Mechanosynthesis of ruthenium trisbipyridyl complexes and application in photoredox catalysis in a ball-mill

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I. General Information

All reagents were purchased from Sigma Aldrich, Fluka, Acros or Alfa Aesar. Hantzsch amide was synthesized according to lit.[1]

Mechanophotochemistry

The milling treatments were carried out in a vibrating Retsch® Mixer Mill 400 (vbm) operating at 25-30 Hz. Milling load (ML) is defined as the ratio between the mass of the reactant over the free volume of the jar. For performing photomechanochemical experiments, the vbm was modified to adapt a 3D-printed ¾-cylinder (90 mm diameter) covered with LEDs (Figure S1, 12VDC SMD3528 LED flexible strip bought from lightingwill.com; 126 LEDs, total power 10.1 W, distance to the milling jar: 35 mm).

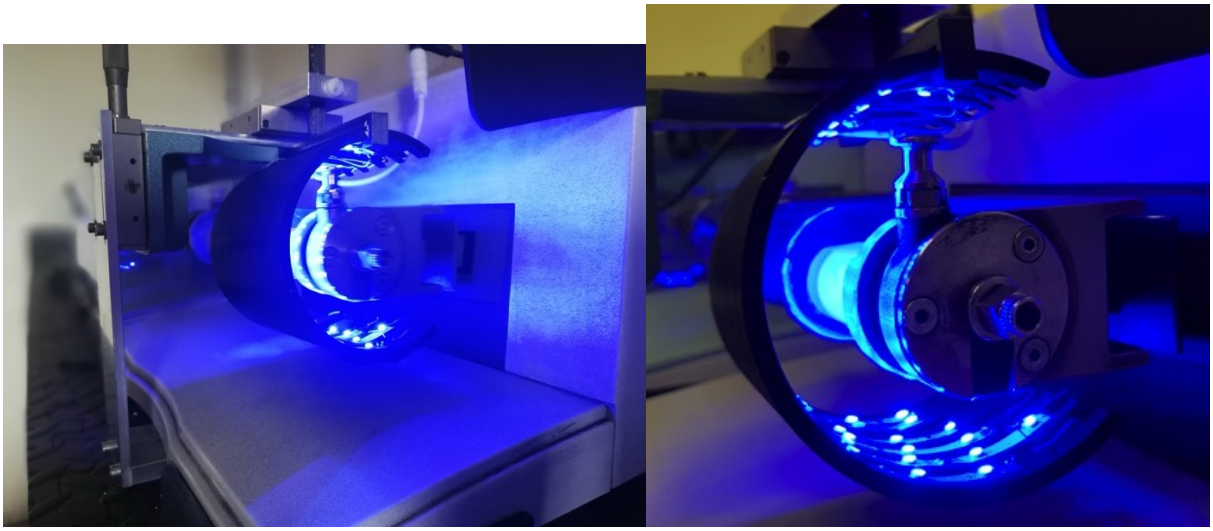


Figure S1. Modified vibratory ball-mill with LEDs

Making epoxy milling jars

A similar protocol to the one depicted in a previous report from our group was used.[2]

A mold of the two parts of a 15 mL milling PMMA jar was made using silicone 3481 and accelerator (catalyst 81-NW) from SF-Composites according to the suppliers' recommendations. Once the mold was ready for use, epoxy resin (SR8500/SD7160) was poured in the molds according to the suppliers' recommendations. After curing, the two parts of the novel milling jar were recovered. If necessary, a light sanding was carried out to obtain suitable jars for use in the vbm.

Analysis

NMR Analyses were performed at the 'Laboratoire de Mesures Physiques' (IBMM, Université de Montpellier). ^{1}H NMR spectra were recorded on a Bruker AVANCE 400 MHz, a Bruker AVANCE III 500 MHz or a Bruker AVANCE III 600 MHz and are reported in ppm using deuterated solvent ($CDCl_3$ at 7.26 ppm or DMSO-d_6 at 2.50 ppm or acetone-d_6 at 2.05 ppm) as internal standards. Data are reported as s = singlet, d = doublet, t = triplet, q = quadruplet, qt = quintuplet, sept = septuplet, m = multiplet; coupling constant in Hz; integration. ^{13}C NMR spectra were recorded on a Bruker AVANCE 101 MHz, a

Bruker AVANCE III 126 MHz or a Bruker AVANCE III 151 MHz and are reported in ppm using deuterated solvent ($CDCl_3$ at 77.2 ppm or DMSO-d_6 at 39.5 ppm or acetone-d_6 at 29.8 ppm) as internal standards.

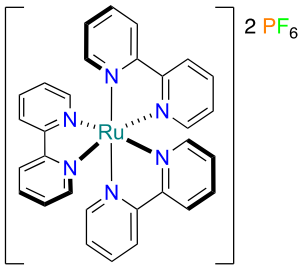
Mass spectra were obtained by LC-MS using as LC a Water Alliance 2695, coupled to a Waters ZQ spectrometer with an electrospray source, a single quadrupole analyzer and a Waters 2489 UV detector. HPLC conversion was measured on an Agilent technologies 1220 Infinity LC using a high-resolution Chromolith® RP-18e50-4.6 mm column and a linear gradient of 0-100% CH_3CN/0.1% TFA in H_2O/0.1% TFA over 3 min, UV lamp detection at 214 nm. Flow rate: 1 $mL.min^{-1}$.

II. Synthesis of ruthenium trisbipyridyl complexes

General procedure

$RuCl_3.xH_2O$ (1.0 equiv.), corresponding bipyridine (4.0 equiv.), KPF_6 (2.0 equiv.), EtOH (12.0 equiv.) and sodium hydroxide (0.25 equiv., 1 M in water) were introduced in a 5 mL WC grinding jar with one WC ball (5 mm diameter). The jar was closed, sealed with parafilm, placed in the vibratory ball-mill and subjected to grinding for 1.5 – 3.5 h at 30 Hz. The solid was dissolved in a minimum of dichloromethane and then filtrated on celite. Solvent was reduced to a minimum under reduced pressure, and the solid was precipitated in Et_2O, filtered and washed with Et_2O, and dried under vacuo.

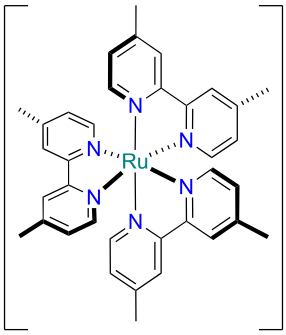
tris(2,2'-bipyridine)ruthenium(II) *bis*(hexafluorophosphate) 1 – CAS [60804-74-2]



General procedure was carried out with 2,2'-bipyridine (35.1 mg, 0.23 mmol) to afford tris(2,2'-bipyridine)ruthenium(II) *bis*(hexafluorophosphate) **1** (46.2 mg, 0.054 mmol, 96%) as a red solid.

^{1}H NMR (500 MHz, Acetone) δ 8.84 (d, *J* = 8.1 Hz, 1H), 8.22 (td, *J* = 8.0, 1.4 Hz, 1H), 8.13 – 7.99 (m, 1H), 7.67 – 7.51 (m, 1H). **^{13}C NMR (126 MHz, Acetone) δ** 158.1, 152.7, 139.0, 128.8, 125.4. Data in agreement with lit.[3]

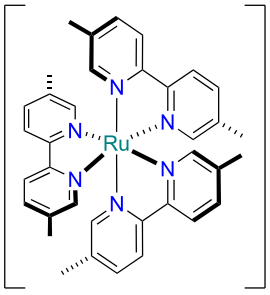
tris(4,4'-dimethylbipyridine)ruthenium(II) *bis*(hexafluorophosphate) 2 – CAS [83605-44-1]



General procedure was carried out for 2 h with 4,4'-dimethylbipyridine (51.2 mg, 0.28 mmol) to afford tris(4,4'-dimethylbipyridine)ruthenium(II) *bis*(hexafluorophosphate) **2** (60.8 mg, 0.064 mmol, 92%) as a dark brown solid.

^{1}H NMR (500 MHz, Acetone) δ 8.67 (s, 1H), 7.83 (d, *J* = 5.8 Hz, 1H), 7.39 (dd, *J* = 5.8, 1.0 Hz, 1H), 2.58 (s, 3H). **^{13}C NMR (126 MHz, Acetone) δ** 157.8, 151.7, 150.9, 129.4, 125.9, 21.1. Data in agreement with lit.[4]

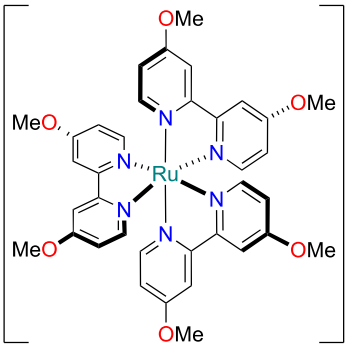
tris(5,5'-dimethylbipyridine)ruthenium(II) *bis*(hexafluorophosphate) 3 – CAS [47837-90-1]



General procedure was carried out for 2 h with 5,5'-dimethylbipyridine (38.9 mg, 0.21 mmol) to afford tris(5,5'-dimethylbipyridine)ruthenium(II) *bis*(hexafluorophosphate) **3** (48.1 mg, 0.051 mmol, 97%) as a grey-brown solid.

^{1}H NMR (500 MHz, Acetone) δ 8.59 (d, *J* = 8.3 Hz, 1H), 7.97 (dd, *J* = 8.3, 1.2 Hz, 1H), 7.79 (d, *J* = 1.0 Hz, 1H), 2.20 (s, 3H). **^{13}C NMR (126 MHz, Acetone) δ** 155.6, 152.2, 139.2, 139.0, 124.1, 18.4. Data in agreement with lit.[5]

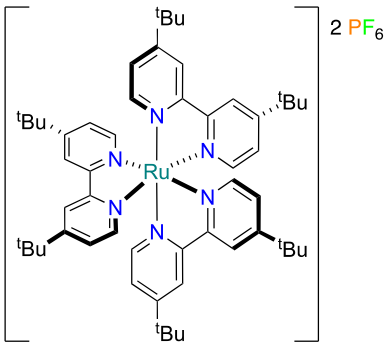
tris(4,4'-dimethoxybipyridine)ruthenium(II) *bis*(hexafluorophosphate) 5 – CAS [630392-00-6]



General procedure was carried out for 3 h with 4,4'-dimethoxybipyridine (42.7 mg, 0.20 mmol) to afford tris(4,4'-dimethoxybipyridine) ruthenium(II) *bis*(hexafluorophosphate) **5** (35.9 mg, 0.035 mmol, 69%) as a red solid.

^{1}H NMR (500 MHz, Acetone) δ 8.37 (d, *J* = 2.6 Hz, 1H), 7.82 (d, *J* = 6.5 Hz, 1H), 7.14 (dd, *J* = 6.5, 2.6 Hz, 1H), 4.07 (s, 3H). **^{13}C NMR (126 MHz, Acetone) δ** 167.7, 159.4, 153.1, 114.7, 111.7, 57.1. Data in agreement with lit.[6]

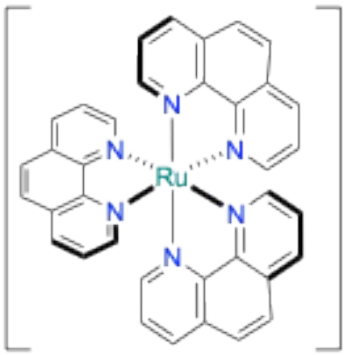
tris(4,4'-di*tert*-butylbipyridine)ruthenium(II) *bis*(hexafluorophosphate) 6 – CAS [75777-87-6]



General procedure was carried out for 3.5 h with 4,4'-di*tert*-butylbipyridine (48.1 mg, 0.18 mmol) to afford tris(4,4'-di*tert*-butylbipyridine) ruthenium(II) *bis*(hexafluorophosphate) **6** (34.7 mg, 0.038 mmol, 85%) as a brown solid.

^{1}H NMR (500 MHz, Acetone) δ 9.10 (d, *J* = 2.0 Hz, 1H), 7.85 (dd, *J* = 6.3, 2.0 Hz, 1H), 7.51 (d, *J* = 6.3 Hz, 1H), 1.41 (s, 9H). **^{13}C NMR (126 MHz, Acetone) δ** 169.6, 156.8, 151.6, 129.4, 125.7, 36.9. Data in agreement with lit.[7]

tris(1,10-phenanthroline)ruthenium(II) *bis*(hexafluorophosphate) 7 – CAS [60828-39-9]



General procedure was carried out for 2 h with 1,10-phenanthroline (38.8 mg, 0.22 mmol) to afford tris(1,10-phenanthroline) ruthenium(II) *bis*(hexafluorophosphate) **7** (43.2 mg, 0.046 mmol, 86%) as a brown solid.

^{1}H NMR (500 MHz, Acetone) δ 8.80 (dd, *J* = 8.3, 1.2 Hz, 1H), 8.45 – 8.38 (m, 2H), 7.81 (dd, *J* = 8.3, 5.3 Hz, 1H). **^{13}C NMR (126 MHz, Acetone) δ** 154.0, 148.9, 137.9, 132.0, 129.1, 127.1. Data in agreement with lit.[3]

III. Calculation of E factor for the synthesis of complexes 1 and 2

The E Factor is the ratio of the weight of generated waste to the total weight of the end product. It is a useful tool for rapid evaluation of processes based on generated waste.

$$E\ Factor = \frac{\sum m(raw\ materials) + \sum m(solvent) + \sum m(water) - m(product)}{m(product)}$$

Due to the difficult measurement of solvent quantity in the work-up process and in particular in laboratory scale, their values will be omitted in the E Factor calculation.

E factor values are reported in the following table for the synthesis of complex **1** in the ball-mill and under MW conditions, and of complex **2** in the ball-mill and under magnetic stirrer conditions. The procedure used are detailed below.

Compounds	Technique	∑ m(raw materials) (mg)	∑ m(solvents) (mg)	∑ m(water) (mg)	m (product) (mg)	E factor
1	vbm	69.1	31.5	14	46.2	1.5
	MW	1080	6660	100000	66	1631
2	vbm	92.2	38.4	14	60.8	1.4
	reflux	1807.2	11835	10000	649.3	35.4

Protocols used for the calculation of E factor for the synthesis of complex 1

Mechanosynthesis (this work)

$RuCl_3.xH_2O$ (11.8 mg), bipyridine (35.6 mg, 4.0 equiv.), KPF_6 (21.2 mg, 2.0 equiv.), EtOH (31.5 mg, 40 µL, 12.0 equiv.) and sodium hydroxide (14 µL (0.57 mg of NaOH), 0.25 equiv., 1 M in water) were introduced in a 5 mL WC grinding jar with one WC ball (5 mm diameter). The jar was closed, sealed with parafilm, placed in the vibratory ball-mill and subjected to grinding for 1.5 – 3.5 h at 30 Hz. The solid was dissolved in a minimum of dichloromethane and then filtrated on celite. Solvent was reduced to a minimum under reduced pressure, and the solid was precipitated in Et_2O, filtered and washed with Et_2O, and dried under vacuo. Complex 1 was isolated in 96% yield (46.2 mg).

Synthesis under MW irradiation.[3]

Dichlorotetrakis(dimethylsulfoxide)ruthenium(II) (40 mg, 0.083 mmol) and 2,2'-bipyridine (40 mg, 0.26 mmol, 3.1 equiv) were dissolved in ethylene glycol (6 mL, 6.66 g) and heated in a microwave reactor at 160 °C for 15 min. The resulting solution was poured into excess aqueous KPF_6 (100 mL, 1 g of KPF_6, 100 g of water), and the precipitate was collected on Celite and washed with water (50 mL). The solid was dissolved in acetonitrile, which was removed under reduced pressure to give $[Ru(bpy)_3](PF_6)_2$ as an orange solid (66 mg, 0.077 mmol, 93%).

In this protocol, details concerning the KPF_6 solution are missing. If saturated, it would imply a mass of KPF_6 of 8.35 g. We considered in the calculations above that 1 g would already be a large excess of KPF_6.

Protocols used for the calculation of E factor for the synthesis of complex 2

Mechanosynthesis (this work)

$RuCl_3.xH_2O$ (14.4 mg), 4,4'-dimethyl-2,2'-bipyridine (51.3 mg, 4.0 equiv.), KPF_6 (25.9 mg, 2.0 equiv.), EtOH (38.4 mg, 50 µL, 12.0 equiv.) and sodium hydroxide (17 µL (0.70 mg of NaOH), 0.25 equiv., 1 M in water) were introduced in a 5 mL WC grinding jar with one WC ball (5 mm diameter). The jar was closed, sealed with parafilm, placed in the vibratory ball-mill and subjected to grinding for 1.5 – 3.5 h at 30 Hz. The solid was dissolved in a minimum of dichloromethane and then filtrated on celite. Solvent was reduced to a minimum under reduced pressure, and the solid was precipitated in Et_2O, filtered and washed with Et_2O, and dried under vacuo. Complex 1 was isolated in 92% yield (60.8 mg).

Synthesis in solution (adapted from lit.[4b])

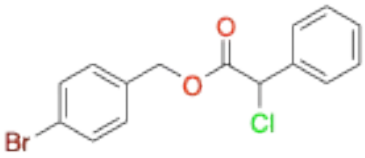
A 25-mL round-bottomed flask equipped with a stir bar was charged with 4,4'dimethyl-2,2'-bipyridine (792.2 mg, 4.3 mmol) dissolved in ethanol (15 mL, 11.8 g) and $RuCl_3$ (0.18 g, 0.86 mmol). This solution was purged with N_2 for 10 minutes and then refluxed 24 h upon which a dark reddish orange solution was obtained. This solution was cooled to room temperature and added a saturated aq. solution of KPF_6 (10 mL, 835 mg of KPF_6, 10 g of water). At this point dark orange red solid precipitated. This solid was isolated by filtration and was washed with diethyl ether (2 3 mL portions) and dried at reduced pressure to obtain the product in 80% yield (649.3 mg).

IV. Photoredox-catalysis experiments

A. Synthesis of substrates **8a-g**

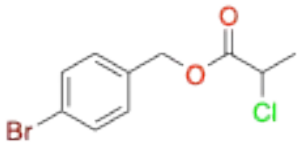
***Synthesis of 4-bromobenzyl 2-chloro-2-phenylacetate* 8a** – CAS [1166870-58-1]
4-bromobenzylalcohol (1.0 equiv.), 2-chloro-2-phenylacetyl chloride (1.1 equiv.) and sodium carbonate (1.1 equiv.) were introduced in a 5 mL WC grinding jar with one WC ball (5 mm diameter). The jar was closed, sealed with parafilm, placed in the vibratory ball-mill and subjected to grinding for 1.5 h at 30 Hz. The solid was dissolved in dichloromethane, filtrated on celite and extracted with H_2O and Et_2O. The aqueous phase was washed with Et_2O, then organic phases were collected, dried on $MgSO_4$ and evaporated under reduced pressure to afford 4-bromobenzyl 2-chloro-2-phenylacetate **8a** (58.1 mg, 0.171 mmol, 94%) as a grey-white solid.

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.42 (m, 7H), 7.14-7.12 (m, 2H), 5,39 (s, 1H), 5.16 (d, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 168.1, 135.6, 134.1, 131.8, 129.8, 129.5, 129.0, 128.1, 122.6, 67.1, 59.1. Data in agreement with lit.[8]



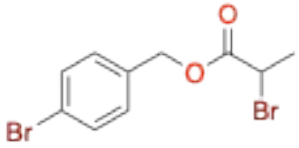
***Synthesis of 4-bromobenzyl 2-chloropropanoate* 8b**
4-bromobenzylalcohol (1.1 equiv., 246.9 mg, 1.32 mmol), 2-chloro-propionyl chloride (1 equiv., 116.7 µL, 1.2 mmol) and triethylamine (1.2 equiv., 200.7 µL, 1.44 mmol) were dissolved in dichloromethane (5 mL) at 0 °C. The mixture was stirred overnight at room temperature. The mixture was extracted with dichloromethane, washed with a saturated solution of NH_4Cl, water, and the organic phases were collected, dried on $MgSO_4$ and evaporated under reduced pressure to afford **8b** (229.7 mg, 0.83 mmol, 69%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.5 Hz, 1H), 5.16 (s, 1H), 4.43 (q, *J* = 6.9 Hz, 1H), 1.70 (d, *J* = 6.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 170.0, 134.3, 132.0, 130.0, 122.8, 66.9, 52.5, 21.6.



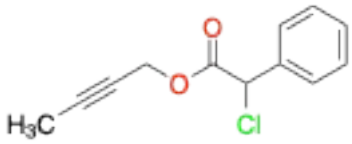
***Synthesis of 4-bromobenzyl 2-bromopropanoate* 8b-Br** – CAS [2172801-87-3]
4-bromobenzylalcohol (1.05 equiv., 295.5 mg, 1.58 mmol), 2-bromo-propionyl bromide (1 equiv., 157 µL, 1.5 mmol) and triethylamine (1.2 equiv., 250.0 µL, 1.8 mmol) were dissolved in 1,3-dioxolane (15 mL) at 0 °C. The mixture was stirred overnight at room temperature. The mixture was filtered, and washed with Et_2O. The solvent was evaporated under reduced pressure and the resulting mixture was filtrated over a pad of silica (Cyclohexane/EtOAc 95:5). After evaporation, pure **8b-Br** was isolated in 49% yield (236.7 mg, 0.74 mmol).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.4 Hz, 1H), 7.25 (d, *J* = 8.4 Hz, 1H), 5.21 – 5.07 (m, 1H), 4.40 (q, *J* = 6.9 Hz, 1H), 1.83 (d, *J* = 6.9 Hz, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 170.1, 134.3, 132.0, 130.0, 122.7, 66.9, 39.9, 21.7.
Data in agreement with lit.[9]



***Synthesis of but-2-yn-1-yl 2-chloro-2-phenylacetate* 8c**

2-Butyn-1-ol (1.1 equiv., 99 µL, 1.32 mmol), 2-chloro-2-phenylacetyl chloride (1 equiv., 189.7 µL, 1.2 mmol) and triethylamine (1.2 equiv., 200.7 µL, 1.44 mmol) were dissolved in dichloromethane (5 mL) at 0 °C. The mixture was stirred overnight at room temperature. The mixture was extracted with dichloromethane, washed with a saturated solution of NH_4Cl, water, and the organic phases were collected, dried on $MgSO_4$ and evaporated under reduced pressure to afford **8c** (264.5 mg, 1.19 mmol, 99%).

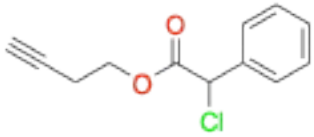


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 – 7.47 (m, 2H), 7.42 – 7.35 (m, 3H), 5.38 (s, 1H), 4.81 – 4.63 (m, 2H), 1.84 (t, *J* = 2.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 167.9, 135.6, 129.5, 129.0, 128.9, 128.2, 84.4, 72.3, 58.9, 54.8, 3.8.

HRMS ASAP-(+) calcd. For $C_{12}H_{12}ClO_2$ $[M+H]^+$ 223.0526, found: 223.0531

***Synthesis of but-3-yn-1-yl 2-chloro-2-phenylacetate* 8d** – CAS [1166870-66-1]

3-Butyn-1-ol (1.1 equiv., 99 µL, 1.32 mmol), 2-chloro-2-phenylacetyl chloride (1 equiv., 189.7 µL, 1.2 mmol) and triethylamine (1.2 equiv., 200.7 µL, 1.44 mmol) were dissolved in dichloromethane (5 mL) at 0 °C. The mixture was stirred overnight at room temperature. The mixture was extracted with dichloromethane, washed with a saturated solution of NH_4Cl, water, and the organic phases were collected, dried on $MgSO_4$ and evaporated under reduced pressure to afford **8d** (227.1 mg, 1.02 mmol, 85%).

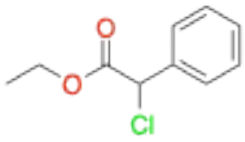


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 – 7.46 (m, 2H), 7.41 – 7.32 (m, 3H), 5.38 (s, 1H), 4.27 (qt, *J* = 10.6, 6.8 Hz, 2H), 2.53 (td, *J* = 6.8, 2.6 Hz, 2H), 1.95 (t, *J* = 2.7 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 168.3, 135.7, 129.5, 129.0, 128.1, 79.3, 70.4, 63.9, 59.0, 18.9.

Data in agreement with lit.[8]

***Synthesis of ethyl 2-chloro-2-phenylacetate* 8e** – CAS [4773-33-5]

Ethanol (1.1 equiv., 77 µL, 1.32 mmol), 2-chloro-2-phenylacetyl chloride (1 equiv., 189.7 µL, 1.2 mmol) and triethylamine (1.2 equiv., 200.7 µL, 1.44 mmol) were dissolved in dichloromethane (5 mL) at 0 °C. The mixture was stirred overnight at room temperature. The mixture was extracted with dichloromethane, washed with a saturated solution of NH_4Cl, water, and the organic phases were collected, dried on $MgSO_4$ and evaporated under reduced pressure to afford **8e** (200.2 mg, 1.00 mmol, 84%).



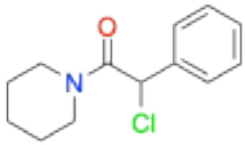
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 – 7.45 (m, 1H), 7.43 – 7.32 (m, 2H), 5.34 (s, 1H), 4.35 – 4.11 (m, 1H), 1.26 (t, *J* = 7.1 Hz, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 168.5, 136.0, 129.4, 129.0, 128.1, 62.6, 59.3, 14.1.

Data in agreement with lit.[10]

***Synthesis of 2-chloro-2-phenyl-1-(piperidin-1-yl)ethan-1-one* 8f** – CAS [18504-70-6]

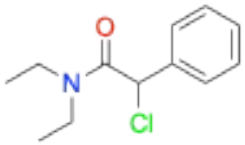
Piperidine (1.1 equiv., 130 µL, 1.32 mmol), 2-chloro-2-phenylacetyl chloride (1 equiv., 189.7 µL, 1.2 mmol) and triethylamine (1.2 equiv., 200.7 µL, 1.44 mmol) were dissolved in dichloromethane (5 mL) at 0 °C. The mixture was stirred overnight at room temperature. The mixture was extracted with

dichloromethane, washed with a saturated solution of NH_4Cl, water, and the organic phases were collected, dried on $MgSO_4$ and evaporated under reduced pressure to afford **8f** (282.4 mg, 1.19 mmol, 99%).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 – 7.44 (m, 2H), 7.42 – 7.31 (m, 3H), 5.72 (s, 1H), 3.61 (dd, *J* = 27.0, 10.1 Hz, 2H), 3.36 (s, 2H), 1.58 (d, *J* = 5.8 Hz, 4H), 1.43 (s, 1H), 1.32 – 1.19 (m, 1H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 165.6, 136.6, 128.9, 127.9, 59.0, 47.3, 44.1, 26.0, 25.5, 24.4.
HRMS ESI-(+) calcd. For $C_{13}H_{17}ClNO$ $[M+H]^+$ 238.09932, found 238.09933.

***Synthesis of 2-chloro-N,N-diethyl-2-phenylacetamide* 8g** – CAS [65117-31-9]
Diethylamine (1.1 equiv., 137 µL, 1.32 mmol), 2-chloro-2-phenylacetyl chloride (1 equiv., 189.7 µL, 1.2 mmol) and triethylamine (1.2 equiv., 200.7 µL, 1.44 mmol) were dissolved in dichloromethane (5 mL) at 0 °C. The mixture was stirred overnight at room temperature. The mixture was extracted with dichloromethane, washed with a saturated solution of NH_4Cl, water, and the organic phases were collected, dried on $MgSO_4$ and evaporated under reduced pressure to afford **8g** (222.2 mg, 0.98 mmol, 82%).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.49 (dt, *J* = 8.5, 2.2 Hz, 2H), 7.41 – 7.30 (m, 3H), 5.64 (s, 1H), 3.49 – 3.23 (m, 4H), 1.11 (dt, *J* = 15.7, 7.1 Hz, 6H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 166.6, 136.7, 129.1, 128.9, 128.2, 58.2, 42.3, 41.4, 14.4, 12.7.
HRMS ESI-(+) calcd. For $C_{12}H_{17}ClNO$ $[M+H]^+$ 226.09932, found 226.09932.
Data in agreement with lit.[11]

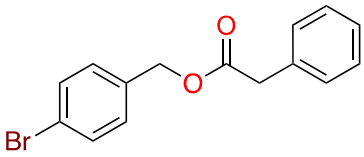
B. General procedure for the photoredox reductive dehalogenation in a vibratory ball-mill

General procedure

4-bromobenzyl 2-chloro-2-phenylacetate **8a** (0.238 mmol, 80.8 mg, 1.0 equiv.), DIPEA (0.472 mmol, 82 µL, 2 equiv.), Hantzsch amide (0.260 mmol, 58.1 mg 1.1 equiv.), DMAc (130 µL, 0.6 µL.mg^{-1}) and catalyst **1** (0.012 mmol, 10.2 mg, 0.05 equiv.) were introduced in a 15 mL grinding jar in epoxy resin with one ZrO_2 ball (1 cm diameter). The jar was loaded and closed put under inert atmosphere of N_2. The milling jar was then placed in the vibratory ball-mill and subjected to grinding at 25 Hz under blue LEDs irradiation for 3.5 h. The mixture was recovered using EtOAc and H_2O and transferred to a separation funnel. The product was extracted twice with EtOAc, and the combined organic phases were then washed with 2M HCl_{aq} and brine. The organic phase was dried over Na_2SO_4 and concentrated in vacuo to afford pure **9a** in 64% yield (46.5 mg, 0.152 mmol). If necessary flash chromatography on silica gel was performed.

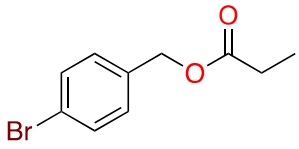
In some cases, toluene or DMAc were also used to recover the reaction mixture from the jar. If so, the recovered mixture was first concentrated in vacuo before performing the extraction.

4-Bromobenzyl 2-phenylacetate **9a** – CAS [1166870-59-2]



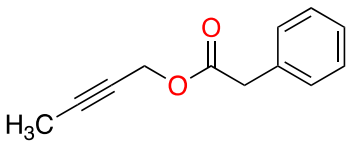
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 – 7.48 (m, 2H), 7.43 – 7.33 (m, 6H), 7.24 (d, *J* = 8.4 Hz, 2H), 5.15 (s, 2H), 3.74 (s, 2H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 171.6, 135.2, 134.0, 132.0, 130.1, 129.6, 128.9, 127.5, 122.5, 66.1, 41.6.
Data in agreement with lit.[8]

4-Bromobenzyl propionate **9b** – CAS [30039-37-3]
General procedure was followed starting from **8b** (56.9 mg, 0.205 mmol) and furnished **9b** in 66% yield (33.1 mg, 0.136 mmol).
Alternatively, general procedure was followed starting from **8b-Br** (76.6 mg, 0.238 mmol) and furnished **9b** in 87% yield (50.5 mg, 0.208 mmol).



^{1}H NMR (600 MHz, $CDCl_3$) δ 7.58 – 7.54 (m, 2H), 7.31 (d, *J* = 8.4 Hz, 2H), 5.14 (s, 2H), 2.45 (q, *J* = 7.5 Hz, 2H), 1.23 (t, *J* = 7.6 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$) δ** 174.5, 135.5, 132.0, 130.2, 122.5, 65.6, 27.9, 9.4.

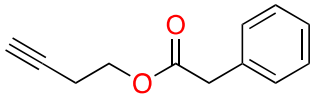
But-2-yn-1-yl 2-phenylacetate **9c** – CAS [144713-04-2]
General procedure was followed starting from **8c** (53.0 mg, 0.238 mmol) and furnished **9c** in 65% yield (29.0 mg, 0.154 mmol).



^{1}H NMR (400 MHz, $CDCl_3$) δ 7.39 – 7.27 (m, 5H), 4.69 (q, *J* = 2.4 Hz, 2H), 3.69 (s, 2H), 1.88 (t, *J* = 2.4 Hz, 3H). **^{13}C NMR (101 MHz, $CDCl_3$) δ** 171.1, 133.7, 129.4, 128.7, 127.3, 83.5, 73.2, 53.4, 41.2, 3.8.
Data in agreement with lit.[12]

But-3-yn-1-yl 2-phenylacetate **9d** – CAS [1166870-68-3]

General procedure was followed starting from **8d** (53.0 mg, 0.238 mmol) and furnished **9d** in 85% yield (38.1 mg, 0.202 mmol).

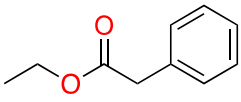


^{1}H NMR (500 MHz, $CDCl_3$) δ 7.36 – 7.25 (m, 4H), 4.21 (t, *J* = 6.8 Hz, 2H), 3.61 (s, 2H), 2.51 (d, *J* = 2.7 Hz, 2H), 1.94 (t, *J* = 2.7 Hz, 1H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 171.62, 134.1, 129.6, 128.8, 127.4, 80.2, 70.2, 62.8, 41.5, 19.2.

Data in agreement with lit.[8]

Ethyl 2-phenylacetate **9e** – CAS [101-97-3]

General procedure was followed starting from **8e** (47.3 mg, 0.238 mmol) and furnished **9e** in 67% yield (26.3 mg, 0.159 mmol).



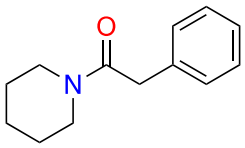
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.40 – 7.21 (m, 5H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.62 (s, 2H), 1.26 (t, *J* = 7.1 Hz, 3H).

^{13}C NMR (151 MHz, $CDCl_3$) δ 171.7, 134.3, 129.4, 128.7, 127.2, 61.0, 41.6, 14.3.

Data in agreement with lit.[13]

2-Phenyl-1-(piperidin-1-yl)ethan-1-one **9f** – CAS [3626-62-8]

General procedure was followed starting from **8f** (56.6 mg, 0.238 mmol) and furnished **9f** in 81% yield (39.0 mg, 0.192 mmol).



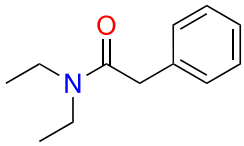
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.27 (m, 2H), 7.27 – 7.19 (m, 3H), 3.72 (s, 2H), 3.61 – 3.53 (m, 2H), 3.42 – 3.33 (m, 2H), 1.63 – 1.46 (m, 4H), 1.39 – 1.29 (m, 2H).

^{13}C NMR (126 MHz, $CDCl_3$) δ 169.4, 135.5, 128.7, 128.7, 126.7, 47.3, 43.0, 41.3, 26.2, 25.6, 24.5.

Data in agreement with lit.[14]

N,*N*-Diethyl-2-phenylacetamide **9g** – CAS [2431-96-1]

General procedure was followed starting from **8g** (53.7 mg, 0.238 mmol) and furnished **9g** in 88% yield (40.0 mg, 0.209 mmol).

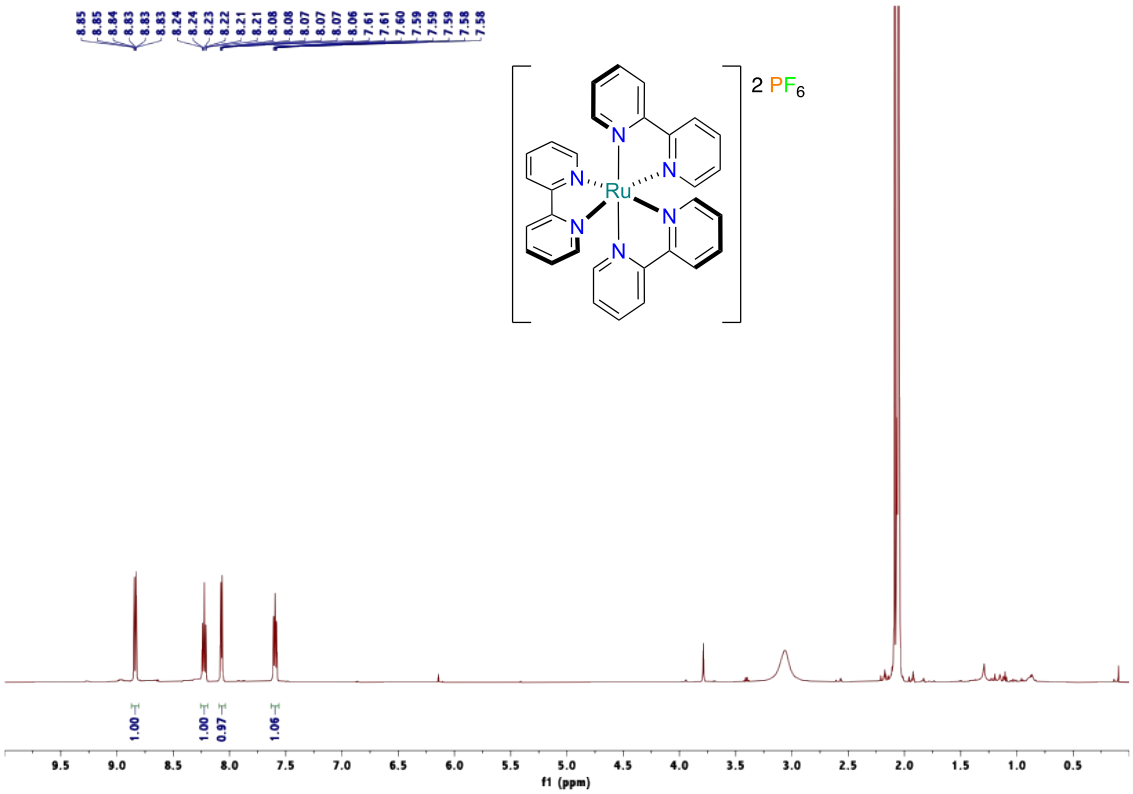


^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.26 (m, 2H), 7.25 – 7.18 (m, 4H), 3.67 (s, 2H), 3.37 (q, *J* = 7.1 Hz, 2H), 3.27 (q, *J* = 7.1 Hz, 2H), 1.08 (dt, *J* = 15.7, 7.1 Hz, 6H). **^{13}C NMR (126 MHz, $CDCl_3$) δ** 170.5, 135.8, 129.0, 129.0, 127.0, 42.7, 41.3, 40.5, 14.5, 13.3.

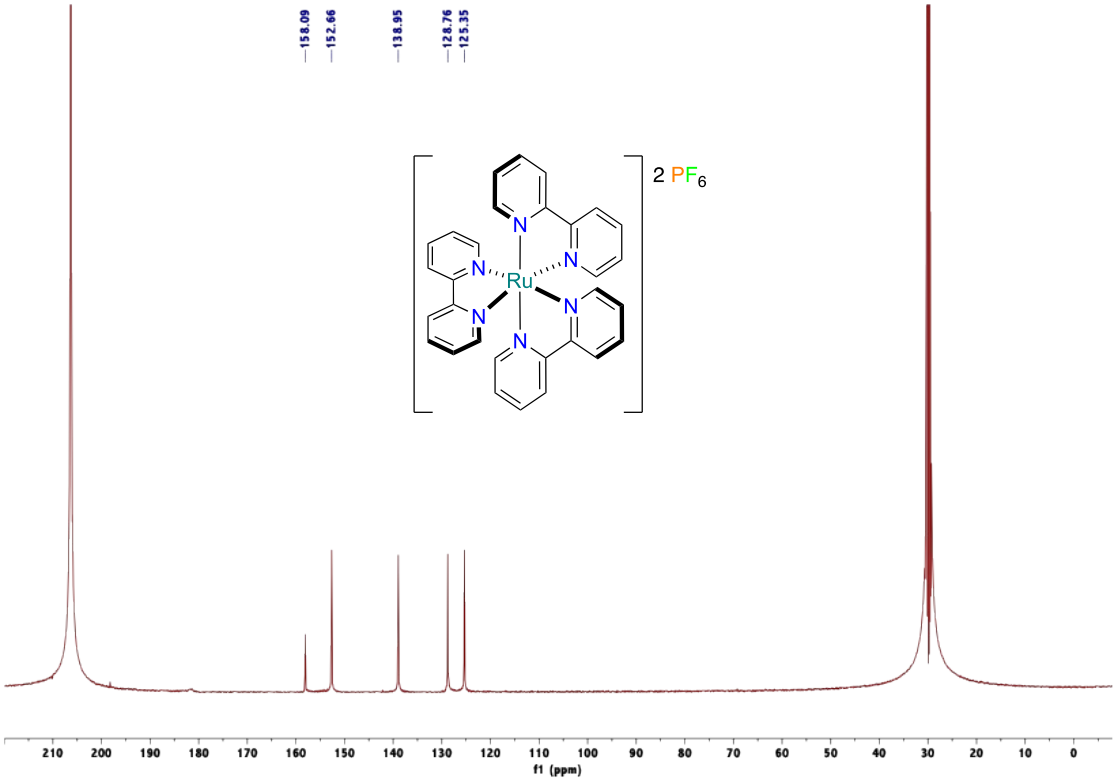
Data in agreement with lit.[15]

V. NMR Spectra

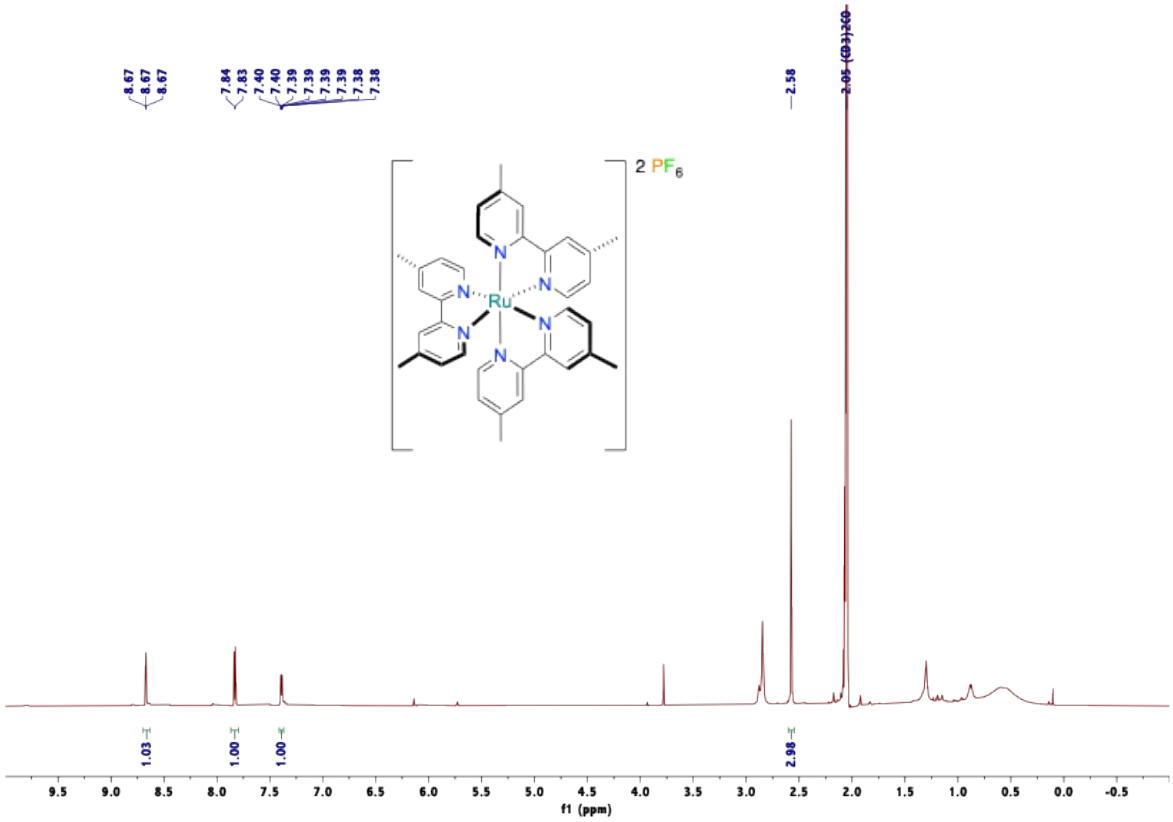
^{1}H NMR (500 MHz, Acetone) of tris(2,2'-bipyridine)ruthenium(II) *bis*(hexafluorophosphate) 1



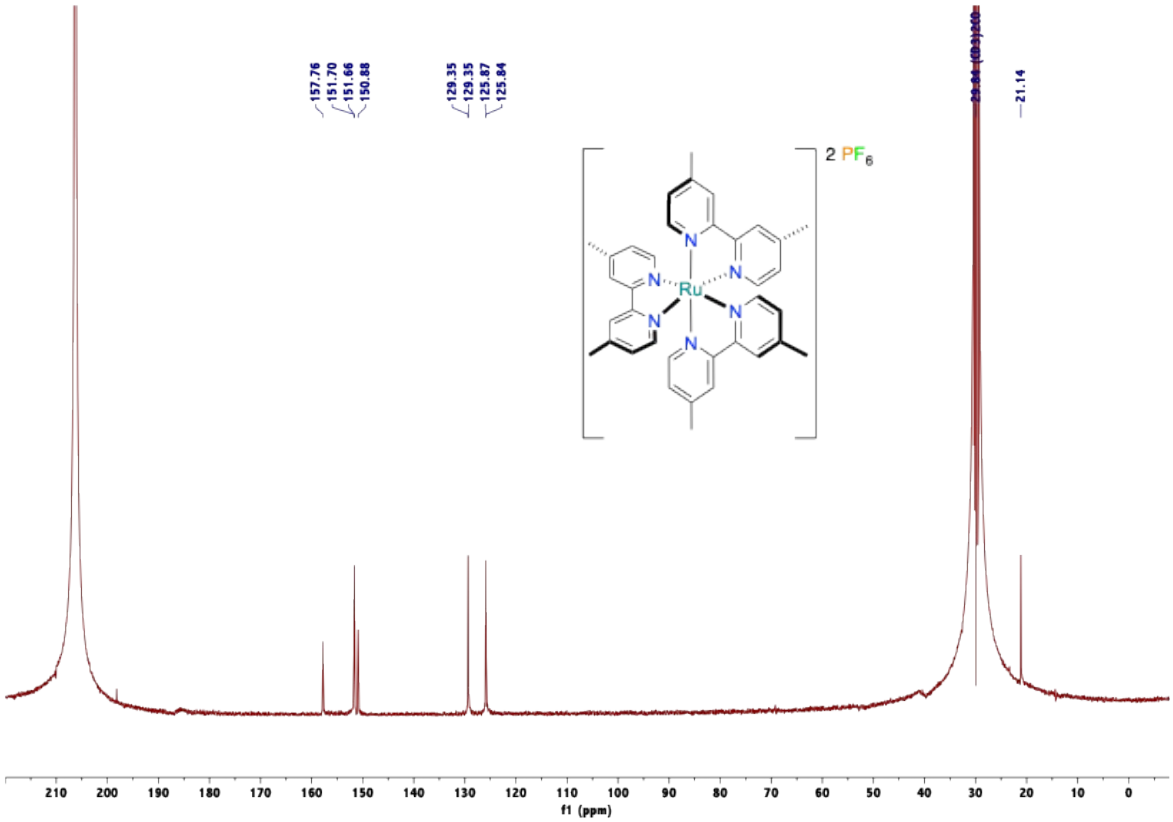
^{13}C NMR (126 MHz, Acetone) of tris(2,2'-bipyridine)ruthenium(II) *bis*(hexafluorophosphate) 1



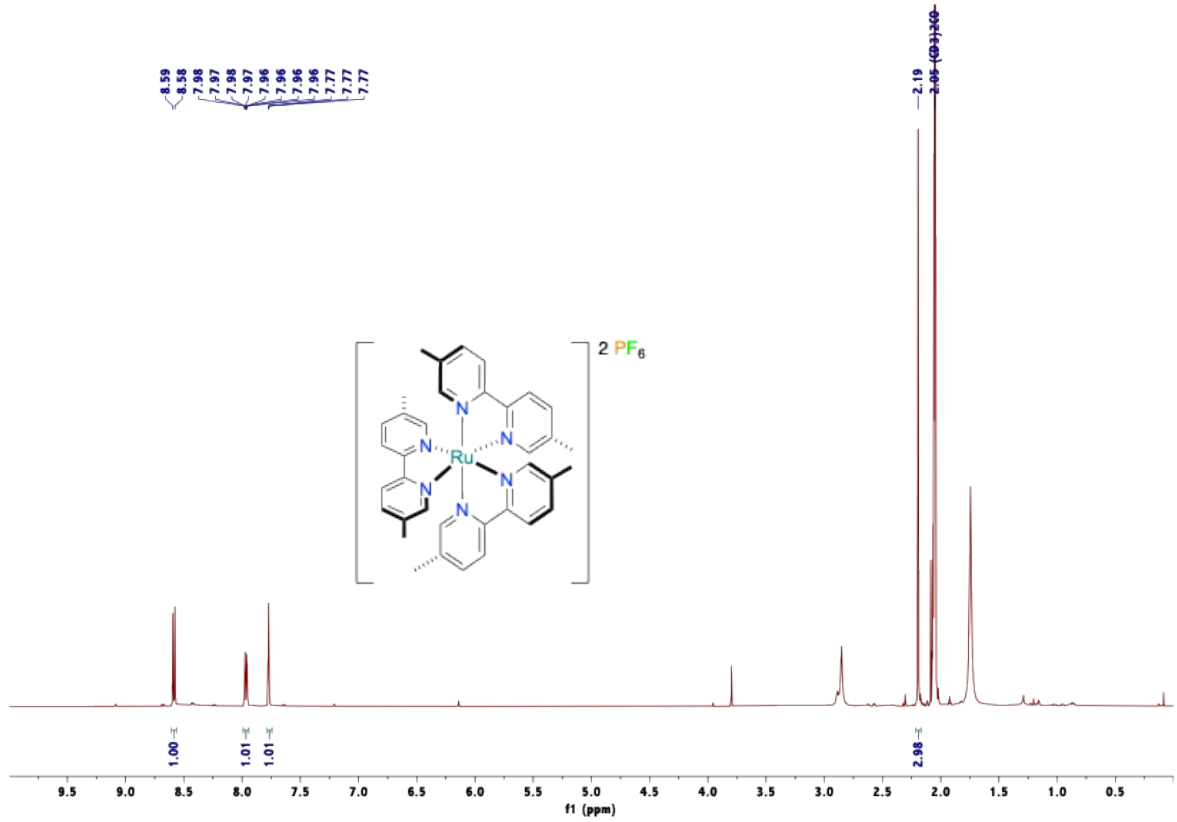
^{1}H NMR (500 MHz, Acetone) of tris(4,4'-dimethylbipyridine)ruthenium(II) *bis*(hexafluorophosphate) 2



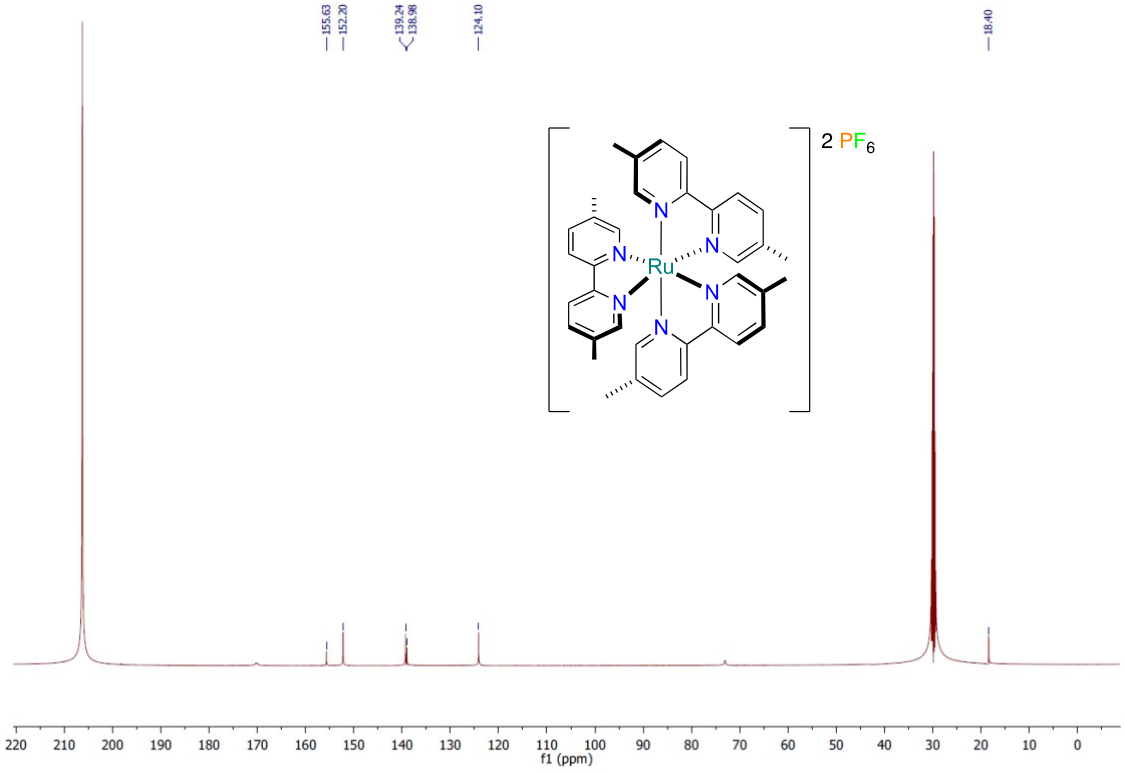
^{13}C NMR (126 MHz, Acetone) of tris(4,4'-dimethylbipyridine)ruthenium(II) *bis*(hexafluorophosphate) 2



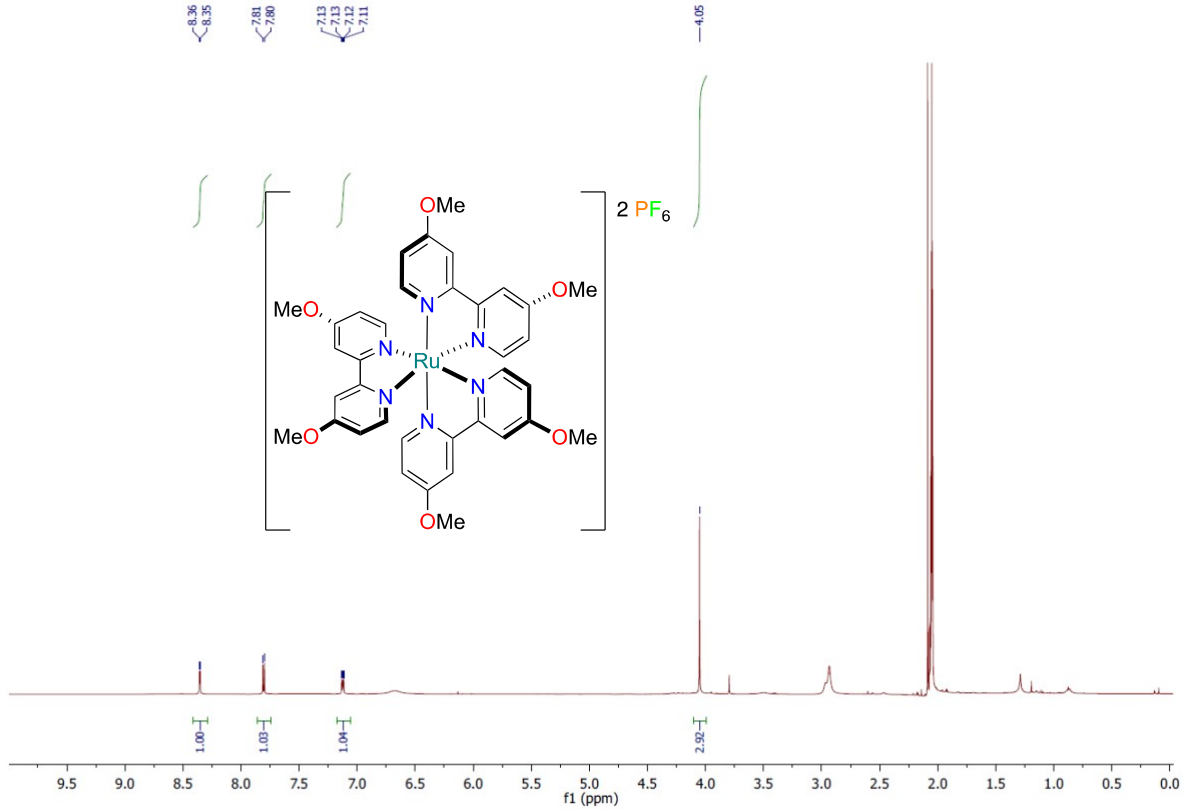
^{1}H NMR (500 MHz, Acetone) of tris(5,5'-dimethylbipyridine)ruthenium(II) *bis*(hexafluorophosphate) 3



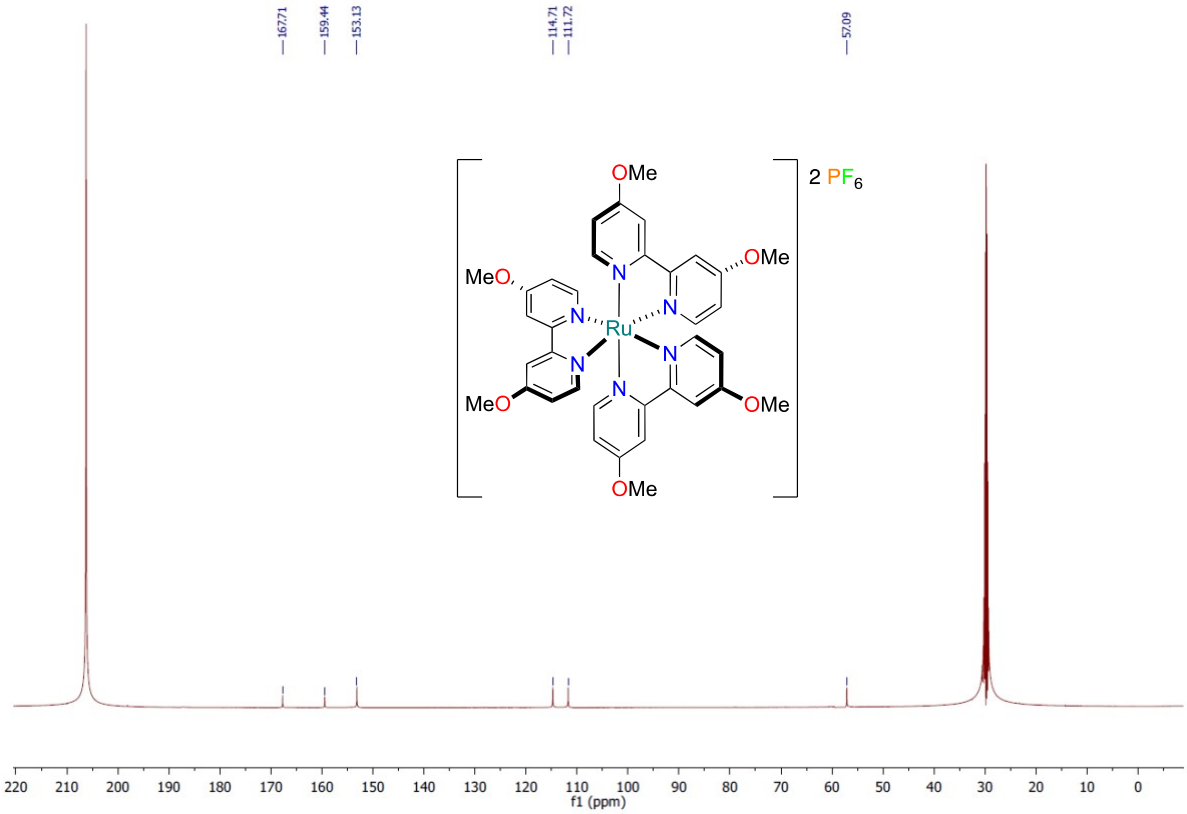
^{13}C NMR (126 MHz, Acetone) of tris(5,5'-dimethylbipyridine)ruthenium(II) *bis*(hexafluorophosphate) 3



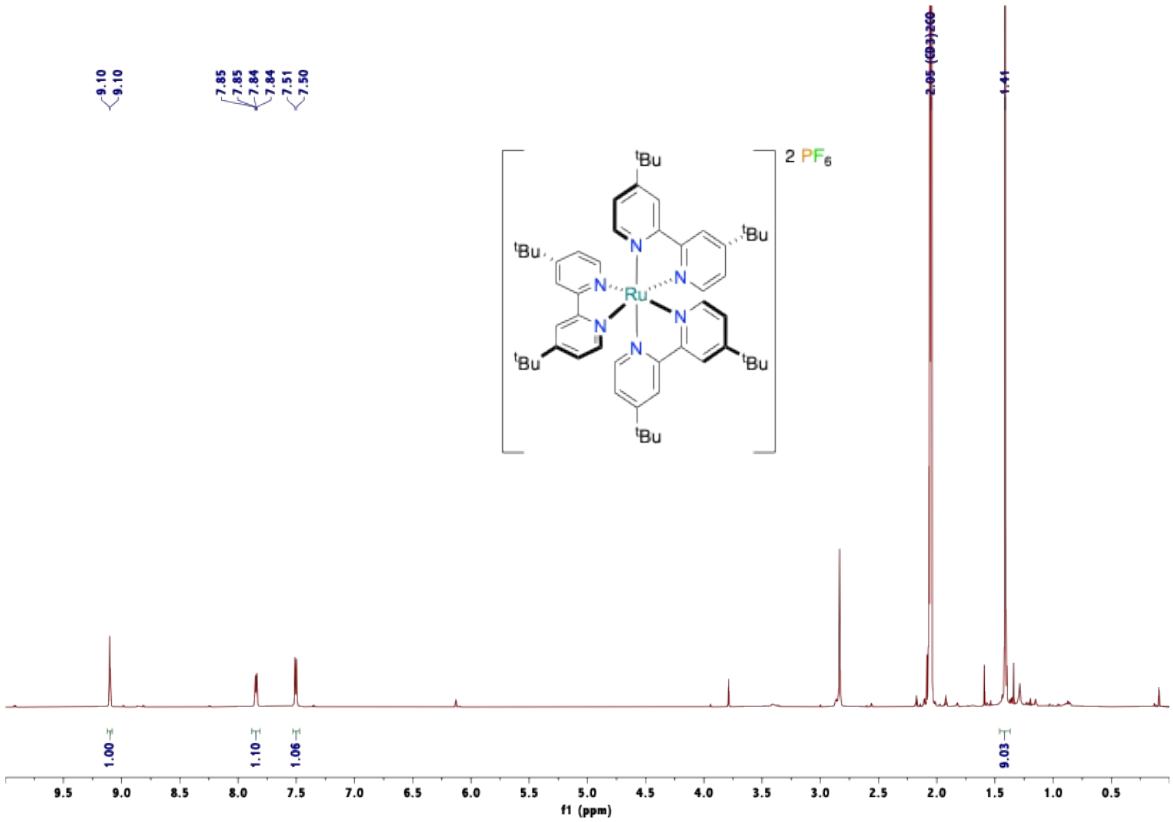
^{1}H NMR (500 MHz, Acetone) of tris(4,4'-dimethoxybipyridine)ruthenium(II) *bis*(hexafluorophosphate) 5



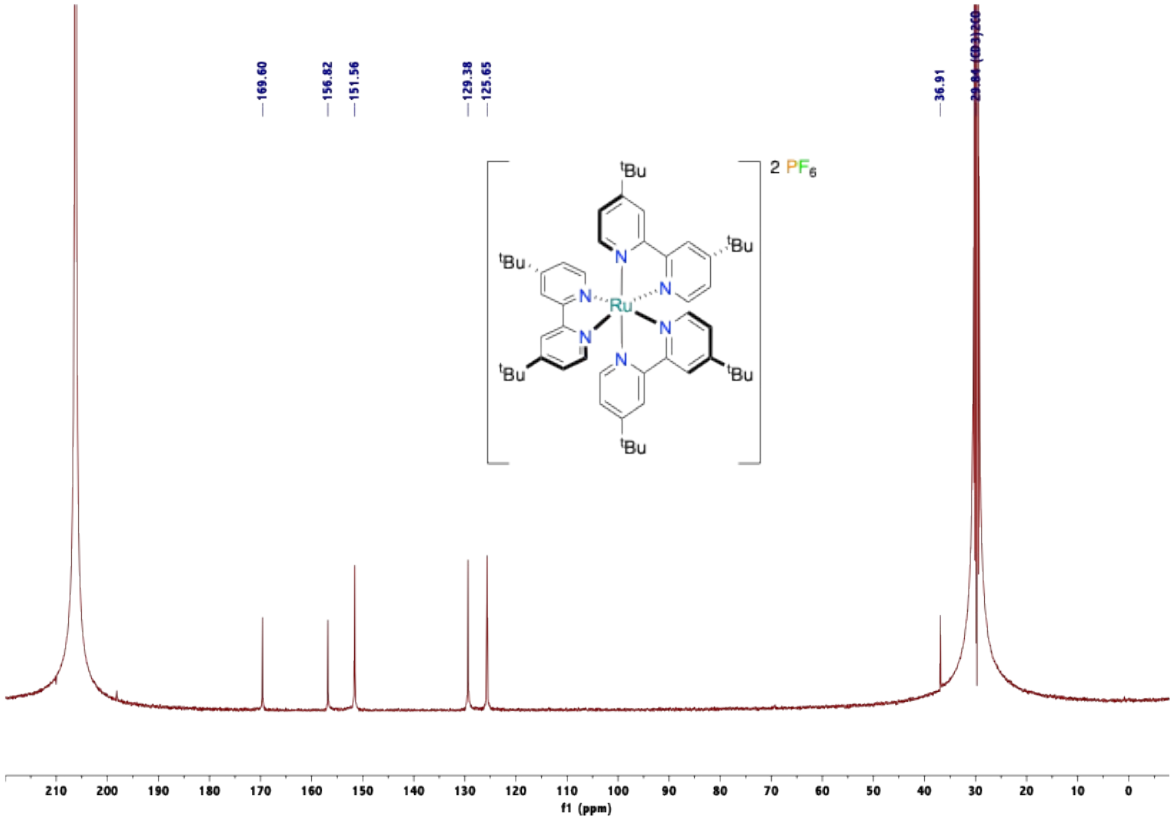
^{13}C NMR (126 MHz, Acetone) of tris(4,4'-dimethoxybipyridine)ruthenium(II) *bis*(hexafluorophosphate) 5



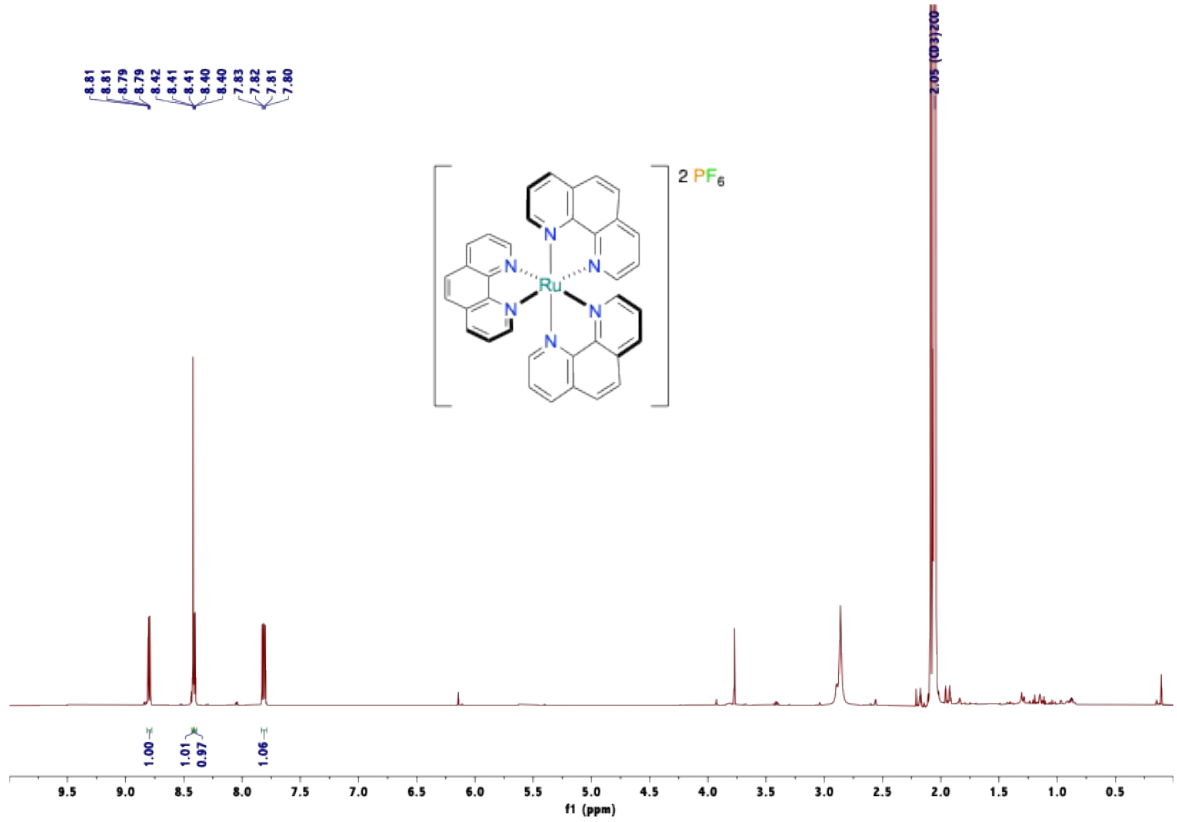
^{1}H NMR (500 MHz, Acetone) of tris(4,4'-di*tert*-butylbipyridine)ruthenium(II) *bis*(hexafluorophosphate) 6



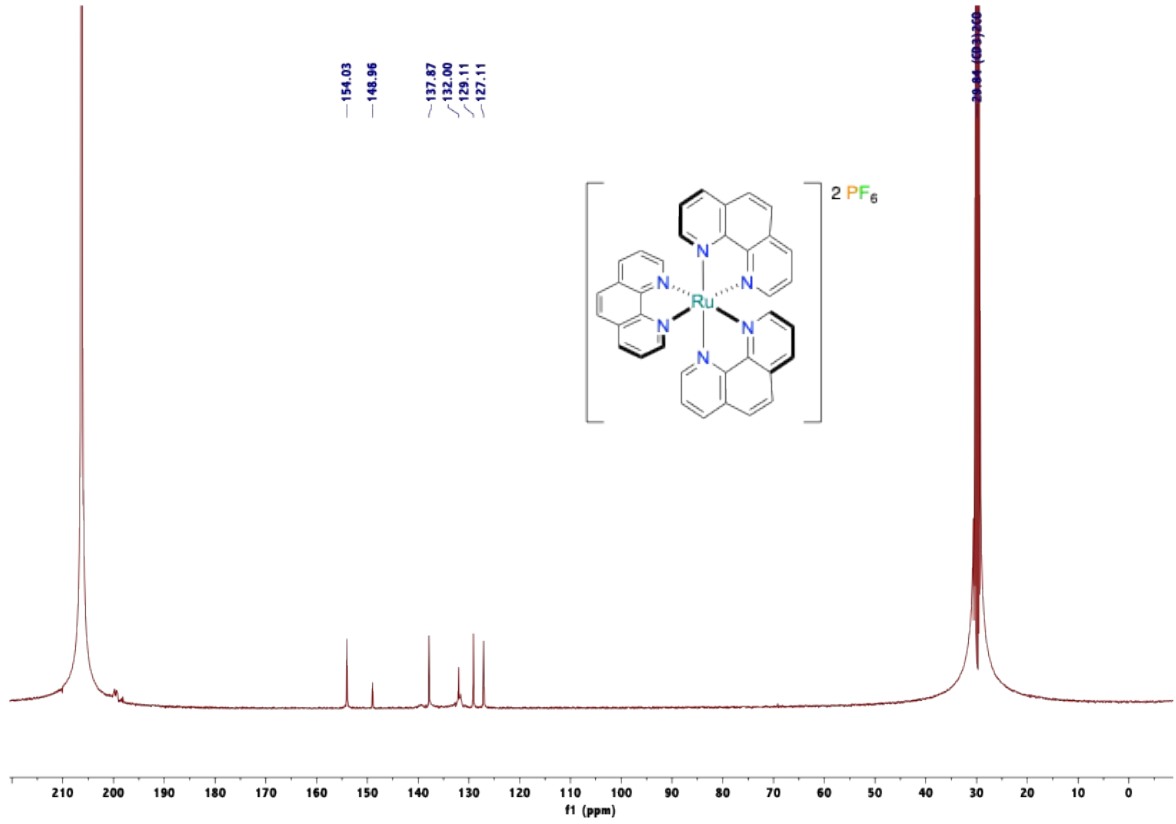
^{13}C NMR (126 MHz, Acetone) of tris(4,4'-di*tert*-butylbipyridine)ruthenium(II) *bis*(hexafluorophosphate) 6



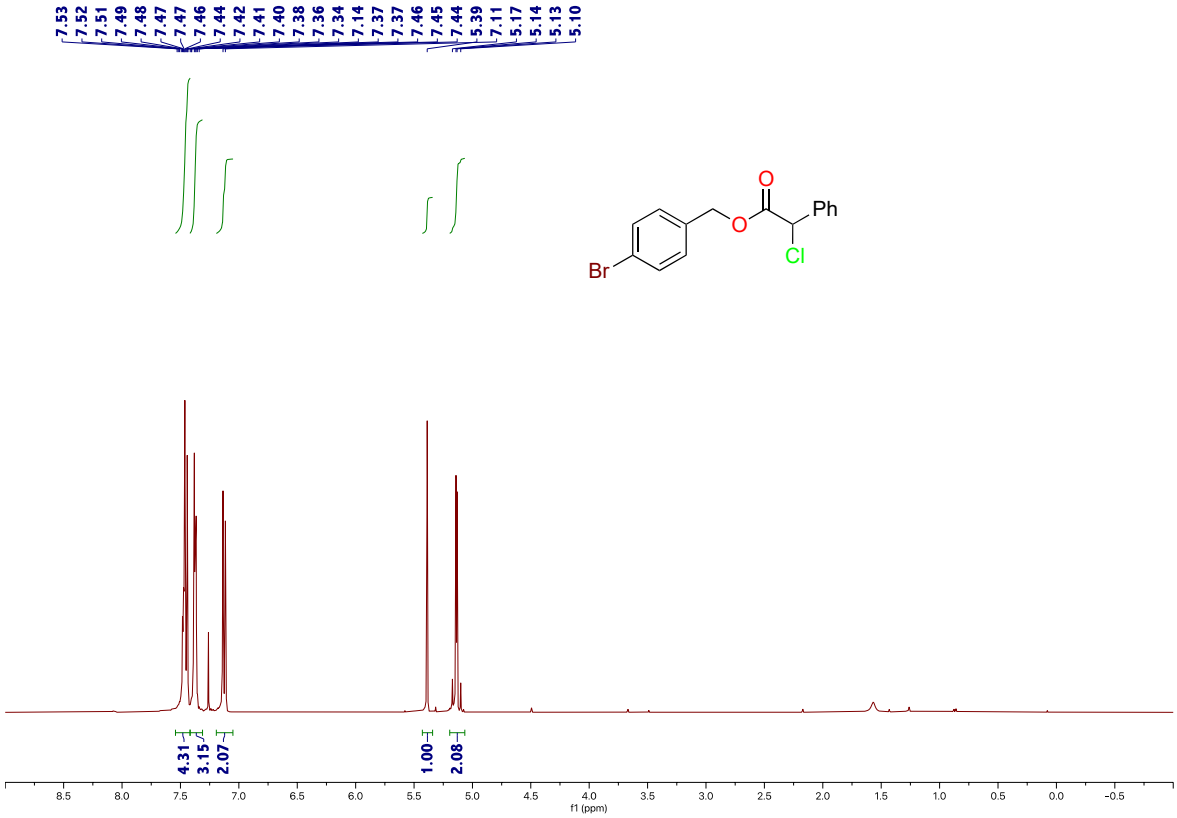
^{1}H NMR (500 MHz, Acetone) of tris(1,10-phenanthroline)ruthenium(II) *bis*(hexafluorophosphate) 7



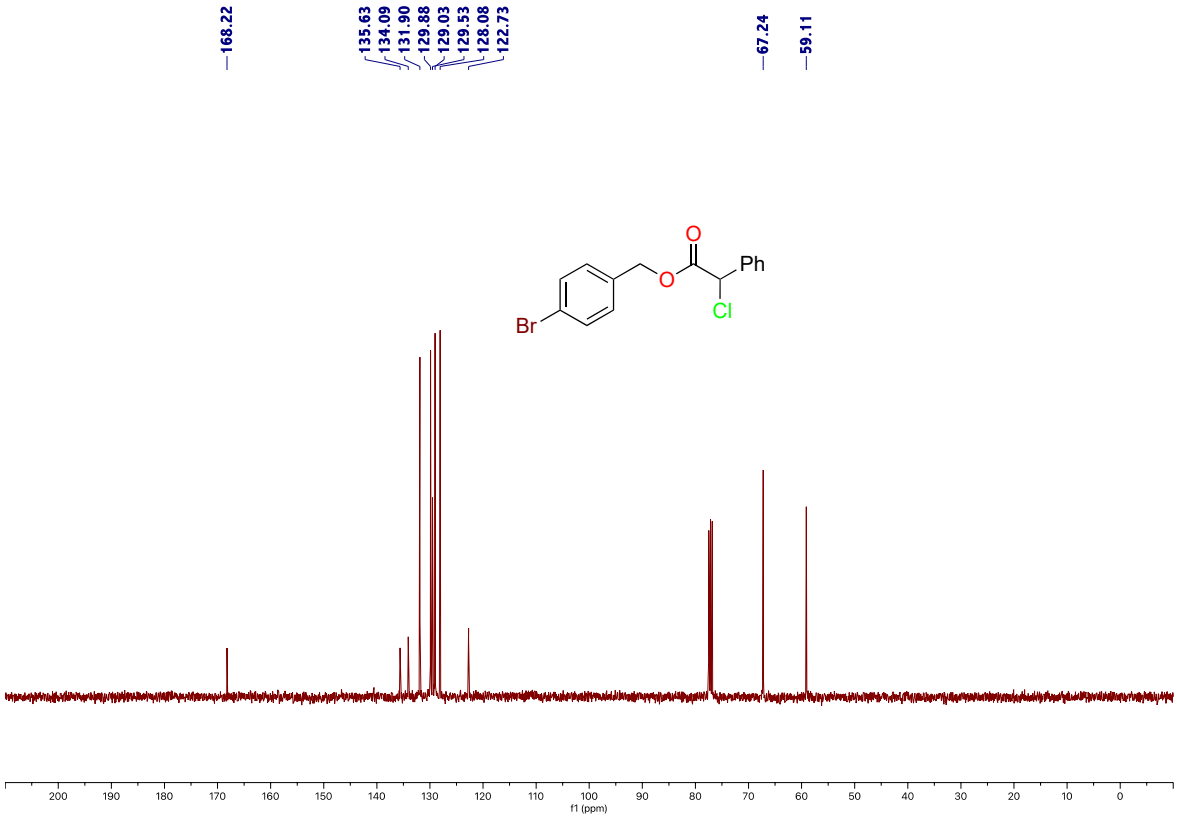
^{13}C NMR (126 MHz, Acetone) of tris(1,10-phenanthroline)ruthenium(II) *bis*(hexafluorophosphate) 7



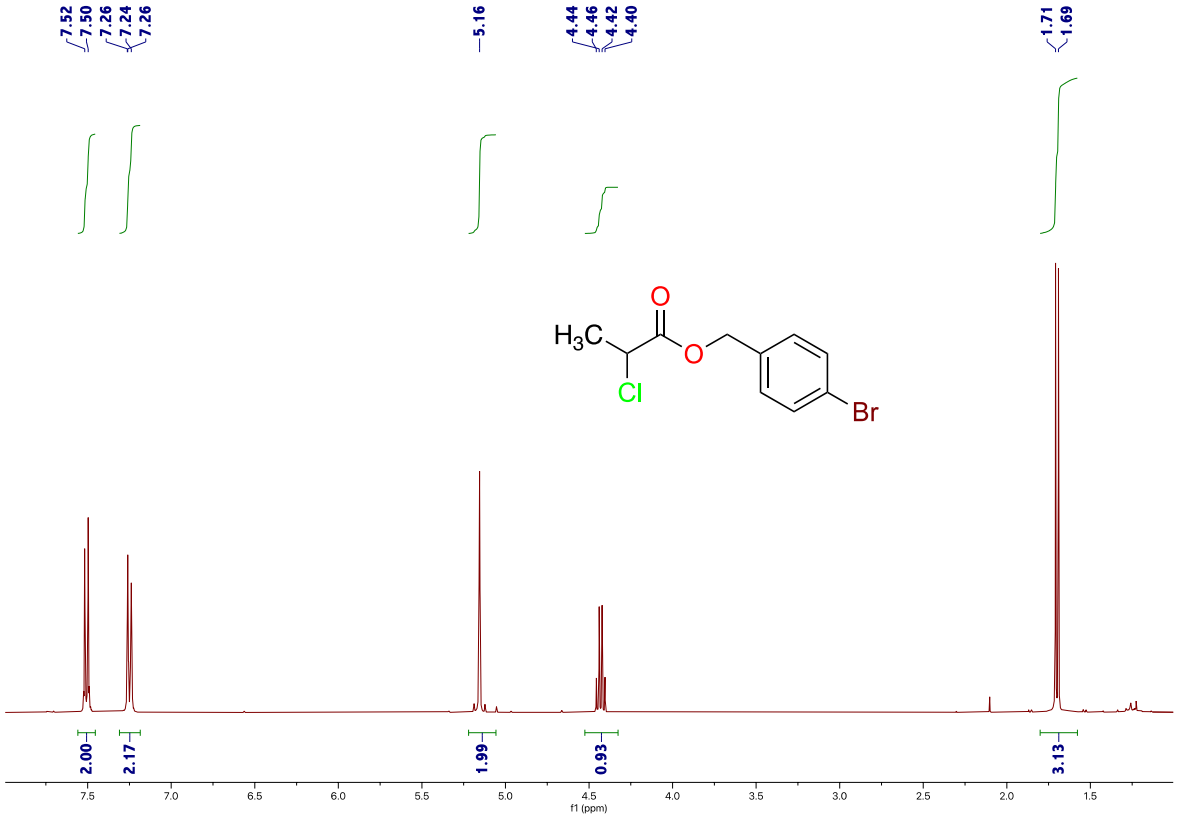
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8a**



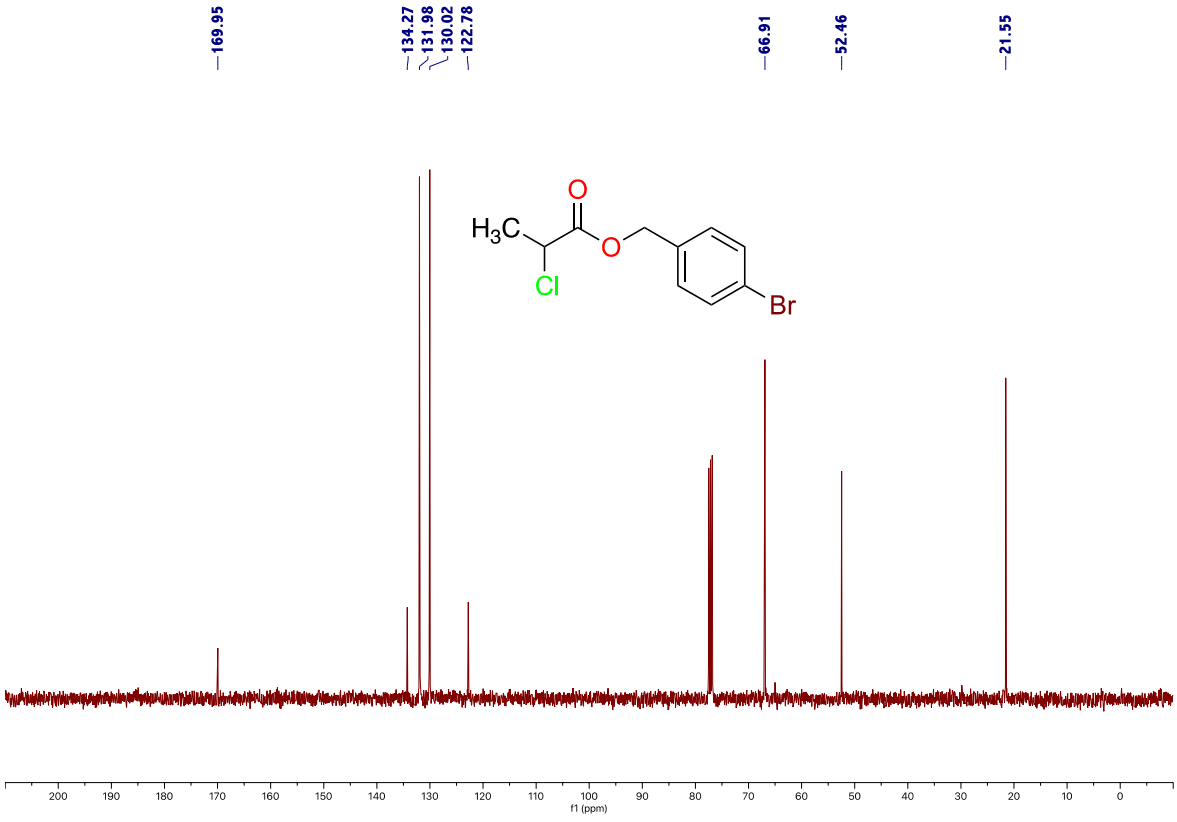
^{13}C NMR (101 MHz, $CDCl_3$) of compound **8a**



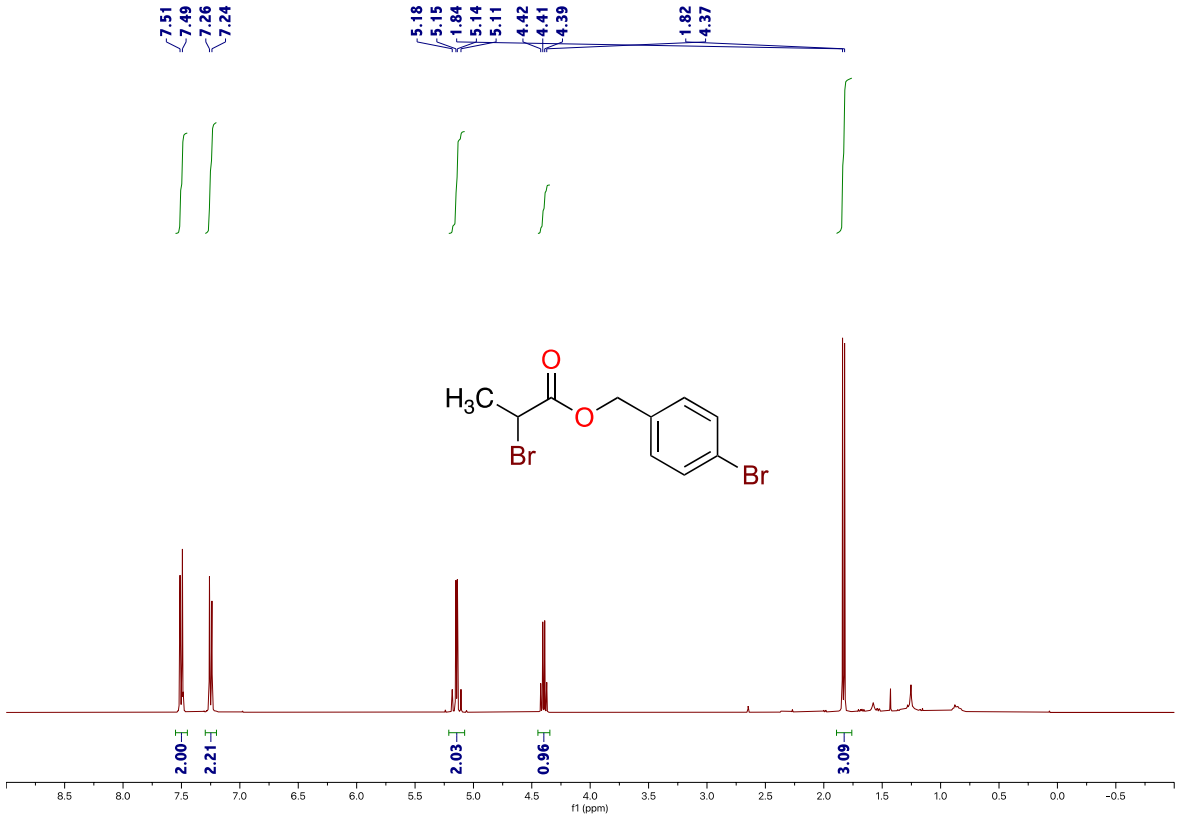
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8b**



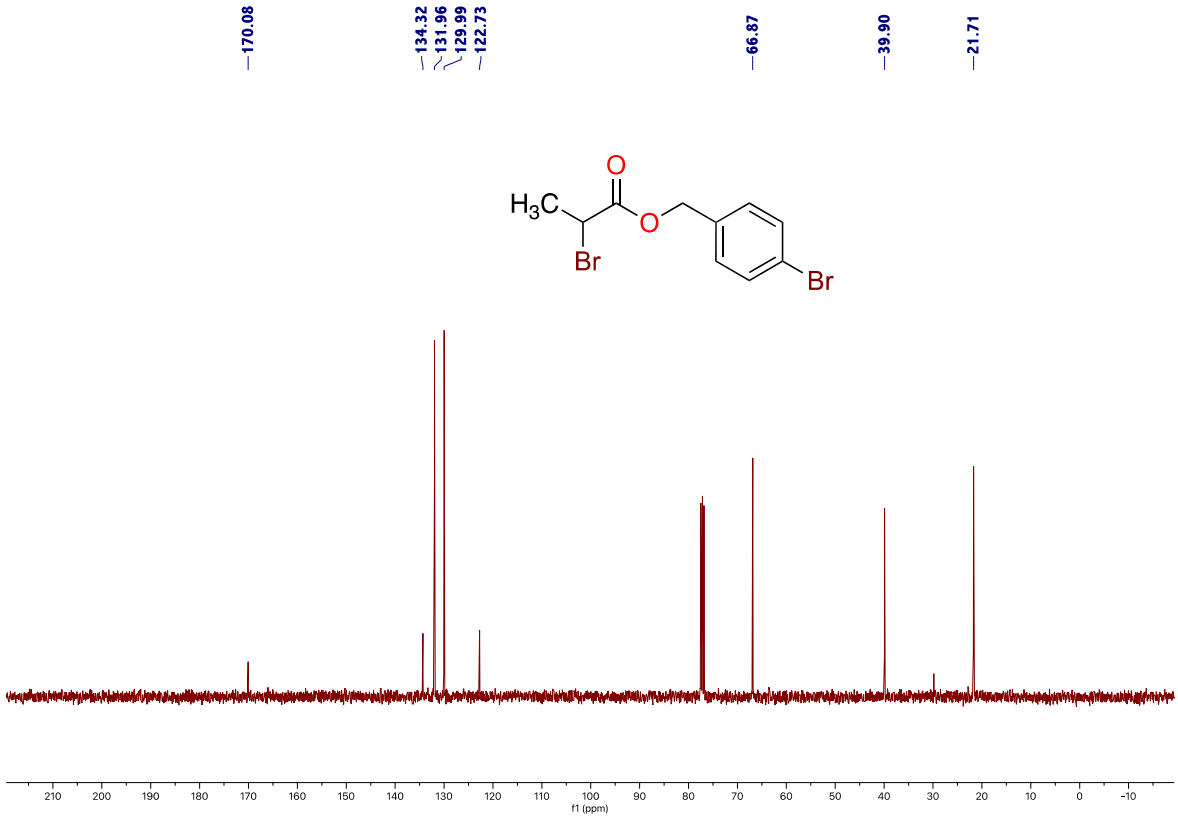
^{13}C NMR (101 MHz, $CDCl_3$) of compound **8b**



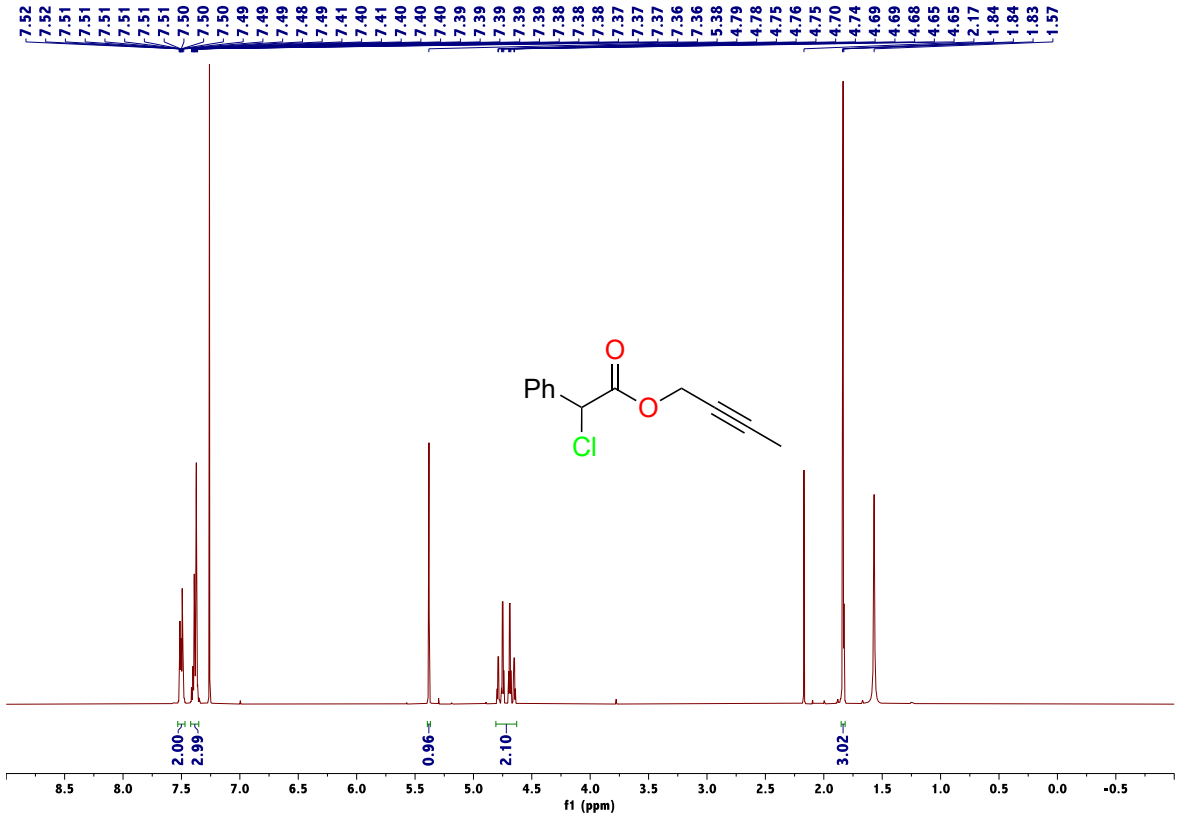
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8b-Br**



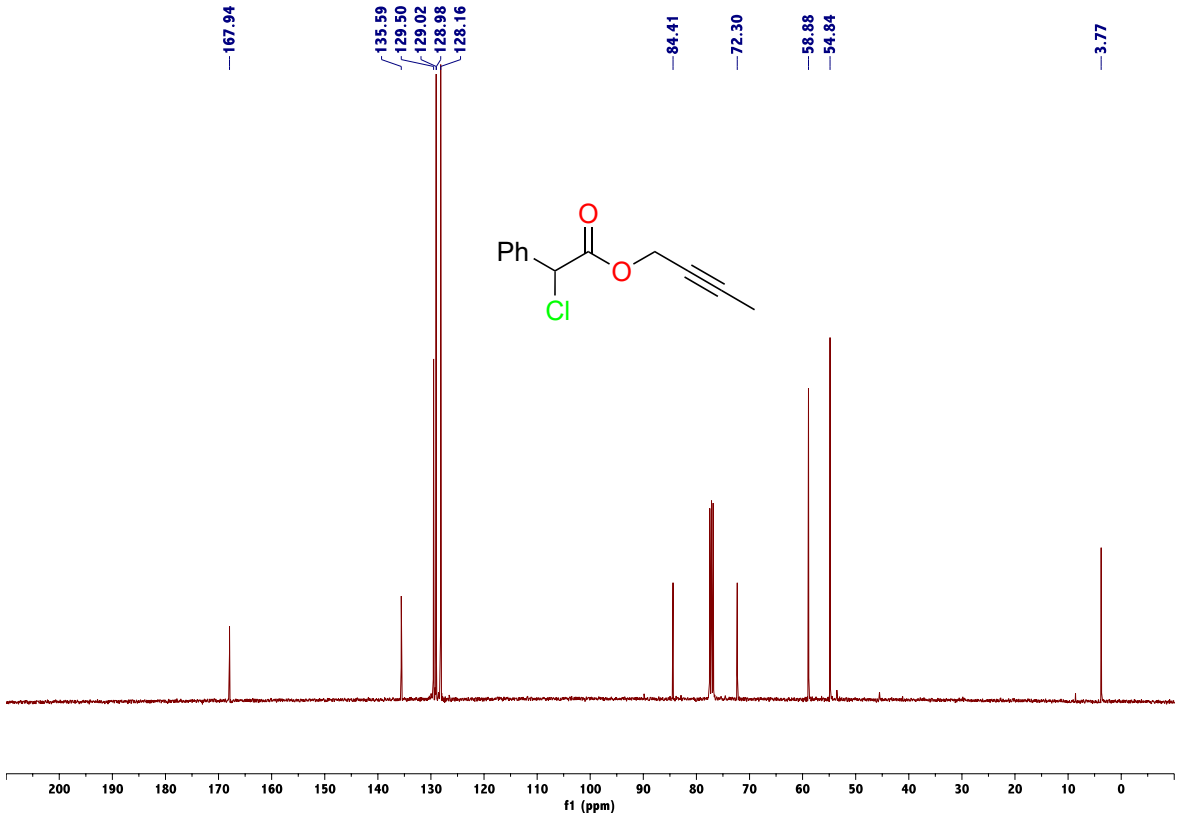
^{13}C NMR (101 MHz, $CDCl_3$) of compound **8b-Br**



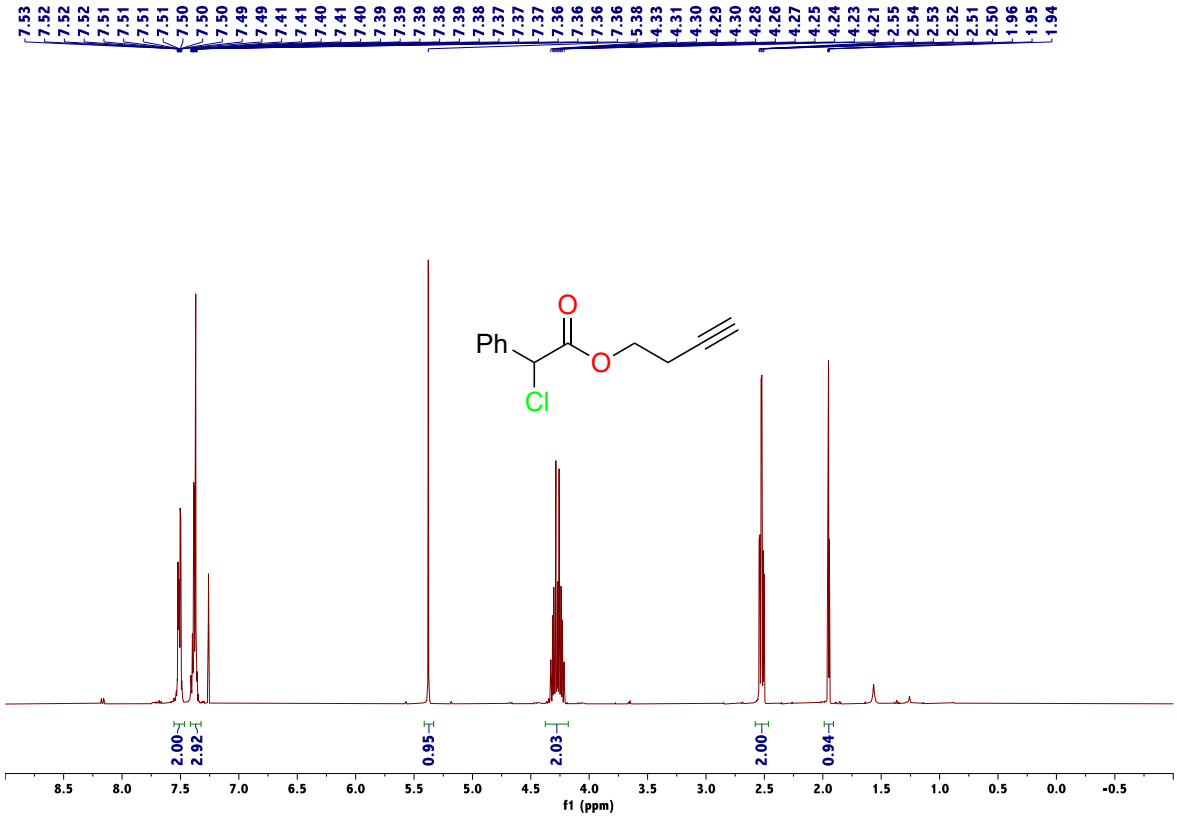
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8c**



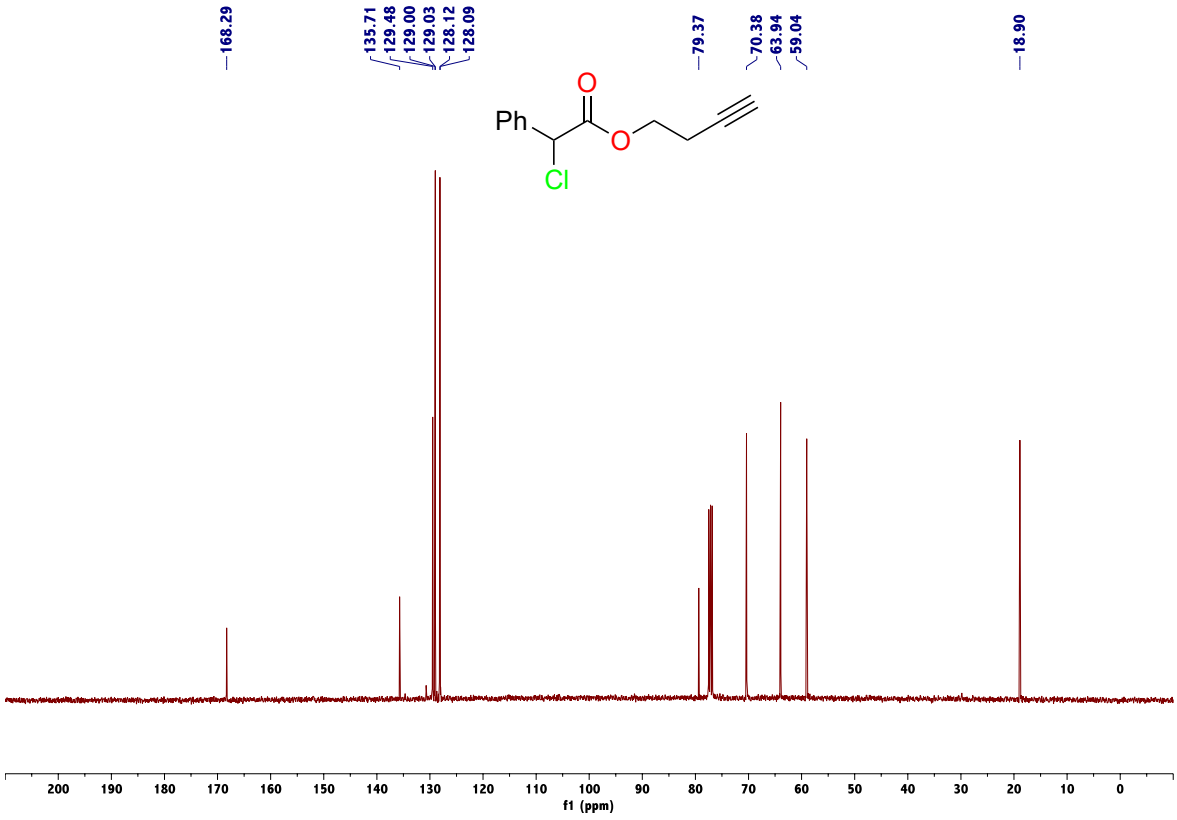
^{13}C NMR (101 MHz, $CDCl_3$) of compound **8c**



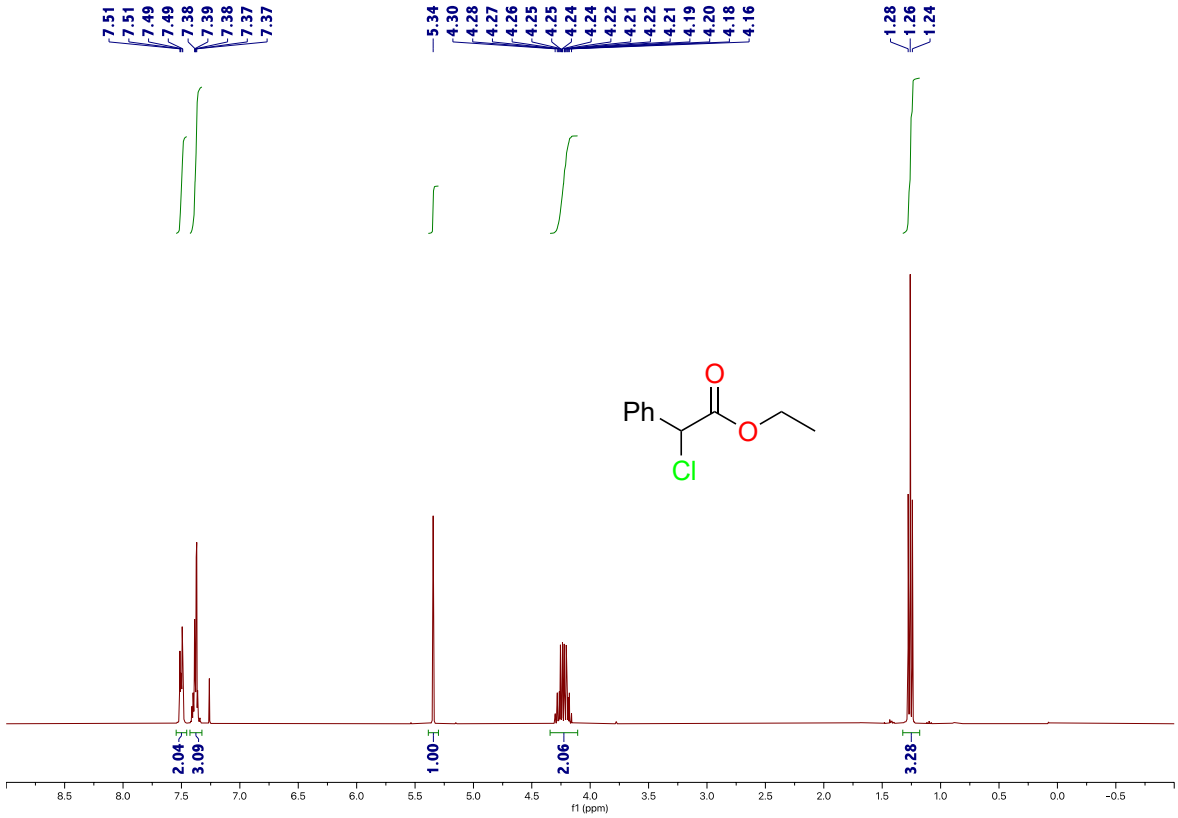
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8d**



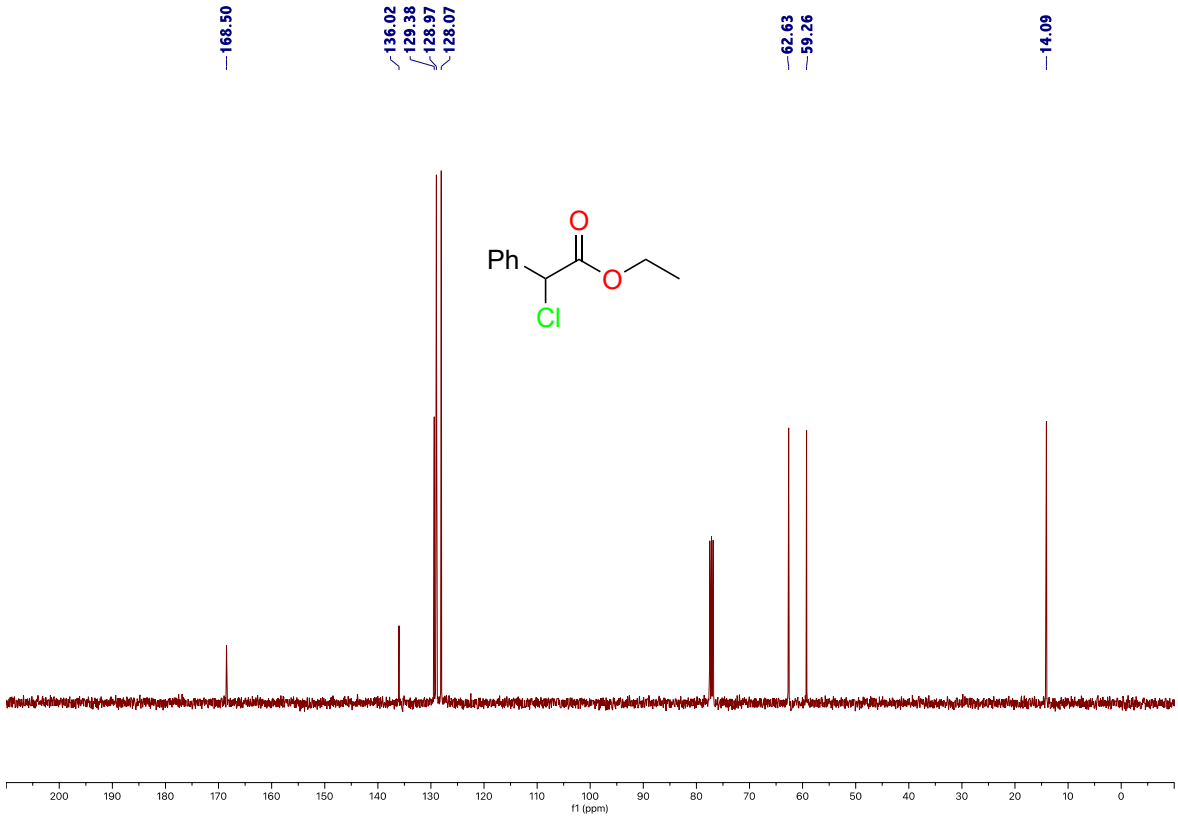
^{13}C NMR (101 MHz, $CDCl_3$) of compound **8d**



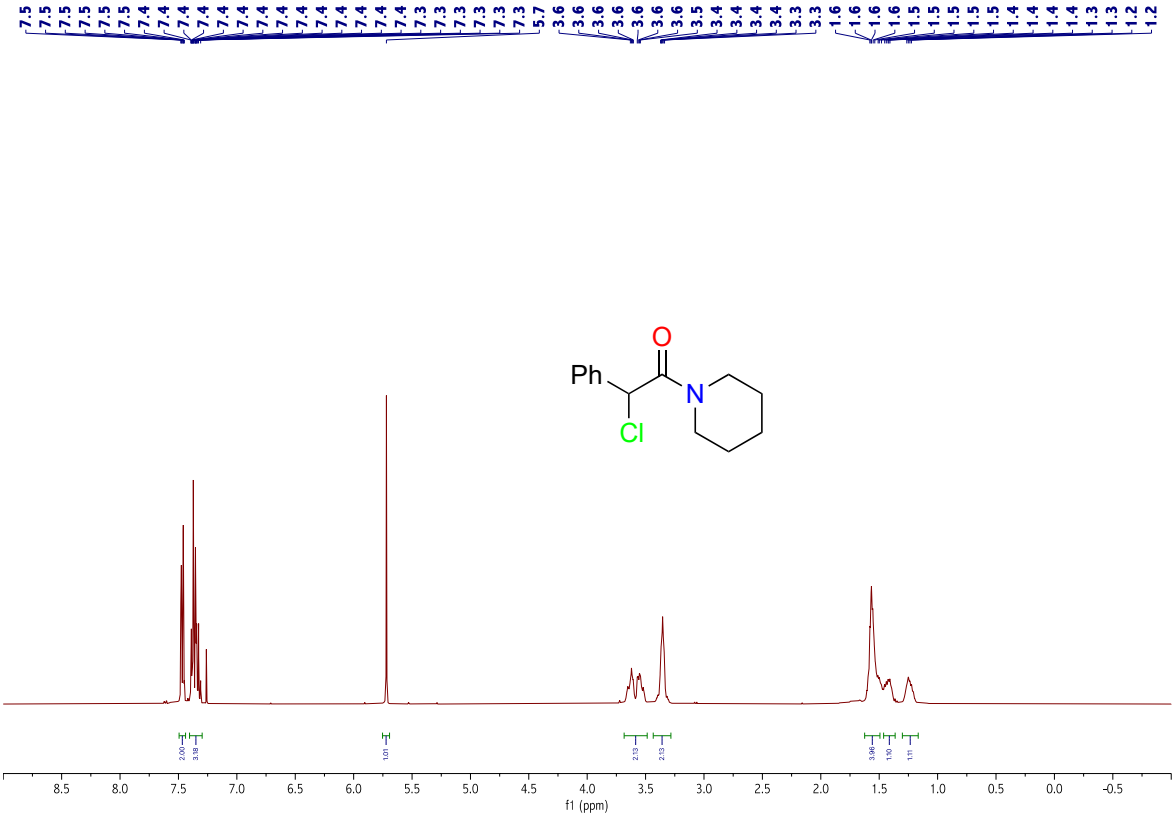
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8e**



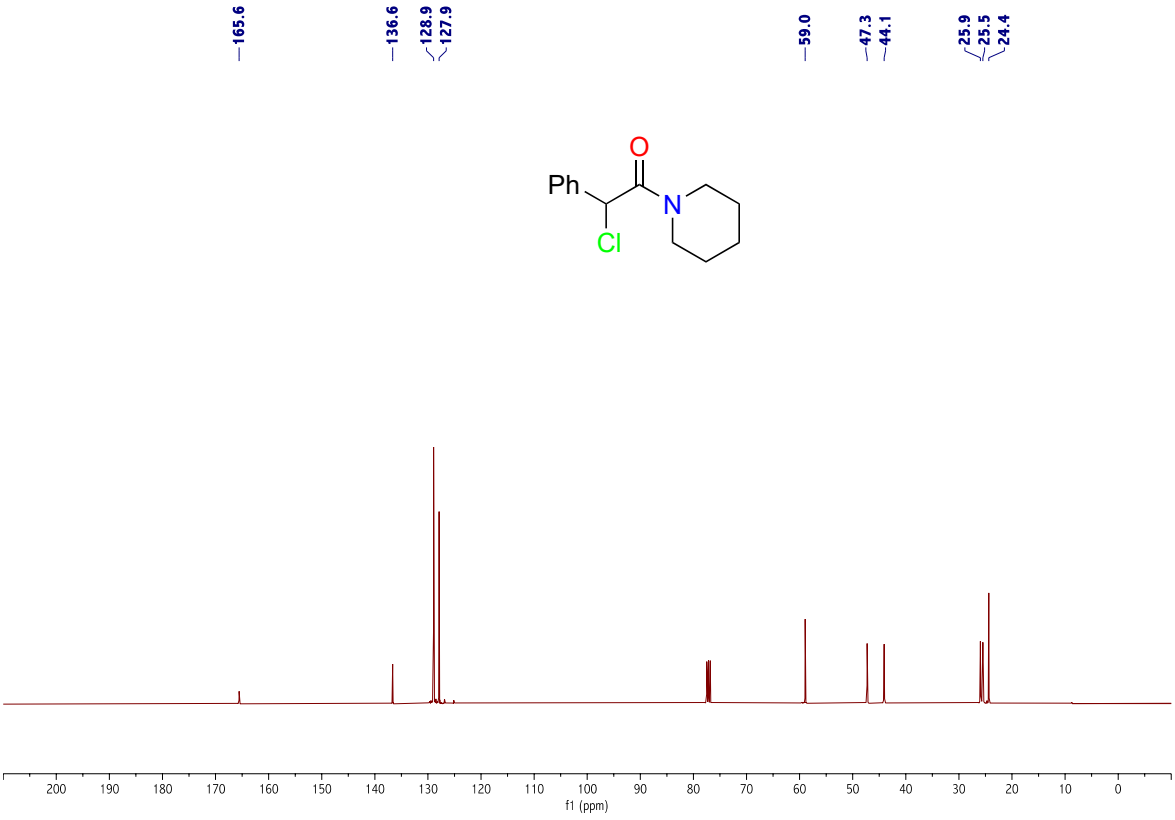
^{13}C NMR (101 MHz, $CDCl_3$) of compound **8e**



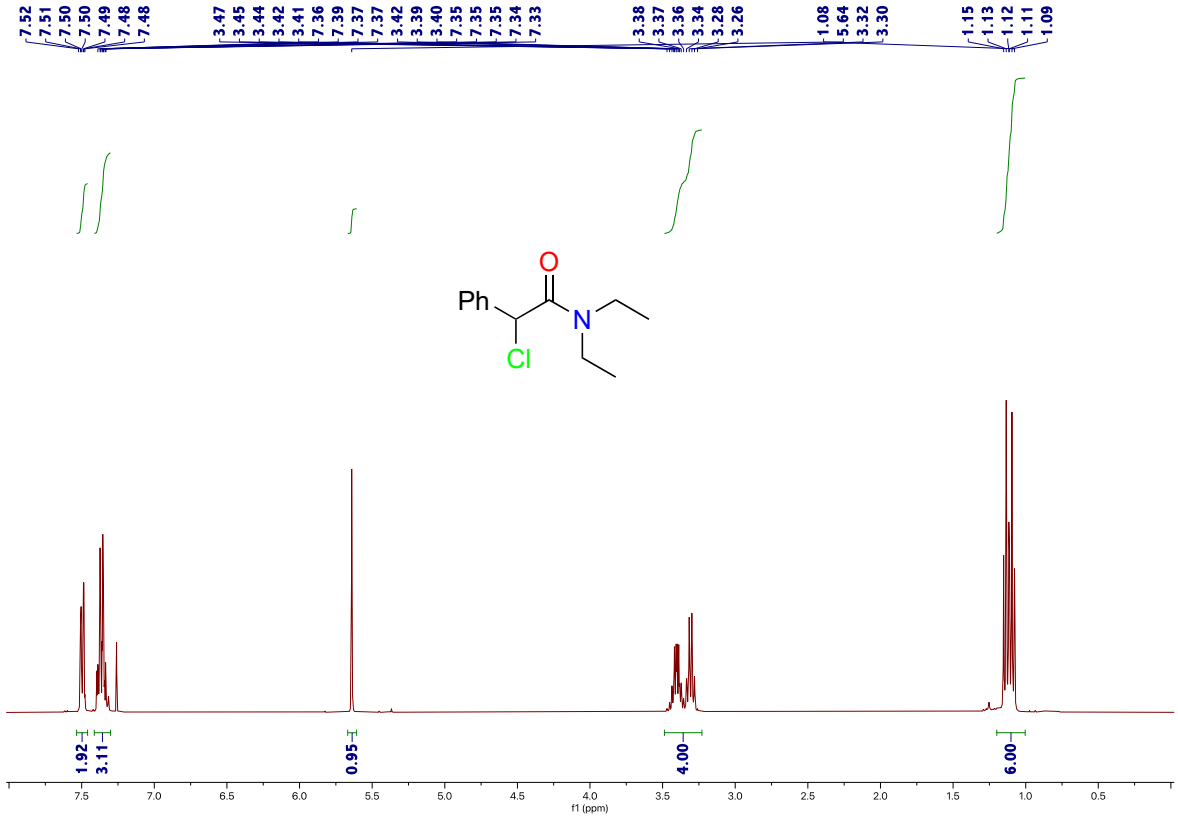
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8f**



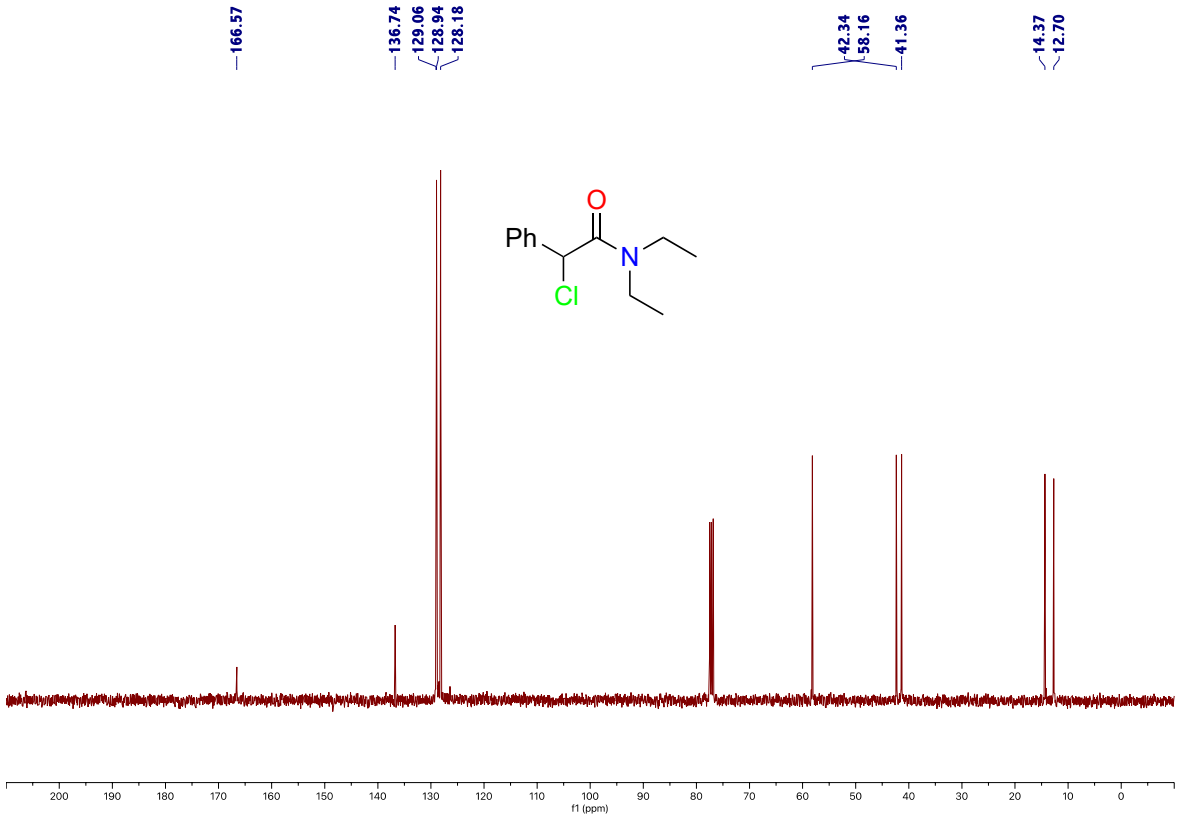
^{13}C NMR (101 MHz, $CDCl_3$) of compound **8f**



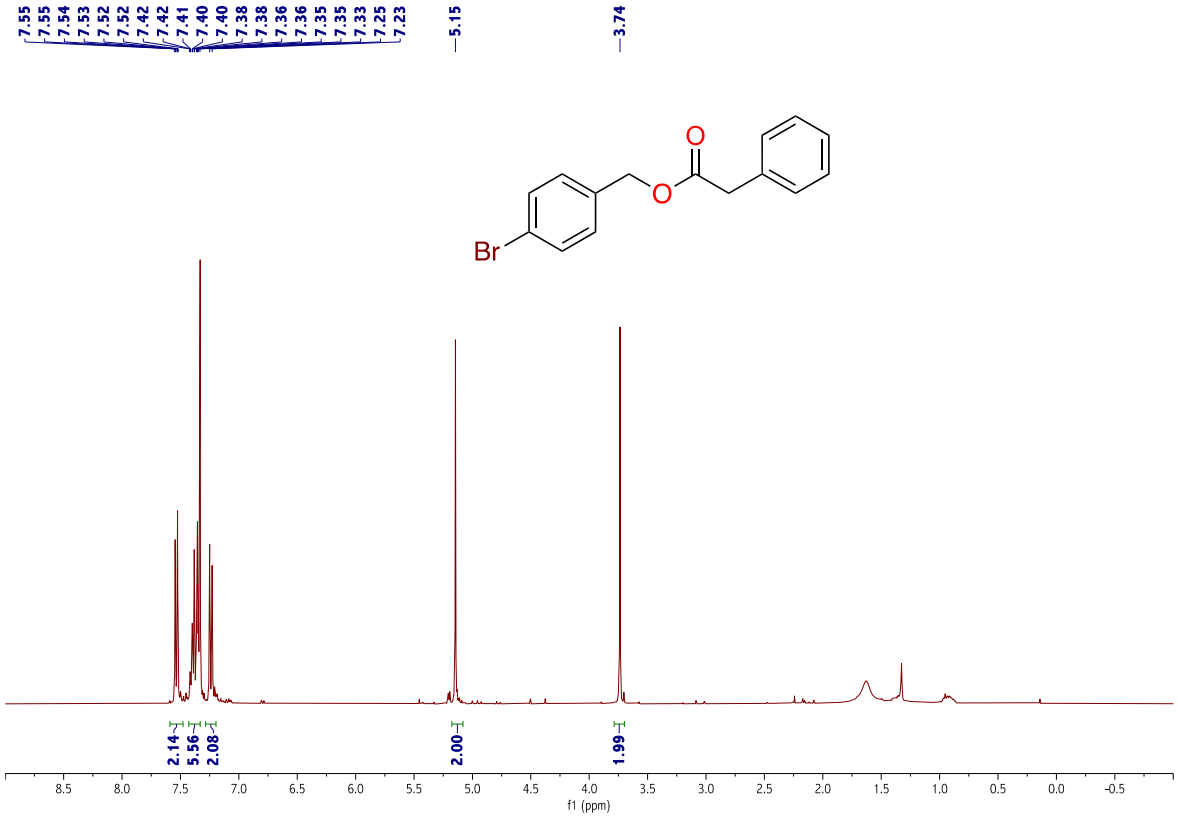
^{1}H NMR (400 MHz, $CDCl_3$) of compound **8g**



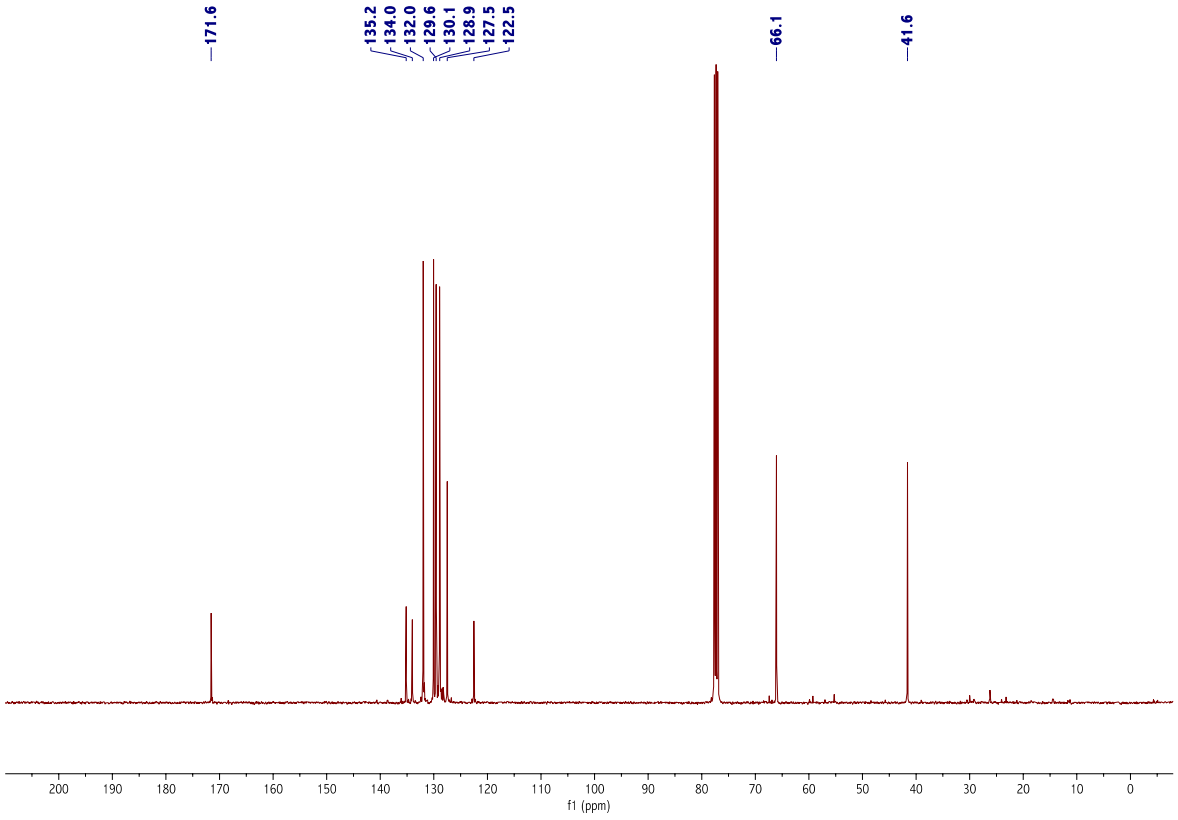
^{13}C NMR (101 MHz, $CDCl_3$) of compound **8g**



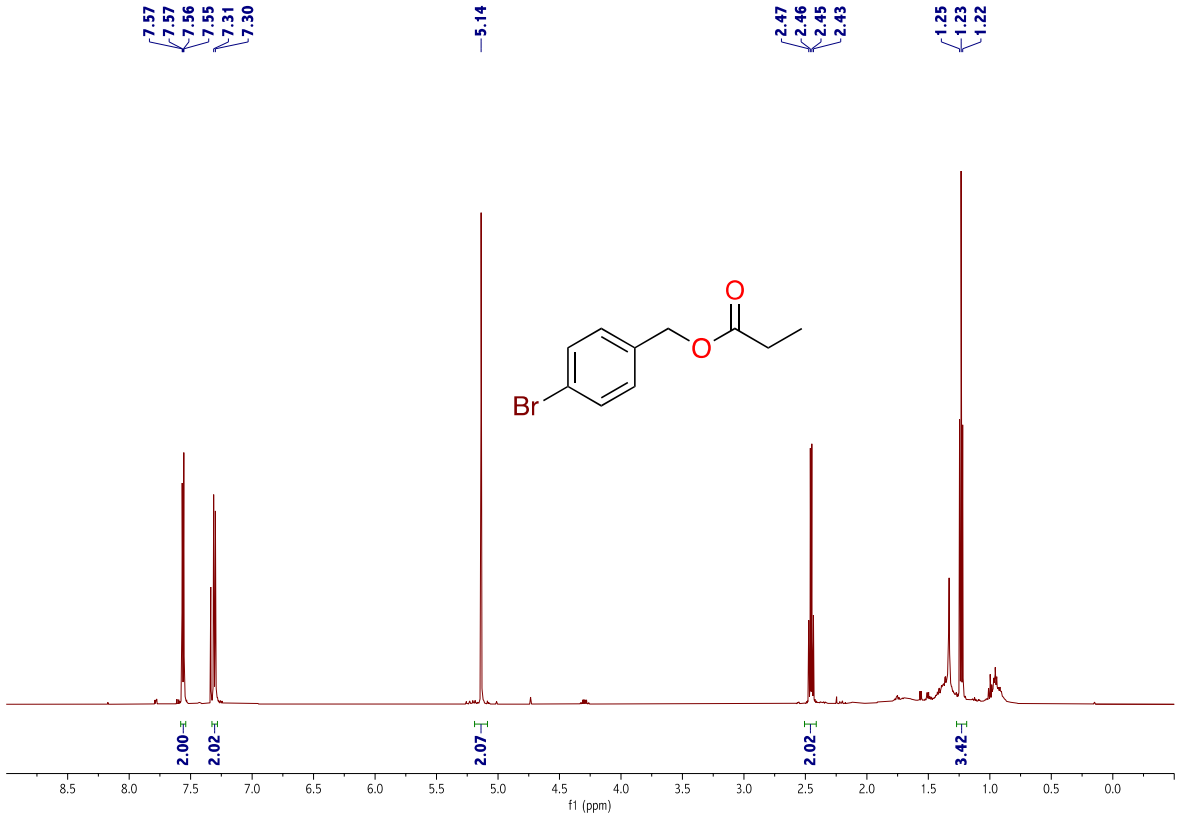
^{1}H NMR (400 MHz, $CDCl_3$) of compound **9a**



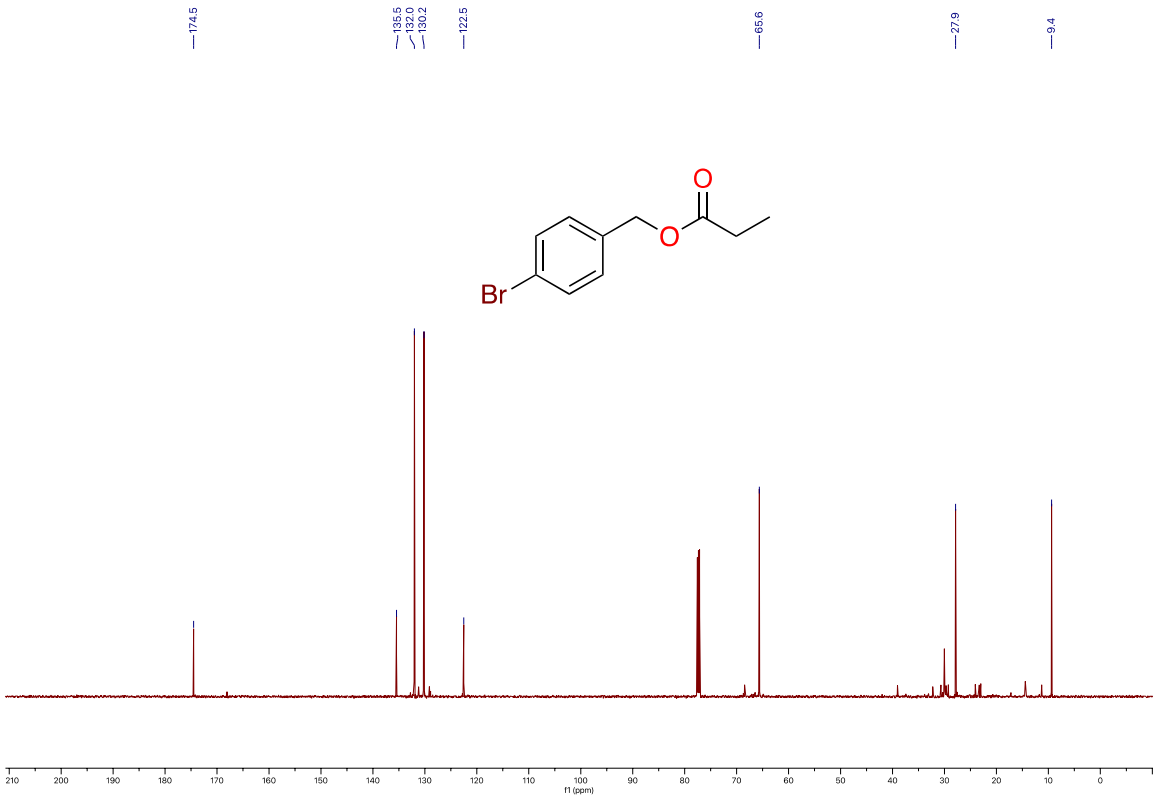
^{13}C NMR (101 MHz, $CDCl_3$) of compound **9a**



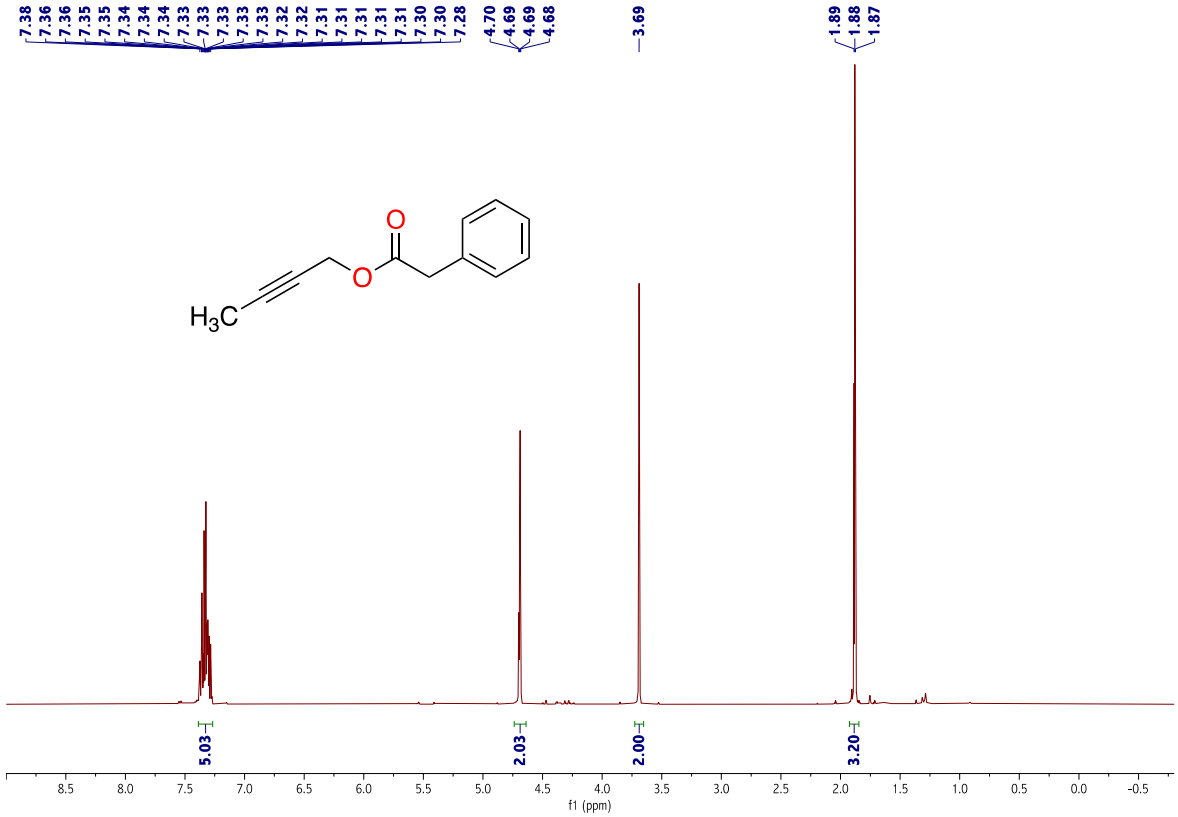
^{1}H NMR (600 MHz, $CDCl_3$) of compound **9b**



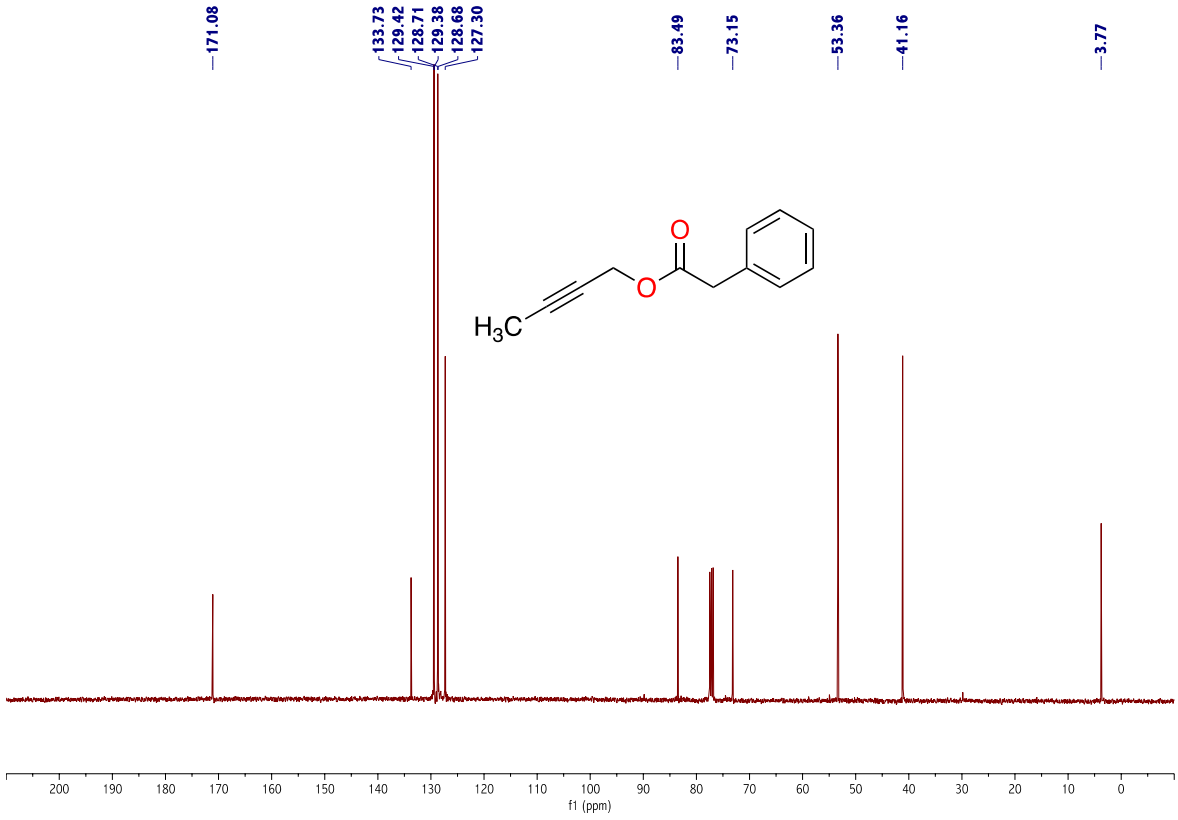
^{13}C NMR (151 MHz, $CDCl_3$) of compound **9b**



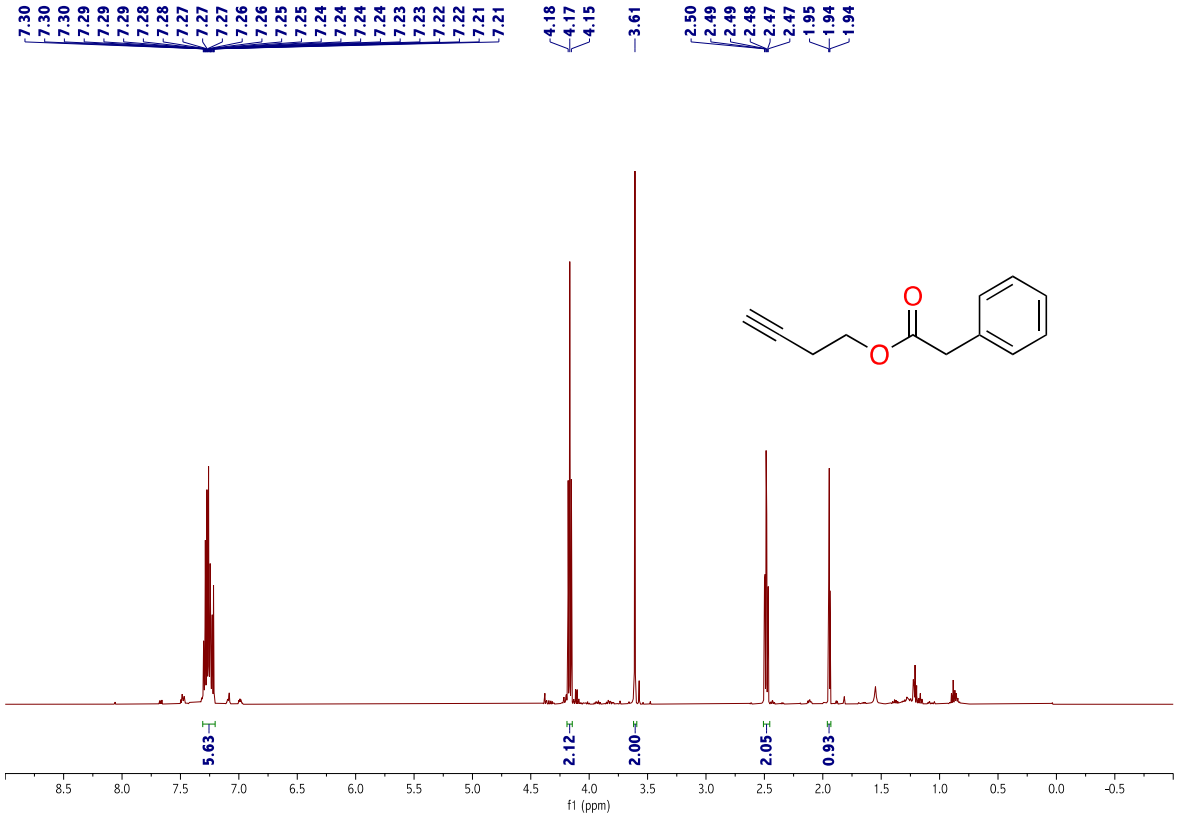
^{1}H NMR (400 MHz, $CDCl_3$) of compound **9c**



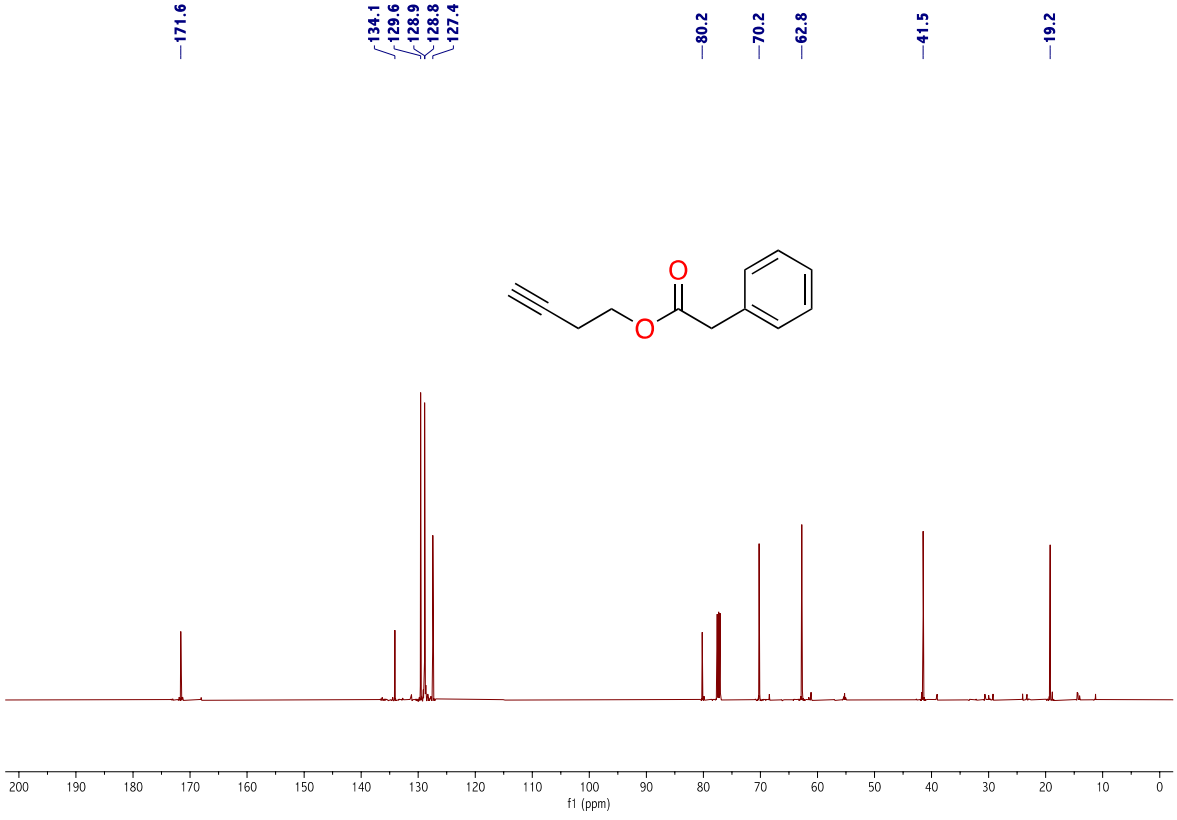
^{13}C NMR (101 MHz, $CDCl_3$) of compound **9c**



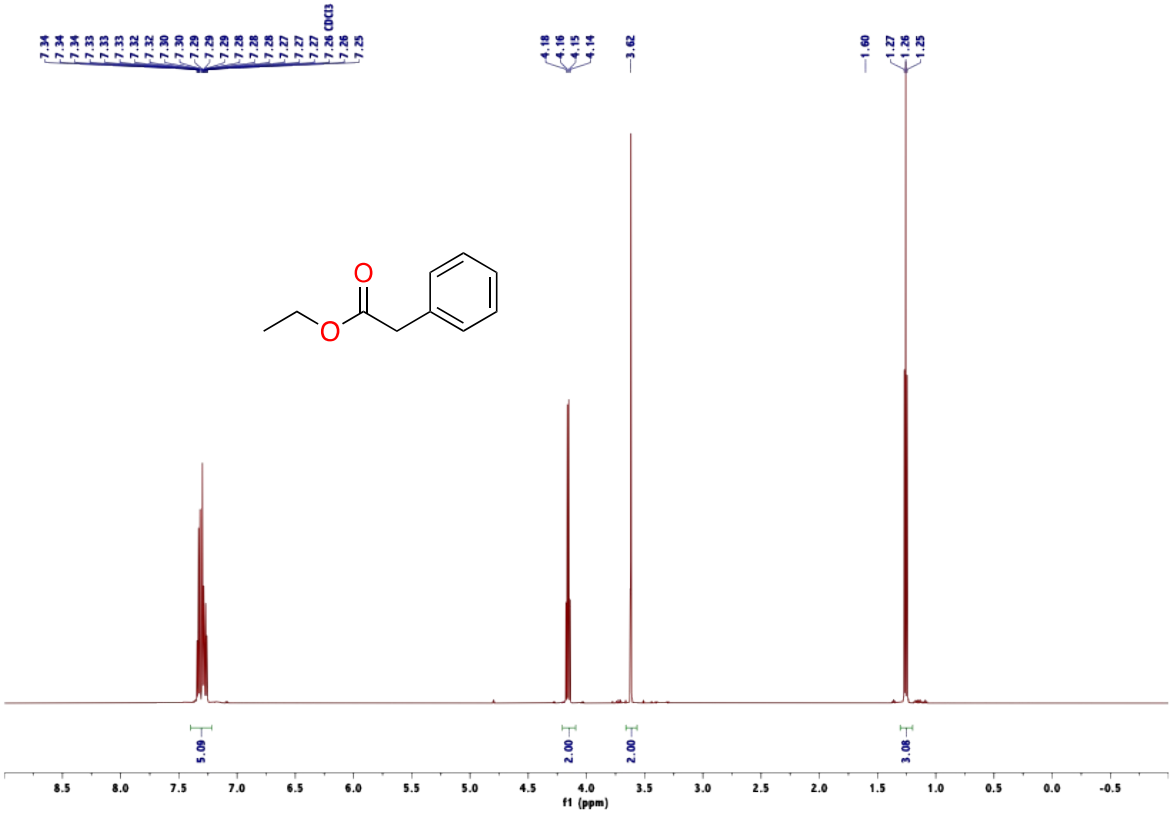
^{1}H NMR (500 MHz, $CDCl_3$) of compound **9d**



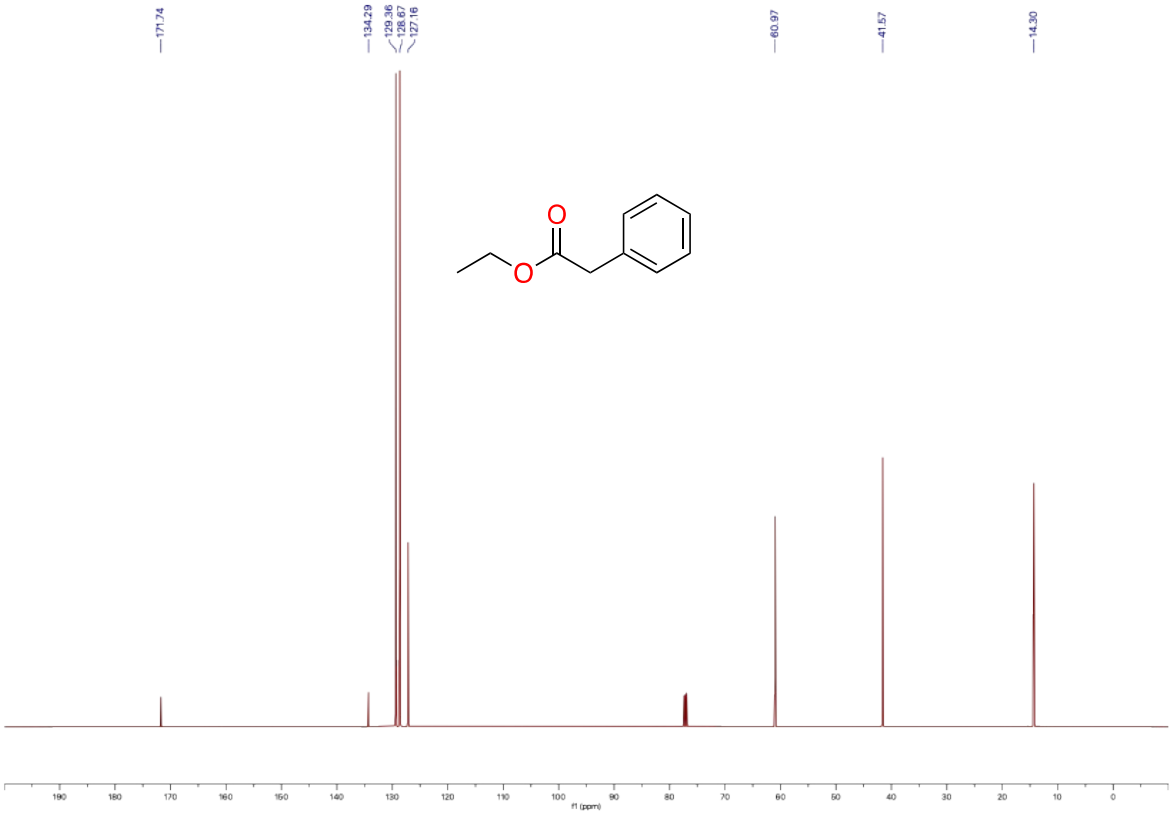
^{13}C NMR (126 MHz, $CDCl_3$) of compound **9d**



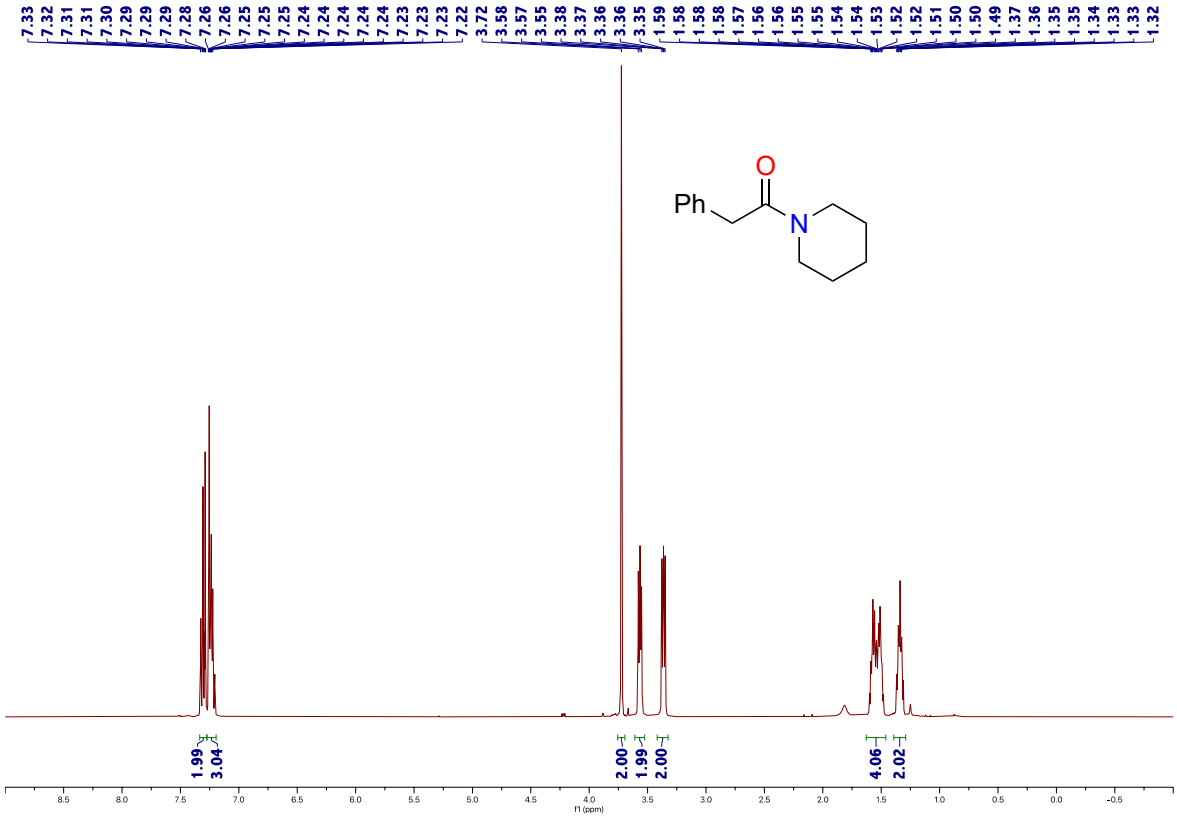
^{1}H NMR (600 MHz, $CDCl_3$) of compound **9e**



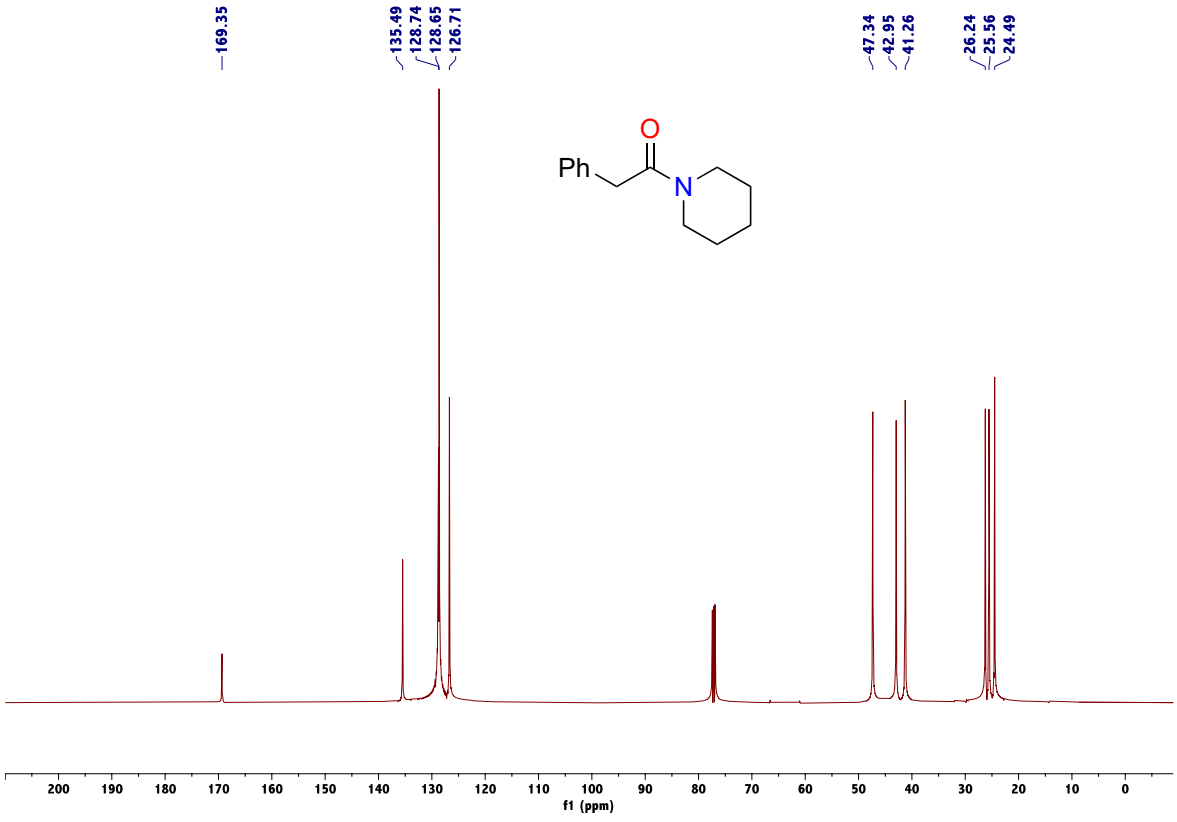
^{13}C NMR (151 MHz, $CDCl_3$) of compound **9e**



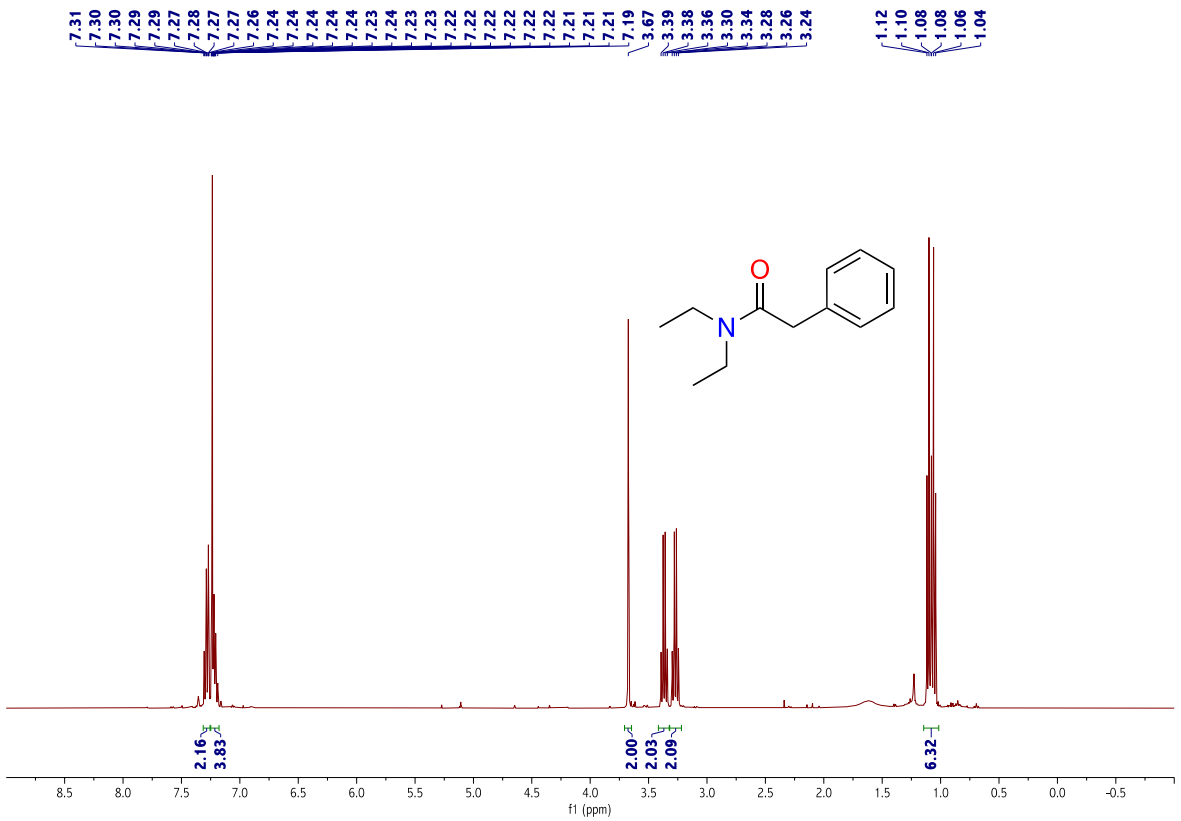
^{1}H NMR (400 MHz, $CDCl_3$) of compound **9f**



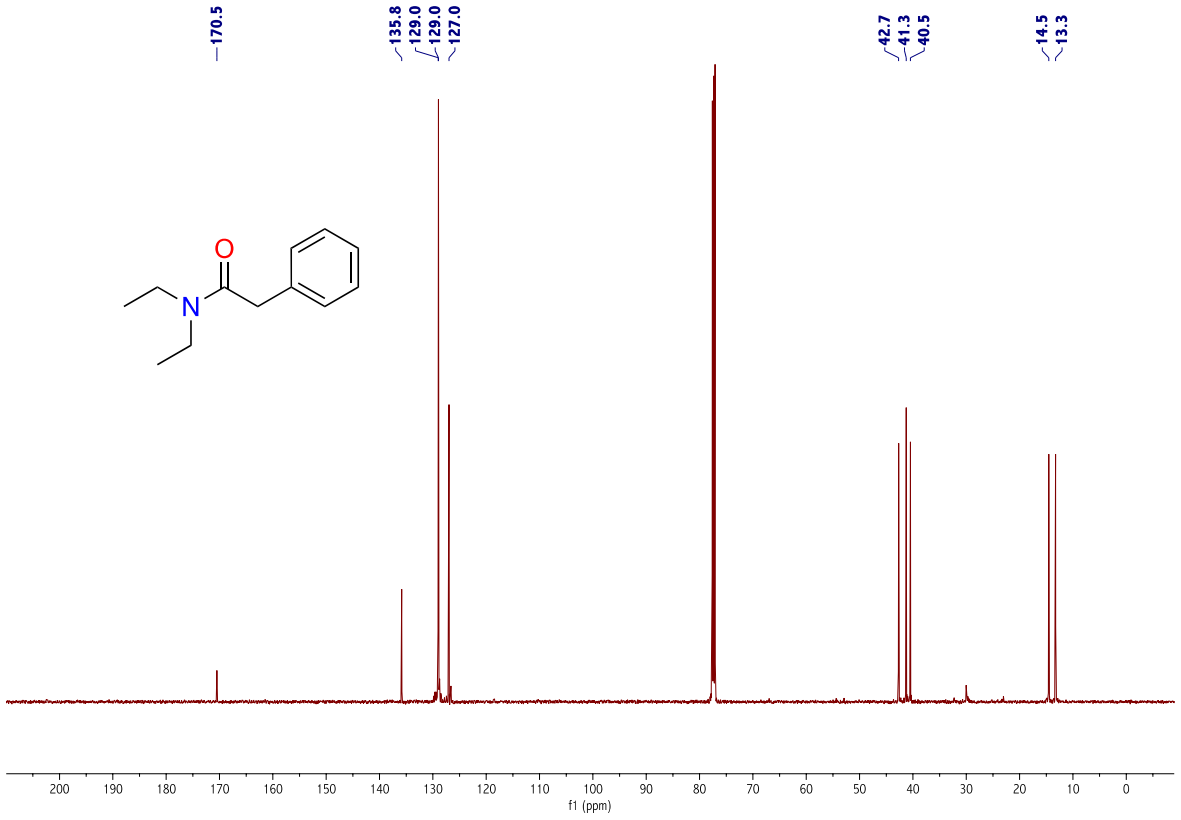
^{13}C NMR (101 MHz, $CDCl_3$) of compound **9f**



^{1}H NMR (400 MHz, $CDCl_3$) of compound **9g**



^{13}C NMR (126 MHz, $CDCl_3$) of compound **9g**



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