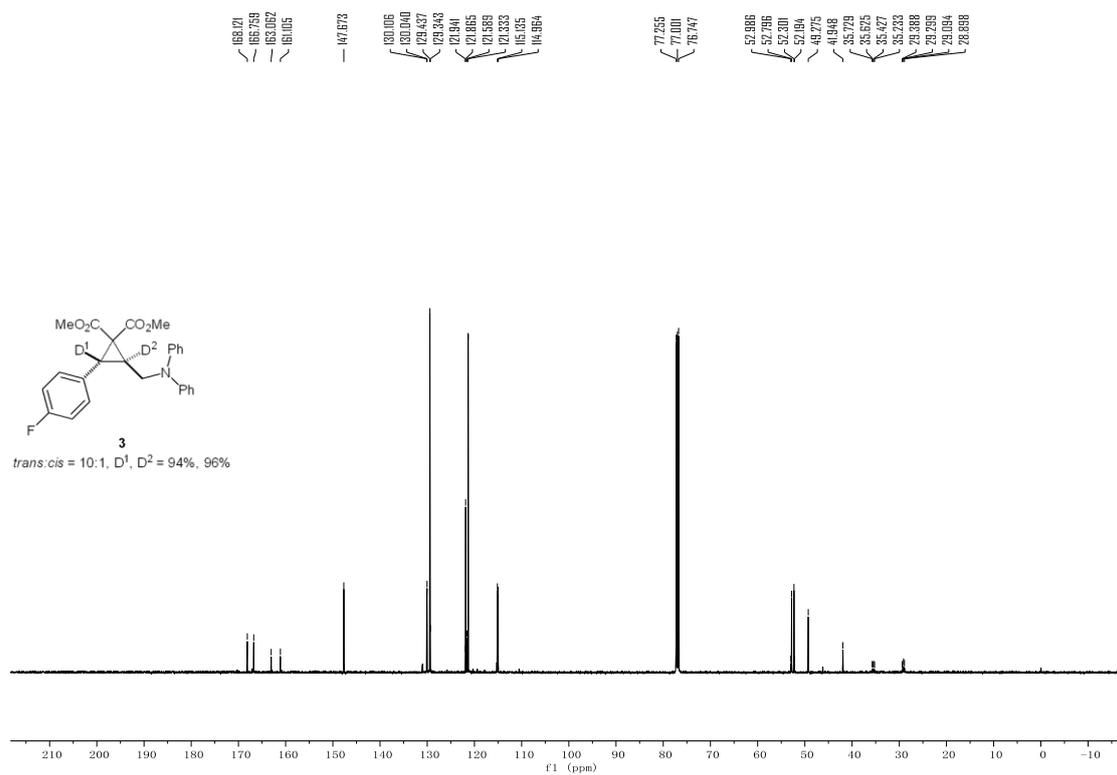
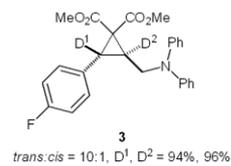
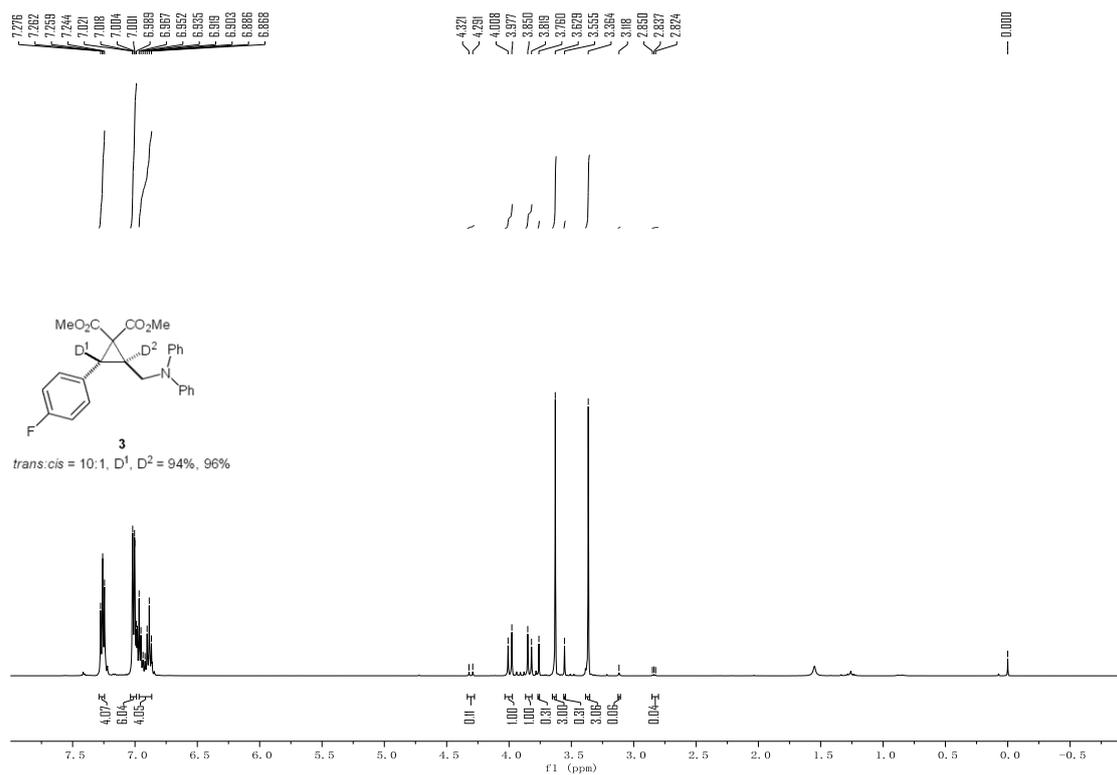
$$\Phi = \frac{\text{mol product}}{\text{flux} \cdot t \cdot f} = \frac{0.1 \times 0.07 \times 10^{-3}}{6.7 \times 10^{-9} \text{ einstein} \cdot \text{s}^{-1} \times 3600 \text{ s} \times 0.98} = 0.30$$

5. References.

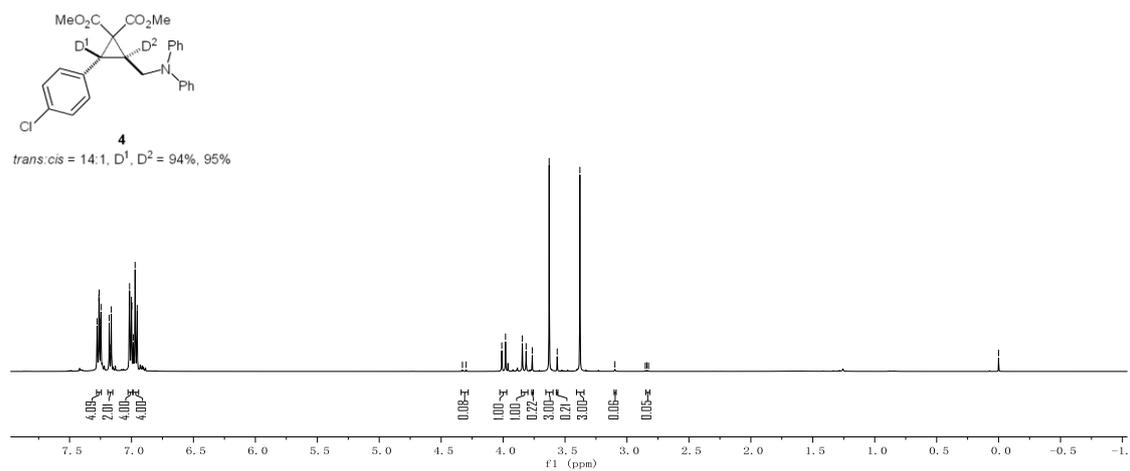
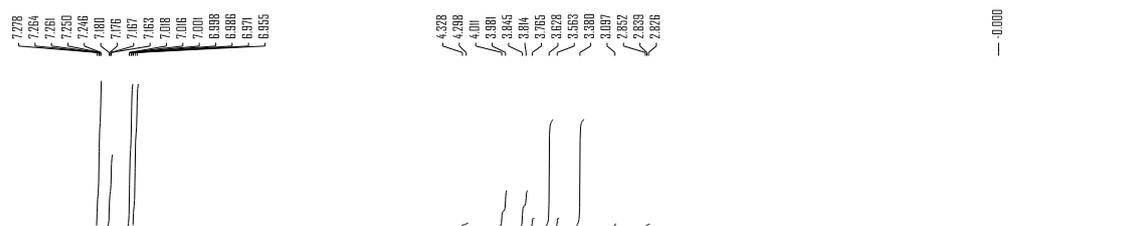
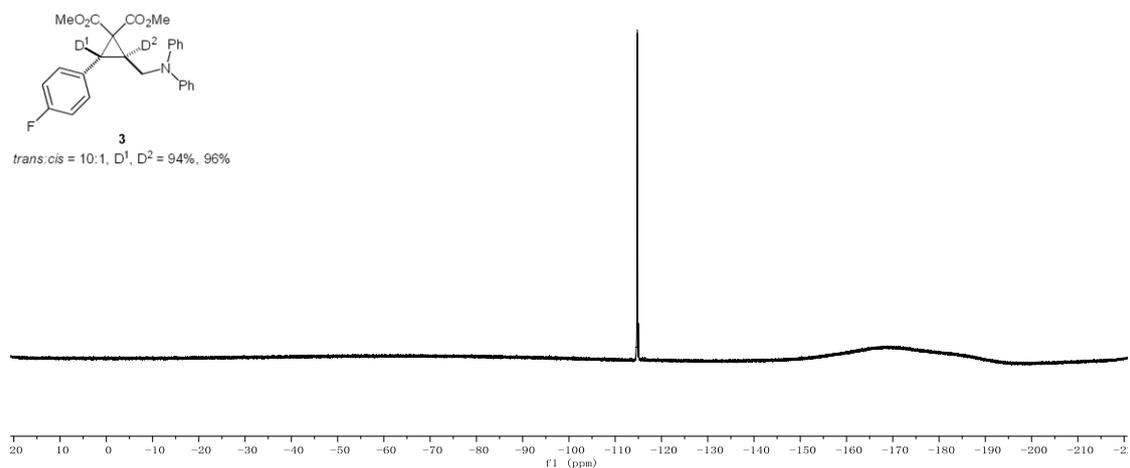
- [1] L.-a. Liao, F. Zhang, N. Yan, J. A. Golen, J. M. Fox, *Tetrahedron.*, **2004**, *60*, 1803.
- [2] S. Chuprakov, M. Rubin, V. Gevorgyan, *J. Am. Chem. Soc.*, **2005**, *127*, 3714.
- [3] Y. Liu, Q. Yu, S. Ma, *Eur. J. Org. Chem.*, **2013**, 3033.
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- [6] C. Peng, F. Gu, X. Lin, N. Ding, Q. Zhan, P. Cao, T. Cao, *Green Chem.*, **2023**, *25*, 671.
- [7] M. A. Cismesia, T. P. Yoon, *Chem. Sci.*, **2015**, *6*, 5426.

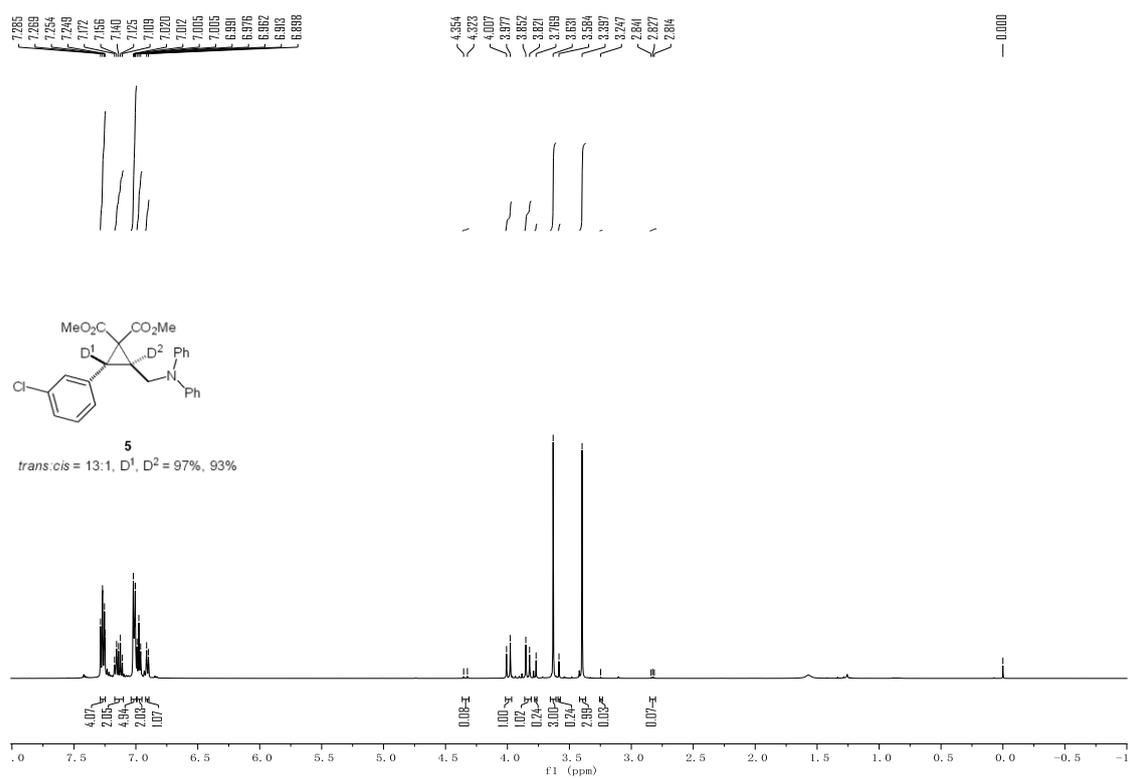
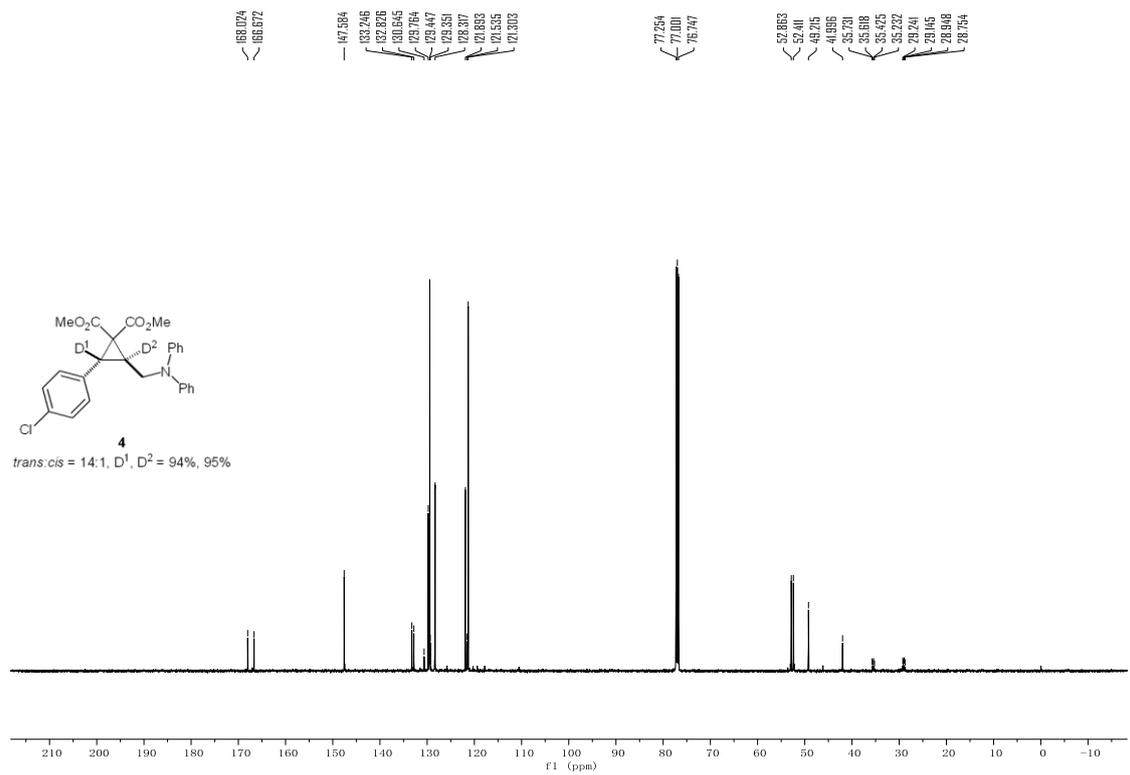
6. ^1H NMR, ^{13}C NMR, ^{19}F NMR spectra for compounds.

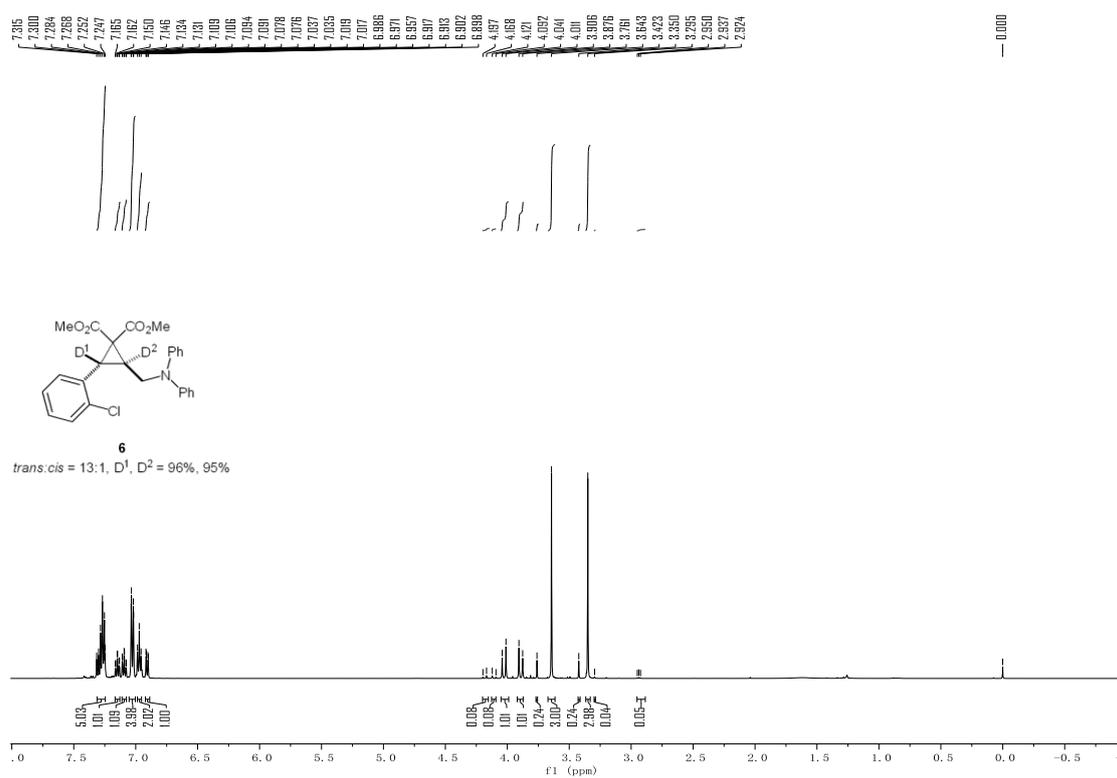
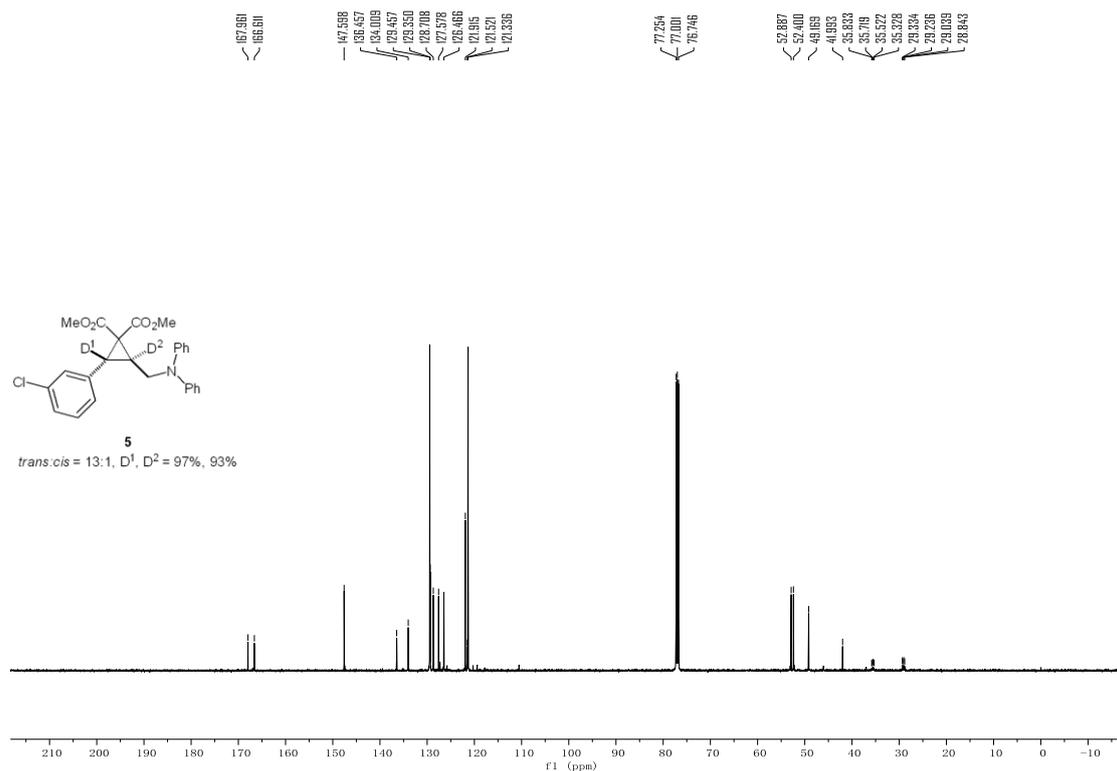




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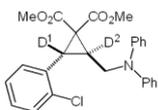


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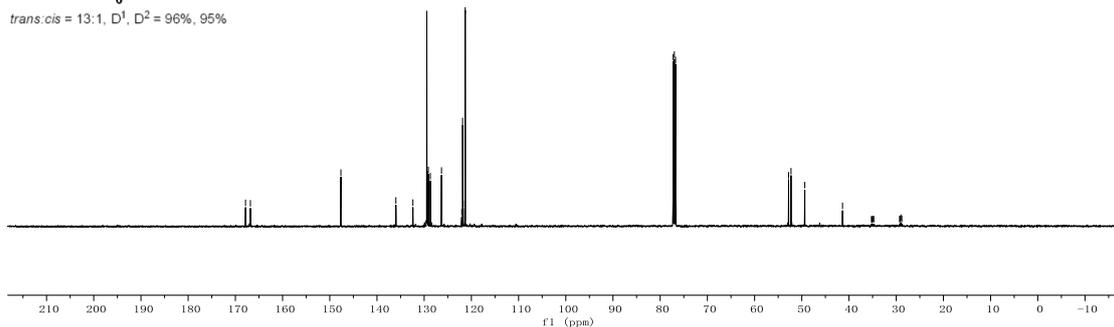
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29.697
28.805



6

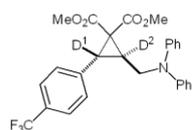
trans:cis = 13:1, D¹, D² = 96%, 95%



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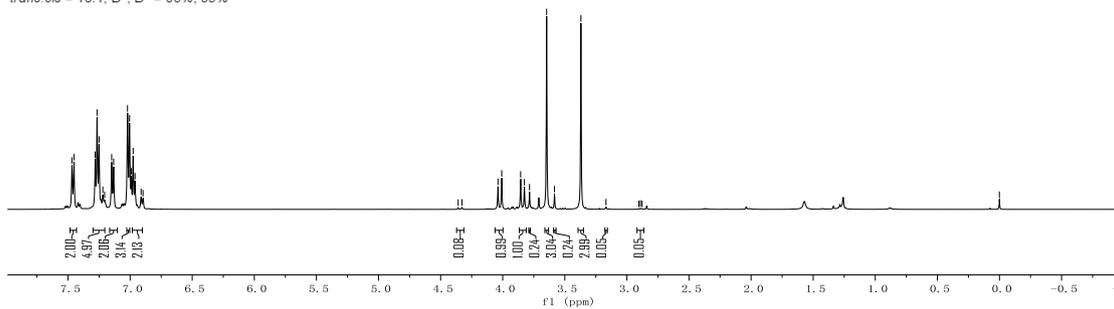
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0.000

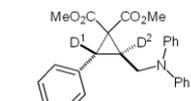


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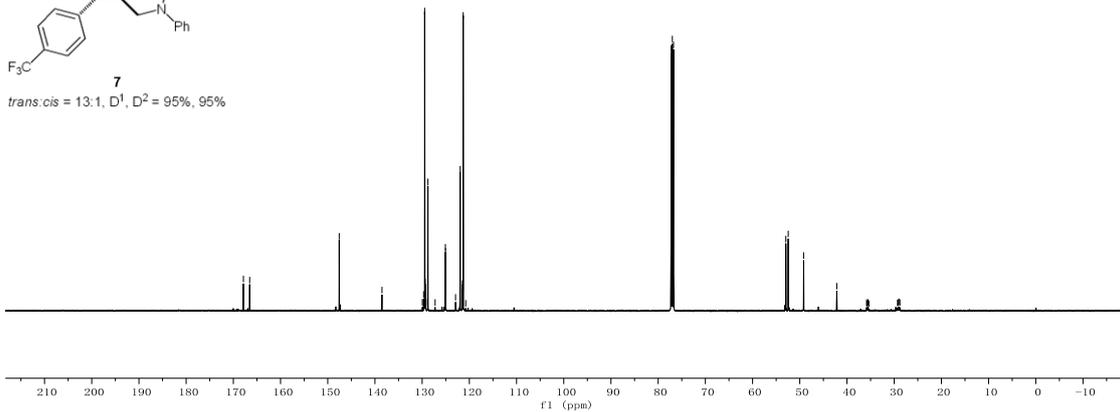
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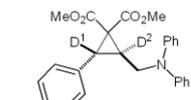
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28.794



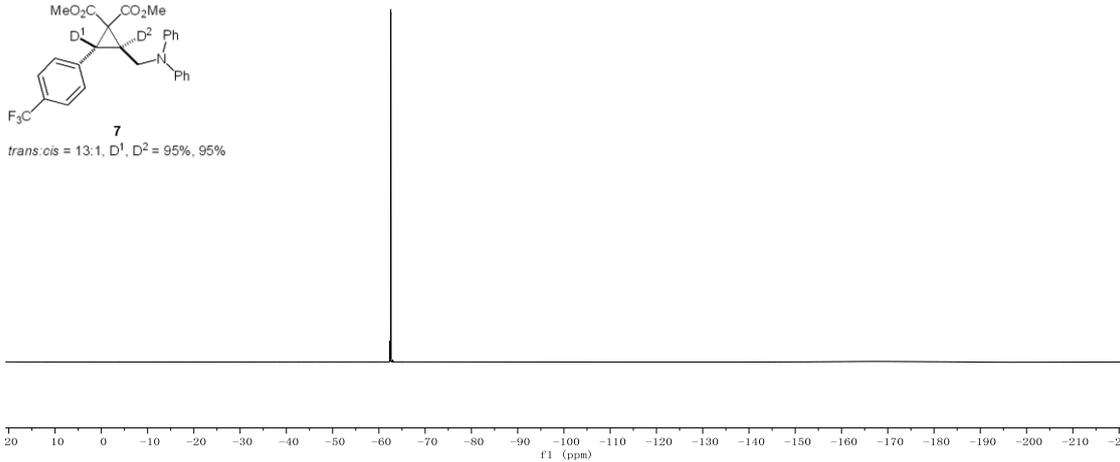
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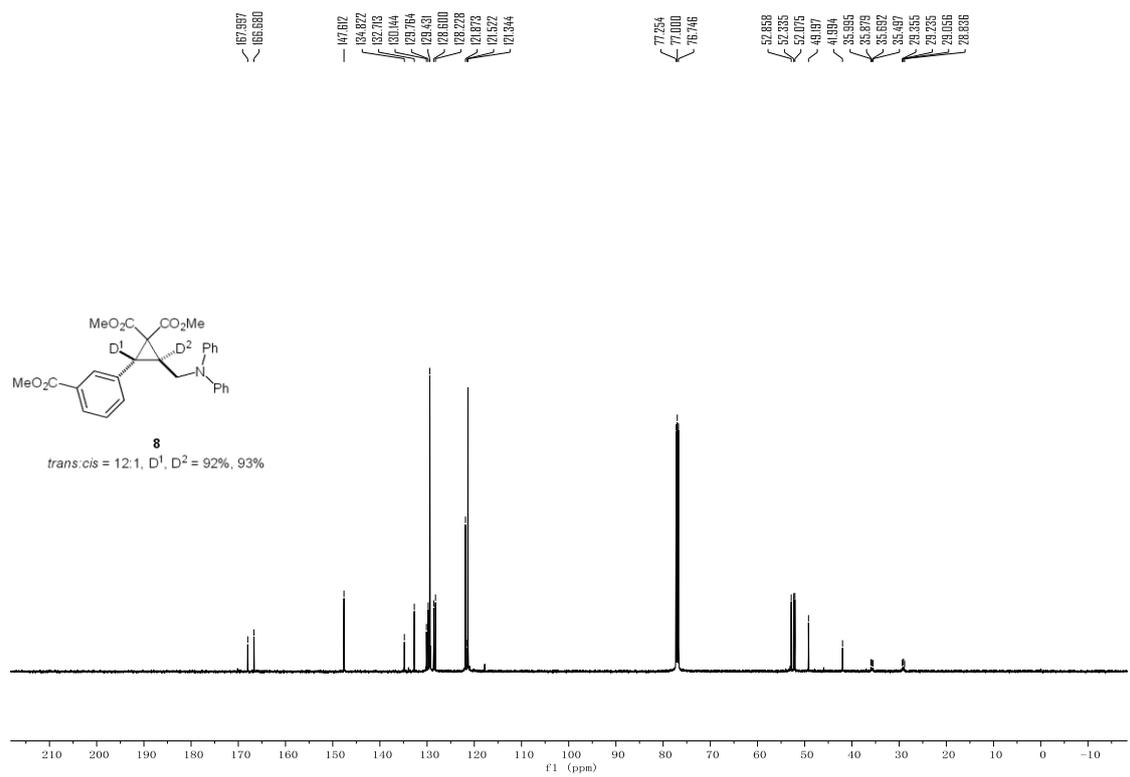
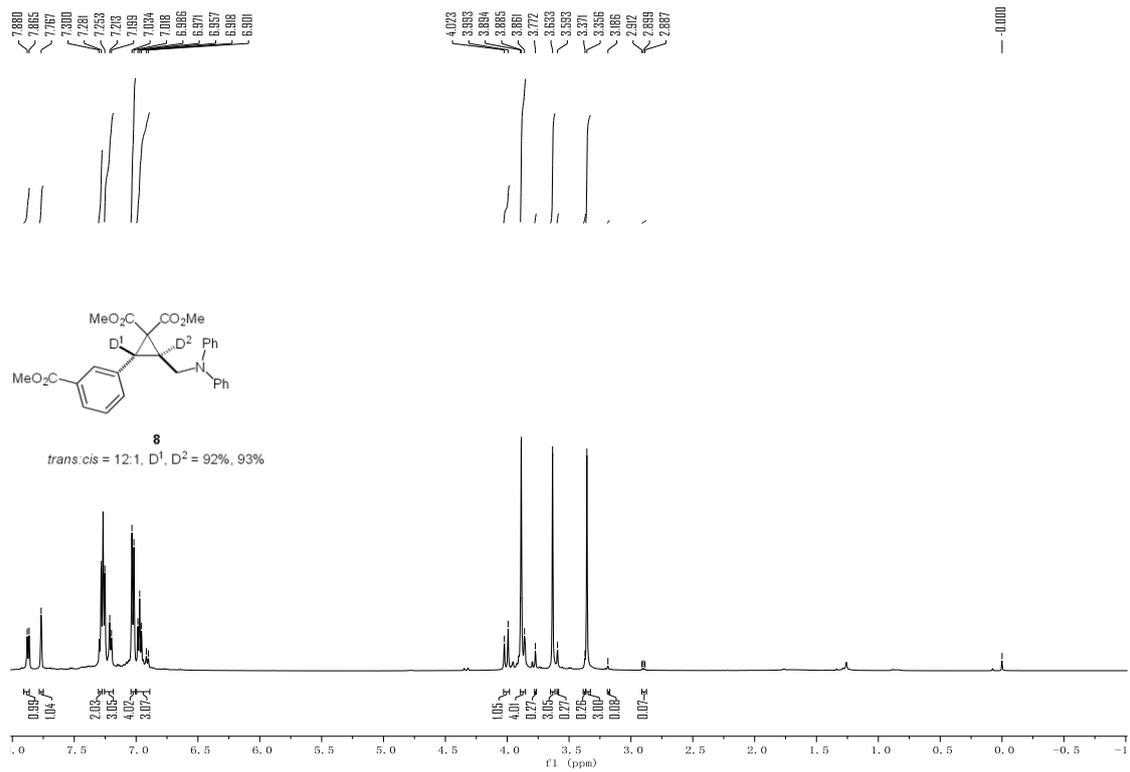


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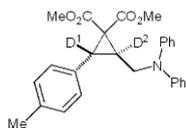




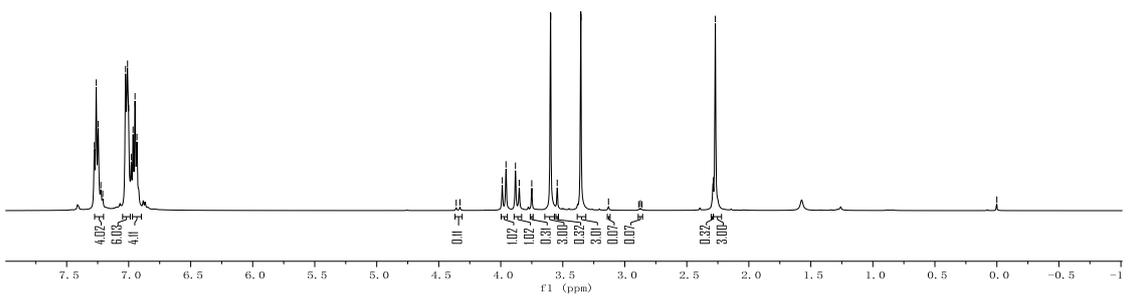
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0.000



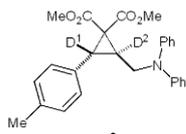
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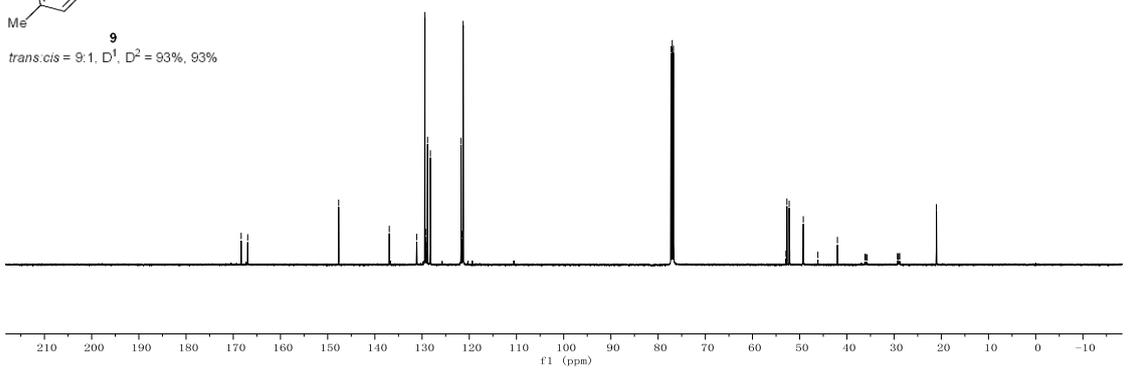
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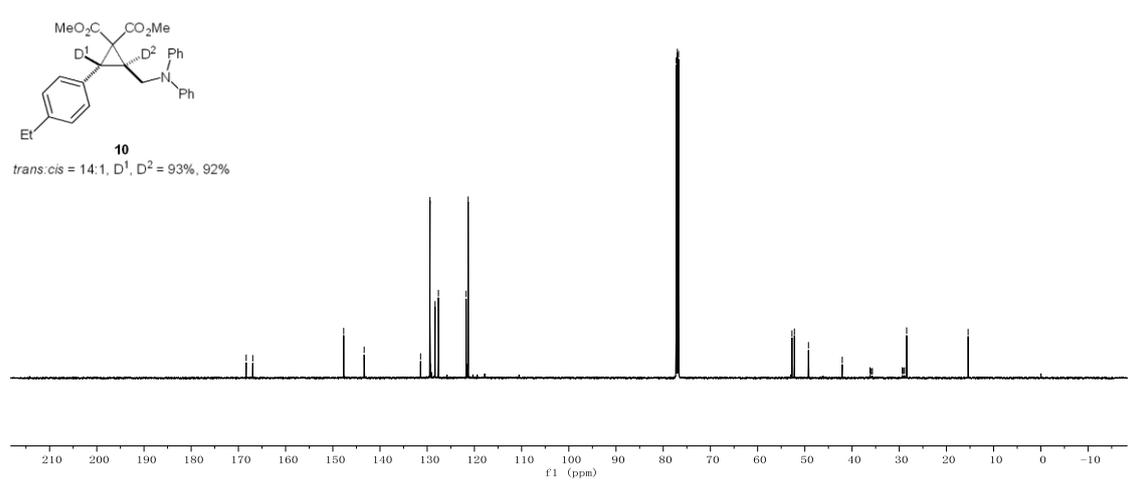
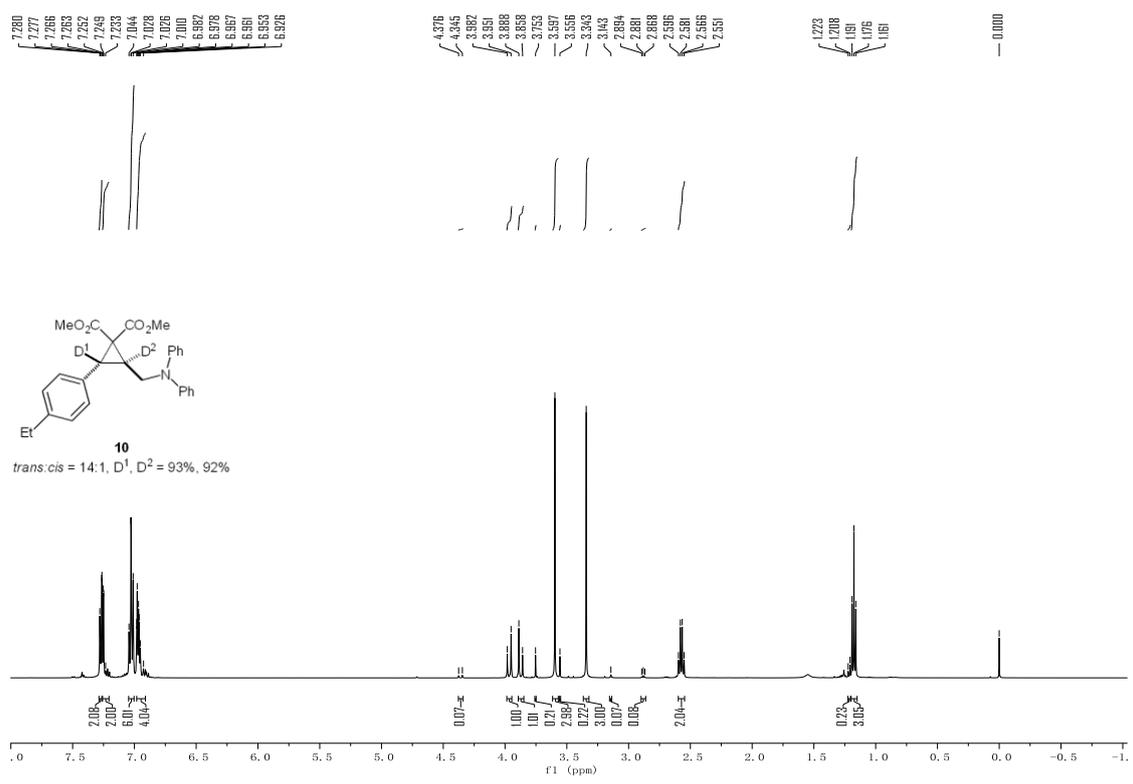
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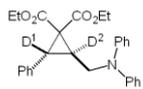
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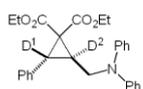
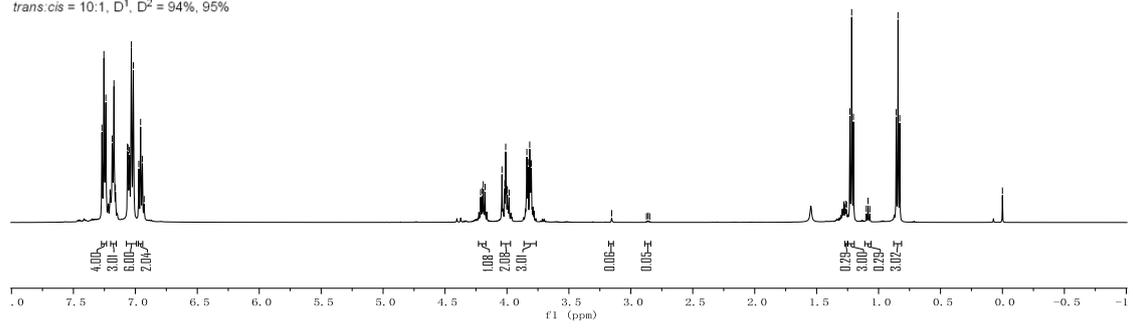






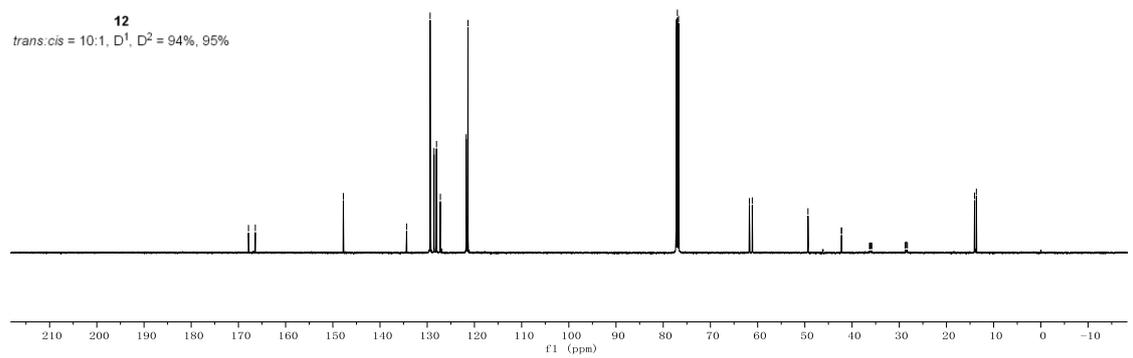
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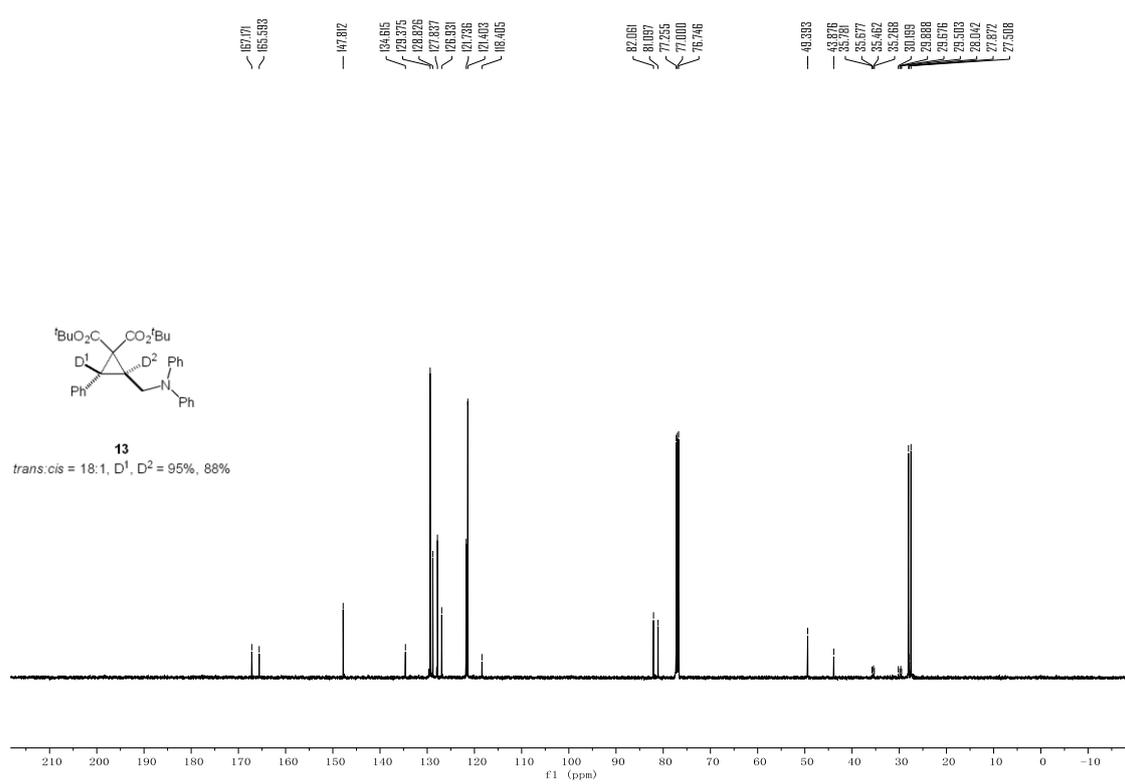
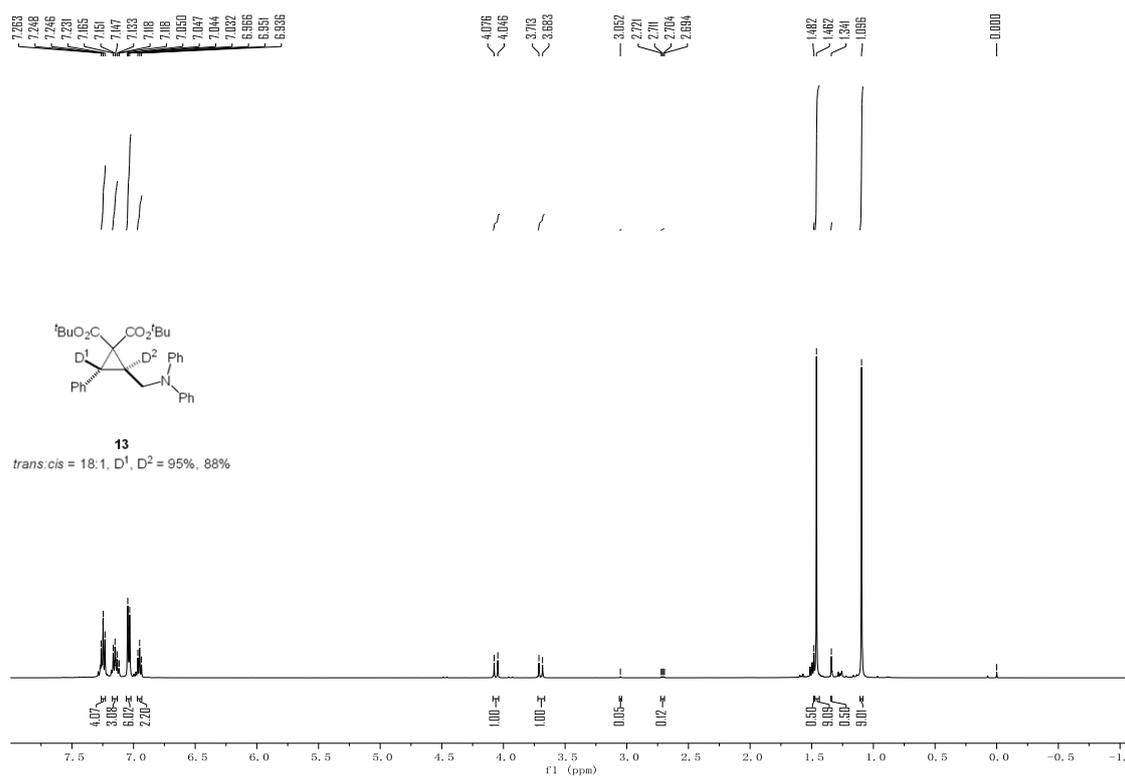
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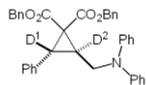
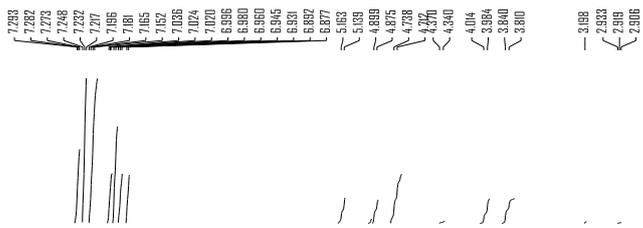


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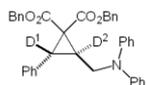
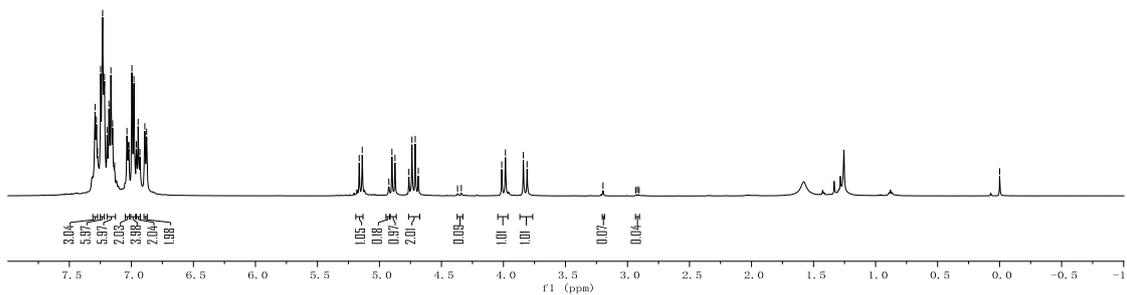






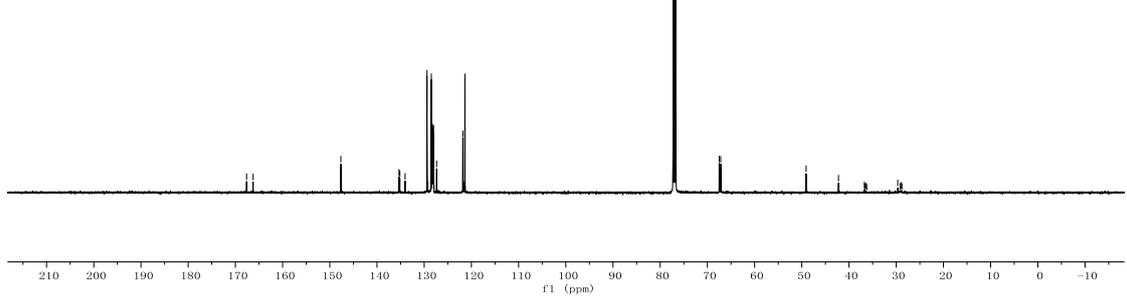
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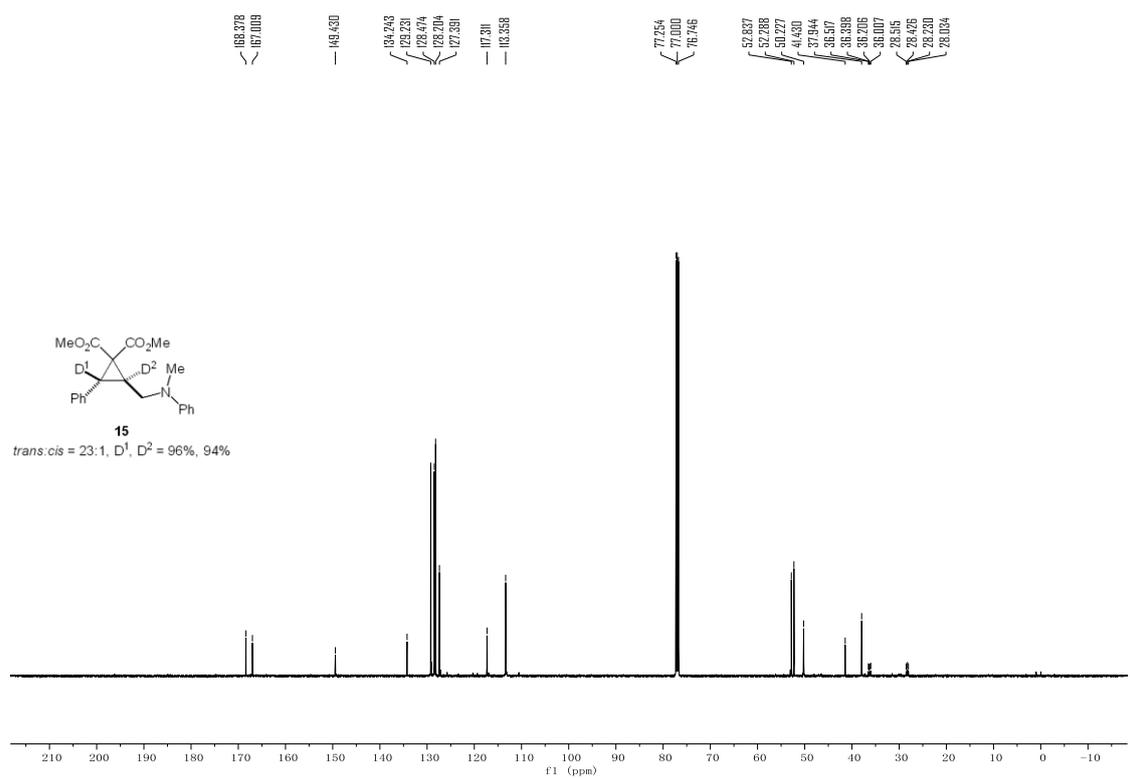
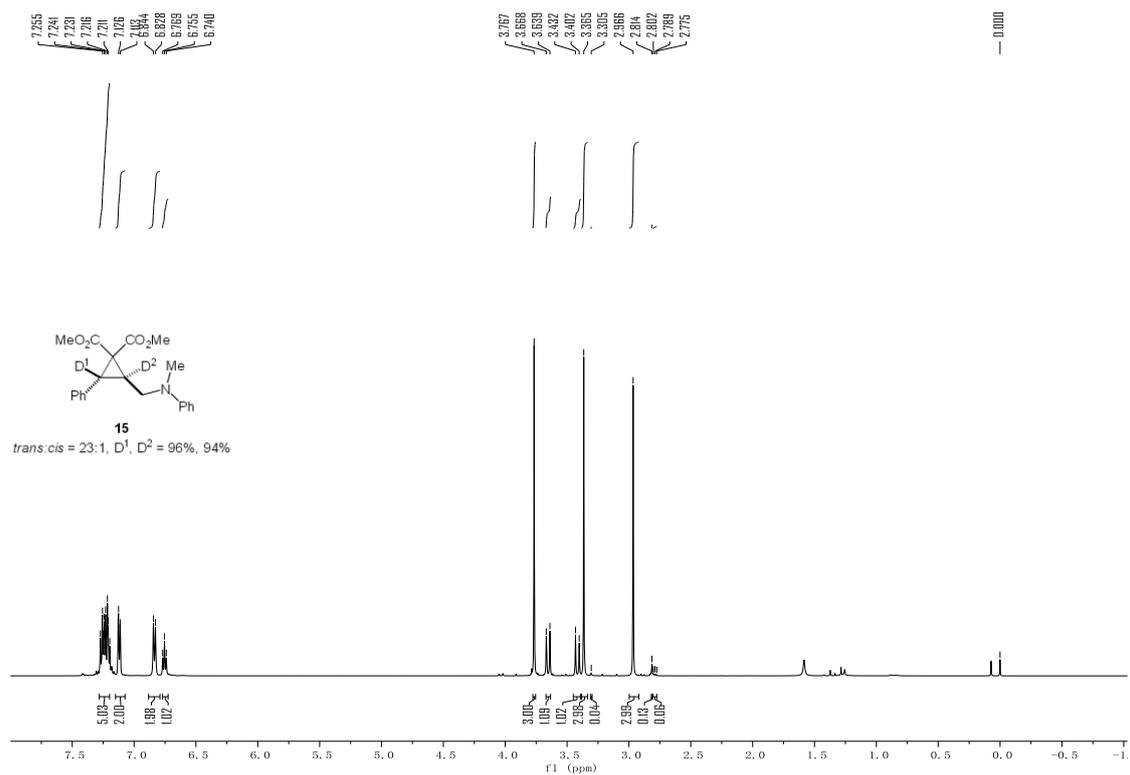
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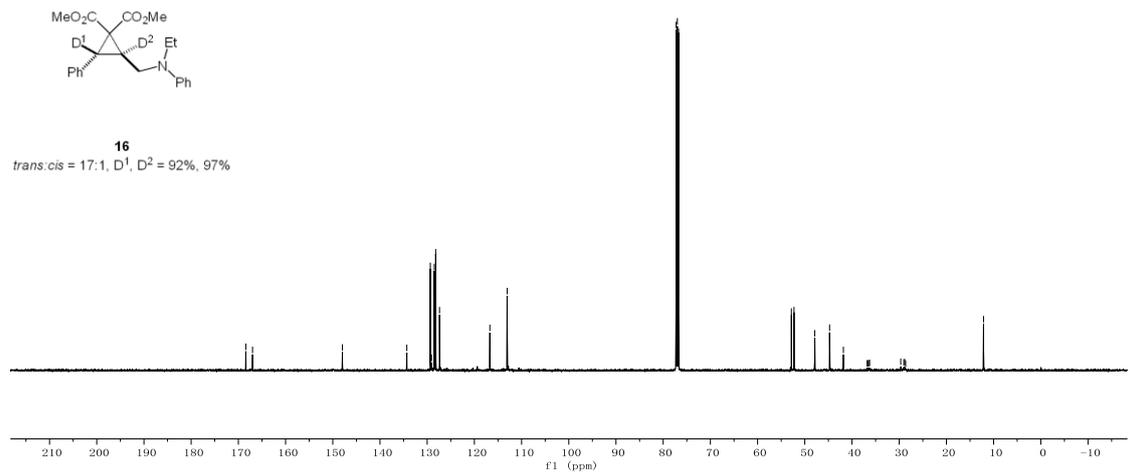
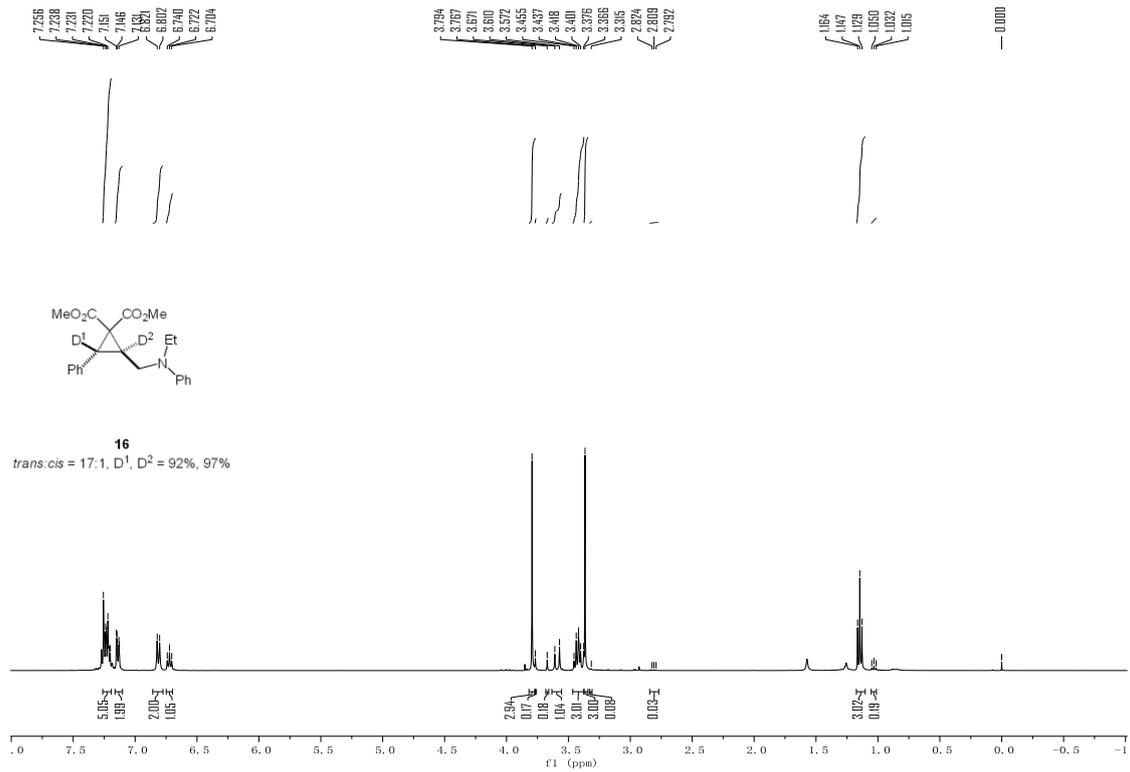


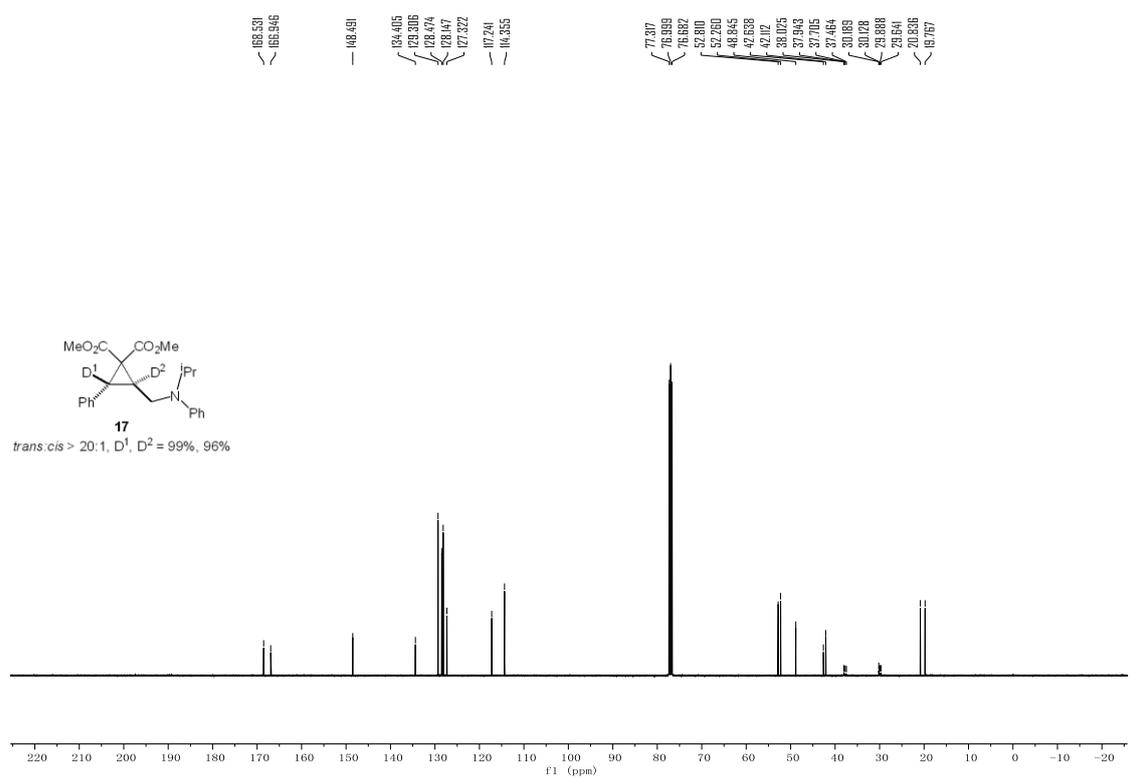
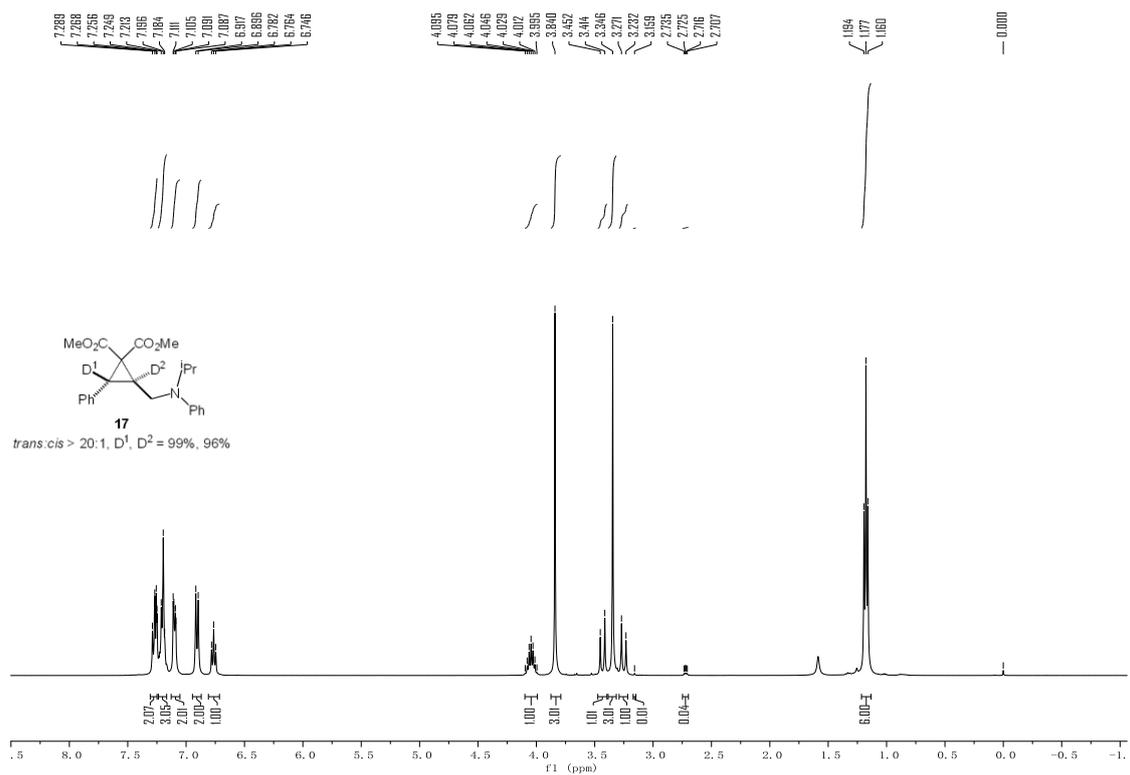
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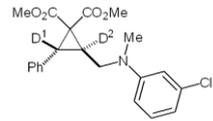
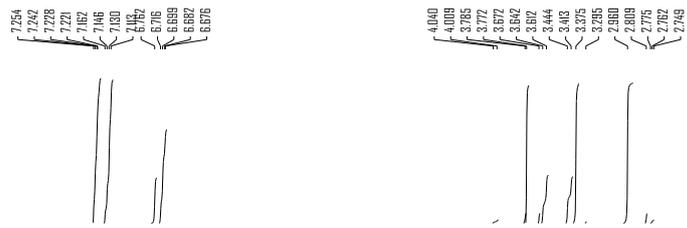
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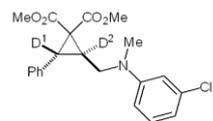
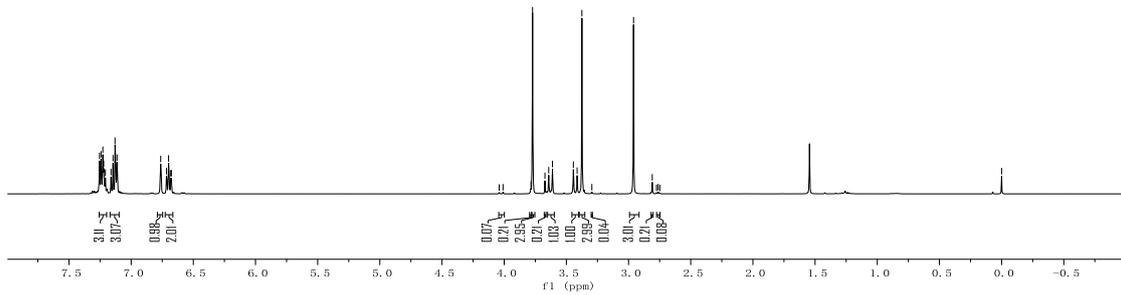




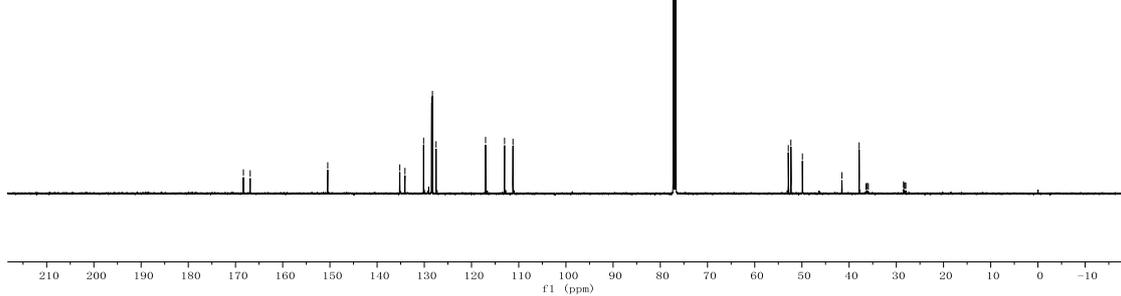


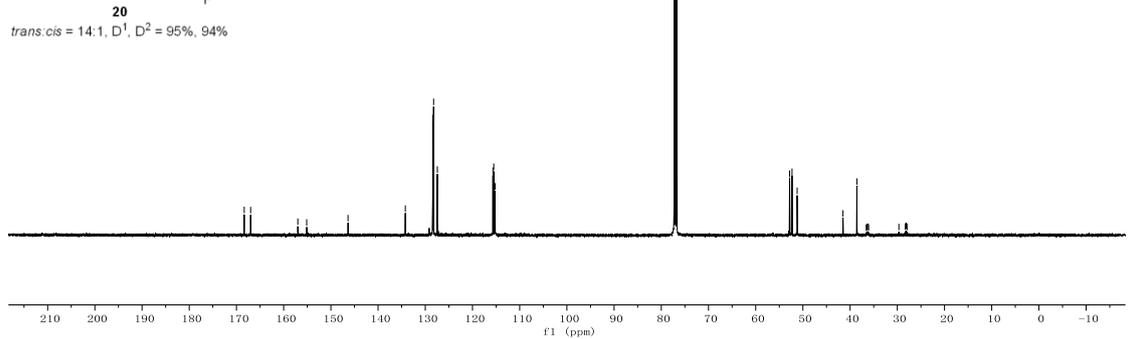
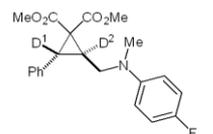
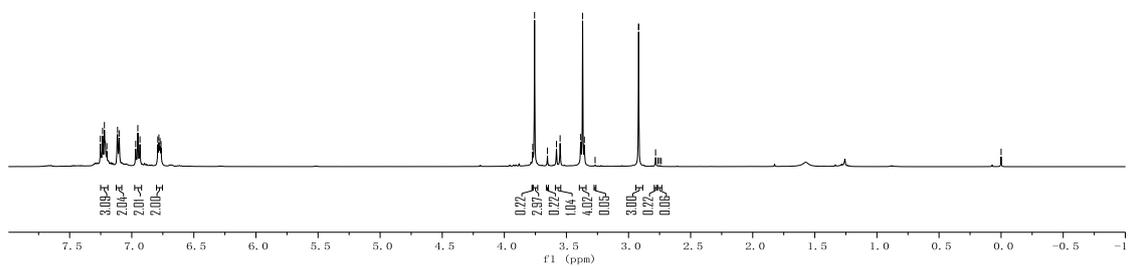
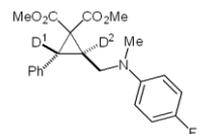


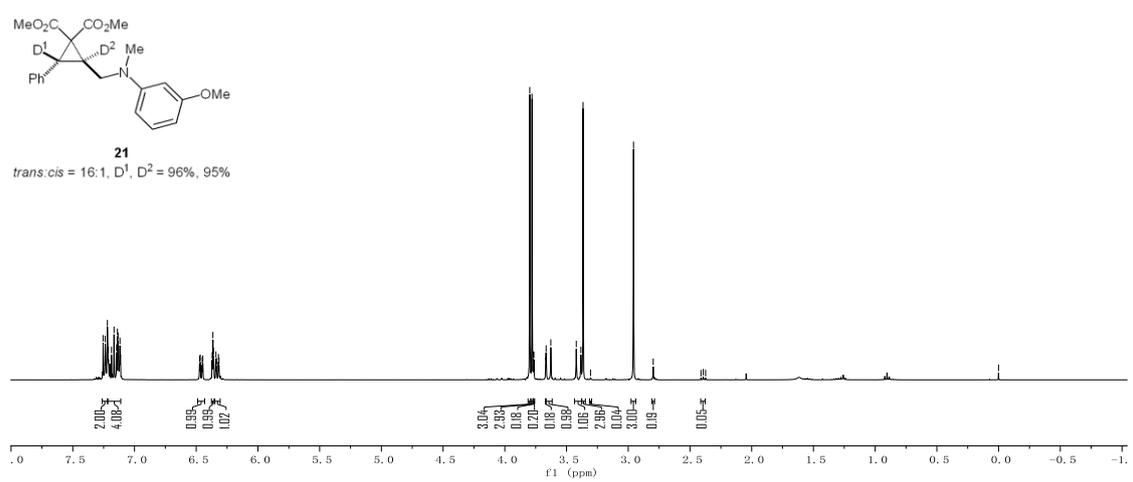
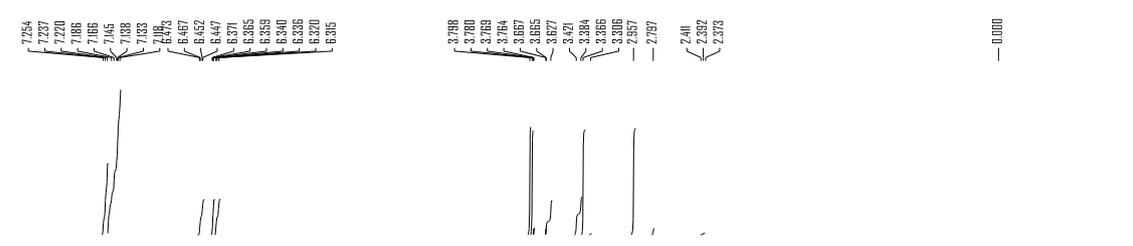
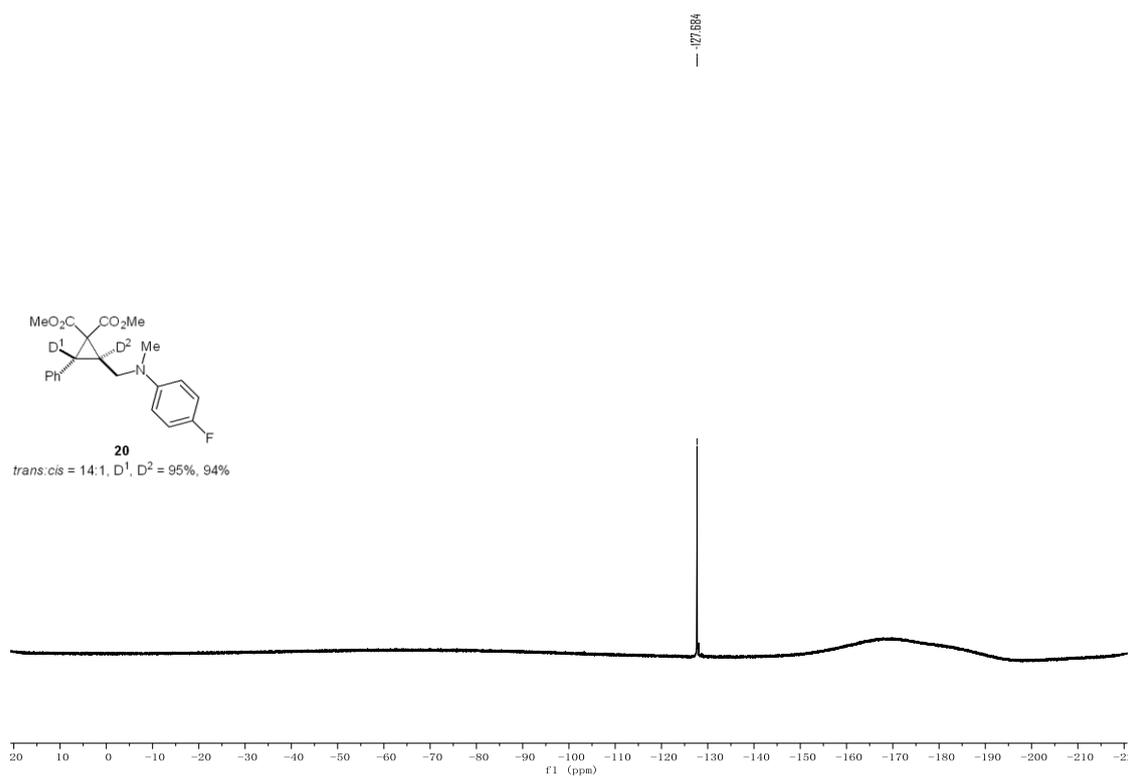
19
trans:*cis* = 14:1, D¹, D² = 96%, 92%

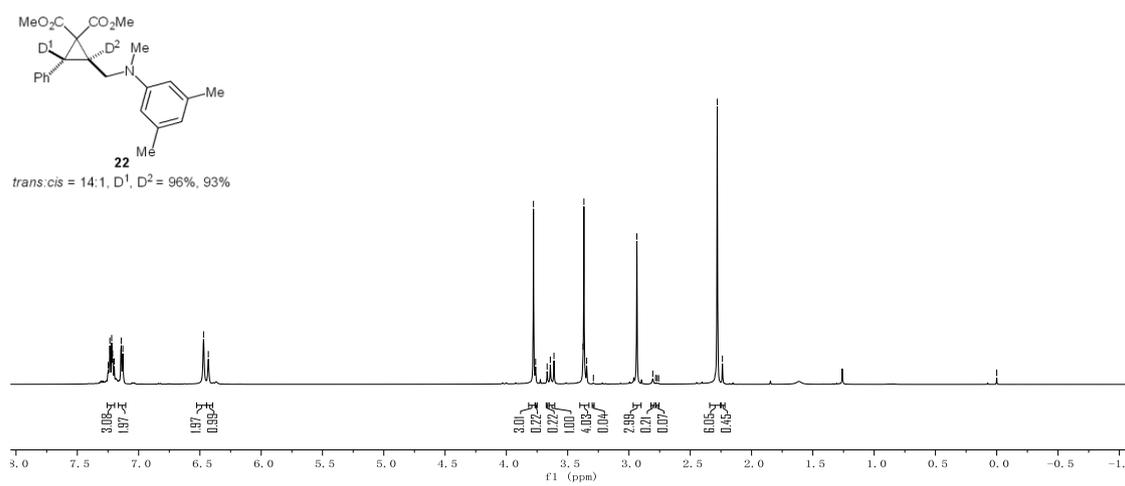
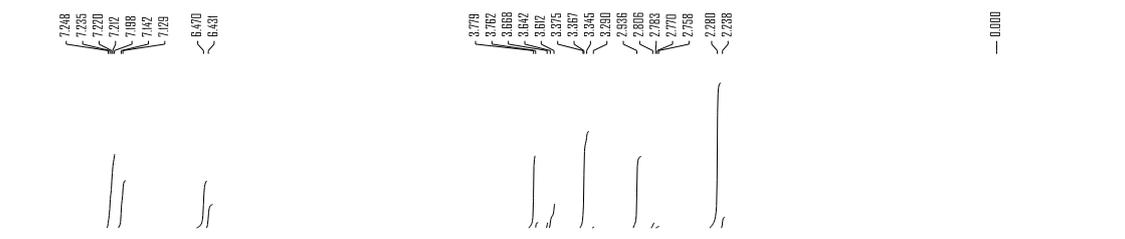
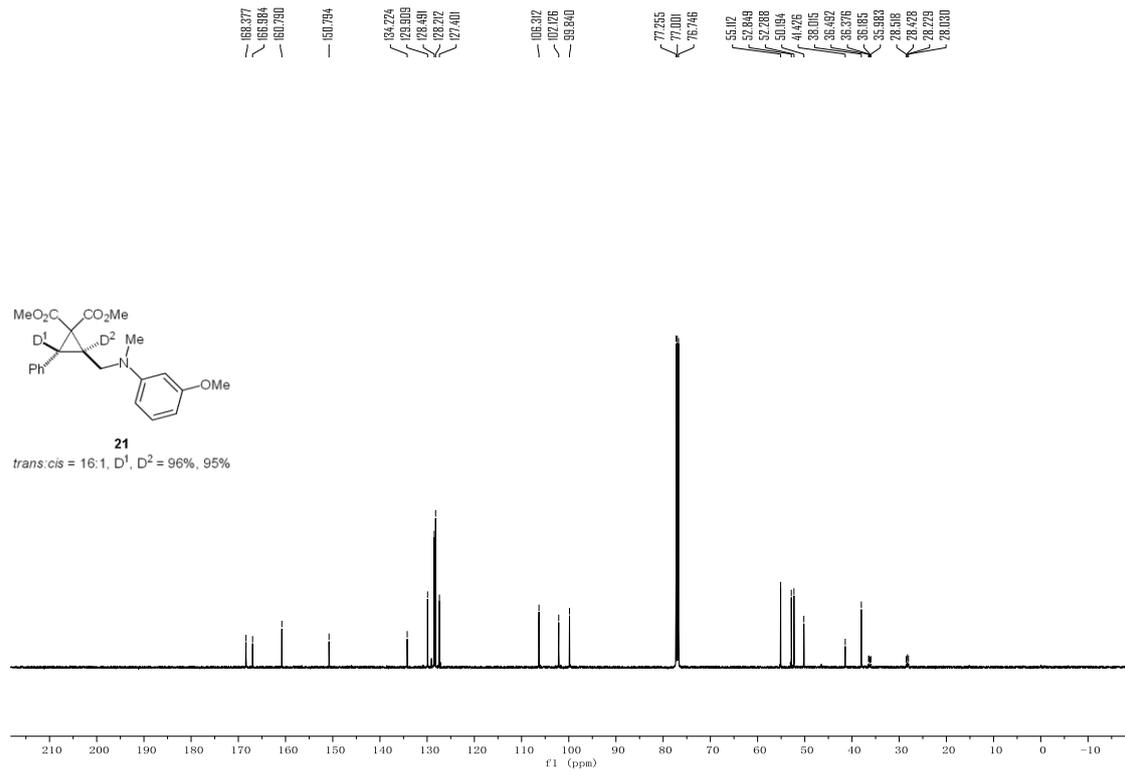


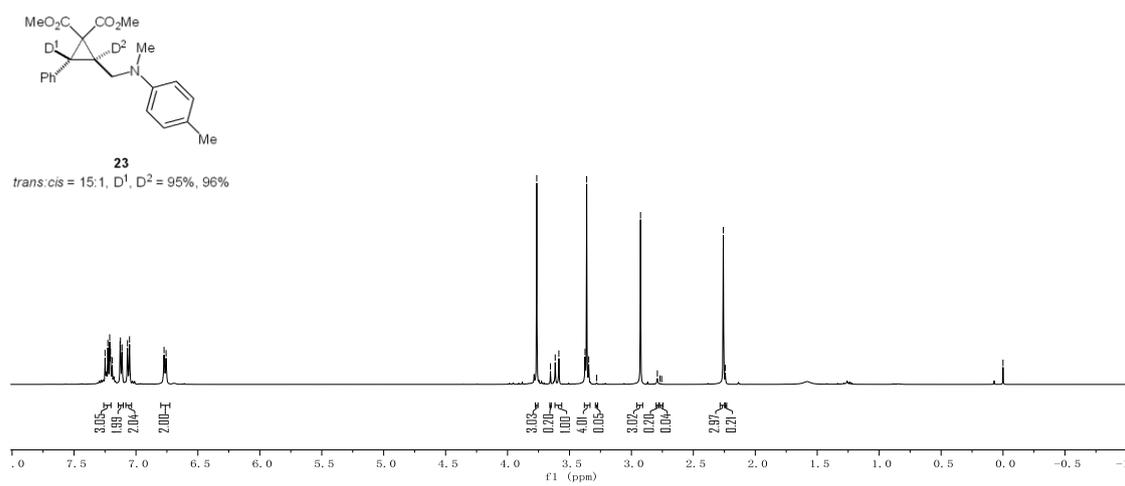
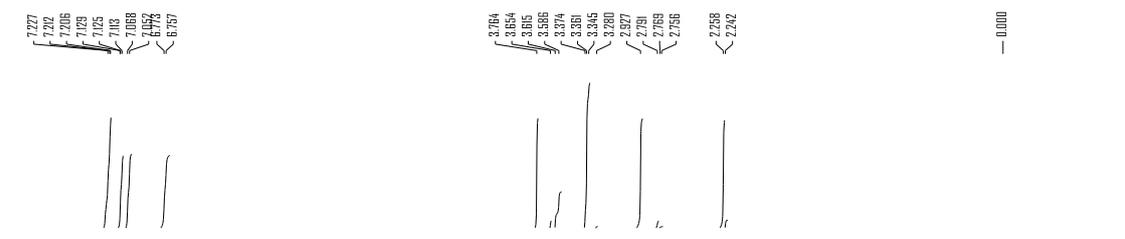
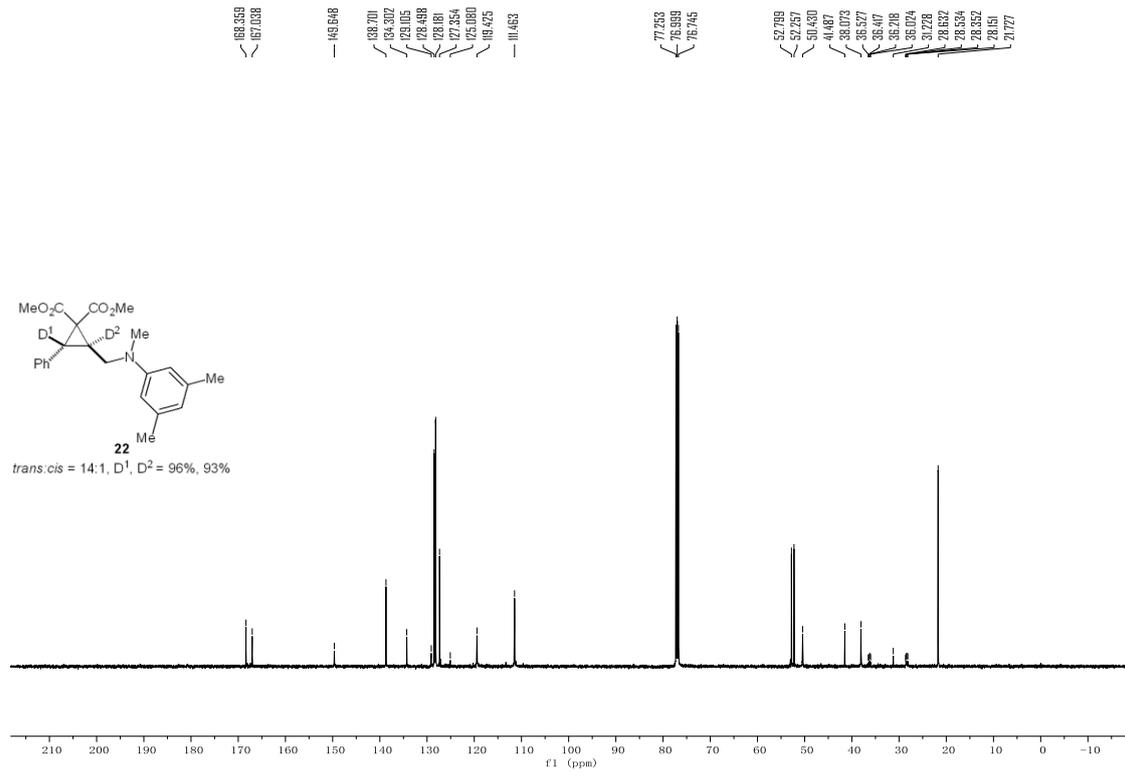
19
trans:*cis* = 14:1, D¹, D² = 96%, 92%

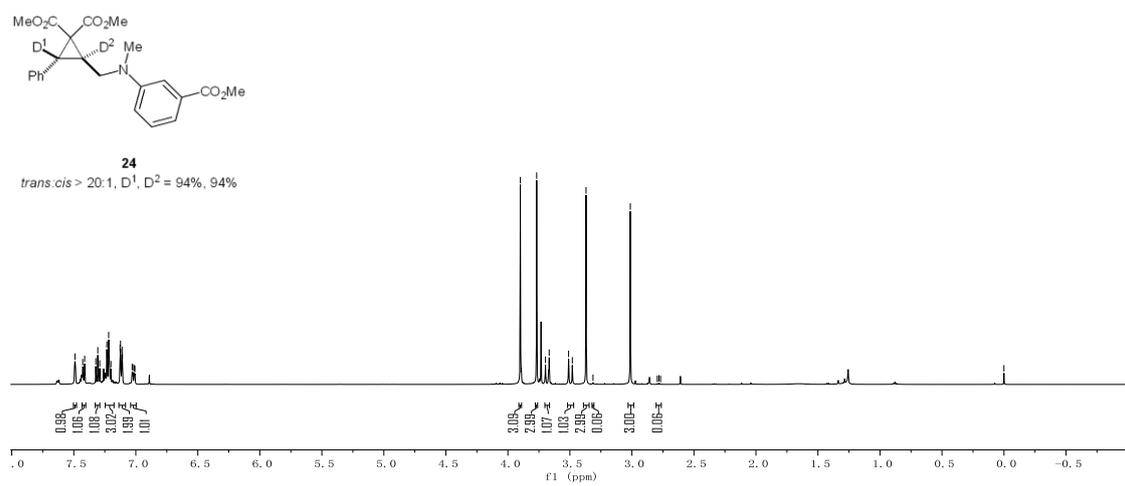
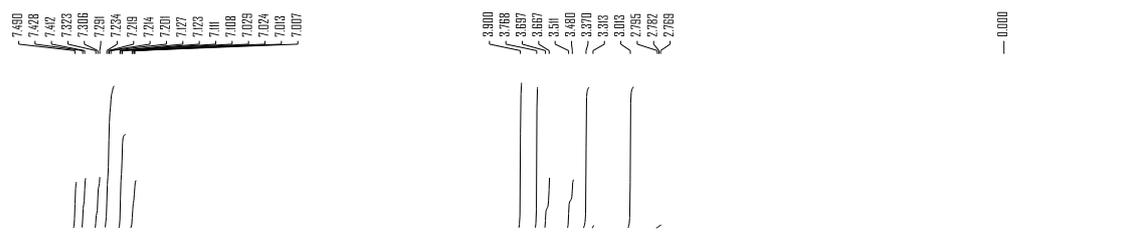
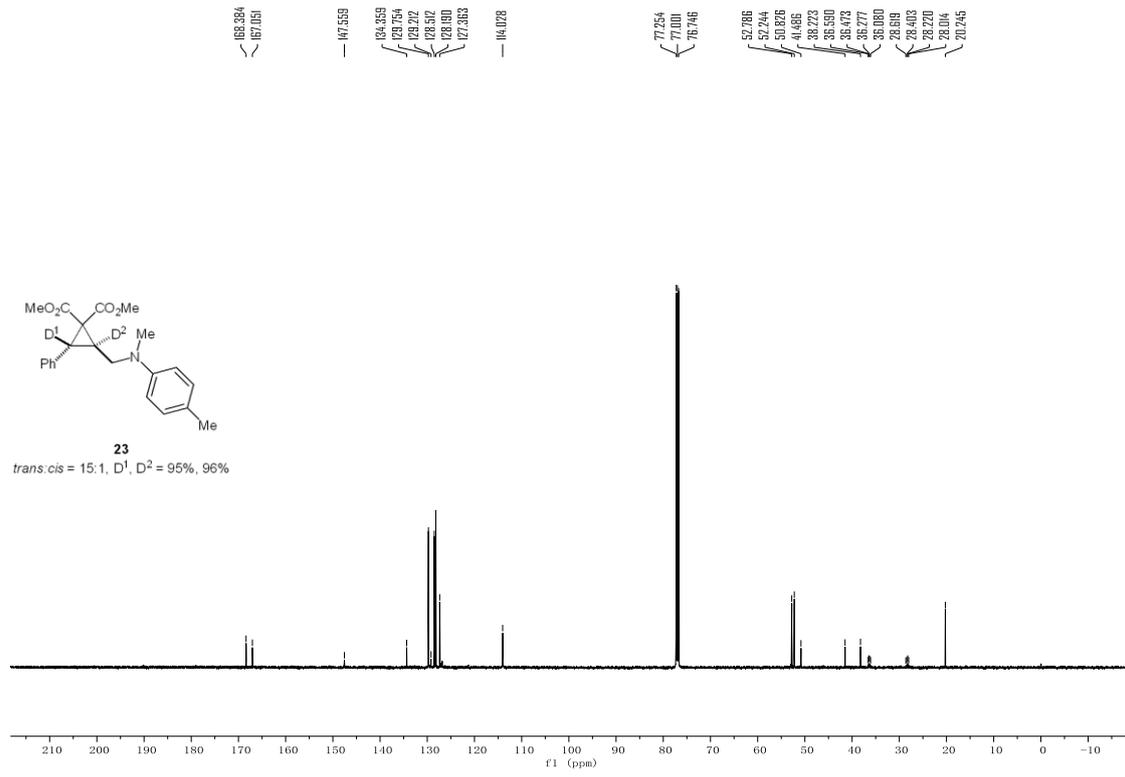












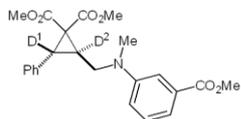
169.214
167.574
166.867

149.313

134.072
131.028
129.153
128.444
128.276
127.442
118.343
117.519
113.976

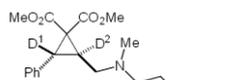
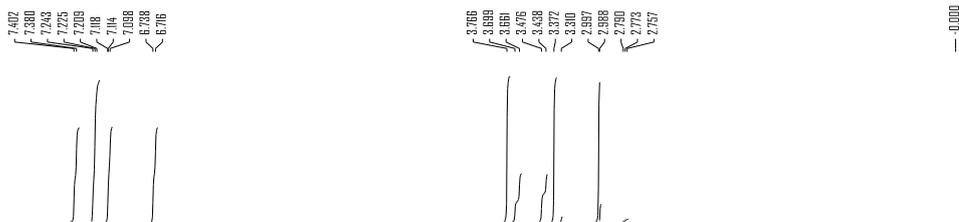
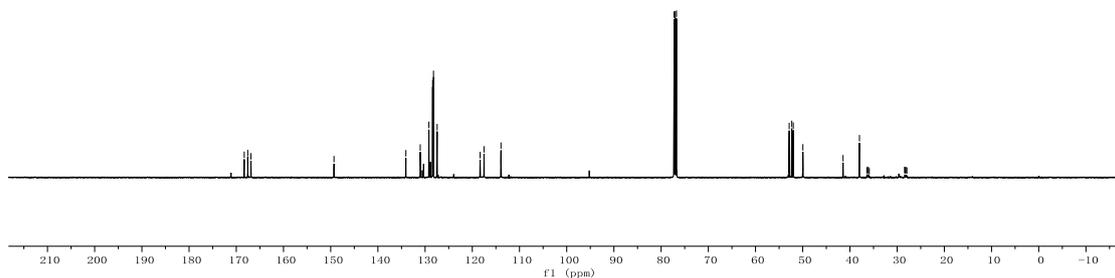
77.255
77.000
76.746

52.867
52.838
52.800
49.864
46.654
37.881
35.405
35.292
35.099
35.898
28.421
28.320
28.165
27.834



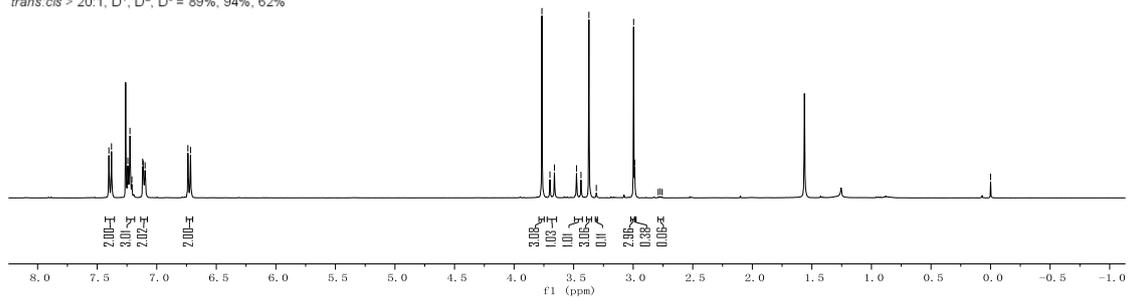
24

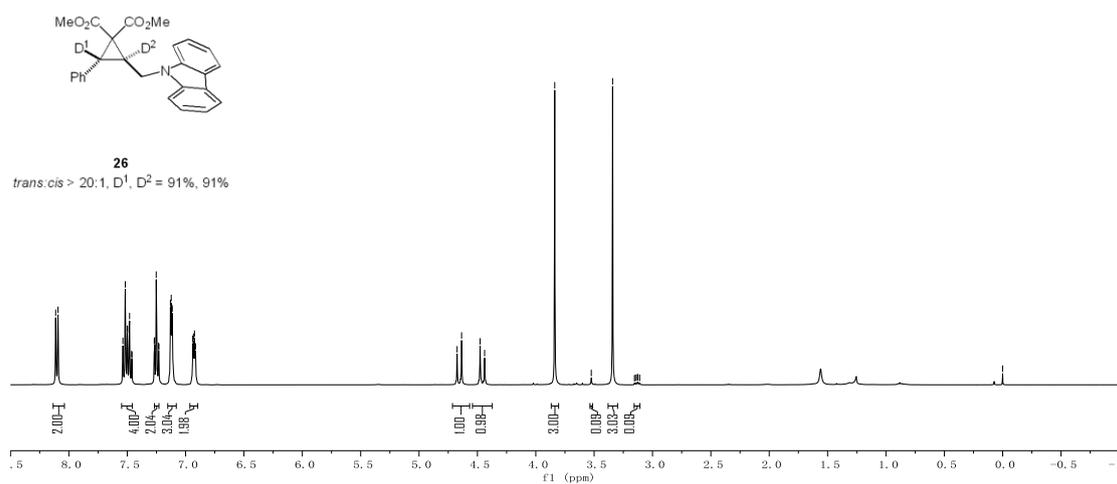
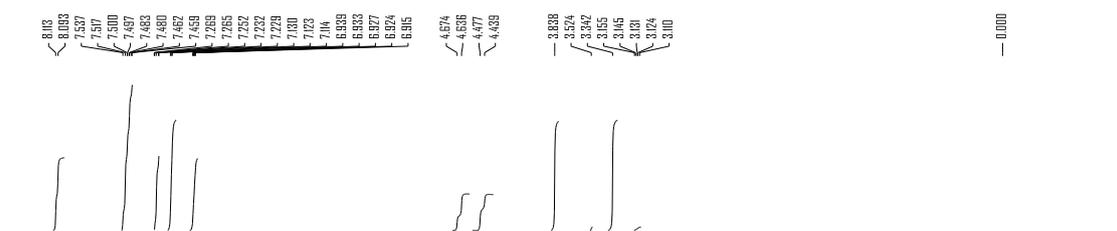
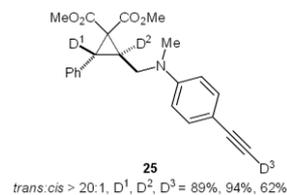
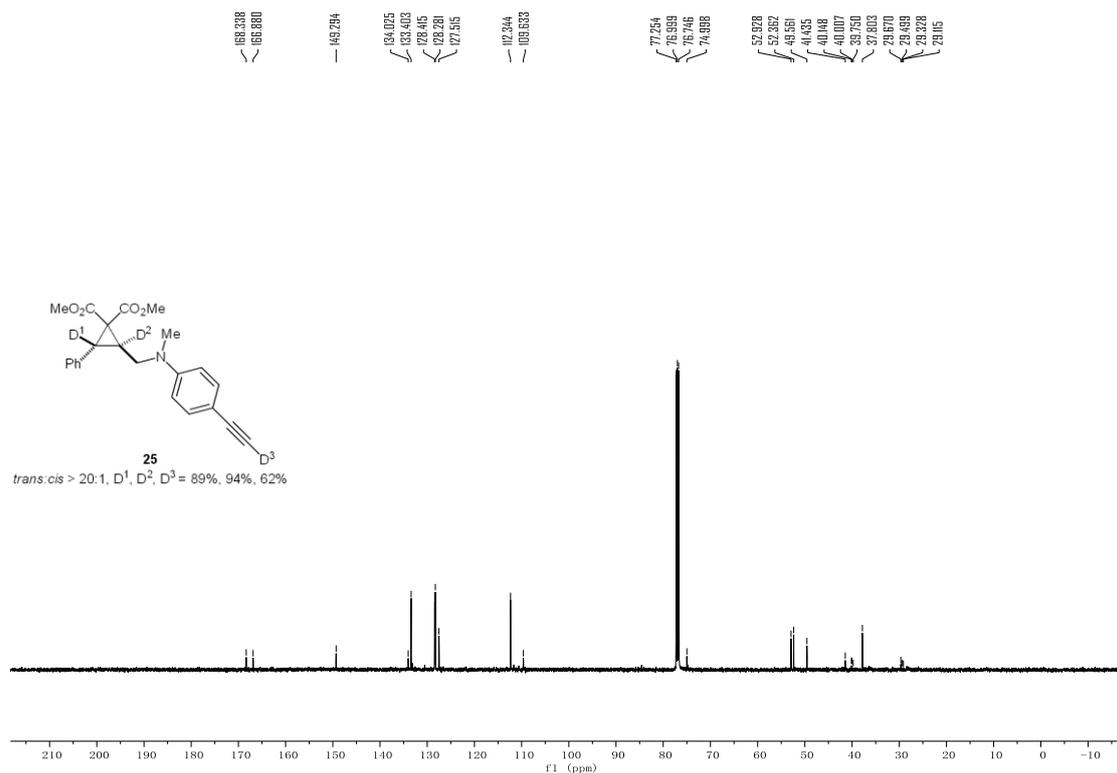
trans:cis > 20:1, D¹, D² = 94%, 94%

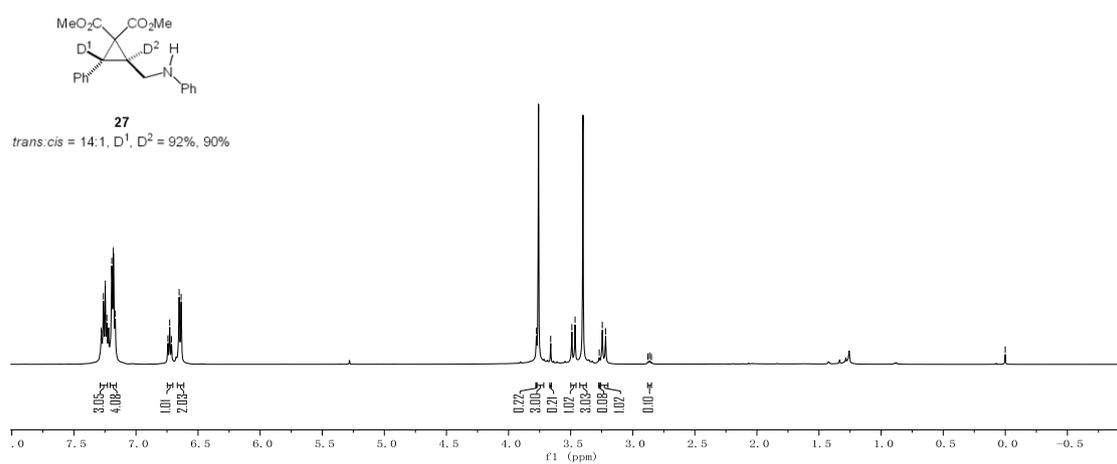
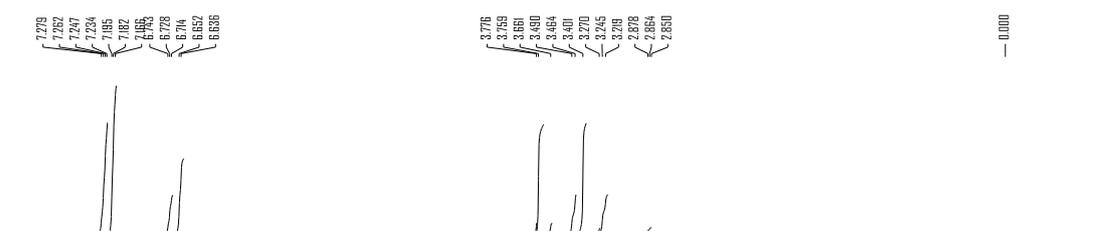
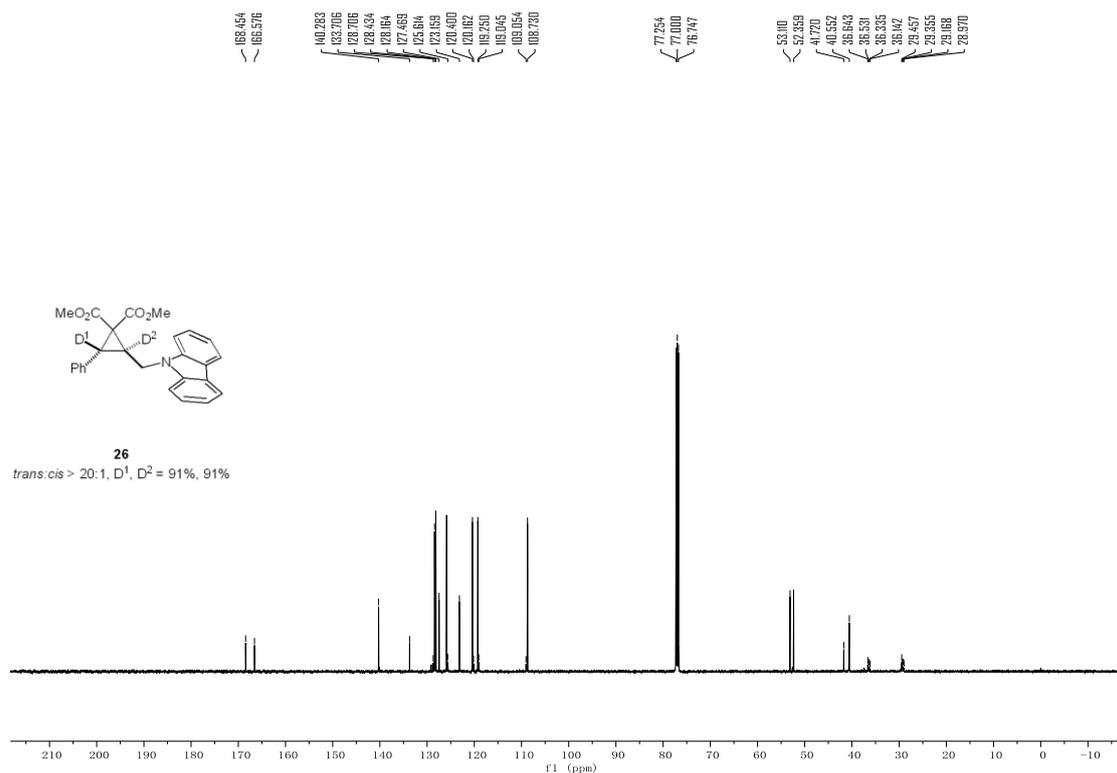


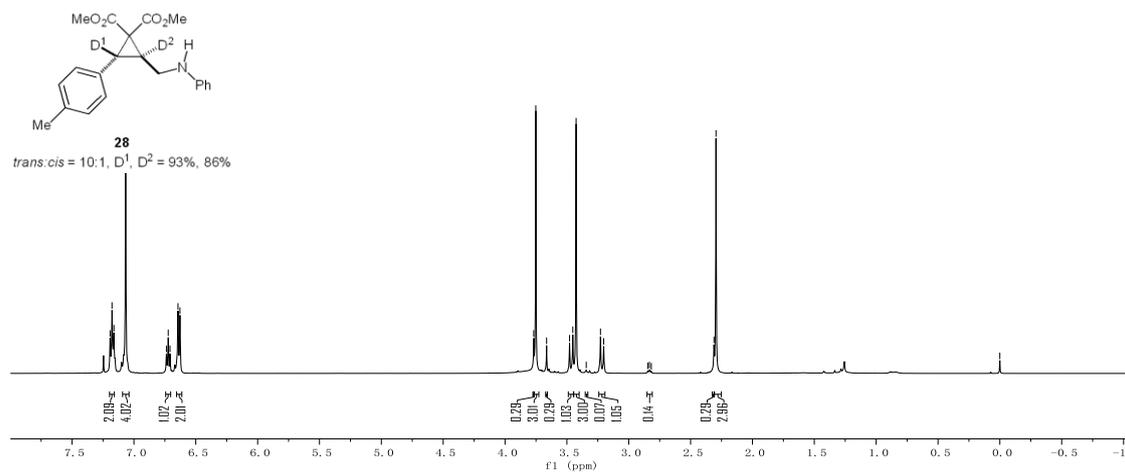
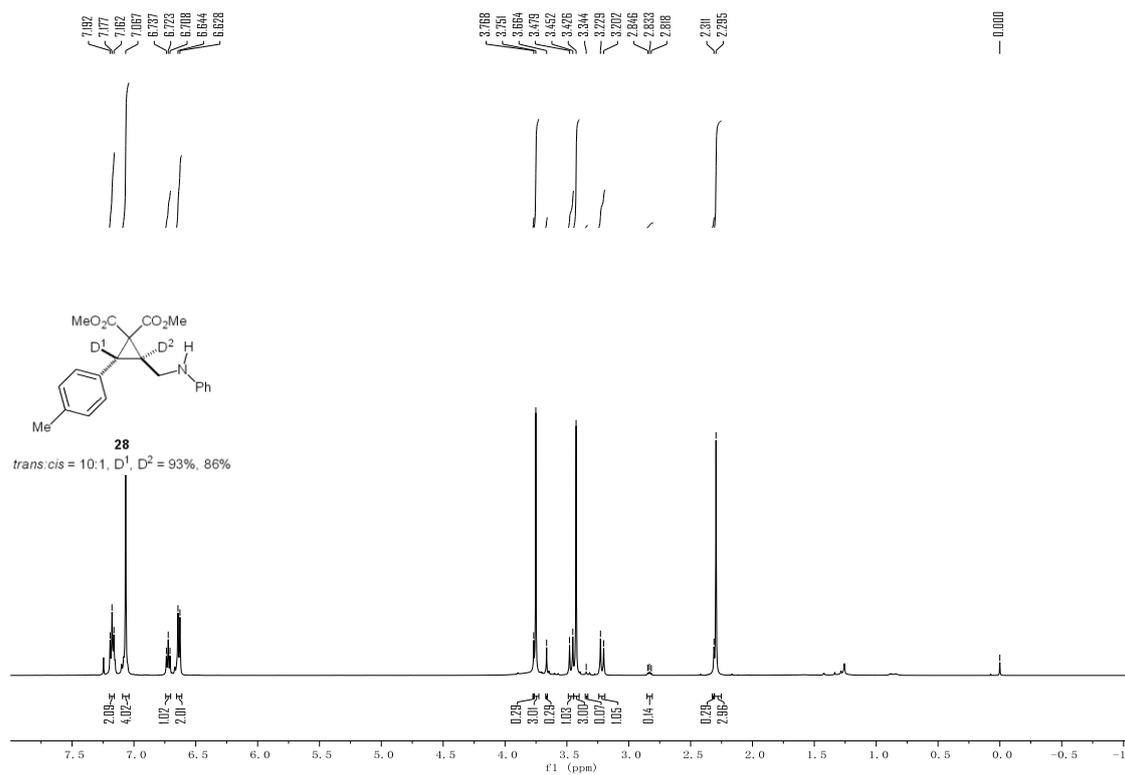
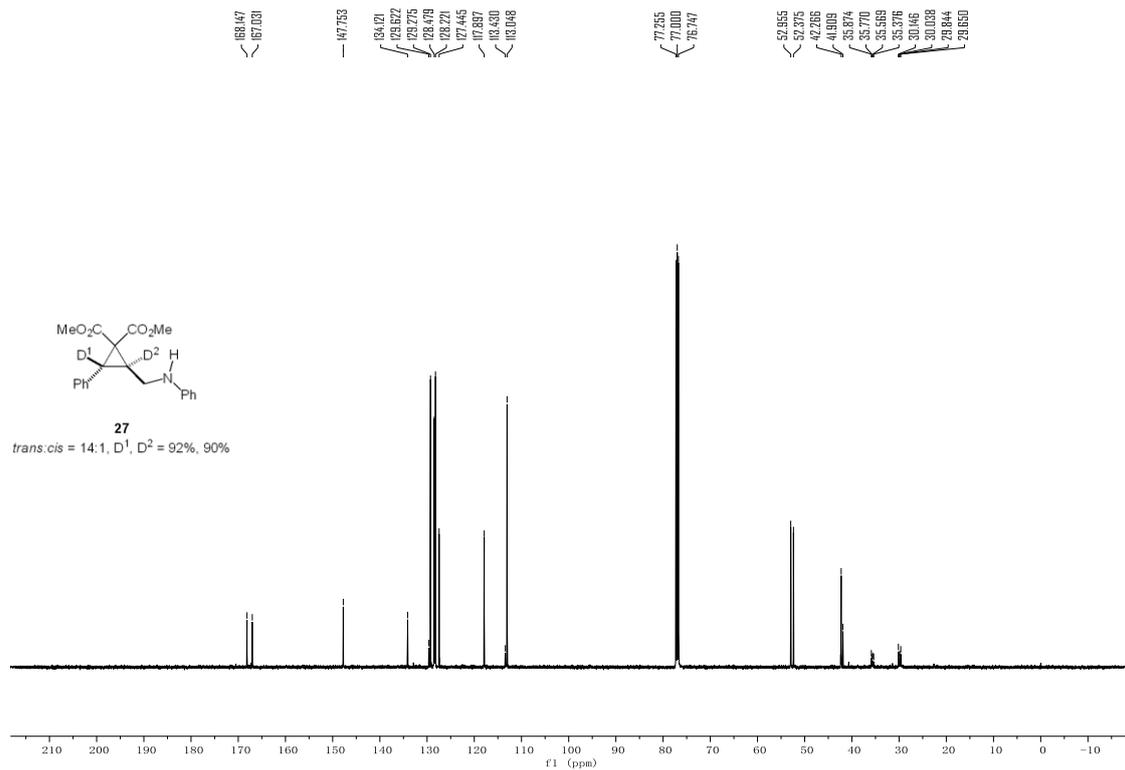
25

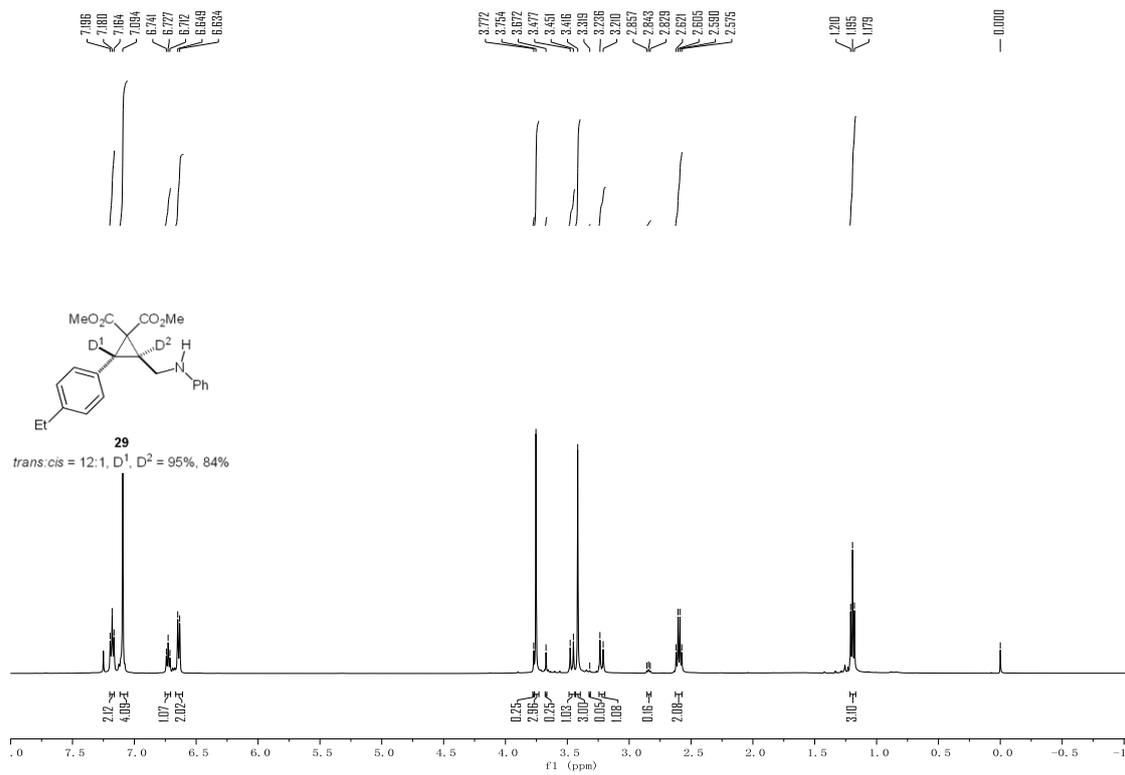
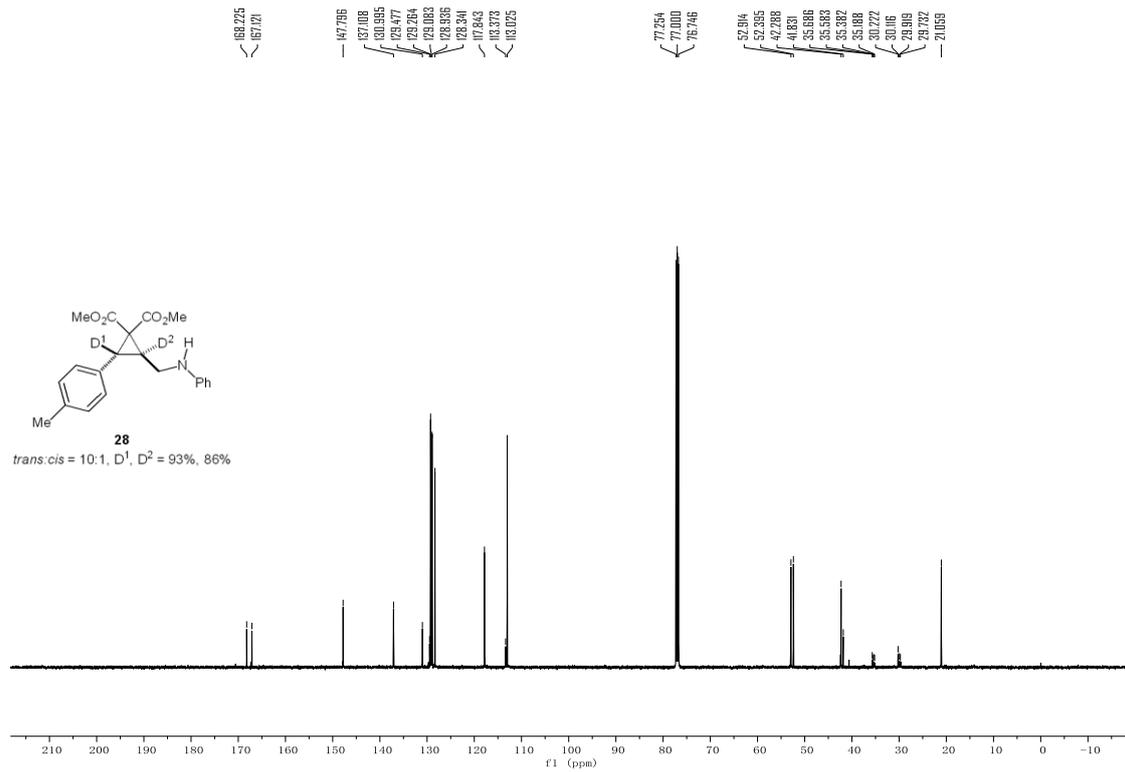
trans:cis > 20:1, D¹, D², D³ = 89%, 94%, 62%

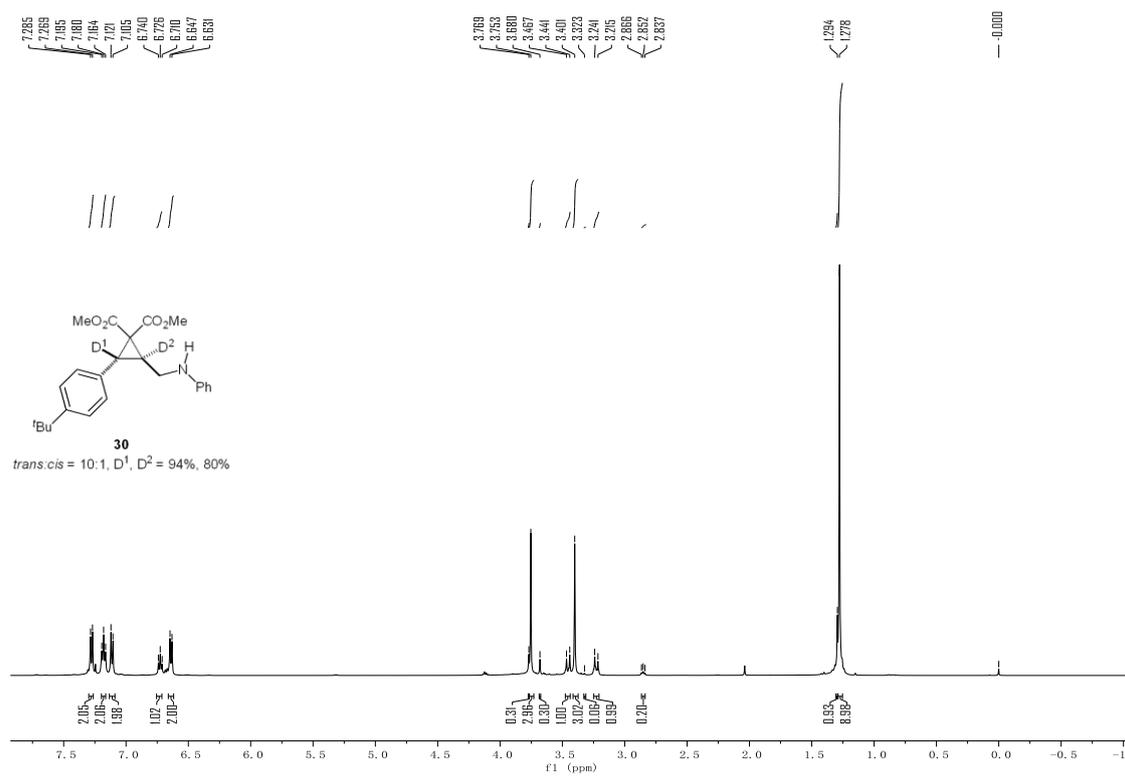
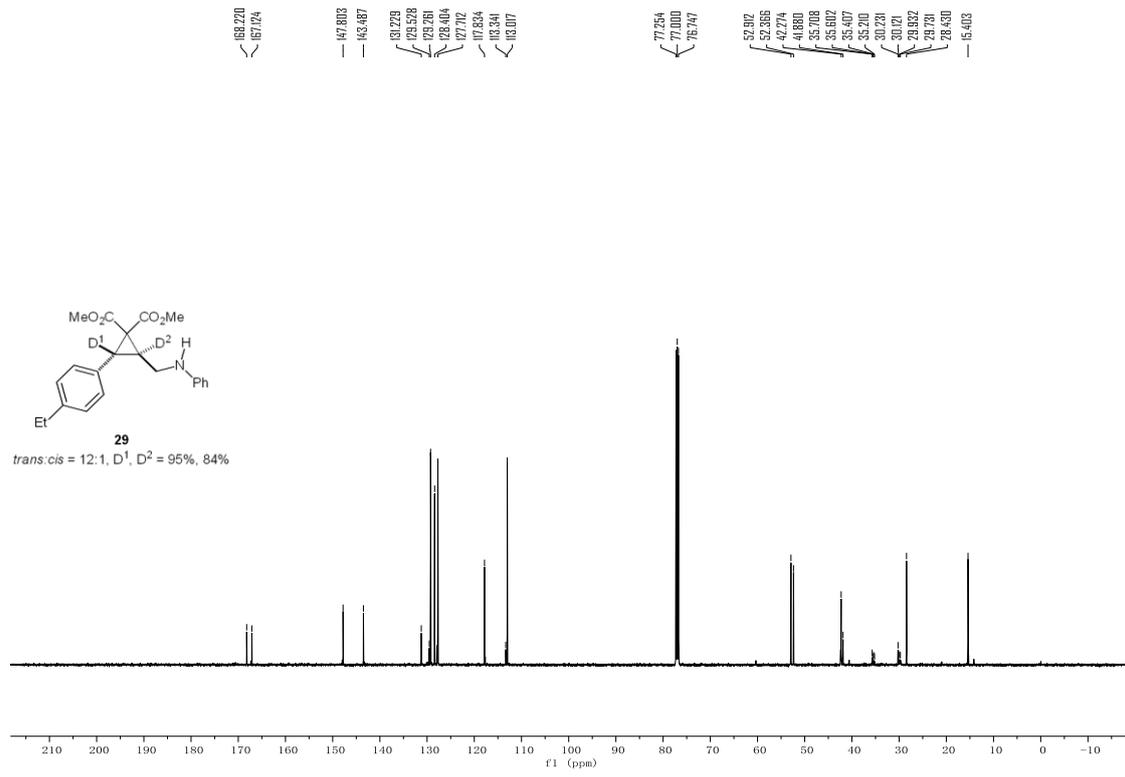


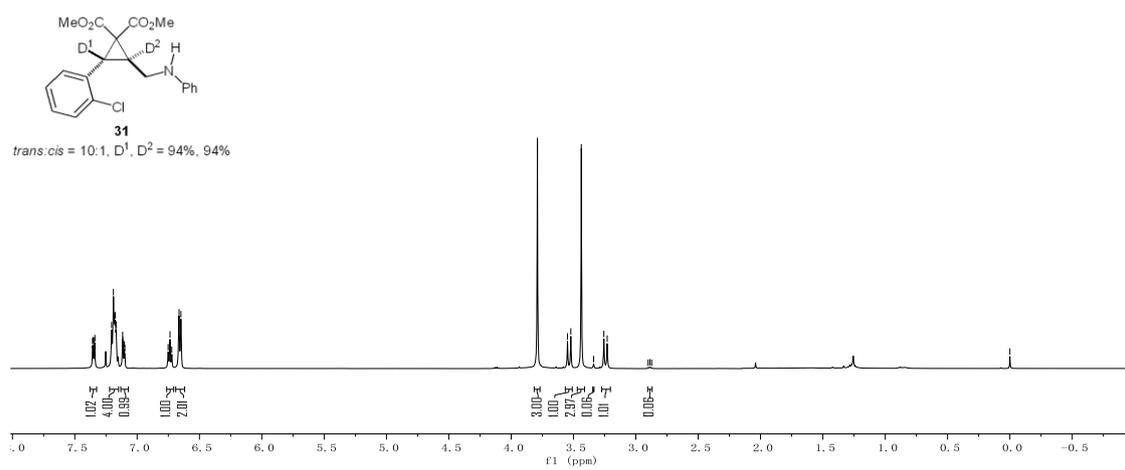
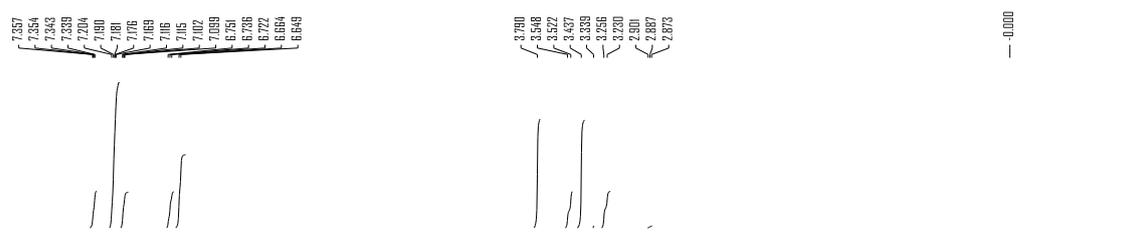
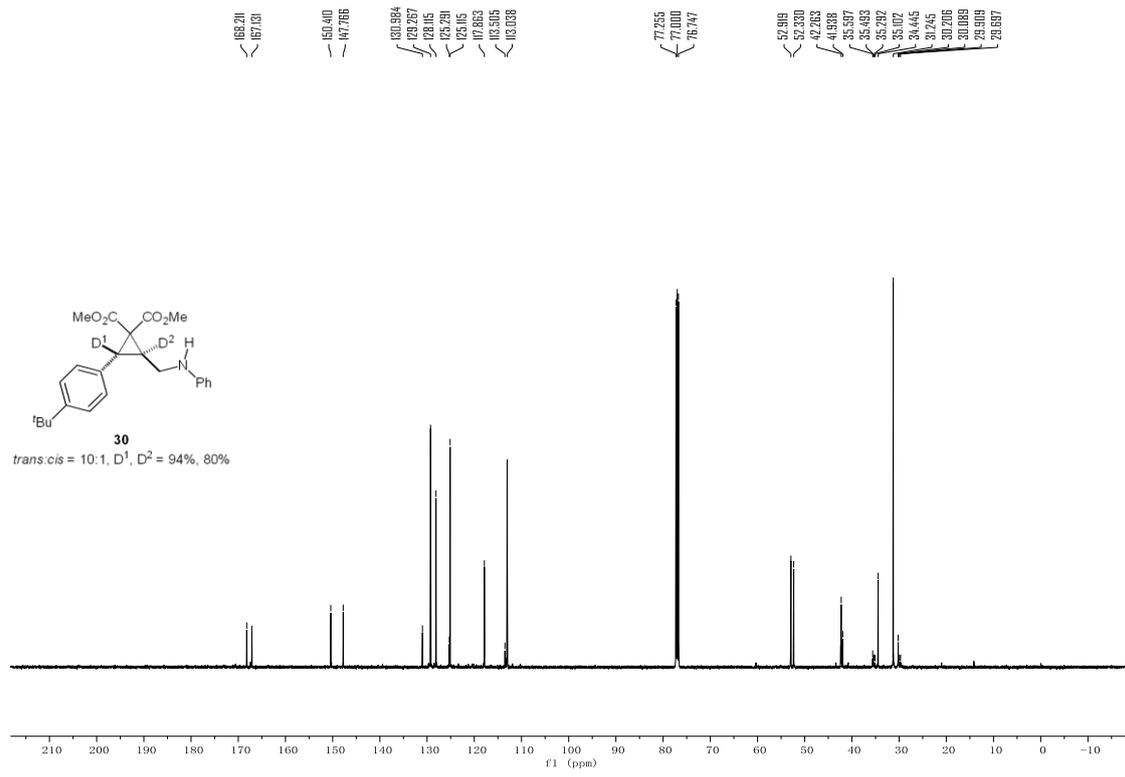


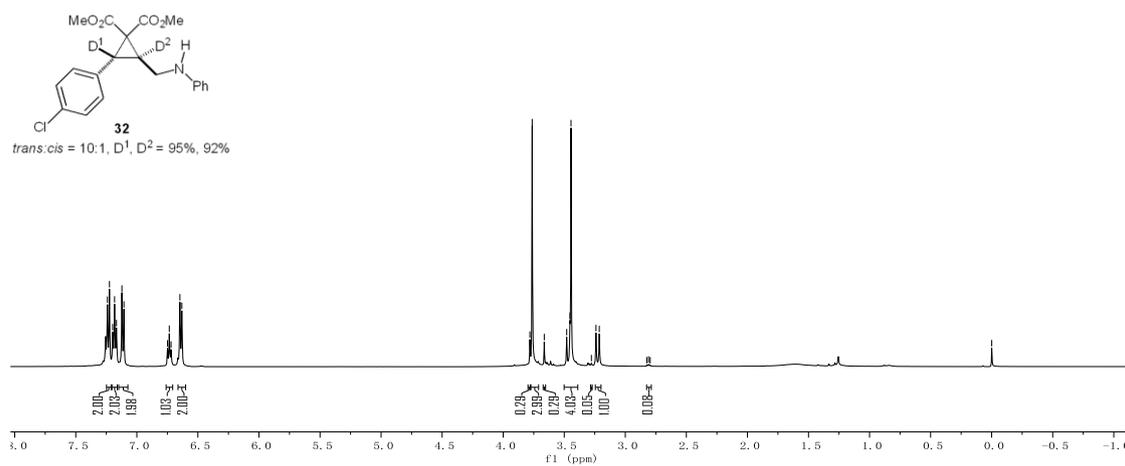
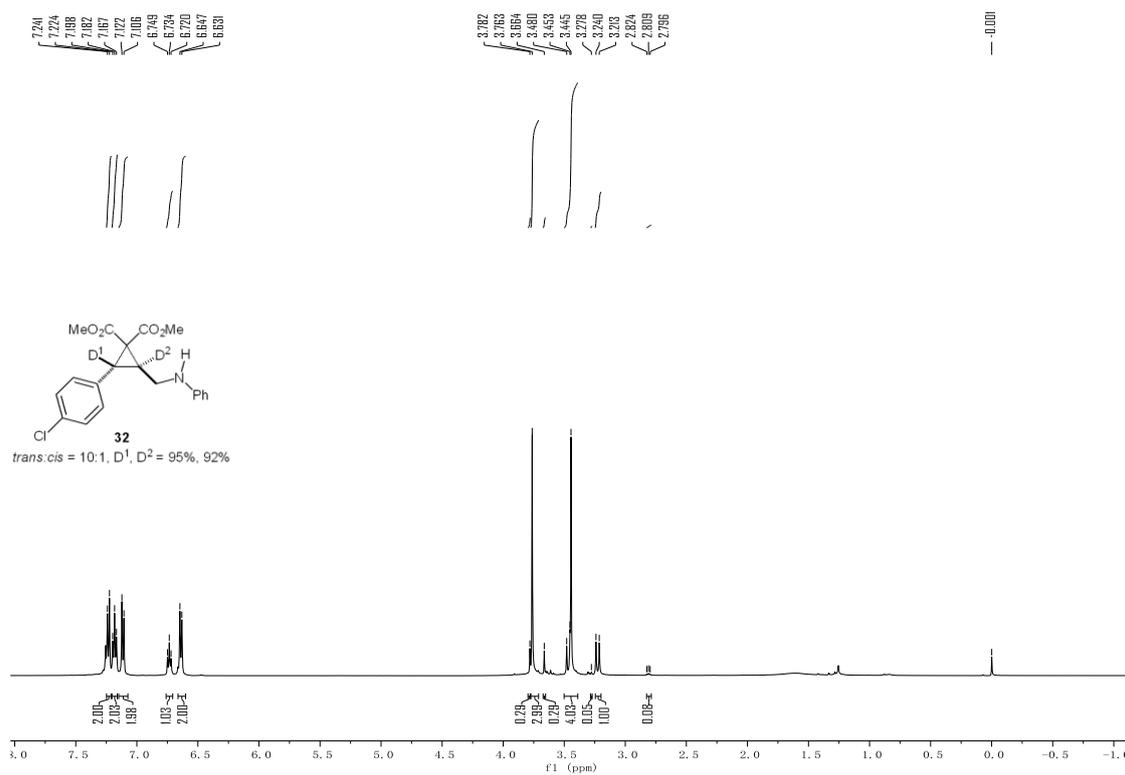
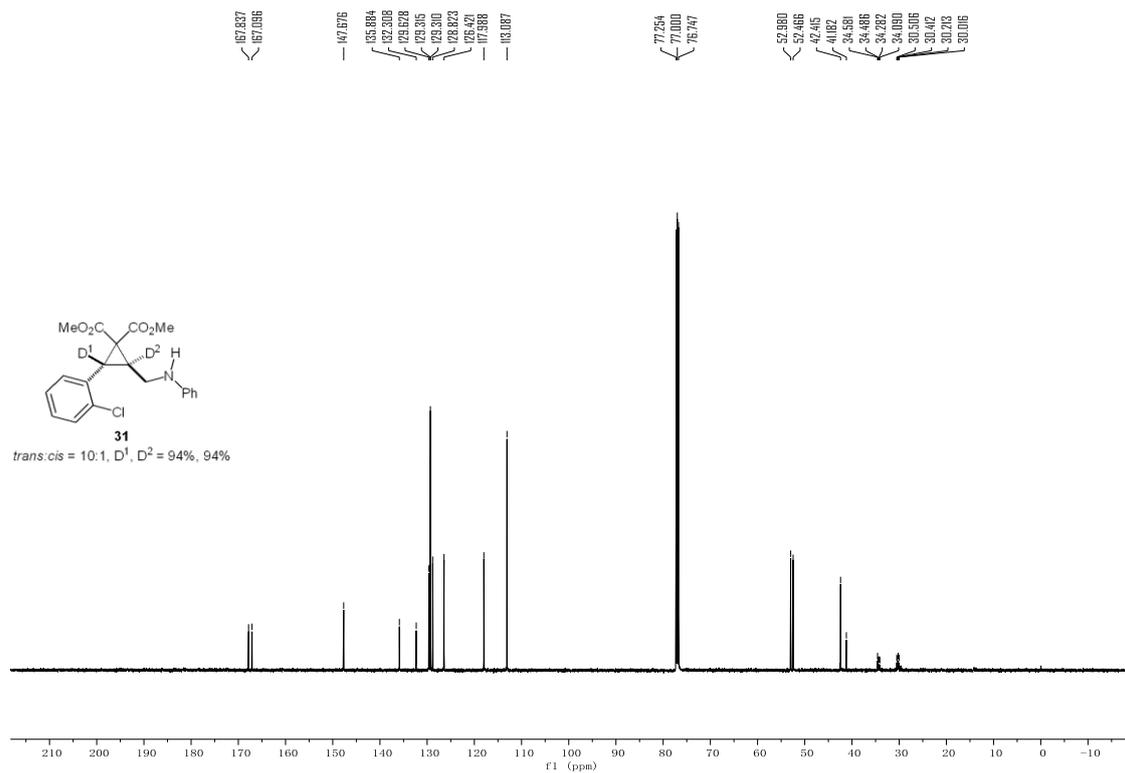


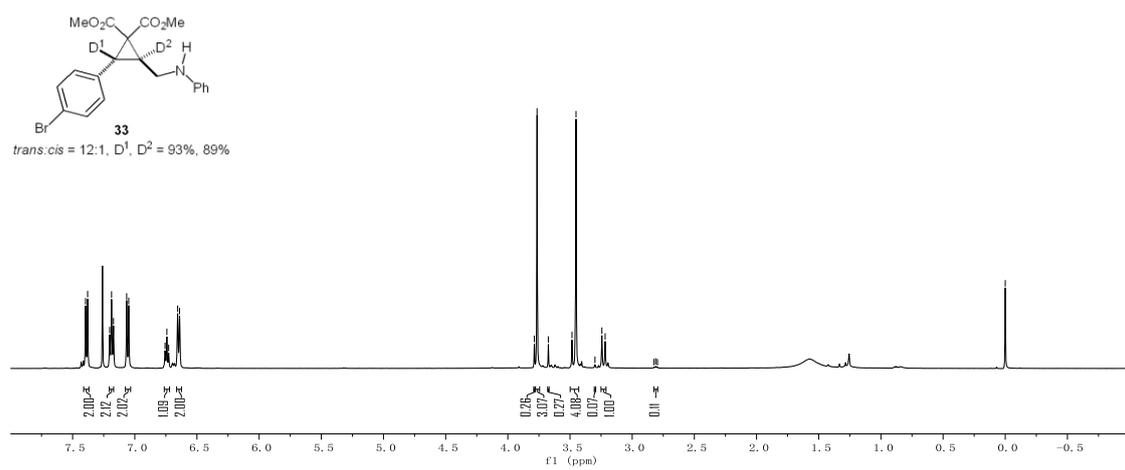
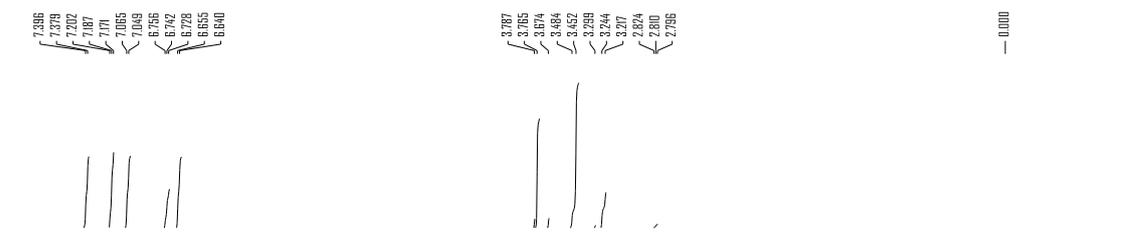
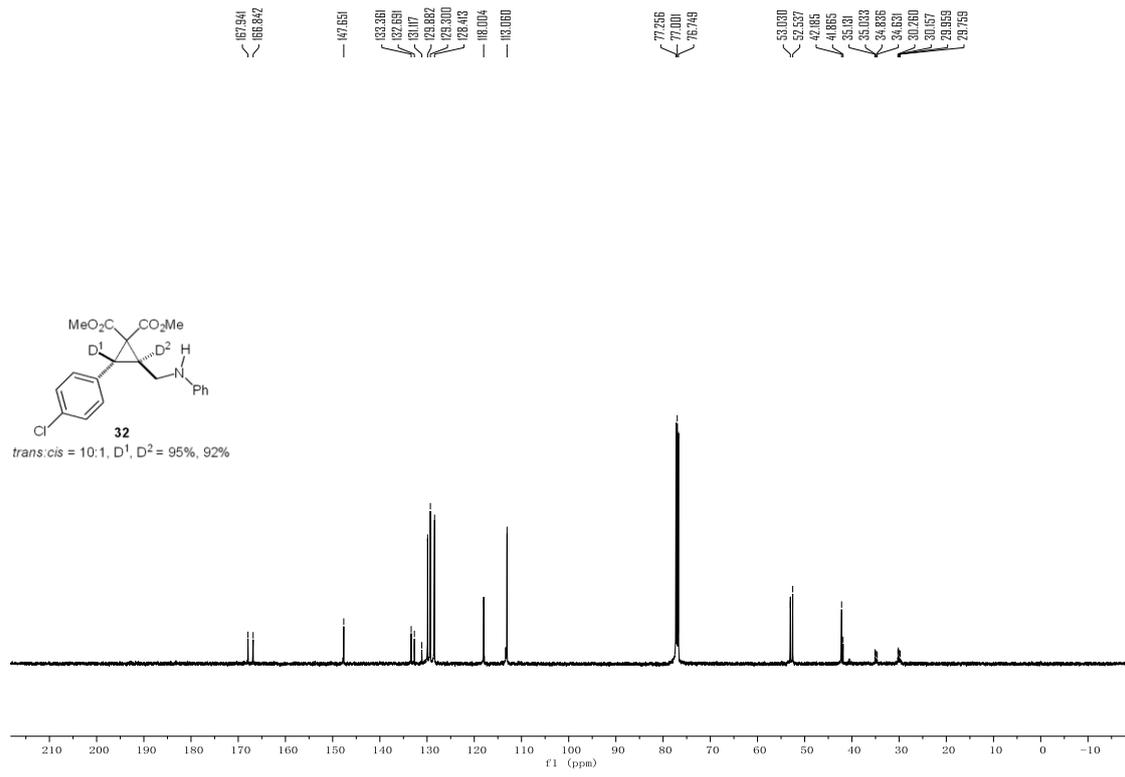


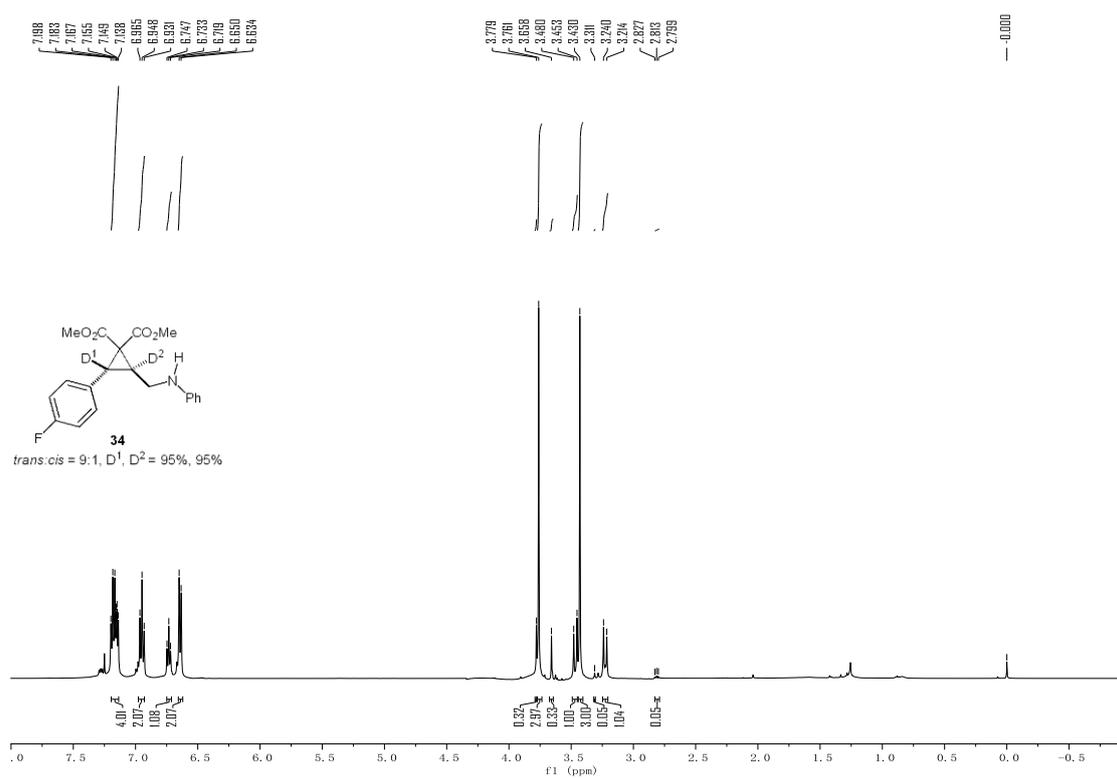
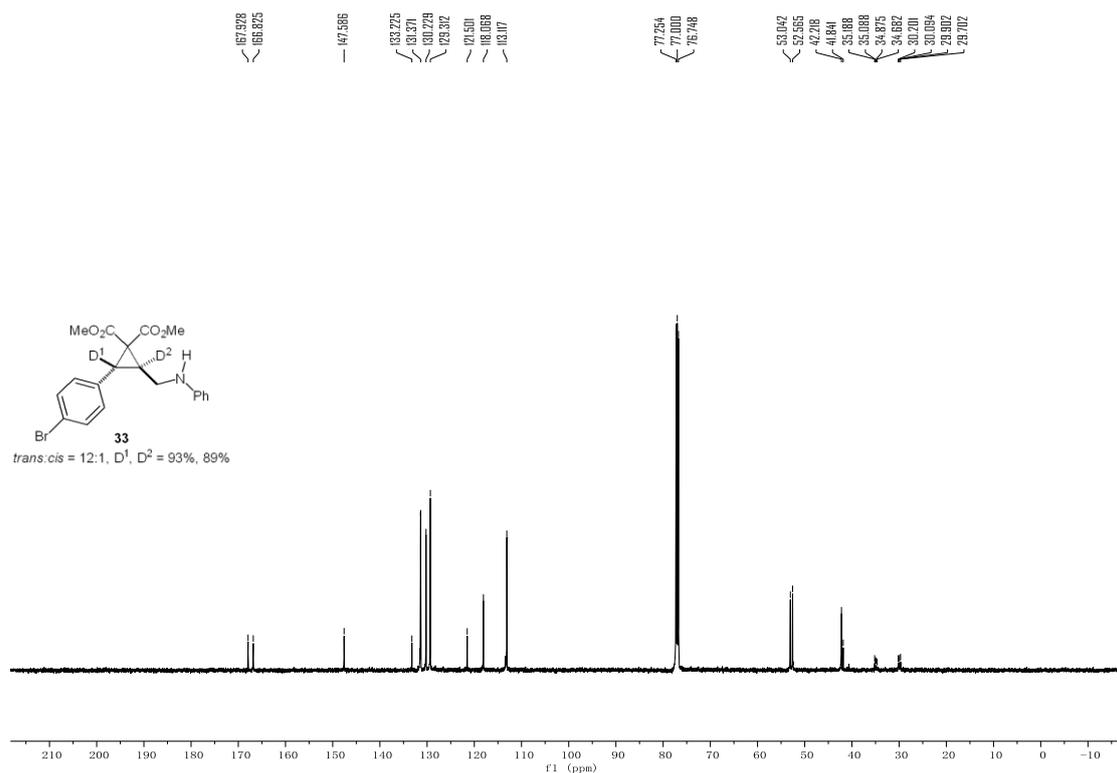




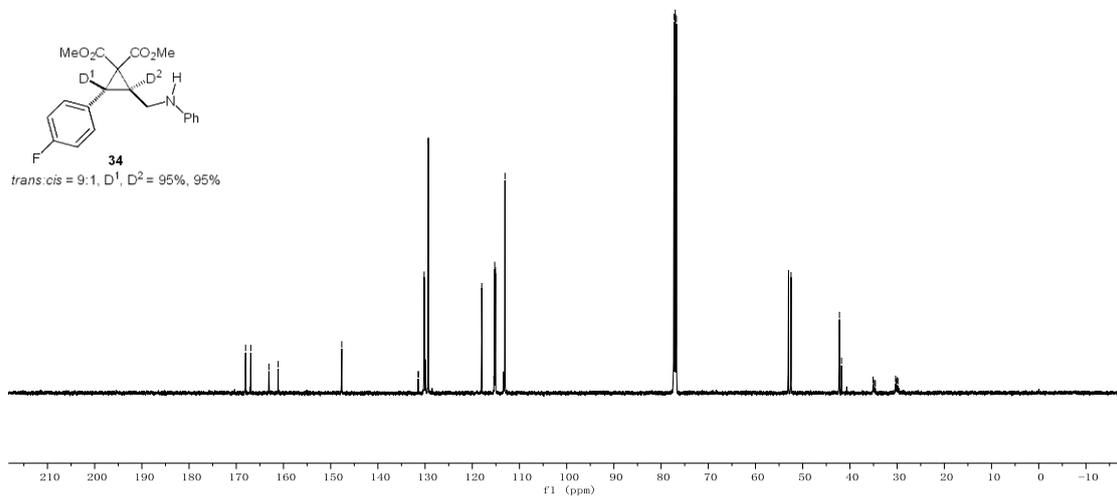
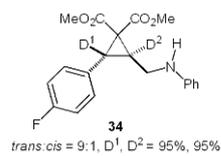




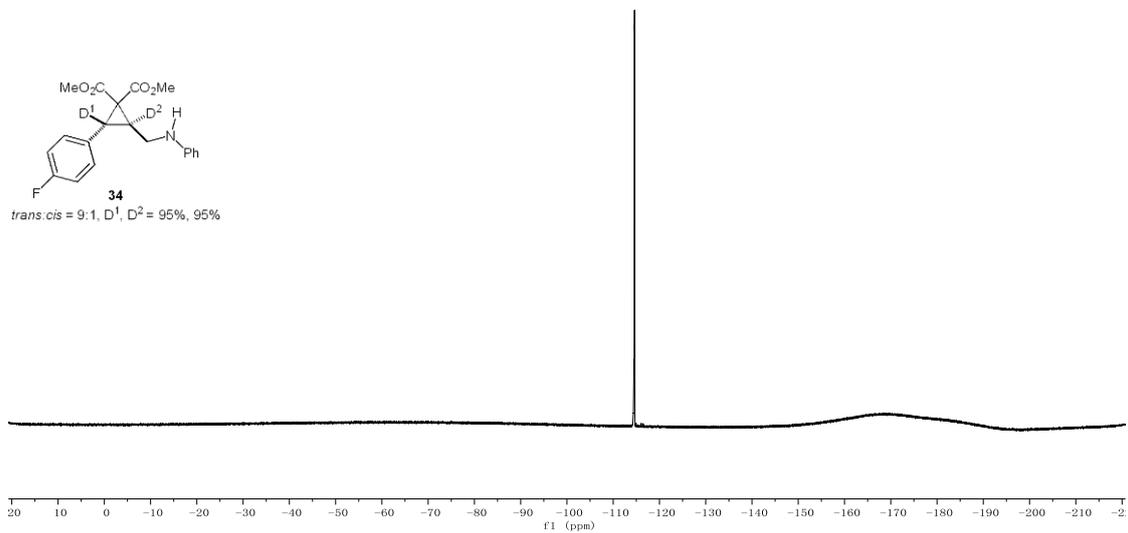
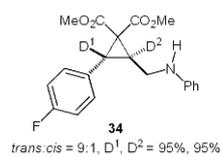


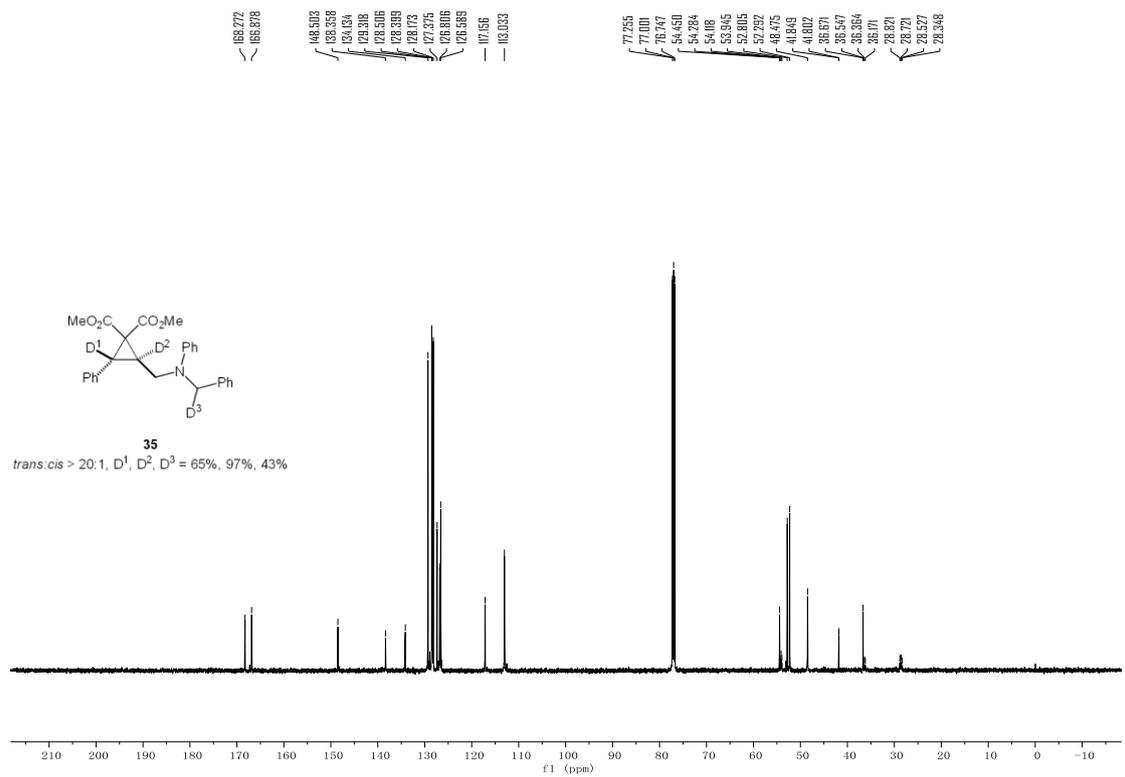
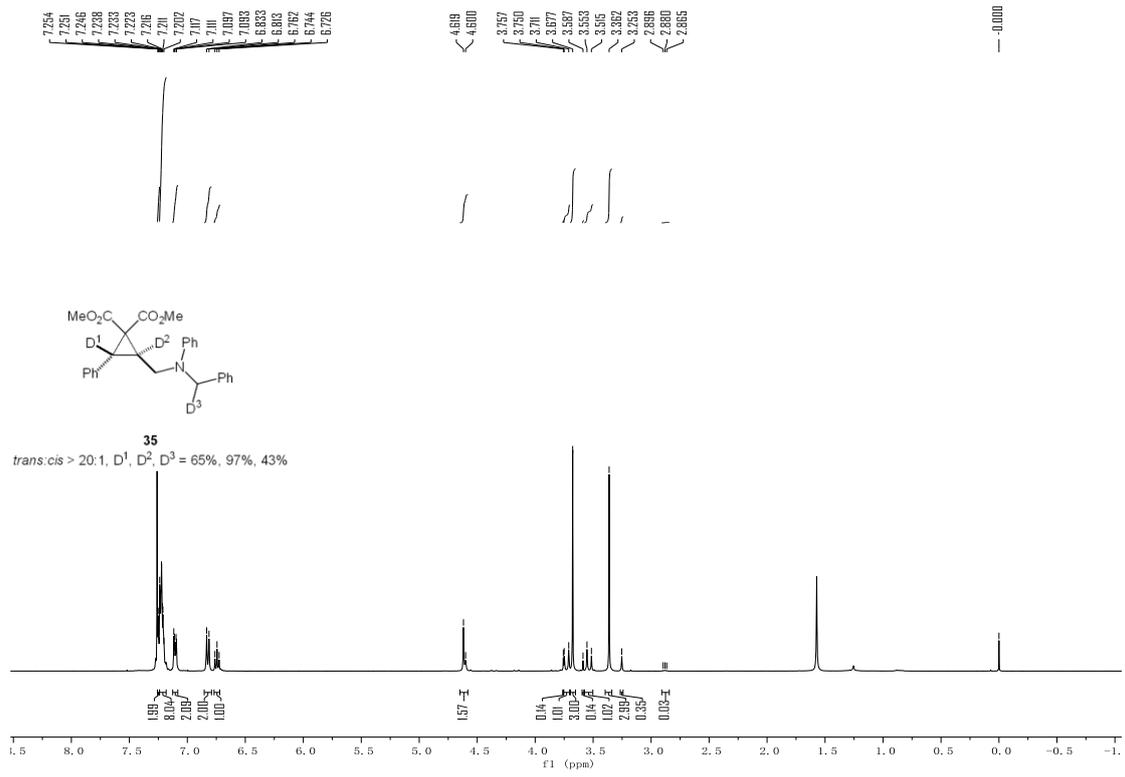


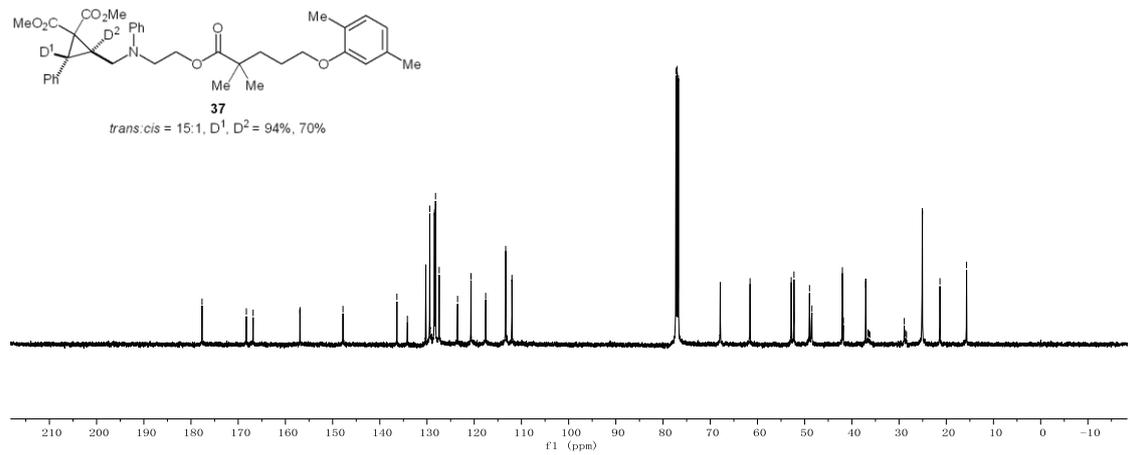
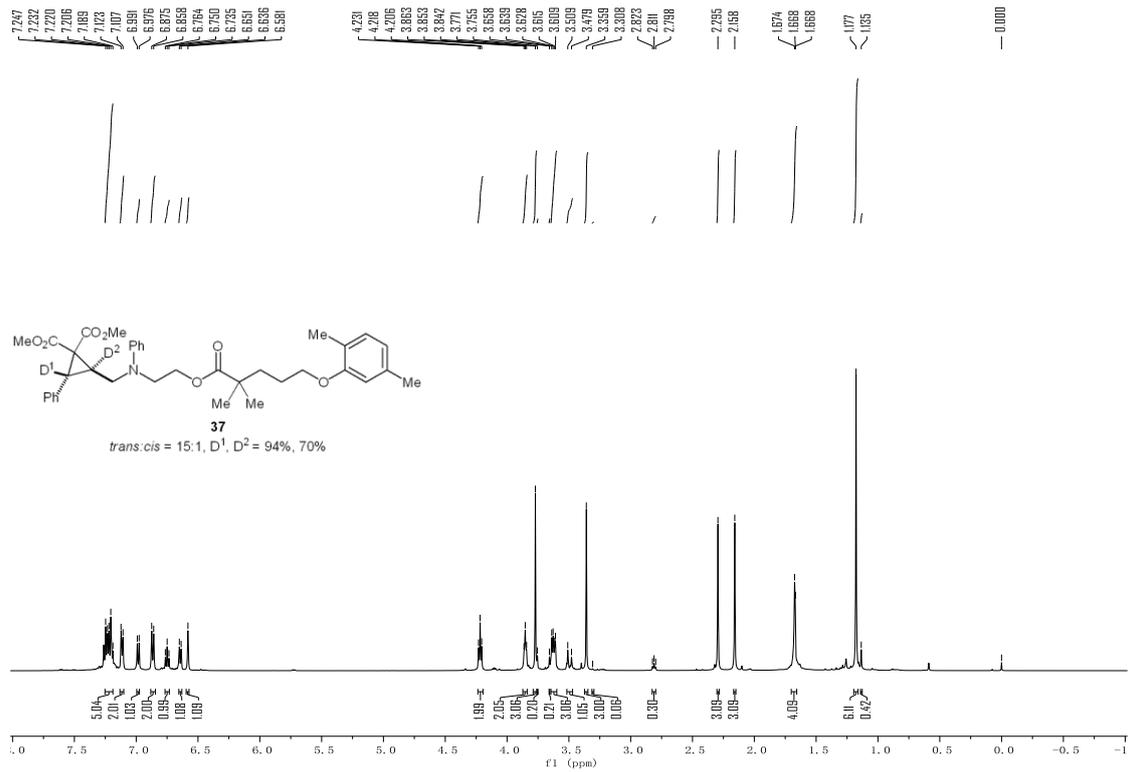
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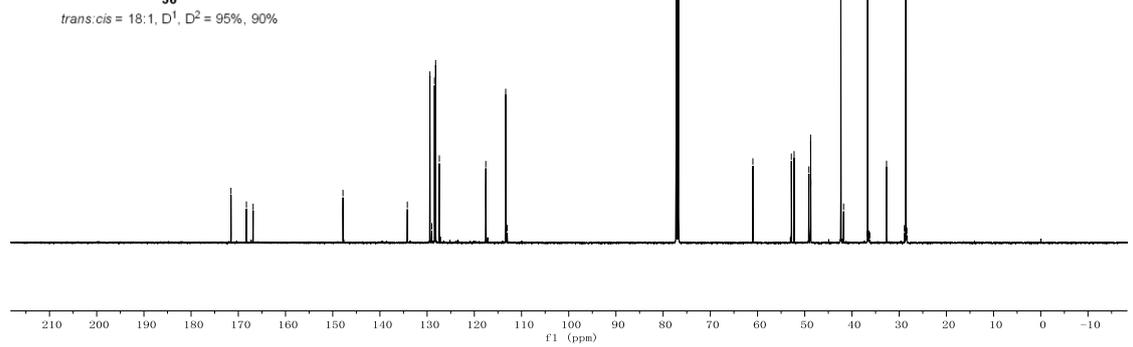
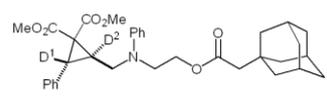
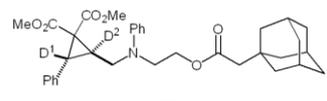
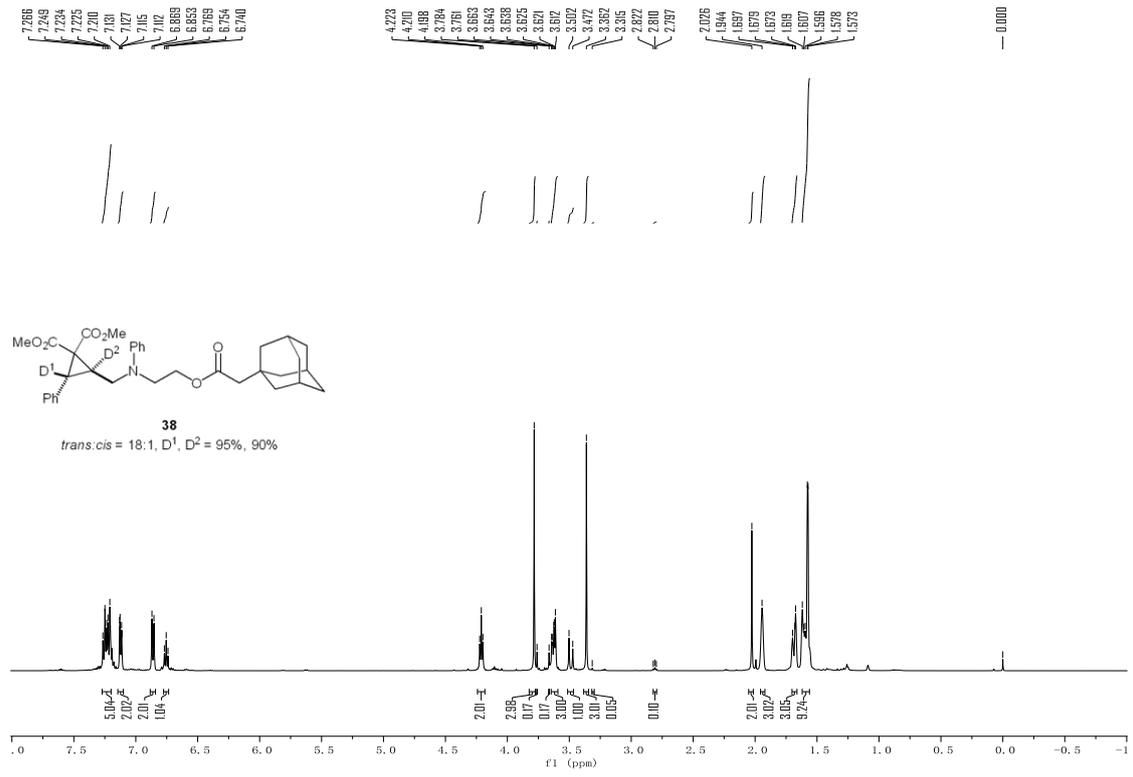


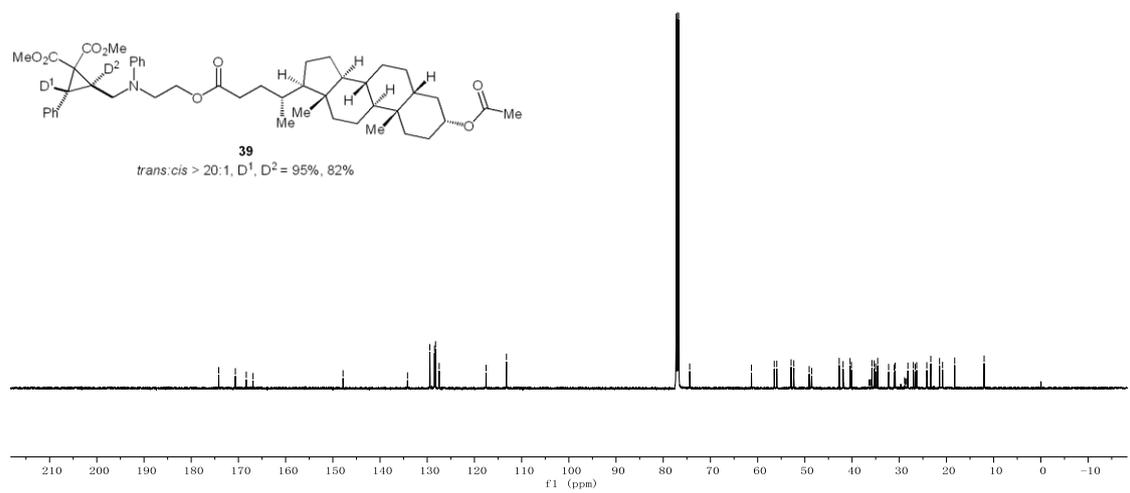
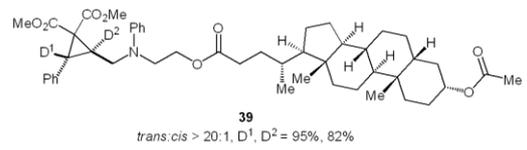
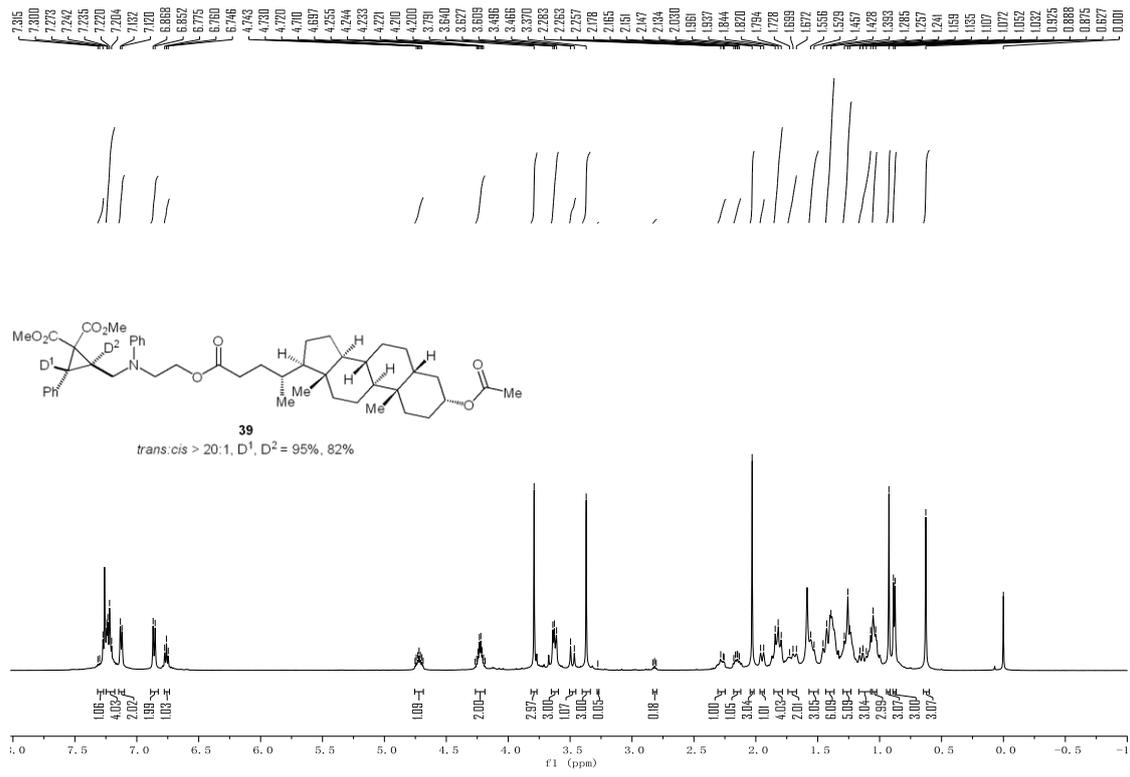
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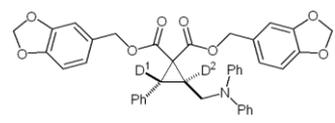




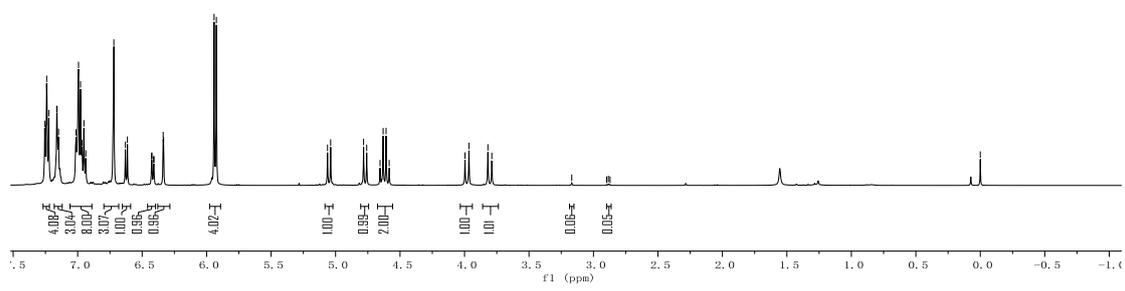


7.255
7.240
7.224
7.163
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6.993
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6.967
6.952
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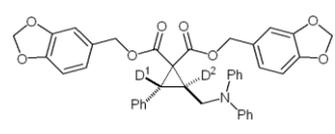
0.000



40 (D¹, D² = 94%, 95%)



167.654
166.866
147.702
147.629
147.658
133.867
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129.871
129.845
129.804
127.302
122.274
122.161
121.788
121.642
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100.029
100.021
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77.101
76.747
67.646
67.160
48.053
42.149
37.044
36.807
36.538
36.566
29.648
29.162
28.533
28.737



40 (D¹, D² = 94%, 95%)

