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Supporting Information

Unlocking catalytic potential: a rhodium(II)-based coordination polymer for efficient carbene transfer reactions with donor/acceptor diazoalkanes

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1. General Information

Unless otherwise noted, all commercially available compounds were used as provided without further purification. Chemicals used in this manuscript were purchased from Sigma Aldrich, Alfa Aesar, Chempur, Fluorochem, Activate Scientific and Carl Roth. Solvents used in reactions were p.A. grade. Solvents for chromatography were technical grade and distilled prior to use. Analytical thin-layer chromatography (TLC) was performed on Macherey-Nagel silica gel aluminium plates with F-254 indicator, visualized by irradiation with UV light. Column chromatography was performed using silica gel Merck 60 (particle size 0.063 – 0.2 mm). Solvent mixtures are understood as volume/volume. ^{1}H-NMR, ^{19}F-NMR and ^{13}C-NMR were recorded on a Varian AV600/AV400, an Agilent DD2 400 or a Bruker Avance III 300 MHz NMR spectrometer in $CDCl_3$ or DMSO-d_6 + D_2SO_4. Data are reported in the following order: chemical shift (δ) in ppm; multiplicities are indicated brs (broadened singlet), s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet); coupling constants (*J*) are in Hertz (Hz). HRMS data were recorded on a ThermoFisher Scientific LTQ Orbitrap XL using ESI ionization or on a Finnigan MAT 95 using EI ionization at 70 eV. IR spectra were recorded on a Perkin Elmer-100 spectrometer and are reported in terms of frequency of absorption (cm^{-1}).
Powder X-ray diffraction (PXRD) analysis was conducted at ambient temperature on a Rigaku Miniflex 600 powder diffractometer (Rigaku, Tokyo, Japan) using Cu Kα1 radiation with λ = 1.5406 Å (40 kV, 15 mA, 600 W) and a flat silicon low background with a small indent in the range of 2 θ = 2 °–50 °. Scanning electron microscopy (SEM) images and energy dispersive X-ray (EDX) analysis were recorded on a Jeol JSM-6510LV QSEM electron microscope equipped with a LaB_6 filament and a Bruker XFlash 410-M EDX detector at an acceleration voltage of 20 kV. Prior to the measurement, samples were coated with gold using a Jeol JFC 1200 sputter coater. Fourier-transform infrared (FT-IR) spectra were recorded on a Bruker FT-IR Tensor 37 spectrometer in the attenuated total reflection (ATR) mode in the range of 4000–550 cm^{-1}. Thermogravimetric analyses (TGA) were performed on a Netzsch Tarsus TG 209 under synthetic air (20.5 ± 0.5% O_2 in N_2) from room temperature to 1000 °C with a heating rate of 5 °C min^{-1} in Al_2O_3-crucibles. Optical measurements were carried out on a FLS1000 photoluminescence spectrometer (Edinburgh Instruments) equipped with a 450 W Xe arc lamp, double grating monochromators (Czerny-Turner) in excitation and emission compartment and a thermoelectrically cooled PMT-980 detector (Hamamatsu). The diffuse reflectance was measured with an integrating sphere (Ulbricht sphere) lined on the inside with BenFlect and exhibiting R > 99% between 350 nm and 2500 nm.

2. Important Safety Note

Handling of diazo compounds should only be done in a well-ventilated fume cupboard using an additional blast shield. No incidents occurred handling of diazoalkanes during the preparation of this manuscript, yet the reader should be aware of carcinogenicity and explosiveness of the herein described diazo compounds. General safety precautions when working with diazomethane and its derivatives should be followed. Any reactions described in this manuscript should not be performed without strict risk assessment and proper safety precautions.

3. Catalyst Synthesis

Synthesis of $Rh_2(OAc)_4$[1]

The amount of 500 mg (1.06 mmol) of rhodium trichloride hydrate and 1 g (7.35 mmol) of sodium acetate trihydrate in a 1 : 1 mixture of glacial acetic acid and absolute ethanol (20 mL) were refluxed under nitrogen atmosphere for one hour to form a green solid. After cooling to room temperature, the green solid was collected by filtration and dissolved in boiling methanol (ca. 50 mL). The solution was filtered, concentrated to 20 mL and placed in a refrigerator overnight. The crystals formed were filtered off and dried in vacuum at 60 °C for 20 h to obtain 188 mg (71%) of green crystals.

Synthesis of Rh-CP[2]

In a 250 mL round bottom flask, $Rh_2(OAc)_4$ (150 mg, 0.34 mmol) and terephthalic acid (173 mg, 1.04 mmol) were dissolved in 150 mL of chlorobenzene. The flask was connected with a Soxhlet extractor. To remove the acetic acid, a cellulose filter tube with 3 g K_2CO_3 and 3 g activated molecular sieve (4 Å) was added to the Soxhlet extractor. The reaction was heated to 150 °C and extracted for 3 days. After 3 days of reaction, the obtained solid was filtered and washed for 5 days in a Soxhlet extractor with 100 mL of chlorobenzene. The product was dried at 80 °C under vacuum for 1 day. The product is a green powder. Yield 178 mg, 97% based on $Rh_2(OAc)_4$.

4. Powder XRD

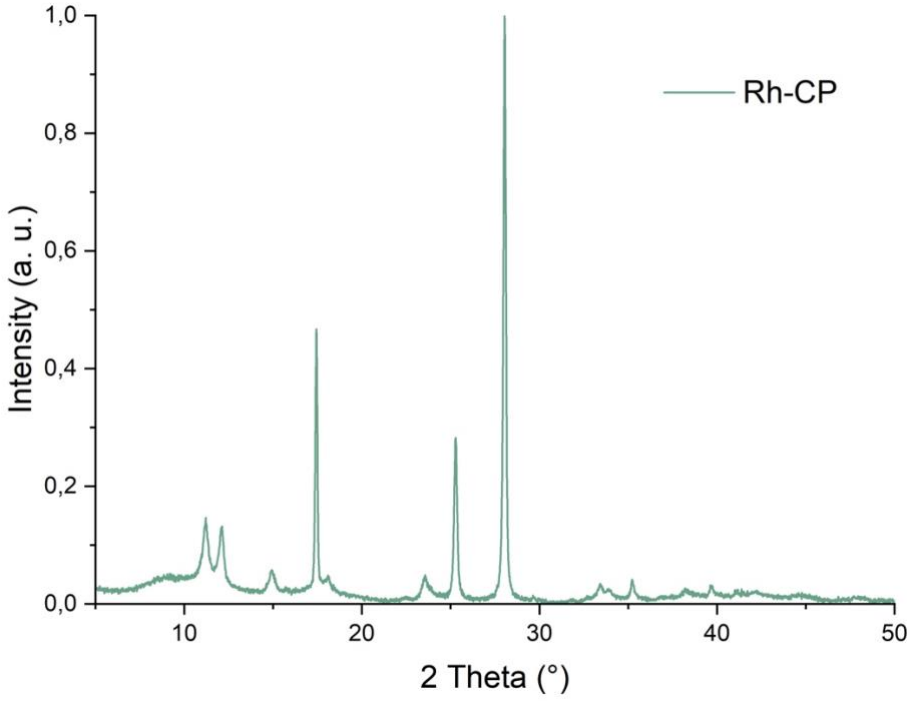


Fig. S1: PXRD of $Rh_2(OAc)_4$.

5. TGA Analysis

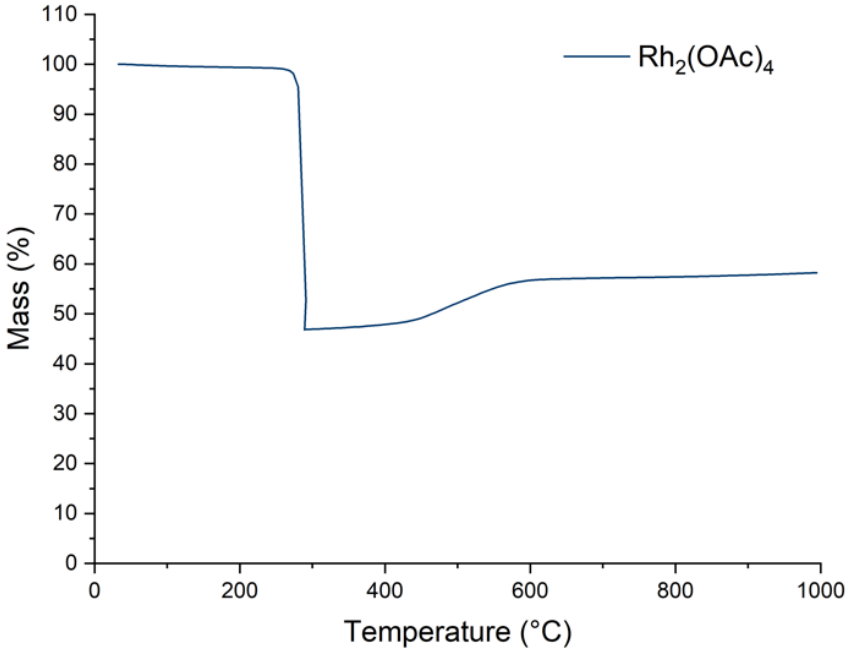


Fig. S2: TGA of $Rh_2(OAc)_4$ in the range of 20 to 1000 °C with a heating rate of 5 K min^{-1}.

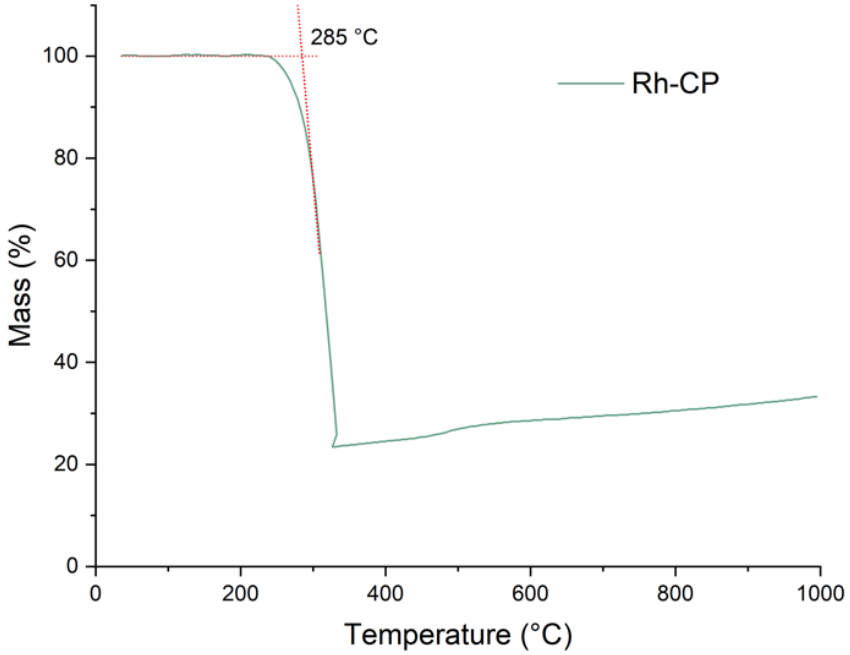


Fig. S3:TGA of Rh-CP in the range of 20 to 1000 °C with a heating rate of 5 K min^{-1}.

6. ATR-IR

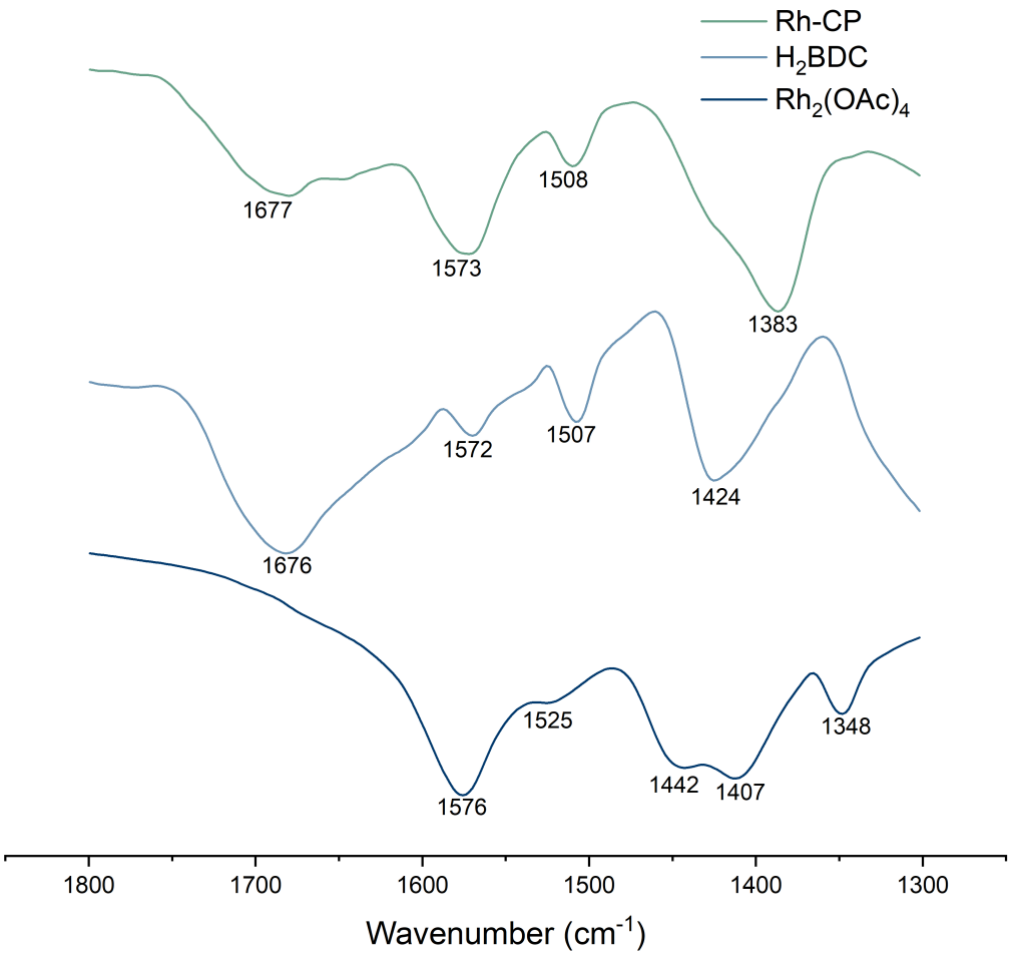


Fig. S4: ATR-IR of the synthesized Rh-CP, the pure linker H_2BDC, and the starting complex $Rh_2(OAc)_4$.

7. SEM

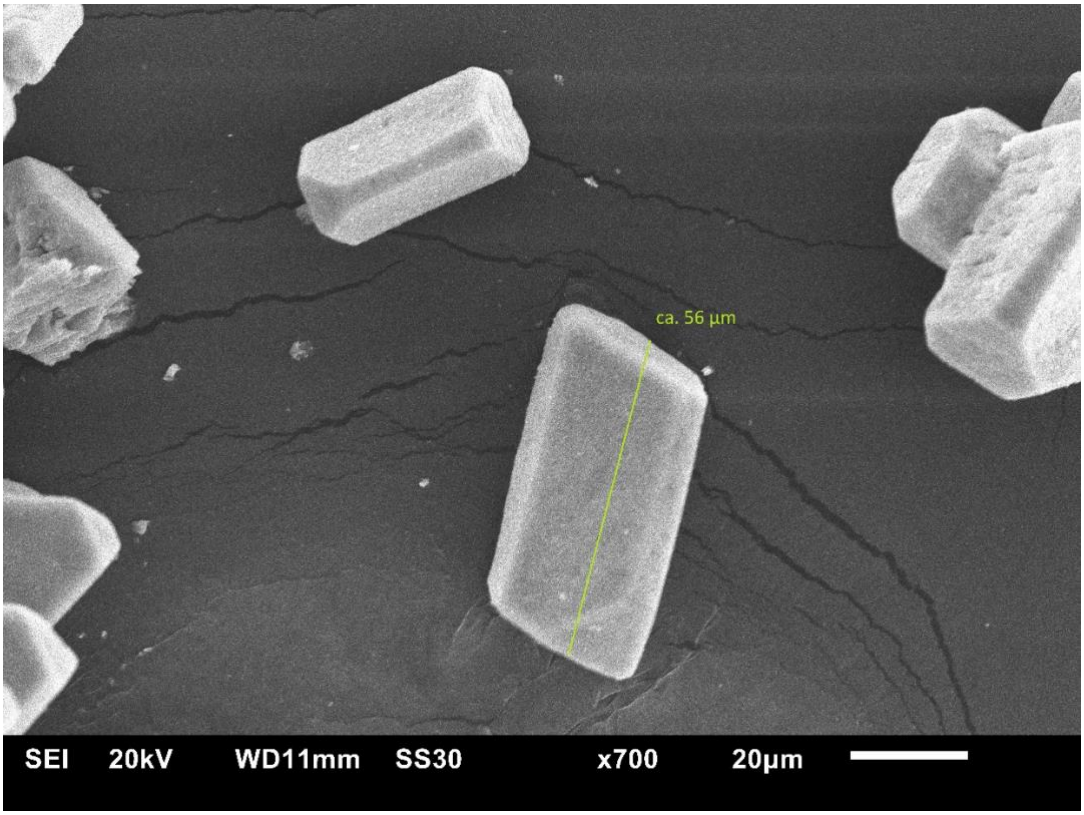


Fig. S5: SEM image of $Rh_2(OAc)_4$ crystal.

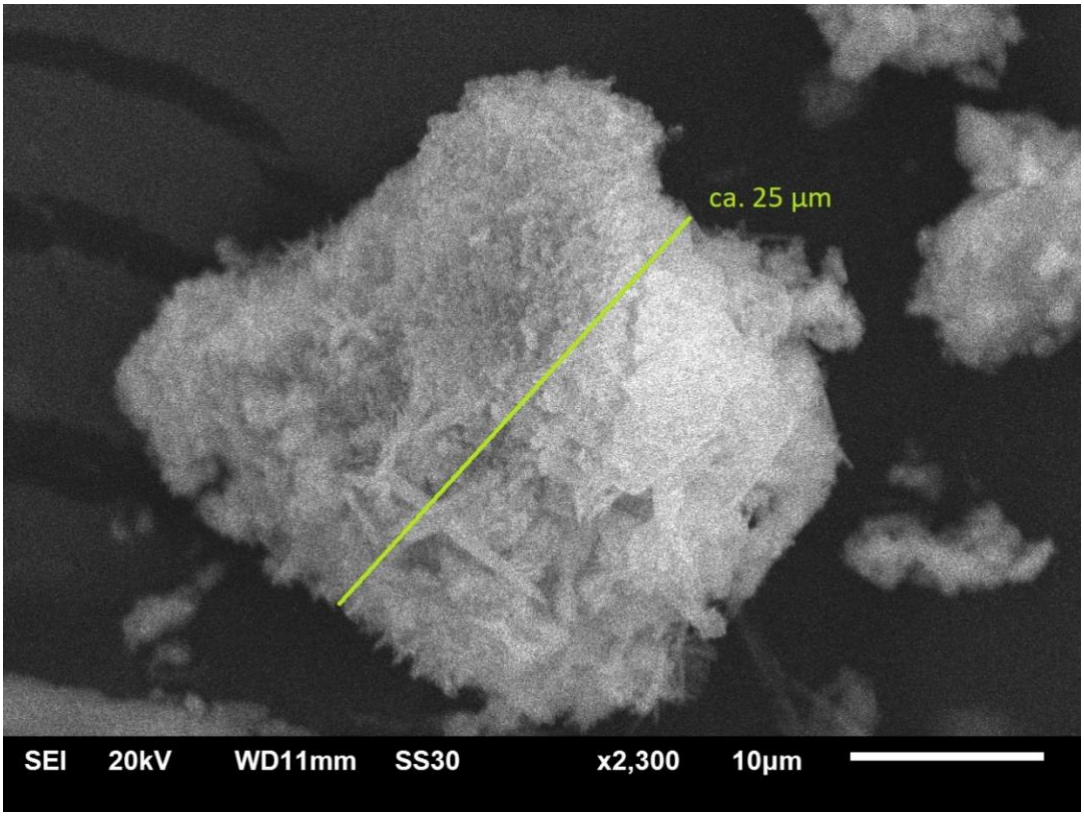


Fig. S6: SEM image of Rh-CP agglomerate.

8. Digestion NMR

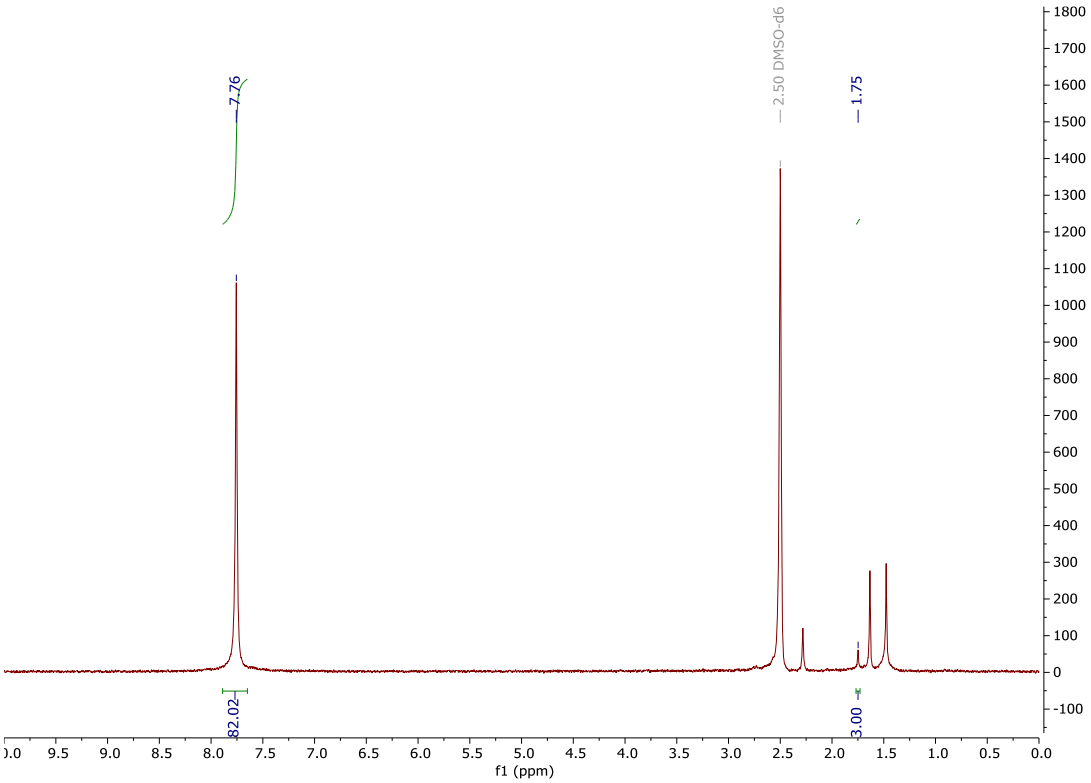


Fig. S7: ^{1}H NMR (300 MHz) of digested Rh-CP in DMSO-d_6 and D_2SO_4 to determine the linker, acetate ratio.

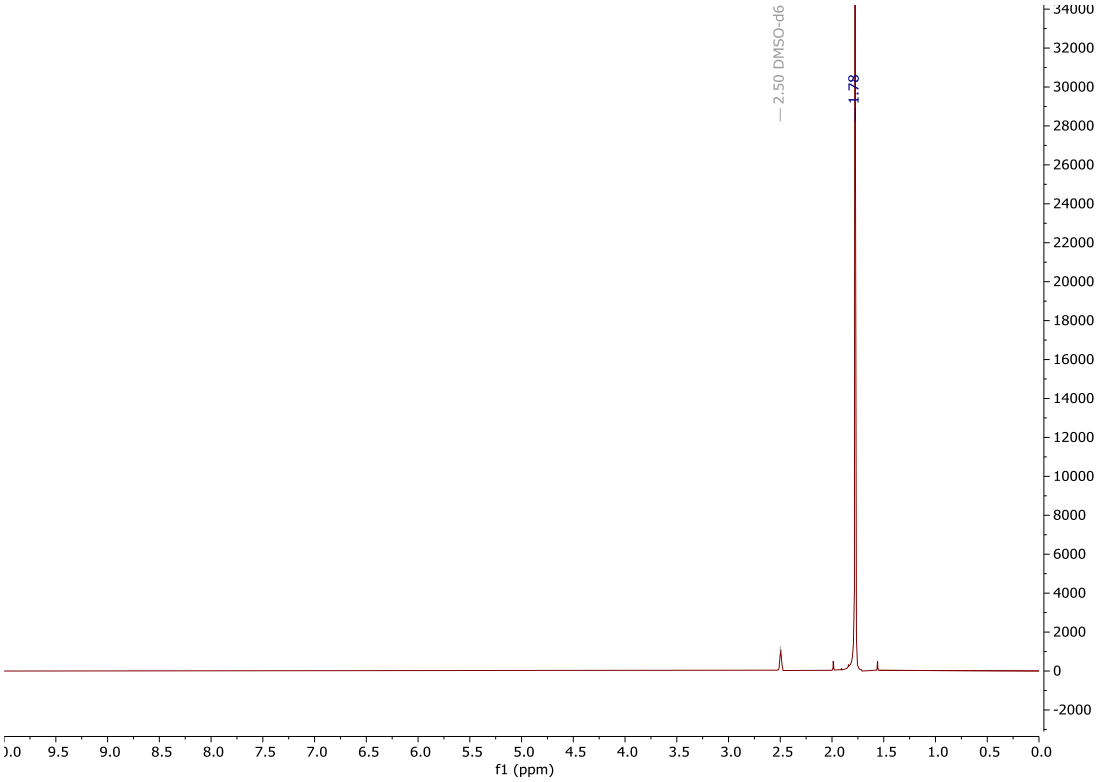


Fig. S8: ^{1}H NMR (300 MHz) of acetic acid as reference for determining the acetic acid chemical shift in DMSO-d_6 and D_2SO_4.

9. Scale Up Experiments

In an oven dried reaction flask Rh-CP or $Rh_2(OAc)_4$ was added. Then the flask was closed with septum and evacuated and backfilled with argon for three times. Then styrene (1.1 equiv., 11.0 mmol) and 10 mL dry, degassed DCM were added. The corresponding diazoalkane **6** (1.0 equiv., 10.0 mmol) was dissolved in a separate reaction test tube in 10 mL of dry and degassed DCM was added to the reaction tube via syringe over 2 h (or 10 h). After the completion of the addition of the diazoalkane, the reaction mixture was stirred until the orange color of the diazoalkane disappeared. The product **7** was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate) to afford the desired pure product.

Rh-CP (0.5 mg)	92%	2.31 g	9.16 mmol
Rh-CP (0.236 mg)	91%	2.29 g	9.08 mmol
$Rh_2(OAc)_4$ (0.25 mg)	94%	2.43 g	9.63 mmol

10. Kinetic Studies

In an oven dried reaction flask Rh-CP (10.0 mg) was added. Then the flask was closed with septum and evacuated and backfilled with argon for three times. Then styrene (1.1 equiv., 2.2 mmol) and 10 mL dry, degassed DCM were added. The corresponding diazoalkane **6** (1.0 equiv., 2.0 mmol) was dissolved in a separate reaction test tube in 10 mL of dry and degassed DCM was added to the reaction tube via syringe in one portion. Then aliquots (0.5 mL each) were taken and quickly filtered through a pluck of silica to remove the Rh-CP. The solvent was removed under reduced pressure and the yield of **7** was determined by ^{1}H NMR spectroscopy using mesitylene as the internal standard. **6** indicates the remaining diazoalkane in the solution.

Table S1: Kinetic studies.

time	0	15 s	30 s	60 s	105 s	180 s	270 s	360 s	480 s	600 s	900s
Yield **7** [%]	0	2	8	21	44	80	88	90	92	94	95
6 [%]	100	91	82	67	41	13	0	0	0	0	0

11. Catalyst Recycling Studies

In an oven dried reaction tube Rh-CP (2.0 mg) was added. Then the tube was closed with septum and evacuated and backfilled with argon for three times. Then styrene (1.1 equiv., 0.22 mmol) and 1 mL dry, degassed DCM were added. The corresponding diazoalkane (1.0 equiv., 0.2 mmol) was dissolved in a separate reaction test tube in 1 mL of dry and degassed DCM was added to the reaction tube via syringe over 1 h. After the completion of the addition of the diazoalkane, the reaction mixture was stirred until the orange color of the diazoalkane disappeared. The catalyst was removed by centrifuge and the clear solution on top of the catalyst was transferred into a reaction flask. The solvent was removed under reduced pressure and the yield was determined by ^{1}H NMR spectroscopy using mesitylene as the internal standard. The remaining catalyst was transferred into a new reaction tube and weight after complete removal of solvent. Then the recycled catalyst was used in the next reaction step.

Table S2: Catalyst recycling studies.

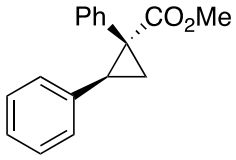
Cycle	1	2	3	4	5	6
Yield **7** [%]	99	92	86	96	98	76
Recovered catalyst [mg]	2.0	1.9	1.7	1.5	1.2	0.6

12. General Procedure (GP-1) Rh-CP catalyzed reactions

In an oven dried reaction tube Rh-CP (1 mg) and the corresponding nucleophile (1.1 equiv., 0.22 mmol, if solid) were added. Then the tube was closed with septum and evacuated and backfilled with argon for three times. Then the corresponding nucleophile (1.1 equiv., 0.22 mmol, if liquid) and 1 mL dry, degassed DCM were added. The corresponding diazoalkane (1.0 equiv., 0.2 mmol) was dissolved in a separate reaction test tube in 1 mL of dry and degassed DCM was added to the reaction tube via syringe over 1 h. After the completion of the addition of the diazoalkane, the reaction mixture was stirred until the orange color of the diazoalkane disappeared. The product was purified by column chromatography on silica gel (*n*-hexane : ethyl acetate) to afford the desired pure product.

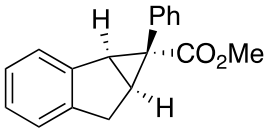
13. Physical Data

Methyl-1,2-diphenylcyclopropane-1-carboxylate (7)



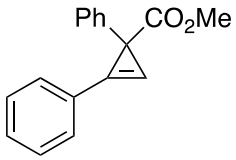
The title compound **7** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless solid (96%, 40.5 mg).
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.21 – 7.08 (m, 3H), 7.08 – 7.00 (m, 5H), 6.81 – 6.72 (m, 2H), 3.67 (s, 3H), 3.18 – 3.05 (m, 1H), 2.14 (ddd, *J* = 9.3, 4.9, 0.7 Hz, 1H), 1.93 – 1.83 (m, 1H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 174.3, 136.3, 134.7, 131.9, 128.0, 127.68, 127.66, 127.0, 126.2, 52.6, 37.3, 33.1, 20.4 ppm.
The data is in accordance with the literature.[3]

Methyl -1-phenyl-1,1a,6,6a-tetrahydrocyclopropa[*a*]indene-1-carboxylate (8)



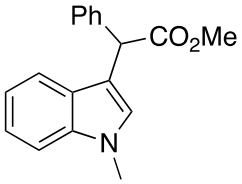
The title compound **8** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless solid (91%, 39.9 mg).
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.40 (d, *J* = 7.5 Hz, 1H), 7.13 – 7.01 (m, 5H), 6.96 – 6.85 (m, 3H), 6.74 – 6.68 (m, 1H), 3.63 (s, 3H), 3.50 – 3.42 (m, 1H), 3.27 – 3.17 (m, 1H), 2.86 (td, *J* = 6.8, 0.7 Hz, 1H), 2.75 (d, *J* = 17.9 Hz, 1H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 174.0, 142.9, 141.4, 132.2, 127.3, 126.5, 126.3, 126.1, 125.0, 124.1, 52.5, 40.7, 38.2, 33.2, 32.0 ppm.
The data is in accordance with the literature.[3]

Methyl 1,2-diphenylcycloprop-2-ene-1-carboxylate (9)



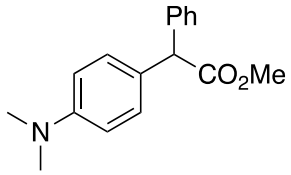
The title compound **9** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless solid (82%, 41.1 mg).
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.67 – 7.60 (m, 2H), 7.51 – 7.34 (m, 5H), 7.35 – 7.26 (m, 2H), 7.24 – 7.20 (m, 2H), 3.72 (s, 3H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 175.0, 140.8, 130.0, 129.9, 128.8, 128.2, 128.0, 126.5, 125.4, 117.3, 100.3, 52.2, 33.5 ppm.
The data is in accordance with the literature.[4]

Methyl 2-(1-methyl-1*H*-indol-3-yl)-2-phenylacetate (10)



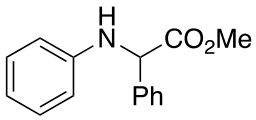
The title compound **10** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (74%, 50.1 mg).
^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.59 – 7.41 (m, 3H), 7.41 – 7.19 (m, 5H), 7.14 – 6.99 (m, 2H), 5.29 (s, 1H), 3.78 (s, 3H), 3.78 (s, 3H) ppm.
^{13}C NMR (101 MHz, Chloroform-*d*): δ = 173.5, 138.7, 137.0, 128.5, 128.4, 127.8, 127.2, 127.0, 121.8, 119.2, 119.0, 112.0, 109.3, 52.3, 48.8, 32.8 ppm.
The data is in accordance with the literature.[3]

Methyl 2-(4-(dimethylamino)phenyl)-2-phenylacetate (11)



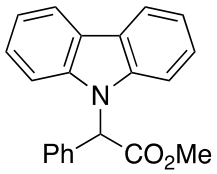
The title compound **11** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (75%, 40.1 mg).
^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.30 (d, *J* = 4.3 Hz, 4H), 7.27 – 7.19 (m, 1H), 7.17 (d, *J* = 8.7 Hz, 2H), 6.77 – 6.63 (m, 2H), 4.94 (s, 1H), 3.72 (s, 3H), 2.91 (s, 6H) ppm
^{13}C NMR (101 MHz, Chloroform-*d*): δ = 173.5, 149.7, 139.3, 129.2, 128.4, 126.9, 126.3, 112.5, 56.1, 52.1, 40.5 ppm.
The data is in accordance with the literature.[5]

Methyl 2-phenyl-2-(phenylamino)acetate (12)



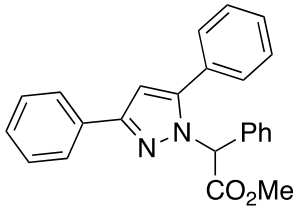
The title compound **12** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless solid (96%, 46.6 mg).
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.53 – 7.48 (m, 2H), 7.38 – 7.33 (m, 2H), 7.33 – 7.27 (m, 1H), 7.17 – 7.10 (m, 2H), 6.71 (tt, *J* = 7.3, 1.1 Hz, 1H), 6.61 – 6.54 (m, 2H), 5.10 (d, *J* = 4.4 Hz, 1H), 4.97 (s, 1H), 3.74 (s, 3H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.3, 145.9, 137.6, 129.2, 128.8, 128.3, 127.2, 118.1, 113.4, 60.7, 52.8 ppm.
The data is in accordance with the literature.[5]

Methyl 2-(9*H*-carbazol-9-yl)-2-phenylacetate (13)



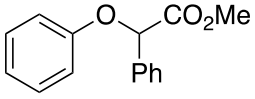
The title compound **13** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (82%, 43.1 mg).
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.15 – 8.09 (m, 2H), 7.40 – 7.34 (m, 2H), 7.34 – 7.30 (m, 3H), 7.27 – 7.21 (m, 6H), 6.62 (s, 1H), 3.78 (s, 3H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 169.8, 140.1, 133.9, 128.6, 128.3, 127.4, 125.7, 123.5, 120.2, 119.7, 119.4, 110.5, 110.1, 60.2, 52.7 ppm.
The data is in accordance with the literature.[5]

Methyl 2-(3,5-diphenyl-1*H*-pyrazol-1-yl)-2-phenylacetate (14)



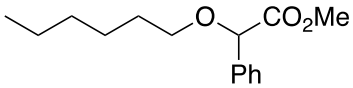
The title compound **14** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (50%, 36.6 mg).
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.94 – 7.82 (m, 2H), 7.48 – 7.29 (m, 14H), 6.65 (s, 1H), 6.07 (s, 1H), 3.76 (s, 3H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 169.0, 151.3, 146.0, 135.2, 133.2, 130.3, 129.1, 128.9, 128.8, 128.7, 128.5, 128.4, 127.8, 125.8, 103.7, 64.7, 53.0 ppm.
HRMS (ESI): m/z: $[M + K]^+$ Calcd. for $C_{24}H_{20}O_2N_2K^+$:407.11564; Found: 407.11559.
IR (KBr): 3061, 2952, 2323, 2083, 1893, 1749, 1603, 1552, 1484, 1455, 1304, 1257, 1204, 1109, 1077, 1002, 957, 919, 865, 805, 762, 735, 694 cm^{-1}.

Methyl 2-phenoxy-2-phenylacetate (15)



The title compound **15** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless solid (56%, 26.9 mg).
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.62 – 7.53 (m, 2H), 7.44 – 7.34 (m, 3H), 7.30 – 7.24 (m, 2H), 7.03 – 6.92 (m, 3H), 5.66 (s, 1H), 3.74 (s, 1H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 170.4, 157.2, 135.4, 129.5, 128.9, 128.8, 127.0, 121.8, 115.4, 52.6 ppm.
The data is in accordance with the literature.[5]

Methyl 2-(hexyloxy)-2-phenylacetate (16)



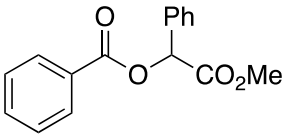
The title compound **16** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (82%, 43.3 mg).

^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.52 – 7.42 (m, 2H), 7.42 – 7.28 (m, 3H), 4.89 (s, 1H), 3.73 (s, 3H), 3.55 (dt, *J* = 9.0, 6.7 Hz, 1H), 3.45 (dt, *J* = 9.0, 6.8 Hz, 1H), 1.74 – 1.56 (m, 2H), 1.45 – 1.23 (m, 6H), 0.90 (t, *J* = 6.8 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*): δ = 171.5, 136.7, 128.5, 127.1, 81.0, 70.0, 52.2, 31.6, 29.5, 25.6, 22.5, 14.0 ppm.

The data is in accordance with the literature.[6]

2-Methoxy-2-oxo-1-phenylethyl benzoate (17)



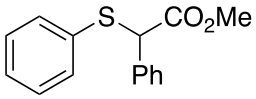
The title compound **17** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (86%, 46.6 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 8.17 – 8.08 (m, 2H), 7.63 – 7.55 (m, 3H), 7.49 – 7.37 (m, 5H), 6.17 (s, 1H), 3.76 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 169.3, 165.8, 133.9, 133.4, 129.9, 129.3, 129.2, 128.8, 128.4, 127.6, 74.8, 52.6 ppm.

The data is in accordance with the literature.[6]

Methyl 2-phenyl-2-(phenylthio)acetate (18)



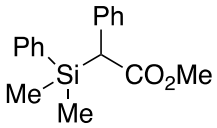
The title compound **18** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (88%, 45.5 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.50 – 7.42 (m, 2H), 7.39 – 7.35 (m, 2H), 7.35 – 7.29 (m, 3H), 7.28 – 7.23 (m, 3H), 4.92 (s, 1H), 3.68 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 170.8, 135.5, 133.6, 132.6, 128.9, 128.6, 128.5, 128.3, 128.0, 56.3, 52.7 ppm.

The data is in accordance with the literature.[7]

Methyl 2-(dimethyl(phenyl)silyl)-2-phenylacetate (19)



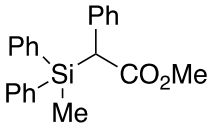
The title compound **19** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (80%, 54.3 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.30 – 7.23 (m, 3H), 7.23 – 7.16 (m, 2H), 7.09 (d, *J* = 4.3 Hz, 4H), 7.02 (dt, *J* = 8.7, 4.2 Hz, 1H), 3.48 (s, 1H), 3.42 (s, 3H), 0.23 (s, 3H), 0.20 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.1, 135.9, 135.5, 134.0, 129.6, 128.3, 128.0, 127.7, 125.6, 51.2, 46.0, -4.0, -4.5 ppm.

The data is in accordance with the literature.[8]

Methyl 2-(methyldiphenylsilyl)-2-phenylacetate (20)



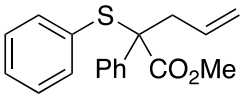
The title compound **20** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (75%, 63.0 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.61 – 7.56 (m, 2H), 7.50 – 7.43 (m, 3H), 7.43 – 7.38 (m, 3H), 7.37 – 7.32 (m, 2H), 7.26 – 7.19 (m, 4H), 7.19 – 7.15 (m, 1H), 4.05 (s, 1H), 3.50 (s, 3H), 0.65 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.0, 135.5, 135.08, 135.00, 134.0, 133.7, 129.8, 129.7, 128.8, 128.0, 127.8, 127.7, 125.8, 51.4, 44.8, -5.2 ppm.

The data is in accordance with the literature.[8]

Methyl 2-phenyl-2-(phenylthio)pent-4-enoate (21)



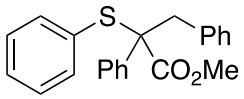
The title compound **21** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (92%, 55.3 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.37 – 7.25 (m, 6H), 7.24 – 7.17 (m, 4H), 5.99 – 5.84 (m, 1H), 5.22 – 4.99 (m, 2H), 3.72 (s, 3H), 3.00 – 2.81 (m, 2H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.3, 139.7, 136.8, 133.2, 130.7, 129.2, 128.5, 128.1, 127.5, 127.4, 118.8, 64.5, 52.6, 40.6 ppm.

The data is in accordance with the literature.[4]

Methyl 2,3-diphenyl-2-(phenylthio)propanoate (22)



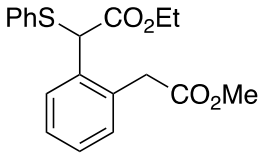
The title compound **22** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (60%, 42.0 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.38 – 7.31 (m, 3H), 7.28 – 7.21 (m, 7H), 7.20 – 7.12 (m, 3H), 7.04 – 6.94 (m, 2H), 3.62 (s, 1H), 3.60 (d, *J* = 14.0, 1H), 3.44 (d, *J* = 13.7 Hz, 1H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.9, 139.2, 136.4, 135.9, 131.3, 130.8, 129.2, 128.5, 128.2, 127.8, 127.6, 127.4, 126.7, 77.2, 65.8, 52.2, 44.5 ppm.

The data is in accordance with the literature.[9]

Ethyl 2-(2-(2-methoxy-2-oxoethyl)phenyl)-2-(phenylthio)acetate (23)



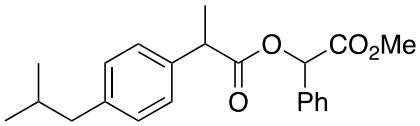
The title compound **23** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (90%, 62.3 mg).

^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.73 – 7.57 (m, 1H), 7.40 (dd, *J* = 6.6, 3.0 Hz, 2H), 7.35 – 7.18 (m, 6H), 5.21 (s, 1H), 4.19 – 3.99 (m, 2H), 3.71 (d, *J* = 4.1 Hz, 2H), 3.63 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*): δ = 171.3, 170.3, 134.2, 133.7, 132.8, 132.5, 131.1, 129.1, 128.9, 128.4, 128.0, 127.9, 61.7, 52.4, 52.1, 38.8, 13.9 ppm.

The data is in accordance with the literature.[9]

2-Methoxy-2-oxo-1-phenylethyl 2-(4-isobutylphenyl)propanoate (24)



The title compound **24** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (91%, 64.3 mg), d.r. = 1 : 1

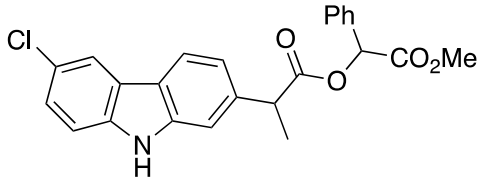
^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.43 – 7.29 (m, 4H), 7.29 – 7.19 (m, 3H), 7.18 – 7.00 (m, 2H), 5.91 (d, *J* = 1.9 Hz, 1H), 3.85 (dt, *J* = 14.1, 7.1 Hz, 1H), 3.70 (s, 1.50 H), 3.62 (s, 1.44 H), 2.44 (dd, *J* = 10.9, 7.2 Hz, 2H), 1.84 (dt, *J* = 10.5, 6.8 Hz, 1H), 1.56 (dd, *J* = 7.2, 5.3 Hz, 3H), 1.03 – 0.78 (m, 6H) ppm.

^{13}C NMR (101 MHz, Chloroform-*d*): δ = 174.0, 173.9, 169.2, 169.0, 140.6, 140.5, 137.0, 136.9, 133.8, 133.7, 129.27, 129.21, 129.08, 129.00, 128.68, 128.61, 127.4, 127.3, 74.5, 74.4, 52.5, 52.3, 45.04, 45.00, 44.9, 44.7, 30.1, 22.3, 18.5, 18.3 ppm.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{22}H_{26}O_4Na^+$: 377.17233; Found: 377.17091.

IR (KBr): 3503, 3156, 3032, 2954, 2870, 2657, 2451, 2335, 2260, 2229, 2174, 2110, 1991, 1956, 1950, 1805, 1742, 1602, 1511, 1454, 1350, 1271, 1213, 1152, 1071, 1028, 967, 922, 848, 780, 733, 695 cm^{-1}.

2-Methoxy-2-oxo-1-phenylethyl 2-(6-chloro-9*H*-carbazol-2-yl)propanoate (25)



The title compound **25** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (90%, 75.2 mg), d.r. 2 : 1.

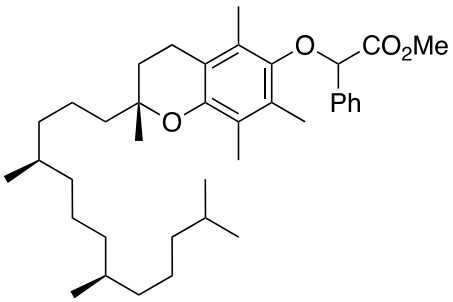
^{1}H NMR (400 MHz, Acetone): δ = 10.50 (s, 0.38H), 10.46 (s, 0.62H), 8.25 – 7.98 (m, 2H), 7.60 – 7.48 (m, 2H), 7.42 (dq, *J* = 7.3, 3.4 Hz, 2H), 7.39 – 7.30 (m, 4H), 7.24 (dt, *J* = 8.1, 1.0 Hz, 0.49H), 7.20 (dt, *J* = 8.2, 1.0 Hz, 0.81H), 5.92 (s, 1H), 4.09 (dd, *J* = 8.9, 7.0 Hz, 1H), 3.68 (d, *J* = 0.8 Hz, 2.31H), 3.57 (d, *J* = 0.7 Hz, 1.35H), 1.58 (t, *J* = 7.2 Hz, 3H) ppm.

^{13}C NMR (101 MHz, Acetone): δ = 173.49, 173.40, 168.9, 168.8, 140.9, 138.8. 134.1, 129.04, 129.00, 128.6, 128.5, 127.5, 127.4, 125.3, 125.2, 124.1, 123.8, 121.3, 120.4, 120.3, 119.6, 119.3, 119.1, 112.16, 112.11, 110.18, 110.10, 74.6, 74.5, 51.8, 51.6, 45.3, 18.6, 18.5 ppm.

HRMS (ESI): m/z: $[M + K]^+$ Calcd. for $C_{24}H_{20}O_4ClK^+$: 460.06960; Found: 460.07124.

IR (KBr): 3409, 3034, 2952, 2230, 2171, 2083, 1990, 1881, 1734, 1610, 1576, 1454, 1333, 1271, 1219, 1159, 1064, 1031, 970, 926, 867, 803, 732, 695 cm^{-1}.

Methyl 2-phenyl-2-(((*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl) chroman-6-yl)oxy)acetate (26)



The title compound **26** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (40%, 44.8 mg), d.r. = 1 : 1.

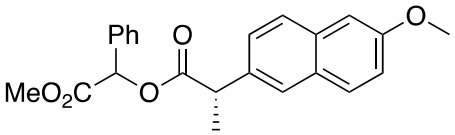
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.62 – 7.41 (m, 2H), 7.36 (dd, *J* = 4.9, 1.8 Hz, 3H), 5.05 (s, 1H), 3.73 (d, *J* = 1.3 Hz, 3H), 2.50 (td, *J* = 6.8, 4.3 Hz, 2H), 2.03 (s, 3H), 1.98 (s, 3H), 1.92 (d, *J* = 2.6 Hz, 3H), 1.85 – 1.70 (m, 2H), 1.66 – 1.48 (m, 3H), 1.43 – 1.33 (m, 2H), 1.33 – 1.23 (m, 5H), 1.22 (s, 3H), 1.18 – 1.10 (m, 2H), 1.09- 1.02 (m, 1H), 0.91 – 0.80 (m, 13H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 171.2, 148.2, 147.9, 136.7, 128.7, 128.5, 127.7, 126.0, 122.9, 117.5, 84.1, 74.8, 52.2, 39.9, 39.3, 37.5, 37.4, 37.3, 37.2, 32.7, 32.6, 27.9, 24.8, 24.4, 23.8, 23.7, 22.7, 22.6, 21.0, 20.7, 19.7, 19.67, 19.60, 13.5, 12.6, 11.8 ppm.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{38}H_{58}O_4Na^+$: 601.42273; Found: 601.42107.

IR (KBr): 3345, 2925, 2865, 2726, 2335, 2098, 1988, 1940, 1759, 1574, 1457, 1409, 1376, 1249, 1204, 1163, 1085, 916, 856, 814, 781, 729, 697 cm^{-1}.

2-Methoxy-2-oxo-1-phenylethyl (2*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (27)



The title compound **27** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (47%, 35.5 mg) d.r. ~1.6:1.

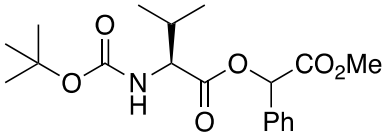
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.82 – 7.61 (m, 3H), 7.58 – 7.25 (m, 6H), 7.15 – 7.04 (m, 2H), 5.92 (s, 0.38H), 5.91 (s, 0.51H), 4.15 – 3.93 (m, 1H), 3.90 (s, 1.08H), 3.89 (s, 1.76H), 3.70 (s, 1.48H), 3.58 (s, 1.26fH), 1.89 – 1.49 (m, 3H).
ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 174.0, 173.9, 169.2, 169.0, 157.6, 134.99, 134.93, 133.7, 133.6, 129.33, 129.30, 129.1, 129.0, 128.9, 128.8, 128.7, 128.6, 127.5, 127.4, 127.1, 127.0, 126.4, 126.3, 126.2, 126.1, 118.93, 118.90, 105.6, 105.5, 74.7, 74.5, 55.2, 52.6, 52.4, 45.2, 45.1, 18.6, 18.4 ppm.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{23}H_{22}O_5Na^+$: 401.13594; Found: 401.13590.

IR (KBr): 2951, 2843, 2327, 2117, 1911, 1739, 1631, 1605, 1487, 1453, 1388, 1350, 1255, 1217, 1151, 1078, 1029, 969, 923, 892, 854, 812, 782, 763, 696 cm^{-1}.
, 1214, 1159, 1096, 1046, 979, 913, 849 cm^{-1}.

2-Methoxy-2-oxo-1-phenylethyl (*tert*-butoxycarbonyl)-*L*-valinate (28)



The title compound **28** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (72%, 41.8 mg) d.r. ~1.6:1.

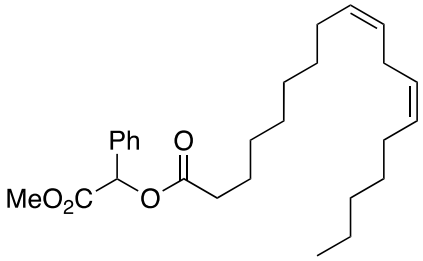
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.54 – 7.42 (m, 2H), 7.42 – 7.33 (m, 3H), 5.96 (s, 0.45H), 5.92 (s, 0.34H), 5.11 – 4.92 (m, 1H), 4.52 – 4.30 (m, 1H), 3.72 (s, 1.86H), 3.71 (s, 1.14H), 2.42 – 2.33 (m, 0.32H), 2.29 – 2.15 (m, 0.51H), 1.43 (s, 3.20H), 1.40 (s, 5.13H), 1.05 (d, *J* = 6.9 Hz, 1.31H), 1.01 (d, *J* = 6.9 Hz, 1.21H), 0.98 (d, *J* = 6.9 Hz, 1.86H), 0.87 (d, *J* = 6.9 Hz, 1.70H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 172.0, 171.5, 168.9, 168.8, 155.6, 155.5, 133.5, 133.2, 129.38, 129.31, 128.8, 128.7, 127.6, 127.5, 79.8, 74.9, 74.8, 58.6, 58.2, 52.6, 52.5, 31.1, 28.29, 28.25, 19.03, 19.00, 17.3, 17.1 ppm.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{19}H_{27}O_6NNa^+$: 388.17306; Found: 388.17306.

IR (KBr): 3387, 2969, 2160, 2022, 1747, 1711, 1499, 1456, 1364, 1310, 1217, 1155, 1089, 1039, 862, 736, 696 cm^{-1}.

2-Methoxy-2-oxo-1-phenylethyl (9*Z*,12*Z*)-octadeca-9,12-dienoate (29)



The title compound **29** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 20:1 → 10:1) as a colorless oil (44%, 37.8 mg).

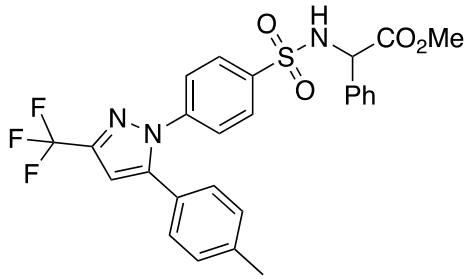
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.57 – 7.43 (m, 2H), 7.43 – 7.28 (m, 3H), 5.92 (s, 1H), 5.33 (tt, *J* = 11.2, 5.2 Hz, 4H), 3.70 (s, 3H), 2.75 (t, *J* = 6.5 Hz, 2H), 2.65 – 2.30 (m, 2H), 2.03 (q, *J* = 7.0 Hz, 4H), 1.67 (p, *J* = 7.4 Hz, 2H), 1.41 – 1.14 (m, 15H), 0.87 (t, *J* = 6.5 Hz, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.1, 169.3, 133.8, 130.2, 130.0, 129.1, 128.7, 128.0, 127.8, 127.5, 74.2, 52.5, 33.9, 31.5, 29.5, 29.3, 29.1, 29.0, 28.9, 27.1, 25.6, 24.7, 22.5, 14.0 ppm.

HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{27}H_{40}O_4Na^+$: 451.28188; Found: 451.28188.

IR (KBr): 3481, 3067, 3009, 2926, 2855, 2664, 2329, 2118, 1992, 1960, 1746, 1649, 1588, 1496, 1456, 1349, 1269

Methyl 2-phenyl-2-((4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonamido)acetate (30)



The title compound **30** was synthesized according to the general procedure (GP-1), and was obtained after silica column chromatography (*n*-hexane : ethyl acetate 10:1 → 4:1) as a colorless oil (27%, 28.7 mg).

^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.72 – 7.64 (m, 2H), 7.41 – 7.30 (m, 2H), 7.30 – 7.24 (m, 3H), 7.23 – 7.19 (m, 2H), 7.19 – 7.15 (m, 2H), 7.11 – 7.05 (m, 2H), 6.72 (s, 1H), 5.80 (d, *J* = 7.4 Hz, 1H), 5.08 (d, *J* = 7.4 Hz, 1H), 3.63 (s, 3H), 2.38 (s, 3H) ppm.

^{13}C NMR (151 MHz, Chloroform-*d*): δ = 170.3, 145.1, 144.0 (d, *J* = 38.6 Hz), 142.4, 139.6 (d, *J* = 51.6 Hz), 134.9, 129.7, 128.9, 128.8, 128.6, 128.0, 127.1, 125.6, 125.2, 121.0 (d, *J* = 269.5 Hz), 106.3, 59.3, 53.2, 21.3 ppm.

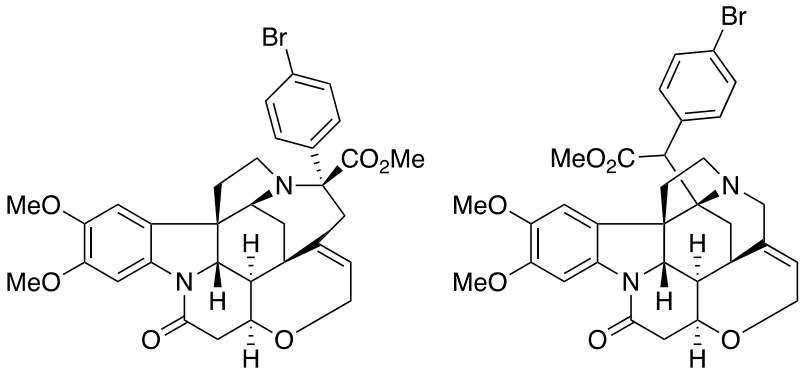
HRMS (ESI): m/z: $[M + Na]^+$ Calcd. for $C_{26}H_{22}O_4N_3F_3SNa^+$: 552.11753; Found: 552.11745.

IR (KBr): 3276, 3067, 3033, 2955, 2523, 2436, 2258, 2230, 2201, 2161, 2121, 2084, 2059, 2024, 1079, 1013, 1742, 1596, 1497, 1470, 1411, 1371, 1342, 1270, 1236, 1160, 1096, 1017, 974, 920, 842, 810, 760, 736, 697 cm^{-1}.

Reaction with Brucine

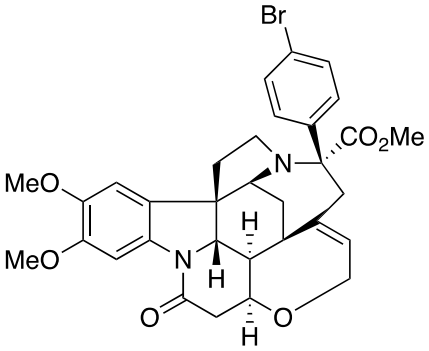
In an oven dried reaction tube Rh-CP (4 mg) and brucine (1.0 equiv., 0.2 mmol,) were added. Then the tube was closed with septum and evacuated and backfilled with argon for three times. Then 1 mL degassed $PhCF_3$ was added. The corresponding diazoalkane (4.0 equiv., 0.8 mmol) was dissolved in a separate reaction test tube in 1 mL of degassed $PhCF_3$ was added to the reaction tube and heated to 83 °C for 16 h. The corresponding products were obtained after column chromatography on silica gel using *n*-hexane : ethyl acetate as eluent.

Methyl (4a*R*,4a1*R*,5a*S*,8a*R*,8a1*S*,15a*S*,16*S*)-16-(4-bromophenyl)-10,11-dimethoxy-14-oxo-2,4a,4a1,5,5a,7,8,8a1,15,15a-decahydro-14*H*-6,4-ethanoindolo[3,2,1-*ij*]oxepino[2,3,4-*de*]pyrrolo[2,3-*h*]quinoline-16-carboxylate (33) & Methyl 2-(4-bromophenyl)-2-((4a*R*,4a1*R*,5a*R*,8a*S*,8a1*S*,15a*S*)-10,11-dimethoxy-14-oxo-4a,4a1,5,7,8,8a1,15,15a-octahydro-14*H*-4,6-methanoindolo[3,2,1-*ij*]oxepino[2,3,4-*de*]pyrrolo[2,3-*h*]quinolin-5a(2*H*)-yl)acetate (34)



The title compound **33** and **34** were obtained as an inseparable 1 : 1 mixture after silica column chromatography (*n*-hexane : ethyl acetate 40:1 → 10:1) as a colorless solid (22%, 45.1 mg).
^{1}H NMR (600 MHz, Chloroform-*d*): δ = 7.92 (s, 1H), 7.82 (s, 1H), 7.53 (d, *J* = 8.6 Hz, 2H), 7.47 – 7.40 (m, 2H), 7.40 – 7.34 (m, 2H), 7.19 (d, *J* = 8.0 Hz, 2H), 6.91 (s, 1H), 6.71 (s, 1H), 5.89 – 5.80 (m, 1H), 5.64 (td, *J* = 6.6, 2.6 Hz, 1H), 4.37 (ddd, *J* = 16.1, 4.9, 1.8 Hz, 1H), 4.28 – 4.21 (m, 2H), 4.15 – 4.05 (m, 5H), 4.01 – 3.86 (m, 2H), 3.91 (d, *J* = 4.0 Hz, 1H), 3.89 (s, 3H), 3.88 (s, 3H), 3.87 (s, 3H), 3.82 (s, 3H), 3.62 (s, 3H), 3.49 (s, 3H), 3.27 (ddd, *J* = 10.2, 7.7, 5.8 Hz, 1H), 3.11 (dd, *J* = 17.7, 8.6 Hz, 1H), 3.08 – 3.00 (m, 4H), 3.00 – 2.94 (m, 1H), 2.91 (dd, *J* = 13.0, 6.5 Hz, 2H), 2.85 – 2.74 (m, 4H), 2.57 (dd, *J* = 17.7, 3.2 Hz, 1H), 2.31 (td, *J* = 12.7, 7.6 Hz, 1H), 2.27 (s, 2H), 2.03 (s, 2H), 1.99 (dt, *J* = 15.2, 3.6 Hz, 1H), 1.95 – 1.84 (m, 2H), 1.79 (dd, *J* = 13.1, 6.3 Hz, 1H), 1.69 (s, 2H), 1.64 – 1.55 (m, 2H), 1.40 (dt, *J* = 16.8, 3.5 Hz, 1H), 1.25 (t, *J* = 7.1 Hz, 3H) ppm.
^{13}C NMR (151 MHz, Chloroform-*d*): δ = 173.0, 172.1, 169.7, 167.4, 149.3, 149.2, 146.1, 145.1, 142.5, 139.3, 138.1, 136.2, 135.7, 135.0, 131.4, 130.3, 128.6, 128.1, 125.7, 123.6, 123.2, 121.4, 121.2, 108.7, 105.8, 100.9, 78.0, 75.6, 68.4, 67.8, 65.2, 65.0, 62.6, 61.5, 60.3, 59.4, 57.9, 56.66, 56.63, 56.3, 56.1, 55.9, 53.0, 52.80, 52.1, 51.8, 49.4, 49.2, 48.0, 46.79, 46.72, 42.4, 42.19, 42.17, 39.3, 35.1, 31.9, 31.5, 28.1 ppm.
The data is in accordance with the literature.[10]

Methyl (4a*R*,4a1*R*,5a*S*,8a*R*,8a1*S*,15a*S*,16*R*)-16-(4-bromophenyl)-10,11-dimethoxy-14-oxo-2,4a,4a1,5,5a,7,8,8a1,15,15a-decahydro-14*H*-6,4-ethanoindolo[3,2,1-*ij*]oxepino[2,3,4-*de*]pyrrolo[2,3-*h*]quinoline-16-carboxylate (35)



The title compound **35** was obtained after silica column chromatography (*n*-hexane : ethyl acetate 40:1 → 10:1) as a colorless solid (17%, 35.0 mg).

^{1}H NMR (400 MHz, Chloroform-*d*): δ = 7.79 (s, 1H), 7.45 (d, *J* = 8.3 Hz, 2H), 7.19 (s, 2H), 6.66 (s, 1H), 5.51 (s, 1H), 4.24 – 4.12 (m, 2H), 4.07 (d, *J* = 10.5 Hz, 1H), 4.02 – 3.94 (m, 1H), 3.91 (s, 3H), 3.87 (s, 3H), 3.85 (s, 3H), 3.76 – 3.67 (m, 1H), 3.52 – 3.38 (m, 1H), 3.07 (dd, *J* = 16.2, 8.2 Hz, 1H), 2.94 (s, 1H), 2.82 – 2.52 (m, 3H), 2.50 – 2.29 (m, 2H), 2.10 – 1.94 (m, 1H), 1.73 – 1.52 (m, 2H), 1.49 – 1.29 (m, 1H) ppm.

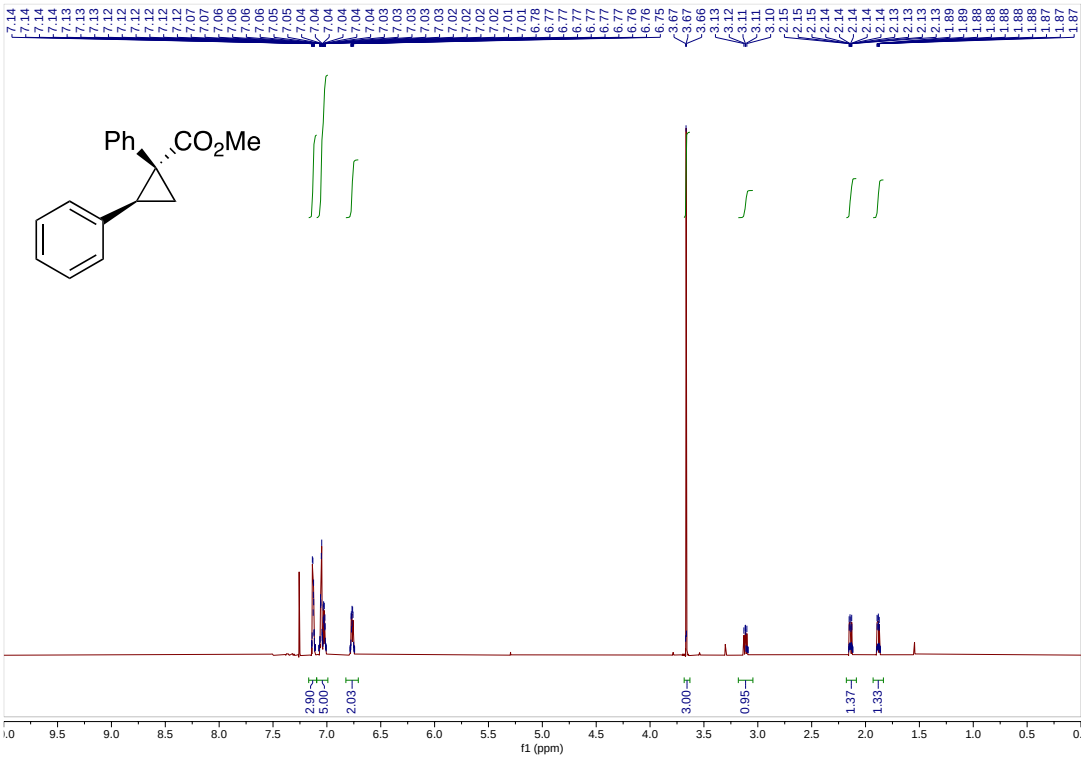
^{13}C NMR (101 MHz, Chloroform-*d*): δ = 173.6, 170.2, 149.0, 146.3, 136.3, 131.3, 128.1, 123.8, 121.4, 105.6, 101.0, 79.0, 68.3, 66.7, 64.2, 60.2, 56.5, 56.1, 52.7, 51.8, 48.9, 47.5, 45.6, 41.8, 40.5, 34.9, 29.0 ppm.

The data is in accordance with the literature.[10]

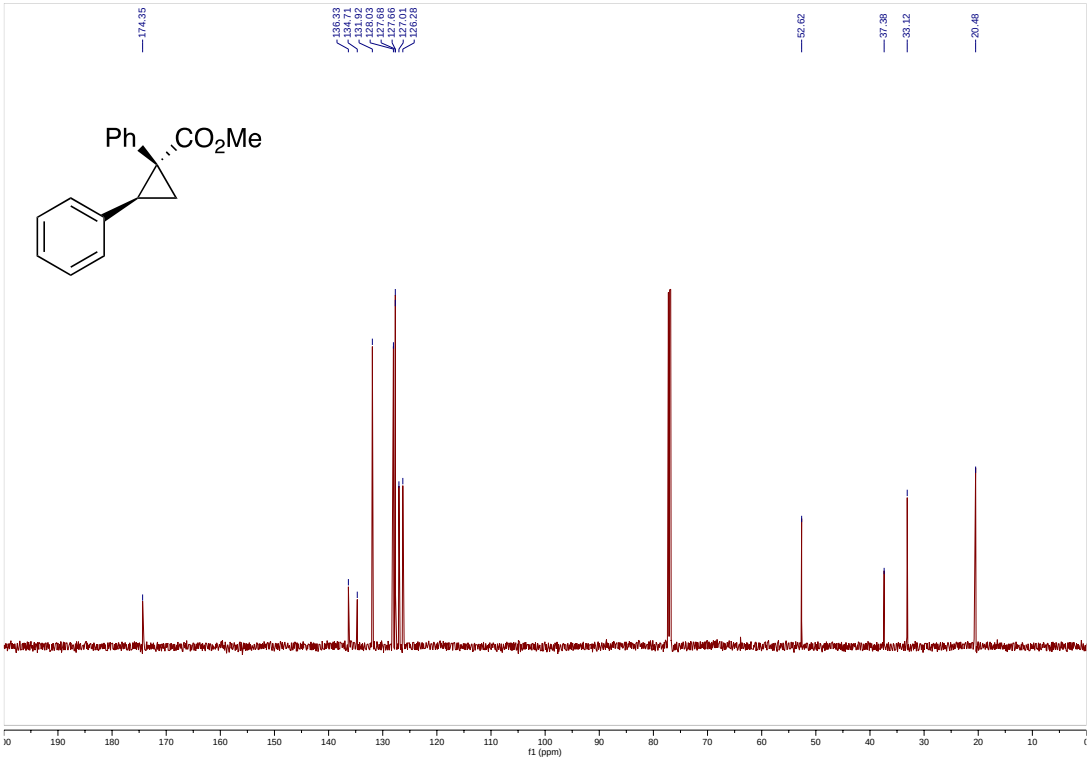
14. NMR Spectra

Methyl-1,2-diphenylcyclopropane-1-carboxylate (7)

^{1}H NMR (600 MHz, Chloroform-*d*)

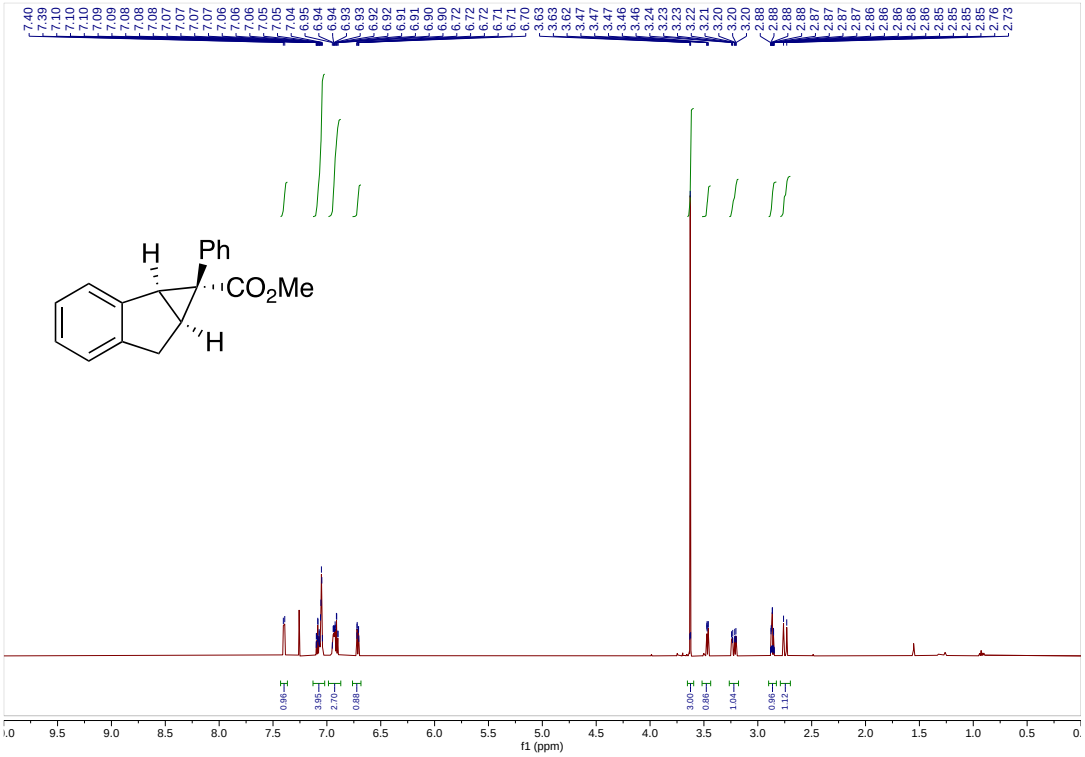


^{13}C NMR (151 MHz, Chloroform-*d*)

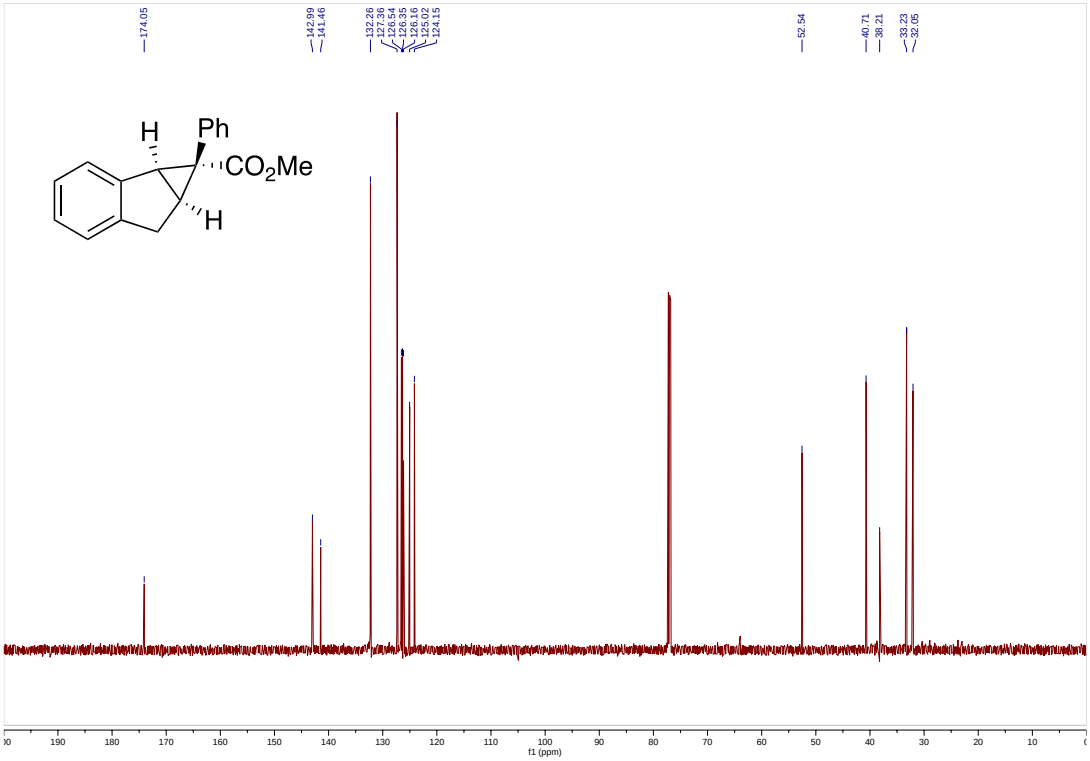


Methyl -1-phenyl-1,1a,6,6a-tetrahydrocyclopropa[*a*]indene-1-carboxylate (8)

^{1}H NMR (600 MHz, Chloroform-*d*)

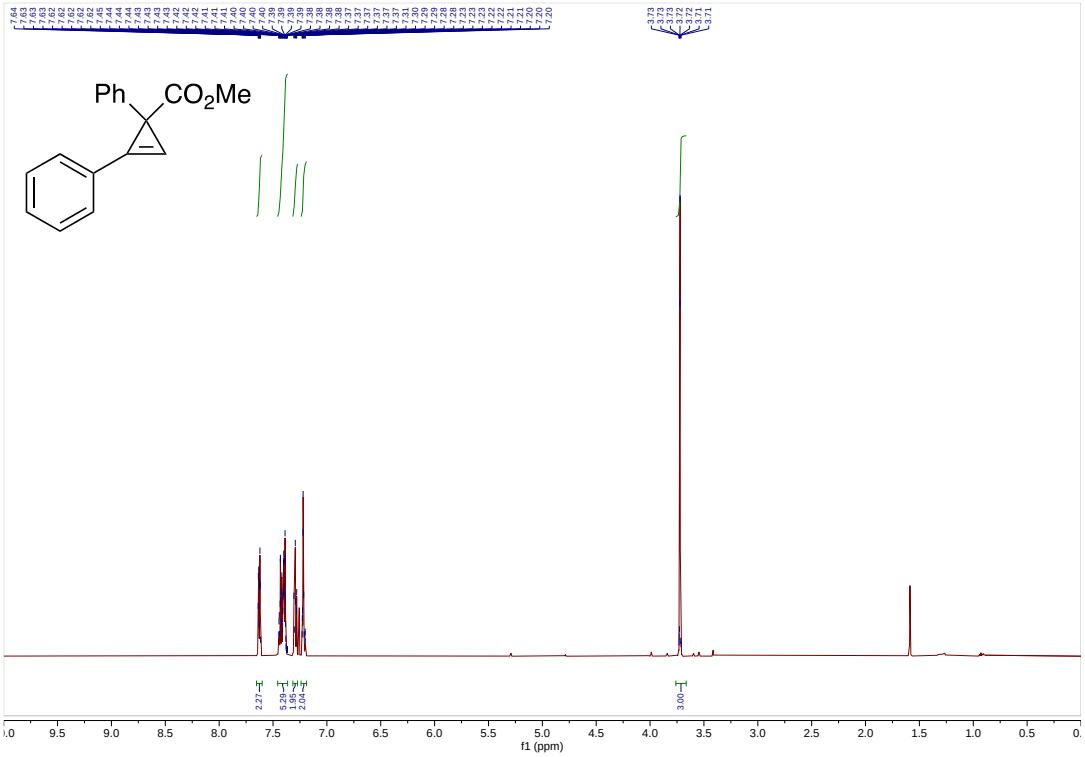


^{13}C NMR (151 MHz, Chloroform-*d*)

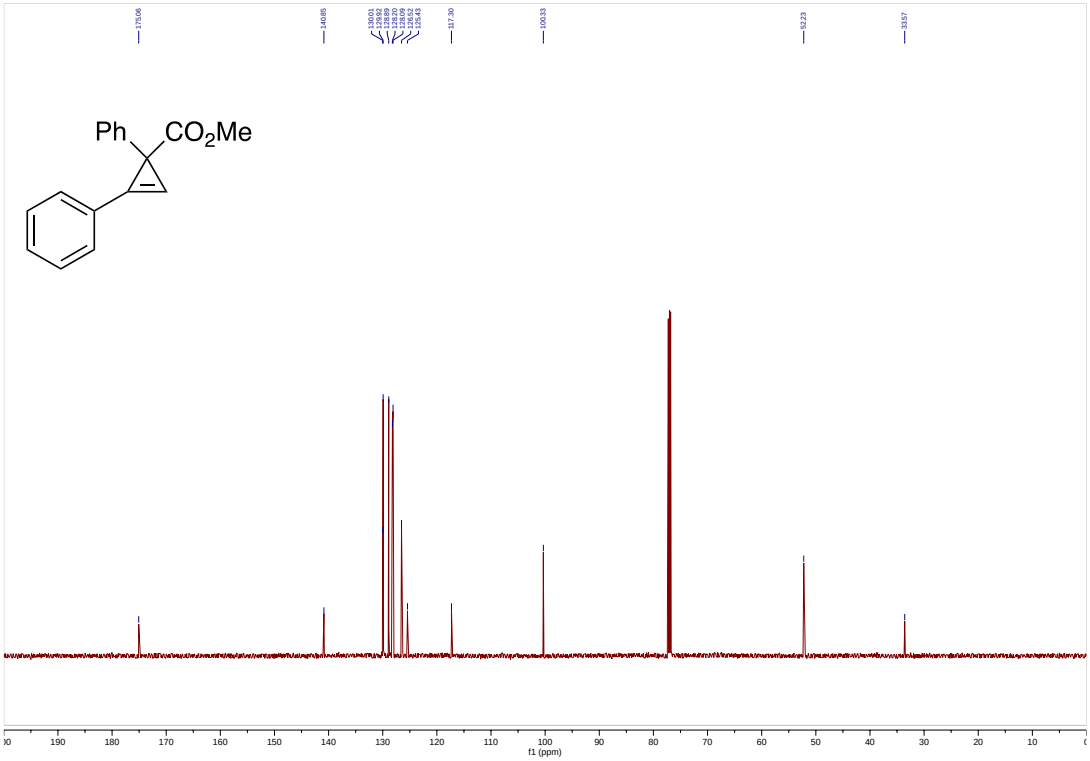


Methyl 1,2-diphenylcycloprop-2-ene-1-carboxylate (9)

^{1}H NMR (600 MHz, Chloroform-*d*)

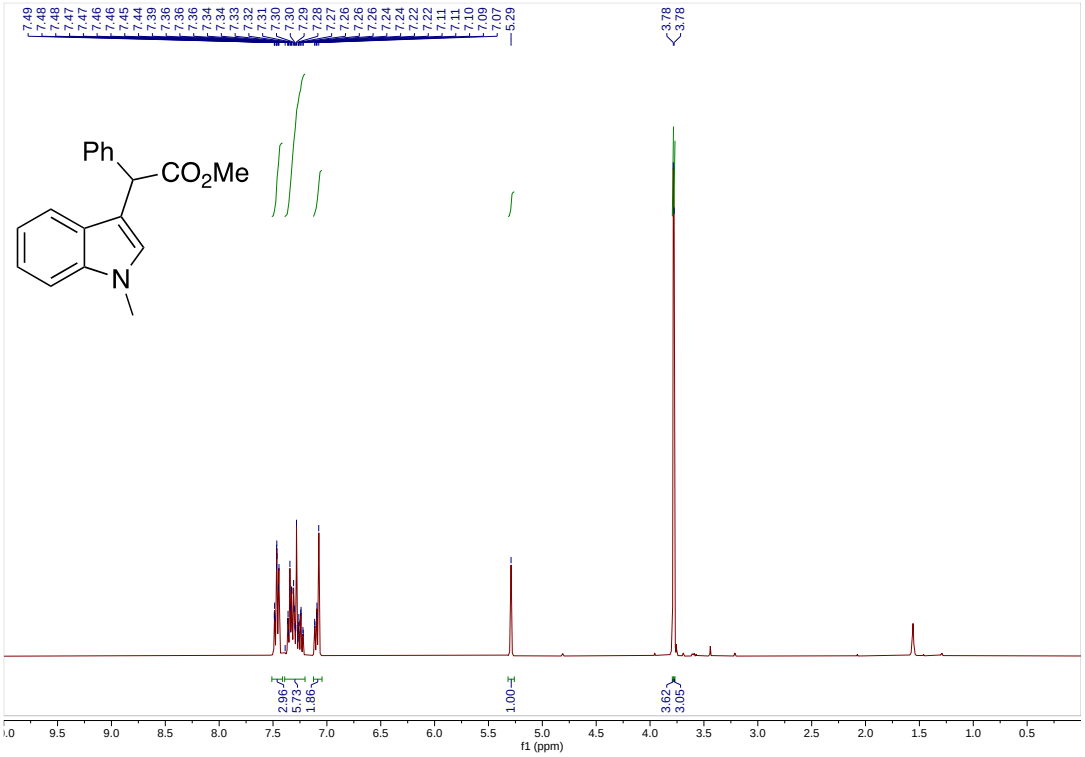


^{13}C NMR (151 MHz, Chloroform-*d*)

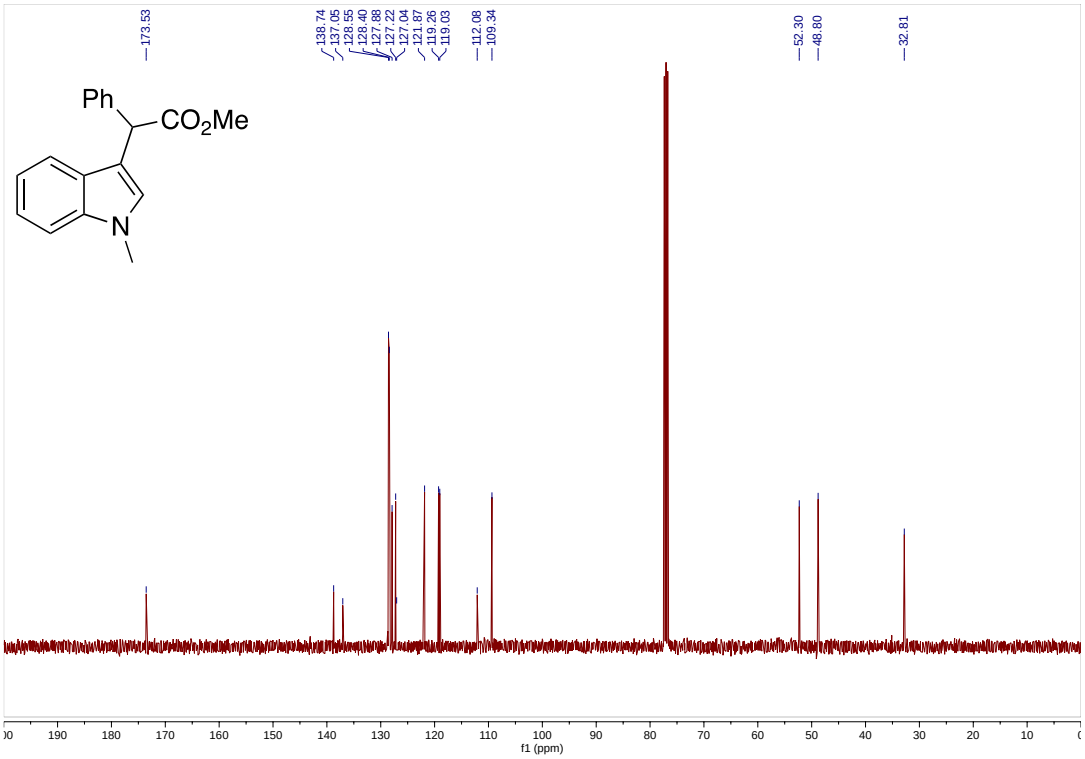


Methyl 2-(1-methyl-1*H*-indol-3-yl)-2-phenylacetate (10)

^{1}H NMR (400 MHz, Chloroform-*d*)

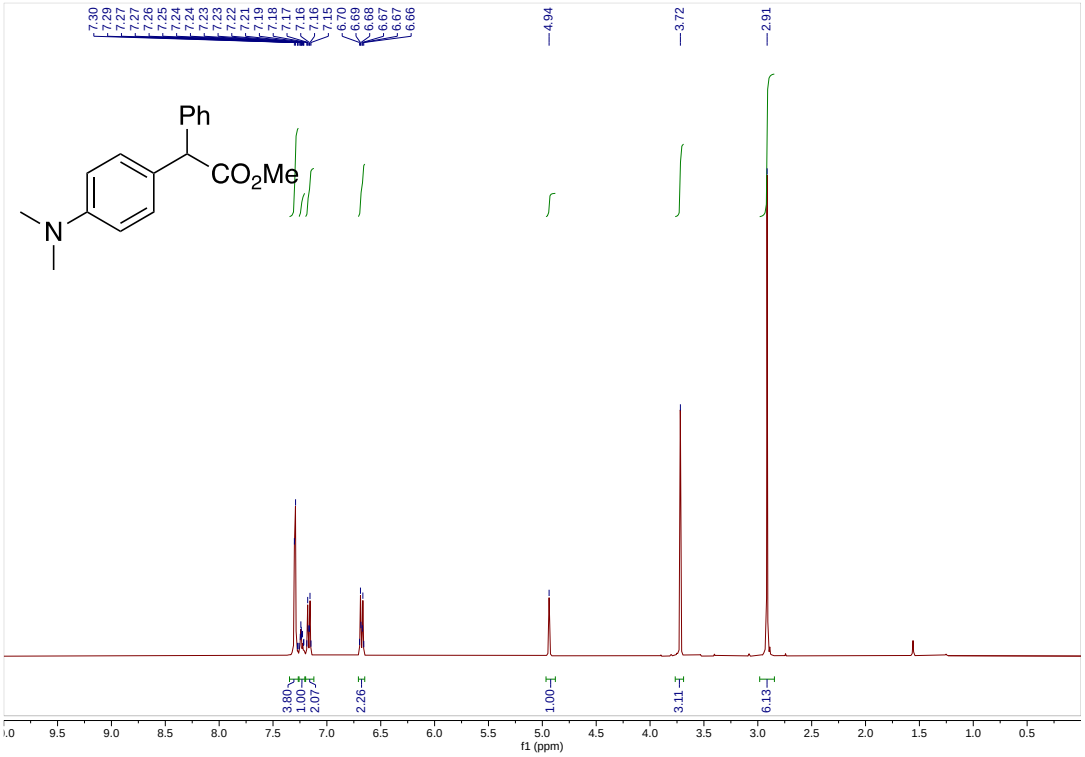


^{13}C NMR (101 MHz, Chloroform-*d*)

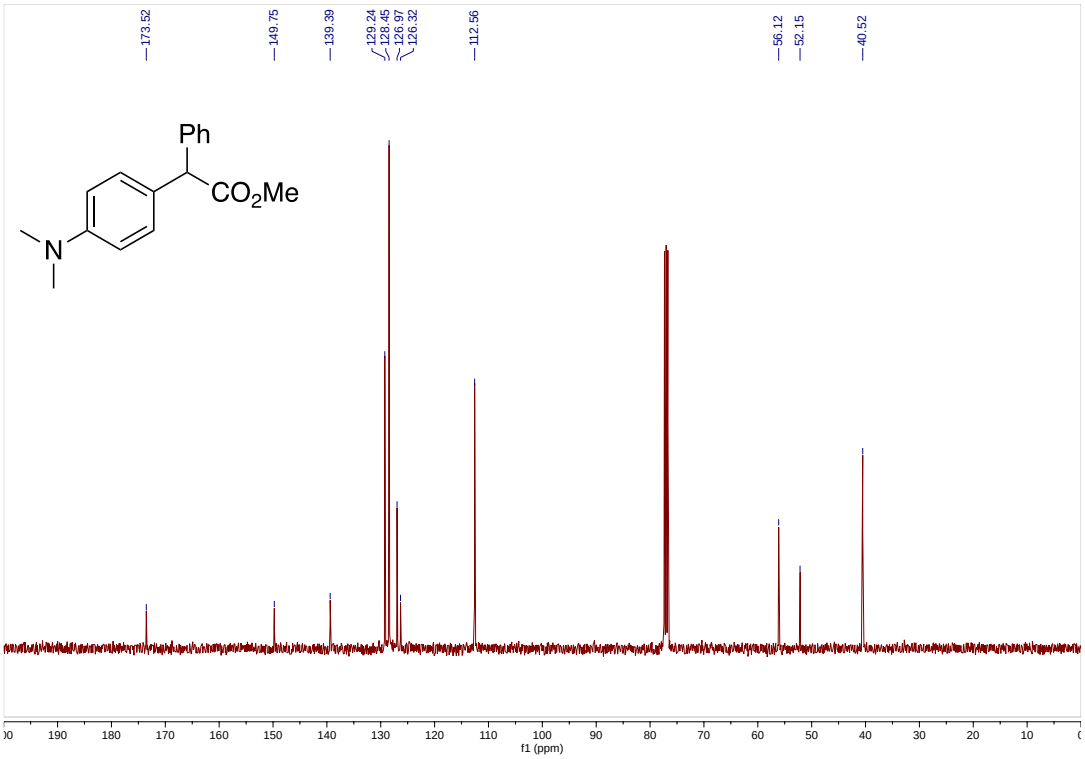


Methyl 2-(4-(dimethylamino)phenyl)-2-phenylacetate (11)

^{1}H NMR (400 MHz, Chloroform-*d*)

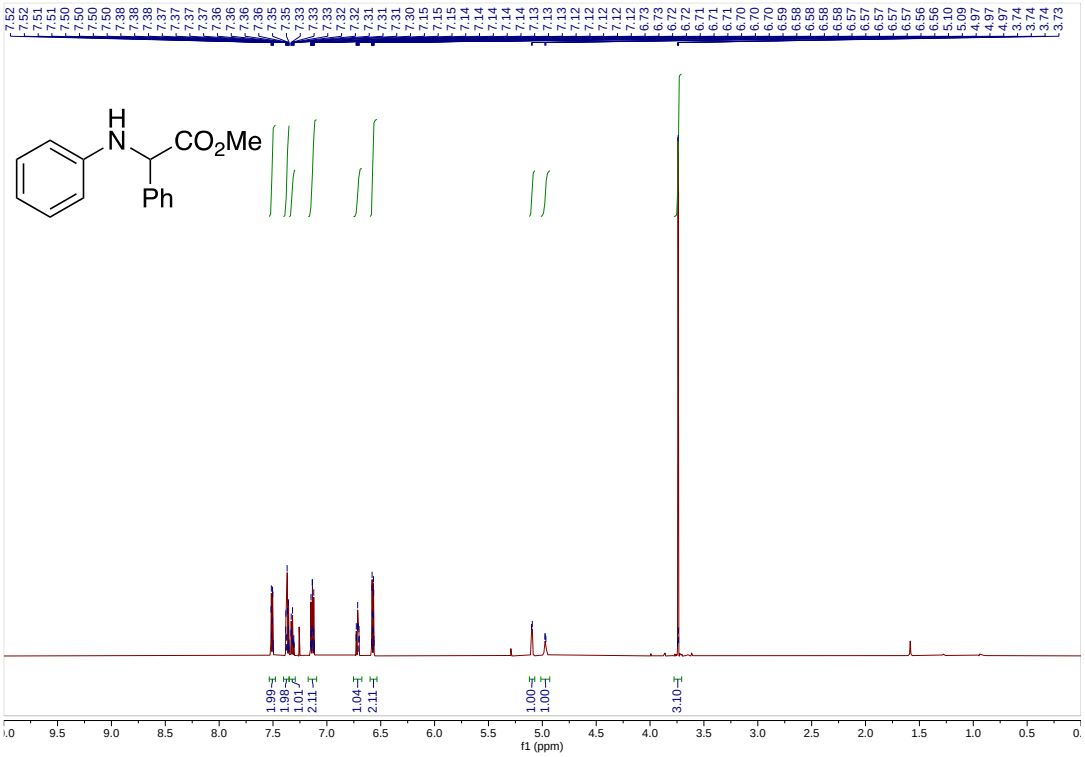


^{13}C NMR (101 MHz, Chloroform-*d*)

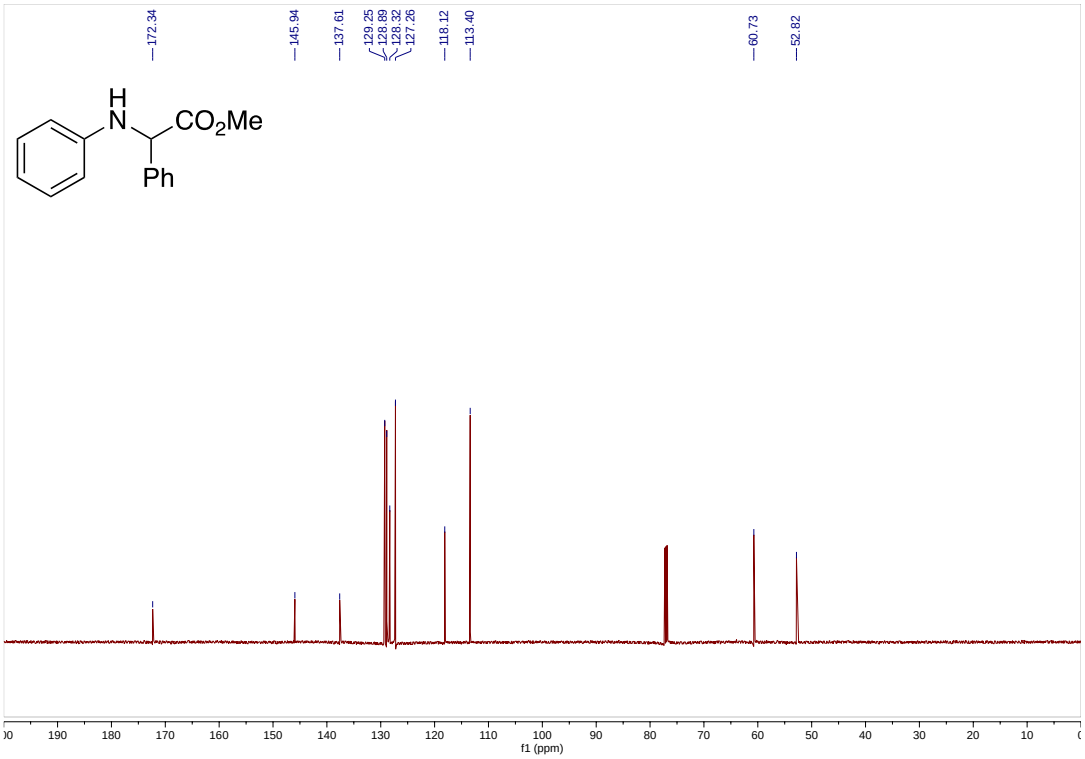


Methyl 2-phenyl-2-(phenylamino)acetate (12)

^{1}H NMR (600 MHz, Chloroform-*d*)

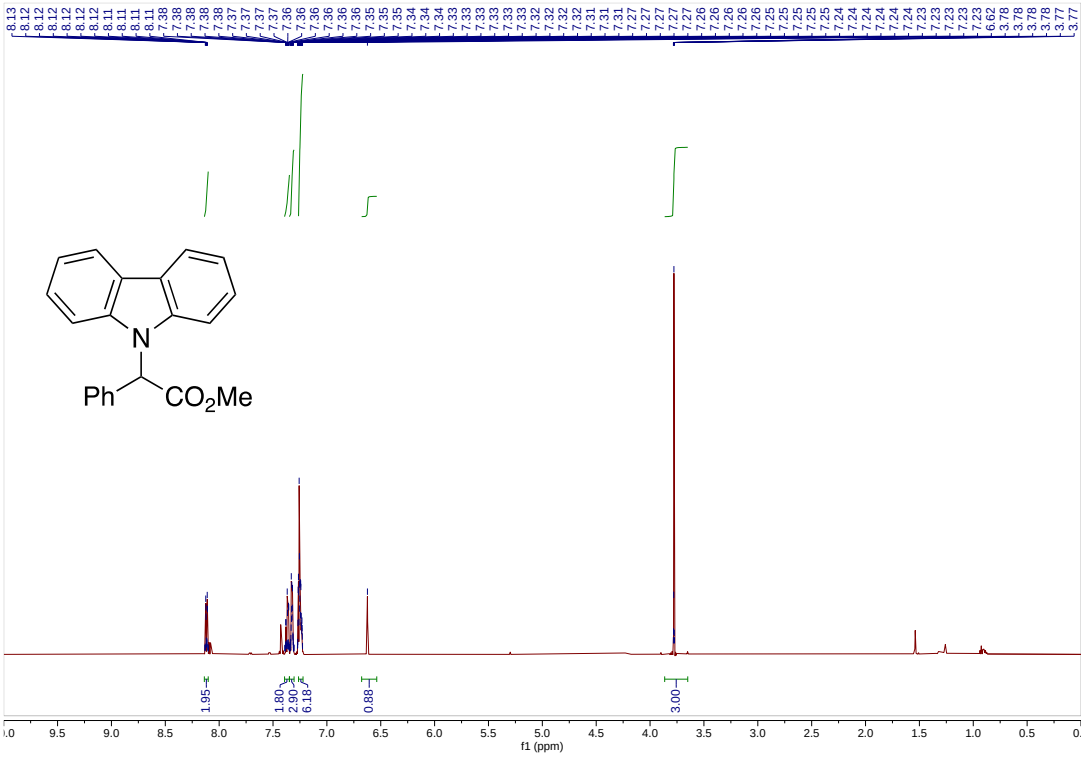


^{13}C NMR (151 MHz, Chloroform-*d*)

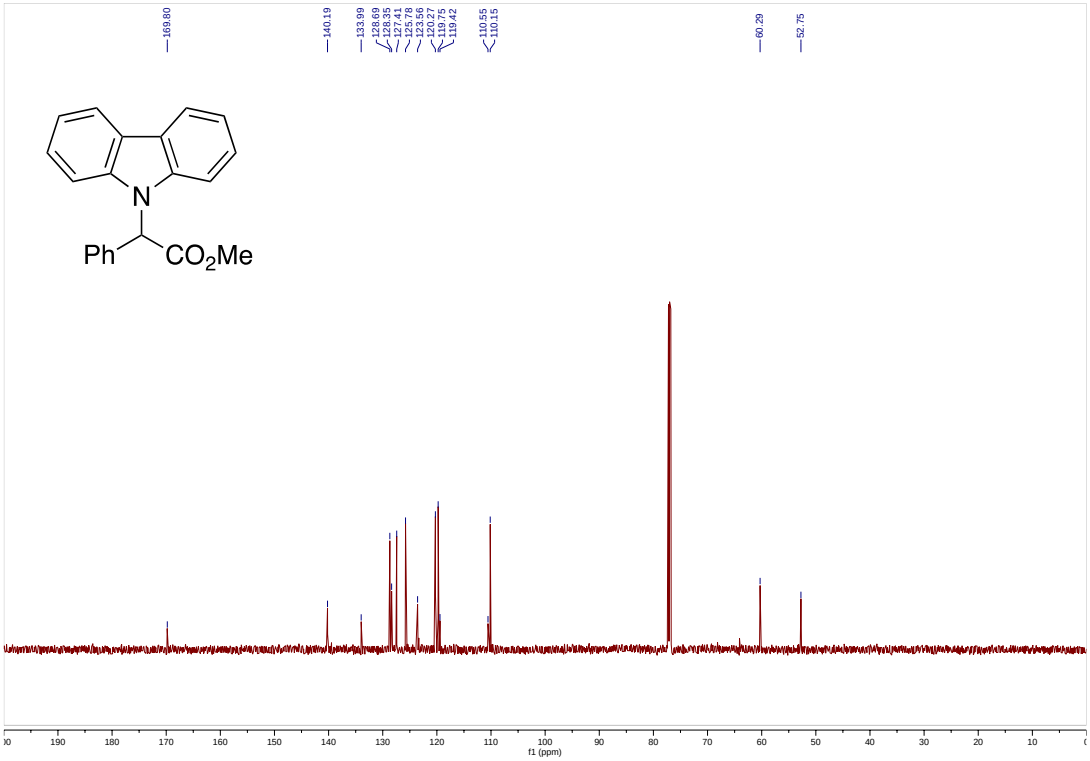


Methyl 2-(9*H*-carbazol-9-yl)-2-phenylacetate (13)

^{1}H NMR (600 MHz, Chloroform-*d*)

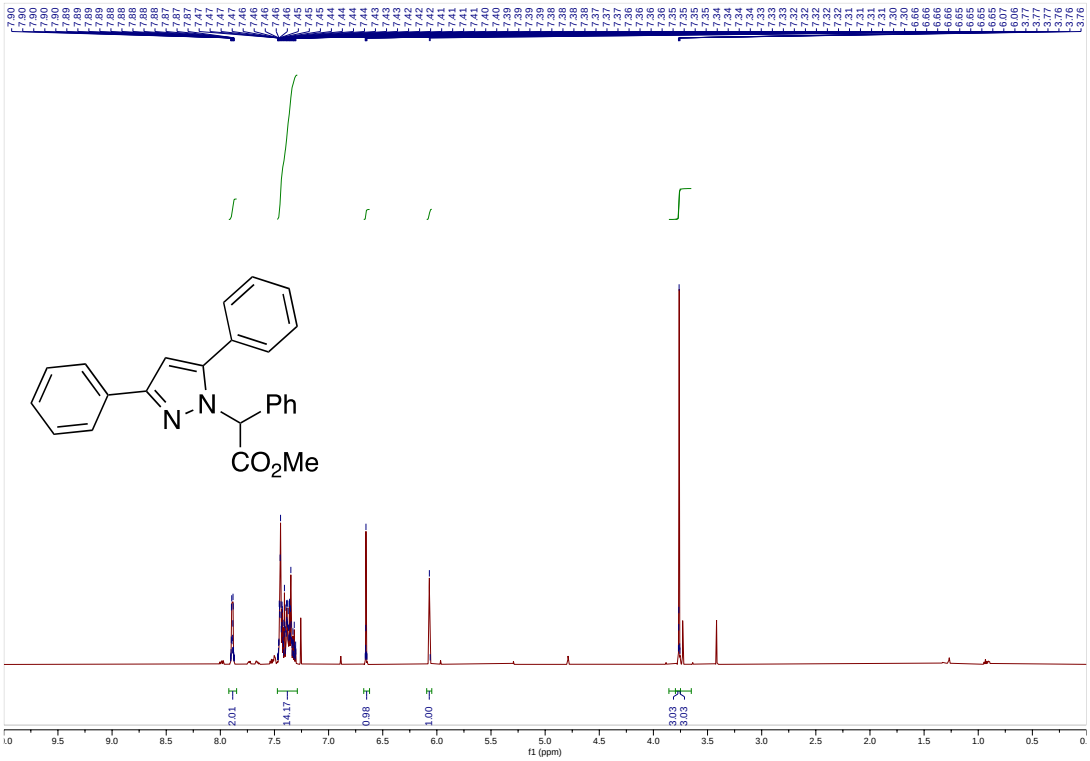


^{13}C NMR (151 MHz, Chloroform-*d*)

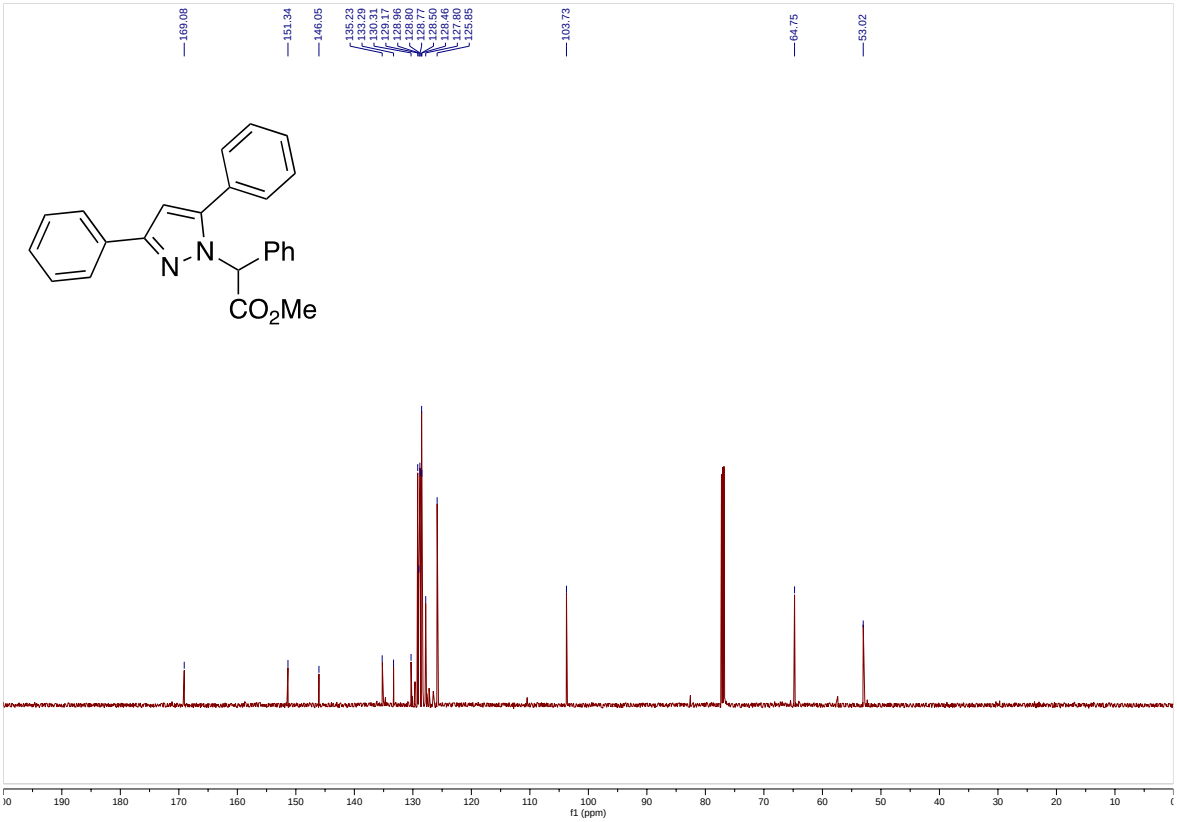


Methyl 2-(3,5-diphenyl-1*H*-pyrazol-1-yl)-2-phenylacetate (14)

^{1}H NMR (600 MHz, Chloroform-*d*)

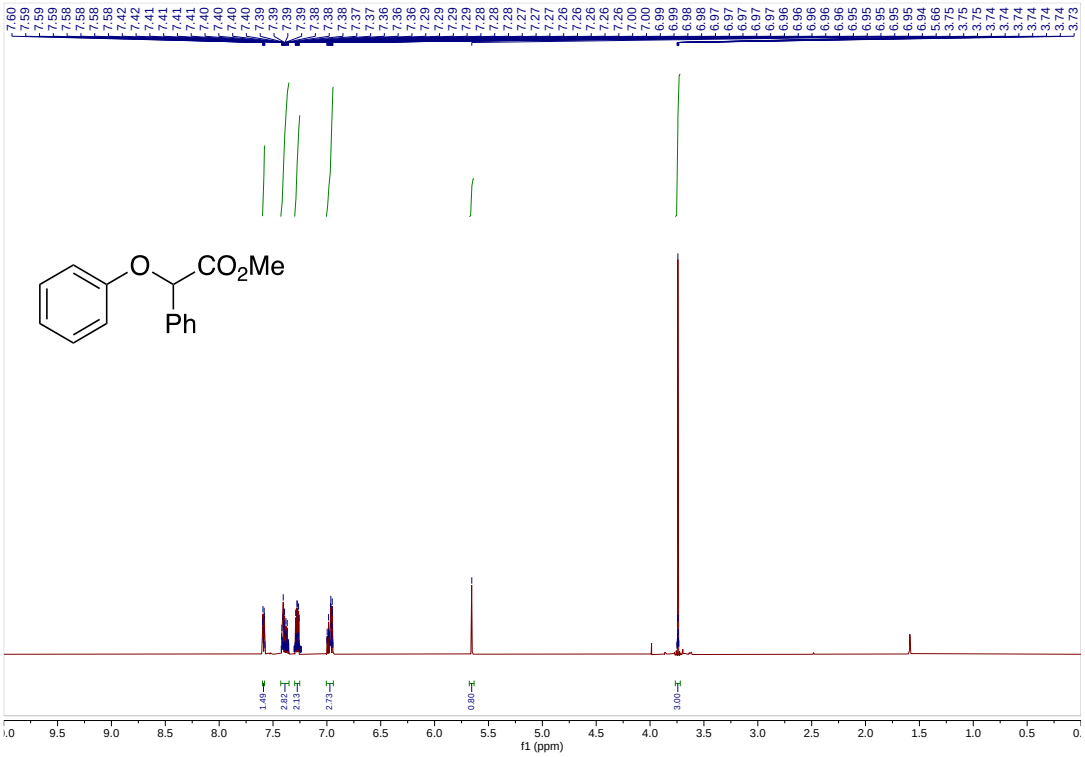


^{13}C NMR (151 MHz, Chloroform-*d*)

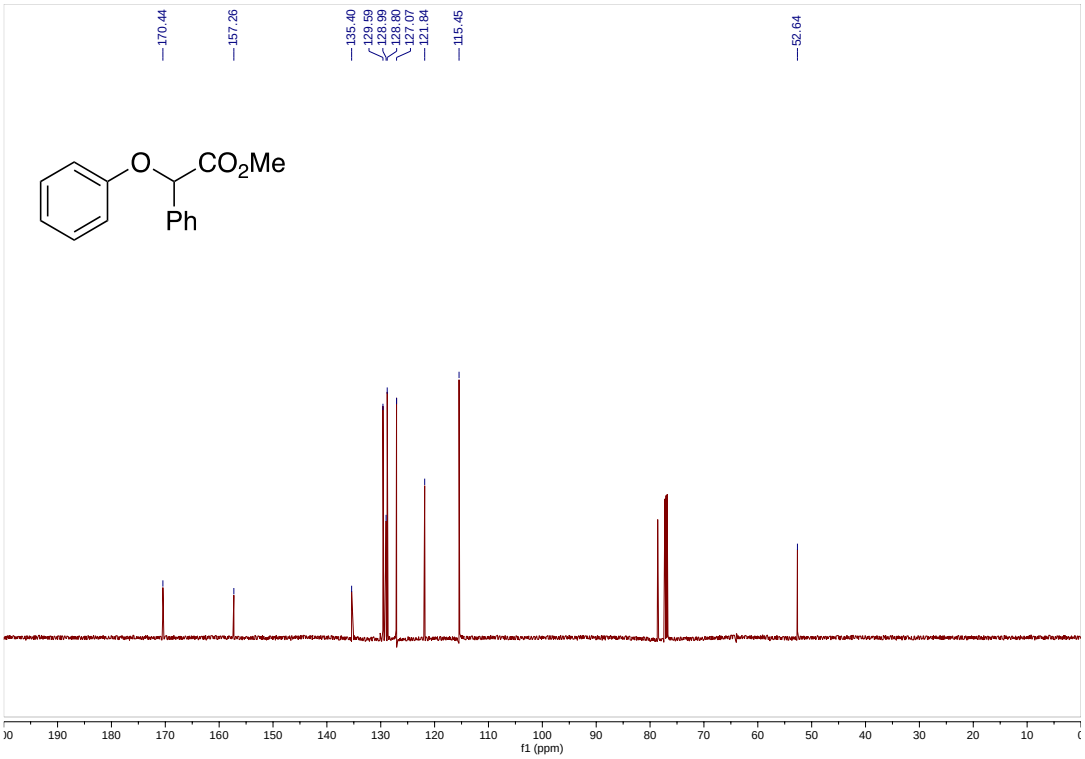


Methyl 2-phenoxy-2-phenylacetate (15)

^{1}H NMR (600 MHz, Chloroform-*d*)

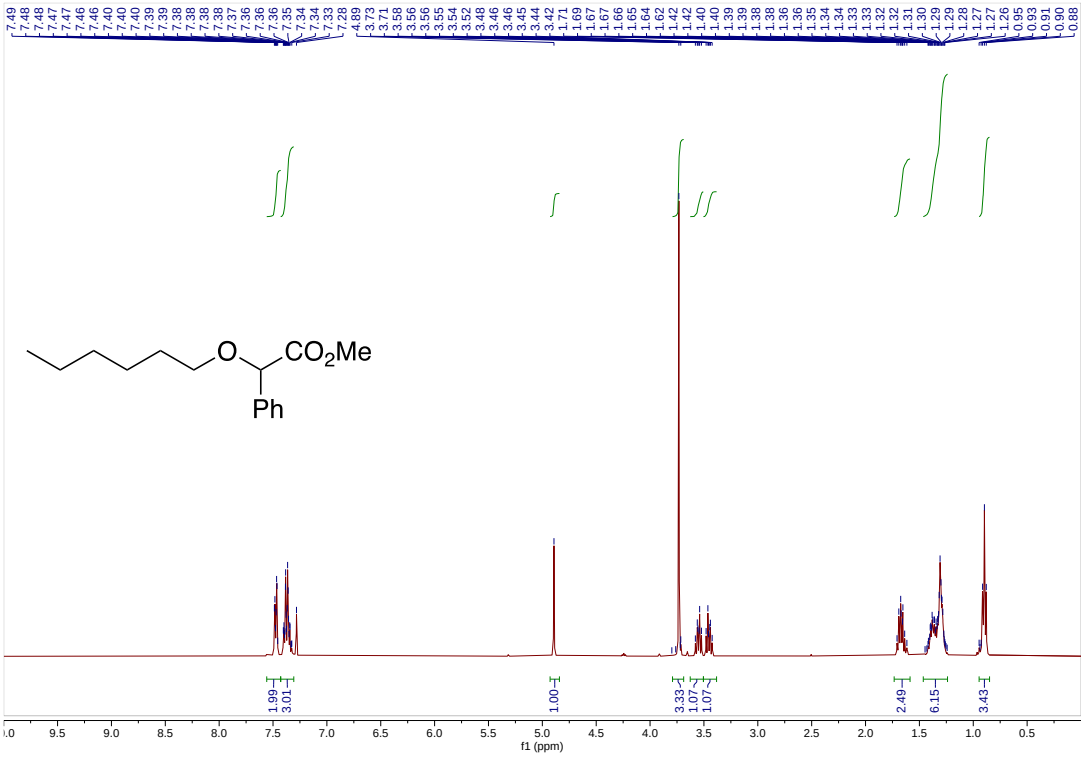


^{13}C NMR (151 MHz, Chloroform-*d*)

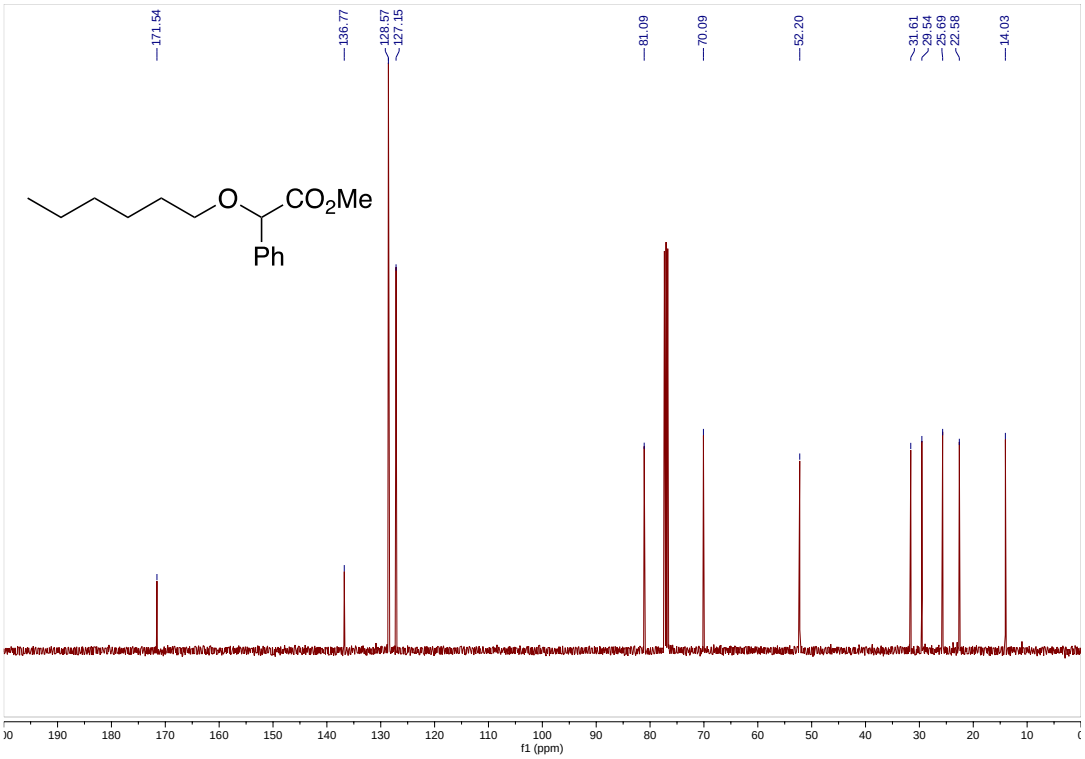


Methyl 2-(hexyloxy)-2-phenylacetate (16)

^{1}H NMR (400 MHz, Chloroform-*d*)

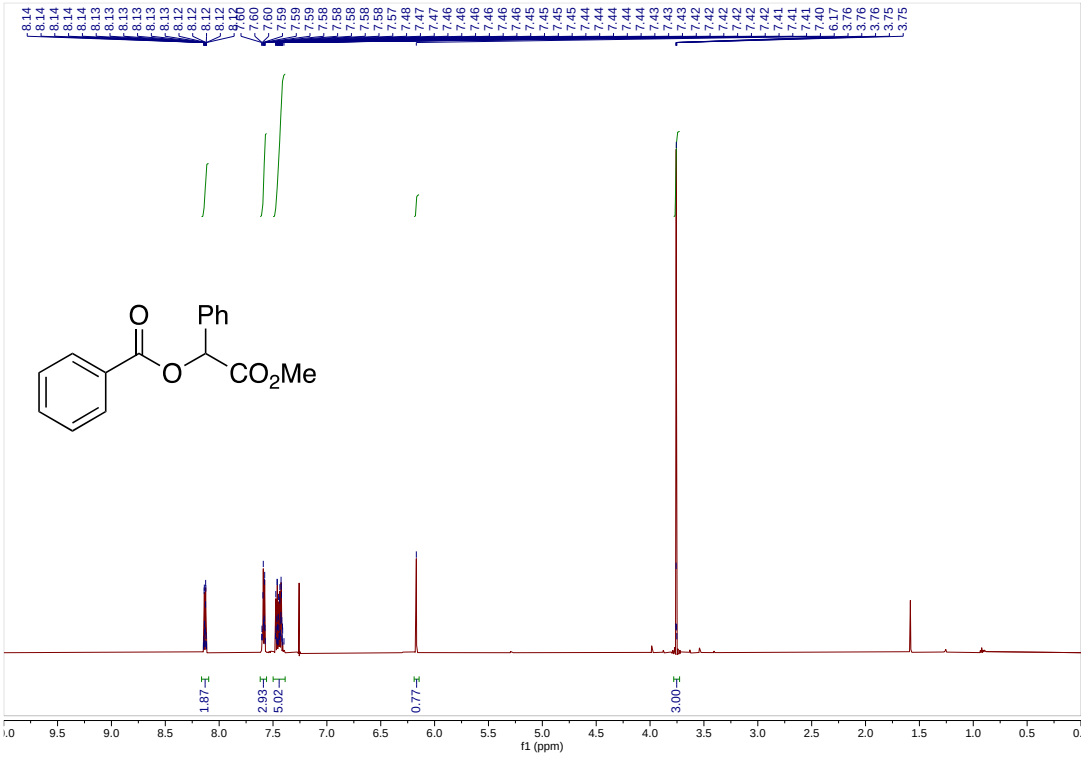


^{13}C NMR (101 MHz, Chloroform-*d*)

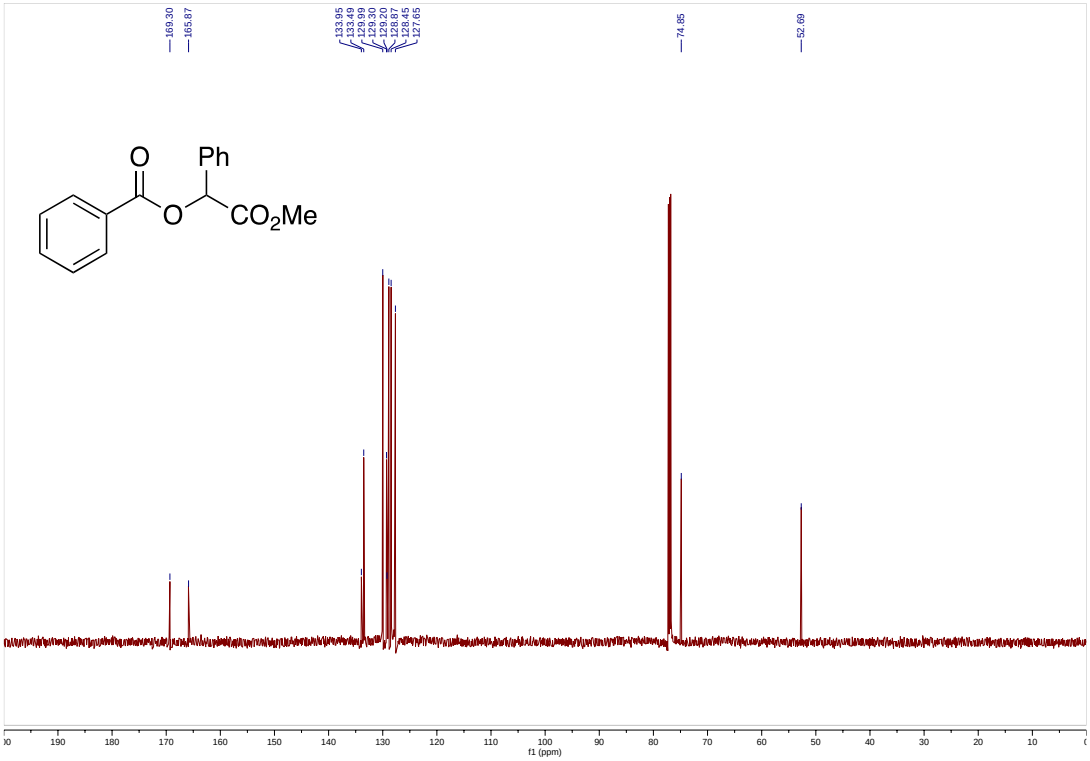


2-Methoxy-2-oxo-1-phenylethyl benzoate (17)

^{1}H NMR (600 MHz, Chloroform-*d*)

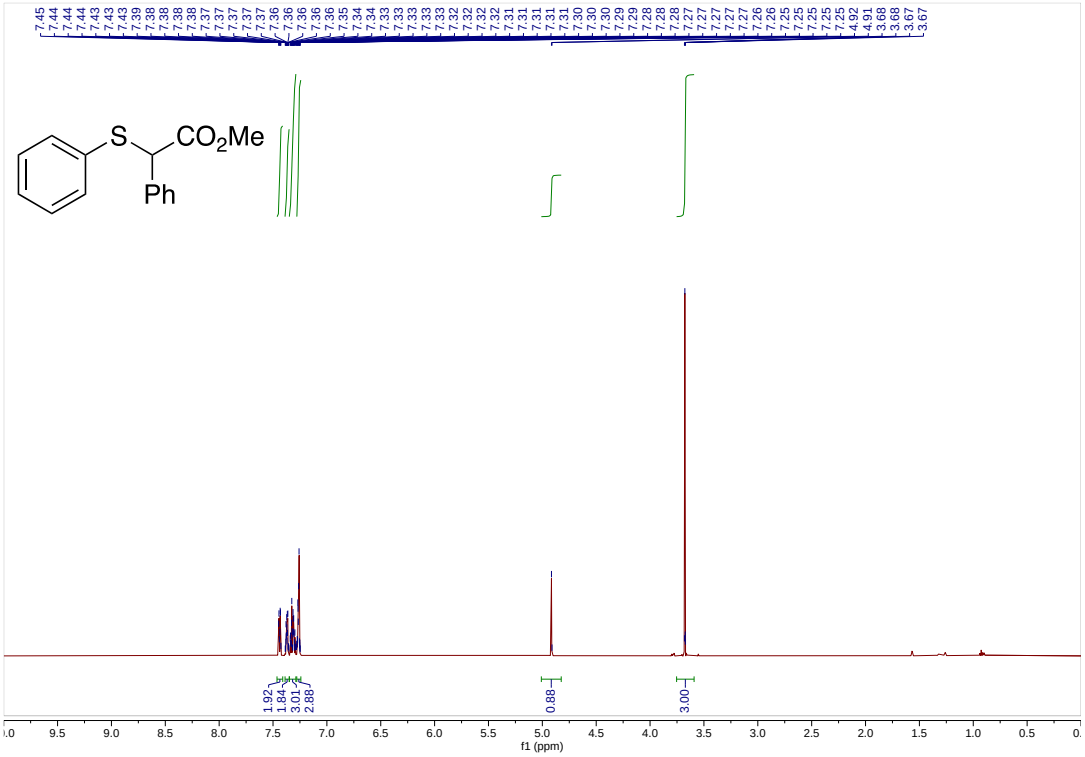


^{13}C NMR (151 MHz, Chloroform-*d*)

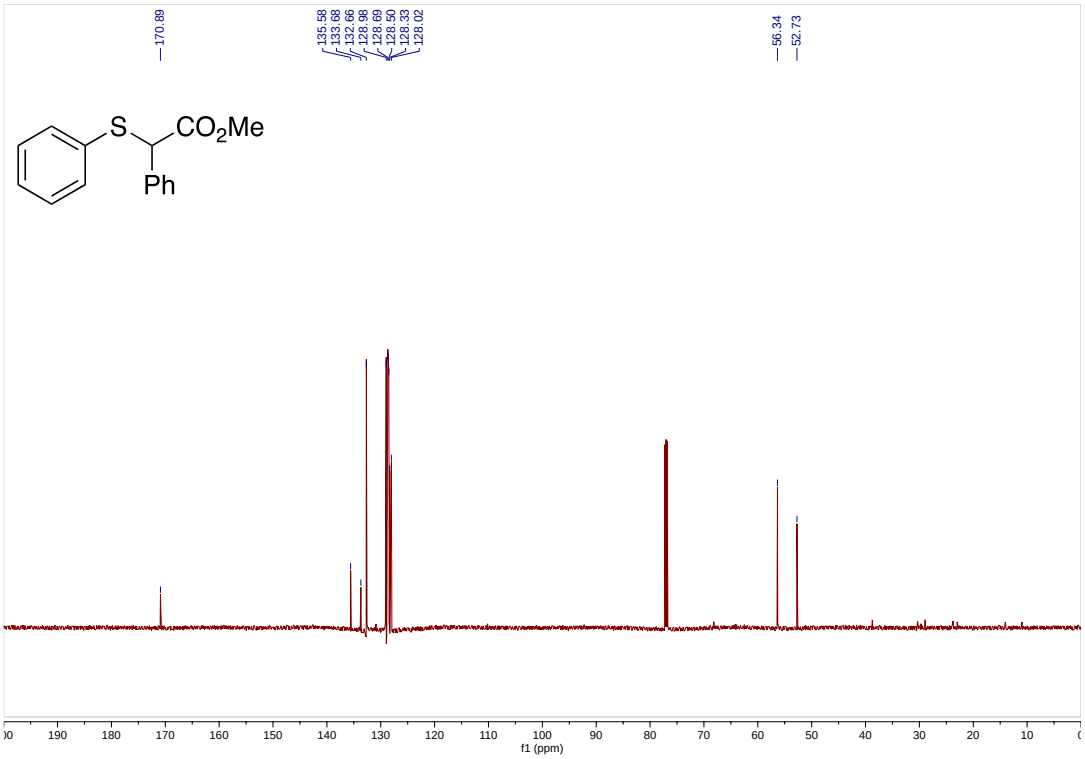


Methyl 2-phenyl-2-(phenylthio)acetate (18)

^{1}H NMR (600 MHz, Chloroform-*d*)

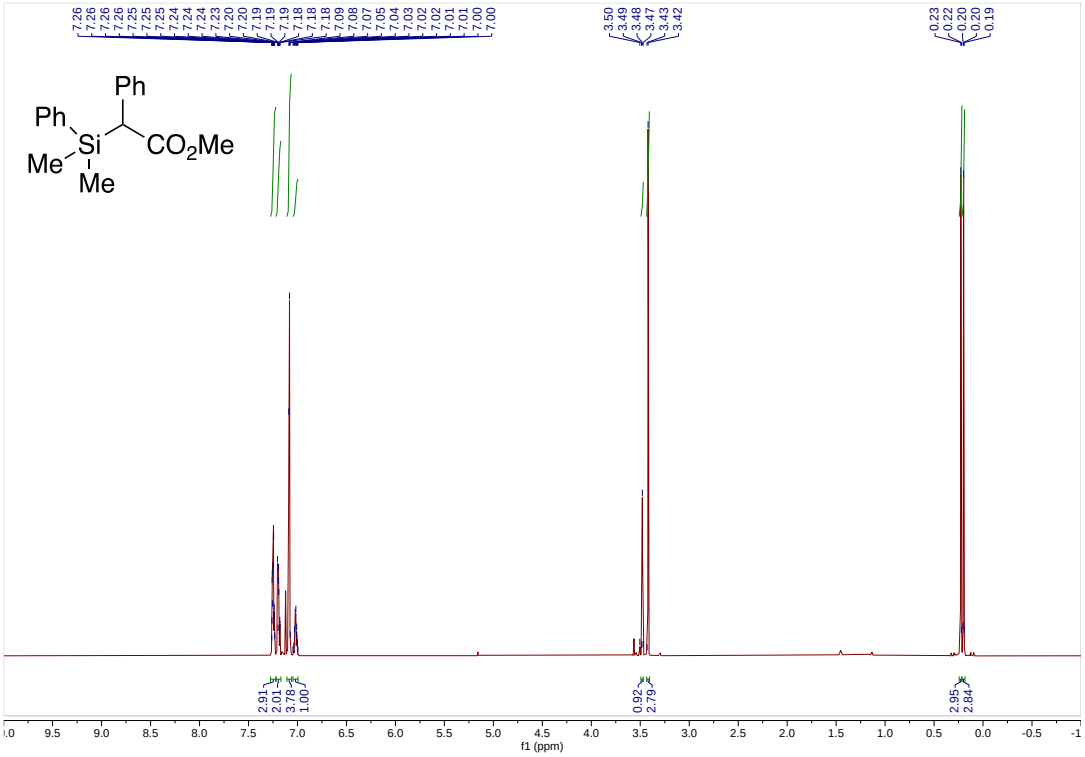


^{13}C NMR (151 MHz, Chloroform-*d*)

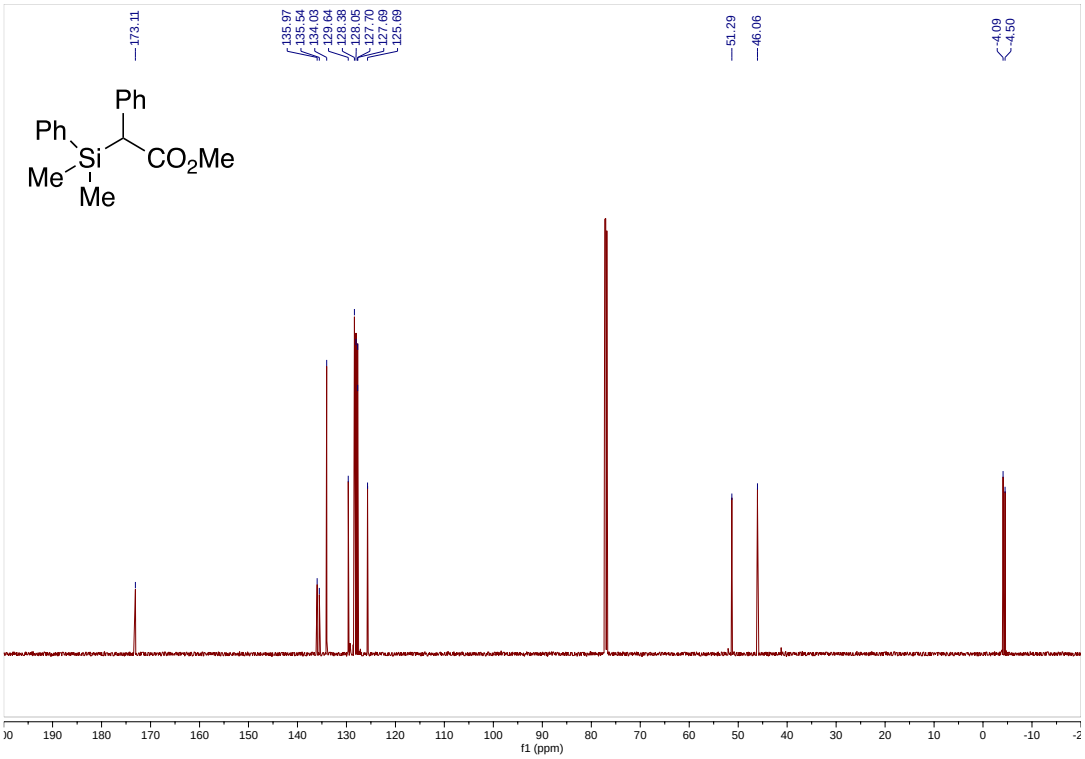


Methyl 2-(dimethyl(phenyl)silyl)-2-phenylacetate (19)

^{1}H NMR (600 MHz, Chloroform-*d*)

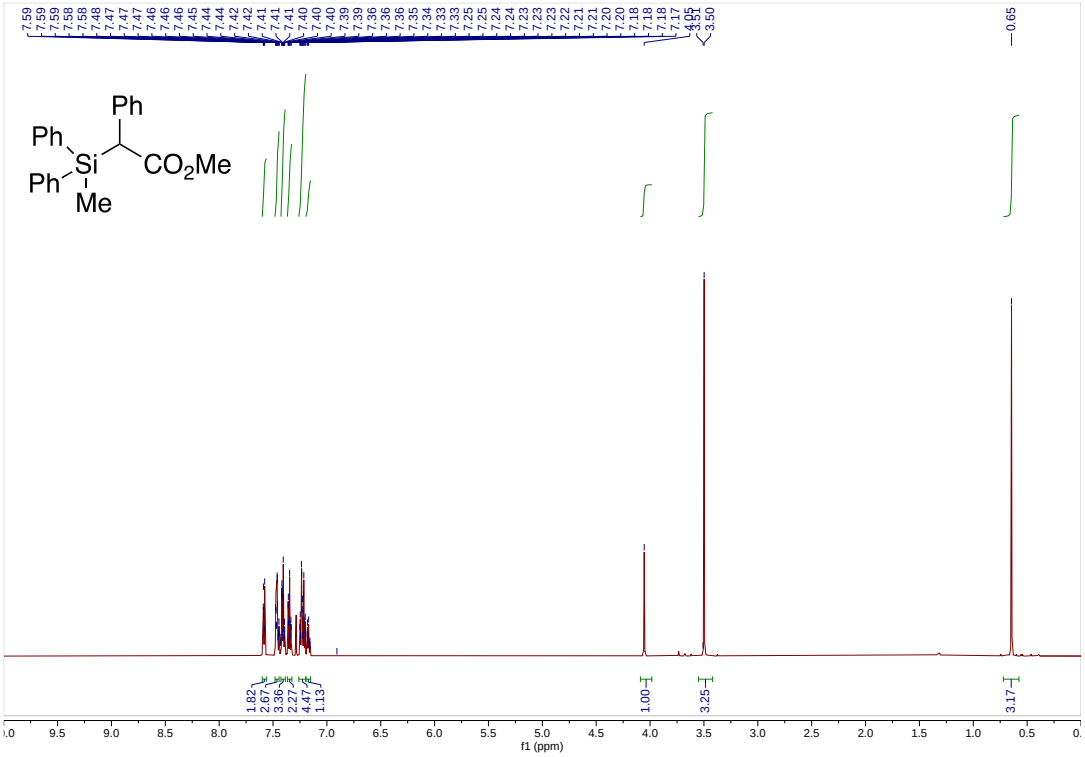


^{13}C NMR (151 MHz, Chloroform-*d*)

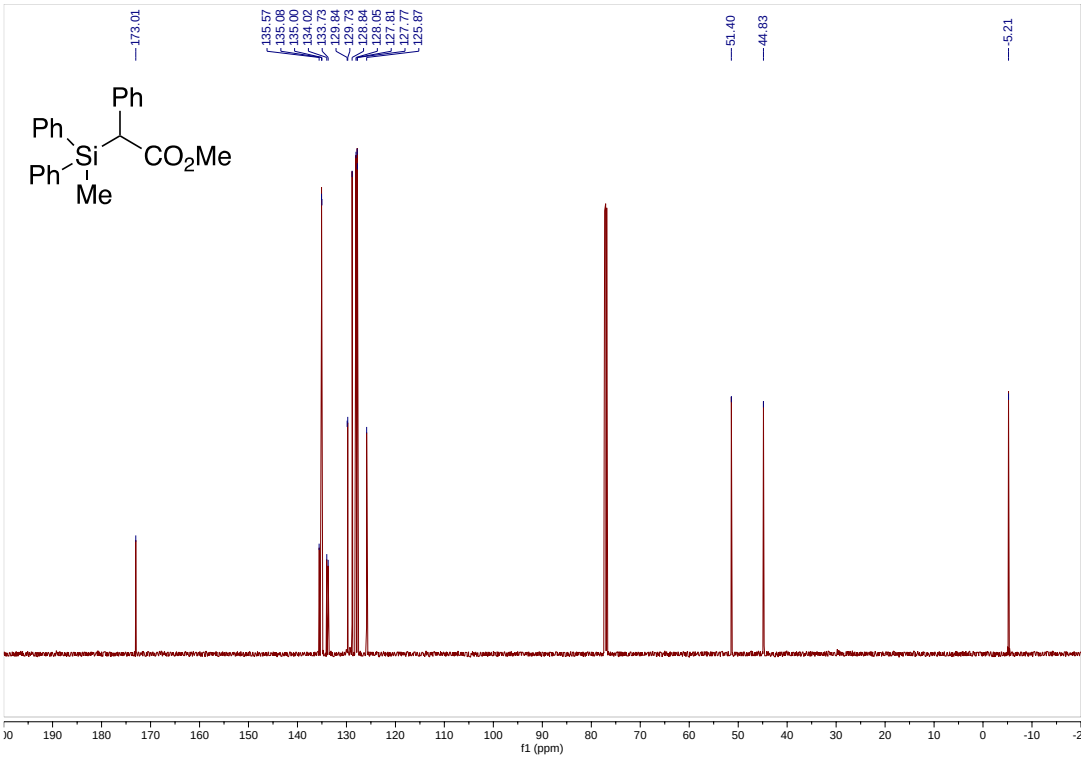


Methyl 2-(methyldiphenylsilyl)-2-phenylacetate (20)

^{1}H NMR (600 MHz, Chloroform-*d*)

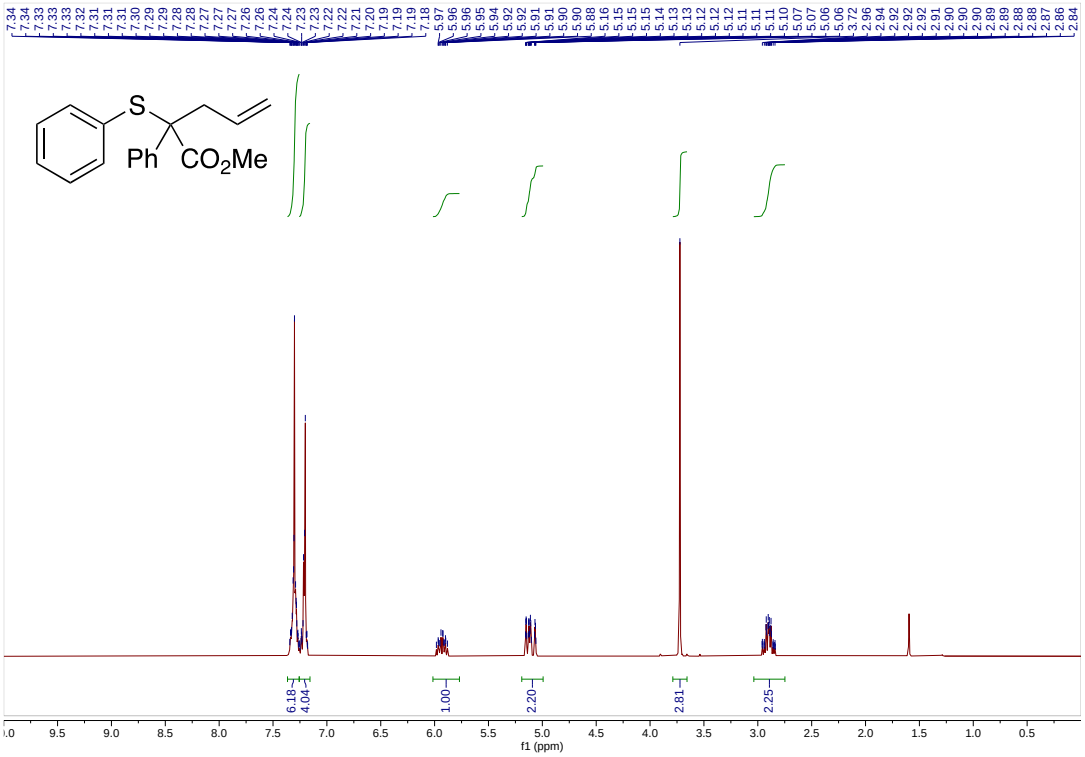


^{13}C NMR (151 MHz, Chloroform-*d*)

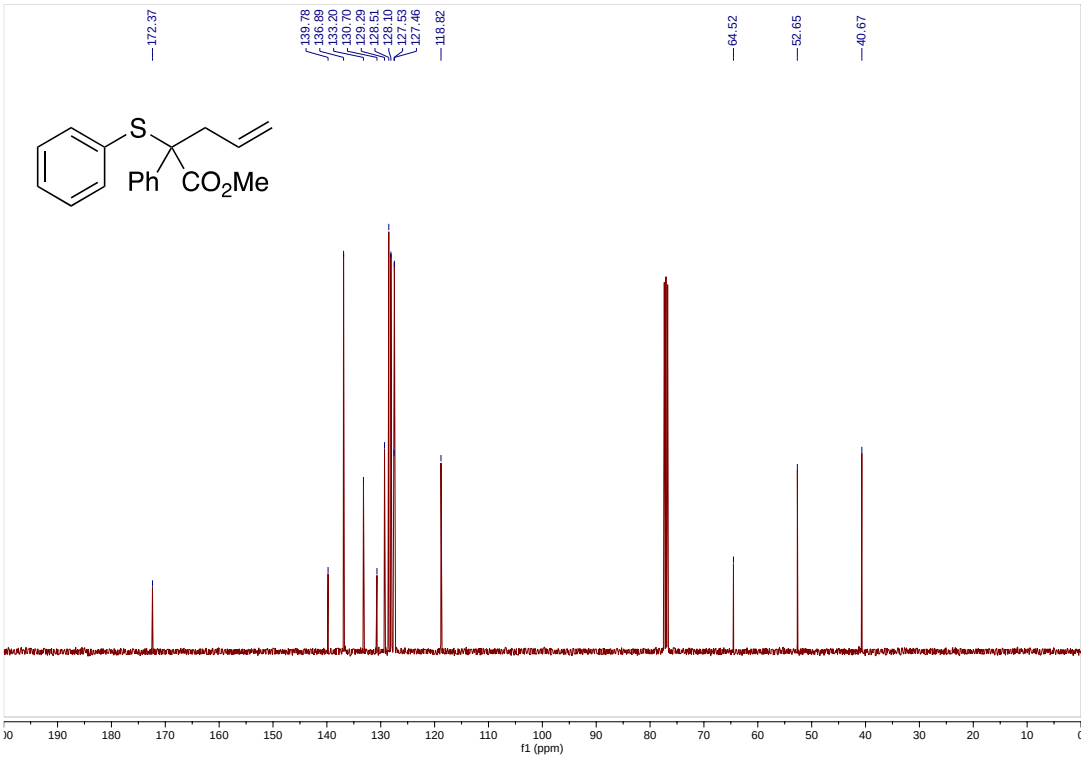


Methyl 2-phenyl-2-(phenylthio)pent-4-enoate (21)

^{1}H NMR (600 MHz, Chloroform-*d*)

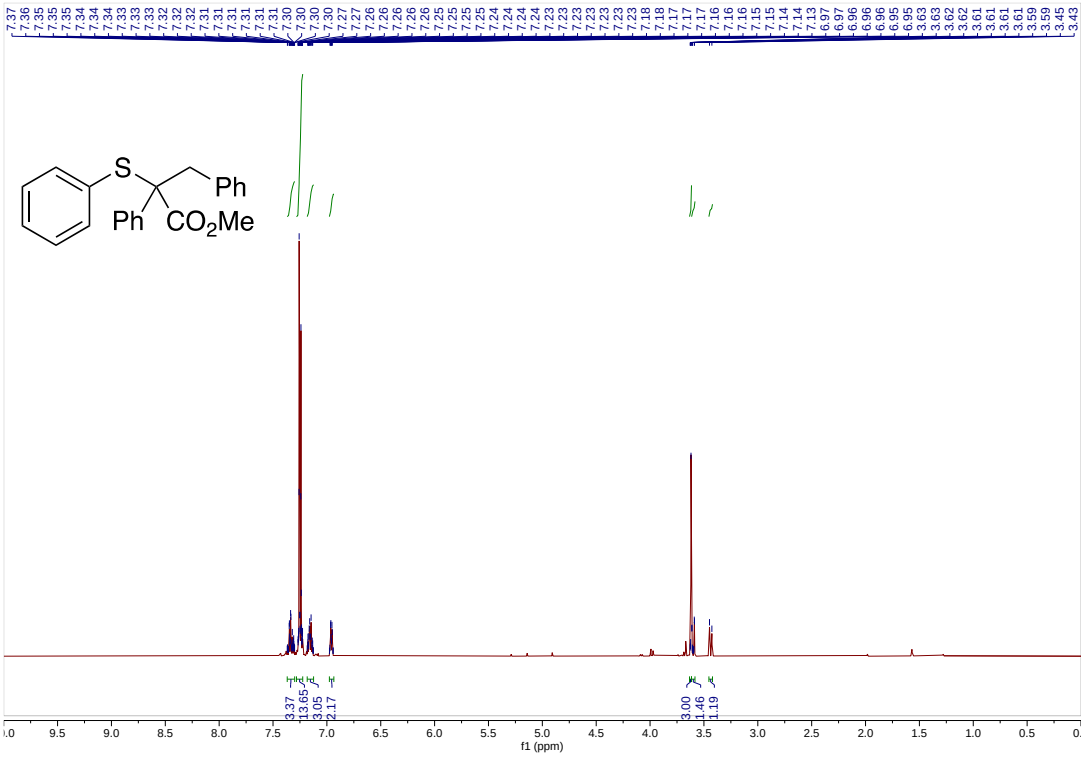


^{13}C NMR (151 MHz, Chloroform-*d*)

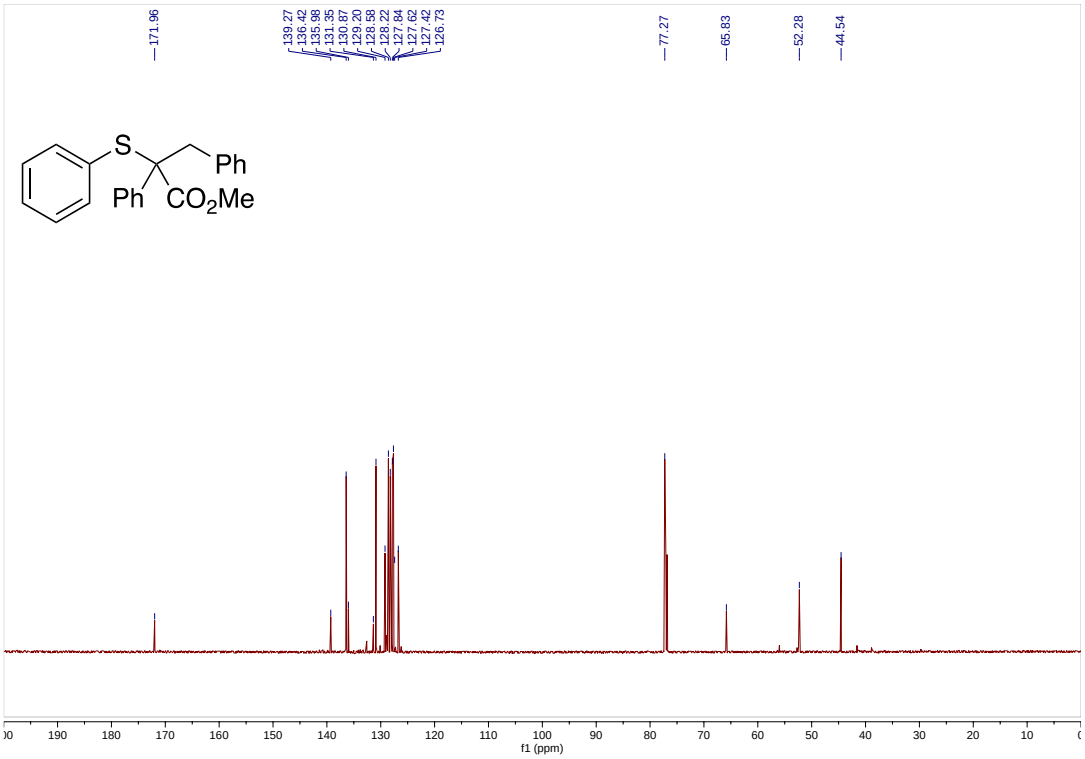


Methyl 2,3-diphenyl-2-(phenylthio)propanoate (22)

^{1}H NMR (600 MHz, Chloroform-*d*)

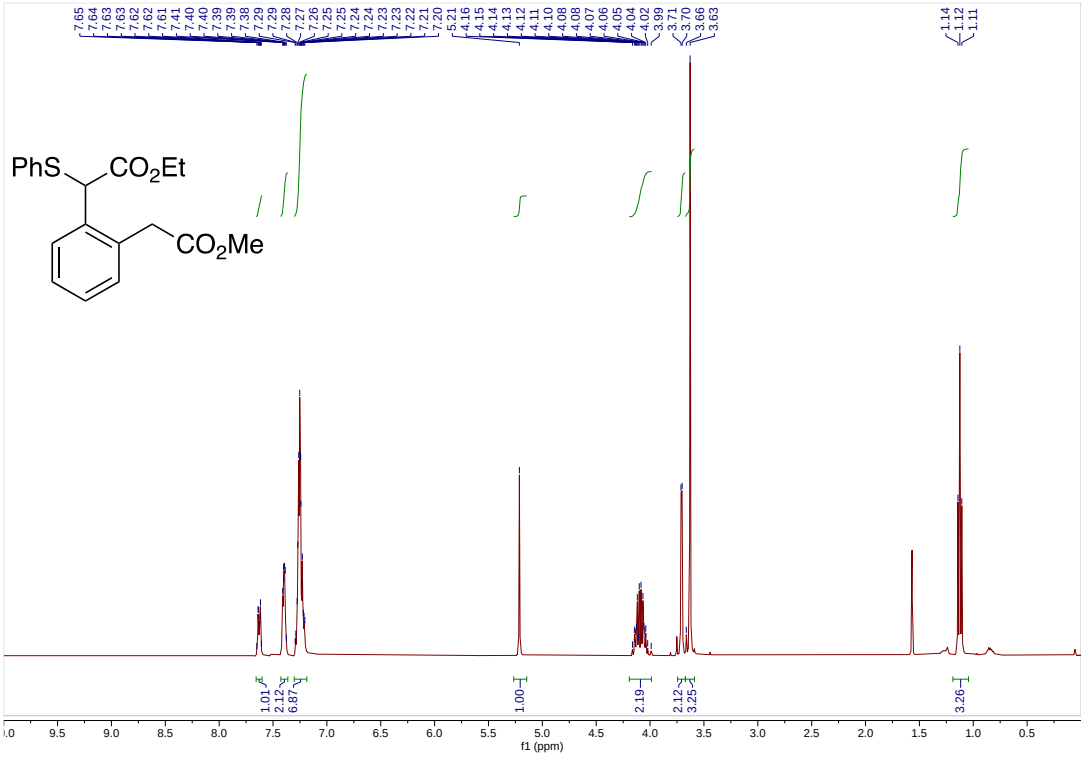


^{13}C NMR (151 MHz, Chloroform-*d*)

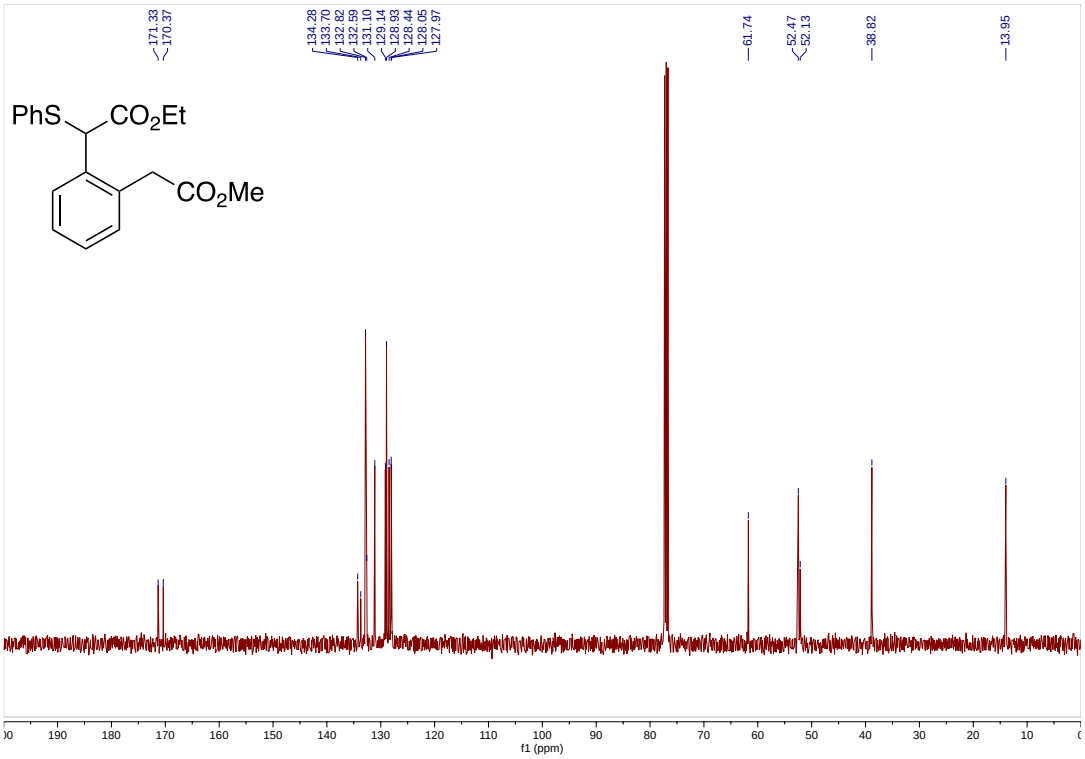


Ethyl 2-(2-(2-methoxy-2-oxoethyl)phenyl)-2-(phenylthio)acetate (23)

^{1}H NMR (400 MHz, Chloroform-*d*)

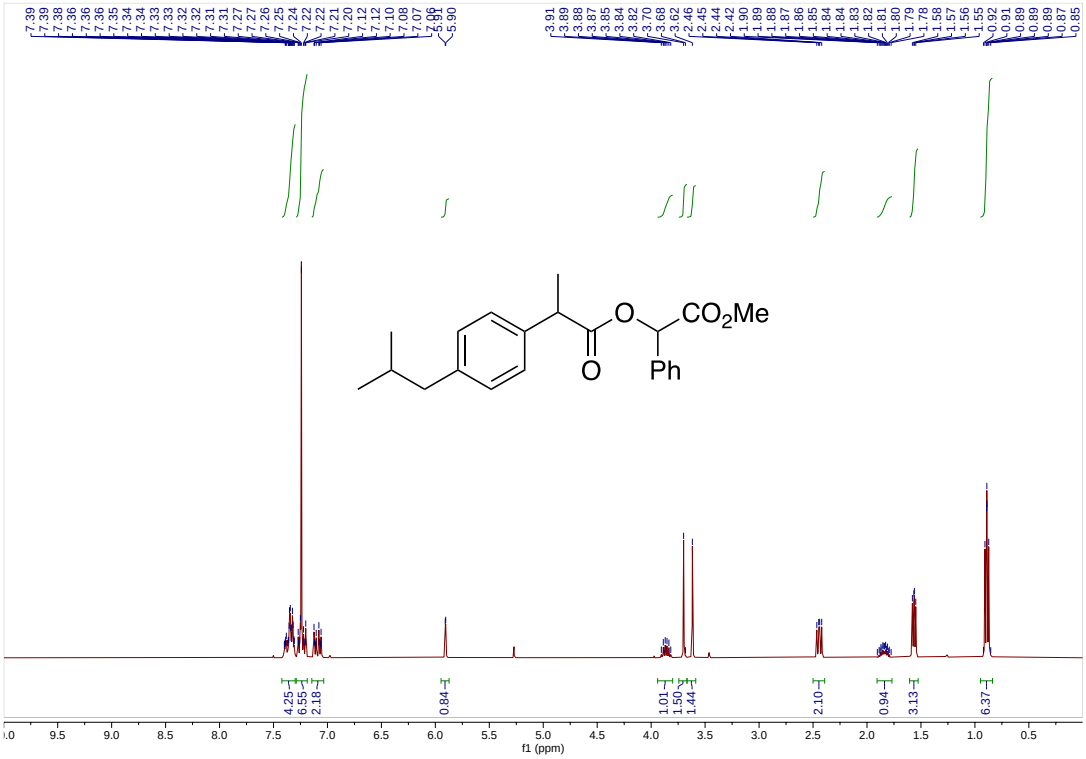


^{13}C NMR (101 MHz, Chloroform-*d*)

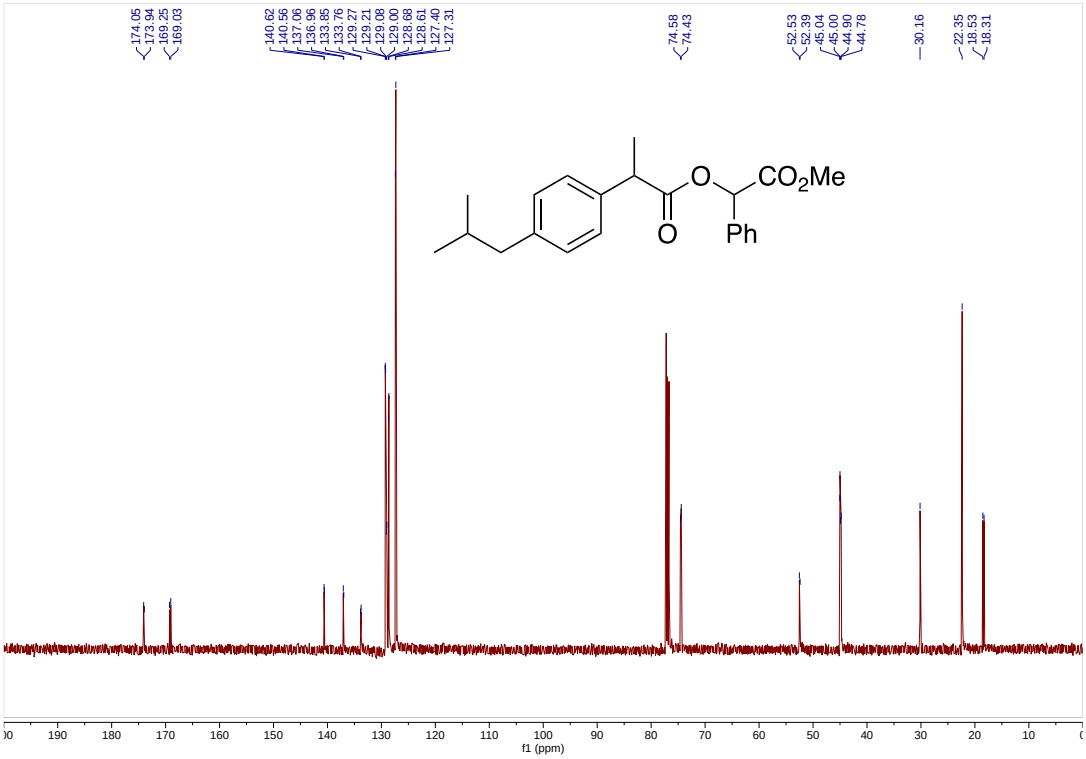


2-Methoxy-2-oxo-1-phenylethyl 2-(4-isobutylphenyl)propanoate (24)

^{1}H NMR (400 MHz, Chloroform-*d*)

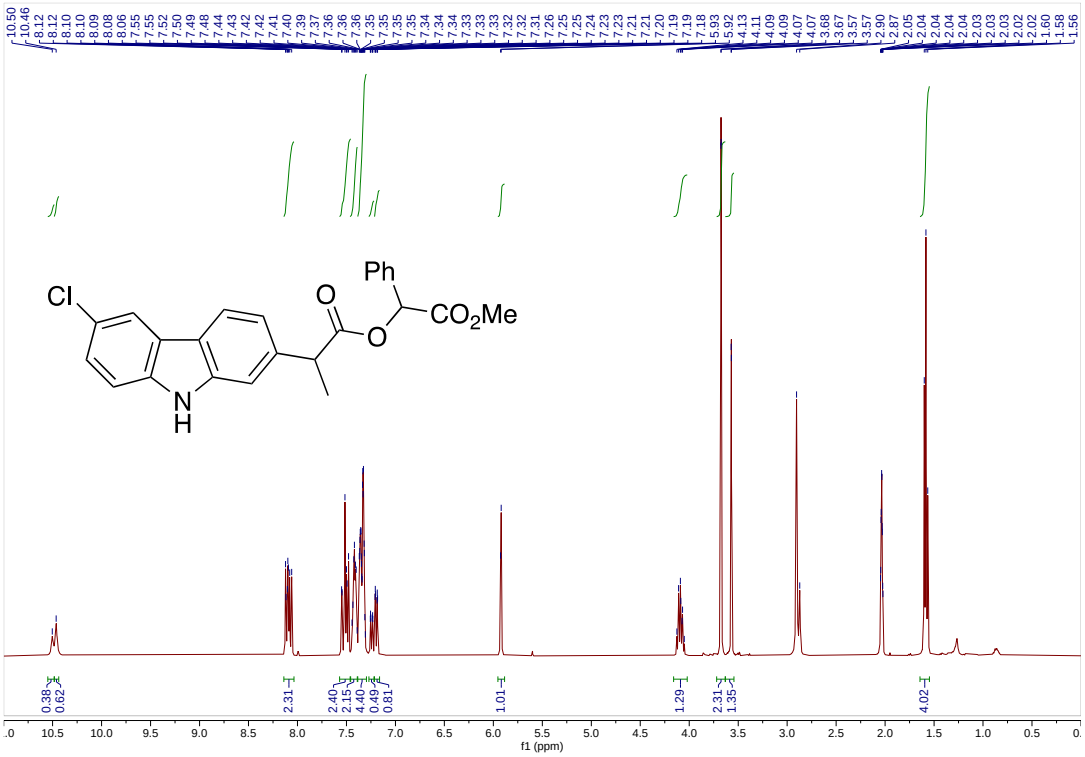


^{13}C NMR (101 MHz, Chloroform-*d*)

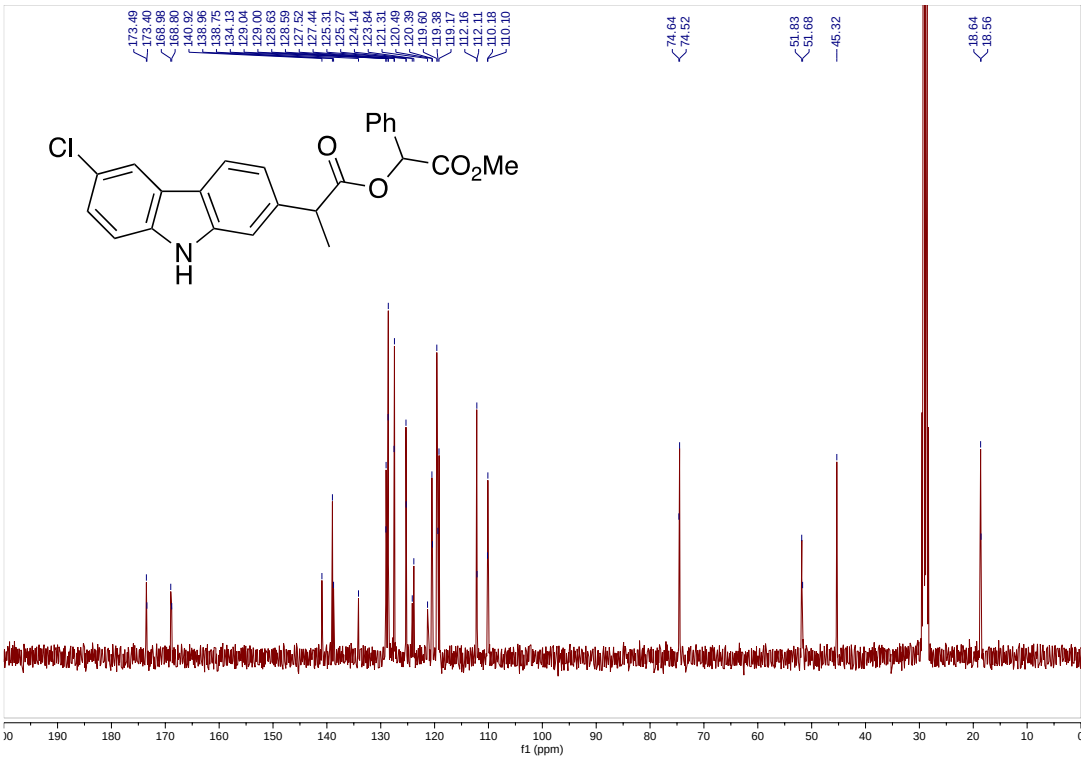


2-Methoxy-2-oxo-1-phenylethyl 2-(6-chloro-9*H*-carbazol-2-yl)propanoate (25)

^{1}H NMR (400 MHz, Acetone)

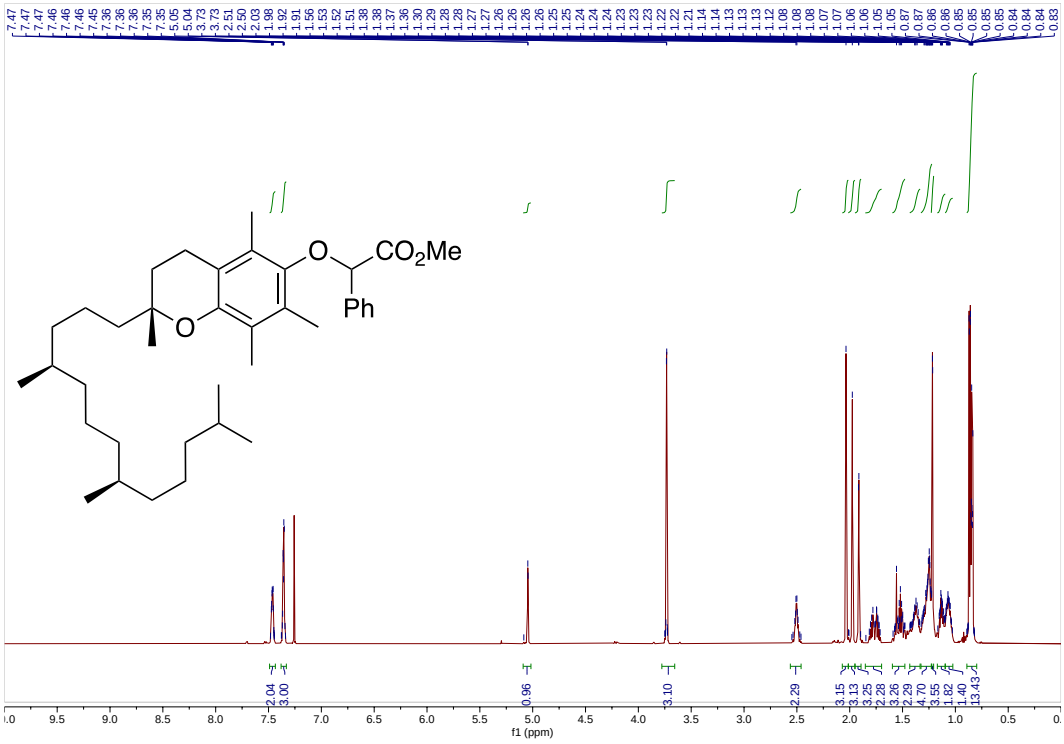


^{13}C NMR (101 MHz, Acetone)

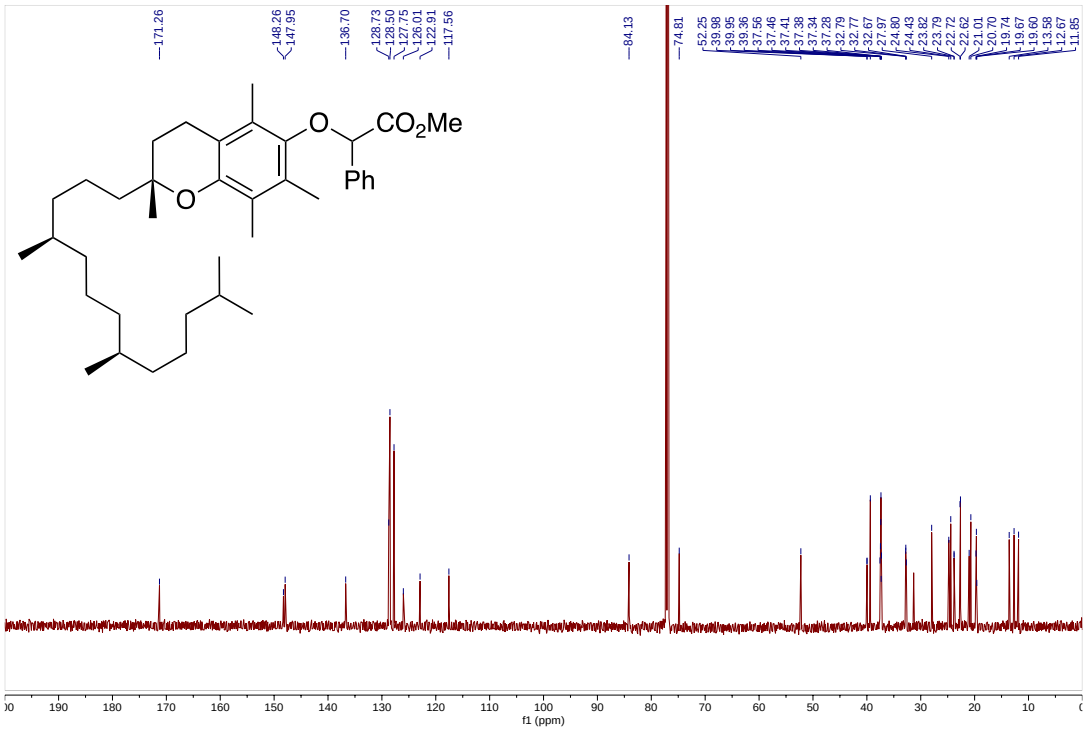


Methyl 2-phenyl-2-(((*R*)-2,5,7,8-tetramethyl-2-((4*R*,8*R*)-4,8,12-trimethyltridecyl) chroman-6-yl)oxy)acetate (26)

^{1}H NMR (400 MHz, Chloroform-*d*)

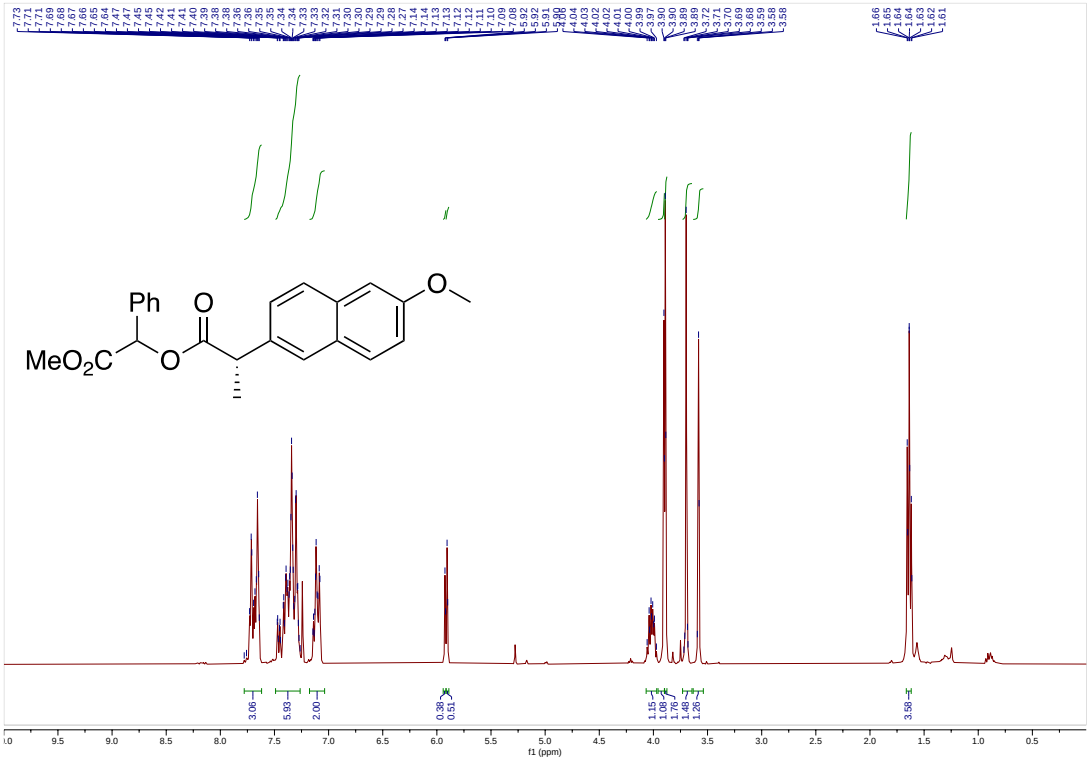


^{13}C NMR (101 MHz, Chloroform-*d*)

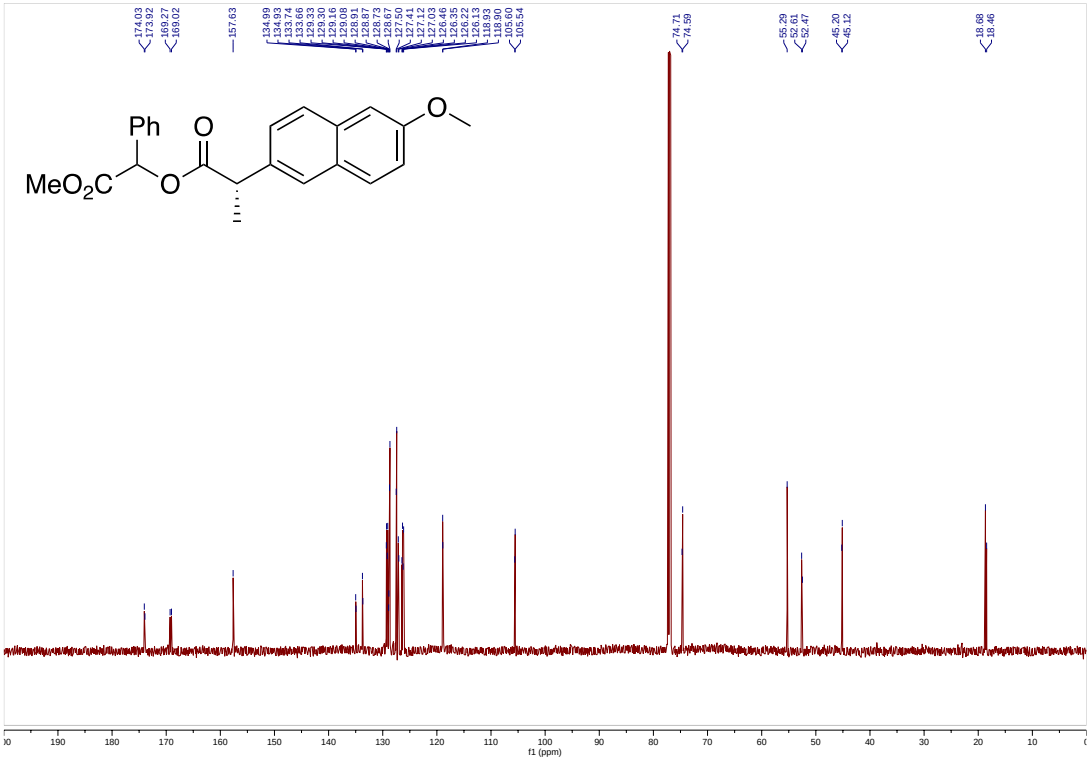


2-Methoxy-2-oxo-1-phenylethyl (2*S*)-2-(6-methoxynaphthalen-2-yl)propanoate (27)

^{1}H NMR (600 MHz, Chloroform-*d*)

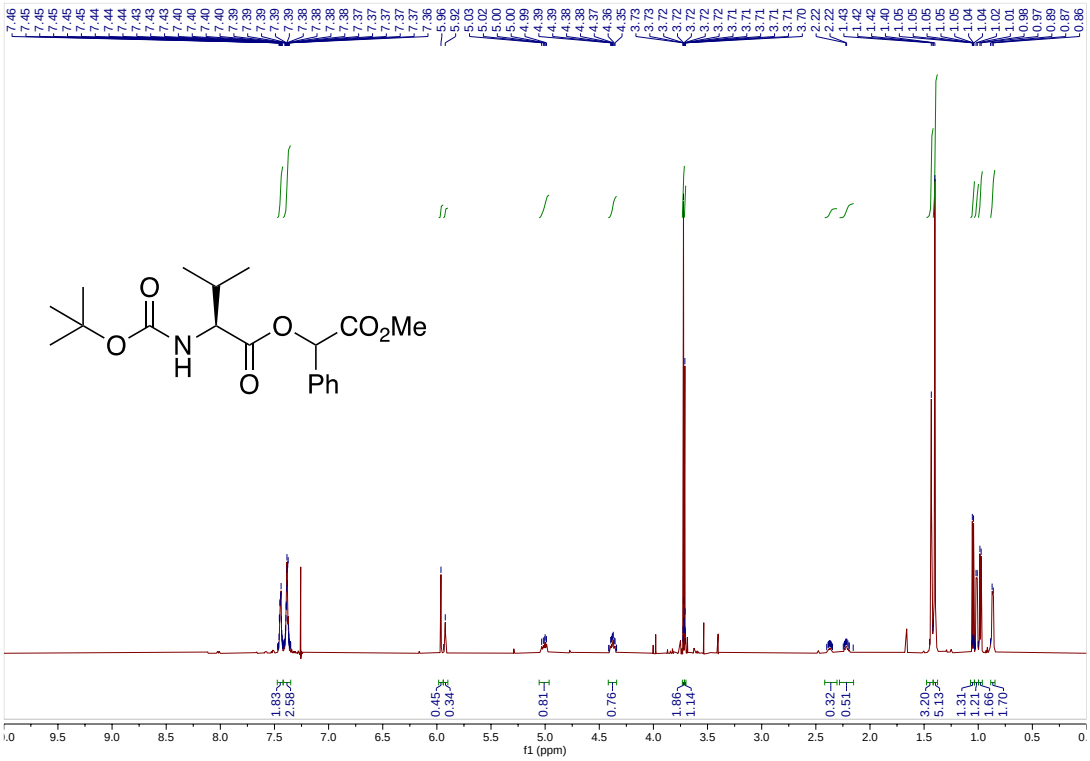


^{13}C NMR (151 MHz, Chloroform-*d*)

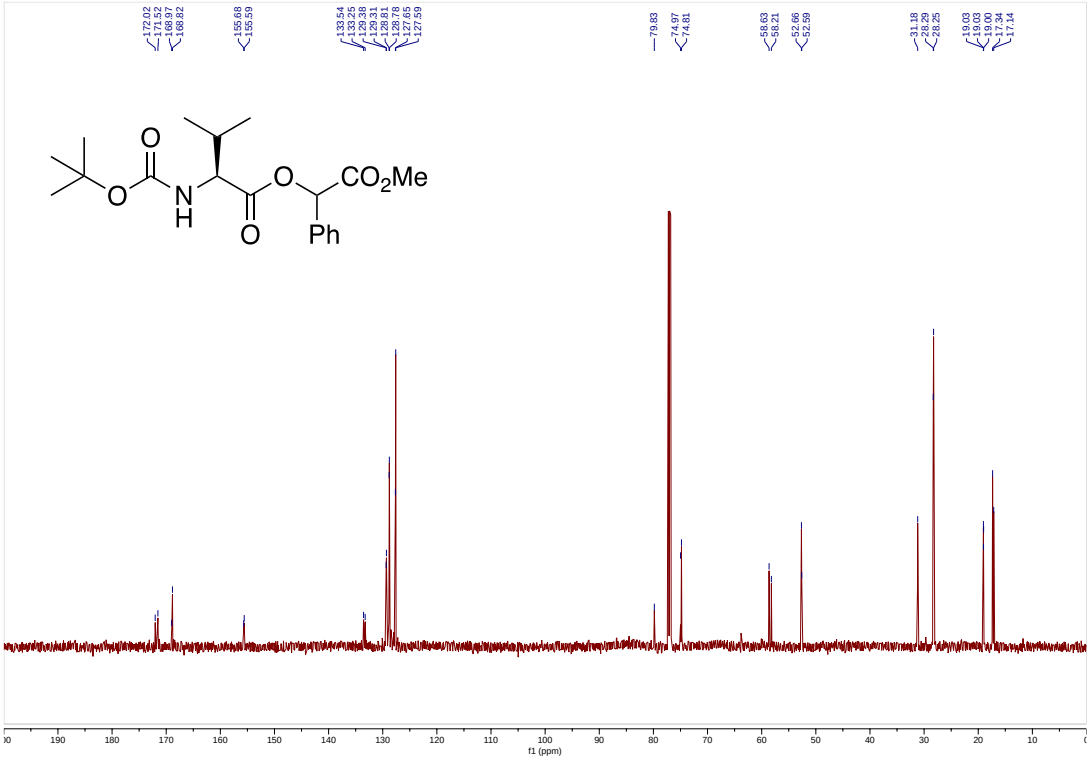


2-Methoxy-2-oxo-1-phenylethyl (*tert*-butoxycarbonyl)-*L*-valinate (28)

^{1}H NMR (600 MHz, Chloroform-*d*)

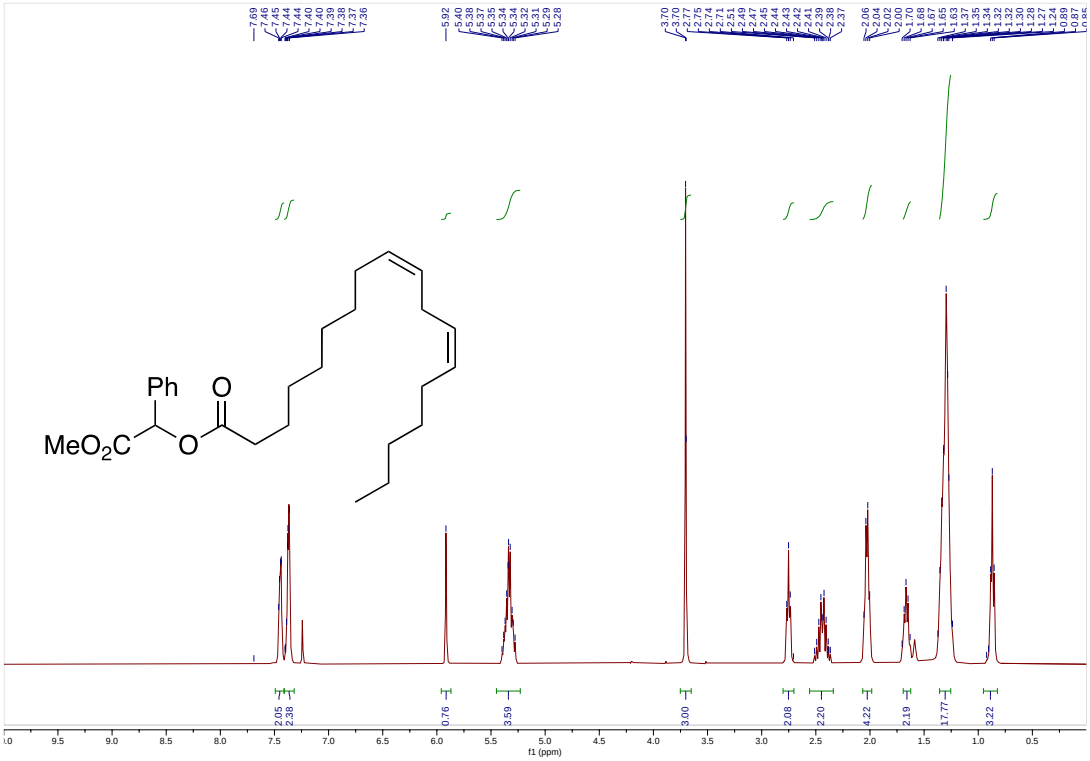


^{13}C NMR (151 MHz, Chloroform-*d*)

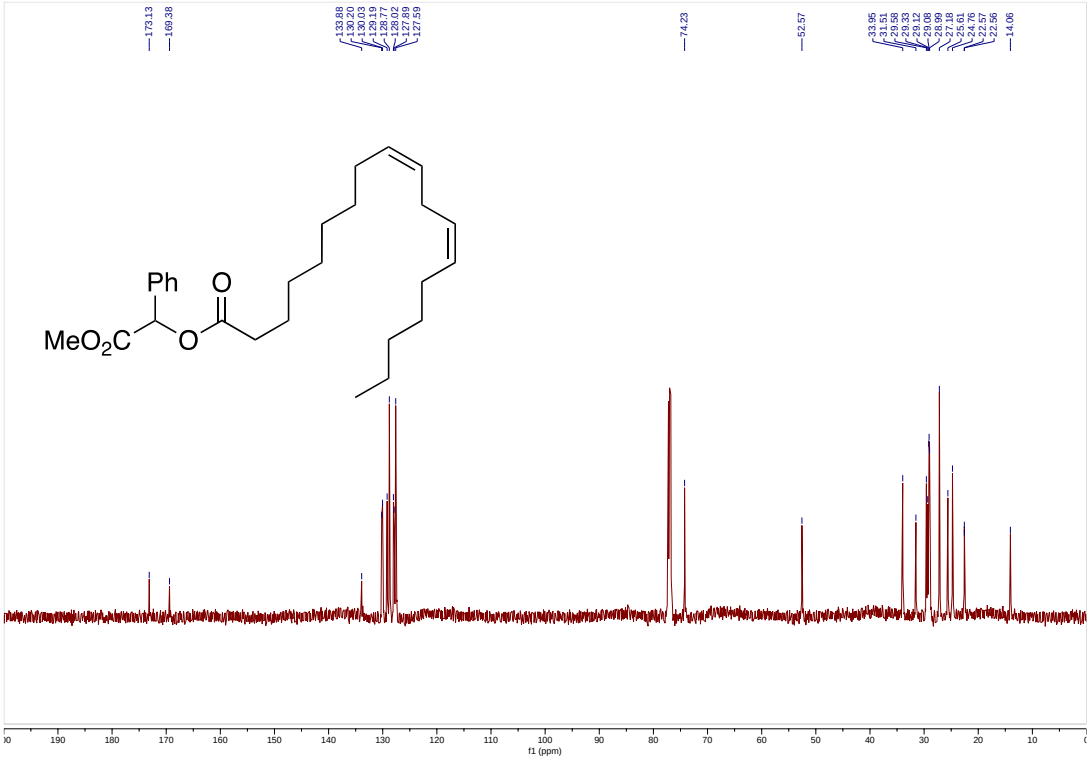


2-Methoxy-2-oxo-1-phenylethyl (9*Z*,12*Z*)-octadeca-9,12-dienoate (29)

^{1}H NMR (600 MHz, Chloroform-*d*)

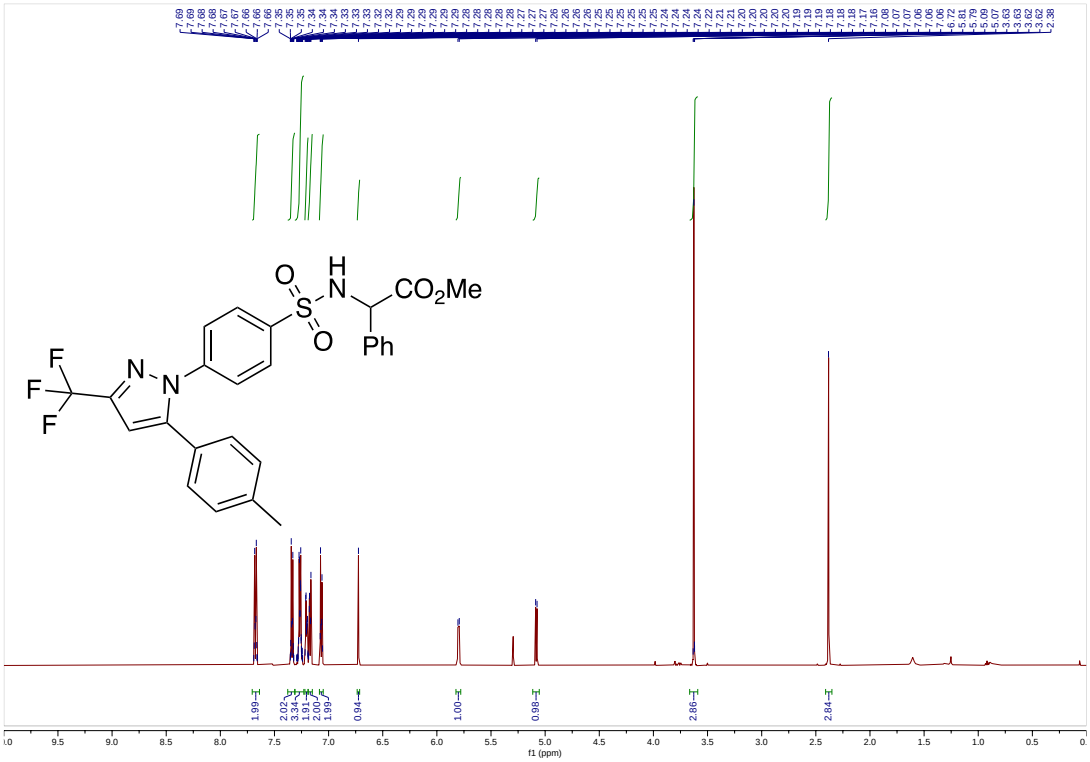


^{13}C NMR (151 MHz, Chloroform-*d*)

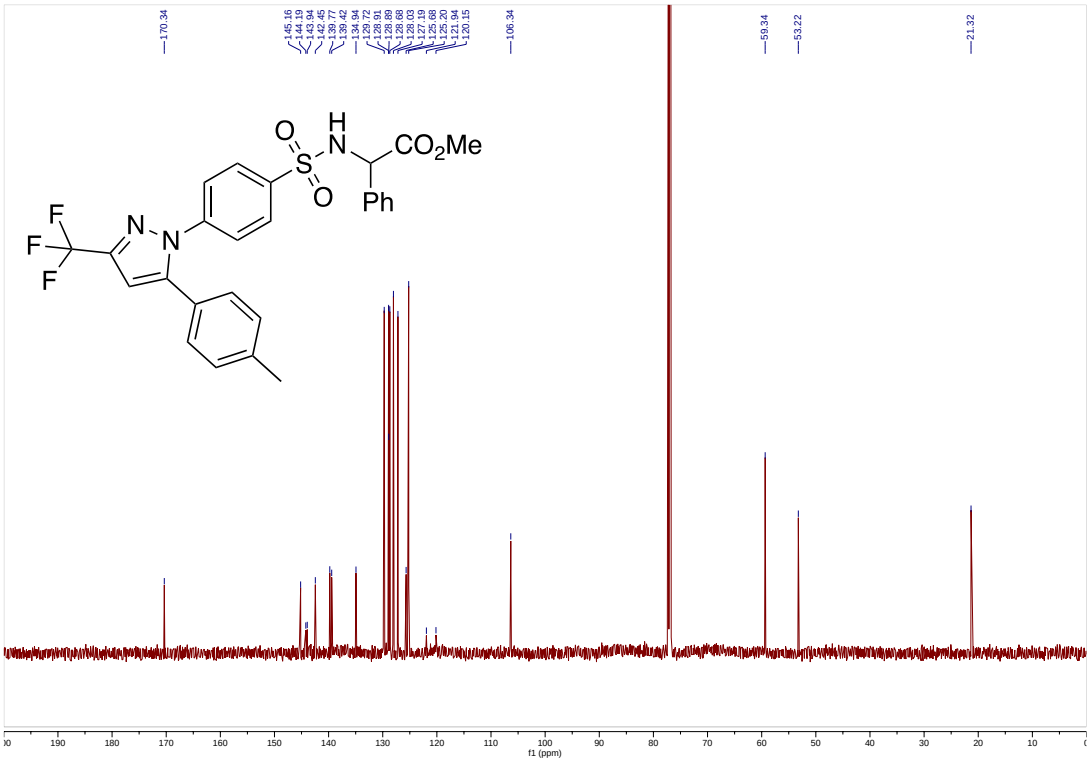


Methyl 2-phenyl-2-((4-(5-(*p*-tolyl)-3-(trifluoromethyl)-1*H*-pyrazol-1-yl)phenyl)sulfonamido)acetate (30)

^{1}H NMR (600 MHz, Chloroform-*d*)

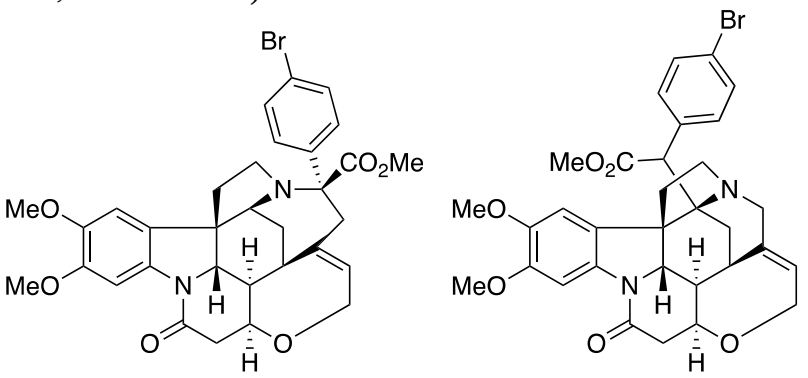


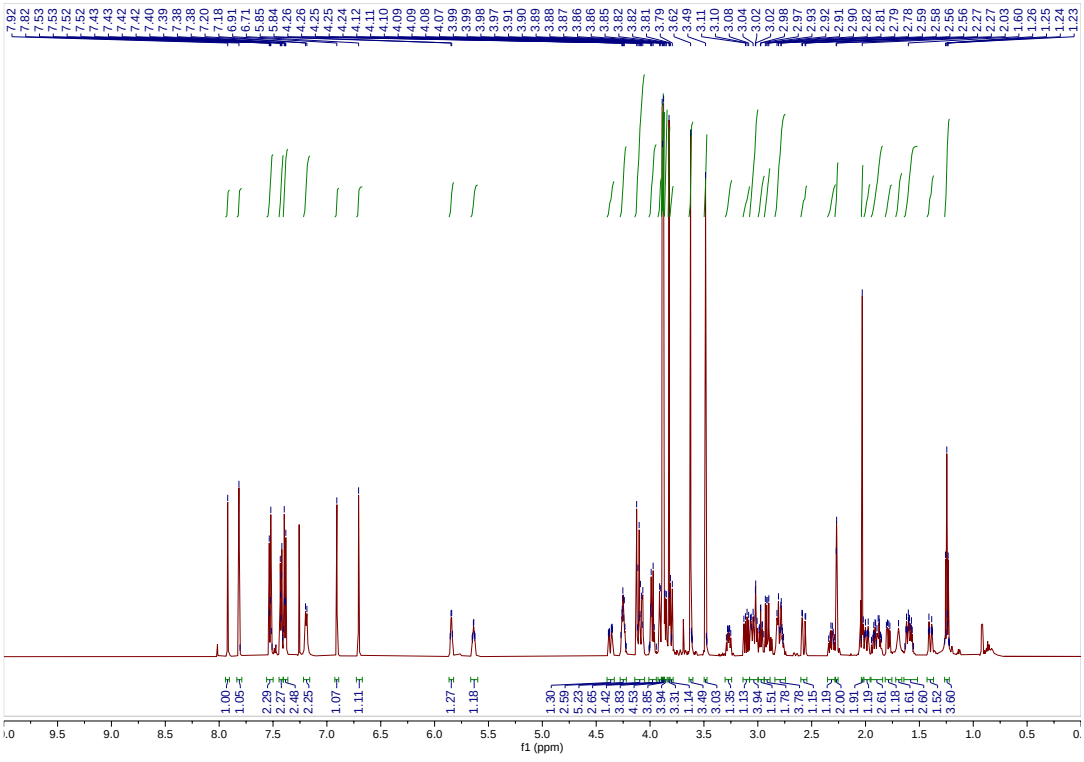
^{13}C NMR (151 MHz, Chloroform-*d*)



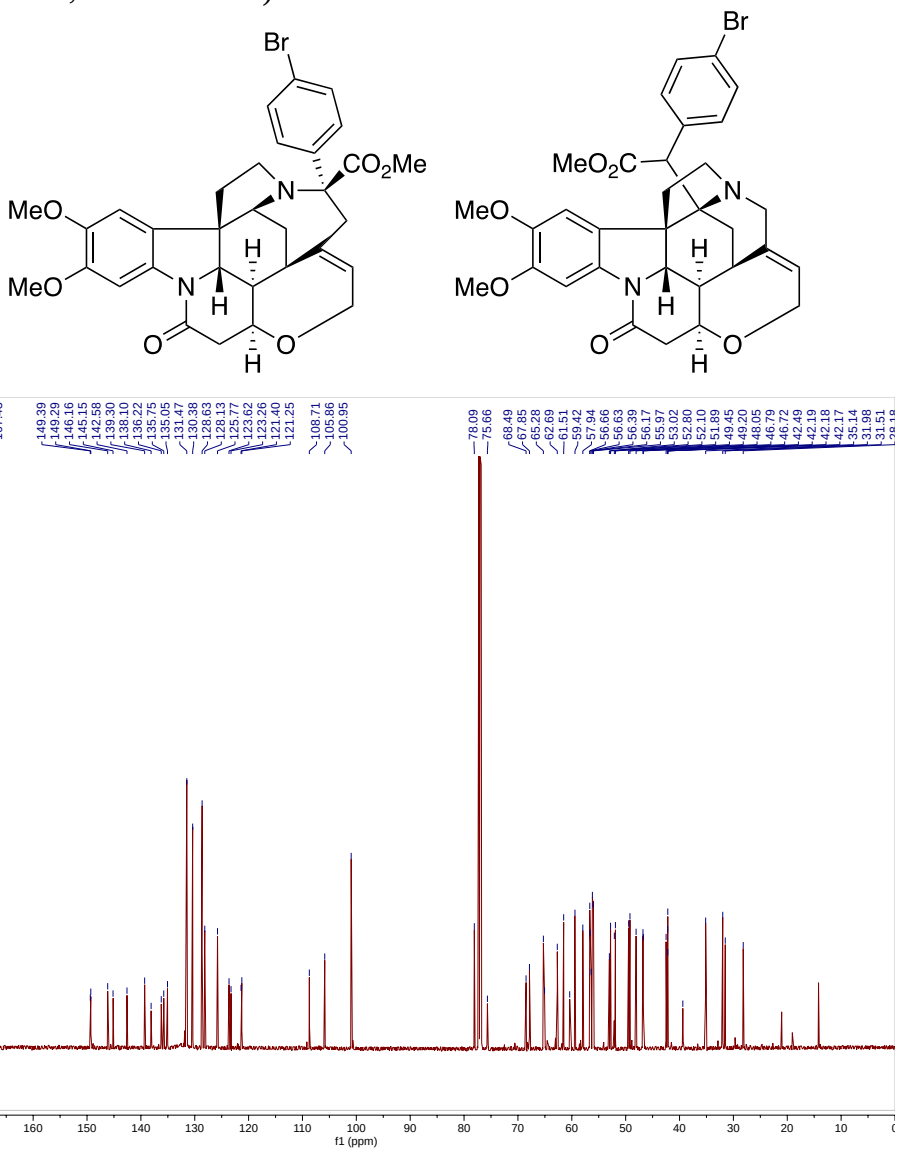
Methyl (4a*R*,4a1*R*,5a*S*,8a*R*,8a1*S*,15a*S*,16*S*)-16-(4-bromophenyl)-10,11-dimethoxy-14-oxo-2,4a,4a1,5,5a,7,8,8a1,15,15a-decahydro-14*H*-6,4-ethanoindolo[3,2,1-*ij*]oxepino[2,3,4-*de*]pyrrolo[2,3-*h*]quinoline-16-carboxylate (33) & Methyl 2-(4-bromophenyl)-2-((4a*R*,4a1*R*,5a*R*,8a*S*,8a1*S*,15a*S*)-10,11-dimethoxy-14-oxo-4a,4a1,5,7,8,8a1,15,15a-octahydro-14*H*-4,6-methanoindolo[3,2,1-*ij*]oxepino[2,3,4-*de*]pyrrolo[2,3-*h*]quinolin-5a(2*H*)-yl)acetate (34)

^{1}H NMR (400 MHz, Chloroform-*d*)



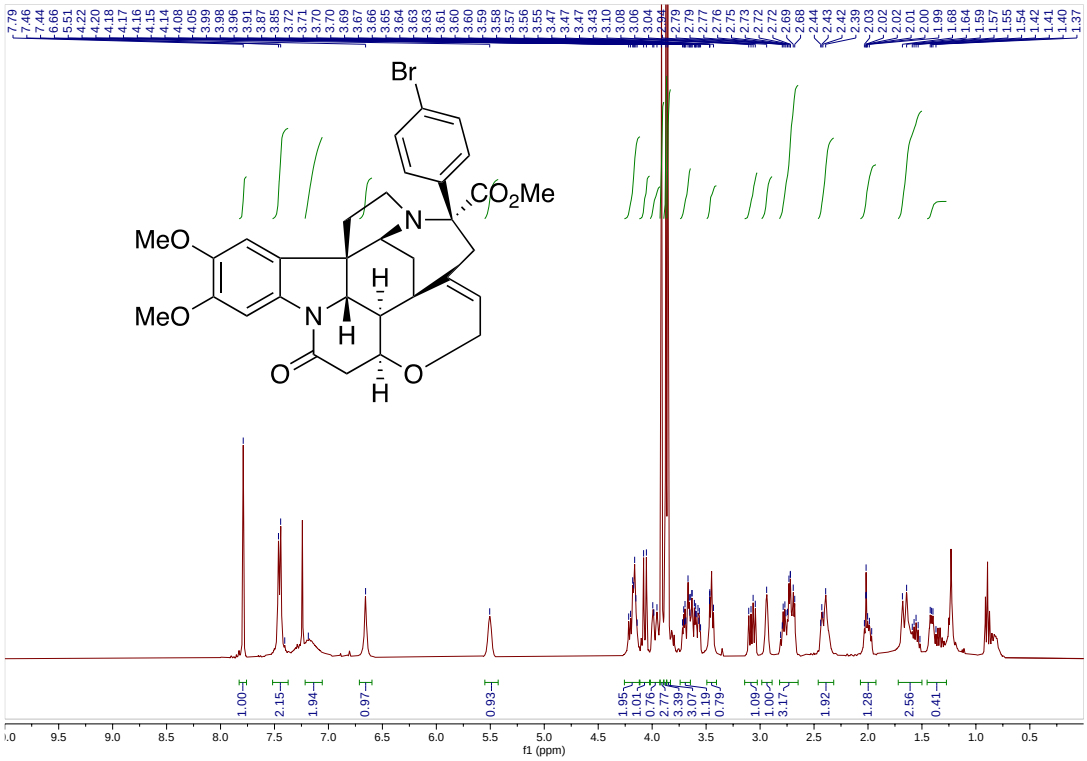


^{13}C NMR (101 MHz, Chloroform-*d*)

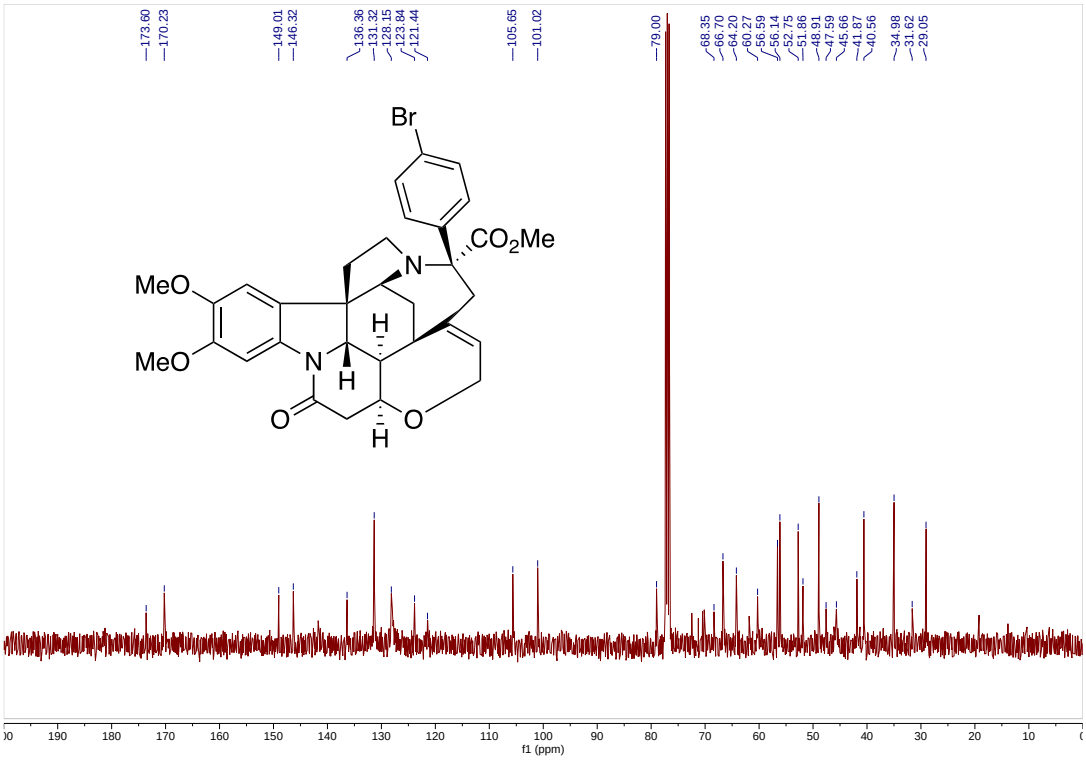


Methyl (4a*R*,4a1*R*,5a*S*,8a*R*,8a1*S*,15a*S*,16*R*)-16-(4-bromophenyl)-10,11-dimethoxy-14-oxo-2,4a,4a1,5,5a,7,8,8a1,15,15a-decahydro-14*H*-6,4-ethanoindolo[3,2,1-*ij*]oxepino[2,3,4-*de*]pyrrolo[2,3-*h*]quinoline-16-carboxylate (35)

^{1}H NMR (400 MHz, Chloroform-*d*)



^{13}C NMR (101 MHz, Chloroform-*d*)



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