Electronic Supplementary Material (ESI) for ChemComm.

Supporting information

Cobaloxime-catalyzed hydration of terminal alkynes without acidic promoters

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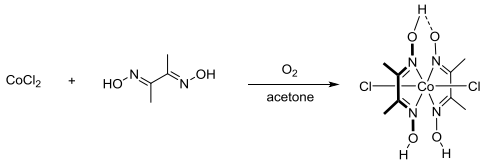
1. General remarks

The reactions were carried out under air in a closed J. Young tube. The catalysts were prepared according to the reported procedure. ^{1}H NMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on a Bruker AM 400 MHz instrument, Varian 300 MHz instrument. High-resolution mass spectral analysis (HRMS) data were measured on a Bruker ApexII mass spectrometer by means of the ESI technique. The IR spectra were recorded on Nicolet Nexus 670 FT-IR spectrometer. Column chromatography was performed on silica gel. ^{1}H and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz (or 300 MHz and 75 MHz) respectively using $CDCl_3$ as a solvent. Yields refer to isolated compounds, estimated to be > 95% pure as determined by ^{1}H-NMR, and GC-analysis. Chemical shifts are reported as δ values relative to internal chloroform (^{1}H and ^{13}C NMR relative to $CHCl_3$, δ 7.26 ppm for ^{1}H NMR and δ 77.0 ppm for ^{13}C NMR), multiplicities are indicated by s (singlet), d (doublet), t (triplet), q (quartet), p (pentet), h (hextet), m (multiplet) and br (broad). Coupling constants (*J*) are reported in Hertz (Hz). The product formation was monitored by ^{1}H NMR using aliquots containing the solvent mixture. All commercial reagents and solvents were obtained from the commercial provider and used without further purification.

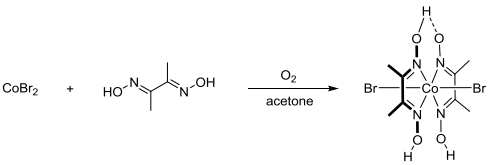
2 Synthesis of cobaloximes

2.1 $[Co(dmgH)(dmgH_2)Cl_2]$[1]



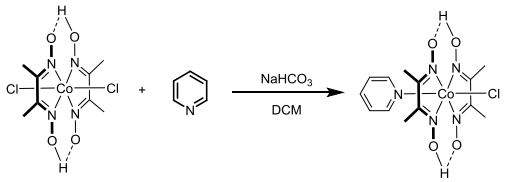
To a solution of $CoCl_2 6H_2O$ (5 g, 21.0 mmol， 1 eq.) in acetone (100 mL) was added a warmed solution of dimethylglyoxime (5 g, 43.1 mmol, 2.1 eq.) in acetone (150 mL). Air was bubbled through the resultant blue mixture and stirred for 20 minutes and then left to stand for 2 hours, yielding green crystals of $[Co(dmgH)(dmgH_2)Cl_2]$, which were filtered off and dried in a desiccator (7.51 g, 99%). ^{1}H NMR (300 MHz, Chloroform-*d*) 2.11 (s,12H).

2.2 $[Co(dmgH)(dmgH_2)Br_2]$[1]



Procedure analogous to the preparation of **2.1**

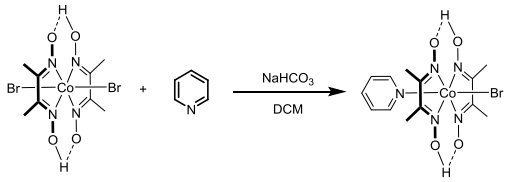
2.3 $[Co(dmgH)_2ClPy]$[1]



To a stirred suspension of $[Co(dmgH)(dmgH_2)Cl_2]$ (1 g, 2.8 mmol， 1 eq.) and pyridine (0.25 mL, 2.8 mmol，1 eq.) in dichloromethane (10 mL) was added $NaHCO_3$ (10 mL), and allowed to stir at room

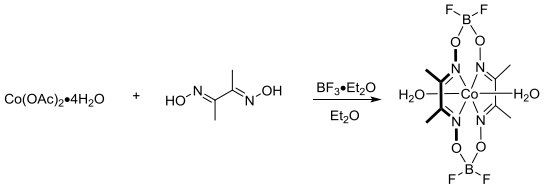
temperature for 1 hour, at which point, the solution was diluted further with dichloromethane (20 mL) and washed with water (2 × 20 mL). The organic fractions were combined, dried over Na_2SO_4, filtered and evaporated to dryness, yielding [Co(dmgH)$_2$ClPy] as a brown crystalline solid (0.99 g, 89%). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.28 (dd, *J* = 5.8 Hz, 2H), 7.69 (tt, *J* = 7.6 Hz, 1H), 7.23 (dt, *J* = 7.6 Hz,1.4 Hz, 2H), 2.40 (s, 12H).

2.4 [Co(dmgH)$_2$BrPy][1]



Procedure analogous to the preparation of **2.3**

2.5 [Co(dmgBF$_2$)$_2$•2H$_2$O][2]



Diethyl ether (150 mL, O_2-free) was added to a flask containing [Co(OAc)$_2$•4H$_2$O] (2.0 g, 8 mmol, 1 eq.) and dmgH$_2$ (1.9 g, 16 mmol, 2 eq.), followed by freshly distilled BF_3•Et_2O (10 mL, an excess). The mixture was stirred for 6 h under argon. The resulting solid was filtered under argon, washed with ice–cold water (3 × 10 mL, O_2-free) and air-dried. A brownish-red solid product was obtained (2.0 g, 4.8 mmol, 60% yield). IR (KBr) 3600, 3533, 3021, 2972, 2931, 1620, 1553, 1444, 1386, 1341, 1208, 1165, 1093, 1010, 954, 829, 627, 605 cm^{-1}.

3. Condition optimization of alkyne hydration

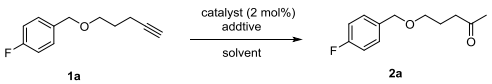


Table 1. condition optimization of cobalt-catalyzed hydratkion of **1a**.[a]

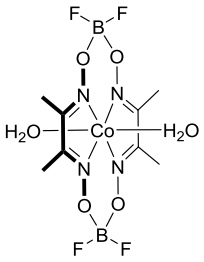
Entry	Catalyst	Additive	Solvent	Temp.(°C)	Time(h)	Yield[%] [b]
1	Co(dmgH)(dmgH$_2$)Cl$_2$	_	MeOH	80	3.5	86
2	Co(dmgH)(dmgH$_2$)Cl$_2$	_	MeOH	65	3.5	53
3	Co(dmgH)(dmgH$_2$)Br$_2$	_	MeOH	80	3.5	85
4	Co(dmgH)(dmgH$_2$)Br$_2$	_	MeOH	65	3.5	50
5[c]	Co(dmgH)(dmgH$_2$)Br$_2$	_	MeOH	65	3.5	85
6[c, d]	Co(dmgH)(dmgH$_2$)Br$_2$	_	MeOH	65	3.5	75
5	Co(dmgH)$_2$ClPy	_	MeOH	80	3.5	< 10
6	Co(dmgH$_2$)BrPy	_	MeOH	80	3.5	< 5

8	$Co(dmgBF_2)_2•2H_2O$	_	MeOH	80	3.5	87
9	$Co(dmgBF_2)_2•2H_2O$	_	MeOH	65	3.5	66
10	$Co(dmgBF_2)_2•2H_2O$	_	MeOH	80	3.5	87
11[c]	$Co(dmgBF_2)_2•2H_2O$	_	MeOH	80	1.5	99
12[c]	$Co(dmgBF_2)_2•2H_2O$	_	MeOH	65	3.5	99
13[c, d]	$Co(dmgBF_2)_2•2H_2O$	_	MeOH	65	3.5	9
14	$Co(dmgH)(dmgH_2)Br_2$	AgOTf (4 mol%)	MeOH	80	3.5	97
15	$Co(dmgH)(dmgH_2)Br_2$	AgOTf (2 mol%)	MeOH	80	3.5	70
16	$Co(dmgH)_2ClPy$	AgOTf (4 mol%)	MeOH	80	9	52
17	$Co(dmgH)(dmgH_2)Cl_2$	AgOTf (4 mol%)	CF_3COOH	rt	1d	< 10
18[e]	$Co(dmgH)(dmgH_2)Cl_2$	AgOTf (4 mol%)	MeOH	rt	1d	< 20
19[d]	$Co(dmgH)(dmgH_2)Cl_2$	AgOTf (4 mol%)	MeOH	80	3.5	97
20	$Co(dmgH)(dmgH_2)Cl_2$	AgOTf (4 mol%)	MeOH	80	3.5	97
21	$Co(dmgH)(dmgH_2)Br_2$	silver salicylate (4 mol%)	MeOH	80	3.5	36
22	$Co(dmgH)(dmgH_2)Br_2$	soldium salicylate (4 mol%)	MeOH	80	3.5	11
23	$Co(dmgH)(dmgH_2)Br_2$	$AgNO_3$ (4 mol%)	MeOH	80	3.5	87
24	$Co(dmgH)(dmgH_2)Br_2$	$AgNO_2$ (4 mol%)	MeOH	80	3.5	26
25	$Co(dmgH)(dmgH_2)Br_2$	$AgNTf_2$ (4 mol%)	MeOH	80	3.5	94
26	$Co(dmgH)(dmgH_2)Br_2$	$AgSbF_6$ (4 mol%)	MeOH	80	3.5	97
27	$Co(dmgH)(dmgH_2)Br_2$	$AgClO_4$ (4 mol%)	MeOH	80	3.5	97
28	$Co(dmgH)(dmgH_2)Br_2$	AgOAc (4 mol%)	MeOH	80	3.5	11
29	$Co(dmgH)(dmgH_2)Br_2$	AgOBz (4 mol%)	MeOH	80	3.5	35
30	$Co(dmgH)(dmgH_2)Br_2$	$AgOCOCF_3$ (4 mol%)	MeOH	80	3.5	60
31	$Co(dmgH)(dmgH_2)Br_2$	AgF (4 mol%)	MeOH	80	3.5	31
32[f]	$Co(dmgBF_2)_2•2H_2O$	_	MeOH	65	3.5	99

[a] reaction conditions: 0.25 mmol of alkyne **1a**, cobaloxime 2 mol%, 4 mol% additives in MeOH (1 mL), heated at the indicating temperature. [b] yield based on ^{19}F NMR. [c] 5 mol% Cobaloxime was used. [d] the reaction was carried out under an argon atmosphere. [e] the reaction was carried out under blue light. [f] the reaction was carried out in the dark.

4. Mechanistic Studies

4.1 XPS data of *Cat 5* recovered after reaction.



(***Cat 5***)

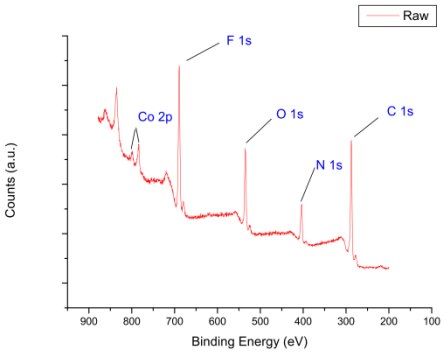


Figure **S1**. XPS survey spectra of the recovered ***Cat 5.***

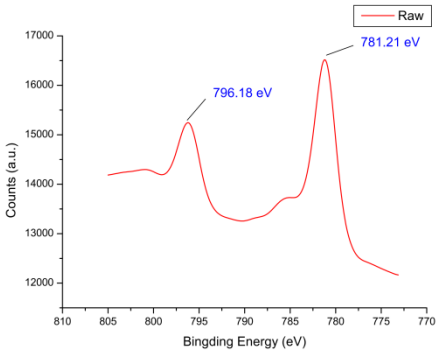
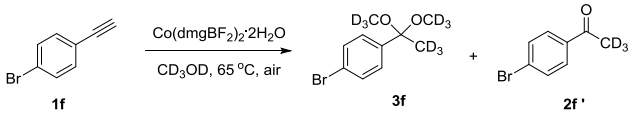


Figure **S2**. Co 2p core level XPS spectra of the recovered ***Cat 5.***

Core level photoemission associated with elemental components of the catalyst is observed. Co 2p core level spectra of the recovered catalyst (Figure S2) show peaks centered at 781.21 eV (2p3/2) and 796.18 eV (2p1/2) with the expected 2:1 branching ratio. The 14.9 eV peak separation and the binding energy value are characteristic of the Co(III) oxidation state.[3]

4.2 GC–MS and ^{1}H NMR spectra of $Co(dmgBF_2)_2{\bullet}2H_2O$ catalyzed hydration of **1f** in CD_3OD.[a]



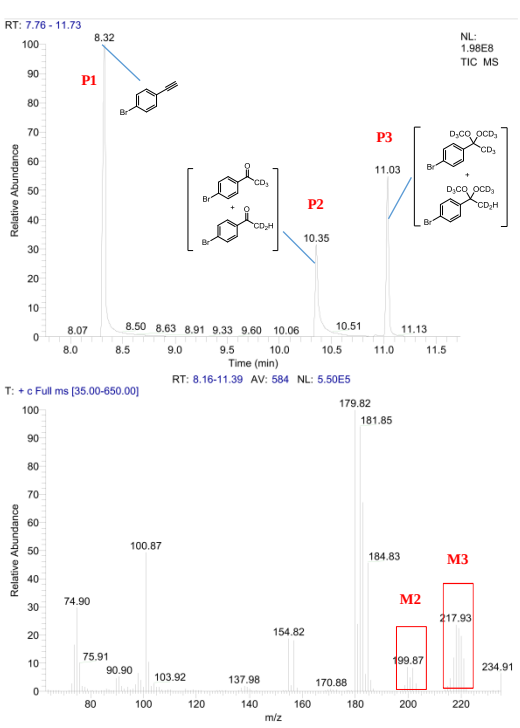


Figure S3. GC–MS spectra after 1.5 hours of reaction.

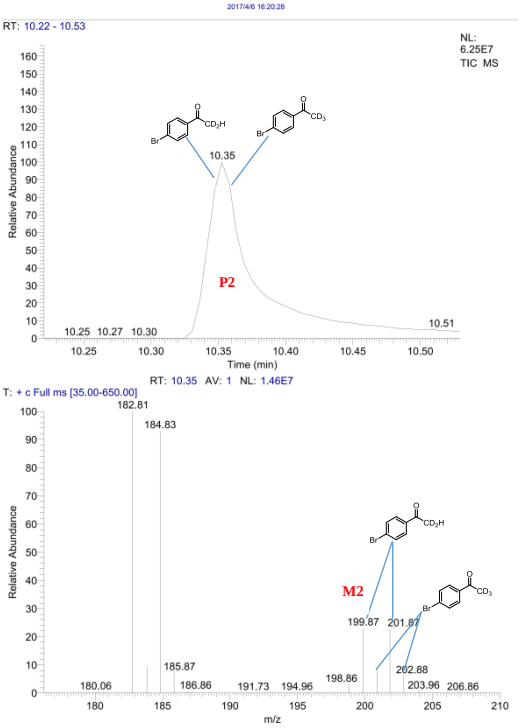


Figure S4. Enlarged GC-MS of P2 and M2.

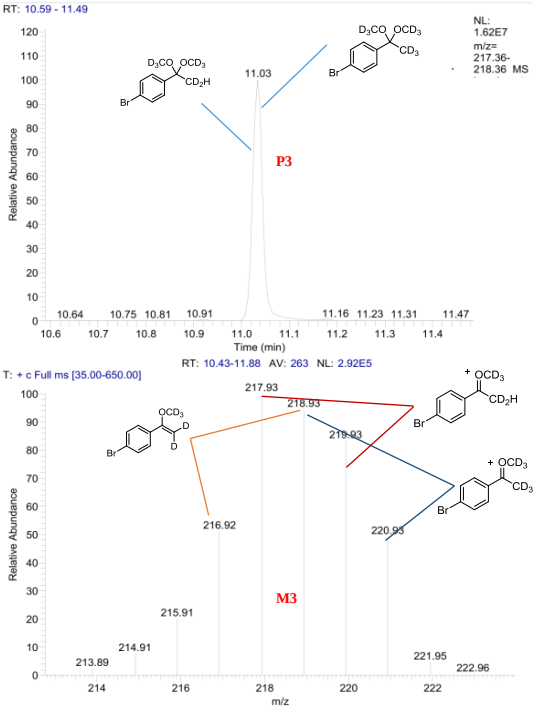


Figure S5. Enlarged GC-MS of P3 and M3

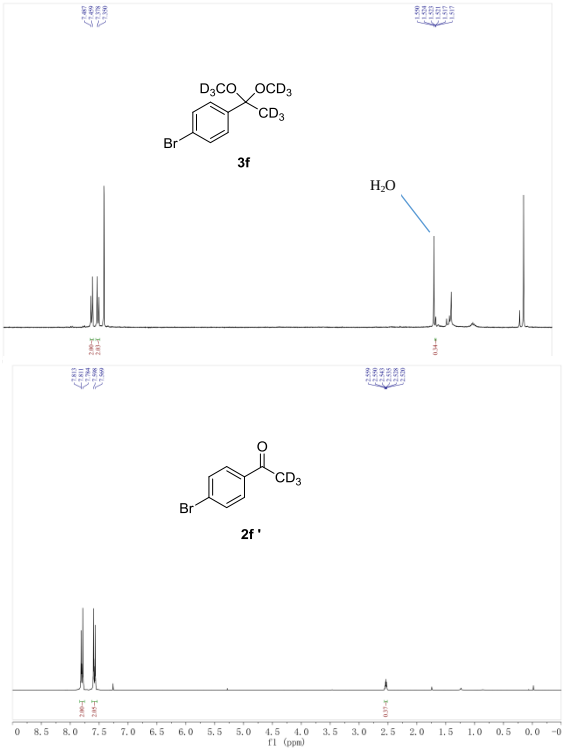
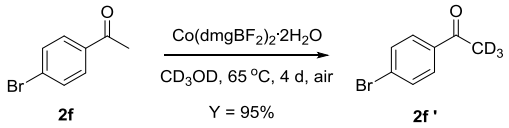


Figure S6. H NMR spectra of **2f'** and **3f**

[a] Reaction conditions: 0.25 mmol of alkyne **1f**, cobaloxime (***Cat 5***.) 5 mol% in CD_3OD (1 mL), heated to the indicating temperature (65 °C) under aerobic conditions. The mixture was stirred for 1.5 h and monitored by GC–MS.

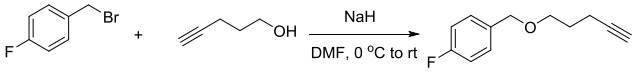


Reaction conditions: 0.25 mmol of alkyne **2f**, cobaloxime (***Cat 5***.) 5 mol% in CD_3OD (1 mL), heated to the indicating temperature (65 °C) under aerobic conditions. The mixture was stirred for 4 d. The reaction mixture was carefully quenched by addition of 0.05 mL H_2O, before the tube was cooled to 25 ℃. The volatiles were removed under reduced pressure and the pure product **2f'** (95%) was obtained by flash chromatography of silica gel.

5. Experimental Procedure and Analytical Data of Products

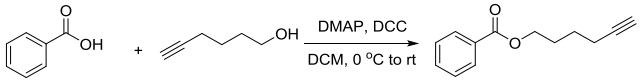
5.1Typical procedures for hydration of alkynes

1a:



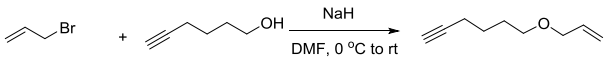
To a solution of NaH (308 mg, 16 mmol, 1.2 eq.) in dry DMF (20 mL) at 0 °C was slowly added pent-4-yn-1-ol (1 mL, 13 mmol， 1 eq.). 1-(bromomethyl)-4-fluorobenzene (2 mL 16 mmol, 1.2 eq.) was added to the solution. The mixture was allowed to warm up to room temperature and to stir overnight. The reaction was quenched by water, and extracted by ethyl acetate. The organic phase was washed by brine and dried with Na_2SO_4. After concentration the crude was purified by silica gel chromatography to provide **1a**[4] (1.01 g, 40% yield) as a colorless oil. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.37 – 7.22 (m, 2H), 7.06 – 6.96 (m, 2H), 4.45 (s, 2H), 3.55 (t, *J* = 6.2 Hz, 2H), 2.30 (td, *J* = 6.9 Hz, 2.7 Hz, 2H), 1.94 (t, *J* = 2.7 Hz, 1H), 1.81 (p, *J* = 6.6 Hz, 2H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ162.2 (d, *J* = 243.8 Hz), 134.1 (d, *J* = 3 Hz), 129.2 (d, *J* = 8 Hz), 115.1 (d, *J* = 21 Hz), 83.8, 72.1, 68.5, 68.5, 28.5, 15.2; HRMS [ESI] calcd for $C_{12}H_{14}FO$ $[M+H]^+$ 193.1023, found 193.1026.

1q:



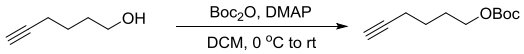
To a solution of 5-hexyn-1-ol (630 mg, 6.4 mmol, 1 eq.) in dry DCM (18 mL) at 0 °C was added DMAP (800 mg, 6.4 mmol, 1 eq.), DCC (1.67 g, 8.2 mmol, 1.3 eq.) and benzoic acid (1 g, 8.2 mmol, 1.3 eq.). After addition, the solution was warmed up to room temperature and stirred for 5 hours. The reaction was quenched by H_2O, and extracted by DCM. The organic phase was washed with brine and dried by Na_2SO_4. After concentration the crude was purified by silica gel chromatography to provide **1q**[5] (0.90 g 70% yield) as a yellow oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.10 – 7.95 (m, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.6 Hz, 2H), 4.34 (t, *J* = 6.4 Hz, 2H), 2.27 (td, *J* = 7.0, 2.6 Hz, 2H), 1.96 (t, *J* = 2.6 Hz, 1H), 1.94 – 1.82 (m, 2H), 1.76 – 1.62 (m, 2H).

1s:



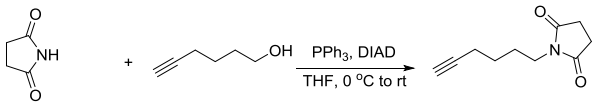
To a solution of NaH (57 mg, 2.4 mmol, 1.2 eq.) in dry DMF (5 mL) at 0 °C was slowly added 5-hexyn-1-ol (196 mg, 2 mmol, 1 eq.). The slurry followed by dropwise addition of 3-bromoprop-1-ene (0.46 g, 3.8 mmol, 1.9 eq.) under constant agitation. The mixture was allowed to warm up to room temperature and to stir overnight. The reaction was quenched by water, and extracted by ethyl acetate. The organic phase was washed by brine and dried with Na_2SO_4. After concentration the crude was purified by silica gel chromatography to provide **1s**[5] (110 mg, 40% yield) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.11 – 5.75 (m, 1H), 5.26 (dd, *J* = 17.2 Hz, 1.6 Hz, 1H), 5.19 – 5.13 (m, 1H), 3.96 (dd, *J* = 5.6, 1.2 Hz, 2H), 3.45 (t, *J* = 6.3 Hz, 2H), 2.22 (td, *J* = 6.9, 2.6 Hz, 2H), 1.94 (t, *J* =2.6 Hz, 1H), 1.81 – 1.48 (m, 4H).

1u



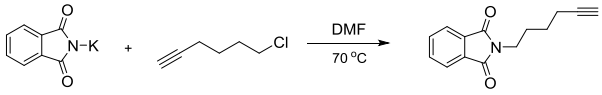
To a solution of 5-hexyn-1-ol (500 mg, 5.1 mmol, 1 eq.) in dry DCM (20 mL) at 0 °C was added DMAP (61 mg, 0.5 mmol, 0.1 eq.) and Boc_2O (1.17g, 5.35 mmol, 1.05 eq.). After addition, the solution was warmed up to room temperature and stirred for 6 hours. The reaction was quenched by H_2O, and extracted by DCM. The organic phase was washed with brine and dried by Na_2SO_4. After concentration the crude was purified by silica gel chromatography to provide **1u** (320 mg 31% yield) as a colorless oil. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 4.08 (t, *J* = 6.3 Hz, 2H), 2.22 (td, *J* = 7.0, 2.7 Hz, 2H), 1.94 (t, *J* = 2.6 Hz, 1H), 1.85 – 1.70 (m, 2H), 1.68 – 1.55 (m, 2H), 1.48 (s, 9H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 153.6, 83.8, 81.9, 68.7, 66.4, 27.8, 27.7, 24.7, 18.0; HRMS [ESI] calcd for $C_{11}H_{18}O_3Na$ $[M+Na]^+$ 221.1148, found 221.1145.

1v



To a stirring solution of 5-hexyn-1-ol (500 mg, 5.1 mmol, 1 eq.), 2,5-Dioxopyrrolidine (555 mg, 5.6 mmol, 1.1 eq.), and PPh_3 (1.47 g, 5.6 mmol, 1.1 eq.) in THF (22 mL) was added diisopropyl azodicarboxylate (957 mg, 5.6 mmol, 1.1 eq.) at 0 ℃. The mixture was stirred for 30 min and allowed to come to room temperature. The reaction was allowed to stir for 7 h. The reaction was quenched by $NaHCO_3$, and extracted by ethyl acetate. The organic phase was washed with brine and dried by Na_2SO_4. After concentration the crude was purified by silica gel to provide **1v**[6] (350 mg, 38% yield) as a colorless oil. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 3.53 (t, *J* = 7.2 Hz, 2H), 2.70 (s, 4H), 2.22 (dt, *J* = 6.9, 1.5 Hz, 2H), 1.94 (t, *J* = 2.6 Hz, 1H), 1.76 – 1.63 (m, 2H), 1.58 – 1.45 (m, 2H).

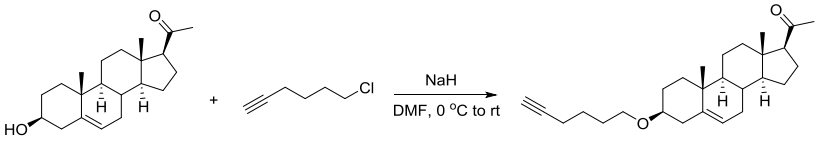
1w:



A round-bottom flask was charged with 6-chlorohex-1-yne (1.05 g 4.5 mmol, 1 eq.) and 20 mL of dry DMF. Potassium phthalimide (2 g, 5.4 mmol, 1.2 eq.) was added to the yellowish solution. The yellowish suspension was heated at 70 ℃ for 24 h. The resulting solution was cooled to room temperature, and 70 mL of H_2O was added into the solution. The mixture was extracted under air with

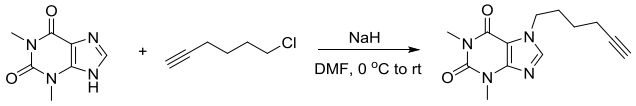
Et_2O (4 × 70 mL), and the combined organic layers were dried over anhydrous $MgSO_4$, filtered, and concentrated on a rotary evaporator. The crude residue was purified by silica gel chromatography to provide **1w**[7] (1.7 g, 85% yield) as a white solid. **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.86-7.83 (m, 2H), 7.73-7.70 (m, 2H), 3.71 (t, *J*= 6.0 Hz, 2H), 2.25 (td, *J*= 7.0, 2.7 Hz, 2H), 1.96 (t, *J* = 2.7 Hz, 1 Hz), 1.86-1.77 (m, 2H), 1.63-1.53 (m, 2H).

1x:



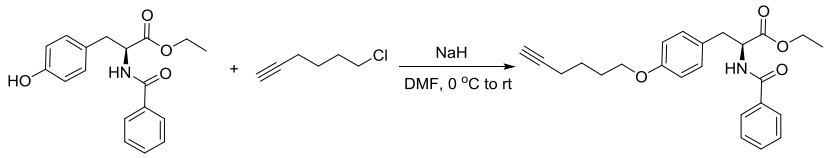
To a clean, dry 25 mL two-neck round-bottom flask were added sodium hydride (364 mg, 15.2 mmol, 12 eq.) and anhydrous DMF (8 mL). The slurry was cooled to 0 ℃ followed by addition of Pregnenolone (0.4 g, 1.26 mmol, 1 eq.). The slurry followed by dropwise addition of 6-Chloro-1-hexyne (221 mg, 1.90 mmol, 1.5 eq.) under constant agitation. The mixture was stirred for 30 min and allowed to come to room temperature. The reaction was allowed to stir for 20 h. The reaction was quenched by water, and extracted by ethyl acetate. The combined organic layers were dried over anhydrous $MgSO_4$ and filtered. After concentration the crude was purified by silica gel to provide **1x** (75 mg, 15% yield) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.34 (d, *J* = 5.2 Hz ,1H), 3.48 (t, *J* = 5.8 Hz, 2H), 3.18-3.07 (m, 1H), 2.52 (t, *J* = 8.8 Hz, 1H), 2.40-2.30 (m, 1H), 2.21 (td, *J* = 7.2, 2.4 Hz, 3H), 2.12 (s, 3H), 2.07 – 1.95 (m, 2H), 1.94 (t, *J* = 2.6 Hz ,1H), 1.92 – 1.83 (m, 2H), 1.74-1.38 (m, 13H), 1.31-1.17 (m, 3H), 1.10-1.02 (m, 1H), 0.99 (s, 3H), 0.62 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 209.5, 141.0, 121.1, 84.4, 78.9, 68.3, 67.3, 63.7, 56.9, 50.0, 44.0, 39.1, 38.8, 37.2, 36.9, 31.82, 31.79, 31.5, 29.2, 28.4, 25.3, 24.5, 22.8, 21.0, 19.4, 18.2, 13.2; HRMS [ESI] calcd for $C_{27}H_{40}O_2Na$ $[M+Na]^+$ 419.2921, found 419.2922.

1y:



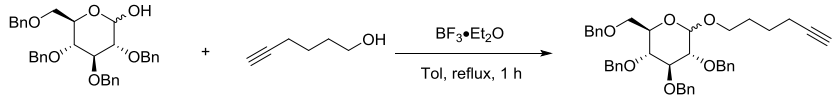
To a clean, dry 20 mL round-bottom flask were added sodium hydride (399 mg, 16.6 mmol, 3 eq.) and anhydrous DMF (10 mL). The slurry was cooled to 0 ℃ followed by addition of Theophylline (1.0 g, 5.55 mmol, 1 eq.). The slurry followed by dropwise addition of 6-Chloro-1-hexyne (776 mg, 6.67 mmol, 1.2 eq.) under constant agitation. The mixture was stirred for 30 min and allowed to come to room temperature and the mixture was allowed to stir for 12 h at room temperature. The reaction was ended by addition of a large excess of water (10 mL) and the product extracted with ethyl acetate (5 × 25 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and filtered. After concentration the crude was purified by silica gel to provide **1y**[8] (72 mg, 5% yield) as a white solid. m.p. 58.4-60.4 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.55 (s, 1H), 4.33 (t, *J* = 7.0 Hz, 2H), 3.60 (s, 3H), 3.41 (s, 3H), 2.25 (td, *J* = 6.8, 2.7 Hz, 2H), 2.07 – 1.98 (m, 2H), 1.97 (t, *J* = 2.6 Hz, 1H), 1.61 – 1.46 (m, 2H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 155.0, 151.6, 148.9, 140.7, 106.9, 83.3, 69.1, 46.7, 29.9, 29.7, 27.9, 25.0, 17.9; HRMS [ESI] calcd for $C_{13}H_{17}N_4O_2$ $[M+H]^+$ 261.1346, found 261.1349.

1z



To a clean, dry 20 mL round-bottom flask were added sodium hydride (115 mg, 4.79 mmol, 3 eq.) and anhydrous DMF (12 mL). The slurry was cooled to 0 ℃ followed by addition of Ethyl N-benzoyl-L-tyrosinate (500 mg, 1.6 mmol, 1 eq.). The slurry followed by dropwise addition of 6-Chloro-1-hexyne (186 mg, 1.6 mmol, 1 eq.) under constant agitation. The mixture was stirred for 30 min and allowed to come to room temperature and the mixture was allowed to stir for 7 h at room temperature. The reaction was ended by addition of a large excess of water (10 mL) and the product extracted with ethyl acetate. (5 × 10 mL). The combined organic layers were dried over anhydrous $MgSO_4$ and filtered. After concentration the crude was purified by silica gel to provide **1z** (43.9 mg, 7% yield) as a white solid. m.p. 69.6-71.6 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 7.2 Hz, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.80 (d, *J* = 8.4 Hz, 2H), 6.61 (d, *J* = 7.6 Hz, 1H), 5.06 – 4.97 (m, 1H), 4.21 (q, *J* = 7.2 Hz, 2H), 3.95 (t, *J* = 6.2 Hz, 2H), 3.26 – 3.12 (m, 2H), 2.27 (td, *J* = 7.2, 2.5 Hz, 2H), 1.96 (t, *J* = 2.6 Hz, 1H), 1.93 – 1.85 (m, 2H), 1.76-1.66 (m, 2H), 1.29 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 171.6, 166.7, 158.1, 134.0, 131.7, 130.4, 128.6, 127.7, 127.0, 114.5, 84.0, 68.6, 67.2, 61.6, 53.6, 37.0, 28.2, 25.0, 18.1, 14.2; HRMS [ESI] calcd for $C_{24}H_{28}NO_4$ $[M+H]^+$ 394.2013, found 394.2013.

1aa



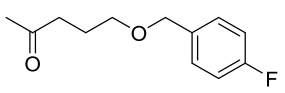
In a 25 mL flask equipped with a stirring bar and a condenser, tetrabenzyl D-glucose (400 mg, 1 mmol, 1 eq.), hex-5-yn-1-ol (363 mg, 5 mmol, 5 eq.), and BF_3 OEt_2 (420 mg, 4 mmol, 4 eq.) were dissolved in toluene (8 mL). The mixture was refluxed, and cooled to room temperature. The mixture was evaporated, and the residue was purified by silica gel column chromatography to afford **1aa**[5] (320 mg, 70%, a mixture of α/β isomers) as a colorless oil. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.42-7.25 (m, 18H), 7.22-7.13 (m, 2H), 5.07-4.40 (m, 9H), 4.05-3.96 (m, 1H), 3.85-3.42 (m, 7H), 2.30-2.20 (m, 2H), 1.98 (t, *J*= 2.6 Hz, 1H), 1.88-1.58 (m, 4H).

5.2 Hydration of Terminal Alkynes 2 to Methyl Ketones.

A Representative Procedure for Hydration of Terminal Alkynes

(A) General Procedures.

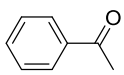
A mixture of alkyne **1a** (50 mg), ***cat.5*** (5 mol%) in CH_3OH (0.25 mol/L) was heated at 65 ℃ under air for 3.5 h in a closed J. Young tube. The progress of the reaction was checked using TLC. The reaction mixture was carefully quenched by addition of H_2O (12 eq.), before the tube was cooled to 25 ℃. The volatiles were removed under reduced pressure and the pure product **2a** as a colorless oil (52.5 mg, 96% yield) was obtained by flash chromatography of silica gel.



5-((4-fluorobenzyl)oxy)pentan-2-one (2a)

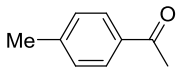
^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.34-7.23 (m, 2H), 7.02 (t, *J* = 8.6 Hz, 2H), 4.43 (s, 2H), 3.47 (t, *J* = 6.2 Hz, 2H), 2.54 (t, *J* = 7.2 Hz, 2H), 2.13 (s, 3H), 1.95 – 1.83 (m, 2H); **^{13}C NMR** (75 MHz, Chloroform-*d*) δ 208.3, 162.1 (d, *J* = 243.8 Hz),

134.0 (d, *J* = 3 Hz), 129.1 (d, *J* = 8.2 Hz), 115.0 (d, *J* = 21 Hz), 71.9, 69.1, 40.1, 29.8, 23.7. Colorless oil,. HRMS [ESI] calcd for $C_{12}H_{15}FO_2Na$ $[M+Na]^+$ 233.0948, found 233.0950.



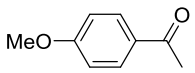
Acetophenone (2b)

Prepared according to general procedure **A** from **1b** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 ^oC for 5 h. Compound **2b** was isolated as a colorless oil (52.9 mg, 96% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.99 – 7.93 (m, 2H), 7.56 (t, *J* = 8.0 Hz, 1H), 7.46 (t, *J* = 7.6 Hz, 2H), 2.61 (s, 3H). The spectral data were in agreement with literature values.[5]



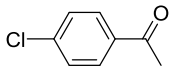
1-(p-tolyl)ethan-1-one (2c)

Prepared according to general procedure **A** from **1c** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 ^oC for 2.5 h. Compound **2c** was isolated as a colorless oil (54.8 mg, 95% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.85 (d, *J* = 8.4 Hz, 2H), 7.25 (d, *J* = 8.1 Hz, 2H), 2.57 (s, 3H), 2.40 (s, 3H). The spectral data were in agreement with literature values.[9]



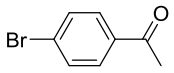
1-(4-methoxyphenyl)ethan-1-one (2d)

Prepared according to general procedure **A** from **1d** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 ^oC for 4 h. Compound **2d** was isolated as a colorless oil (51.1 mg, 90% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.92 (d, *J* = 9.0 Hz, 2H), 6.92 (d, *J* = 8.9 Hz, 2H), 3.85 (s, 3H), 2.54 (s, 3H). The spectral data were in agreement with literature values.[5]



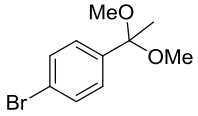
1-(4-chlorophenyl)ethan-1-one (2e)

Prepared according to general procedure **A** from **1e** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 ^oC for 3.5 h. Compound **2e** was isolated as a colorless oil (53.2 mg, 94% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.88 (d, *J* = 8.8 Hz, 2H), 7.41 (d, *J* = 8.8 Hz, 2H), 2.57 (s, 3H). The spectral data were in agreement with literature values.[10]



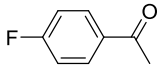
1-(4-bromophenyl)ethan-1-one (2f)

Prepared according to general procedure **A** from **1f** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 ^oC for 4.5 h. Compound **2f** was isolated as a white solid (50.6 mg, 92% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.82 (d, *J* = 8.4 Hz, 2H), 7.60 (d, *J* = 8.4 Hz, 2H), 2.59 (s, 3H). The spectral data were in agreement with literature values.[10]



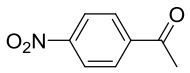
1-bromo-4-(1,1-dimethoxyethyl)benzene (2f-Intermediate)

^{1}H NMR (300 MHz, Chloroform-*d*) δ 7.47 (d, *J* = 8.4 Hz, 2H), 7.36 (d, *J* = 8.4 Hz, 2H), 3.17 (s, 6H), 1.51 (s, 3H). Colorless oil. The spectral data were in agreement with literature values.[12]



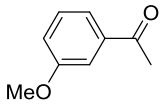
1-(4-fluorophenyl)ethan-1-one (2g)

Prepared according to general procedure **A** from **1g** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 3.5 h. Compound **2g** was isolated as a colorless oil (54.0 mg, 94% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.02-7.93 (m, 2H), 7.12 (t, *J* =8.7 Hz, 2H), 2.58 (s, 3H). The spectral data were in agreement with literature values.[5]



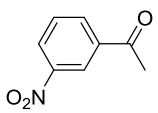
1-(4-nitrophenyl)ethan-1-one (2h)

Prepared according to general procedure **A** from **1h** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 60 h. Compound **2h** was isolated as a yellow solid (46.0 mg, 82% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.29 (d, *J* = 8.7 Hz, 2H), 8.10 (d, *J* = 8.7 Hz, 2H), 2.67 (s, 3H). The spectral data were in agreement with literature values.[13]



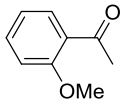
1-(3-methoxyphenyl)ethan-1-one (2i)

Prepared according to general procedure **A** from **1i** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 2.5 h. Compound **2i** was isolated as a colorless oil (54.5 mg, 96% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.52 (d, *J* = 7.5 Hz, 1H), 7.48 (s, 1H), 7.36 (t, *J* = 8.0 Hz, 1H), 7.10 (dd, *J* = 8.4, 2.7 Hz, 1H), 3.84 (s, 3H), 2.58 (s, 3H). The spectral data were in agreement with literature values.[14]



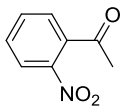
1-(3-nitrophenyl)ethan-1-one (2j)

Prepared according to general procedure **A** from **1j** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 49 h. Compound **2j** was isolated as a yellow solid (51.1 mg, 91% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.75 (t, *J* = 1.8 Hz, 1H), 8.44-8.37 (m, 1H), 8.28 (dt, *J* = 7.8 Hz, 1.4 Hz, 1H), 7.68 (t, *J* = 8.0 Hz, 1H), 2.68 (s, 3H). The spectral data were in agreement with literature values.[11]



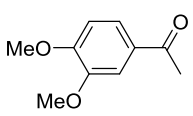
1-(2-methoxyphenyl)ethan-1-one (2k)

Prepared according to general procedure **A** from **1k** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 2.5 h. Compound **2k** was isolated as a colorless oil (52.8 mg, 93% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.72 (dd, *J* = 7.6, 1.6 Hz, 1H), 7.47 – 7.42 (m, 1H), 7.01 – 6.91 (m, 2H), 3.89 (s, 3H), 2.60 (s, 3H). The spectral data were in agreement with literature values.[15]



1-(2-nitrophenyl)ethan-1-one (2l)

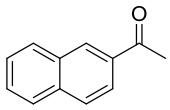
Prepared according to general procedure **A** from **1l** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 60 h. Compound **2l** was isolated as a white solid (33.7 mg, 60% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.09 (d, *J* = 8.1 Hz, 1H), 7.72 (t, *J* = 7.2 Hz, 1H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.43 (d, *J* = 7.2 Hz, 1H), 2.56 (s, 3H). The spectral data were in agreement with literature values.[14]



1-(3,4-dimethoxyphenyl)ethan-1-one (2m)

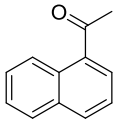
Prepared according to general procedure **A** from **1m** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 2.5 h. Compound **2m** was isolated as a white

solid (52.8 mg, 95% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.56 (d, *J* = 8.4 Hz, 1H), 7.51 (s, 1H), 6.87 (d, *J* = 8.4 Hz, 1H), 3.93 (s, 3H), 3.92 (s, 3H), 2.55 (s, 3H). The spectral data were in agreement with literature values.[10]



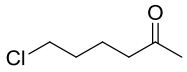
1-(naphthalen-2-yl)ethan-1-one (2n)

Prepared according to general procedure **A** from **1n** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 3.5 h. Compound **2n** was isolated as a white solid (53.1 mg, 95% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.46 (s, 1H), 8.04 (dd, *J* = 8.4, 1.5 Hz, 1H), 7.97 (d, *J* = 7.8 Hz, 1H), 7.92-7.84 (m, 2H), 7.65-7.50 (m, 2H), 2.73 (s, 3H). The spectral data were in agreement with literature values.[16]



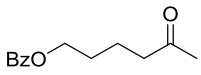
1-(naphthalen-1-yl)ethan-1-one (2o)

Prepared according to general procedure **A** from **1o** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 2.5 h. Compound **2o** was isolated as a yellow oil (52.0 mg, 93% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 8.76 (d, *J* = 8.4 Hz, 1H), 8.00 (d, *J* = 8.4 Hz, 1H), 7.94 (d, *J* = 7.2 Hz, 1H), 7.88 (d, *J* = 7.6 Hz, 1H), 7.61 (t, *J* = 7.2 Hz, 1H), 7.57-7.47 (m, 2H), 2.75 (s, 3H). The spectral data were in agreement with literature values.[10]



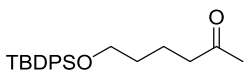
6-chlorohexan-2-one (2p)

Prepared according to general procedure **A** from **1p** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 2.5 h. Compound **2p** was isolated as a colorless oil (56.6 mg, 98% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 3.43 (t, *J* = 6.3 Hz, 2H), 2.38 (t, *J* = 6.8 Hz, 2H), 2.04 (s, 3H), 1.75-1.47 (m, 4H). The spectral data were in agreement with literature values.[15]



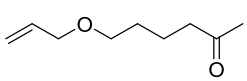
5-oxohexyl benzoate (2q)

Prepared according to general procedure **A** from **1q** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 12 h. Compound **2q** was isolated as a colorless oil (52.8 mg, 97% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 8.04 (d, *J* = 7.2 Hz, 2H), 7.56 (t, *J* = 7.4 Hz, 1H), 7.43 (t, *J* = 7.5 Hz, 2H), 4.32 (t, *J* = 6.0 Hz, 2H), 2.52 (t, *J* = 6.8 Hz, 2H), 2.15 (s, 3H), 1.82 – 1.72 (m, 4H). The spectral data were in agreement with literature values.[5]



6-tert-Butyldiphenylsilyloxy-2-hexanone (2r)

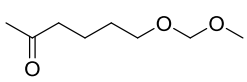
Prepared according to general procedure **A** from **1r** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 3 h. Compound **2r** was isolated as a light yellow oil (31.6 mg, 60% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.70 – 7.61 (m, 4H), 7.46 – 7.34 (m, 6H), 3.66 (t, *J* = 6.2 Hz, 2H), 2.41 (t, *J* = 7.2 Hz, 2H), 2.12 (s, 3H), 1.72 – 1.61 (m, 2H), 1.58 – 1.49 (m, 2H), 1.05 (s, 9H). The spectral data were in agreement with literature values.[5]



6-(allyloxy)hexan-2-one (2s)

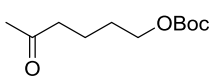
Prepared according to general procedure **A** from **1s** (50 mg) and ***cat.5*** (5

mol%) in MeOH (0.25 mol/mL) at 65 °C for 4.5 h. Compound **2s** was isolated as a colorless oil (53.7 mg, 96% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 6.02 – 5.73 (m, 1H), 5.25 (d, *J* = 17.2 Hz, 1H), 5.16 (d, *J* = 10.4 Hz, 1H), 3.95 (d, *J* = 6.0 Hz, 2H), 3.43 (t, *J* = 6.2 Hz, 2H), 2.45 (t, *J* = 7.2 Hz, 2H), 2.13 (s, 3H), 1.70 – 1.50 (m, 4H). The spectral data were in agreement with literature values.[5]



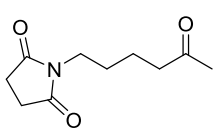
6-(methoxymethoxy)hexan-2-one (2t)

Prepared according to general procedure **A** from **1t** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 13 h. Compound **2t** was isolated as a colorless oil (51.3 mg, 91% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 4.56 (s, 2H), 3.48 (t, *J* = 6.2 Hz, 2H), 3.31 (s, 3H), 2.43 (t, *J* = 7.2 Hz, 2H), 2.10 (s, 3H), 1.66 – 1.51 (m, 4H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 208.7, 96.3, 67.3, 55.0, 43.2, 29.8, 29.0, 20.4. HRMS [ESI] calcd for $C_8H_{16}O_3Na$ $[M+Na]^+$ 183.0992, found 183,0989.



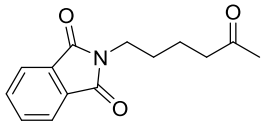
tert-butyl (5-oxohexyl) carbonate (2u)

Prepared according to general procedure **A** from **1u** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 20 h. Compound **2u** was isolated as a colorless oil (46.9 mg, 86% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 4.04 (t, *J* = 5.8 Hz, 2H), 2.45 (t, *J* = 6.6 Hz, 2H), 2.12 (s, 3H), 1.68-1.60 (m, 4H), 1.46 (s, 9H); **^{13}C NMR** (101 MHz, Chloroform-*d*) δ 208.3, 153.5, 81.9, 66.5, 43.0, 29.9, 28.0, 27.7, 20.0. HRMS [ESI] calcd for $C_{11}H_{20}O_4Na$ $[M+Na]^+$ 239.1254, found 239.1251.



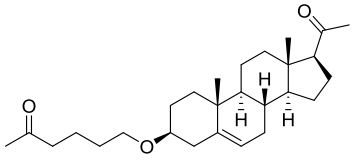
1-(5-oxohexyl)pyrrolidine-2,5-dione (2v)

Prepared according to general procedure **A** from **1v** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 6 h. Compound **2v** was isolated as a colorless oil (44.0 mg, 80% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 3.45 (t, *J* = 6.3 Hz, 2H), 2.66 (s, 4H), 2.42 (t, *J* = 6.4 Hz, 2H), 2.08 (s, 3H), 1.53 – 1.48 (m, 4H). **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 208.2, 177.2, 42.6, 38.2, 29.9, 28.0, 26.9, 20.5. HRMS [ESI] calcd for $C_{10}H_{16}NO_3$ $[M+H]^+$ 198.1125, found 198.1122.



2-(5-oxohexyl)isoindoline-1,3-dione (2w)

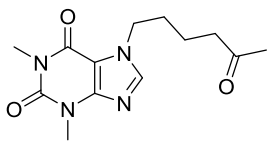
Prepared according to general procedure **A** from **1w** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 3.5 h. Compound **2w** was isolated as a white solid (53.4 mg, 99% yield). **^{1}H NMR** (300 MHz, Chloroform-*d*) δ 7.84 – 7.76 (m, 2H), 7.72-7.65 (m, 2H), 3.66 (t, *J* = 6.8 Hz, 2H), 2.46 (t, *J* = 6.9 Hz, 2H), 2.11 (s, 3H), 1.75 – 1.51 (m, 4H). The spectral data were in agreement with literature values.[17]



6-(((3S,8S,9S,10R,13S,14S,17S)-17-acetyl-10,13-dimethyl-2,3,4,7,8,9,10,11,12,13,14,15,16,17-tetradecahydro-1H-cyclopenta[a]phenanthren-3-yl)oxy)hexan-2-one (2x)

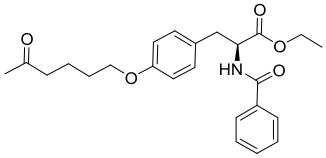
Prepared according to general procedure **A** from **1x** (50 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 5 h. Compound **2x** was isolated as a white solid (51.2 mg, 98% yield). m.p. 94.8 – 96.8 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 5.33 (d, *J* = 5.6 Hz, 1H), 3.45 (td, *J* = 6.4, 1.6 Hz, 2H), 3.16-3.06 (m, 1H), 2.52 (t, *J* = 8.8 Hz, 1H), 2.45 (t, *J* = 7.4 Hz, 2H), 2.38-2.31 (m, 1H), 2.22-2.14 (m, 2H), 2.13 (s, 3H), 2.11 (s, 3H), 2.06 – 1.81 (m, 4H), 1.71 – 1.37 (m, 13H), 1.25 – 1.02 (m, 3H), 0.98 (s, 3H), 0.62 (s, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 209.5, 209.0, 141.0, 121.1, 78.9, 67.6, 63.7, 56.9, 50.0, 44.0, 43.5, 39.1, 38.8, 37.2, 36.9, 31.8, 31.77, 31.5,

29.9, 29.6, 28.4, 24.4, 22.8, 21.0, 20.6, 19.3, 13.2; HRMS [ESI] calcd for $C_{27}H_{42}O_3Na$ $[M+Na]^+$ 437.3026, found 437.3026.



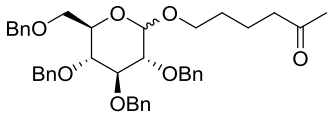
1,3-dimethyl-7-(5-oxohexyl)-3,7-dihydro-1H-purine-2,6-dione (2y)

Prepared according to general procedure **A** from **1y** (40 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 20 h. Compound **2y** was isolated as a white solid (40.2 mg, 94% yield). m.p. 38.0 – 40.0 °C. **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.54 (s, 1H), 4.24 (t, *J* = 6.8 Hz, 2H), 3.54 (s, 3H), 3.36 (s, 3H), 2.46 (t, *J* = 6.4 Hz, 2H), 2.09 (s, 3H), 1.92-1.75 (m, 2H), 1.64 – 1.46 (m, 2H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 207.9, 155.0, 151.5, 148.8, 140.8, 106.8, 46.9, 42.5, 30.2, 29.9, 29.7, 27.9, 20.1; HRMS [ESI] calcd for $C_{13}H_{19}N_4O_3$ $[M+H]^+$ 279.1452, found 279.1453.



(S)-ethyl 2-benzamido-3-(4-((5-oxohexyl)oxy)phenyl)propanoate (2z)

Prepared according to general procedure **A** from **1z** (20 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 18.5 h. Compound **2z** was isolated as a colorless oil (19.4 mg, 90% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.73 (d, *J* = 6.8 Hz, 2H), 7.54 – 7.48 (m, 1H), 7.42 (t, *J* = 7.4 Hz, 2H), 7.04 (d, *J* = 8.4 Hz, 2H), 6.79 (d, *J* = 8.8 Hz, 2H), 6.59 (d, *J* = 7.2 Hz, 1H), 5.06-4.97 (m, 1H), 4.22 (q, *J* = 7.2 Hz, 2H), 3.92 (t, *J* = 5.8 Hz, 2H), 3.28 – 3.10 (m, 2H), 2.51 (t, *J* = 6.6 Hz, 2H), 2.15 (s, 3H), 1.81-1.69 (m, 4H), 1.29 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR** (100 MHz, Chloroform-*d*) δ 208.6, 171.6, 166.7, 158.1, 134.0, 131.7, 130.4, 128.6, 127.7, 127.0, 114.5, 67.4, 61.6, 53.6, 43.2, 37.0, 29.9, 28.6, 20.4, 14.2; HRMS [ESI] calcd for $C_{24}H_{29}NO_5Na$ $[M+Na]^+$ 434.1938, found 434.1938.



6-(((3R,4S,5R,6R)-3,4,5-tris(benzyloxy)-6-((benzyloxy)methyl)tetrahydro-2H-pyran-2-yl)oxy)hexan-2-one (2aa)

Prepared according to general procedure **A** from **1aa** (47.7 mg) and ***cat.5*** (5 mol%) in MeOH (0.25 mol/mL) at 65 °C for 34 h. Compound **2aa** was isolated as a colorless oil (45.1mg, 92% yield). **^{1}H NMR** (400 MHz, Chloroform-*d*) δ 7.38 – 7.30 (m, 12H), 7.28 – 7.24 (m, 6H), 7.17 – 7.11 (m, 2H), 5.00 – 4.70 (m, 5H), 4.66-4.36 (m, 4H), 3.97 (t, *J* = 9.3 Hz, 1H), 3.80 – 3.49 (m, 6H), 3.48 – 3.38 (m, 1H), 2.48 – 2.39 (m, 2H), 2.10 (s, 3H), 1.72 – 1.55 (m, 4H). The spectral data were in agreement with literature values.[5]

6. References

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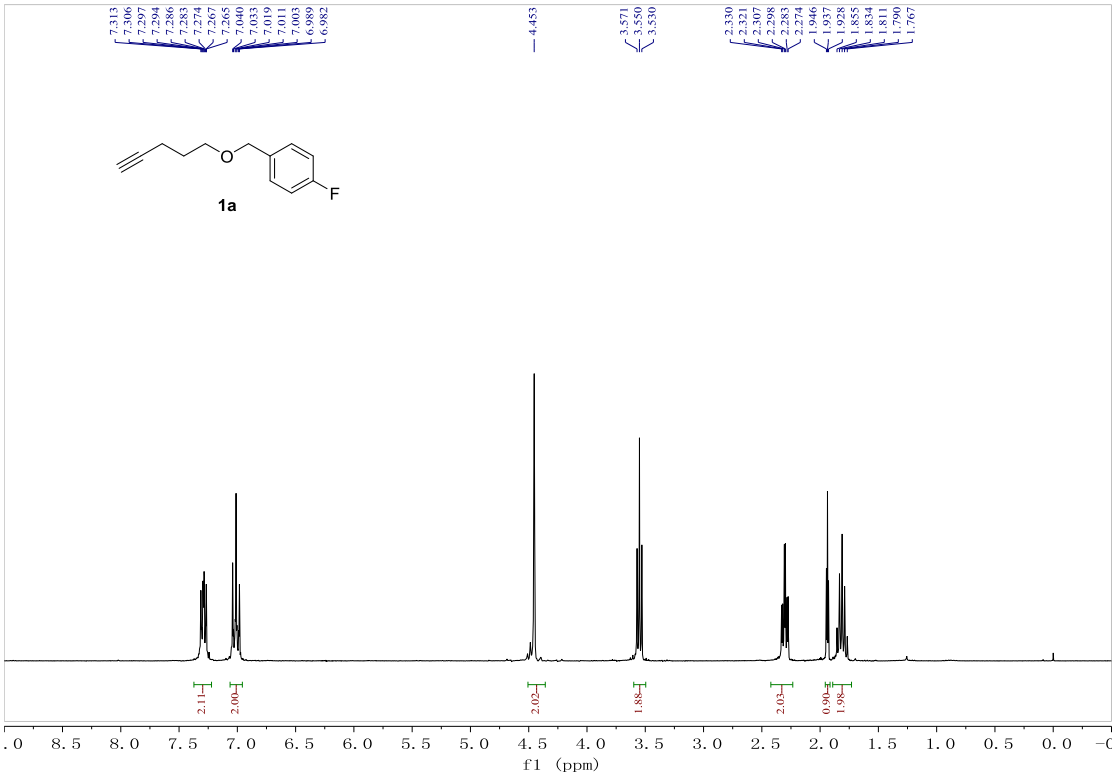
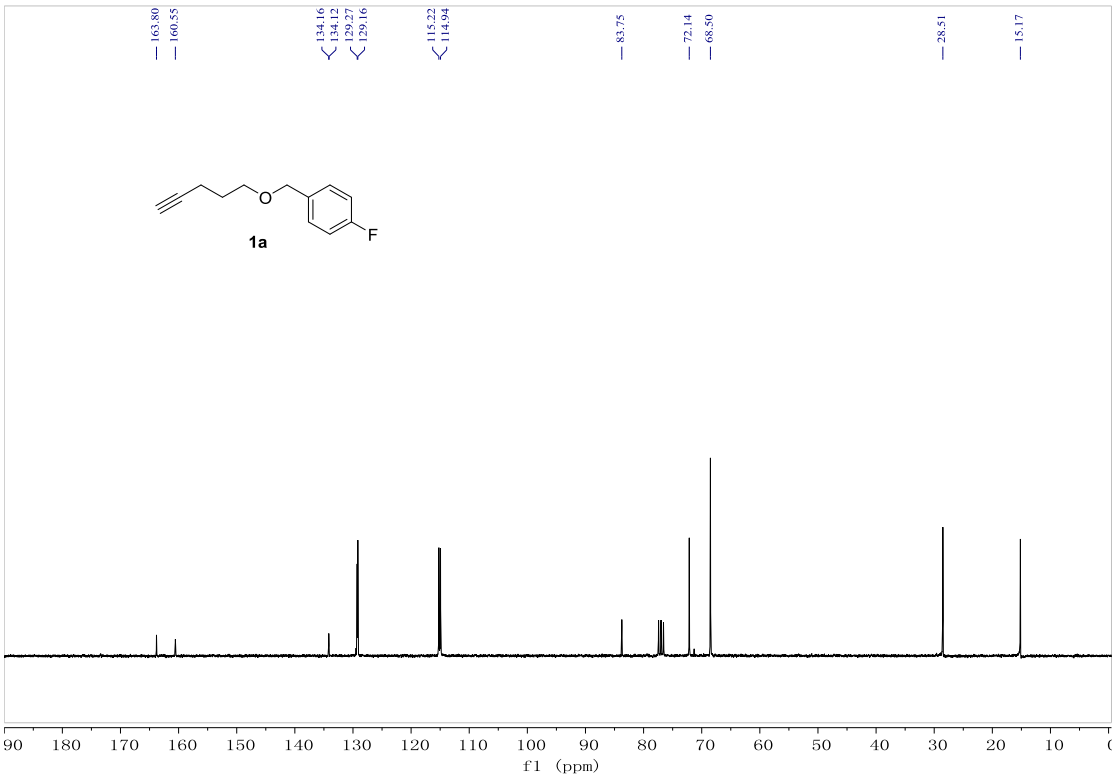
7. ^{1}H NMR, ^{13}C NMR spectra



^{1}H NMR was recorded on Bruker 300 MHz; Solvent: $CDCl_3$



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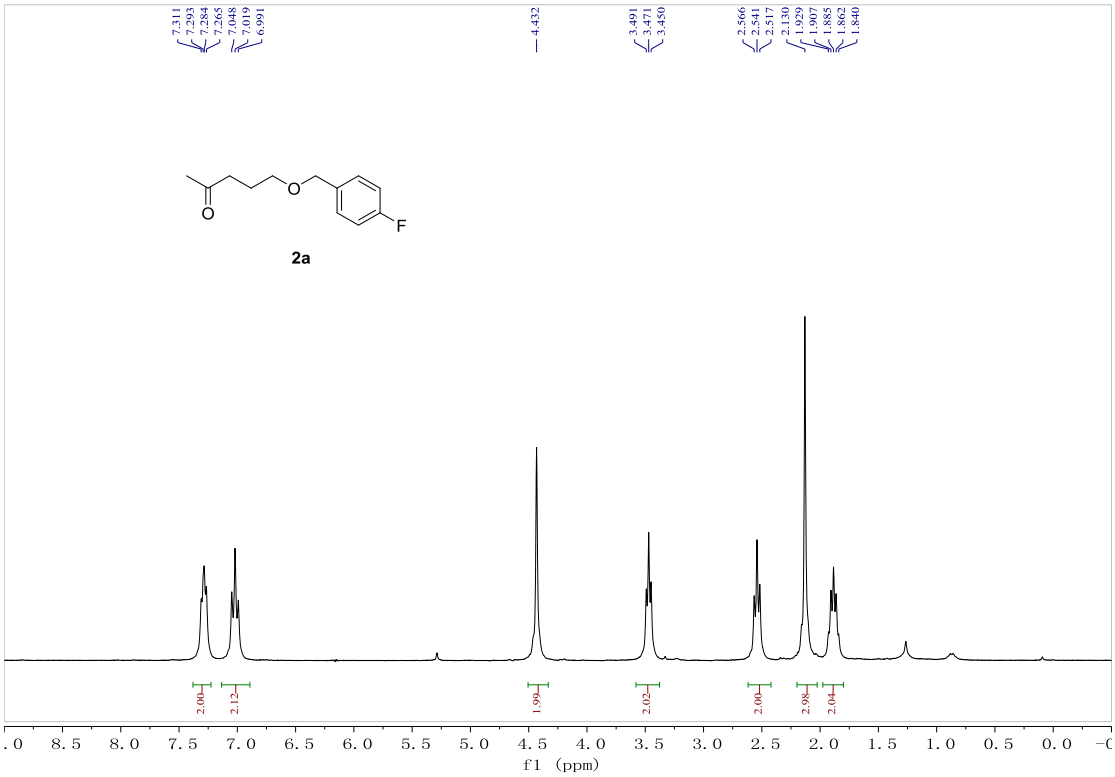

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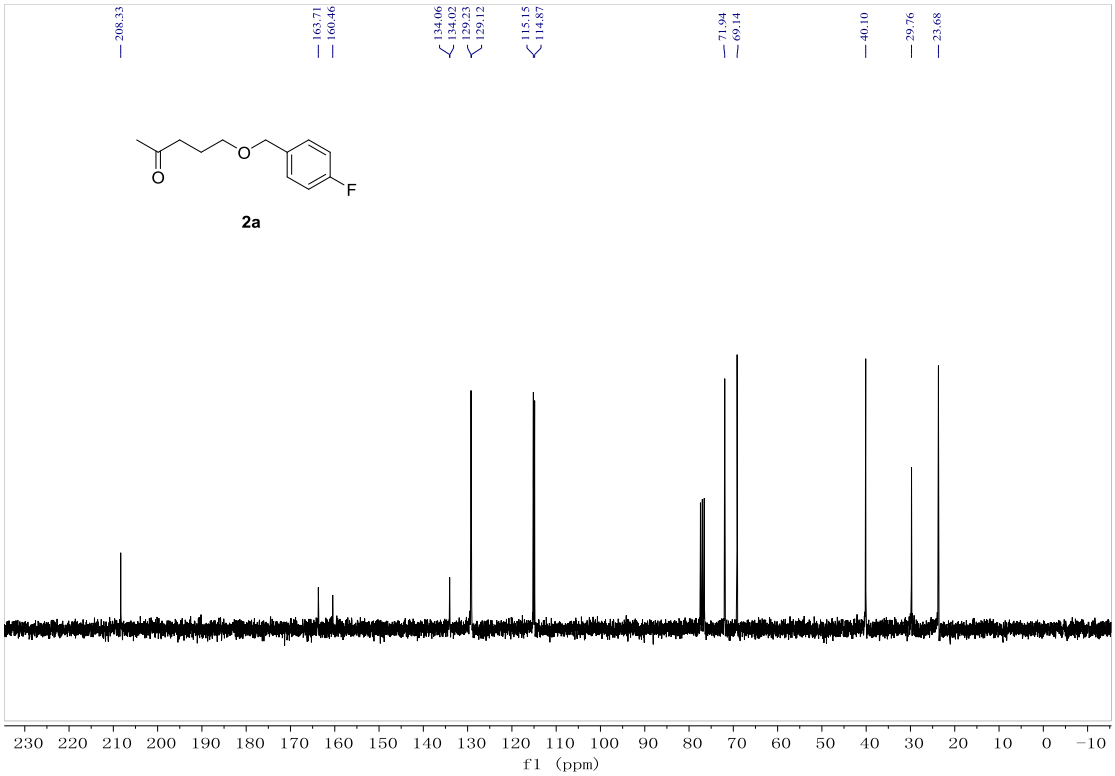
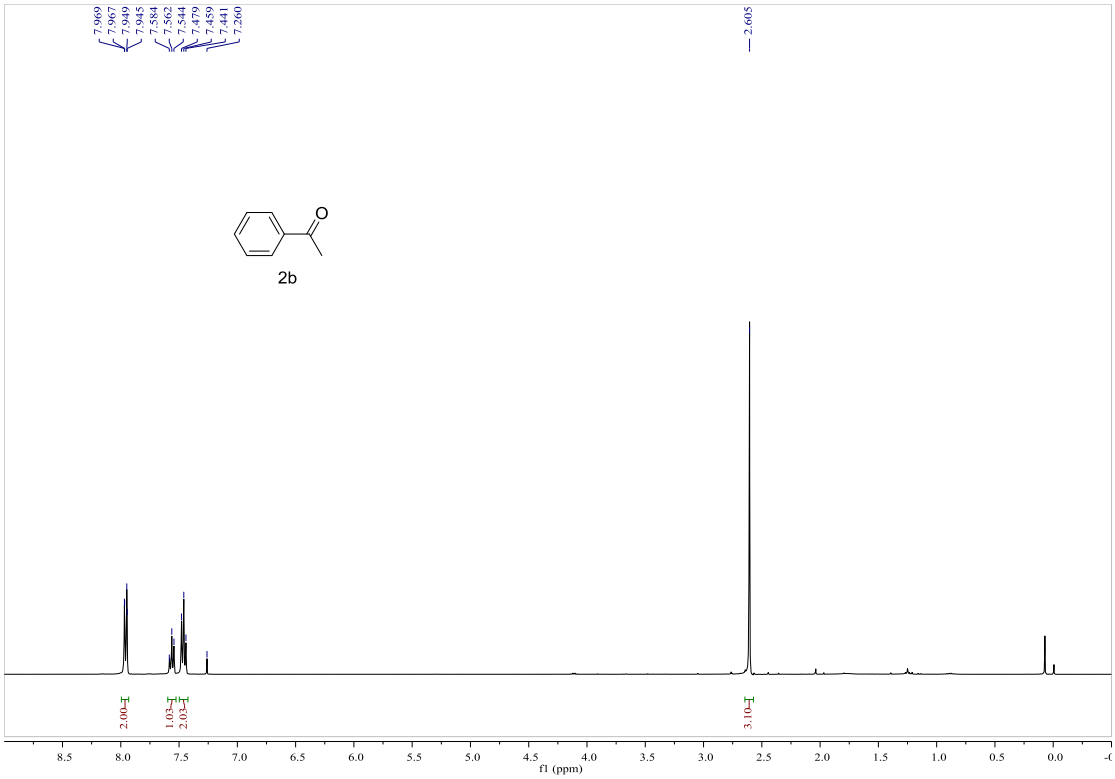
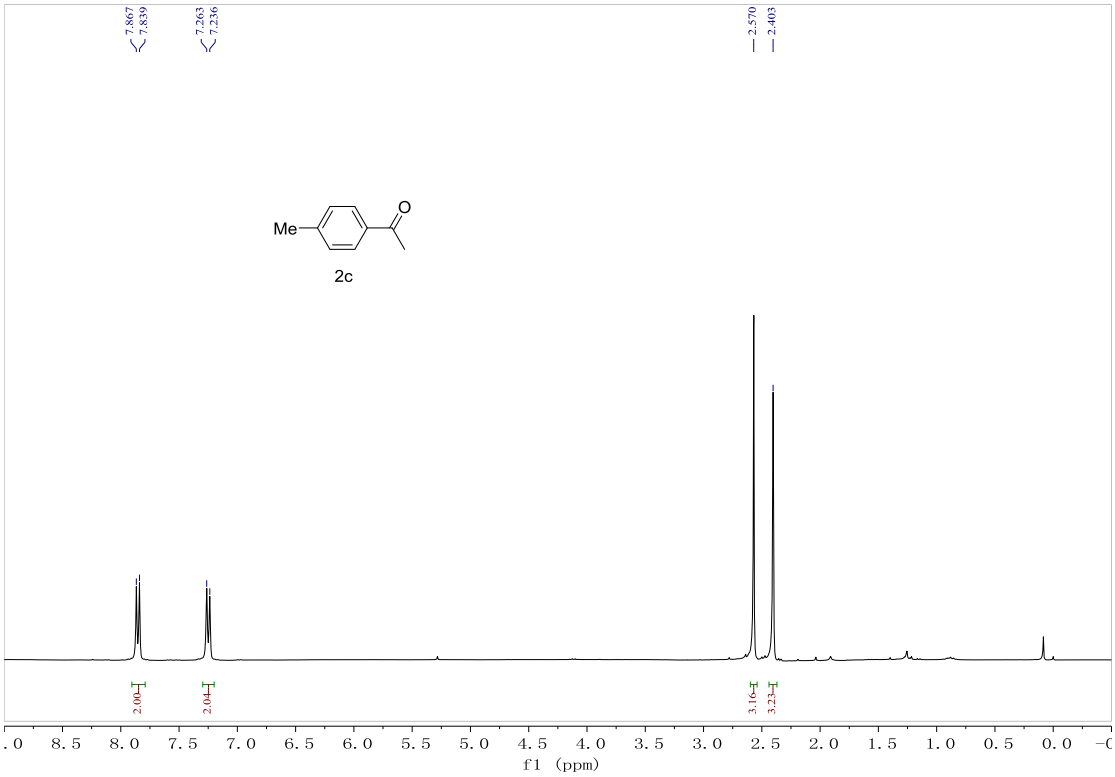


^{13}C NMR was recorded on Bruker 75 MHz; Solvent: $CDCl_3$



^{1}H NMR was recorded on Bruker 400 MHz; Solvent: $CDCl_3$



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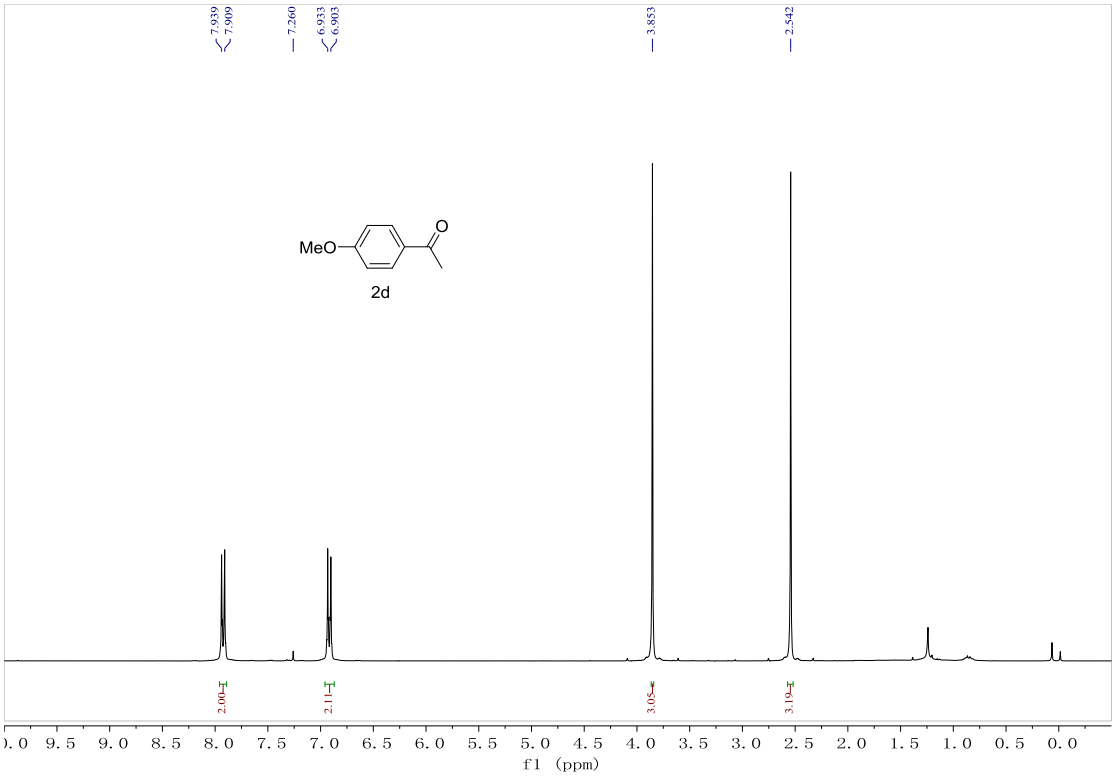

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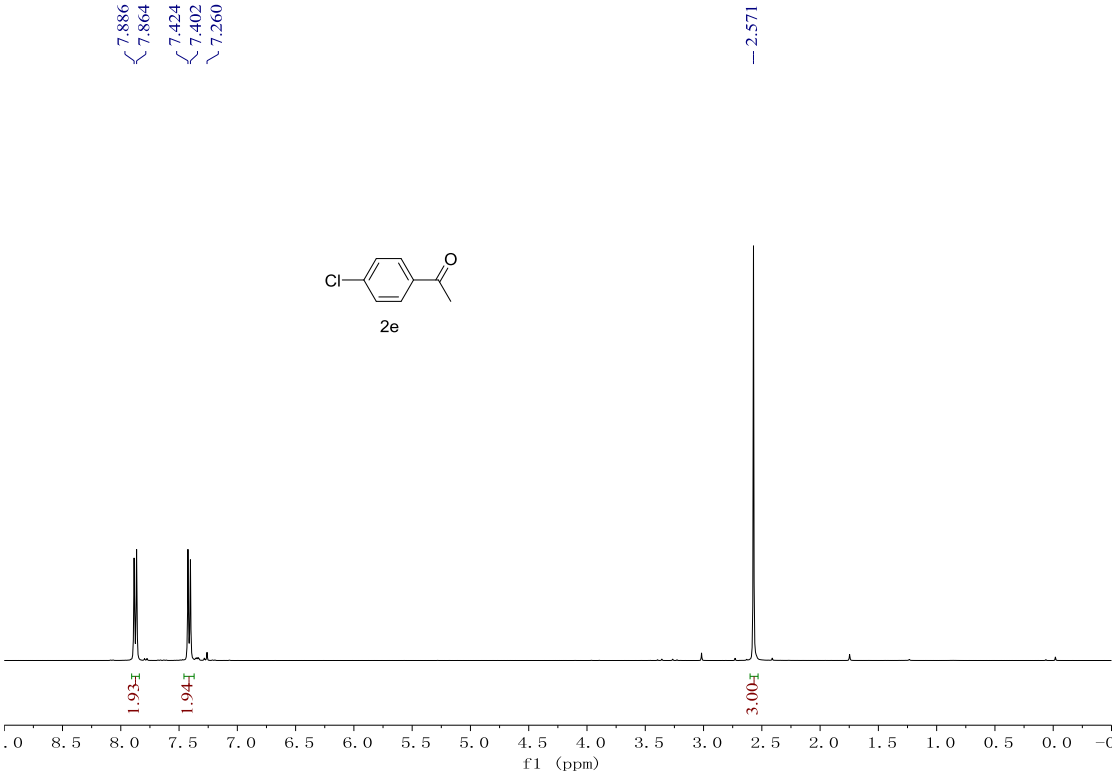
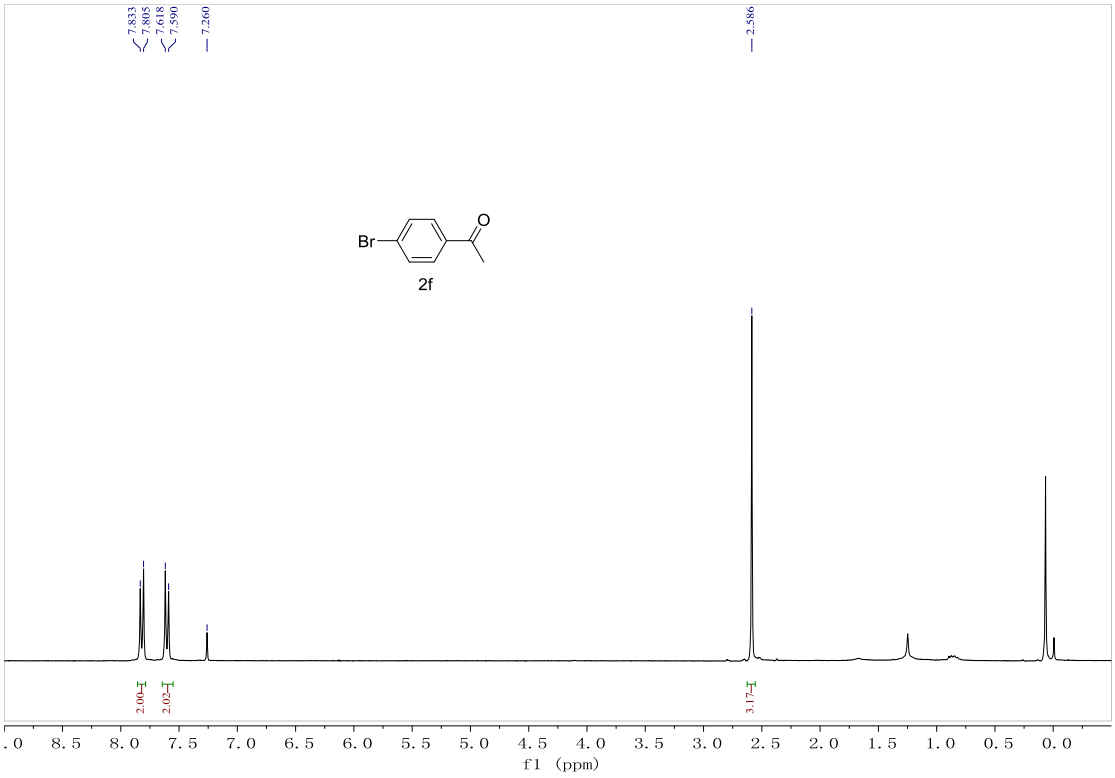
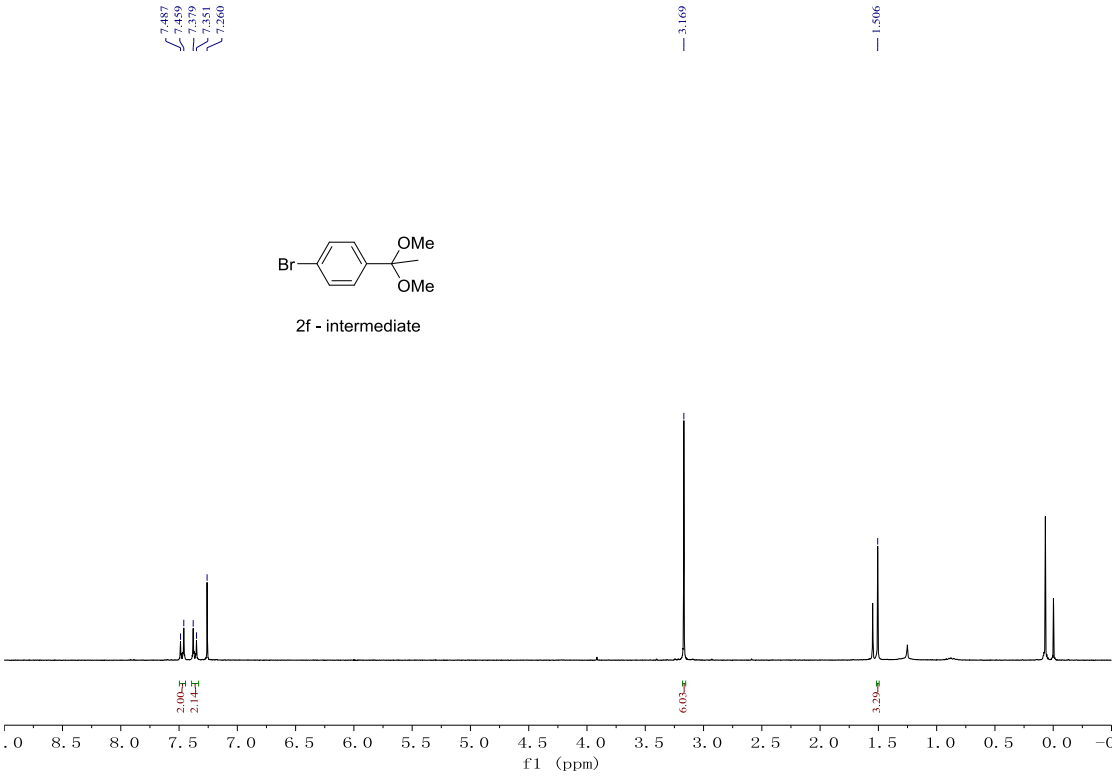


^{1}H NMR was recorded on Bruker 400 MHz; Solvent: $CDCl_3$



^{1}H NMR was recorded on Bruker 300 MHz; Solvent: $CDCl_3$



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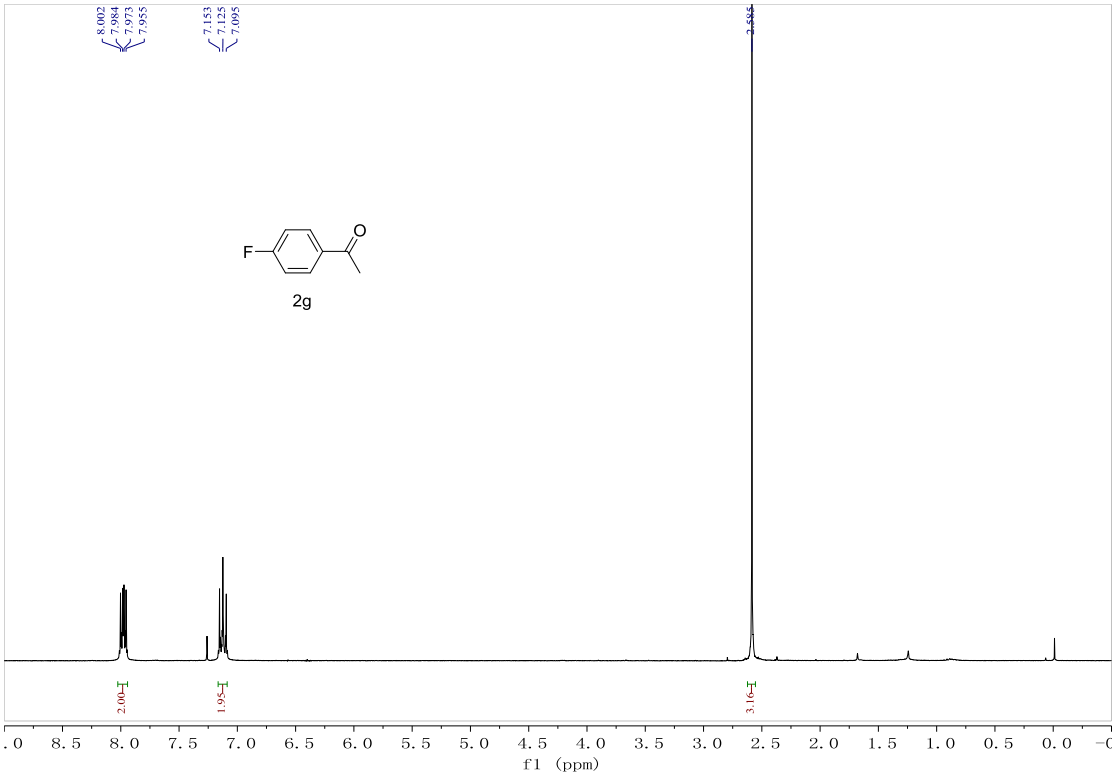

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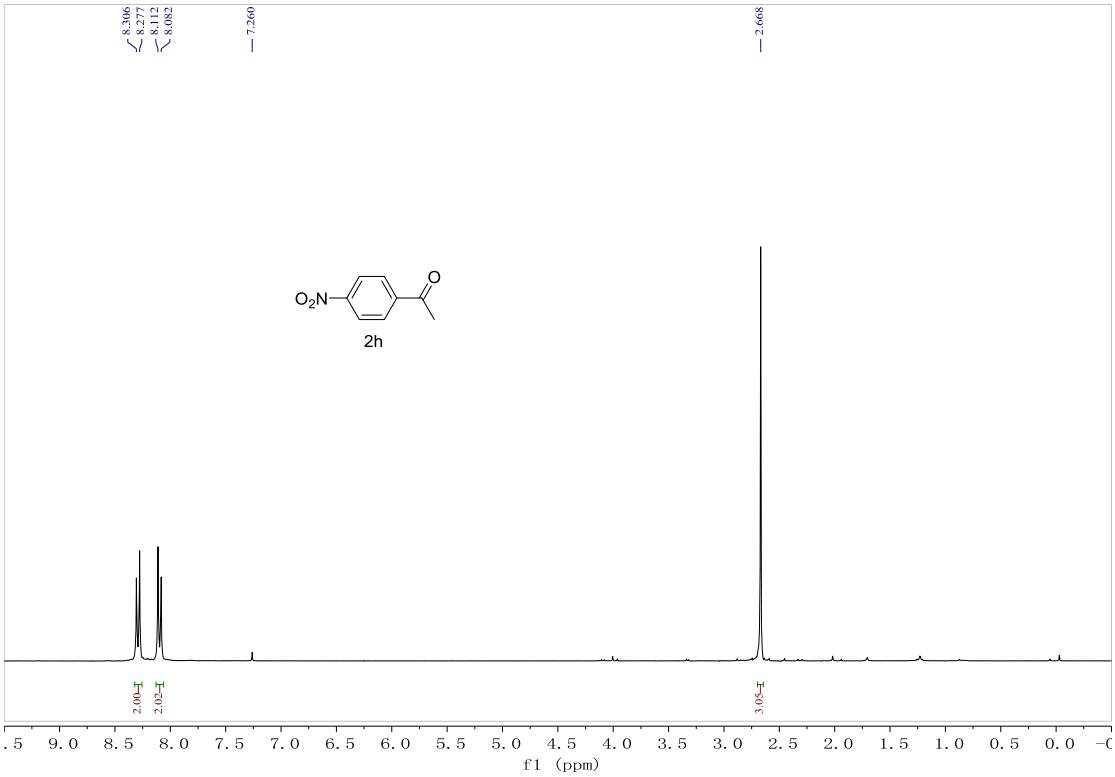

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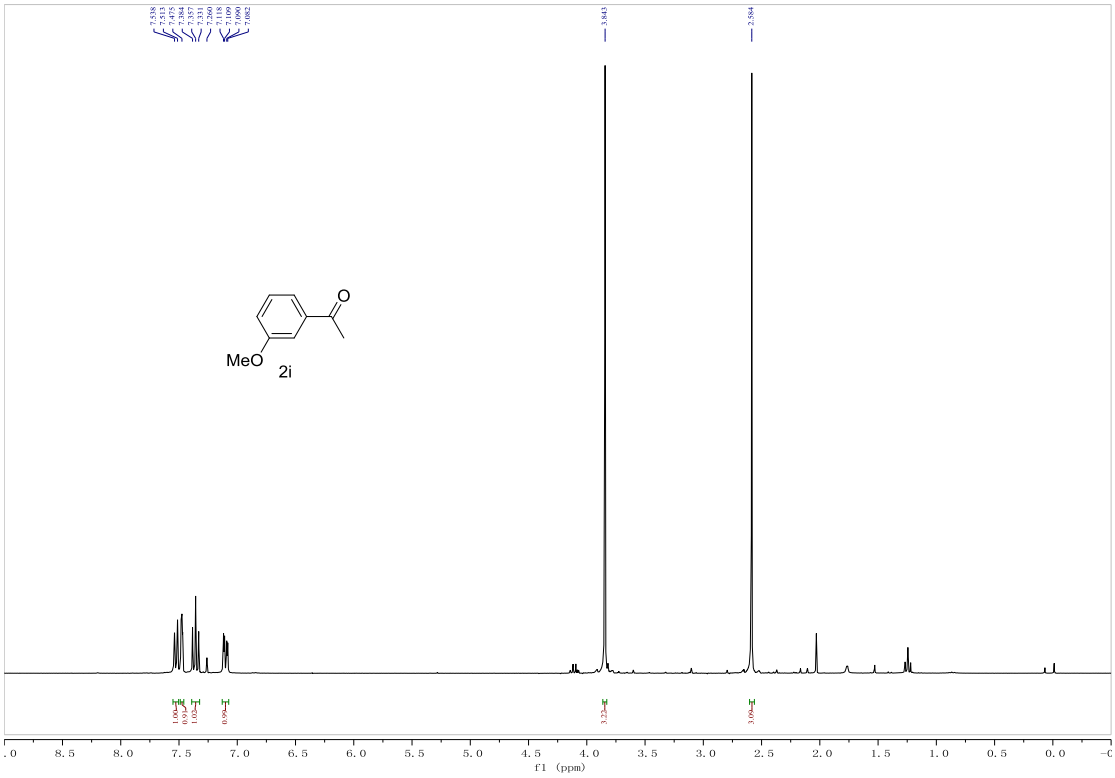

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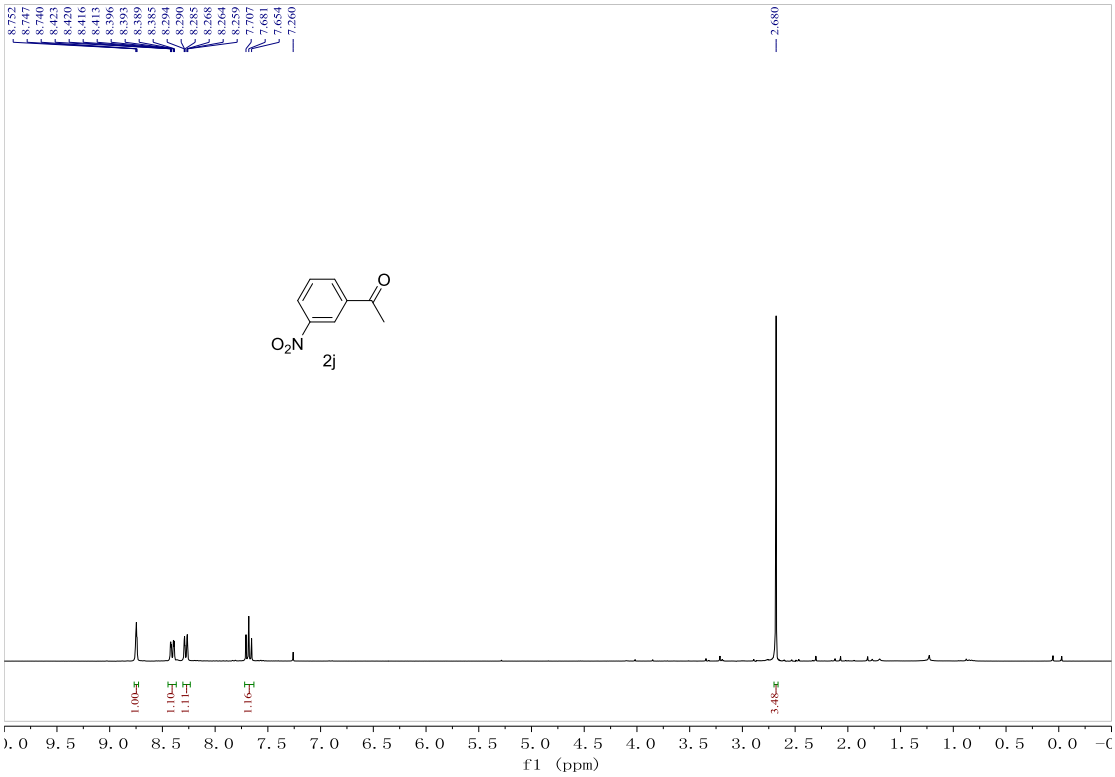
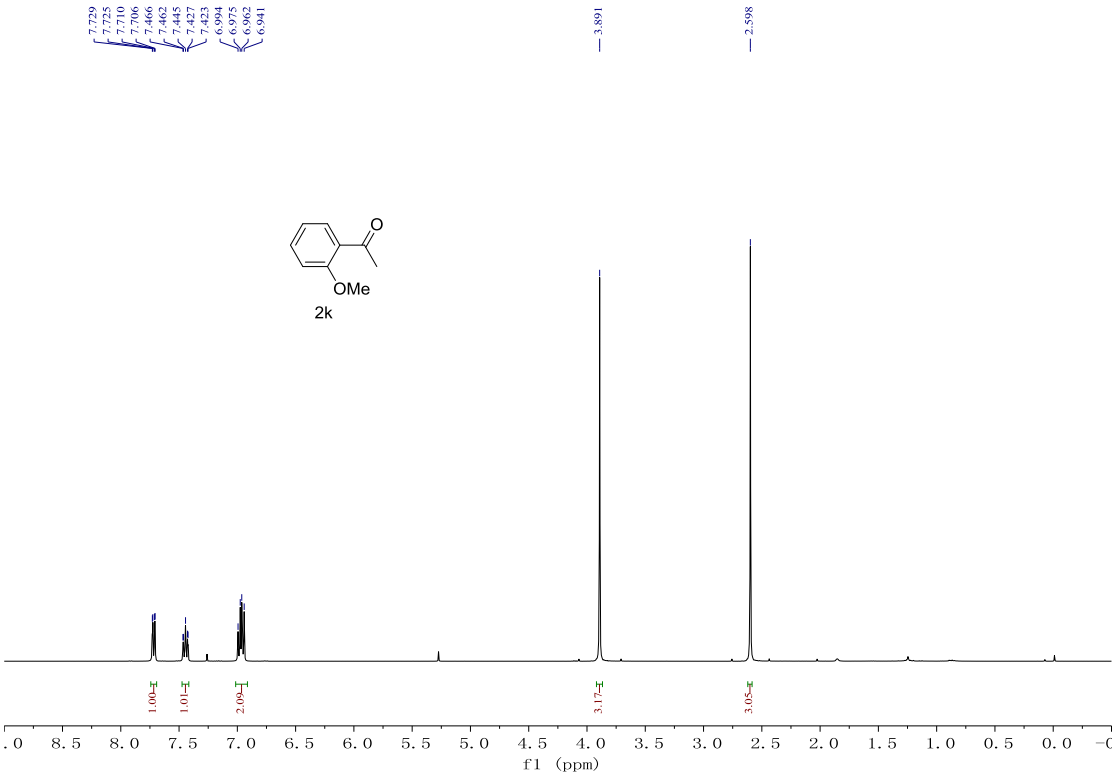
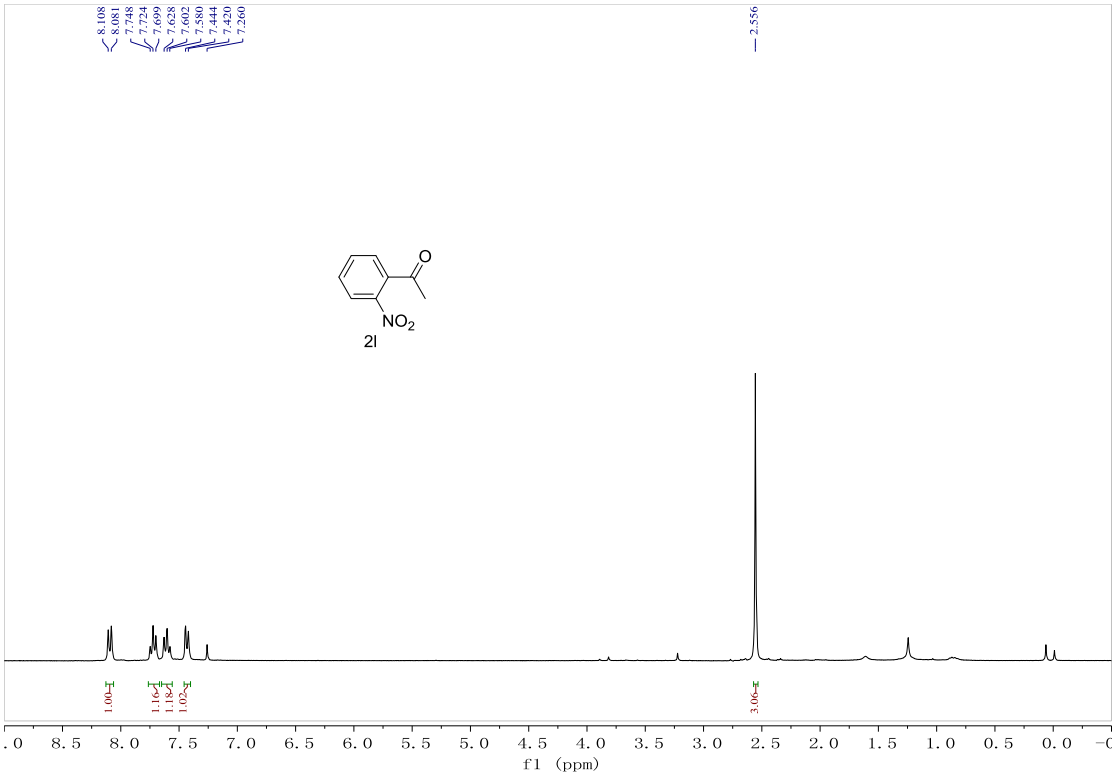


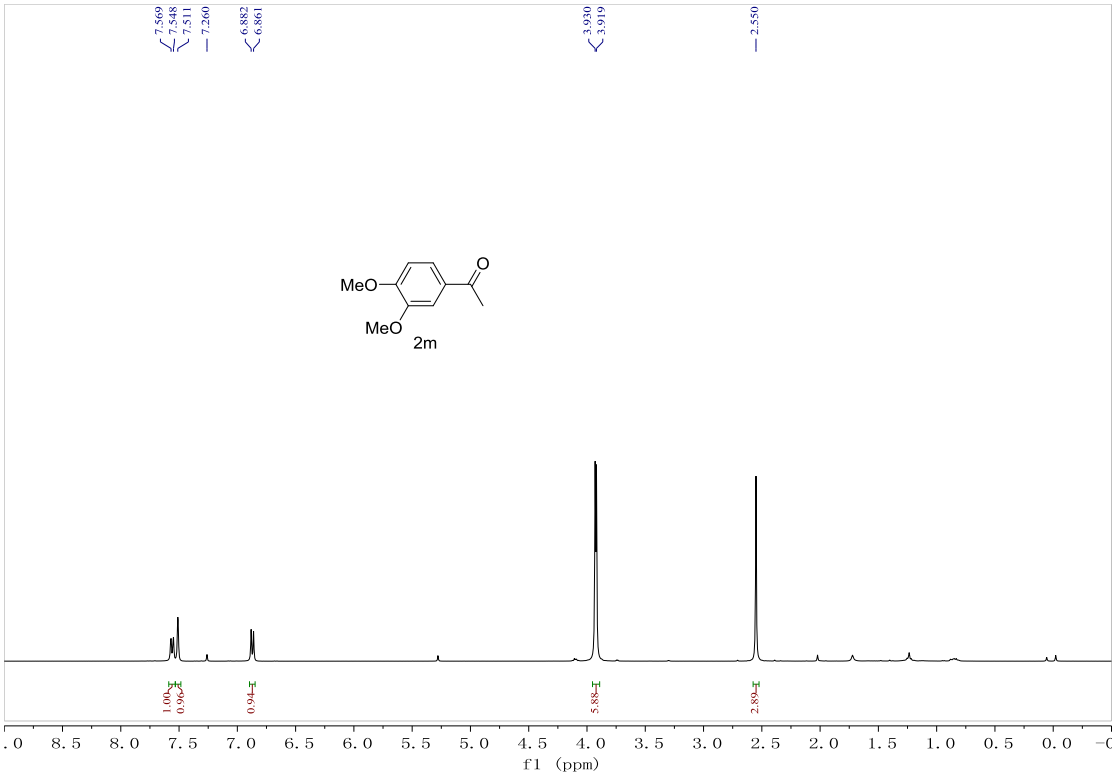
^{1}H NMR was recorded on Bruker 300 MHz; Solvent: $CDCl_3$



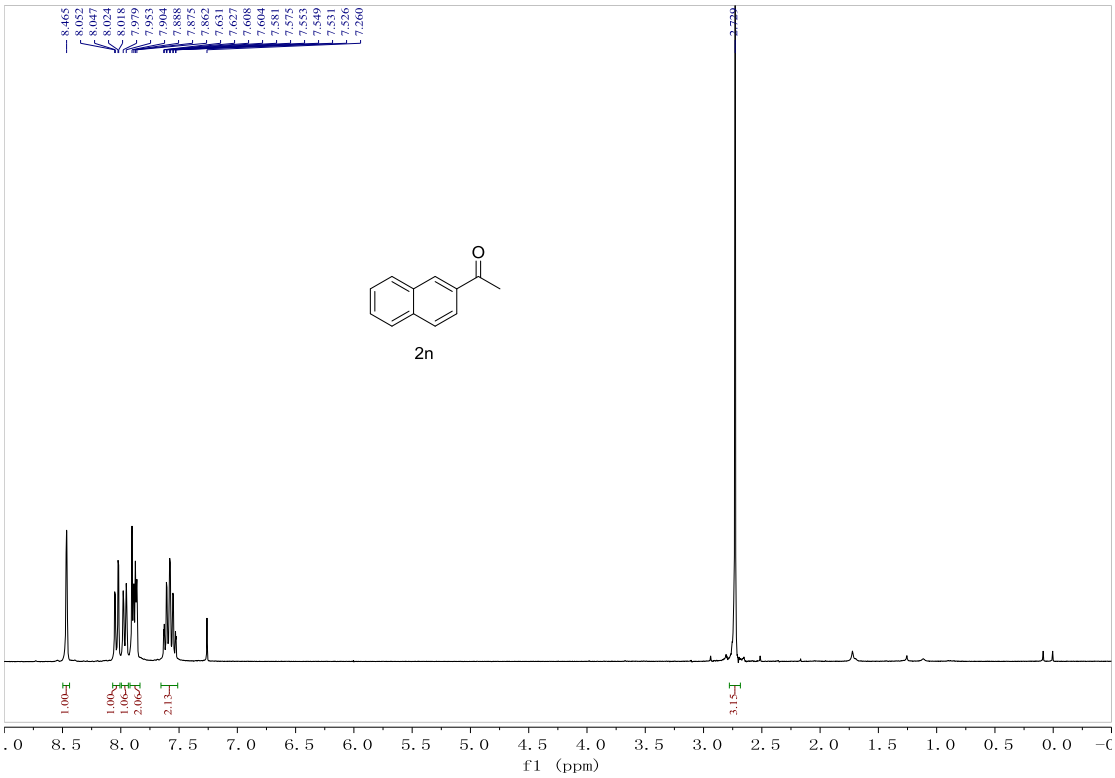
^{1}H NMR was recorded on Bruker 400 MHz; Solvent: $CDCl_3$



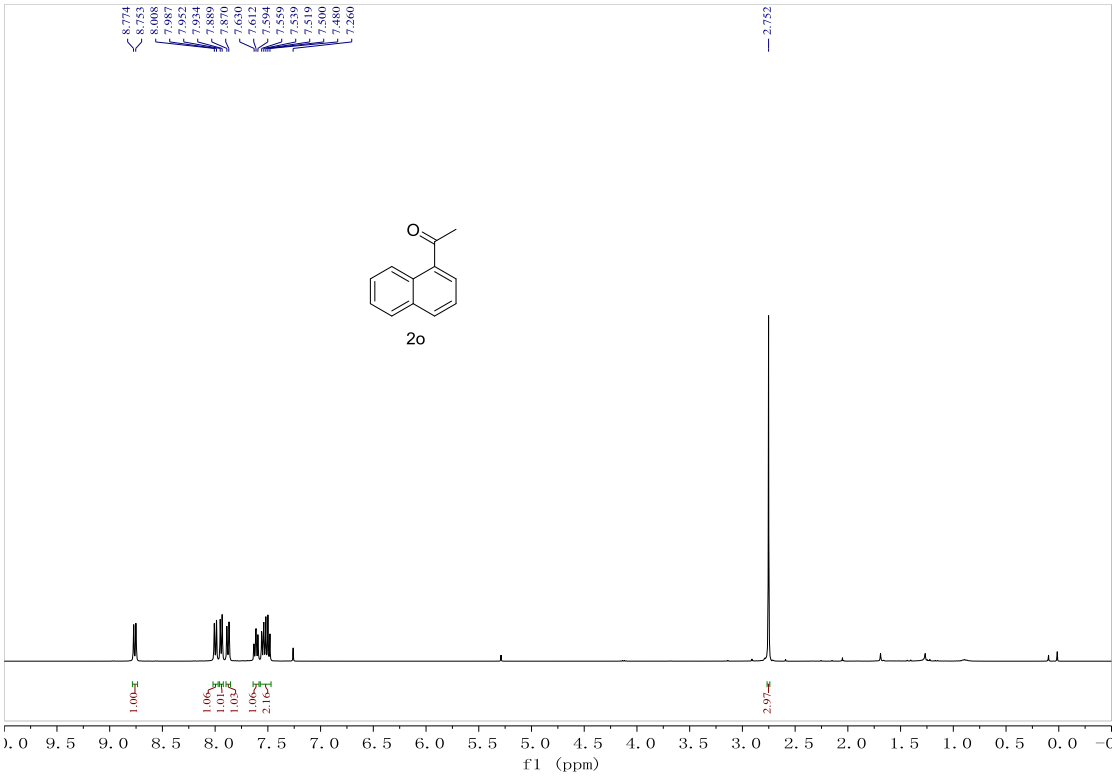
^{1}H NMR was recorded on Bruker 300 MHz; Solvent: $CDCl_3$



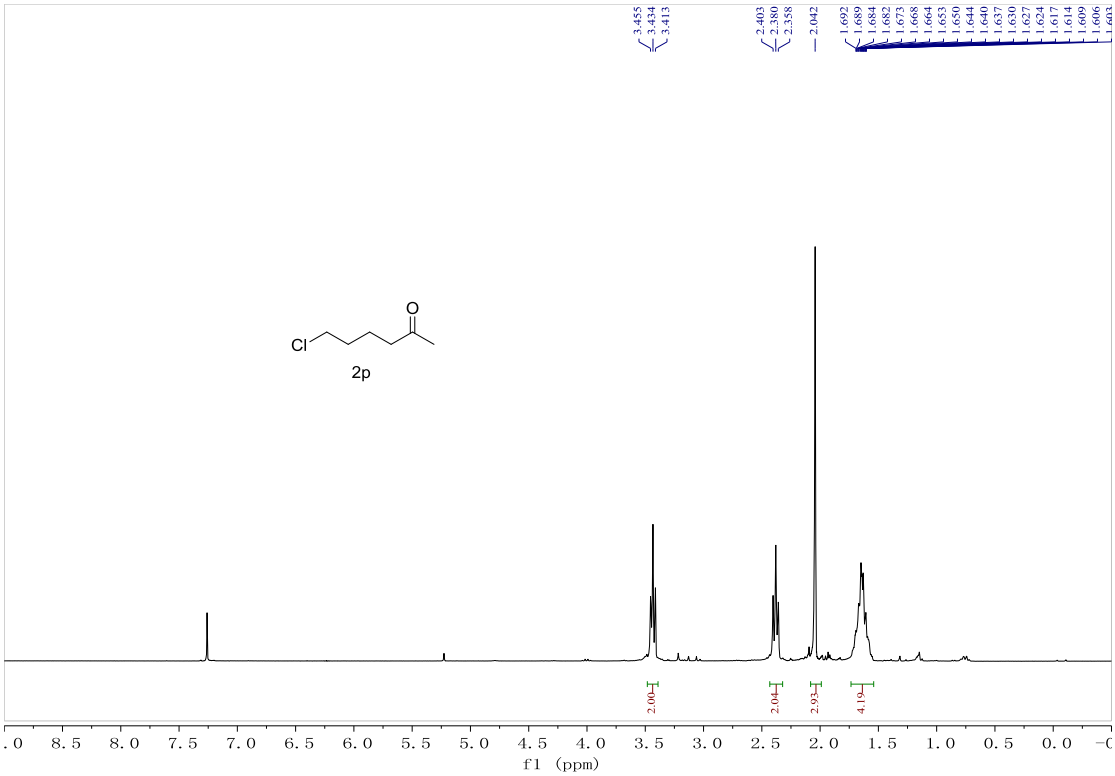
^{1}H NMR was recorded on Bruker 400 MHz; Solvent: $CDCl_3$



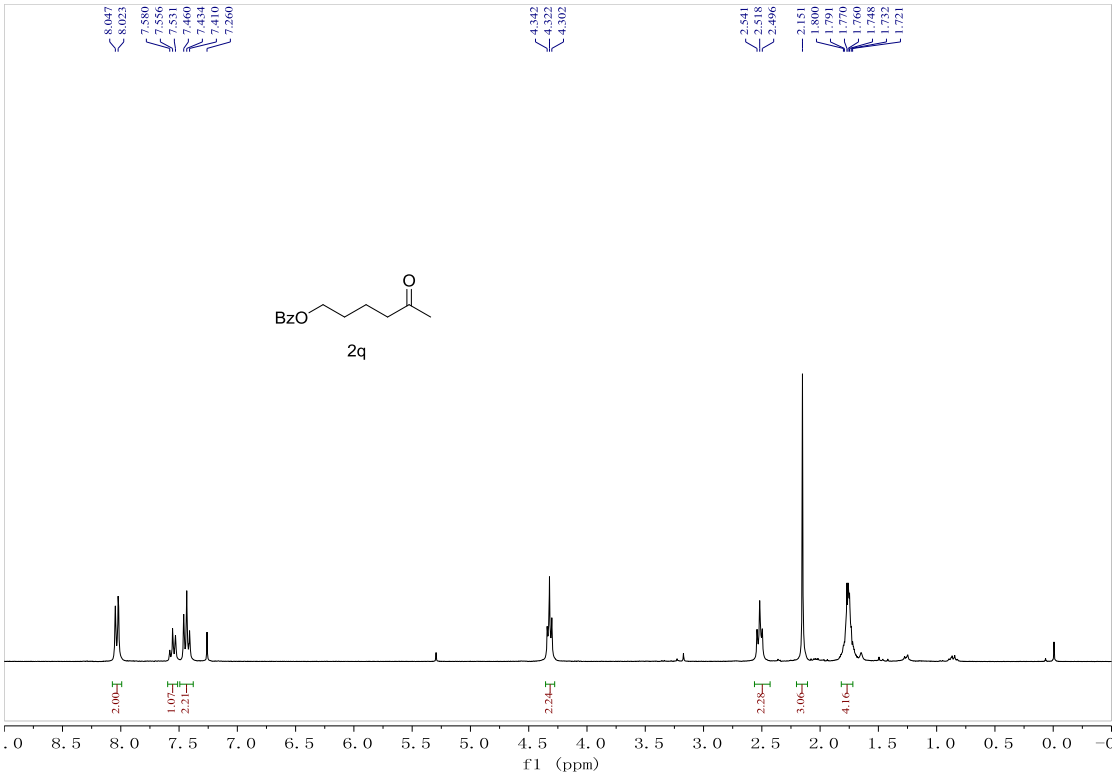
^{1}H NMR was recorded on Bruker 300 MHz; Solvent: $CDCl_3$



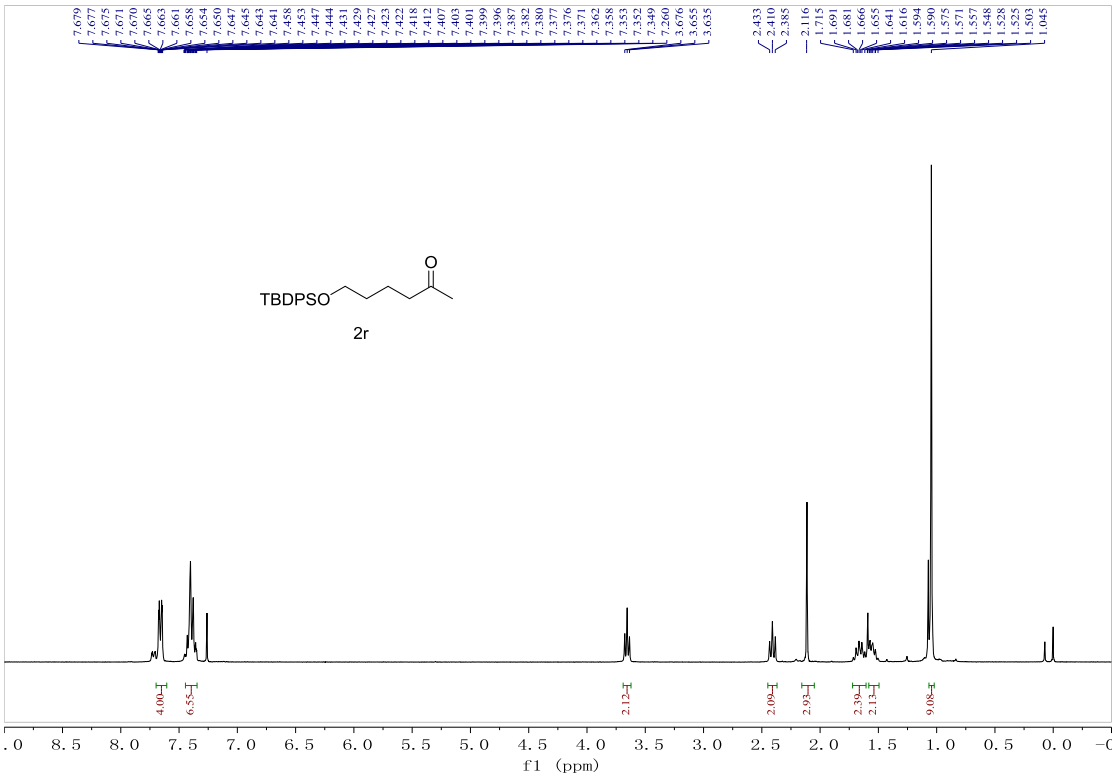
^{1}H NMR was recorded on Bruker 400 MHz; Solvent: $CDCl_3$



^{1}H NMR was recorded on Bruker 300 MHz; Solvent: $CDCl_3$



^{1}H NMR was recorded on Bruker 300 MHz; Solvent: $CDCl_3$



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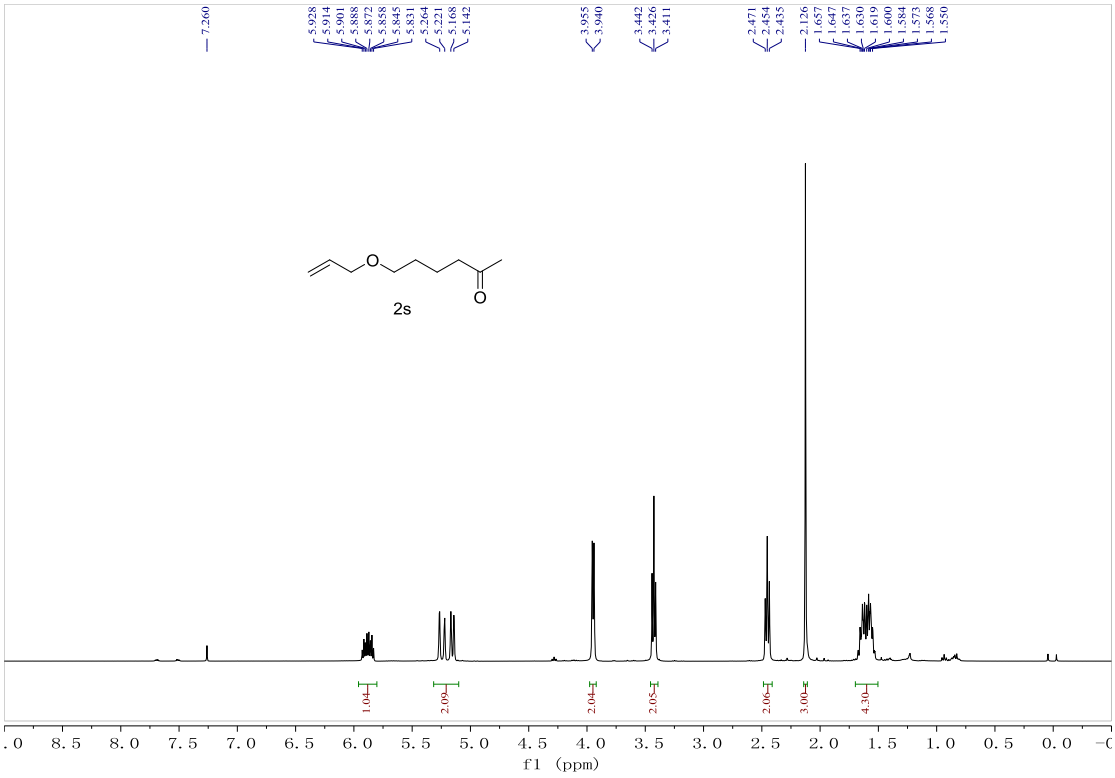
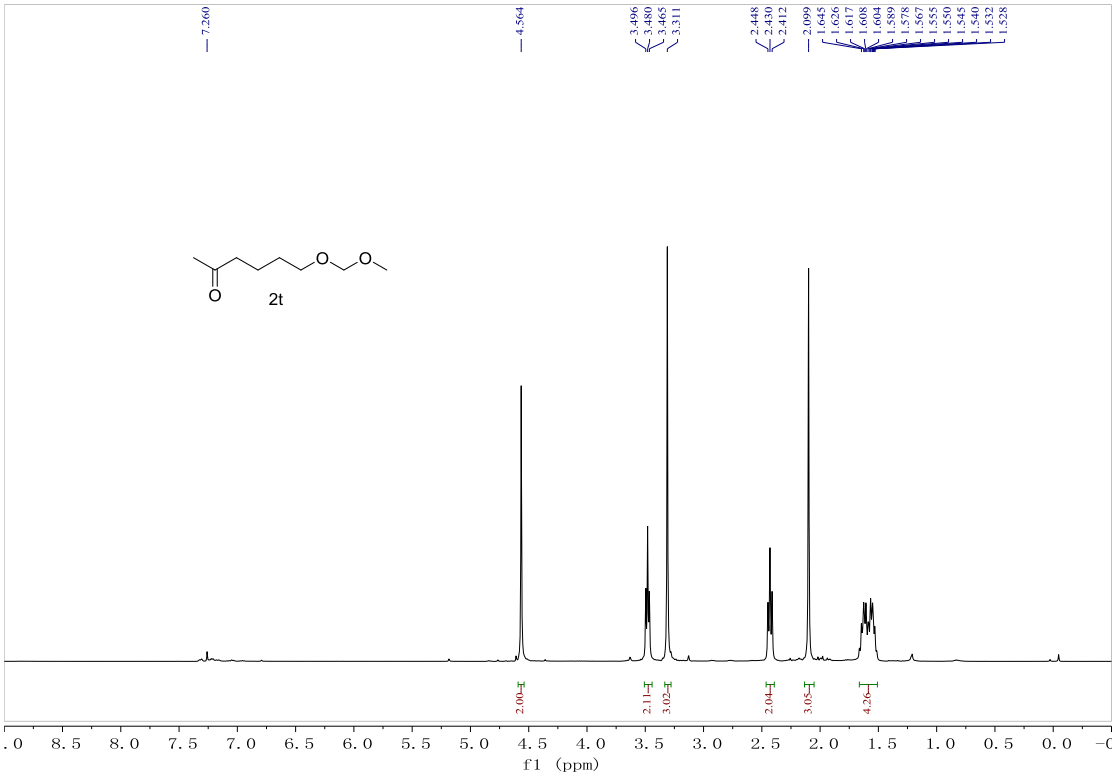


^{1}H NMR was recorded on Bruker 400 MHz; Solvent: $CDCl_3$



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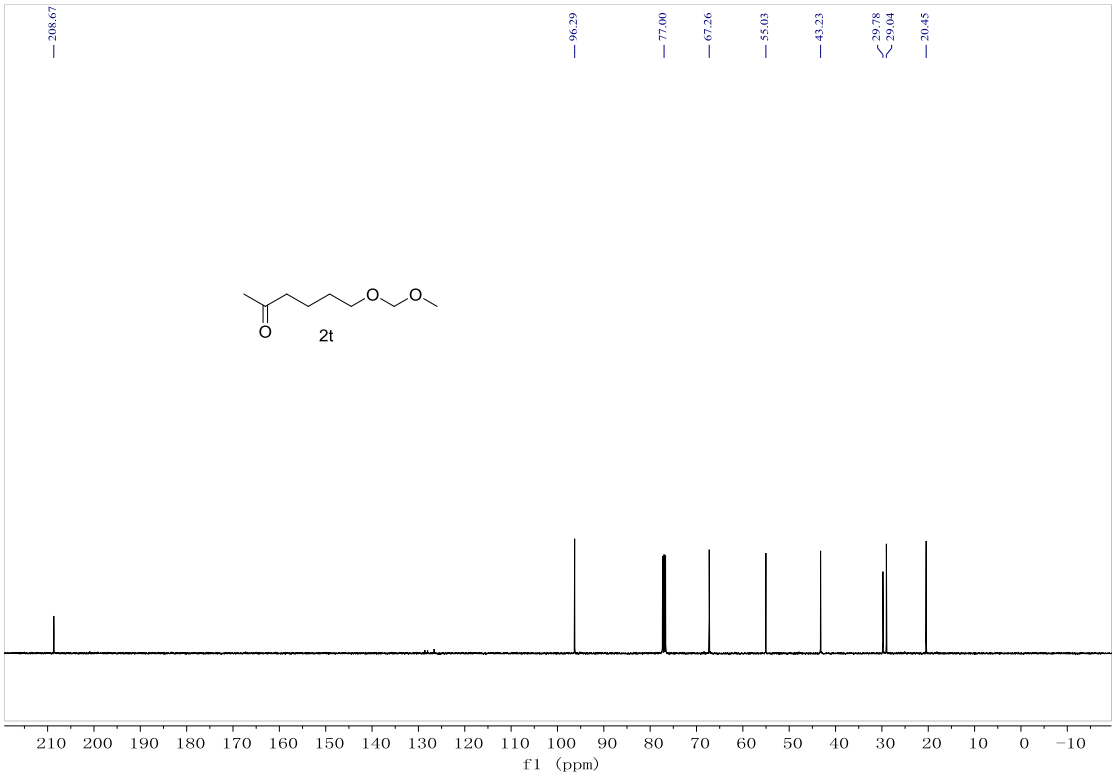
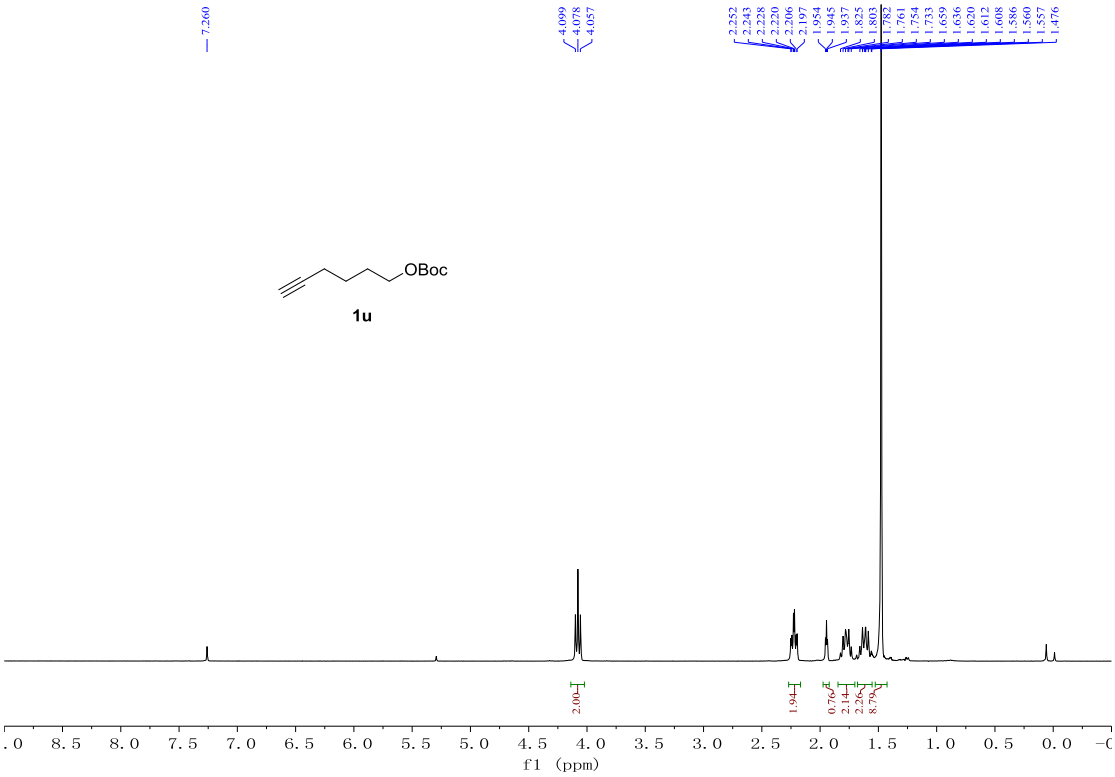
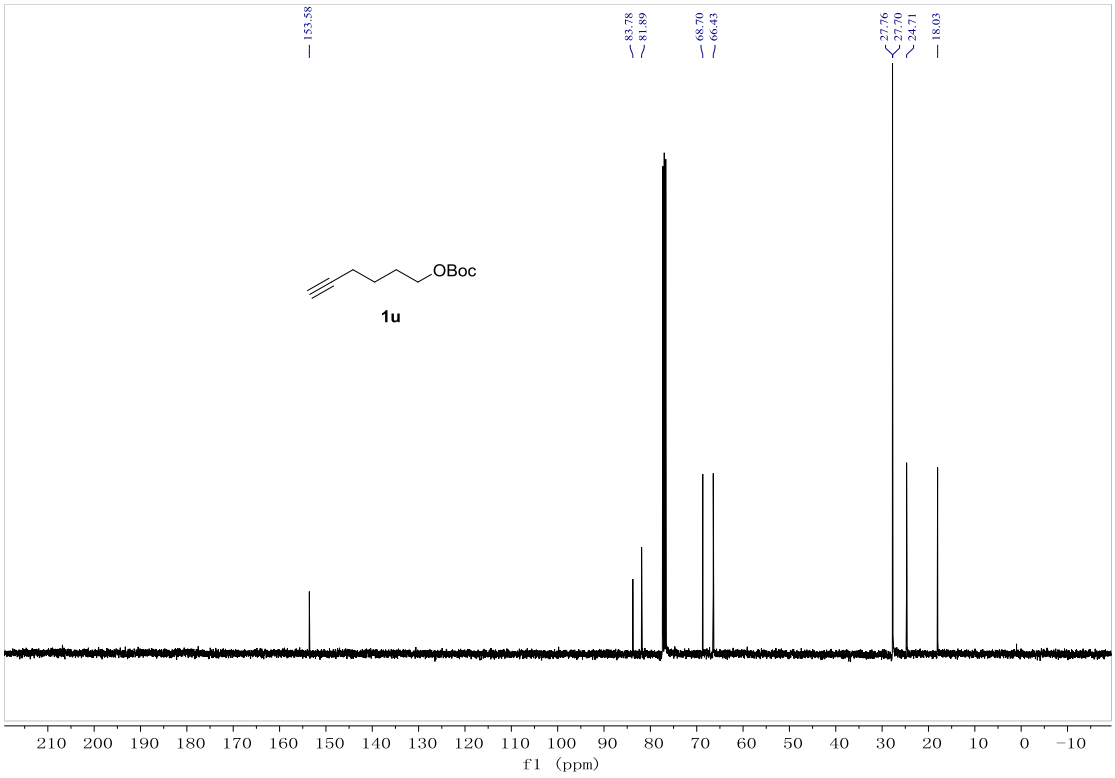


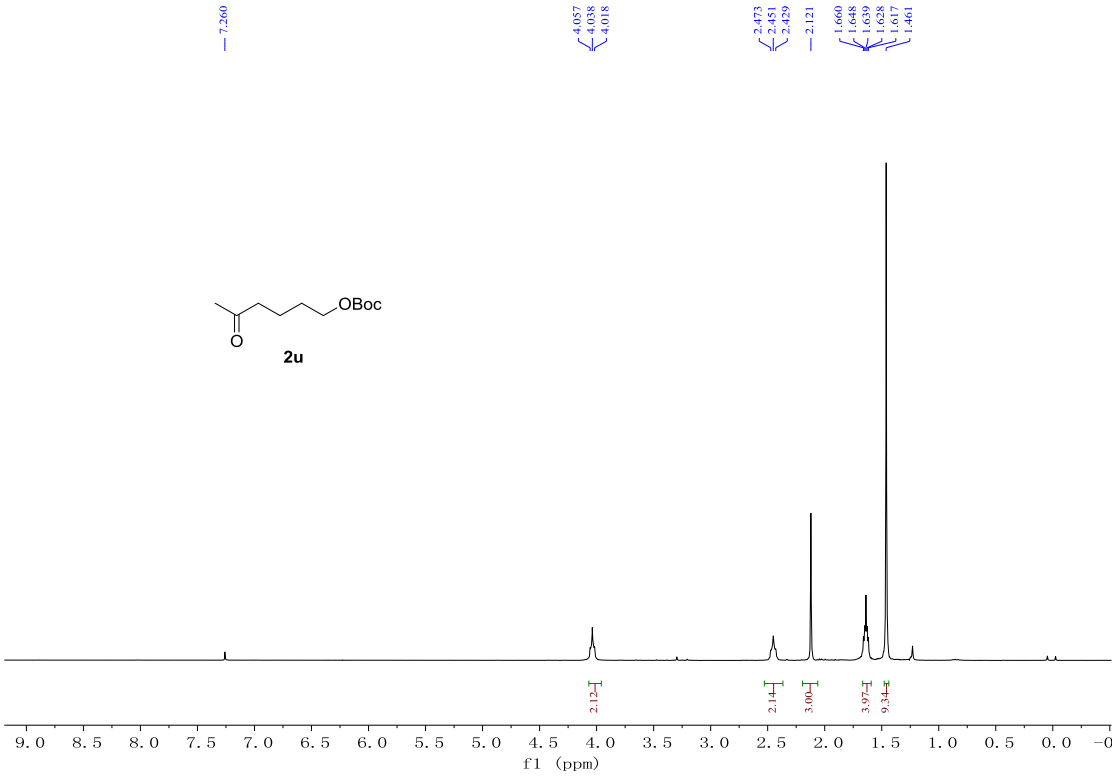
^{13}C NMR was recorded on Bruker 100 MHz; Solvent: $CDCl_3$



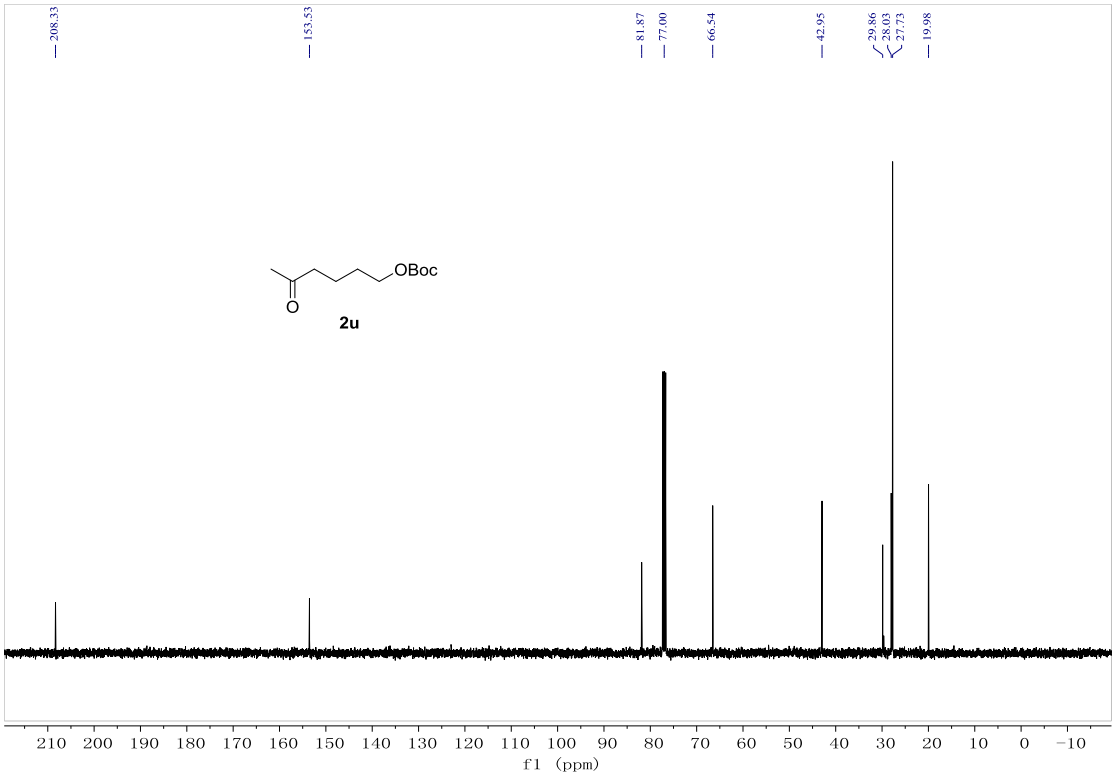
^{1}H NMR was recorded on Bruker 300 MHz; Solvent: $CDCl_3$



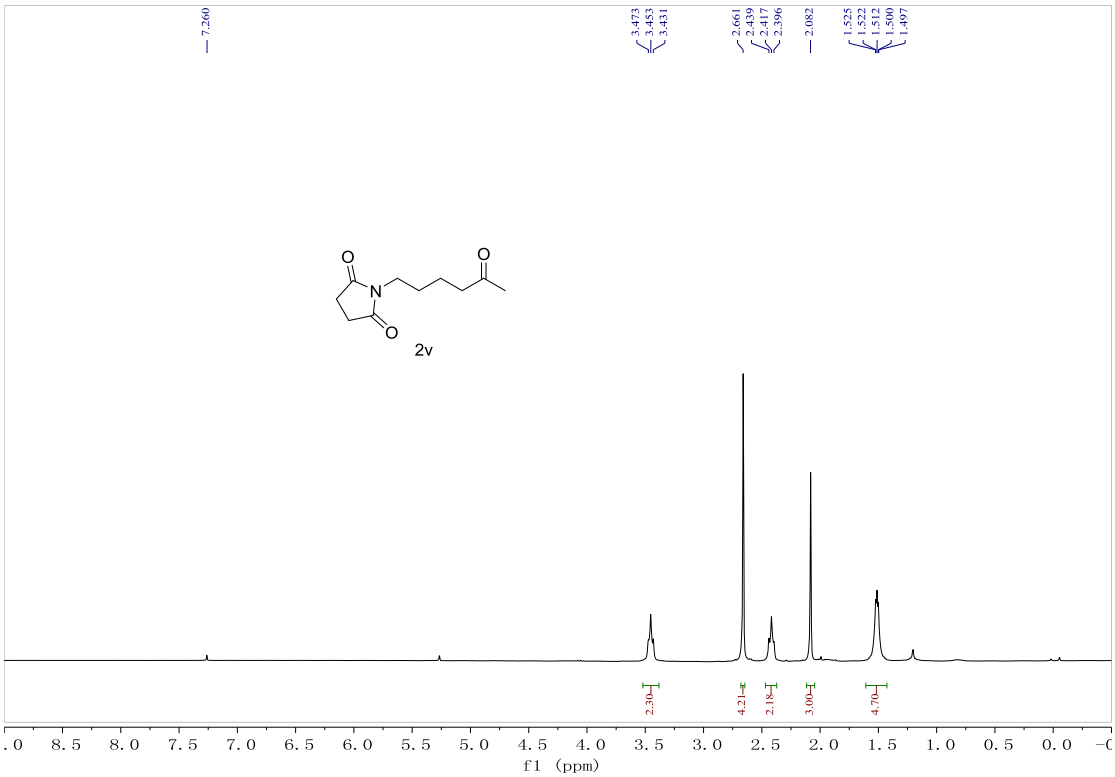
^{13}C NMR was recorded on Bruker 100 MHz; Solvent: $CDCl_3$



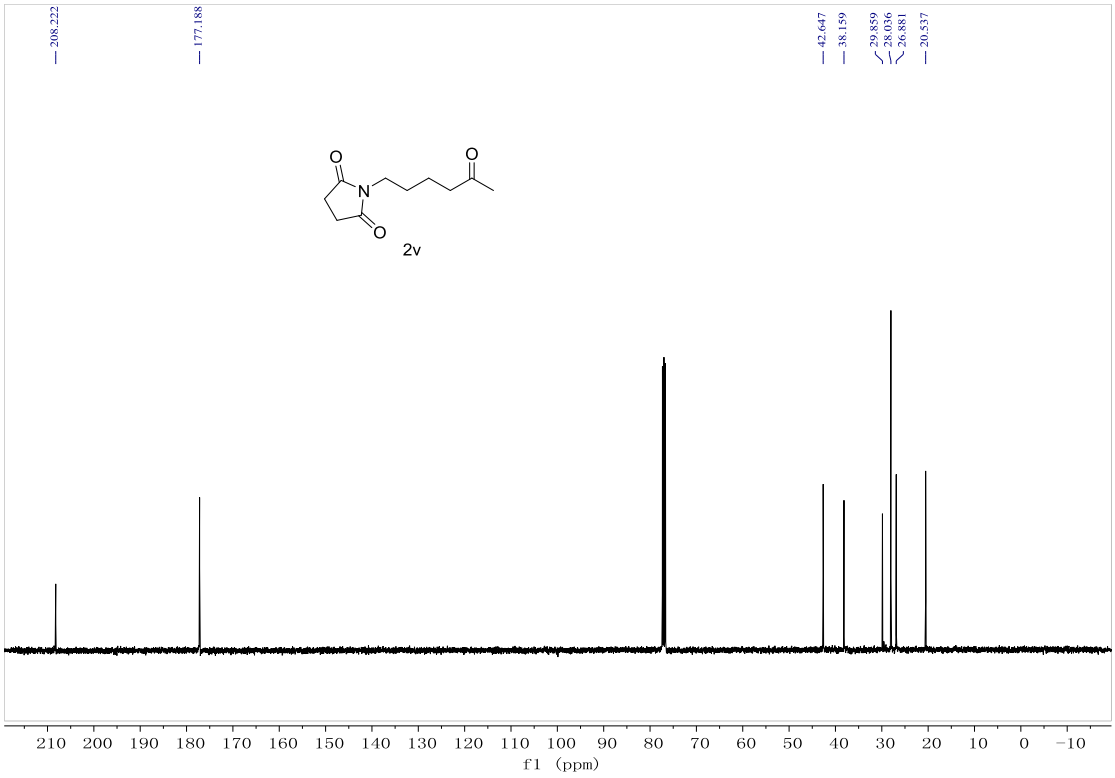
^{1}H NMR was recorded on Bruker 300 MHz; Solvent: $CDCl_3$



^{13}C NMR was recorded on Bruker 100 MHz; Solvent: $CDCl_3$



^{1}H NMR was recorded on Bruker 300 MHz; Solvent: $CDCl_3$



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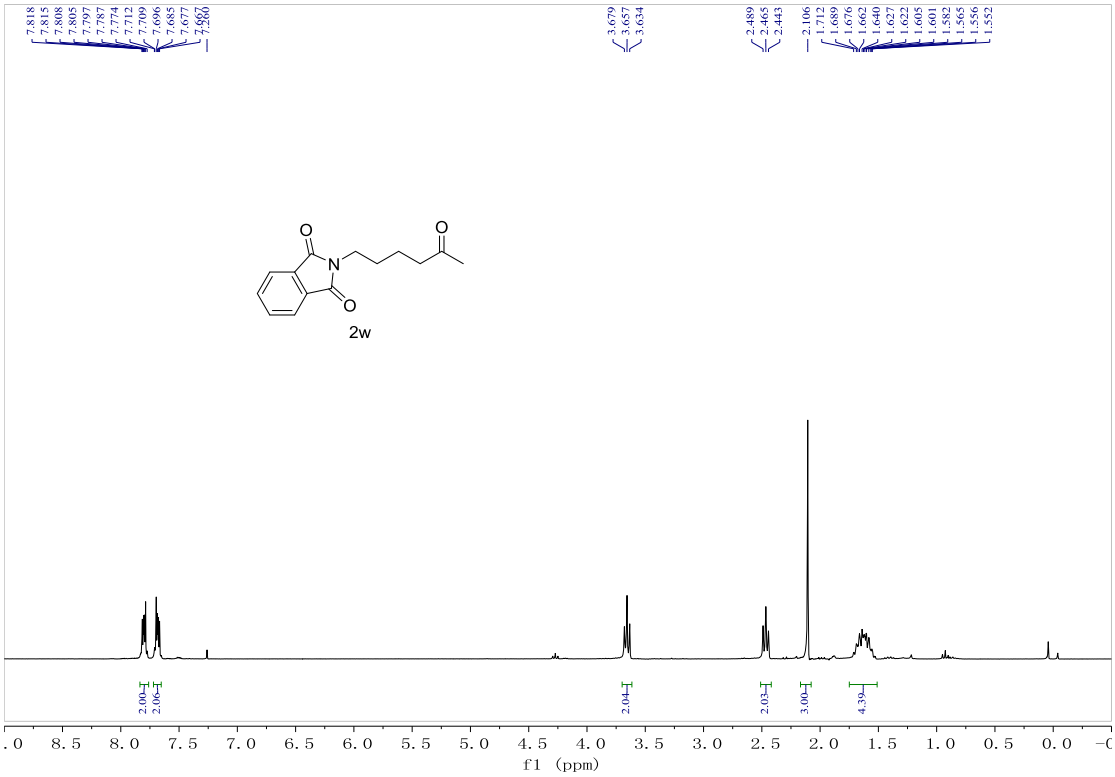

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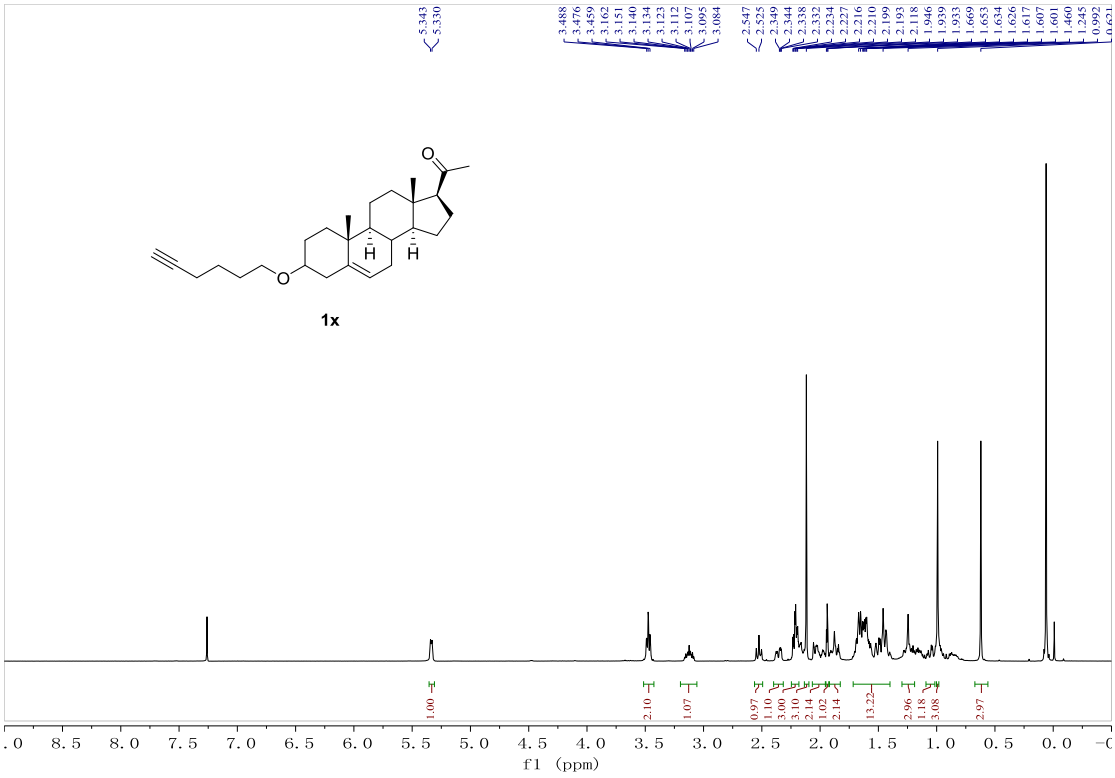
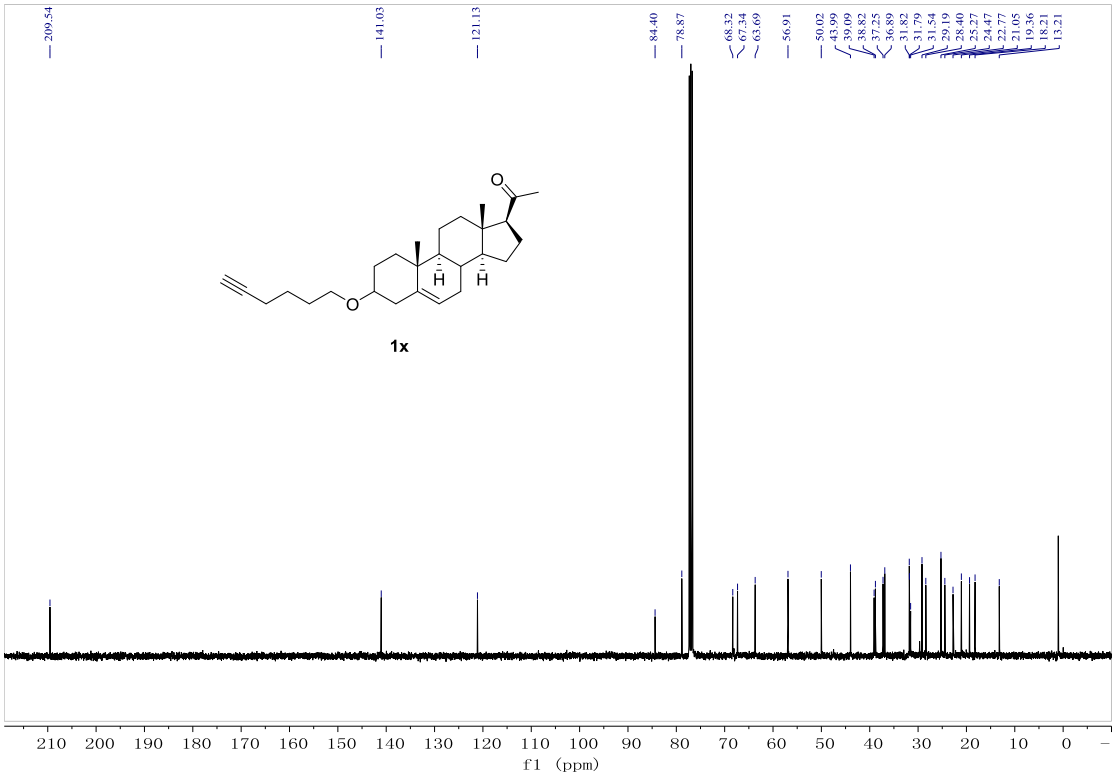


^{1}H NMR was recorded on Bruker 400 MHz; Solvent: $CDCl_3$



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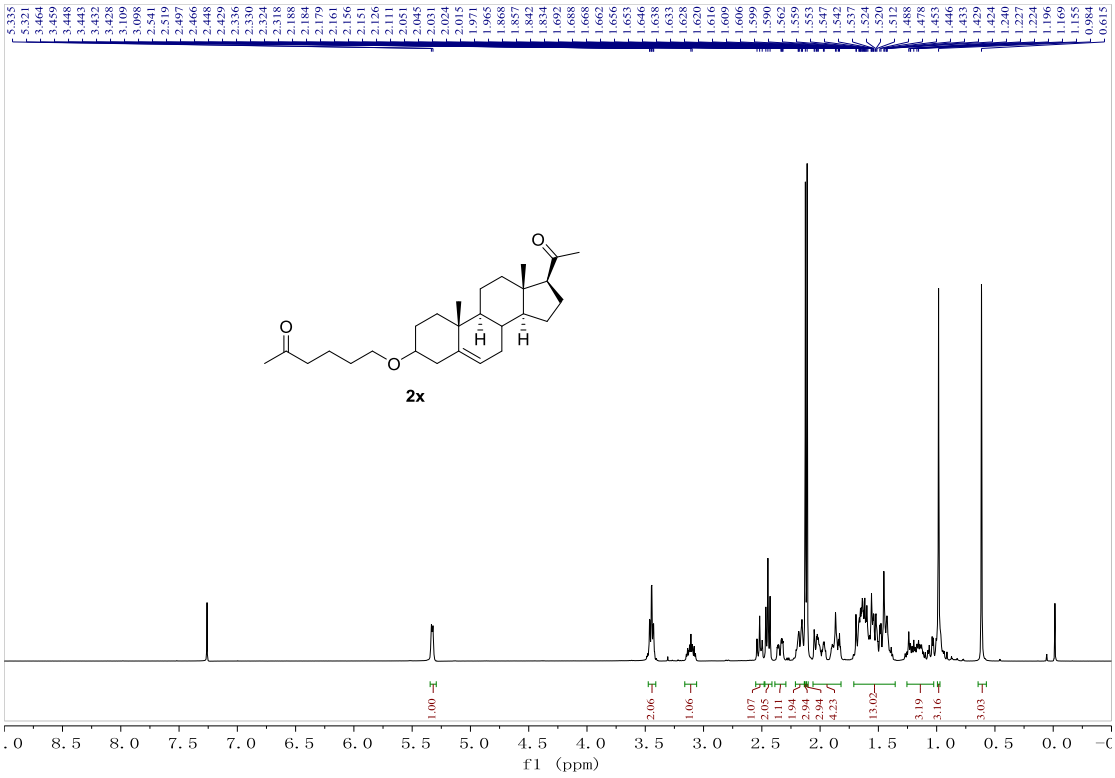

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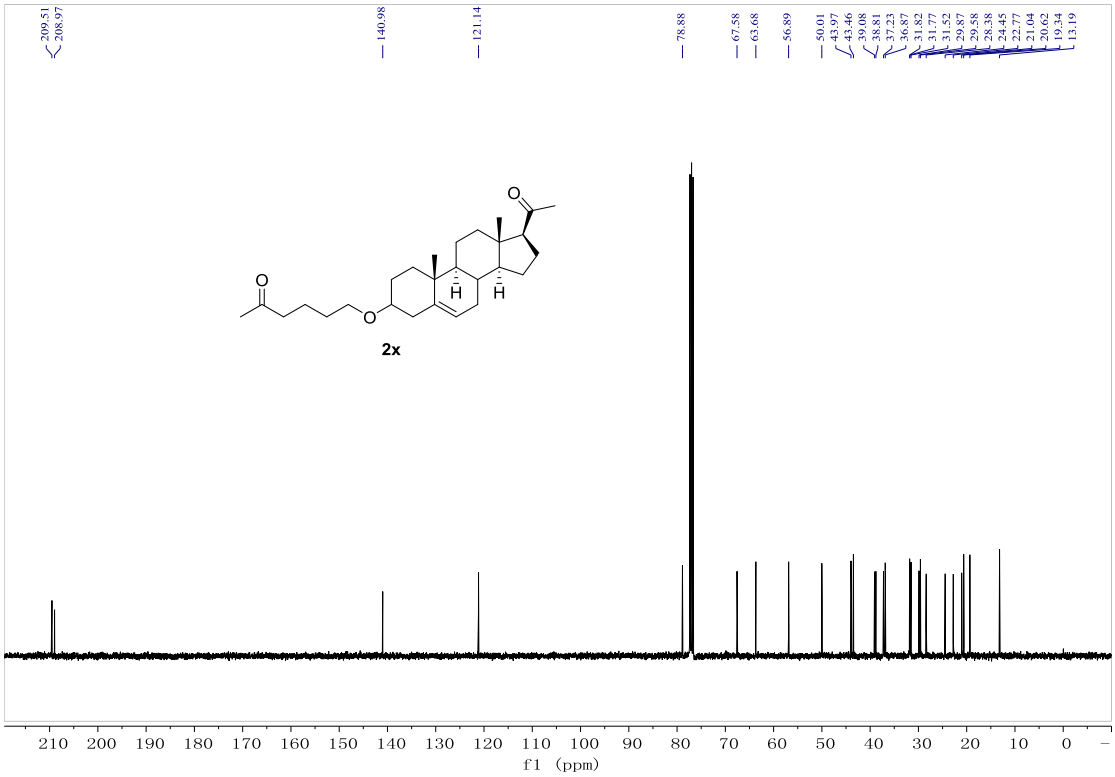
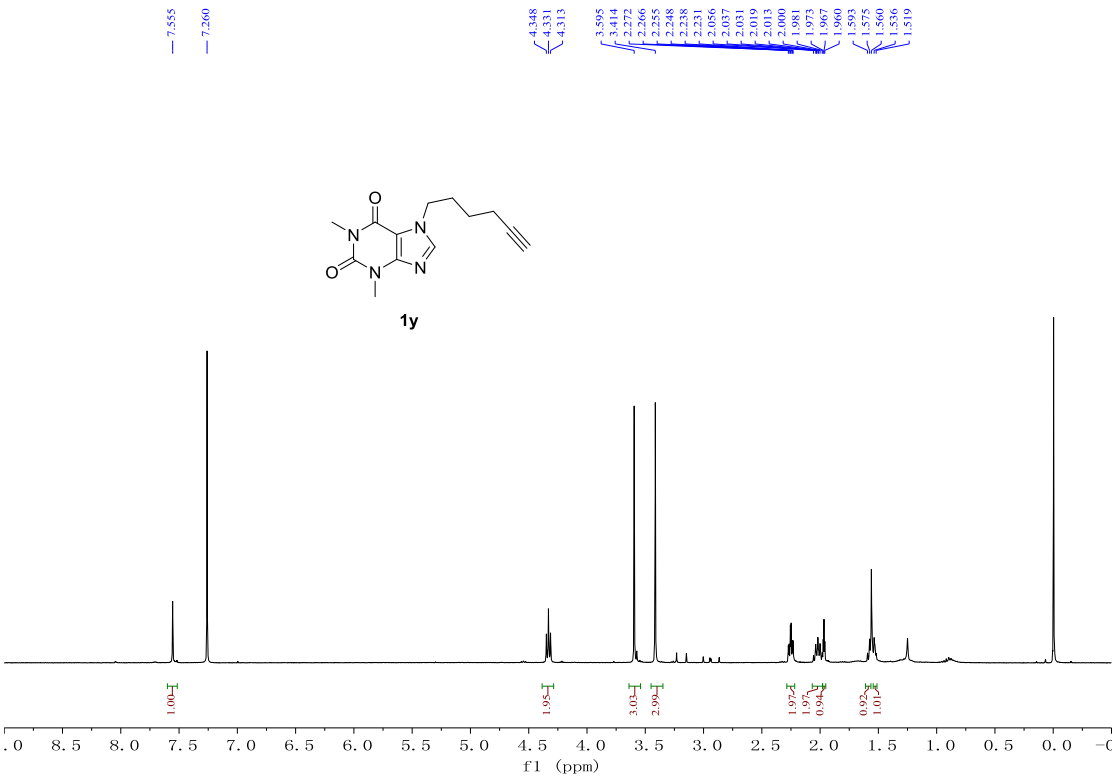


^{13}C NMR was recorded on Bruker 100 MHz; Solvent: $CDCl_3$



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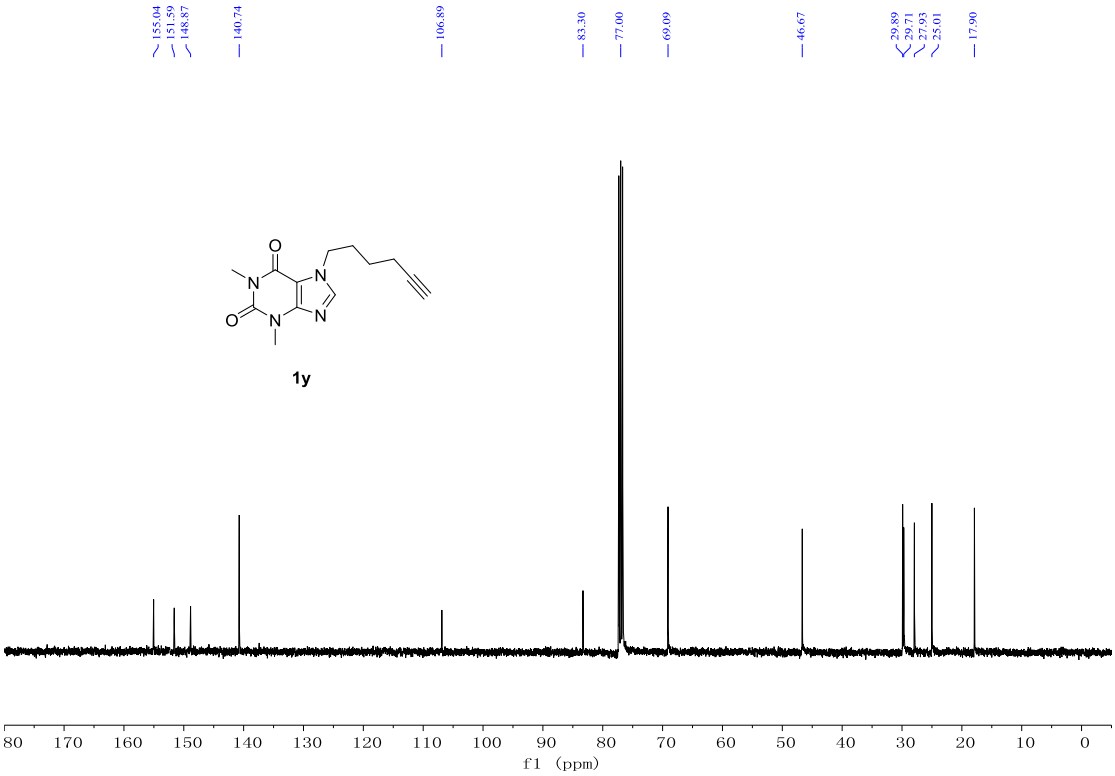

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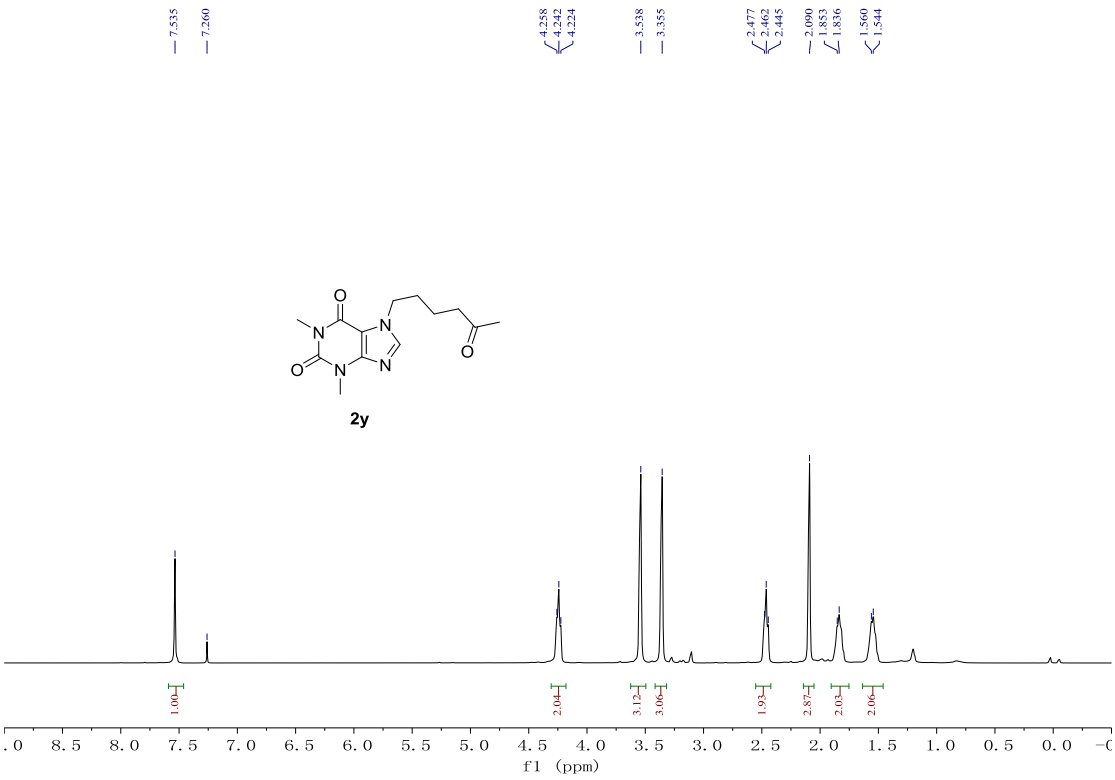

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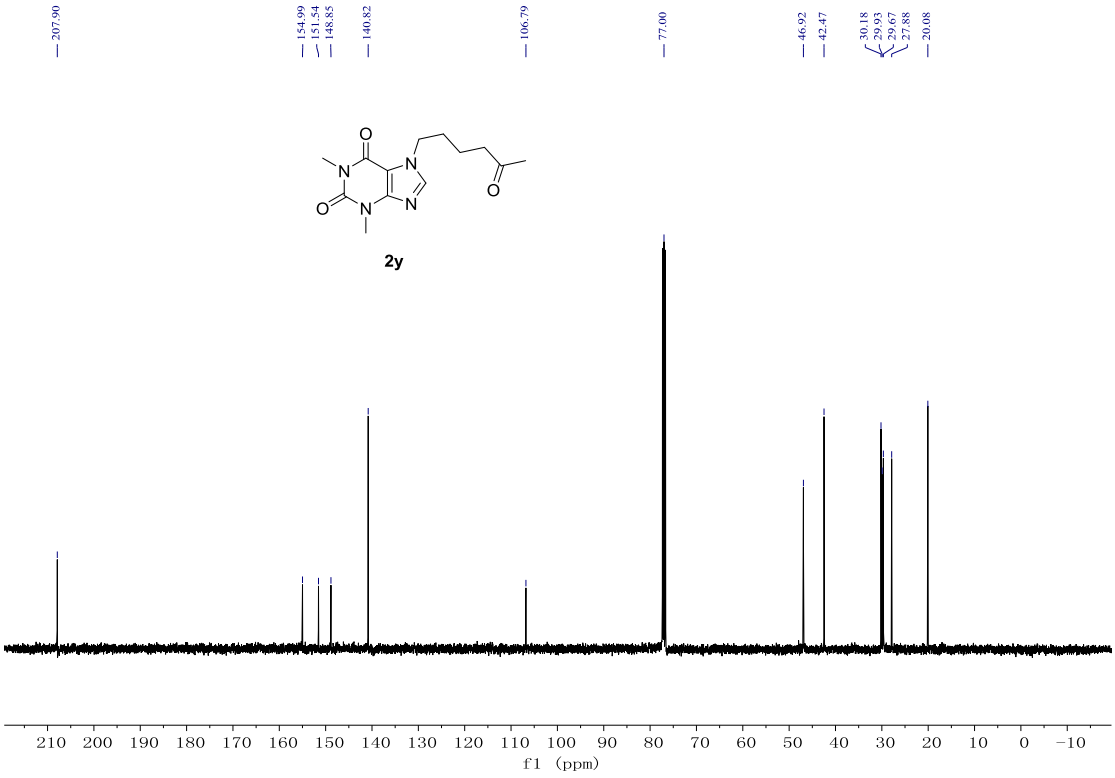

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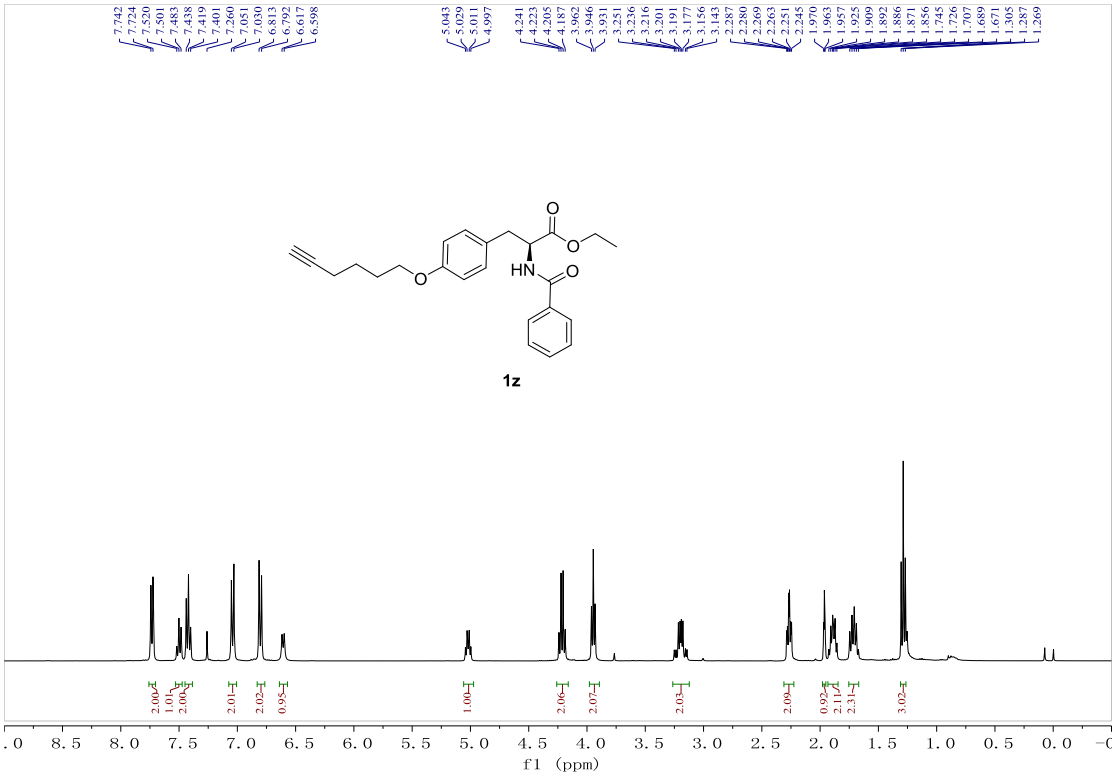

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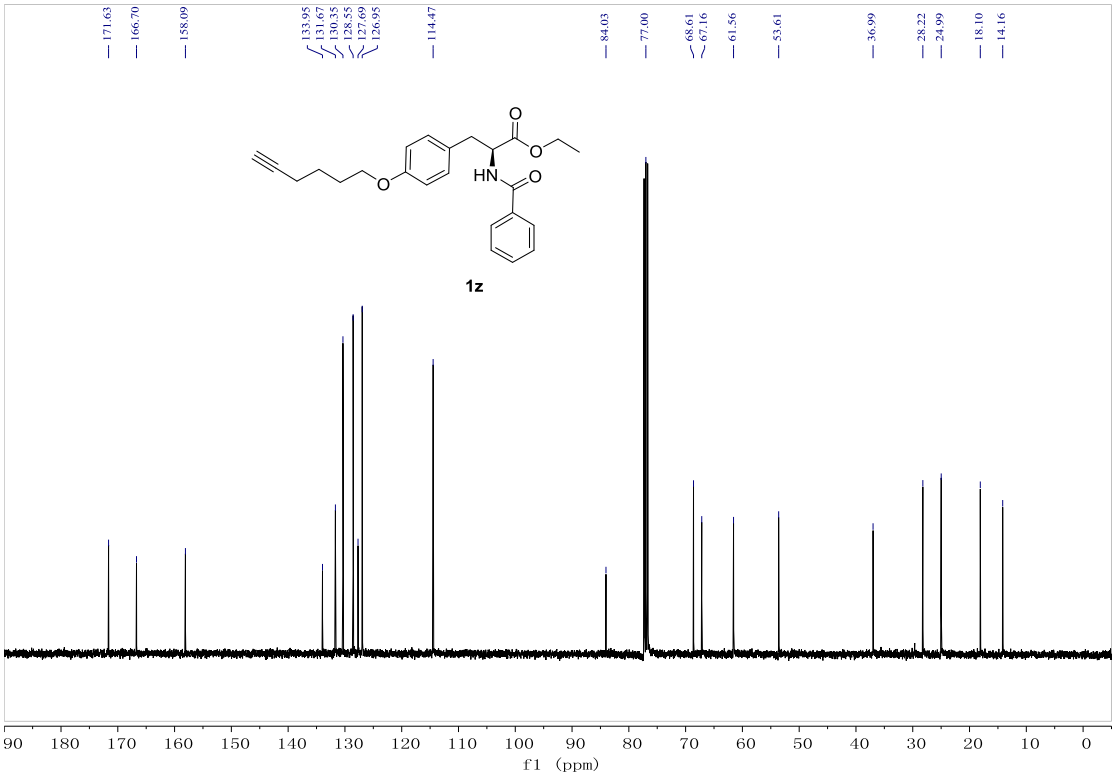

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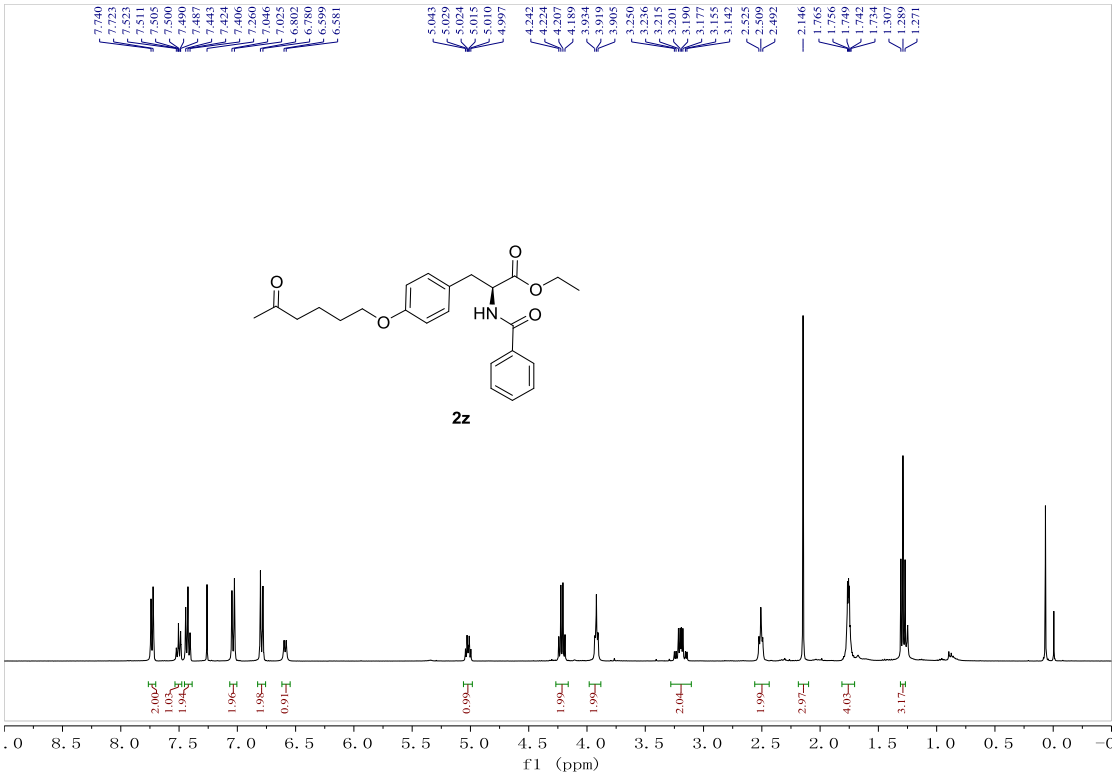

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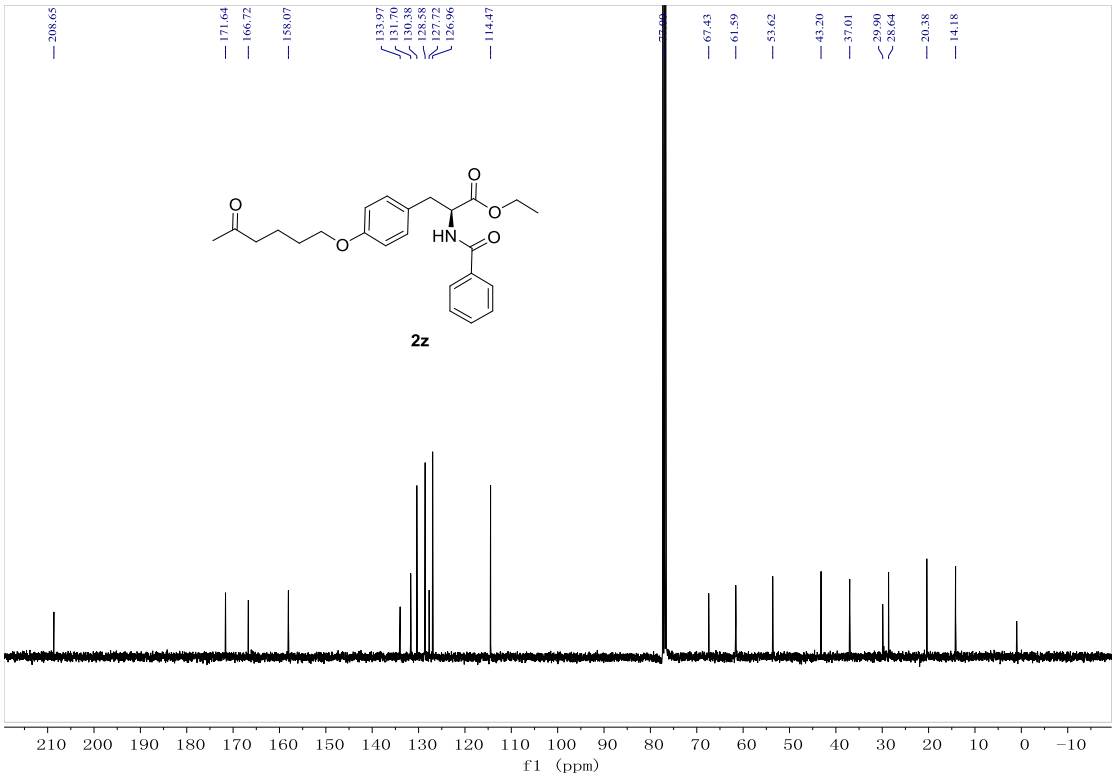

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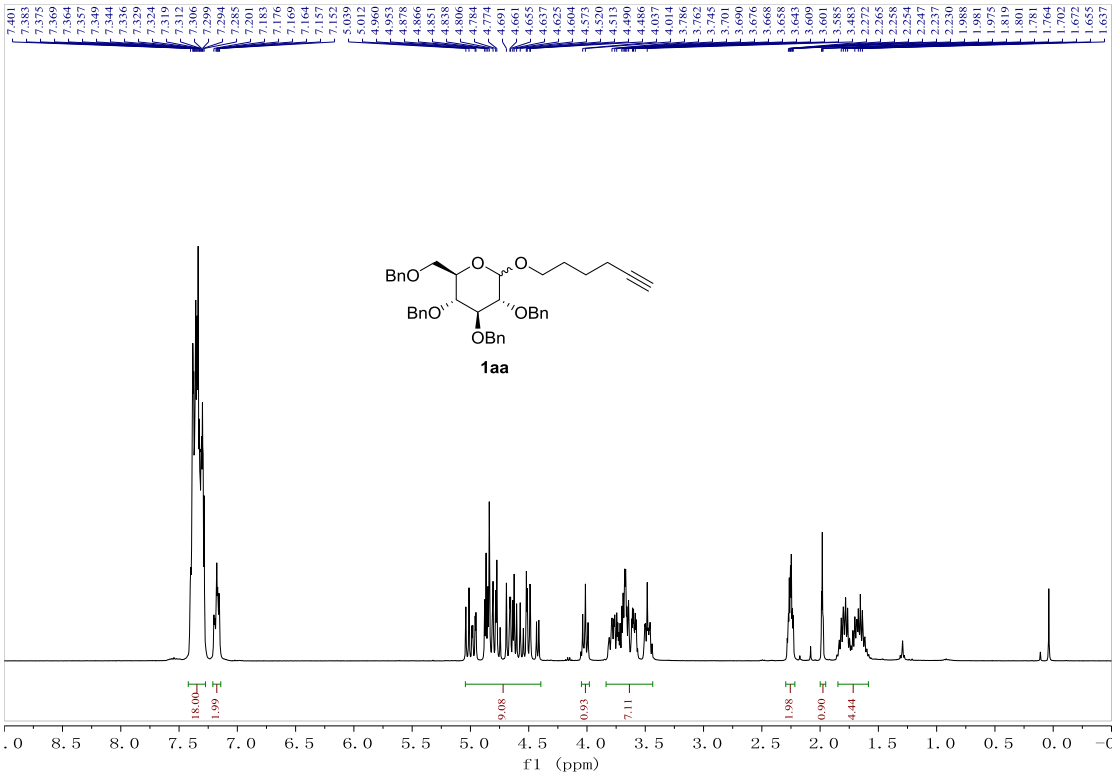

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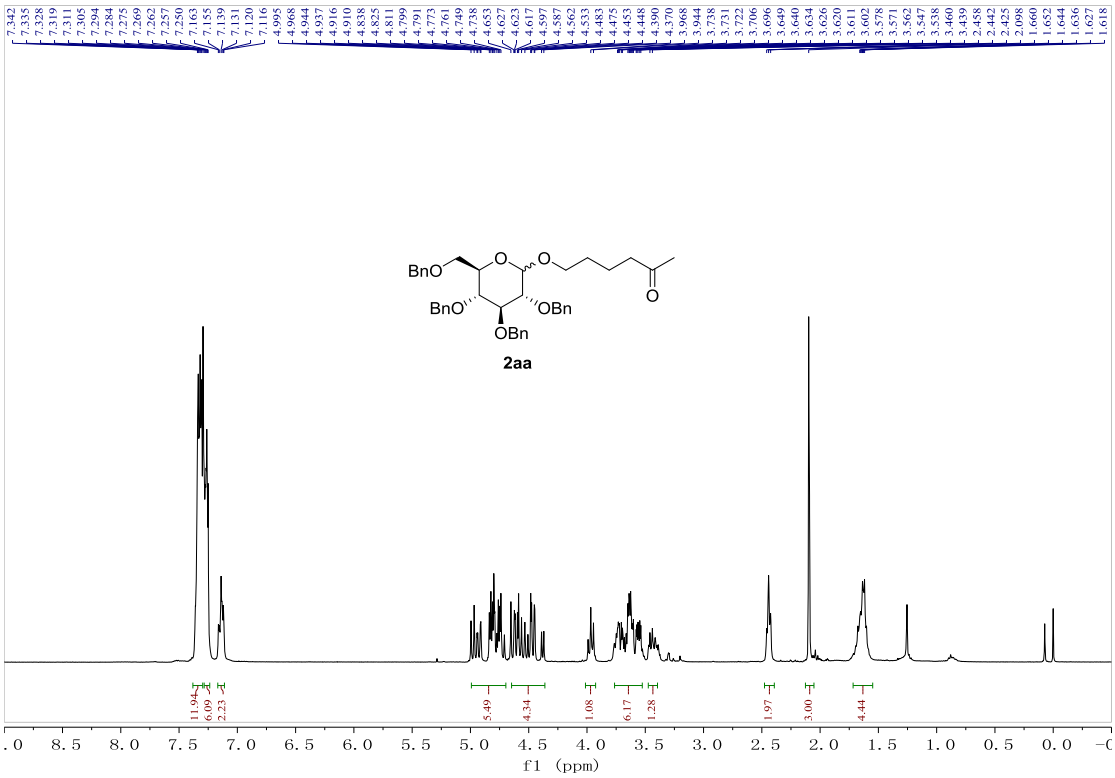

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