

Supporting information for

Ni-Catalyzed [8+3] Cycloaddition of Tropones with 1,1-Cyclopropanediester

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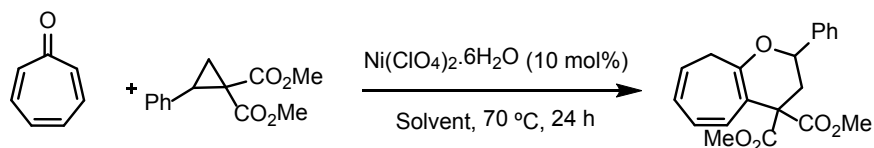
1. General methods

Good quality commercially available solvents were used in the [8+3] cycloadditions. Anhydrous solvents were not required in this transformation. Melting points were taken in open-end capillary tubes. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm silica gel plates (230-400 mesh). Flash column chromatographies were performed using silica gel (230-400 mesh). NMR spectra were recorded on AU-300 MHz instrument and calibrated using residual undeuterated solvent (CDCl₃, methanol-d₄ or D₂O) as internal reference. MS spectra were recorded on a VG *AutoSpec* mass spectrometer. The HPLC chromatograms of the racemic and enantiomerically enriched cycloadducts are also included. 1,1-Cyclopropanediester were synthesized according to literature procedures: (**2a-2l**)¹, **2h**², (**2m-2o**)³, **2p**⁴, **2q**⁵; (*S*)-**2a** and (*S*)-**2d**⁶.

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1. S. R. Goudreau, D. Marcoux and A. B. Charette, *J. Org. Chem.*, 2009, **74**, 470.
 2. B. H. Xianran, Q. Guanpeng, Y. Jin, X. Yuling, W. Zhongyuan, Q. Guofu and H. Xianming, *European Journal of Medicinal Chemistry*, 2010, **45**, 3818.
 3. E. J. Corey and M. Chaykovsky, *J. Am. Chem. Soc.*, 1965, **87**, 1353.
 4. A. P. Dieskan, M. S. Holzwarth and B. Plietker, *J. Am. Chem. Soc.*, 2012, **11**, 134.
 5. F. Benfatti, F. De Nanteuil and J. Waser, *Chem. Eur. J.*, 2012, **18**, 4844.
 6. C. Deng, L-J. Wang, J. Zhu and Y. Tang, *Angew. Chem. Int. Ed.*, 2012, **51**, 11620.

1. Solvent and catalyst optimization studies

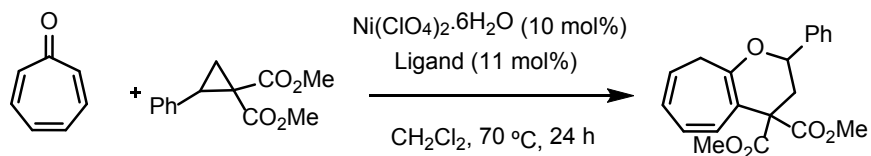
2a. Optimization of the solvent



Entry	Solvent	Conversion (%) ^[a]
1	CH ₃ CN	0
2	DMF	41
3	MeOH	53
4	Toluene	60
5	CH ₂ Cl ₂	>99

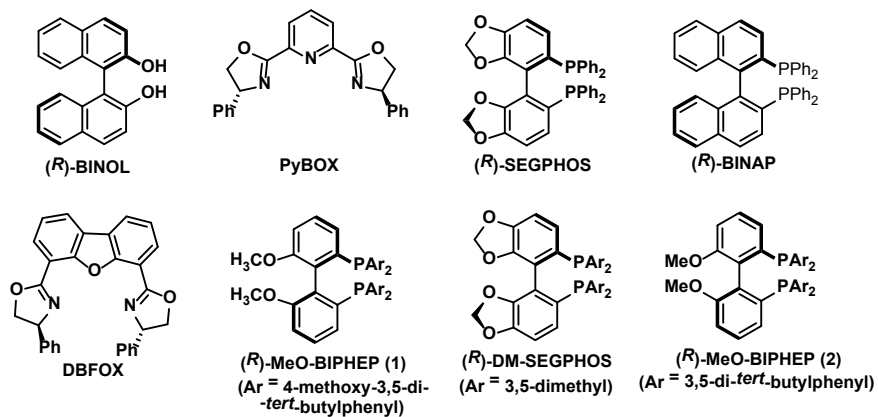
[a] Determined by ¹H-NMR.

2b. Optimization of the chiral ligand

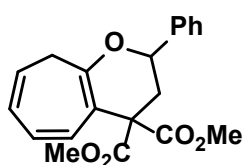


Entry	Ligand	Conversion (%) ^[a]	ee (%) ^[b]
1	(<i>R</i>)-BINOL	60	0
2	PyBOX	30	0
3	(<i>R</i>)-SEGPHOS	65	32
4	(<i>R</i>)-BINAP	62	41
5	DBFOX	49	51
6	(<i>R</i>)-MeO-BIPHEP (1)	70	54
7	(<i>R</i>)-DM-SEGPHOS	68	60
8	(<i>R</i>)-MeO-BIPHEP (2)	70	80

[a] Determined by ¹H-NMR. [b] Determined by HPLC.



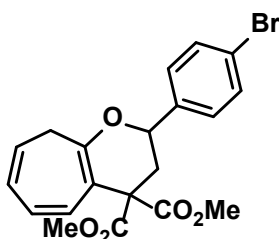
2. Typical procedure for the [8+3] cycloaddition of tropone with 1,1-cyclopropanediester: Dimethyl 2-phenyl-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (**3a**).



A solution of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (3.1 mg, 0.0085 mmol), 1,1-cyclopropanediester **2a** (20.0 mg 0.085 mmol) and tropone **1** (9.1 mg, 0.085 mmol) in CH_2Cl_2 (1.0 ml) was stirred at 70 °C for 24 h. The resulting solution was filtered through a plug of celite® with the aid of CH_2Cl_2 (10.0 ml), and the solvent was removed under reduced pressure. The residue was purified by silica gel flash chromatography (hexane-EtOAc 10:1) to afford the cycloadduct **3a** (26.3 mg, 91%, colorless oil).

^1H NMR (300 MHz, CDCl_3): δ 7.42-7.31 (m, 5H), 6.53 (d, $J = 11.4$ Hz, 1H), 6.33 (dd, $J = 5.3, 11.4$ Hz, 1H), 6.20 (dd, $J = 5.3, 8.9$ Hz, 1H), 5.40 (m, 1H), 4.92 (dd, $J = 1.4, 11.4$ Hz, 1H), 3.76 (s, 3H), 3.75 (s, 3H), 3.02 (dd, $J = 7.9, 13.2$ Hz, 1H), 2.80 (dd, $J = 1.4, 13.6$ Hz, 1H), 2.26 (dd, $J = 5.9, 13.2$ Hz, 1H), 2.15 (dd, $J = 11.4, 13.6$ Hz, 1H). **^{13}C NMR** (75 MHz, CDCl_3): 171.7, 171.3, 147.1, 139.7, 130.6, 128.6 (2C), 128.3, 127.8, 126.1 (2C), 124.7, 119.4, 103.7, 76.0, 55.9, 53.0, 52.7, 37.6, 33.0. **MS** (EI+): 340.1 ($[\text{M}]^+$, 100). **HRMS** (EI+): Calculated for $\text{C}_{20}\text{H}_{20}\text{O}_5$, 340.1311; found, 340.1310.

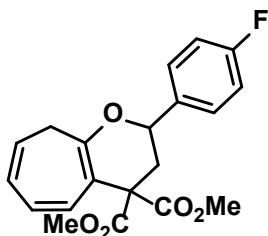
Dimethyl 2-(4-bromophenyl)-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (**3b**).



Following the typical procedure, the reaction of tropone **1** (6.8 mg, 0.064 mmol) with cyclopropane **2b** (20.0 mg, 0.064 mmol) in the presence of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (2.3 mg, 0.0064 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3b** (23.9 mg, 89%, white solid).

M.p.: 126-128°C. **^1H NMR** (300 MHz, CDCl_3): δ 7.51 (d, $J = 8.3$ Hz, 2H), 7.29 (d, $J = 8.3$ Hz, 2H), 6.52 (d, $J = 11.4$ Hz, 1H), 6.33 (dd, $J = 5.3, 11.4$ Hz, 1H), 6.19 (dd, $J = 5.3, 8.6$ Hz, 1H), 5.41 (m, $J = 8.6$ Hz, 1H), 4.88 (d, $J = 11.7$ Hz, 1H), 3.76 (s, 6H), 3.01 (dd, $J = 7.9, 13.3$ Hz, 1H), 2.76 (dd, $J = 1.6, 13.7$ Hz, 1H), 2.26 (dd, $J = 6.0, 13.3$ Hz, 1H), 2.09 (dd, $J = 11.7, 13.7$ Hz, 1H). **^{13}C NMR** (75 MHz, CDCl_3): 171.4, 171.2, 146.8, 138.8, 131.7 (2C), 130.5, 127.8, 127.7, 124.9, 122.1, 119.4, 103.8, 75.2, 55.7, 53.0, 52.8, 37.5, 32.9. **MS** (EI+): 418.0 ($[\text{M}]^+$, 100). **HRMS** (EI+): Calculated for $\text{C}_{20}\text{H}_{19}\text{BrO}_5$, 418.0416; found, 418.0413.

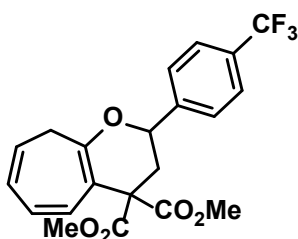
Dimethyl 2-(4-fluorophenyl)-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (**3c**).



Following the typical procedure, the reaction of tropone **1** (8.4 mg, 0.079 mmol) with cyclopropane **2c** (20 mg, 0.079 mmol) in the presence of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (2.9 mg, 0.0079 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3c** (24.3 mg, 86%, colorless oil).

^1H NMR (300 MHz, CDCl_3): δ 7.40 (dd, $J = 5.4, 8.6$ Hz, 2H), 7.07 (t, $J = 8.6$ Hz, 2H), 6.53 (d, $J = 11.5$ Hz, 1H), 6.34 (dd, $J = 5.3, 11.5$ Hz, 1H), 6.19 (dd, $J = 5.3, 9.0$ Hz, 1H), 5.41 (m, 1H), 4.91 (d, $J = 11.7$ Hz, 1H), 3.77 (s, 6H), 3.01 (dd, $J = 7.9, 13.3$ Hz, 1H), 2.78 (dd, $J = 1.8, 13.6$ Hz, 1H), 2.26 (dd, $J = 6.0, 13.3$ Hz, 1H), 2.13 (dd, $J = 11.7, 13.6$ Hz, 1H). **^{13}C NMR** (75 MHz, CDCl_3): 171.5, 171.3, 147.0, 135.6-135.5 (d, $^4J_{\text{C-F}} = 3.8$ Hz), 130.6, 127.9-124.8 (d, $^1J_{\text{C-F}} = 232.3$ Hz), 127.9-127.7 (d, $^3J_{\text{C-F}} = 8.2$ Hz), 119.4, 115.6-115.3 (d, $^2J_{\text{C-F}} = 21.9$ Hz), 103.8, 75.3, 55.8, 53.0, 52.7, 37.6, 33.0. **MS** (EI+): 358.1 ($[\text{M}]^+$, 100). **HRMS** (EI+): Calculated for $\text{C}_{20}\text{H}_{19}\text{FO}_5$, 358.1217; found, 358.1201.

Dimethyl 2-(4-(trifluoromethyl)phenyl)-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (3d).

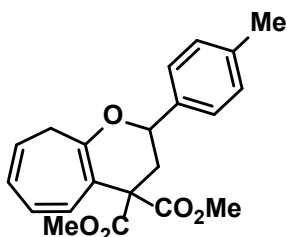


Following the typical procedure, the reaction of tropone **1** (7.0 mg, 0.066 mmol) with cyclopropane **2d** (20 mg, 0.066 mmol) in the presence of Ni(ClO₄)₂·6H₂O (2.4 mg, 0.0066 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3d** (21.3 mg, 76%, white solid).

M.p.: 138-140°C. **¹H NMR** (300 MHz, CDCl₃): δ 7.65 (d, *J* = 8.2 Hz, 2H), 7.54 (d, *J* = 8.2 Hz, 2H), 6.52 (d, *J* = 11.4 Hz, 1H), 6.34 (dd, *J* = 5.3, 11.4 Hz, 1H), 6.19 (dd, *J* = 5.3, 8.9 Hz, 1H), 5.42 (m, 1H), 4.99 (d, *J* = 11.3 Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.02 (dd, *J* = 7.9, 13.3 Hz, 1H), 2.80 (dd, *J* = 1.7, 13.6 Hz, 1H), 2.28 (dd, *J* = 6.0, 13.3 Hz, 1H), 2.10 (dd, *J* = 11.3, 13.6 Hz, 1H). **¹³C NMR** (75 MHz, CDCl₃): 171.3, 171.2, 146.6, 143.7, 130.5 (2C), 127.9-125.0 (d, ¹*J*_{C-F} = 213.2 Hz), 126.3, 126.3-125.8 (d, ²*J*_{C-F} = 55.6 Hz), 126.3-125.6 (d, ²*J*_{C-F} = 58.7 Hz), 125.9-125.5 (d, ³*J*_{C-F} = 4.0 Hz), 125.0, 119.5, 103.9, 75.2, 55.6, 53.0, 52.7, 37.6, 32.9. **MS** (EI⁺): 408.1 ([M]⁺, 100). **HRMS** (EI): Calculated for C₂₁H₁₉F₃O₅, 408.1185; found, 408.1168.

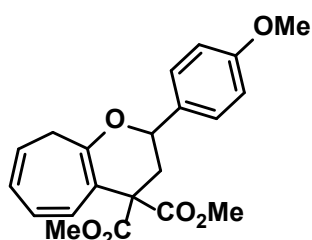
Dimethyl 2-p-tolyl-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (3e).

Following the typical procedure, the reaction of tropone **1** (8.5 mg, 0.081 mmol) with cyclopropane **2e** (20. mg, 0.081 mmol) in the presence of Ni(ClO₄)₂·6H₂O (2.9 mg, 0.0081 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3e** (26.4 mg, 92%, colorless oil).



¹H NMR (300 MHz, CDCl₃): δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.20 (d, *J* = 8.0 Hz, 2H), 6.53 (d, *J* = 11.4 Hz, 1H), 6.33 (dd, *J* = 5.3, 11.4 Hz, 1H), 6.21 (dd, *J* = 5.3, 8.9 Hz, 1H), 5.41 (m, 1H), 4.87 (d, *J* = 11.8 Hz, 1H), 3.77 (s, 6H), 3.02 (dd, *J* = 7.9, 13.2 Hz, 1H), 2.77 (dd, *J* = 1.5, 13.6 Hz, 1H), 2.37 (s, 3H), 2.27 (dd, *J* = 7.2, 13.2 Hz, 1H), 2.16 (dd, *J* = 11.8, 13.6 Hz, 1H). **¹³C NMR** (75 MHz, CDCl₃): 171.6, 171.3, 147.3, 134.9, 130.8, 130.7, 130.5, 127.9, 127.8, 126.3, 125.3, 124.6, 119.3, 103.6, 73.1, 55.8, 52.9, 52.7, 36.8, 33.1, 18.8. **MS** (EI⁺): 354.1 ([M]⁺, 100). **HRMS** (EI): Calculated for C₂₁H₂₂O₅, 354.1417; found, 354.1469.

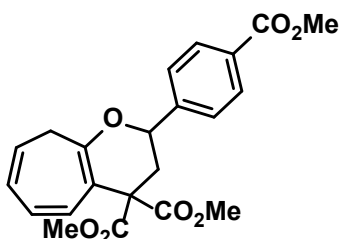
Dimethyl 2-(4-methoxyphenyl)-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (3f).



Following the typical procedure, the reaction of tropone **1** (8.0 mg, 0.076 mmol) with cyclopropane **2f** (20.0 mg, 0.076 mmol) in the presence of Ni(ClO₄)₂·6H₂O (2.8 mg, 0.0076 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3f** (26.2 mg, 92%, colorless oil).

¹H NMR (300 MHz, CDCl₃): δ 7.33 (d, *J* = 8.6 Hz, 2H), 6.91 (d, *J* = 8.6 Hz, 2H), 6.53 (d, *J* = 11.4 Hz, 1H), 6.32 (dd, *J* = 5.3, 11.4 Hz, 1H), 6.19 (dd, *J* = 5.3, 8.8 Hz, 1H), 5.41 (m, 1H), 4.85 (d, *J* = 11.4 Hz, 1H), 3.81 (s, 3H), 3.76 (s, 3H), 3.75 (s, 3H), 3.00 (dd, *J* = 7.9, 13.2 Hz, 1H), 2.75 (dd, *J* = 1.6, 13.6 Hz, 1H), 2.24 (dd, *J* = 6.0, 13.2 Hz, 1H), 2.15 (dd, *J* = 11.4, 13.6 Hz, 1H). **¹³C NMR** (75 MHz, CDCl₃): 171.6, 171.3, 159.6, 147.2, 131.8, 130.6, 127.8, 127.5 (2C), 124.6, 119.3, 114.0 (2C), 103.6, 75.6, 56.0, 55.3, 52.9, 52.6, 37.4, 33.1. **MS** (EI⁺): 370.1 ([M]⁺, 100). **HRMS** (EI): Calculated for C₂₁H₂₂O₆, 370.1416; found, 370.1402.

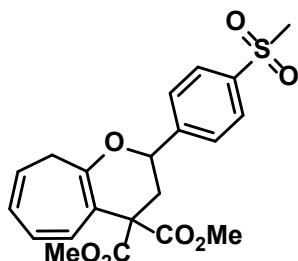
Dimethyl 2-(4-(methoxycarbonyl)phenyl)-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (3g).



Following the typical procedure, the reaction of tropone **1** (7.3 mg, 0.068 mmol) with cyclopropane **2g** (20.0 mg, 0.068 mmol) in the presence of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (2.5 mg, 0.0068 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3g** (22.8 mg, 84%, colorless oil).

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 8.06 (d, $J = 8.2$ Hz, 2H), 7.49 (d, $J = 8.2$ Hz, 2H), 6.52 (d, $J = 11.4$ Hz, 1H), 6.34 (dd, $J = 5.3, 11.4$ Hz, 1H), 6.20 (dd, $J = 5.3, 8.6$ Hz, 1H), 5.42 (m, 1H), 4.98 (d, $J = 11.7$ Hz, 1H), 3.93 (s, 3H), 3.78 (s, 3H), 3.76 (s, 3H), 3.04 (dd, $J = 7.9, 13.3$ Hz, 1H), 2.81 (dd, $J = 1.6, 13.6$ Hz, 1H), 2.28 (dd, $J = 6.4, 13.3$ Hz, 1H), 2.10 (dd, $J = 11.7, 13.6$ Hz, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): 171.4, 171.2, 166.7, 146.7, 144.7, 130.5, 129.9, 129.8 (2C), 127.8, 125.8 (2C), 124.9, 119.4, 103.9, 75.4, 55.7, 52.9, 52.8, 52.1, 37.6, 32.9. **MS** (EI+): 398.1 ($[\text{M}]^+$, 100). **HRMS** (EI): Calculated for $\text{C}_{22}\text{H}_{22}\text{O}_7$, 398.1366; found, 398.1363.

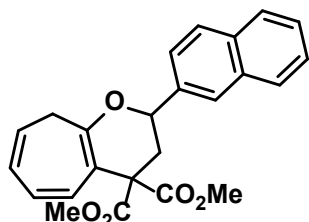
Dimethyl 2-(4-(methylsulfonyl)phenyl)-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (3h).



Following the typical procedure, the reaction of tropone **1** (7.5 mg, 0.07 mmol) with cyclopropane **2h** (20.0 mg, 0.07 mmol) in the presence of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (2.6 mg, 0.007 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3h** (17.4 mg, 62%, colorless oil).

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.90 (d, $J = 8.3$ Hz, 2H), 7.57 (d, $J = 8.3$ Hz, 2H), 6.46 (d, $J = 11.5$ Hz, 1H), 6.29 (dd, $J = 11.5, 5.3$ Hz, 1H), 6.13 (dd, $J = 9.3, 5.0$ Hz, 1H), 5.36 (q, $J = 8.1, 7.5$ Hz, 1H), 4.96 (d, $J = 11.3$ Hz, 1H), 3.71 (s, 3H), 3.69 (s, 3H), 2.99 (s, 3H), 2.94 (d, $J = 7.9$ Hz, 1H), 2.75 (dd, $J = 13.6, 1.9$ Hz, 1H), 2.22 (dd, $J = 13.3, 6.0$ Hz, 1H), 1.99 (dd, $J = 11.8, 1.4$ Hz, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): 171.2, 171.1, 146.4, 146.0, 140.3, 130.3, 127.9, 127.8, 126.9 (2C), 125.2, 119.5, 104.0, 75.0, 55.5, 53.1, 52.8, 44.6, 37.6, 32.8, 29.7. **MS** (ESI+): 419.1 ($[\text{M}+\text{H}]^+$, 100). **HRMS** (ESI): Calculated for $\text{C}_{21}\text{H}_{23}\text{O}_7\text{S}$, 419.1159; found, 419.1141.

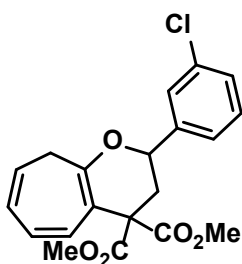
Dimethyl 2-(naphthalen-2-yl)-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (3i).



Following the typical procedure, the reaction of tropone **1** (7.5 mg, 0.07 mmol) with cyclopropane **2i** (20.0 mg, 0.07 mmol) in the presence of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (2.6 mg, 0.007 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3i** (24.6 mg, 90%, colorless oil).

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.88 (d, $J = 8.9$ Hz, 3H), 7.50 (m, 4H), 6.57 (d, $J = 11.4$ Hz, 1H), 6.36 (dd, $J = 5.3, 11.4$ Hz, 1H), 6.22 (dd, $J = 5.3, 8.7$ Hz, 1H), 5.45 (m, 1H), 5.10 (d, $J = 11.7$ Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.09 (dd, $J = 7.9, 13.3$ Hz, 1H), 2.90 (dd, $J = 1.5, 13.6$ Hz, 1H), 2.33 (dd, $J = 6.0, 13.3$ Hz, 1H), 2.24 (dd, $J = 11.7, 13.6$ Hz, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): 171.6, 171.4, 147.1, 137.1, 133.3 (2C), 130.7, 128.4, 128.1, 127.8, 127.7, 126.3, 126.2, 125.1, 124.8, 123.8, 119.4, 103.8, 76.1, 55.9, 53.0, 52.8, 37.6, 33.1. **MS** (EI+): 390.1 ($[\text{M}]^+$, 100). **HRMS** (EI): Calculated for $\text{C}_{24}\text{H}_{22}\text{O}_5$, 390.1467; found, 390.1466.

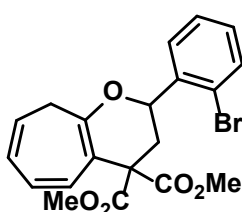
Dimethyl 2-(3-chlorophenyl)-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (**3j**).



Following the typical procedure, the reaction of tropone **1** (7.9 mg, 0.074 mmol) with cyclopropane **2j** (20.0 mg, 0.074 mmol) in the presence of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (2.7 mg, 0.0074 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3j** (21.8 mg, 78%, colorless oil).

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.44 (s, 1H), 7.36-7.22 (m, 3H), 6.54 (d, $J = 11.5$ Hz, 1H), 6.34 (dd, $J = 5.3, 11.5$ Hz, 1H), 6.20 (dd, $J = 5.3, 8.2$ Hz, 1H), 5.42 (m, 1H), 4.90 (dd, $J = 1.8, 11.7$ Hz, 1H), 3.77 (s, 3H), 3.74 (s, 3H), 3.02 (dd, $J = 7.8, 13.3$ Hz, 1H), 2.80 (dd, $J = 1.8, 13.6$ Hz, 1H), 2.28 (dd, $J = 5.8, 13.3$ Hz, 1H), 2.11 (dd, $J = 11.7, 13.6$ Hz, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): 171.4, 171.2, 146.7, 141.7, 134.5, 130.5, 129.9, 128.3, 127.8, 126.2, 124.9, 124.2, 119.4, 103.8, 75.2, 55.7, 53.0, 52.7, 37.6, 32.9. **MS** (EI⁺): 374.0 ($[\text{M}]^+$, 100). **HRMS** (EI): Calculated for $\text{C}_{20}\text{H}_{19}\text{ClO}_5$, 374.0921; found, 374.0914.

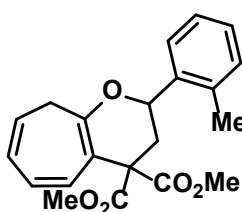
Dimethyl 2-(2-bromophenyl)-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (**3k**).



Following the typical procedure, the reaction of tropone **1** (6.8 mg, 0.064 mmol) with cyclopropane **2i** (20.0 mg, 0.064 mmol) in the presence of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (2.3 mg, 0.0064 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3i** (16.4 mg, 61%, white solid).

M.p.: 110-112°C. $^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.57 (m, $J = 1.3, 6.9$ Hz, 2H), 7.37 (t, $J = 7.6$ Hz, 1H), 7.18 (m, $J = 1.3, 7.6$ Hz, 1H), 6.54 (d, $J = 11.4$ Hz, 1H), 6.35 (dd, $J = 5.3, 11.4$ Hz, 1H), 6.21 (dd, $J = 5.3, 8.9$ Hz, 1H), 5.42 (m, 1H), 5.28 (dd, $J = 1.5, 11.5$ Hz, 1H), 3.77 (s, 3H), 3.75 (s, 3H), 3.00 (dd, $J = 7.8, 13.3$ Hz, 1H), 2.90 (dd, $J = 1.5, 13.8$ Hz, 1H), 2.28 (dd, $J = 6.0, 13.3$ Hz, 1H), 2.06 (dd, $J = 11.5, 13.8$ Hz, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): 171.3, 170.9, 146.4, 139.1, 132.9, 130.2, 129.6, 127.8, 127.7, 127.6, 125.0, 121.7, 119.4, 104.0, 74.8, 55.8, 53.0, 52.7, 36.3, 33.0. **MS** (EI⁺): 418.0 ($[\text{M}]^+$, 100). **HRMS** (EI): Calculated for $\text{C}_{20}\text{H}_{19}\text{BrO}_5$, 418.0416; found, 418.0421.

Dimethyl 2-o-tolyl-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (**3l**).

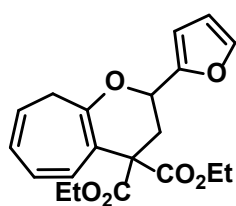


Following the typical procedure, the reaction of tropone **1** (8.5 mg, 0.081 mmol) with cyclopropane **2j** (20.0 mg, 0.081 mmol) in the presence of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (2.9 mg, 0.0081 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3l** (25.3 mg, 88%, colorless oil).

$^1\text{H NMR}$ (300 MHz, CDCl_3): δ 7.50 (m, $J = 1.8, 8.4$ Hz, 1H), 7.25-7.17 (m, 3H), 6.56 (d, $J = 11.4$ Hz, 1H), 6.34 (dd, $J = 5.3, 11.4$ Hz, 1H), 6.20 (dd, $J = 5.3, 8.9$ Hz, 1H), 5.42 (m, 1H), 5.12 (d, $J = 11.5$ Hz, 1H), 3.77 (s, 3H), 3.76 (s, 3H), 3.05 (dd, $J = 7.9, 13.2$ Hz, 1H), 2.77 (dd, $J = 1.4, 13.8$ Hz, 1H), 2.40 (s, 3H), 2.28 (dd, $J = 6.4, 13.2$ Hz, 1H), 2.05 (dd, $J = 11.5, 13.8$ Hz, 1H). $^{13}\text{C NMR}$ (75 MHz, CDCl_3): 171.6, 171.3, 147.3, 138.0, 134.9, 130.7, 130.5, 127.9, 127.8, 126.3, 125.3, 124.6, 119.3, 103.6, 73.1, 55.8, 53.0, 52.7, 36.8, 33.1, 18.9. **MS** (EI⁺): 354.1 ($[\text{M}]^+$, 100). **HRMS** (EI): Calculated for $\text{C}_{21}\text{H}_{22}\text{O}_5$, 354.1467; found, 354.1476.

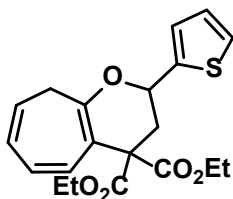
Diethyl 2-(furan-2-yl)-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (**3m**).

Following the typical procedure, the reaction of tropone **1** (8.4 mg, 0.079 mmol) with cyclopropane **2m** (20.0 mg, 0.079 mmol) in the presence of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (2.9 mg, 0.0079 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3m** (21.2 mg, 75%, colorless oil).



¹H NMR (300 MHz, CDCl₃): δ 7.45 (d, 1H), 6.57 (d, *J* = 11.4 Hz, 1H), 6.41-6.37 (m, 2H), 6.31 (dd, *J* = 5.6, 11.4 Hz, 1H), 6.17 (dd, *J* = 5.6, 8.2 Hz, 1H), 5.41 (m, *J* = 7.9 Hz, 1H), 4.98 (dd, *J* = 1.5, 11.9 Hz, 1H), 4.23 (m, *J* = 7.1 Hz, 4H), 2.96 (dd, *J* = 7.9, 13.3 Hz, 1H), 2.80 (dd, *J* = 1.8, 13.6 Hz, 1H), 2.43 (dd, *J* = 11.9, 13.6 Hz, 1H), 2.21 (dd, *J* = 6.0, 13.3 Hz, 1H), 1.27 (m, *J* = 7.1 Hz, 6H). **¹³C NMR** (75 MHz, CDCl₃): 170.9, 170.6, 151.9, 146.4, 142.8, 130.7, 127.7, 124.7, 119.5, 110.3, 108.3, 103.8, 69.2, 61.8, 61.6, 55.2, 33.3, 32.8, 14.1, 14.0. **MS** (EI+): 358.1 ([M]⁺, 100). **HRMS** (EI): Calculated for C₂₀H₂₂O₆, 358.1416; found, 358.1414.

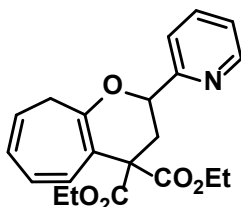
Diethyl 2-(thiophen-2-yl)-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (3n).



Following the typical procedure, the reaction of tropone **1** (7.9 mg, 0.075 mmol) with cyclopropane **2n** (20.0 mg, 0.075 mmol) in the presence of Ni(ClO₄)₂·6H₂O (2.7 mg, 0.0075 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3n** (23.9 mg, 85%, colorless oil).

¹H NMR (300 MHz, CDCl₃): δ 7.33 (d, *J* = 5.1 Hz, 1H), 7.10 (d, *J* = 3.3 Hz, 1H), 7.01 (dd, *J* = 3.3, 5.1 Hz, 1H), 6.57 (d, *J* = 11.4 Hz, 1H), 6.32 (dd, *J* = 5.3, 11.4 Hz, 1H), 6.18 (dd, *J* = 6.1, 8.9 Hz, 1H), 5.43 (m, *J* = 7.9 Hz, 1H), 5.20 (dd, *J* = 11.7 Hz, 1H), 4.24 (m, *J* = 7.2 Hz, 4H), 3.00 (dd, *J* = 7.9, 13.3 Hz, 1H), 2.88 (dd, *J* = 1.8, 13.5 Hz, 1H), 2.29 (dd, *J* = 11.7, 13.5 Hz, 1H), 2.23 (dd, *J* = 6.0, 13.3 Hz, 1H), 1.26 (m, *J* = 7.2 Hz, 6H). **¹³C NMR** (75 MHz, CDCl₃): 170.9, 170.6, 146.6, 142.5, 130.7, 127.7, 126.7, 125.5, 125.2, 124.7, 119.6, 103.9, 72.0, 61.9, 61.6, 55.5, 37.4, 32.9, 14.1, 14.0. **MS** (EI+): 374.1 ([M]⁺, 100). **HRMS** (EI): Calculated for C₂₀H₂₂O₅S, 374.1188; found, 374.0903.

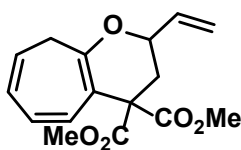
Diethyl 2-(pyridin-2-yl)-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (3o).



Following the typical procedure, the reaction of tropone **1** (8.1 mg, 0.076 mmol) with cyclopropane **2o** (20.0 mg, 0.076 mmol) in the presence of Ni(ClO₄)₂·6H₂O (2.8 mg, 0.0076 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3o** (17.4 mg, 62%, yellow oil).

¹H NMR (300 MHz, CDCl₃): δ 8.64 (d, *J* = 4.2 Hz, 1H), 7.73 (td, *J* = 1.8, 7.7 Hz, 1H), 7.48 (d, *J* = 7.7 Hz, 1H), 7.24 (m, 1H), 6.59 (dd, *J* = 11.4 Hz, 1H), 6.33 (dd, *J* = 5.4, 11.4 Hz, 1H), 6.19 (dd, *J* = 5.4, 8.1 Hz, 1H), 5.42 (m, *J* = 8.1 Hz, 1H), 5.04 (dd, *J* = 1.8, 11.6 Hz, 1H), 4.22 (m, *J* = 7.2 Hz, 4H), 3.02 (dd, *J* = 7.9, 13.4 Hz, 1H), 2.98 (dd, *J* = 2.0, 10.9 Hz, 1H), 2.30 (dd, *J* = 11.6, 13.7 Hz, 1H), 2.28 (dd, *J* = 13.4 Hz, 1H), 1.26 (m, *J* = 7.2 Hz, 6H). **¹³C NMR** (75 MHz, CDCl₃): 171.0, 170.6, 158.6, 149.4, 146.4, 136.7, 130.8, 127.7, 124.6, 123.0, 121.0, 119.4, 104.3, 76.4, 61.8, 61.6, 55.3, 35.4, 33.0, 14.0 (2C). **MS** (EI+): 369.1 ([M]⁺, 100). **HRMS** (EI): Calculated for C₂₁H₂₃NO₅, 369.1576; found, 369.1583.

Dimethyl 2-vinyl-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (3p).

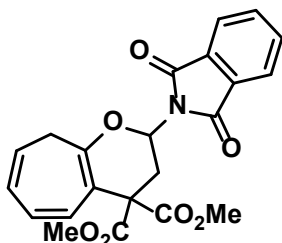


Following the typical procedure, the reaction of tropone **1** (11.8 mg, 0.11 mmol) with cyclopropane **2p** (20.0 mg, 0.11 mmol) in the presence of Ni(ClO₄)₂·6H₂O (3.95 mg, 0.011 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3p** (25.9 mg, 82%, colorless oil).

¹H NMR (300 MHz, CDCl₃): δ 6.48 (d, *J* = 10.1 Hz, 1H), 6.25 (dd, *J* = 5.5, 10.1 Hz, 1H), 6.10 (dd, *J* = 5.5, 9.2 Hz, 1H), 5.80 (m, 1H), 5.30 (m, 2H), 5.20 (m, 1H), 4.25 (m, 1H), 3.65 (s, 3H), 3.60 (s, 3H), 2.85 (dd, *J* = 8.0, 13.9 Hz, 1H), 2.65 (dd, *J* = 1.6, 12.9 Hz, 1H), 2.15 (dd, *J* = 6.2,

13.9 Hz, 1H), 1.90 (dd, $J = 12.0, 12.9$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3): 171.6, 171.2, 146.5, 135.8, 130.6, 127.7, 124.5, 119.3, 117.3, 103.5, 74.3, 55.3, 52.9, 52.6, 35.2, 32.9. **MS** (ESI+): 313.1 ([M+Na], 100). **HRMS** (ESI): Calculated for $\text{C}_{16}\text{H}_{18}\text{O}_5\text{Na}$, 313.1046; found, 313.1020.

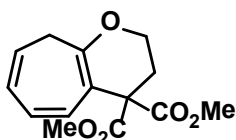
Dimethyl 2-(1,3-dioxoisindolin-2-yl)-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (3q).



Following the typical procedure, the reaction of tropone **1** (7.21 mg, 0.066 mmol) with cyclopropane **2q** (20.0 mg, 0.066 mmol) in the presence of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (2.41 mg, 0.0066 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3q** (17.3 mg, 64%, colorless oil).

^1H NMR (300 MHz, CDCl_3): δ 7.85 (m, 2H), 7.70 (m, 2H), 6.50 (dd, $J = 11.4$ Hz, 1H), 6.25 (dd, $J = 5.3, 11.4$ Hz, 1H), 6.10 (dd, $J = 5.3, 8.6$ Hz, 1H), 5.80 (d, $J = 11.7$ Hz, 1H), 5.30 (m, $J = 8.6$ Hz, 1H), 3.70 (s, 3H), 3.65 (s, 3H), 3.30 (dd, $J = 7.9, 13.3$ Hz, 1H), 2.80 (dd, $J = 1.6, 13.7$ Hz, 1H), 2.60 (dd, $J = 6.0, 13.3$ Hz, 1H), 2.25 (dd, $J = 11.7, 13.7$ Hz, 1H). ^{13}C NMR (75 MHz, CDCl_3): 167.3, 167.0, 164.7, 162.5, 149.1, 138.0. **MS** (ESI+): 432.1 ([M+Na], 100). **HRMS** (ESI): Calculated for $\text{C}_{22}\text{H}_{19}\text{NO}_7\text{Na}$, 432.1053; found, 432.1065.

Dimethyl 2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (3r).

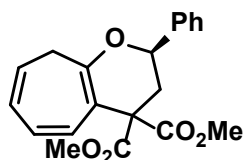


Following the typical procedure, the reaction of tropone **1** (13.8 mg, 0.13 mmol) with cyclopropane **2r** (20.0 mg, 0.13 mmol) in the presence of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (4.8 mg, 0.013 mmol) for 24 h afforded, after chromatography (hexane-EtOAc 10:1), the cycloadduct **3r** (28.5 mg, 83%, colorless oil).

^1H NMR (300 MHz, CDCl_3): δ 6.38 (d, $J = 10.5$ Hz, 1H), 6.20 (dd, $J = 5.4, 10.5$ Hz, 1H), 6.08 (dd, $J = 5.4, 9.5$ Hz, 1H), 5.31 (m, 1H), 3.93 (dd, $J = 5.6$ Hz, 2H), 3.67 (s, 6H), 2.46 (d, $J = 7.3$ Hz, 2H), 2.29 (dd, $J = 5.6$ Hz, 2H). ^{13}C NMR (75 MHz, CDCl_3): 171.5 (2C), 146.7, 130.9, 127.7, 124.4, 119.1, 103.6, 63.9, 54.7, 52.7 (2C), 32.9, 30.0. **MS** (ESI+): 264.1 ([M], 100). **HRMS** (EI): Calculated for $\text{C}_{14}\text{H}_{16}\text{O}_5$, 264.0998; found, 264.1006.

4. [8+3] cycloaddition reaction with enantioenriched cyclopropanes

(-)-(R)-Dimethyl 2-phenyl-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate ((R)-3a).

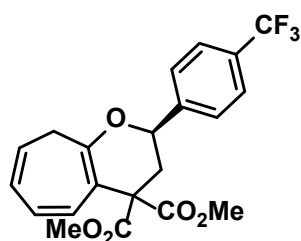


A solution of Nickel perchlorate hexahydrate (3.1 mg, 0.0085 mmol), (-)-(S)-dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (**S**)-**2a** (20.0 mg, 0.085 mmol) and tropone **1** (9.1 mg, 0.085 mmol) in CH_2Cl_2 (1.0 ml) was stirred at 70 °C for 24 h. The resulting solution was filtered through a plug of celite[®] with the aid of CH_2Cl_2 (10.0 ml), and the solvent was removed under reduced pressure. The residue was purified by silica gel flash chromatography (hexane-EtOAc 10:1) to afford the cycloadduct (**R**)-**3a**.

$T = 70$ °C: (26.9 mg, 93% *rdto*, colorless oil). $[\alpha]_D^{20} = -41.2$ ($c = 1.00$ g/mL, CHCl_3), 76% *ee*. **HPLC**: Daicel Chiralpak IA, isopropanol-hexane 99-1, flow rate 0.7 mL/min ($\lambda = 254.4$ nm), t_R : 30 min (minor), 36 min (major).

$T = 55$ °C: (21.4 mg, 74% *rdto*, colorless oil). $[\alpha]_D^{20} = -51.2$ ($c = 1.00$ g/mL, CHCl_3), 95% *ee*. **HPLC**: Daicel Chiralpak IA, isopropanol-hexane 99-1, flow rate 0.7 mL/min ($\lambda = 254.4$ nm), t_R : 30 min (minor), 36 min (major).

(-)-(R)-Dimethyl 2-(4-(trifluoromethyl)phenyl)-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-



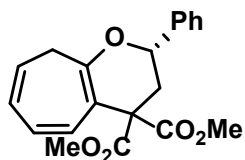
dicarboxylate ((R)-3d). A solution of Nickel perchlorate hexahydrate (19.3 mg, 0.053 mmol), (-)-(S)-dimethyl 2-(4-(trifluoromethyl)phenyl)cyclopropane-1,1-dicarboxylate (S)-2d (160.0 mg, 0.53 mmol) and tropone **1** (57.9 mg, 0.53 mmol) in CH₂Cl₂ (1.0 ml) was stirred at 55 °C for 72 h. The resulting solution was filtered through a plug of celite[®] with the aid of CH₂Cl₂ (10.0 ml), and the solvent was removed under reduced pressure. The residue was purified by silica gel flash chromatography (hexane-

EtOAc 10:1) to afford the cycloadduct (R)-3d (164.2 mg, 76%, brown solid).

$[\alpha]_D^{20} = -58.3$ (c = 1.00 g/mL, CHCl₃), 88% ee. **HPLC:** Daicel Chiralpak OD, isopropanol-hexane 95-5, flow rate 0.7 mL/min ($\lambda = 254.4$ nm), t_R : 11 min (major), 13 (minor).

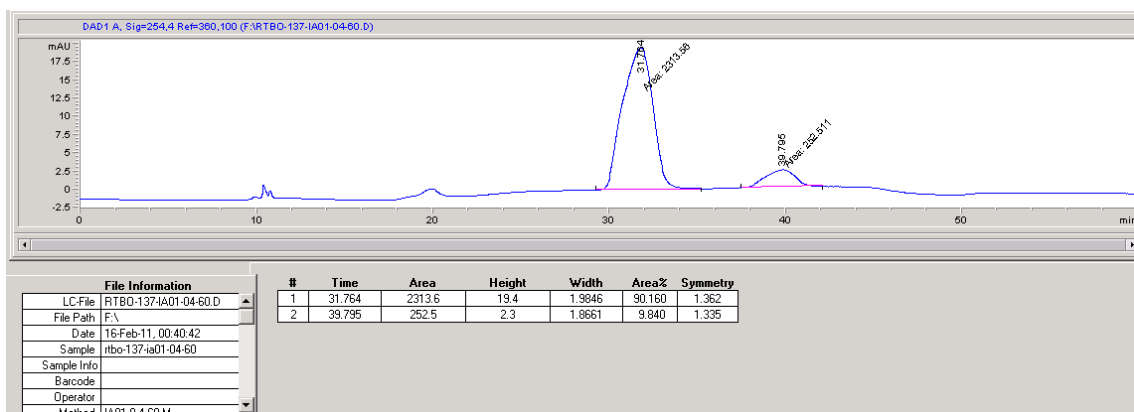
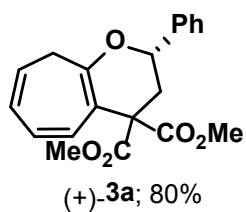
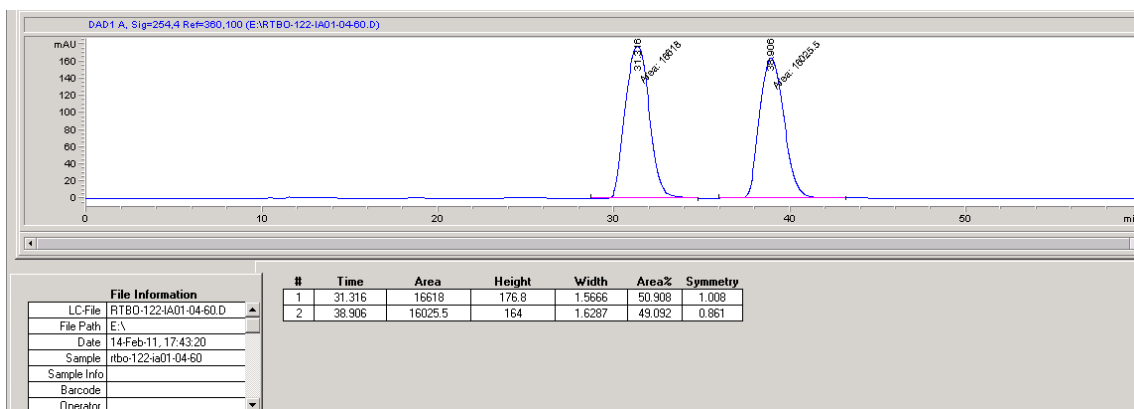
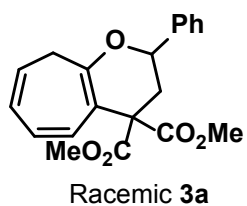
5. Enantioselective [8+3] cycloaddition: (+)-(S)-Dimethyl 2-phenyl-2,3-dihydrocyclohepta[b]pyran-4,4-(9H)-dicarboxylate (3a).

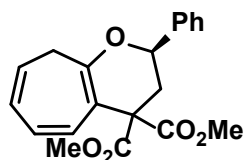
A solution of Ni(ClO₄)₂·6H₂O (3.1 mg, 0.0085 mmol), (R)-MeO-BIPHEP (0.0094 mmol), 1,1-cyclopropanediester **2a** (20.0 mg, 0.085 mmol) and tropone (9.1mg, 0.085 mmol) in CH₂Cl₂ (1.0 ml) was stirred at 70 °C for 24 h. The resulting solution was filtered through a plug of celite[®] with the aid of CH₂Cl₂ (10.0 ml), and the solvent was removed under reduced pressure. The residue was purified by silica gel flash chromatography (hexane-EtOAc 10:1) to afford the cycloadduct (R)-3a (19.6 mg, 68%, colorless oil).



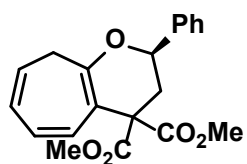
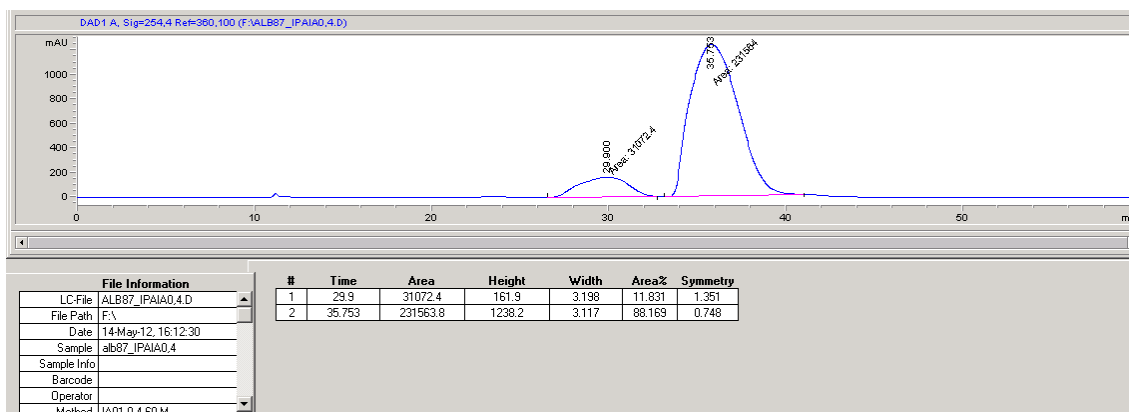
$[\alpha]_D^{20} = +42.4$ (c = 1.00 g/mL, CHCl₃), 80% ee. **HPLC:** Daicel Chiralpak IA, isopropanol-hexane 99-1, flow rate 0.7 mL/min ($\lambda = 254.4$ nm), t_R : 32 min (major), 39 min (minor).

6. HPLC chart.

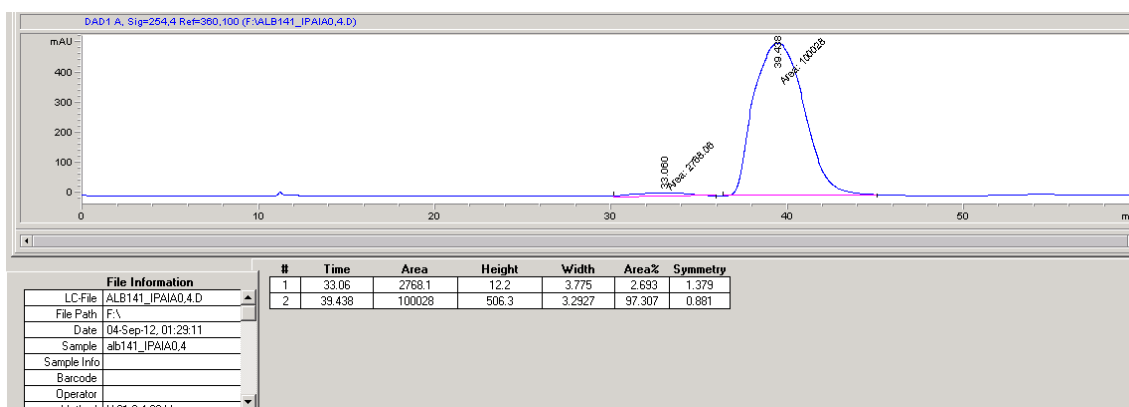


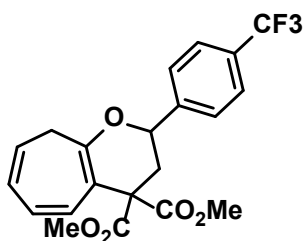


(-)-3a; 76% ee

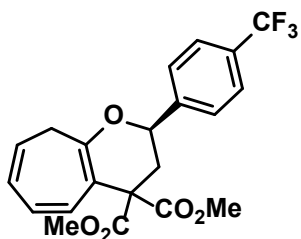
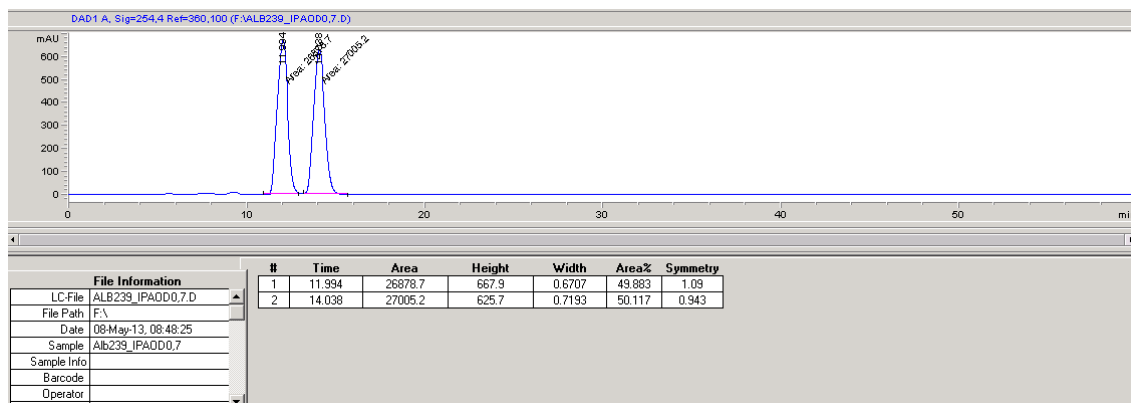


(-)-3a; 95% ee

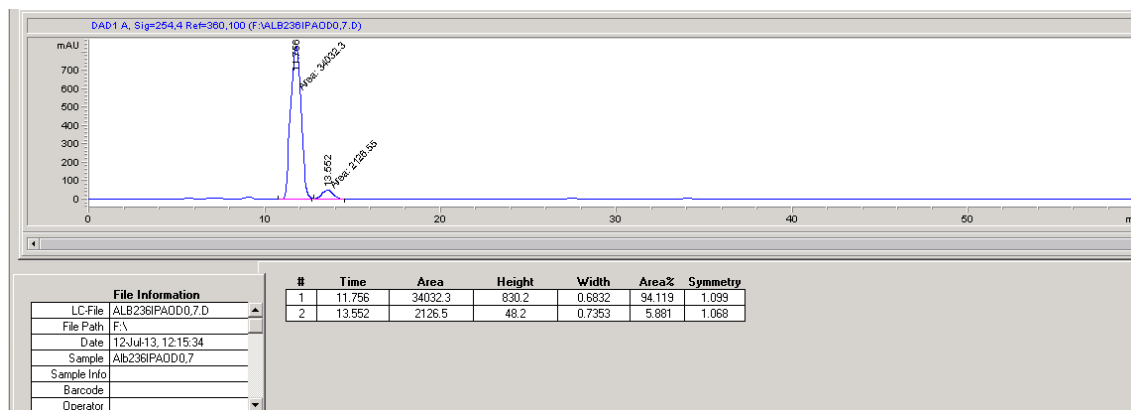




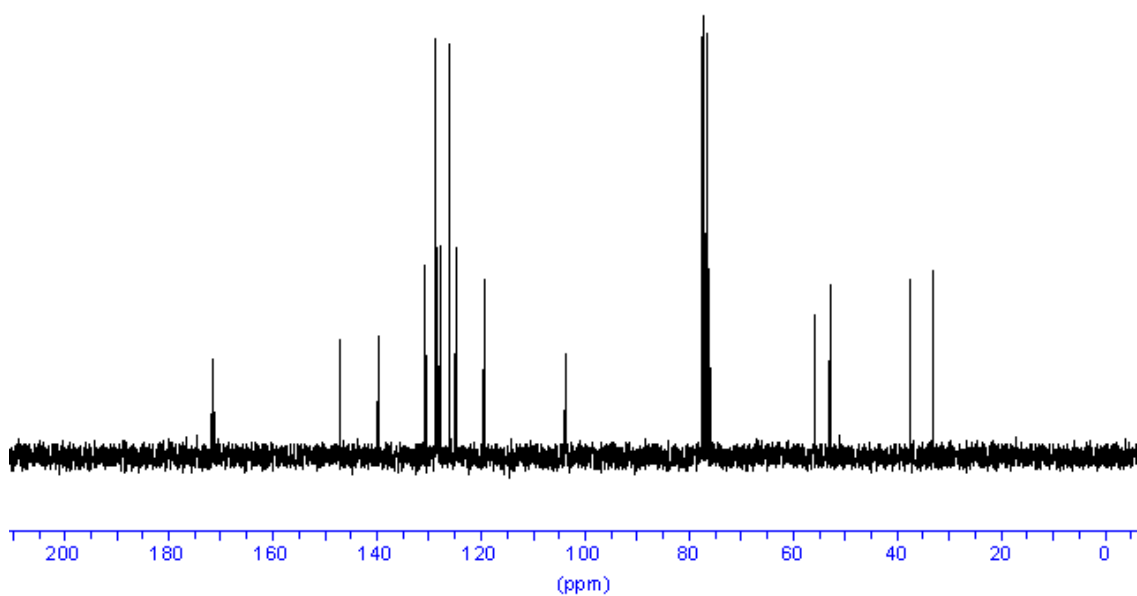
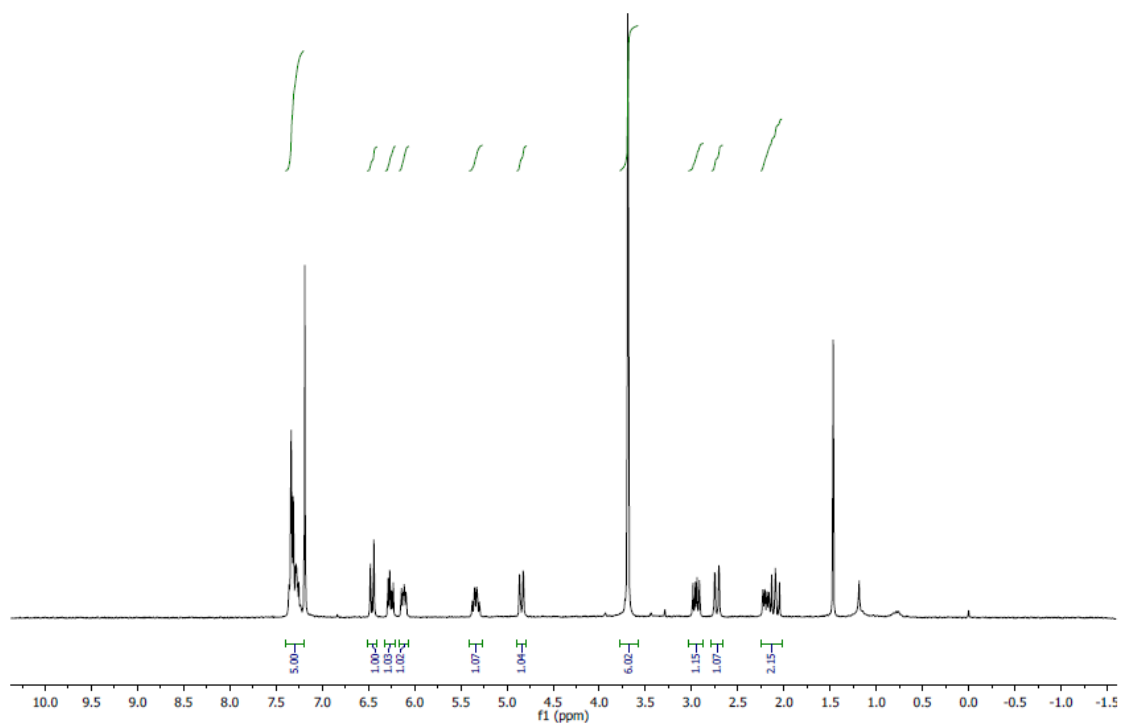
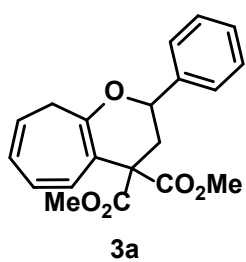
Racemic **3d**

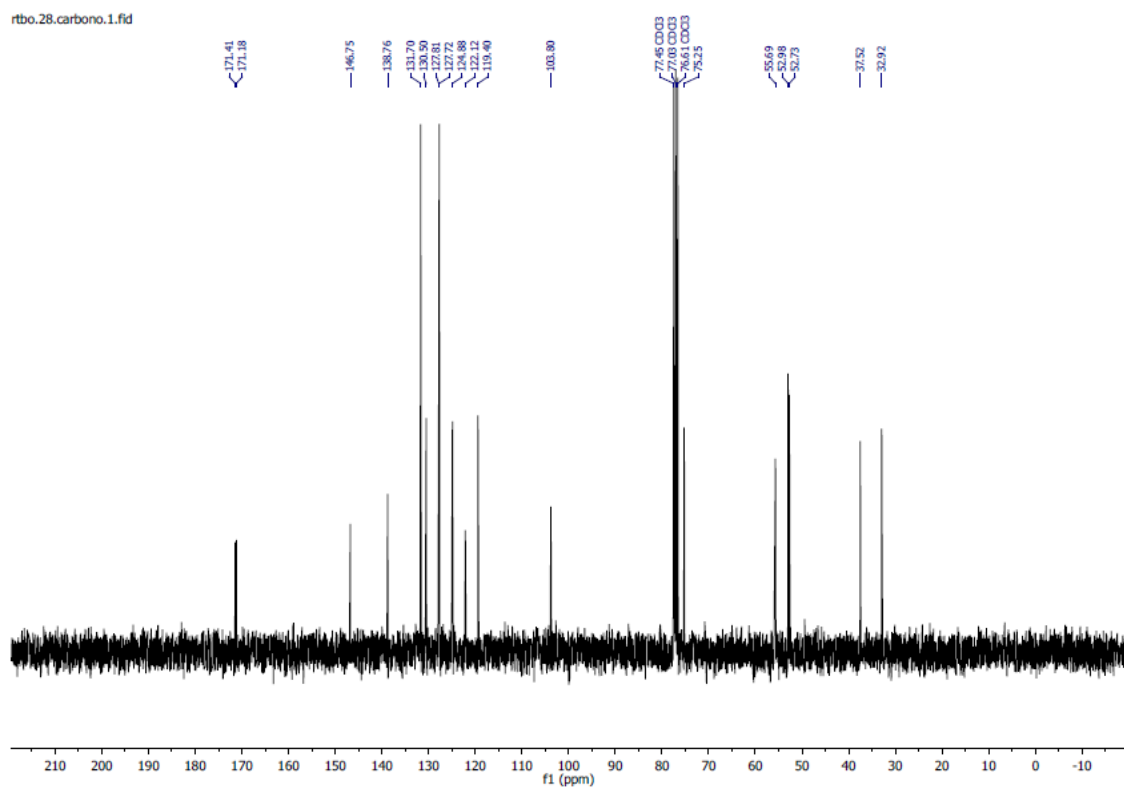
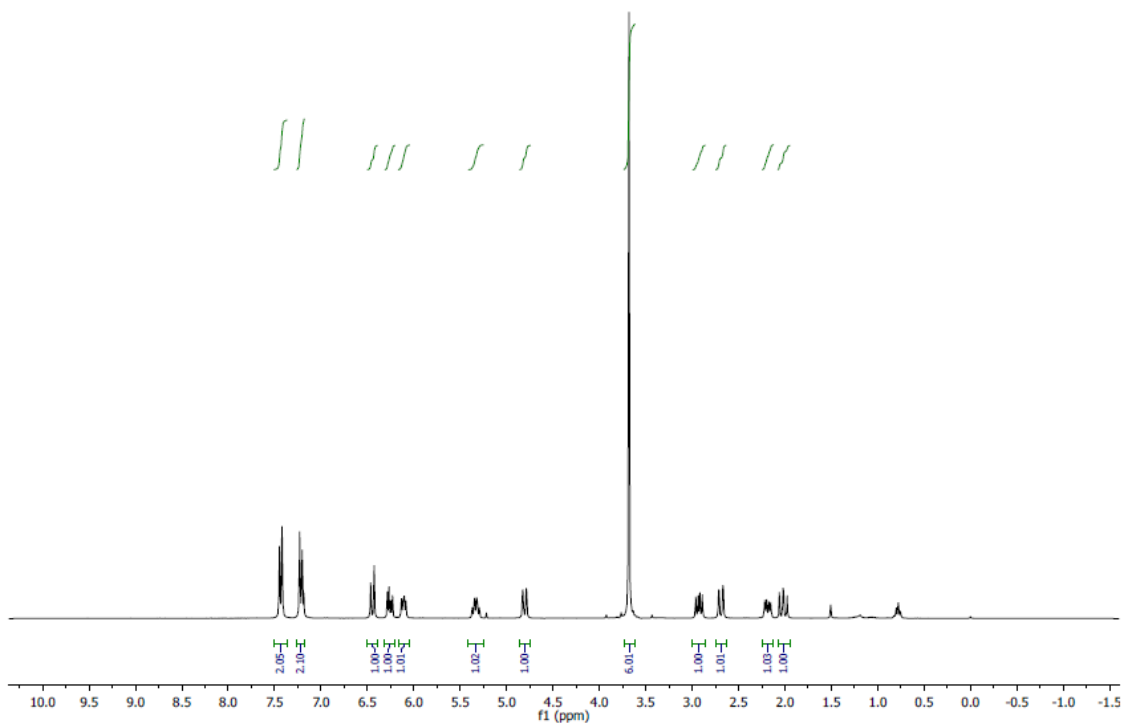
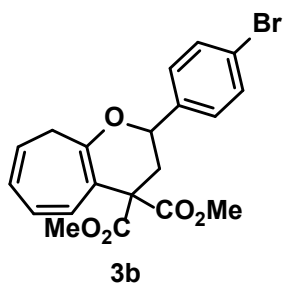


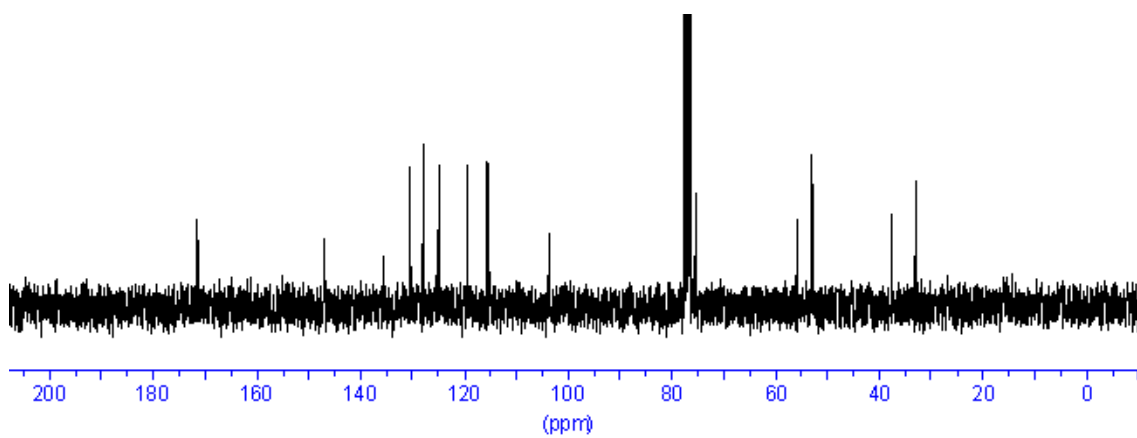
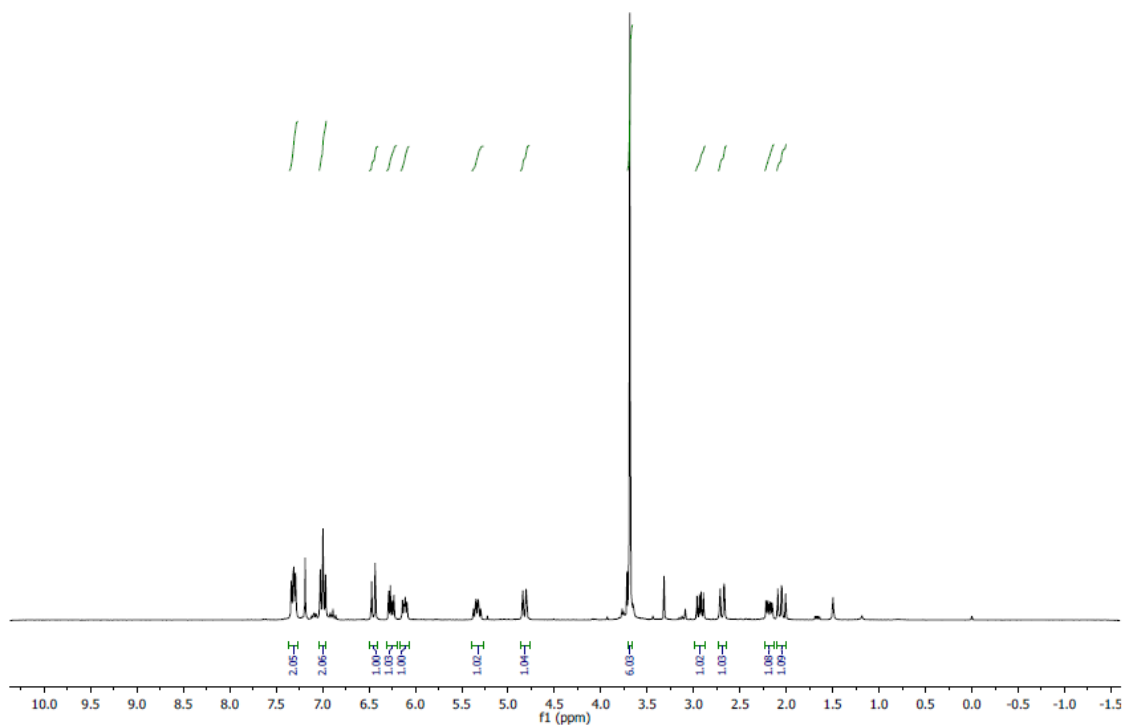
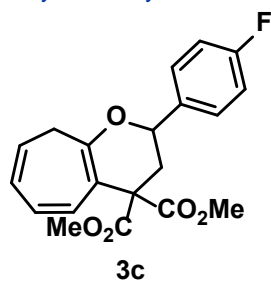
(-)-**3d**; 88% ee

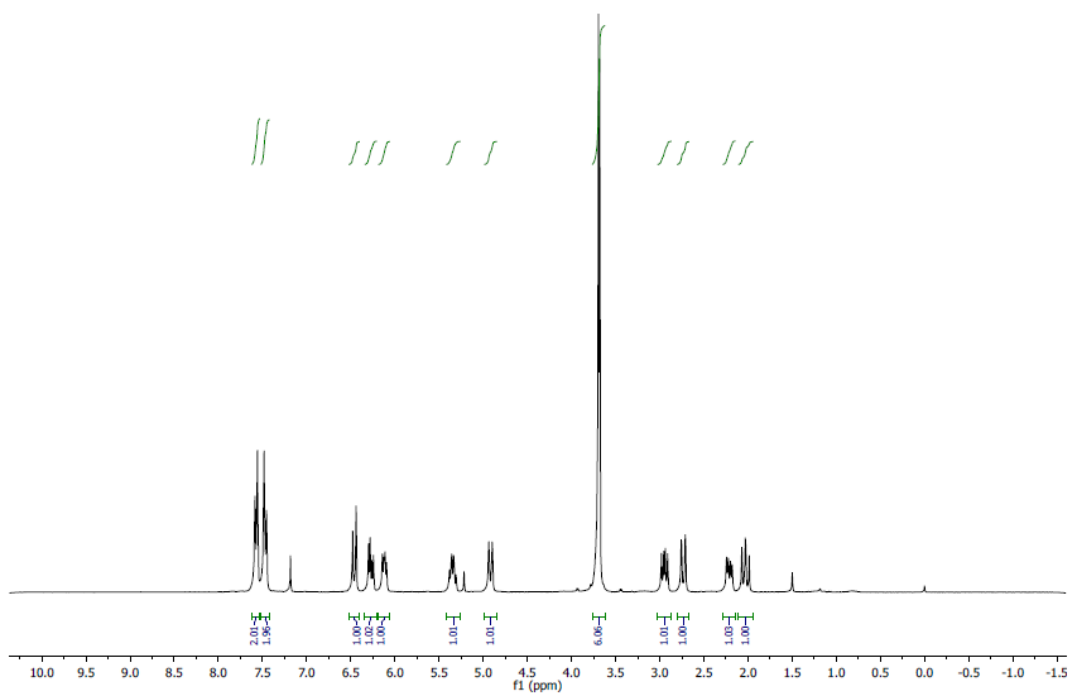
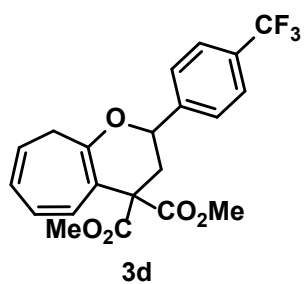


7. NMR spectra collection.

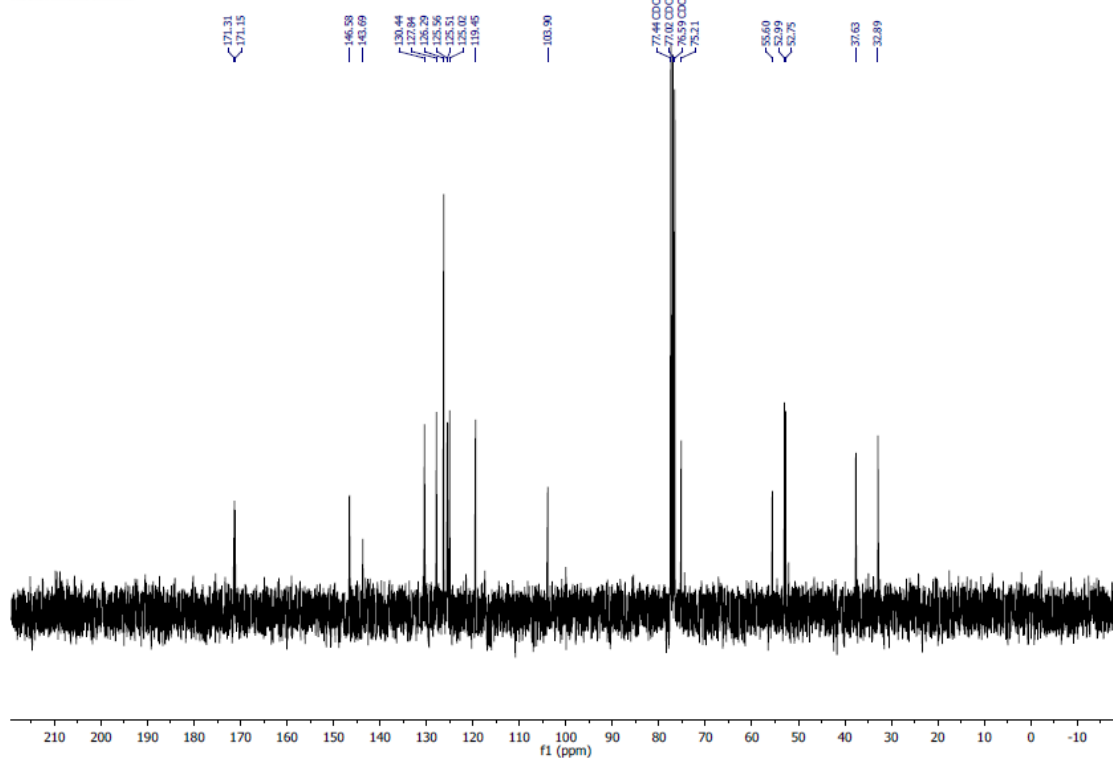


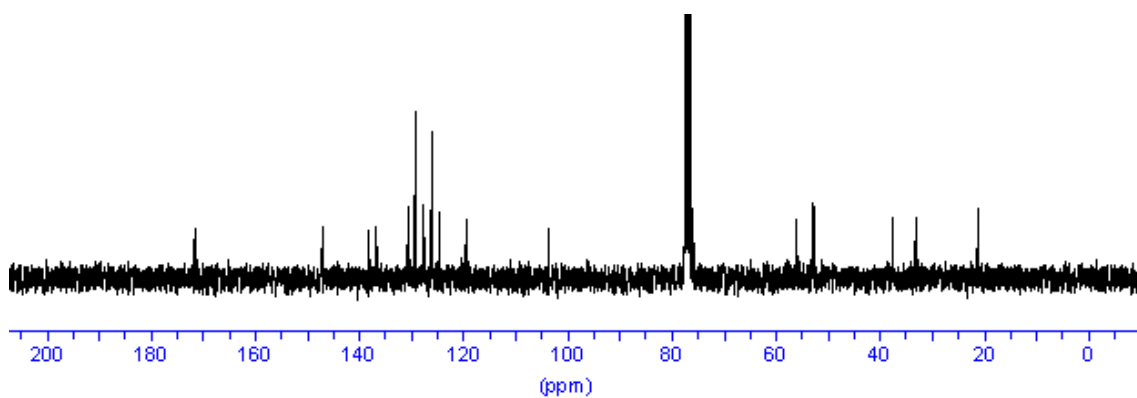
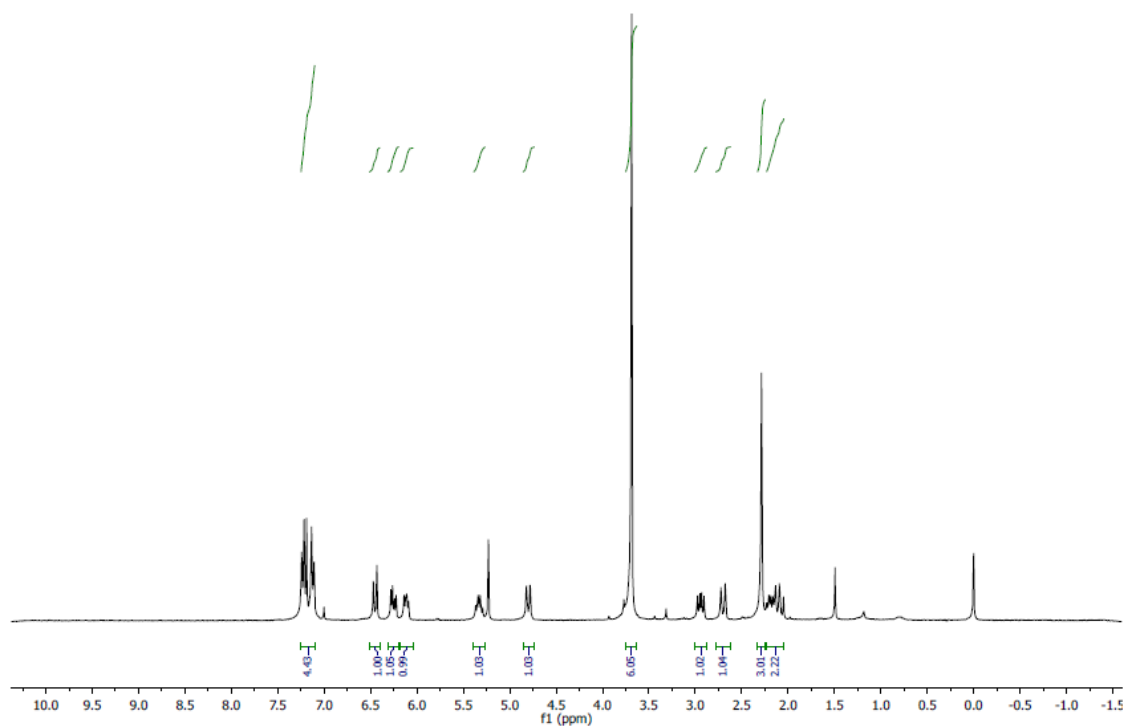
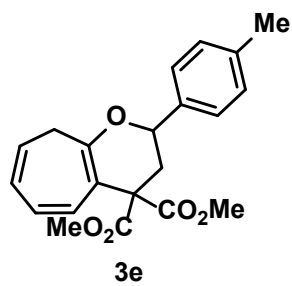


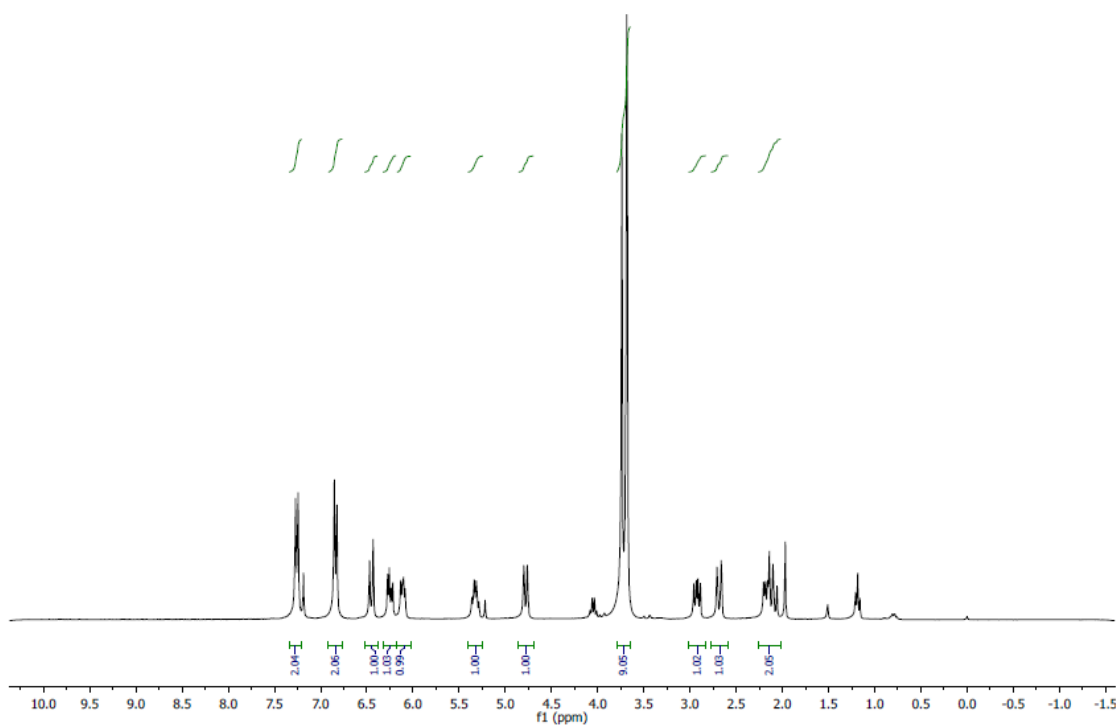
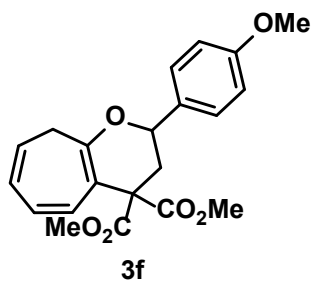




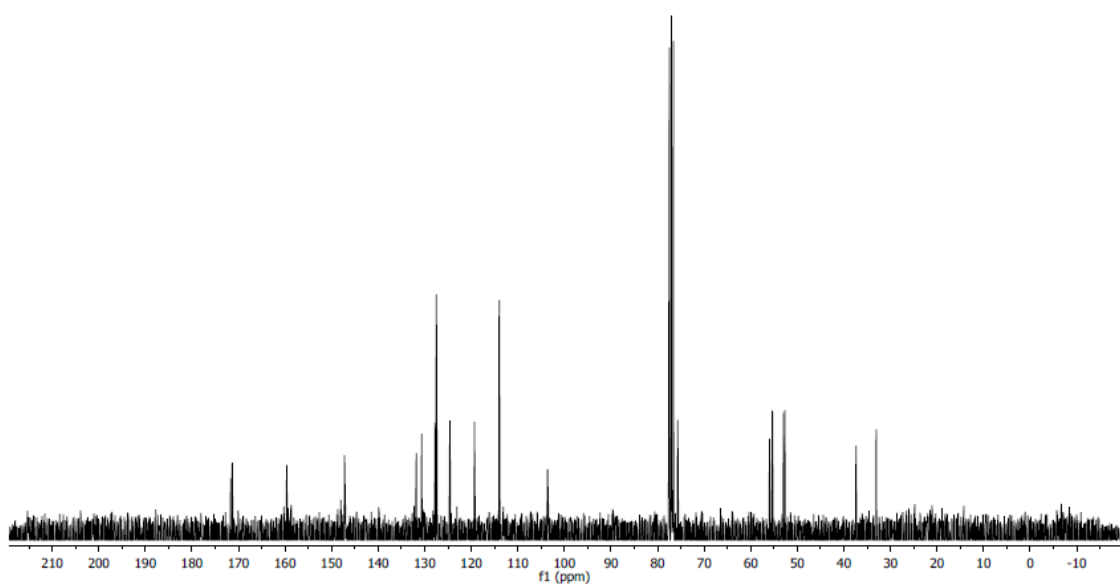
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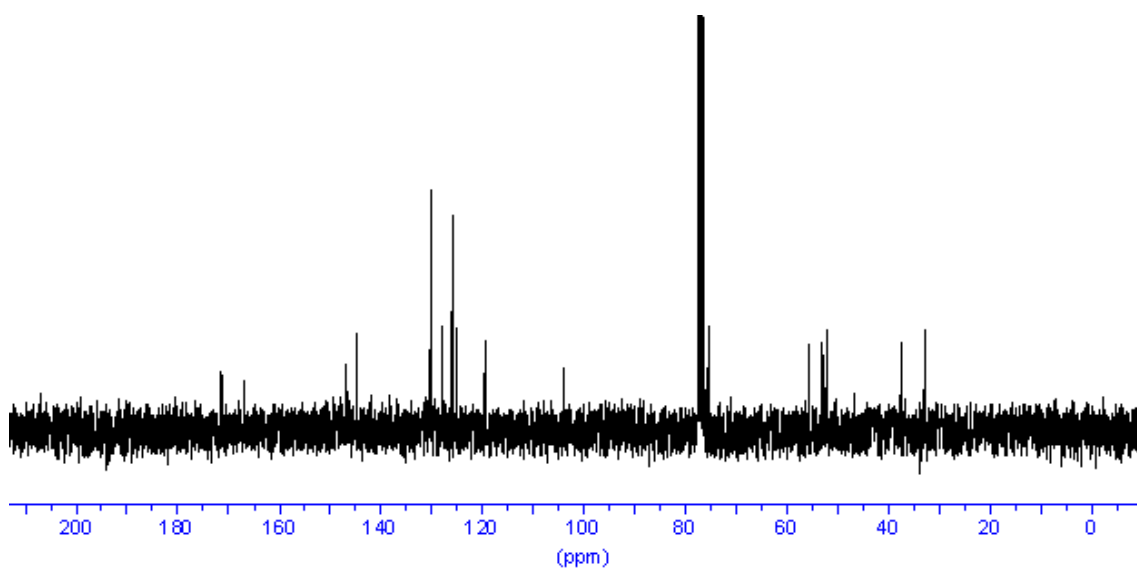
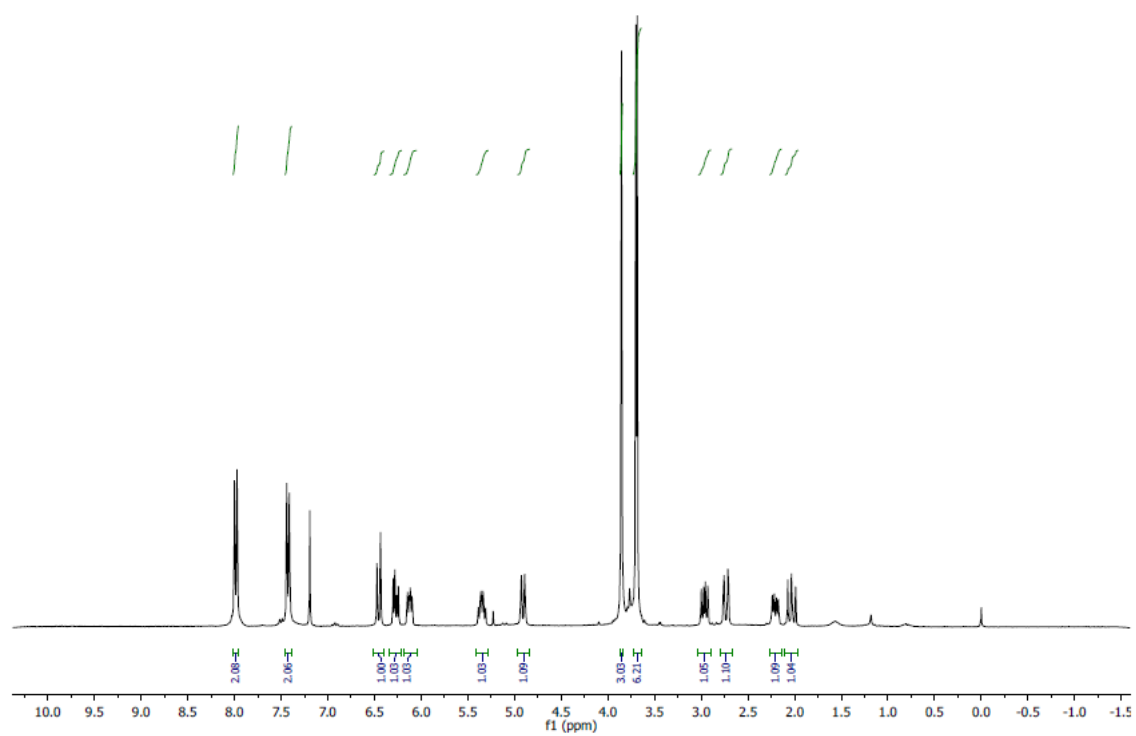
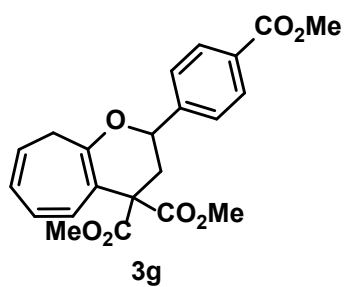


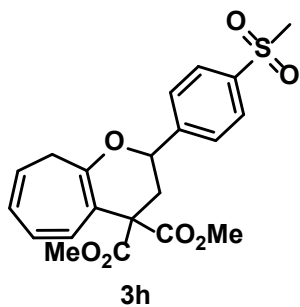




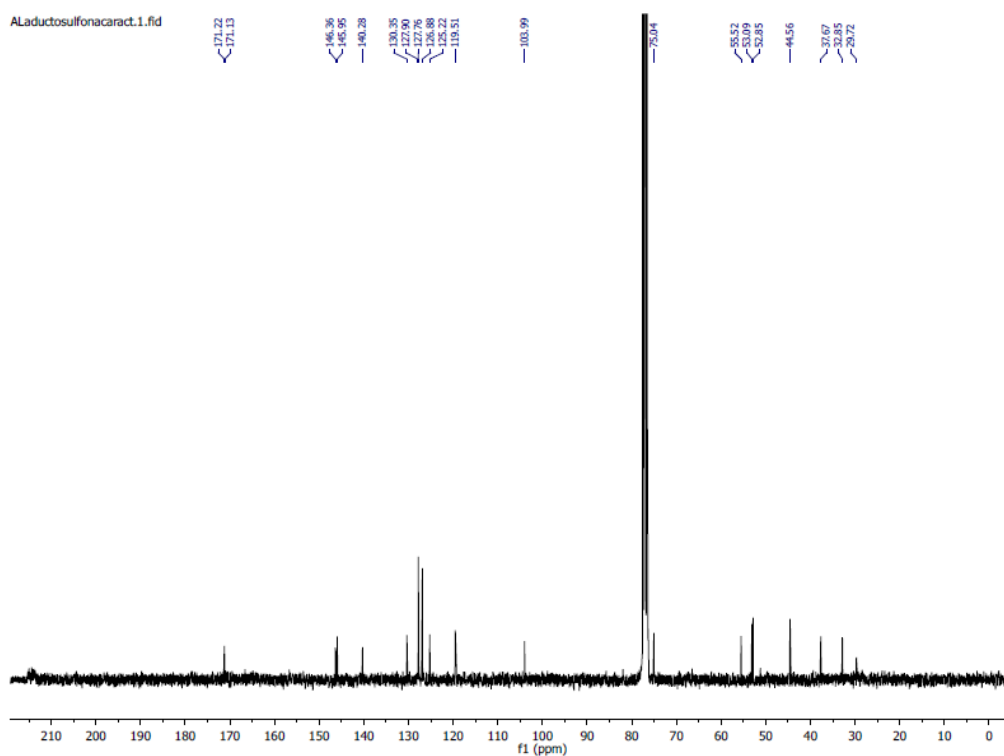
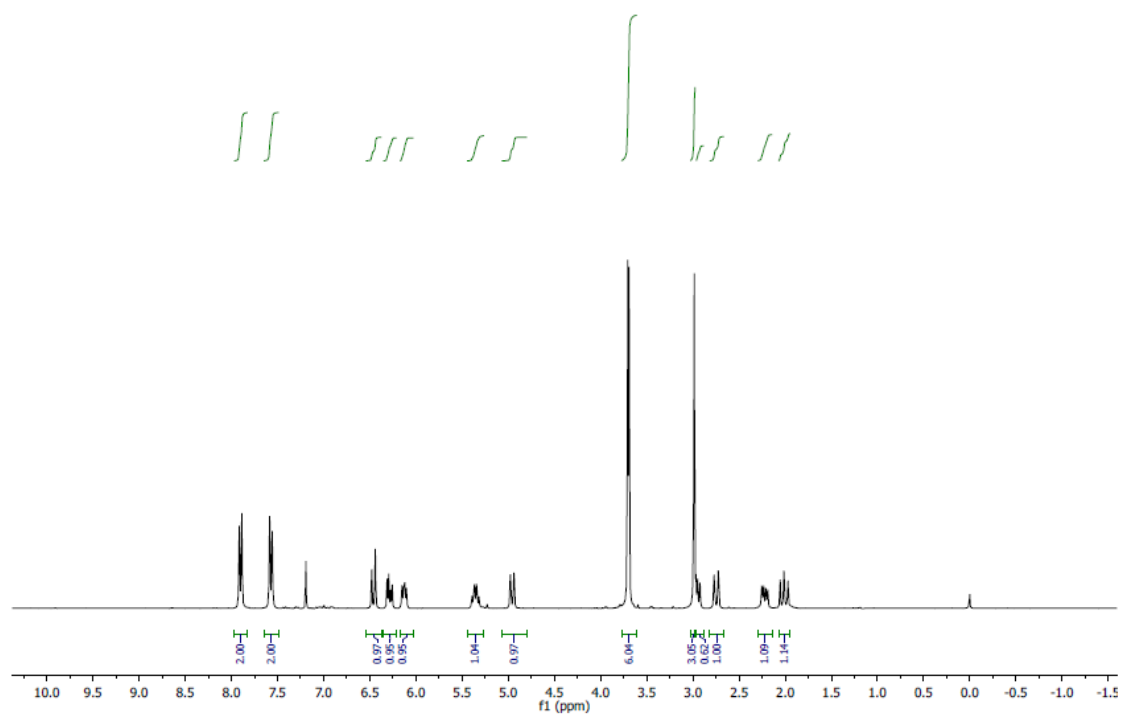
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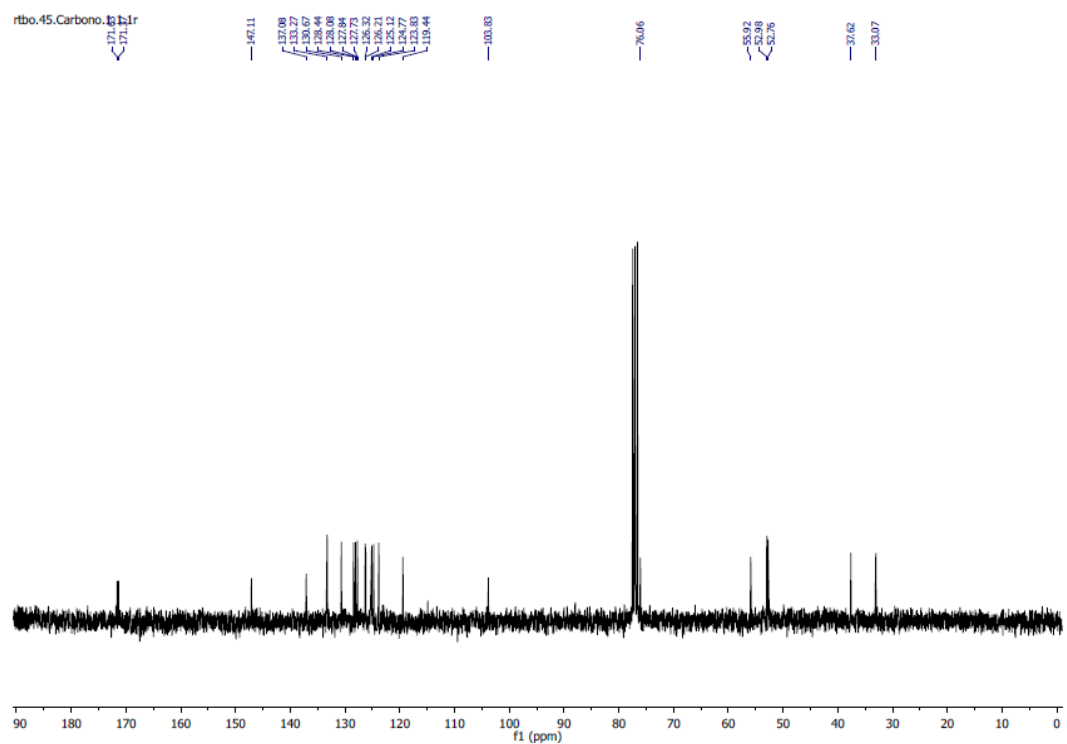
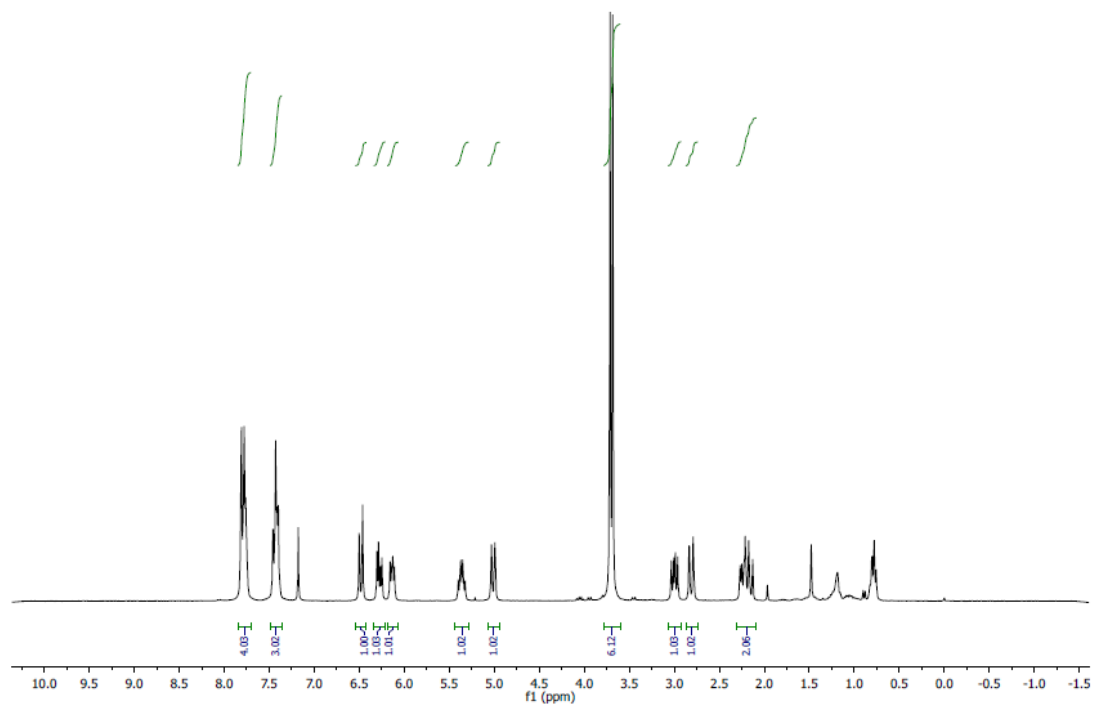
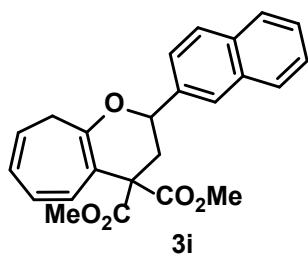


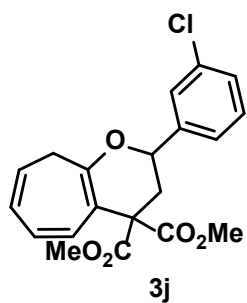




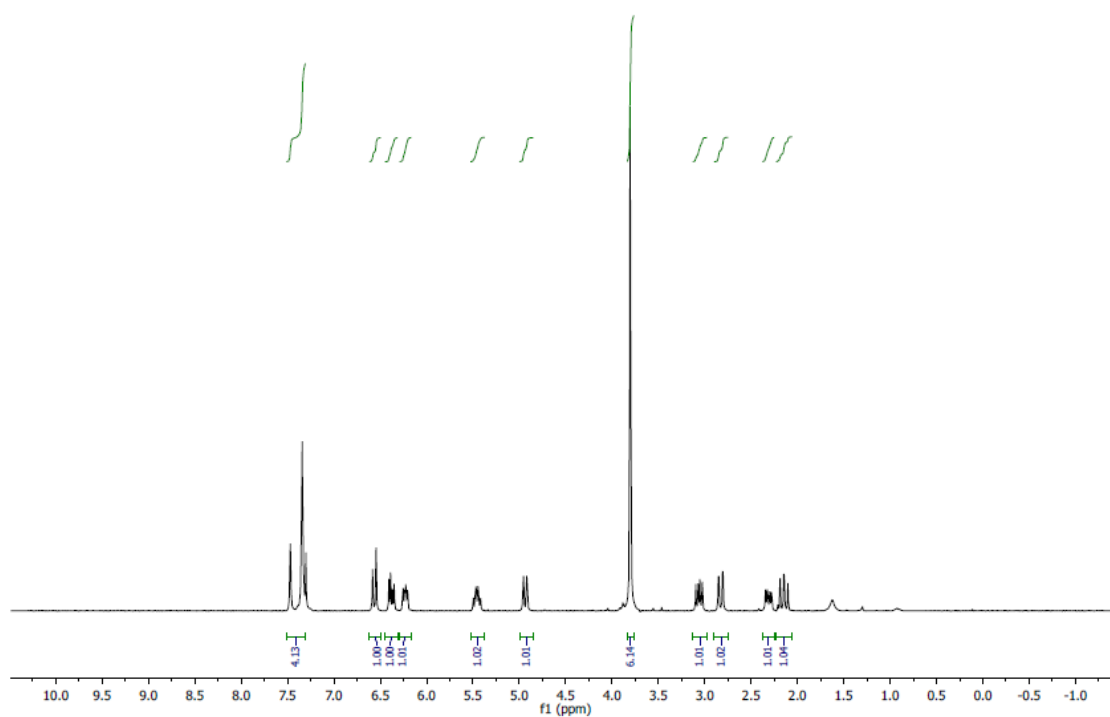
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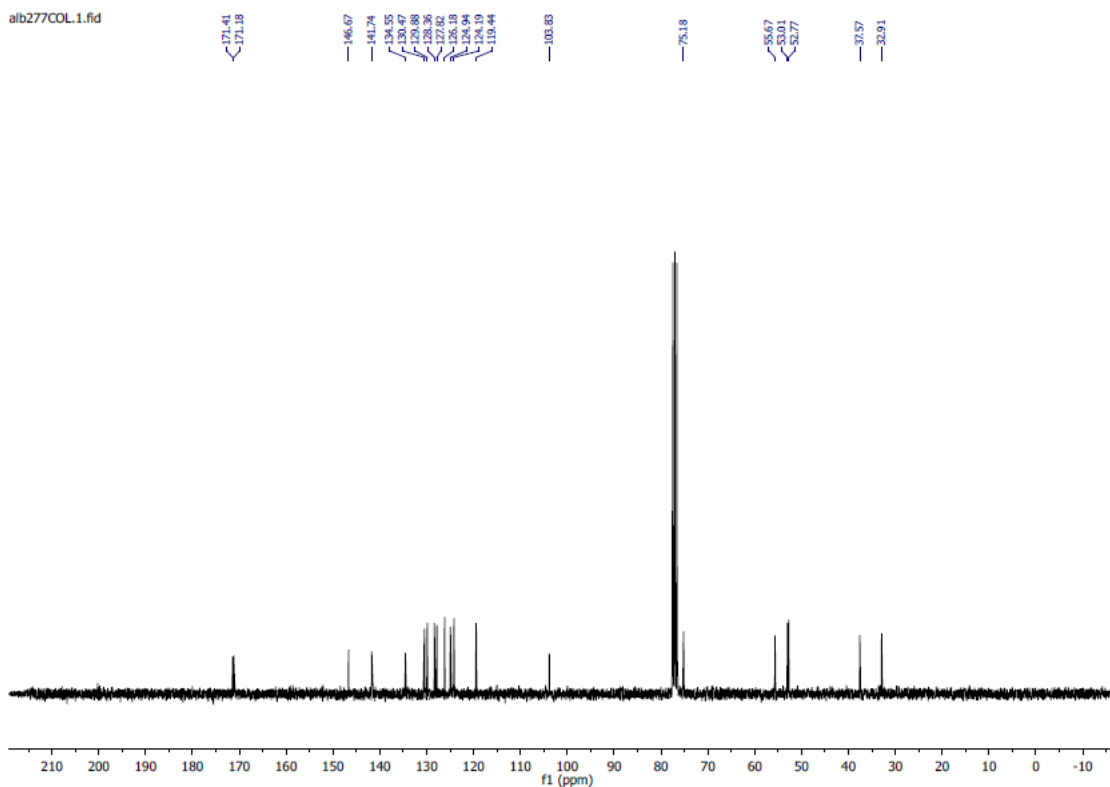


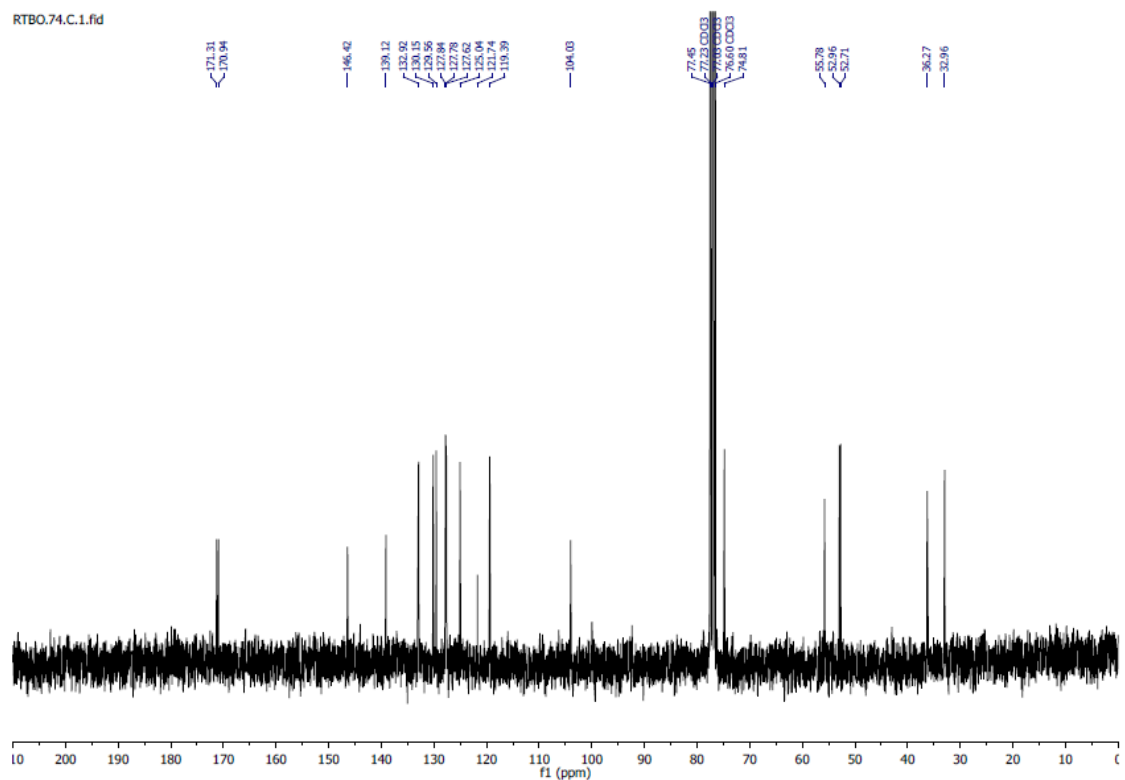
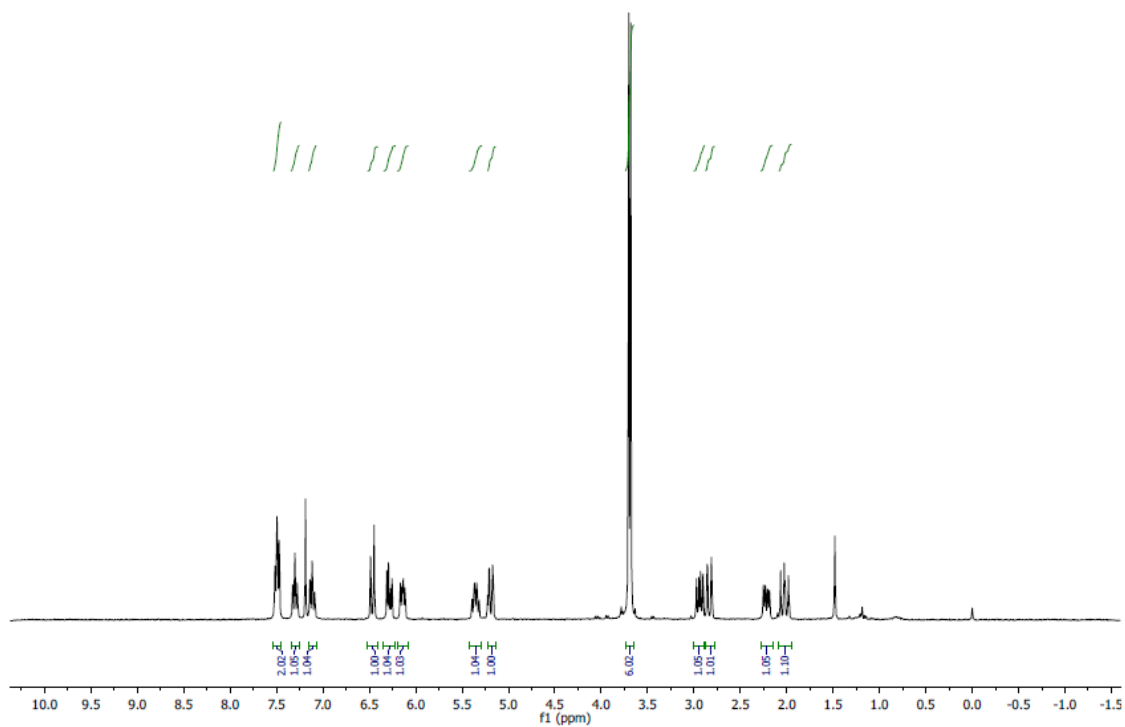
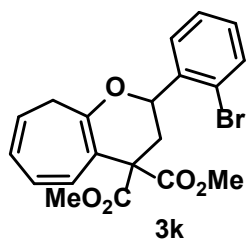


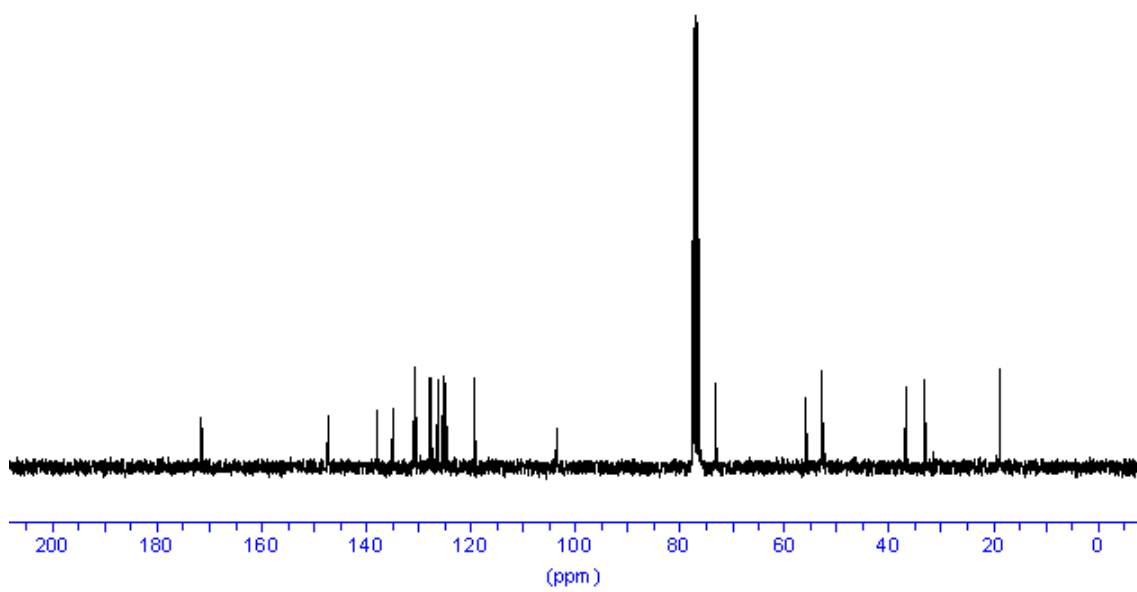
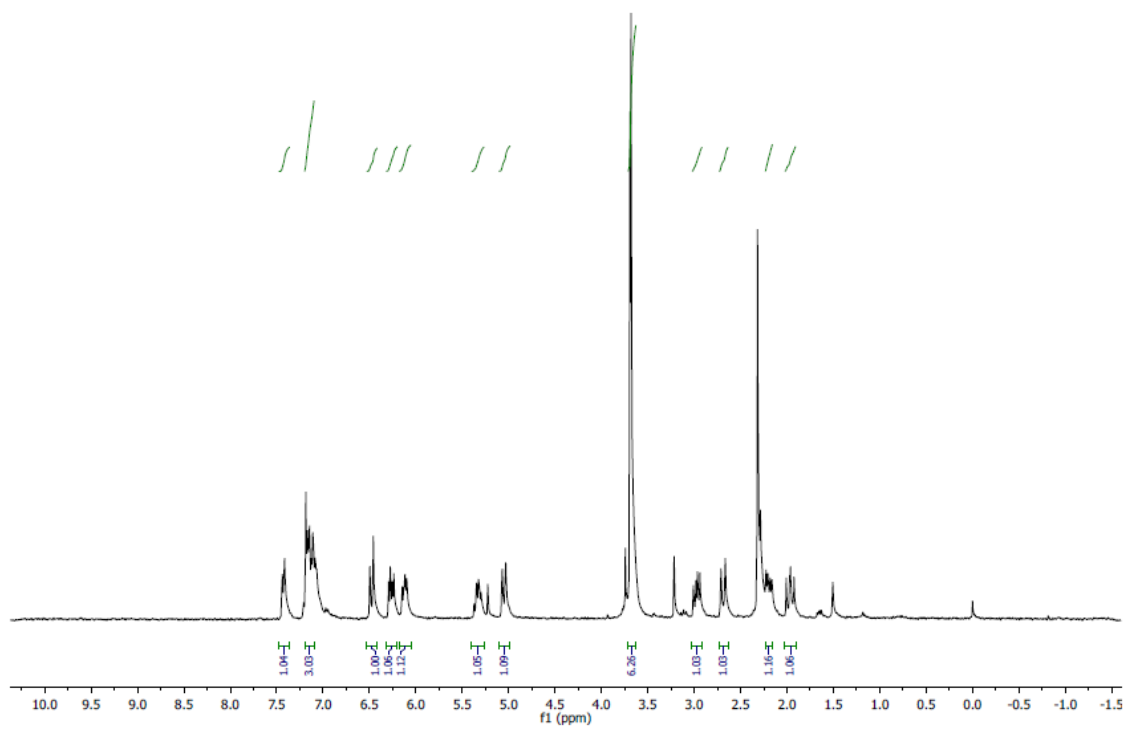
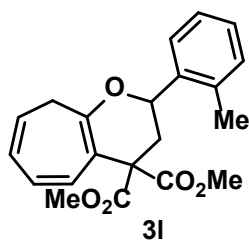
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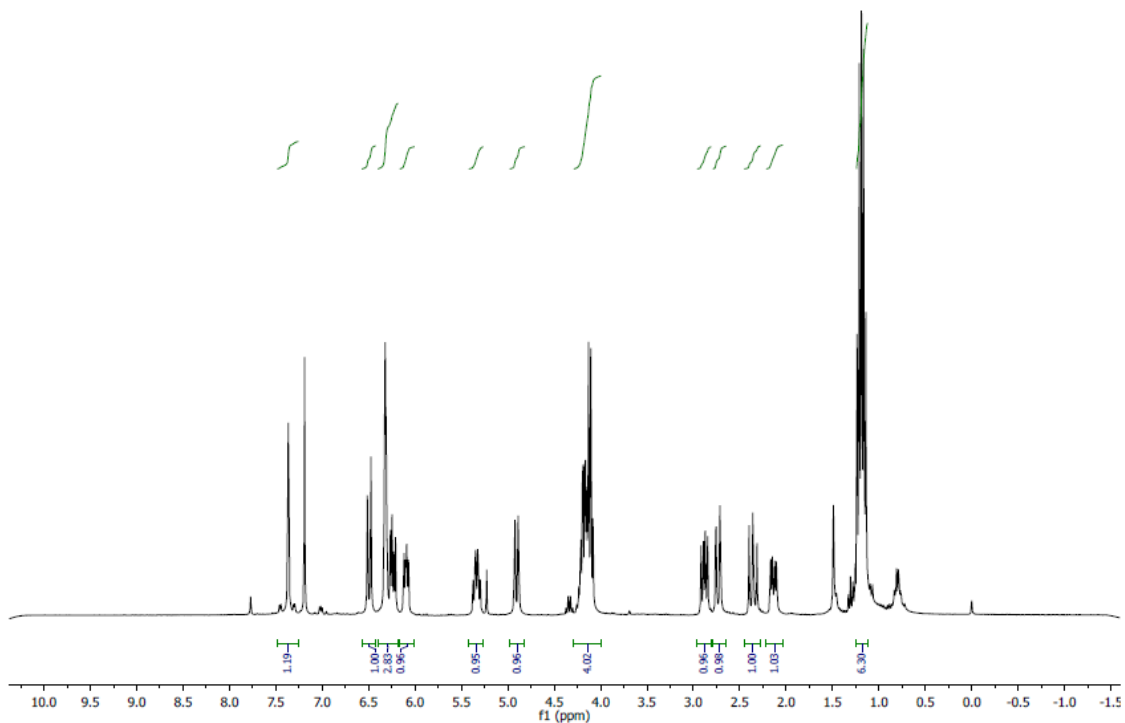
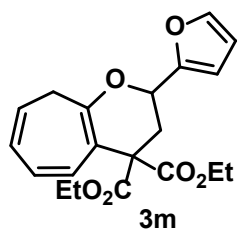


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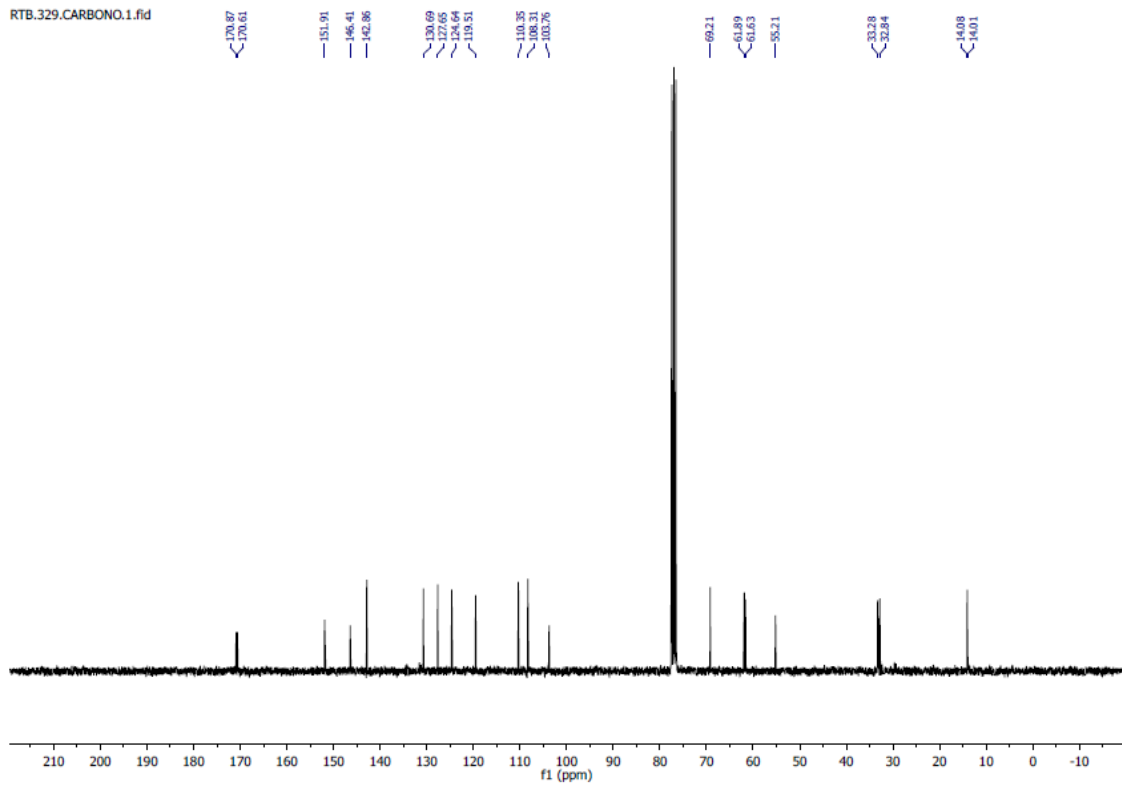


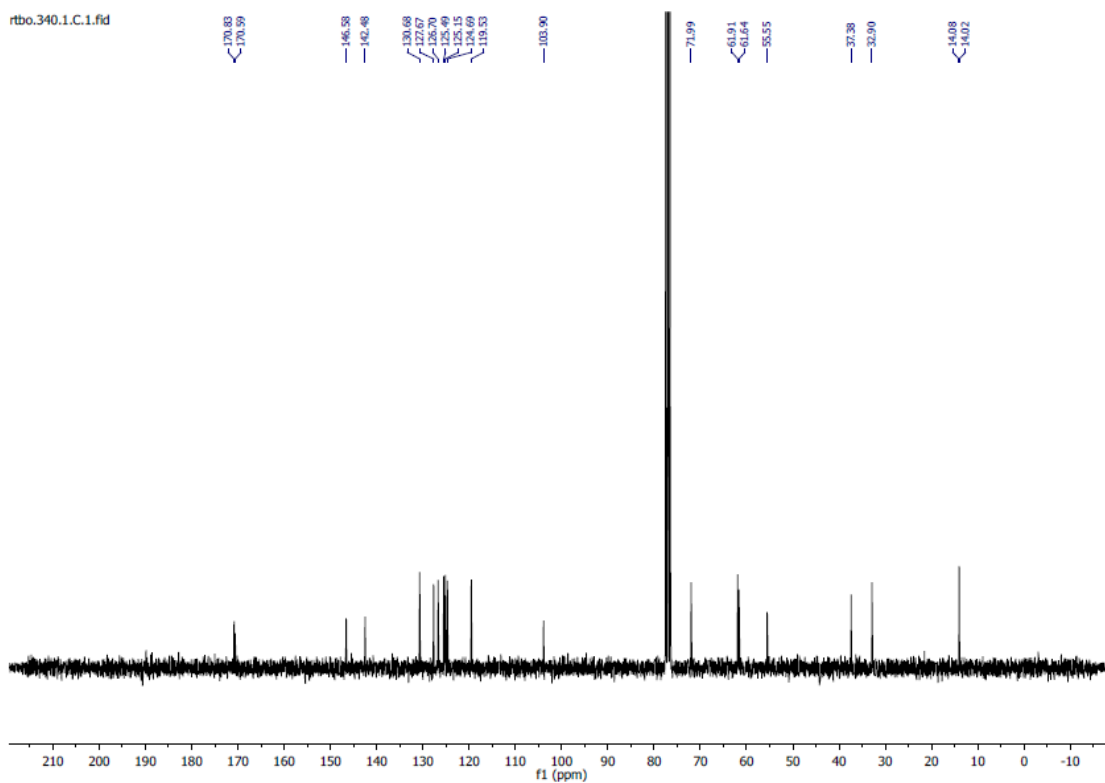
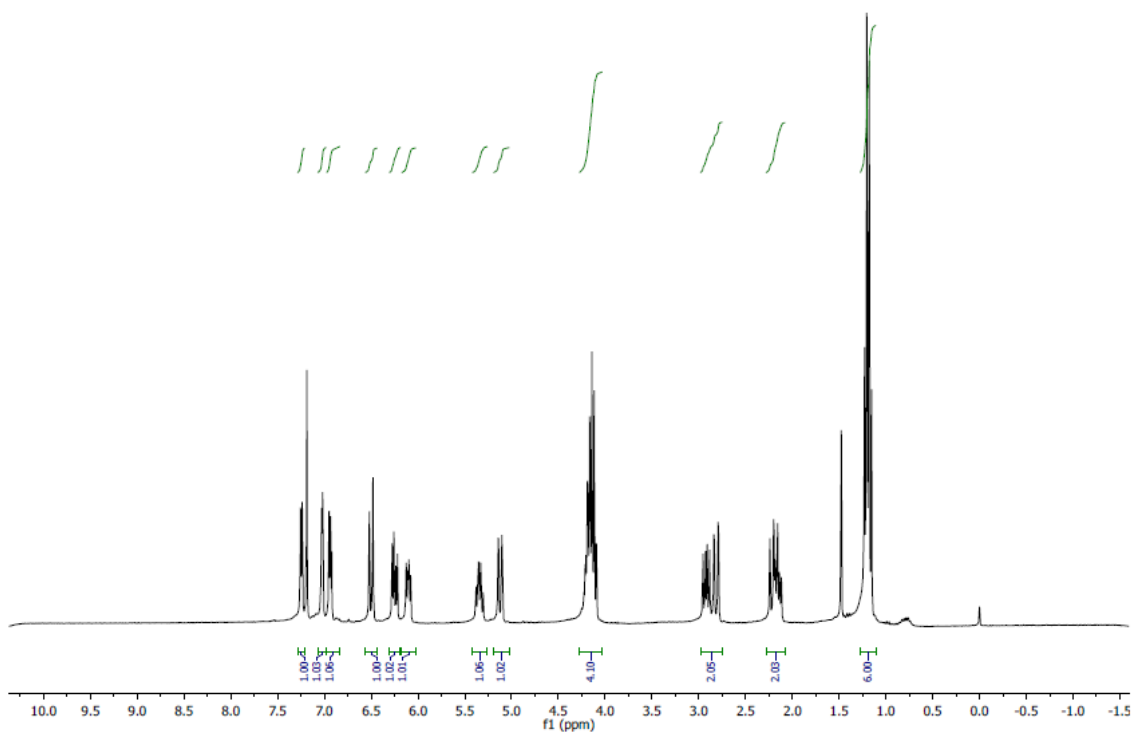
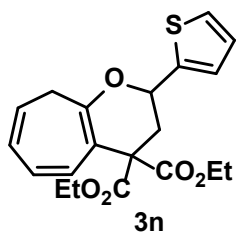


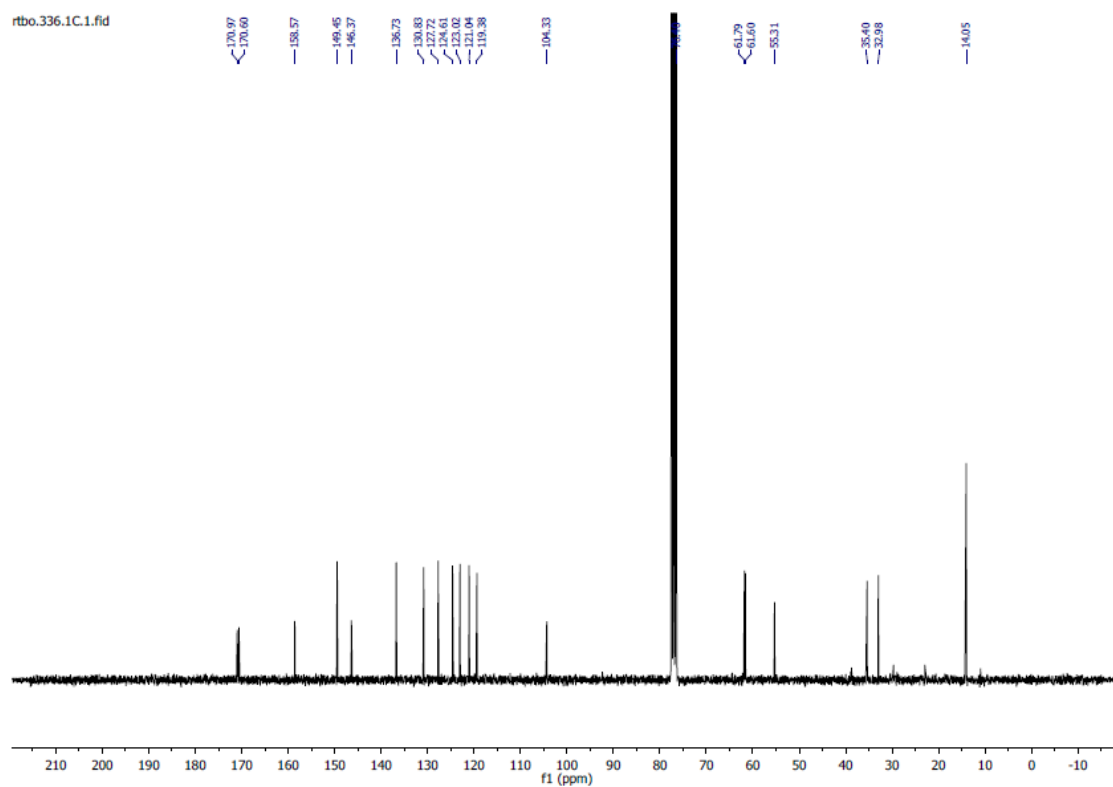
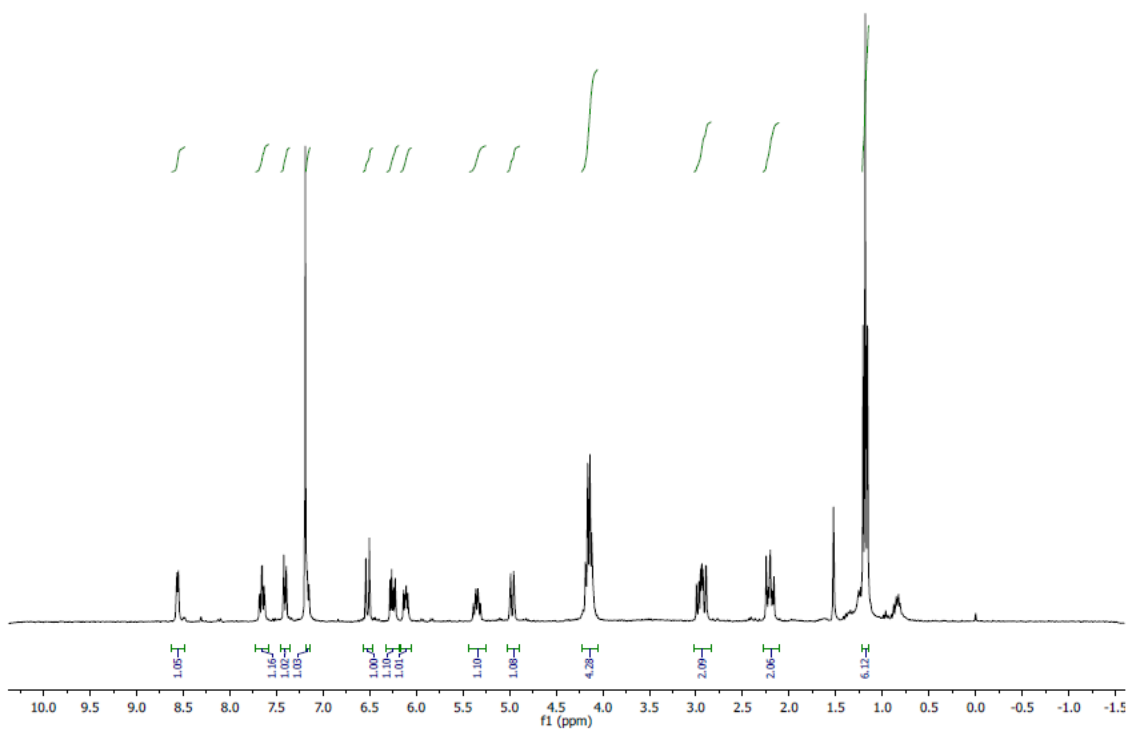
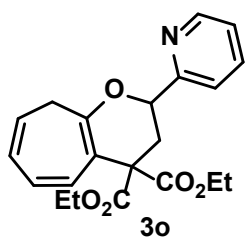


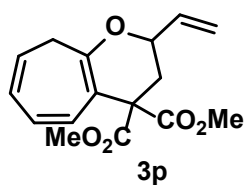


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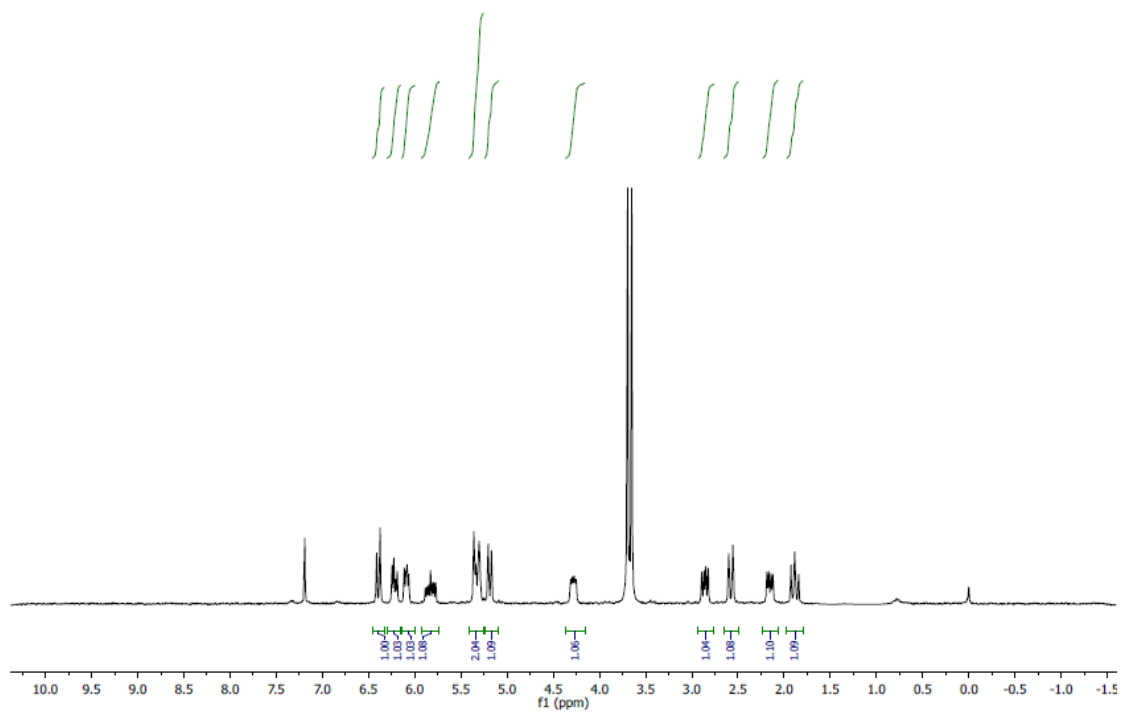




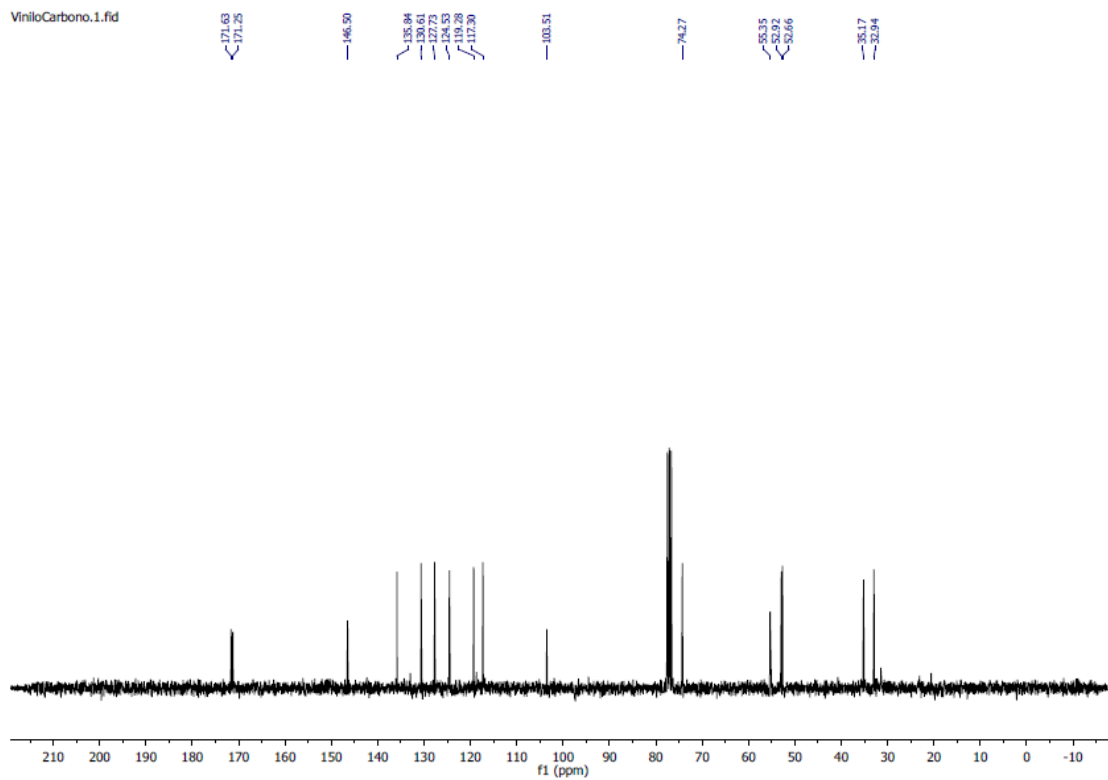


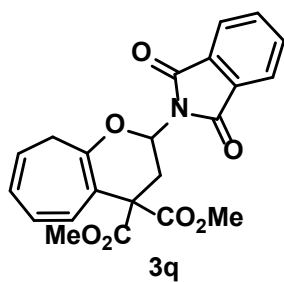


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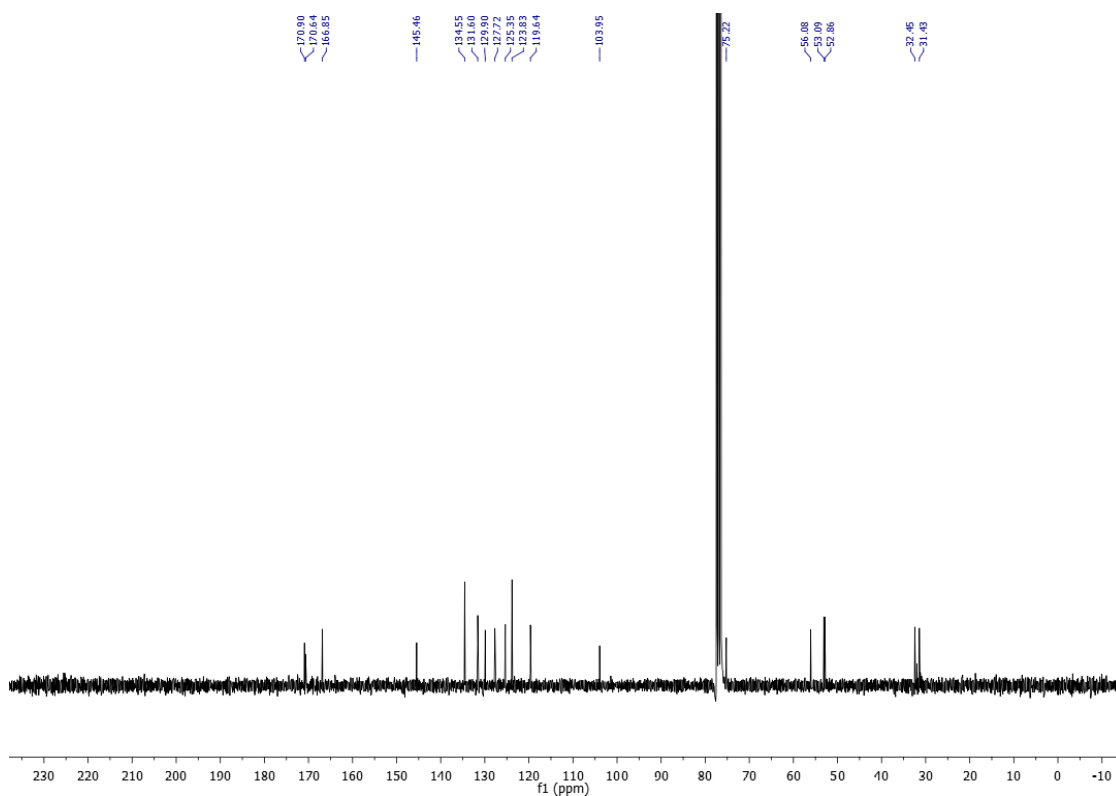
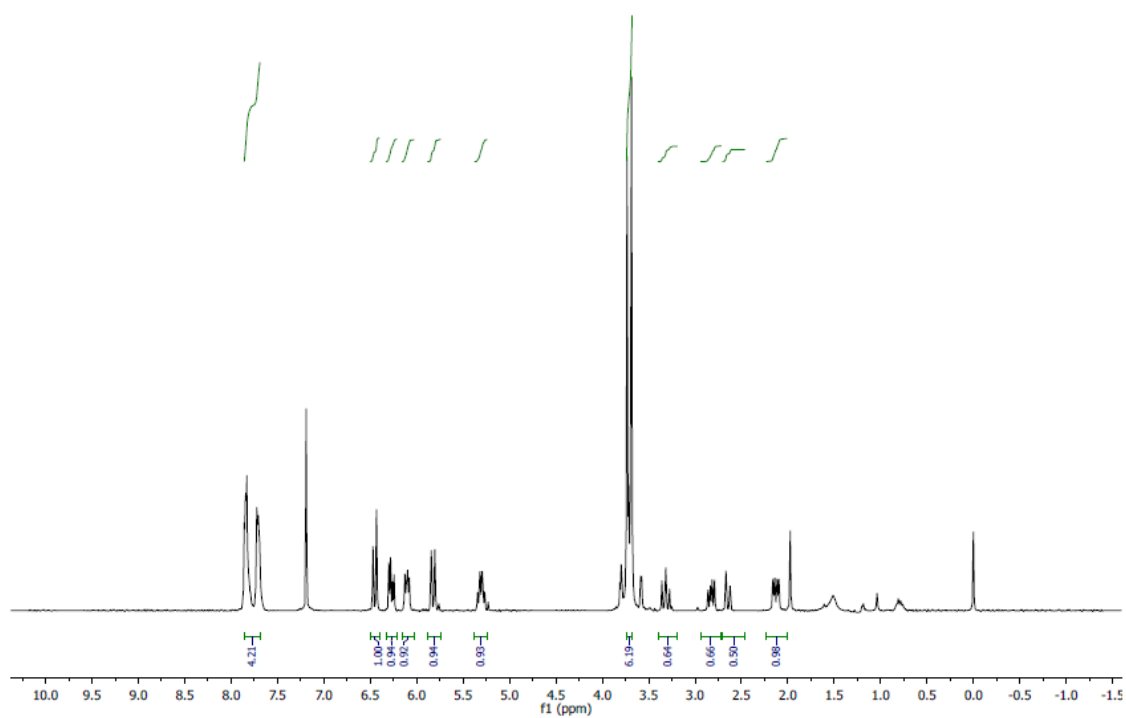


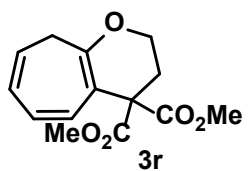
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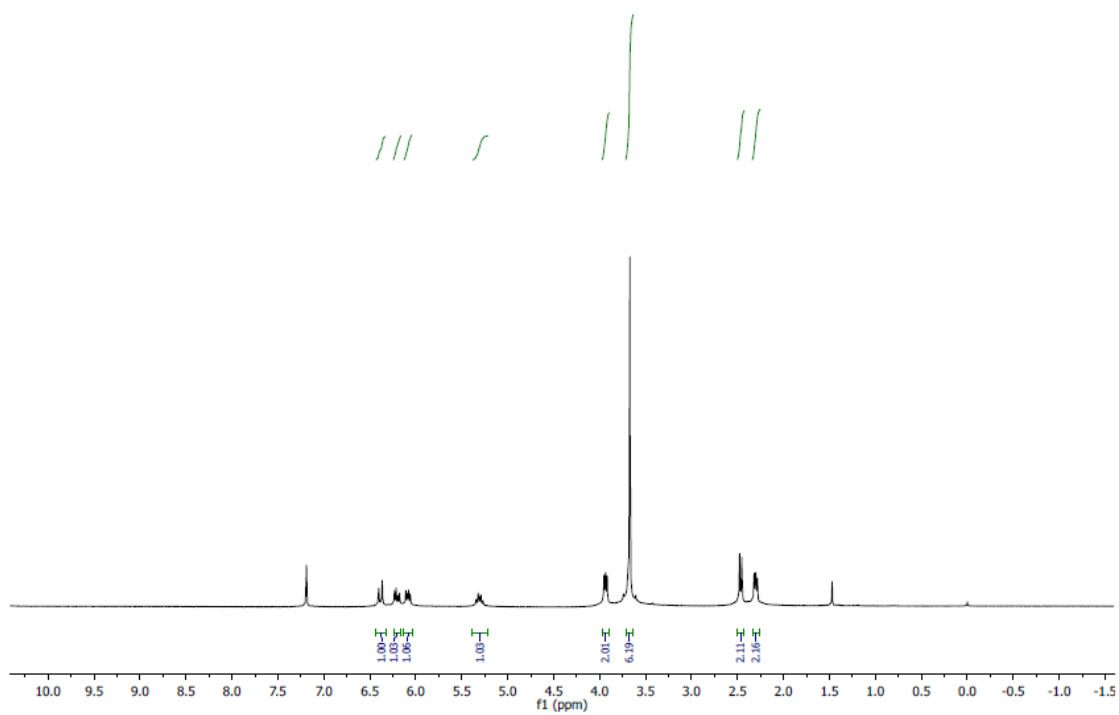


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RTBO.94.1.1.1.1r



rtbo.94.carbono.1.fid

