

Supporting Information

Nucleophilic Ring-Opening of Donor-Acceptor Cyclopropanes Catalyzed by Brønsted acid in Hexafluoroisopropanol

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General Information, Materials & General Procedures

All arylation/cyclopropane opening reactions were performed in 10 mL glass pressure tubes under an atmosphere of air. Elevated temperatures were achieved by way of a stirrer-hotplate, metal heating block and thermocouple. Purification of reaction products was carried out by flash column chromatography using Merck silica gel (40-63 µm). Analytical thin layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel 60 F254 (Merck), cut to size. Visualization was accomplished with UV light followed by staining with basic KMnO₄ solution and heating.

¹H-NMR spectra were recorded on a Bruker UltraShield 400 (400 MHz) spectrometer at ambient temperature and are reported in ppm using solvent as internal standard (CDCl₃ at 7.26 ppm). ¹³C-NMR spectra were recorded on a Bruker UltraShield Plus 400 (100 MHz) spectrometer at ambient temperature and are reported in ppm using solvent as internal standard (CDCl₃ at 77.16 ppm). ¹⁹F-NMR spectra were recorded on a Bruker UltraShield 400 (376.5 MHz) spectrometer at ambient temperature and are reported in ppm using trifluoroacetic acid as external standard (at -76.55 ppm). Data are reported as: multiplicity (ap = apparent, br = broad, s = singlet, d = doublet, t = triplet, q = quartet, quint = quintet, sext = sextet, m = multiplet, dd = doublet of doublets, ddd = doublet of doublet of doublets, dddd = doublet of doublet of doublet of doublets, qd = quartet of doublets, dt = doublet of triplets, dm = doublet of multiplets, td = triplet of doublets, quintd = quintet of doublets), coupling constants (in Hz) and integration. In cases where compounds were isolated as mixtures of regioisomers, signals corresponding to protons of the major regioisomer were integrated as integer values matching the number of protons in the molecule. Non-integer integration values correspond to signals of protons of minor regioisomers or to overlapping signals of regioisomers.

High resolution mass spectrometry (HRMS) analysis was performed on MicroTOF-Q Bruker (ESI) and ThermoScientific Exactive Plus EMR/Trace 1300 GC (APPI) instruments.

Materials: All commercial materials were purchased from Sigma-Aldrich, Alfa Aesar and FluoroChem, and were used as received, without further purification. Triflic acid (TfOH) ReagentPlus[®], ≥99% (CAS: 1493-13-6) was purchased from Sigma Aldrich, and HFIP (CAS: 920-66-1) from FluoroChem. Tris(pentafluorophenyl)borane B(C₆F₅) was purchased from Alfa Aesar and used without precaution to exclude air or moisture. It is known to rapidly hydrate to B(C₆F₅)•H₂O under such conditions.¹

Preparation of Donor-Acceptor Cyclopropanes: Donor-acceptor cyclopropane diesters **1a- 1j** were prepared via a two-step Knoevenagel/Corey-Chaykovsky sequence, according to unchanged literature procedures, in comparable yields to those reported and with corresponding analytical data.^{2,3} Donor-acceptor cyclopropane **1k**⁴ was prepared by Corey-Chaykovsky cyclopropanation of *trans*-chalcone according to a literature procedure and with corresponding analytical data. Cyclopropanes **1l-1p** were prepared according to a two-step aldol condensation/Corey-Chaykovsky sequence, according to unchanged literature procedures, in comparable yields to those reported and with corresponding analytical data.

General Procedure A – A 10 mL Pyrex tube was charged with a stir bar, followed by the requisite cyclopropane (0.25 mmol), nucleophile (0.50 mmol), HFIP (0.125mL) and finally TfOH (2.2 µL, 10 mol%). The reaction was then stirred at ambient temperature until TLC showed disappearance of starting material (typically ca. 3 hours). At completion, the crude reaction mixture was concentrated *in vacuo* onto silica gel and purified by flash column chromatography over silica in the eluent system stated to give the desired ring-opened product.

General Procedure B – A 10 mL Pyrex tube was charged with a stir bar, followed by the requisite cyclopropane (0.25 mmol), nucleophile (0.50 mmol), HFIP or MeNO₂ (0.125 mL) and finally B(C₆F₅)•H₂O (6.6 mg, 5 mol%). The reaction was then stirred at ambient temperature until TLC showed disappearance of starting material (typically ca. 3 hours). At completion, the crude reaction mixture was concentrated *in vacuo* onto silica gel and purified by flash column chromatography over silica in the eluent system stated to give the desired ring-opened product.

¹ Bergquist, C.; Bridgewater, B. M.; Harlan, C. J.; Norton, J. R.; Friesner, R. A.; Parkin, G. *J. Am. Chem. Soc.* **2000**, 122, 10581.

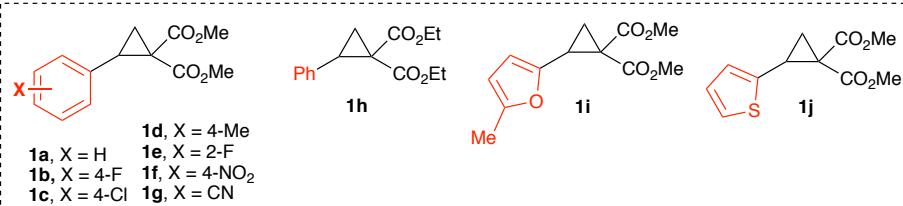
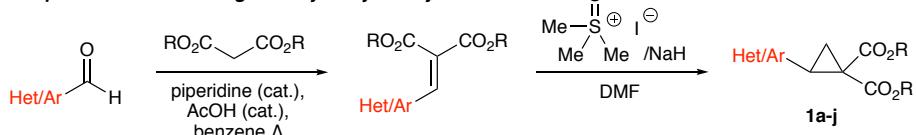
² M. K. Ghorai, R. Talukdar, D. P. Tiwari *Org. Lett.* **2014**, 16, 2204.

³ A. F. G. Goldberg, N. R. O'Connor, R. A. Craigill, B. M. Stoltz *Org. Lett.* **2012**, 14, 5314.

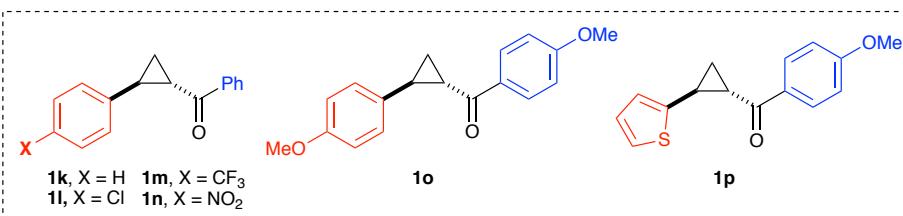
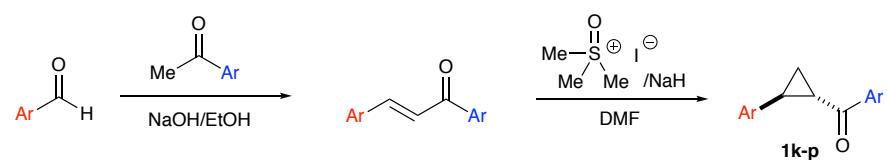
⁴ J. A. Ciaccio, C. E. Aman *Synth. Commun.* **2006**, 36, 1333.

1. Synthetic Overview & Characterization Data for Cyclopropanes

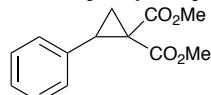
Preparation 1: Knoevenagel/Corey-Chaykovsky



Preparation 2: Aldol Condensation/Corey-Chaykovsky



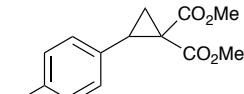
Dimethyl 2-phenylcyclopropane-1,1-dicarboxylate (1a)



Prepared via a two-step Knoevenagel/Corey-Chaykovsky sequence according to a literature procedure and with corresponding analytical data.²

Yield: 1.37 g, 97%; **¹H NMR:** (400 MHz, CDCl₃) δ 7.31–7.20 (5H, m), 3.81 (3H, s), 3.38 (3H, s), 3.25 (1H, t, *J* = 8.6 Hz), 2.22 (1H, dd, *J* = 8.0, 5.2 Hz), 1.77 (1H, dd, *J* = 9.3, 5.2 Hz).

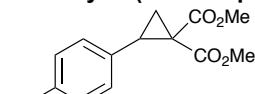
Dimethyl 2-(4-fluorophenyl)cyclopropane-1,1-dicarboxylate (1b)



Prepared via a two-step Knoevenagel/Corey-Chaykovsky sequence according to a literature procedure and with corresponding analytical data.²

Yield: 1.03 g, 82%; **¹H NMR:** (400 MHz, CDCl₃) δ 7.16 (2H, dd, *J* = 8.6, 5.4 Hz), 6.96 (2H, t, *J* = 8.6 Hz), 3.79 (3H, s), 3.75 (3H, s), 3.19 (1H, t, *J* = 8.6 Hz), 2.15 (1H, dd, *J* = 8.0, 5.3 Hz), 1.74 (1H, dd, *J* = 9.3, 5.3 Hz); **¹⁹F NMR:** (376 MHz, CDCl₃) δ -116.8.

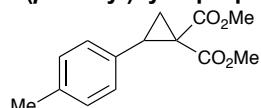
Dimethyl 2-(4-chlorophenyl)cyclopropane-1,1-dicarboxylate (1c)



Prepared via a two-step Knoevenagel/Corey-Chaykovsky sequence according to a literature procedure and with corresponding analytical data.²

Yield: 0.126 g, 9%; **¹H NMR:** (400 MHz, CDCl₃) δ 7.24 (2H, d, *J* = 8.4 Hz), 7.12 (2H, d, *J* = 8.4 Hz), 3.79 (3H, s), 3.40 (3H, s), 3.18 (1H, t, *J* = 8.8 Hz), 2.15 (1H, dd, *J* = 8.0, 5.6 Hz), 1.74 (1H, dd, *J* = 9.2, 5.2 Hz).

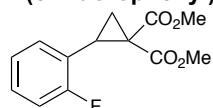
2-(*p*-Tolyl)cyclopropane-1,1-dicarboxylate (1d)



Prepared via a two-step Knoevenagel/Corey-Chaykovsky sequence according to a literature procedure and with corresponding analytical data.⁵

Yield: 0.380 g, 31%; **¹H NMR:** (400 MHz, CDCl₃) δ 7.07 (4H, s), 3.78 (3H, s), 3.38 (3H, s), 3.19 (1H, t, *J* = 8.8 Hz), 2.30 (3H, s), 2.17 (1H, dd, *J* = 8.4, 5.0 Hz), 1.72 (1H, dd, *J* = 9.6, 5.0 Hz).

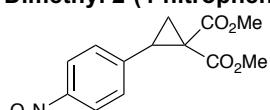
2-(*o*-Fluorophenyl)cyclopropane-1,1-dicarboxylate (1e)



Prepared via a two-step Knoevenagel/Corey-Chaykovsky sequence according to a literature procedure and with corresponding analytical data.⁶

Yield: 0.270 g, 37%; **¹H NMR:** (400 MHz, CDCl₃) δ 7.25–7.18 (1H, m), 7.10–6.97 (3H, m), 3.80 (3H, s), 3.39 (3H, s), 3.27 (1H, t, *J* = 8.6 Hz), 2.20 (1H, dd, *J* = 8.0, 5.2 Hz), 1.78 (1H, dd, *J* = 9.2, 5.2 Hz); **¹⁹F NMR** (376.5 MHz, CDCl₃, CF₃CO₂H - ext. std.) δ (ppm): –114.76 to –114.90 (1F, m).

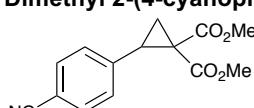
Dimethyl 2-(4-nitrophenyl)cyclopropane-1,1-dicarboxylate (1f)



Prepared via a two-step Knoevenagel/Corey-Chaykovsky sequence according to a literature procedure and with corresponding analytical data.⁷

Yield: 0.408 g, 29%; **¹H NMR:** (400 MHz, CDCl₃) δ 8.14 (2H, d, *J* = 8.4 Hz), 7.36 (2H, d, *J* = 8.8 Hz), 3.81 (3H, s), 3.42 (3H, s), 3.28 (1H, t, *J* = 8.6 Hz), 2.22 (1H, dd, *J* = 7.6, 5.4 Hz), 1.83 (1H, dd, *J* = 9.2, 5.6 Hz).

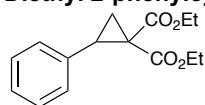
Dimethyl 2-(4-cyanophenyl)cyclopropane-1,1-dicarboxylate (1g)



Prepared via a two-step Knoevenagel/Corey-Chaykovsky sequence according to a literature procedure and with corresponding analytical data.⁸

Yield: 0.691 g, 67%; **¹H NMR:** (400 MHz, CDCl₃) δ 7.58 (2H, d, *J* = 8.2 Hz), 7.31 (2H, d, *J* = 8.2 Hz), 3.81 (3H, s), 3.41 (3H, s), 3.25 (1H, t, *J* = 8.5 Hz), 2.20 (1H, dd, *J* = 8.0, 5.5 Hz), 1.81 (1H, dd, *J* = 9.1, 5.4 Hz).

Diethyl 2-phenylcyclopropane-1,1-dicarboxylate (1h)



Prepared via a two-step Knoevenagel/Corey-Chaykovsky sequence according to a literature procedure and with corresponding analytical data.⁹

Yield: 0.850 g, 65%; **¹H NMR:** (400 MHz, CDCl₃) δ 7.30–7.22 (5H, m), 4.23 (2H, q, *J* = 6.9 Hz), 3.86 (2H, q, *J* = 7.1 Hz), 3.24 (1H, t, *J* = 8.6 Hz), 2.20 (1H, dd, *J* = 8.0, 5.2 Hz), 1.73 (1H, dd, *J* = 9.2, 5.2 Hz), 1.32–1.29 (3H, m), 0.88 (3H, t, *J* = 7.1 Hz).

⁵ R. Talukdar, Tiwari, D. P., Saha, A., Ghorai, M. K. *Org. Lett.* **2014**, *16*, 3954.

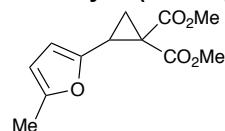
⁶ J. Zhang, H. Jiang, S. Zhu *Adv. Synth. Catal.* **2017**, *359*, 2924.

⁷ C. Perreault, S. R. Goudreau, L. E. Zimmer, A. B. Charette *Org. Lett.* **2008**, *10*, 689.

⁸ K. L. Ivanov, E. V. Vilemson, E. M. Budynina, O. A. Ivanova, I. V. Trushkov, M. Y. Melnikov *Chem. Eur. J.* **2015**, *21*, 4975.

⁹ R. Dey, P. Banerjee *Org. Lett.* **2017**, *19*, 304.

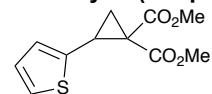
Dimethyl 2-(5-methylfuran-2-yl)cyclopropane-1,1-dicarboxylate (1i)



Prepared via a two-step Knoevenagel/Corey-Chaykovsky sequence according to a literature procedure and with corresponding analytical data.¹⁰

Yield: 1.12 g, 94%; **¹H NMR:** (400 MHz, CDCl₃) δ 5.98 (1H, d, *J* = 3.1 Hz), 5.84 (1H, d, *J* = 2.3 Hz), 3.80 (3H, s), 3.56 (3H, s), 3.04 (1H, t, *J* = 8.6 Hz), 2.22 (3H, s), 2.04 (1H, ddd, *J* = 7.7, 5.0 Hz), 1.75 (1H, dd, *J* = 9.5, 5.0 Hz).

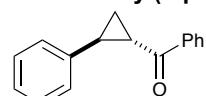
Dimethyl 2-(thiophen-2-yl)cyclopropane-1,1-dicarboxylate (1j)



Prepared via a two-step Knoevenagel/Corey-Chaykovsky sequence according to a literature procedure and with corresponding analytical data.²

Yield: 1.17g, 97%; **¹H NMR:** (400 MHz, CDCl₃) δ 7.16 (1H, dd, *J* = 5.1, 0.6 Hz), 6.90 (1H, dd, *J* = 5.1, 3.5 Hz), 6.83 (1H, d, *J* = 3.5 Hz), 3.78 (3H, s), 3.48 (3H, s), 3.29 (1H, t, *J* = 8.5 Hz), 2.15 (1H, dd, *J* = 7.7, 5.2 Hz), 1.83 (1H, dd, *J* = 9.2, 5.2 Hz).

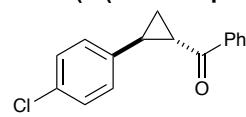
trans-Phenyl(2-phenylcyclopropyl)methanone (1k)



Donor-acceptor cyclopropane **1k** was prepared by Corey-Chaykovsky cyclopropanation of *trans*-chalcone according to a literature procedure and with corresponding analytical data.⁴

Yield: 0.829 g, 75%; **¹H NMR:** (400 MHz, CDCl₃) δ 8.01-7.99 (2H, m), 7.58-7.54 (1H, m), 7.46 (2H, t, *J* = 7.5 Hz), 7.32 (2H, t, *J* = 7.6 Hz), 7.25-7.22 (1H, m), 7.19 (2H, dd, *J* = 8.0, 1.0 Hz), 2.91 (1H, ddd, *J* = 8.1, 5.1, 4.0 Hz), 2.71 (1H, ddd, *J* = 9.1, 6.5, 4.0 Hz).

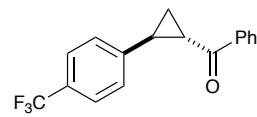
trans-(2-(4-Chlorophenyl)cyclopropyl)(phenyl)methanone (1l)



Prepared via a two-step aldol condensation/Corey-Chaykovsky sequence, according to a literature procedure and with corresponding analytical data.¹¹

Yield: 0.726 g, 57%; **¹H NMR:** (400 MHz, CDCl₃) δ 8.01 (2H, d, *J* = 7.4 Hz), 7.60 (1H, t, *J* = 7.4 Hz), 7.49 (2H, t, *J* = 7.7 Hz), 7.30 (2H, d, *J* = 8.4 Hz), 7.13 (2H, d, *J* = 8.4 Hz), 2.91-2.86 (1H, m), 2.72-2.67 (1H, m), 1.94 (1H, dt, *J* = 9.1, 4.6 Hz), 1.54 (1H, ddd, *J* = 8.0, 6.6, 4.3 Hz).

trans-Phenyl(2-(4-(trifluoromethyl)phenyl)cyclopropyl)methanone (1m)



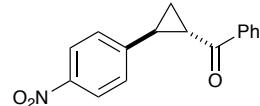
Prepared via a two-step aldol condensation/Corey-Chaykovsky sequence, according to a literature procedure and with corresponding analytical data.¹¹

Yield: 1.08 g, 74%; **¹H NMR:** (400 MHz, CDCl₃) δ 7.98 (2H, d, *J* = 8.8 Hz), 7.11 (2H, d, *J* = 8.7 Hz), 6.94 (2H, d, *J* = 8.8 Hz), 6.85 (2H, d, *J* = 8.7 Hz), 3.87 (3H, s), 3.80 (3H, s), 2.80-2.76 (1H, m), 2.65-2.60 (1H, m), 1.86 (1H, ddd, *J* = 9.1, 4.9, 4.2 Hz), 1.47 (1H, ddd, *J* = 7.9, 6.7, 4.1 Hz); **¹⁹F NMR:** (376 MHz, CDCl₃) δ -62.4.

¹⁰ Ivanova, Olga A.; Budynina, Ekaterina M.; Chagarovskiy, Alexey O.; Kaplun, Alexey E.; Trushkov, Igor V.; Melnikov, Mikhail Ya *Adv. Synth. Catal.* **2011**, 353, 1125.

¹¹ P. Cotugno, A. Monopoli, F. Ciminale, A. Milella, A. Nacci *Angew. Chem. Int. Ed.* **2014**, 53, 13563.

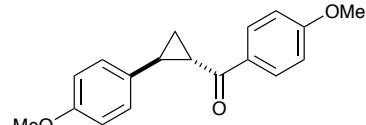
***trans*-(2-(4-Nitrophenyl)cyclopropyl)(phenyl)methanone (1n)**



Prepared as a yellow solid via a two-step aldol condensation/Corey-Chaykovsky sequence, according to a literature procedure and with corresponding analytical data.¹²

Yield: 0.765 g, 57%; **¹H NMR:** (400 MHz, CDCl₃) δ 8.21 (2H, d, *J* = 8.8 Hz), 7.99 (2H, dd, *J* = 8.3, 1.1 Hz), 7.65 (1H, tt, *J* = 7.4, 1.4 Hz), 7.53 (2H, t, *J* = 7.7 Hz), 7.34 (2H, d, *J* = 8.8 Hz), 3.05 (1H, ddd, *J* = 8.3, 5.4, 4.0 Hz), 2.82 (1H, ddd, *J* = 9.0, 6.6, 4.0 Hz), 2.04 (1H, dt, *J* = 9.0, 5.0 Hz), 1.72 (1H, ddd, *J* = 8.2, 6.6, 4.6 Hz).

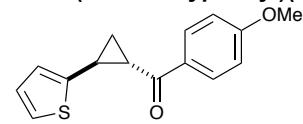
***trans*-(4-Methoxyphenyl)(2-(4-methoxyphenyl)cyclopropyl)methanone (1o)**



Prepared via a two-step aldol condensation/Corey-Chaykovsky sequence, according to a literature procedure and with corresponding analytical data.¹³

Yield: 0.801 g, 57%; **¹H NMR:** (400 MHz, CDCl₃) δ 8.01 (2H, d, *J* = 8.6 Hz), 7.13 (2H, d, *J* = 8.5 Hz), 6.96 (2H, d, *J* = 8.6 Hz), 6.87 (2H, d, *J* = 8.5 Hz), 3.89 (3H, s), 3.82 (3H, s), 2.80 (1H, dt, *J* = 8.2, 4.3 Hz), 2.67-2.62 (1H, m), 1.88 (1H, dt, *J* = 9.0, 4.5 Hz), 1.49 (1H, td, *J* = 7.1, 4.1 Hz).

***trans*-(4-Methoxyphenyl)(2-(thiophen-2-yl)cyclopropyl)methanone (1p)**



Prepared via a two-step aldol condensation/Corey-Chaykovsky sequence, according to a literature procedure.¹⁴

Yield: 0.959 g, 74%; **¹H NMR:** (400 MHz, CDCl₃) δ 8.00 (2H, d, *J* = 8.8 Hz), 7.12 (1H, dd, *J* = 4.9, 1.0 Hz), 6.97-6.92 (3H, m), 6.88 (1H, dt, *J* = 3.5, 0.5 Hz), 3.88 (3H, s), 2.91-2.82 (2H, m), 1.91 (1H, ddd, *J* = 9.0, 5.2, 4.0 Hz), 1.51 (1H, ddd, *J* = 8.1, 6.5, 4.0 Hz); **¹³C NMR:** (100 MHz, CDCl₃) δ 196.3, 163.5, 145.0, 130.6, 130.4, 127.0, 124.0, 123.1, 113.8, 55.5, 29.6, 24.6, 19.8.

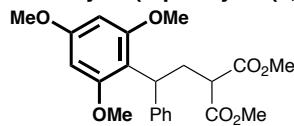
¹² L. A. Yanovskaya, V. A. Dombrovsky, O. S. Chizov, B. M. Zolotarev, O. A. Subbotin, V. F. Kucherov *Tetrahedron*, **1972**, *28*, 1565.

¹³ L. Feng, H. Yan, C. Yang, D. Chen, W. Xia *J. Org. Chem.* **2016**, *81*, 7008.

¹⁴ Paxton, R. J.; Taylor, R. J. *K Synlett*, **2007**, *4*, 633.

2. Characterization Data for Ring-Opened Products

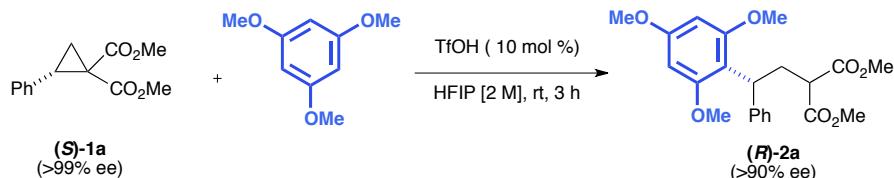
Dimethyl 2-(2-phenyl-2-(2,4,6-trimethoxyphenyl)ethyl)malonate (2a)



The title compound was prepared according to *General Procedure A* from cyclopropane **1a** (0.059 g, 0.25 mmol), 1,3,5-trimethoxybenzene (0.084 g, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-30% EtOAc in petroleum ether) gave **2a** as a colourless liquid. Analytical data are in agreement with the literature.¹⁵

Yield: 0.096 g, 95%; **R_f** = 0.23 (petroleum ether/EtOAc 8:2); **IR v_{max} / cm⁻¹ (film)**: 2955, 2839, 1751, 1732, 1603, 1589; **¹H NMR**: (400 MHz, CDCl₃) δ 7.29 (2H, d, *J* = 7.4 Hz), 7.21 (2H, t, *J* = 7.6 Hz), 7.11 (1H, t, *J* = 7.3 Hz), 6.10 (2H, s), 4.63 (1H, dd, *J* = 10.9, 5.6 Hz), 3.78 (3H, s), 3.71 (3H, s), 3.70 (6H, s), 3.63 (3H, s), 3.26 (1H, dd, *J* = 9.4, 5.4 Hz), 2.92 (1H, ddd, *J* = 13.3, 11.6, 5.4 Hz), 2.74 (1H, ddd, *J* = 13.3, 9.4, 5.6 Hz); **¹³C NMR**: (100 MHz, CDCl₃) δ 170.3, 170.0, 160.0, 159.4, 144.4, 127.7, 127.7, 125.4, 111.3, 91.1, 55.6, 55.2, 52.4, 52.3, 50.7, 37.0, 31.0.

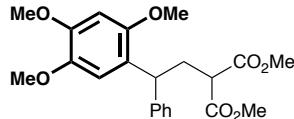
(R)-Dimethyl 2-(2-phenyl-2-(2,4,6-trimethoxyphenyl)ethyl)malonate ((R)-2a)



The title compound was prepared according to *General Procedure A* from enantiopure cyclopropane (**S**)-1a (0.059 g, 0.25 mmol), 1,3,5-trimethoxybenzene (0.084 g, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-30% EtOAc in petroleum ether) gave (**R**)-2a as a colourless liquid.

Yield: 0.082 g, 81%; **Optical rotation:** $\alpha_D^{25} = +55.6$ (CHCl₃, *c* 0.196); {lit.¹⁵ +49.3 (CHCl₃, *c* 0.142). **Chiral HPLC Analysis:** >90% ee (full baseline separation could not be obtained for a precise ee value) Chiralpak IB Column (Hexane/iPrOH 97:3, 1.0 mL/min).

Dimethyl 2-(2-phenyl-2-(2,4,5-trimethoxyphenyl)ethyl)malonate (2b)

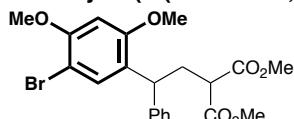


The title compound was prepared according to *General Procedure A* from cyclopropane **1a** (0.059 g, 0.25 mmol), 1,2,4-trimethoxybenzene (0.075 mL, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-40% EtOAc in petroleum ether) gave **2b** as a colourless oil.

Yield: 0.086 g, 85%; **R_f** = 0.14 (petroleum ether/EtOAc 8:2); **IR v_{max} / cm⁻¹ (film)**: 2953, 1751, 1732, 1514; **¹H NMR**: (400 MHz, CDCl₃) δ 7.31-7.26 (4H, m), 7.21-7.16 (1H, m), 6.75 (1H, s), 6.51 (1H, s), 4.39 (1H, t, *J* = 8.1 Hz), 3.88 (3H, s), 3.81 (3H, s), 3.75 (3H, s), 3.72 (3H, s), 3.71 (3H, s), 3.32 (1H, dd, *J* = 7.6, 7.0 Hz), 2.73-2.56 (2H, m); **¹³C NMR**: (100 MHz, CDCl₃) δ 170.0, 169.8, 151.6, 148.3, 143.8, 143.2, 128.4, 128.0, 126.3, 123.2, 112.4, 98.0, 56.9, 56.5, 56.2, 52.6, 52.5, 50.2, 40.8, 33.9; **HRMS**: (ESI⁺) [M+Na]⁺ C₂₂H₂₆O₇Na Found: 425.1546, requires 425.1571 (+5.9 ppm).

¹⁵ R. Talukdar, A. Saha, D. P. Tiwari, M. K. Ghorai *Tetrahedron* **2016**, 72, 613.

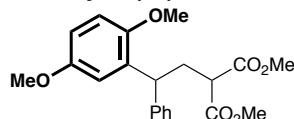
Dimethyl 2-(2-(5-bromo-2,4-dimethoxyphenyl)-2-phenylethyl)malonate (2c)



The title compound was prepared according to *General Procedure A* from cyclopropane **1a** (0.059 g, 0.25 mmol), 1-bromo-2,4-dimethoxybenzene (0.072 mL, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-35% EtOAc in petroleum ether) gave **2c** as a colourless oil.

Yield: 0.057 g, 51%; **R_f** = 0.21 (petroleum ether/EtOAc 8:2); **IR v_{max} / cm⁻¹ (film)**: 2953, 2845, 1751, 1732, 1599; **¹H NMR**: (400 MHz, CDCl₃) δ 7.33 (1H, s), 7.31-7.28 (2H, m), 7.25 (1H, d, *J* = 6.9 Hz), 7.22-7.17 (1H, m), 6.45 (1H, s), 4.32 (1H, t, *J* = 8.1 Hz), 3.89 (3H, s), 3.79 (3H, s), 3.73 (3H, s), 3.71 (3H, s), 3.29 (1H, t, *J* = 7.4 Hz), 2.69-2.54 (2H, m); **¹³C NMR**: (100 MHz, CDCl₃) δ 169.9, 169.8, 157.4, 155.3, 143.0, 131.8, 128.5, 128.1, 126.5, 125.8, 102.1, 96.9, 56.5, 55.9, 52.7, 52.6, 50.2, 40.6, 33.8; **HRMS**: (ESI⁺) [M+Na]⁺ C₂₁H₂₃⁷⁹BrO₆Na Found: 473.0554, requires 473.0570 (+3.4 ppm).

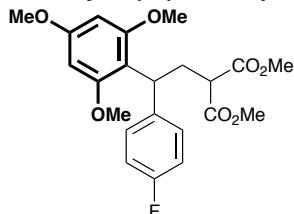
Dimethyl 2-(2-(2,5-dimethoxyphenyl)-2-phenylethyl)malonate (2d)



The title compound was prepared according to *General Procedure A* from cyclopropane **1a** (0.059 g, 0.25 mmol), 1,4-dimethoxybenzene (0.069 g, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-30% EtOAc in petroleum ether) gave **2d** as a colourless oil.

Yield: 0.045 g, 48%; **R_f** = 0.42 (petroleum ether/EtOAc 8:2); **IR v_{max} / cm⁻¹ (film)**: 2955, 2842, 1743, 1737, 1604; **¹H NMR**: (400 MHz, CDCl₃) δ 7.29 (2H, s), 7.28 (2H, s), 7.20 (1H, dq, *J* = 8.7, 4.3 Hz), 6.82 (1H, d, *J* = 3.0 Hz), 6.79 (1H, d, *J* = 8.8 Hz), 6.72 (1H, dd, *J* = 8.8, 3.0 Hz), 4.43 (1H, t, *j* = 8.1 Hz), 3.76 (3H, s), 3.73 (3H, s), 3.73 (3H, s), 3.71 (3H, s), 3.33 (1H, t, *J* = 7.4 Hz), 2.72-2.58 (2H, m); **¹³C NMR**: (100 MHz, CDCl₃) δ 170.0, 169.8, 153.8, 151.5, 143.2, 133.2, 128.4, 128.2, 126.4, 114.8, 111.9, 111.4, 56.2, 55.7, 52.6, 52.5, 50.2, 41.2, 33.8; **HRMS**: (ESI⁺) [M+Na]⁺ C₂₁H₂₄O₆Na Found: 395.1449, requires 395.1465 (+4.0 ppm).

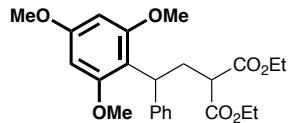
Dimethyl 2-(2-(4-fluorophenyl)-2-(2,4,6-trimethoxyphenyl)ethyl)malonate (2e)



The title compound was prepared according to *General Procedure A* from cyclopropane **1b** (0.063 g, 0.25 mmol), 1,3,5-trimethoxybenzene (0.084 g, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-30% EtOAc in petroleum ether) gave **2e** as a colourless liquid. Analytical data are in agreement with the literature.¹⁵

Yield: 0.081 g, 71%; **R_f** = 0.23 (petroleum ether/EtOAc 8:2); **IR v_{max} / cm⁻¹ (film)**: 2953, 2843, 1751, 1732, 1603, 1593; **¹H NMR**: (400 MHz, CDCl₃) δ 7.28-7.24 (2H, m), 6.91 (2H, t, *J* = 8.8 Hz), 6.12 (2H, s), 4.60 (1H, dd, *J* = 10.9, 5.6 Hz), 3.81 (3H, s), 3.73 (3H, s), 3.72 (6H, s), 3.64 (3H, s), 3.25 (1H, dd, *J* = 9.4, 5.4 Hz), 2.90 (1H, ddd, *J* = 13.3, 10.9, 5.4 Hz), 2.71 (1H, ddd, *J* = 13.3, 9.4, 5.6 Hz); **¹³C NMR**: (100 MHz, CDCl₃) δ 170.3, 170.0, 161.1 (d, *J* = 242.8 Hz), 160.2, 159.4, 140.2 (d, *J* = 3.3 Hz), 129.2 (d, *J* = 7.8 Hz), 114.4 (d, *J* = 20.8 Hz), 111.2, 91.2, 55.7, 55.4, 52.6, 52.5, 50.8, 36.5, 31.3; **¹⁹F NMR**: (376 MHz, CDCl₃) δ -118.5.

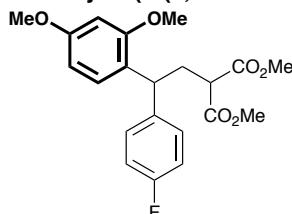
Diethyl 2-(2-phenyl-2-(2,4,6-trimethoxyphenyl)ethyl)malonate (2f)



The title compound was prepared according to *General Procedure A* from cyclopropane **1h** (0.066 g, 0.25 mmol), 1,3,5-trimethoxybenzene (0.084 g, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-25% EtOAc in petroleum ether) gave **2f** as a colourless liquid.

Yield: 0.087 g, 81%; **R_f** = 0.35 (petroleum ether/EtOAc 8:2); **IR ν_{max} / cm⁻¹ (film)**: 2940, 2839, 1748, 1730, 1605, 1592; **¹H NMR**: (400 MHz, CDCl₃) δ 7.30 (2H, d, *J* = 7.5 Hz), 7.21 (2H, t, *J* = 7.6 Hz), 7.10 (1H, t, *J* = 7.3 Hz), 6.10 (2H, s), 4.64 (1H, dd, *J* = 10.7, 5.8 Hz), 4.25-4.04 (4H, m), 3.78 (3H, s), 3.71 (6H, s), 3.21 (1H, dd, *J* = 9.3, 5.4 Hz), 2.90 (1H, ddd, *J* = 13.4, 10.8, 5.4 Hz), 2.73 (1H, ddd, *J* = 13.4, 9.3, 5.8 Hz), 1.25 (3H, t, *J* = 7.2 Hz), 1.21 (3H, t, *J* = 7.2 Hz); **¹³C NMR**: (100 MHz, CDCl₃) δ 170.1, 169.7, 160.1, 159.5, 144.7, 127.9, 127.8, 125.5, 111.5, 91.2, 61.3, 61.2, 55.7, 55.4, 51.2, 37.3, 31.2, 14.2, 14.1; **HRMS**: (ESI⁺) [M+H]⁺ C₂₄H₃₁O₇ Found: 431.2063, requires 431.2064 (+0.3 ppm).

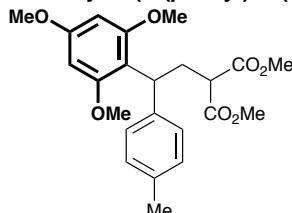
Dimethyl 2-(2-(2,4-dimethoxyphenyl)-2-(4-fluorophenyl)ethyl)malonate (2g)



The title compound was prepared according to *General Procedure A* from cyclopropane **1b** (0.063 g, 0.25 mmol), 1,3-dimethoxybenzene (0.065 mL, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-30% EtOAc in petroleum ether) gave **2g**, as the major regioisomer, as a colourless liquid.

Yield: 0.061 g, 63%; **R_f** = 0.30 (petroleum ether/EtOAc 8:2); **IR ν_{max} / cm⁻¹ (film)**: 2955, 2839, 1751, 1730, 1605, 1585, 1505; **¹H NMR**: (400 MHz, CDCl₃) δ (only data from the major regioisomer is reported) 7.21 (2H, dd, *J* = 8.6, 5.5 Hz), 7.09 (1H, d, *J* = 8.4 Hz), 6.96 (2H, t, *J* = 8.7 Hz), 6.47 (1H, dd, *J* = 8.4, 2.4 Hz), 6.43 (1H, d, *J* = 2.4 Hz), 4.31 (1H, t, *J* = 8.1 Hz), 3.80 (3H, s), 3.75 (3H, s), 3.72 (3H, s), 3.71 (3H, s), 3.29 (1H, t, *J* = 7.4 Hz), 2.67-2.54 (2H, m); **¹³C NMR**: (100 MHz, CDCl₃) δ (only data from the major regioisomer is reported) 169.9, 169.7, 161.3 (d, *J* = 244.0 Hz), 159.5, 158.0, 139.5 (d, *J* = 2.9 Hz), 129.4 (d, *J* = 7.9 Hz), 128.1, 123.9, 115.0 (d, *J* = 21.1 Hz), 104.3, 98.6, 55.4, 55.3, 52.5, 52.4, 50.1, 40.0, 33.9; **¹⁹F NMR**: (376 MHz, CDCl₃) δ -117.3 (major) and -118.3 (minor).

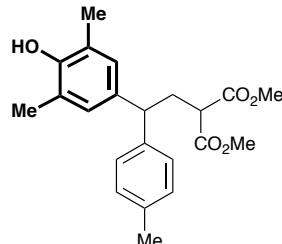
Dimethyl 2-(2-(*p*-tolyl)-2-(2,4,6-trimethoxyphenyl)ethyl)malonate (2h)



The title compound was prepared according to *General Procedure A* from cyclopropane **1d** (0.064 g, 0.25 mmol), 1,3,5-trimethoxybenzene (0.086 g, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (15% EtOAc in petroleum ether) gave **2h** as a colourless oil. with analytical data in agreement with the literature.¹⁵

Yield: 0.114 g, quantitative; **¹H NMR**: (400 MHz, CDCl₃) δ 7.18 (2H, d, *J* = 8.0 Hz), 7.02 (2H, d, *J* = 7.9 Hz), 6.09 (2H, s), 4.58 (1H, dd, *J* = 10.9, 5.7 Hz), 3.78 (3H, s), 3.71 (6H, s), 3.70 (3H, s), 3.62 (3H, s), 3.24 (1H, dd, *J* = 9.3, 5.5 Hz), 2.91 (1H, ddd, *J* = 13.4, 10.9, 5.5 Hz), 2.71 (1H, ddd, *J* = 13.4, 9.3, 5.7 Hz), 2.27 (3H, s).

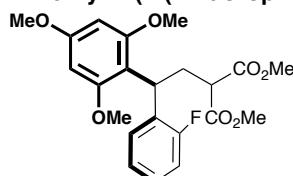
Dimethyl 2-(2-(4-hydroxy-3,5-dimethylphenyl)-2-(*p*-tolyl)ethyl)malonate (2i)



The title compound was prepared according to *General Procedure A* from cyclopropane **1d** (0.059 g, 0.24 mmol), 2,6-dimethylphenol (0.059 g, 0.48 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 1 h. Purification by flash column chromatography over silica (10-15% EtOAc in petroleum ether) gave **2i** as a yellow oil.

Yield: 0.085 g, 97%; **R_f** = 0.10 (petroleum ether/EtOAc 9:1); **¹H NMR**: (400 MHz, CDCl₃) δ 7.09 (s, 4H), 6.81 (s, 2H), 4.48 (s, 1H), 3.75 (t, *J* = 8.0 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.27 (t, *J* = 7.6 Hz, 1H), 2.58 (t, *J* = 7.6 Hz, 2H), 2.29 (s, 3H), 2.19 (s, 6H); **¹³C NMR**: (100 MHz, CDCl₃) δ 170.0, 150.9, 141.0, 136.1, 135.3, 129.4, 128.0, 127.7, 123.1, 52.6, 50.2, 47.6, 34.8, 21.1, 16.2; **HRMS**: (APPI⁺) [M+H]⁺ C₂₂H₂₆O₅ Found: 371.1856, requires 371.1853 (+0.32 ppm).

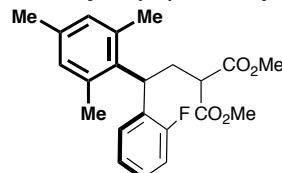
Dimethyl 2-(2-(2-fluorophenyl)-2-(2,4,6-trimethoxyphenyl)ethyl)malonate (2j)



The title compound was prepared according to *General Procedure A* from cyclopropane **1e** (0.051 g, 0.20 mmol), 1,3,5-trimethoxybenzene (68.9 mg, 0.410 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at 40 °C for 4 h. Purification by flash column chromatography over silica (15-18% EtOAc in petroleum ether) gave **2j** as an off-white solid.

Yield: 0.089 g, quantitative; **R_f** = 0.07 (petroleum ether/EtOAc 9:1); **¹H NMR**: (400 MHz, CDCl₃) δ 7.47–7.39 (m, 1H), 7.12–7.07 (m, 1H), 7.07–6.98 (m, 1H), 6.91–6.87 (m, 1H), 6.08 (s, 2H), 4.83 (dd, *J* = 11.2, 5.2 Hz, 1H), 3.77 (s, 3H), 3.73 (s, 3H), 3.70 (6H), 3.61 (3H), 3.28 (dd, *J* = 8.8, 5.6 Hz, 1H), 2.89 (ddd, *J* = 13.2, 11.2, 5.6 Hz, 1H), 2.65 (ddd, *J* = 13.6, 8.8, 5.2 Hz, 1H); **¹³C NMR**: (100 MHz, CDCl₃) δ 170.4, 170.0, 161.0 (d, *J* = 244.5 Hz), 160.3, 159.6, 131.0 (d, *J* = 13.7 Hz), 129.7 (d, *J* = 4.5 Hz), 127.1 (d, *J* = 8.2 Hz), 123.2 (d, *J* = 3.3 Hz), 114.9 (d, *J* = 22.4 Hz), 110.1, 91.2, 55.8, 55.7, 55.4, 55.3, 52.5, 52.5, 50.6, 31.2 (d, *J* = 2.0 Hz), 30.8; **¹⁹F NMR** (376.5 MHz, CDCl₃, CF₃CO₂H - ext. std.) δ (ppm): –115.14 to –115.25 (m, 1F); **HRMS**: (APPI⁺) [M]⁺ C₂₂H₂₅FO₇ Found: 420.1578, requires 420.1579 -0.20 ppm).

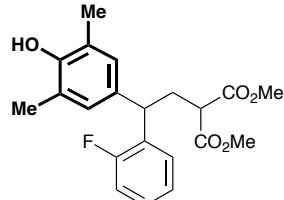
Dimethyl 2-(2-(2-fluorophenyl)-2-mesitylethyl)malonate (2k)



The title compound was prepared according to *General Procedure A* from cyclopropane **1e** (0.052 g, 0.20 mmol), mesitylene (56.8 μ L, 0.408 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at 50 °C for 24 h. Purification by flash column chromatography over silica (3% EtOAc in petroleum ether) gave **2k** as a colourless oil.

Yield: 0.068 g, 89%; **R_f** = 0.42 (petroleum ether/EtOAc 9:1); **¹H NMR**: (400 MHz, CDCl₃) δ 7.32 (t, *J* = 7.6 Hz, 1H), 7.23–7.18 (m, 1H), 7.08 (td, *J* = 7.6, 0.8 Hz, 1H), 7.00–6.90 (m, 1H), 6.79 (s, 2H), 4.65 (t, *J* = 8.0 Hz, 1H), 3.75 (s, 3H), 3.62 (s, 3H), 3.38 (t, *J* = 7.2 Hz, 1H), 2.91 (dt, *J* = 14.0 Hz, 7.2 Hz, 1H), 2.99–2.85 (m, 1H), 2.78–2.64 (m, 1H), 2.23 (br s, 9H); **¹³C NMR**: (100 MHz, CDCl₃) δ 169.9, 169.9, 161.7 (d, *J* = 245.5 Hz), 137.3, 136.2, 134.7, 130.5 (m), 129.3, 129.2 (d, *J* = 2.3 Hz), 127.9 (d, *J* = 8.4 Hz), 123.6 (d, *J* = 3.4 Hz), 115.8 (d, *J* = 22.4 Hz), 52.8, 52.7, 50.0, 37.5, 30.4, 21.3, 21.3, 20.8; **¹⁹F NMR** (376.5 MHz, CDCl₃, CF₃CO₂H - ext. std.) δ (ppm): –112.44 to –112.57 (m, 1F); **HRMS**: (APPI⁺) [M-H]⁺ C₂₂H₂₄FO₄ Found: 371.1654, requires 371.1653 (+0.10 ppm).

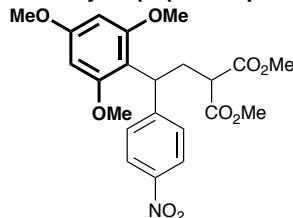
Dimethyl-2-(2-(2-fluorophenyl)-2-(3,5-dimethyl-4-hydroxophenyl)ethyl)malonate (2l)



The title compound was prepared according to *General Procedure A* from cyclopropane **1e** (0.052 g, 0.21 mmol), 2,6-dimethylphenol (50.2 mg, 0.411 mmol) and TfOH (2.2 μL , 10 mol%) in HFIP (0.125 mL) and stirred at 50 °C for 24 h. Purification by flash column chromatography over silica (10% EtOAc in petroleum ether) gave **2l** as a pale yellow oil.

Yield: 0.072 g, 93%; R_f = 0.07 (petroleum ether/EtOAc 9:1); **1H NMR:** (400 MHz, CDCl_3) δ 7.33–7.25 (m, 1H), 7.22–7.13 (m, 1H), 7.09 (t, J = 7.4 Hz, 1H), 7.02–6.94 (m, 1H), 6.85 (s, 2H), 4.52 (s, 1H), 4.15 (t, J = 8.0 Hz, 1H), 3.71 (s, 3H), 3.70 (s, 3H), 3.29 (t, J = 7.4 Hz, 1H), 2.70–2.54 (m, 2H), 2.19 (s, 6H); **13C NMR:** (100 MHz, CDCl_3) δ 169.8, 169.8, 160.7 (d, J = 244.0 Hz), 151.0, 133.9, 130.9 (d, J = 14.2 Hz), 128.4 (d, J = 4.2 Hz), 128.2, 128.1, 124.4 (d, J = 3.5 Hz), 123.2, 115.7 (d, J = 22.5 Hz), 52.7, 52.7, 50.1, 40.5 (d, J = 2.4 Hz), 33.8, 31.1, 16.2; **19F NMR** (376.5 MHz, CDCl_3 , $\text{CF}_3\text{CO}_2\text{H}$ - ext. std.) δ (ppm): –116.27 to –116.47 (m, 1F); **HRMS:** (APPI⁺) [M-H]⁺ $\text{C}_{21}\text{H}_{22}\text{FO}_5$ Found: 373.1446, requires 373.1446 (+0.09 ppm).

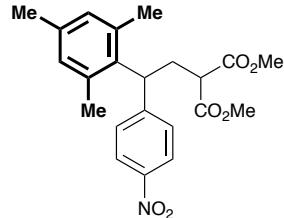
Dimethyl 2-(2-(4-nitrophenyl)-2-(2,4,6-trimethoxyphenyl)ethyl)malonate (2m)



The title compound was prepared according to *General Procedure A* from cyclopropane **1f** (0.062 g, 0.22 mmol), 1,3,5-trimethoxybenzene (0.075 g, 0.45 mmol) and TfOH (2.2 μL , 10 mol%) in HFIP (0.125 mL) and stirred at 50 °C for 24 h. Purification by flash column chromatography over silica (20–25% EtOAc in petroleum ether) gave **2m** as a yellow oil.

Yield: 0.092 g, 94%; R_f = 0.06 (petroleum ether/EtOAc 9:1); **1H NMR:** (400 MHz, CDCl_3) δ 8.06 (d, J = 8.4 Hz, 2H), 7.41 (d, J = 8.8 Hz, 2H), 6.09 (s, 2H), 4.69 (dd, J = 11.2, 4.8 Hz, 1H), 3.79 (s, 3H), 3.73 (s, 3H), 3.69 (s, 6H), 3.62 (s, 3H), 3.22 (dd, J = 9.6, 5.2 Hz, 1H), 2.90 (ddd, J = 13.2, 11.6, 5.2 Hz, 1H), 2.72 (ddd, J = 13.2, 9.6, 5.2 Hz, 1H); **13C NMR:** (100 MHz, CDCl_3) δ 170.1, 169.8, 160.8, 159.3, 152.8, 146.0, 128.5, 123.1, 109.8, 91.1, 55.7, 55.4, 52.7, 52.6, 50.5, 37.0, 30.4; **HRMS:** (APPI⁺) [M]⁺ $\text{C}_{22}\text{H}_{25}\text{NO}_9$ Found: 447.1524, requires 447.1534 (+1.06 ppm).

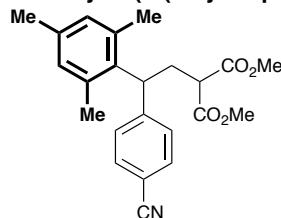
Dimethyl 2-(2-mesityl-2-(4-nitrophenyl)ethyl)malonate (2n)



The title compound was prepared according to *General Procedure A* from cyclopropane **1f** (0.062 g, 0.22 mmol), mesitylene (60.2 μL , 0.433 mmol) and TfOH (2.2 μL , 10 mol%) in HFIP (0.125 mL) and stirred at 50 °C for 24 h. Purification by flash column chromatography over silica (5% EtOAc in petroleum ether) gave **2n** as a yellow oil.

Yield: 0.085 g, 99%; R_f = 0.28 (petroleum ether/EtOAc 9:1); **1H NMR:** (400 MHz, CDCl_3) δ 8.11 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.4 Hz, 2H), 6.85 (s, 2H), 4.61 (dd, J = 10.4, 5.4 Hz, 1H), 3.75 (s, 3H), 3.62 (s, 3H), 3.23 (dd, J = 9.2, 5.0 Hz, 1H), 3.02 (ddd, J = 13.6, 9.2, 6.0 Hz, 1H), 2.80–2.68 (m, 1H), 2.43–1.75 (m, 9H); **13C NMR:** (100 MHz, CDCl_3) δ 169.8, 169.8, 151.4, 146.3, 137.3, 137.1, 134.4, 128.0, 123.6, 52.9, 52.8, 49.8, 41.6, 30.6, 21.2, 20.9; **HRMS:** (APPI⁺) [M]⁺ $\text{C}_{22}\text{H}_{25}\text{NO}_6$ Found: 399.1678, requires 399.1676 (+0.50 ppm).

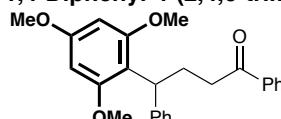
Dimethyl 2-(2-(4-cyanophenyl)-2-mesitylethyl)malonate (2o)



The title compound was prepared according to *General Procedure A* from cyclopropane **1g** (0.065 g, 0.25 mmol), mesitylene (0.070 mL, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at 50 °C for 3 h. Purification by flash column chromatography over silica (20% EtOAc in petroleum ether) gave **2o** as a colourless oil.

Yield: 0.056 g, 60%; R_f = 0.44 (petroleum ether/EtOAc 8:2); **1H NMR:** (400 MHz, CDCl₃) δ 7.56 (2H, d, J = 8.4 Hz), 7.28 (2H, d, J = 8.0 Hz), 6.86 (2H, br s), 4.60 (1H, dd, J = 10.7, 5.7 Hz), 3.76 (3H, s), 3.63 (3H, s), 3.25 (1H, dd, J = 9.1, 5.2 Hz), 3.01 (1H, ddd, J = 14.1, 8.8, 5.5 Hz), 2.73 (1H, ddd, J = 13.8, 10.8, 5.2 Hz), 2.27 (3H, s), 2.11 (6H, br s); **^{13}C NMR:** (100 MHz, CDCl₃) δ 169.6, 149.0, 137.2, 136.8, 134.3, 132.1, 130.7 (br), 127.8, 118.9, 109.7, 52.7, 52.6, 49.7, 41.5, 30.3, 21.1, 20.7; **HRMS:** (APPI⁺) [M]⁺ C₂₃H₂₅NO₄ Found: 379.1179, requires 379.1178 (+0.10 ppm).

1,4-Diphenyl-4-(2,4,6-trimethoxyphenyl)butan-1-one (2p)



The title compound was prepared according to *General Procedure A* from cyclopropane **1k** (0.056 g, 0.25 mmol), 1,3,5-trimethoxybenzene (0.084 g, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-25% EtOAc in petroleum ether) gave **2p** as a white solid.

Yield: 0.098 g, 98%

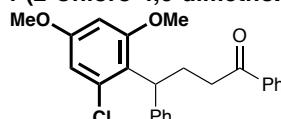
10 x Scale-Up Procedure

The title compound was prepared according to *General Procedure A* from cyclopropane **1k** (0.556 g, 2.50 mmol), 1,3,5-trimethoxybenzene (0.841 g, 5.00 mmol) and TfOH (11.1 μ L, 5 mol%) in HFIP (1.25 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-25% EtOAc in petroleum ether) gave **2p** as a white solid.

Yield: 0.971 g, 99%

R_f = 0.38 (petroleum ether/EtOAc 8:2); **mp:** 96-97 °C; **IR ν_{max} / cm⁻¹ (film):** 2933, 2834, 1682; **1H NMR:** (400 MHz, CDCl₃) δ 7.91-7.89 (2H, m), 7.54 (1H, t, J = 7.4 Hz), 7.44 (2H, t, J = 7.6 Hz), 7.38 (2H, d, J = 7.5 Hz), 7.26 (2H, t, J = 7.6 Hz), 7.15 (1H, t, J = 7.3 Hz), 6.14 (2H, s), 4.72 (1H, dd, J = 10.0, 6.2 Hz), 3.82 (3H, s), 3.70 (6H, s), 2.99 (1H, ddd, J = 16.2, 9.4, 6.7 Hz), 2.87 (1H, ddd, J = 15.9, 9.8, 5.7 Hz), 2.87 (1H, ddd, J = 15.9, 9.8, 5.7 Hz), 2.77-2.60 (2H, m); **^{13}C NMR:** (100 MHz, CDCl₃) δ 200.9, 159.8, 159.4, 145.3, 137.3, 132.7, 128.5, 128.1, 127.9, 127.7, 125.3, 112.9, 91.2, 55.6, 55.3, 38.8, 37.6, 26.7; **HRMS:** (ESI⁺) [M+Na]⁺ C₂₅H₂₆O₄Na Found: 413.1690, requires 413.1723 (+8.0 ppm).

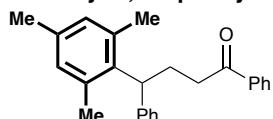
4-(2-Chloro-4,6-dimethoxyphenyl)-1,4-diphenylbutan-1-one (2q)



The title compound was prepared according to *General Procedure A* from cyclopropane **1k** (0.056 g, 0.25 mmol), 5-chloro-1,3-dimethoxybenzene (0.067 mL, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-15% EtOAc in petroleum ether) gave a 2:1 mixture of **2q** and **2q'** as a pale yellow oil. **Combined Yield:** 0.072 g, 71%. **Repurification by careful column chromatography allowed partial separation of the regioisomers and the major regioisomer (as depicted) to be characterized.**

Major regioisomer (2q): A pale yellow oil; R_f = 0.53 (petroleum ether/EtOAc 8:2); **1H NMR:** (400 MHz, CDCl₃) δ 7.90 (2H, d, J = 7.1 Hz), 7.55 (1H, t, J = 7.4 Hz), 7.44 (2H, t, J = 7.6 Hz), 7.36 (2H, d, J = 7.6 Hz), 7.27 (2H, t, J = 7.4 Hz), 7.17 (1H, t, J = 7.3 Hz), 6.56 (1H, d, J = 2.4 Hz), 6.33 (1H, d, J = 2.4 Hz), 4.82 (1H, dd, J = 9.7, 6.1 Hz), 3.79 (3H, s), 3.62 (3H, s), 3.03 (1H, ddd, J = 16.5, 9.8, 6.4 Hz), 2.87 (1H, ddd, J = 16.6, 9.7, 5.2 Hz), 2.80-2.65 (2H, m); **^{13}C NMR:** (100 MHz, CDCl₃) δ 200.3, 159.8, 159.1, 143.6, 137.0, 135.5, 132.8, 128.4, 128.0, 127.7, 125.6, 122.7, 106.1, 98.6, 55.5, 37.2, 25.7; **HRMS:** (ESI⁺) [M+Na]⁺ C₂₄H₂₃³⁵ClO₃Na Found: 417.1236, requires 417.1228 (-1.9 ppm).

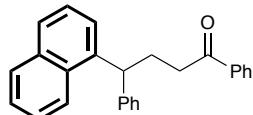
4-Mesityl-1,4-diphenylbutan-1-one (2r)



The title compound was prepared according to *General Procedure A* from cyclopropane **1k** (0.056 g, 0.25 mmol), mesitylene (0.070 mL, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-5% EtOAc in petroleum ether) gave **2r** as a white solid.

Yield: 0.078 g, 89%; **R_f** = 0.70 (petroleum ether/EtOAc 8:2); **mp:** 92-94 °C; **IR v_{max} / cm⁻¹ (film):** 1688; **¹H NMR:** (400 MHz, CDCl₃) δ 7.89-7.87 (2H, m), 7.57 (1H, t, *J* = 7.4 Hz), 7.45 (2H, t, *J* = 7.6 Hz), 7.32-7.25 (4H, m), 7.21 (1H, t, *J* = 6.9 Hz), 6.87 (2H, s), 4.68 (1H, dd, *J* = 10.3, 5.3 Hz), 3.04 (1H, td, *J* = 13.6, 6.6 Hz), 2.95-2.83 (2H, m), 2.60-2.46 (1H, m), 2.31 (3H, s), 2.21 (6H, br s); **¹³C NMR:** (100 MHz, CDCl₃) δ 200.3, 144.1, 137.4, 137.2, 137.0, 135.8, 133.0, 130.4 (br), 128.6, 128.3, 128.1, 127.3, 125.6, 42.7, 36.8, 25.6, 21.5, 20.9; **HRMS:** (ESI⁺) [M+Na]⁺ C₂₅H₂₆ONa Found: 365.1908, requires 365.1876 (-8.9 ppm).

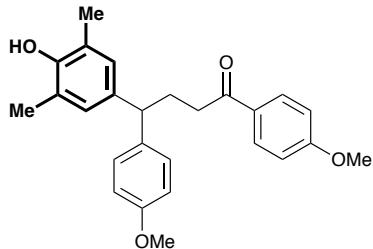
4-(Naphthalen-1-yl)-1,4-diphenylbutan-1-one (2s)



The title compound was prepared according to *General Procedure A* from cyclopropane **1k** (0.056 g, 0.25 mmol), naphthalene (0.064 g, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-10% EtOAc in petroleum ether) gave a 2:1 regioisomeric mixture of **2s** and its regioisomer as a yellow oil.

Yield: 0.072 g, 82%; **R_f** = 0.58 (petroleum ether/EtOAc 8:2); **IR v_{max} / cm⁻¹ (film):** 3053, 3026, 1680, 1597, 1578; **¹H NMR:** (400 MHz, CDCl₃) δ (*only characteristic peaks reported*) 4.92 (2.3H, t, *J* = 7.7 Hz) *major regioisomer* and 4.25 (1H, t, *J* = 7.8 Hz) *minor regioisomer*; **HRMS:** (ESI⁺) [M+Na]⁺ C₂₆H₂₂ONa Found: 373.1533, requires 373.1563 (+8.1 ppm).

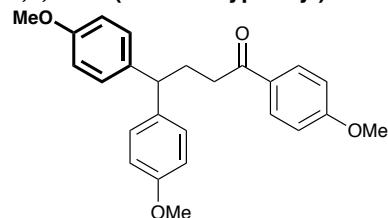
4-(4-Hydroxy-3,5-dimethylphenyl)-1,4-bis(4-methoxyphenyl)butan-1-one (2t)



The title compound was prepared according to *General Procedure A* from cyclopropane **1o** (0.071 g, 0.25 mmol), 2,6-dimethylphenol (0.061 g, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-35% EtOAc in petroleum ether) gave **2t** as a yellow oil.

Yield: 0.079 g, 78%; **R_f** = 0.26 (petroleum ether/EtOAc 8:2); **IR v_{max} / cm⁻¹ (film):** 3446 (br), 1667, 1599, 1572, 1510; **¹H NMR:** (400 MHz, CDCl₃) δ 7.84 (2H, d, *J* = 8.9 Hz), 7.18 (2H, d, *J* = 8.7 Hz), 6.89 (2H, d, *J* = 8.9 Hz), 6.86 (2H, s), 6.83 (2H, d, *J* = 8.7 Hz), 4.61 (1H, br s), 3.85 (3H, s), 3.82 (1H, t, *J* = 8.0 Hz), 3.77 (3H, s), 2.86 (2H, t, *J* = 7.5 Hz), 2.40 (2H, q, *J* = 7.6 Hz), 2.20 (6H, s); **¹³C NMR:** (100 MHz, CDCl₃) δ 199.1, 163.5, 158.0, 150.7, 137.4, 136.6, 130.4, 130.2, 128.8, 128.0, 123.1, 114.0, 113.7, 55.6, 55.3, 49.2, 36.9, 30.6, 16.2; **HRMS:** (ESI⁺) [M+K]⁺ C₂₆H₂₈O₄K Found: 443.1635, requires 443.1619 (-3.5 ppm).

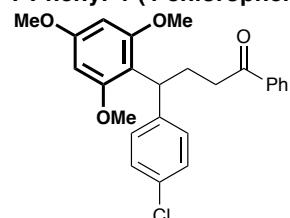
1,4,4-Tris(4-methoxyphenyl)butan-1-one (2u)



The title compound was prepared according to *General Procedure A* from cyclopropane **1o** (0.071 g, 0.25 mmol), anisole (0.054 mL g, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-25% EtOAc in petroleum ether) gave **2u** as a white solid.

Yield: 0.081 g, 83%; **R_f** = 0.37 (petroleum ether/EtOAc 8:2); **mp:** 95-96 °C; **IR v_{max} / cm⁻¹ (film):** 1672, 1595; **¹H NMR:** (400 MHz, CDCl₃) δ 7.85 (2H, d, *J* = 8.9 Hz), 7.17 (4H, d, *J* = 8.7 Hz), 6.89 (2H, d, *J* = 8.9 Hz), 6.84 (4H, d, *J* = 8.7 Hz), 3.92 (1H, t, *J* = 7.9 Hz), 3.85 (3H, s), 3.77 (3H, s), 2.87 (2H, t, *J* = 7.5 Hz), 2.43 (2H, q, *J* = 7.6 Hz); **¹³C NMR:** (100 MHz, CDCl₃) δ 198.8, 163.4, 158.0, 137.1, 130.4, 130.2, 128.8, 114.0, 113.7, 55.5, 55.3, 49.0, 36.7, 30.6; **HRMS:** (ESI⁺) [M+H]⁺ C₂₅H₂₇O₄ Found: 391.1912, requires 391.1904 (-2.1 ppm).

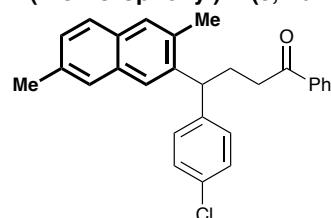
1-Phenyl-4-(4-chlorophenyl)-4-(2,4,6-trimethoxyphenyl)butan-1-one (2v)



The title compound was prepared according to *General Procedure A* from cyclopropane **1l** (0.064 g, 0.25 mmol), 1,3,5-trimethoxybenzene (0.084 g, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-30% EtOAc in petroleum ether) gave **2v** as a white solid.

Yield: 0.100 g, 94%; **R_f** = 0.39 (petroleum ether/EtOAc 8:2); **mp:** 116-117 °C; **IR v_{max} / cm⁻¹ (film):** 2839, 1688, 1593; **¹H NMR:** (400 MHz, CDCl₃) δ 7.87 (2H, d, *J* = 8.3 Hz), 7.54 (1H, t, *J* = 7.3 Hz), 7.43 (2H, t, *J* = 7.7 Hz), 7.28 (2H, d, *J* = 7.5 Hz), 7.20 (2H, d, *J* = 8.5 Hz), 6.11 (2H, s), 4.64 (1H, dd, *J* = 10.0, 6.1 Hz), 3.81 (3H, s), 3.68 (3H, s), 2.95 (1H, ddd, *J* = 16.4, 9.0, 7.1 Hz), 2.83 (1H, ddd, *J* = 16.0, 9.5, 5.9 Hz), 2.70-2.53 (2H, m); **¹³C NMR:** (100 MHz, CDCl₃) δ 200.7, 160.0, 159.3, 143.9, 143.9, 137.3, 132.8, 130.9, 129.4, 128.5, 128.2, 127.8, 112.4, 91.2, 55.7, 55.4, 38.2, 37.4, 26.4; **HRMS:** (ESI⁺) [M+H]⁺ C₂₅H₂₆³⁵ClO₄ Found: 425.1530, requires 425.1514 (-3.7 ppm).

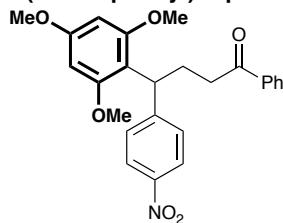
4-(4-Chlorophenyl)-4-(3,7-dimethylnaphthalen-2-yl)-1-phenylbutan-1-one (2w)



The title compound was prepared according to *General Procedure A* from cyclopropane **1l** (0.064 g, 0.25 mmol), 2,6-dimethylnaphthalene (0.078 g, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-10% EtOAc in petroleum ether) gave a 3:1 regioisomeric mixture of **2w** and **2w'** as an off-white solid.

Yield: 0.085 g, 82%; **R_f** = 0.67 (petroleum ether/EtOAc 8:2); **mp:** 129-132 °C; **IR v_{max} / cm⁻¹ (film):** 1682; **¹H NMR:** (400 MHz, CDCl₃) δ (only characteristic peaks reported) 4.82 (3.4H, t, *J* = 7.8 Hz), 2.52 (10H, s), 2.48 (10H, s) *major regioisomer* and 4.33 (1H, t, *J* = 7.8 Hz), 2.54 (3H, s), 2.35 (3H, s) *minor regioisomer*; **HRMS:** (ESI⁺) [M+Na]⁺ C₂₈H₂₅³⁵ClONa Found: 435.1502, requires 435.1486 (-3.6 ppm).

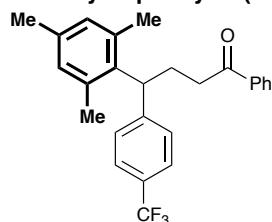
4-(4-Nitrophenyl)-1-phenyl-4-(2,4,6-trimethoxyphenyl)butan-1-one (2x)



The title compound was prepared according to *General Procedure A* from cyclopropane **1n** (0.067 g, 0.25 mmol), 1,3,5-trimethoxybenzene (0.084 g, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at 80 °C for 3 h. Purification by flash column chromatography over silica (0-25% EtOAc in petroleum ether) gave **2x** as a yellow oil.

Yield: 0.097 g, 89%; **R_f** = 0.21 (petroleum ether/EtOAc 8:2); **IR v_{max} / cm⁻¹ (film)**: 2837, 1682, 1593, 1512; **¹H NMR**: (400 MHz, CDCl₃) δ 8.07 (2H, d, *J* = 8.8 Hz), 7.86-7.83 (2H, m), 7.52 (1H, t, *J* = 7.4 Hz), 7.45 (2H, d, *J* = 8.5 Hz), 7.41 (2H, t, *J* = 7.7 Hz), 6.08 (2H, s), 4.73 (1H, dd, *J* = 10.2, 5.8 Hz), 3.79 (3H, s), 3.63 (6H, s), 2.95 (1H, dt, *J* = 16.9, 7.8 Hz), 2.82 (1H, ddd, *J* = 16.9, 8.3, 5.4 Hz), 2.71-2.56 (2H, m); **¹³C NMR**: (100 MHz, CDCl₃) δ 200.3, 160.4, 159.2, 153.8, 145.8, 137.2, 132.9, 128.6, 128.5, 128.1, 123.0, 111.2, 91.0, 55.6, 55.4, 38.5, 36.8, 25.7; **HRMS**: (ESI⁺) [M+H]⁺ C₂₅H₂₆NO₆ Found: 436.1765, requires 436.1755 (-2.3 ppm).

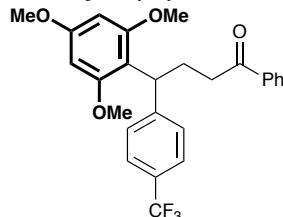
4-Mesityl-1-phenyl-4-(4-(trifluoromethyl)phenyl)butan-1-one (2y)



The title compound was prepared according to *General Procedure A* from cyclopropane **1m** (0.073 g, 0.25 mmol), mesitylene (0.070 mL, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-10% EtOAc in petroleum ether) gave **2y** as a white solid.

Yield: 0.095 g, 93%; **R_f** = 0.70 (petroleum ether/EtOAc 8:2); **mp**: 129-130 °C; **IR v_{max} / cm⁻¹ (film)**: 1680, 1614; **¹H NMR**: (400 MHz, CDCl₃) δ 7.83 (2H, dd, *J* = 8.3, 1.2 Hz), 7.56-7.51 (3H, m), 7.42 (2H, t, *J* = 7.7 Hz), 7.33 (2H, d, *J* = 8.2 Hz), 6.84 (2H, s), 4.65 (1H, dd, *J* = 10.5, 4.3 Hz), 3.01-2.94 (1H, m), 2.91-2.82 (2H, m), 2.55-2.47 (1H, m), 2.27 (3H, s), 2.14 (6H, br s); **¹³C NMR**: (100 MHz, CDCl₃) δ 199.9, 148.4, 137.0, 136.8, 136.3, 136.2, 133.0, 130.3, 128.5, 128.0, 127.9 (app. d, *J* = 32.2 Hz), 127.4, 125.1 (q, *J* = 3.5 Hz), 124.4 (q, *J* = 271.7 Hz), 42.6, 36.3, 25.4, 21.3, 20.8; **¹⁹F NMR**: (376 MHz, CDCl₃) δ -62.3; **HRMS**: (ESI⁺) [M+H]⁺ C₂₆H₂₆F₃O Found: 411.1943, requires 411.1930 (-3.2 ppm).

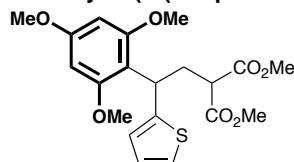
1-Phenyl-4-(4-(trifluoromethyl)phenyl)-4-(2,4,6-trimethoxyphenyl)butan-1-one (2z)



The title compound was prepared according to *General Procedure A* from cyclopropane **1m** (0.073 g, 0.25 mmol), 1,3,5-trimethoxybenzene (0.084 g, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 16 h. Purification by flash column chromatography over silica (0-30% EtOAc in petroleum ether) gave **2z** as a colourless oil.

Yield: 0.097 g, 85%; **R_f** = 0.41 (petroleum ether/EtOAc 8:2); **IR v_{max} / cm⁻¹ (film)**: 2839, 1684, 1608, 1589; **¹H NMR**: (400 MHz, CDCl₃) δ 7.86-7.84 (2H, m), 7.54-7.50 (1H, m), 7.47-7.39 (6H, m), 6.09 (2H, s), 4.70 (1H, dd, *J* = 10.1, 6.0 Hz), 3.79 (3H, s), 3.65 (3H, s), 2.94 (1H, ddd, *J* = 16.4, 9.0, 7.1 Hz), 2.82 (1H, ddd, *J* = 16.7, 8.8, 5.3 Hz), 2.72-2.55 (2H, m); **¹³C NMR**: (100 MHz, CDCl₃) δ 200.5, 160.1, 159.2, 149.5, 137.2, 132.7, 128.4, 128.1, 128.0, 127.4 (q, *J* = 32.0), 124.6 (q, *J* = 271.7 Hz), 124.5 (q, *J* = 3.4 Hz), 111.8, 91.0, 55.5, 55.2, 38.5, 37.1, 26.0; **¹⁹F NMR**: (376 MHz, CDCl₃) δ -62.1; **HRMS**: (ESI⁺) [M+Na]⁺ C₂₆H₂₅F₃O₄Na Found: 481.1604, requires 481.1597 (-1.5 ppm).

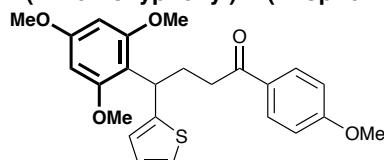
Dimethyl 2-(2-(thiophen-2-yl)-2-(2,4,6-trimethoxyphenyl)ethyl)malonate (3a)



The title compound was prepared according to *General Procedure B* from cyclopropane **1j** (0.061 g, 0.25 mmol), 1,3,5-trimethoxybenzene (0.084 g, 0.50 mmol) and B(C₆F₅)•H₂O (6.6 mg, 5 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-35% EtOAc in petroleum ether) gave **3a** as a colourless liquid. Analytical data are in agreement with the literature.¹⁵

Yield: 0.061 g, 60%; **R_f** = 0.29 (petroleum ether/EtOAc 8:2); **¹H NMR:** (400 MHz, CDCl₃) δ 7.04 (1H, dd, *J* = 4.9, 1.4 Hz), 6.86-6.83 (2H, m), 6.11 (2H, s), 4.85 (1H, dd, *J* = 10.3, 6.1 Hz), 3.79 (3H, s), 3.74 (6H, s), 3.71 (3H, s), 3.63 (3H, s), 3.25 (1H, dd, *J* = 9.2, 5.7 Hz), 2.90 (1H, ddd, *J* = 13.4, 10.4, 5.7 Hz), 2.76 (1H, ddd, *J* = 13.4, 9.2, 6.1 Hz); **¹³C NMR:** (100 MHz, CDCl₃) δ 170.1, 169.8, 160.3, 148.6, 125.9, 123.7, 122.7, 110.6, 91.1, 55.6, 55.3, 52.4, 52.4, 50.5, 33.5, 32.9.

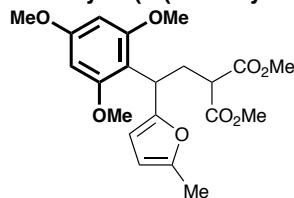
1-(4-Methoxyphenyl)-4-(thiophen-2-yl)-4-(2,4,6-trimethoxyphenyl)butan-1-one (3b)



The title compound was prepared according to *General Procedure B* from cyclopropane **1p** (0.065 g, 0.25 mmol), 1,3,5-trimethoxybenzene (0.084 g, 0.50 mmol) and B(C₆F₅)•H₂O (6.6 mg, 5 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-20% EtOAc in petroleum ether) gave **3b** as a colourless oil.

Yield: 0.099 g, 93%; **R_f** = 0.22 (petroleum ether/EtOAc 8:2); **IR ν_{max} / cm⁻¹ (film):** 2938; 2835, 1672, 1599; **¹H NMR:** (400 MHz, CDCl₃) δ 7.84 (2H, d, *J* = 8.9 Hz), 7.05 (app. t, *J* = 3.2 Hz), 6.89-6.86 (4H, m), 6.12 (2H, s), 4.89 (1H, dd, *J* = 9.3, 6.8 Hz), 3.84 (3H, s), 3.80 (3H, s), 3.72 (6H, s), 2.88 (1H, ddd, *J* = 15.9, .1, 6.8 Hz), 2.77 (1H, ddd, *J* = 15.6, 9.6, 5.7 Hz), 2.72-2.57 (2H, m); **¹³C NMR:** (100 MHz, CDCl₃) δ 199.3, 163.2, 160.1, 159.3, 149.7, 130.4, 130.3, 126.0, 123.6, 122.5, 113.6, 112.1, 91.2, 55.7, 55.5, 55.3, 37.1, 35.3, 29.1; **HRMS:** (ESI⁺) [M+Na]⁺ C₂₄H₂₆O₅SNa Found: 449.1408, requires 449.1393 (-3.4 ppm).

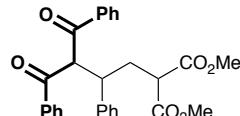
Dimethyl 2-(2-(5-methylfuran-2-yl)-2-(2,4,6-trimethoxyphenyl)ethyl)malonate (3c)



The title compound was prepared according to *General Procedure B* from cyclopropane **1i** (0.060 g, 0.25 mmol), 1,3,5-trimethoxybenzene (0.084 g, 0.50 mmol) and B(C₆F₅)•H₂O (6.6 mg, 5 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-35% EtOAc in petroleum ether) gave **3c** as a colourless liquid.

Yield: 0.004 g, trace; **R_f** = 0.30 (petroleum ether/EtOAc 8:2); **¹H NMR:** (400 MHz, CDCl₃) δ 6.11 (2H, s), 5.82-5.80 (2H, m), 4.58 (1H, t, *J* = 8.0 Hz), 3.80 (3H, s), 3.72 (3H, s), 3.71 (6H, s), 3.60 (3H, s), 3.26 (1H, t, *J* = 7.5 Hz), 2.71 (2H, t, *J* = 7.8 Hz), 2.20 (3H, s); **¹³C NMR:** (100 MHz, CDCl₃) δ 170.2, 169.8, 160.2, 159.6, 155.7, 149.5, 108.9, 105.7, 105.0, 91.2, 55.7, 55.2, 52.4 (app. d, *J* = 3.1 Hz), 50.3, 32.0, 30.5, 13.6; **HRMS:** (APPI⁺) [M]⁺ C₂₁H₂₆O₈ Found: 406.1624, requires 406.1622 (+0.19 ppm).

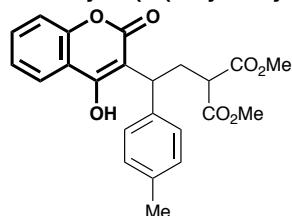
Dimethyl 2-(3-benzoyl-4-oxo-2,4-diphenylbutyl)malonate (4a)



The title compound was prepared according to *General Procedure A* from cyclopropane **1a** (0.059 g, 0.25 mmol), dibenzoylmethane (0.056 g, 0.25 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (10-30% EtOAc in petroleum ether) gave **4a** as a white solid.

Yield: 0.089 g, 78%; **R_f** = 0.23 (petroleum ether/EtOAc 8:2); **mp:** 98-101 °C; **IR v_{max} / cm⁻¹ (film):** 1751, 1730, 1688, 1665; **¹H NMR:** (400 MHz, CDCl₃) δ 8.05 (2H, d, *J* = 7.3 Hz), 7.74 (2H, d, *J* = 7.3 Hz), 7.56 (1H, t, *J* = 7.4 Hz), 7.47-7.40 (4H, m), 7.31-7.27 (2H, m), 7.25-7.23 (2H, m), 7.18 (2H, t, *J* = 7.5 Hz), 7.09 (1H, t, *J* = 7.2 Hz), 5.67 (1H, d, *J* = 10.3 Hz), 3.98 (1H, td, *J* = 10.4, 4.6 Hz), 3.76 (3H, d, *J* = 2.3 Hz), 3.50 (3H, d, *J* = 2.3 Hz), 3.16 (1H, dd, *J* = 9.1, 5.6 Hz), 2.40-2.35 (2H, m); **¹³C NMR:** (100 MHz, CDCl₃) δ 194.2, 194.1, 169.5, 169.1, 139.2, 136.9, 136.7, 133.7, 133.2, 128.9 (2C), 128.9, 128.6, 128.5, 128.5, 127.3, 64.5, 52.6, 52.4, 49.9, 44.7, 32.9; **HRMS:** (ESI⁺) [M+Na]⁺ C₂₈H₂₆O₆Na Found: 481.1617, requires 481.1622 (+0.9 ppm).

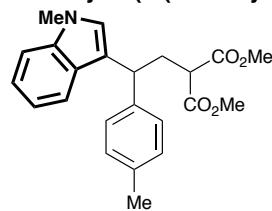
Dimethyl 2-(2-(4-hydroxy-2-oxo-2H-chromen-3-yl)-2-(p-tolyl)ethyl)malonate (4b)



The title compound was prepared according to *General Procedure A* from cyclopropane **1d** (0.063 g, 0.25 mmol), 4-hydroxycoumarin (0.049 g, 0.30 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (10-30% EtOAc in petroleum ether) gave **4b** as a white solid.

Yield: 0.052 g, 50%; **R_f** = 0.21 (petroleum ether/EtOAc 7:3); **mp:** 152-154 °C; **¹H NMR:** (400 MHz, CDCl₃) δ 7.90 (1H, d, *J* = 7.9 Hz), 7.52 (1H, td, *J* = 7.8, 1.1 Hz), 7.34 (2H, d, *J* = 7.8 Hz), 7.27 (2H, app. d, *J* = 8.1 Hz), 7.14 (2H, d, *J* = 7.9 Hz), 4.51 (1H, dd, *J* = 9.6, 6.0 Hz), 3.76 (3H, s), 3.72 (3H, s), 3.51 (1H, dd, *J* = 8.6, 6.1 Hz), 2.96 (1H, ddd, *J* = 14.4, 9.3, 5.6 Hz), 2.82 (1H, ddd, *J* = 14.1, 8.3, 6.1 Hz), 2.32 (3H, s); **¹³C NMR:** (100 MHz, CDCl₃) δ 170.9, 170.1, 162.6, 161.0, 152.7, 137.3, 136.8, 132.0, 129.4, 127.7, 123.9, 123.4, 116.4, 116.1, 107.2, 53.1, 52.8, 49.8, 37.5, 29.6, 21.0.

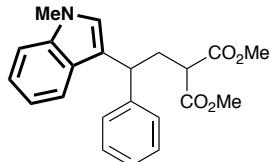
Dimethyl 2-(2-(1-methyl-1*H*-indol-3-yl)-2-(p-tolyl)ethyl)malonate (4c)



The title compound was prepared according to *General Procedure B* from cyclopropane **1d** (0.063 g, 0.25 mmol), 1-methylindole (0.062 mL, 0.50 mmol) and B(C₆F₅)₂·H₂O (6.6 mg, 5 mol%) in MeNO₂ (0.125 mL) and stirred at 80 °C for 24 h. Purification by flash column chromatography over silica (10-30% EtOAc in petroleum ether) gave **4c** as an off-white solid.

Yield: 0.081 g, 85%; **R_f** = 0.34 (petroleum ether/EtOAc 8:2); **mp:** 96-98 °C; **¹H NMR:** (400 MHz, CDCl₃) δ 7.50 (1H, d, *J* = 8.0 Hz), 7.29 (1H, d, *J* = 7.8 Hz), 7.24-7.19 (3H, m), 7.13 (2H, d, *J* = 7.9 Hz), 7.06 (1H, t, *J* = 7.4 Hz), 6.90 (1H, s), 4.21 (1H, t, *J* = 7.9 Hz), 3.77 (6H, s), 3.70 (3H, s), 3.43 (1H, dd, *J* = 8.1, 6.6 Hz), 2.85 (1H, dt, *J* = 14.1, 7.2 Hz), 2.62 (1H, ddd, *J* = 13.9, 8.9, 6.5 Hz), 2.34 (3H, s); **¹³C NMR:** (100 MHz, CDCl₃) δ 170.0, 169.9, 140.4, 137.3, 135.9, 129.2, 127.8, 127.2, 126.0, 121.7, 119.6, 118.9, 117.5, 109.1, 52.5, 52.4, 50.1, 40.2, 35.1, 32.7, 21.0; **HRMS:** (APPI⁺) [M]⁺ C₂₃H₂₅NO₄ Found: 379.1778, requires 379.1778 (+0.03 ppm).

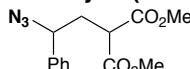
Dimethyl 2-(2-(1-methyl-1*H*-indol-3-yl)-2-phenylethyl)malonate (**4d**)



The title compound was prepared according to *General Procedure B* from cyclopropane **1a** (0.059 g, 0.25 mmol), 1-methylindole (0.062 mL, 0.50 mmol) and $B(C_6F_5)_2\cdot H_2O$ (13.2 mg, 10 mol%) in $MeNO_2$ (0.125 mL) and stirred at 80 °C for 24 h. Purification by flash column chromatography over silica (10-25% EtOAc in petroleum ether) gave **4d** as a colourless oil. Analytical data are in agreement with the literature.¹⁵

Yield: 0.062 g, 68%; **¹H NMR:** (400 MHz, $CDCl_3$) δ 7.49 (1H, d, J = 8.0 Hz), 7.36-7.28 (5H, m), 7.24-7.20 (2H, m), 7.07-7.03 (1H, m), 6.91 (1H, s), 4.25 (1H, t, J = 7.9 Hz), 3.78 (3H, s), 3.77 (3H, s), 3.70 (3H, s), 3.44 (1H, dd, J = 7.8, 6.9 Hz), 2.89-2.82 (1H, m), 2.65 (1H, ddd, J = 13.9, 8.7, 6.7 Hz).

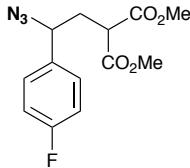
Dimethyl 2-(2-azido-2-phenylethyl)malonate (**4e**)



The title compound was prepared according to *General Procedure A* from cyclopropane **1a** (0.059 g, 0.25 mmol), azidotrimethylsilane (0.066 mL, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (10% EtOAc in petroleum ether) gave **4e** as a colourless liquid. Analytical data are in agreement with the literature.¹⁶

Yield: 0.045 g, 65%; **R_f** = 0.66 (petroleum ether/EtOAc 8:2); **¹H NMR:** (400 MHz, $CDCl_3$) δ 7.42-7.35 (3H, m), 7.34-7.31 (2H, m), 4.55 (1H, t, J = 7.3 Hz), 3.75 (3H, s), 3.74 (3H, s), 3.54 (1H, t, J = 7.3 Hz), 2.34 (2H, dd, J = 7.7, 7.0 Hz); **¹³C NMR:** (100 MHz, $CDCl_3$) δ 169.3, 169.2, 138.4, 129.0, 128.7, 126.9, 63.9, 52.8, 48.7, 35.3.

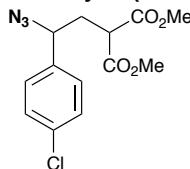
Dimethyl 2-(2-azido-2-(4-fluorophenyl)ethyl)malonate (**4f**)



The title compound was prepared according to *General Procedure A* from cyclopropane **1b** (0.063 g, 0.25 mmol), azidotrimethylsilane (0.066 mL, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-15% EtOAc in petroleum ether) gave **4f** as a colourless liquid. Analytical data are in agreement with the literature.¹⁶

Yield: 0.048 g, 65%; **R_f** = 0.65 (petroleum ether/EtOAc 8:2); **¹H NMR:** (400 MHz, $CDCl_3$) δ 7.30 (2H, dd, J = 8.7, 5.3 Hz), 7.08 (2H, t, J = 8.6 Hz), 4.54 (1H, t, J = 7.3 Hz), 3.75 (3H, s), 3.74 (3H, s), 3.52 (1H, t, J = 7.2 Hz), 2.30 (2H, t, J = 6.9 Hz); **¹³C NMR:** (100 MHz, $CDCl_3$) δ 169.2, 169.1, 162.7 (d, J = 247.6 Hz), 134.3 (d, J = 3.0 Hz), 128.7 (d, J = 8.4 Hz), 116.0 (d, J = 21.8 Hz), 63.2, 52.8, 48.6, 35.4; **¹⁹F NMR:** (376 MHz, $CDCl_3$) δ -112.9.

Dimethyl 2-(2-azido-2-(4-chlorophenyl)ethyl)malonate (**4g**)

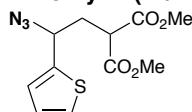


The title compound was prepared according to *General Procedure A* from cyclopropane **1c** (0.067 g, 0.25 mmol), azidotrimethylsilane (0.066 mL, 0.50 mmol) and TfOH (2.2 μ L, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-15% EtOAc in petroleum ether) gave **4g** as a colourless liquid.

Yield: 0.044 g, 56%; **R_f** = 0.60 (petroleum ether/EtOAc 8:2); **IR ν_{max} / cm⁻¹ (film):** 2955, 2100, 1732; **¹H NMR:** (400 MHz, $CDCl_3$) δ 7.39 (2H, d, J = 8.5 Hz), 7.28 (2H, d, J = 8.5 Hz), 4.57 (1H, t, J = 7.3 Hz), 3.78 (3H, s), 3.76 (3H, s), 3.55 (1H, t, J = 7.3 Hz), 2.32 (1H, t, J = 7.3 Hz); **¹³C NMR:** (100 MHz, $CDCl_3$) δ 169.2, 169.2, 137.1, 134.7, 129.3, 128.4, 63.3, 52.9, 48.7, 35.4; **HRMS:** (ESI⁺) [M+Na]⁺ $C_{13}H_{14}{^{35}Cl}N_3O_4Na$ Found: 334.0560, requires 334.0565 (+1.6 ppm).

¹⁶ K. L. Ivanov, E. V. Villemson, E. M. Budynina, O. A. Ivanova, I. V. Trushkov, M. Y. Melnikov, *Chem. Eur.-J.* **2015**, *21*, 4975.

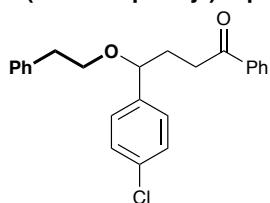
Dimethyl 2-(2-azido-2-(thiophen-2-yl)ethyl)malonate (4h)



The title compound was prepared according to *General Procedure B* from cyclopropane **1j** (0.061 g, 0.25 mmol), azidotrimethylsilane (0.066 mL, 0.50 mmol) and B(C₆F₅)•H₂O (6.6 mg, 5 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-15% EtOAc in petroleum ether) gave **4h** as a colourless liquid. Analytical data are in agreement with the literature.¹⁶

Yield: 0.048 g, 68%; **R_f** = 0.60 (petroleum ether/EtOAc 8:2); **¹H NMR**: (400 MHz, CDCl₃) δ 7.32 (1H, dd, *J* = 5.1, 1.0 Hz), 7.05 (1H, dd, *J* = 3.4, 0.5 Hz), 7.01 (1H, dd, *J* = 5.0, 3.5 Hz), 4.81 (1H, t, *J* = 7.4 Hz), 3.76 (3H, s), 3.75 (3H, s), 3.58 (1H, t, *J* = 7.2 Hz), 2.43 (2H, t, *J* = 7.4 Hz); **¹³C NMR**: (100 MHz, CDCl₃) δ 169.2, 169.1, 141.2, 127.0, 126.3, 126.1, 59.2, 52.9, 48.7, 35.6.

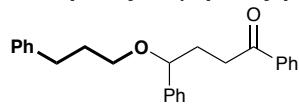
4-(4-Chlorophenyl)-4-phenethoxy-1-phenylbutan-1-one (4i)



The title compound was prepared according to *General Procedure A* from cyclopropane **1i** (0.064 g, 0.25 mmol), 2-phenylethanol (0.060 mL, 0.50 mmol) and TfOH (2.2 μL, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-10% EtOAc in petroleum ether) gave **4i** as an off-white solid.

Yield: 0.085 g, 90%; **R_f** = 0.83 (petroleum ether/EtOAc 8:2); **mp:** 87-88 °C; **IR v_{max} / cm⁻¹ (film)**: 1680; **¹H NMR**: (400 MHz, CDCl₃) δ 7.92 (2H, dd, *J* = 8.3, 1.3 Hz), 7.61-7.57 (1H, m), 7.48 (2H, t, *J* = 7.6 Hz), 7.33-7.26 (4H, m), 7.23-7.19 (5H, m), 4.35 (1H, t, *J* = 6.5 Hz), 3.59 (1H, dt, *J* = 9.3, 6.8 Hz), 3.48 (1H, dt, *J* = 9.3, 6.9 Hz), 3.02 (2H, t, *J* = 7.2 Hz), 2.92-2.81 (2H, m), 2.11 (2H, q, *J* = 6.9 Hz); **¹³C NMR**: (100 MHz, CDCl₃) δ 200.0, 141.1, 139.2, 137.1, 133.2, 133.1, 129.1, 128.7, 128.6, 128.4, 128.2, 127.9, 126.3, 80.6, 69.8, 36.5, 34.5, 32.7; **HRMS**: (ESI⁺) [M+K]⁺ C₂₄H₂₃³⁵ClO₂K Found: 417.1054, requires 417.1018 (-8.7 ppm).

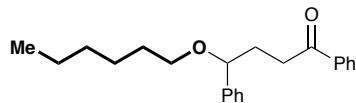
1,4-Diphenyl-4-(3-phenylpropoxy)butan-1-one (4j)



The title compound was prepared according to *General Procedure A* from cyclopropane **1k** (0.056g, 0.25 mmol), 3-phenylpropanol (0.068 mL, 0.50 mmol) and TfOH (2.2 μL, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-10% EtOAc in petroleum ether) gave **4j** as an off-white solid.

Yield: 0.065 g, 73%; **R_f** = 0.83 (petroleum ether/EtOAc 8:2); **mp:** 76-77 °C; **IR v_{max} / cm⁻¹ (film)**: 1680; **¹H NMR**: (400 MHz, CDCl₃) δ 7.99 (2H, d, *J* = 7.3 Hz), 7.58 (1H, t, *J* = 7.3 Hz), 7.48 (2H, t, *J* = 7.6 Hz), 7.41-7.36 (4H, m), 7.34-7.26 (3H, m), 7.20 (1H, d, *J* = 7.2 Hz), 7.16 (2H, d, *J* = 7.3 Hz), 4.38 (1H, dd, *J* = 7.6, 5.5 Hz), 3.41 (1H, dt, *J* = 9.3, 6.3 Hz), 3.31 (1H, dt, *J* = 9.3, 6.3 Hz), 3.13 (2H, td, *J* = 7.1, 2.6 Hz), 2.77-2.63 (2H, m), 2.28-2.14 (2H, m), 1.93-1.86 (2H, m); **¹³C NMR**: (100 MHz, CDCl₃) δ 200.2, 142.7, 142.2, 137.2, 133.1, 128.7, 128.5, 128.4, 128.2, 127.7, 126.7, 125.8, 81.2, 68.2, 34.8, 32.8, 32.6, 31.6; **HRMS**: (ESI⁺) [M+Na]⁺ C₂₅H₂₆O₂Na Found: 381.1829, requires 381.1825 (-1.1 ppm).

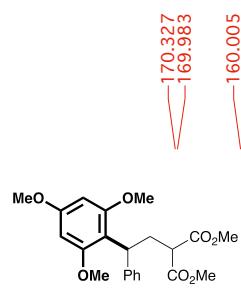
4-(Hexyloxy)-1,4-diphenylbutan-1-one (4k)



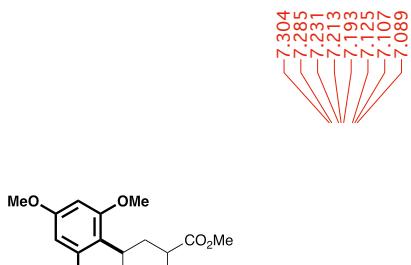
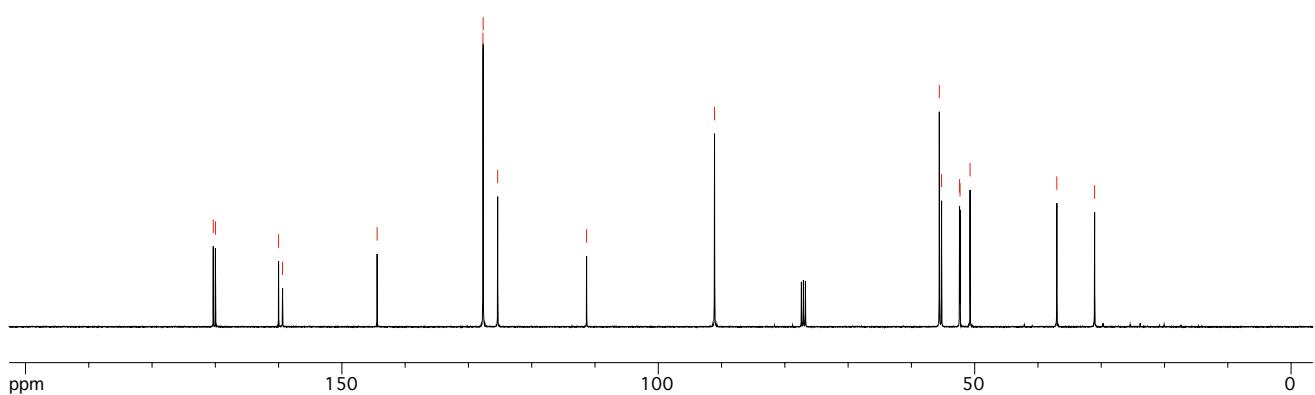
The title compound was prepared according to *General Procedure A* from cyclopropane **1k** (0.056g, 0.25 mmol), 1-hexanol (0.093 mL, 0.75 mmol) and TfOH (2.2 μL, 10 mol%) in HFIP (0.125 mL) and stirred at room temperature for 3 h. Purification by flash column chromatography over silica (0-5% EtOAc in petroleum ether) gave **4k** as a colourless liquid.

Yield: 0.060 g, 74%; **R_f** = 0.84 (petroleum ether/EtOAc 8:2); **IR v_{max} / cm⁻¹ (film)**: 1681; **¹H NMR**: (400 MHz, CDCl₃) δ 7.98-7.96 (2H, m), 7.59-7.56 (1H, m), 7.47 (2H, t, *J* = 7.6 Hz), 7.39-7.27 (5H, m), 4.35 (1H, t, *J* = 6.6 Hz), 3.36 (1H, dt, *J* = 9.2, 6.7 Hz), 3.25 (1H, dt, *J* = 9.2, 6.6 Hz), 3.18-3.04 (2H, m), 2.19-2.14 (2H, m), 1.61-1.52 (2H, m), 1.37-1.22 (6H, m), 0.88 (3H, t, *J* = 7.0 Hz); **¹³C NMR**: (100 MHz, CDCl₃) δ 200.1, 142.7, 137.1, 132.9, 128.5, 128.4, 128.0, 127.4, 126.5, 81.0, 69.0, 34.7, 32.8, 31.7, 29.9, 25.9, 22.6, 14.0; **HRMS**: (APPI⁺) [M]⁺ C₂₂H₂₈O₂ Found: 324.2084, requires 324.2084 (+0.04 ppm).

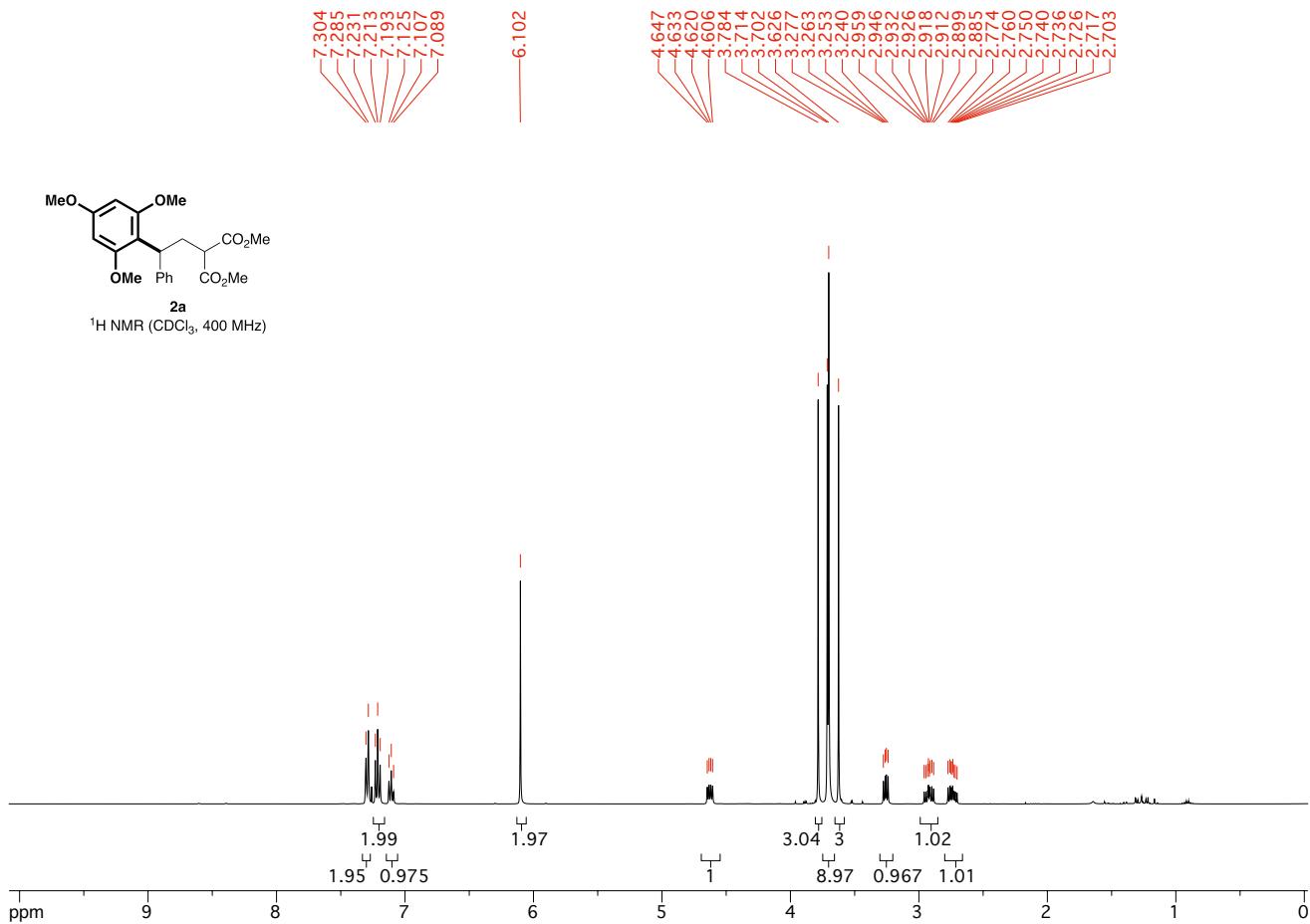
3. NMR Spectra of Products

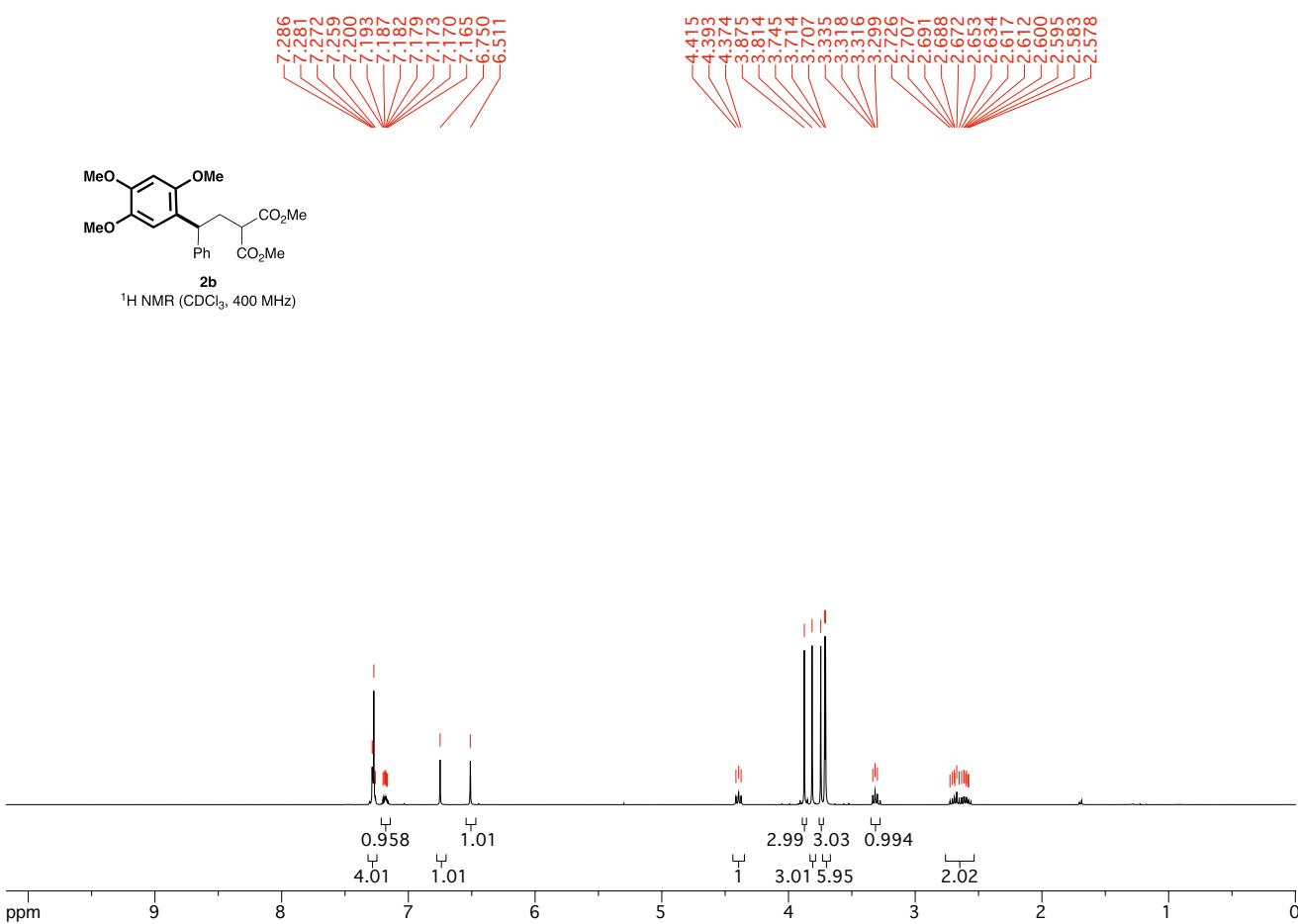
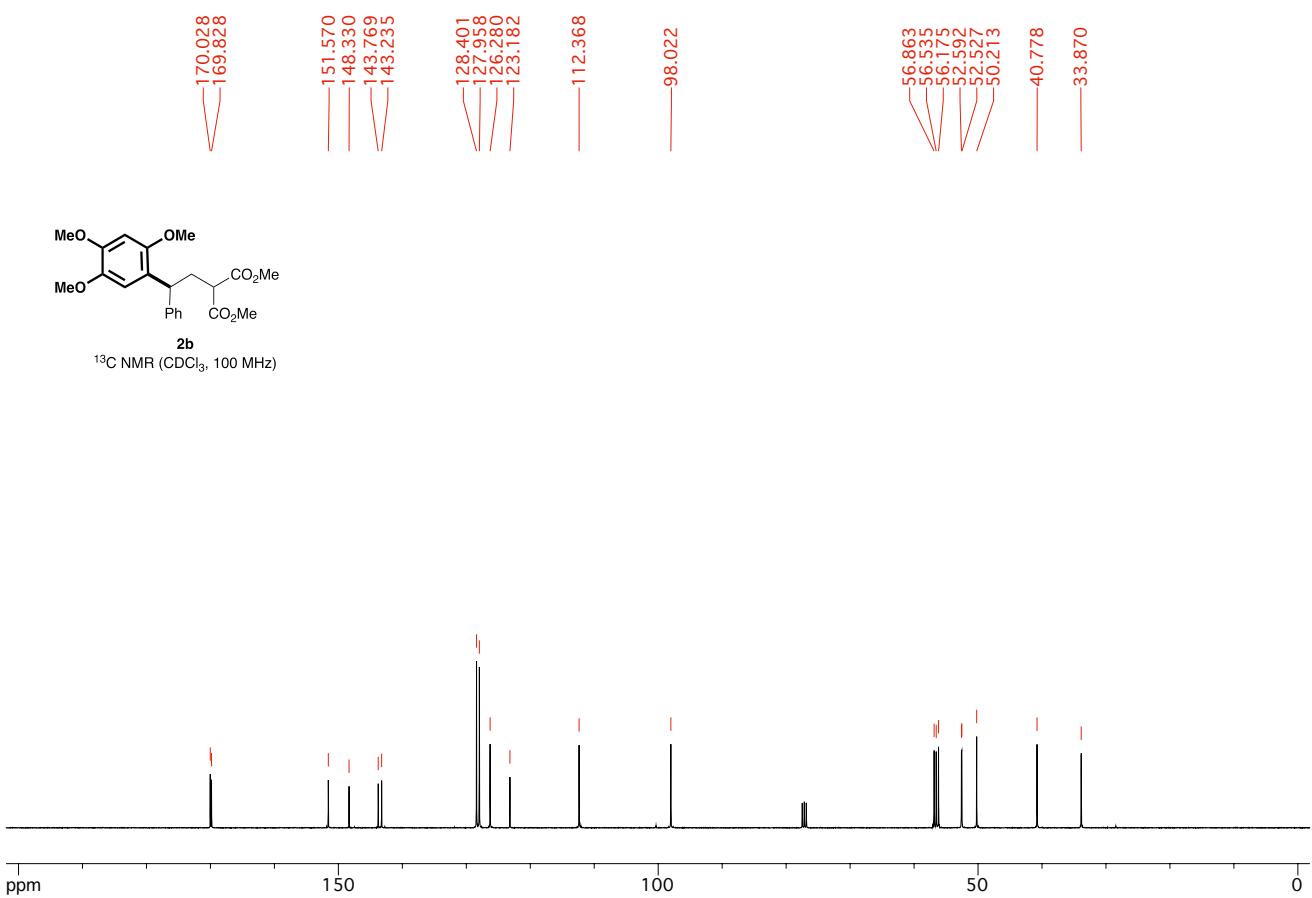


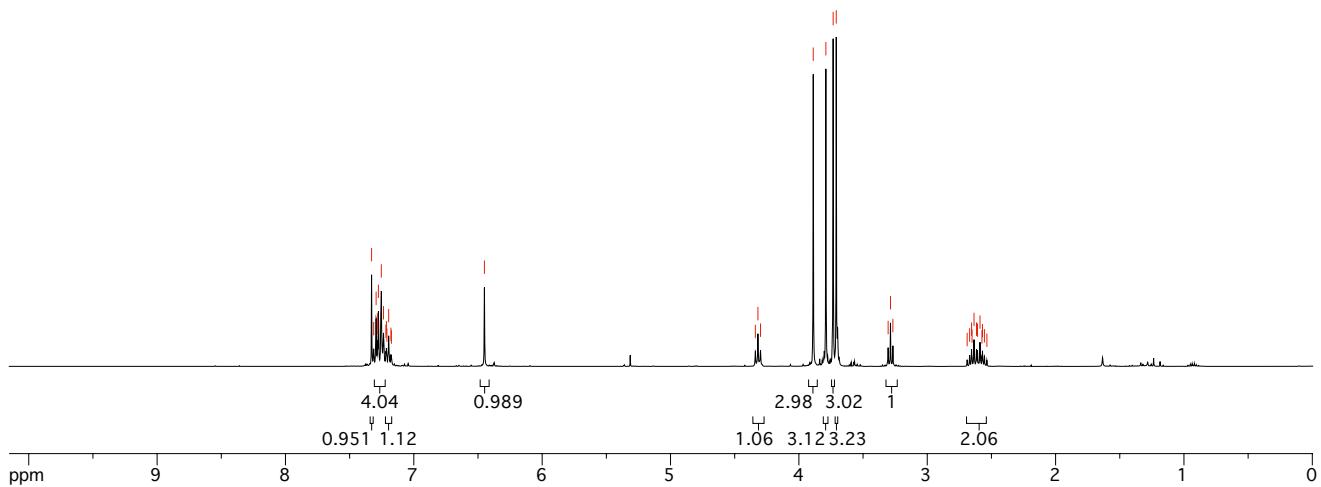
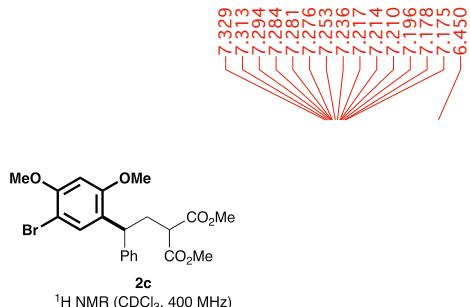
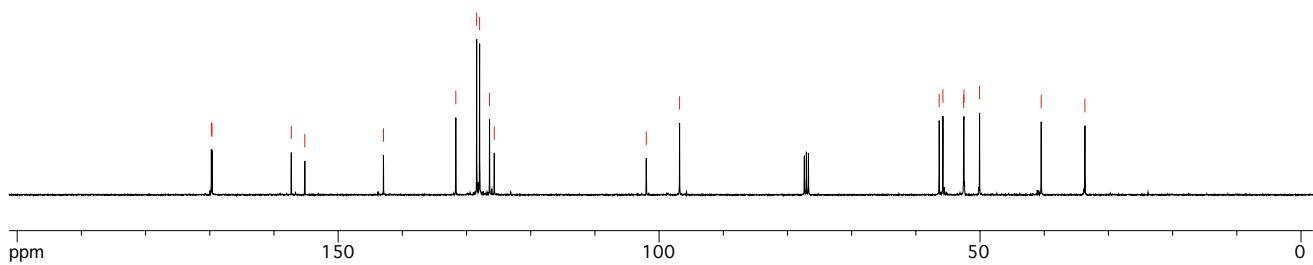
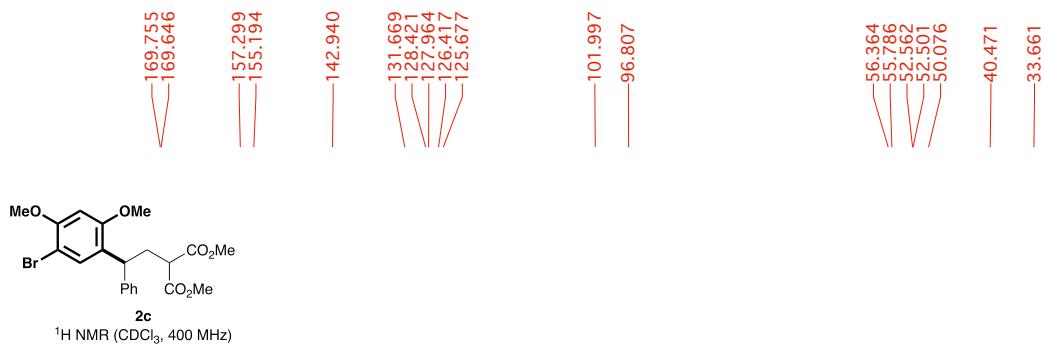
¹³C NMR (CDCl_3 , 100 MHz)

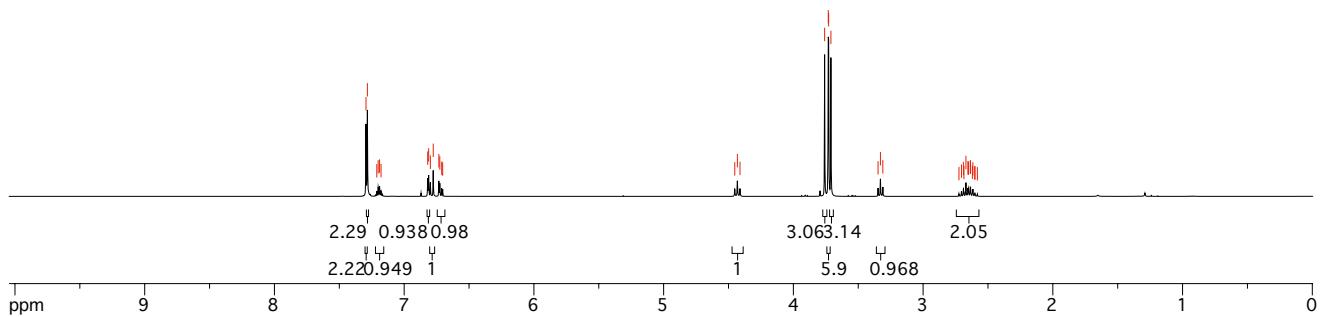
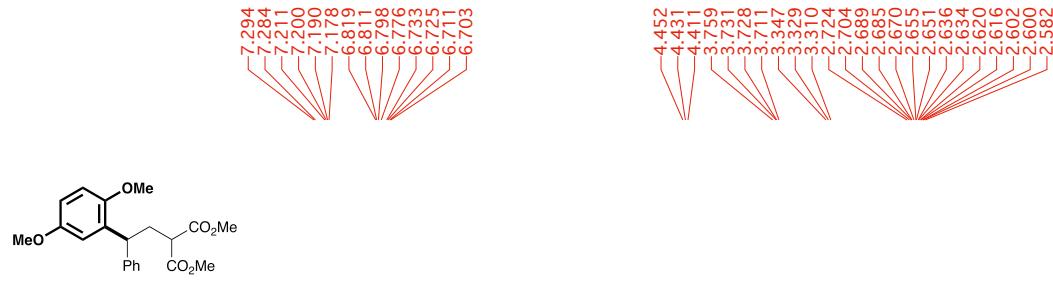
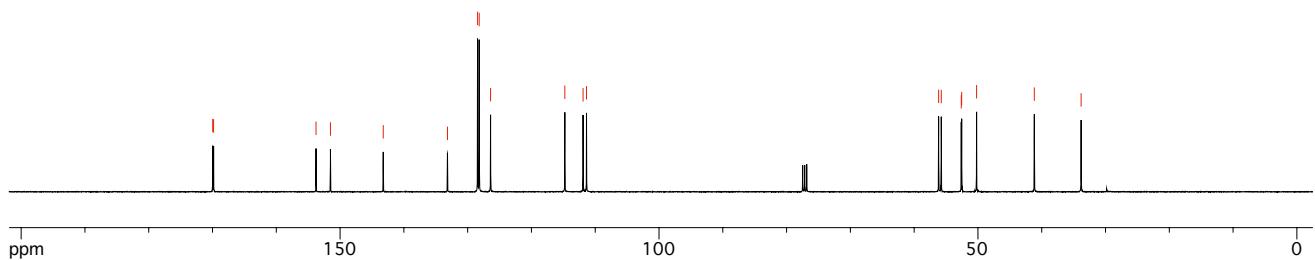
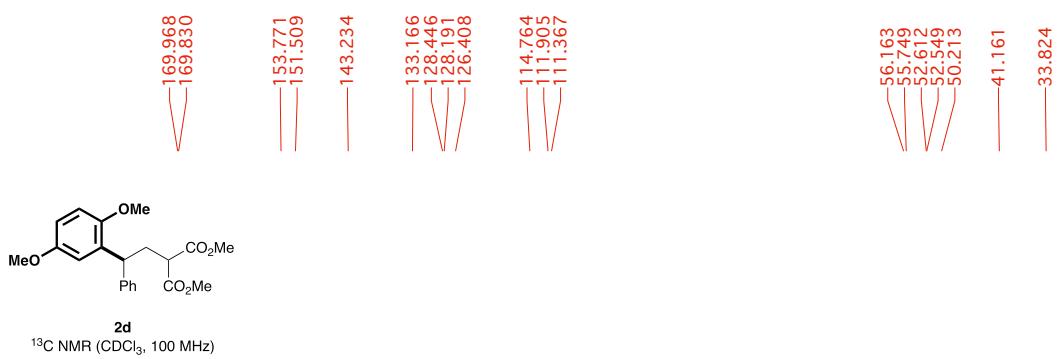


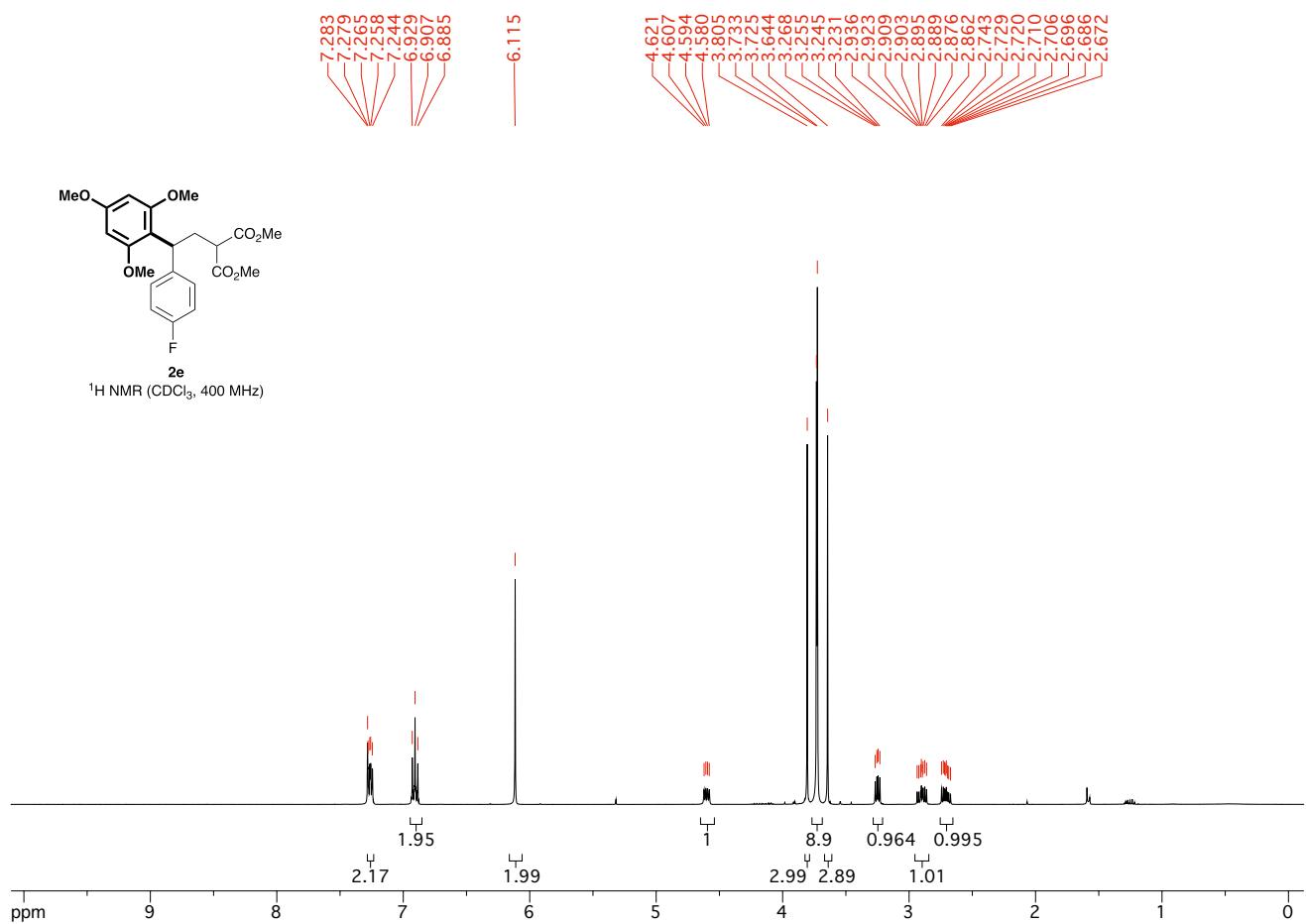
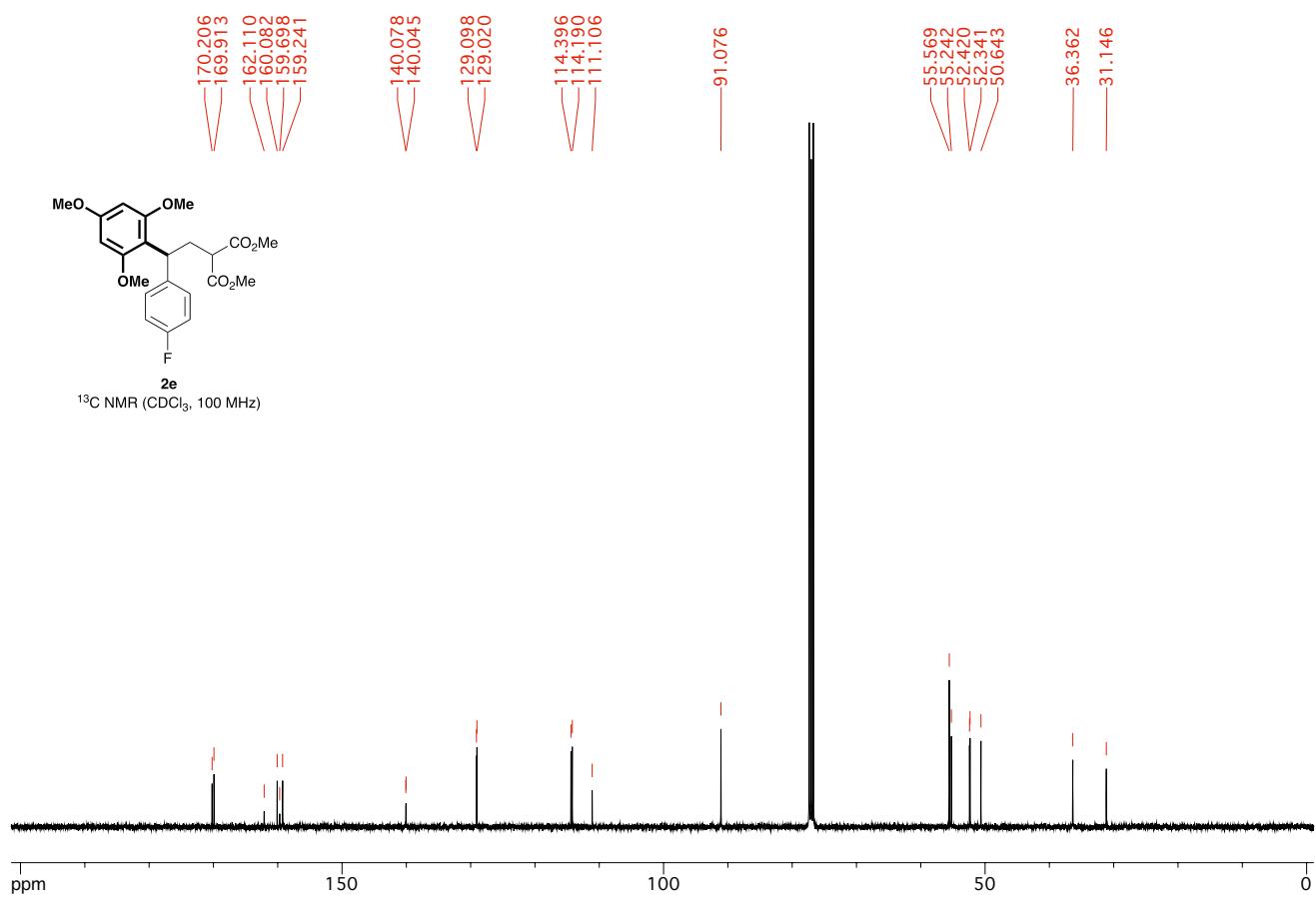
¹H NMR (CDCl_3 , 400 MHz)

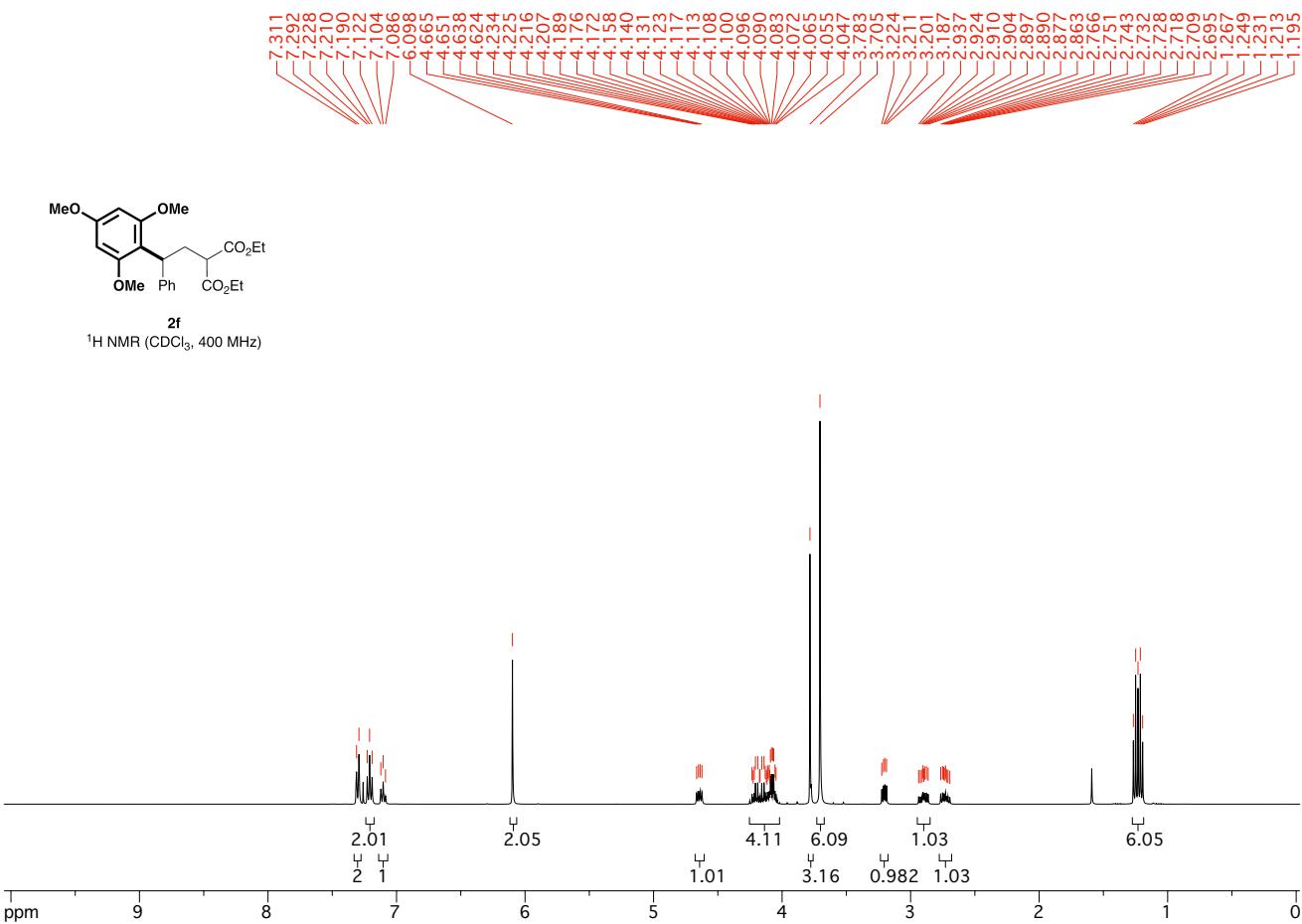
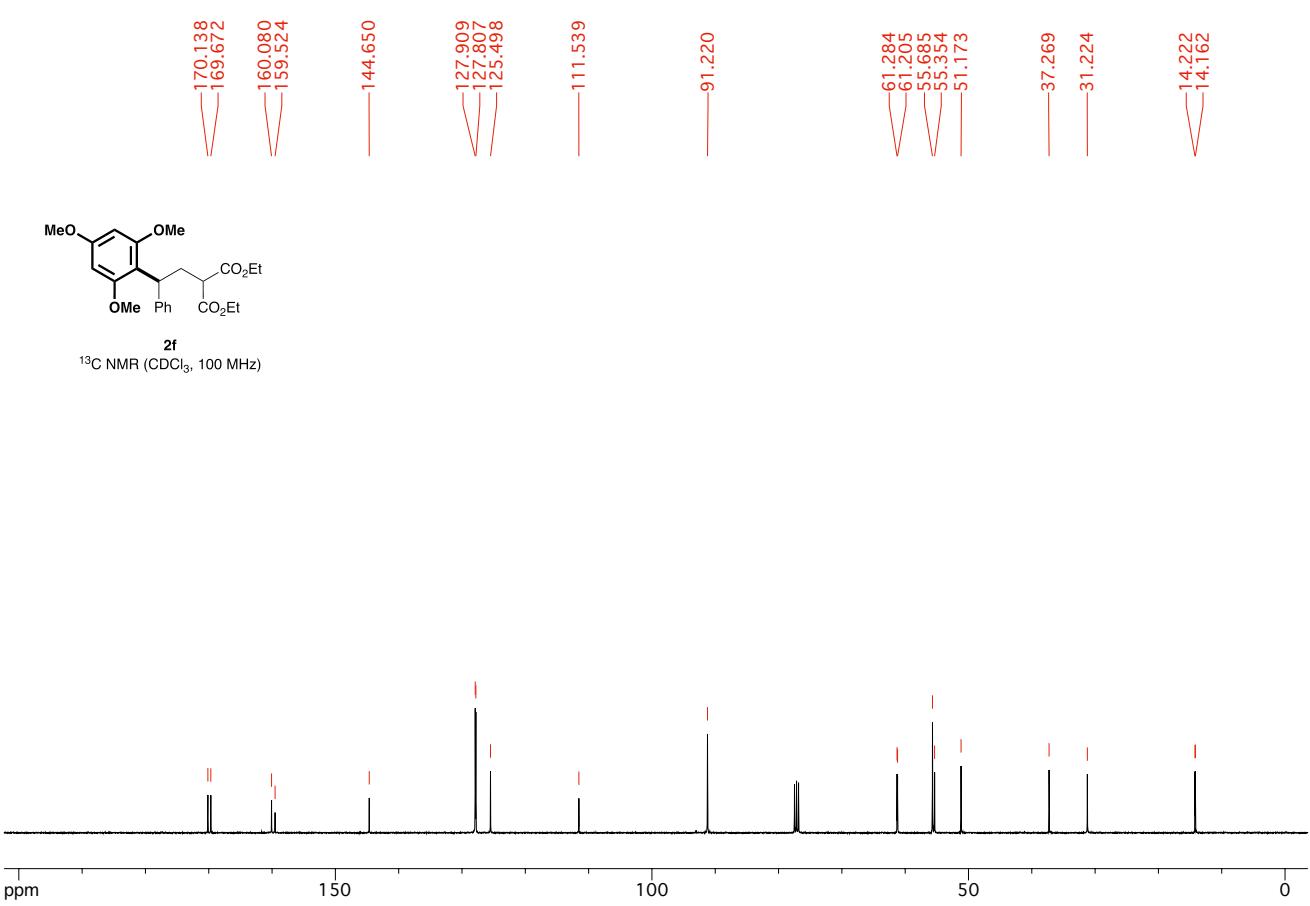


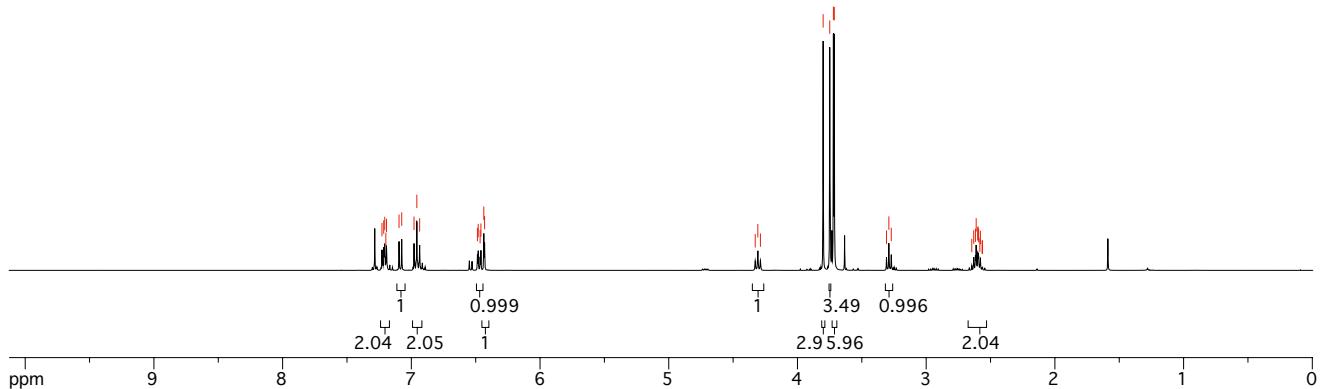
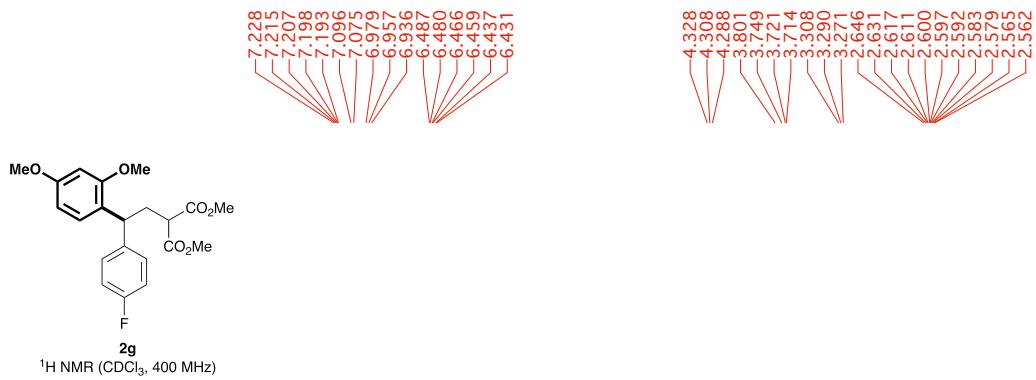
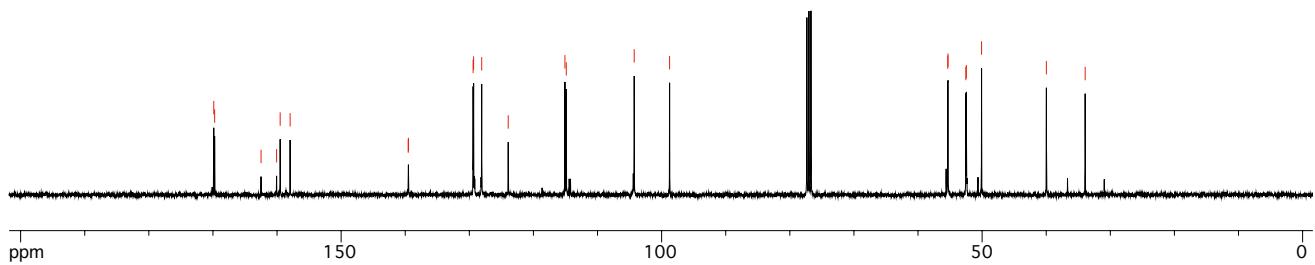
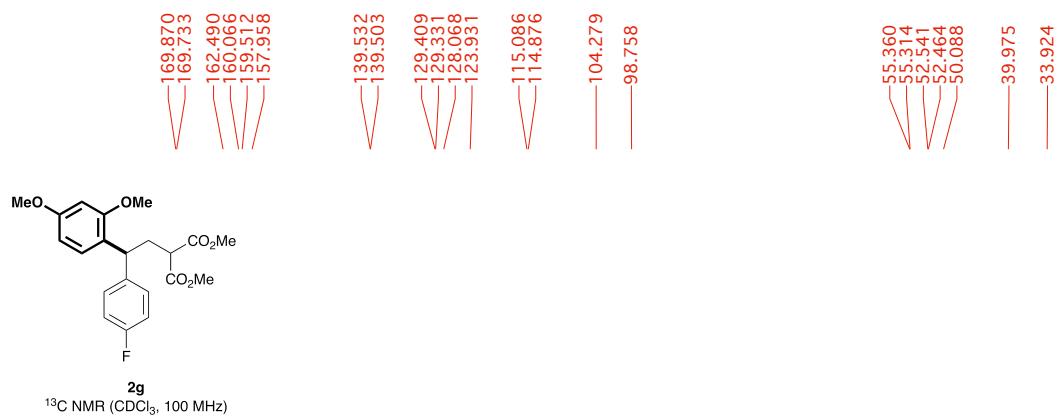


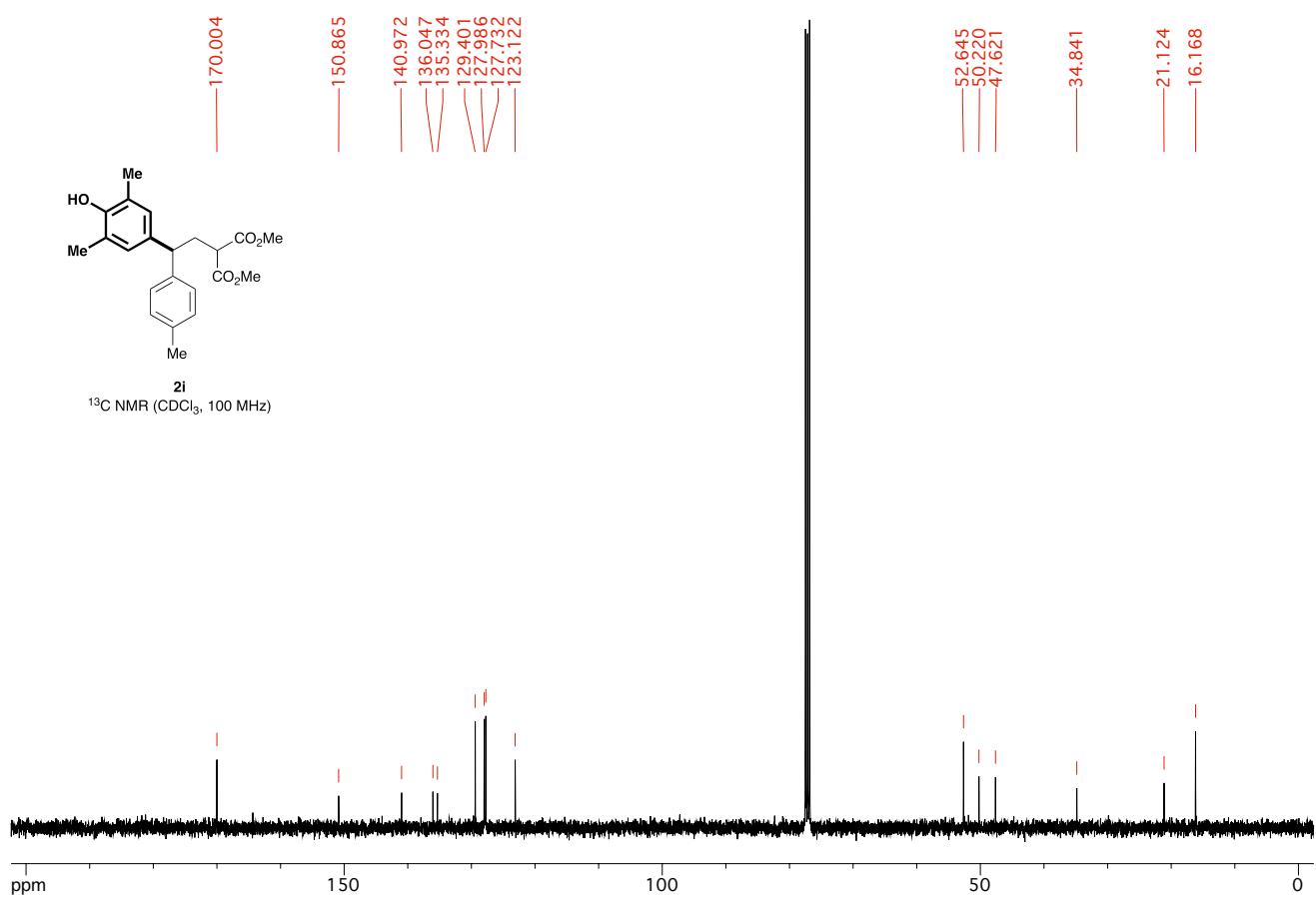
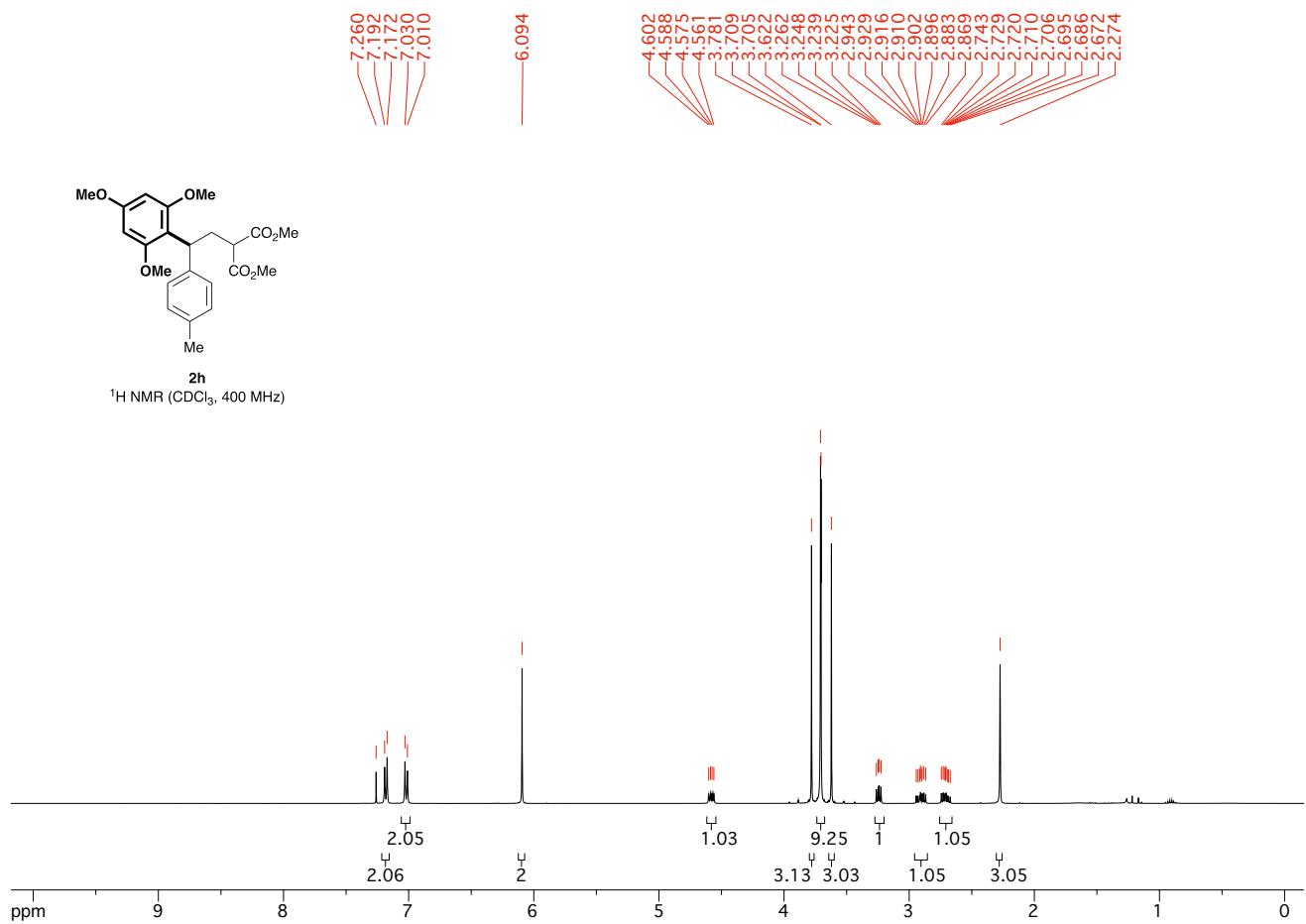


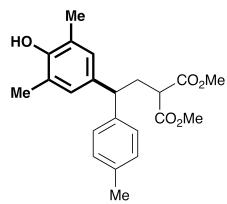




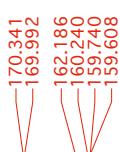
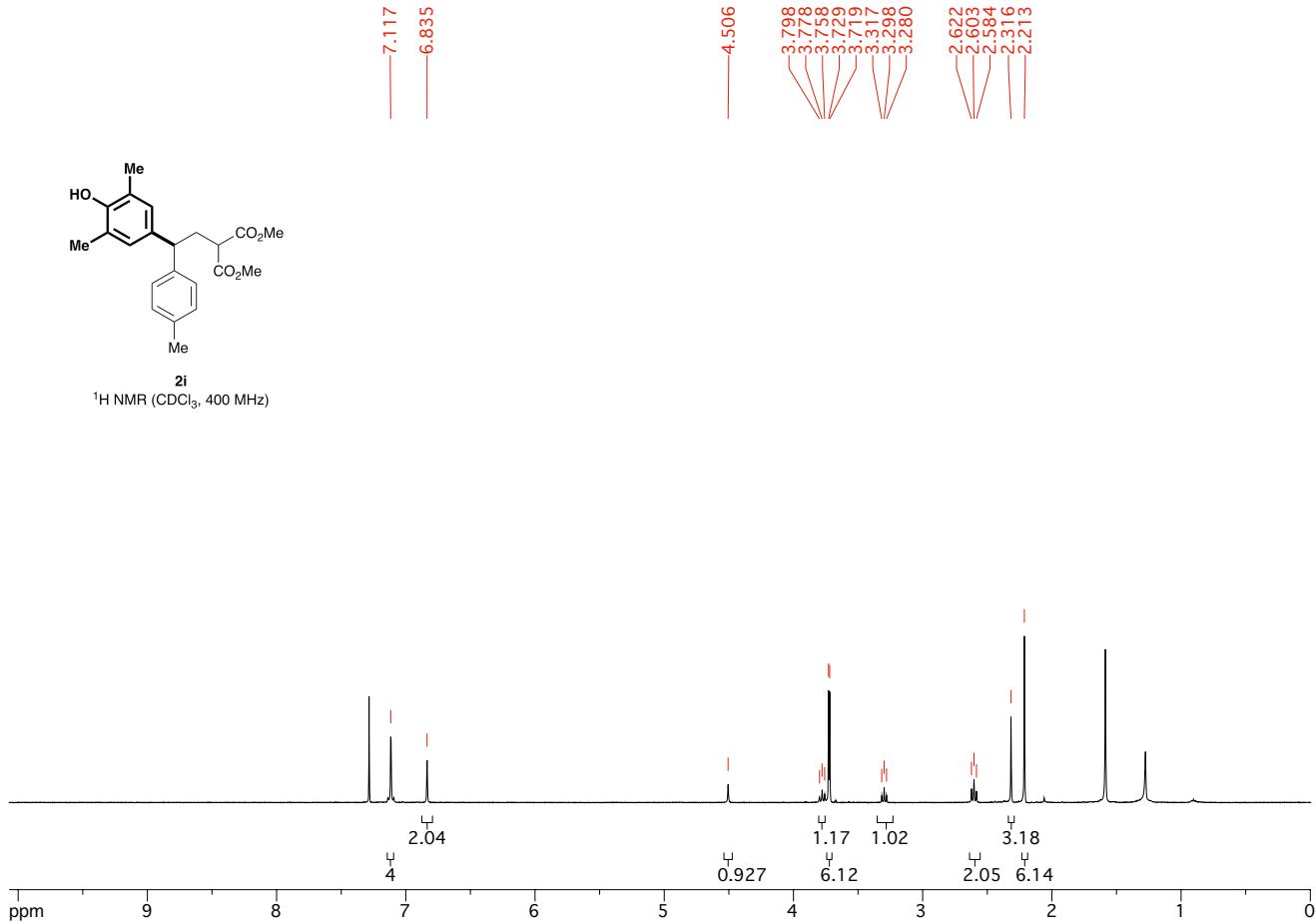




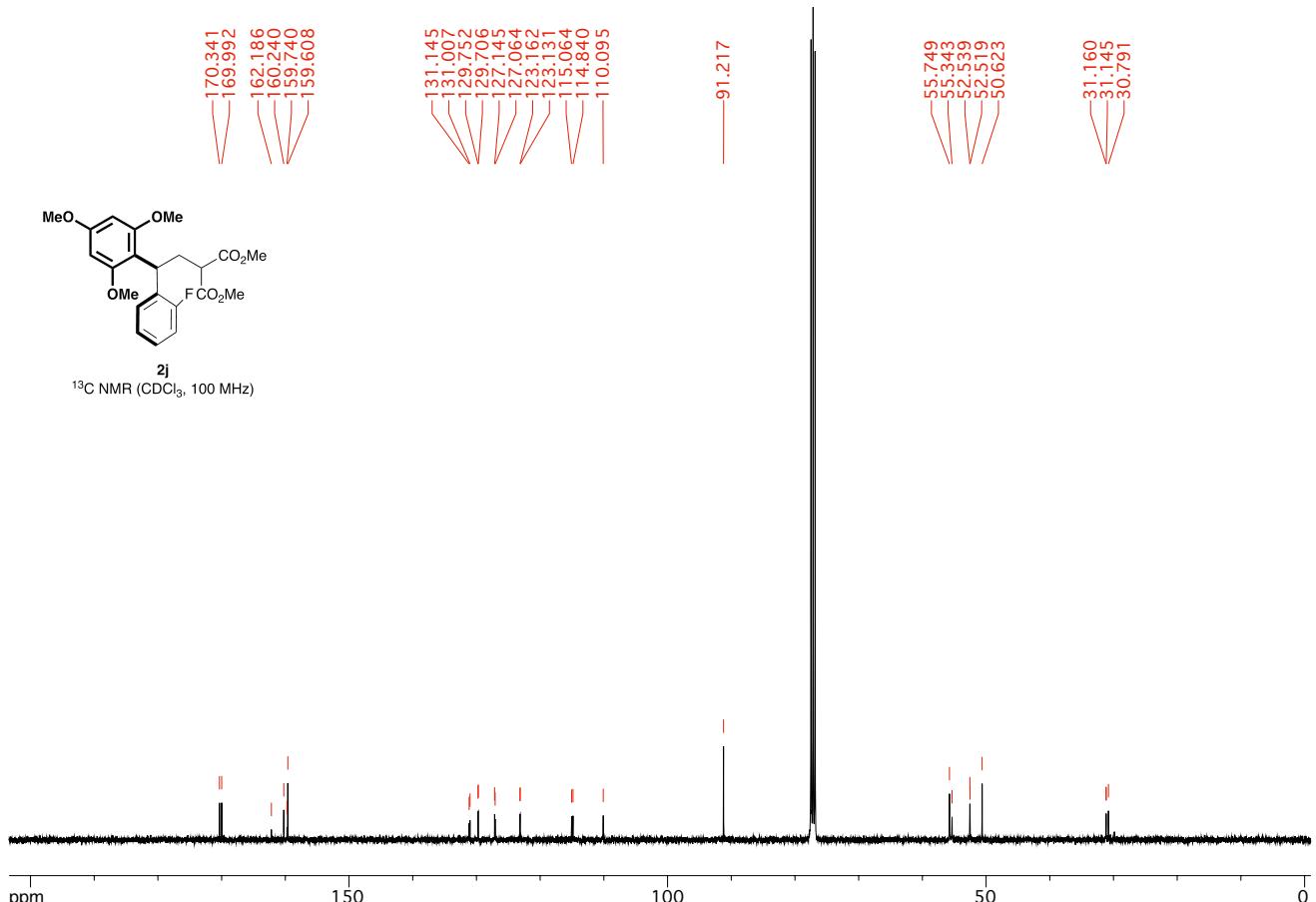


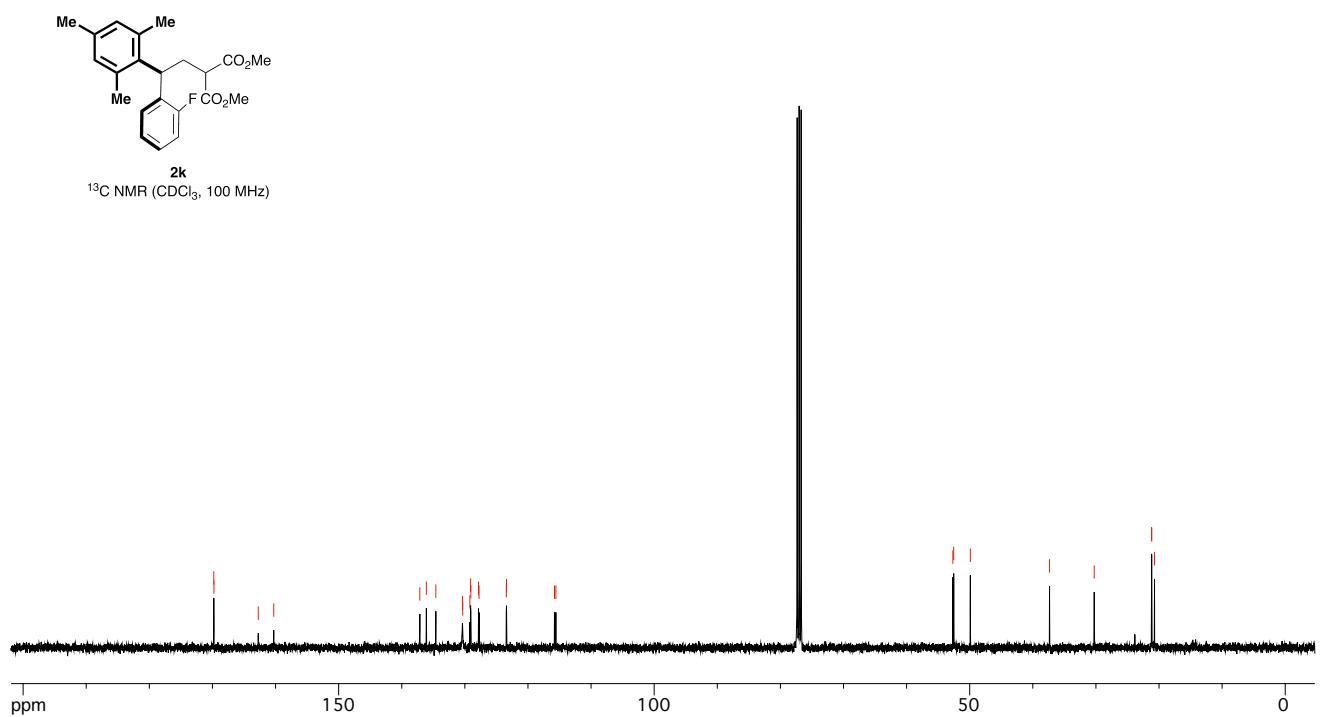
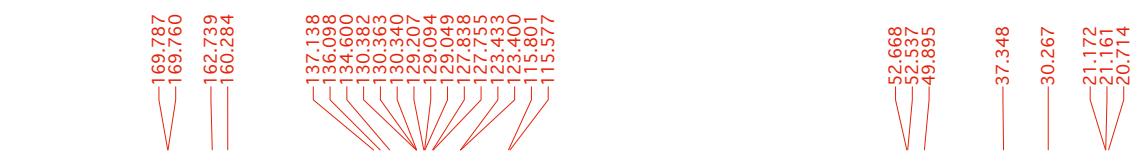
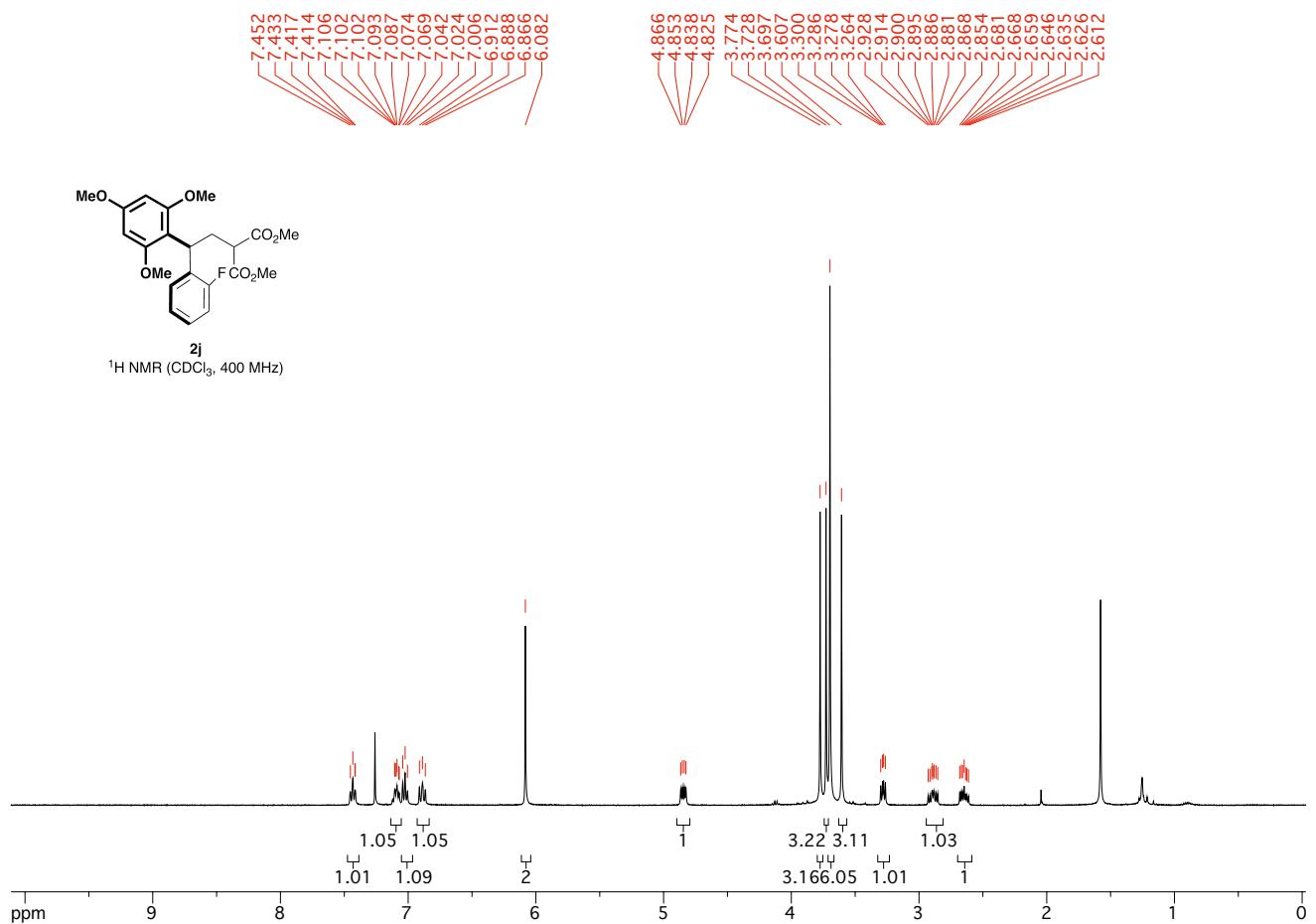


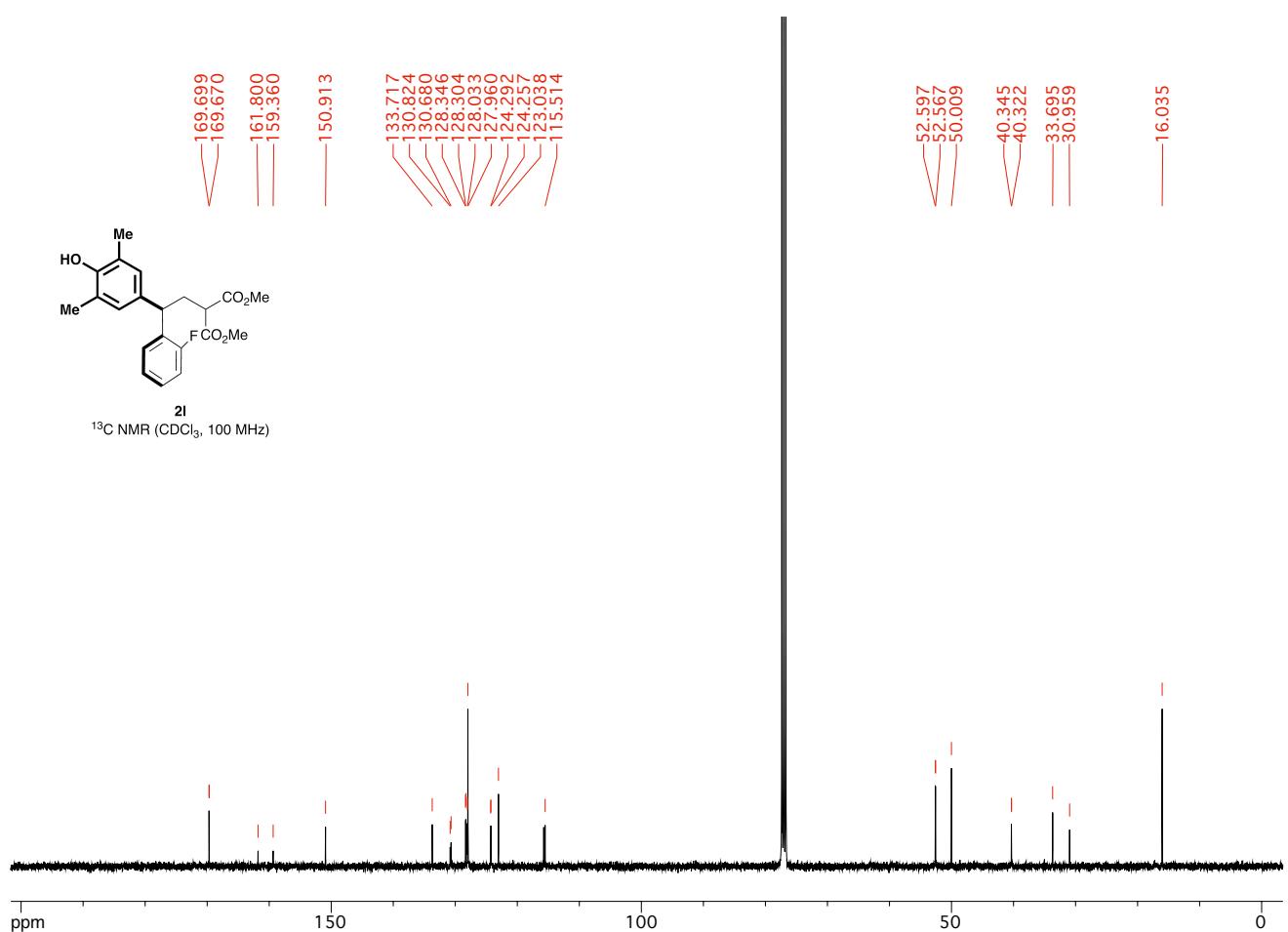
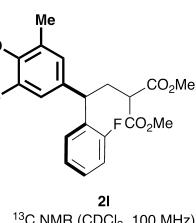
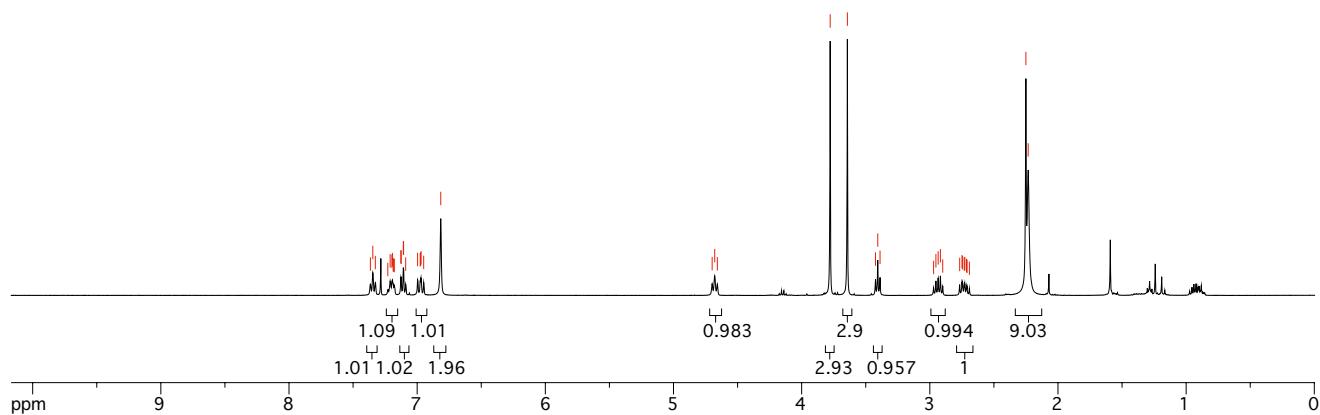
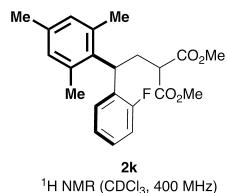
2i
¹H NMR (CDCl₃, 400 MHz)

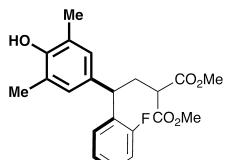


2j
¹³C NMR (CDCl₃, 100 MHz)

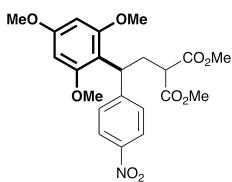
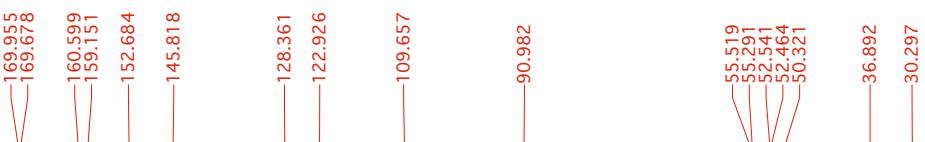
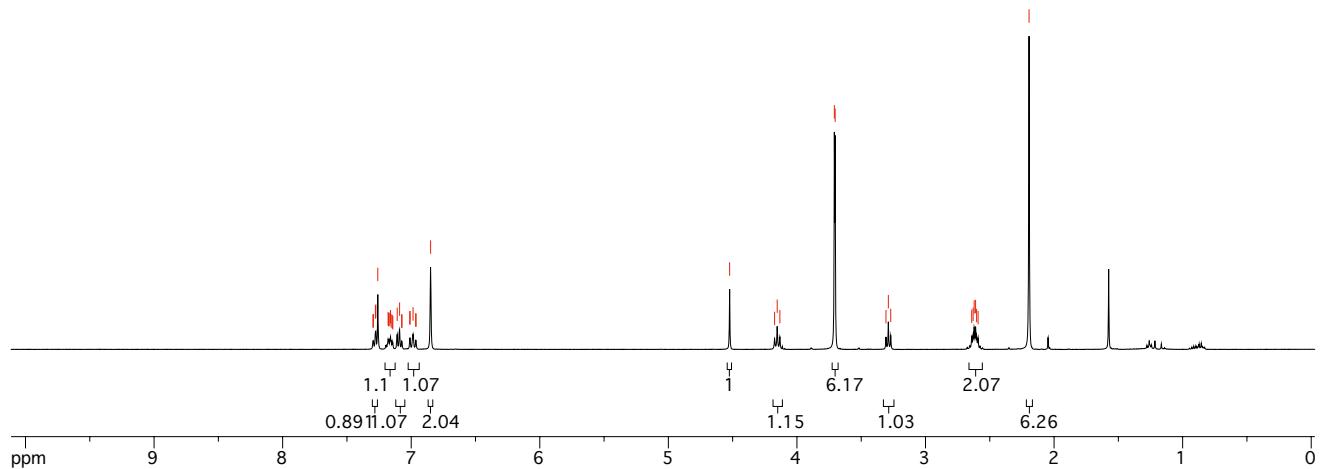




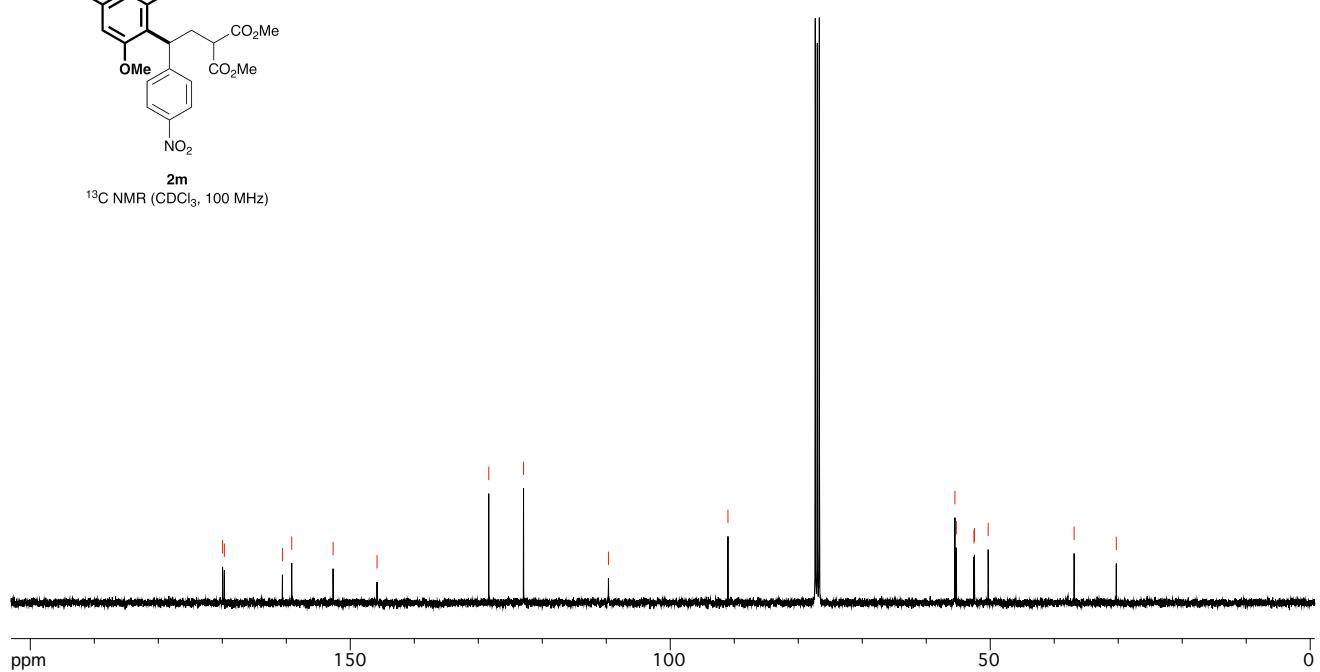


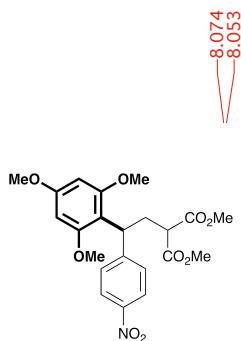


¹H NMR (CDCl₃, 400 MHz)

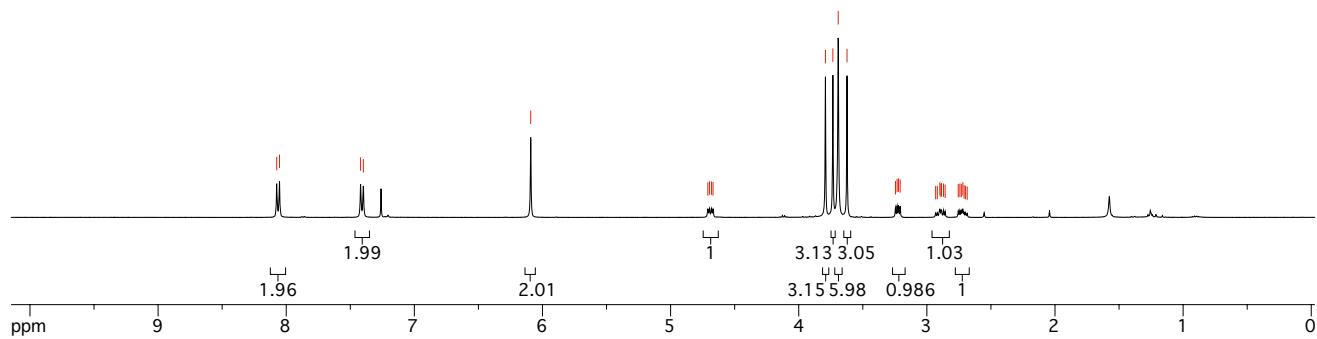


¹³C NMR (CDCl₃, 100 MHz)





2m
¹H NMR (CDCl₃, 400 MHz)



169.615

151.221

146.153

137.182

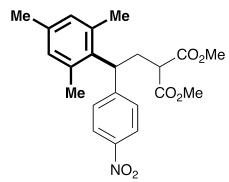
136.923

134.246

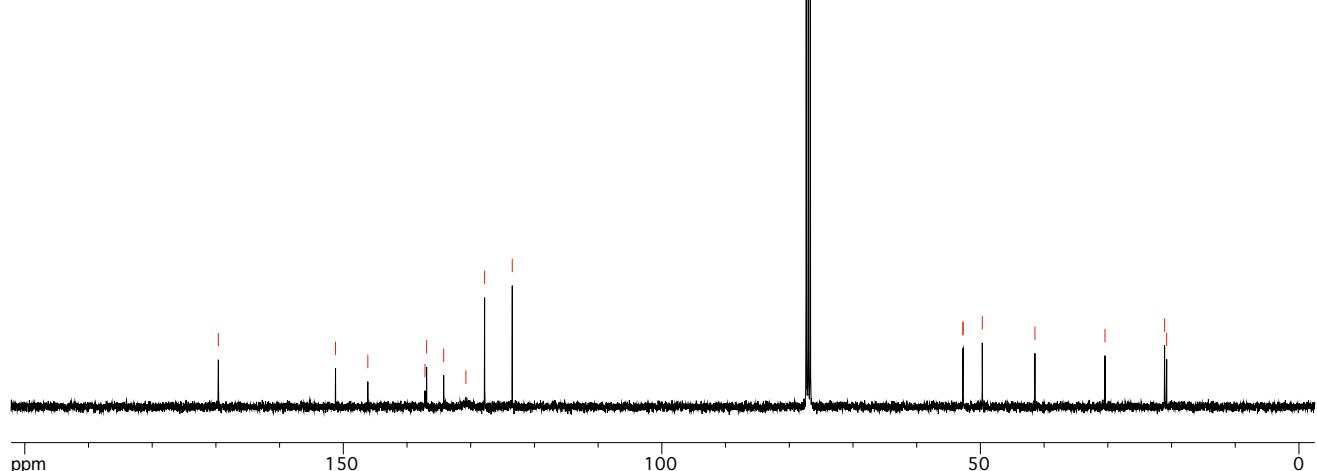
130.759

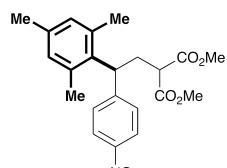
127.846

123.480

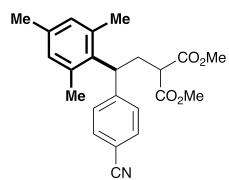
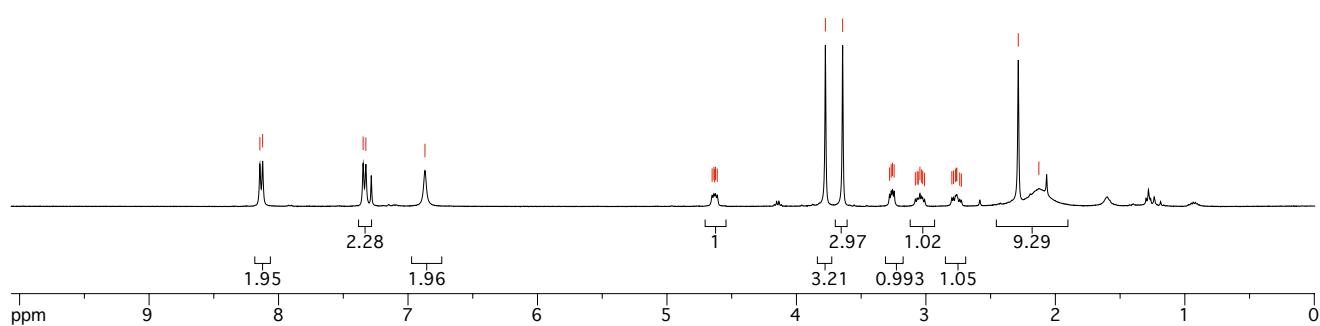


2n
¹³C NMR (CDCl₃, 100 MHz)

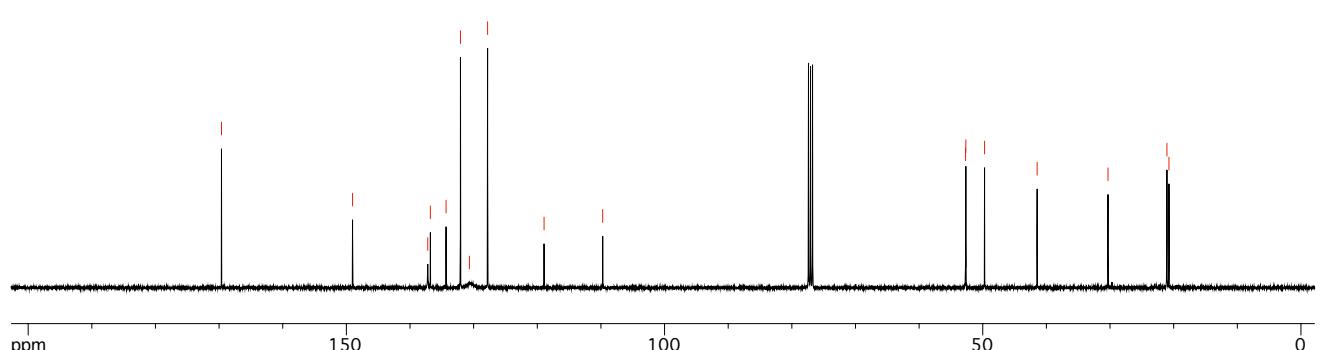


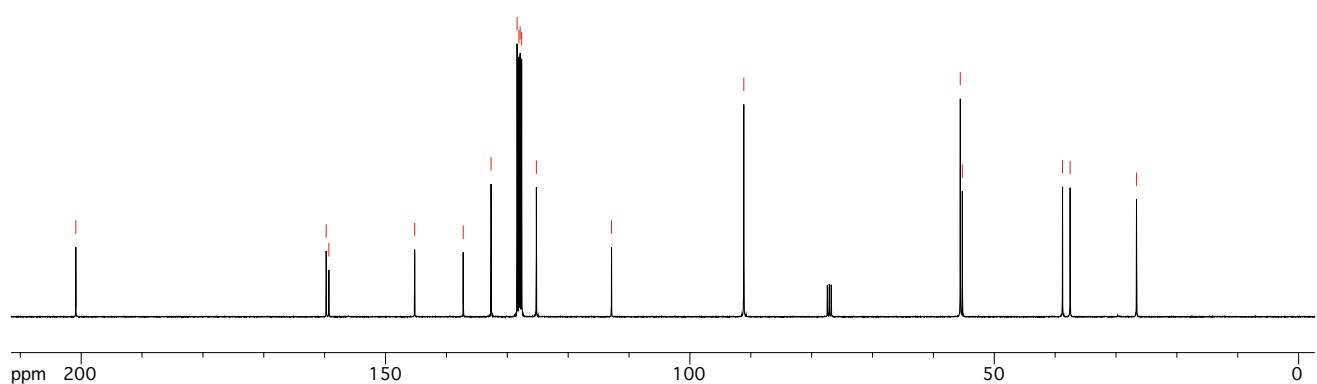
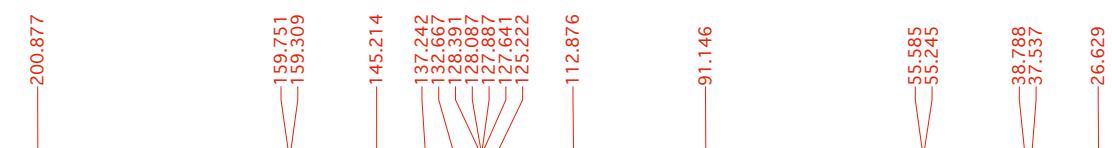
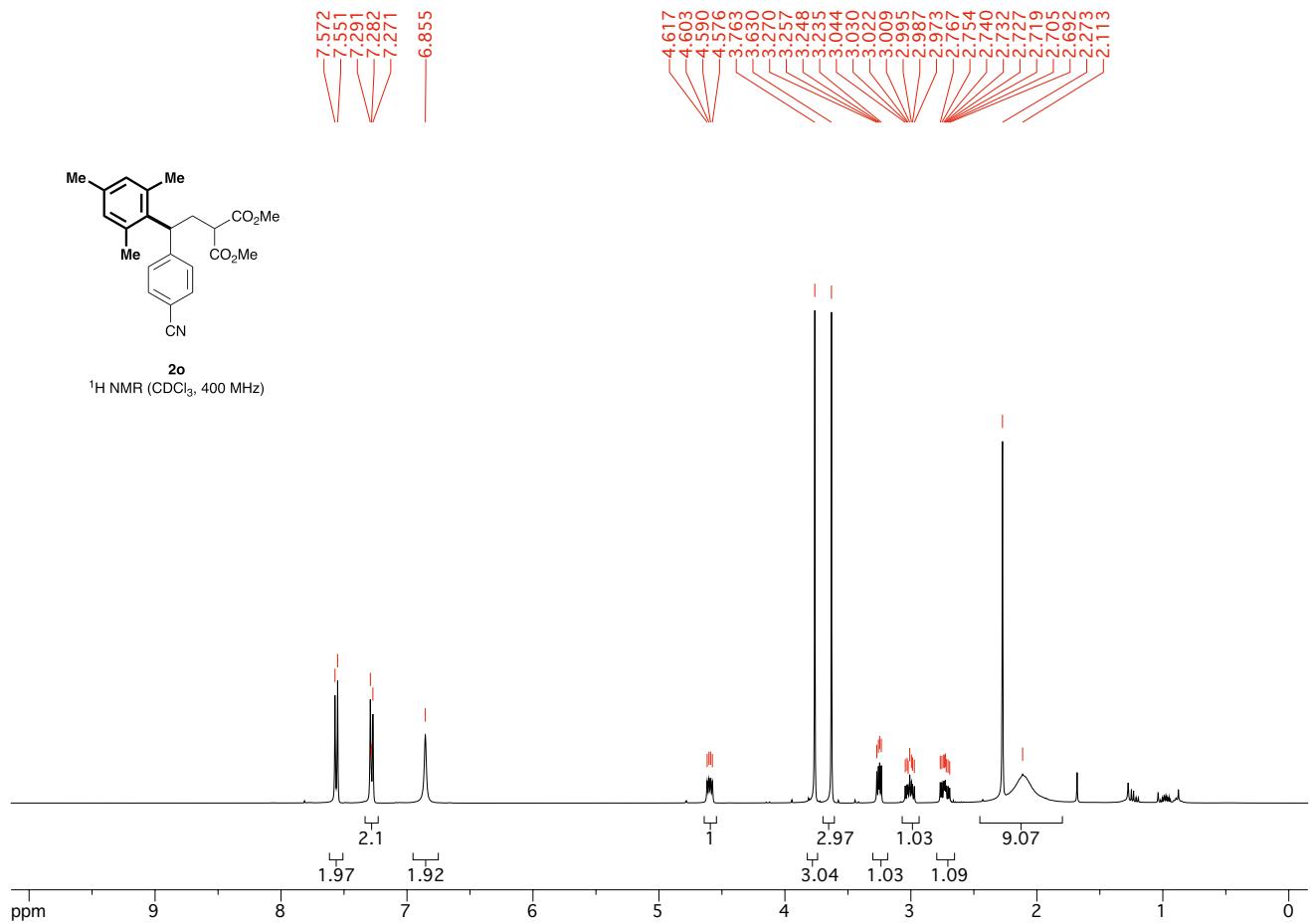


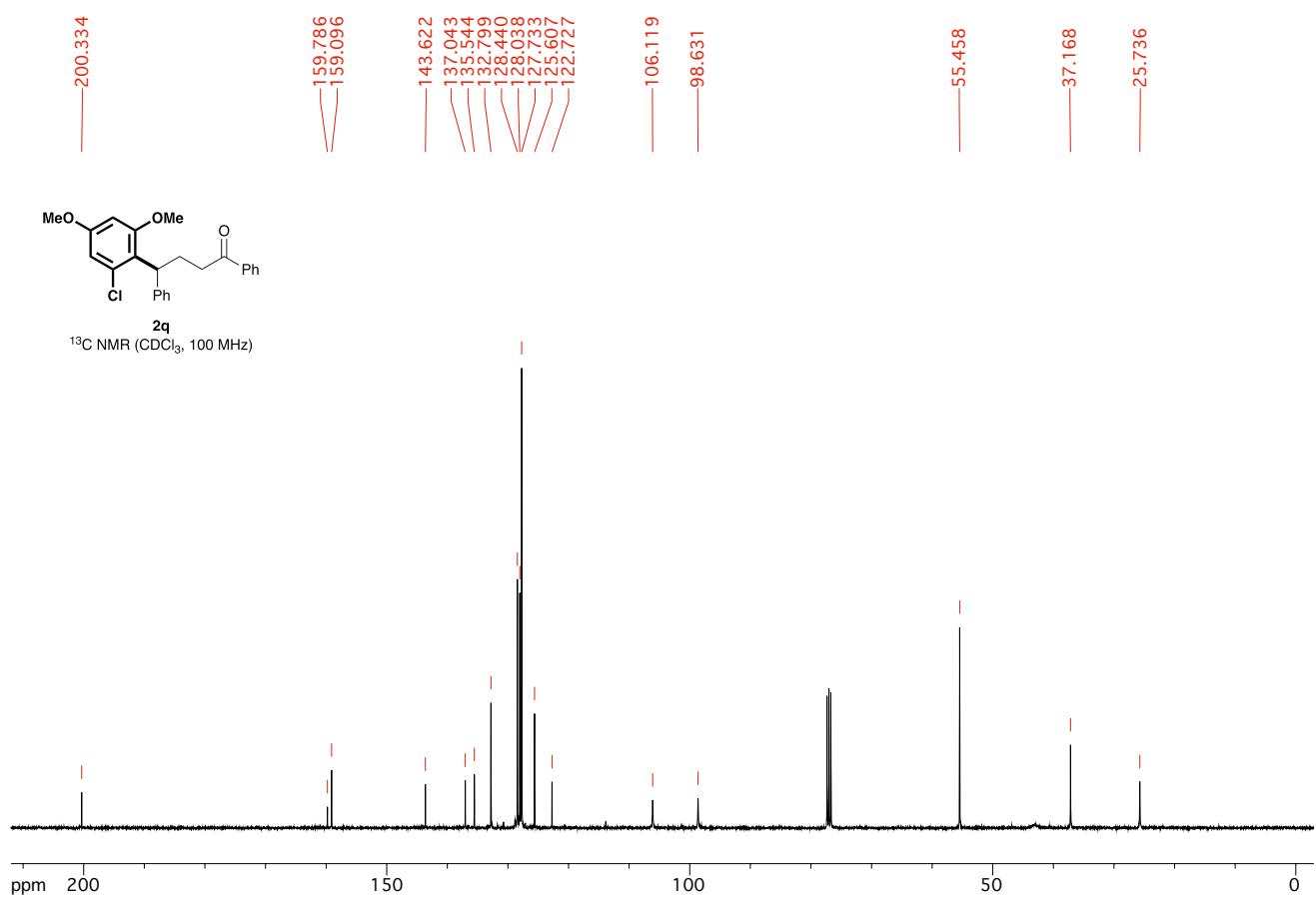
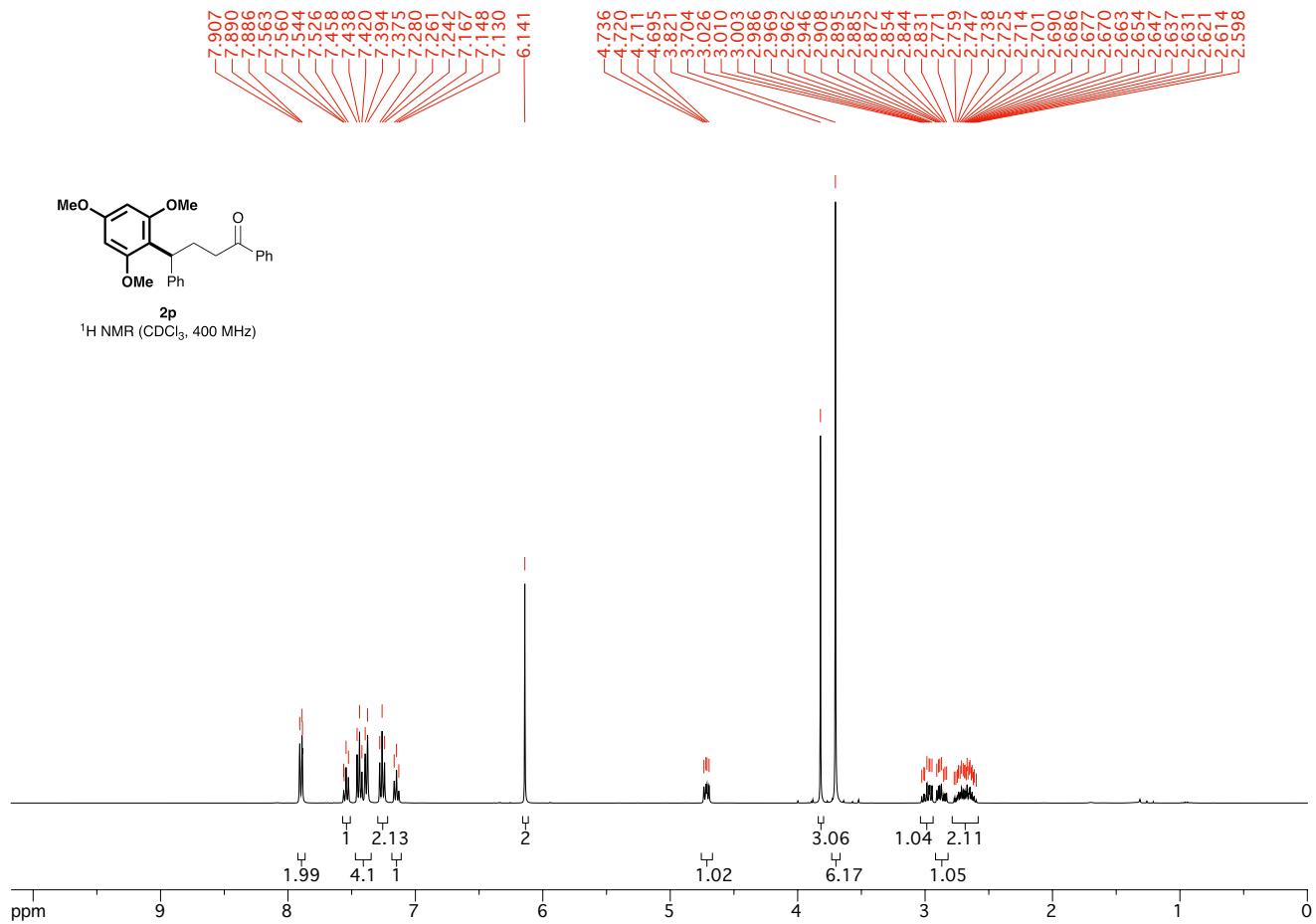
2n
 ^1H NMR (CDCl_3 , 400 MHz)

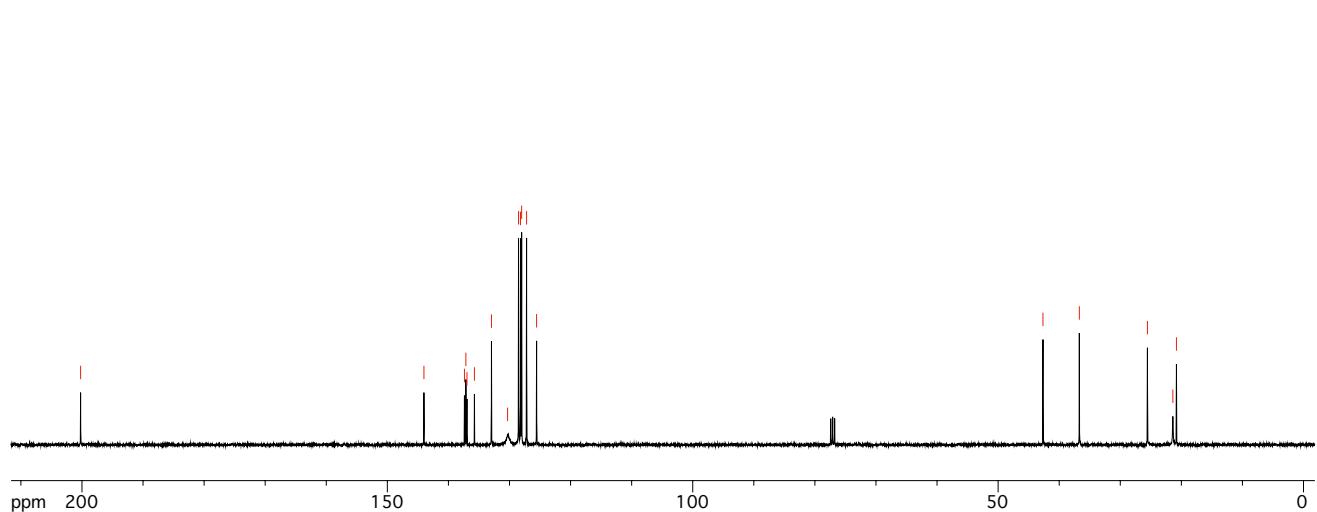
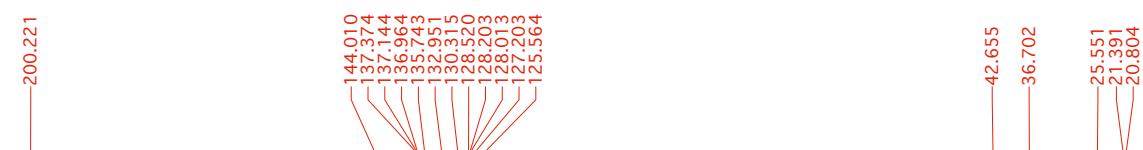
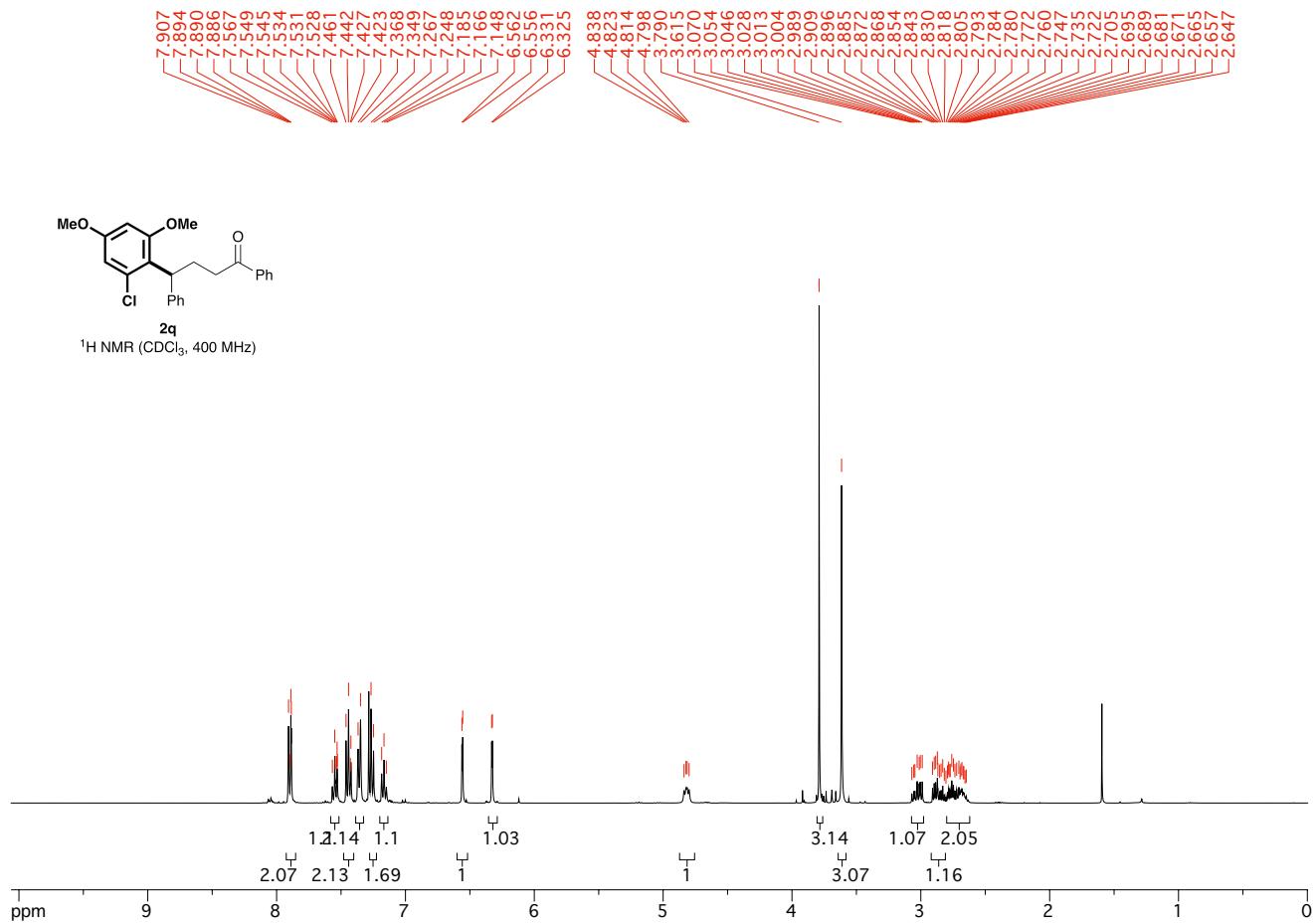


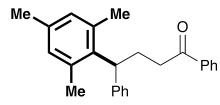
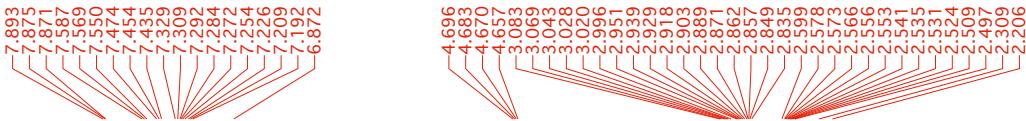
2o
 ^{13}C NMR (CDCl_3 , 100 MHz)



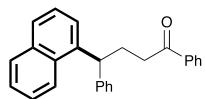
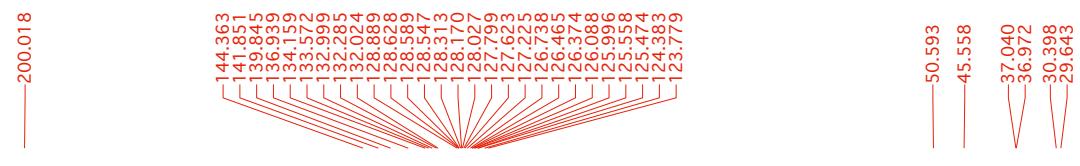
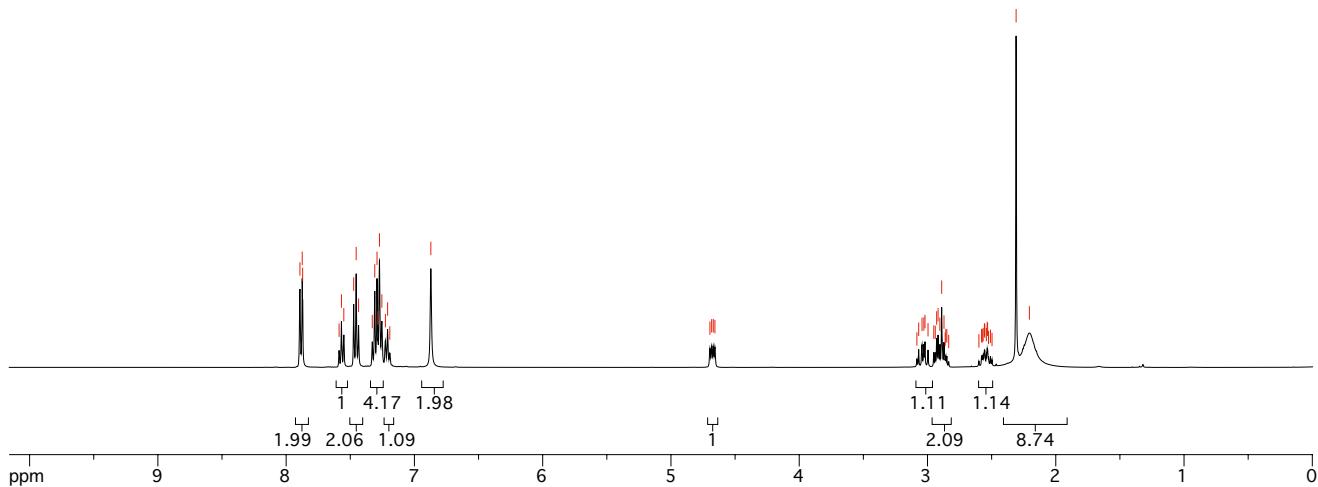




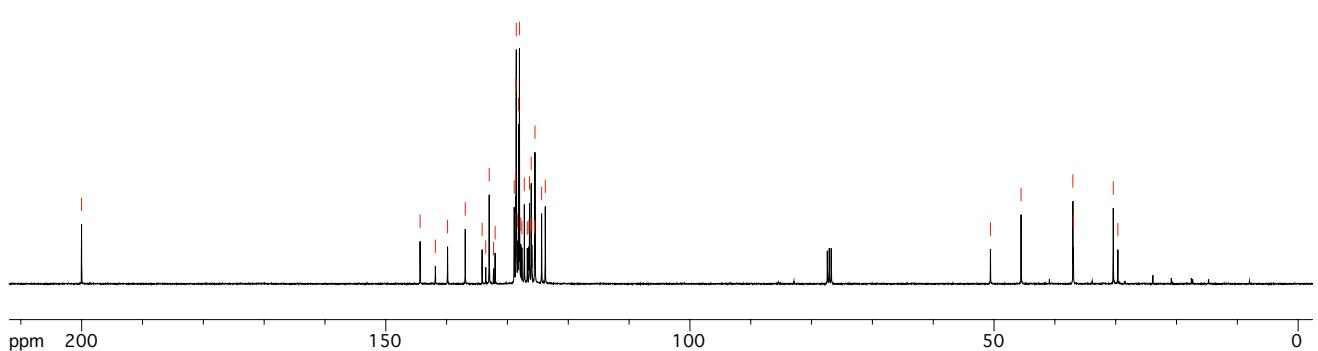


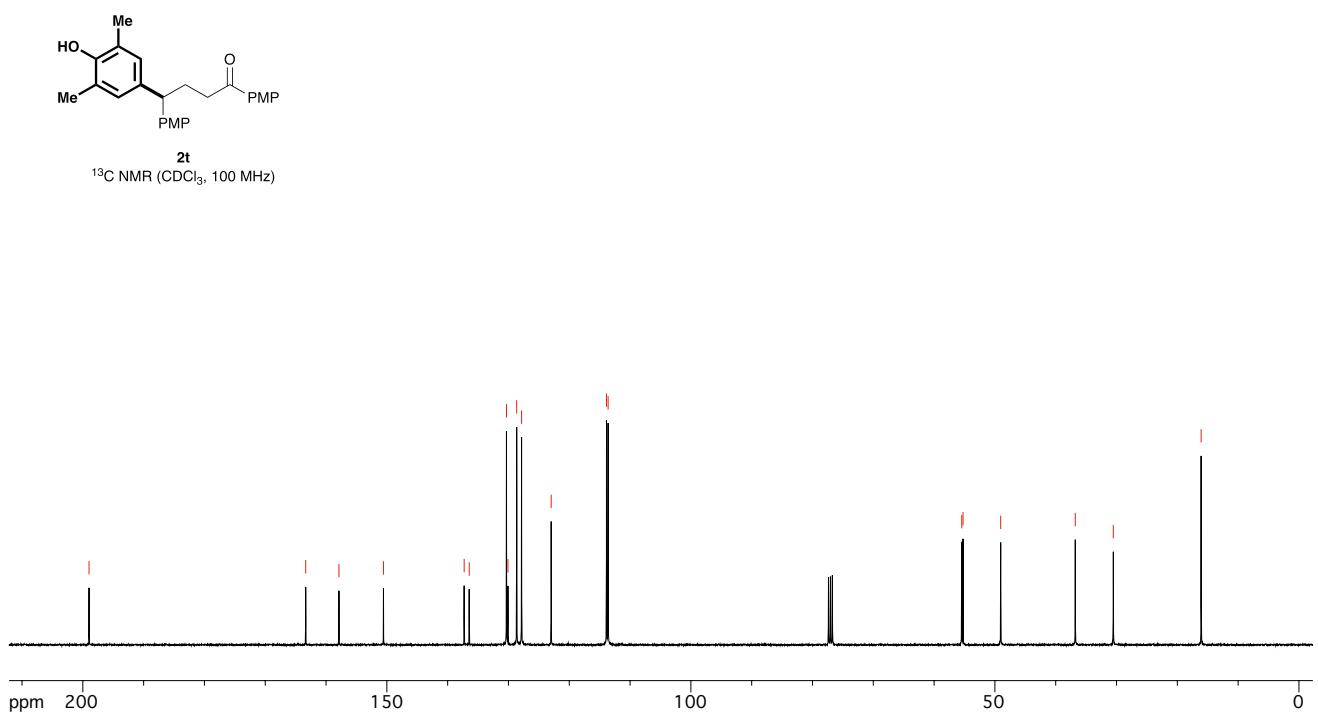
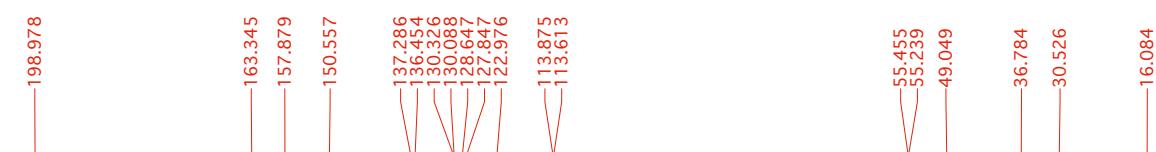
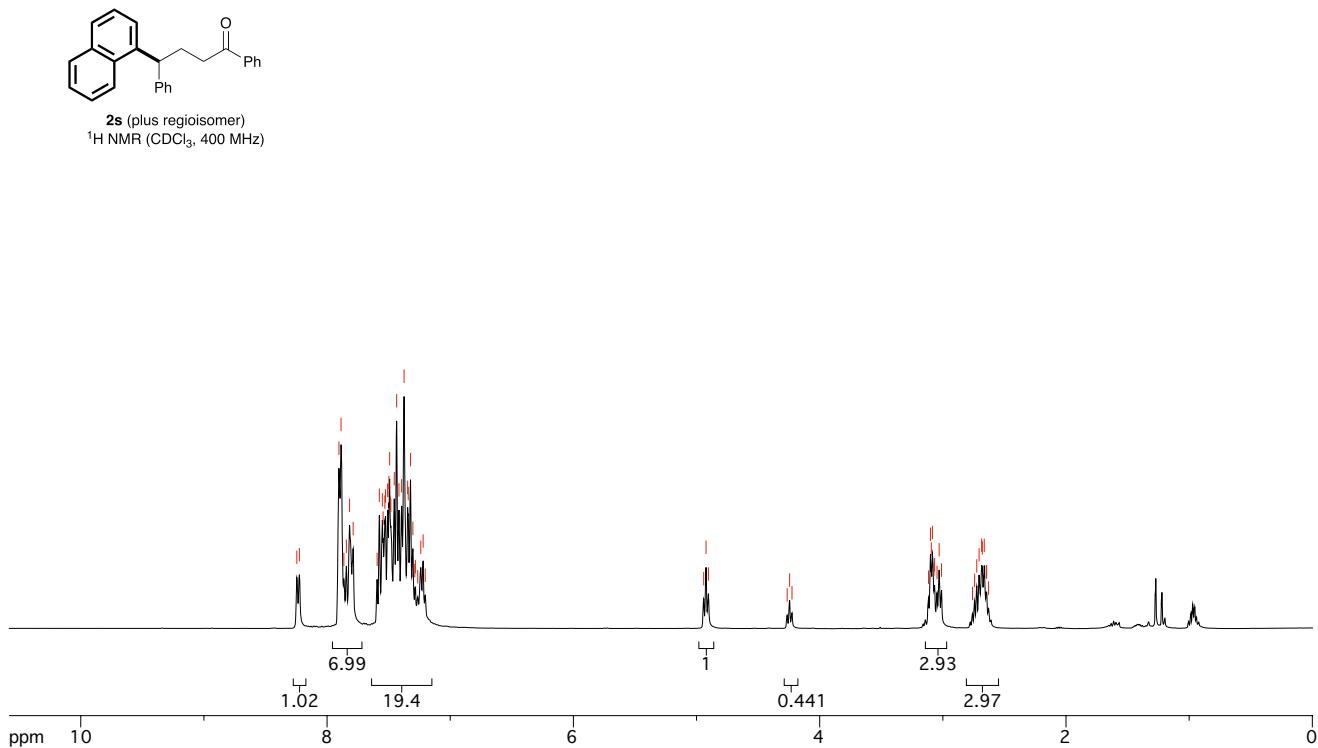
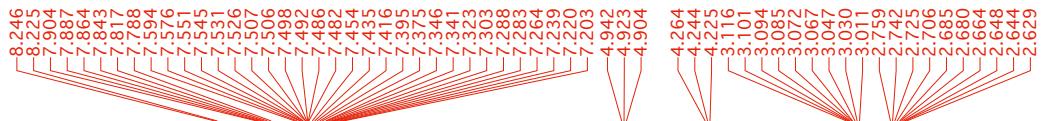


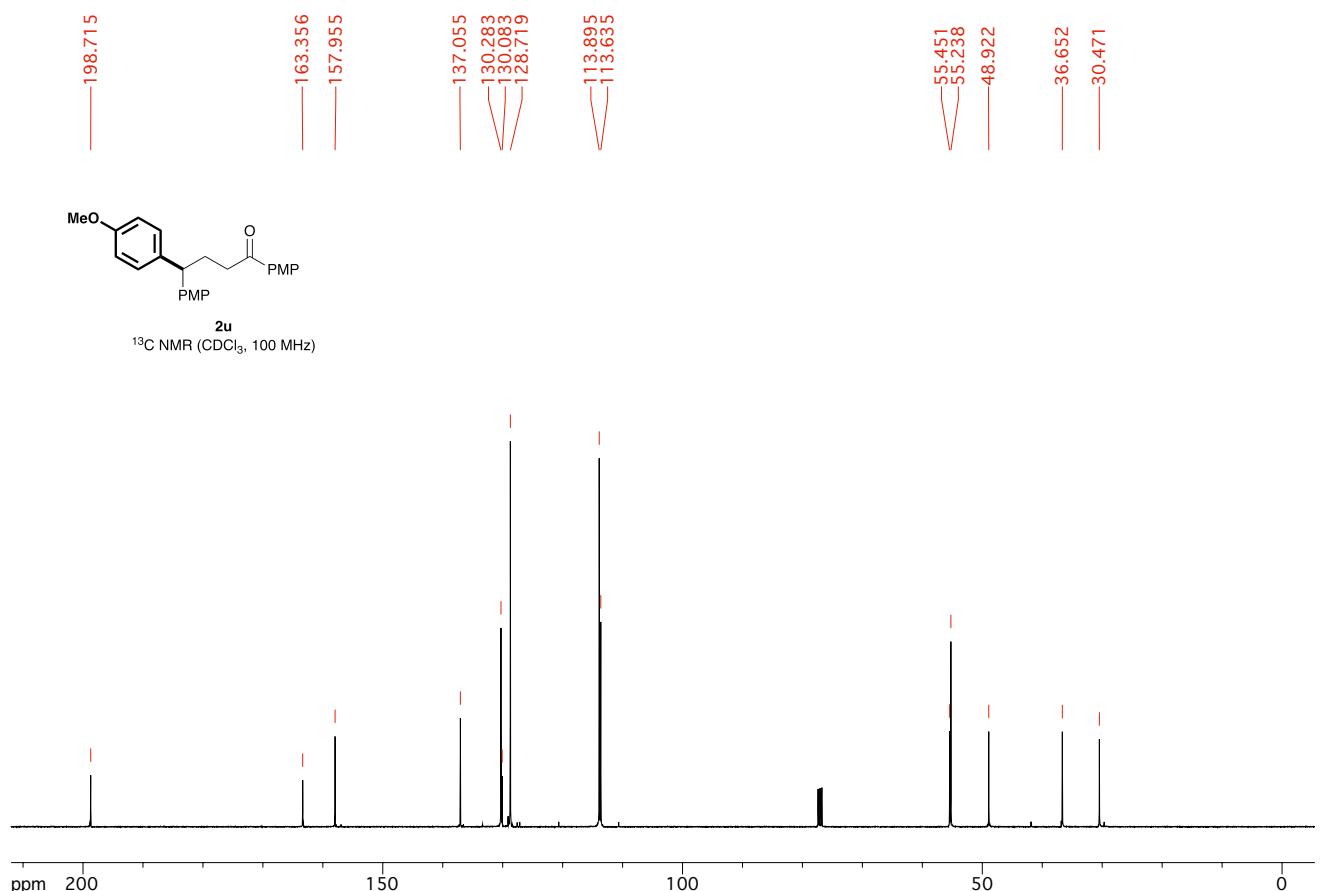
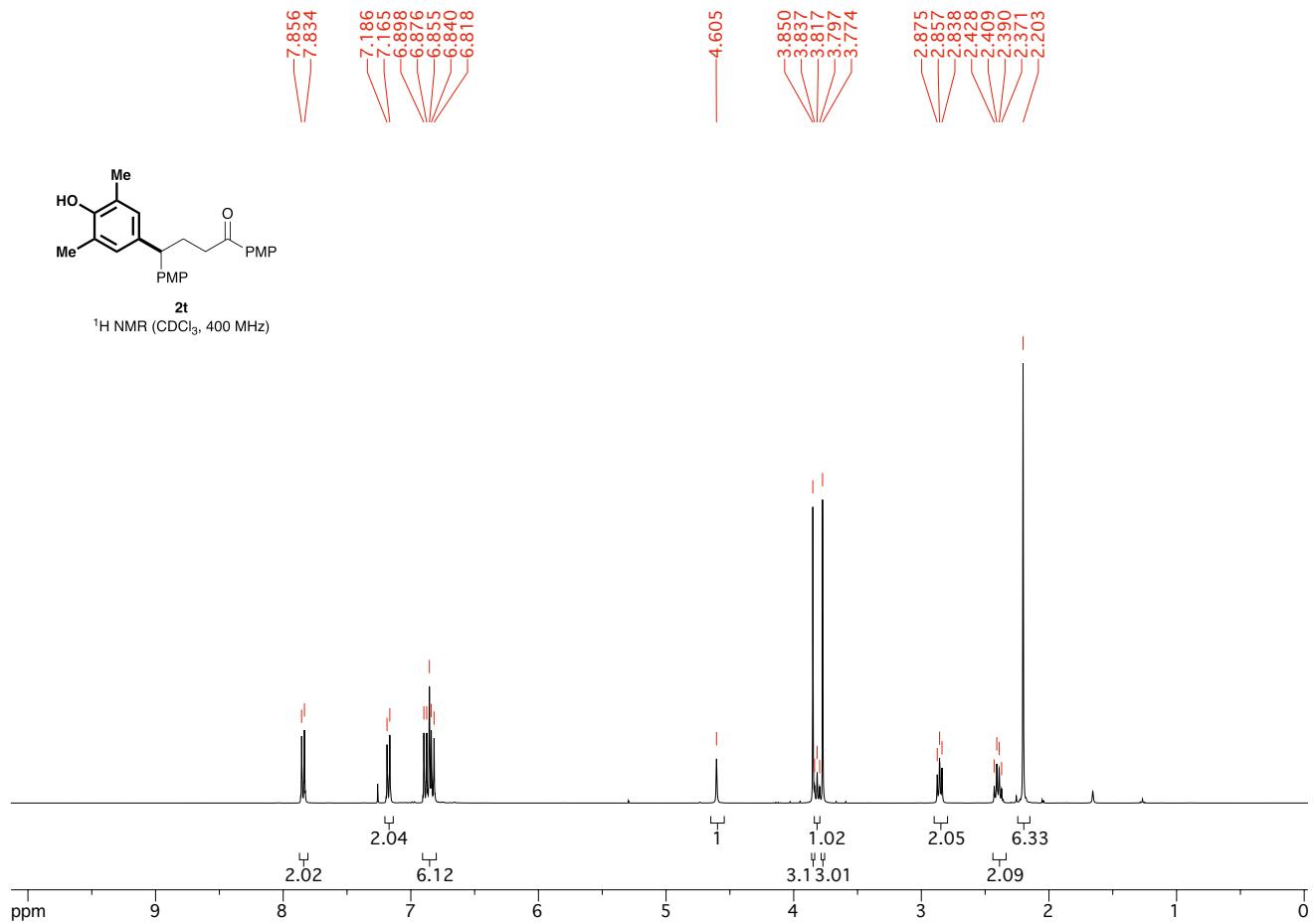
2r
¹H NMR (CDCl₃, 400 MHz)

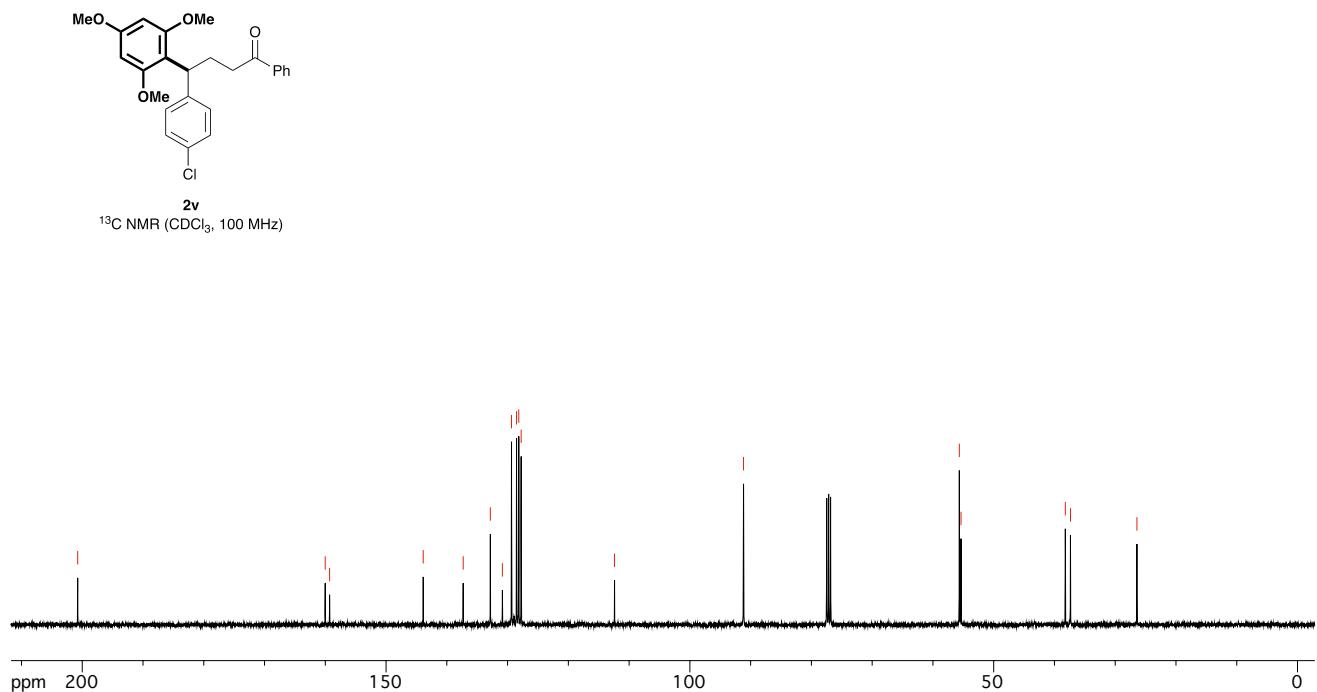
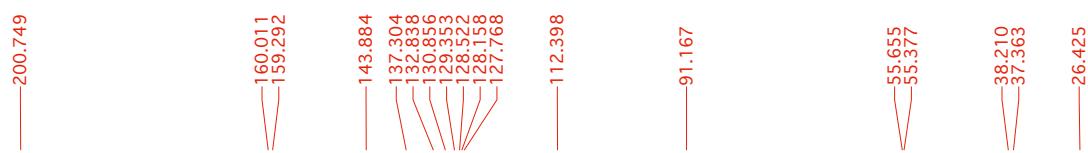
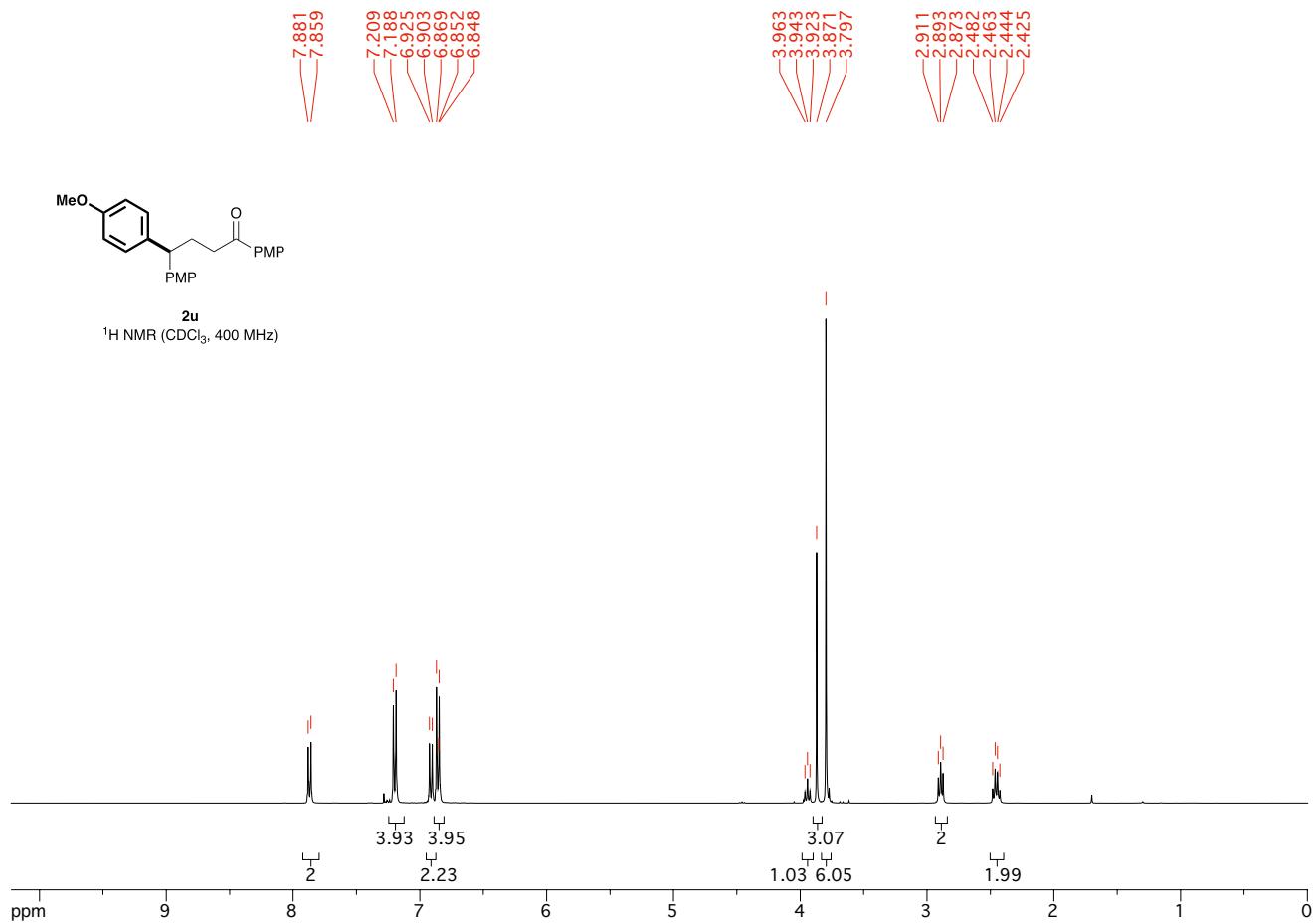


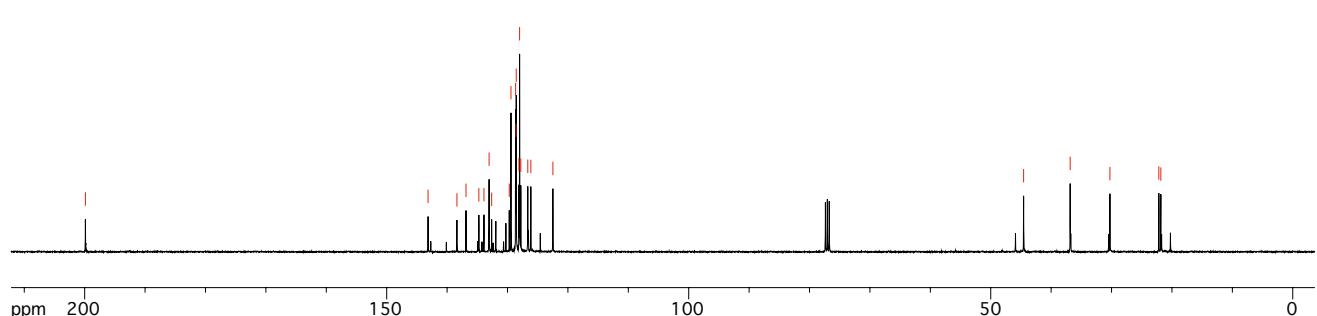
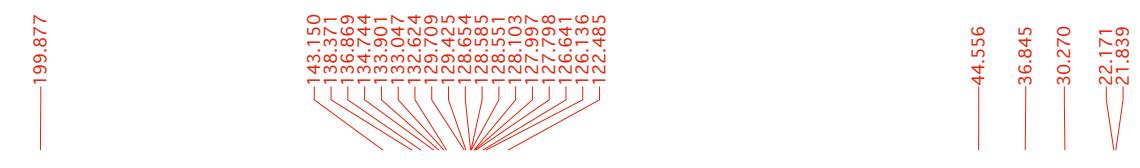
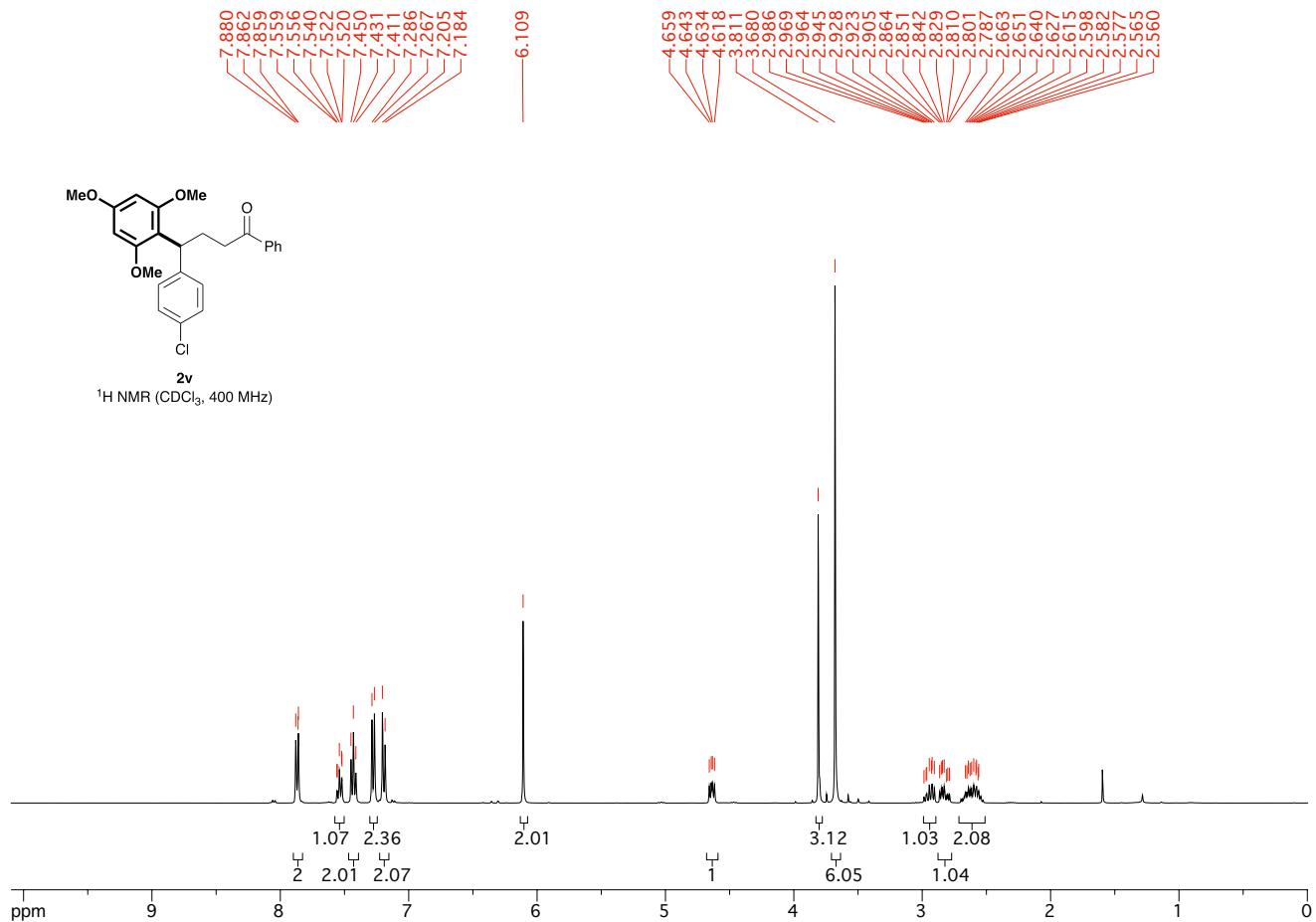
2s (plus regioisomer)
¹³C NMR (CDCl_3 , 100 MHz)

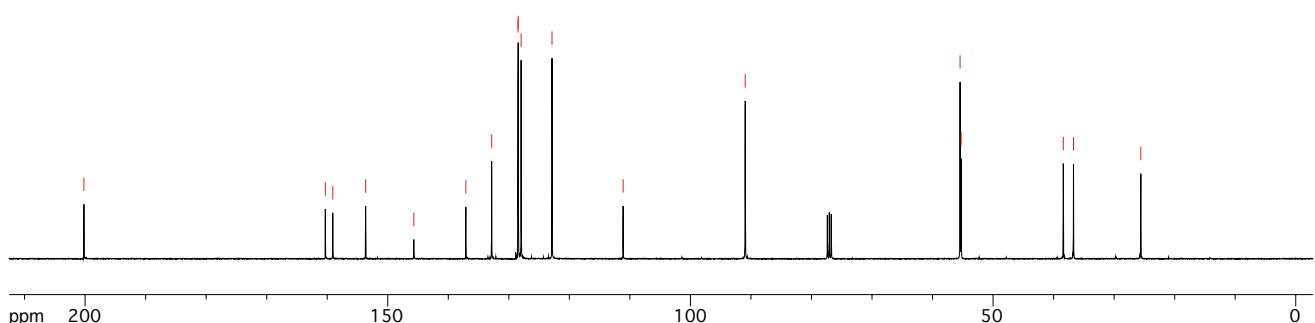
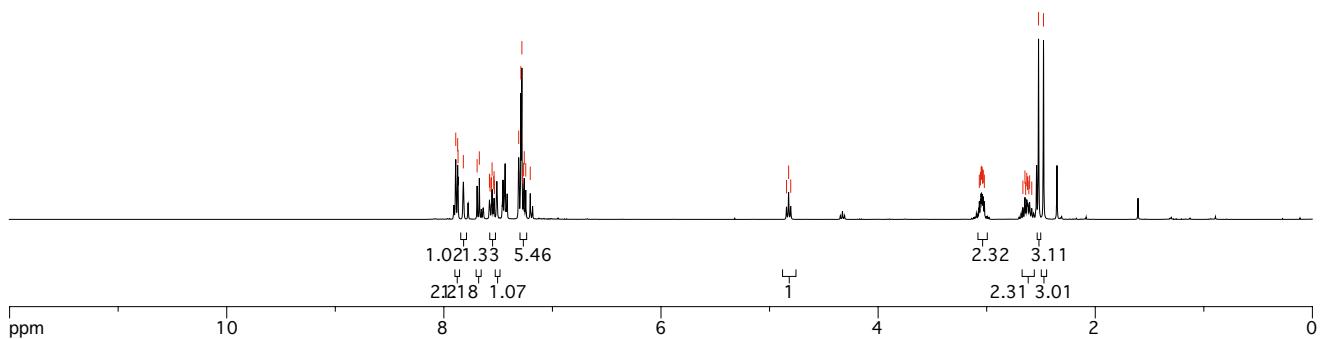
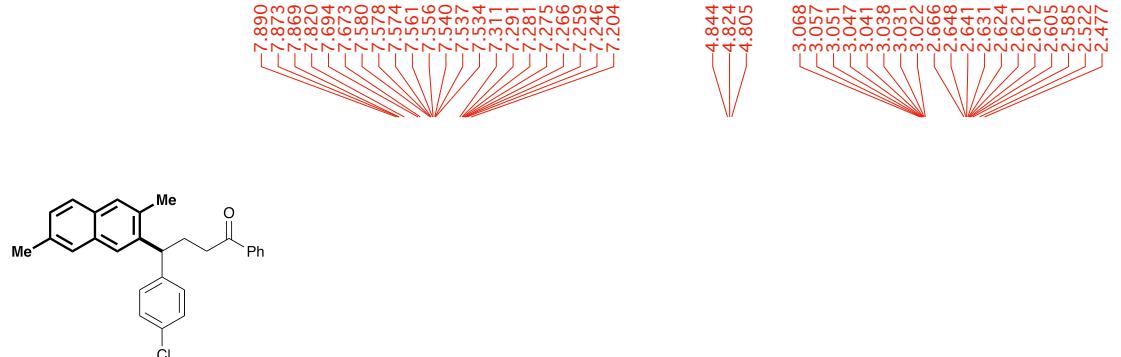


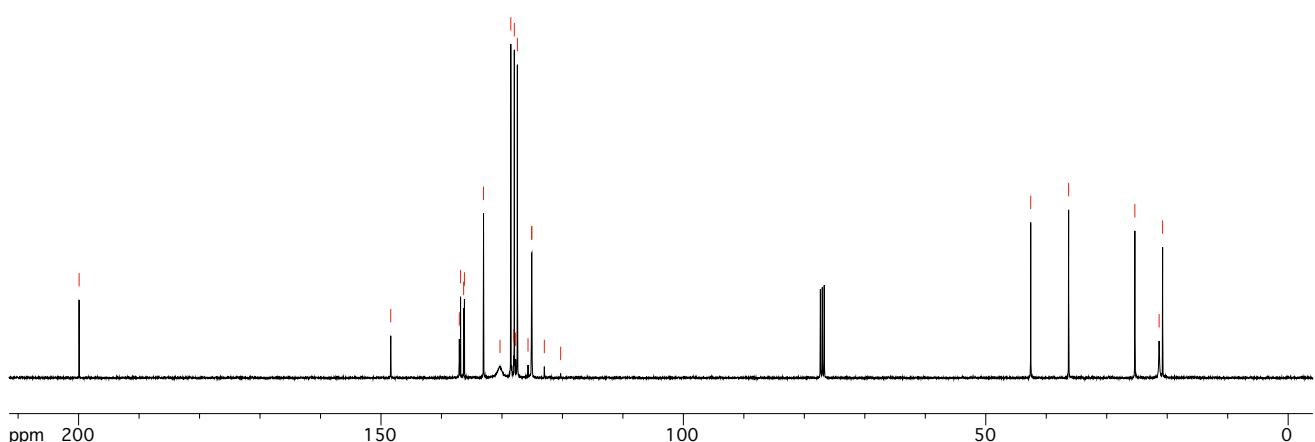
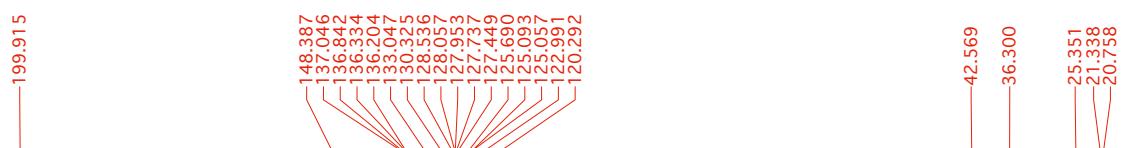
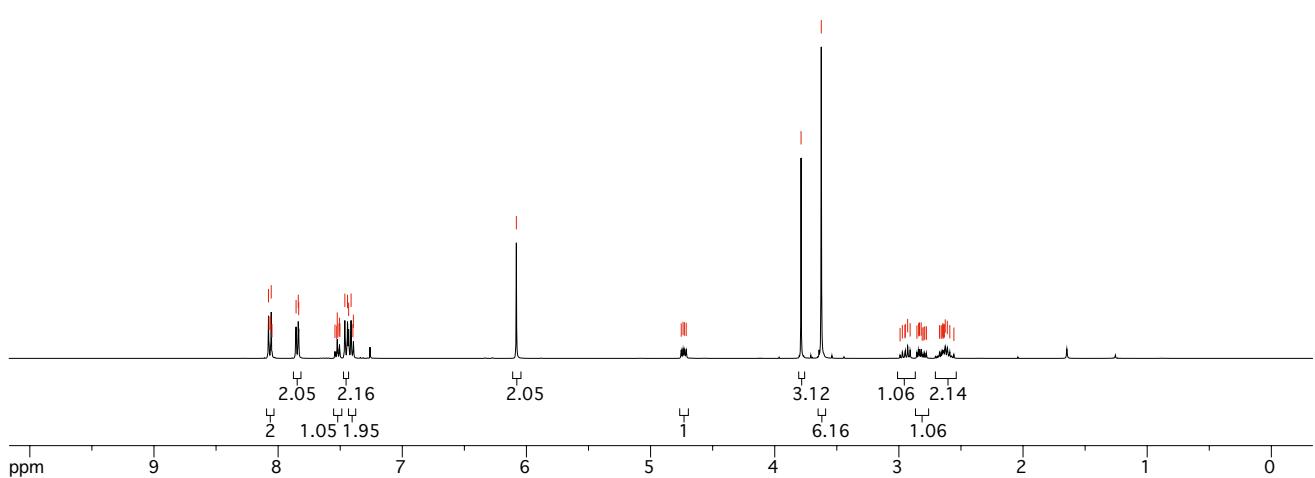
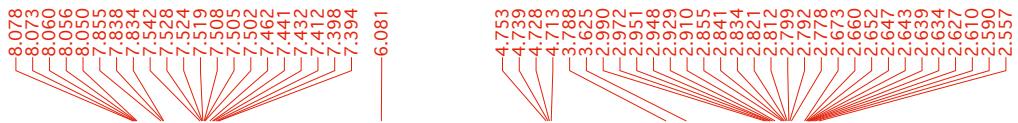


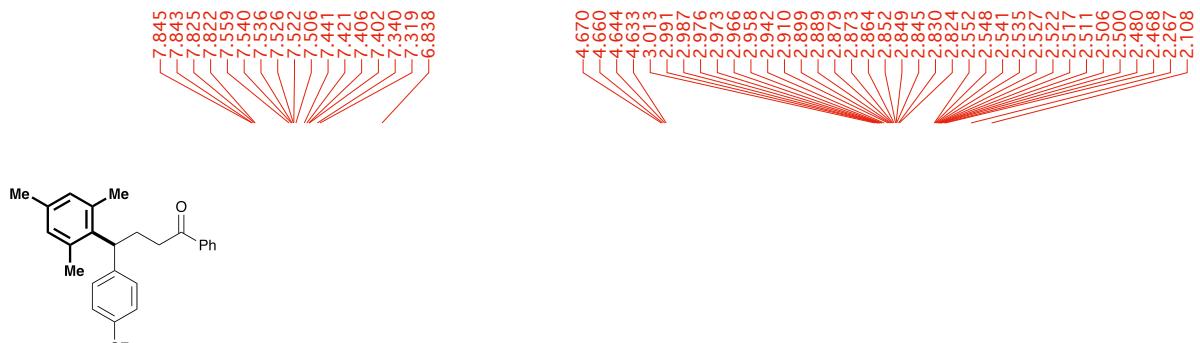




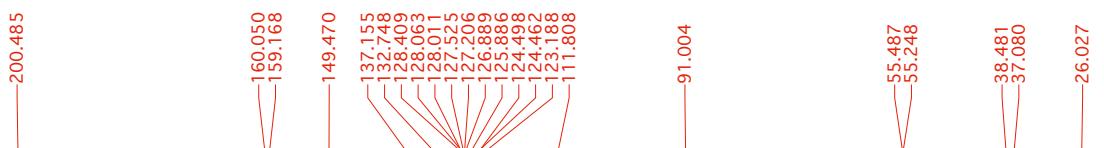
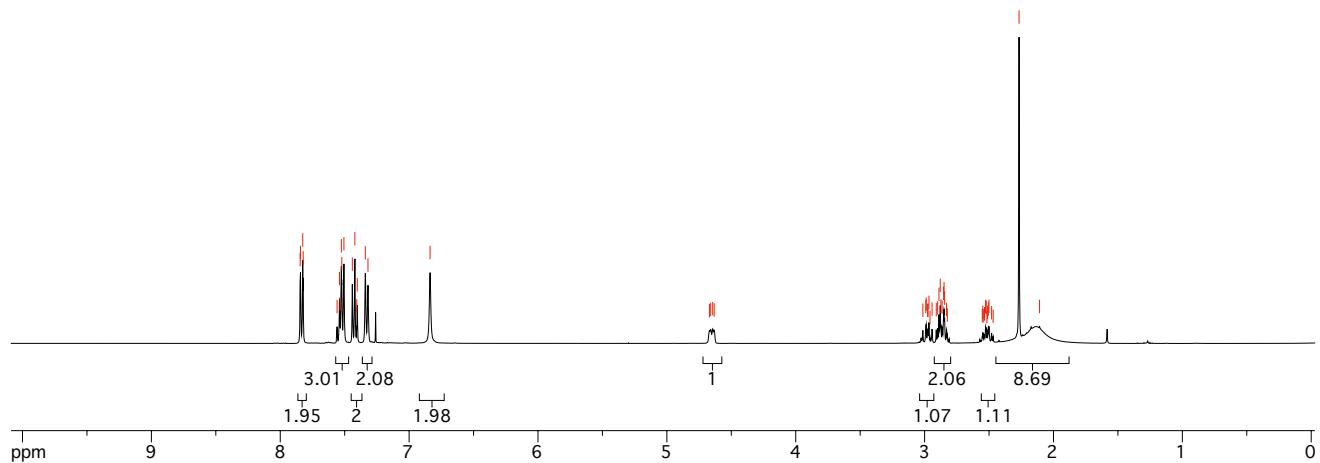








2y
¹H NMR (CDCl_3 , 400 MHz)



2z
¹³C NMR (CDCl_3 , 100 MHz)

