Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Supporting Information

Cr-mediated Photocatalytic Decarboxylative Coupling of alpha-Oxo Acids with Benzylic Pyridinium Salts

Jia Cao*, Yan Liu, Zhixiang Wang, Le Liu

China Shaanxi Key Laboratory of Chemical Reaction Engineering, School of Chemistry and Chemical Engineering, Yan'an University, Yan'an 716000 (P. R. China).

Corresponding Author: caojia213@126.com

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1. General Information

All reactions were carried out with standard schlenk techniques under argon or in an argon-filled glove-box. $CrCl_2$, $CoCl_2$, $NiCl_2$, photocatalysis, base and α-oxo acids were purchased from Sigma-Aldrich, J&K, Alfa Aesar Chemical Companies and Acros used as received without purification. Anhydrous THF and other anhydrous solvents were purchased from J&K and used as received (water < 30 ppm, J&KSeal). Analytical thin-layer chromatography (TLC) was performed on silica gel 60 F_{254} aluminum sheets from Qingdao Haiyang Chemical Co., Ltd. Flash chromatography was performed on silica gel (200–300 mesh, Qingdao Haiyang Chemical Co., Ltd). All of Katritzky salts were synthesized according to the literature procedure.[1]

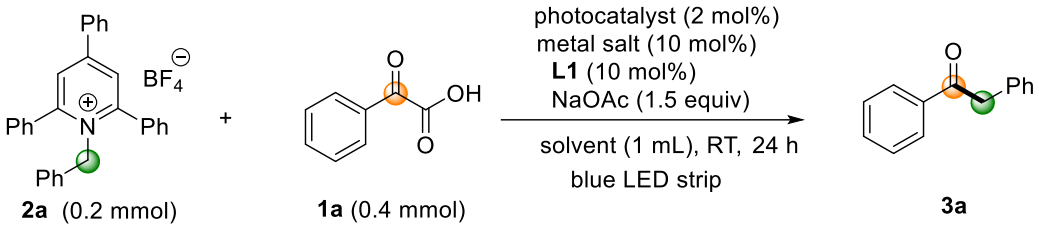
^1H, ^{13}C, and ^{19}F NMR spectra were recorded in $CDCl_3$ on a Bruker AVANCE Avance III 400 instrument. Chemical shifts are reported in parts per million (ppm) and are referenced to the residual solvent resonance as the internal standard ($CDCl_3$: 7.26 ppm for ^1H NMR, and 77.16 ppm for $^{13}C\{^1H$ NMR). Data are reported as follows: chemical shift (δ ppm), multiplicity (s = singlet, d = doublet, t = triplet, q =quartet, m = multiplet), coupling constants (Hz) and integration. Infrared spectra were recorded on a ThermoFisher Nicolet iS5 FTIR using a neat thin-film technique. High-resolution mass spectra (HRMS) were recorded on the Thermo Quest Finnigan LCQDECA system equipped with an ESI ionization source and a TOF detector mass spectrometer. All the photochemical reactions were performed with blue LED strips (8 W, λ = 450 nm).

2. Experimental Details for the Decarboxylative Coupling of α-Oxo Acids with Benzylic pyridinium Salts

2.1 Optimization Studies

General procedure. In an argon-filled glovebox, to an oven-dried 10 mL vial equipped with a stir bar was added metal salt (0.02 mmol, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (L1, dtbbpy, 0.02 mmol, 10 mol%), and anhydrous CH_3CN (0.5 mL). The reaction solution was stirred for 20 minutes. After the indicated time, α-oxo acids (0.4 mmol, 2.0 equiv.), alkylpyridinium salts (0.2 mmol, 1.0 equiv.), base (0.3 mmol, 1.5 equiv.), photocatalysis (2 mol%) and anhydrous CH_3CN (0.5 mL) were added to the reaction vessel for the solution of ligated metal salt. The reaction vial was capped, removed from the glovebox, and stirred with 8 W blue LED strips (λ = 450 nm) for 24 hours. The temperature of the reaction was maintained at room temperature via a fan. Then, the reaction mixture was diluted by ethyl acetate, and filtered through a plug of silica (eluting with ethyl acetate). Finally, the filtrate was concentrated under reduced pressure and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl acetate) to afford the corresponding product.

Table S1. Optimization on the base.[a]

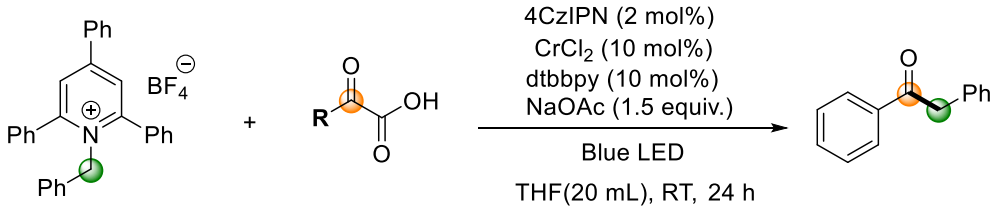


2a (0.2 mmol) **1a** (0.4 mmol) **3a**

Entry	photocatalysis	Metal salt	base	ligand	solvent	isolated yield
1					CH_3CN	7%
2			NaOAc		CH_3CN	15%
3	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$		NaOAc	**L1**	CH_3CN	22%
4	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiCl_2$		**L1**	CH_3CN	28%
5	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiCl_2$	NaI	**L1**	CH_3CN	N D
6	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiCl_2$	Cs_2CO_3	**L1**	CH_3CN	N D
7	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiCl_2$	Na_2CO_3	**L1**	CH_3CN	15%
8	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiCl_2$	Li_2CO_3	**L1**	CH_3CN	16%
9	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiCl_2$	K_2HPO_4	**L1**	CH_3CN	18%
10	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiCl_2$	NaOMe	**L1**	CH_3CN	27%
11	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiCl_2$	K_2CO_3	**L1**	CH_3CN	29%
12	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiCl_2$	NaOAc	**L1**	CH_3CN	38%
13	$Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$	$NiCl_2$	NaOAc	**L1**	THF	50%

[a]Reaction conditions: **1a** (0.4 mmol, 1.0 equiv.), **2a** (0.2 mmol, 2.0 equiv.), $NiCl_2$ (10 mol%), 4,4'-Di-tert-butyl-2,2'-bypyridine ligand (**L1**), base (2.0 equiv.) and $Ir[dF(CF_3)ppy]_2(dtbbpy)PF_6$ [(4,4'-Di-t-butyl-2,2'-bipyridine)bis[3,5-difluoro-2-[5-trifluoromethyl-2-pyridinyl-kN)phenyl-kC]iridium(III), 2 mol%] in CH_3CN (1.0 mL). Yields were solated yield of analytically pure material after purification on preparative thin-layer chromatography. ND = Not detected.

2.2 Gram-scale experiment

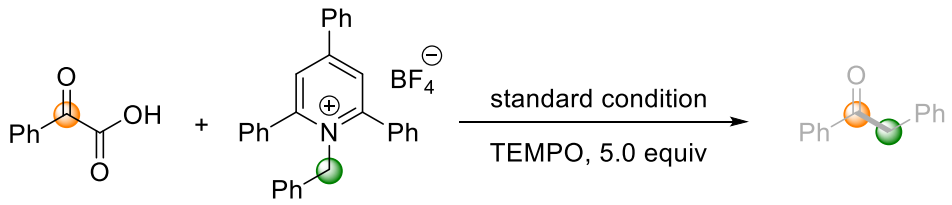


2a (10 mmol) **1** (20 mmol) **3a,** 68%

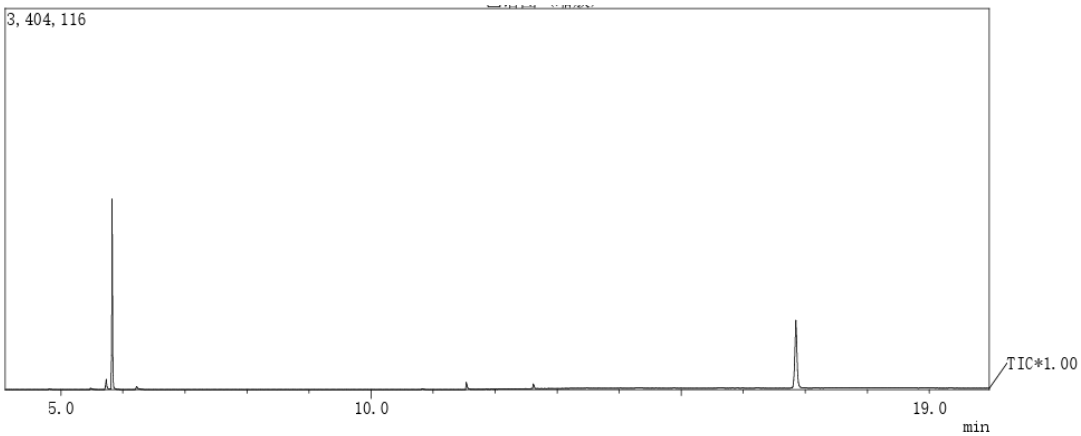
Experimental procedure: In an argon-filled glovebox, to an oven-dried 10 mL vial equipped with a stir bar was added $CrCl_2$ (122 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 268.4 mg, 0.02 mmol, 10 mol%), and THF (5 mL). The reaction solution was stirred for 20 minutes. After the indicated time, α-oxo acids (3.0 g, 20.0 mmol, 2.0 equiv.), NaOAc (1.23 mg, 15 mmol, 1.5 equiv.), 4CzIPN (2 mol%, 157.6 mg) and THF (25 mL) were added to the reaction vessel for the solution of ligated $CrCl_2$. The reaction vial was capped, removed from the glovebox, and stirred with 8 W blue LED strips (λ=450 nm) for 24 hours. The temperature of the reaction was maintained at room temperature via a fan. After 24 hours, the reaction mixture was diluted by ethyl acetate, and filtered through a plug of silica (eluting with ethyl acetate). The solvent were removed under reduced pressure and the crude product was purified by flash chromatography on silica gel with petroleum ether/ethyl acetate (100:1). The corresponding product **3a** as colorless oil was isolated in 68% yield.

2.3 Experimental Studies on the Reaction Mechanism

2.3.1 Radical trapping experiment



1a (0.4 mmol) **2a** (0.2 mmol) **3a, ND**



Experimental procedure: In an argon-filled glovebox, to an oven-dried 10 mL vial equipped with a stir bar was added $CrCl_2$ (2.5 mg, 0.02 mmol, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 0.02 mmol, 10 mol%), and THF (0.5 mL). The reaction solution was stirred for 20 minutes. After the indicated time, α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (97.0 mg, 0.2 mmol, 1.0 equiv.), 2,2,6,6-tetramethylpiperidinooxy (TEMPO, 1 mmol, 156.2 mg, 5 equiv.), NaOAc (24.6 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (2 mol%, 3.2 mg) and THF (0.5 mL) were added to the reaction vessel for the solution of ligated $CrCl_2$. The reaction vial was capped, removed from the glovebox, and stirred with 8 W blue LED strips (λ=450 nm) for 24 hours. The temperature of the reaction was maintained at room temperature via a fan. After 24 hours, the crude reaction mixture was subject to the GC-MS analysis.

2.3.2 Control experiments

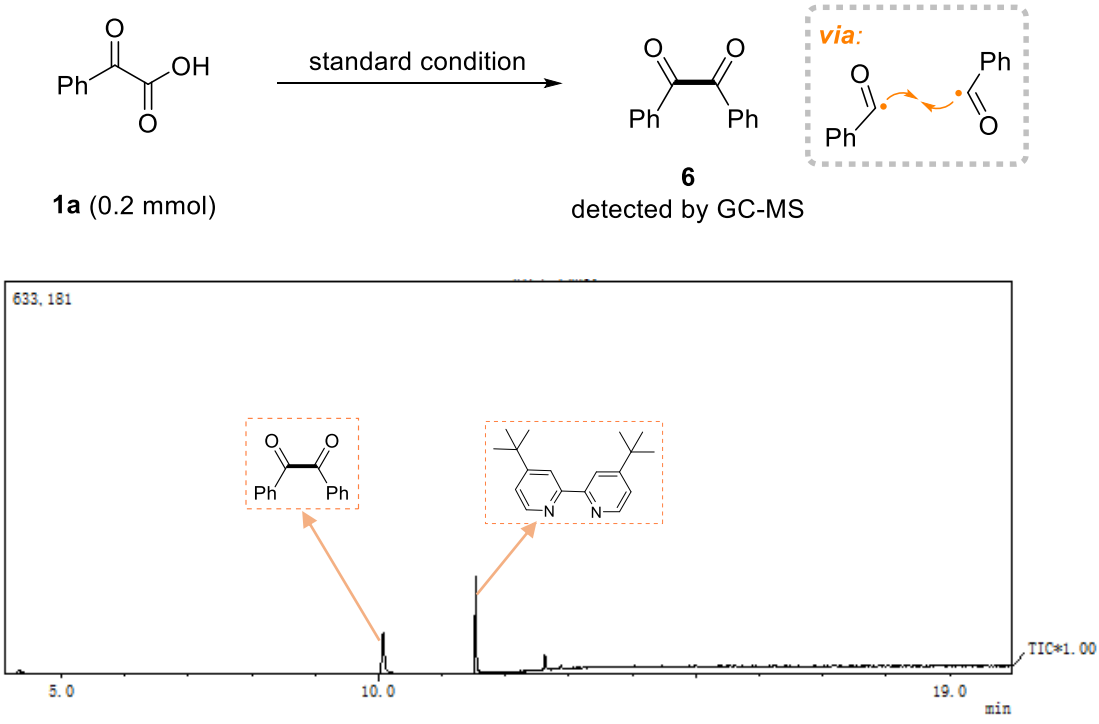
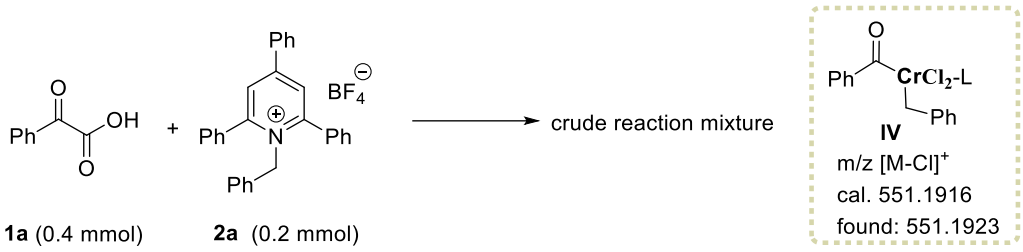


Figure S1

Experimental procedure: In an argon-filled glovebox, to an oven-dried 10 mL vial equipped with a stir bar was added $CrCl_2$ (0.02 mmol, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 0.02 mmol, 10 mol%), and THF (0.5 mL). The reaction solution was stirred for 20 minutes. After the indicated time, α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), NaOAc (24.6 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (2 mol%, 3.2 mg) and THF (0.5 mL) were added to the reaction vessel for the solution of ligated $CrCl_2$. The reaction vial was capped, removed from the glovebox, and stirred with 8 W blue LED strips (λ=450 nm) for 24 hours. The temperature of the reaction was maintained at room temperature via a fan. After 24 hours, the crude reaction mixture was subject to the GC-MS analysis.

2.3.3 Trapping the intermediates by HRMS analysis



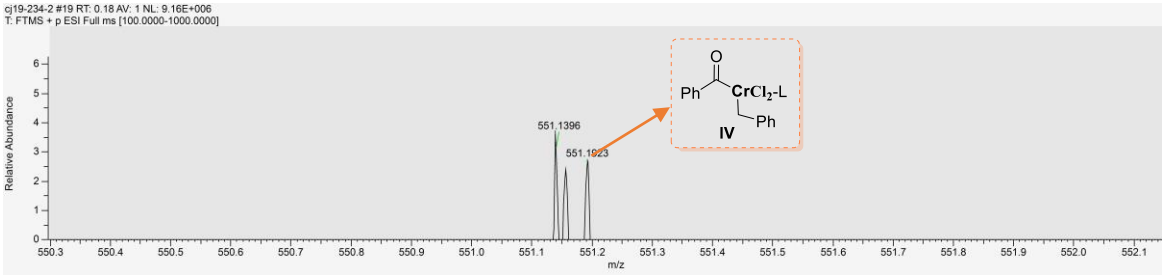
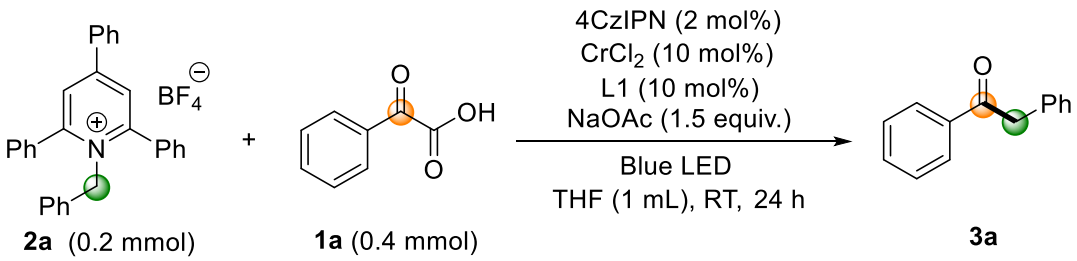


Figure S2

Experimental procedure: In an argon-filled glovebox, to an oven-dried 10 mL vial equipped with a stir bar was added $CrCl_2$ (2.5 mg, 0.02 mmol, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 0.02 mmol, 5.4 mg, 10 mol%), and THF (0.5 mL). The reaction solution was stirred for 20 minutes. After the indicated time, α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), alkylpyridinium salts (97 mg, 0.2 mmol, 1.0 equiv.), NaOAc (24.6 mg, 0.3 mmol, 1.5 equiv.), 4CzIPN (2 mol%, 3.2 mg) and THF (0.5 mL) were added to the reaction vessel for the solution of ligated $CrCl_2$. The reaction vial was capped, removed from the glovebox, and stirred with 8 W blue LED strips (λ=450 nm) for 16 hours. The temperature of the reaction was maintained at room temperature via a fan. After 16 hours, the reaction vial was transfered to the glovebox for the sample preparation of HRMS analysis. Then, the prepared sample of crude reaction mixture was subject to the HRMS analysis using anhydrous CH_3CN as the solvent.

2.3.4 Light on/off experiment



We carried out the light on/off experiments by the reaction of **2a** and **1a** under standard conditions, suggesting light irradiation is essential for this protocol.

Experimental procedure: according to the general procedure, six oven-dried reaction vials were charged respectively $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10

mol%), α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (97.0 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) in an argon-filled glove box. The vials were irritated under blue LED (8 W, λ=450 nm) irradiation. After 1.5 hour, the lamps were turned off, and one vial was removed from the irradiation setup for analysis. The remaining five vials were stirred in the absence of light for an additional 1.5 hour. Then, one vial was removed for analysis, and the other lamps were turned back on to irradiate. After an additional 1.5 hours of irradiation, the lamps were turned off, and one vial was removed for analysis. The remaining vials were stirred in the absence of light for an additional 1.5 hour. Then, a vial was removed for analysis, and the other lamps were turned back on to irradiate the remaining one reaction mixture. After an additional 1.5 hours of irradiation, the lamps were turned off, and the last vial was removed for analysis. The reaction mixtures were diluted by ethyl acetate, and filtered through a plug of silica (eluting with ethyl acetate). Finally, the filtrate was concentrated under reduced pressure and the resulting crude material was purified by preparative TLC (petroleum ether/ethyl acetate) to afford the corresponding product.

2.3.3 Stern-Volmer luminescence quenching experiments

Stern-Volmer luminescence quenching analysis was conducted using a HITACHI F-7000 spectrofluorometer. All the mixed degassed anhydrous THF solutions were excited at 420 nm and the emission intensity at 512 nm was observed. All samples used in the luminescence quenching experiments were freshly prepared under oxygen free conditions (or in a glovebox under a positive pressure of argon) and placed in a 4 mL screw-top quartz cuvette at room temperature. I_0 = emission intensity of the photocatalyst in isolation at the specified wavelength; I = observed emission intensity of the photocatalyst with added quencher.

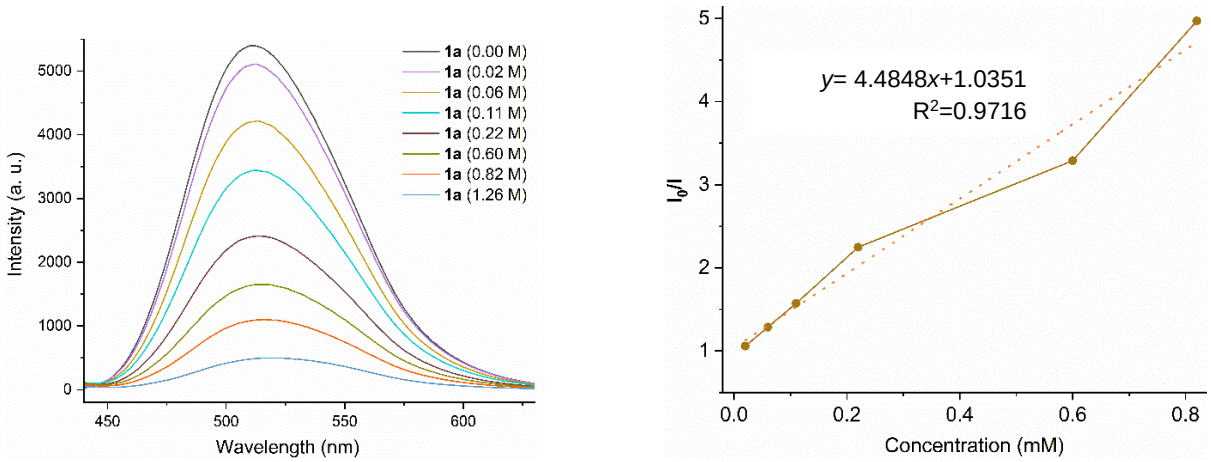


Figure S3. Luminescence spectrum of 4CzIPN as a function of concentration of benzoylformic acid **1a** in degassed THF with excitation at 420 nm, [4CzIPN] = 2×10^{-5} M.

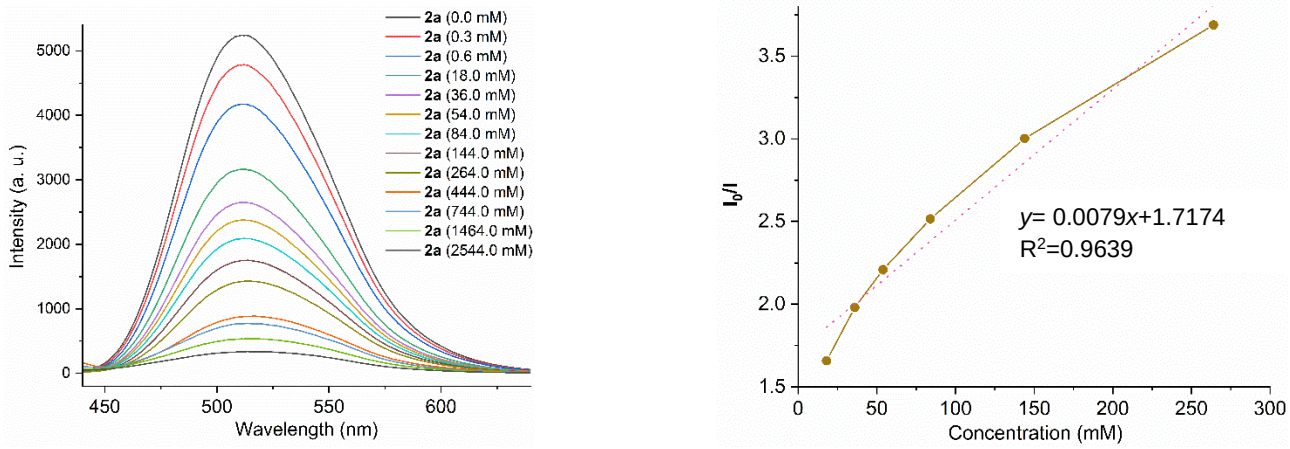


Figure S4. Luminescence spectrum of 4CzIPN as a function of concentration of benzylic pyridinium salt **2a** in degassed THF with excitation at 420 nm, [4CzIPN] = 2×10^{-5} M.

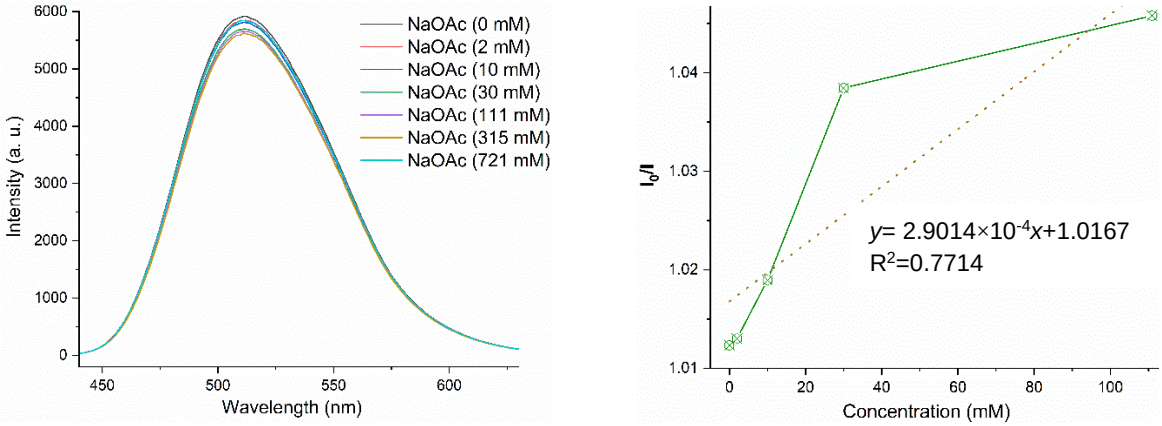
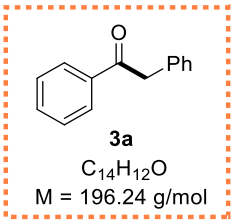


Figure S5. Luminescence spectrum of 4CzIPN as a function of concentration of NaOAc in degassed THF with excitation at 420 nm, [4CzIPN] = 2×10^{-5} M.

2.4 Characterization Data of the Products

2.4.1 Characterization data of 1,2-diphenylethan-1-one (**3a**)

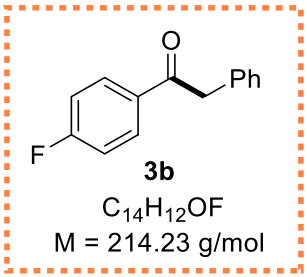


3a
$C_{14}H_{12}O$
M = 196.24 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (97.0 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **3a** as white solid (30.5 mg, 78% yield), mp = 47-50

°C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.98 – 7.95 (m, 2H), 7.52 – 7.47 (m, 1H), 7.42 – 7.37 (m, 2H), 7.30 – 7.25 (m, 2H), 7.23 – 7.15 (m, 3H), 4.23 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 197.7, 136.7, 134.6, 133.2, 129.5, 128.7, 128.7, 128.7, 126.9, 45.5 ppm. **IR** (film): 3007, 1520, 1480, 1380, 1275, 764, 750 cm^{-1}. **HRMS** (ESI): calculated for $C_{14}H_{13}O^+$ $[M+H]^+$ 197.0961, found 197.0959. Spectra data of this compound are consistent with literature data.[2]

2.4.2 Characterization data of 1-(4-fluorophenyl)-2-phenylethan-1-one (**3b**)



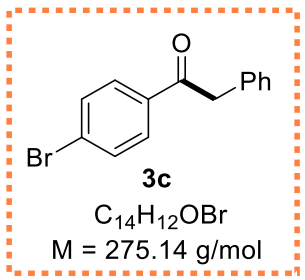
3b

$C_{14}H_{12}OF$

M = 214.23 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), 2-(4-fluorophenyl)-2-oxoacetic acid (67.2 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (97.0 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **3b** as white solid (26.1 mg, 61% yield), mp = 70-72 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.05 – 8.00 (m, 2H), 7.37 – 7.29 (m, 2H), 7.28 – 7.20 (m, 3H), 7.14 – 7.07 (m, 2H), 4.17 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 196.1, 165.8 (d, $J_{C\text{-}F}$ = 255.1 Hz), 134.4, 133.1, 133.0, 131.3 (d, $J_{C\text{-}F}$ = 9.2 Hz), 129.5, 128.8, 127.1, 115.8 (d, $J_{C\text{-}F}$ = 21.9 Hz), 45.6 ppm. **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -104.9 ppm. **IR** (film): 3005, 2326, 1510, 1275, 1261, 760, 745 cm^{-1}. **HRMS** (ESI): calculated for $C_{14}H_{12}OF^+$ $[M+H]^+$ 215.0867, found 215.0864. Spectra data of this compound are consistent with literature data.[3]

2.4.3 Characterization data of 1-(4-bromophenyl)-2-phenylethan-1-one (**3c**)



3c

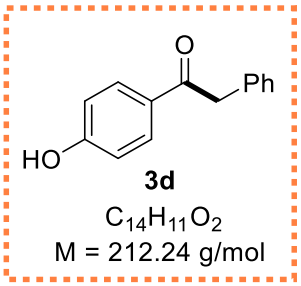
$C_{14}H_{12}OBr$

M = 275.14 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), 2-(4-bromophenyl)-2-oxoacetic acid (91.6 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (97.0 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24

hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **3c** as white solid (43.4 mg, 79% yield), mp = 103-105 ℃. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.89 – 7.85 (m, 2H), 7.63 – 7.56 (m, 2H), 7.38 – 7.30 (m, 2H), 7.26 – 7.20 (m, 3H), 4.25 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 196.7, 135.3, 134.2, 132.0, 130.2, 129.4, 128.8, 128.4, 127.1, 45.6 ppm. **IR** (film): 3006, 2991, 2350, 2410, 1620, 1500, 1260, 740, 720 cm^{-1}. **HRMS** (ESI): calculated for $C_{14}H_{12}OBr^+$ $[M+H]^+$ 275.0066, found 275.0065. Spectra data of this compound are consistent with literature data.[4]

2.4.4 Characterization data of 1-(4-hydroxyphenyl)-2-phenylethan-1-one (**3d**)



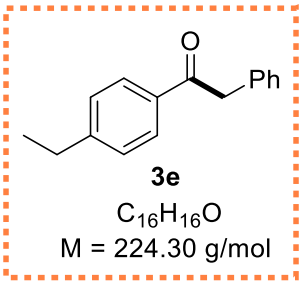
3d

$C_{14}H_{11}O_2$

M = 212.24 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), 2-(4-hydroxyphenyl)-2-oxoacetic acid (66.4 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (97.0 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **3d** as white solid (31.4 mg, 74% yield), mp = 100-102 ℃; **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.02 – 7.94 (m, 2H), 7.43 – 7.32 (m, 2H), 7.32 – 7.21 (m, 3H), 6.93 – 6.85 (m, 2H), 6.03 (br, 1H, -OH), 4.24 (s, 2H), 1.31 (br, 1H). **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 196.9, 160.4, 134.9, 131.4, 129.7, 129.5, 128.8, 127.0, 115.6, 45.3 ppm. **IR** (film): 3014, 2378, 2324, 1510, 1480, 1270, 740 cm^{-1}. **HRMS** (ESI): calculated for $C_{14}H_{13}O_2^+$ $[M+H]^+$ 213.0910, found 213.0909. Spectra data of this compound are consistent with literature data.[5]

2.4.5 Characterization data of 1-(4-ethylphenyl)-2-phenylethan-1-one (**3e**)



3e

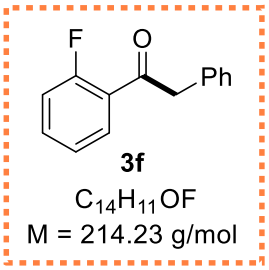
$C_{16}H_{16}O$

M = 224.30 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), 2-(4-ethylphenyl)-2-oxoacetic acid (71.2 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (97.0 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6

mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **3e** as gum (31.4 mg, 70% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.97 – 7.94 (m, 2H), 7.38 – 7.21 (m, 7H), 4.27 (s, 2H), 2.71 (q, J = 7.6 Hz, 2H), 1.26 (t, J = 7.6 Hz, 3H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 197.4, 150.2, 134.9, 134.4, 129.5, 128.9, 128.7, 128.2, 126.9, 45.5, 29.0, 15.2 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -109.0 ppm. **IR** (film): 3004, 2320, 1600, 1550, 1268, 740 cm^{-1}. **HRMS** (ESI): calculated for $C_{16}H_{17}O^+$ $[M+H]^+$ 225.1274, found 225.1270. Spectra data of this compound are consistent with literature data.[6]

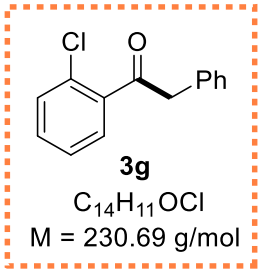
2.4.6 Characterization data of 1-(2-fluorophenyl)-2-phenylethan-1-one (**3f**)



3f
$C_{14}H_{11}OF$
M = 214.23 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), 2-(2-fluorophenyl)-2-oxoacetic acid (67.2 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (97.0 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **3f** as gum (24.4 mg, 57% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.87 – 7.82 (m, 1H), 7.53 – 7.47 (m, 1H), 7.34 – 7.21 (m, 6H), 7.15 – 7.09 (m, 1H), 4.30 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$):δ 196.3, 161.8 (d, J_{C-F} = 254.3 Hz), 134.7 (d, J_{C-F} = 9.1 Hz), 134.1, 131.1, 129.8, 128.6, 127.0, 124.6, 116.8, 116.6, 50.0 ppm. ^{19}F NMR (376 MHz, $CDCl_3$) δ -109.01 ppm. **IR** (film): 3015, 2317, 1540, 1260, 758 cm^{-1}. **HRMS** (ESI): calculated for $C_{12}H_{14}OF^+$ $[M+H]^+$ 215.0867, found 215.0866. Spectra data of this compound are consistent with literature data.[7]

2.4.7 Characterization data of 1-(2-chlorophenyl)-2-phenylethan-1-one (**3g**)

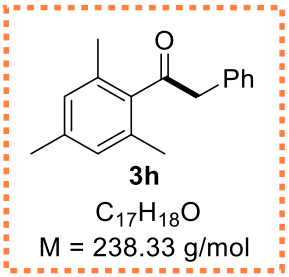


3g
$C_{14}H_{11}OCl$
M = 230.69 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), 2-(2-chlorophenyl)-2-oxoacetic acid (73.6 mg, 0.4 mmol, 2.0

equiv.), benzylicpyridinium salts (97.0 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **3g** as gum (29.9 mg, 65% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.48 – 7.29 (m, 3H), 7.28 – 7.22 (m, 2H), 7.22 – 6.98 (m, 4H), 4.19 (s, 2H).ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 201.0, 134.9, 133.7, 131.7, 130.5, 129.8, 129.1, 128.7, 127.2, 126.9, 49.6. **IR** (film): 3020, 2322, 1650, 1470, 1270, 750 cm^{-1}. **HRMS** (ESI): calculated for $C_{12}H_{14}OCl^+$ $[M+H]^+$ 231.0571, found 231.0567. Spectra data of this compound are consistent with literature data.[7]

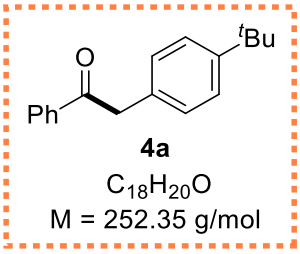
2.4.8 Characterization data of 1-mesityl-2-phenylethan-1-one (**3h**)



3h
$C_{17}H_{18}O$
M = 238.33 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), 2-mesityl-2-oxoacetic acid (76.8 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (97.0 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **3h** as gum (23.8 mg, 50% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 7.26 – 7.17 (m, 3H), 7.15 – 7.09 (m, 2H), 6.75 (s, 2H), 3.92 (s, 2H), 2.20 (s, 3H), 2.05 (s, 6H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 207.6, 139.2, 138.6, 133.4, 132.8, 130.0, 128.6, 128.6, 127.2, 51.9, 21.1, 19.3 ppm. **IR** (film): 3014, 2311, 1508, 1260, 730 cm^{-1}. **HRMS** (ESI): calculated for $C_{17}H_{19}O^+$ $[M+H]^+$ 239.1430, found 239.1427. Spectra data of this compound are consistent with literature data.[8]

2.4.9 Characterization data of 2-(4-(tert-butyl)phenyl)-1-phenylethan-1-one (**4a**)

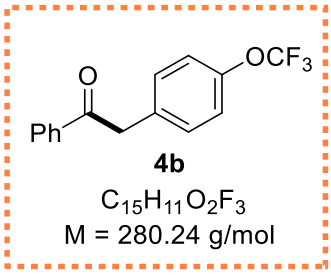


4a
$C_{18}H_{20}O$
M = 252.35 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium

salts (108.3 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4a** as gum (35.3 mg, 70% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.08 – 8.01 (m, 2H), 7.50 – 7.44 (m, 2H), 7.38 – 7.35 (m, 2H), 7.24 – 7.20 (m, 2H), 4.27 (s, 2H), 1.32 (s, 9H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 197.9, 149.8, 136.8, 133.2, 131.5, 130.0, 129.2, 128.7, 125.7, 45.0, 34.5, 31.4 ppm. **IR** (film): 3081, 3014, 2370, 1620, 1247, 720 cm^{-1}. **HRMS** (ESI): calculated for $C_{18}H_{21}O^+$ $[M+H]^+$ 253.1587, found 253.1584. Spectra data of this compound are consistent with literature data.[9]

2.4.10 Characterization data of 1-phenyl-2-(4-(trifluoromethoxy)phenyl)ethan-1-one (**4b**)



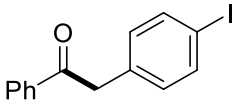
4b

$C_{15}H_{11}O_2F_3$

M = 280.24 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (113.8 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4b** as white solid (40.3 mg, 72% yield), mp = 100-101 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.03 – 7.98 (m, 2H), 7.62 – 7.53 (m, 1H), 7.51 – 7.43 (m, 2H), 7.31 – 7.26 (m, 2H), 7.21 – 7.14 (m, 2H), 4.29 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 197.1, 148.3, 136.5, 133.5, 133.3, 131.0, 128.8, 128.6, 121.2, 44.6 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -57.8 ppm. **IR** (film): 3028, 2328, 1700, 1271, 765, 751 cm^{-1}. **HRMS** (ESI): calculated for $C_{15}H_{12}O_2F_3^+$ $[M+H]^+$ 281.0784, found 281.0778.

2.4.11 Characterization data of 2-(4-iodophenyl)-1-phenylethan-1-one (**4c**)



4c

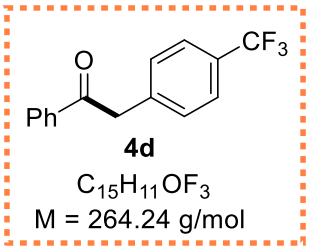
$C_{14}H_{11}OI$

M = 322.14 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (122.2 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2

mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4c** as white solid (46.3 mg, 72% yield), mp = 130-132 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.02 – 7.97 (m, 2H), 7.69 – 7.61 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.49 – 7.43 (m, 2H), 7.03 – 6.99 (m, 2H), 4.22 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 197.1, 137.8, 136.5, 134.2, 133.5, 131.6, 128.8, 128.6, 92.5, 45.0 ppm. **IR** (film): 3018, 2350, 1602, 1280, 749, 540 cm^{-1}. **HRMS** (ESI): calculated for $C_{14}H_{12}OI^+$ $[M+H]^+$ 322.9927, found 322.9918. Spectra data of this compound are consistent with literature data.[10]

2.4.12 Characterization data of 1-phenyl-2-(4-(trifluoromethyl)phenyl)ethan-1-one (**4d**)



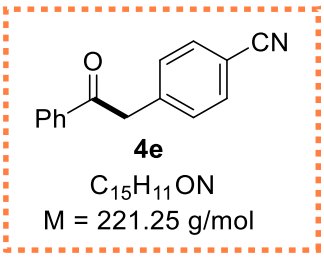
4d

$C_{15}H_{11}OF_3$

M = 264.24 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (110.6 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4d** as white solid (36.9 mg, 70% yield), mp = 130-132 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.04 – 8.00 (m, 2H), 7.63 – 7.56 (m, 3H), 7.53 – 7.45 (m, 2H), 7.41 – 7.36 (m, 2H), 4.36 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 196.7, 138.6, 136.4, 135.0, 133.6, 130.1, 129.1, 128.9, 128.6, 125.6 (q, J = 3.9 Hz), 45.1 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -62.5 ppm. **IR** (film): 3013, 2369, 1670, 1240, 1102, 750 cm^{-1}. **HRMS** (ESI): calculated for $C_{15}H_{12}OF_3^+$ $[M+H]^+$ 265.0835, found 265.0827. Spectra data of this compound are consistent with literature data.[8]

2.4.13 Characterization data of 4-(2-oxo-2-phenylethyl)benzonitrile (**4e**)



4e

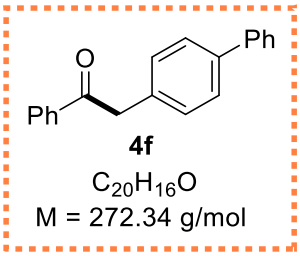
$C_{15}H_{11}ON$

M = 221.25 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (102.0 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by

preparative TLC (petroleum PE/EA = 20:1) to afford **4e** as white solid (24.3 mg, 55% yield), mp = 150-153 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.02 – 7.98 (m, 2H), 7.66 – 7.56 (m, 3H), 7.52 – 7.47 (m, 2H), 7.39 – 7.36 (m, 2H), 4.36 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 196.2, 140.1, 136.3, 133.8, 132.4, 130.6, 128.9, 128.5, 118.9, 111.0, 45.3 ppm. **IR** (film): 3027, 2318, 1721, 1533, 1275, 740 cm^{-1}. **HRMS** (ESI): calculated for $C_{15}H_{12}NO^+$ $[M+H]^+$ 222.0913, found 222.0906. Spectra data of this compound are consistent with literature data.[8]

2.4.14 Characterization data of 2-([1,1'-biphenyl]-4-yl)-1-phenylethan-1-one (**4f**)



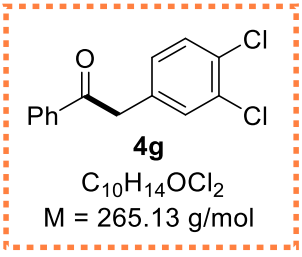
4f

$C_{20}H_{16}O$

M = 272.34 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (112.2 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4f** as white solid (38.1 mg, 70% yield), mp = 218-220 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.09 – 8.02 (m, 2H), 7.60 – 7.54 (m, 5H), 7.50 – 7.41 (m, 4H), 7.37 – 7.32 (m, 3H), 4.34 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 197.7, 140.9, 140.0, 136.7, 133.6, 133.3, 130.0, 128.8, 128.8, 128.7, 127.5, 127.3, 127.2, 45.2 ppm. **IR** (film): 3030, 2324, 1705, 1515, 1230, 710 cm^{-1}. **HRMS** (ESI): calculated for $C_{20}H_{17}O^+$ $[M+H]^+$ 273.1274, found 273.1270. Spectra data of this compound are consistent with literature data.[11]

2.4.15 Characterization data of 2-([1,1'-biphenyl]-4-yl)-1-phenylethan-1-one (**4g**)



4g

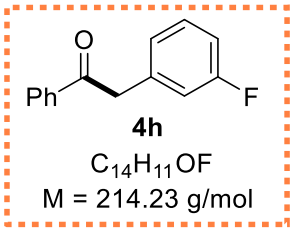
$C_{10}H_{14}OCl_2$

M = 265.13 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (126.0 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4g** as white solid (34.4 mg, 65% yield), mp = 70-

71 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.01 – 7.98 (m, 2H), 7.61 – 7.57 (m, 1H), 7.49 (dd, J = 8.3, 7.0 Hz, 2H), 7.42 – 7.33 (m, 2H), 7.10 (dd, J = 8.2, 2.1 Hz, 1H), 4.25 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): 196.5, 136.3, 134.7, 133.6, 132.6, 131.6, 131.2, 130.5, 129.2, 128.9, 128.5, 44.3 ppm. **IR** (film): 3005, 2991, 2379, 2317, 1261, 750 cm^{-1}. **HRMS** (ESI): calculated for $C_{14}H_{11}OCl_2^+$ $[M+H]^+$ 265.0181, found 265.0177. Spectra data of this compound are consistent with literature data.[12]

2.4.16 Characterization data of 2-(3-fluorophenyl)-1-phenylethan-1-one (**4h**)



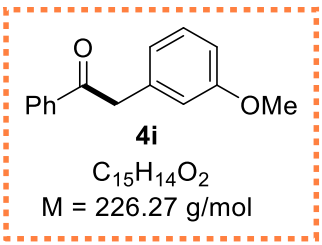
4h

$C_{14}H_{11}OF$

M = 214.23 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (115.8 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4h** as gum (25.7 mg, 60% yield). **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.02 – 7.99 (m, 2H), 7.60 – 7.55 (m, 1H), 7.50 – 7.45 (m, 2H), 7.32 – 7.26 (m, 1H), 7.09 – 6.91 (m, 3H), 4.28 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 197.0, 163.0 (d, J_{C-F} = 246.1 Hz), 136.9 (d, J_{C-F} = 7.7 Hz), 136.5, 133.4, 130.1 (d, J_{C-F} = 8.5 Hz), 128.8, 128.6, 125.3, 116.6 (d, J_{C-F} = 21.8 Hz), 114.0 (d, J_{C-F} = 21.1 Hz), 45.1 ppm. **^{19}F NMR** (376 MHz, $CDCl_3$) δ -113.0 (s, 1F) ppm. **IR** (film): 3004, 2970, 2370, 2331, 1508, 1266, 700 cm^{-1}. **HRMS** (ESI): calculated for $C_{14}H_{12}OF^+$ $[M+H]^+$ 215.0867, found 265.0860. Spectra data of this compound are consistent with literature data.[13]

2.4.17 Characterization data of 2-(3-methoxyphenyl)-1-phenylethan-1-one (**4i**)



4i

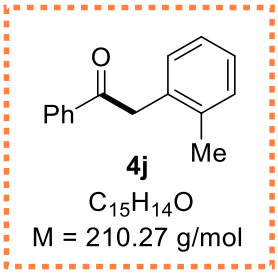
$C_{15}H_{14}O_2$

M = 226.27 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (118.3 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4i** as gum (36.2 mg, 80% yield). **^{1}H NMR** ($CDCl_3$,

400 MHz): δ 8.04 – 8.00 (m, 2H), 7.58 – 7.53 (m, 1H), 7.49 – 7.43 (m, 2H), 7.25 (t, J = 7.8 Hz, 1H), 6.90 – 6.74 (m, 3H), 4.26 (s, 2H), 3.78 (s, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$): δ 197.6, 159.9, 136.6, 136.1, 133.2, 129.7, 128.7, 128.7, 121.9, 115.2, 112.4, 55.2, 45.6 ppm. **IR** (film): 3029, 2336, 1633, 1274, 884, 710 cm^{-1}. **HRMS** (ESI): calculated for $C_{15}H_{15}O_2^+$ $[M+H]^+$ 227.1067, found 227.1063. Spectra data of this compound are consistent with literature data.[13]

2.4.18 Characterization data of 1-phenyl-2-(o-tolyl)ethan-1-one (**4j**)



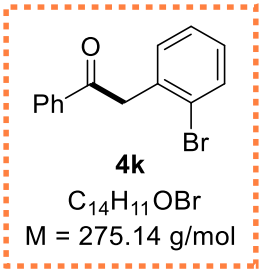
4j

$C_{15}H_{14}O$

M = 210.27 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (115.0 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4j** as white solid (31.1 mg, 74% yield), mp = 55-57 °C. **^1H NMR** ($CDCl_3$, 400 MHz): δ 8.07 – 8.03 (m, 2H), 7.64 – 7.55 (m, 1H), 7.52 – 7.47 (m, 2H), 7.29 – 7.10 (m, 4H), 4.33 (s, 2H), 2.29 (s, 3H) ppm. **$^{13}C\{^1H\}$ NMR** (100 MHz, $CDCl_3$): δ 197.5, 136.9, 133.5, 133.2, 130.4, 130.3, 128.7, 128.4, 128.3, 127.3, 126.2, 43.5, 19.8 ppm. **IR** (film): 2989, 2300, 1602, 1527, 1233, 699 cm^{-1}. **HRMS** (ESI): calculated for $C_{15}H_{15}O^+$ $[M+H]^+$ 211.1117, found 211.1115. Spectra data of this compound are consistent with literature data.[13]

2.4.19 Characterization data of 2-(2-bromophenyl)-1-phenylethan-1-one (**4k**)



4k

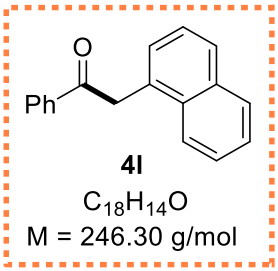
$C_{14}H_{11}OBr$

M = 275.14 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (128.0 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4k** as white solid (40.7 mg, 72% yield), mp = 59-61

°C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.06 – 8.02 (m, 2H), 7.64 – 7.53 (m, 2H), 7.50 – 7.45 (m, 2H), 7.29 – 7.22 (m, 2H), 7.16 – 7.11 (m, 1H), 4.44 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 196.4, 136.7, 135.1, 133.4, 132.9, 131.8, 128.8, 128.8, 128.4, 127.6, 125.2, 45.8 ppm. **IR** (film): 3030, 2340, 1759, 1672, 1658, 1289, 810 cm^{-1}. **HRMS** (ESI): calculated for $C_{14}H_{12}OBr^{+}$ $[M+H]^{+}$ 275.0066, found 275.0060. Spectra data of this compound are consistent with literature data.[14]

2.4.20 Characterization data of 2-(naphthalen-1-yl)-1-phenylethan-1-one (**4l**)



4l

$C_{18}H_{14}O$

M = 246.30 g/mol

Prepared according to general procedure from $CrCl_2$ (2.5 mg, 10 mol%), 4,4'-Di-tert-butyl-2,2'-bipyridine (dtbbpy, 5.4 mg, 10 mol%), α-oxo acids (60 mg, 0.4 mmol, 2.0 equiv.), benzylicpyridinium salts (122.2 mg, 0.2 mmol, 1.0 equiv.), NaOAc (0.3 mmol, 1.5 equiv. 24.6 mg,), 4CzIPN (2 mol%, 3.2 mg) and THF (1 mL) under blue LED (8 W, λ=450 nm) irradiation for 24 hours. Purification by preparative TLC (petroleum PE/EA = 20:1) to afford **4l** as white solid (29.5 mg, 60% yield), mp = 90-92 °C. **^{1}H NMR** ($CDCl_3$, 400 MHz): δ 8.13 – 8.06 (m, 2H), 7.92 – 7.86 (m, 2H), 7.84 – 7.78 (m, 1H), 7.63 – 7.56 (m, 1H), 7.55 – 7.42 (m, 5H), 7.39 – 7.35 (m, 1H), 4.75 (s, 2H) ppm. **^{13}C{^{1}H} NMR** (100 MHz, $CDCl_3$): δ 197.7, 136.8, 134.0, 133.3, 132.3, 131.4, 128.9, 128.8, 128.6, 128.1, 128.0, 126.4, 125.8, 125.5, 123.9, 43.2 ppm. **IR** (film): 3017, 2340, 1536, 1269, 1100, 750, 680 cm^{-1}. **HRMS** (ESI): calculated for $C_{18}H_{15}O^{+}$ $[M+H]^{+}$ 247.1117, found 2471113. Spectra data of this compound are consistent with literature data.[9]

3. Computational Investigations

3.1 Computational Details

All calculations were performed with the Gaussian 16 package.[15] The 3D structures of the optimized species were generated using CYLview.[16] Geometry optimizations and frequencies calculations of the reactants, transition states, intermediates and products were performed by using the UB3LYP method.[17] The LANL2DZ basis set is employed for the chromium atom,[18] and the 6-31G(d,p) basis set is used for all the other atoms. Intrinsic reaction coordinate calculations are performed to confirm that each transition state connects with the desired reactants and products.[19] To get more accurate energies, single-point energy calculations were done with the UB3LYP(BJ)-D3 functional in conjugation with solvent model density (SMD) for tetraHydrofuran.[20] The SDD basis set is employed for the chromium atom,[21] and the cc-PVTZ basis set is used for all the other atoms. On the basis of previous work,[22] an active quartet anionic $Cr^{I}Cl_2$/dtbbpy ($LCr^{I}Cl_2$) catalyst is considered as the ground-states. Vertical excited energies were calculated by time-dependent density function theory (TD-DFT) calculations at the B3LYP-D3(SMD-THF)/cc-PVTZ level of theory.[23]

The barrier heights of single electron transfer steps were calcualted by using Marcus-Hush theory.[24] The free energy barrier of a single electron transfer process of outer-sphere electron transfer can be applied according to the following equation:

$$\Delta G_{ET}^{\dagger} = \frac{(\Delta G_{\mathrm{r}} + \lambda)^2}{4\lambda}$$

Where ΔG_{r} is the Gibbs free energy change of the studied single electron transfer step, λ is the reorganization energy which includes two components, inner reorganization energy (λ_i) and outer reorganization energy (λ_0). The outer-sphere electron transfer model is applicable and the activation barrier may be estimated from the outer-sphere Marcus-Hush model. Since the inner reorganization energies are usually small and could be neglected. Thus, the total reorganization energy $\lambda \approx \lambda_0$.

$$\lambda = \lambda_{\mathrm{o}} = 332\left(\frac{1}{2\mathrm{a}_1} + \frac{1}{2\mathrm{a}_2} - \frac{1}{R}\right)\left(\frac{1}{\varepsilon_{opt}} - \frac{1}{\varepsilon}\right)$$

Where, a_1 and a_2 are the radii of donor and acceptor, R is the sum of a_1 and a_2, ε_{opt} and ε is the optical dielectric constant and static dielectric constant of solvent respectively (for THF ε_{opt} = 1.98, ε = 7.43). a_1 and a_2 are calculated by using Multiwfn package.[25]

Table S2. Calculated free energy barriers ($\Delta G_{ET}^{\dagger}$, kcal/mol) of single electron transfer steps and their relevant parameters.

entry	a_1 (Å)	a_2 (Å)	R (Å)	λ	ΔG_r	$\Delta G_{ET}^{\dagger}$
SET1	4.92	8.69	13.61	10.59	-37.2	16.7
SET2	8.69	8.17	16.86	7.57	-1.1	1.3
SET3	4.92	8.17	13.09	10.64	19.2	20.9
SET4	8.69	7.02	15.71	8.79	7.7	7.8

3.2 Computational fragmentation mechanism of the radical anion the **2a**$^{\cdot-}$

The fragmentation of the radical anion the **2a**$^{\cdot-}$ proceeded through transition state **TS'** with the barrier height of 13.2 kcal/mol. This step is exergonic by 12.6 kcal/mol (with respect to **2a**$^{\cdot-}$).

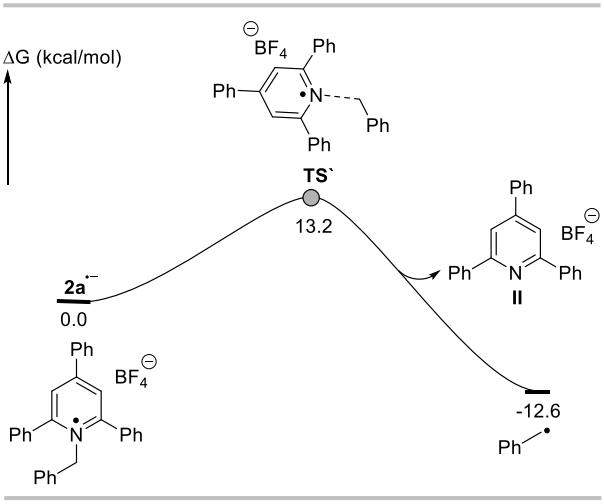
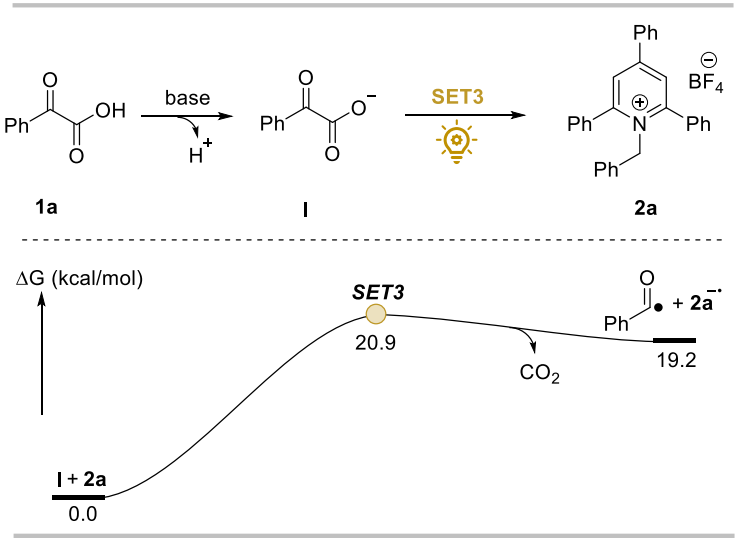


Figure S3. calculated Gibbs energy profile of fragmentation mechanism of the radical anion the **2a**$^{\cdot-}$.

3.3 Single electron transfer from the α-oxocarboxylate **I** to pyridinium salt **2a** (SET3)

When the absence of photocatalyst, photocatalytic cycle maybe proceeded through the direct single electron transfer (SET3) from the α-oxocarboxylate **I** to pyridinium salt **2a**, leading to the radical anion **2a**$^{\cdot-}$, benzoyl radical and CO_2. As shown below, the calculated barrier height of SET3 was 20.9 kcal/mol, which indicate the SET3 step was possible. Overall, these calculated results were qualitative agreement with the experimental data (the yield of **3a**, 35% without photocatalyst, and ~78% using 4CzIPN as photocatalyst).



3.4 Single electron transfer from the reduced 4CzIPN$^{\cdot-}$ to $CrCl_2$/dtbbpy by photocatalysis (SET4)

The barrier height of single electron transfer from 4CzIPN$^{\cdot-}$ to $CrCl_2$/dtbbpy is 7.8 kcal/mol.

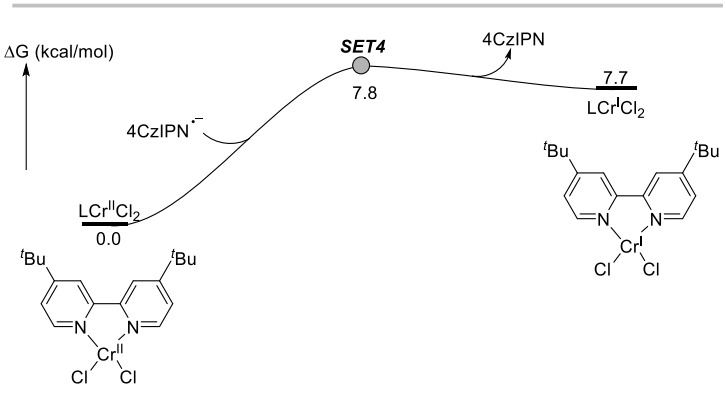
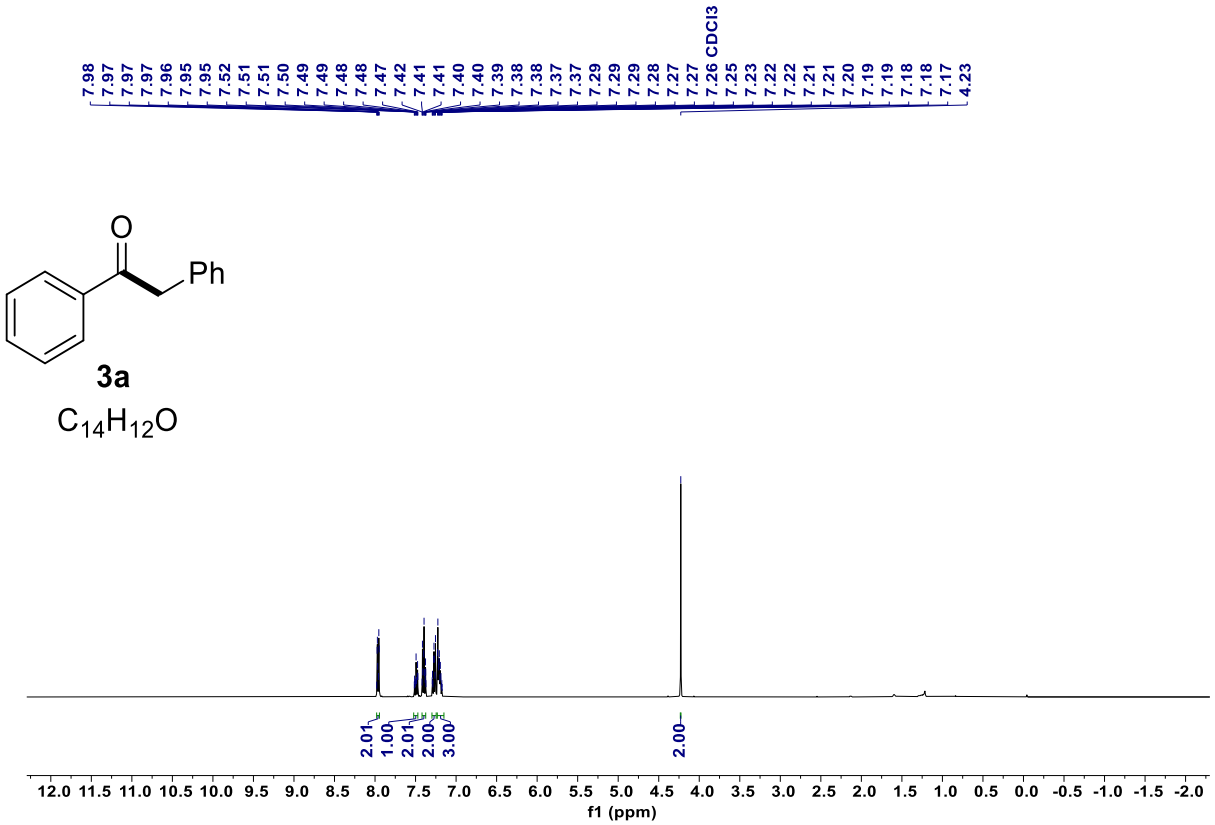


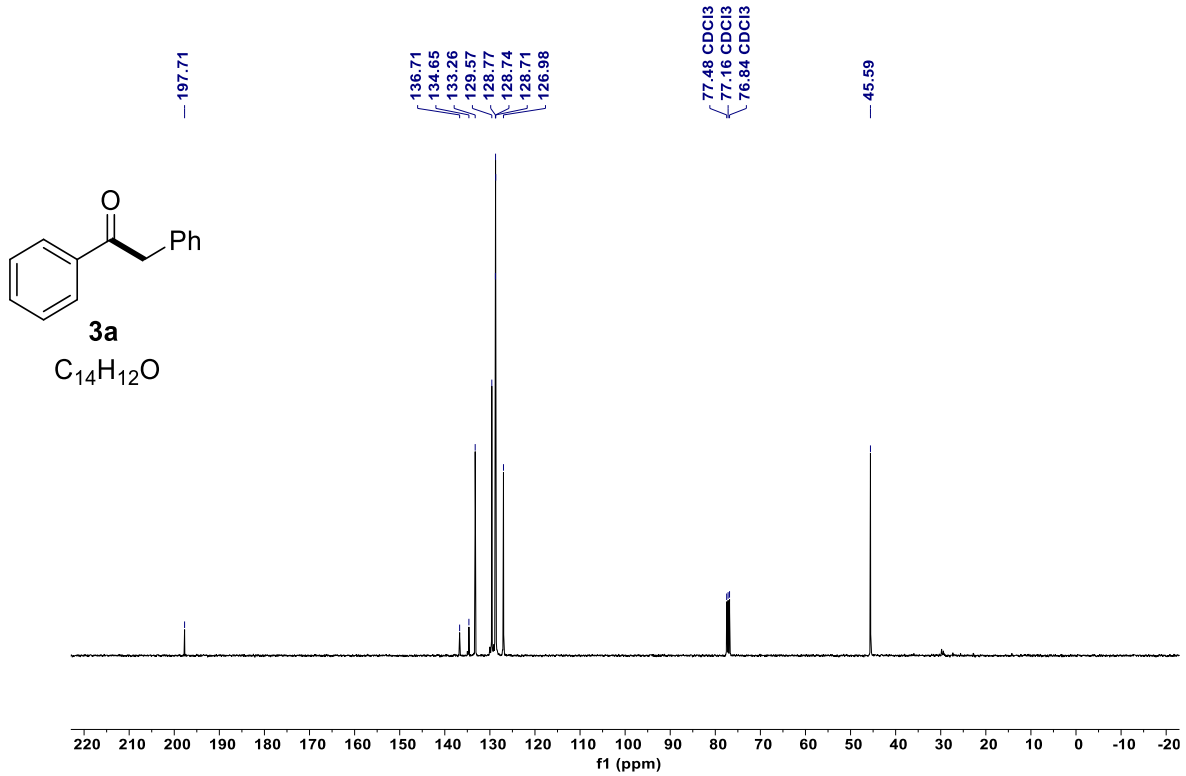
Figure S4

4. NMR Spectra

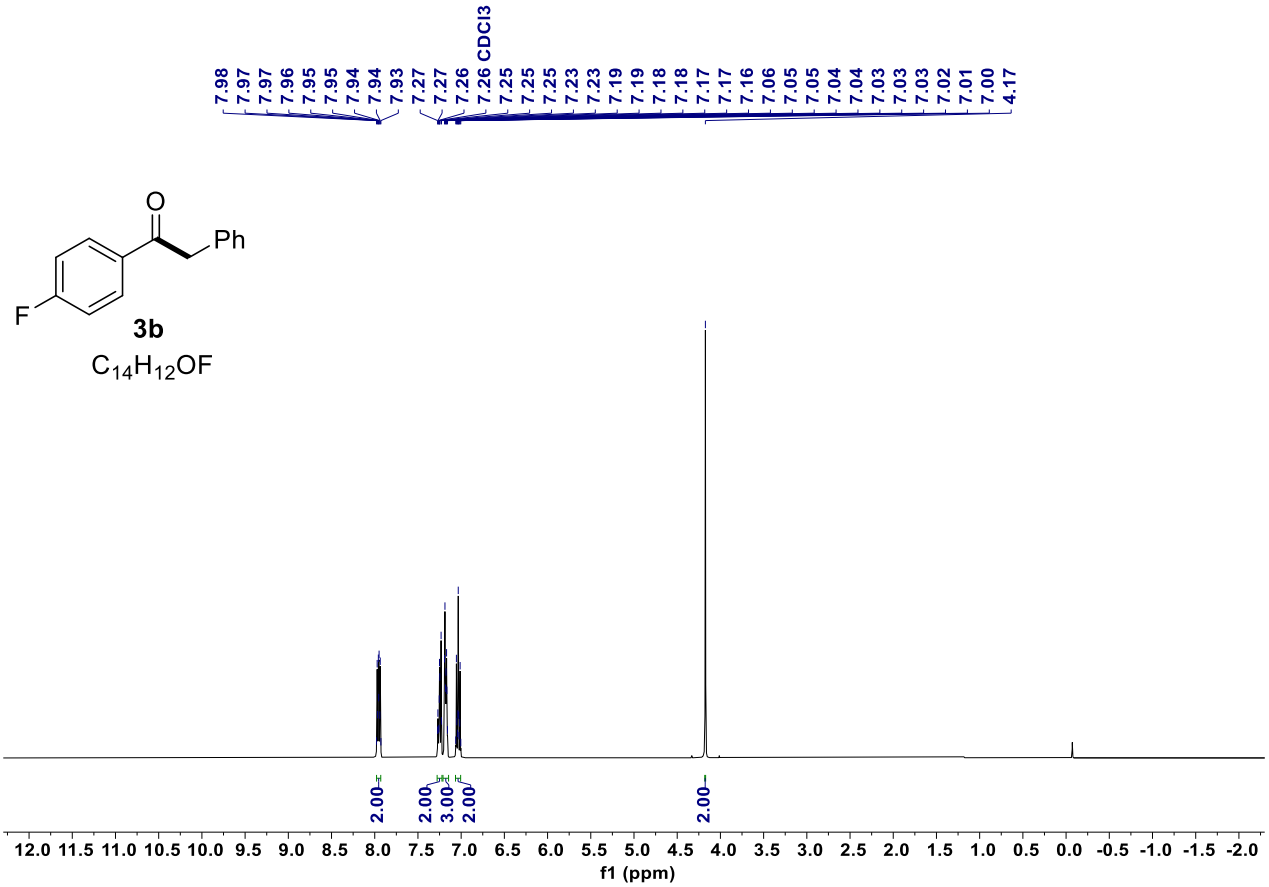
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3a**.



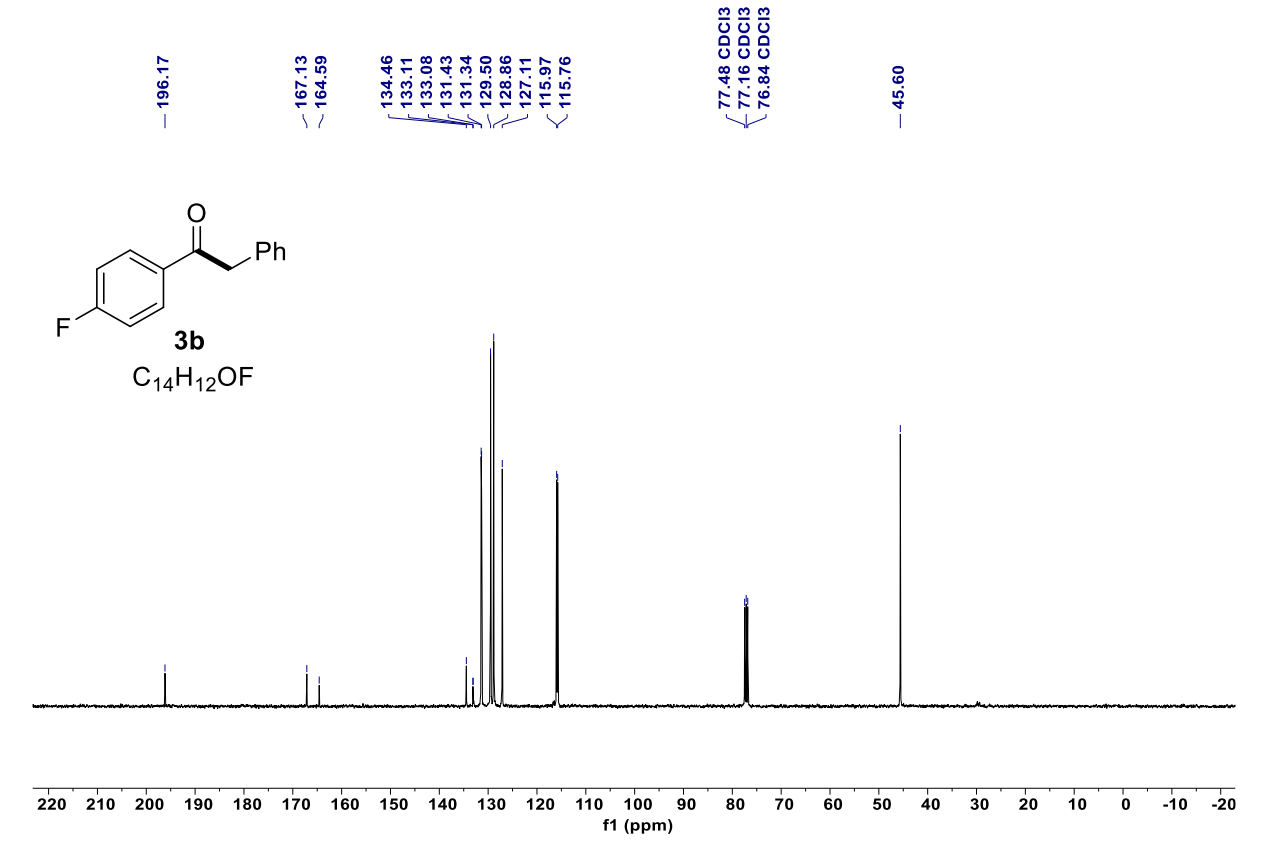
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **3a**.



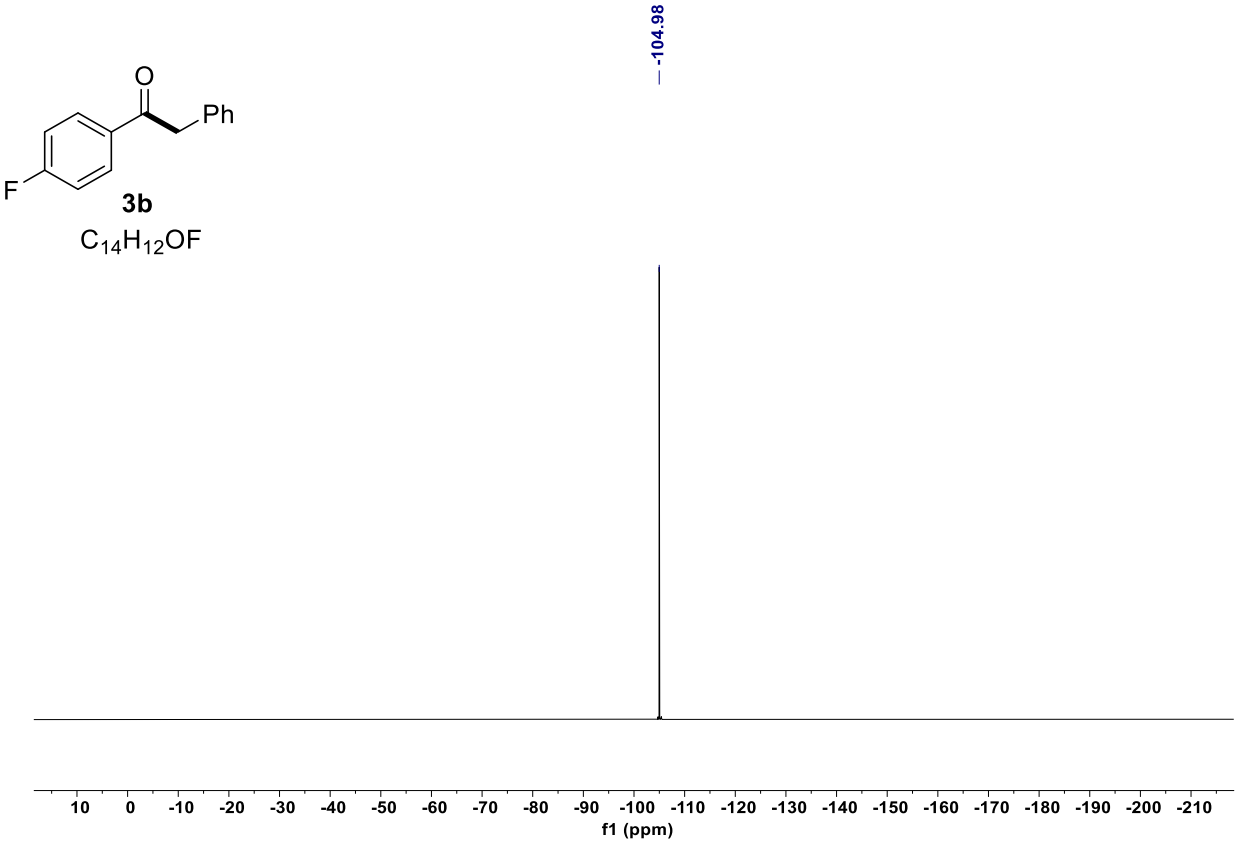
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3b**.



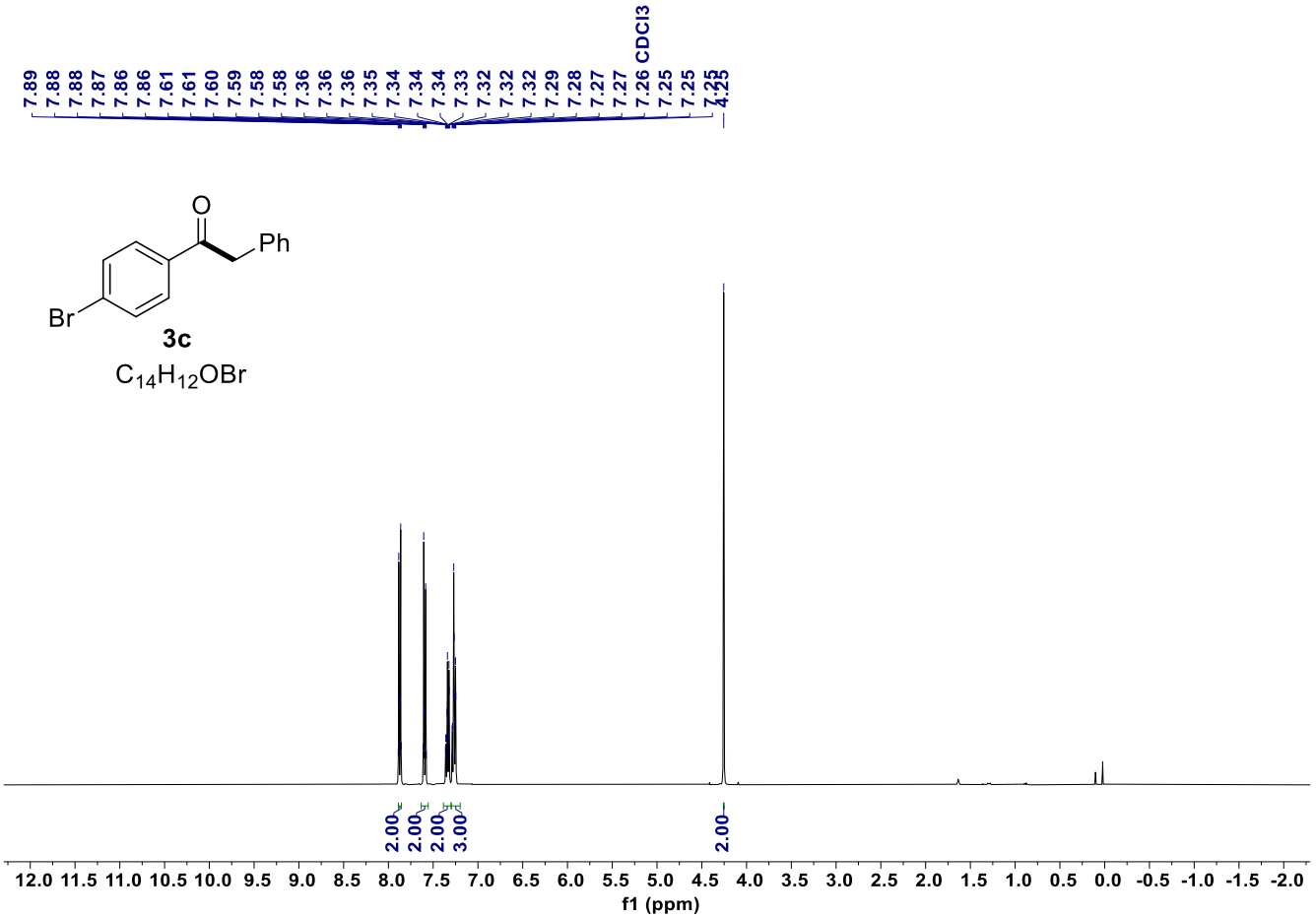
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **3b**.



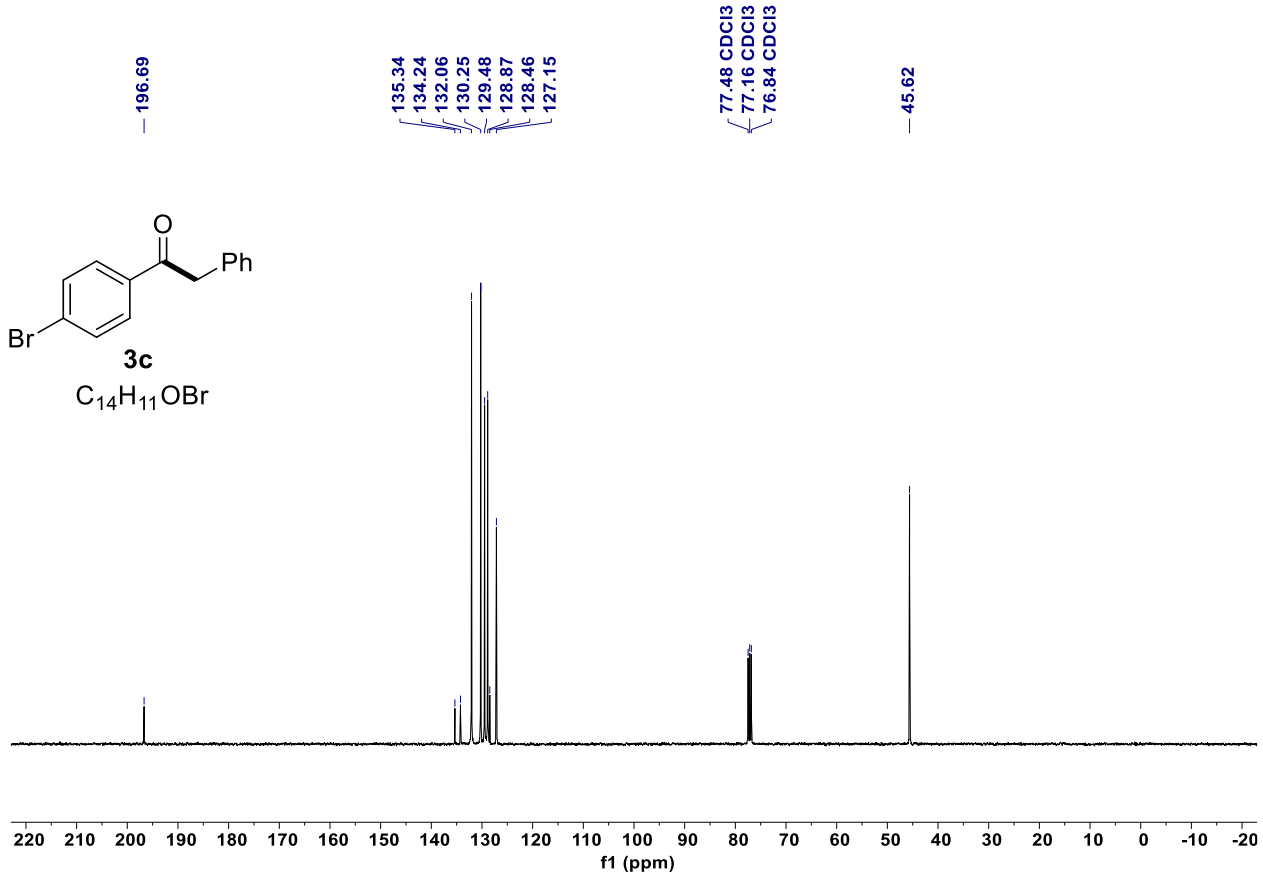
^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of the compound **3b**



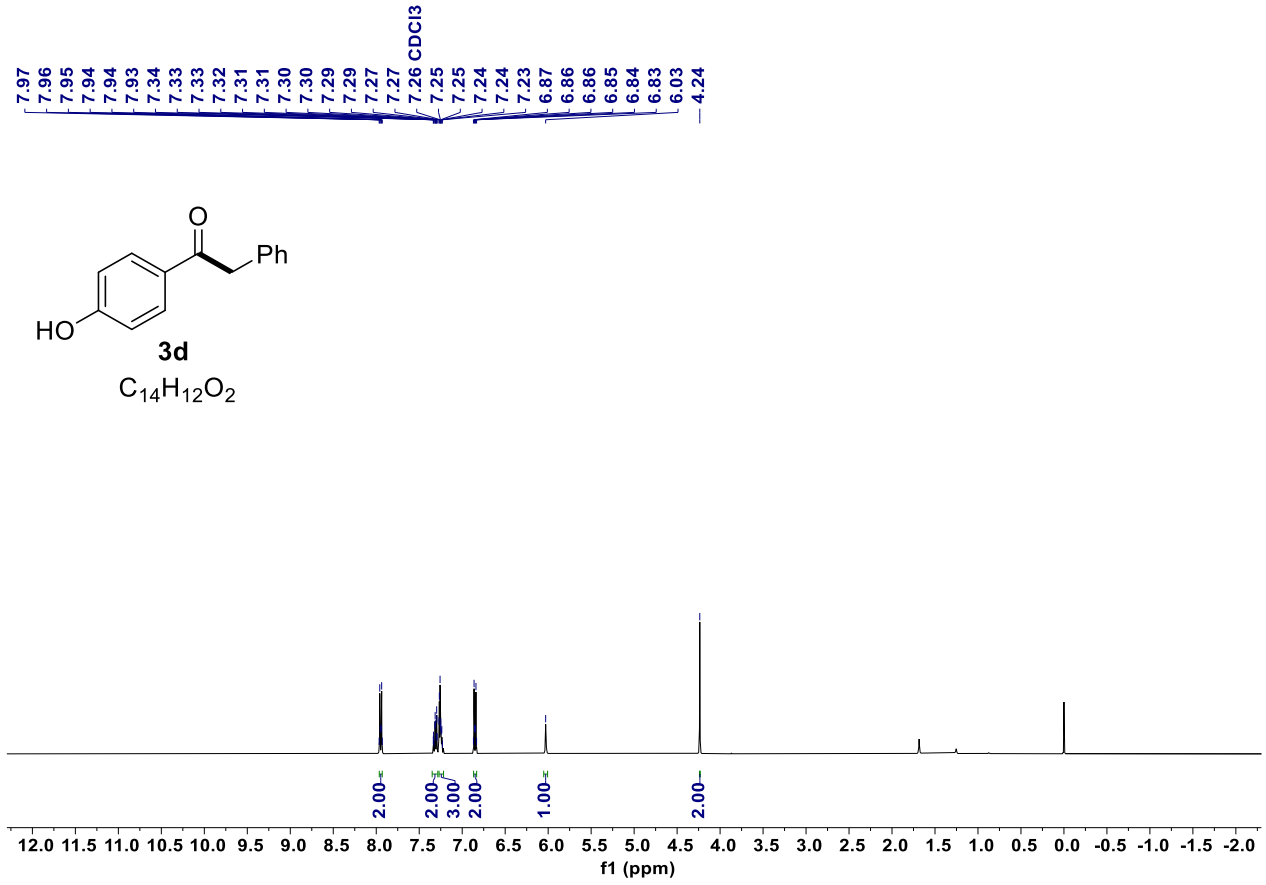
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3c**.



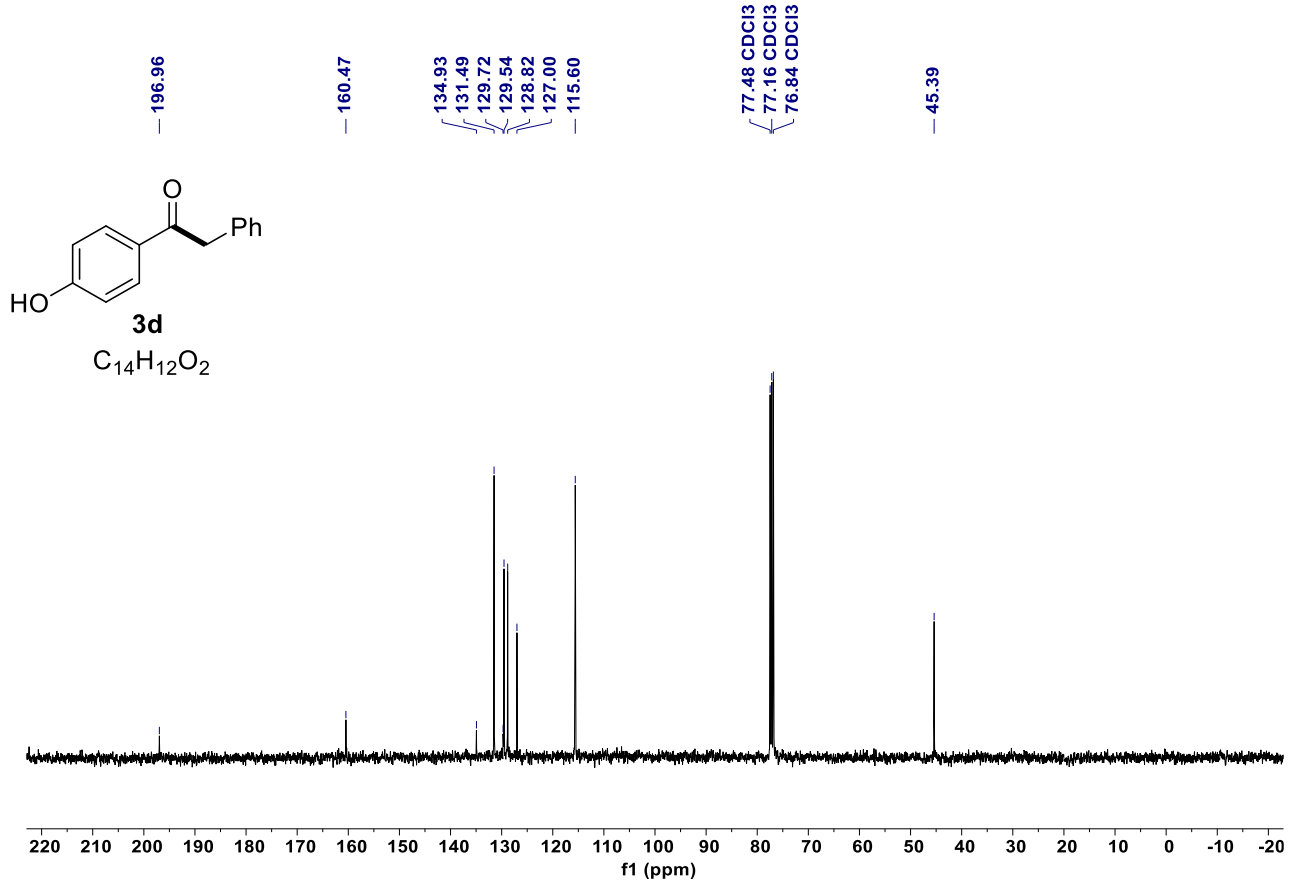
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3c**.



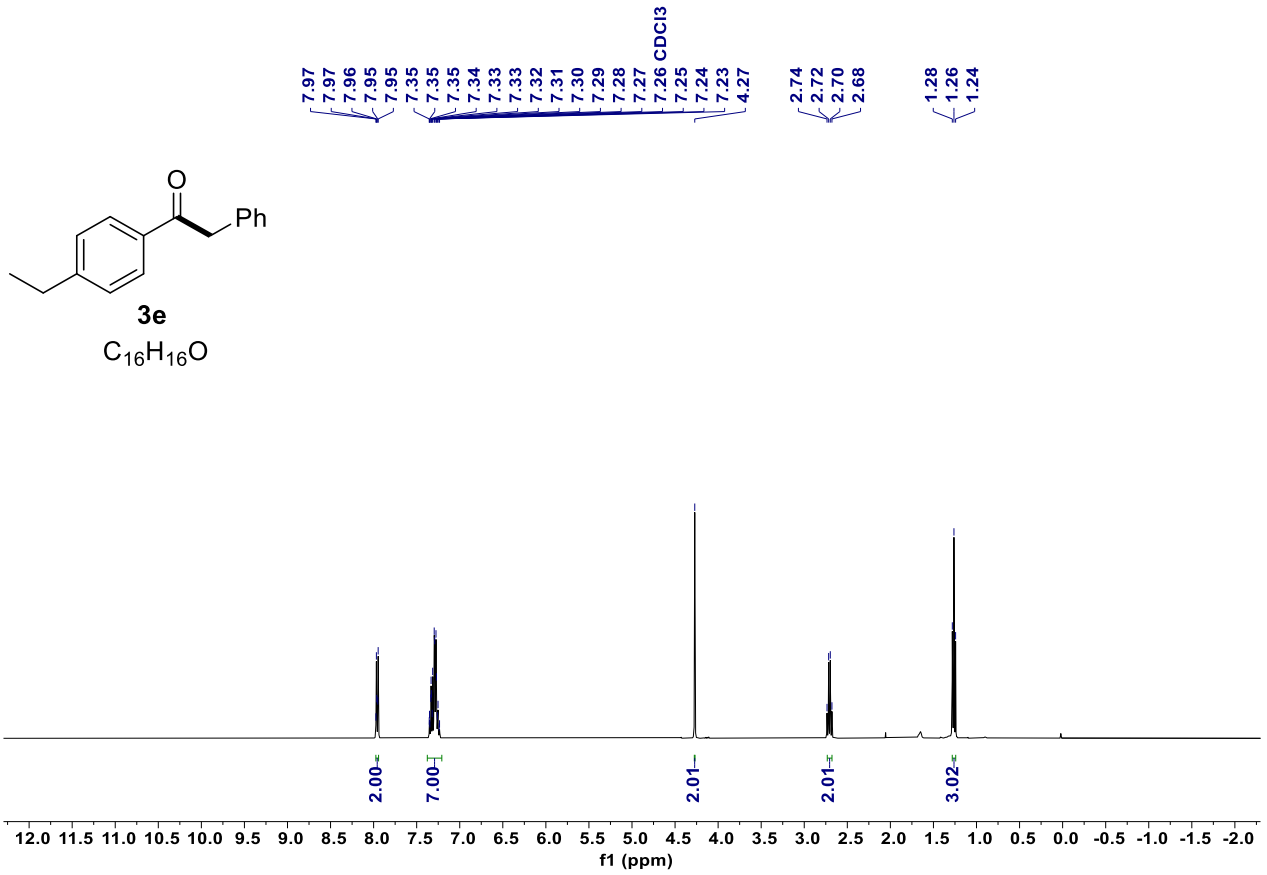
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3d**.



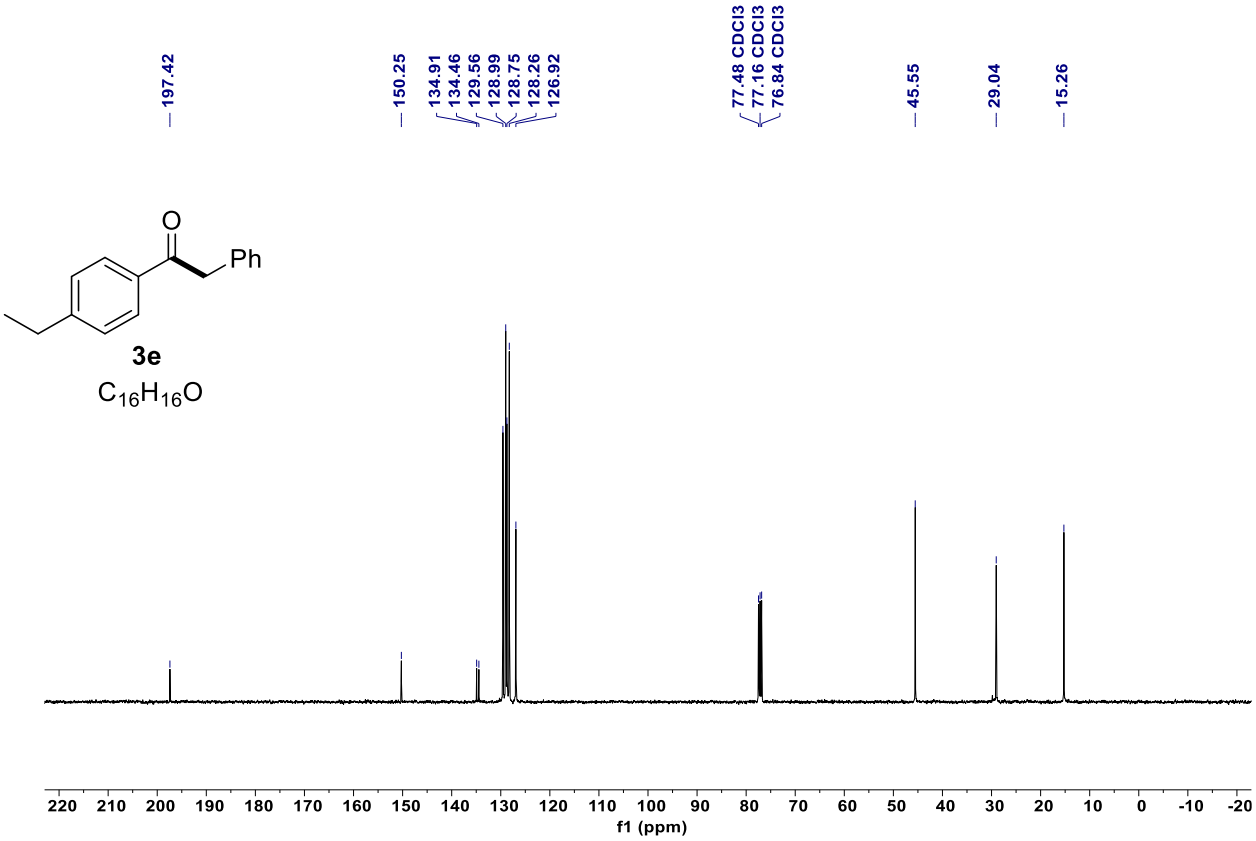
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3d**.



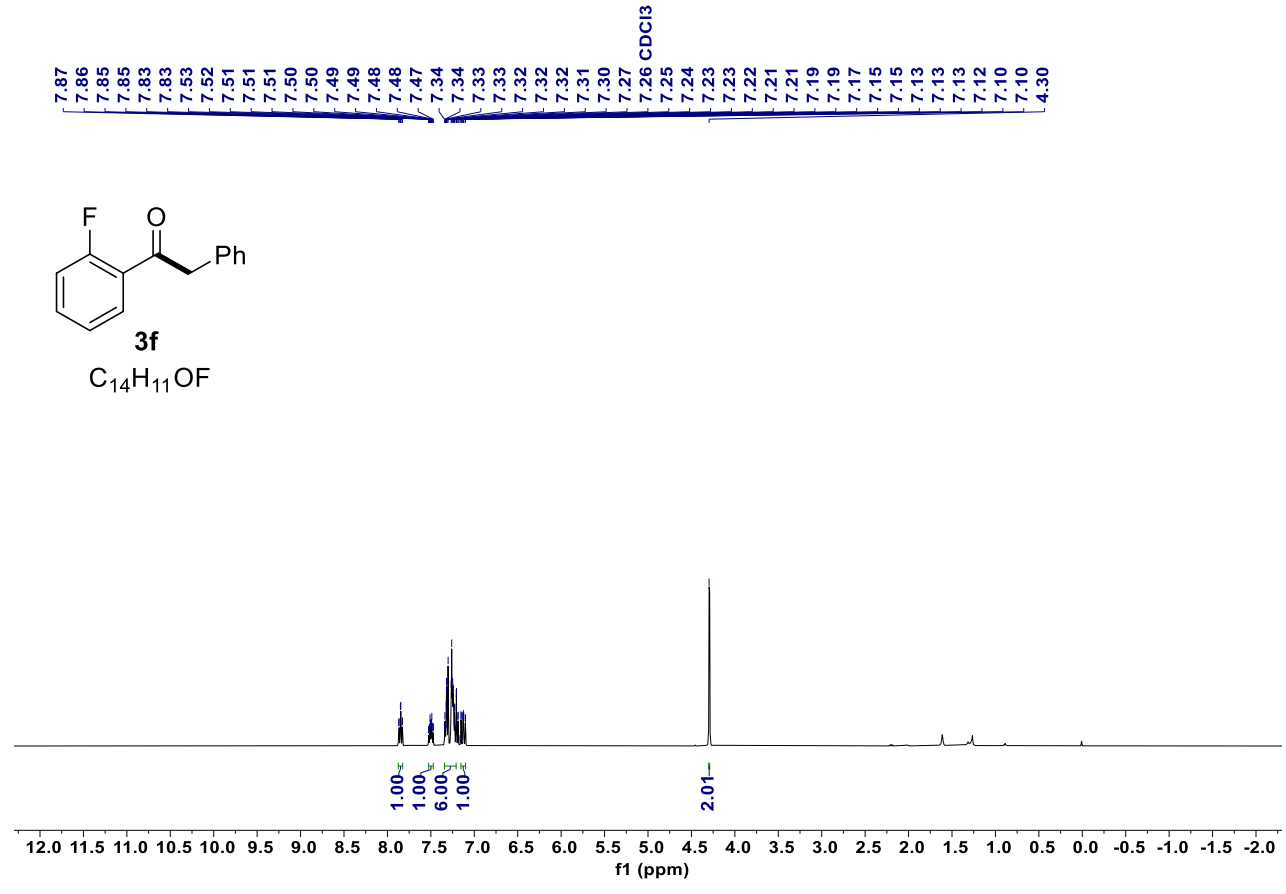
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3e**.



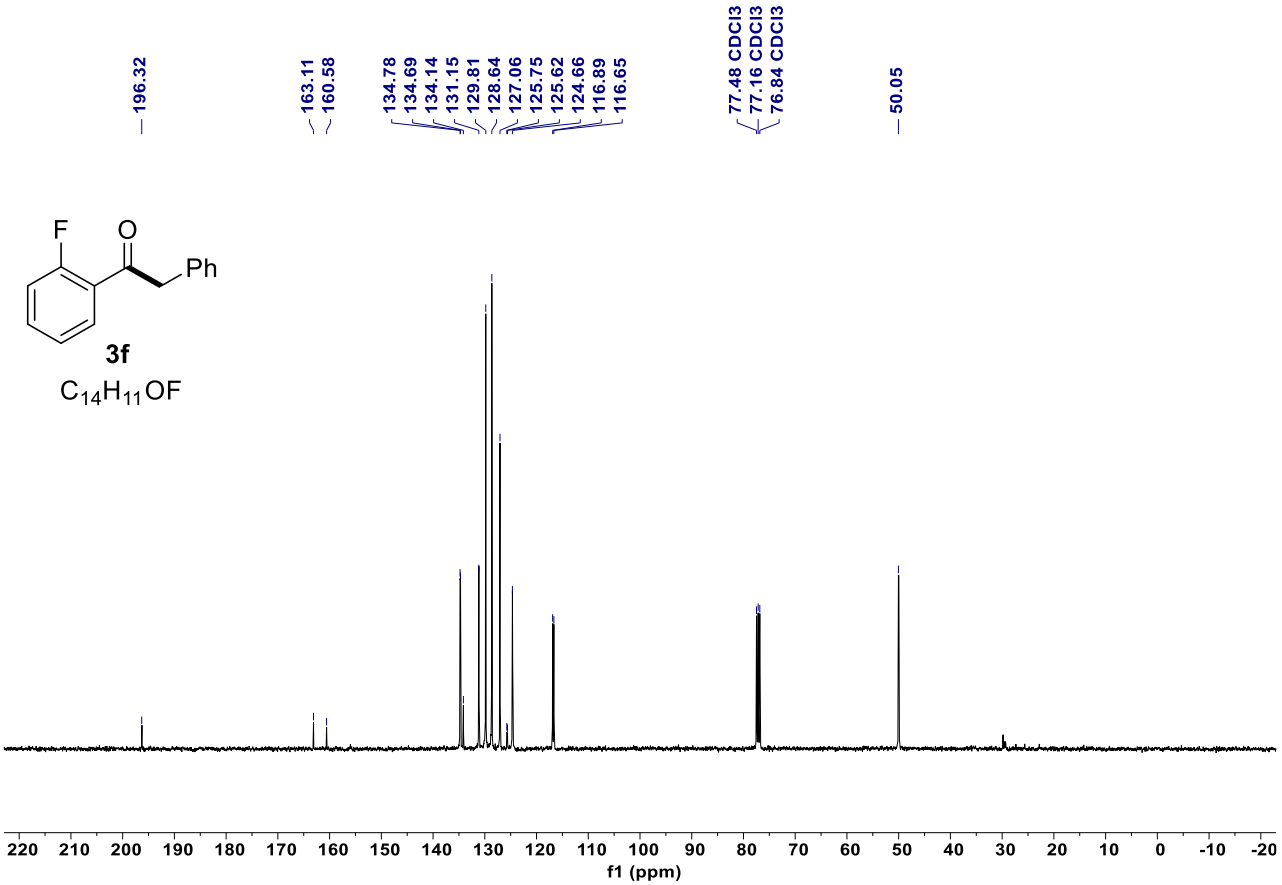
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3e**.



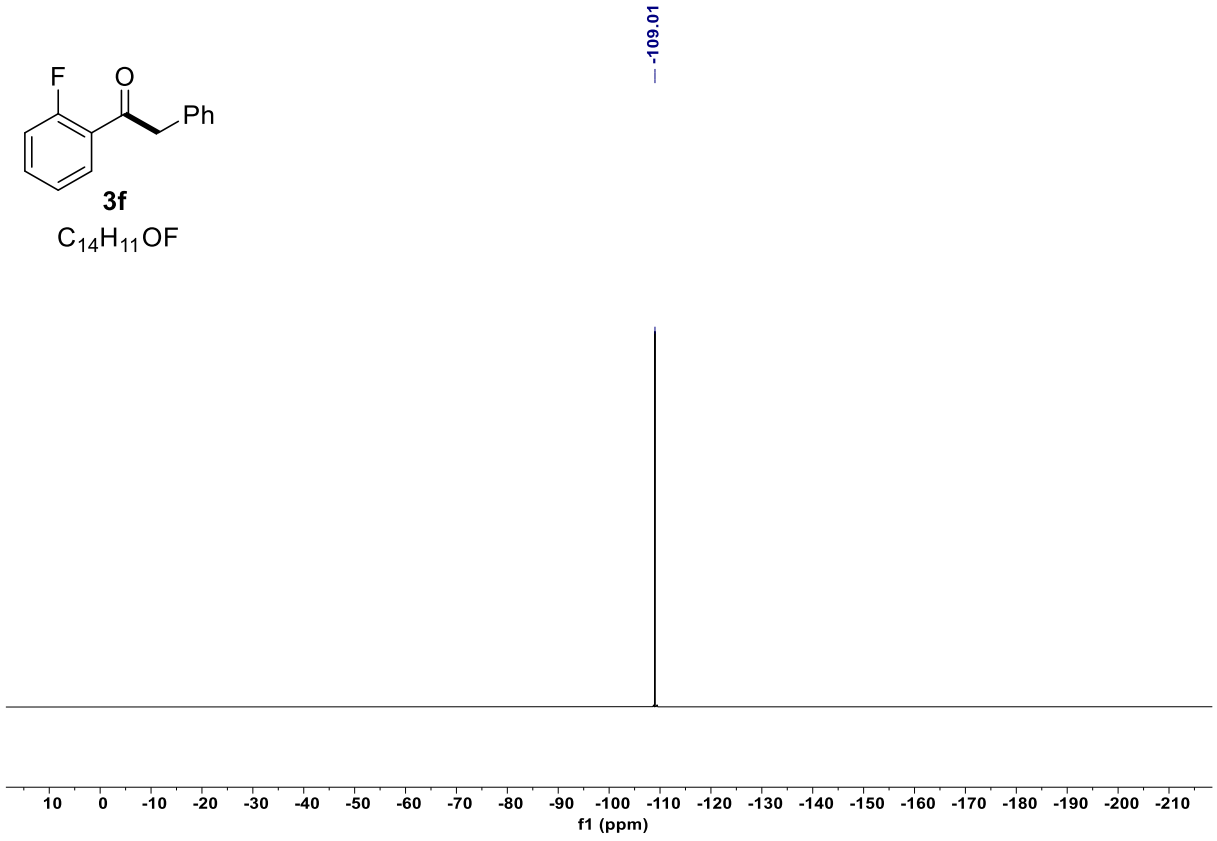
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3f**.



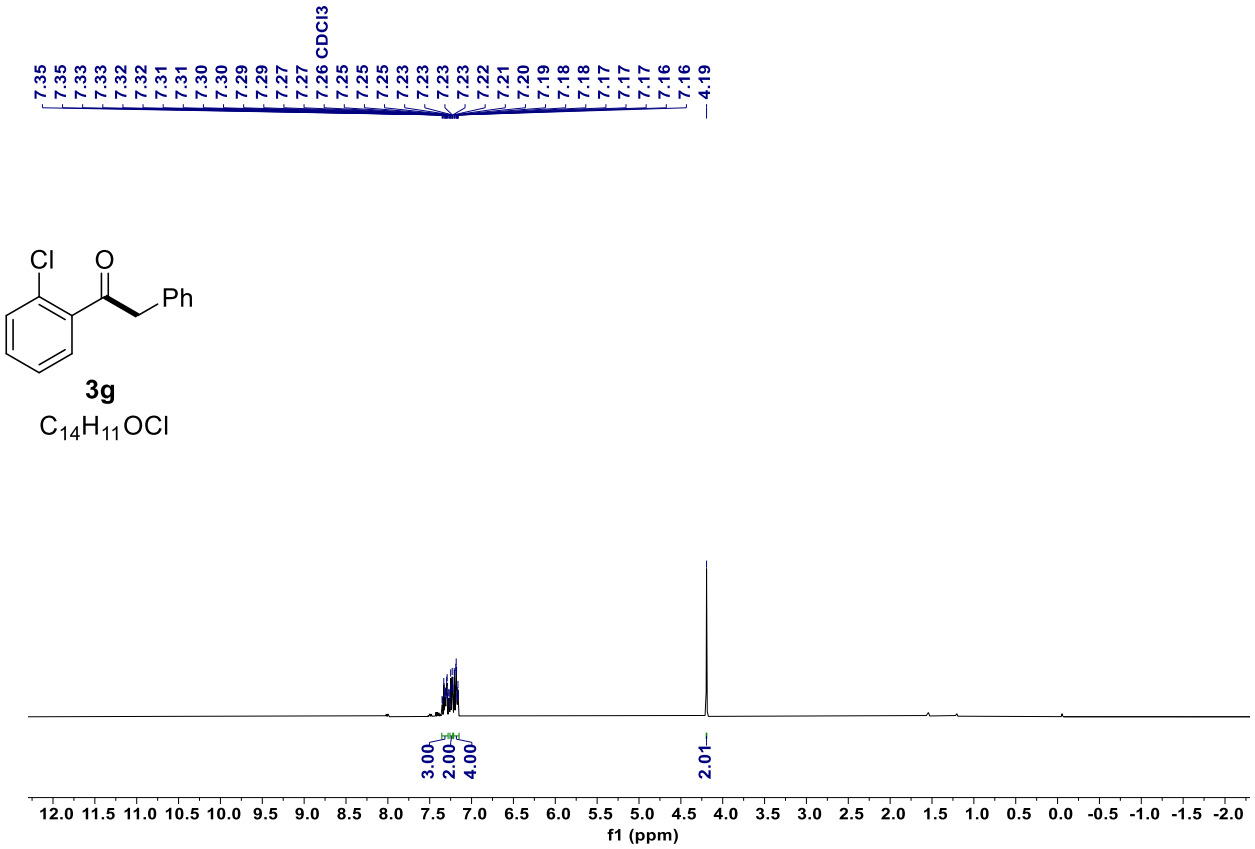
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **3f**.



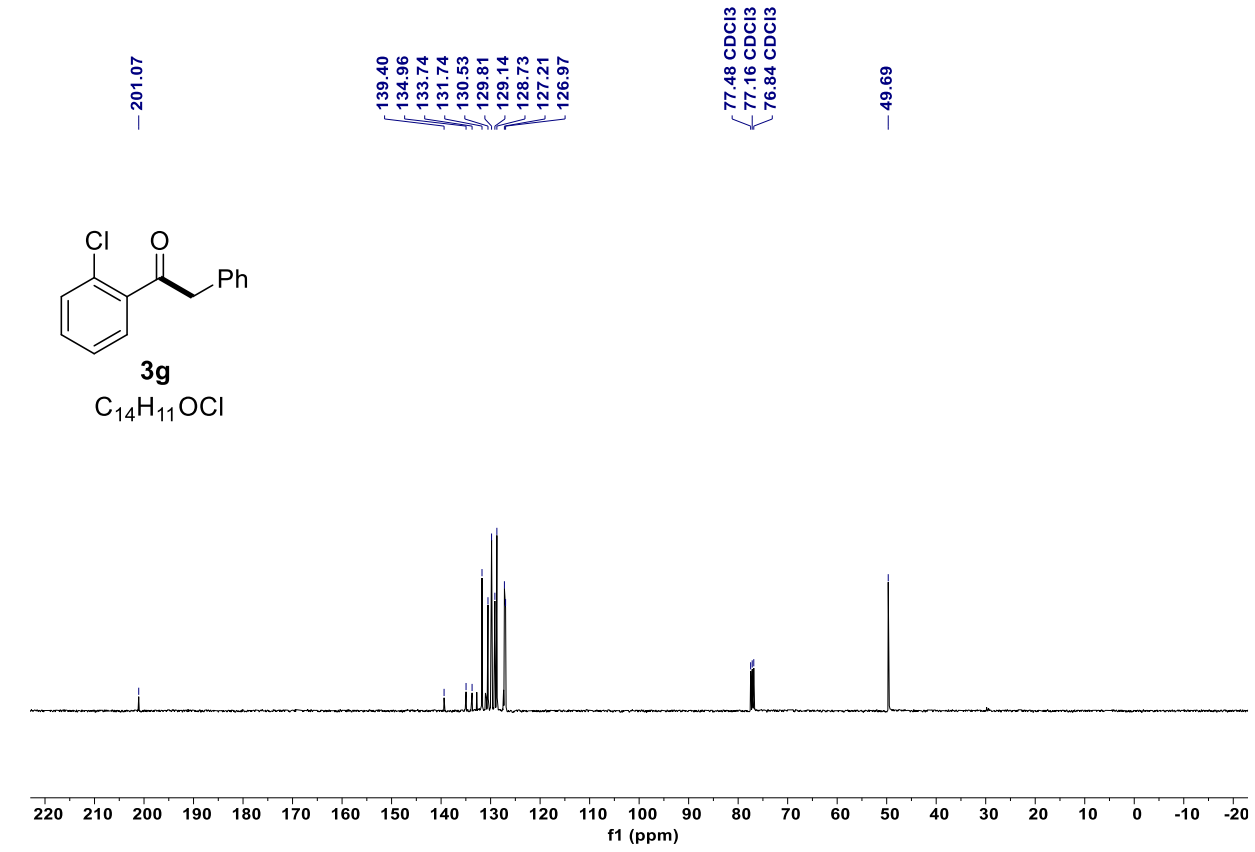
^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of the compound **3f**



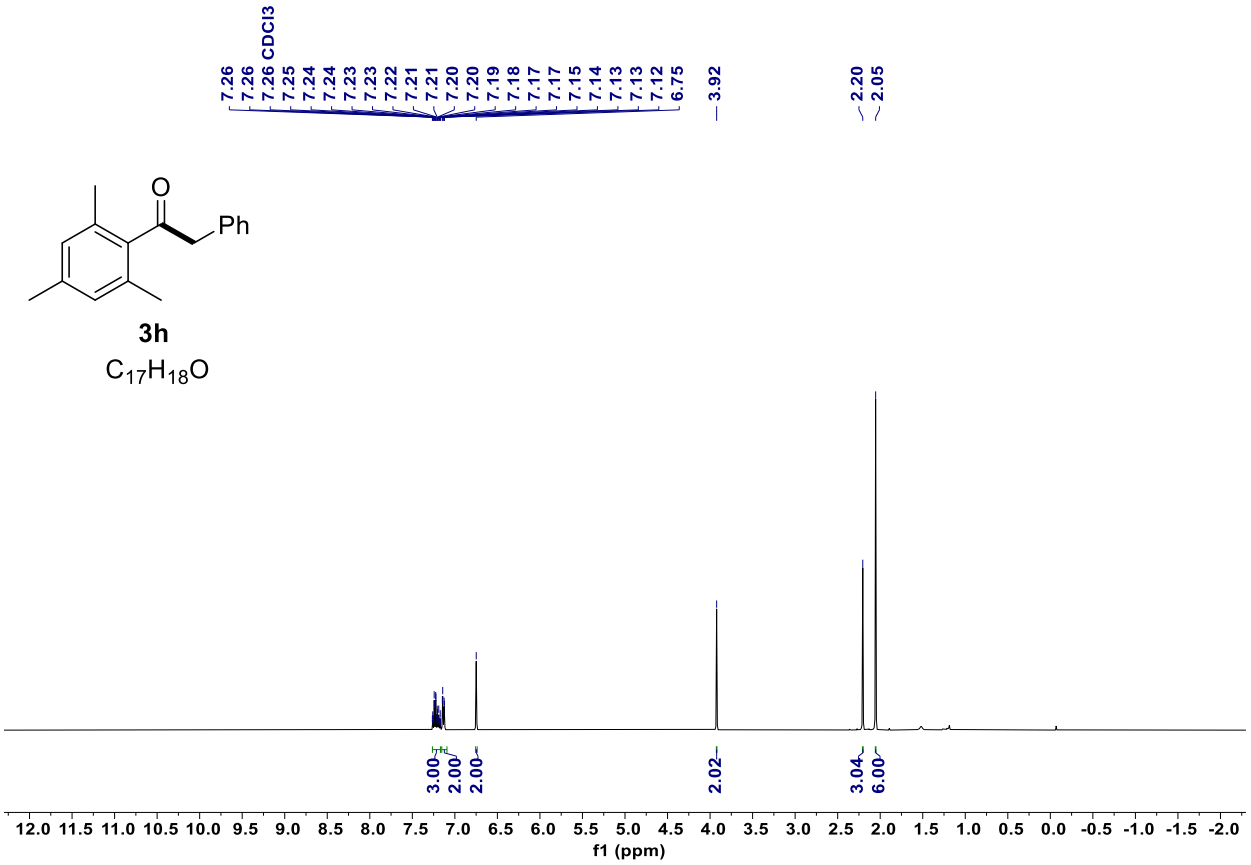
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3g**.



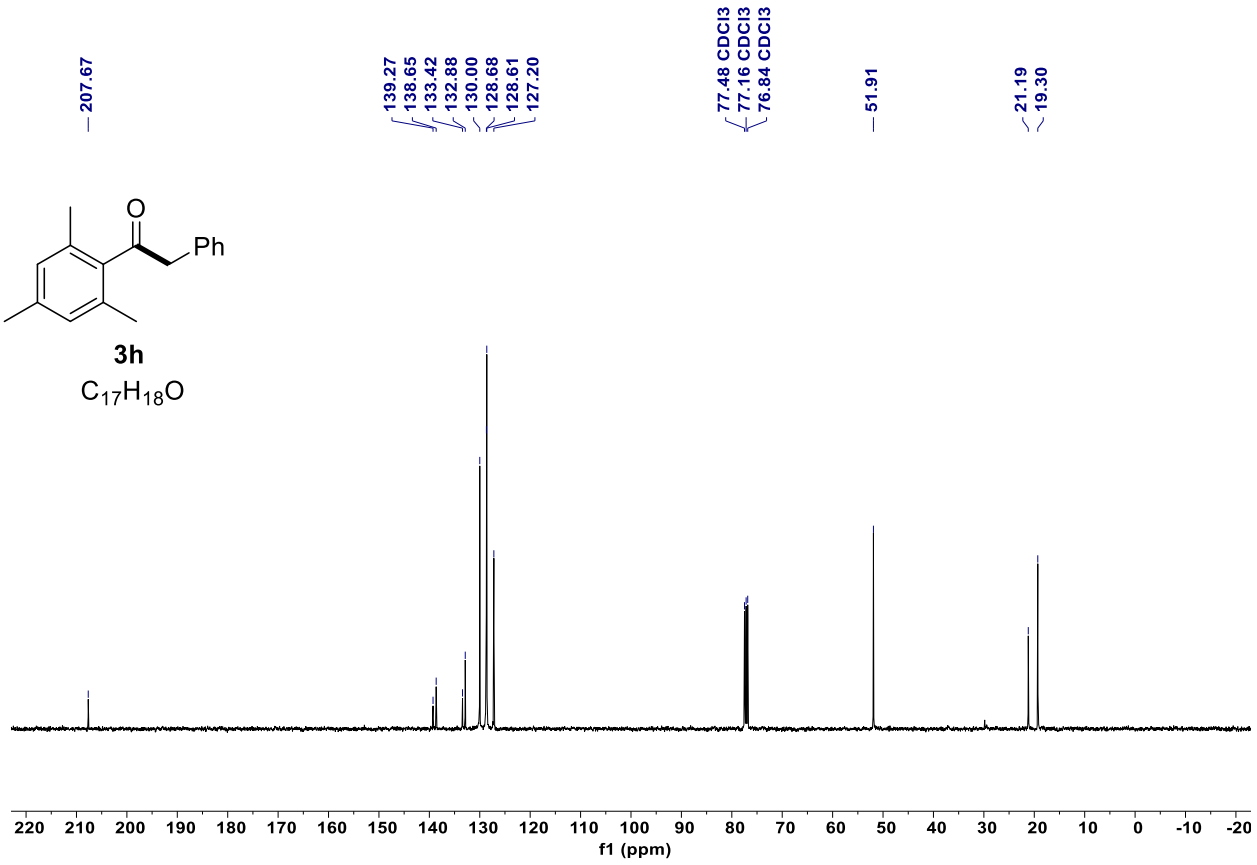
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **3g**.



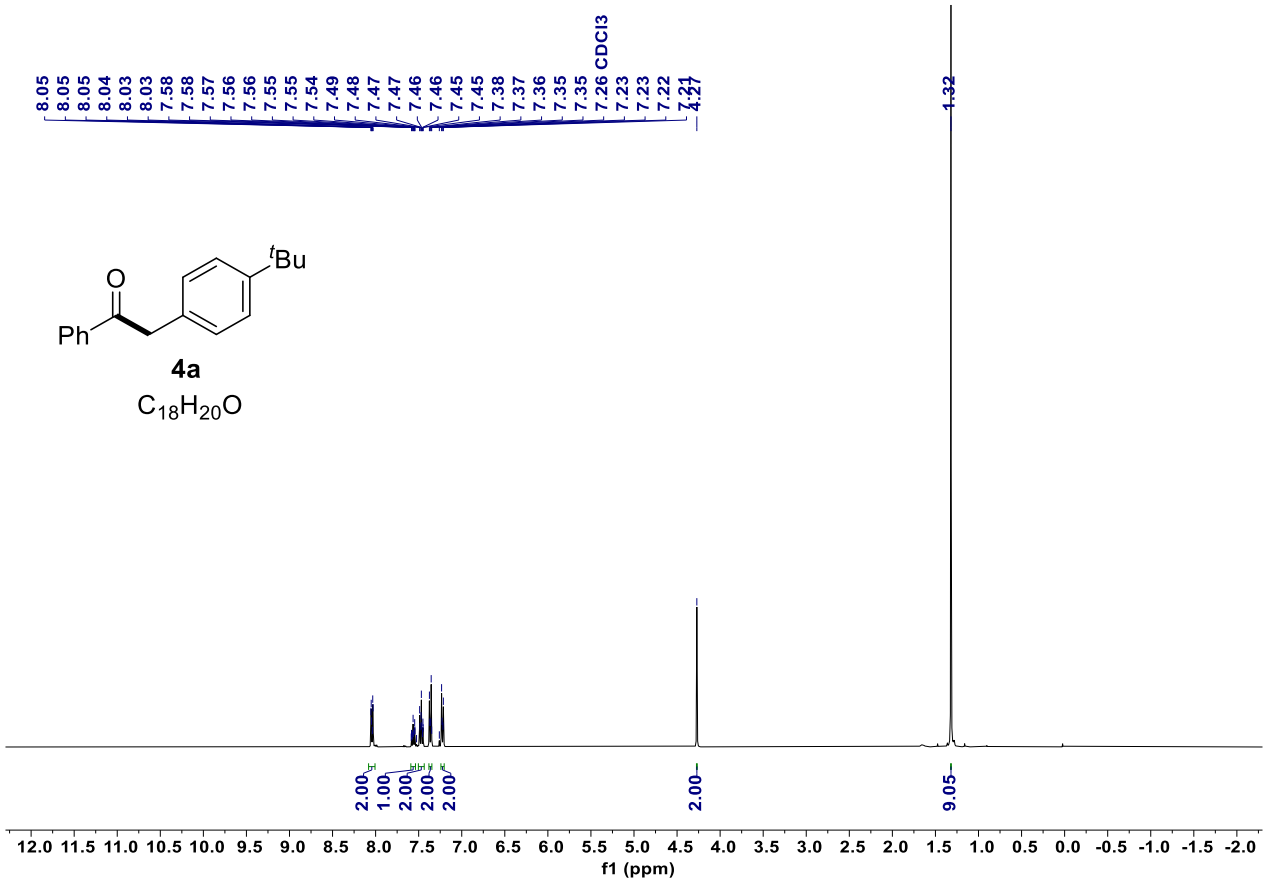
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **3h**.



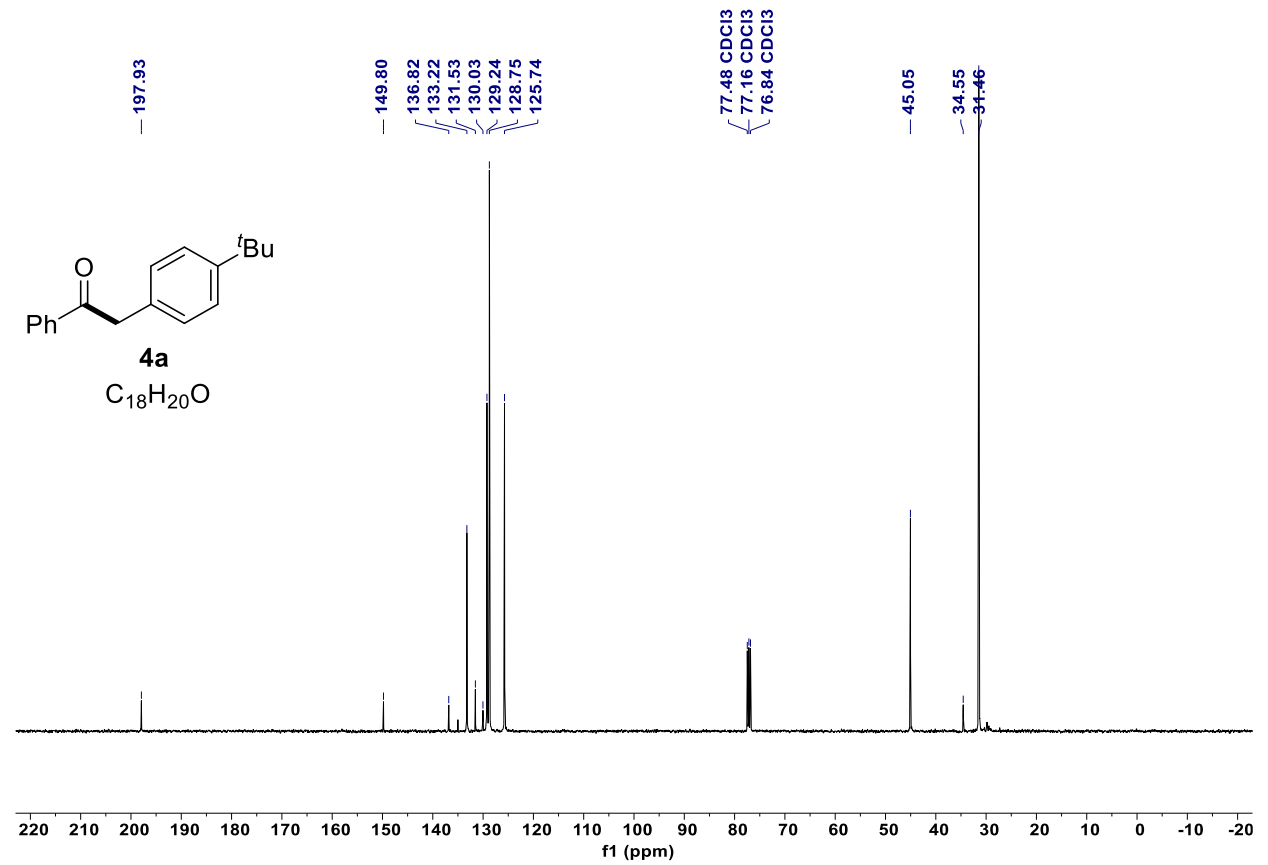
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **3h**.



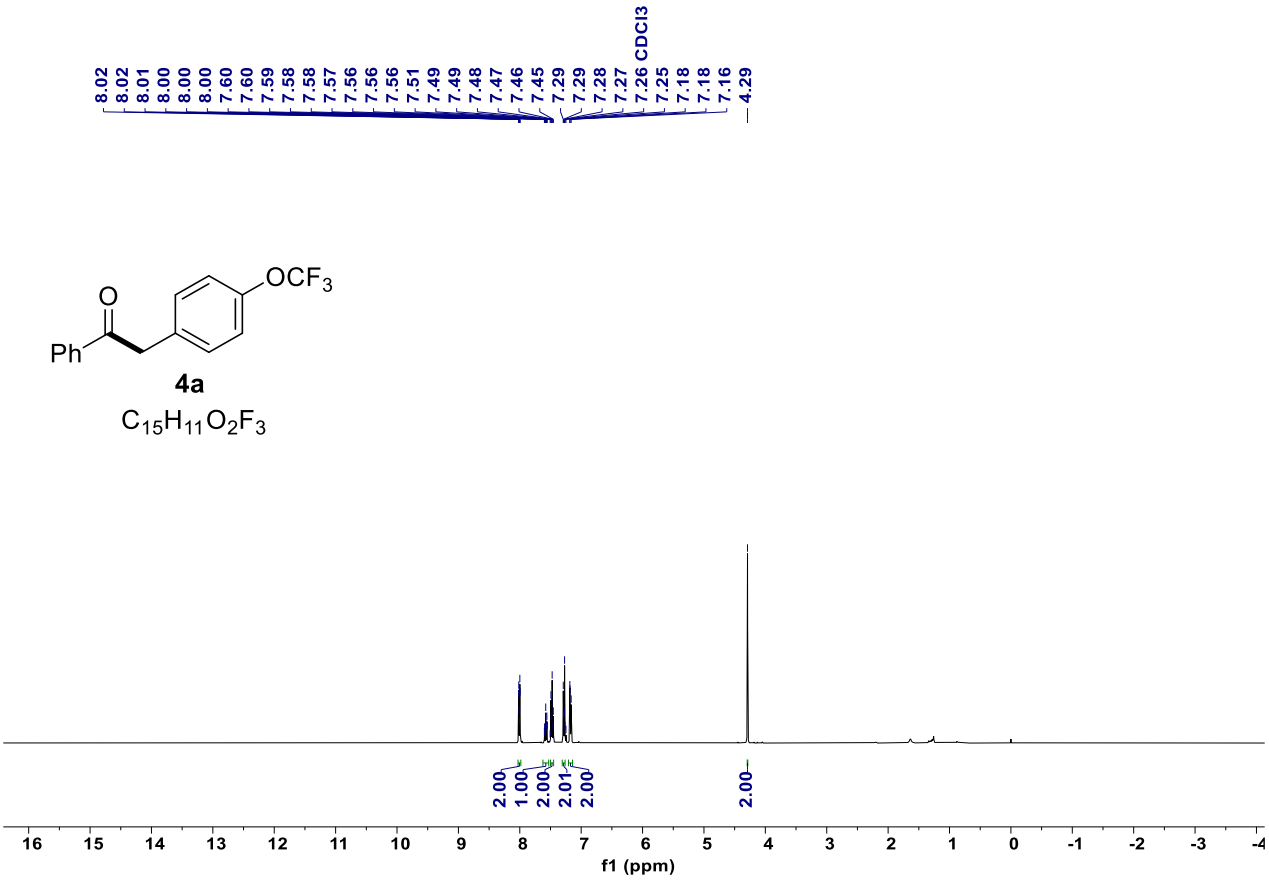
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4a**.



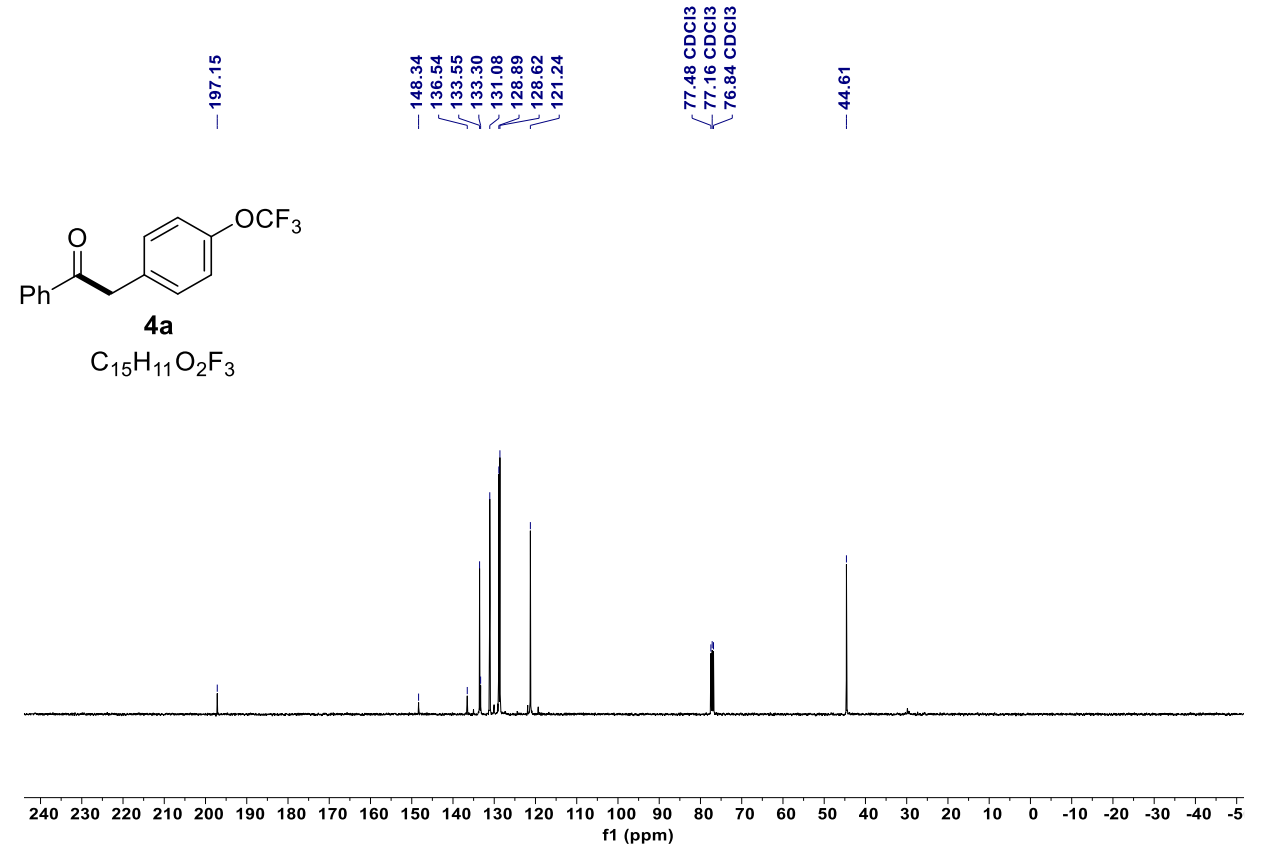
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4a**.



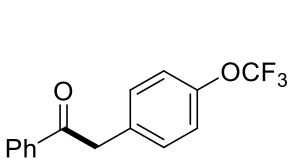
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4b**.



^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4b**.



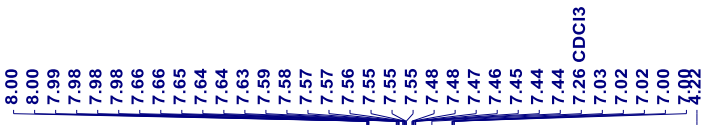
^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of the compound **4b**

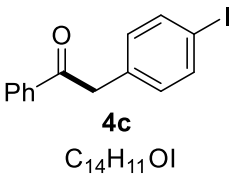


4a

$C_{15}H_{11}O_2F_3$

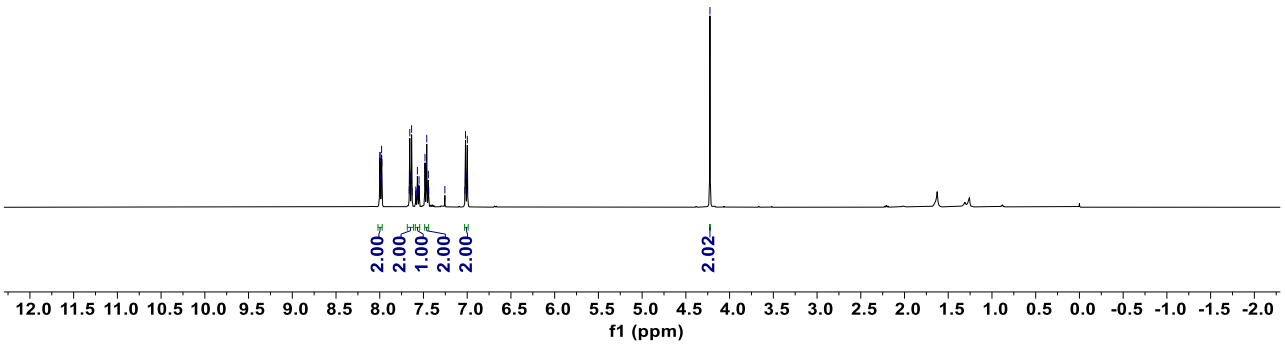
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4c**.



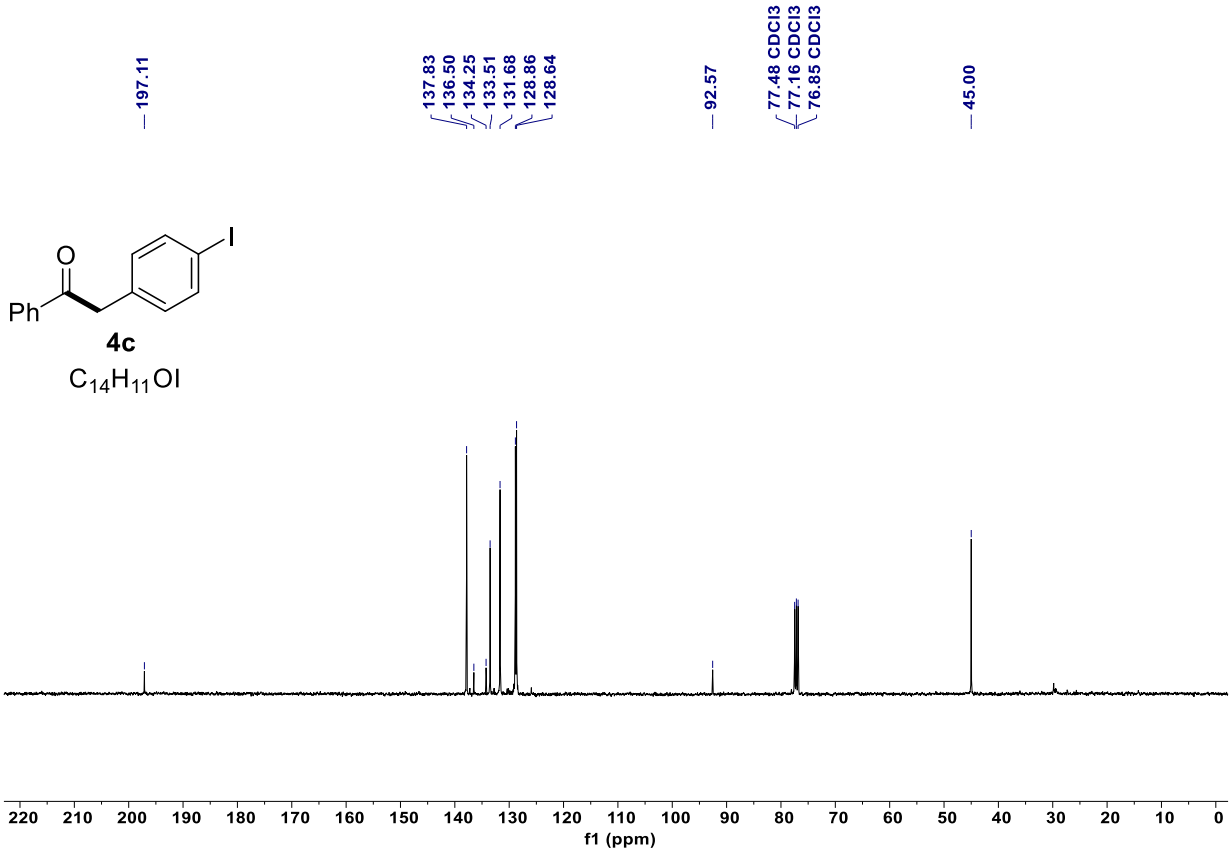


4c

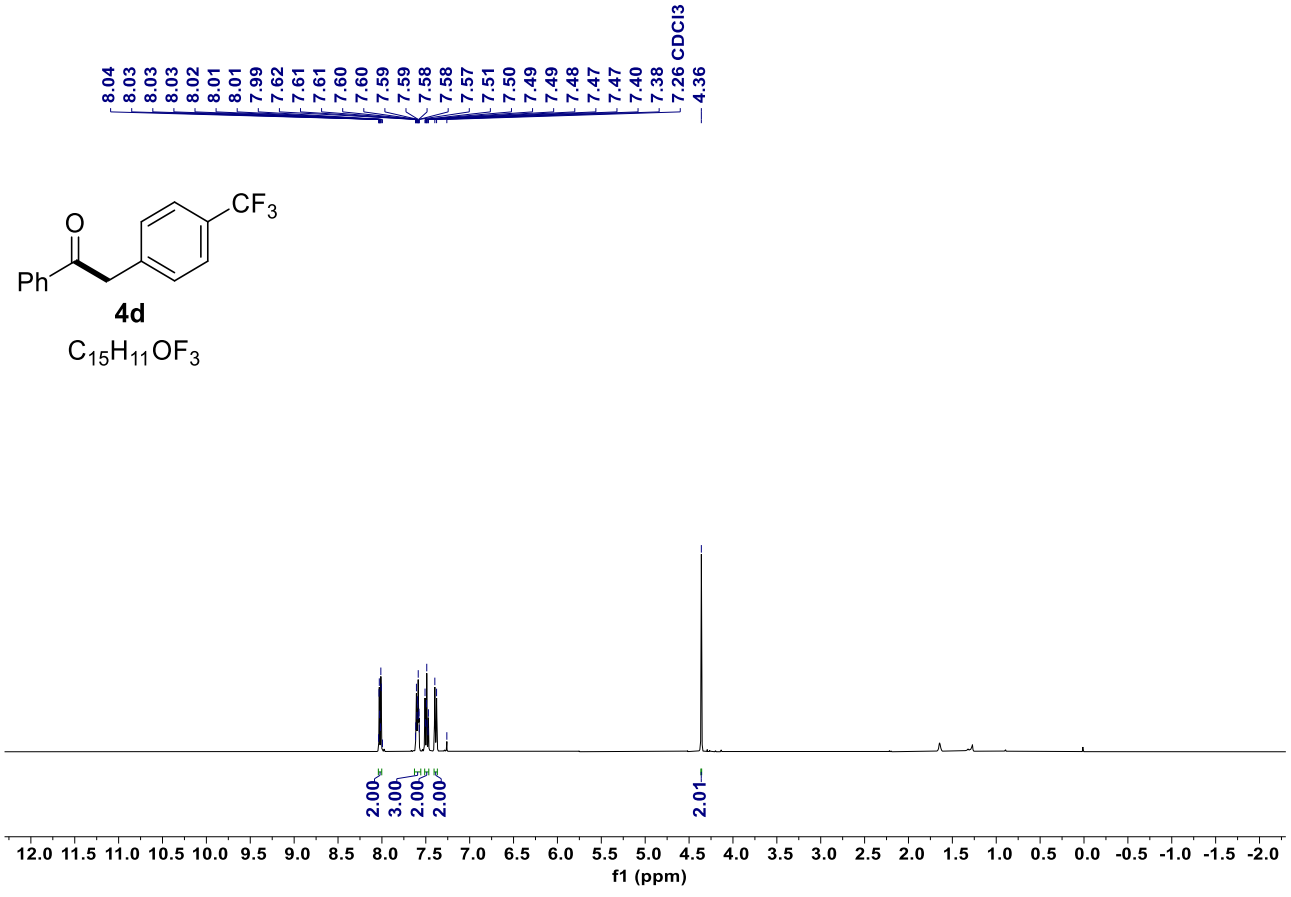
$C_{14}H_{11}OI$



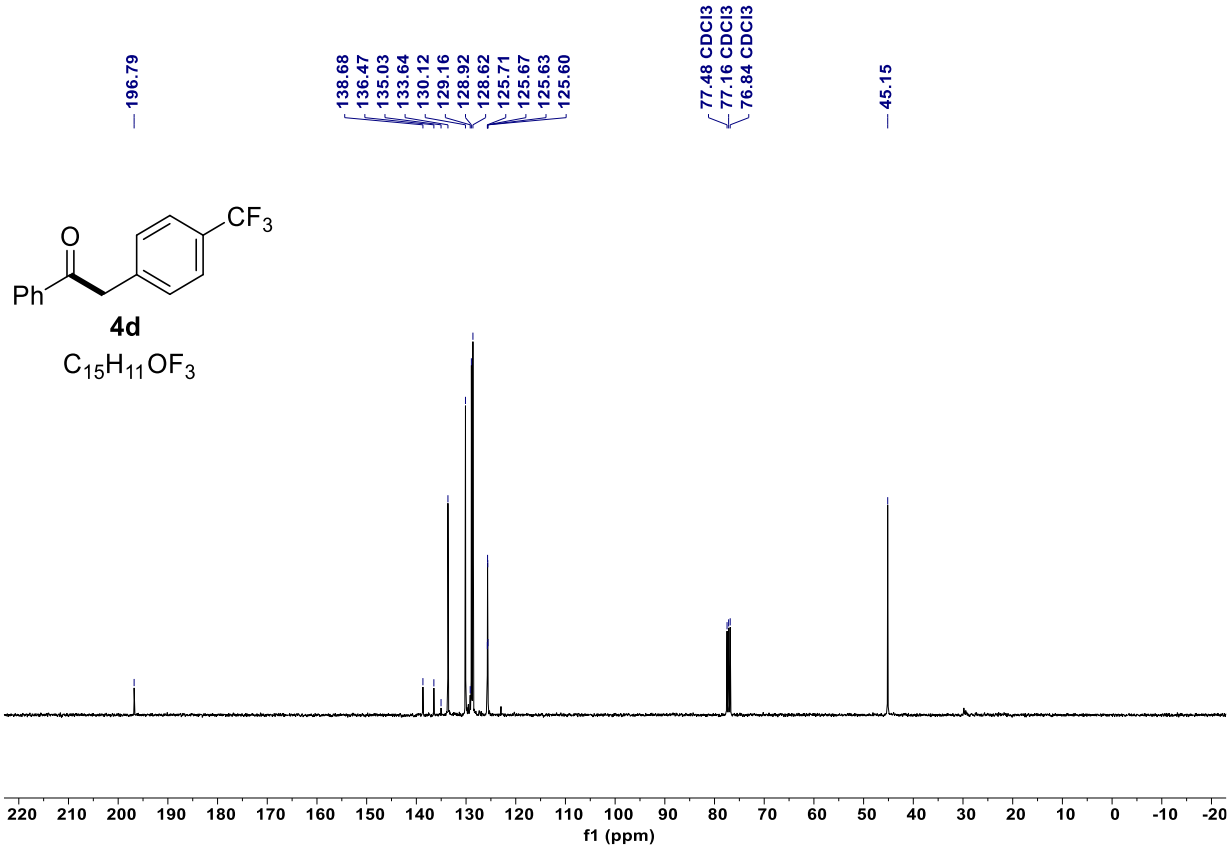
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **4c**.



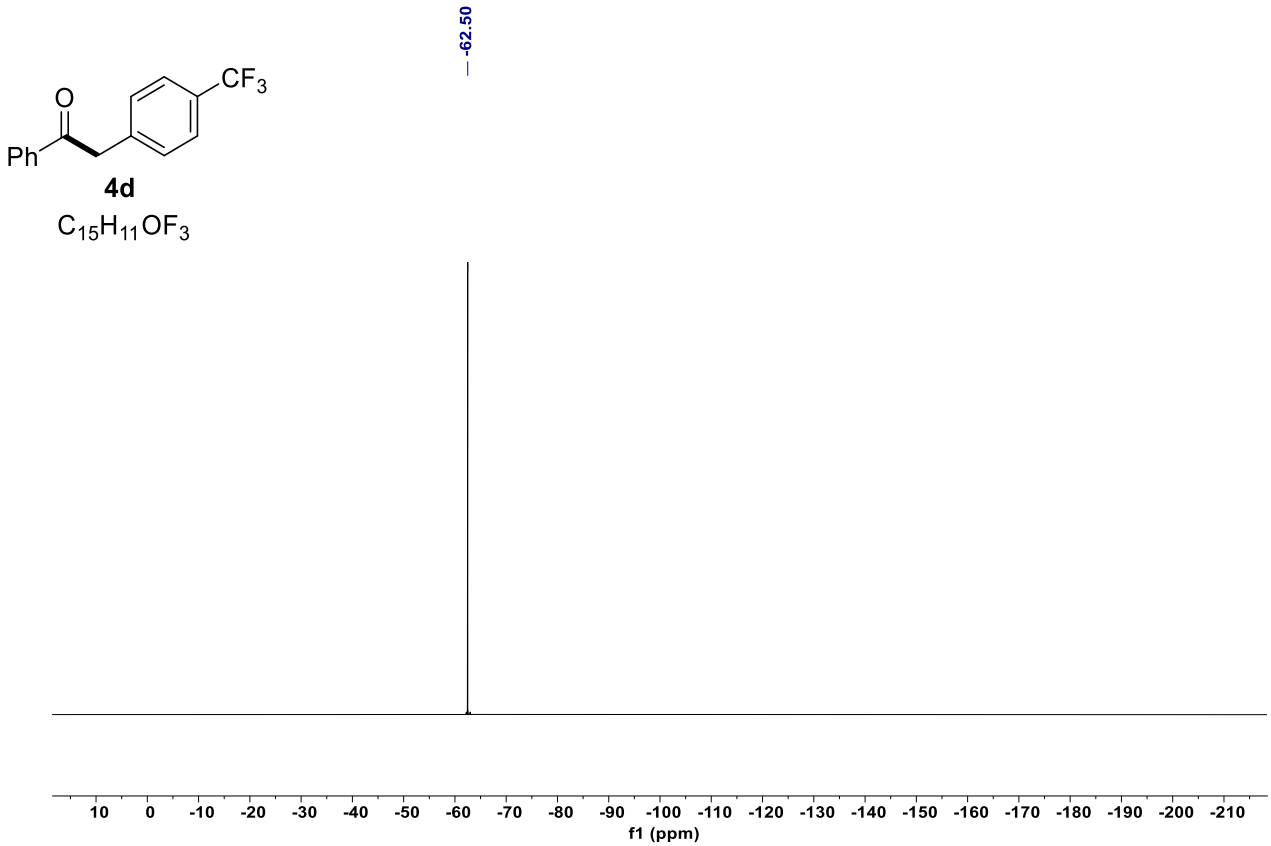
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4d**.



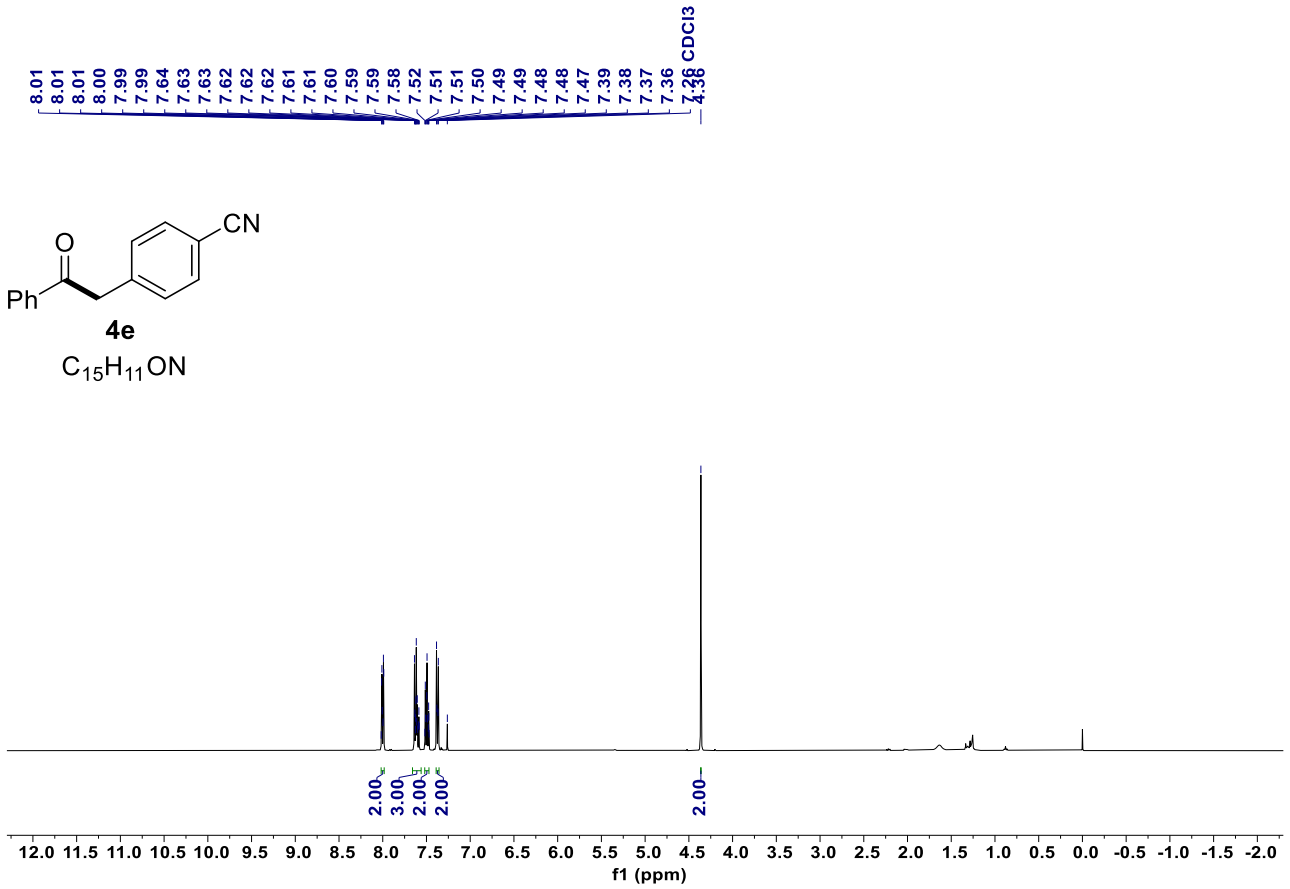
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **4d**.



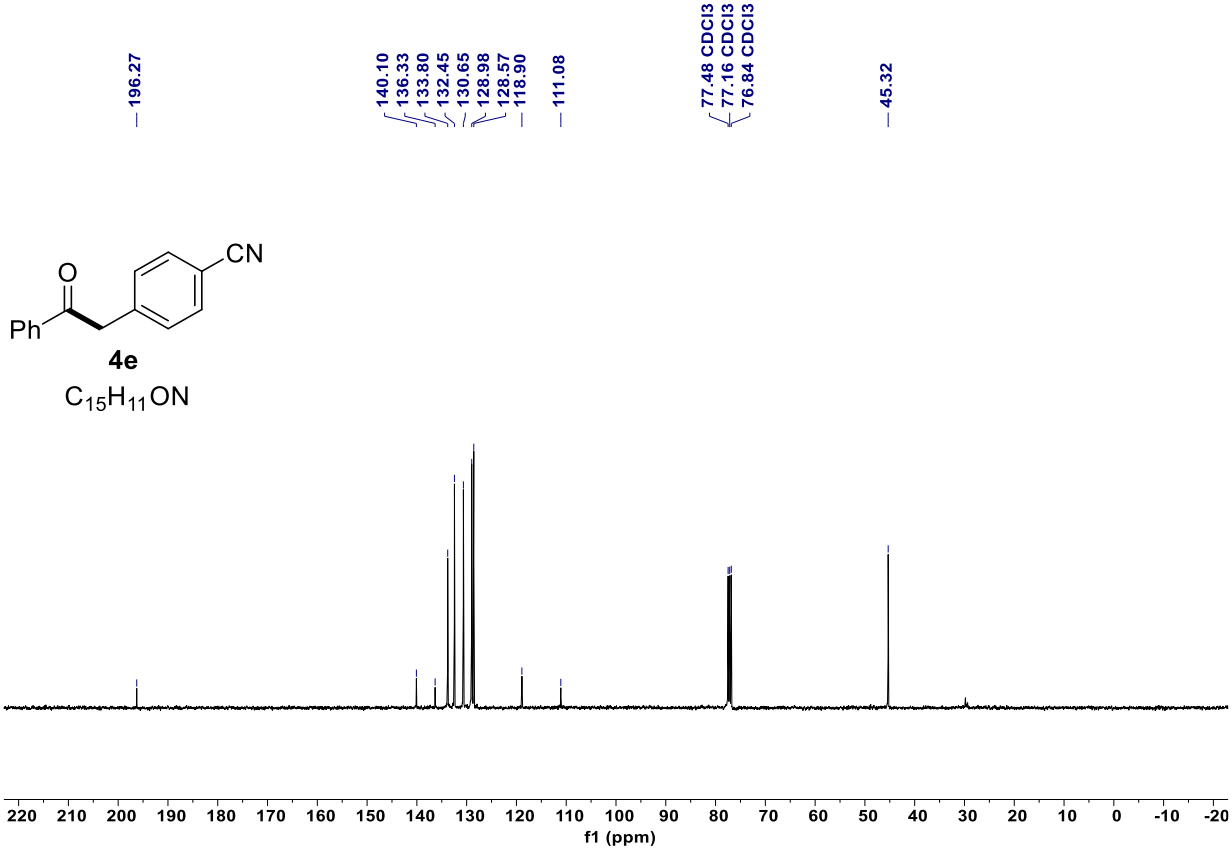
^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of the compound **4d.**



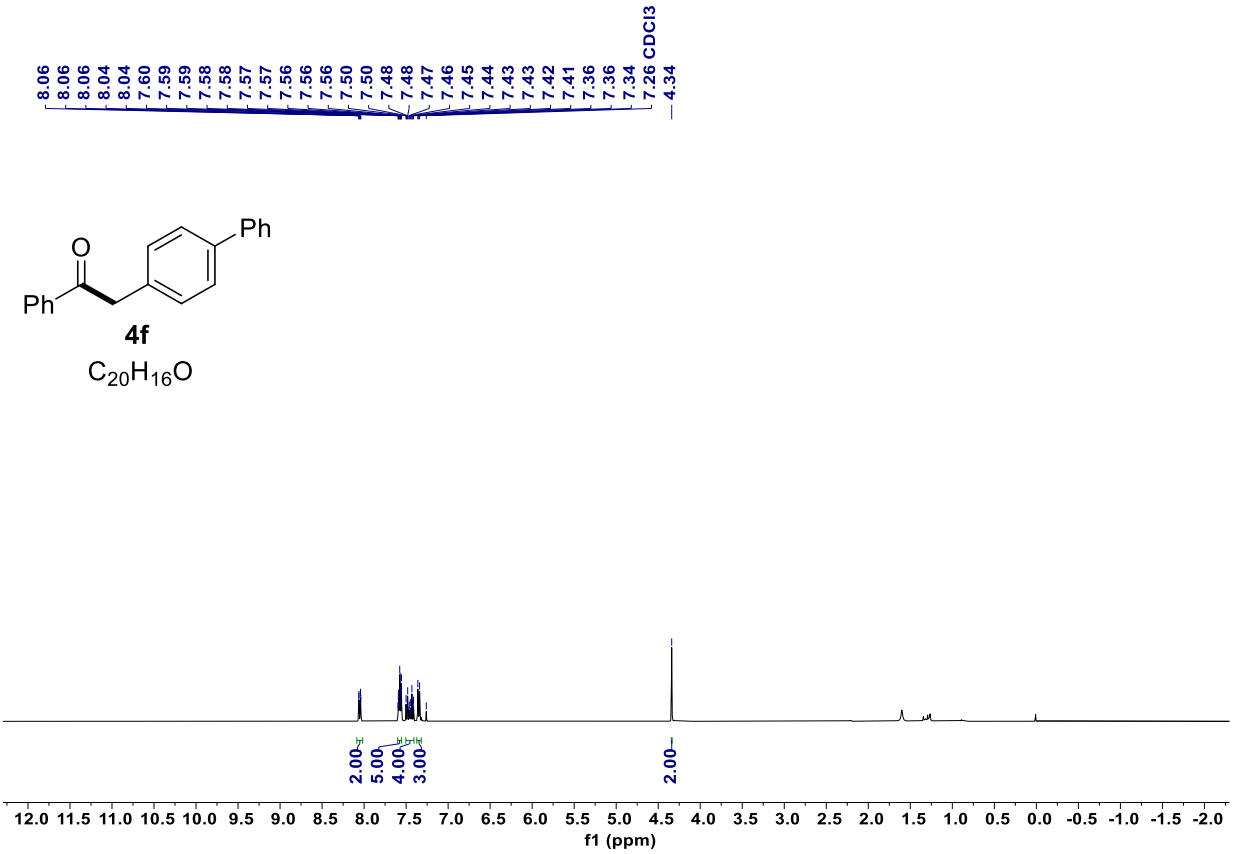
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4e**.



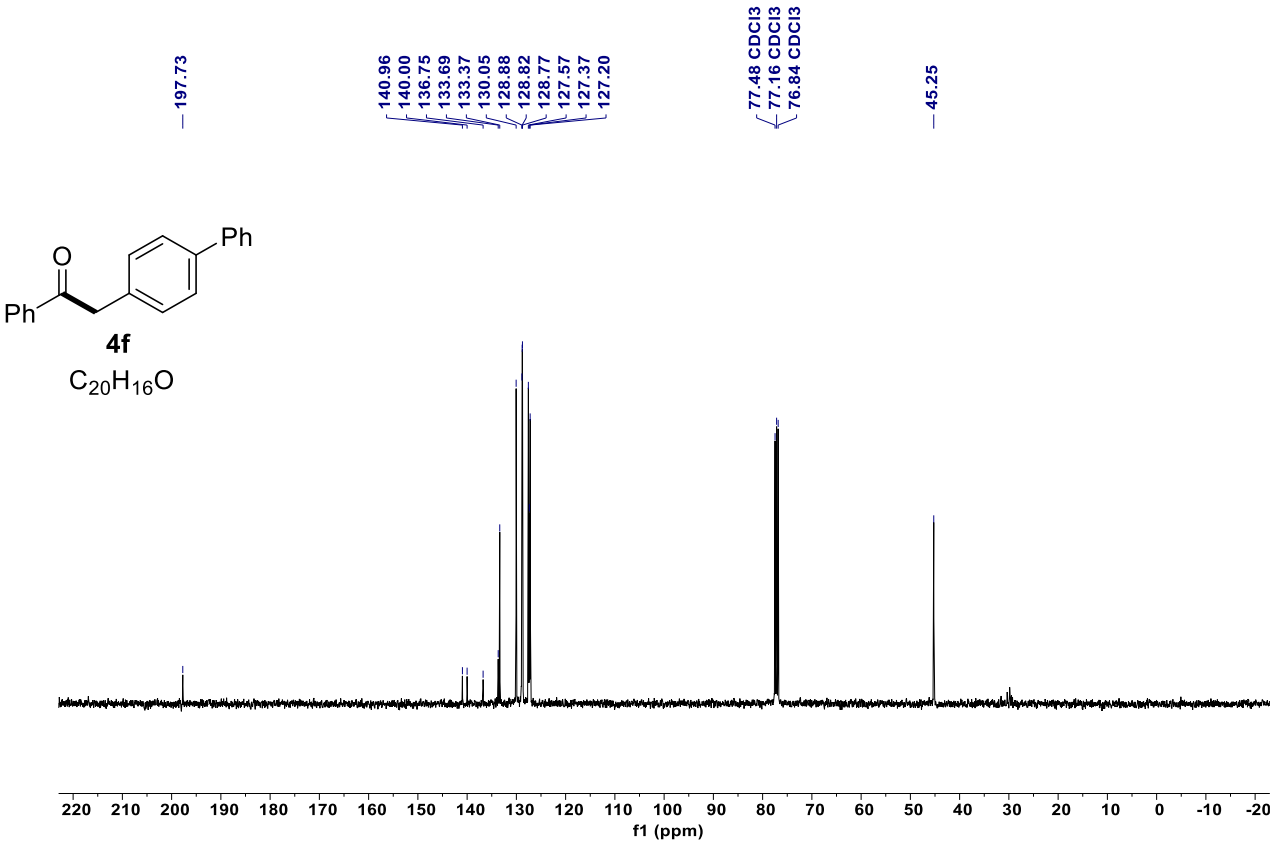
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4e**.



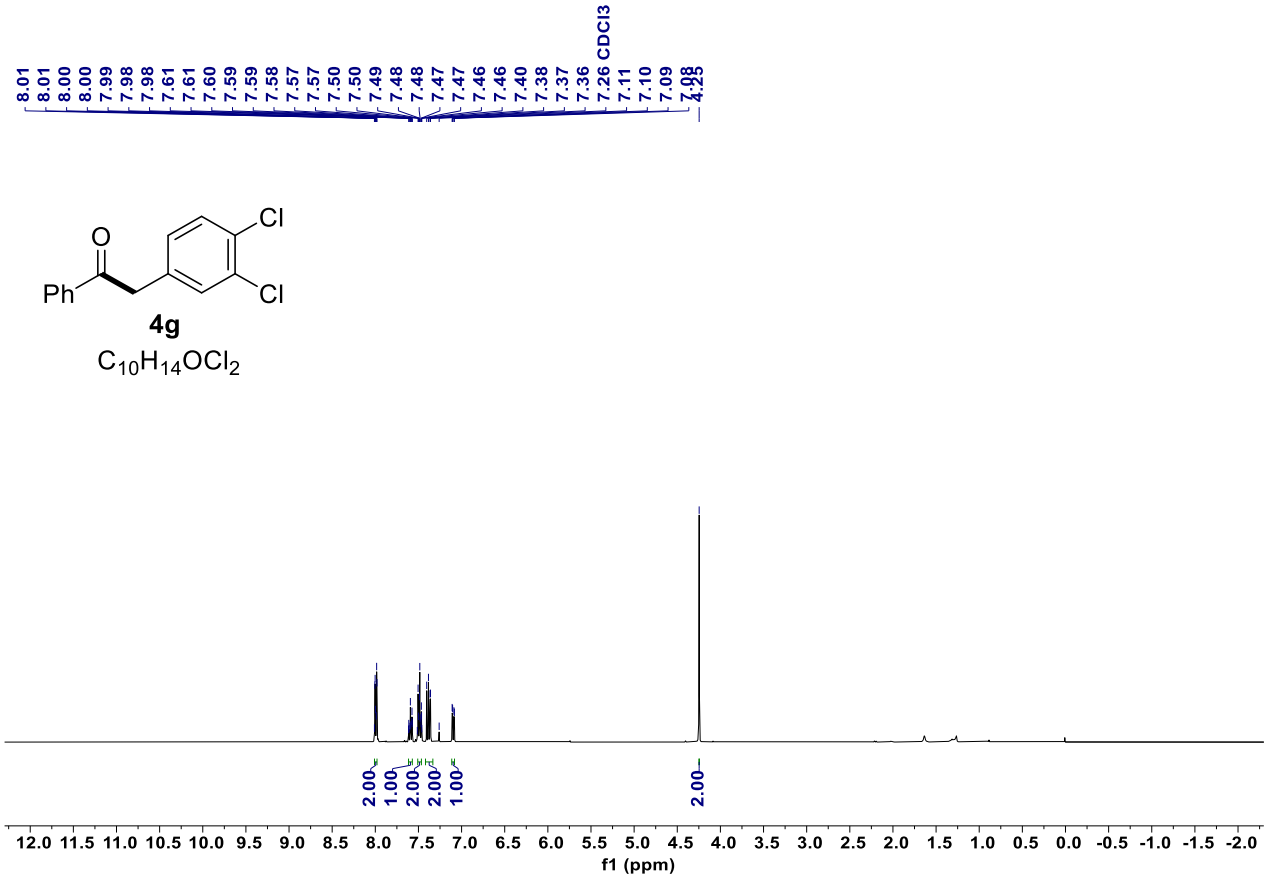
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4f**.



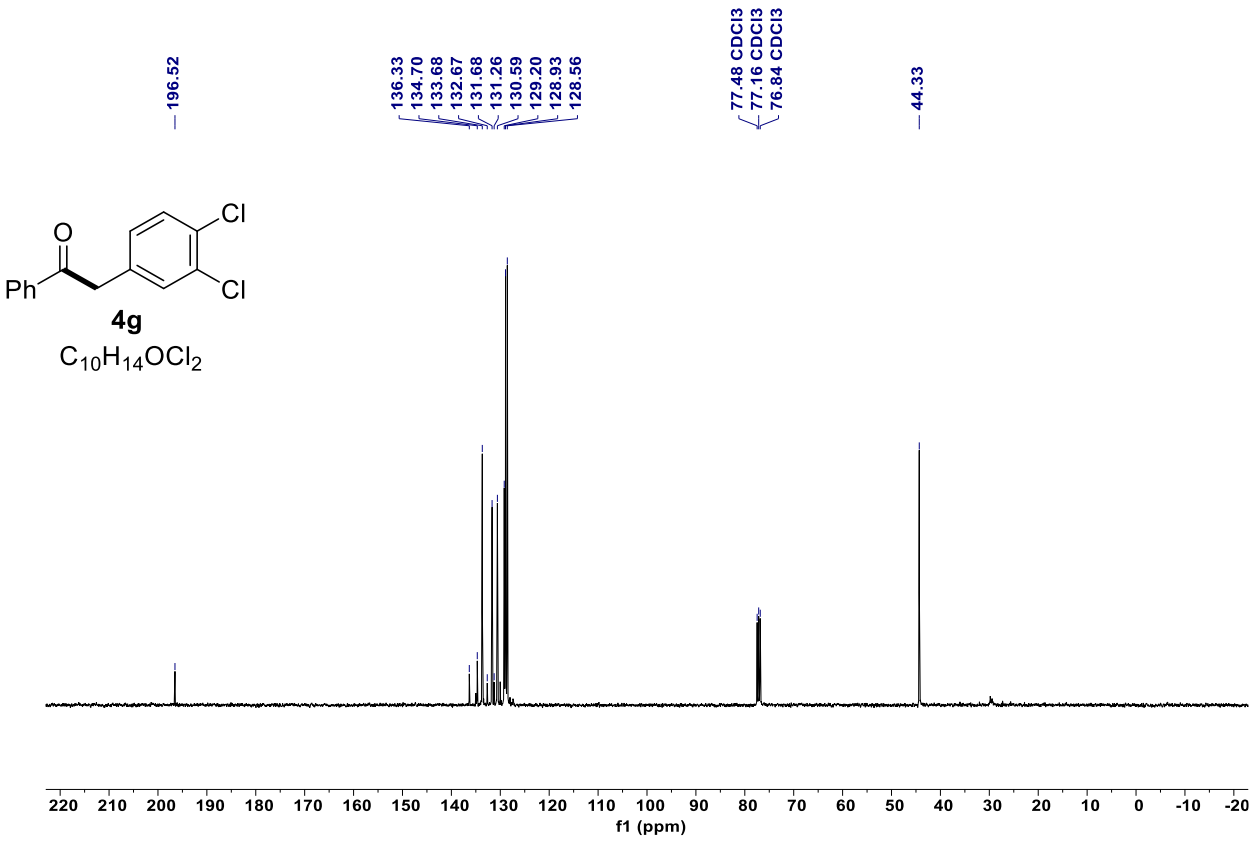
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4f**.



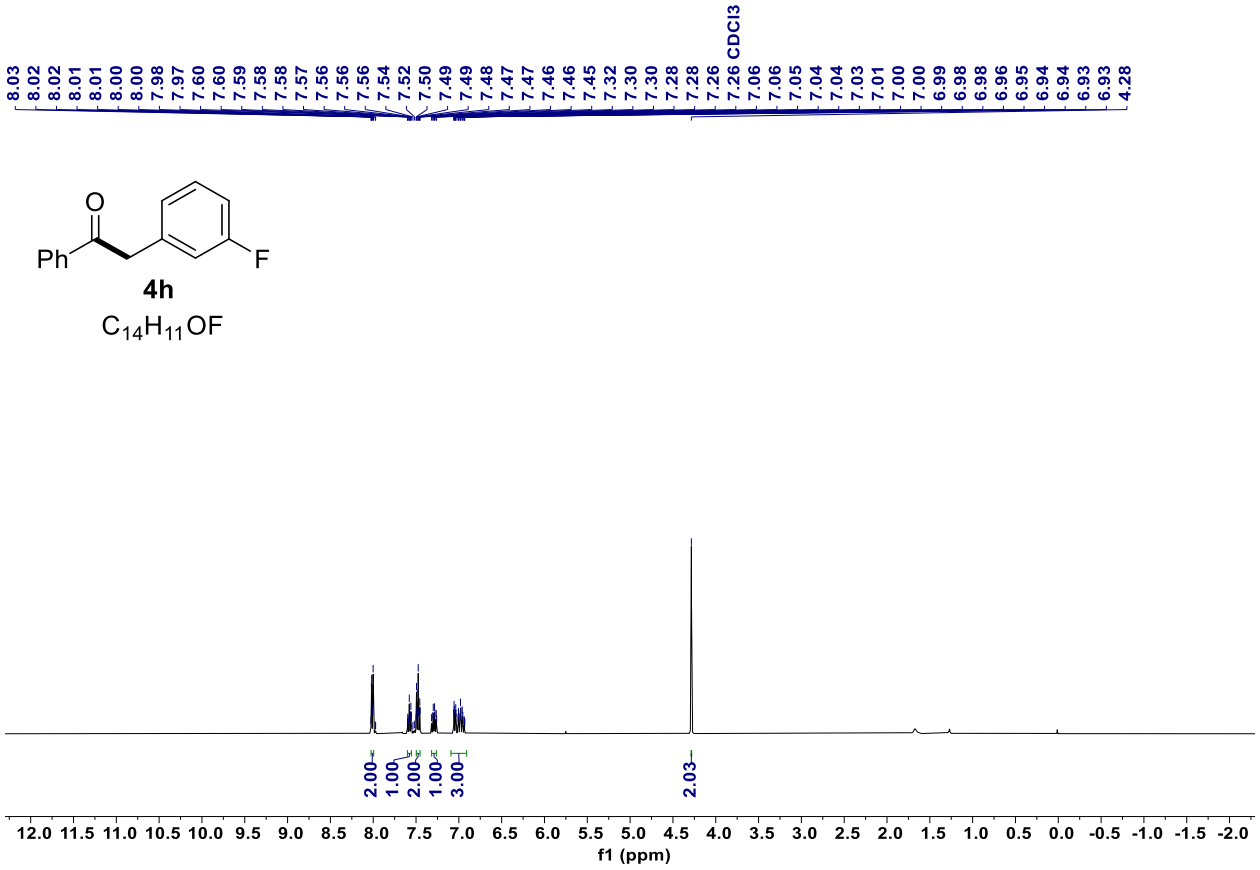
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4g**.



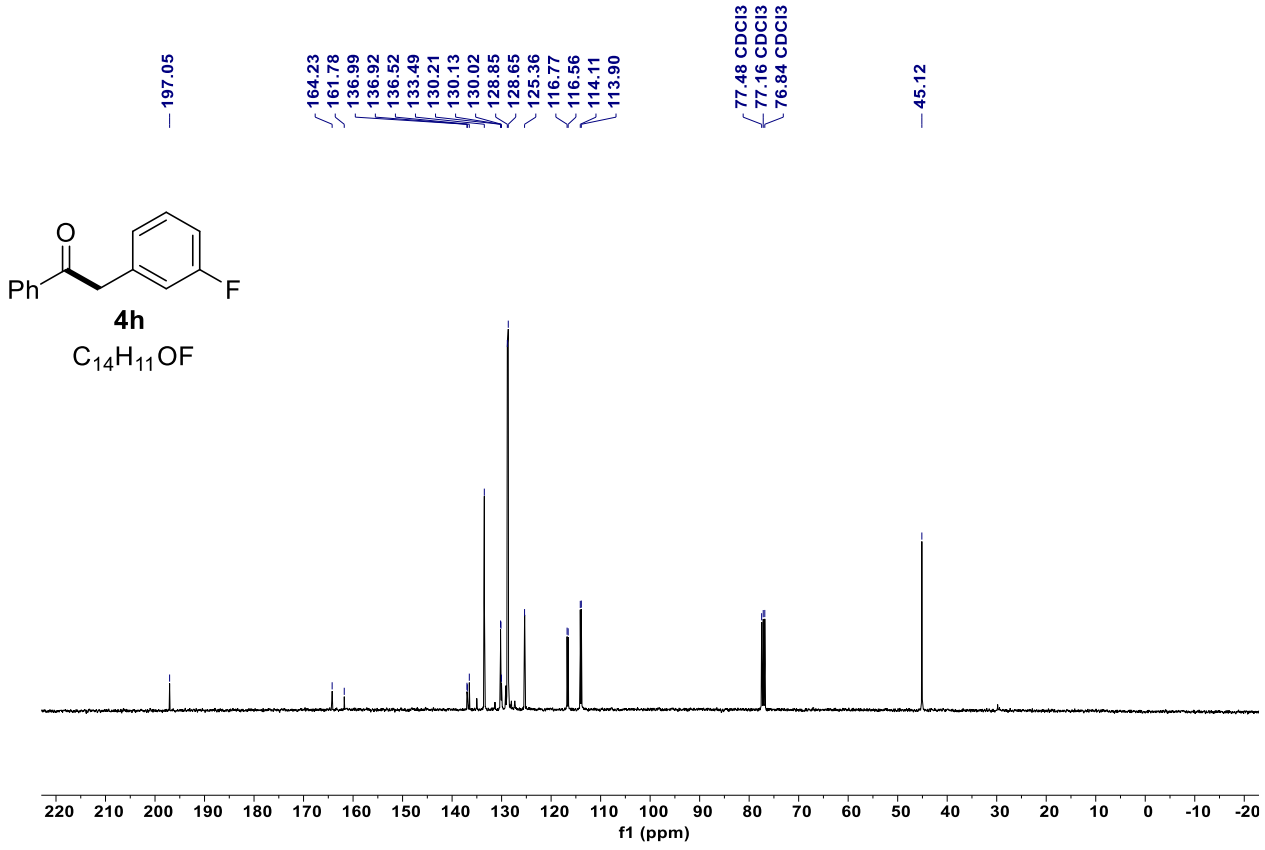
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **4g**.



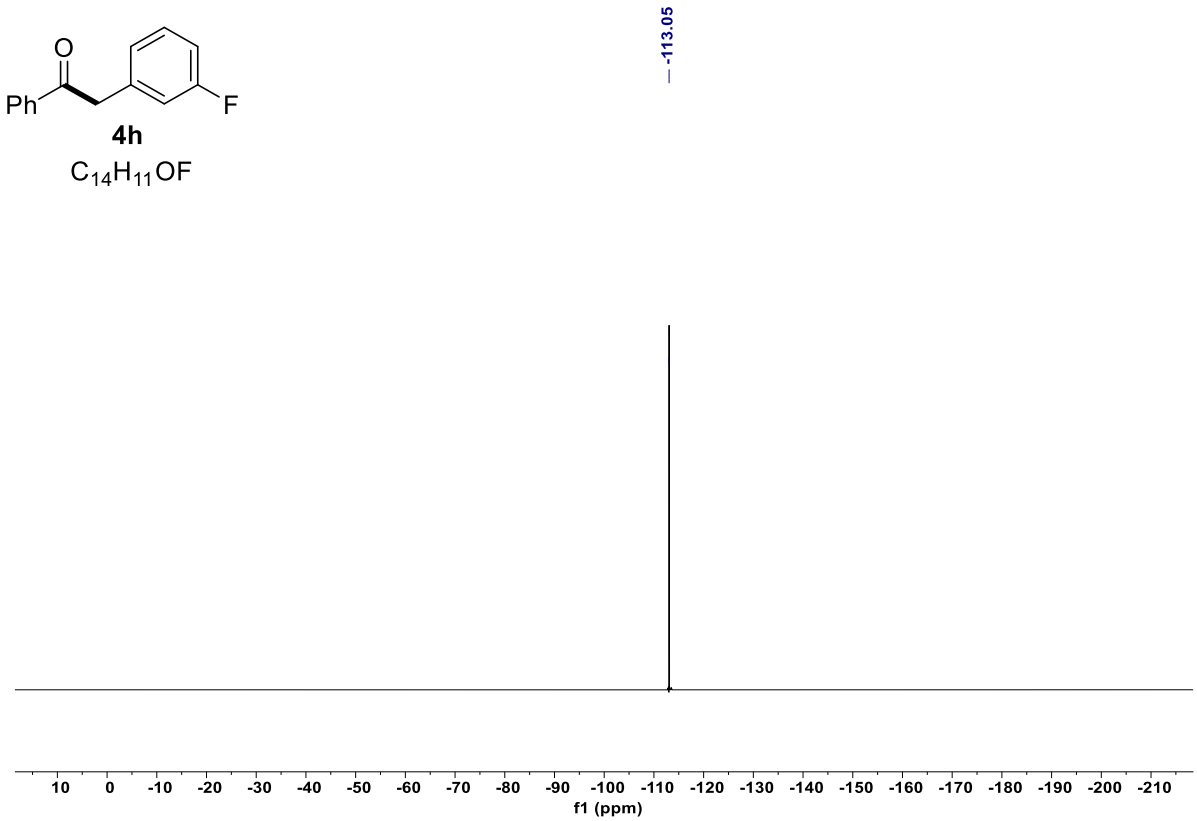
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4h**



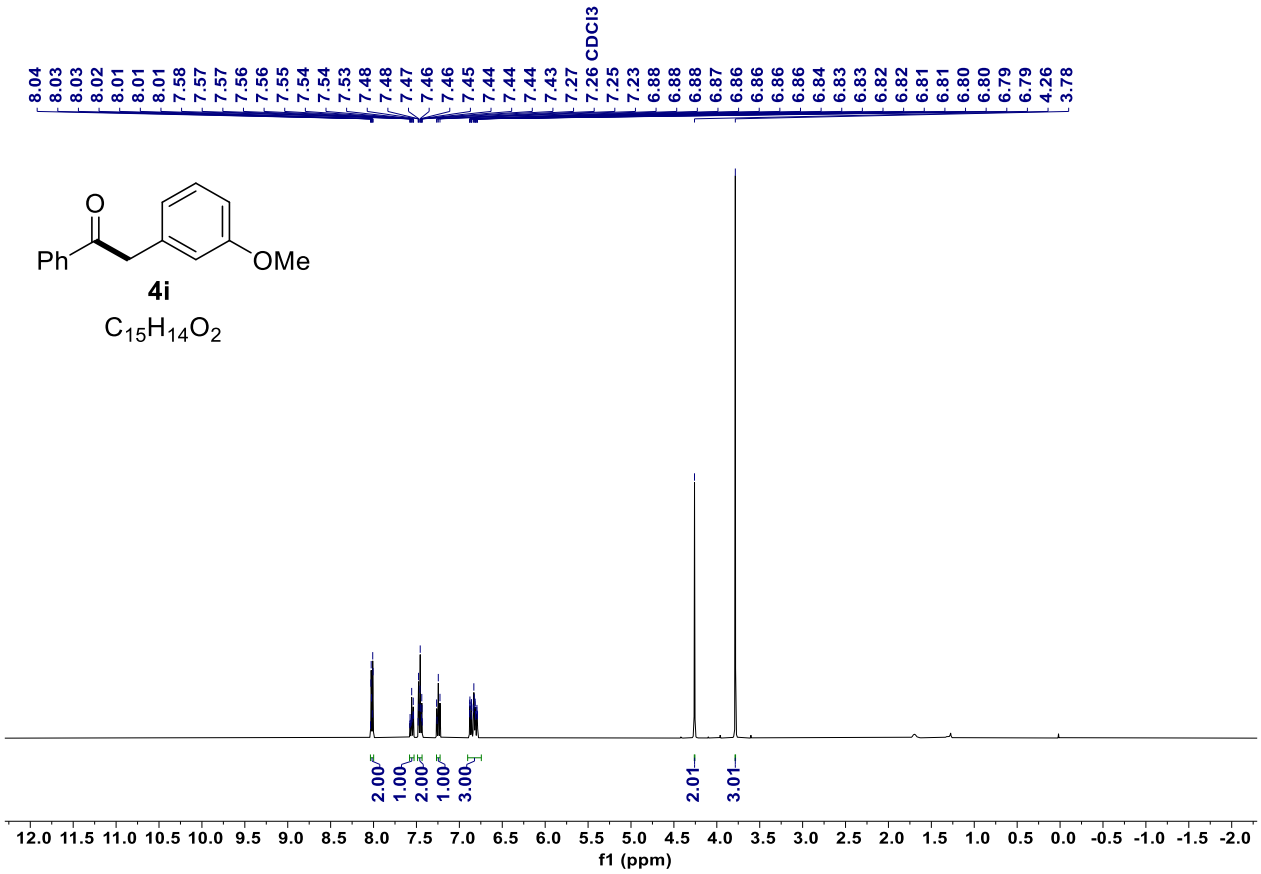
$^{13}C\{^{1}H\}$ NMR spectrum (100 MHz, $CDCl_3$) of compound **4h**.



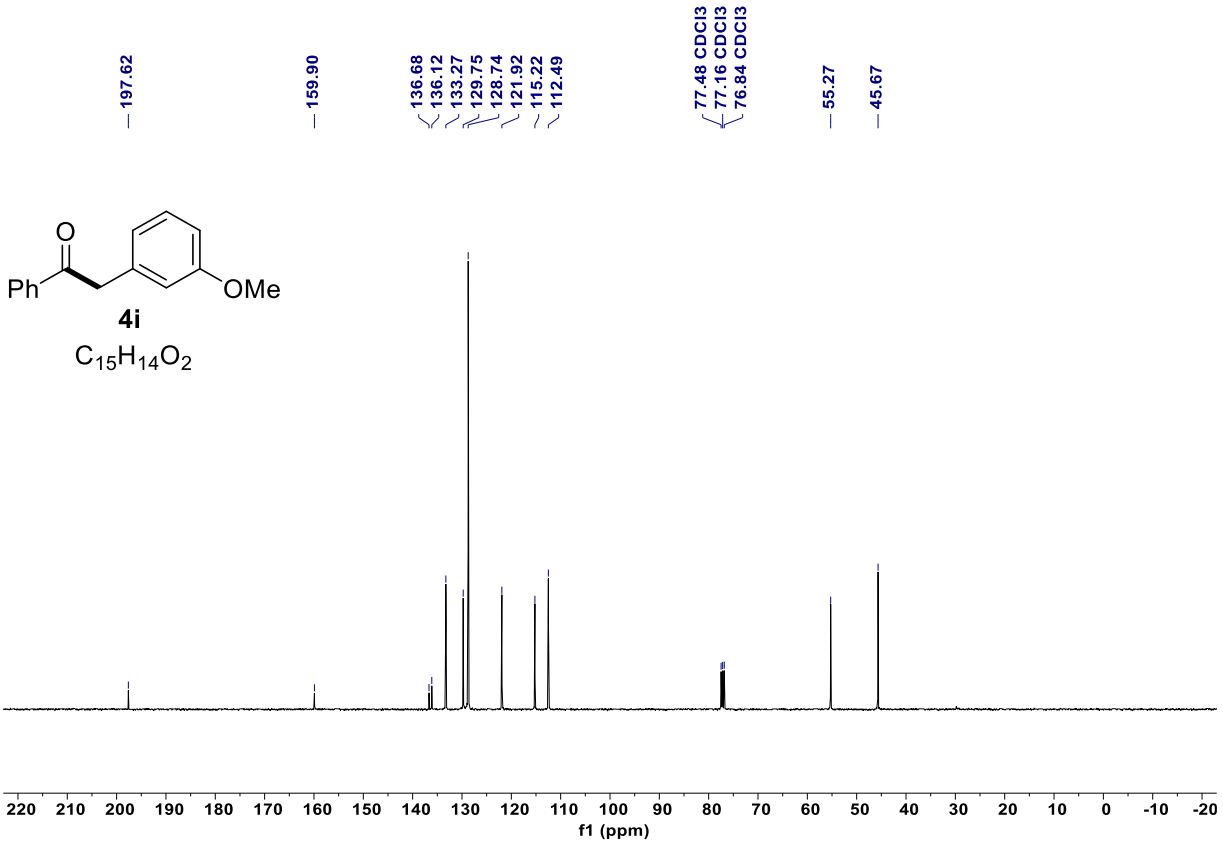
^{19}F NMR spectrum ($CDCl_3$, 376 MHz) of the compound **4h.**



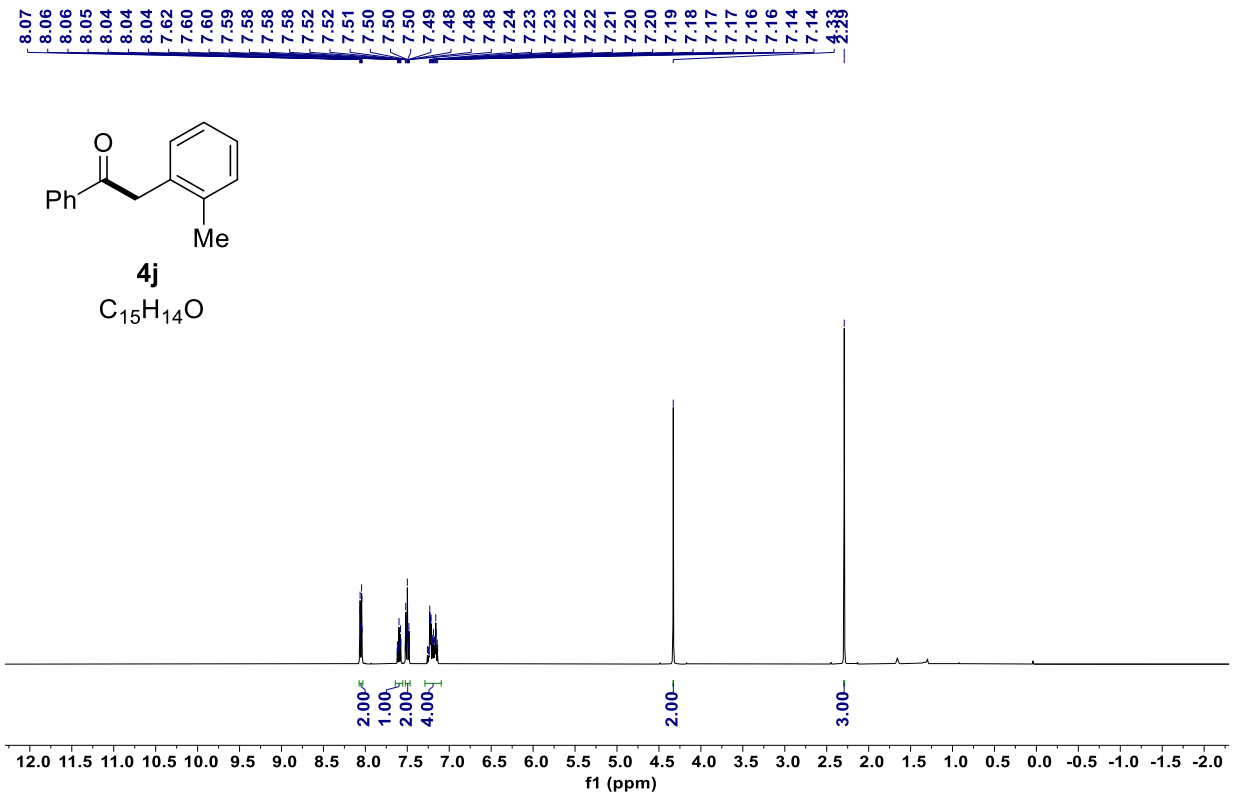
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4i**



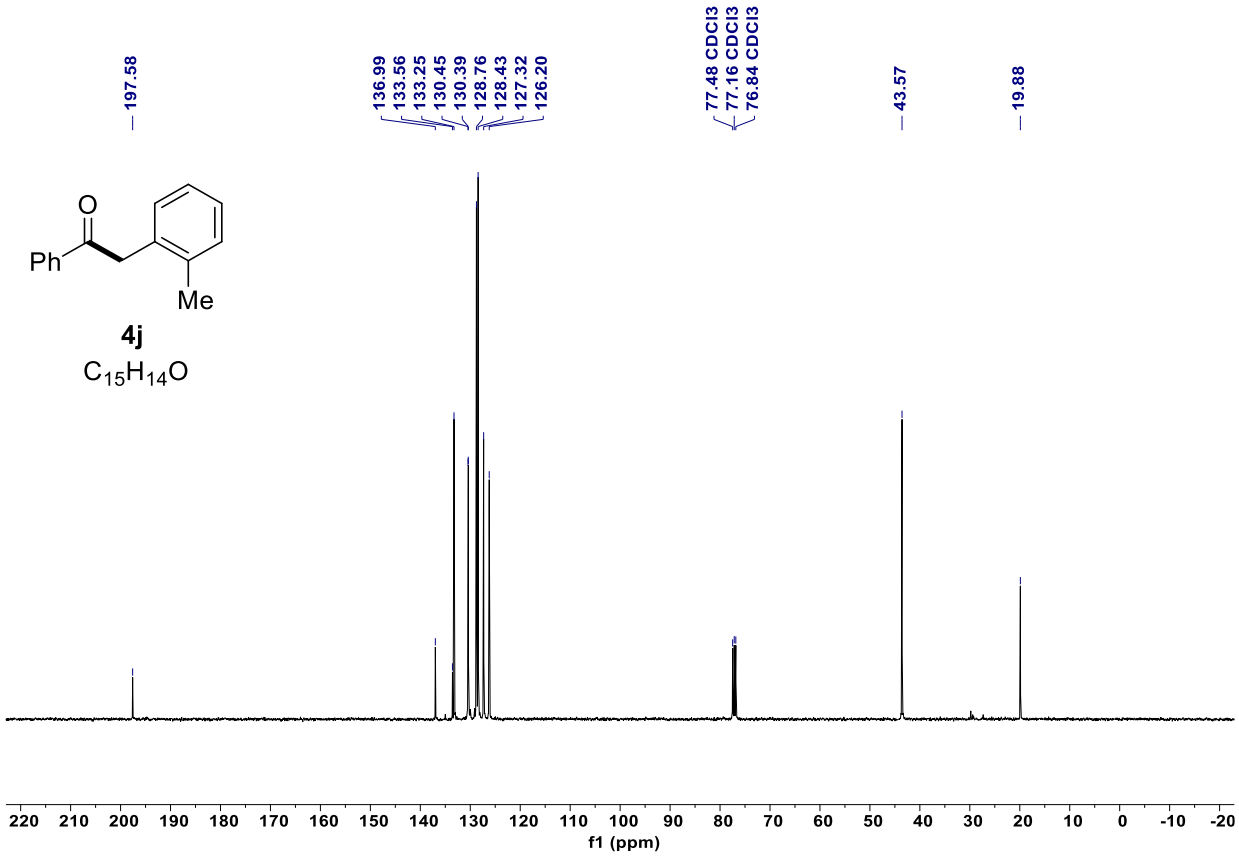
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4i**.



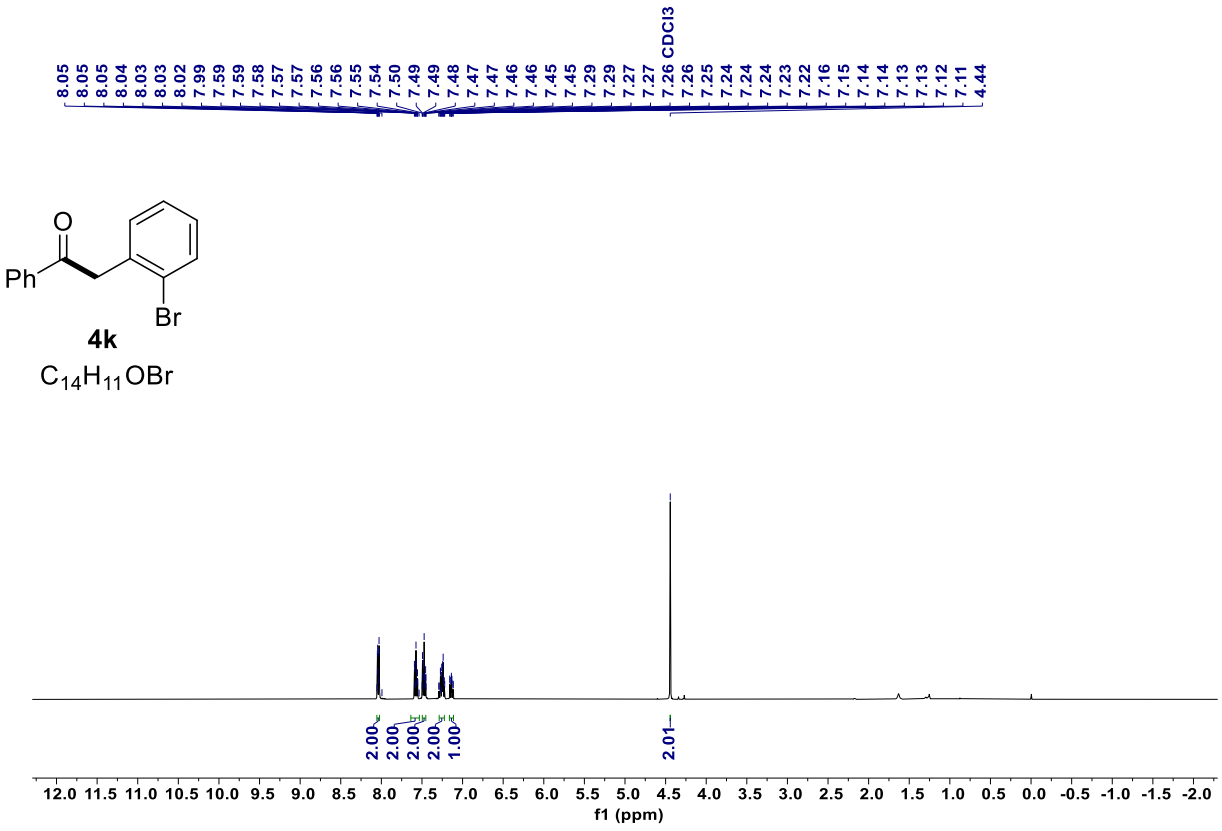
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4j**



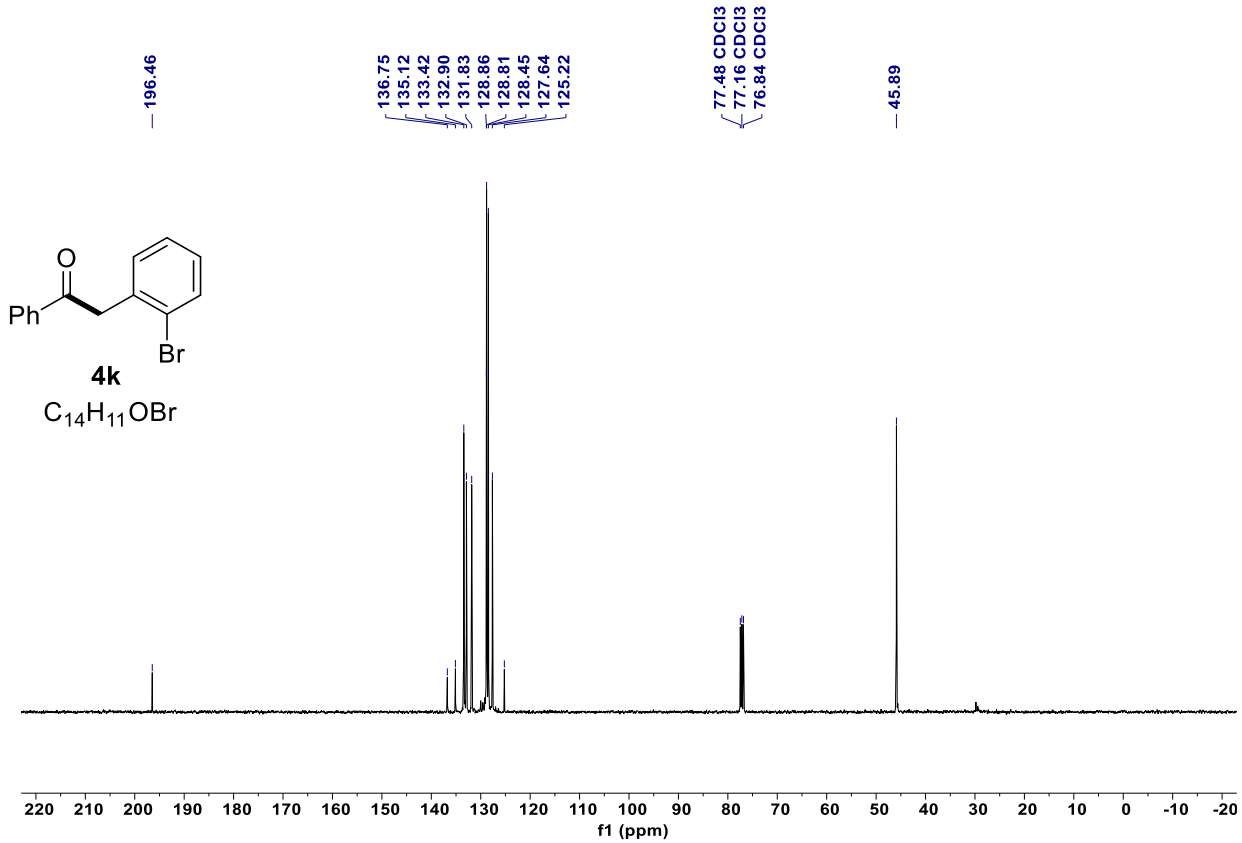
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4j**.



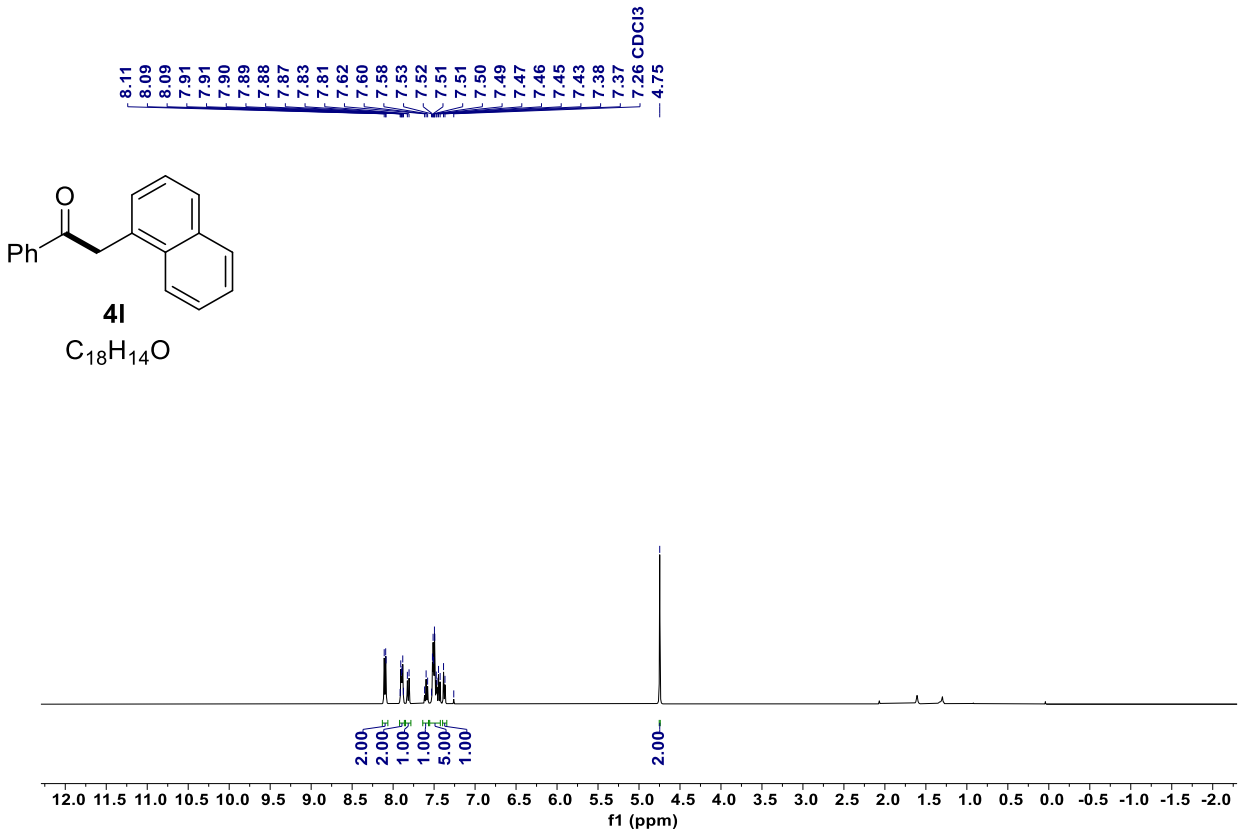
^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4k**



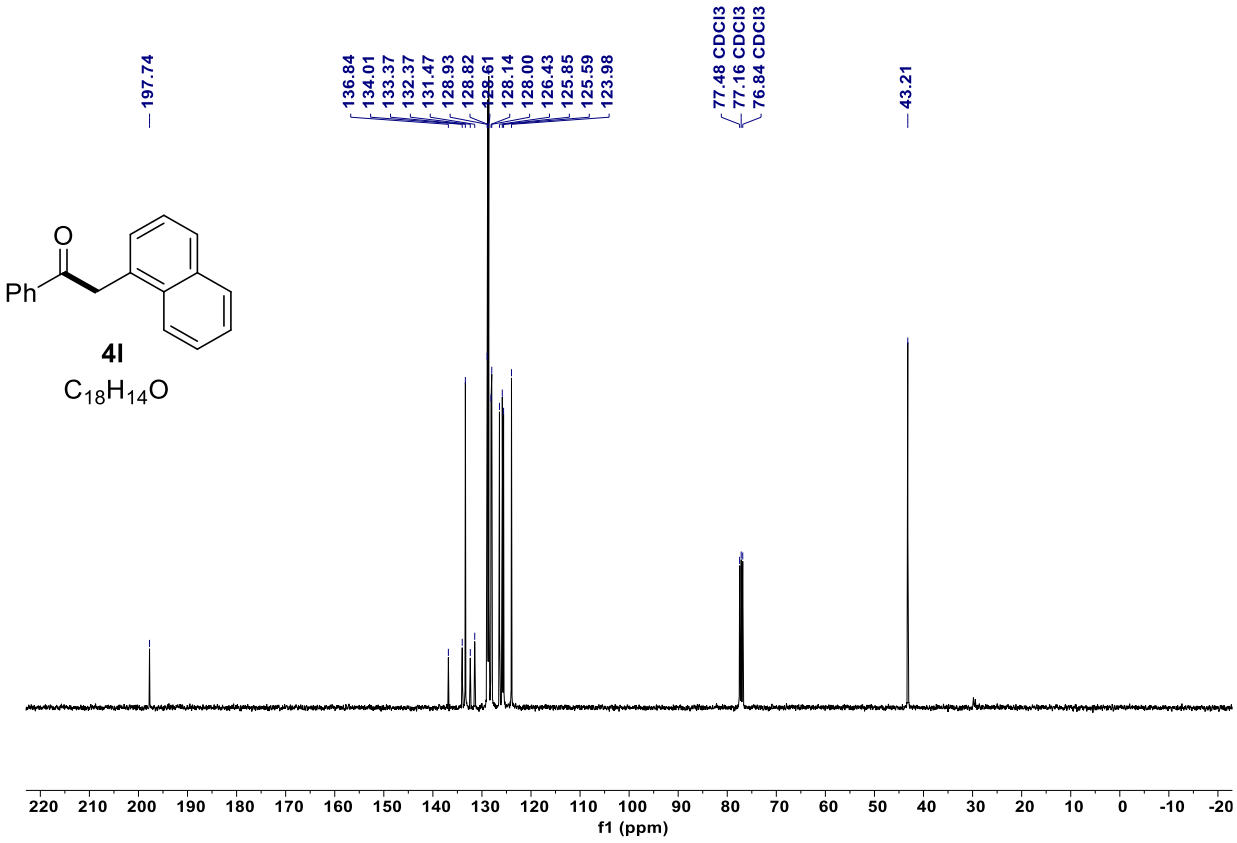
^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4k**.



^{1}H NMR spectrum (400 MHz, $CDCl_3$) of compound **4l**



^{13}C{^{1}H} NMR spectrum (100 MHz, $CDCl_3$) of compound **4l**.


197.74
136.84
134.01
133.37
132.37
131.47
128.93
128.82
128.61
128.14
128.00
126.43
125.85
125.59
123.98
77.48 CDCl3
77.16 CDCl3
76.84 CDCl3
43.21
O
Ph
4l
C18H14O
220 210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10 -20
f1 (ppm)

5. Energies and Cartesian Coordinates of the Optimized Structures

4CzIPN

B3LYP/6-31G(d,p) Electronic Energy: -2481.8307517 a.u.
B3LYP/6-31G(d,p) Gibbs free Energy: -2481.189211 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -2482.7787559 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
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14	6	0	4.491873	-2.093217	-1.444561
15	6	0	6.224775	-0.717903	-0.374871
16	6	0	6.243212	0.452790	0.480688
17	6	0	4.554329	1.897194	1.529424
18	6	0	5.507647	-2.866533	-2.003502
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20	6	0	7.225365	-1.508781	-0.949640
21	6	0	7.267827	1.202713	1.067930
22	6	0	5.593593	2.628880	2.101088
23	1	0	3.518714	2.158147	1.720498
24	6	0	6.860340	-2.581317	-1.758451
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34	6	0	-1.297195	3.264439	-2.861992
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37	6	0	-2.046643	1.019483	-4.331656
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52	6	0	-2.123800	-2.089777	-1.294080
53	6	0	-3.795238	-0.548289	-0.377660
54	6	0	-3.773146	0.697621	0.360250
55	6	0	-2.048639	2.166105	1.297991
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77	6	0	-0.998968	-5.566869	1.811419
78	6	0	-2.291092	-3.348542	3.992284
79	6	0	-2.145727	-0.948679	4.330699
80	1	0	-0.950138	0.180796	2.936340
81	6	0	-0.308131	-6.204213	0.784725
82	1	0	1.015280	-5.979429	-0.903865
83	1	0	-1.610074	-6.138955	2.503139
84	6	0	-2.630780	-2.208455	4.714781
85	1	0	-2.650530	-4.325689	4.300893
86	1	0	-2.411955	-0.071172	4.911663
87	1	0	-0.067475	7.280391	-0.659494
88	1	0	7.723044	2.879074	2.332526
89	1	0	7.627918	-3.202624	-2.208831
90	1	0	-0.375463	-7.282042	0.676257
91	1	0	-5.302132	-3.122328	-1.994107
92	1	0	-3.268684	-2.293399	5.588878
93	1	0	-5.188185	3.333845	1.959427
94	1	0	-3.095349	2.407318	-5.606998

4CzIPN$^{\bullet-}$

B3LYP/6-31G(d,p) Electronic Energy: -2481.8904876 a.u.
B3LYP/6-31G(d,p) Gibbs free Energy: -2481.255434 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -2482.8822779 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	0.456440	-1.004760	0.740030
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6	6	0	1.919280	-1.000043	0.793333
7	6	0	2.610982	-1.887057	1.653941
8	7	0	3.172275	-2.623723	2.368441
9	6	0	2.706265	1.766915	-1.593609
10	7	0	3.306193	2.479707	-2.300903
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12	6	0	4.854671	-1.001968	-0.646448
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14	6	0	4.476182	-2.053676	-1.482879
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17	6	0	4.536582	1.858299	1.566950
18	6	0	5.487344	-2.815709	-2.061552
19	1	0	3.429933	-2.267556	-1.670972
20	6	0	7.214175	-1.486872	-0.985836
21	6	0	7.255306	1.180892	1.103729
22	6	0	5.570542	2.578820	2.158375
23	1	0	3.497609	2.114448	1.742147
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26	1	0	8.263417	-1.272453	-0.800875
27	6	0	6.917967	2.247614	1.931605
28	1	0	8.297210	0.924079	0.931739
29	1	0	5.328052	3.415217	2.807967
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31	6	0	-0.800168	1.944190	-2.634112
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55	6	0	-2.077316	2.054570	1.449285
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64	1	0	-5.893741	-1.002619	-0.840956
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72	6	0	-0.945043	-4.137117	2.039875
73	6	0	-1.384828	-3.197797	3.048714
74	6	0	-1.124617	-0.787611	3.437566
75	6	0	0.224545	-5.381631	-0.164697
76	1	0	0.946103	-3.425906	-0.744633
77	6	0	-1.082914	-5.520164	1.877710
78	6	0	-2.102440	-3.327151	4.243251
79	6	0	-1.837541	-0.943200	4.623284
80	1	0	-0.747402	0.180888	3.132860
81	6	0	-0.499640	-6.136494	0.774262
82	1	0	0.686355	-5.882154	-1.011312
83	1	0	-1.634973	-6.105628	2.608320
84	6	0	-2.328353	-2.197826	5.024674
85	1	0	-2.470707	-4.299786	4.559062
86	1	0	-2.017361	-0.073269	5.248707
87	1	0	-0.289737	7.217416	-0.620737
88	1	0	7.700841	2.830900	2.407866
89	1	0	7.608606	-3.154019	-2.284628
90	1	0	-0.595666	-7.210228	0.640508
91	1	0	-5.313367	-2.970571	-2.243956
92	1	0	-2.883680	-2.284944	5.954280
93	1	0	-5.213846	3.179255	2.201582
94	1	0	-2.714923	2.388056	-5.961548

B3LYP/6-31G(d,p) Electronic Energy: -344.921214 a.u.
B3LYP/6-31G(d,p) Gibbs free Energy: -344.854813 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -345.0617292 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.136330	-5.754913	3.070358
2	6	0	1.546897	-5.005114	2.053580
3	6	0	1.045942	-3.726515	2.329734
4	6	0	1.136143	-3.196396	3.629181
5	6	0	1.725435	-3.948525	4.640343
6	6	0	2.224595	-5.226213	4.360420
7	1	0	2.525760	-6.746449	2.860393
8	1	0	1.467083	-5.395238	1.043381
9	1	0	0.741553	-2.203337	3.820553
10	1	0	1.798480	-3.545683	5.646422
11	1	0	2.684087	-5.810338	5.152790
12	6	0	0.422349	-2.944825	1.235829
13	8	0	-0.052039	-1.849104	1.290252

CO_2

B3LYP/6-31G(d,p) Electronic Energy: -188.6617569 a.u.
B3LYP/6-31G(d,p) Gibbs free Energy: -188.6617569 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -188.6617569 a.u.

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	0.122602	-3.288960	-0.600587
2	8	0	0.635602	-4.333130	-0.484717
3	8	0	-0.390706	-2.245169	-0.718398

Quartet anionic $Cr^{I}Cl_2$/dtbbpy ($LCr^{I}Cl_2$)

B3LYP/6-31G(d,p) Electronic Energy: -1816.7975047 a.u.
B3LYP/6-31G(d,p) Gibbs free Energy: -1816.466922 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -1817.9376363 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.079944	0.794106	-0.178347
2	6	0	-1.178837	1.860133	-0.969003
3	6	0	-1.721595	3.116010	-0.708856
4	6	0	-3.002042	3.228410	-0.158149
5	6	0	-3.673152	2.023334	0.102787
6	6	0	-3.738187	-0.511493	0.074636
7	6	0	-3.537236	-2.817218	-0.063491
8	6	0	-4.807059	-3.004167	0.476938
9	6	0	-5.587640	-1.901113	0.836681
10	6	0	-5.014615	-0.638156	0.619301
11	1	0	-0.188674	1.730733	-1.395962
12	1	0	-1.127050	3.989273	-0.944274
13	1	0	-4.667892	2.048378	0.529044
14	1	0	-2.900572	-3.647248	-0.355318
15	1	0	-5.163754	-4.017718	0.607120
16	1	0	-5.572595	0.252437	0.878861
17	7	0	-1.835002	0.718633	-0.713263
18	7	0	-3.005429	-1.602361	-0.264180
19	6	0	-3.672314	4.573232	0.157968
20	6	0	-4.986317	4.687673	-0.652214
21	6	0	-3.989331	4.638366	1.671708
22	6	0	-2.769802	5.767635	-0.203887
23	1	0	-4.791718	4.642815	-1.728448
24	1	0	-5.693310	3.889976	-0.404818
25	1	0	-5.475954	5.642771	-0.435682
26	1	0	-3.076327	4.557640	2.270090
27	1	0	-4.468661	5.593105	1.911615
28	1	0	-4.668335	3.839472	1.984903
29	1	0	-3.285933	6.701709	0.037171
30	1	0	-1.831231	5.756225	0.359460
31	1	0	-2.530898	5.790624	-1.271970
32	6	0	-6.995377	-2.020730	1.438117
33	6	0	-7.008129	-1.354454	2.835273
34	6	0	-8.005565	-1.301541	0.511633
35	6	0	-7.434541	-3.488778	1.593209
36	1	0	-6.299713	-1.842727	3.511947
37	1	0	-6.749716	-0.292244	2.787261
38	1	0	-8.007197	-1.432413	3.276422
39	1	0	-8.016522	-1.752189	-0.485840
40	1	0	-9.014733	-1.378173	0.929426
41	1	0	-7.774701	-0.238036	0.397597
42	1	0	-8.439915	-3.525736	2.023167
43	1	0	-7.469723	-4.008856	0.630561
44	1	0	-6.770631	-4.045600	2.262218
45	24	0	-1.053485	-1.247915	-1.092726
46	17	0	-0.623591	-3.511692	-1.328495
47	17	0	0.939159	-0.412915	-1.927856

$PhCOCO_2^-$ (I)

B3LYP/6-31G(d,p) Electronic Energy: -533.5908956 a.u.

B3LYP/6-31G(d,p) Gibbs free Energy: -533.514581 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -533.8833244 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.079944	0.794106	-0.178347
2	6	0	-1.178837	1.860133	-0.969003
3	6	0	-1.721595	3.116010	-0.708856
4	6	0	-3.002042	3.228410	-0.158149
5	6	0	-3.673152	2.023334	0.102787
6	6	0	-3.738187	-0.511493	0.074636
7	6	0	-3.537236	-2.817218	-0.063491
8	6	0	-4.807059	-3.004167	0.476938
9	6	0	-5.587640	-1.901113	0.836681
10	6	0	-5.014615	-0.638156	0.619301
11	1	0	-0.188674	1.730733	-1.395962
12	1	0	-1.127050	3.989273	-0.944274
13	1	0	-4.667892	2.048378	0.529044
14	1	0	-2.900572	-3.647248	-0.355318
15	1	0	-5.163754	-4.017718	0.607120
16	1	0	-5.572595	0.252437	0.878861
17	7	0	-1.835002	0.718633	-0.713263
18	7	0	-3.005429	-1.602361	-0.264180
19	6	0	-3.672314	4.573232	0.157968
20	6	0	-4.986317	4.687673	-0.652214
21	6	0	-3.989331	4.638366	1.671708
22	6	0	-2.769802	5.767635	-0.203887
23	1	0	-4.791718	4.642815	-1.728448
24	1	0	-5.693310	3.889976	-0.404818
25	1	0	-5.475954	5.642771	-0.435682
26	1	0	-3.076327	4.557640	2.270090
27	1	0	-4.468661	5.593105	1.911615
28	1	0	-4.668335	3.839472	1.984903
29	1	0	-3.285933	6.701709	0.037171
30	1	0	-1.831231	5.756225	0.359460
31	1	0	-2.530898	5.790624	-1.271970
32	6	0	-6.995377	-2.020730	1.438117
33	6	0	-7.008129	-1.354454	2.835273
34	6	0	-8.005565	-1.301541	0.511633
35	6	0	-7.434541	-3.488778	1.593209
36	1	0	-6.299713	-1.842727	3.511947
37	1	0	-6.749716	-0.292244	2.787261
38	1	0	-8.007197	-1.432413	3.276422
39	1	0	-8.016522	-1.752189	-0.485840
40	1	0	-9.014733	-1.378173	0.929426
41	1	0	-7.774701	-0.238036	0.397597
42	1	0	-8.439915	-3.525736	2.023167
43	1	0	-7.469723	-4.008856	0.630561
44	1	0	-6.770631	-4.045600	2.262218
45	24	0	-1.053485	-1.247915	-1.092726
46	17	0	-0.623591	-3.511692	-1.328495
47	17	0	0.939159	-0.412915	-1.927856

2a

B3LYP/6-31G(d,p) Electronic Energy: -1636.8849586 a.u.
B3LYP/6-31G(d,p) Gibbs free Energy: -1636.480371 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -1637.5595671 a.u.

Center	Atomic	Atomic	Coordinates (Angstroms)

Number	Number	Type	X	Y	Z
1	6	0	-1.150792	0.045689	-3.218215
2	6	0	-0.732633	0.265754	-1.903523
3	6	0	-0.353277	-0.806597	-1.099586
4	6	0	-0.383433	-2.118212	-1.593084
5	6	0	-0.803928	-2.329593	-2.909847
6	6	0	-1.185116	-1.254600	-3.717928
7	1	0	-1.446782	0.881191	-3.845134
8	1	0	-0.702393	1.274585	-1.502847
9	1	0	-0.029788	-0.625930	-0.077542
10	1	0	-0.837566	-3.336376	-3.315689
11	1	0	-1.508202	-1.439155	-4.738287
12	6	0	0.054181	-3.227750	-0.655921
13	1	0	1.091293	-3.100850	-0.349470
14	1	0	-0.540833	-3.217999	0.256927
15	6	0	-1.220192	-5.298914	-1.047729
16	6	0	1.072347	-5.211013	-1.706040
17	6	0	-1.280558	-6.632324	-1.415452
18	6	0	1.024177	-6.558631	-2.022163
19	6	0	-0.141645	-7.311045	-1.858305
20	1	0	-2.204801	-7.166297	-1.234783
21	1	0	1.932444	-7.026813	-2.377135
22	7	0	-0.051005	-4.600314	-1.210076
23	6	0	-2.385878	-4.681452	-0.347491
24	6	0	-2.572962	-5.003830	1.007370
25	6	0	-3.314363	-3.869635	-1.011661
26	6	0	-3.678307	-4.492668	1.687721
27	1	0	-1.845757	-5.643443	1.499919
28	6	0	-4.419419	-3.370926	-0.321603
29	1	0	-3.177605	-3.629137	-2.060380
30	6	0	-4.600534	-3.678505	1.027656
31	1	0	-3.818374	-4.737309	2.736222
32	1	0	-5.138358	-2.744275	-0.840613
33	1	0	-5.461310	-3.287264	1.562028
34	6	0	2.361163	-4.477142	-1.850766
35	6	0	2.542709	-3.469387	-2.809427
36	6	0	3.439781	-4.882986	-1.046890
37	6	0	3.789968	-2.863285	-2.954908
38	1	0	1.719222	-3.163916	-3.445197
39	6	0	4.680558	-4.265452	-1.199549
40	1	0	3.280838	-5.660668	-0.307446
41	6	0	4.859058	-3.257976	-2.149094
42	1	0	3.925097	-2.086923	-3.701892
43	1	0	5.509137	-4.573815	-0.569361
44	1	0	5.829060	-2.782982	-2.263639
45	6	0	-0.136140	-8.772601	-2.067683
46	6	0	0.884447	-9.534766	-1.473803
47	6	0	-1.138916	-9.410803	-2.812573
48	6	0	0.900750	-10.917909	-1.642767
49	1	0	1.607418	-9.038019	-0.832909
50	6	0	-1.106378	-10.792806	-2.987915
51	1	0	-1.927165	-8.822032	-3.273708
52	6	0	-0.085737	-11.547274	-2.405130
53	1	0	1.679312	-11.506371	-1.167065
54	1	0	-1.876082	-11.280406	-3.578588
55	1	0	-0.065480	-12.624998	-2.537426
56	9	0	1.612664	-6.695762	2.841498
57	9	0	1.301151	-5.107078	1.200798
58	9	0	-0.113364	-6.910670	1.326290
59	9	0	2.066664	-7.202374	0.636936

60	5	0	1.222026	-6.486274	1.538899

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B3LYP/6-31G(d,p) Electronic Energy: -1636.9516479 a.u.
B3LYP/6-31G(d,p) Gibbs free Energy: -1636.551040 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -1637.6673859 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-2.106623	-0.905445	-3.231199
2	6	0	-1.742741	-0.541920	-1.932697
3	6	0	-0.961306	-1.396053	-1.154793
4	6	0	-0.525235	-2.623933	-1.671679
5	6	0	-0.885821	-2.980158	-2.976483
6	6	0	-1.675840	-2.127788	-3.749769
7	1	0	-2.722273	-0.242414	-3.833858
8	1	0	-2.074644	0.407243	-1.519749
9	1	0	-0.668506	-1.124028	-0.144118
10	1	0	-0.553825	-3.930103	-3.385599
11	1	0	-1.953600	-2.419495	-4.759688
12	6	0	0.391883	-3.469542	-0.809587
13	1	0	1.421745	-3.213035	-1.058166
14	1	0	0.274790	-3.203311	0.238902
15	6	0	-0.996770	-5.547185	-0.970274
16	6	0	1.358655	-5.675969	-1.496598
17	6	0	-1.204842	-6.715747	-1.661484
18	6	0	1.128360	-6.838712	-2.191284
19	6	0	-0.174770	-7.383099	-2.385063
20	1	0	-2.195328	-7.148424	-1.593683
21	1	0	1.998865	-7.407244	-2.496035
22	7	0	0.268677	-4.933748	-1.002191
23	6	0	-2.079579	-4.959869	-0.147440
24	6	0	-1.842163	-4.491098	1.158527
25	6	0	-3.395149	-4.920015	-0.646609
26	6	0	-2.895743	-4.006651	1.932465
27	1	0	-0.842292	-4.498773	1.579625
28	6	0	-4.443676	-4.444024	0.136191
29	1	0	-3.584143	-5.241397	-1.666452
30	6	0	-4.198779	-3.983374	1.431800
31	1	0	-2.685798	-3.645141	2.934930
32	1	0	-5.450328	-4.416281	-0.273376
33	1	0	-5.013914	-3.600569	2.040292
34	6	0	2.736009	-5.238343	-1.174561
35	6	0	3.769252	-5.382187	-2.120358
36	6	0	3.052146	-4.691612	0.084809
37	6	0	5.075014	-5.007820	-1.811214
38	1	0	3.537035	-5.767422	-3.109235
39	6	0	4.354067	-4.292246	0.379086
40	1	0	2.286260	-4.561850	0.842627
41	6	0	5.372671	-4.456181	-0.561979
42	1	0	5.857243	-5.124932	-2.557353
43	1	0	4.536347	-3.830800	1.343759
44	1	0	6.387599	-4.141973	-0.332416
45	6	0	-0.405639	-8.587677	-3.171026
46	6	0	0.561758	-9.062749	-4.093846
47	6	0	-1.601665	-9.343477	-3.069594
48	6	0	0.351652	-10.211047	-4.848174
49	1	0	1.479183	-8.501775	-4.239265
50	6	0	-1.807889	-10.489339	-3.828434

51	1	0	-2.371047	-9.041126	-2.367006
52	6	0	-0.835006	-10.941049	-4.726530
53	1	0	1.119021	-10.534876	-5.547565
54	1	0	-2.737053	-11.042466	-3.712048
55	1	0	-0.999091	-11.836977	-5.318283
56	9	0	1.056544	-2.073412	3.911769
57	9	0	0.899942	-1.589371	1.665609
58	9	0	0.988589	-3.781826	2.366891
59	9	0	2.858313	-2.456800	2.525949
60	5	0	1.459851	-2.451678	2.637553

III

B3LYP/6-31G(d,p) Electronic Energy: -2161.8082867 a.u.
B3LYP/6-31G(d,p) Gibbs free Energy: -2161.391741 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -2163.1353427 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.504561	0.638117	-0.100216
2	6	0	-1.367397	1.432380	-0.644276
3	6	0	-1.748838	2.747965	-0.468687
4	6	0	-3.085605	3.050370	-0.084557
5	6	0	-3.935603	1.972891	0.088881
6	6	0	-4.330599	-0.516771	0.047535
7	6	0	-4.446097	-2.853635	-0.124624
8	6	0	-5.775600	-2.871537	0.241548
9	6	0	-6.446771	-1.648845	0.536124
10	6	0	-5.694397	-0.494157	0.425674
11	1	0	-0.354853	1.170711	-0.932172
12	1	0	-1.009802	3.523464	-0.624596
13	1	0	-4.967112	2.141730	0.379092
14	1	0	-3.913559	-3.767759	-0.363253
15	1	0	-6.280454	-3.827570	0.297498
16	1	0	-6.149536	0.467411	0.638350
17	7	0	-2.194591	0.378746	-0.476153
18	7	0	-3.705558	-1.726472	-0.229936
19	6	0	-3.589955	4.488003	0.134182
20	6	0	-4.751243	4.786468	-0.843680
21	6	0	-4.094607	4.646113	1.588171
22	6	0	-2.483410	5.533578	-0.104144
23	1	0	-4.419983	4.687571	-1.882767
24	1	0	-5.588751	4.098190	-0.696481
25	1	0	-5.125998	5.807935	-0.700049
26	1	0	-3.290323	4.443190	2.302766
27	1	0	-4.459188	5.666481	1.762647
28	1	0	-4.913527	3.954972	1.808122
29	1	0	-2.881364	6.541126	0.062259
30	1	0	-1.639463	5.391686	0.578562
31	1	0	-2.100828	5.491804	-1.129127
32	6	0	-7.924860	-1.584137	0.959732
33	6	0	-8.035193	-0.947742	2.365755
34	6	0	-8.720377	-0.725101	-0.051793
35	6	0	-8.574000	-2.980633	1.014811
36	1	0	-7.483578	-1.538908	3.104012
37	1	0	-7.625018	0.066292	2.382147
38	1	0	-9.083767	-0.892154	2.685232
39	1	0	-8.665318	-1.156894	-1.056636
40	1	0	-9.777459	-0.665065	0.237227
41	1	0	-8.330043	0.295361	-0.108379

42	1	0	-9.623282	-2.891672	1.318695
43	1	0	-8.550682	-3.476673	0.039031
44	1	0	-8.072030	-3.631623	1.737823
45	24	0	-1.693845	-1.626828	-0.643166
46	17	0	-1.666528	-3.824685	-1.516557
47	17	0	0.505766	-1.148597	-1.357960
48	6	0	0.629096	-4.038606	3.899812
49	6	0	-0.217855	-3.097353	3.321905
50	6	0	-0.260535	-2.933184	1.926630
51	6	0	0.565796	-3.722964	1.117684
52	6	0	1.422054	-4.659878	1.700826
53	6	0	1.454315	-4.823080	3.086735
54	1	0	0.650928	-4.162658	4.980328
55	1	0	-0.861098	-2.466946	3.928295
56	1	0	0.533912	-3.597770	0.042159
57	1	0	2.063781	-5.265916	1.066491
58	1	0	2.119107	-5.558718	3.534338
59	6	0	-1.202737	-1.888847	1.365468
60	8	0	-1.741998	-1.108002	2.131266

III′

B3LYP/6-31G(d,p) Electronic Energy: -2087.7963096 a.u.
B3LYP/6-31G(d,p) Gibbs free Energy: -2087.360411 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -2089.0950695 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.204433	0.578937	-0.315502
2	6	0	-1.275996	1.670905	-1.087129
3	6	0	-1.720942	2.896538	-0.636447
4	6	0	-2.985455	2.995938	0.015388
5	6	0	-3.698471	1.819507	0.155826
6	6	0	-3.884364	-0.671133	-0.205701
7	6	0	-3.793629	-2.968910	-0.659956
8	6	0	-5.040543	-3.183447	-0.109353
9	6	0	-5.773037	-2.090376	0.434252
10	6	0	-5.166422	-0.849586	0.367336
11	1	0	-0.326276	1.566213	-1.601418
12	1	0	-1.091470	3.762788	-0.795611
13	1	0	-4.666524	1.830860	0.645617
14	1	0	-3.213618	-3.781577	-1.083304
15	1	0	-5.431516	-4.192808	-0.100439
16	1	0	-5.676159	0.022318	0.763480
17	7	0	-1.969458	0.517806	-0.950119
18	7	0	-3.196550	-1.757855	-0.728288
19	6	0	-3.553400	4.324698	0.545204
20	6	0	-4.899107	4.631320	-0.154156
21	6	0	-3.785272	4.220376	2.071439
22	6	0	-2.600051	5.507367	0.286291
23	1	0	-4.763600	4.716730	-1.237392
24	1	0	-5.635556	3.842614	0.025940
25	1	0	-5.320809	5.575539	0.213378
26	1	0	-2.846255	4.009765	2.593879
27	1	0	-4.193307	5.159356	2.466730
28	1	0	-4.487910	3.419102	2.318518
29	1	0	-3.039582	6.432075	0.677286
30	1	0	-1.633429	5.363590	0.779843
31	1	0	-2.416082	5.652298	-0.783165
32	6	0	-7.163607	-2.248611	1.074388

33	6	0	-7.107275	-1.792810	2.551934
34	6	0	-8.191433	-1.380057	0.311020
35	6	0	-7.653997	-3.709036	1.042347
36	1	0	-6.382906	-2.390128	3.114937
37	1	0	-6.808125	-0.744020	2.638231
38	1	0	-8.089454	-1.903124	3.029127
39	1	0	-8.256600	-1.686250	-0.738369
40	1	0	-9.188901	-1.477656	0.758163
41	1	0	-7.917877	-0.320942	0.330286
42	1	0	-8.645248	-3.778737	1.504717
43	1	0	-7.737136	-4.085684	0.017671
44	1	0	-6.981388	-4.373358	1.594252
45	24	0	-1.326573	-1.358312	-1.534888
46	17	0	-1.098292	-3.556671	-2.397785
47	17	0	0.372528	-0.467793	-2.922487
48	6	0	-1.767219	-1.900050	3.505666
49	6	0	-1.179777	-1.360706	2.362490
50	6	0	-0.697495	-2.184563	1.324232
51	6	0	-0.839592	-3.579457	1.487395
52	6	0	-1.425093	-4.118309	2.630394
53	6	0	-1.892803	-3.284166	3.651113
54	1	0	-2.126331	-1.236314	4.289616
55	1	0	-1.086342	-0.282016	2.260715
56	1	0	-0.494986	-4.230942	0.688755
57	1	0	-1.518393	-5.198080	2.726945
58	1	0	-2.348164	-3.706102	4.543794
59	6	0	-0.065923	-1.617000	0.118143
60	1	0	0.339429	-0.614812	0.274840
61	1	0	0.683203	-2.270844	-0.331013

IV

B3LYP/6-31G(d,p) Electronic Energy: -2432.7461658 a.u.
B3LYP/6-31G(d,p) Gibbs free Energy: -2432.219849 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -2434.2044876 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-3.280412	0.632359	-0.190557
2	6	0	-1.284533	1.647978	-0.755252
3	6	0	-1.760800	2.904083	-0.383580
4	6	0	-3.059003	3.037787	0.114919
5	6	0	-3.809385	1.858363	0.216457
6	6	0	-4.024116	-0.647388	-0.080555
7	6	0	-3.903967	-2.942738	-0.289499
8	6	0	-5.241463	-3.095078	0.075129
9	6	0	-6.015767	-1.968555	0.368444
10	6	0	-5.370486	-0.727260	0.280159
11	1	0	-0.272049	1.513289	-1.109897
12	1	0	-1.098642	3.754881	-0.484040
13	1	0	-4.811283	1.892235	0.626709
14	1	0	-3.279409	-3.788219	-0.563979
15	1	0	-5.656188	-4.094907	0.109542
16	1	0	-5.926393	0.182282	0.473643
17	7	0	-2.026394	0.540606	-0.684238
18	7	0	-3.305161	-1.753186	-0.359852
19	6	0	-3.663788	4.381189	0.553207
20	6	0	-4.936427	4.664616	-0.279846
21	6	0	-4.034539	4.311132	2.053707
22	6	0	-2.682922	5.551452	0.351289

23	1	0	-4.701391	4.717807	-1.347624
24	1	0	-5.692953	3.885899	-0.145261
25	1	0	-5.382314	5.619926	0.020880
26	1	0	-3.149543	4.112020	2.666588
27	1	0	-4.470949	5.261763	2.381877
28	1	0	-4.764227	3.521609	2.256627
29	1	0	-3.154966	6.487280	0.669033
30	1	0	-1.770312	5.423466	0.942248
31	1	0	-2.396806	5.664030	-0.699378
32	6	0	-7.501701	-2.041312	0.756450
33	6	0	-7.699463	-1.405641	2.153051
34	6	0	-8.339652	-1.265202	-0.287352
35	6	0	-8.016810	-3.491939	0.808758
36	1	0	-7.117671	-1.938517	2.912259
37	1	0	-7.388522	-0.356828	2.170922
38	1	0	-8.756066	-1.445431	2.442503
39	1	0	-8.213499	-1.693743	-1.286502
40	1	0	-9.403881	-1.307499	-0.027207
41	1	0	-8.050011	-0.211622	-0.340179
42	1	0	-9.074605	-3.497512	1.092725
43	1	0	-7.932095	-3.987802	-0.163396
44	1	0	-7.472022	-4.090207	1.546355
45	24	0	-1.301398	-1.385526	-1.323635
46	17	0	-0.971744	-3.719912	-1.785538
47	17	0	-2.743597	-0.894849	-3.333521
48	6	0	-0.254742	-2.564281	4.188289
49	6	0	-0.151963	-1.741856	3.069289
50	6	0	-0.414482	-2.237901	1.780514
51	6	0	-0.770922	-3.584895	1.637310
52	6	0	-0.858117	-4.415588	2.758249
53	6	0	-0.609236	-3.909157	4.035081
54	1	0	-0.055536	-2.164208	5.180681
55	1	0	0.141465	-0.699768	3.156465
56	1	0	-0.947299	-3.974271	0.639296
57	1	0	-1.120082	-5.463851	2.631724
58	1	0	-0.686649	-4.556554	4.906160
59	6	0	-0.330477	-1.266606	0.601062
60	8	0	0.278830	-0.221306	0.823591
61	6	0	4.429711	-1.207172	-0.899230
62	6	0	3.841192	0.052691	-1.025903
63	6	0	2.544296	0.179117	-1.522674
64	6	0	1.779789	-0.941309	-1.908126
65	6	0	2.395951	-2.205457	-1.771122
66	6	0	3.691881	-2.334233	-1.277939
67	1	0	5.441690	-1.310170	-0.514154
68	1	0	4.396750	0.944392	-0.739973
69	1	0	2.110441	1.171858	-1.628504
70	1	0	1.824401	-3.088003	-2.043967
71	1	0	4.132172	-3.325589	-1.186037
72	6	0	0.406550	-0.805893	-2.442347
73	1	0	0.195726	0.216830	-2.776564
74	1	0	0.225043	-1.479375	-3.284032

TS

B3LYP/6-31G(d,p) Electronic Energy: -2432.7208231 a.u.
B3LYP/6-31G(d,p) Gibbs free Energy: -2432.193921 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -2434.1745073 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-3.337097	0.790519	-0.482938
2	6	0	-1.518009	1.936853	-1.337433
3	6	0	-2.008713	3.152050	-0.873950
4	6	0	-3.225792	3.202302	-0.182189
5	6	0	-3.884109	1.980454	0.002602
6	6	0	-3.957976	-0.533595	-0.308505
7	6	0	-3.740237	-2.804161	-0.709145
8	6	0	-4.948150	-3.078060	-0.076782
9	6	0	-5.709343	-2.034806	0.470030
10	6	0	-5.180254	-0.746674	0.334573
11	1	0	-0.597657	1.882195	-1.902741
12	1	0	-1.427286	4.045150	-1.065217
13	1	0	-4.828461	1.950466	0.533148
14	1	0	-3.131256	-3.583432	-1.157446
15	1	0	-5.276374	-4.108729	-0.024074
16	1	0	-5.721820	0.103662	0.731977
17	7	0	-2.163082	0.776522	-1.155439
18	7	0	-3.240795	-1.563810	-0.825695
19	6	0	-3.837491	4.503545	0.361080
20	6	0	-5.226729	4.727343	-0.282241
21	6	0	-3.993186	4.394734	1.896725
22	6	0	-2.958948	5.730237	0.051145
23	1	0	-5.144517	4.810106	-1.370770
24	1	0	-5.913715	3.904520	-0.062684
25	1	0	-5.679115	5.650945	0.098118
26	1	0	-3.022579	4.235347	2.377106
27	1	0	-4.429570	5.315374	2.302179
28	1	0	-4.644844	3.563157	2.181321
29	1	0	-3.429816	6.633256	0.454567
30	1	0	-1.966244	5.642711	0.504152
31	1	0	-2.830968	5.875682	-1.026346
32	6	0	-7.052856	-2.251503	1.184739
33	6	0	-6.947934	-1.735992	2.639945
34	6	0	-8.162505	-1.470629	0.441123
35	6	0	-7.453491	-3.738225	1.226767
36	1	0	-6.168480	-2.273022	3.189891
37	1	0	-6.706054	-0.669675	2.677271
38	1	0	-7.899336	-1.881627	3.165009
39	1	0	-8.259759	-1.817889	-0.592561
40	1	0	-9.127867	-1.611734	0.941359
41	1	0	-7.955293	-0.396765	0.412858
42	1	0	-8.412920	-3.847349	1.743714
43	1	0	-7.569051	-4.156288	0.221583
44	1	0	-6.716081	-4.342245	1.765096
45	24	0	-1.359673	-1.049565	-1.795658
46	17	0	-1.120694	-3.319643	-2.622812
47	17	0	-1.580801	-0.026170	-4.060755
48	6	0	0.112335	-2.452894	3.356284
49	6	0	0.075161	-1.479817	2.359989
50	6	0	-0.042421	-1.834235	1.003113
51	6	0	-0.108906	-3.195270	0.671878
52	6	0	-0.059415	-4.169262	1.670735
53	6	0	0.046157	-3.806826	3.015576
54	1	0	0.199624	-2.157365	4.400214
55	1	0	0.140786	-0.423503	2.599521
56	1	0	-0.203824	-3.489091	-0.367774
57	1	0	-0.101126	-5.219929	1.392321
58	1	0	0.078649	-4.570517	3.789757
59	6	0	-0.159565	-0.695380	0.006480
60	8	0	0.116388	0.442335	0.413658

61	6	0	4.536062	-2.811775	-0.202675
62	6	0	4.222583	-1.502575	0.175032
63	6	0	3.082411	-0.876055	-0.322477
64	6	0	2.216151	-1.536839	-1.219349
65	6	0	2.541499	-2.861345	-1.581626
66	6	0	3.682478	-3.485421	-1.081527
67	1	0	5.428694	-3.298841	0.182707
68	1	0	4.872526	-0.965664	0.863379
69	1	0	2.832940	0.133990	-0.009189
70	1	0	1.878323	-3.391021	-2.260148
71	1	0	3.909301	-4.506088	-1.383052
72	6	0	1.024510	-0.865441	-1.773488
73	1	0	1.128152	0.217297	-1.820151
74	1	0	0.765707	-1.276306	-2.752150

3a

B3LYP/6-31G(d,p) Electronic Energy: -615.9491016 a.u.
B3LYP/6-31G(d,p) Gibbs free Energy: -615.770568 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -616.1993124 a.u.

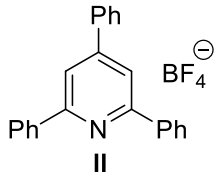
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	2.139283	-5.763492	3.078305
2	6	0	1.562127	-5.027697	2.043061
3	6	0	1.054860	-3.741297	2.283557
4	6	0	1.137185	-3.207482	3.579950
5	6	0	1.716257	-3.940188	4.611252
6	6	0	2.218686	-5.221100	4.362168
7	1	0	2.527059	-6.758880	2.882426
8	1	0	1.507320	-5.465668	1.051905
9	1	0	0.737469	-2.213164	3.748392
10	1	0	1.776905	-3.516825	5.609675
11	1	0	2.670382	-5.794567	5.166695
12	6	0	0.413579	-2.896092	1.219670
13	8	0	-0.058496	-1.806197	1.496181
14	6	0	-1.126880	-0.713094	-3.202844
15	6	0	-1.977418	-1.185631	-2.200205
16	6	0	-1.498823	-2.066087	-1.231432
17	6	0	-0.163123	-2.490331	-1.247618
18	6	0	0.680440	-2.008681	-2.254801
19	6	0	0.204869	-1.126691	-3.227460
20	1	0	-1.500873	-0.028045	-3.958411
21	1	0	-3.015542	-0.866512	-2.172367
22	1	0	-2.164384	-2.422964	-0.450760
23	1	0	1.719922	-2.327592	-2.280068
24	1	0	0.875004	-0.765566	-4.002599
25	6	0	0.356605	-3.455888	-0.209850
26	1	0	-0.271046	-4.358323	-0.173877
27	1	0	1.357863	-3.805483	-0.486736

TS′

B3LYP/6-31G(d,p) Electronic Energy: -1636.9225205 a.u.
B3LYP/6-31G(d,p) Gibbs free Energy: -1636.524797 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -1637.6433379 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z

1	6	0	-2.796727	-1.273642	-2.871804
2	6	0	-2.314923	-0.987348	-1.587854
3	6	0	-1.175740	-1.618711	-1.104498
4	6	0	-0.476551	-2.551584	-1.907495
5	6	0	-0.972629	-2.826485	-3.202308
6	6	0	-2.119207	-2.195964	-3.675573
7	1	0	-3.691375	-0.780247	-3.243012
8	1	0	-2.836344	-0.268462	-0.961385
9	1	0	-0.790211	-1.406814	-0.111450
10	1	0	-0.445256	-3.540994	-3.829800
11	1	0	-2.486669	-2.419871	-4.674319
12	6	0	0.715288	-3.190122	-1.399034
13	1	0	1.455834	-3.488188	-2.133134
14	1	0	1.107798	-2.809334	-0.463573
15	6	0	-0.875768	-5.562078	-0.983074
16	6	0	1.436267	-5.875064	-1.309940
17	6	0	-1.154374	-6.662014	-1.788405
18	6	0	1.194135	-6.979491	-2.115305
19	6	0	-0.123357	-7.388230	-2.413800
20	1	0	-2.184166	-6.984089	-1.891531
21	1	0	2.031521	-7.590119	-2.434449
22	7	0	0.407871	-5.107136	-0.813705
23	6	0	-1.936961	-4.882557	-0.203800
24	6	0	-1.614470	-4.260701	1.015785
25	6	0	-3.276692	-4.871064	-0.632637
26	6	0	-2.609894	-3.659870	1.784684
27	1	0	-0.588541	-4.233591	1.366207
28	6	0	-4.266650	-4.270121	0.140163
29	1	0	-3.540019	-5.301380	-1.594414
30	6	0	-3.938203	-3.663783	1.355792
31	1	0	-2.329439	-3.182569	2.719158
32	1	0	-5.294297	-4.261255	-0.214881
33	1	0	-4.711232	-3.190677	1.956238
34	6	0	2.806131	-5.469668	-0.914266
35	6	0	3.925745	-5.763475	-1.715345
36	6	0	3.005543	-4.755180	0.280850
37	6	0	5.202227	-5.363257	-1.326702
38	1	0	3.793896	-6.281401	-2.661424
39	6	0	4.280836	-4.335217	0.656146
40	1	0	2.165340	-4.522283	0.925851
41	6	0	5.384047	-4.643540	-0.141792
42	1	0	6.054304	-5.595076	-1.961415
43	1	0	4.373923	-3.746222	1.562779
44	1	0	6.379309	-4.315547	0.147891
45	6	0	-0.393483	-8.555108	-3.272910
46	6	0	0.500334	-8.921770	-4.300588
47	6	0	-1.546354	-9.350206	-3.105378
48	6	0	0.256203	-10.025161	-5.114492
49	1	0	1.382485	-8.314042	-4.476432
50	6	0	-1.791665	-10.450309	-3.922263
51	1	0	-2.241870	-9.118460	-2.304987
52	6	0	-0.892601	-10.798365	-4.933885
53	1	0	0.962589	-10.275823	-5.901888
54	1	0	-2.685649	-11.047255	-3.760465
55	1	0	-1.084725	-11.657572	-5.570303
56	9	0	0.914229	-1.625817	3.688341
57	9	0	1.014193	-1.681873	1.387980
58	9	0	1.049206	-3.645064	2.589803
59	9	0	2.870491	-2.243844	2.637955
60	5	0	1.466694	-2.283226	2.594117



II

B3LYP/6-31G(d,p) Electronic Energy: -1366.0242335 a.u.
B3LYP/6-31G(d,p) Gibbs free Energy: -1365.735593 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -1366.6336678 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.582889	-5.213282	-0.983191
2	6	0	0.720866	-5.158130	-1.221213
3	6	0	-1.591510	-6.612448	-0.991778
4	6	0	0.786728	-6.560558	-1.267806
5	6	0	-0.386601	-7.314148	-1.141795
6	1	0	-2.524030	-7.154012	-0.885916
7	1	0	1.735088	-7.062202	-1.426466
8	7	0	-0.449015	-4.503303	-1.100352
9	6	0	-2.843599	-4.427197	-0.846740
10	6	0	-4.001979	-4.968011	-0.264997
11	6	0	-2.891895	-3.099985	-1.304407
12	6	0	-5.171061	-4.215101	-0.159293
13	1	0	-3.985684	-5.977648	0.132980
14	6	0	-4.059895	-2.348498	-1.201414
15	1	0	-1.993442	-2.676793	-1.738533
16	6	0	-5.208253	-2.902195	-0.630580
17	1	0	-6.052085	-4.654205	0.301529
18	1	0	-4.074578	-1.325550	-1.568811
19	1	0	-6.119185	-2.315342	-0.548344
20	6	0	1.954614	-4.324343	-1.292881
21	6	0	1.859460	-2.945538	-1.548361
22	6	0	3.226390	-4.883252	-1.080226
23	6	0	3.001632	-2.150511	-1.600817
24	1	0	0.876780	-2.512866	-1.698675
25	6	0	4.366236	-4.081558	-1.125504
26	1	0	3.362724	-5.936641	-0.869420
27	6	0	4.262652	-2.715432	-1.388414
28	1	0	2.907940	-1.086455	-1.805575
29	1	0	5.328327	-4.550185	-0.942174
30	1	0	5.153624	-2.093010	-1.423962
31	6	0	-0.347953	-8.800162	-1.162604
32	6	0	0.789752	-9.487771	-0.706654
33	6	0	-1.440126	-9.550193	-1.633841
34	6	0	0.825779	-10.880865	-0.715683
35	1	0	1.662502	-8.961455	-0.340240
36	6	0	-1.401032	-10.943428	-1.640345
37	1	0	-2.315686	-9.040308	-2.026050
38	6	0	-0.266864	-11.615481	-1.177766
39	1	0	1.727224	-11.370455	-0.360476
40	1	0	-2.253027	-11.503814	-2.017548
41	1	0	-0.235353	-12.702153	-1.186046
42	9	0	5.488172	-9.229016	-1.129884
43	9	0	4.929539	-7.340990	0.067827
44	9	0	3.724161	-9.291957	0.353193
45	9	0	3.540591	-8.092918	-1.597432
46	5	0	4.444619	-8.499107	-0.569144

B3LYP/6-31G(d,p) Electronic Energy: -270.9202558 a.u.
B3LYP/6-31G(d,p) Gibbs free Energy: -270.835136 a.u.
B3LYP-D3(SMD-THF) Electronic Energy: -271.0269556 a.u.

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	6	0	-1.119278	-0.667227	-3.172020
2	6	0	-1.975678	-1.214633	-2.205314
3	6	0	-1.508092	-2.160797	-1.306953
4	6	0	-0.151035	-2.601605	-1.339478
5	6	0	0.698077	-2.028901	-2.333349
6	6	0	0.219090	-1.083374	-3.226453
7	1	0	-1.490106	0.073725	-3.873781
8	1	0	-3.013215	-0.895088	-2.159690
9	1	0	-2.176233	-2.581503	-0.560030
10	1	0	1.736085	-2.347685	-2.380480
11	1	0	0.885886	-0.662120	-3.973857
12	6	0	0.329500	-3.561842	-0.430437
13	1	0	-0.319935	-3.995899	0.321934
14	1	0	1.361547	-3.893939	-0.459121

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