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Precise manipulation of electron transfers to enable the site-selective hydropyridylation of ynones

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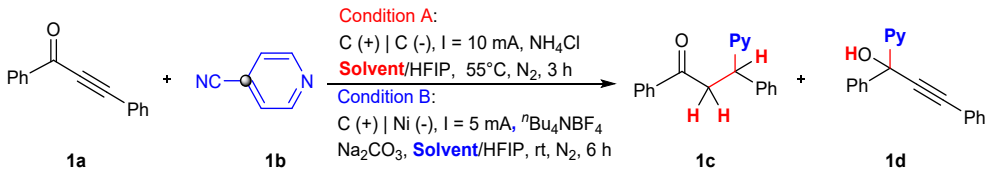
Contents

1. General information

All glassware was oven dried at 100 °C for hours and cooled down under vacuum. Ynones was prepared according to reported procedures. [1] Unless otherwise noted, materials were obtained from commercial suppliers and used without further purification. The instrument for electrolysis is dual display potentiostat (DJS-292B) (made in China), carbon rods (ϕ = 6 mm), nickel plate (1.5 × 1.5 cm^2), and Pt plate (1.5 × 1.5 cm^2). Thin layer chromatography (TLC) employed glass 0.25 mm silica gel plates. Flash chromatography columns were packed with 200-300 mesh silica gel in petroleum (b. p. 60-90 °C). ^1H, ^{13}C, and ^{19}F NMR data were recorded with Bruker Advance III (500 MHz) spectrometers with tetramethylsilane as an internal standard. All chemical shifts (δ) are reported in ppm and coupling constants (*J*) in Hz. All chemical shifts are reported relative to tetramethylsilane and d-solvent peaks (77.00 ppm, chloroform, 40.00 ppm, DMSO-d_6), respectively.

2. Investigation of solvents and Investigating the electron transfer properties of ynones

Table S1. Investigation of solvents



Entry	Condition A: **Solvent** [a]	**1c** [%][c]	**1d** [%][c]	Entry	Condition B: **Solvent** [b]	**1c** [%][c]	1d [%][c]
1	DMSO	83	n. d.	12	DCM	n. d.	81
2	DMF	21	18	13	DCE	34	13
3	Acetone	66	trace	14	$CHCl_3$	11	47
4	MeCN	37	trace	15	DBE	trace	trace
5	1,4-dioxane	41	n. d.	16	MeCN	n. d.	9
6	THF	35	n. d.	17	DMSO	21	n. d.
7	Toluene	n. d.	n. d.	18	HFIP	0	41
8	HFIP	23	5	19	MeOH	50	trace
9	MeOH	58	n. d.	20	EtOH	28	trace
10	EtOH	50	n. d.	21	TFEA	n. d.	n. d.
11	TFEA	17	n. d.				

[a] Reaction condition A: carbon rods as the anode, carbon rods as the cathode, constant current 10 mA, **1a** (0.25 mmol), **1b** (0.5 mmol), NH_4Cl (1.0 mmol), Solvent/HFIP (5.0 mL, v = 4 : 1), 55 °C, N_2, 3 h. [b] Reaction condition B: carbon rods as the anode, Ni plate as the cathode, constant current 5 mA, **1a** (0.25 mmol), **1b** (0.5 mmol), $^nBu_4NBF_4$ (0.25 mmol), Na_2CO_3 (0.5 mmol), Solvent/HFIP (10.0 mL, v = 9 : 1), N_2, 6 h. [c] Isolated yield.

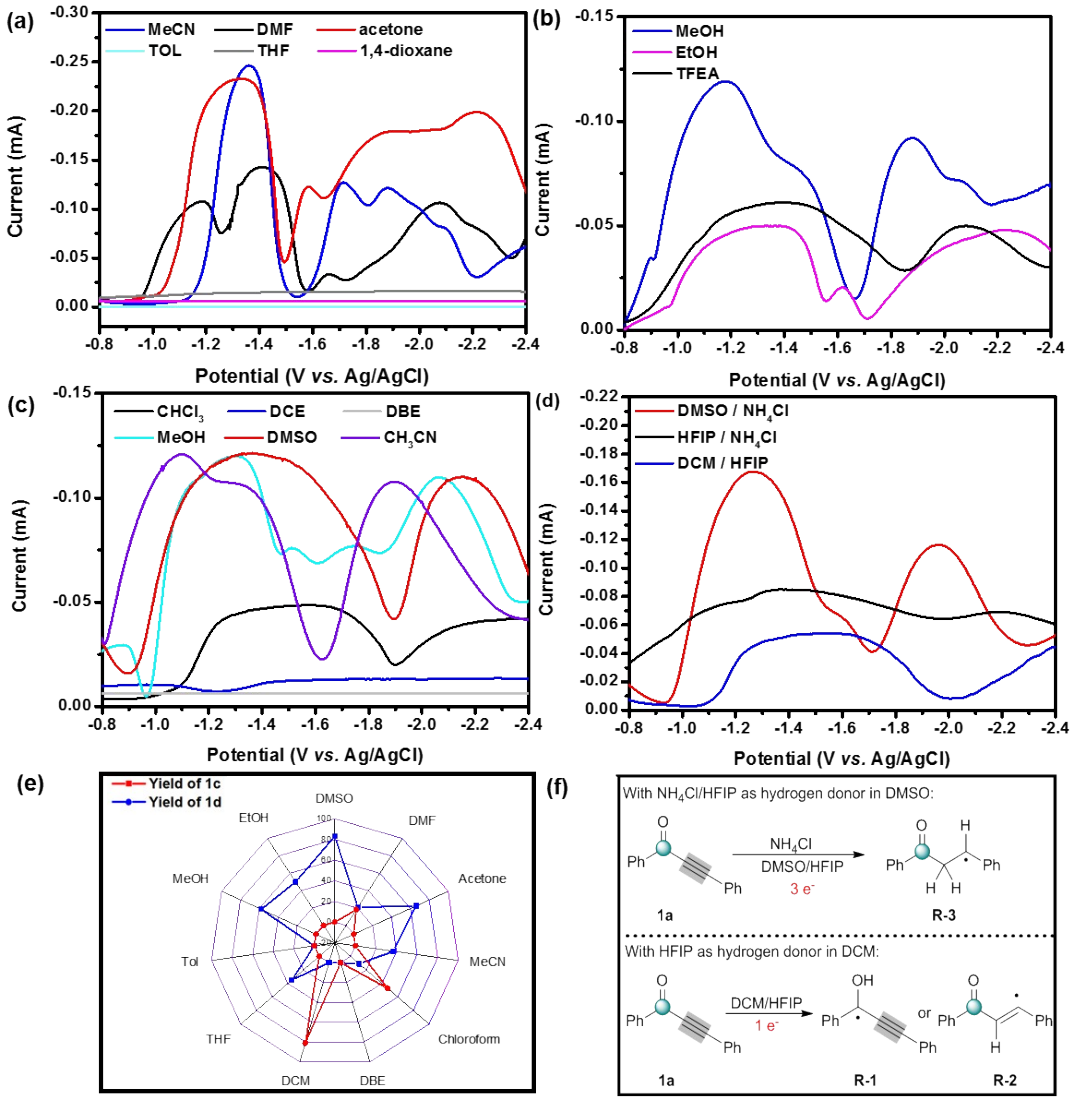
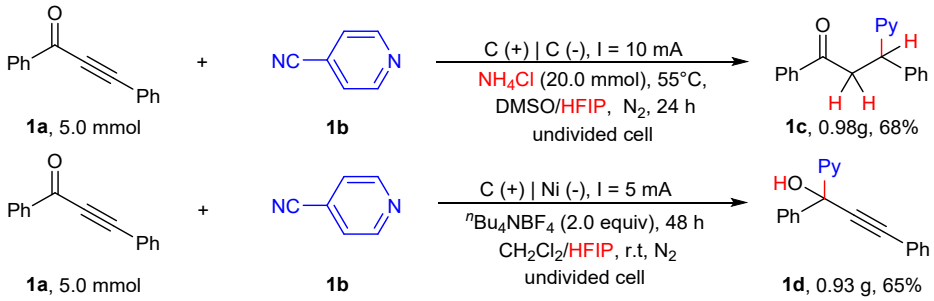


Figure S1. Investigating the electron transfer properties of ynones. Square wave voltammetry (SWV) was performed on solutions containing 0.1 M $^{n}Bu_4NBF_4$ in DMSO or CH_2Cl_2 at room temperature in the presence of HFIP (1.0 mL), or/and NH_4Cl (2.0 mM), at a pulse height of 25 mV, step height of 4 mV, with the frequency of 10 Hz, **1a** (0.25 mM). (a) Varying solvent with NH_4Cl (2.0 mM), and HFIP (1.0 mL). (b) Varying solvent with NH_4Cl (2.0 mM). (c) Varying solvent with HFIP (1.0 mL). (d) SWV results in DMSO (HFIP, 1.0 mL), HFIP, and DCM. (e) The effect of solvent on selectivity. (f) Conclusion of the SWV experiments.

3. Gram-scale synthesis

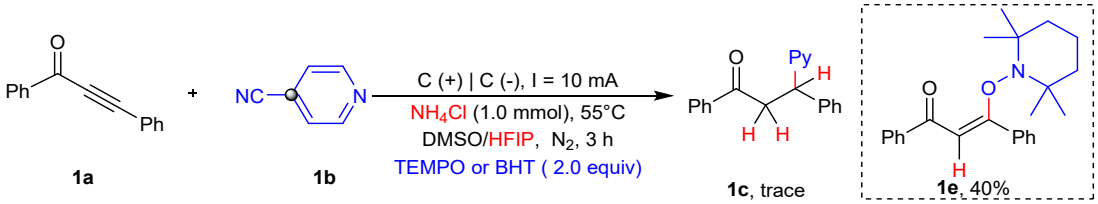


1c: In an oven-dried undivided three-necked flask (100 mL) equipped with a stir bar, **1a** (5.0 mmol, 1.03 g), **1b** (10.0 mmol, 2.08 g), NH_4Cl (20.0 mmol, 1.06 g) were combined and added. The flask was equipped with carbon rods (ϕ = 6 mm) as the electrodes and was then charged with nitrogen. Under the protection of nitrogen, DMSO/HFIP (50.0 mL, v = 4 : 1) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under 55 °C for 24 h. When the reaction was finished, the reaction mixture was washed with water and extracted with CH_2Cl_2 (20 mL × 3). The organic layers were combined, dried over Na_2SO_4, and then concentrated. The pure product **1c** was obtained a yield of 68% by flash column chromatography on silica gel.

1d: In an oven-dried undivided three-necked flask (150 mL) equipped with a stir bar, **1a** (5.0 mmol, 1.03 g), **1b** (10.0 mmol, 2.08 g), and $^{n}Bu_4NBF_4$ (5.0 mmol, 1.65 g) were combined and added. The flask was equipped with a carbon rod (ϕ = 6 mm) as the anode and nickel plate (1.5 × 1.5 cm^2) as the cathode and was then charged with nitrogen. Under the protection of nitrogen, CH_2Cl_2/HFIP (100.0 mL, v = 9 : 1) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 48 h. When the reaction was finished, the reaction mixture was washed with water and extracted with CH_2Cl_2 (20 mL × 3). The organic layers were combined, dried over Na_2SO_4, and concentrated. The pure product **1d** was obtained a yield of 65% by flash column chromatography on silica gel.

4. Mechanistic studies

4.1 Radical trapping experiments

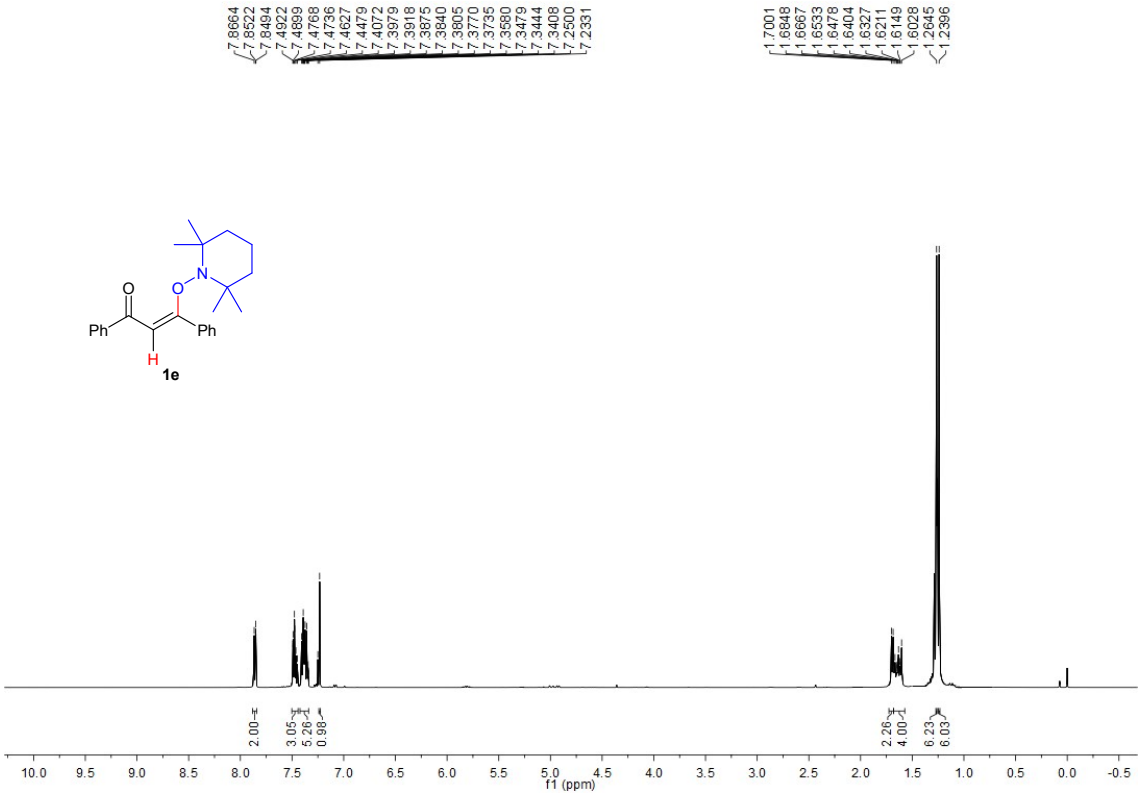


In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **1a** (0.25 mmol,

51.5 mg), **1b** (0.5 mmol, 52.0 mg), NH_4Cl (1.0 mmol, 53.0 mg), TEMPO or BHT (0.5 mmol) were combined and added. The flask was equipped with carbon rods (ϕ = 6 mm) as the electrodes and was then charged with nitrogen. Under the protection of nitrogen, DMSO/HFIP (5.0 mL, v = 4 : 1) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under 55 °C for 3 h. When the reaction was finished, the solution was concentrated in a vacuum and not detected the desired product **1c**. The pure product **1e** was obtained in 40% yield by flash column chromatography on silica gel.

1e: ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 – 7.84 (m, 2H), 7.47 – 7.44 (m, 3H), 7.40 -7.34 (m, 5H), 7.23 (s, 1H), 1.70 - 1.68 (m, 2H), 1.66 -1.60 (m, 4H), 1.26 (s, 6H), 1.24 (s, 6H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.9, 173.7, 140.2, 134.3, 131.7, 129.7, 128.8, 128.2, 128.1, 127.9, 101.7, 61.0, 39.8, 32.4, 20.8, 16.9.

^{1}H NMR



^{13}C NMR

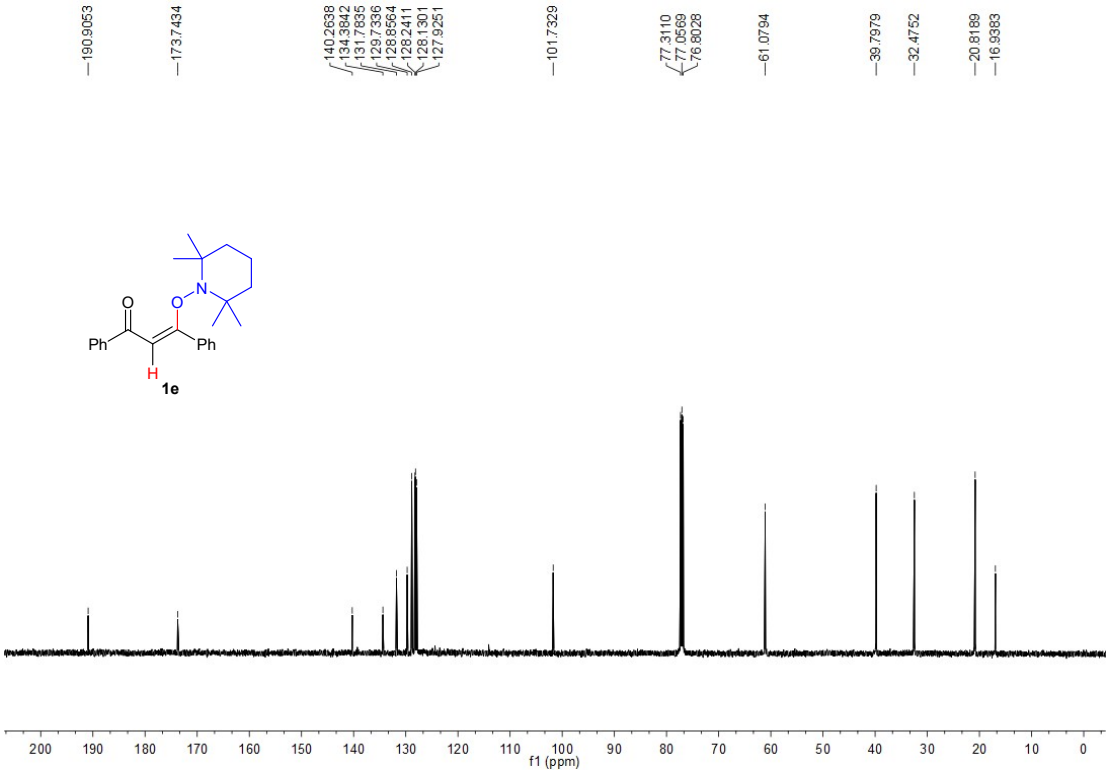
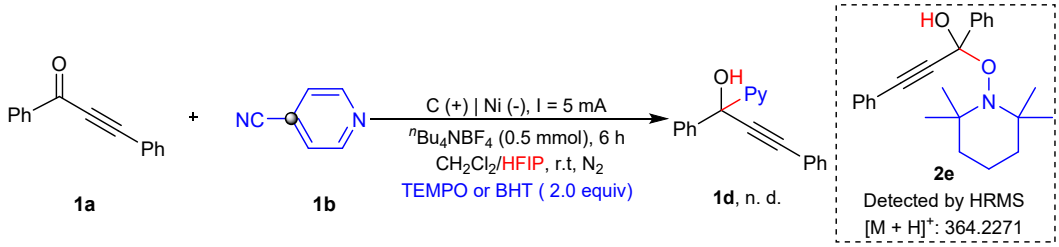


Figure S2. NMR results of **1e**.



In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **1a** (0.25 mmol, 51.5 mg), **1b** (0.5 mmol, 52.0 mg), ^{n}Bu$_4$NBF$_4$ (0.25 mmol, 82.5 mg), TEMPO or BHT (0.5 mmol) were combined and added. The flask was equipped with a carbon rod (ϕ = 6 mm) as the anode and nickel plate (1.5 × 1.5 cm^2) as the cathode and was then charged with nitrogen. Under the protection of nitrogen, CH$_2$Cl$_2$/HFIP (10.0 mL, v = 9 : 1) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 5 mA under room temperature for 6 h. When the reaction was finished, the solution was concentrated in a vacuum and not detected the desired product **1d**. The compound **2e** can be detected by HRMS. HRMS (ESI) calcd for C$_{24}$H$_{30}$NO$_2$ [M + H]$^+$: 364.2271; found: 364.2271.

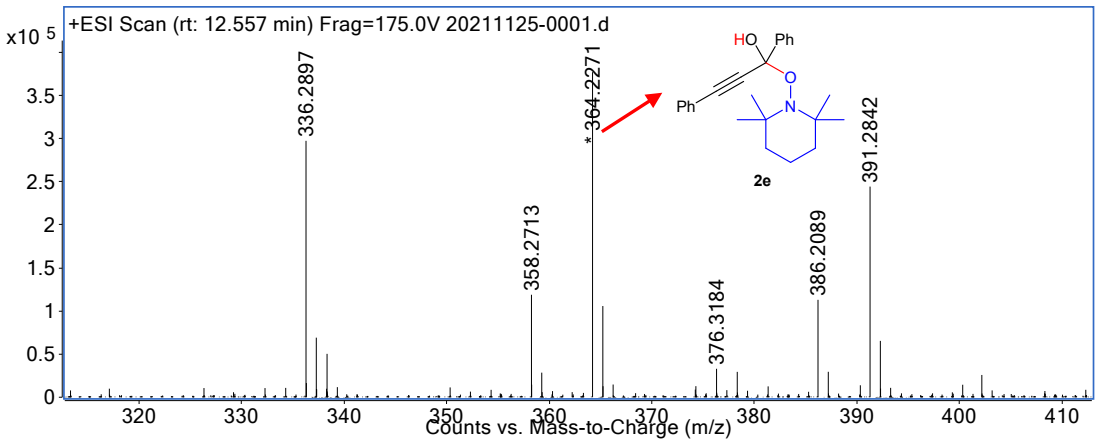
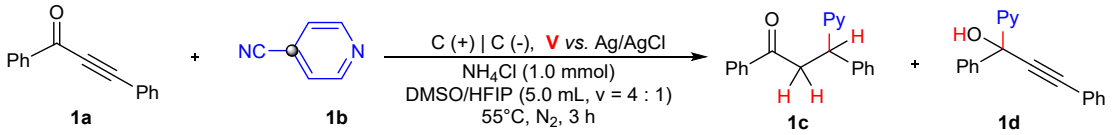


Figure S3. HRMS results of **2e**.

4.2 Potentiostatic experiments

Table S2. Potentiostatic experiments

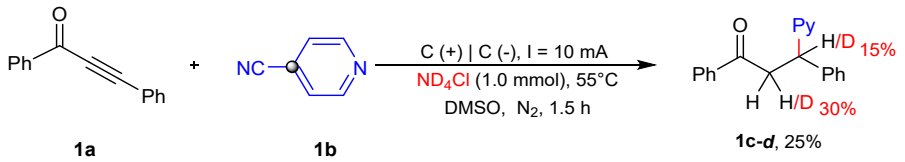


Entry	V *vs.* Ag/AgCl	Yield of **1c** [a]	Yield of **1d** [a]
1	1.0	trace	0
2	1.1	11	0
3	1.2	28	0
4	1.3	42	0

[a] The yield of product **1c** and **1d** was monitored by GC with diphenylmethane as the internal standard.

4.3 Deuteration experiments

In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **1a** (0.25 mmol, 51.5 mg), **1b** (0.5 mmol, 52.0 mg), ND_4Cl or NH_4Cl were combined and added. The flask was equipped with carbon rods (ϕ = 6 mm) as the electrodes and was then charged with nitrogen. Under the protection of nitrogen, DMSO (5.0 mL) or DMSO/CD_3OD (5.0 mL, v = 4 : 1) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 10 mA under 55 °C for 1.5 h. When the reaction was finished, the solution was concentrated in vacuum, the pure product **1c-*d*** was obtained by flash column chromatography on silica gel, and the deuteration rate is quantified by ^1H NMR.



(1)

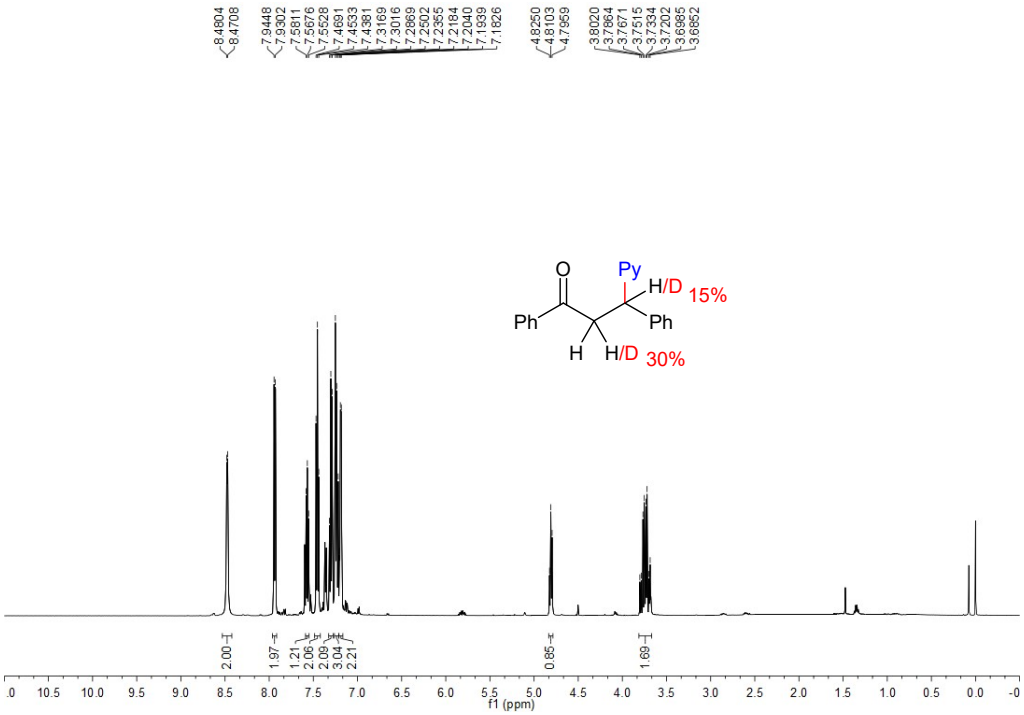


Figure S4. ^{1}H NMR results **1c** with ND_4Cl as hydrogen donor.

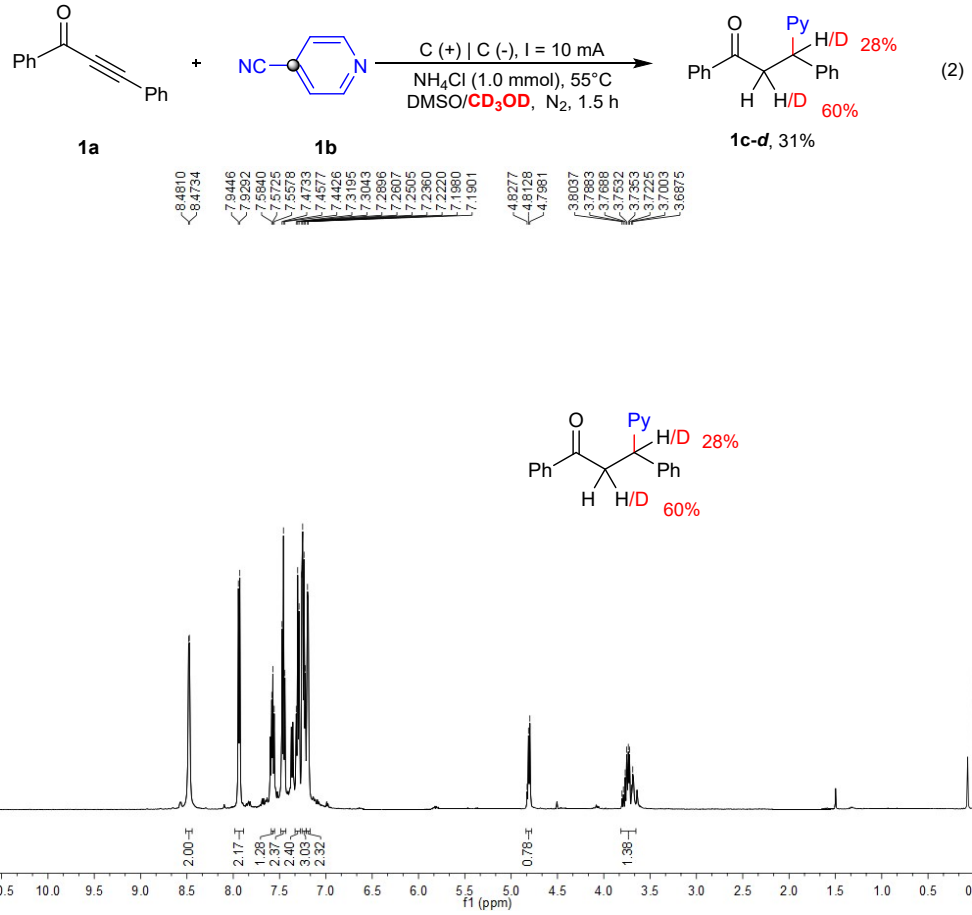
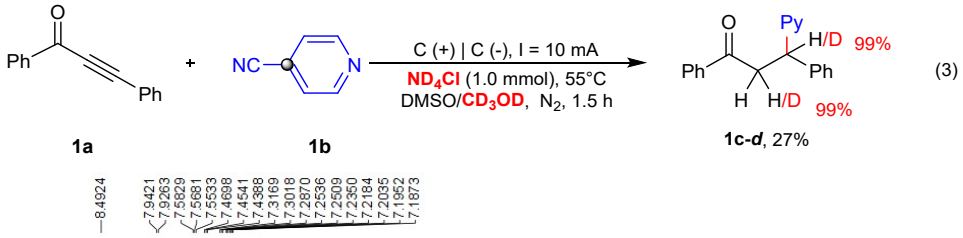


Figure S5. ^{1}H NMR results **1c** with CD_3OD as hydrogen donor.



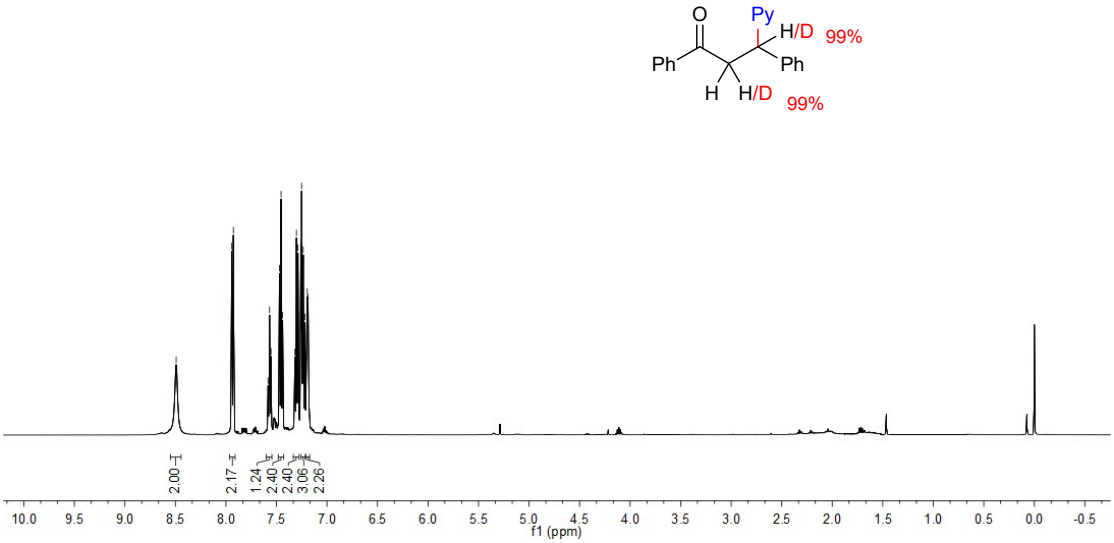


Figure S6. ^{1}H NMR results **1c** with CD_3OD and ND_4Cl as hydrogen donor.

4.4 General procedure for kinetic studies

In an oven-dried undivided three-necked flask (25 mL) equipped with a stir bar, **1a** (0.25 mmol, 51.5 mg), **1b** (0.5 mmol, 52.0 mg), and NH_4Cl (1.0 mmol, 53.0 mg) were combined and added. The flask was equipped with carbon rods (ϕ = 6 mm) as the electrodes and was then charged with nitrogen. Under the protection of nitrogen, DMSO/HFIP (5.0 mL, v = 4 : 1) were slowly injected into the reaction flask. The reaction mixture was stirred and electrolyzed at a constant current of 10.0 mA under 55 °C for designated time interval (20, 40, 60, 80, 100, 120 min). The reaction was quenched by ethyl acetate and then analyzed by GC analysis with diphenylmethane as the internal standard. As the same as above procedure, the similar sets of experiments were conducted by using different concentration of **1a**, **1b**, NH_4Cl, HFIP. Moreover, the similar sets of experiments were also conducted with different constant current under condition A or B. Only one parameter was changed from the general procedure in one reaction.

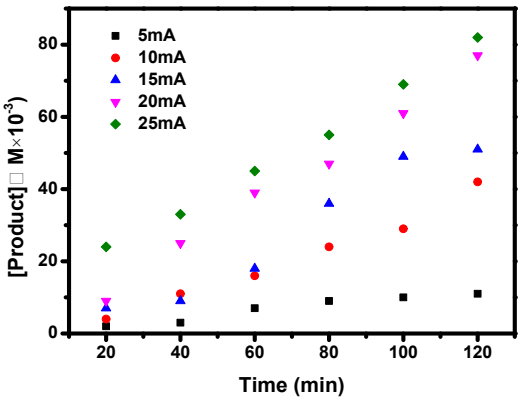


Figure S7. The yield of **1c** with different constant current and different time under condition A.

Linear fitting:

Current	Linear Fitting Results
5 mA	$y = 0.097x + 0.2$ $R^2 = 0.93$
10 mA	$y = 0.360x - 4.2$ $R^2 = 0.97$
15 mA	$y = 0.511x - 7.47$ $R^2 = 0.93$
20 mA	$y = 0.651x - 2.6$ $R^2 = 0.99$
25 mA	$y = 0.583x - 10.5$ $R^2 = 0.99$

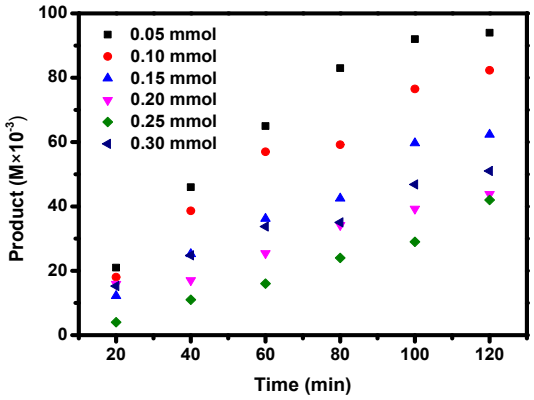


Figure S8. The yield of different concentration **1a** with different time.

Linear fitting:

Concentration of **1a**	Linear Fitting Results
0.01 M	$y = 0.744x + 14.7$ $R^2 = 0.91$
0.02 M	$y = 0.625x + 11.6$ $R^2 = 0.94$
0.03 M	$y = 0.515x + 3.66$ $R^2 = 0.97$
0.04 M	$y = 0.307x + 7.77$ $R^2 = 0.97$
0.05 M	$y = 0.36x - 4.20$ $R^2 = 0.97$
0.06 M	$y = 0.352x + 8.50$ $R^2 = 0.96$

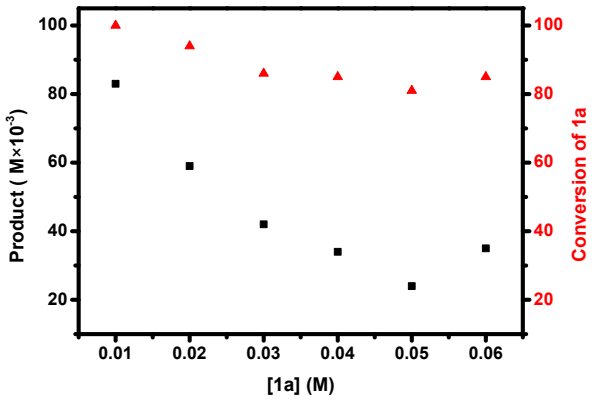


Figure S9. The yield and conversion of different concentration **1a** at 80 min with 10 mA.

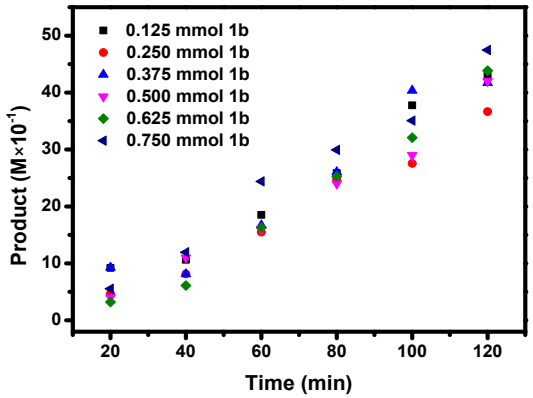


Figure S10. The yield of different concentration **1b** with different time.

Linear fitting:

Concentration of **1b**	Linear Fitting Results
0.025 M	y = 0.368x - 1.6 R^2 = 0.97
0.050 M	y = 0.325x - 3.2 R^2 = 0.97
0.075 M	y = 0.383x - 3.11 R^2 = 0.91
0.100 M	y = 0.36x - 4.2 R^2 = 0.97
0.125 M	y = 0.415x - 7.88 R^2 = 0.98
0.150 M	y = 0.406x - 2.73 R^2 = 0.98

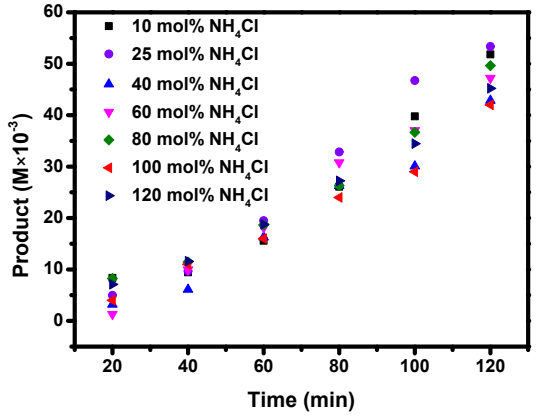


Figure S11. The yield of different concentration NH_4Cl with different time.

Linear fitting:

Concentration of NH_4Cl	Linear Fitting Results
0.02 M	y = 0.456x - 6.71 R^2 = 0.92
0.05 M	y = 0.523x - 8.79 R^2 = 0.98
0.08 M	y =0.400x - 7.21 R^2 = 0.97
0.12 M	y = 0.462x - 8.26 R^2 = 0.99
0.16 M	y = 0.415x - 3.86 R^2 = 0.95
0.20 M	y = 0.36x - 4.2 R^2 = 0.97
0.24 M	y = 0.382x - 2.7 R^2 = 0.98

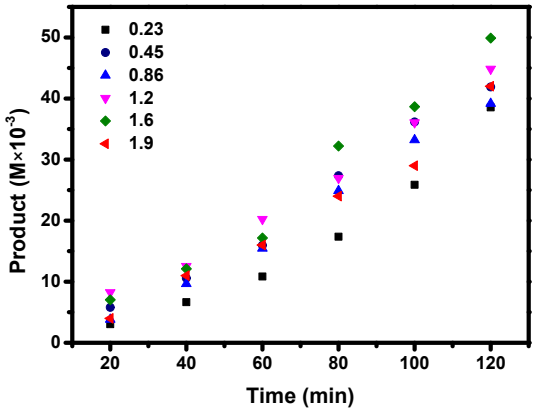


Figure S12. The yield of different concentration HFIP with different time.

Linear fitting:

Concentration of HFIP	Linear Fitting Results
0.23 M	y = 0.345x - 7.11 R^2 = 0.93
0.45 M	y = 0.384x - 3.9 R^2 = 0.98
0.86 M	y = 0.367x-4.65 R^2 = 0.99
1.2 M	y = 0.372x-1.21 R^2 = 0.99
1.6 M	y = 0.441x-4.72 R^2 = 0.97
1.9 M	y = 0.36x - 4.2 R^2 = 0.97

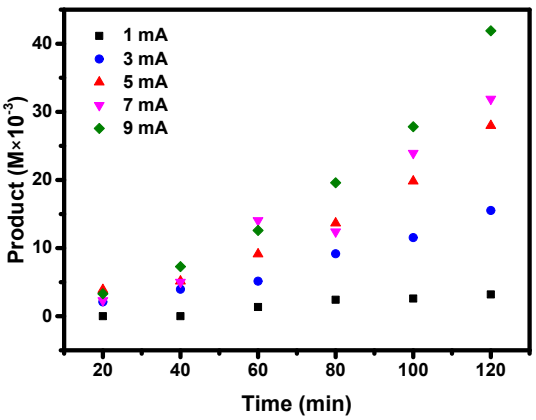


Figure S13. The yield of different concentration NH_4Cl with different time.

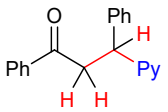
Linear fitting:

Condition B: current	Linear Fitting Results
1 mA	y = 0.035x - 0.89 R^2=0.92
3 mA	y = 0.134x - 1.48 R^2=0.96
5 mA	y = 0.24x - 3.63 R^2=0.93
7 mA	y = 0.29x - 5.37 R^2=0.91
9 mA	y = 0.374x - 7.41 R^2=0.94

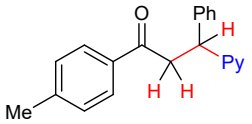
5. Reference

1. (a) Waldo, J. P.; Larock, R. C., *J. Org. Chem.* **2007**, *72*, 9643; (b) Yuan, J.; Wang, J.; Zhang, G.; Liu, C.; Qi, X.; Lan, Y.; Miller, J. T.; Kropf, A. J.; Bunel, E. E.; Lei, A., *Chem. Commun.* **2015**, *51*, 576; (c) Tang, S.; Zeng, L.; Liu, Y.; Lei, A., *Angew. Chem. Int. Ed. Engl.* **2015**, *54*, 15850. (d) Wen, J.; Shi, W.; Zhang, F.; Liu, D.; Tang, S.; Wang, H.; Lin, X.-M.; Lei, A., *Org. Lett.* **2017**, *19*, 3131.
2. (a) Yang, J.; Ma, J.; Yan, K.; Tian, L.; Li, B.; Wen, J., *Adv. Synth. Catal.*, 2022. *364*, 845; (b) Zhang, S.; Li, L.; Li, X.; Zhang, J.; Xu, K.; Li, G.; Findlater, M. *Org. Lett.*, **2020**, *22*, 3570. (c) Liu, Y.; Yu, Y.; Sun, C.; Fu, Y.; Mang, Z.; Shi,L.; Li, H., *Org. Lett*. **2020**, *22*, 8127. (d) Hoshikawa, T.; Inoue, M., *Chem. Sci.,* **2013**, *4*, 3118; (e) Mccarty, F. J.; Tilford, C. H.; Van Campen Jr. M. G. *J. Org. Chem.* **1961**, *26*, 4084; (f) Zeng, X.; Cai, J.; Gu, Y., *Tetrahedron Lett.*, **1995**, *36*, 7275.

6. Detail descriptions for products.

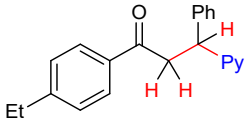


1,3-Diphenyl-3-(pyridin-4-yl)propan-1-one (1c):[2] yellow oil was obtained with 83% isolated yield (59.5 mg). ^{1}H NMR (500 MHz, CDCl3) δ 8.48 (d, J = 2.8 Hz, 2H), 7.94 (d, J = 7.3 Hz, 2H), 7.56 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.7 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.26–7.21 (m, 3H), 7.19 (d, J = 5.3 Hz, 2H), 4.81 (t, J = 7.2 Hz, 1H), 3.74 (ddd, J = 25.3, 17.5, 7.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.1, 153.4, 149.4, 142.3, 136.6, 133.4, 128.9, 128.7, 128.0, 127.8, 127.0, 45.2, 43.8.

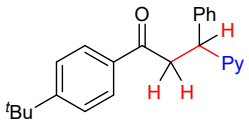


3-Phenyl-3-(pyridin-4-yl)-1-(p-tolyl)propan-1-one (2c):[2] yellow oil was obtained with 78% isolated yield (58.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 3.0 Hz, 2H), 7.84 (d, *J* = 8.1 Hz, 2H), 7.33–7.28 (m, 2H), 7.27–7.21 (m, 7H), 4.82 (t, *J* = 7.2 Hz, 1H), 3.72 (ddd, *J* = 25.4, 17.4, 8.1 Hz, 2H), 2.41 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 149.1, 144.3, 143.1, 142.3, 134.1, 129.4, 128.9,

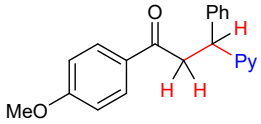
128.1, 127.8, 127.0, 45.3, 43.7, 21.6.



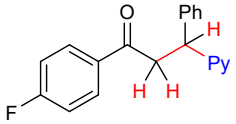
1-(4-Ethylphenyl)-3-phenyl-3-(pyridin-4-yl)propan-1-one (3c):[2] yellow oil was obtained with 74% isolated yield (58.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.46 (d, *J* = 4.2 Hz, 2H), 7.87 (d, *J* = 8.2 Hz, 2H), 7.32–7.26 (m, 4H), 7.2–7.21 (m, 3H), 7.19 (t, *J* = 5.1 Hz, 2H), 4.81 (t, *J* = 7.2 Hz, 1H), 3.72 (ddd, *J* = 24.0, 17.4, 7.3 Hz, 2H), 2.70 (q, *J* = 7.6 Hz, 2H), 1.25 (t, *J* = 6.6 Hz, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 153.1, 150.4, 149.8, 142.5, 134.4, 128.8, 128.2, 128.2, 127.9, 126.9, 123.2, 45.2, 43.7, 28.9, 15.1.



1-(4-(*Tert*-butyl)phenyl)-3-phenyl-3-(pyridin-4-yl)propan-1-one (4c):[2] yellow oil was obtained with 75% isolated yield (64.4mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 5.8 Hz, 2H), 7.89 (d, *J* = 8.5 Hz, 2H), 7.47 (d, *J* = 8.5 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.26–7.21 (m, 3H), 7.21–7.18 (m, 2H), 4.82 (t, *J* = 7.2 Hz, 1H), 3.72 (ddd, *J* = 24.0, 17.4, 7.2 Hz, 2H), 1.33 (s, 9H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.7, 157.2, 153.3, 149.6, 142.5, 134.1, 128.8, 128.0, 127.9, 126.9, 125.6, 123.3, 45.2, 43.7, 35.1, 31.0.

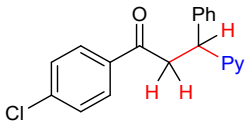


1-(4-Methoxyphenyl)-3-phenyl-3-(pyridin-4-yl)propan-1-one (5c):[2] yellow oil was obtained with 77% isolated yield (61.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, *J* = 5.9 Hz, 2H), 7.92 (d, *J* = 8.8 Hz, 2H), 7.29 (t, *J* = 7.5 Hz, 2H), 7.25–7.20 (m, 3H), 7.19–7.16 (m, 2H), 6.91 (d, *J* = 8.8 Hz, 2H), 4.80 (t, *J* = 7.2 Hz, 1H), 3.84 (s, 3H), 3.68 (ddd, *J* = 25.1, 17.2, 7.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.7, 163.7, 153.2, 149.8, 142.6, 130.3, 129.8, 128.8, 127.9, 126.9, 123.2, 113.8, 55.5, 45.3, 43.4.

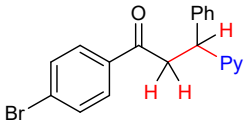


1-(4-Fluorophenyl)-3-phenyl-3-(pyridin-4-yl)propan-1-one (6c):[2] yellow oil was obtained with 60% isolated yield (45.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 2H), 8.01–7.90 (m, 2H), 7.31 (t, *J* = 7.4 Hz, 2H), 7.26–7.20 (m, 3H), 7.19 (d, *J* = 4.4 Hz, 2H), 7.12 (t, *J* = 8.3 Hz, 2H), 4.79 (t, *J* = 7.1

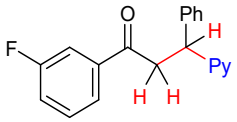
Hz, 1H), 3.71 (ddd, J = 25.2, 17.4, 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.5, 165.9 (d, J = 255.5 Hz), 152.9, 149.8, 142.3, 133.1, 130.6 (d, J = 9.4 Hz), 128.9, 127.8, 127.0, 123.1, 115.8 (d, J = 21.9 Hz), 45.2, 43.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -101.1.



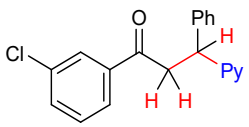
1-(4-Chlorophenyl)-3-phenyl-3-(pyridin-4-yl)propan-1-one (7c): [2] yellow oil was obtained with 74% isolated yield (59.5 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 2H), 7.87 (d, J = 8.6 Hz, 2H), 7.42 (d, J = 8.6 Hz, 2H), 7.33–7.27 (m, 2H), 7.22 (d, J = 7.2 Hz, 3H), 7.18 (d, J = 4.5 Hz, 2H), 4.78 (t, J = 7.2 Hz, 1H), 3.70 (ddd, J = 25.2, 17.4, 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.0, 152.9, 149.8, 142.2, 139.9, 134.9, 129.4, 129.0, 128.9, 127.8, 127.1, 123.2, 45.2, 43.8.



1-(4-Bromophenyl)-3-phenyl-3-(pyridin-4-yl)propan-1-one (8c): [2] yellow oil was obtained with 70% isolated yield (64.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, J = 4.7 Hz, 2H), 7.79 (d, J = 8.5 Hz, 2H), 7.59 (d, J = 8.5 Hz, 2H), 7.30 (t, J = 7.5 Hz, 2H), 7.24–7.19 (m, 3H), 7.17 (d, J = 5.4 Hz, 2H), 4.78 (t, J = 7.2 Hz, 1H), 3.69 (ddd, J = 24.6, 17.4, 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.2, 152.8, 149.9, 142.2, 135.3, 132.0, 129.5, 128.9, 128.6, 127.8, 127.1, 123.1, 45.2, 43.8.

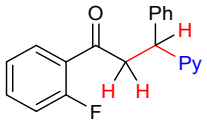


1-(3-Fluorophenyl)-3-phenyl-3-(pyridin-4-yl)propan-1-one (9c): [2] yellow oil was obtained with 66% isolated yield (50.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 2H), 7.72 (d, J = 7.7 Hz, 1H), 7.60 (d, J = 9.3 Hz, 1H), 7.47–7.41 (m, 1H), 7.33–7.28 (m, 2H), 7.27–7.21 (m, 4H), 7.19 (d, J = 5.0 Hz, 2H), 4.79 (t, J = 7.2 Hz, 1H), 3.72 (ddd, J = 25.6, 17.6, 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.9, 162.8 (d, J = 248.5 Hz), 152.9, 149.8, 142.1, 138.6, 130.4 (d, J = 7.6 Hz), 128.9, 127.8, 127.1, 123.7 (d, J = 2.9 Hz), 123.2, 120.4 (d, J = 21.5 Hz), 114.8 (d, J = 22.3 Hz), 45.2, 44.0. ^{19}F NMR (471 MHz, $CDCl_3$) δ -107.5.

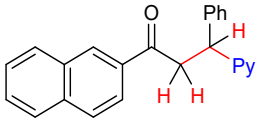


1-(3-chlorophenyl)-3-phenyl-3-(pyridin-4-yl)propan-1-one (10c):[2] yellow oil was obtained with 63% isolated yield (50.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, J = 5.2 Hz, 2H), 7.89 (s, 1H),

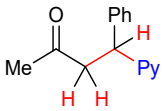
7.80 (d, J = 7.8 Hz, 1H), 7.55–7.51 (m, 1H), 7.39 (t, J = 7.9 Hz, 1H), 7.33–7.28 (m, 2H), 7.24–7.20 (m, 3H), 7.18 (d, J = 5.8 Hz, 2H), 4.78 (t, J = 7.2 Hz, 1H), 3.71 (ddd, J = 25.4, 17.6, 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.9, 152.9, 149.7, 142.1, 138.1, 135.1, 133.3, 130.0, 128.9, 128.1, 127.8, 127.1, 126.0, 123.2, 45.1, 43.9.



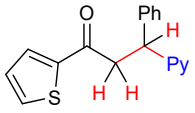
1-(2-Fluorophenyl)-3-phenyl-3-(pyridin-4-yl)propan-1-one (11c): [2] yellow oil was obtained with 64% isolated yield (48.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 2H), 7.74 (t, J = 7.5 Hz, 1H), 7.58–7.50 (m, 1H), 7.30 (t, J = 7.5 Hz, 2H), 7.26–7.21 (m, 4H), 7.21–7.12 (m, 3H), 4.78 (t, J = 7.1 Hz, 1H), 3.77 (ddd, J = 25.9, 18.1, 7.7 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.6, 162.9, 153.3, 149.6, 142.2, 134.9 (d, J = 9.0 Hz), 130.7, 128.8, 127.8, 127.0, 125.4 (d, J = 13.0 Hz), 124.6 (d, J = 3.3 Hz), 123.3, 116.7 (d, J = 23.8 Hz), 48.7, 45.2. ^{19}F NMR (471 MHz, $CDCl_3$) δ -105.6.



1-(Naphthalen-2-yl)-3-phenyl-3-(pyridin-4-yl)propan-1-one (12c): [2] yellow oil was obtained with 65% isolated yield (54.8 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, J = 5.4 Hz, 2H), 8.47 (s, 1H), 8.00 – 7.97 (m, 1H), 7.95 (d, J = 8.1 Hz, 1H), 7.91–7.85 (m, 2H), 7.63–7.59 (m, 1H), 7.58–7.54 (m, 1H), 7.34–7.29 (m, 2H), 7.28 (d, J = 7.0 Hz, 2H), 7.26–7.22 (m, 3H), 4.88 (t, J = 7.2 Hz, 1H), 3.88 (ddd, J = 25.2, 17.4, 7.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 153.5, 149.4, 142.4, 135.7, 134.0, 132.4, 129.7, 129.5, 128.9, 128.7, 128.6, 127.9, 127.8, 127.0, 126.9, 123.7, 123.3, 45.4, 43.94.

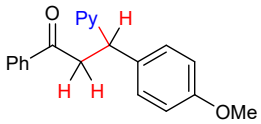


4-Phenyl-4-(pyridin-4-yl)butan-2-one (13c): [2] yellow oil was obtained with 84% isolated yield (47.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.47 (d, J = 4.4 Hz, 2H), 7.31–7.27 (m, 2H), 7.25–7.21 (m, 1H), 7.19 (d, J = 7.5 Hz, 2H), 7.13 (d, J = 5.2 Hz, 2H), 4.57 (t, J = 7.4 Hz, 1H), 3.19 (d, J = 7.4 Hz, 2H), 2.11 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 205.8, 152.9, 149.8, 142.0, 128.8, 127.7, 127.0, 123.1, 48.7, 45.1, 29.7.

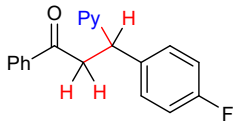


3-Phenyl-3-(pyridin-4-yl)-1-(thiophen-2-yl)propan-1-one (14c): [2] yellow oil was obtained with

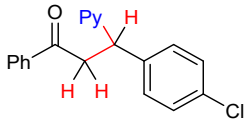
66% isolated yield (48.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (s, 2H), 7.73 (d, *J* = 3.7 Hz, 1H), 7.64 (d, *J* = 4.9 Hz, 1H), 7.31 (t, *J* = 7.6 Hz, 2H), 7.26–7.22 (m, 3H), 7.21 (d, *J* = 4.5 Hz, 2H), 7.13–7.11 (m, 1H), 4.80 (t, *J* = 7.3 Hz, 1H), 3.66 (ddd, *J* = 24.7, 16.9, 7.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 190.0, 152.9, 149.7, 143.9, 142.1, 134.1, 132.0, 128.8, 128.2, 127.8, 127.1, 123.2, 45.3, 44.5.



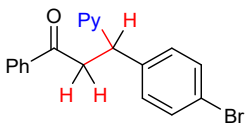
3-(4-Methoxyphenyl)-1-phenyl-3-(pyridin-4-yl)propan-1-one (15c): [2] yellow oil was obtained with 67% isolated yield (53.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.48 (d, *J* = 4.8 Hz, 2H), 7.96–7.90 (m, 2H), 7.57 (t, *J* = 7.4 Hz, 1H), 7.45 (t, *J* = 7.7 Hz, 2H), 7.20–7.12 (m, 4H), 6.86–6.80 (m, 2H), 4.76 (t, *J* = 7.2 Hz, 1H), 3.76 (s, 3H), 3.70 (ddd, *J* = 24.4, 17.4, 7.0 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.3, 158.5, 153.5, 149.7, 136.7, 134.5, 133.4, 128.8, 128.7, 128.0, 123.1, 114.2, 55.2, 44.4, 44.0.



3-(4-Fluorophenyl)-1-phenyl-3-(pyridin-4-yl)propan-1-one (16c):[2] yellow oil was obtained with 69% isolated yield (52.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.49 (d, *J* = 5.3 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 2H), 7.60–7.54 (m, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.24–7.16 (m, 4H), 7.04–6.95 (m, 2H), 4.81 (t, *J* = 7.2 Hz, 1H), 3.72 (ddd, *J* = 25.1, 17.4, 7.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 161.7 (d, *J* = 246.0 Hz), 153.2, 149.6, 138.0 (d, *J* = 3.3 Hz), 136.5, 133.5, 129.3 (d, *J* = 8.0 Hz), 128.7, 128.0, 123.1, 115.7 (d, *J* = 21.4 Hz), 44.4, 43.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.7.

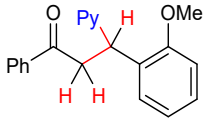


3-(4-Chlorophenyl)-1-phenyl-3-(pyridin-4-yl)propan-1-one (17c):[2] yellow oil was obtained with 68% isolated yield (54.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.51 (d, *J* = 2.9 Hz, 2H), 7.94 (d, *J* = 7.3 Hz, 2H), 7.59 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.7 Hz, 2H), 7.28 (d, *J* = 8.6 Hz, 2H), 7.22–7.14 (m, 4H), 4.80 (t, *J* = 7.2 Hz, 1H), 3.72 (ddd, *J* = 24.4, 17.5, 7.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 152.7, 149.8, 140.8, 136.5, 133.5, 132.8, 129.2, 129.0, 128.7, 128.0, 123.1, 44.6, 43.7.

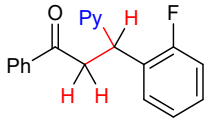


3-(4-Bromophenyl)-1-phenyl-3-(pyridin-4-yl)propan-1-one (18c):[2] yellow oil was obtained with 78% isolated yield (71.2 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (d, *J* = 3.2 Hz, 2H), 7.93 (d, *J*

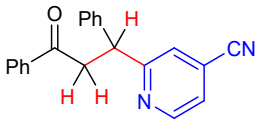
= 7.6 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.7 Hz, 2H), 7.42 (d, *J* = 8.4 Hz, 2H), 7.16 (d, *J* = 5.3 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 4.77 (t, *J* = 7.2 Hz, 1H), 3.71 (ddd, *J* = 24.1, 17.6, 7.3 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 152.4, 150.0, 141.4, 136.5, 133.5, 131.9, 129.6, 128.7, 128.0, 123.1, 120.9, 44.6, 43.6.



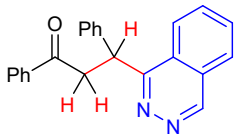
3-(2-Methoxyphenyl)-1-phenyl-3-(pyridin-4-yl)propan-1-one (19c): [2] yellow oil was obtained with 49% isolated yield (38.9 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.45 (s, 2H), 7.95 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 6.6 Hz, 1H), 7.45 (t, *J* = 7.0 Hz, 2H), 7.25–7.15 (m, 3H), 7.11 (d, *J* = 7.1 Hz, 1H), 6.90 (t, *J* = 7.0 Hz, 1H), 6.85 (d, *J* = 7.9 Hz, 1H), 5.13 (t, *J* = 6.2 Hz, 1H), 3.76 (s, 3H), 3.70 (ddd, *J* = 22.8, 17.2, 5.5 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.6, 156.8, 153.1, 149.4, 136.8, 133.2, 130.8, 128.6, 128.2, 128.0, 123.4, 120.7, 110.9, 55.3, 42.6, 39.3.



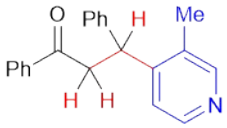
3-(2-Fluorophenyl)-1-phenyl-3-(pyridin-4-yl)propan-1-one (20c):[2] yellow oil was obtained with 52% isolated yield (39.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.50 (s, 2H), 7.96 (d, *J* = 7.5 Hz, 2H), 7.58 (t, *J* = 7.4 Hz, 1H), 7.47 (t, *J* = 7.8 Hz, 2H), 7.26–7.21 (m, 4H), 7.10 (t, *J* = 7.5 Hz, 1H), 7.07–7.01 (m, 1H), 5.05 (t, *J* = 7.2 Hz, 1H), 3.79 (ddd, *J* = 25.4, 17.6, 7.8 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 160.6 (d, *J* = 246.5 Hz), 152.0, 149.7, 136.5, 133.5, 129.3 (d, *J* = 14.1 Hz), 129.1 (d, *J* = 4.3 Hz), 128.8 (d, *J* = 8.5 Hz), 128.7, 128.0, 124.4 (d, *J* = 3.5 Hz), 123.2, 116.0 (d, *J* = 22.2 Hz), 42.5, 39.3. ^{19}F NMR (471 MHz, $CDCl_3$) δ -105.6.



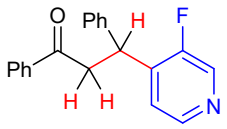
2-(3-Oxo-1,3-diphenylpropyl)isonicotinonitrile (21c):[2] yellow oil was obtained with 67% isolated yield (52.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.57 (d, *J* = 4.7 Hz, 1H), 7.95 (d, *J* = 7.7 Hz, 2H), 7.63–7.56 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 2H), 7.43 (d, *J* = 4.5 Hz, 1H), 7.34 (t, *J* = 7.3 Hz, 2H), 7.27 (d, *J* = 7.6 Hz, 1H), 7.24 (d, *J* = 7.8 Hz, 2H), 4.85 (t, *J* = 6.8 Hz, 1H), 3.78 (ddd, *J* = 26.2, 17.9, 8.2 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 154.9, 151.1, 141.2, 136.3, 134.0, 133.7, 129.2, 128.8, 128.1, 128.0, 127.8, 127.5, 126.4, 117.3, 45.0, 43.6.



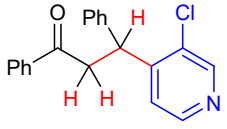
1,3-Diphenyl-3-(phthalazin-1-yl)propan-1-one (22c):[2] yellow oil was obtained with 47% isolated yield (39.7 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 9.36 (s, 1H), 8.26 (d, *J* = 8.1 Hz, 1H), 8.00 (d, *J* = 8.1 Hz, 2H), 7.88–7.83 (m, 1H), 7.83–7.74 (m, 2H), 7.51 (t, *J* = 7.0 Hz, 1H), 7.47 (d, *J* = 7.8 Hz, 2H), 7.41 (t, *J* = 7.7 Hz, 2H), 7.26 (t, *J* = 7.4 Hz, 2H), 7.17 (t, *J* = 6.9 Hz, 1H), 5.74 – 5.68 (m, 1H), 4.89 – 4.80 (m, 1H), 3.66 – 3.57 (m, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 198.6, 159.5, 150.7, 142.3, 136.9, 133.0, 132.6, 131.8, 128.9, 128.5, 128.2, 128.2, 127.0, 126.9, 125.7, 124.2, 44.9, 43.1.



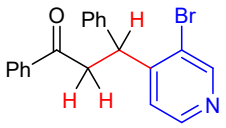
3-(3-methylpyridin-4-yl)-1,3-diphenylpropan-1-one (23c):[2] yellow oil was obtained with 56% isolated yield (42.4 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.36 (d, J = 4.8 Hz, 1H), 8.33 (s, 1H), 7.83 (d, J = 8.2 Hz, 2H), 7.27 – 7.21 (m, 4H), 7.18 (t, J = 6.6 Hz, 3H), 7.15 (d, J = 5.1 Hz, 1H), 4.95 (t, 1H), 3.69 (ddd, J = 23.9, 17.5, 7.3 Hz, 2H), 2.39 (s, 3H), 2.29 (s, 3H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.9, 151.1, 150.7, 147.5, 144.2, 142.0, 134.2, 132.2, 129.4, 128.7, 128.1, 128.0, 126.8, 121.0, 44.1, 41.6, 21.6, 16.6.



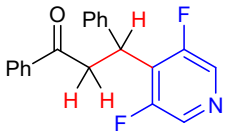
3-(3-fluoropyridin-4-yl)-1,3-diphenylpropan-1-one (24c):[2] yellow oil was obtained with 44% isolated yield (33.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.41 (d, *J* = 2.4 Hz, 1H), 8.35 (d, *J* = 6.2 Hz, 1H), 8.02 – 7.95 (m, 2H), 7.61 (t, *J* = 9.2 Hz, 1H), 7.49 (t, *J* = 9.6 Hz, 2H), 7.38 – 7.30 (m, 4H), 7.29 – 7.22 (m, 2H), 5.10 (t, *J* = 9.2 Hz, 1H), 3.84 (ddd, *J* = 32.0, 22.1, 9.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.8, 157.8 (d, *J* = 318.7 Hz), 145.8 (d, *J* = 6.4 Hz), 141.1, 139.6 (d, *J* = 14.8 Hz), 138.3 (d, *J* = 31.4 Hz), 136.5, 133.4, 128.9, 128.7, 128.0, 127.7, 127.2, 123.2 (d, *J* = 2.0 Hz), 42.8, 39.4. ^{19}F NMR (471 MHz, $CDCl_3$) δ -130.5.



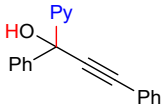
3-(3-chloropyridin-4-yl)-1,3-diphenylpropan-1-one (25c):[2] yellow oil was obtained with 48% isolated yield (38.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (s, 1H), 8.38 (d, J = 5.1 Hz, 1H), 7.96 – 7.92 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.45 (t, J = 7.8 Hz, 2H), 7.32 – 7.27 (m, 2H), 7.27 – 7.21 (m, 3H), 7.18 (d, J = 5.1 Hz, 1H), 5.23 (t, J = 7.4 Hz, 1H), 3.80 – 3.70 (m, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.6, 150.2, 149.8, 147.7, 140.6, 136.4, 133.5, 132.2, 128.8, 128.7, 128.0, 128.0, 127.1, 122.8, 43.3, 42.0.



3-(3-bromopyridin-4-yl)-1,3-diphenylpropan-1-one (26c):[2] yellow oil was obtained with 47% isolated yield (43.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.70 (s, 1H), 8.42 (s, 1H), 7.97 – 7.90 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.32 – 7.28 (m, 2H), 7.27 – 7.21 (m, 3H), 7.17 (d, J = 4.8 Hz, 1H), 5.21 (t, J = 7.3 Hz, 1H), 3.75 (d, J = 7.4 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 196.5, 152.4, 151.8, 148.3, 140.6, 136.4, 133.4, 128.8, 128.7, 128.1, 128.0, 127.1, 124.2, 123.4, 44.4, 43.5.

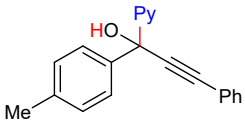


3-(3,5-difluoropyridin-4-yl)-1,3-diphenylpropan-1-one (27c):[2] yellow oil was obtained with 47% isolated yield (38.1 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.26 (s, 2H), 7.99 – 7.93 (m, 2H), 7.57 (t, J = 7.4 Hz, 1H), 7.46 (t, J = 7.8 Hz, 2H), 7.39 (d, J = 7.6 Hz, 2H), 7.32 (t, J = 7.6 Hz, 2H), 7.26 – 7.22 (m, 1H), 5.20 – 5.15 (m, 1H), 3.96 (ddd, J = 24.0, 18.2, 7.6 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 197.0, 157.6 (d, J = 255.3 Hz), 140.4, 136.3, 134.6 (d, J = 4.8 Hz), 134.4 (d, J = 4.8 Hz), 133.5, 128.9, 128.7, 128.0, 127.7, 127.3, 42.0, 35.9. ^{19}F NMR (471 MHz, $CDCl_3$) δ -128.0.

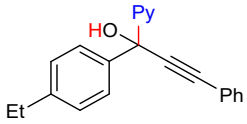


1,3-Diphenyl-1-(pyridin-4-yl)prop-2-yn-1-ol (1d): white powder was obtained with 81% isolated yield (57.7 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.55 (d, J = 4.6 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H), 7.59 (d, J = 5.8 Hz, 2H), 7.58–7.55 (m, 2H), 7.46–7.42 (m, 3H), 7.38 (t, J = 7.7 Hz, 2H), 7.29 (t, J = 7.1 Hz, 1H), 7.23 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.1, 150.1, 145.4, 131.9, 129.5, 129.2, 128.8, 128.1, 126.0, 122.1, 121.0, 92.3, 86.4, 72.9. HRMS (ESI) calcd for $C_{20}H_{16}NO$ [M + H]

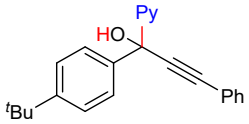
$^{+}$: 286.1226; found: 286.1224.



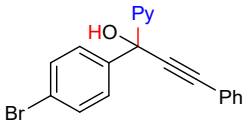
3-Phenyl-1-(pyridin-4-yl)-1-(p-tolyl)prop-2-yn-1-ol (2d): white powder was obtained with 84% isolated yield (59.8 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.55 (s, 2H), 7.62–7.53 (m, 4H), 7.51 (d, J = 8.0 Hz, 2H), 7.46–7.40 (m, 3H), 7.21–7.14 (m, 3H), 2.27 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.4, 150.0, 142.5, 137.3, 131.9, 129.4, 129.3, 129.2, 126.0, 122.2, 121.0, 92.5, 86.3, 72.8, 21.0. HRMS (ESI) calcd for $C_{21}H_{17}NO$ [M + H] $^{+}$: 300.1383; found: 300.1383. m. p.: 180 - 184 °C.



1-(4-Ethylphenyl)-3-phenyl-1-(pyridin-4-yl)prop-2-yn-1-ol (3d): white powder was obtained with 73% isolated yield (57.1 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.54 (d, J = 6.1 Hz, 2H), 7.60–7.57 (m, 2H), 7.56 (d, J = 2.2 Hz, 1H), 7.56–7.54 (m, 1H), 7.54 (t, J = 1.9 Hz, 1H), 7.52 (t, J = 1.9 Hz, 1H), 7.44 (d, J = 2.1 Hz, 2H), 7.43 (d, J = 1.5 Hz, 1H), 7.20 (d, J = 8.4 Hz, 2H), 7.16 (s, 1H), 2.57 (q, J = 7.6 Hz, 2H), 1.15 (t, J = 7.6 Hz, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.3, 150.0, 143.6, 142.7, 131.9, 129.4, 129.2, 128.1, 126.1, 122.2, 121.0, 92.5, 86.2, 72.8, 28.1, 16.0. HRMS (ESI) calcd for $C_{22}H_{19}NO$ [M + H] $^{+}$: 314.1539; found: 314.1539. m. p.: 157 - 163 °C.

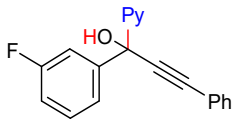


1-(4-(*Tert*-butyl)phenyl)-3-phenyl-1-(pyridin-4-yl)prop-2-yn-1-ol (4d): white powder was obtained with 76% isolated yield (64.8 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.54 (d, J = 6.1 Hz, 2H), 7.62–7.59 (m, 2H), 7.57–7.53 (m, 4H), 7.45–7.41 (m, 3H), 7.39 (d, J = 8.5 Hz, 2H), 7.16 (s, 1H), 1.25 (s, 9H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.2, 150.5, 150.1, 142.5, 131.9, 129.4, 129.2, 125.8, 125.5, 122.2, 121.0, 92.5, 86.2, 72.8, 34.6, 31.5. HRMS (ESI) calcd for $C_{24}H_{23}NO$ [M + H] $^{+}$: 342.1852; found: 324.1852. m. p.: 187 - 192 °C.

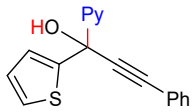


1-(4-Bromophenyl)-3-phenyl-1-(pyridin-4-yl)prop-2-yn-1-ol (5d): white powder was obtained with 67% isolated yield (60.8 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.59 (d, J = 6.1 Hz, 2H), 7.60–7.58 (m, 2H), 7.58–7.55 (m, 6H), 7.45–7.43 (m, 3H), 7.37 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ

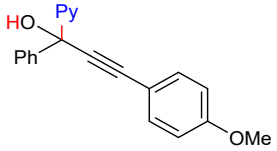
154.7, 150.1, 144.8, 131.9, 131.7, 129.6, 129.2, 128.4, 121.9, 121.4, 120.9, 91.7, 86.7, 72.6. HRMS (ESI) calcd for $C_{20}H_{14}BrNO$ $[M + H]^+$: 364.0332; found: 364.0332. m. p.: 175 - 179 °C.



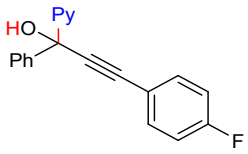
1-(3-Fluorophenyl)-3-phenyl-1-(pyridin-4-yl)prop-2-yn-1-ol (6d): white powder was obtained with 61% isolated yield (46.3 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.60 (d, J = 4.1 Hz, 2H), 7.64–7.60 (m, 2H), 7.60–7.56 (m, 2H), 7.50–7.39 (m, 7H), 7.13 (t, J = 8.0 Hz, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 162.4 (d, J = 244.0 Hz), 154.5, 150.2, 148.3 (d, J = 6.7 Hz), 132.0, 130.9 (d, J = 8.2 Hz), 129.6, 129.2, 122.3 (d, J = 2.6 Hz), 121.9, 120.9, 115.0 (d, J = 21.0 Hz), 112.8 (d, J = 23.1 Hz), 91.7, 86.6, 72.5. ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.9. HRMS (ESI) calcd for $C_{20}H_{14}FNO$ $[M + H]^+$: 304.1132; found: 304.1129. m. p.: 159 - 162 °C.



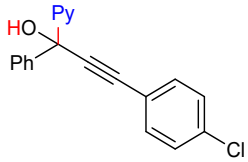
3-Phenyl-1-(pyridin-4-yl)-1-(thiophen-2-yl)prop-2-yn-1-ol (7d): white powder was obtained with 86% isolated yield (62.5 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.59 (d, J = 6.0 Hz, 2H), 7.67–7.61 (m, 2H), 7.59–7.54 (m, 3H), 7.50–7.47 (m, 1H), 7.46 –7.41 (m, 3H), 7.16 (d, J = 3.6 Hz, 1H), 7.00 – 6.95 (m, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.5, 150.5, 150.2, 131.9, 129.6, 129.2, 127.2, 126.7, 125.3, 121.8, 120.7, 91.7, 85.8, 70.5. HRMS (ESI) calcd for $C_{18}H_{13}NOS$ $[M + H]^+$: 292.0791; found: 292.0792. m. p.: 171 -175 °C.



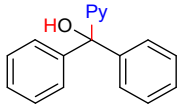
3-(4-Methoxyphenyl)-1-phenyl-1-(pyridin-4-yl)prop-2-yn-1-ol (8d): white powder was obtained with 72% isolated yield (56.7 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.54 (d, J = 6.1 Hz, 2H), 7.65–7.61 (m, 2H), 7.60–7.57 (m, 2H), 7.52–7.48 (m, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.27 (t, J = 7.3 Hz, 1H), 7.17 (s, 1H), 6.99 (d, J = 8.9 Hz, 2H), 3.79 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 160.1, 155.4, 150.1, 145.6, 133.5, 128.7, 128.0, 126.1, 121.0, 114.8, 114.0, 90.9, 86.5, 72.9, 55.7. HRMS (ESI) calcd for $C_{21}H_{17}NO_2$ $[M + H]^+$: 316.1332; found: 316.1333. m. p.: 177 - 180 °C.



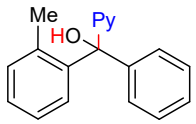
3-(4-Fluorophenyl)-1-phenyl-1-(pyridin-4-yl)prop-2-yn-1-ol (9d): white powder was obtained with 65% isolated yield (49.2 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.55 (d, J = 6.1 Hz, 2H), 7.66–7.61 (m, 4H), 7.61–7.58 (m, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.31–7.25 (m, 3H), 7.25 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 167.4 (d, J = 247.9 Hz), 159.8, 154.9 (d, J = 15.9 Hz), 150.1, 139.1, 133.5, 132.8, 130.8, 125.8, 123.3 (d, J = 3.3 Hz), 121.2 (d, J = 22.2 Hz), 96.8, 90.1, 77.7. ^{19}F NMR (471 MHz, $CDCl_3$) δ -111.9. HRMS (ESI) calcd for $C_{20}H_{14}FNO$ [M + H] $^{+}$:304.1132; found: 304.1134. m. p.: 155 - 159 ^{o}C.



3-(4-Chlorophenyl)-1-phenyl-1-(pyridin-4-yl)prop-2-yn-1-ol (10d): white powder was obtained with 58% isolated yield (46.3 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.55 (d, J = 6.0 Hz, 2H), 7.63 (d, J = 7.9 Hz, 2H), 7.59 (d, J = 7.0 Hz, 4H), 7.50 (d, J = 8.5 Hz, 2H), 7.37 (t, J = 7.7 Hz, 2H), 7.32–7.23 (m, 2H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 155.0, 150.1, 145.2, 134.2, 133.7, 129.4, 128.8, 128.1, 126.0, 121.0, 121.0, 93.4, 85.3, 72.9. HRMS (ESI) calcd for $C_{20}H_{14}ClNO$ [M + H] $^{+}$: 320.0837; found: 320.0838. m. p.: 185 - 188 ^{o}C.

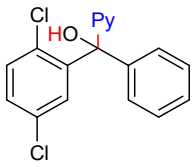


Diphenyl(pyridin-4-yl)methanol (11d): [2c, 2d] white powder was obtained with 76% isolated yield (49.7 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.51 (d, J = 5.8 Hz, 2H), 7.36–7.31 (m, 4H), 7.30–7.26 (m, 2H), 7.25–7.22 (m, 2H), 7.22 – 7.19 (m, 4H), 6.74 (s, 1H). ^{13}C NMR (126 MHz, MDSO-d_6) δ 161.2, 154.4, 151.5, 133.0, 132.8, 132.3, 127.8, 85.1.

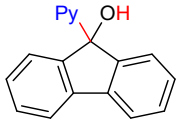


Phenyl(pyridin-4-yl)(o-tolyl)methanol (12d):[2e] white powder was obtained with 55% isolated yield (37.9 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.52 (d, J = 6.1 Hz, 2H), 7.34 (t, J = 7.4 Hz, 2H), 7.31–7.25 (m, 1H), 7.24–7.17 (m, 6H), 7.05 (t, J = 6.6 Hz, 1H), 6.75 (s, 1H), 6.57 (d, J = 7.5 Hz, 1H),

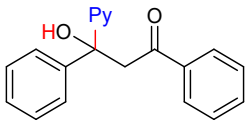
2.04 (s, 3H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 156.5, 149.6, 146.5, 144.4, 138.4, 132.8, 129.1, 128.3, 128.1, 127.6, 127.4, 125.2, 122.9, 81.4, 22.1.



(2,5-Dichlorophenyl)(phenyl)(pyridin-4-yl)methanol (13d): white oil was obtained with 59% isolated yield (48.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.53 (d, J = 5.3 Hz, 2H), 7.37–7.32 (m, 4H), 7.30–7.24 (m, 3H), 7.24–7.17 (m, 3H), 6.81 (s, 1H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 153.6, 149.6, 144.0, 143.2, 132.9, 132.6, 131.4, 131.0, 129.5, 128.4, 128.1, 127.4, 122.5, 81.4. HRMS (EI) calcd for $C_{18}H_{13}Cl_2NO$ [M + H] $^{+}$:330.0447; found: 330.0447.



9-(Pyridin-4-yl)-9H-fluoren-9-ol (14d):[2f] white powder was obtained with 63% isolated yield (40.8 mg). ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.43 (d, J = 5.9 Hz, 2H), 7.86 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 5.9 Hz, 2H), 7.30–7.24 (m, 4H), 7.20 (d, J = 6.0 Hz, 2H), 6.61 (s, 1H). ^{13}C NMR (126 MHz, DMSO-d_6) δ 154.6, 150.6, 149.9, 139.7, 129.4, 128.7, 125.0, 120.8, 82.3.

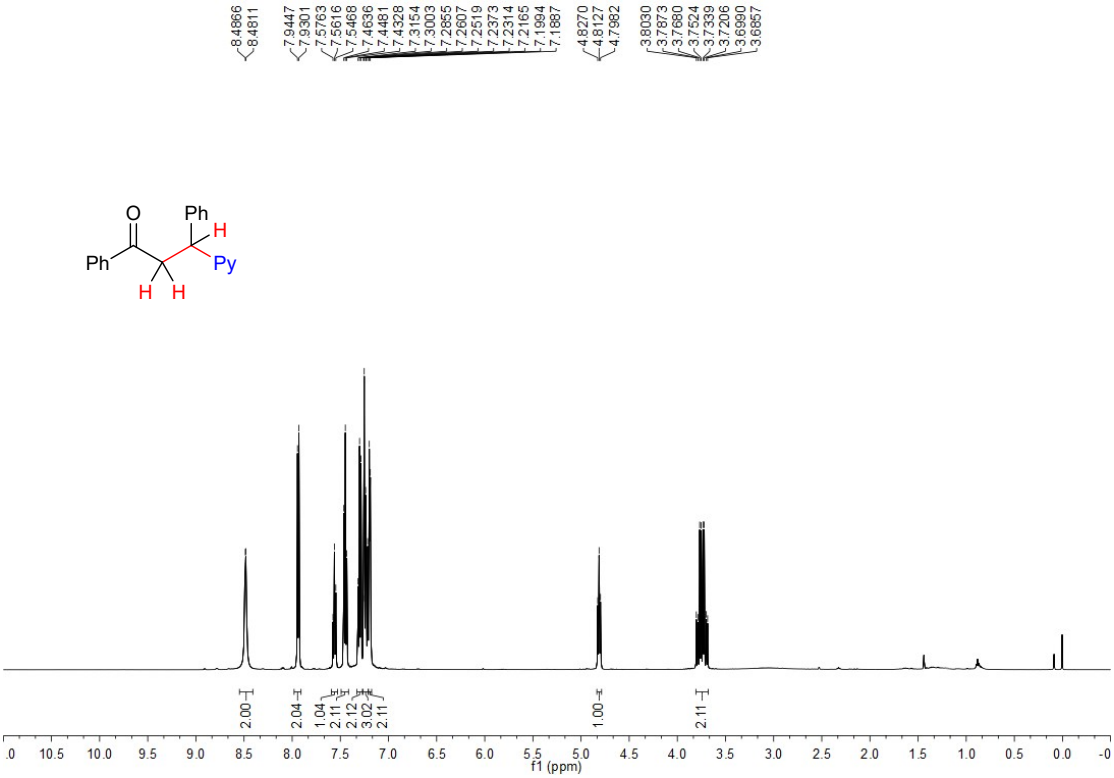


3-Hydroxy-1,3-diphenyl-3-(pyridin-4-yl)propan-1-one (15d): yellow oil was obtained with 47% isolated yield (35.6 mg). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.54 (s, 2H), 7.95 (d, J = 7.6 Hz, 2H), 7.63 (t, J = 7.4 Hz, 1H), 7.50 (t, J = 7.7 Hz, 2H), 7.43–7.37 (m, 4H), 7.32 (t, J = 7.6 Hz, 2H), 7.24 (d, J = 7.2 Hz, 1H), 5.48 (s, 1H), 3.92 (q, J = 17.9 Hz, 2H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 200.4, 156.3, 149.6, 144.8, 136.4, 134.2, 128.9, 128.6, 128.1, 127.5, 125.5, 120.8, 76.6, 47.5. HRMS (ESI) calcd for $C_{20}H_{17}NO_2$ [M + H] $^{+}$: 304.1332; found: 304.1332.

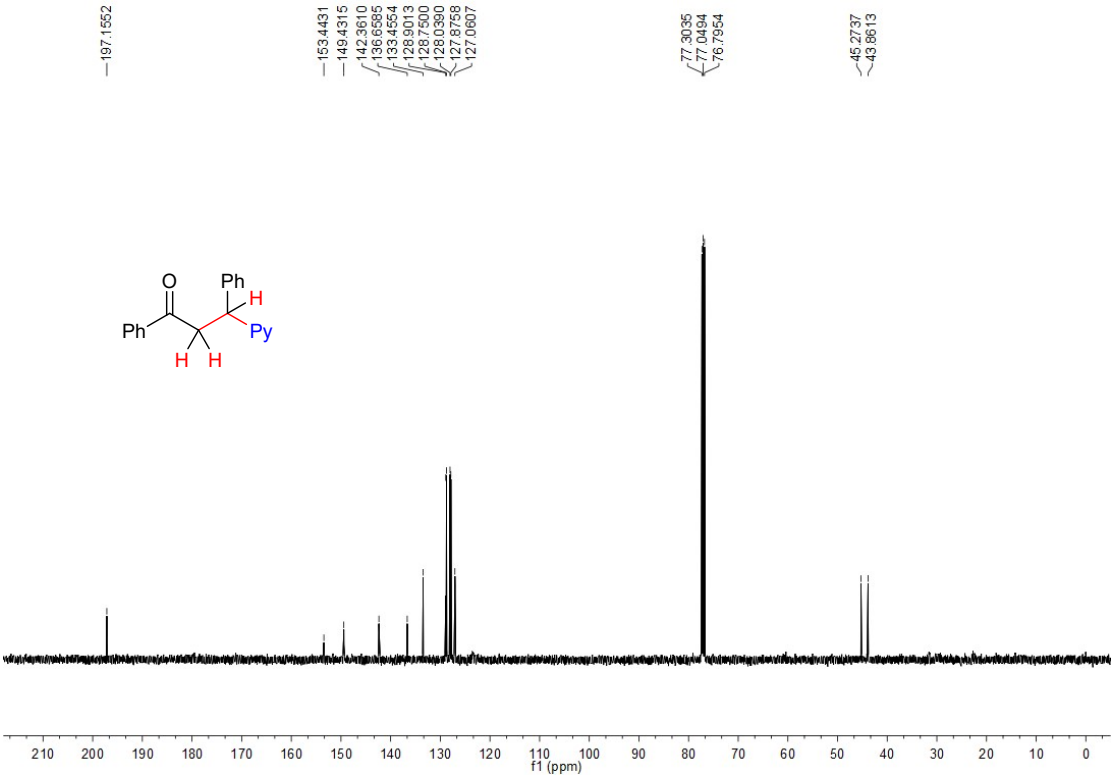
7. Copies of product NMR spectra

1c

^{1}H NMR

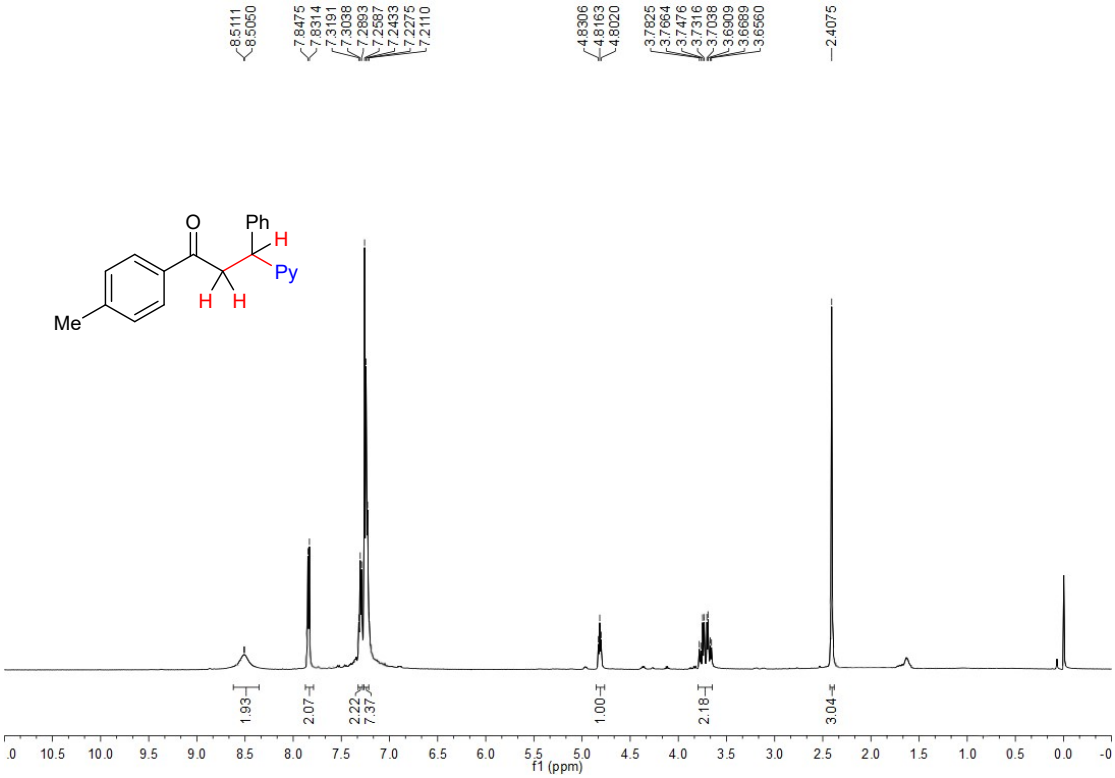


^{13}C NMR

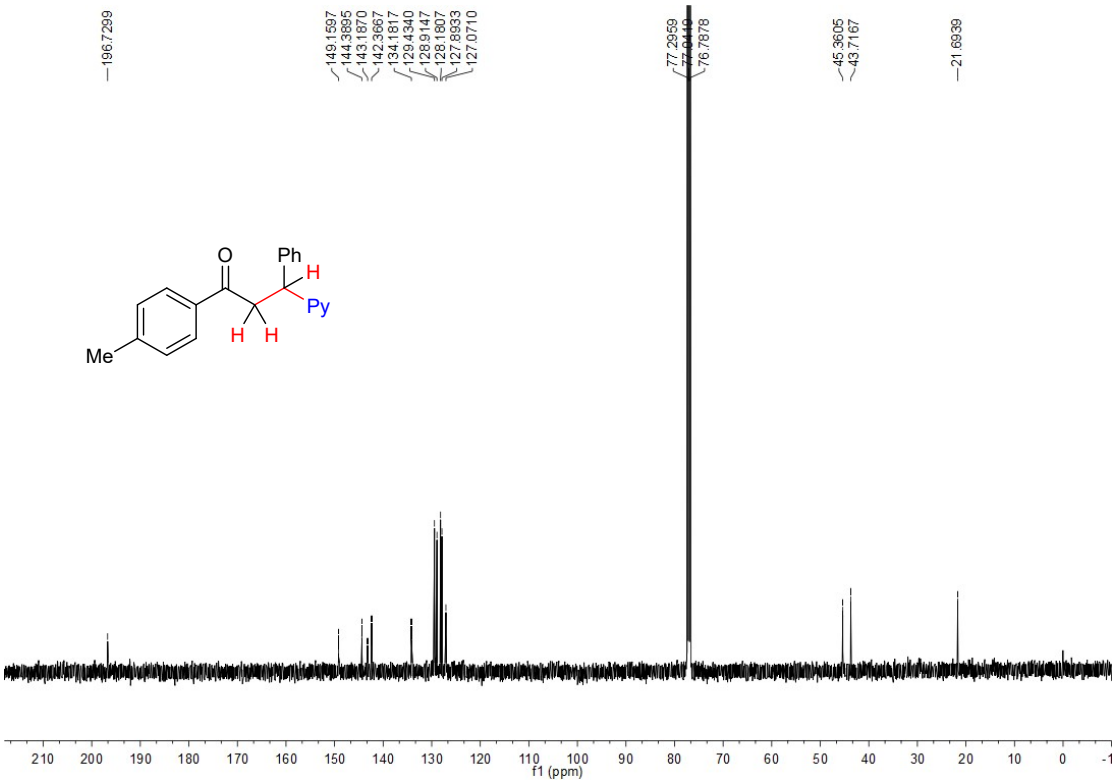


2c

^{1}H NMR

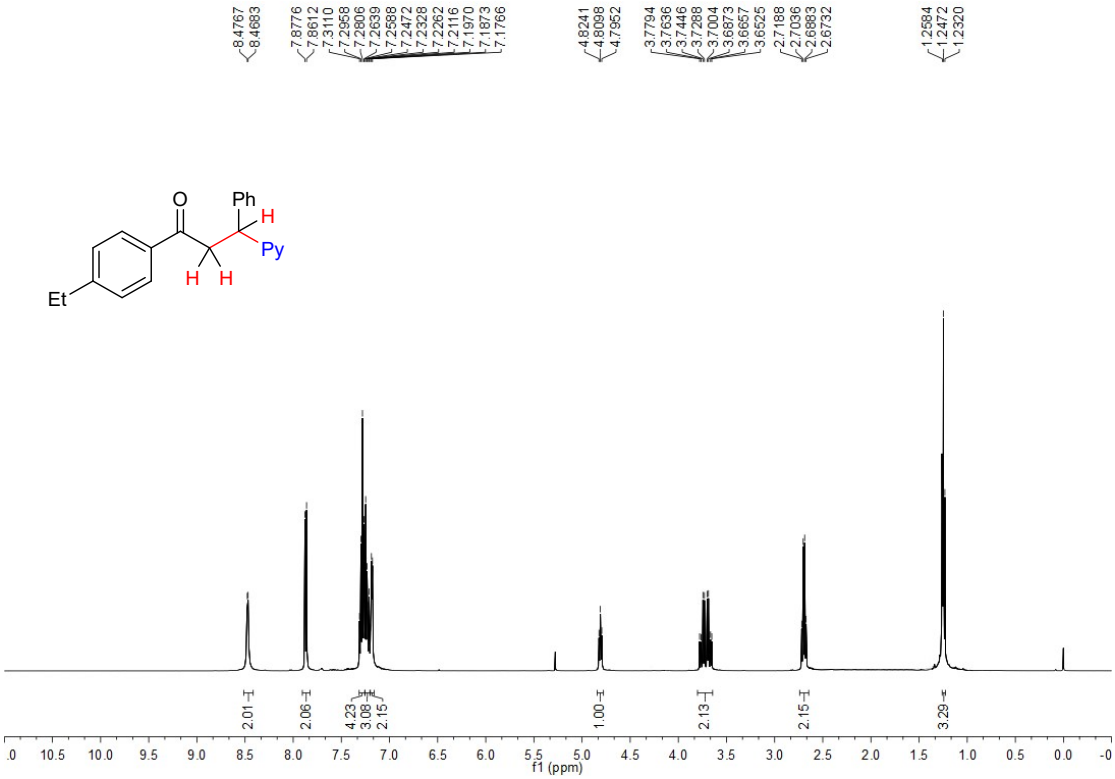


^{13}C NMR

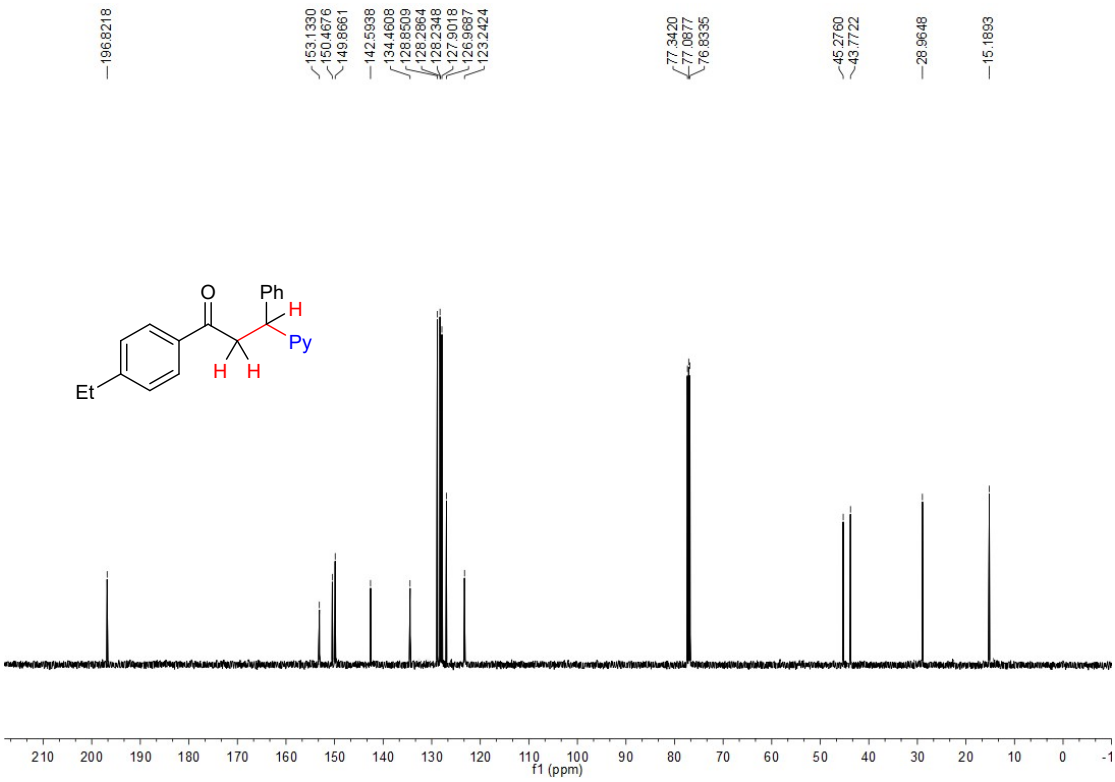


3c

^{1}H NMR

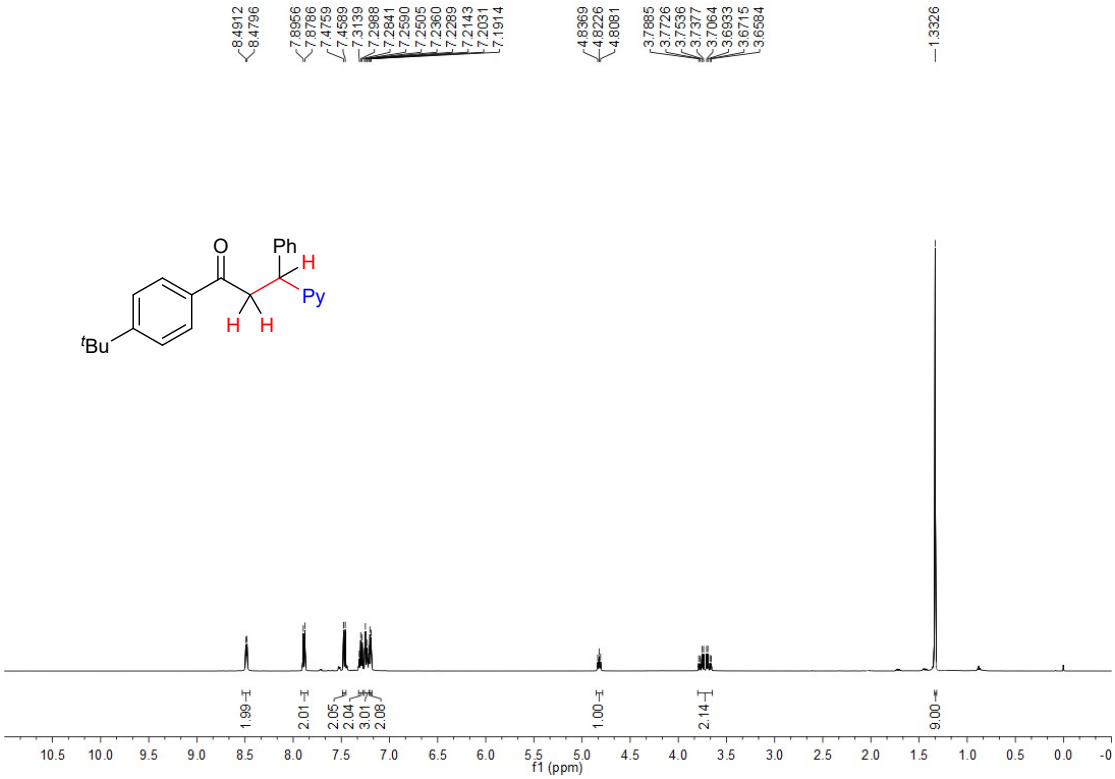


^{13}C NMR

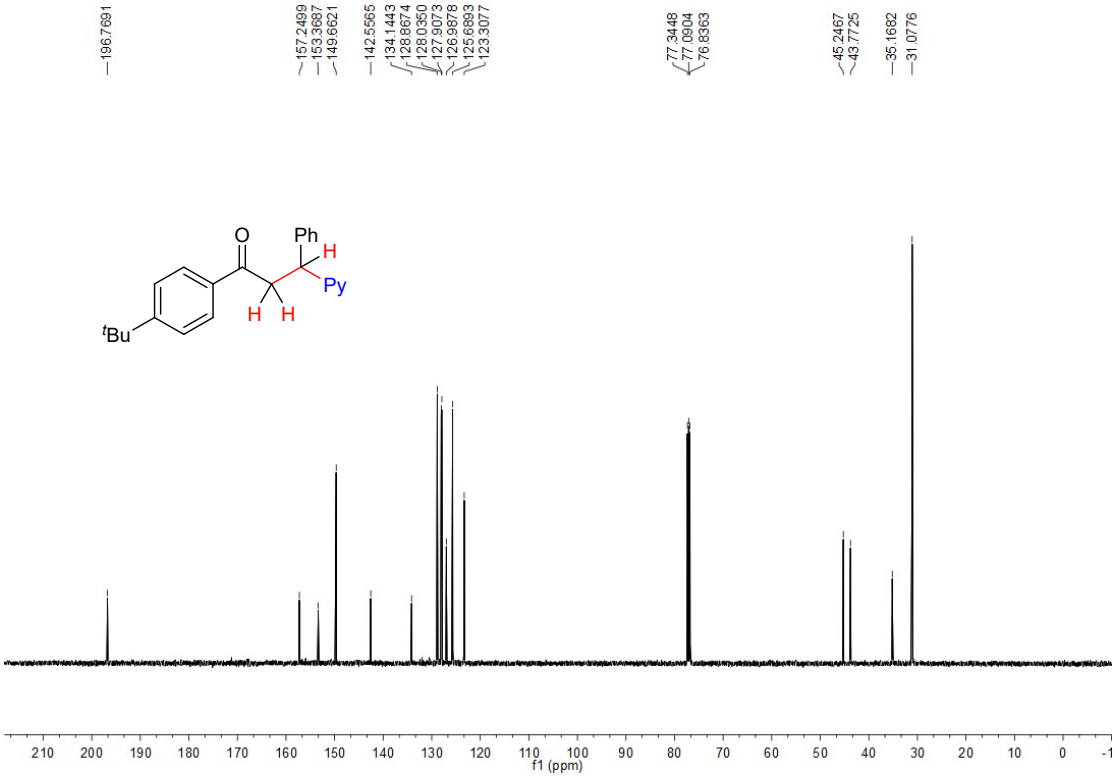


4c

^{1}H NMR

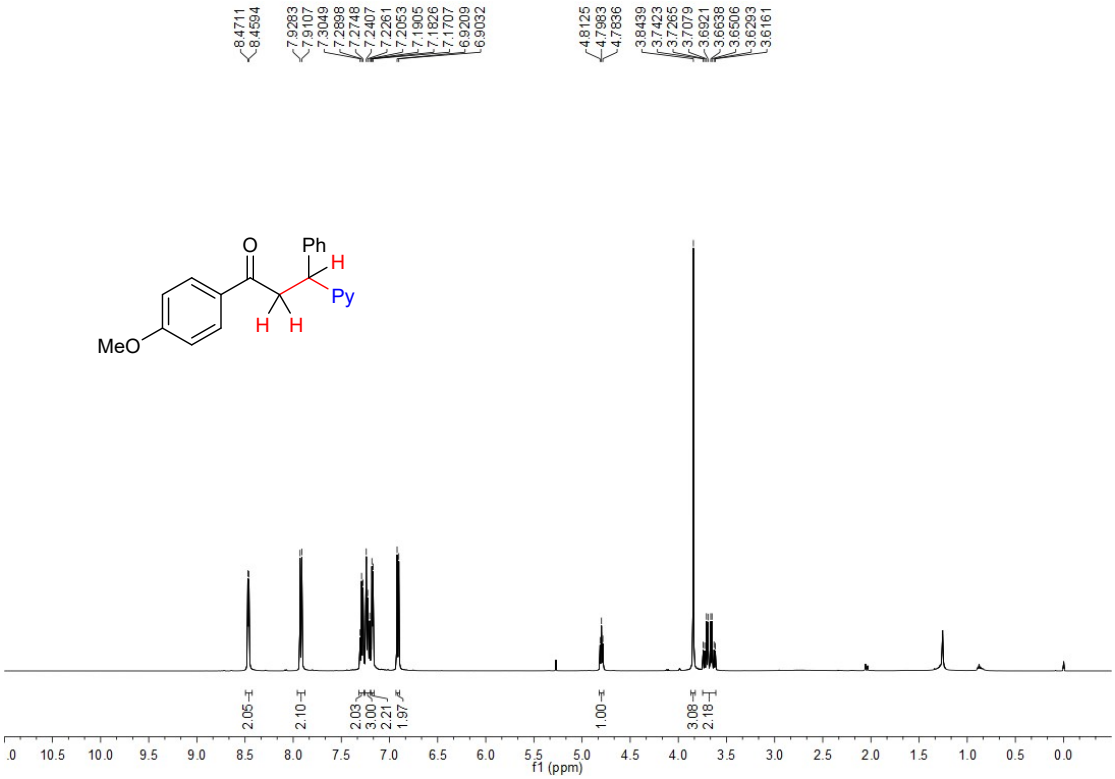


^{13}C NMR

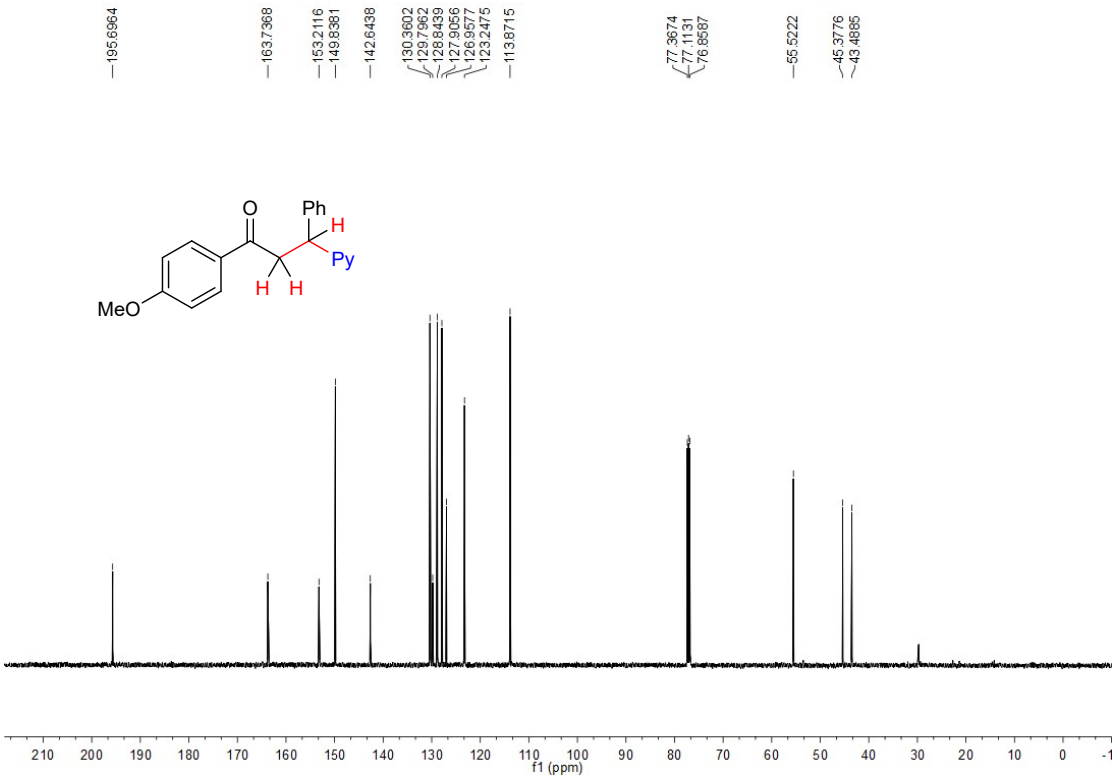


5c

^{1}H NMR

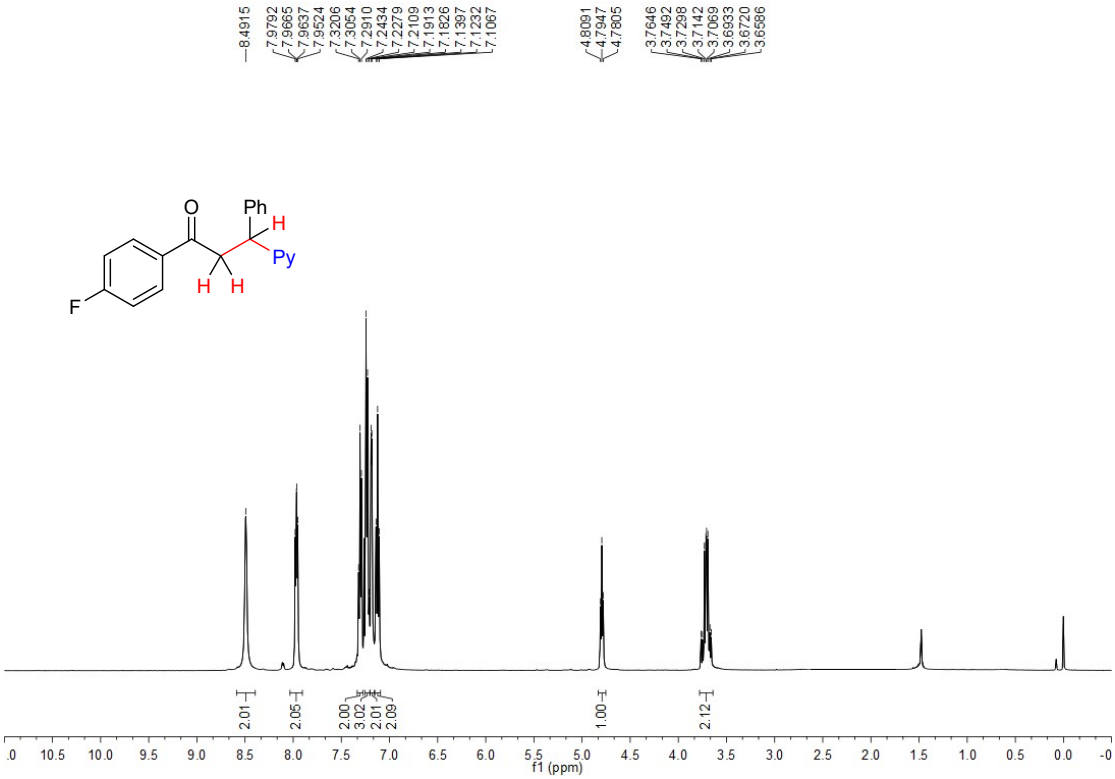


^{13}C NMR

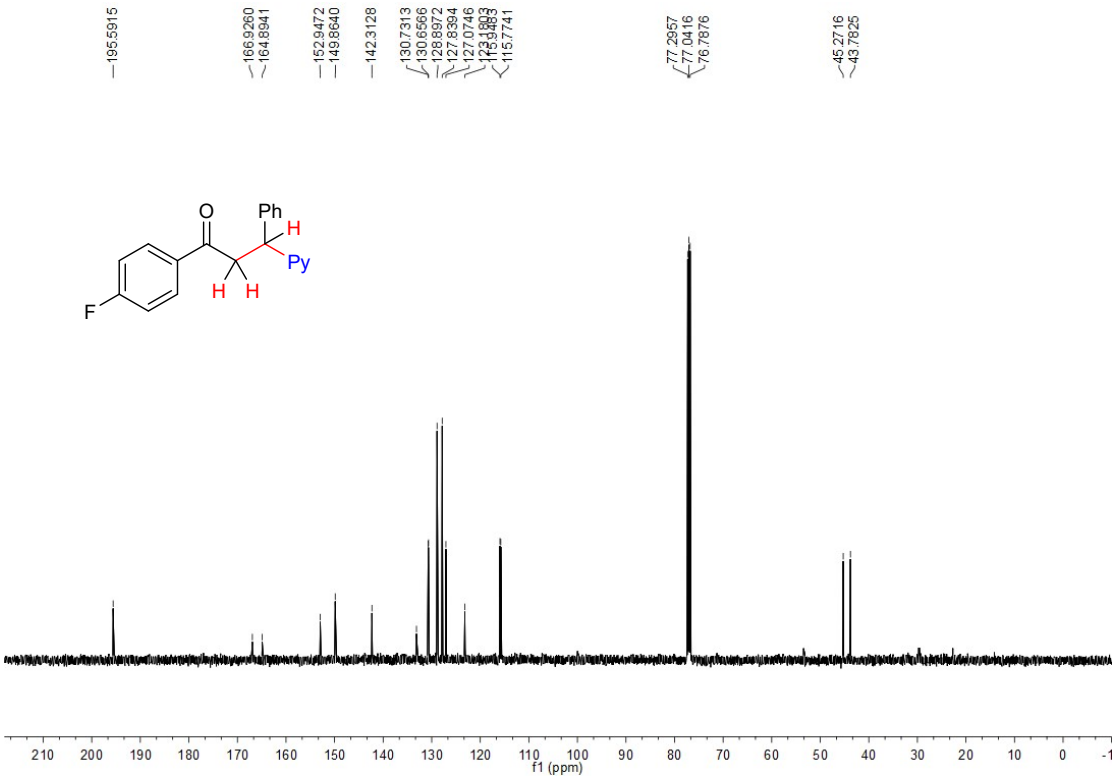


6c

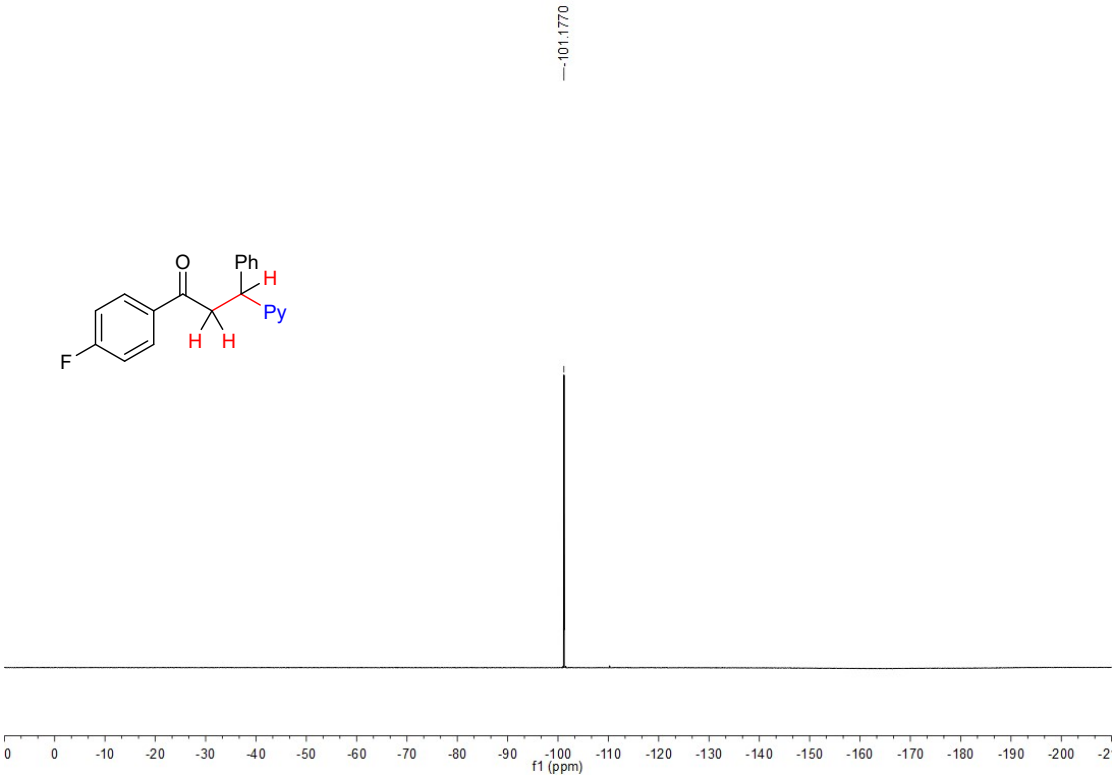
^{1}H NMR



^{13}C NMR

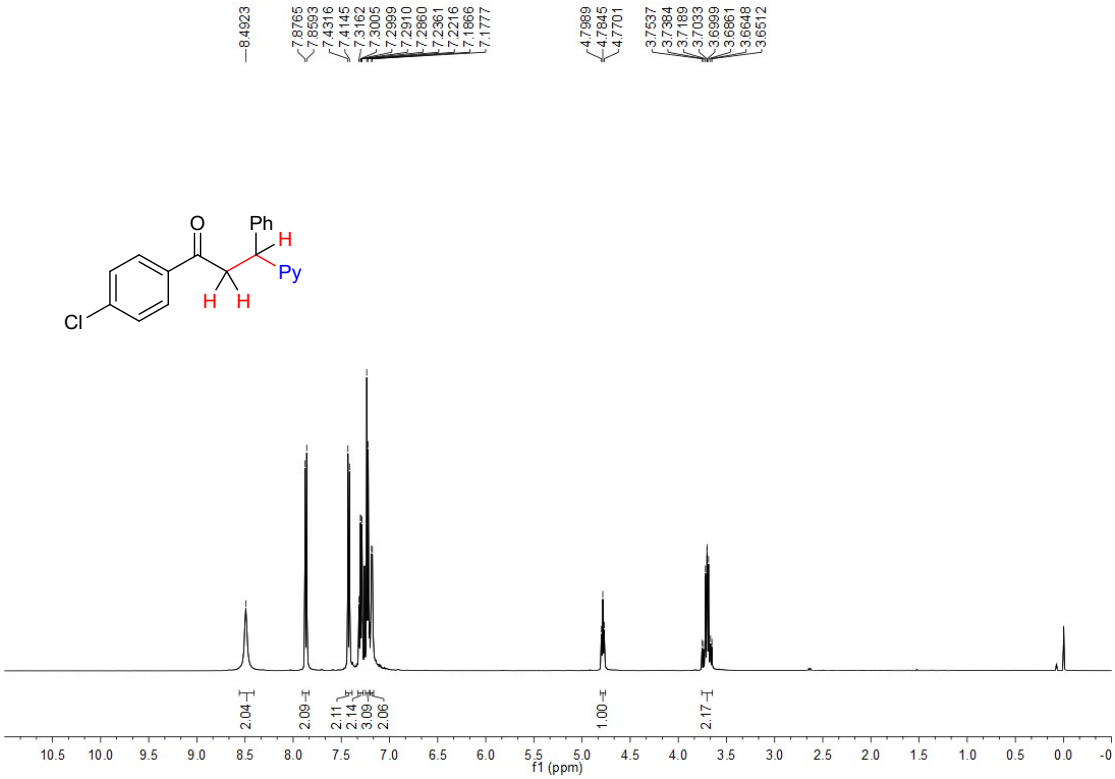


^{19}F NMR

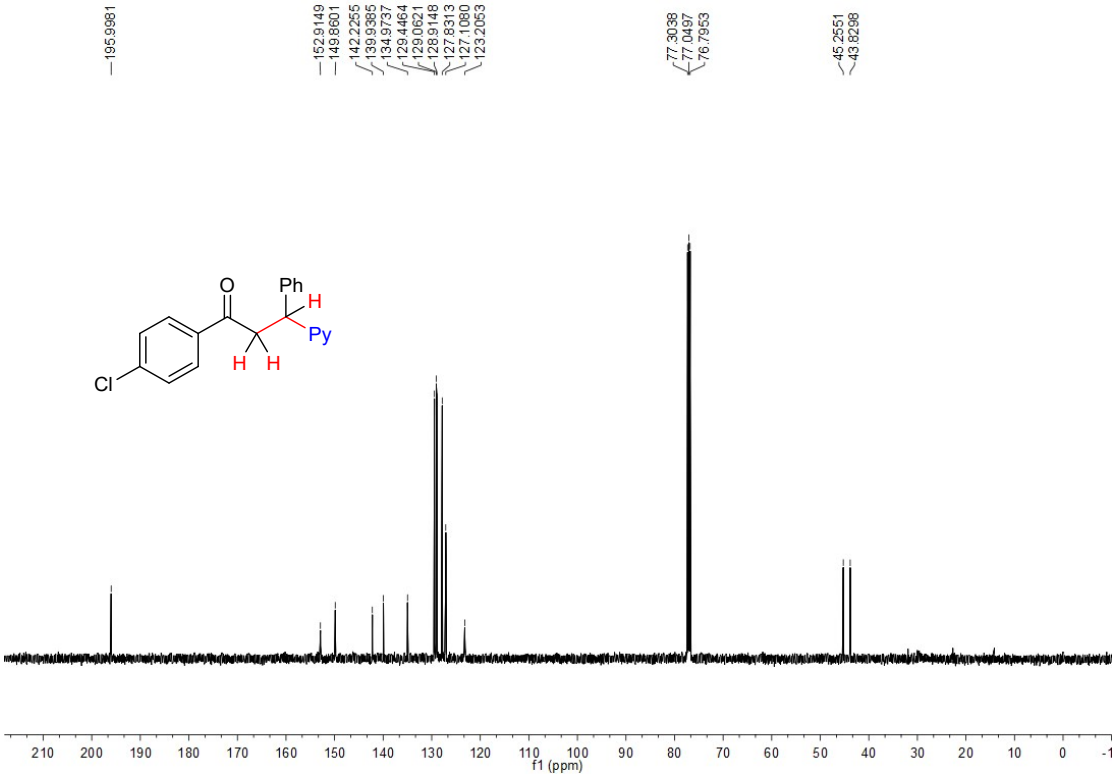

-101.770
O
Ph
H
Py
H H
F
0 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -2
f1 (ppm)

7c

^{1}H NMR

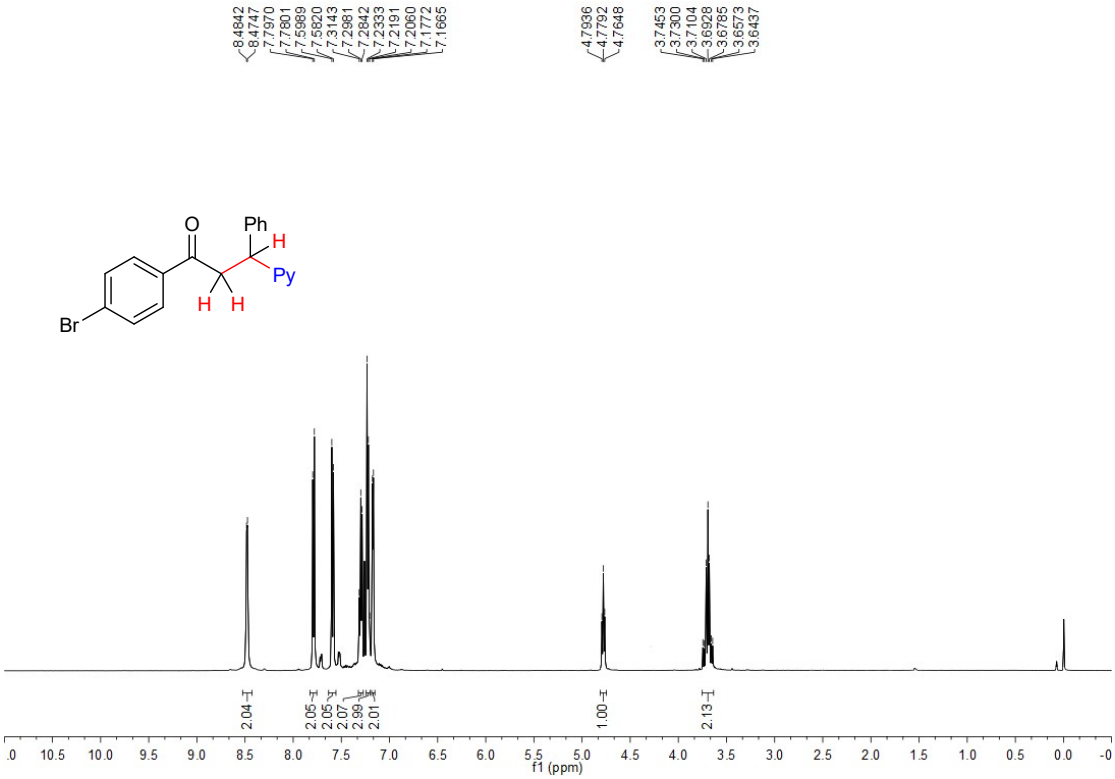


^{13}C NMR

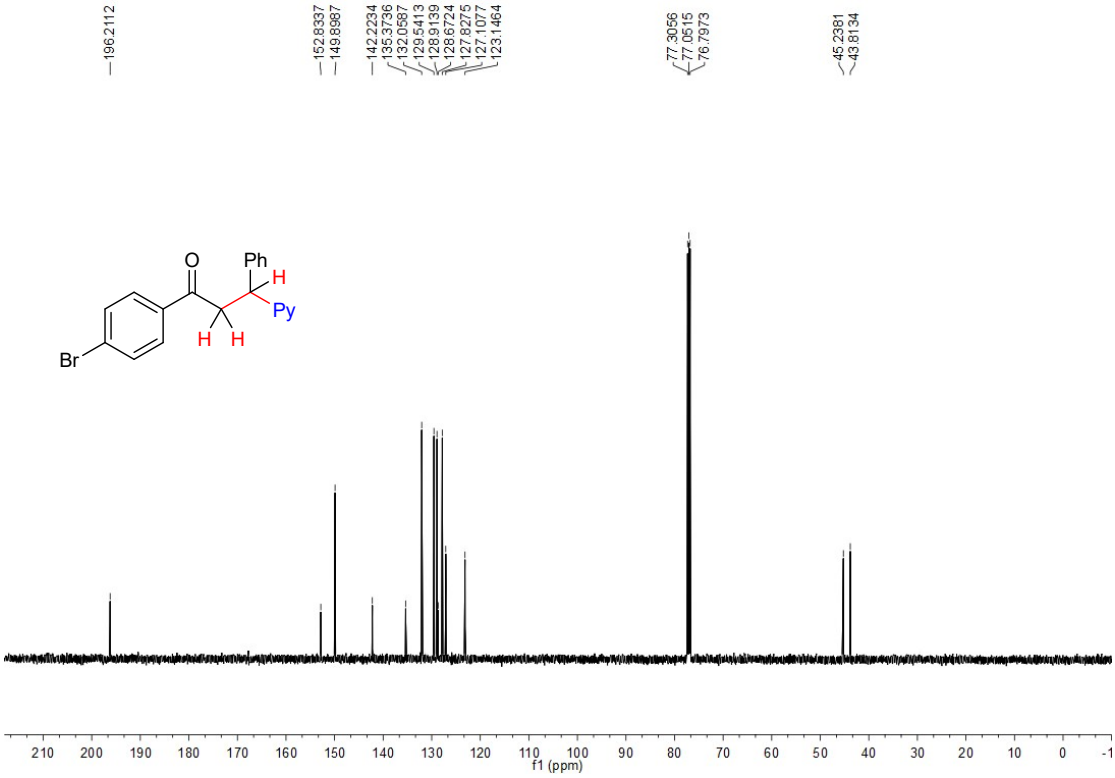


8c

^{1}H NMR

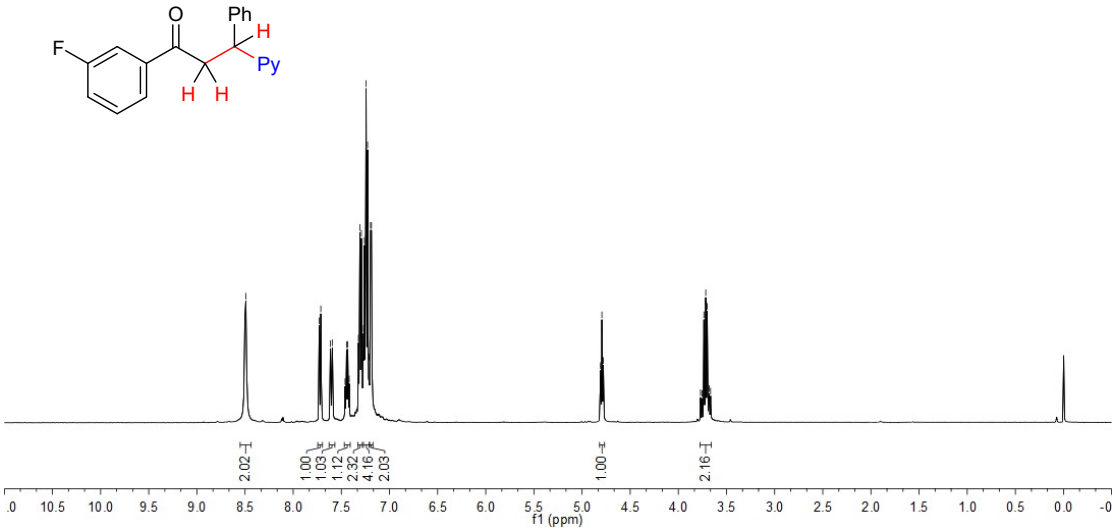


^{13}C NMR

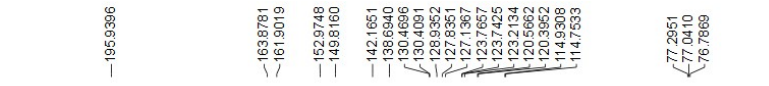


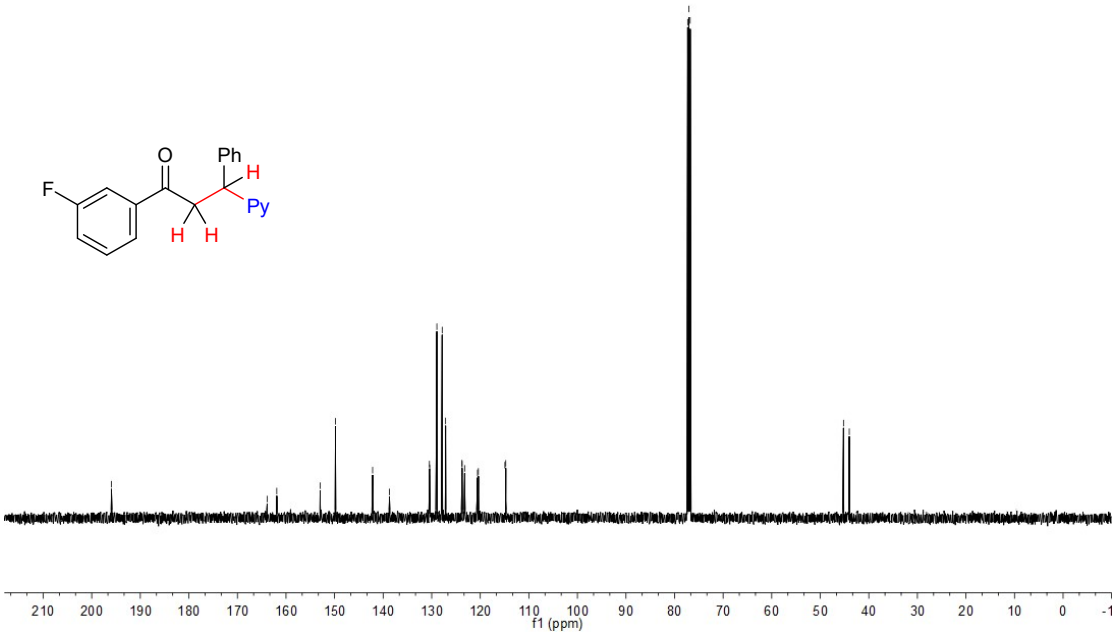
9c

^{1}H NMR

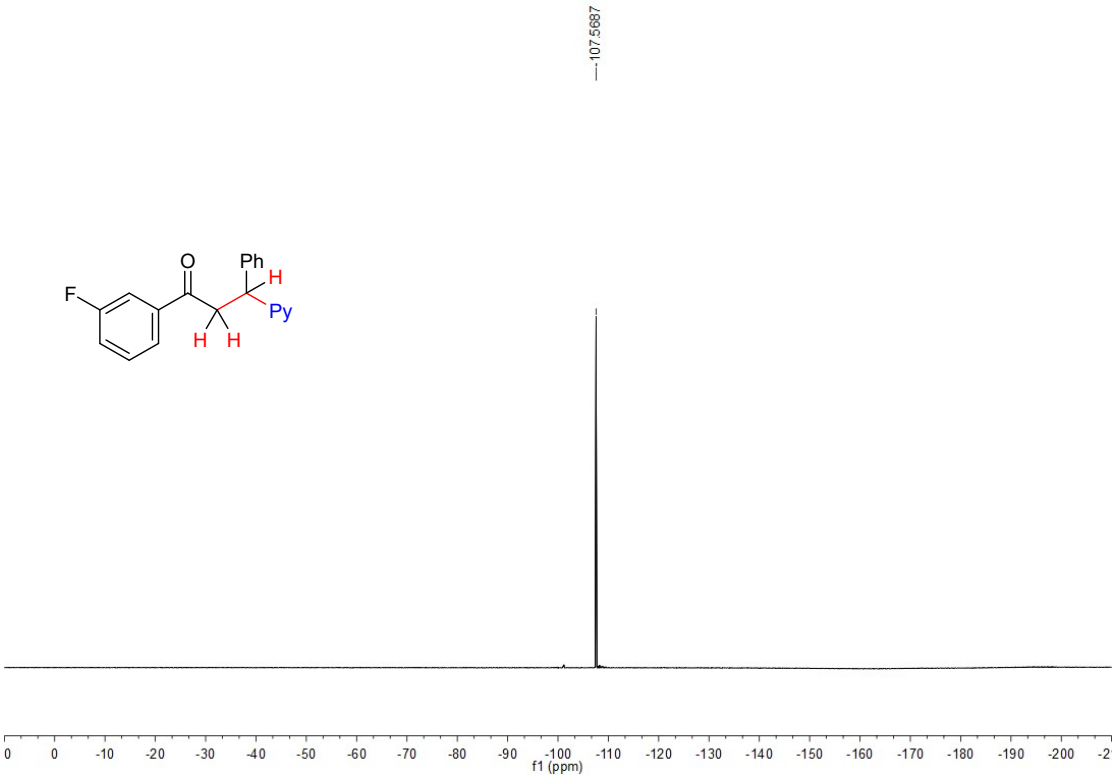


^{13}C NMR





^{19}F NMR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H
F
Py
H
H
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0
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-50
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-100
-110
-120
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-140
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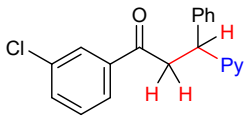
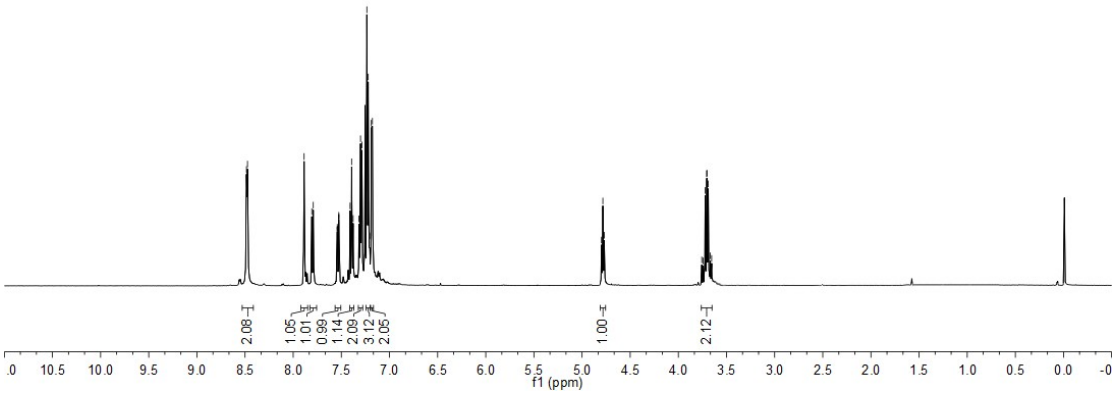
-160
-170
-180
-190
-200
-2
f1 (ppm)

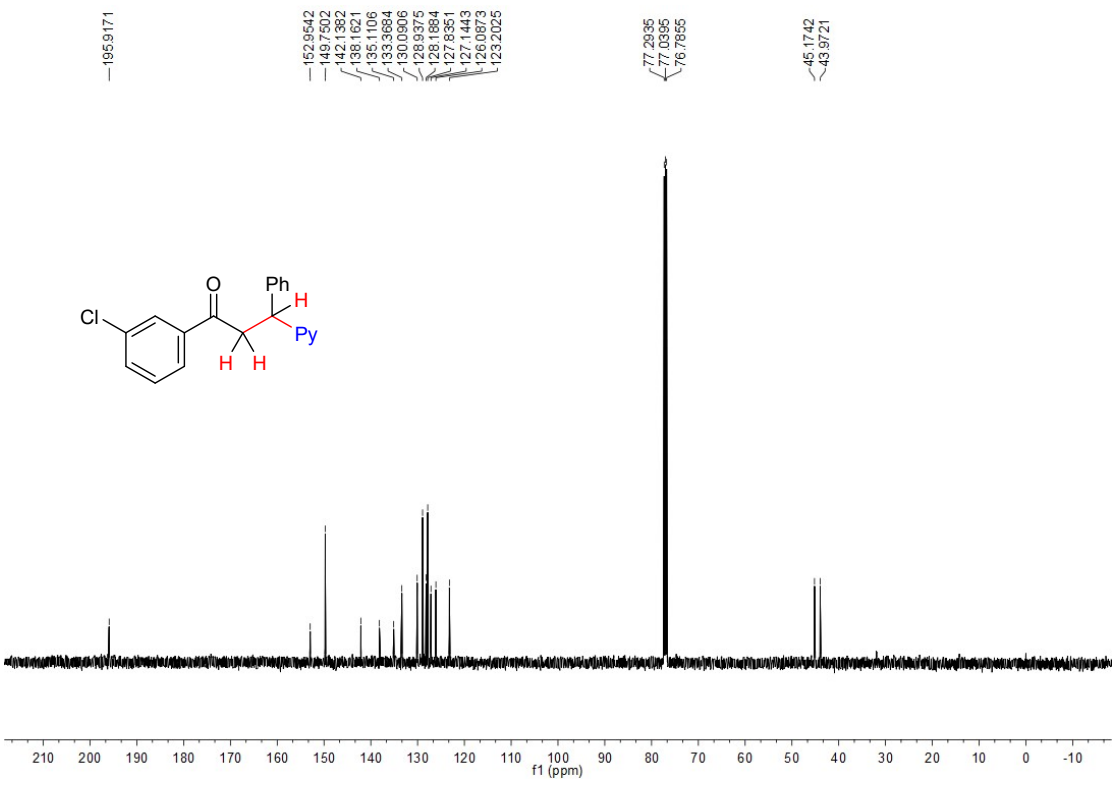
10c

^{1}H NMR



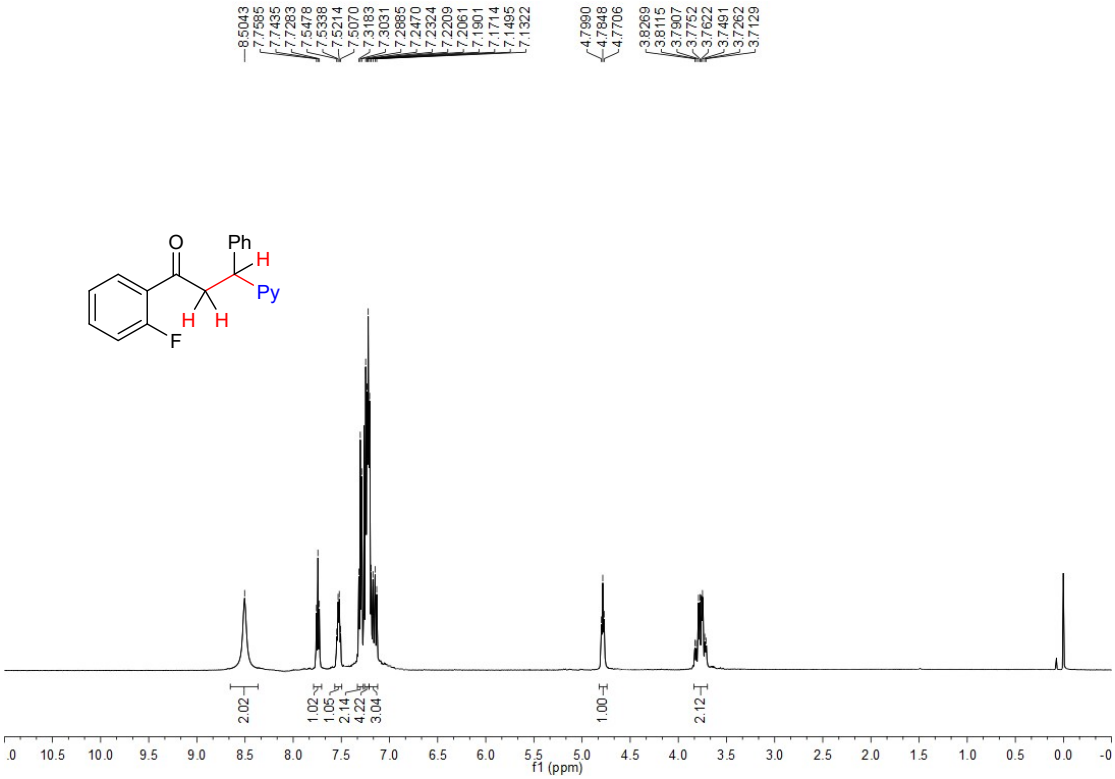


^{13}C NMR

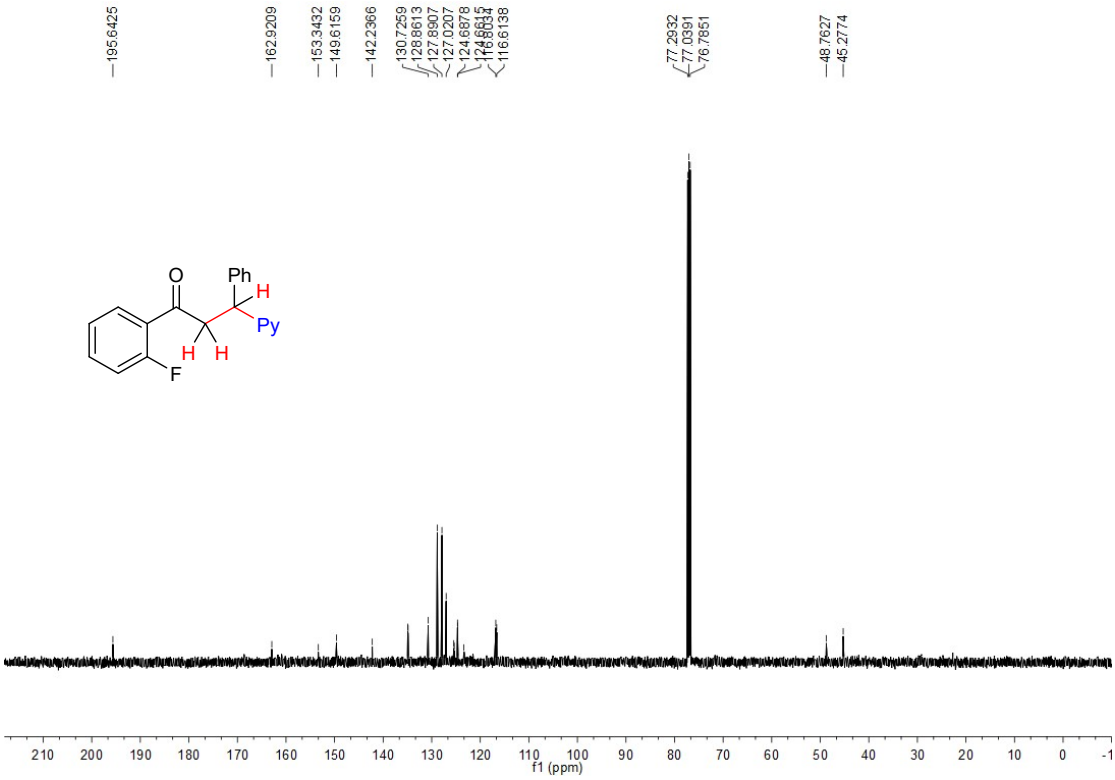


11c

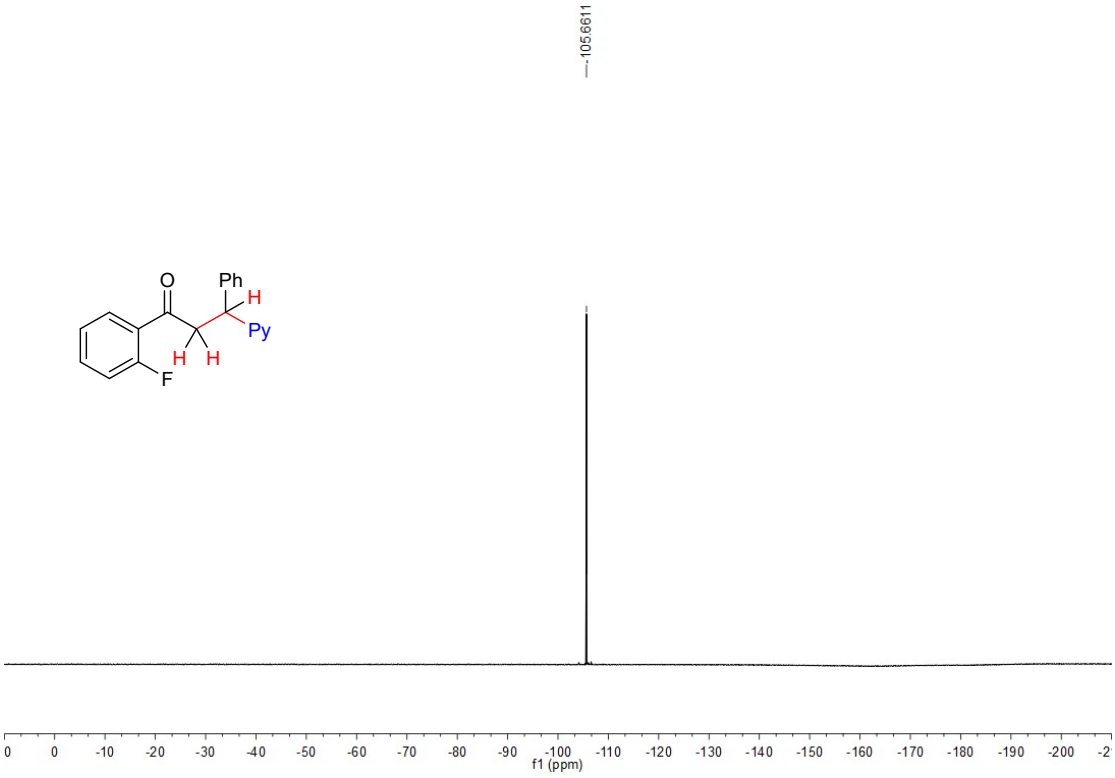
^{1}H NMR



^{13}C NMR



^{19}F NMR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Py
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H
F
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-170
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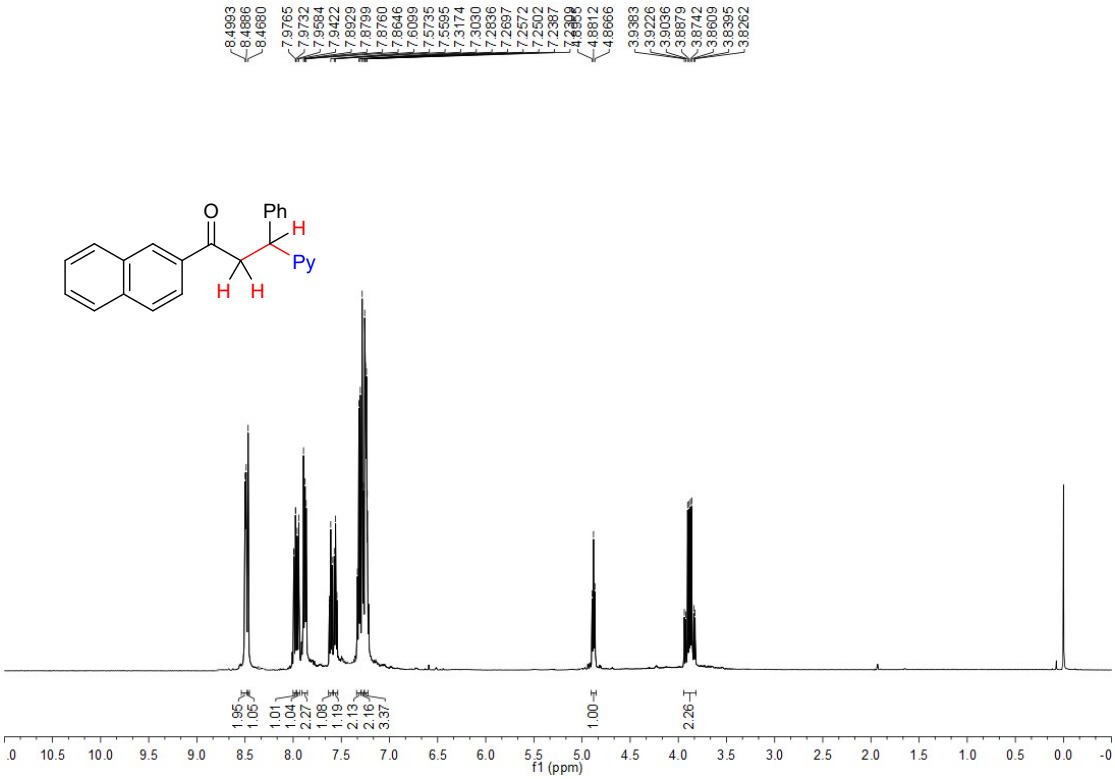
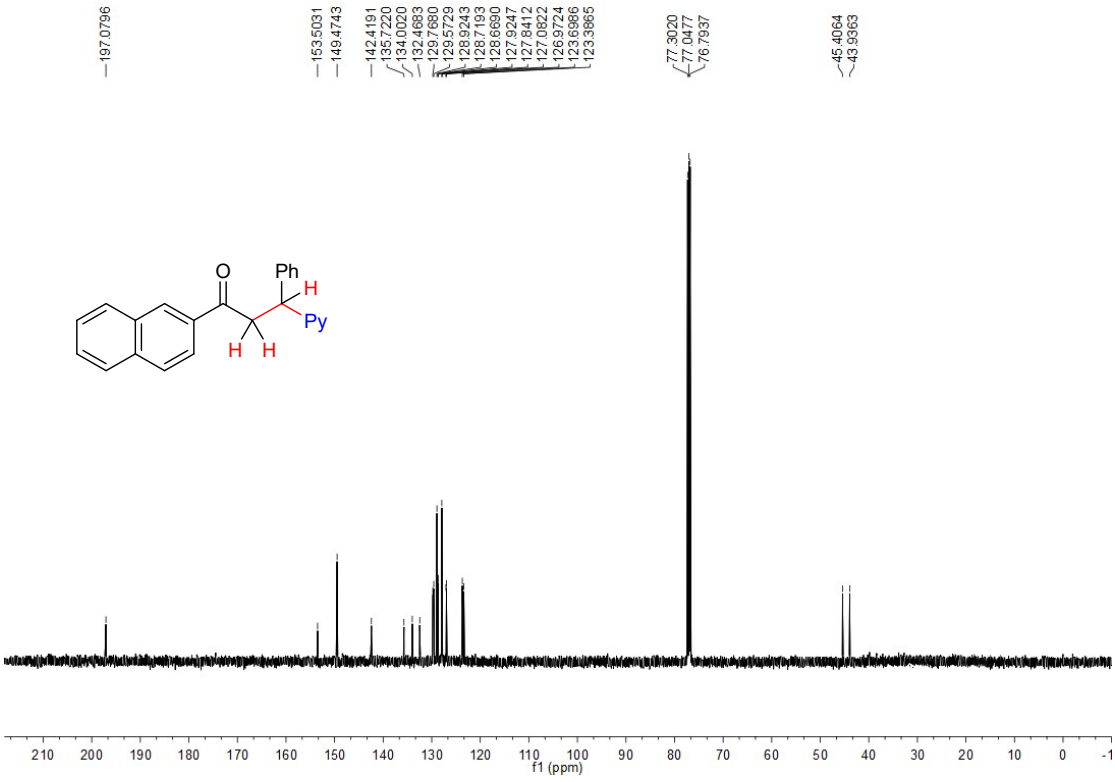
-190
-200
-2
f1 (ppm)

12c

^{1}H NMR

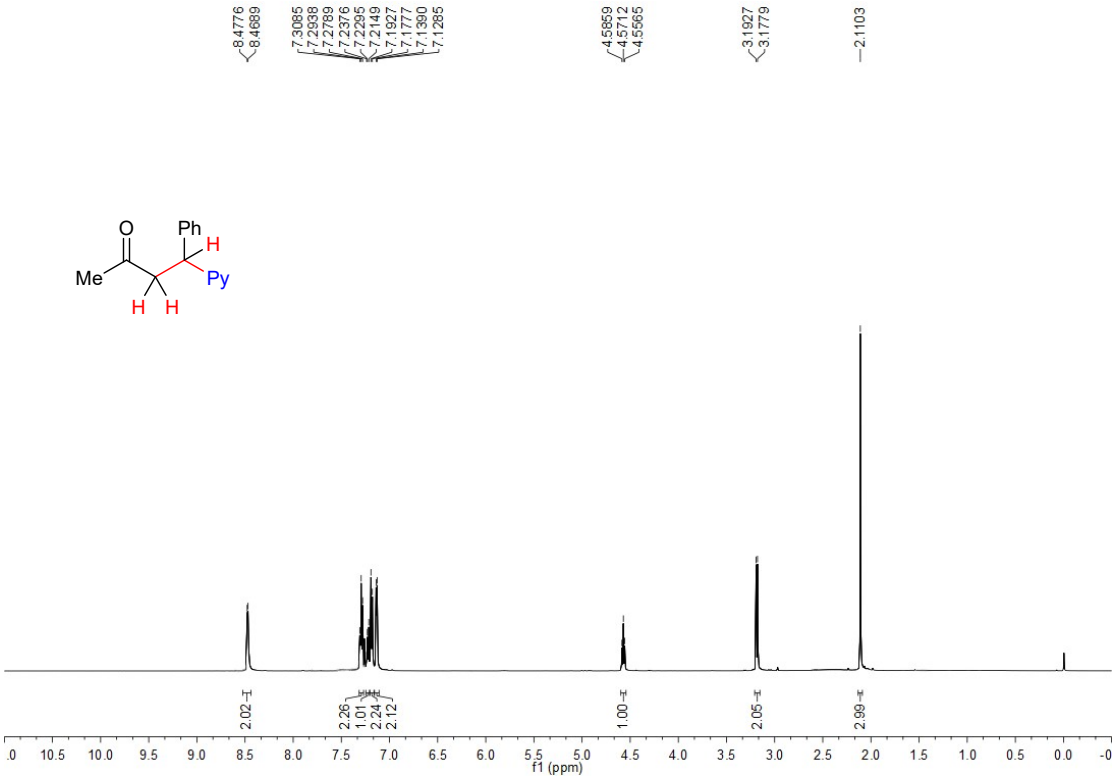


^{13}C NMR

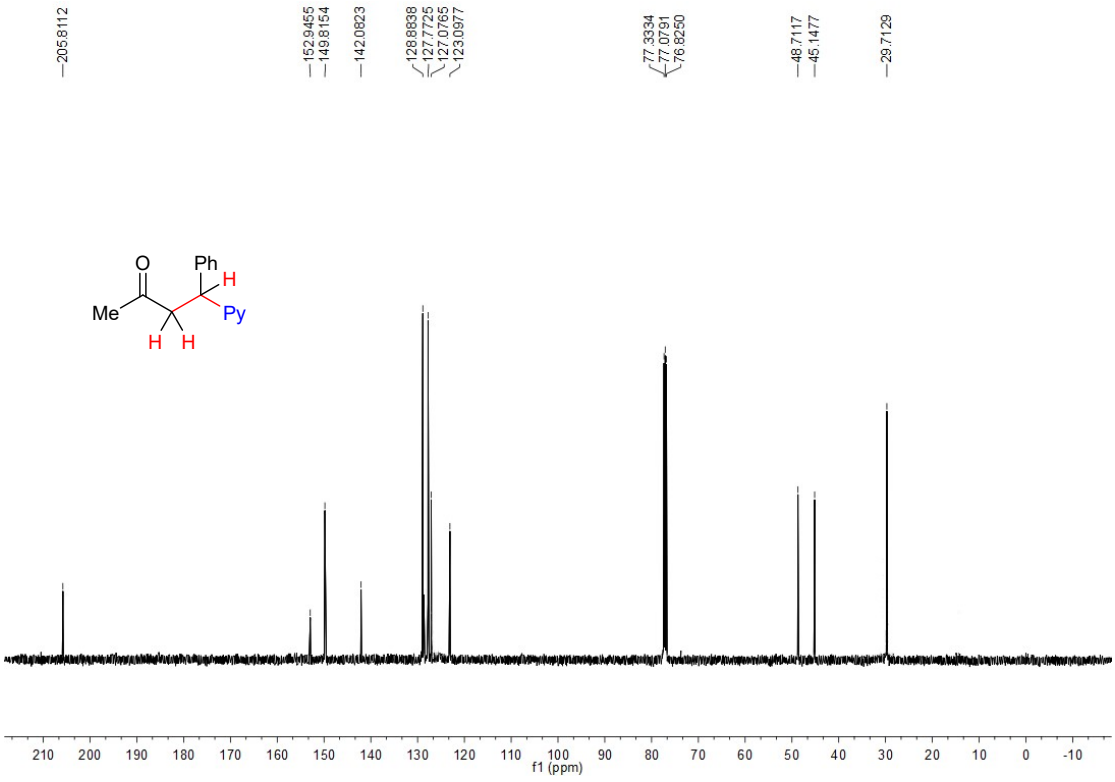


13c

^{1}H NMR

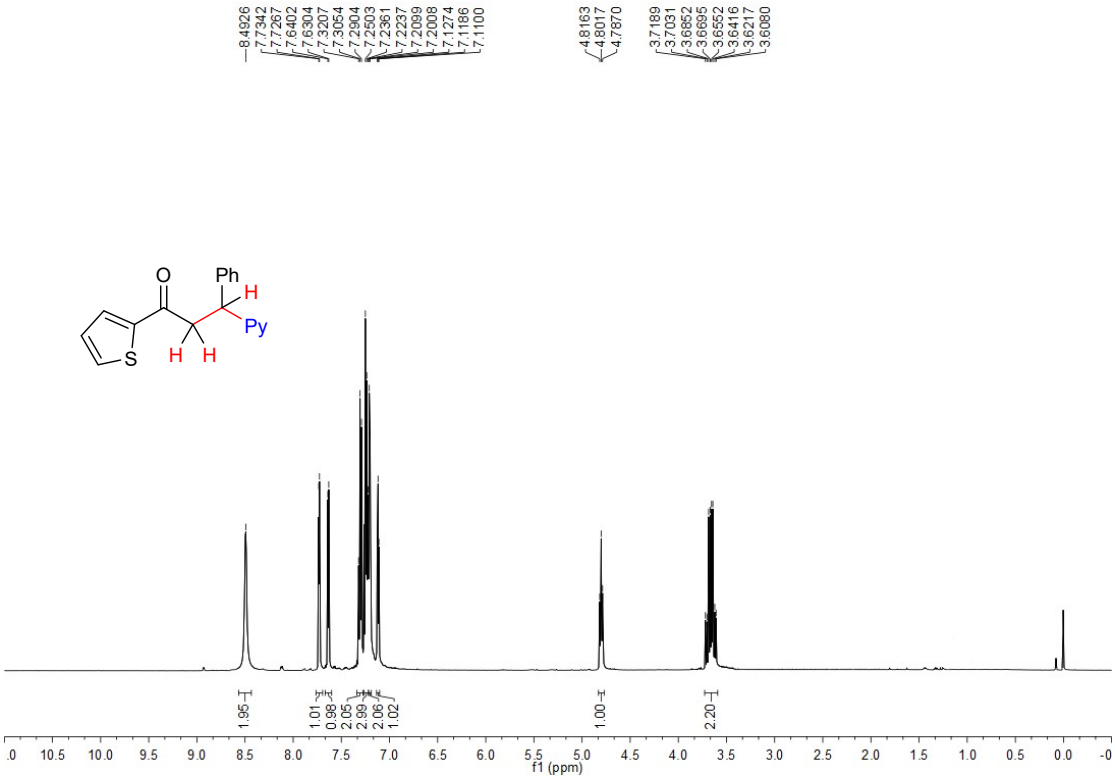


^{13}C NMR

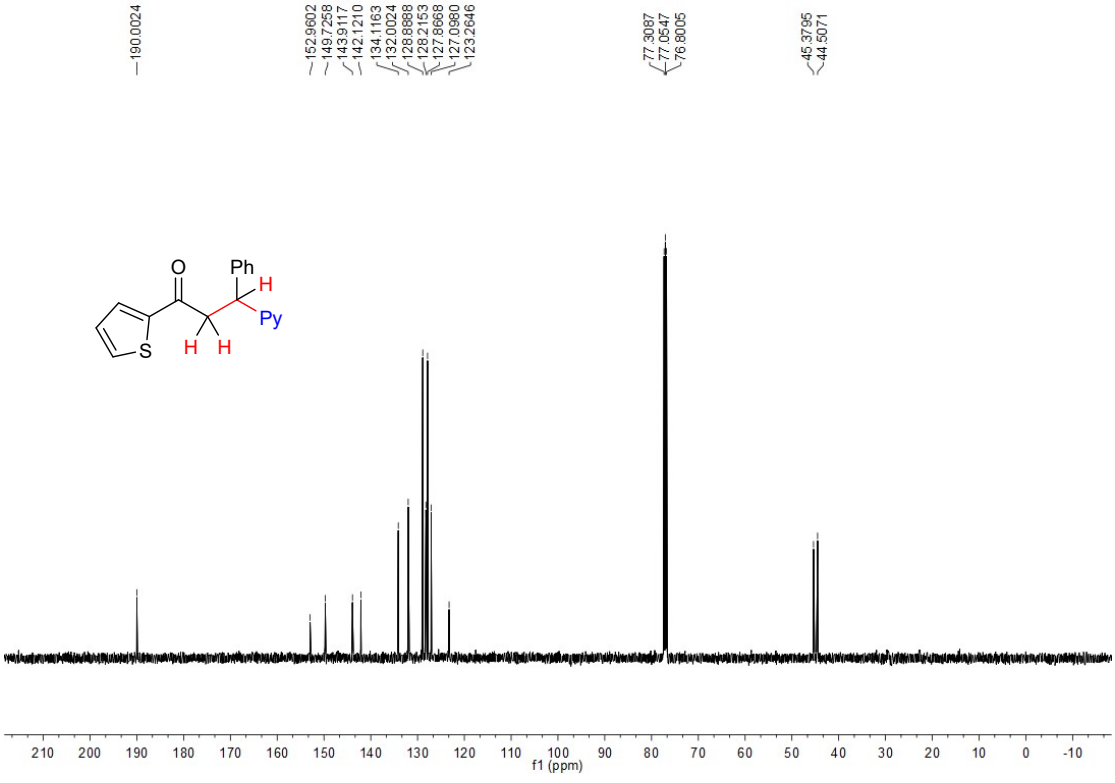


14c

^{1}H NMR

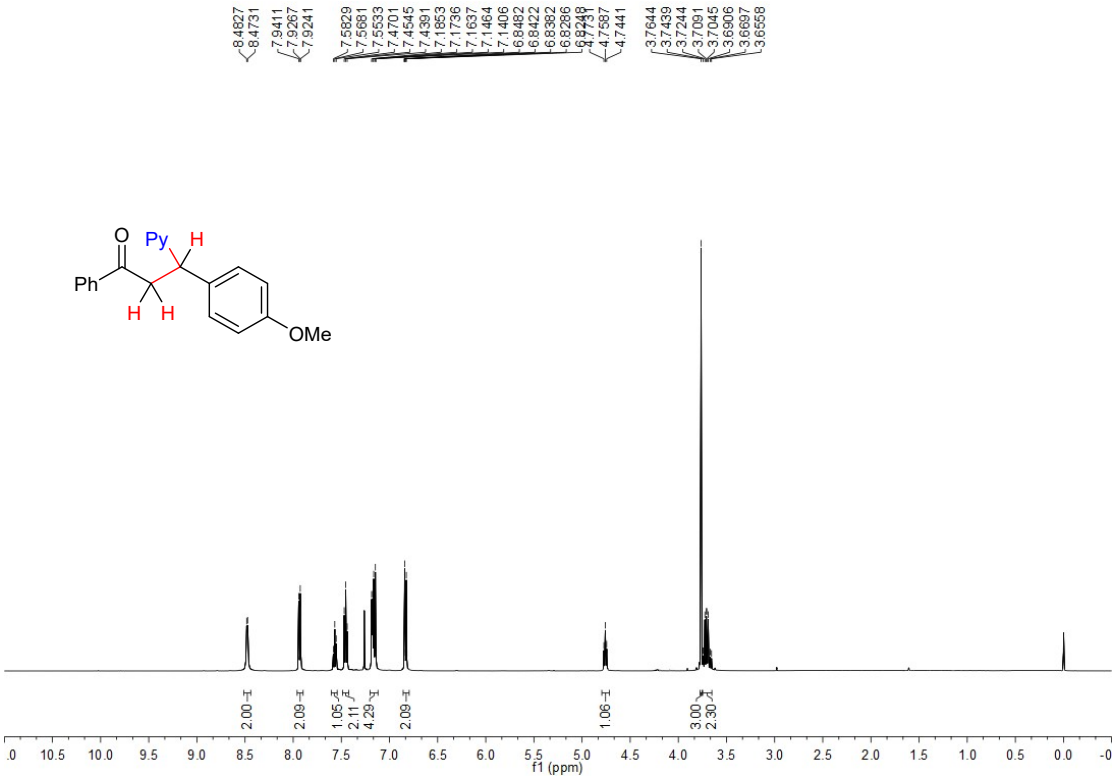


^{13}C NMR

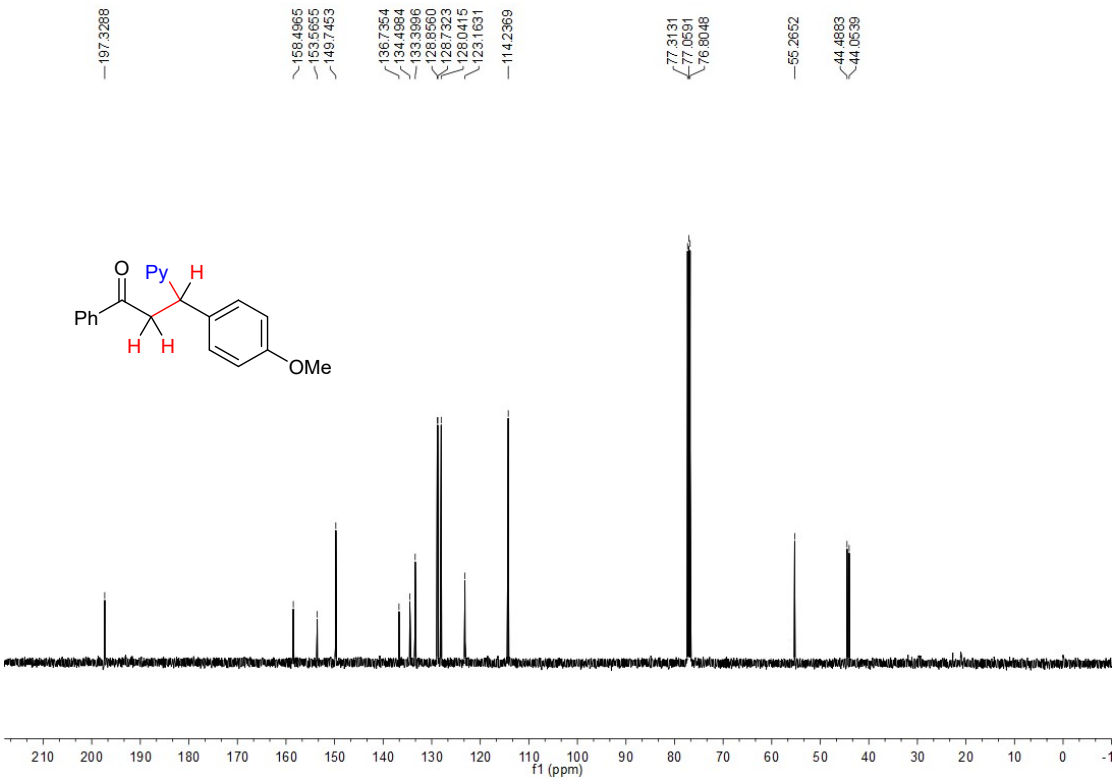


15c

^{1}H NMR

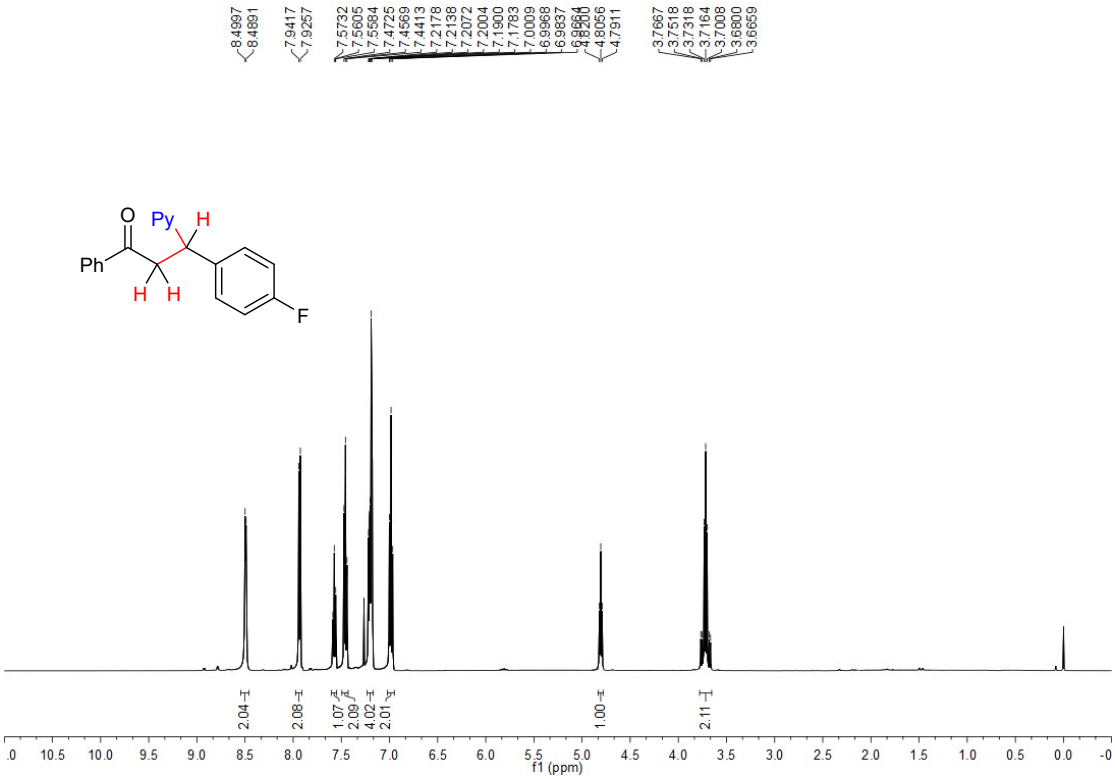


^{13}C NMR

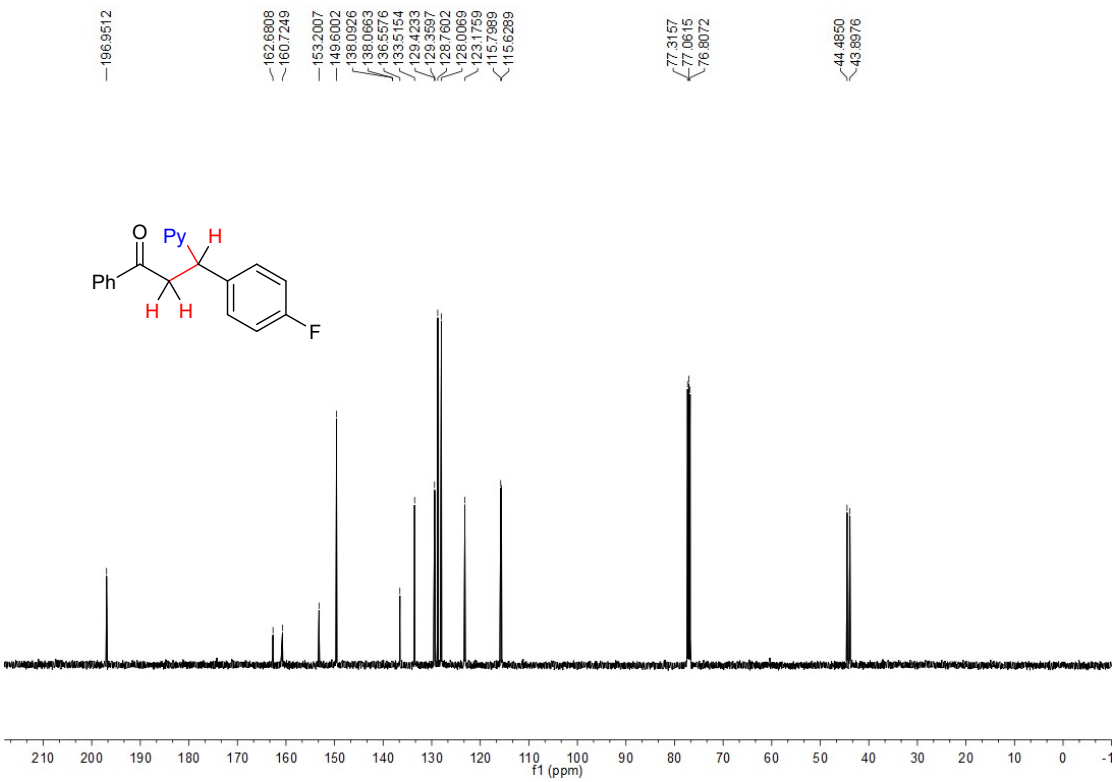


16c

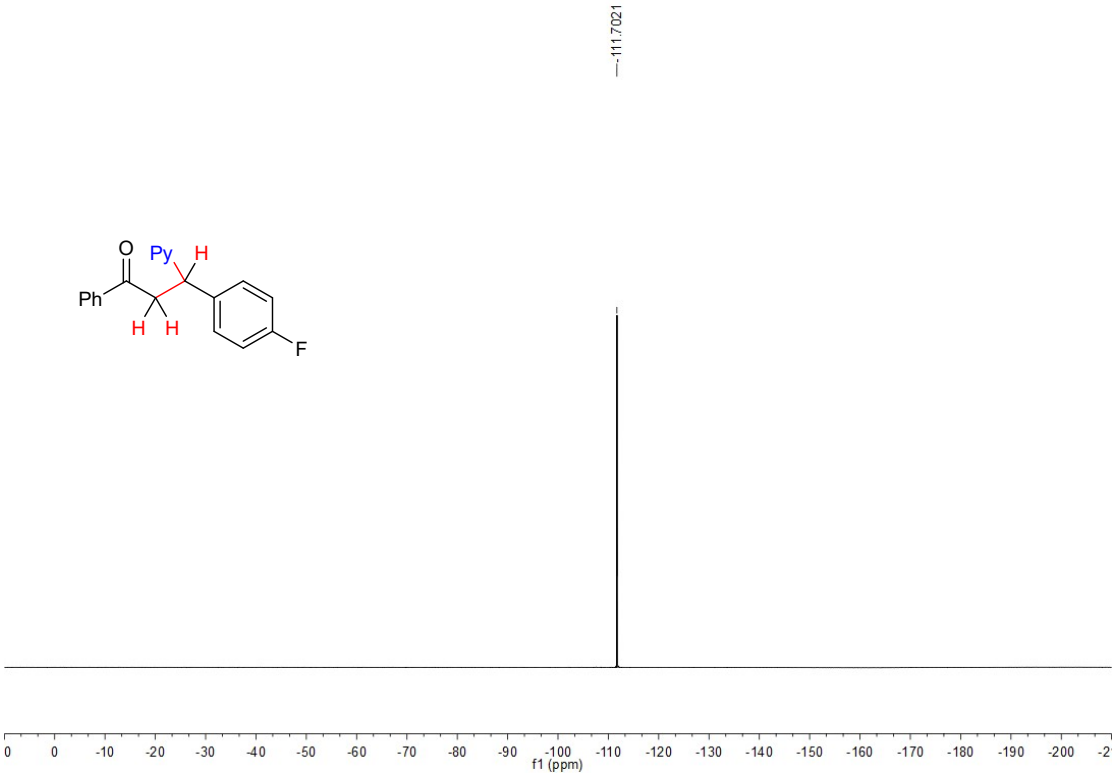
^{1}H NMR



^{13}C NMR

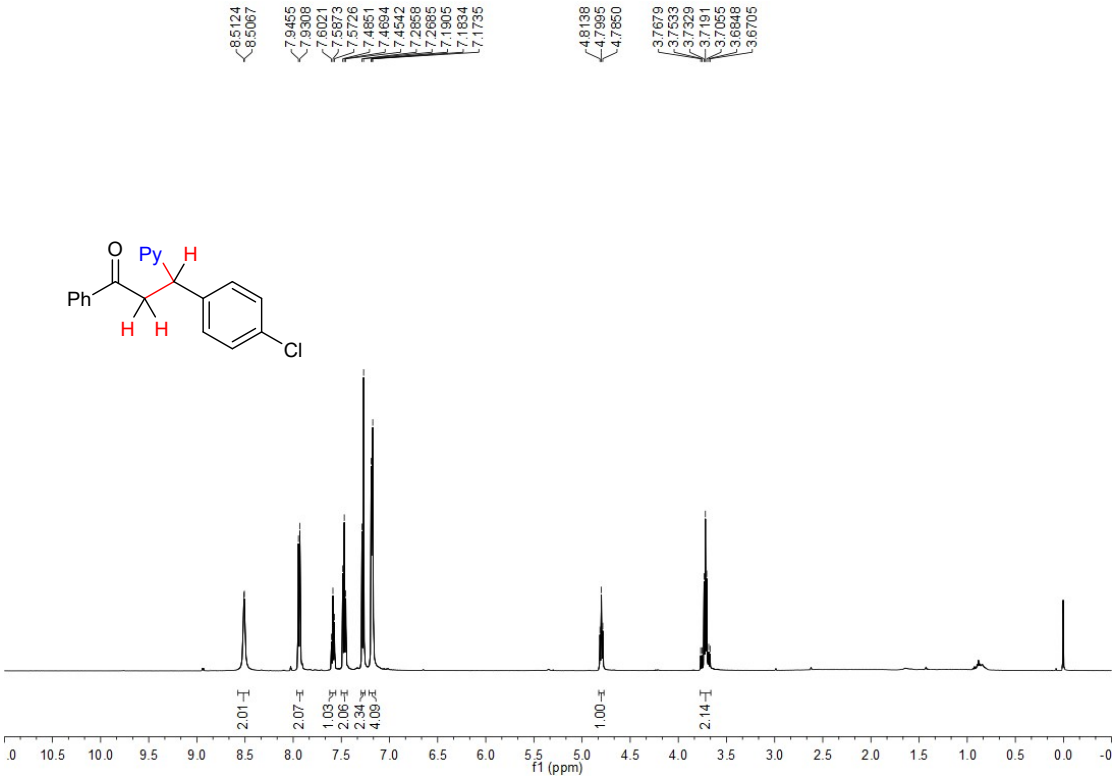


^{19}F NMR

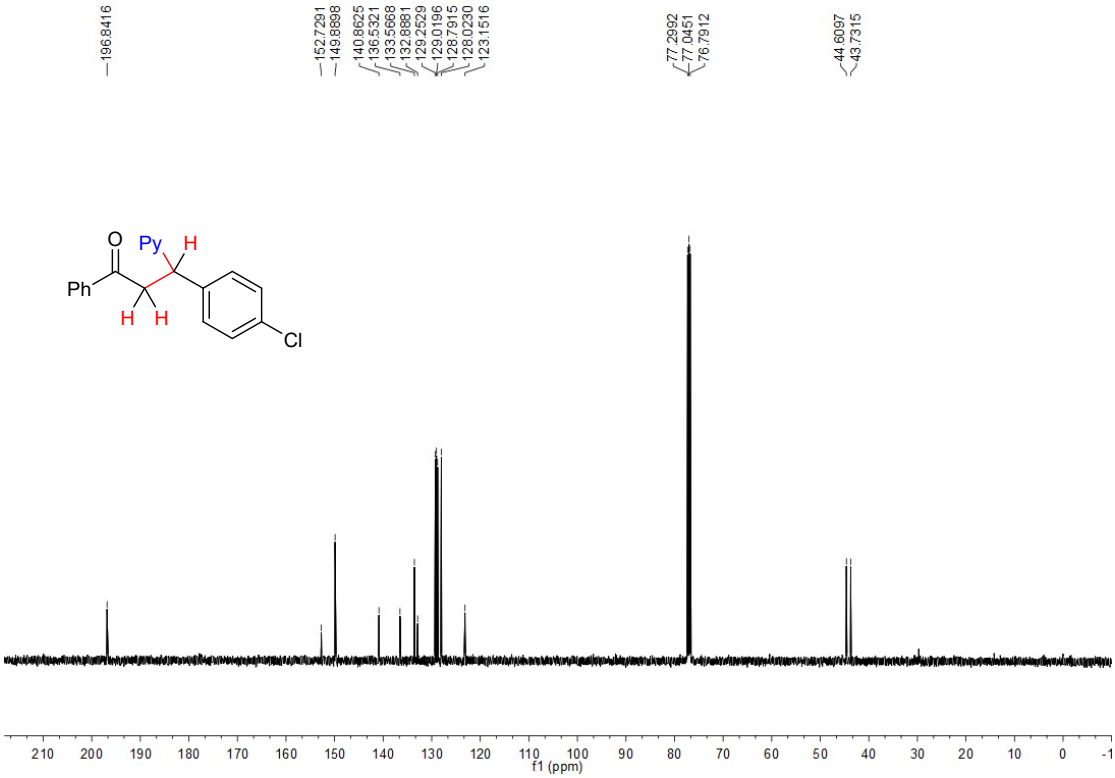

-111.7021
O
Py
H
Ph
H
H
F
0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-2
f1 (ppm)

17c

^{1}H NMR

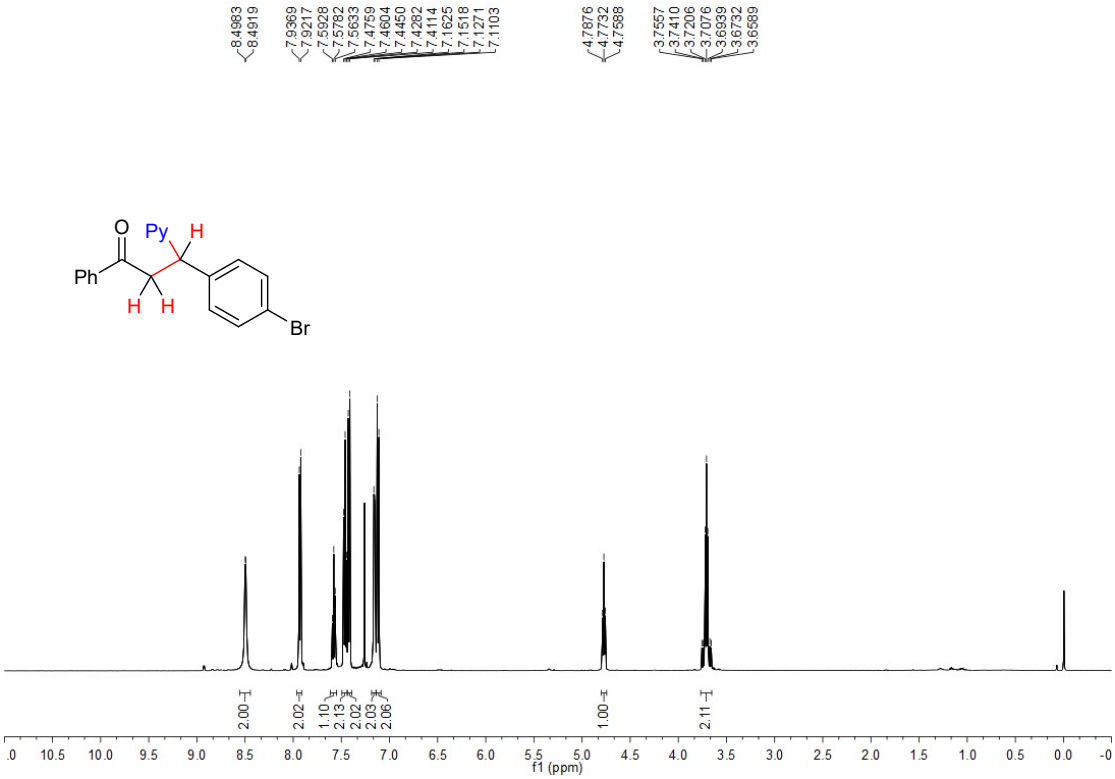


^{13}C NMR

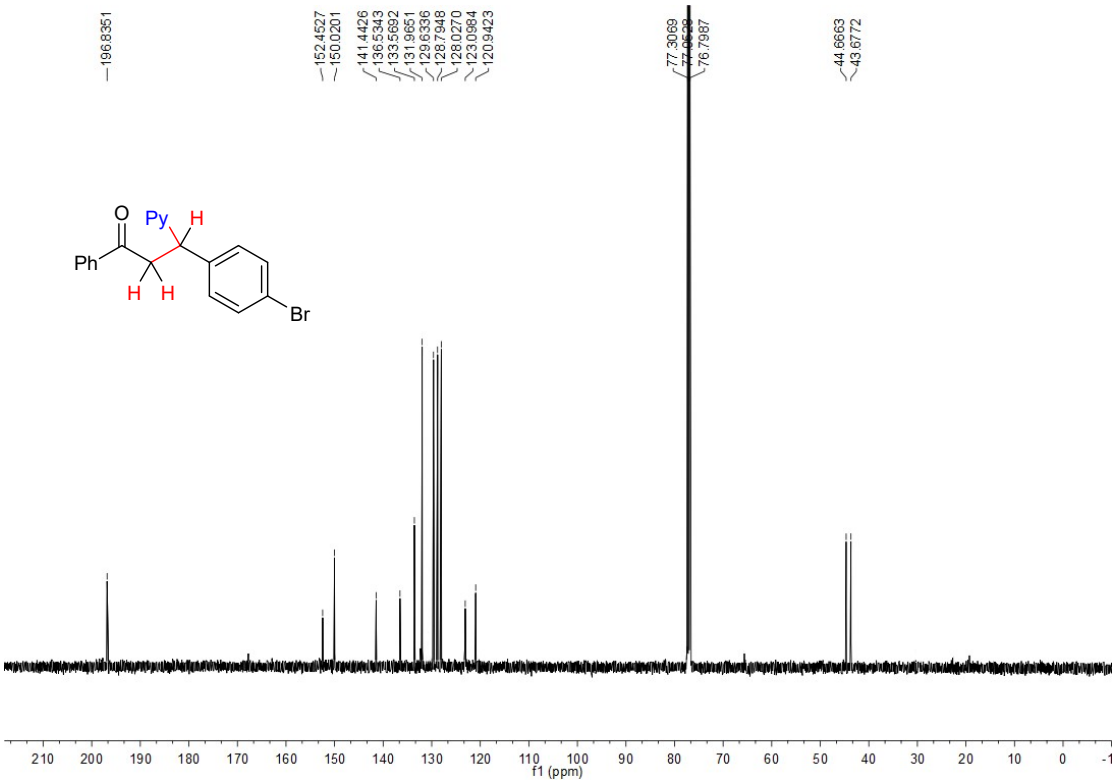


18c

^{1}H NMR

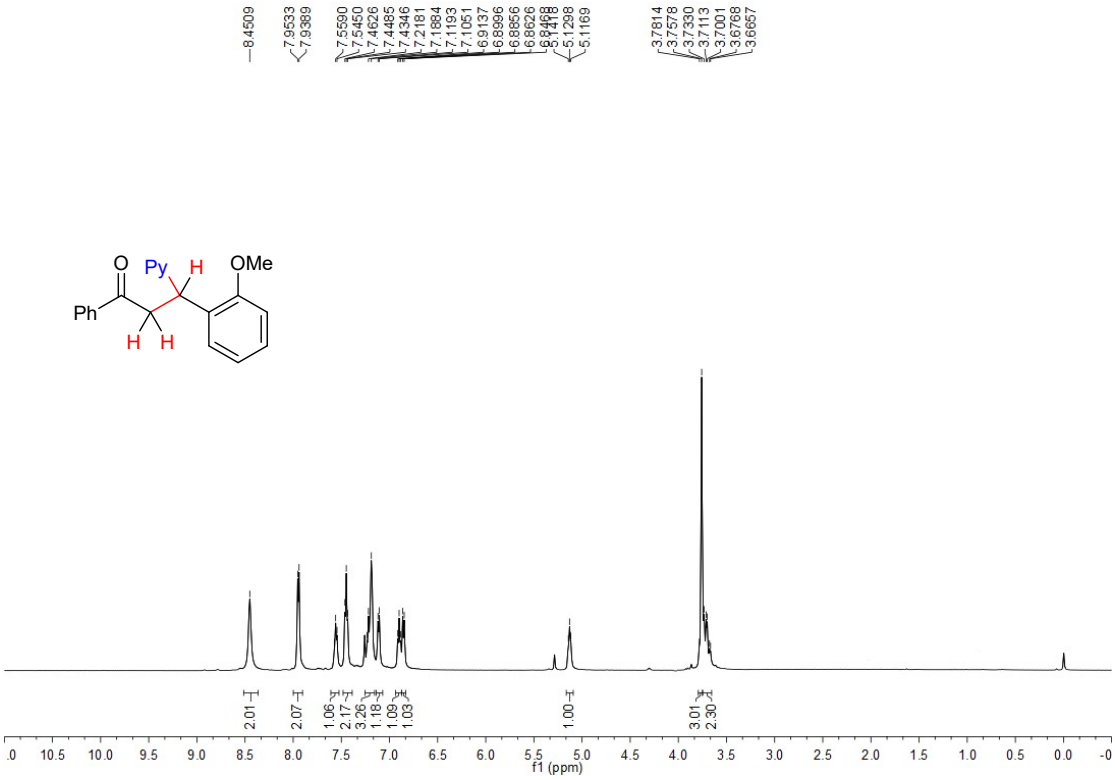


^{13}C NMR

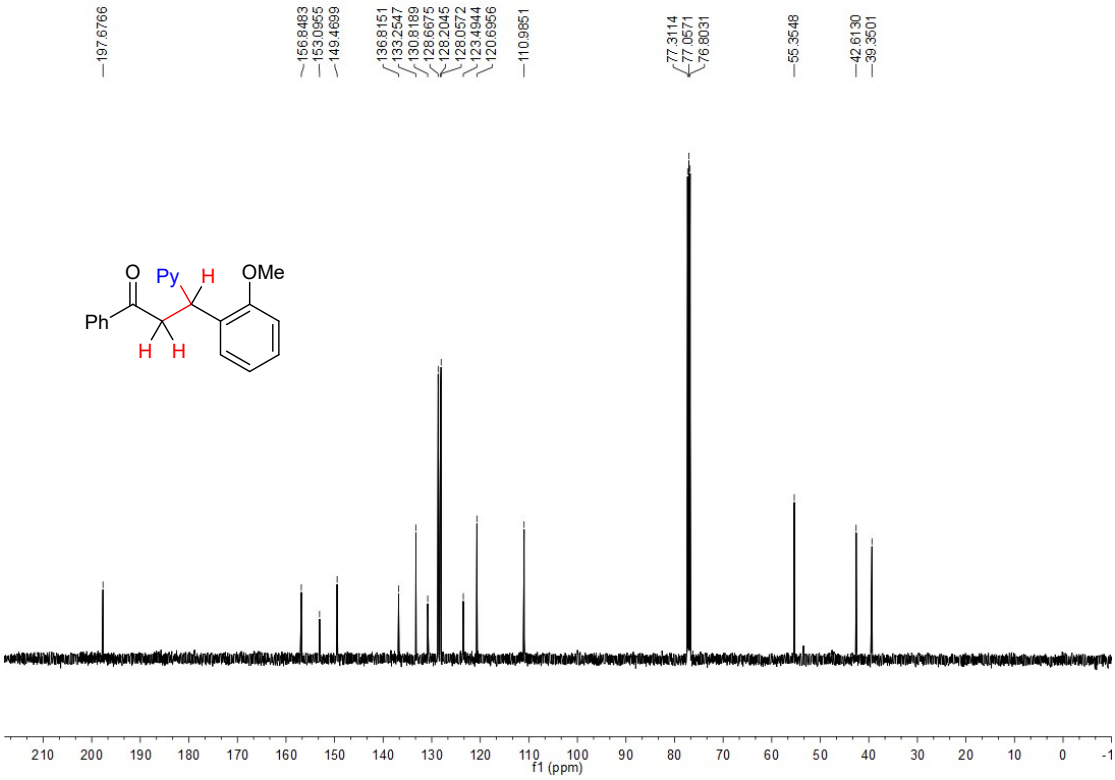


19c

^{1}H NMR

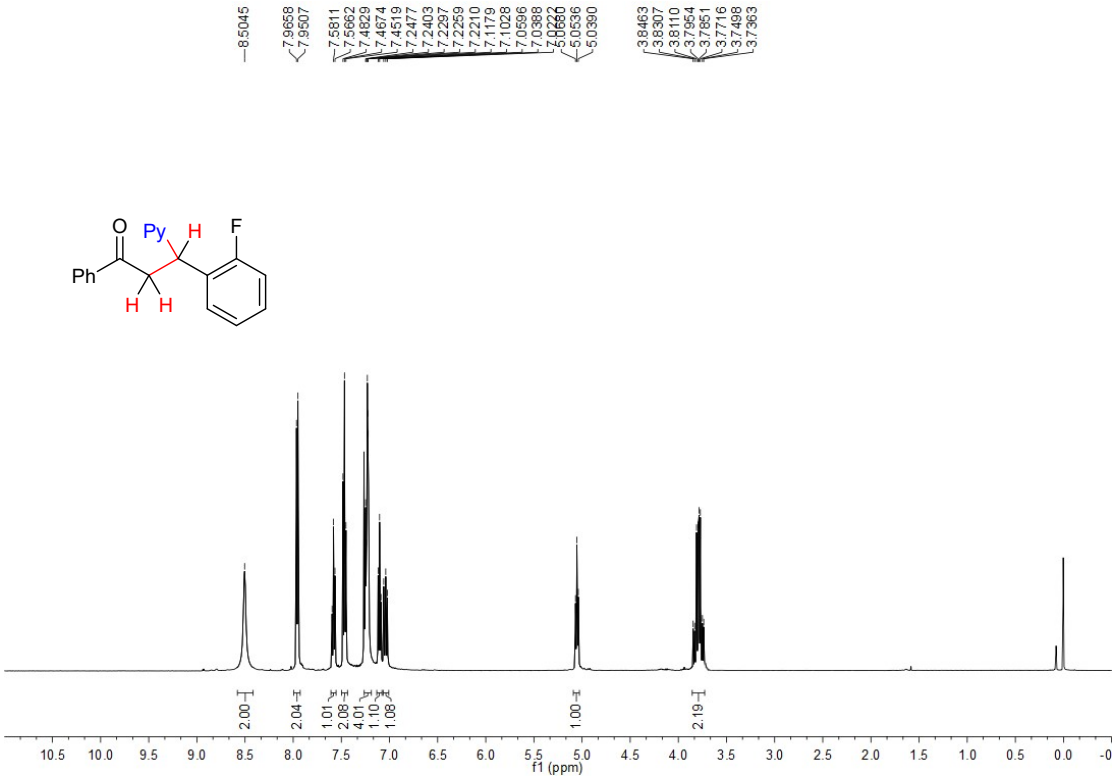


^{13}C NMR

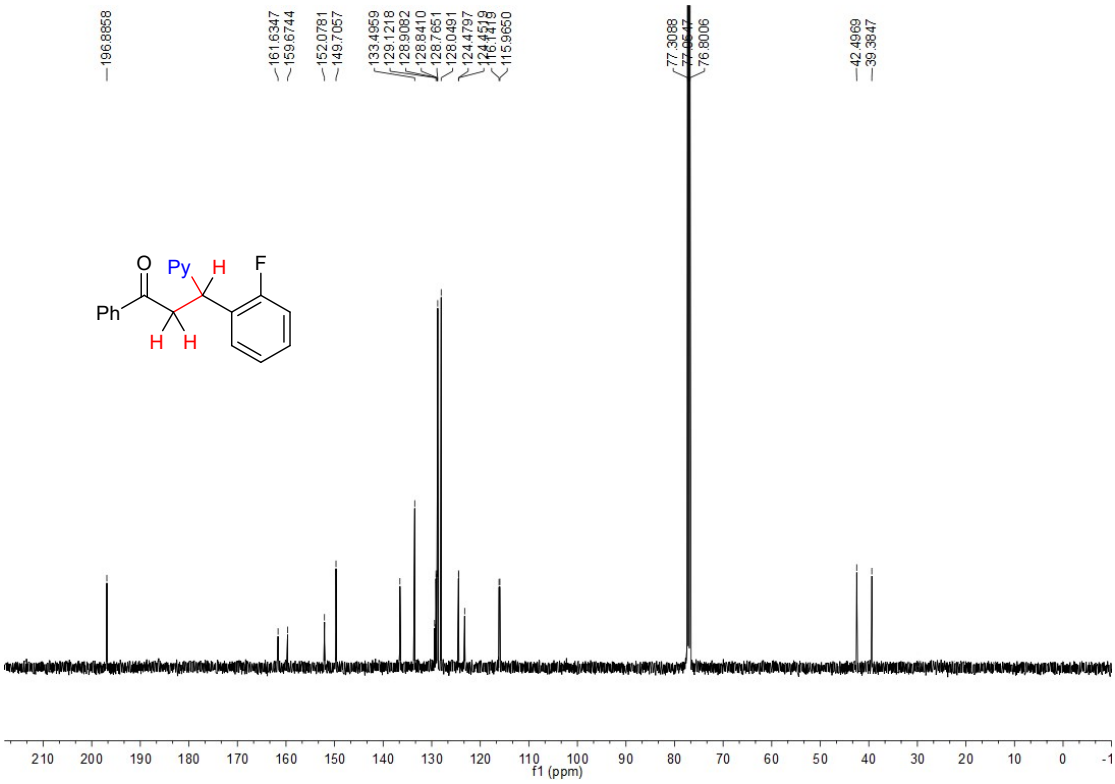


20c

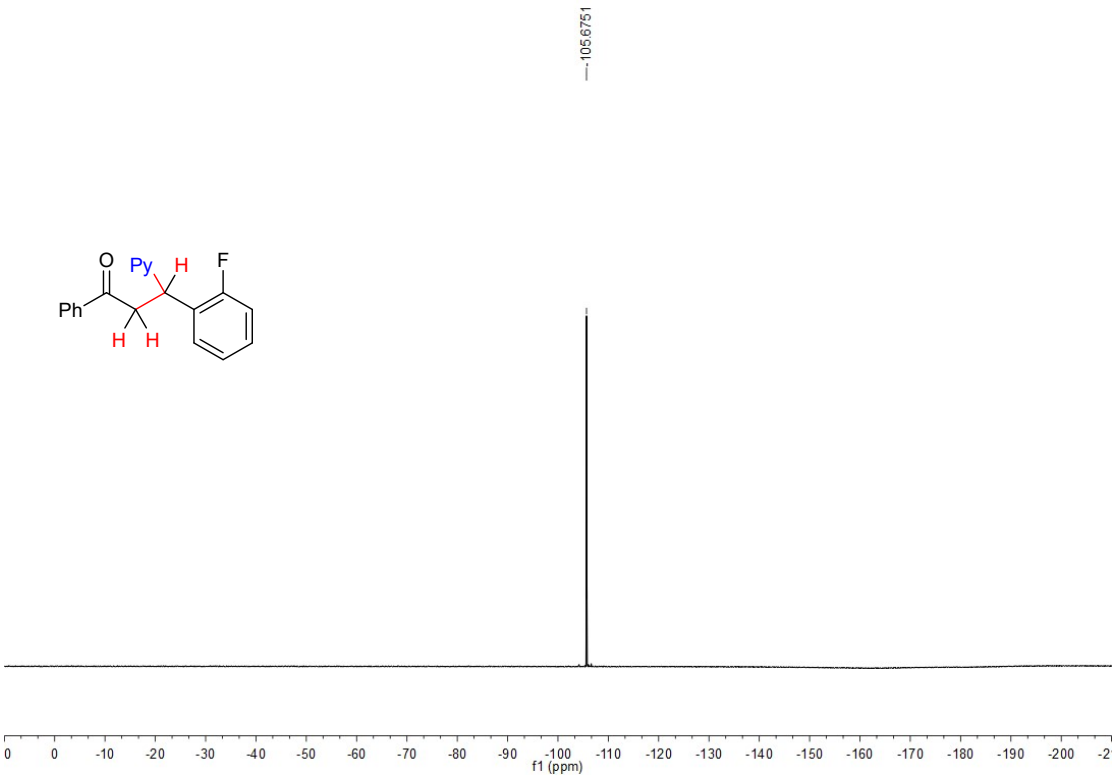
^{1}H NMR



^{13}C NMR

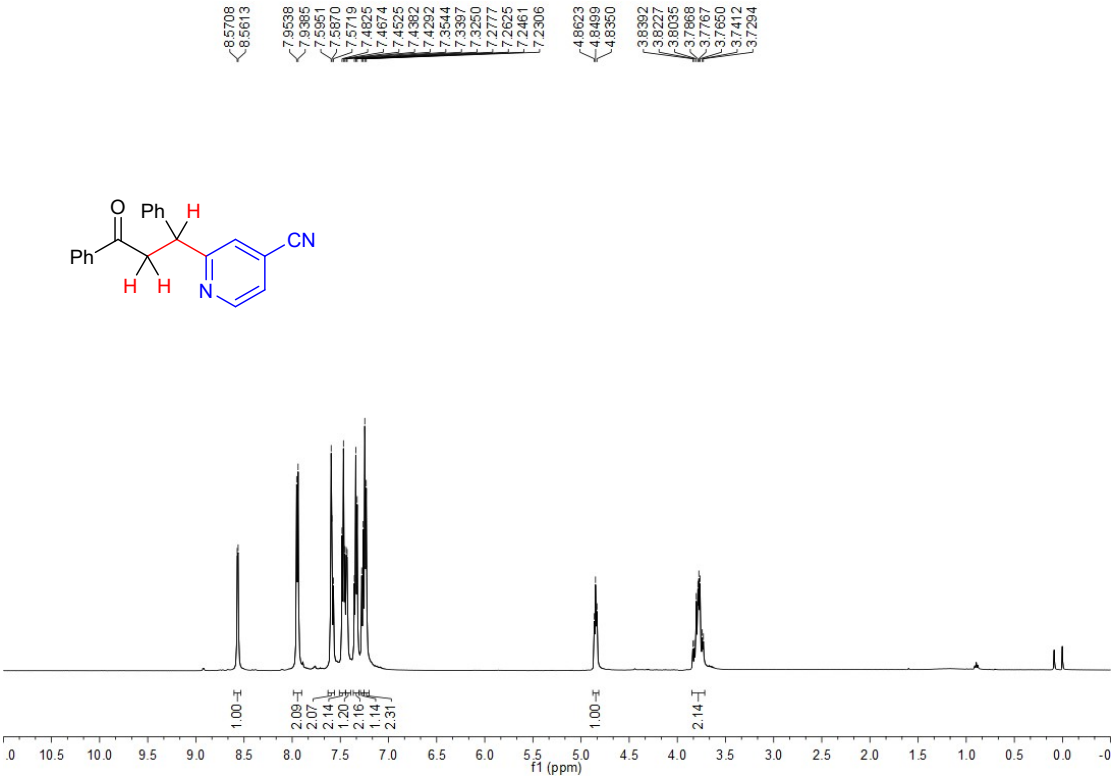


^{19}F NMR

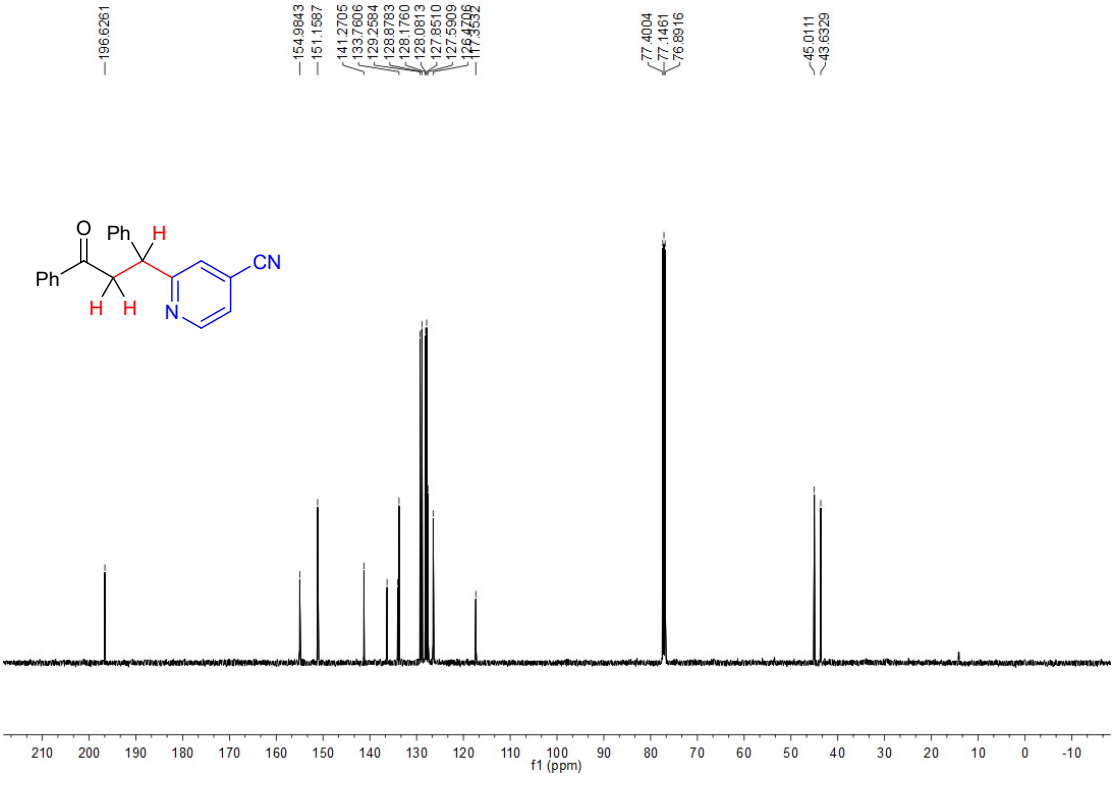

-105.6751
O
Py
H
F
Ph
H
H
0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-2
f1 (ppm)

21c

^{1}H NMR

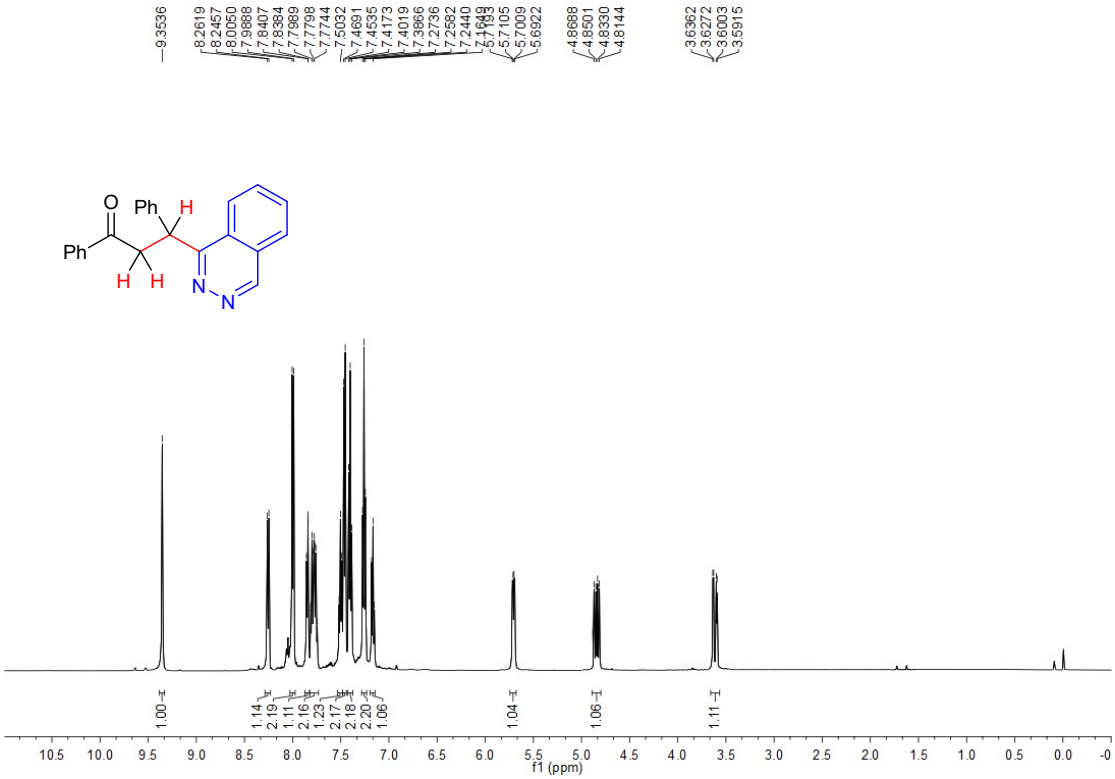


^{13}C NMR

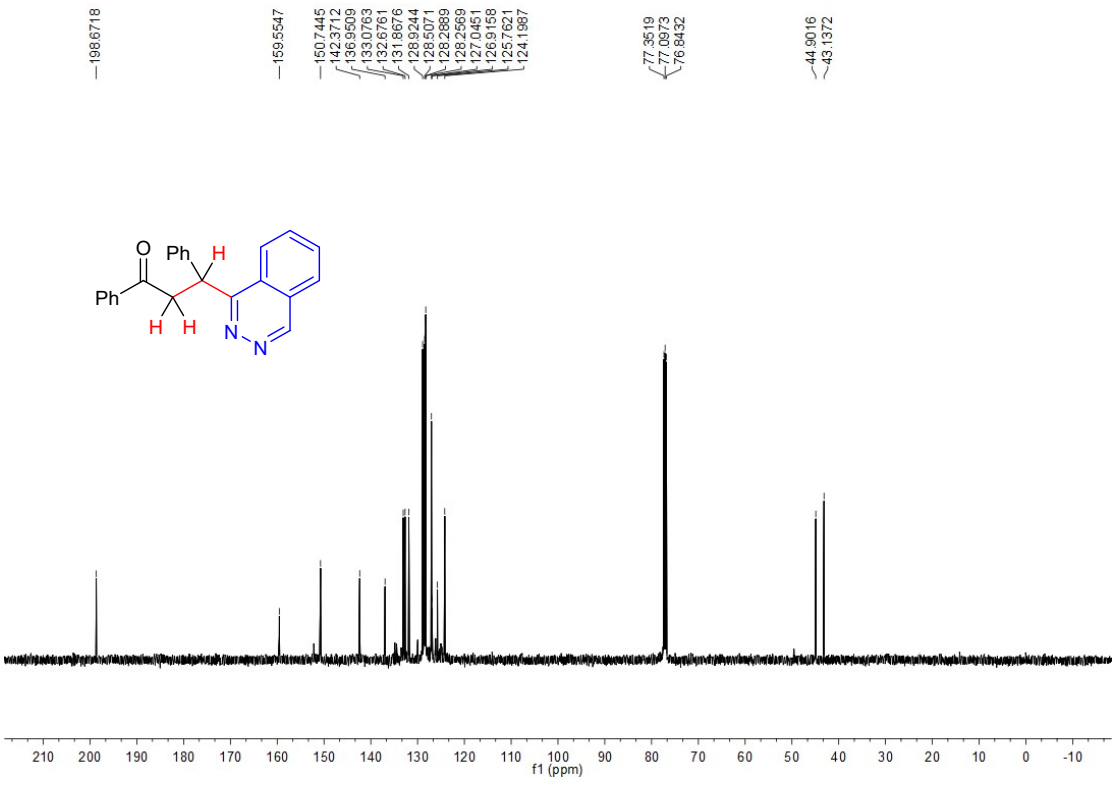


22c

^{1}H NMR

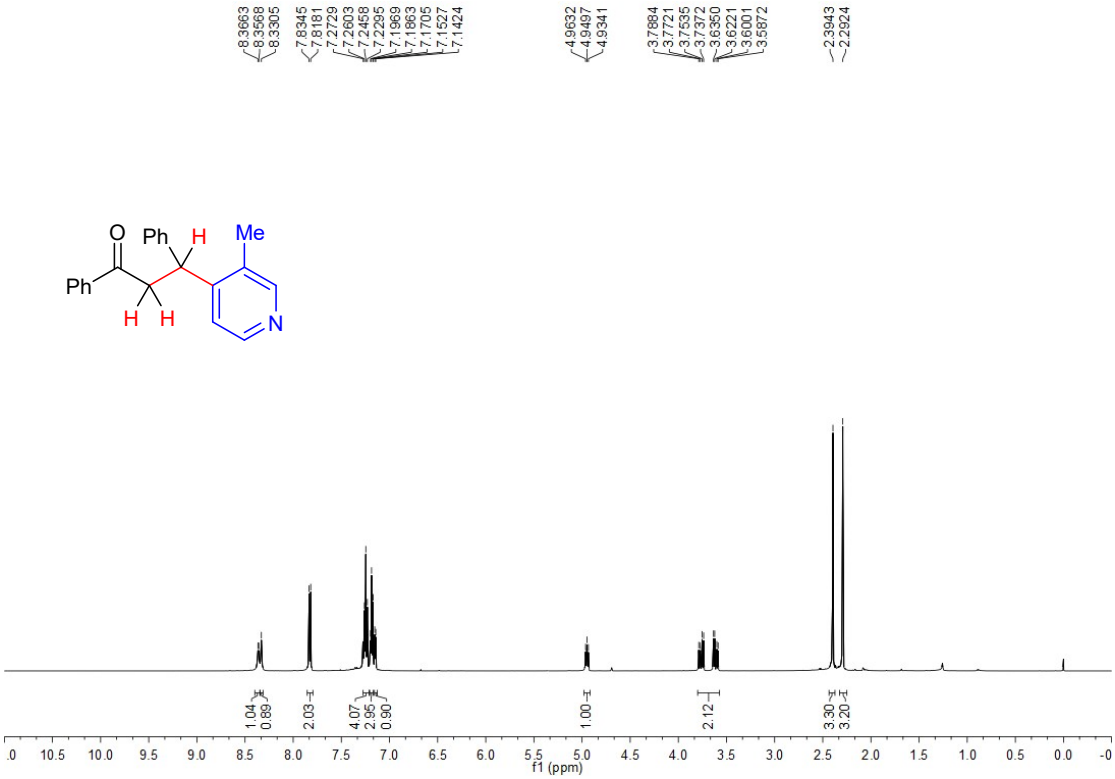


^{13}C NMR

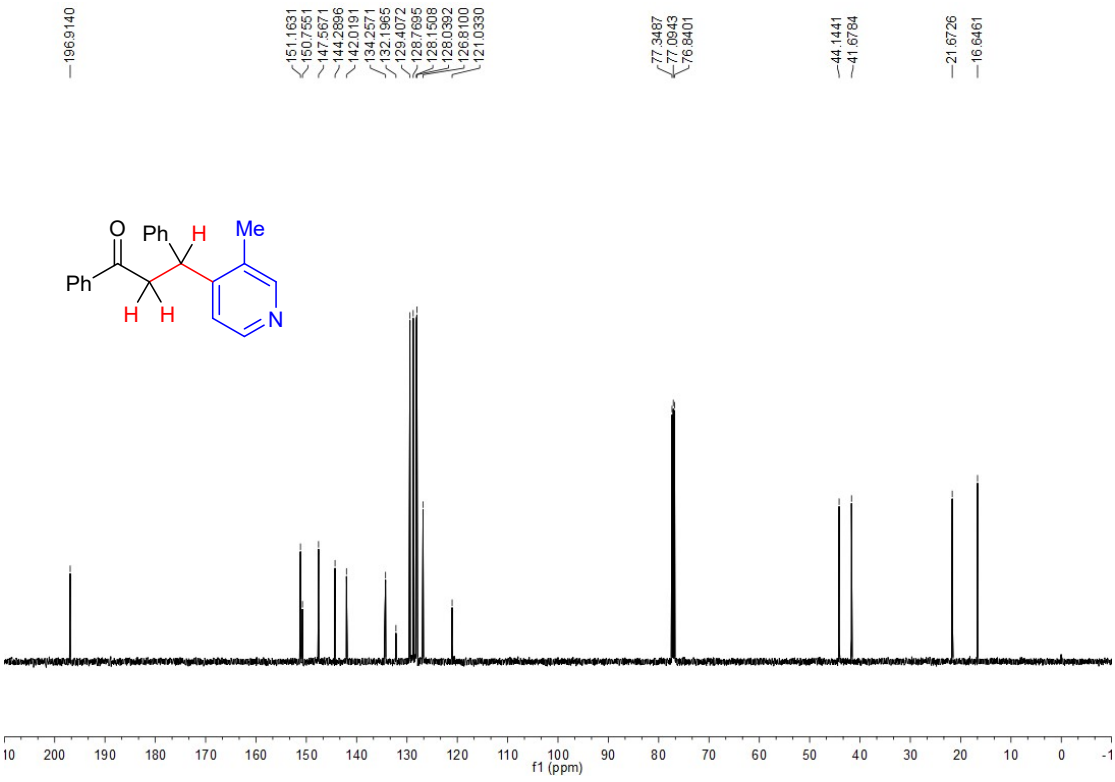


23c

^{1}H NMR

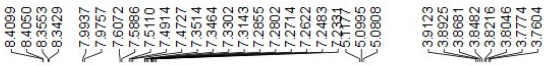


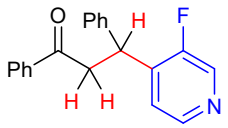
^{13}C NMR

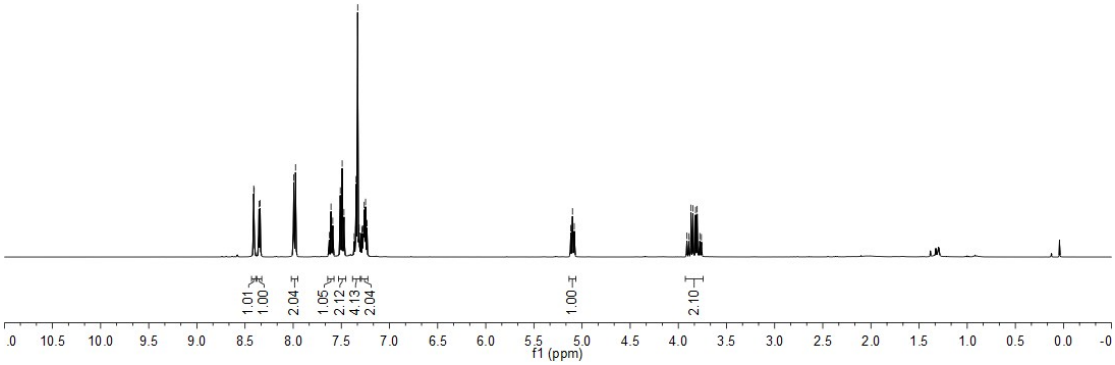


24c

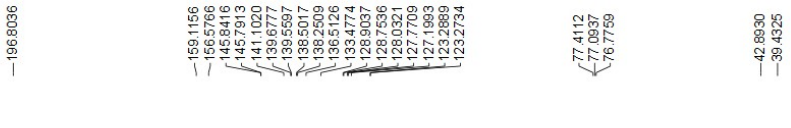
^{1}H NMR

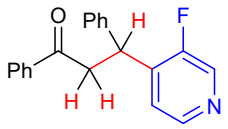


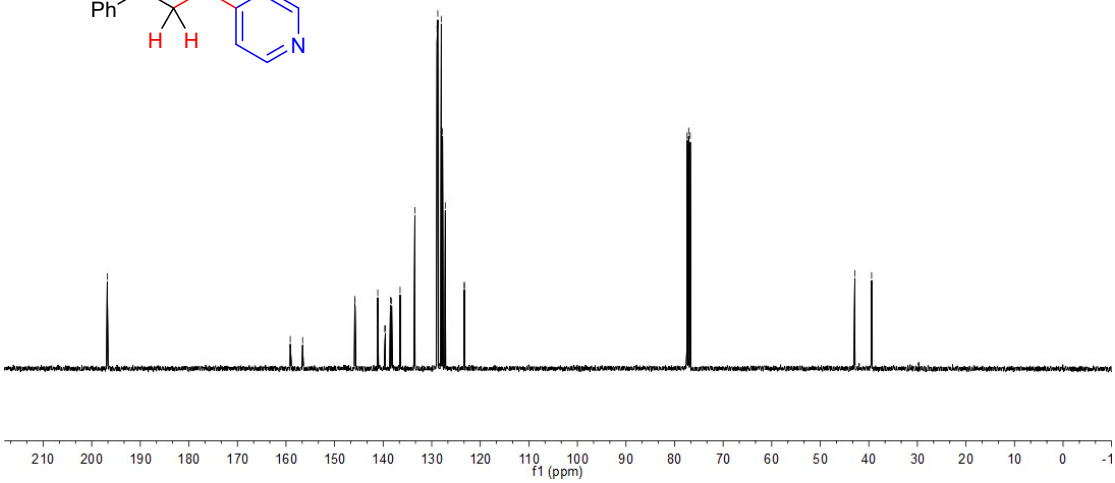




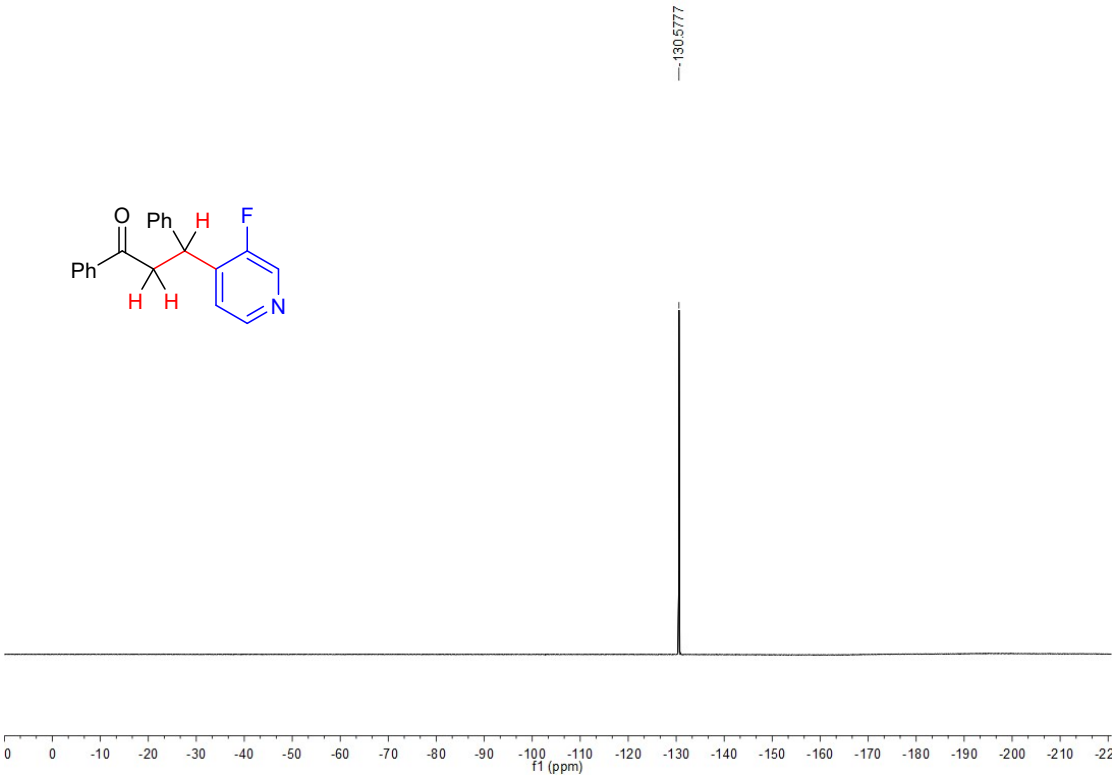
^{13}C NMR





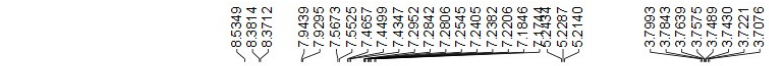


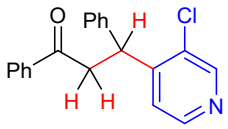
^{19}F NMR

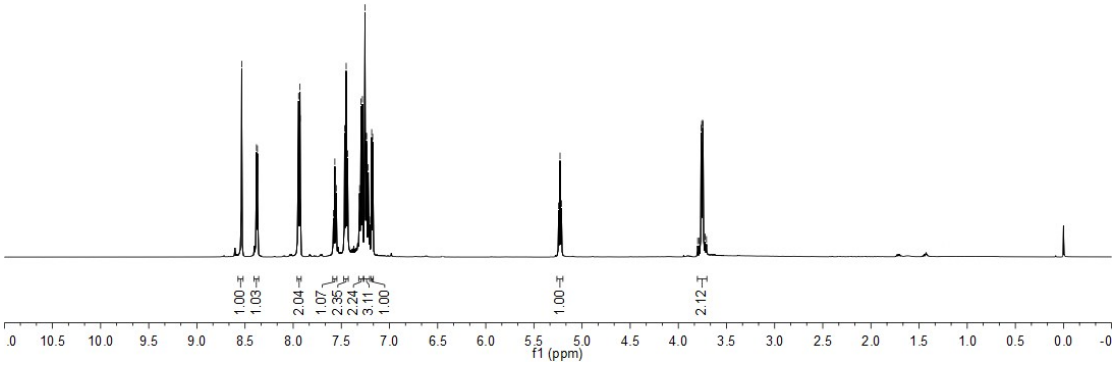

-130.5777
O
Ph
H
F
Ph
H
H
N
0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

25c

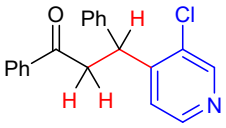
^{1}H NMR

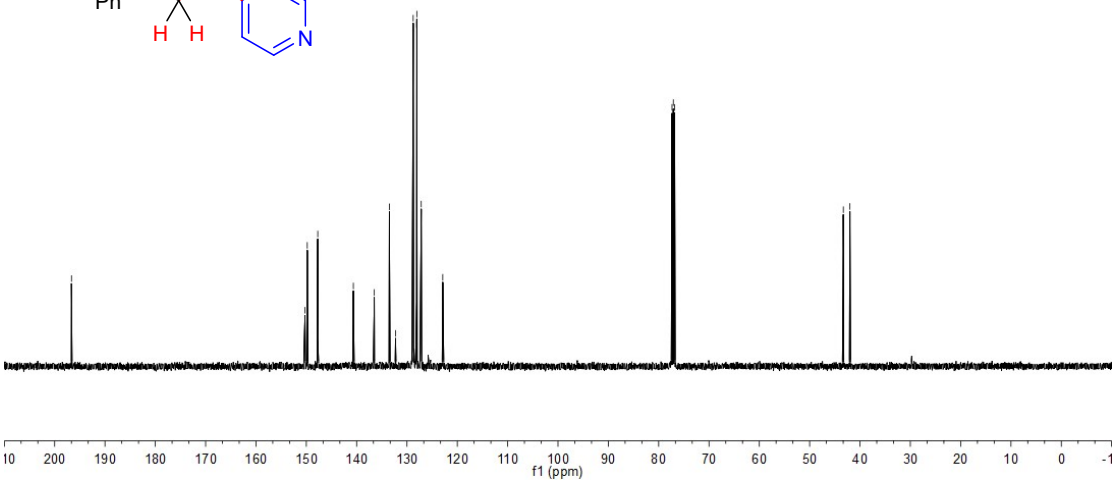






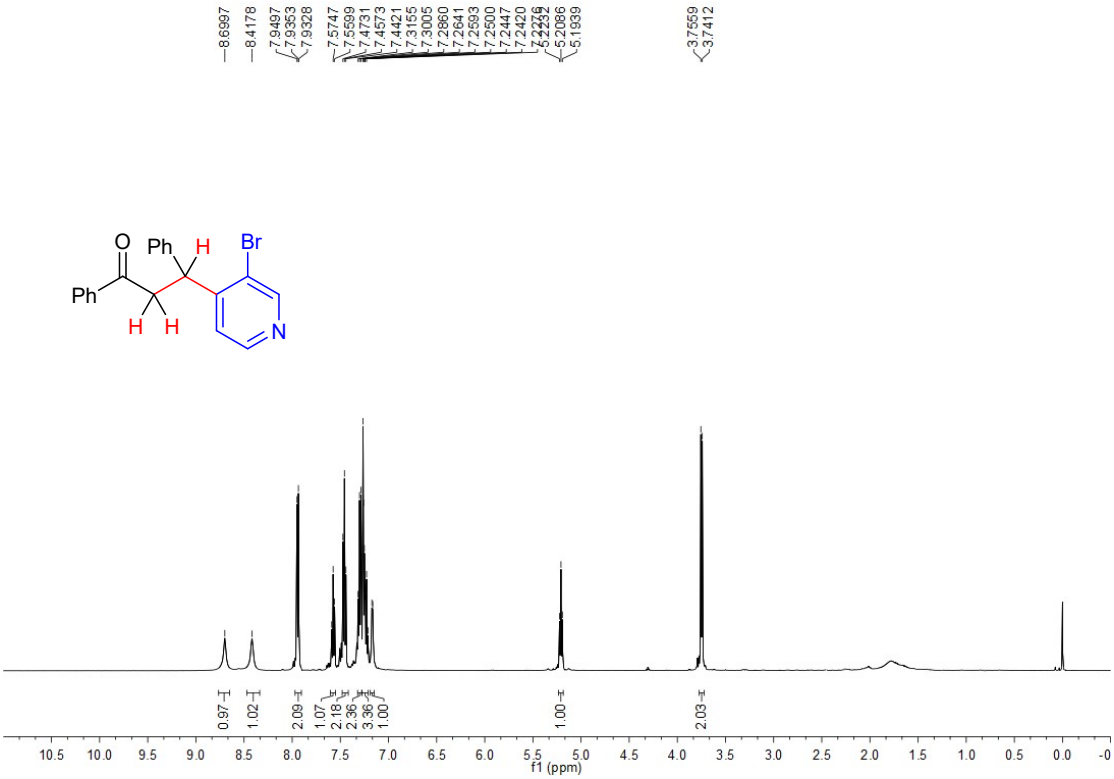
^{13}C NMR



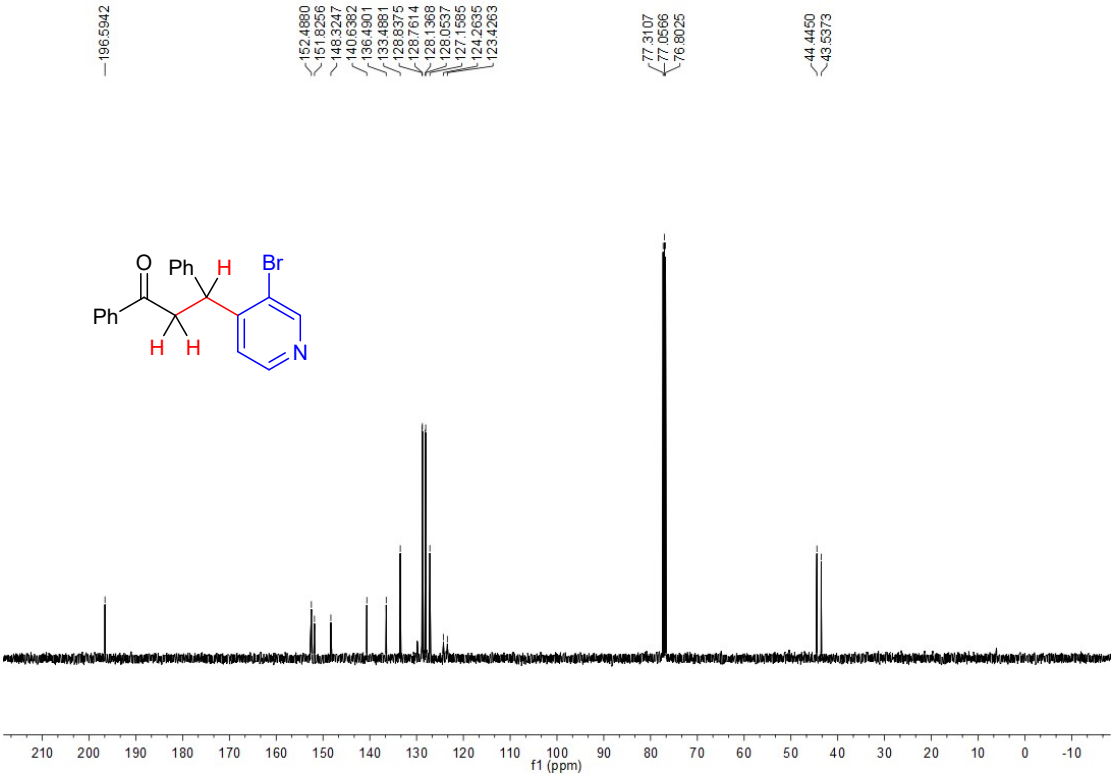


26c

^{1}H NMR

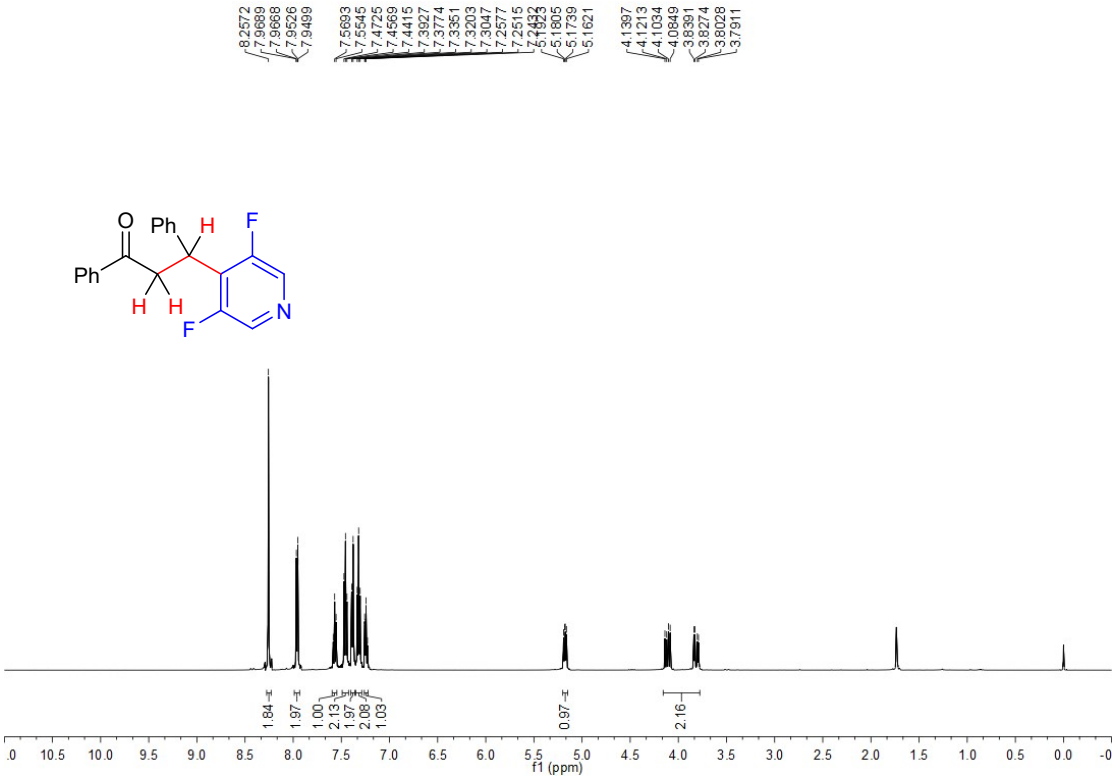


^{13}C NMR

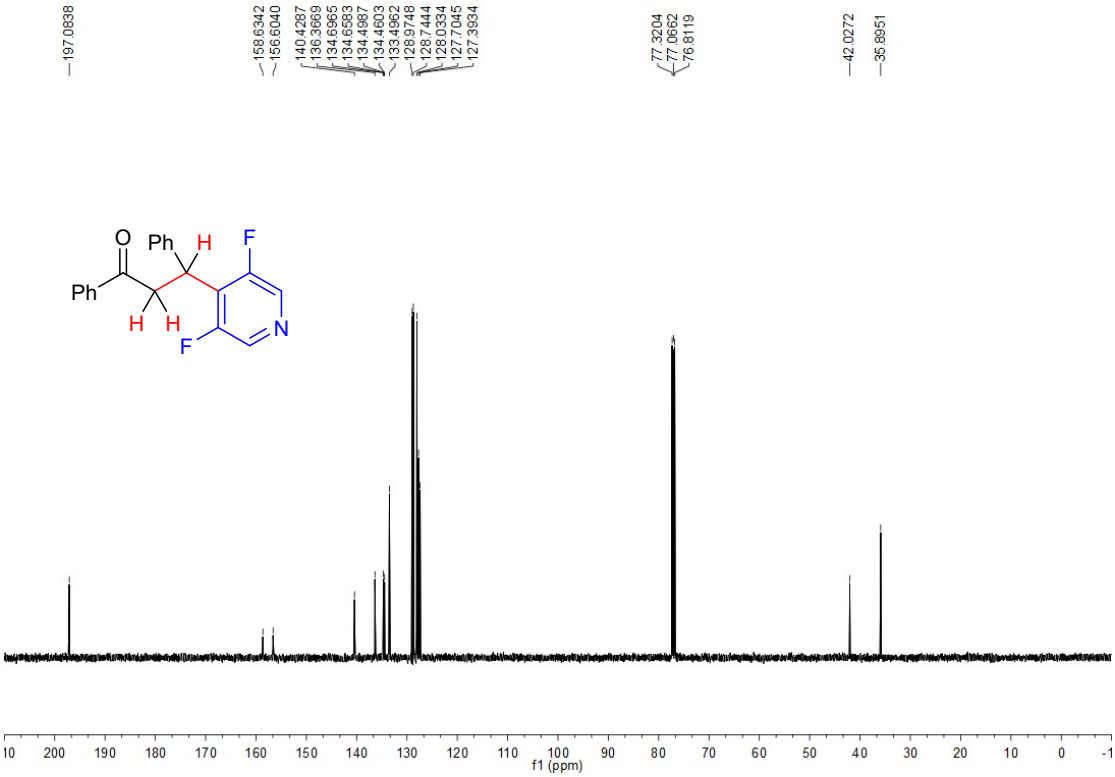


27c

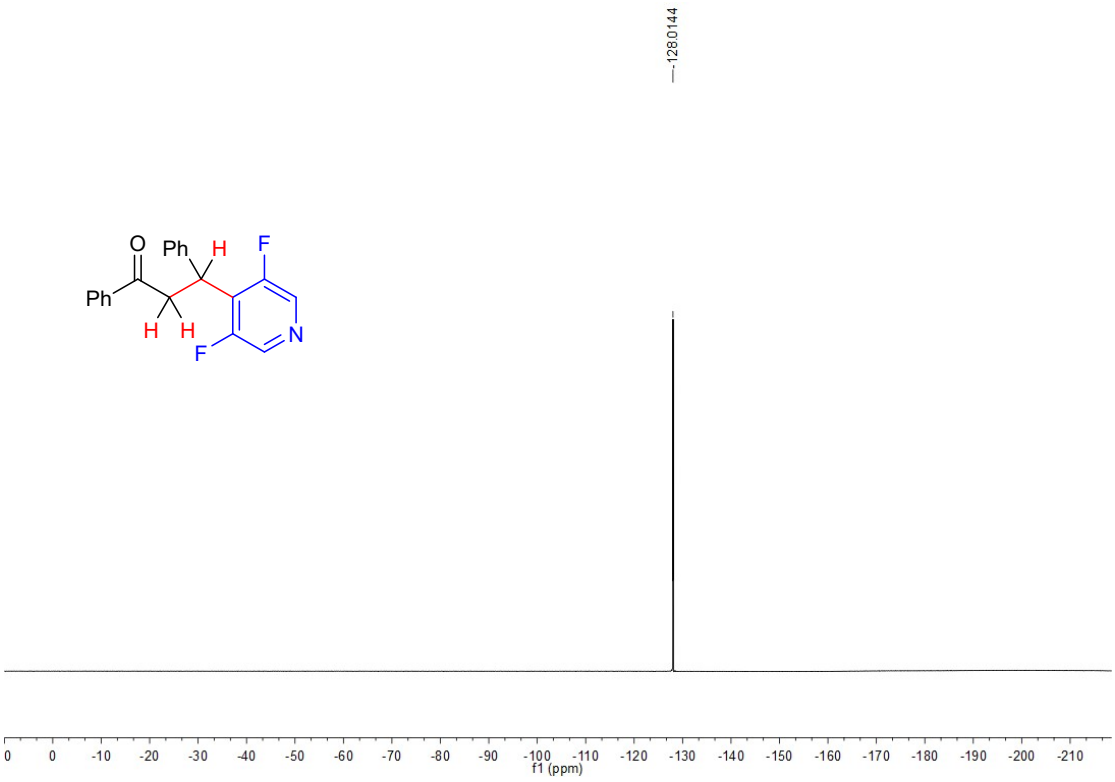
^{1}H NMR



^{13}C NMR

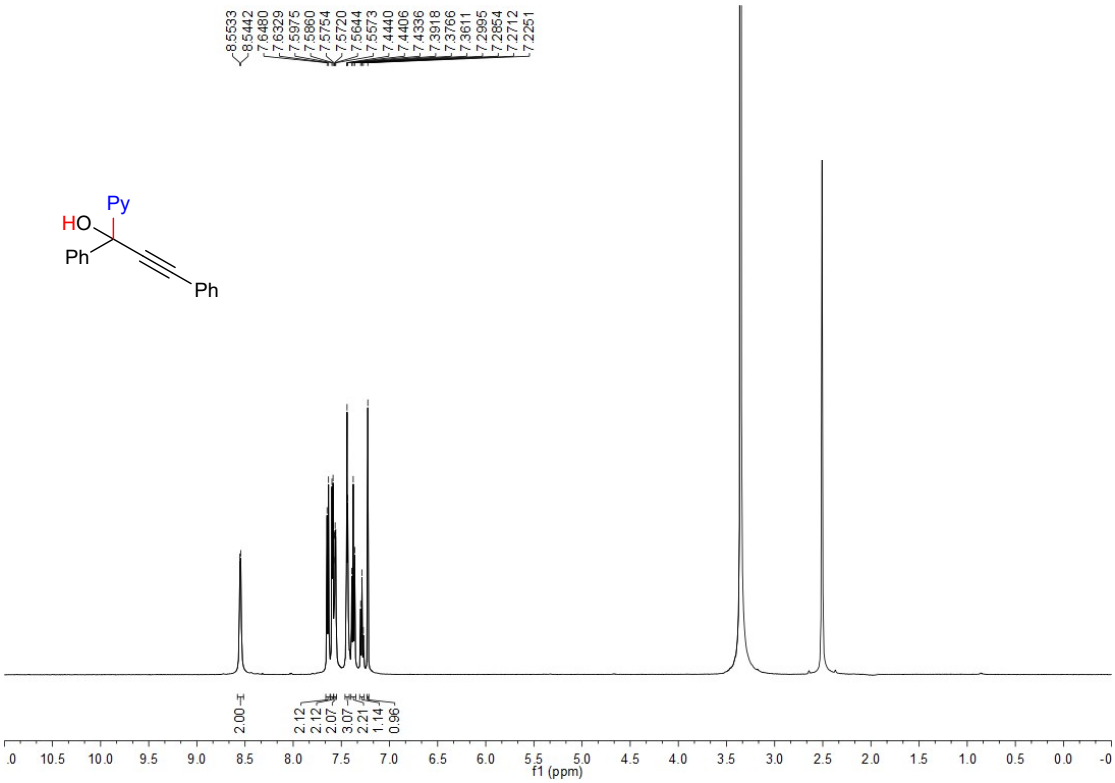


^{19}F NMR

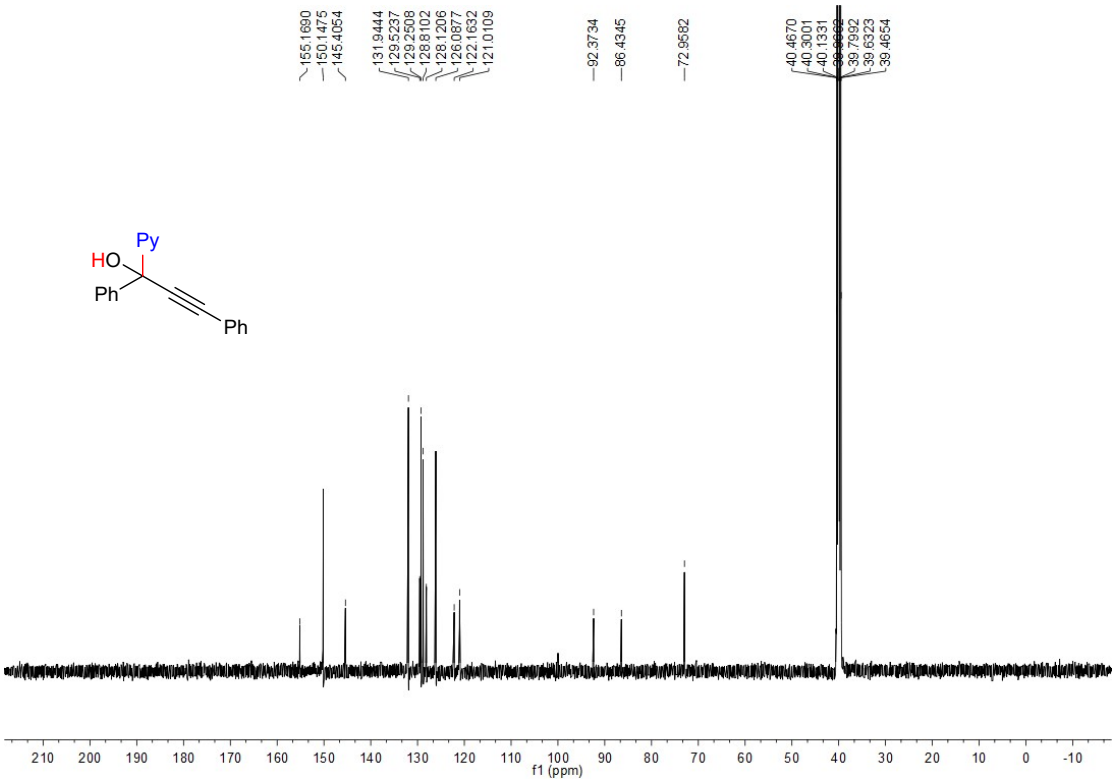

-128.0144
O
Ph
H
F
Ph
H
H
F
N
0
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

1d

^{1}H NMR

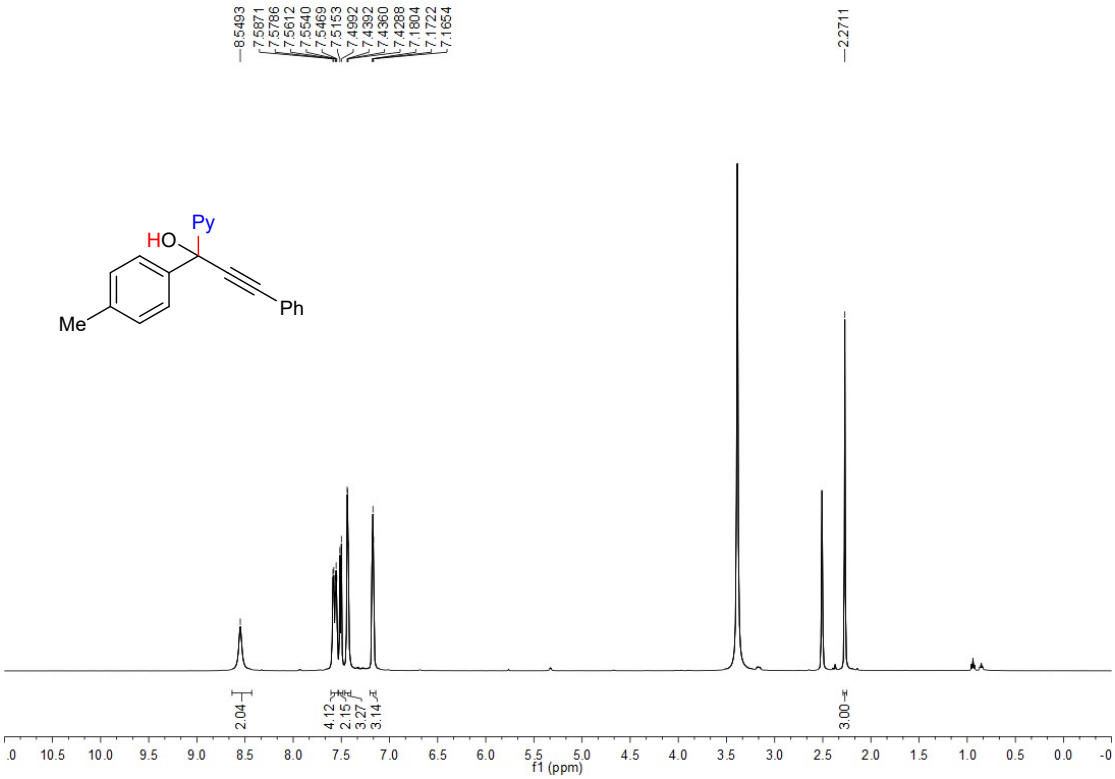


^{13}C NMR

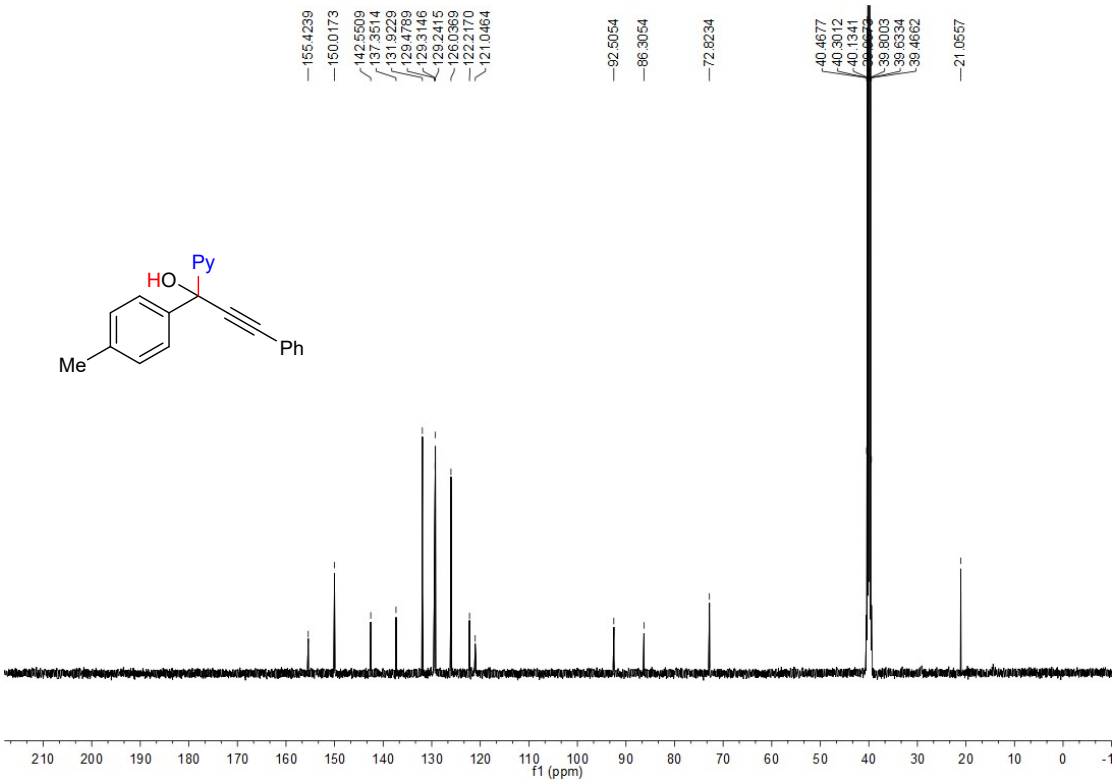


2d

^{1}H NMR

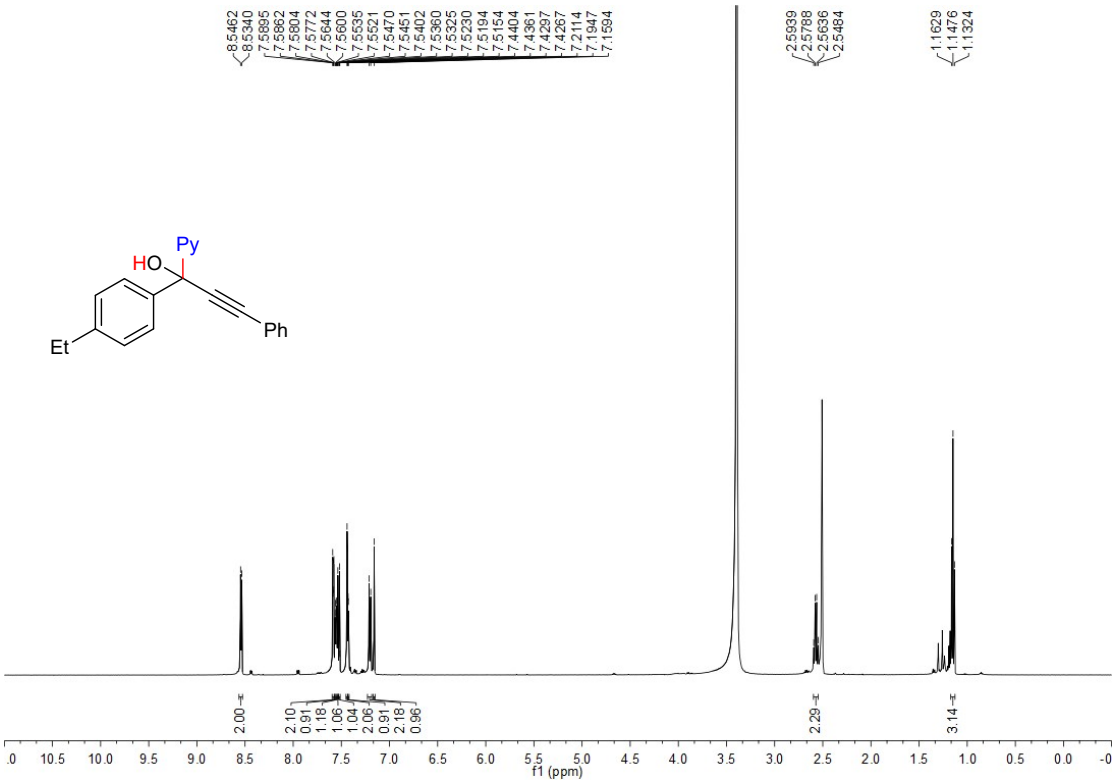


^{13}C NMR

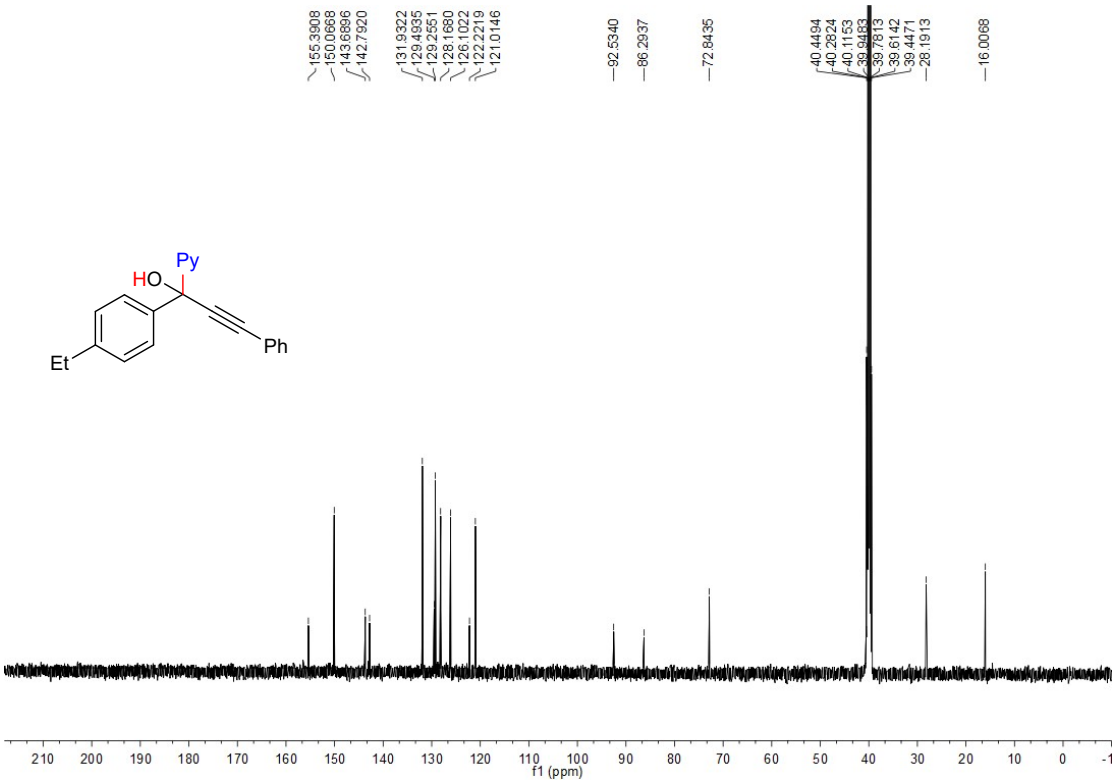


3d

^{1}H NMR

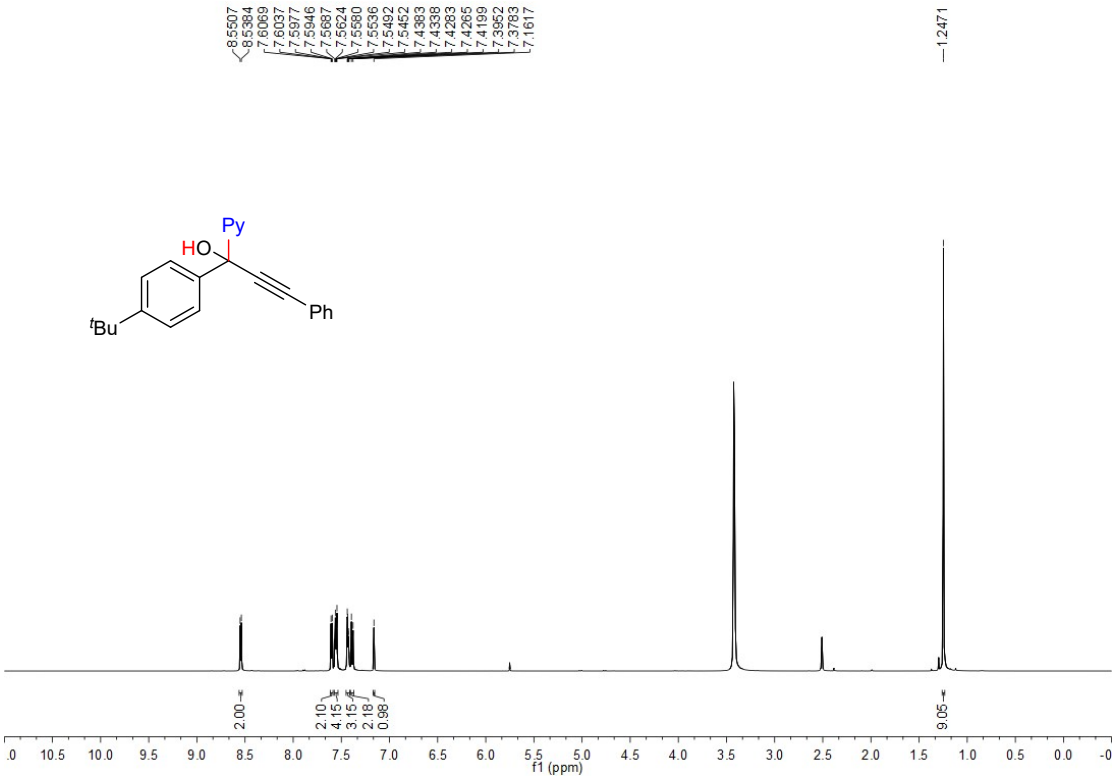


^{13}C NMR

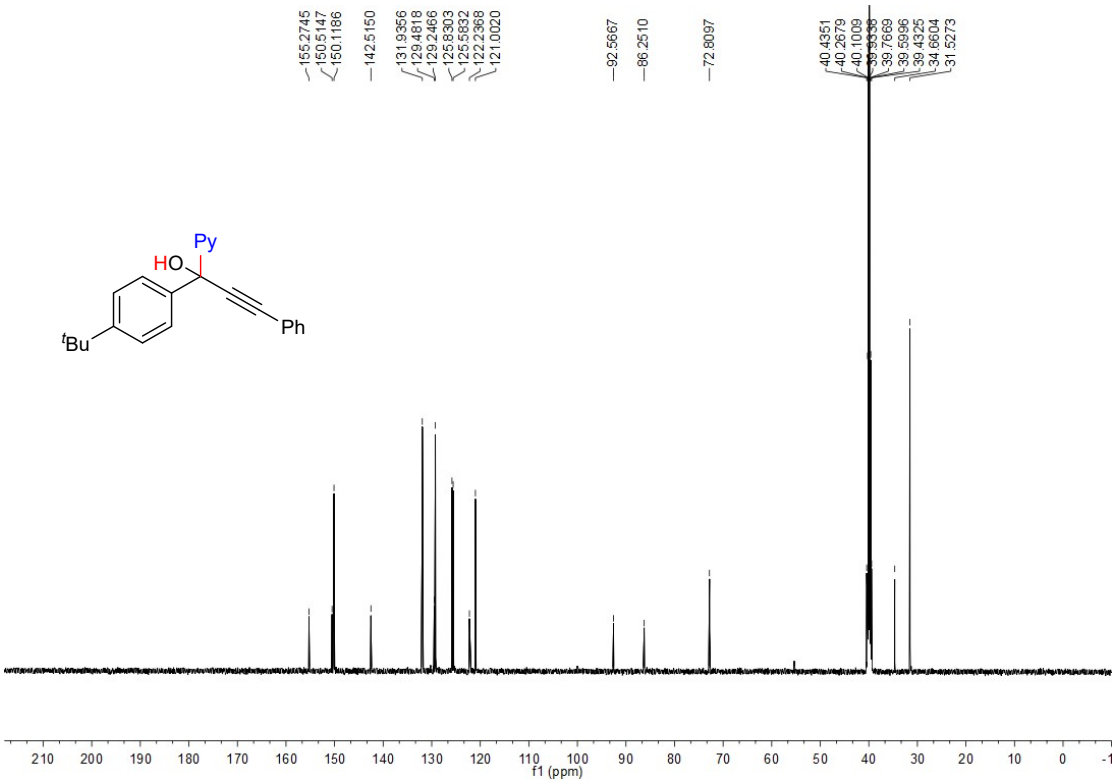


4d

^{1}H NMR

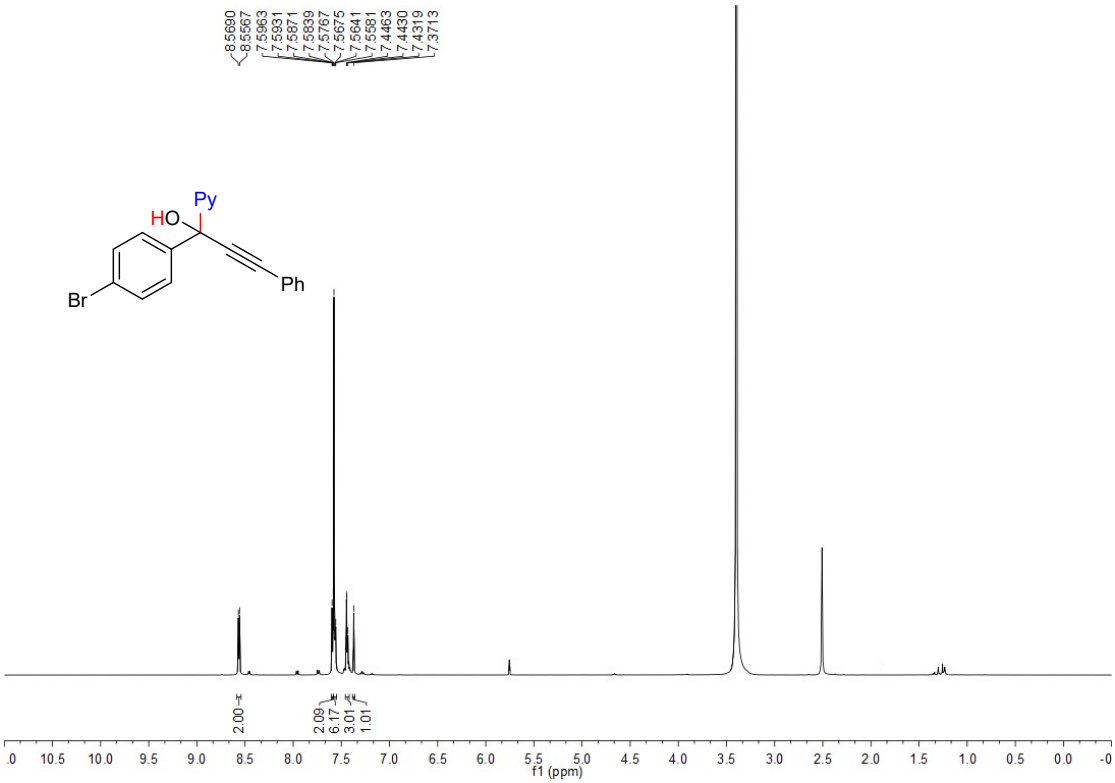


^{13}C NMR

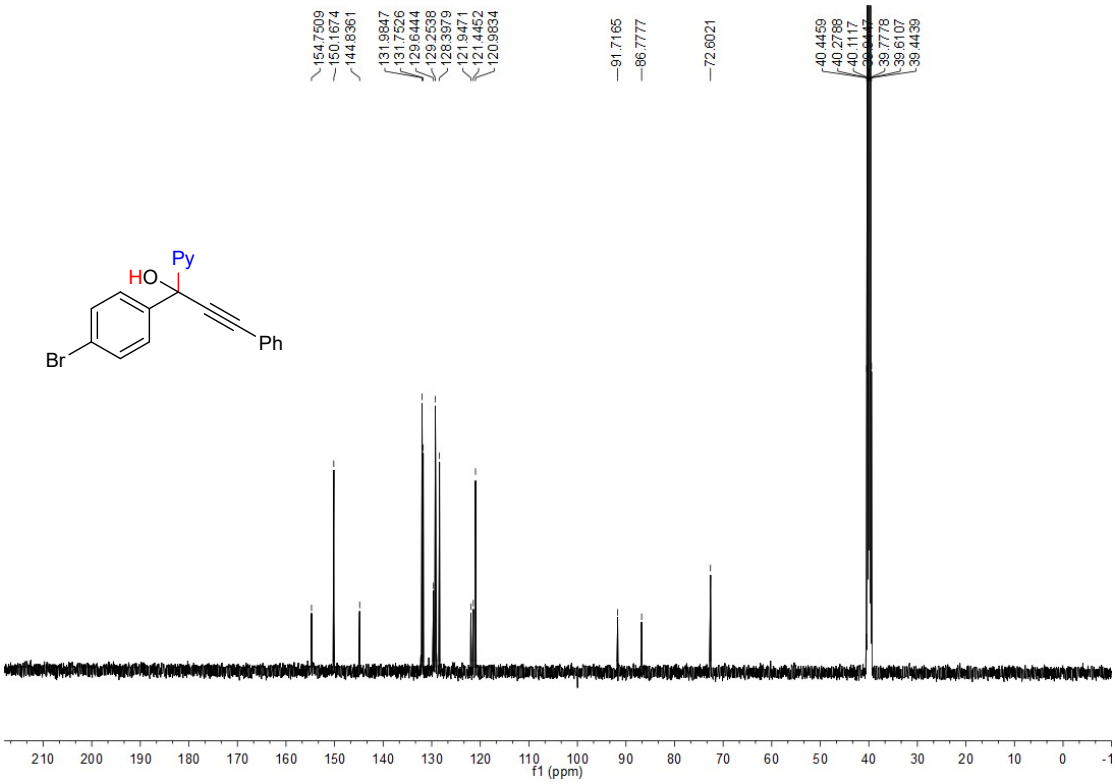


5d

^{1}H NMR

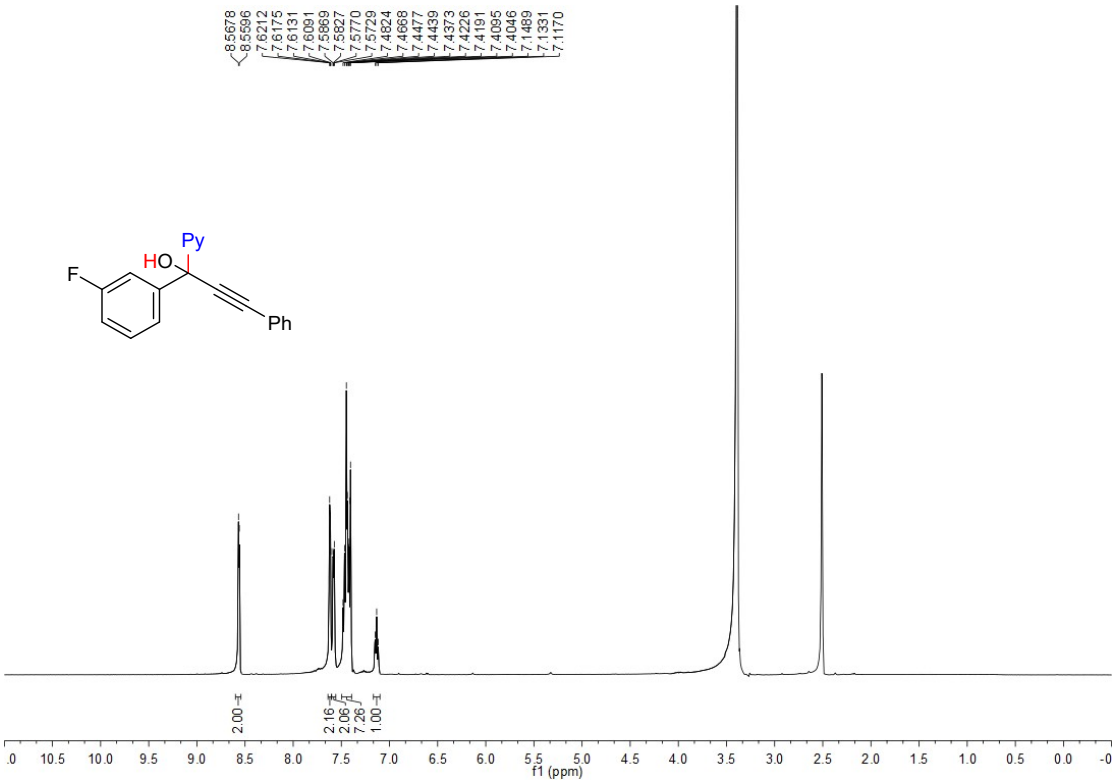


^{13}C NMR

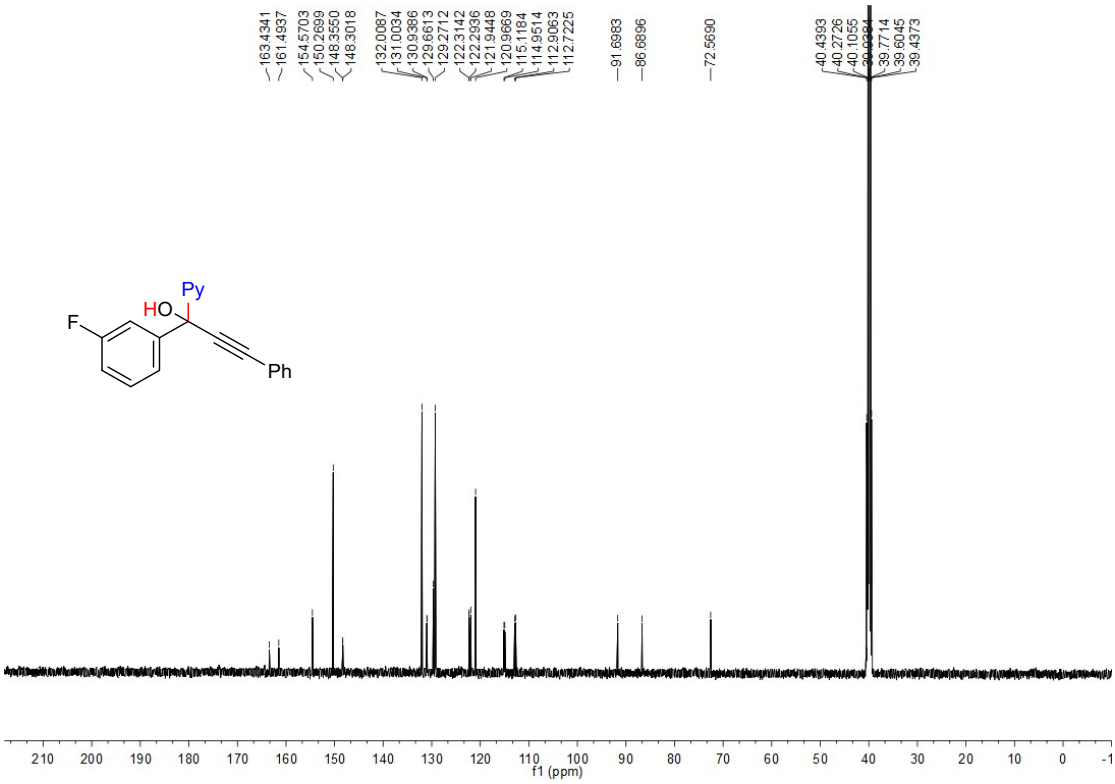


6d

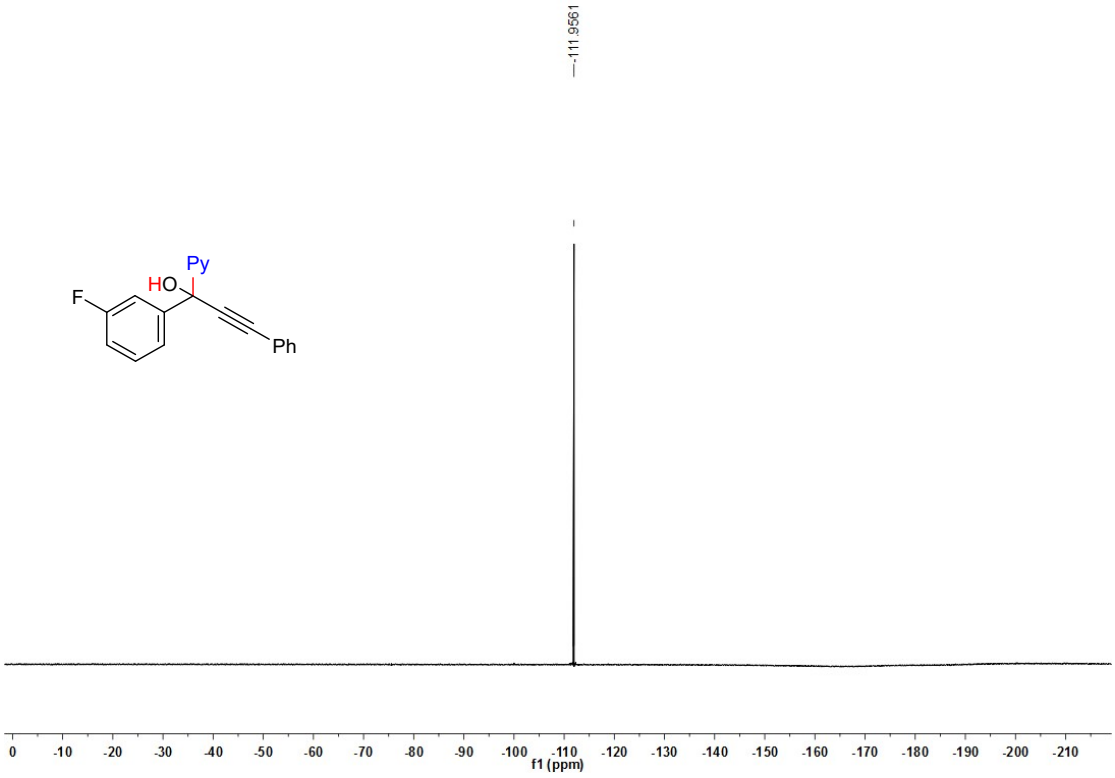
^{1}H NMR



^{13}C NMR

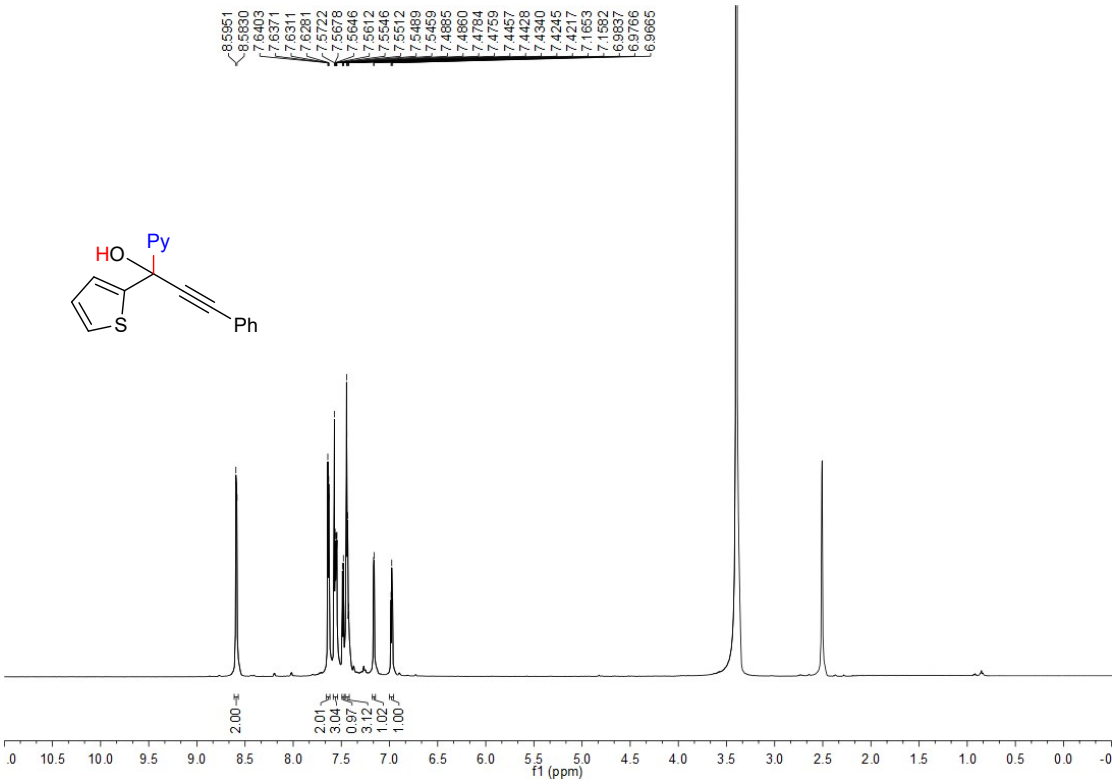


^{19}F NMR

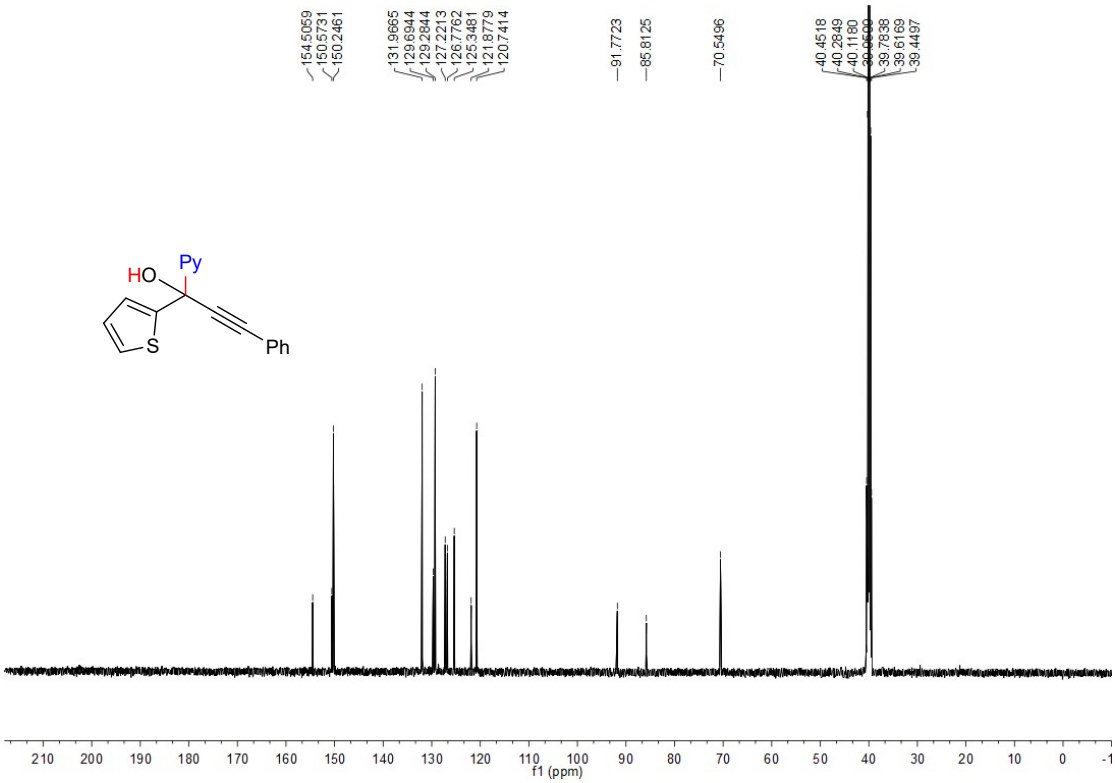

-111.9561
Py
HO
F
Ph
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

7d

^{1}H NMR

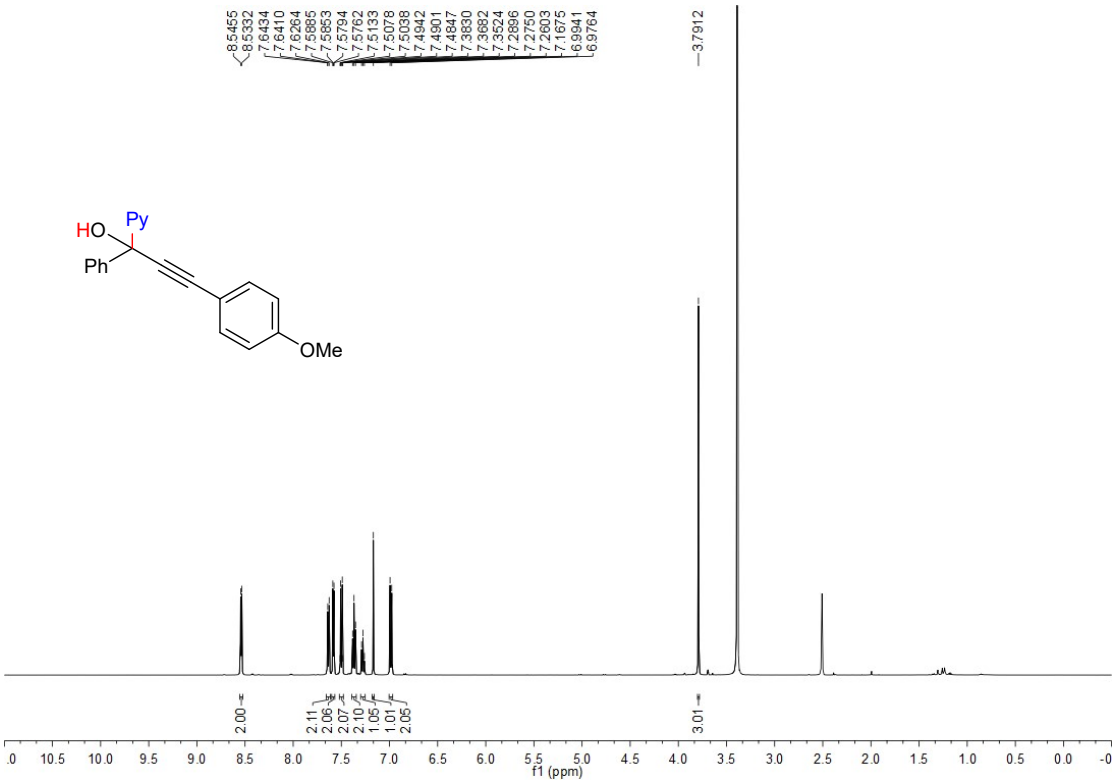


^{13}C NMR

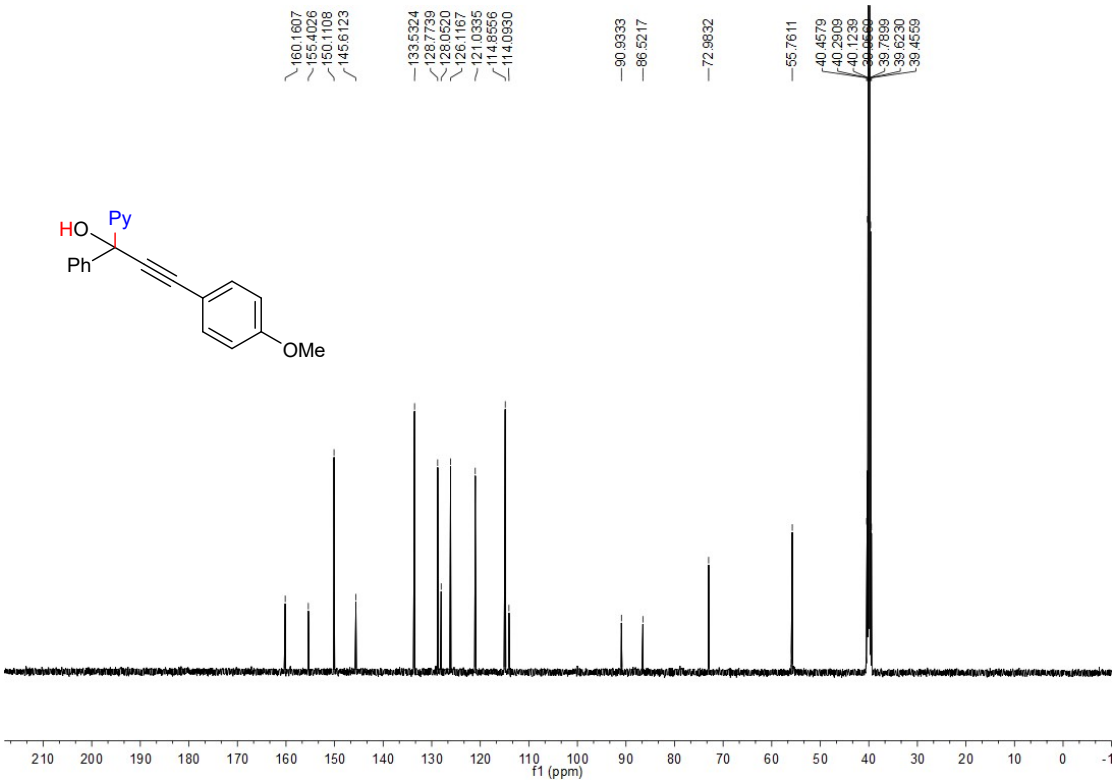


8d

^{1}H NMR

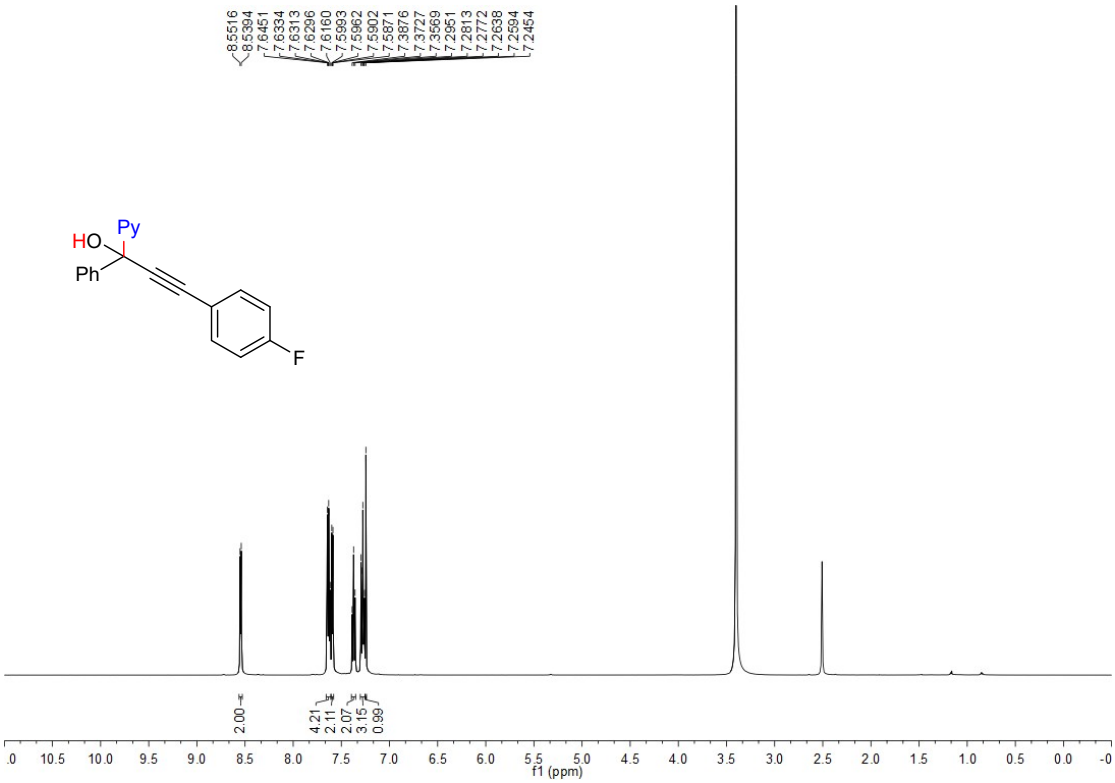


^{13}C NMR

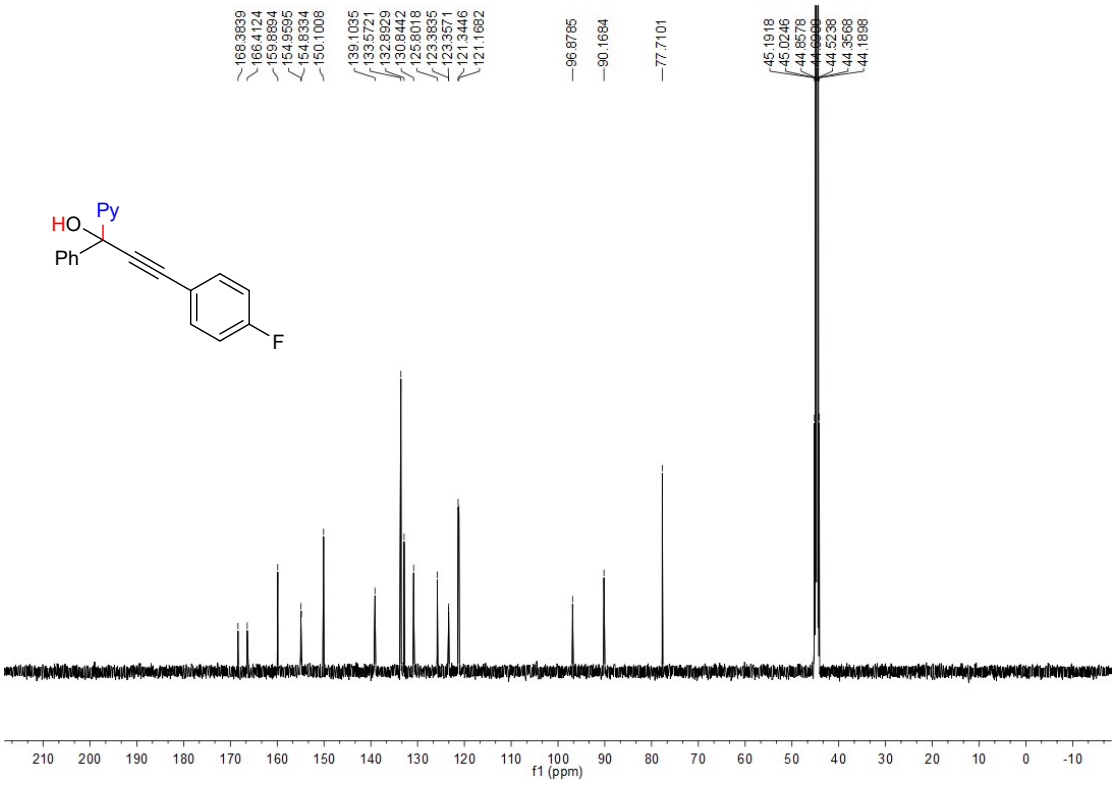


9d

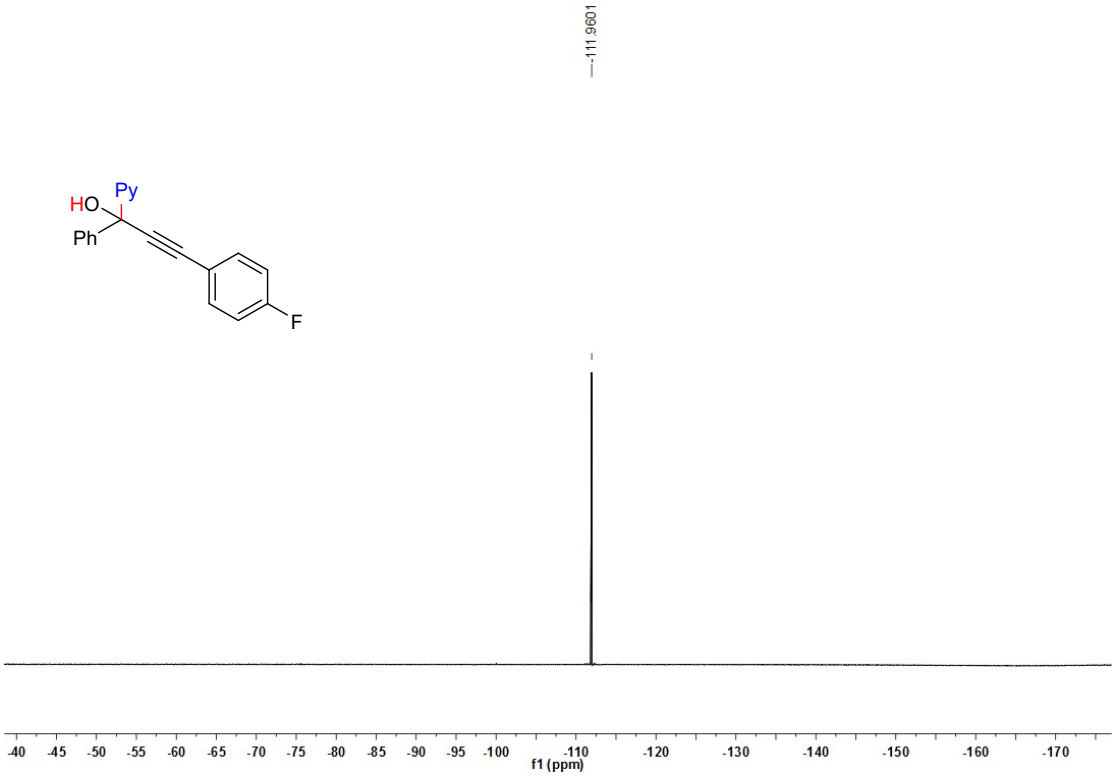
^{1}H NMR



^{13}C NMR

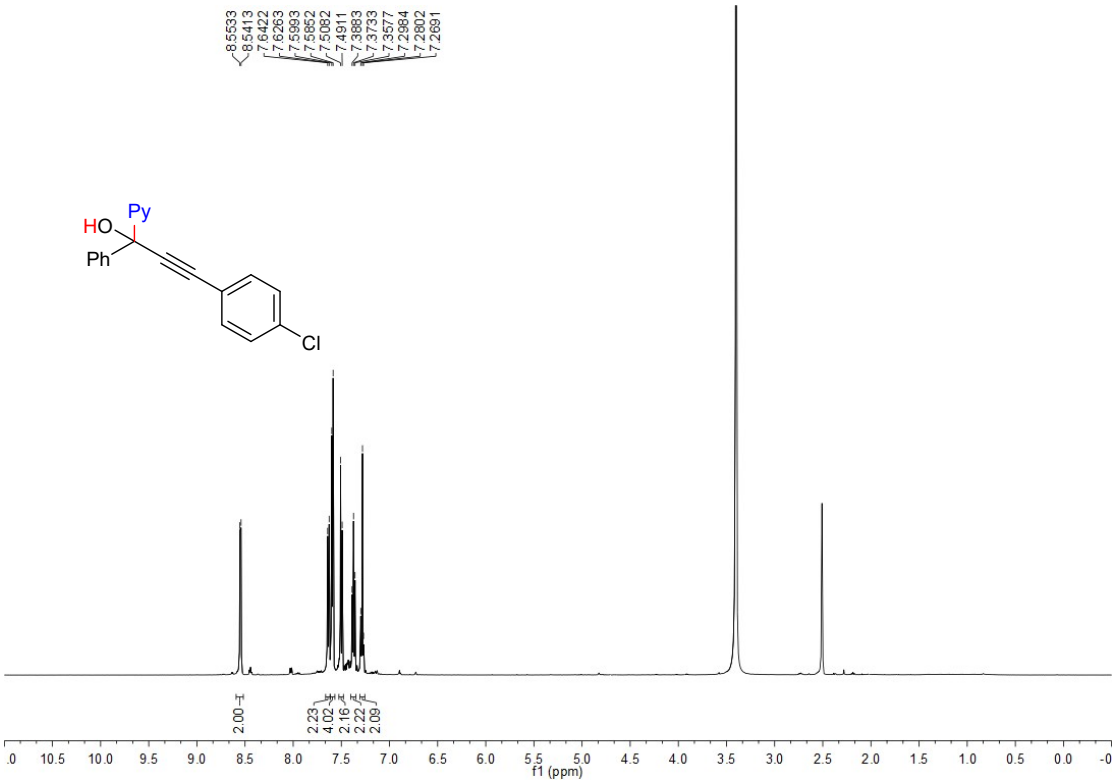


^{19}F NMR

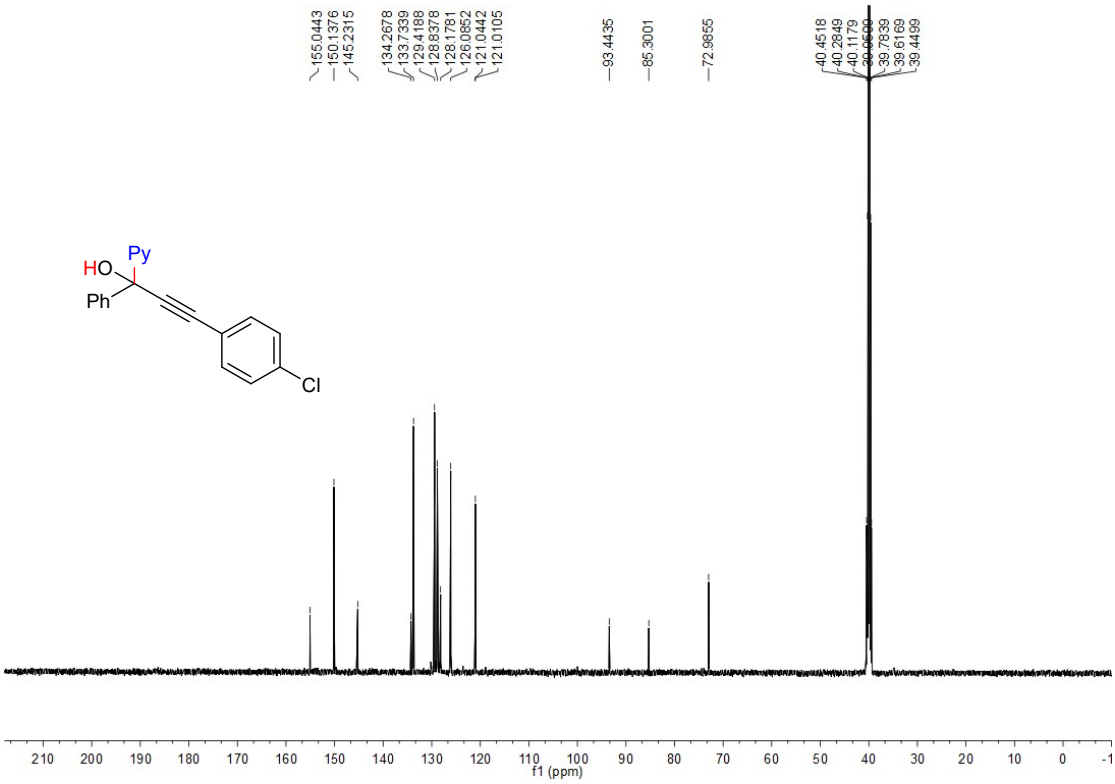

-111.9601
HO
Py
Ph
F
-40
-45
-50
-55
-60
-65
-70
-75
-80
-85
-90
-95
-100
-110
-120
-130
-140
-150
-160
-170
f1 (ppm)

10d

^{1}H NMR

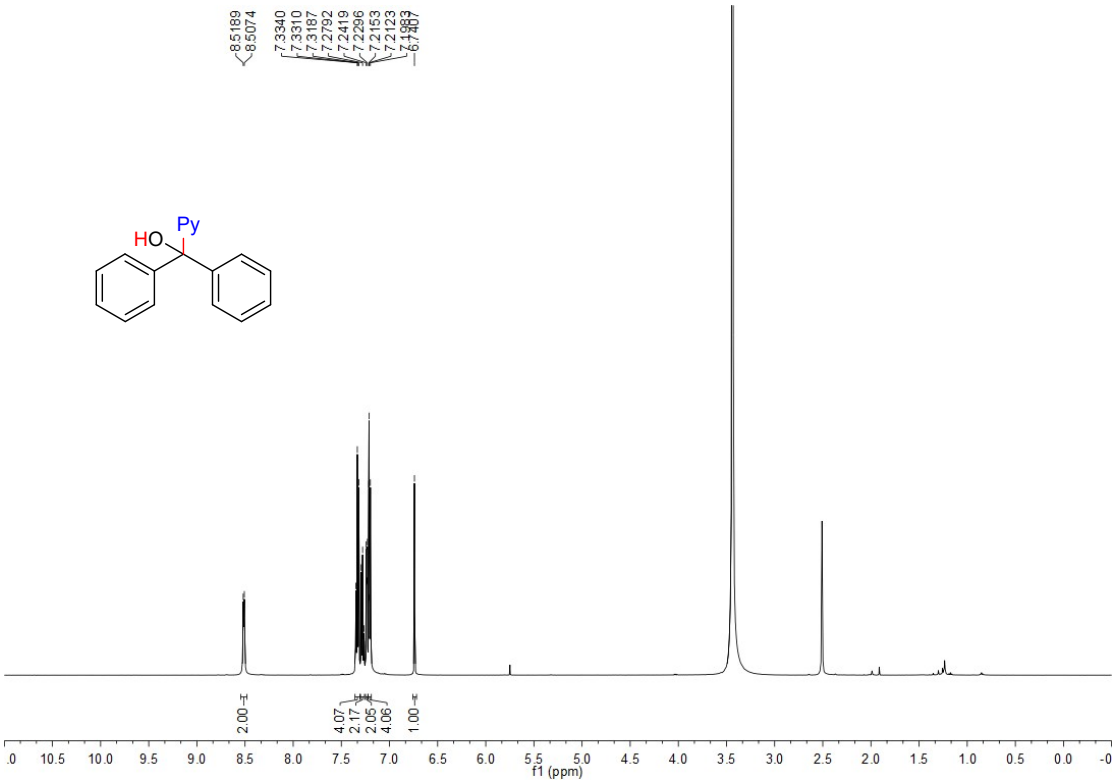


^{13}C NMR

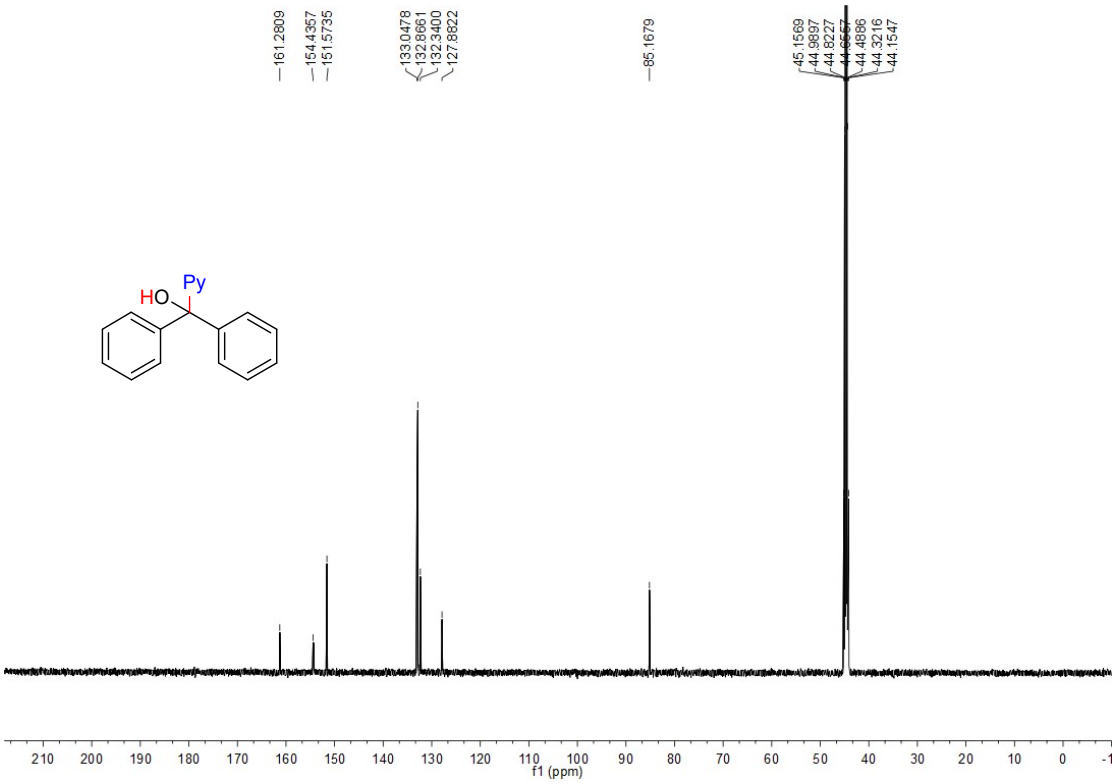


11d

^{1}H NMR

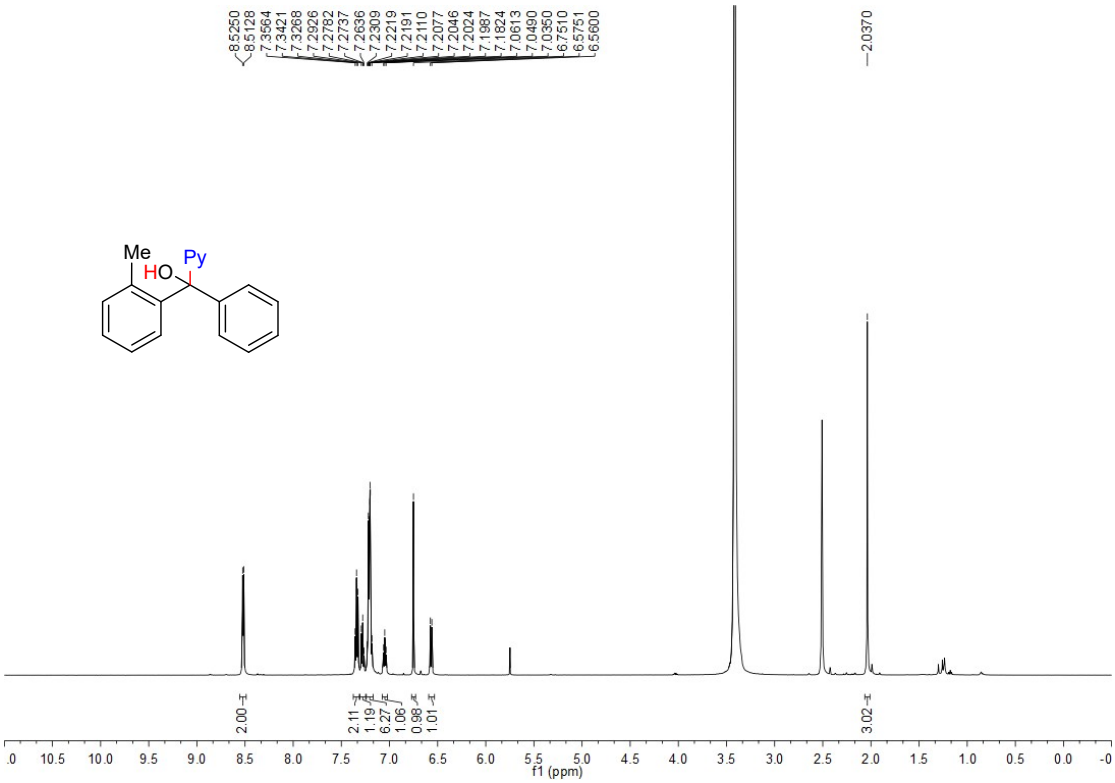


^{13}C NMR

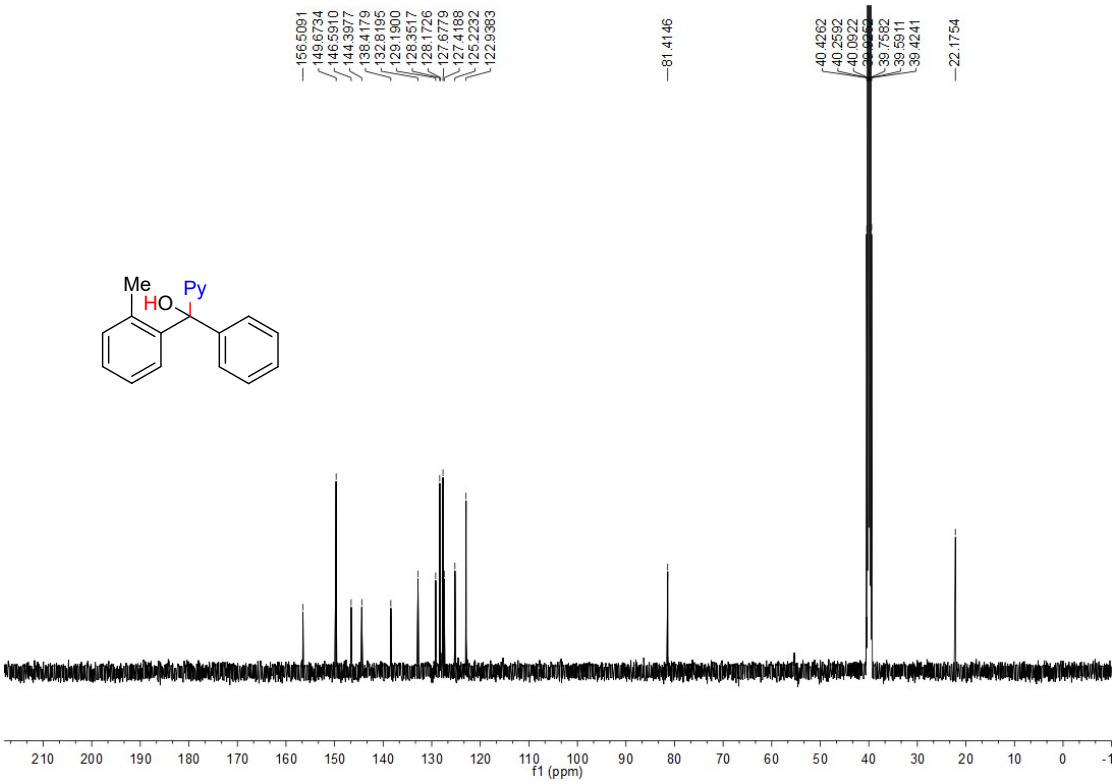


12d

^{1}H NMR

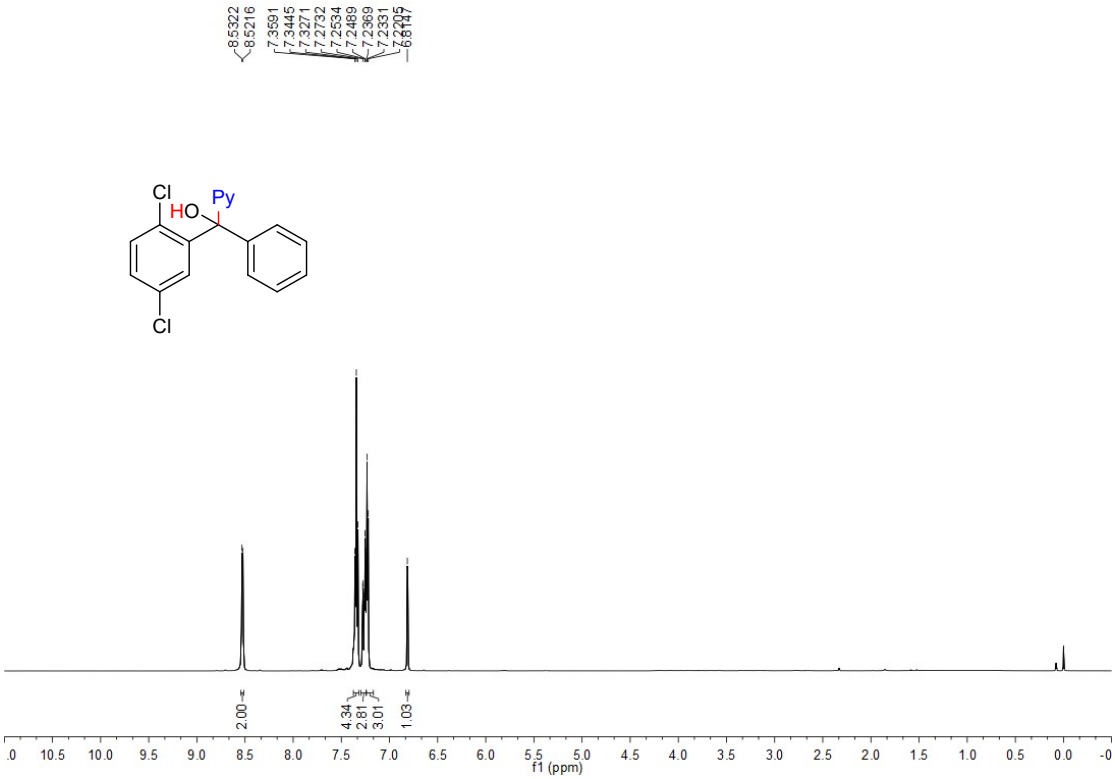


^{13}C NMR

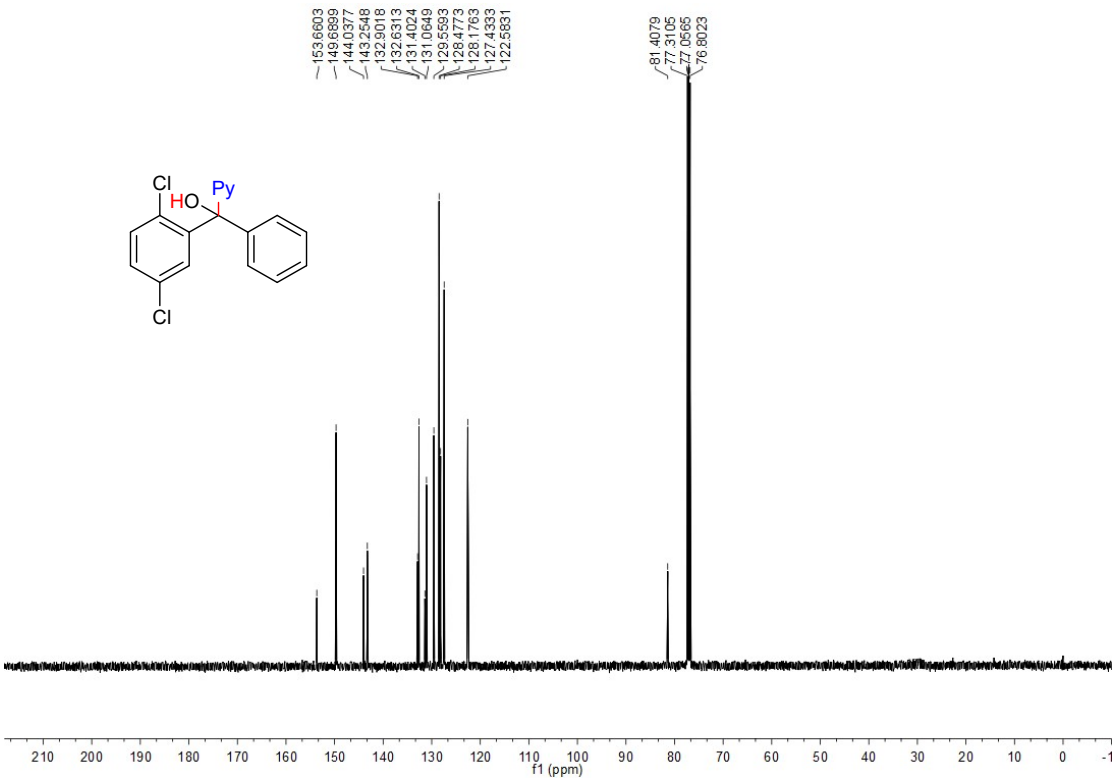


13d

^{1}H NMR

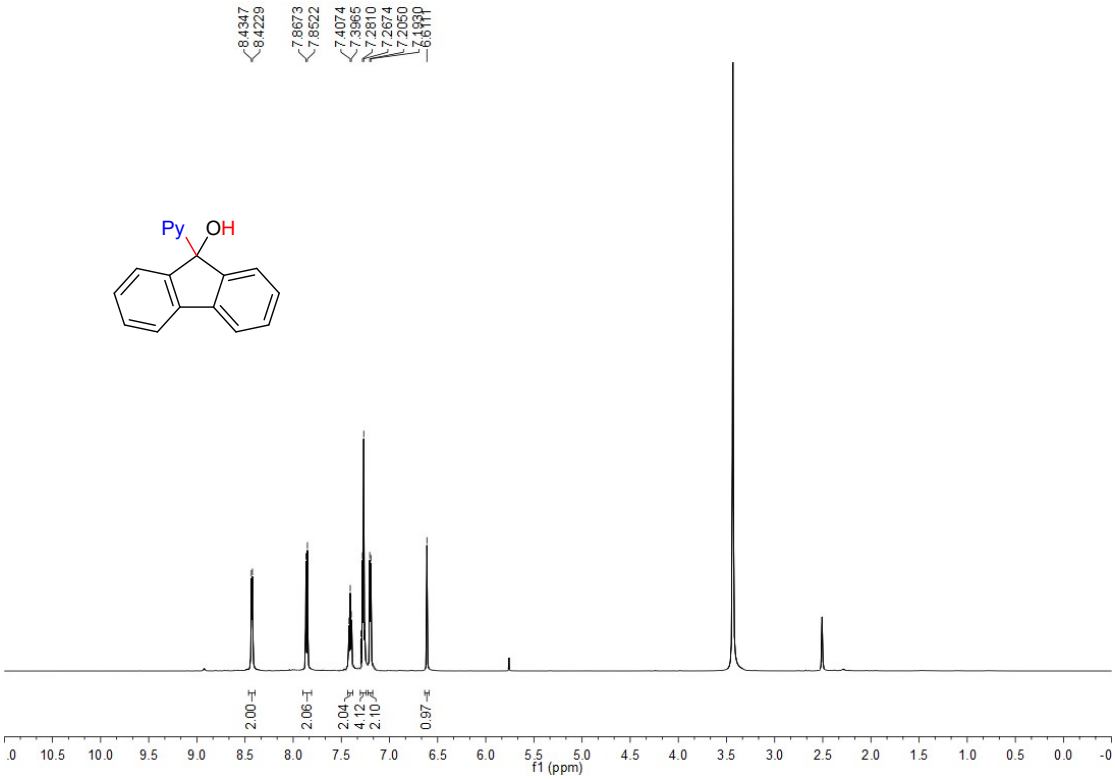


^{13}C NMR

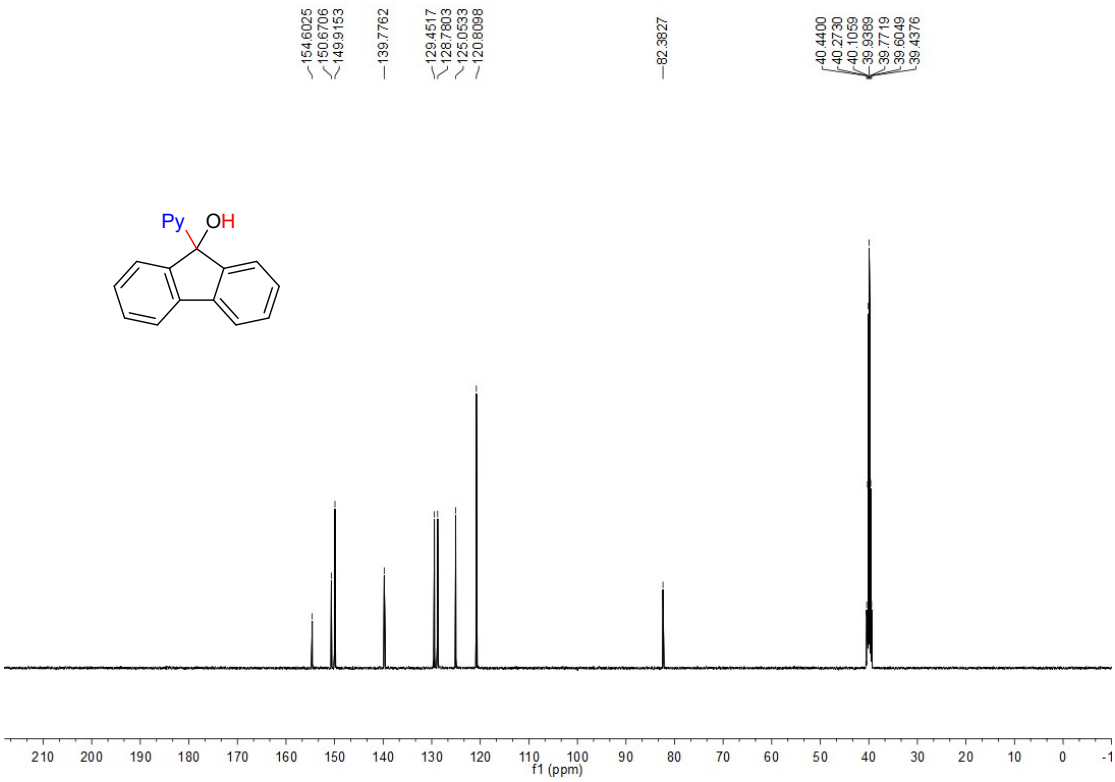


14d

^{1}H NMR

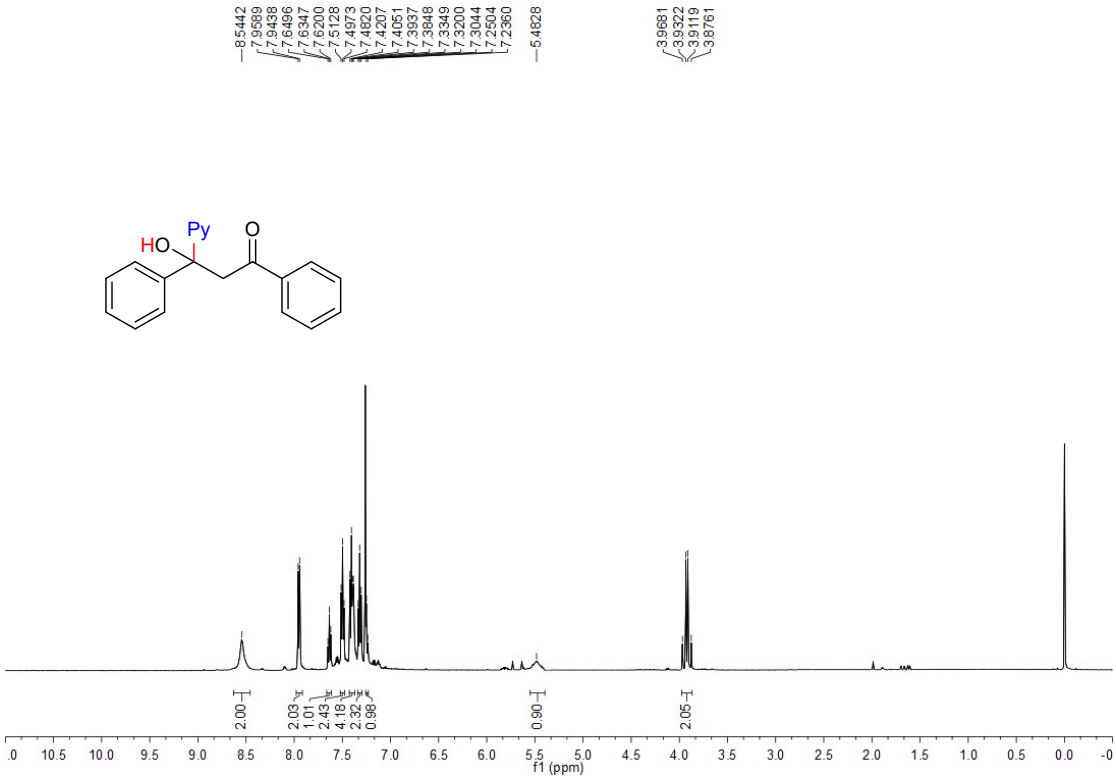


^{13}C NMR



15d

^{1}H NMR



^{13}C NMR