Supplementary Information

Photoinduced Iron-Catalyzed LMCT Enables Propargylic C(sp^3)-H Activation to Access Polysubstituted α-Bromoenones

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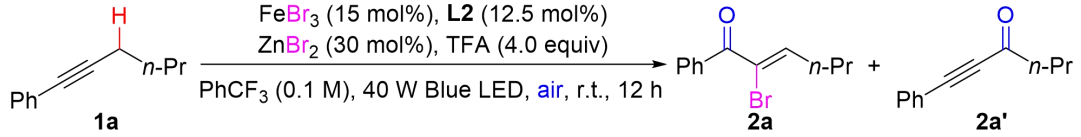
General Information

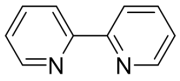
All reactions were performed at 40 W blue LED (450-455 nm) irradiation (SSSTECH-LAL1CV1.0, Shanghai 3S Technology Co., Ltd) under air atmosphere in a 25 mL sealed tube. The materials, solvents and alkynes **1** were purchased from common commercial sources and used without additional purification, if there is no special version. ^{1}H NMR spectra were recorded at 400 MHz using TMS as internal standard, ^{13}C NMR spectra was recorded at 100 MHz using TMS as internal standard. The multiplicities are reported as follows: singlet (s), doublet (d), doublet of doublets (dd), multiplet (m), and and triplet (t). Mass spectroscopy data of the products were collected on an HRMS-TOF instrument.

Table S1 Optimization of Reaction Conditions[a]

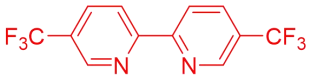


no ligand

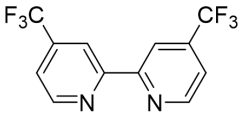
2a (38%, Z/E = 5:1)
2a' (19%), **1a** (41%)



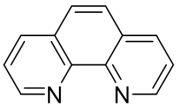
L1
2a (21%, Z/E = 12:1)
2a' (10%), **1a** (66%)



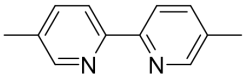
L2
2a (83%, Z/E > 20:1)
2a' (ND), **1a** (15%)



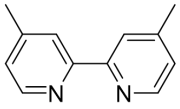
L3
2a (51%, Z/E = 15:1)
2a' (ND), **1a** (45%)



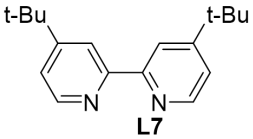
L4
2a (35%, Z/E = 11:1)
2a' (ND), **1a** (58%)



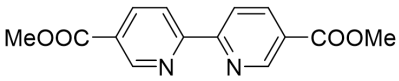
L5
2a (56%, Z/E > 20:1)
2a' (ND), **1a** (42%)



L6
2a (44%, Z/E = 16:1)
2a' (ND), **1a** (52%)



L7
2a (39%, Z/E = 15:1)
2a' (ND), **1a** (55%)



L8
2a (67%, Z-configuration)
2a' (ND), **1a** (29%)

Entry	Catalyst	"Br" salt	Acid	Solvent	Yield (%)[b]
1	**$FeBr_3$**	**$ZnBr_2$**	**TFA**	**$PhCF_3$**	**83**
2	$FeCl_3$	$ZnBr_2$	TFA	$PhCF_3$	35
3	$Fe(NO_3)_3·6H_2O$	$ZnBr_2$	TFA	$PhCF_3$	0
4	$Fe(acac)_3$	$ZnBr_2$	TFA	$PhCF_3$	0
5	$FeCl_2$	$ZnBr_2$	TFA	$PhCF_3$	28
7	$Fe(OAc)_2$	$ZnBr_2$	TFA	$PhCF_3$	37
8	$CoBr_2$	$ZnBr_2$	TFA	$PhCF_3$	0
9	$NiBr_2$	$ZnBr_2$	TFA	$PhCF_3$	0
10	$CuBr_2$	$ZnBr_2$	TFA	$PhCF_3$	0
11	$FeBr_3$	KBr	TFA	$PhCF_3$	67
12	$FeBr_3$	NaBr	TFA	$PhCF_3$	15
13	$FeBr_3$	$MgBr_2$	TFA	$PhCF_3$	60
14	$FeBr_3$	TBAB	TFA	$PhCF_3$	44
15	$FeBr_3$	$ZnBr_2$ (10 mol%)	TFA	$PhCF_3$	34
16	$FeBr_3$	$ZnBr_2$ (20 mol%)	TFA	$PhCF_3$	46
17	$FeBr_3$	$ZnBr_2$ (40 mol%)	TFA	$PhCF_3$	65
18	$FeBr_3$	$ZnBr_2$ (50 mol%)	TFA	$PhCF_3$	54
19	$FeBr_3$	$ZnBr_2$	HOAc	$PhCF_3$	55
20	$FeBr_3$	$ZnBr_2$	PivOH	$PhCF_3$	37
21	$FeBr_3$	$ZnBr_2$	PhCOOH	$PhCF_3$	15

22	$FeBr_3$	$ZnBr_2$	*o*-NO_2PhCOOH	$PhCF_3$	0
23	$FeBr_3$	$ZnBr_2$	TFA (1.0 equiv)	$PhCF_3$	19
24	$FeBr_3$	$ZnBr_2$	TFA (2.0 equiv)	$PhCF_3$	33
25	$FeBr_3$	$ZnBr_2$	TFA (3.0 equiv)	$PhCF_3$	63
26	$FeBr_3$	$ZnBr_2$	TFA (5.0 equiv)	$PhCF_3$	59
27	$FeBr_3$	$ZnBr_2$	TFA	DMF	0
29	$FeBr_3$	$ZnBr_2$	TFA	1,4-dioxane	0
30	$FeBr_3$	$ZnBr_2$	TFA	THF	0
32	$FeBr_3$	$ZnBr_2$	TFA	NMP	0
33	$FeBr_3$	$ZnBr_2$	TFA	TFE	0
34	$FeBr_3$	$ZnBr_2$	TFA	DMSO	62
35	$FeBr_3$	$ZnBr_2$	TFA	DCE	35
36	$FeBr_3$	$ZnBr_2$	TFA	MeCN	72
37[c]	$FeBr_3$	$ZnBr_2$	TFA	MeCN	trace
38[d]	$FeBr_3$	$ZnBr_2$	TFA	MeCN	83
39[e]	$FeBr_3$	$ZnBr_2$	TFA	MeCN	0
40	$FeBr_3$	$ZnBr_2$	-	MeCN	18
41	-	$ZnBr_2$	TFA	MeCN	<10
42	$FeBr_3$	-	TFA	MeCN	40

[a]Reactions were carried out by using **1a** (0.1 mmol), Catalyst (0.015 mmol), ligand (0.0125 mmol), Br salt (0.03 mmol), acid (0.4 mmol), and solvent (1.0 mL) with 40 W blue LED irradiation under air at room temperature for 12 h. [b]Isolated yield. The ratio of Z/E configuration was determined by ^{1}H NMR. [c]N_2 atmosphere. [d]O_2 atmosphere. [e]No light.

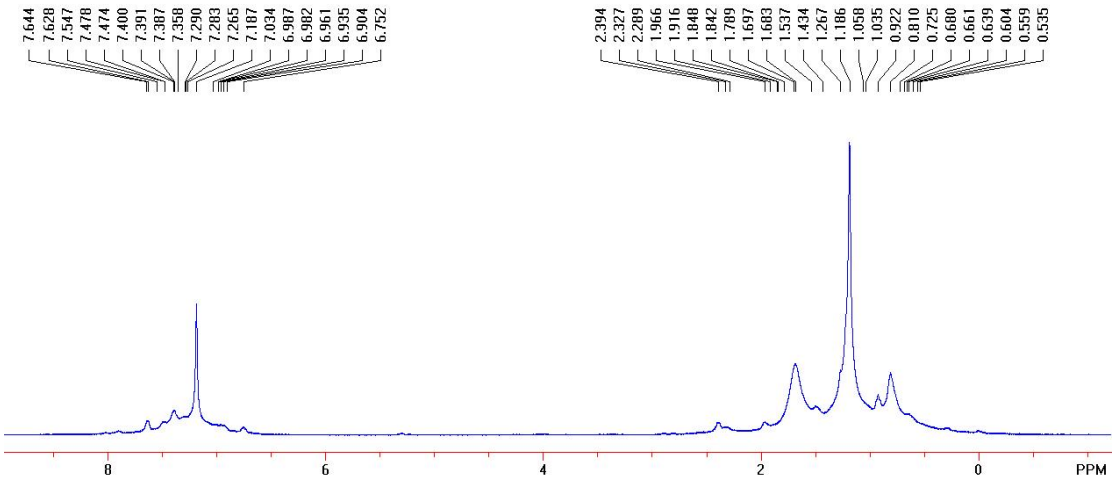
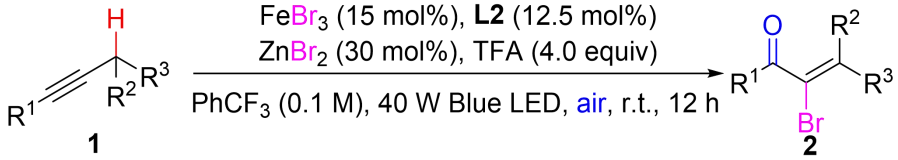


Figure S1 The crude reaction mixture of entry 1 was analyzed by ^{1}H NMR

Typical Procedure for Photoinduced Iron-Catalyzed LMCT Enables Propargylic C(sp^3)-H Activation to Access Polysubstituted Z-Configured α-Bromoenones

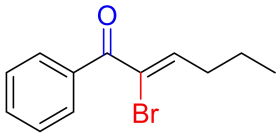


A 25 mL thick wall pressure sealed tube was charged with **1** (0.1 mmol), $FeBr_3$ (4.4 mg, 0.015 mmol), **L2** (3.6 mg, 0.0125 mmol), $ZnBr_2$ (6.8 mg, 0.03 mmol), TFA (45.8 mg, 0.4 mmol), and $PhCF_3$ (1.0 mL) with 40 W blue LED irradiation under air at room temperature for 12 h. The mixture was then cooled to room temperature, diluted with EtOAc, filtered through a celite pad, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/PE (1:40 ~ 1:30, v/v), to give the corresponding product **2**.

Figure S2 Reaction setup

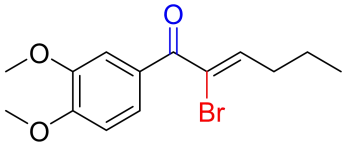
Analytical Data for Products

(Z)-2-bromo-1-phenylhex-2-en-1-one (2a)



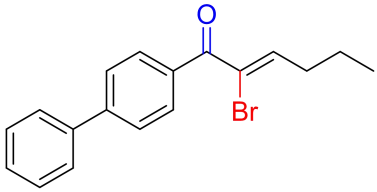
Rf 0.36 (PE/EtOAc = 40/1). 83%, 20.9 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63 (d, J = 7.6 Hz, 2H), 7.49 (t, J = 7.6 Hz, 1H), 7.40-7.36 (m, 2H), 6.76 (t, J = 7.2 Hz, 1H), 2.39 (dd, J_1 = 7.2 Hz; J_2 = 16.8 Hz, 2H), 1.51-1.43 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.5, 147.9, 136.7, 132.4, 129.5, 128.4, 126.2, 34.5, 21.1, 13.8. HRMS (EI-TOF) calcd for $C_{12}H_{13}BrO$ (M^+): 252.0150, found: 252.0151.

(Z)-2-bromo-1-(3,4-dimethoxyphenyl)hex-2-en-1-one (2b)



Rf 0.30 (PE/EA = 5/1). 57%, 17.8 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.01 (d, J = 8.0 Hz, 1H), 7.52 (d, J = 8.4 Hz, 1H), 7.46 (s, 1H), 6.81 (d, J = 8.4 Hz, 1H), 3.87 (s, 6H), 2.85 (t, J = 7.2 Hz, 2H), 1.66 (s, 2H), 0.84 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 199.3, 153.1, 149.0, 130.4, 123.4, 122.7, 110.2, 109.9, 56.0, 55.9, 38.1, 22.5, 14.0. HRMS (EI-TOF) calcd for $C_{14}H_{17}BrO_3$ (M^+): 312.0361, found: 312.0368.

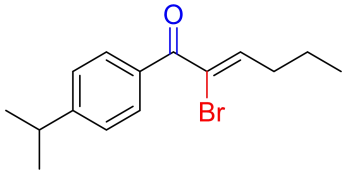
(Z)-1-([1,1'-biphenyl]-4-yl)-2-bromohex-2-en-1-one (2c)



Rf 0.32 (PE/EA = 40/1). 62%, 20.3 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, J = 7.6 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 7.57 (d, J = 6.8 Hz, 2H), 7.42-7.35 (m, 3H), 6.81 (t, J = 6.8 Hz, 1H), 2.43-2.39 (m, 2H), 1.51 (dd, J_1 = 7.2 Hz; J_2 = 14.8

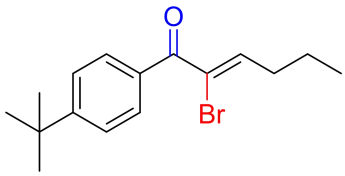
Hz, 2H), 0.94 (t, J = 7.2 Hz, 3H).^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.2, 147.6, 145.4, 139.8, 135.3, 130.2, 129.0, 128.7, 128.3, 127.3, 127.1, 34.5, 21.1, 13.9. HRMS (EI-TOF) calcd for $C_{18}H_{17}BrO$ (M^+): 328.0463, found: 328.0469.

(Z)-2-bromo-1-(4-isopropylphenyl)hex-2-en-1-one (2d)



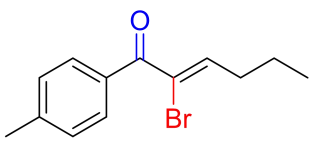
Rf 0.28 (PE/EtOAc = 40/1). 72%, 21.1 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59 (d, J = 8.4 Hz, 2H), 7.20 (d, J = 13.2 Hz, 2H), 6.73 (t, J = 7.2 Hz, 1H), 2.92-2.84 (m, 1H), 2.40-2.35 (m, 2H), 1.55-1.44 (m, 2H), 1.21 (s, 3H), 1.19 (s, 3H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.4, 154.3, 147.2, 135.0, 129.9, 128.3, 126.6, 38.5, 34.2, 23.7, 22.5, 14.0. HRMS (EI-TOF) calcd for $C_{15}H_{19}BrO$ (M^+): 294.0619, found: 294.0622.

(Z)-2-bromo-1-(4-(tert-butyl)phenyl)hex-2-en-1-one (2e)



Rf 0.28 (PE/EtOAc = 40/1). 73%, 22.5 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.60 (d, J = 8.4 Hz, 2H), 7.40 (t, J = 6.0 Hz, 2H), 6.73 (t, J = 7.2 Hz, 1H), 2.41-2.35 (m, 2H), 1.53-1.44 (m, 2H), 1.27 (s, 9H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.4, 156.6, 147.2, 134.6, 129.6, 128.1, 125.4, 38.5, 35.1, 31.1, 22.5, 13.9. HRMS (EI-TOF) calcd for $C_{16}H_{21}BrO$ (M^+): 308.0776, found: 308.0778.

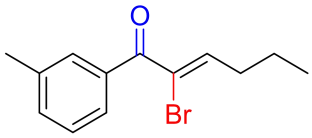
(Z)-2-bromo-1-(p-tolyl)hex-2-en-1-one (2f)



Rf 0.28 (PE/EtOAc = 40/1). 72%, 19.1 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ

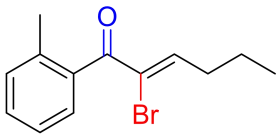
7.56 (d, J = 7.6 Hz, 2H), 7.19 (t, J = 7.6 Hz, 2H), 6.71 (t, J = 7.2 Hz, 1H), 2.40-2.35 (m, 5H), 1.51-1.45 (m, 2H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.3, 146.9, 143.3, 133.9, 129.8, 129.1, 126.0, 34.4, 29.7, 21.1, 13.8. HRMS (EI-TOF) calcd for $C_{13}H_{15}BrO$ (M^+): 266.0306, found: 266.0306.

(Z)-2-bromo-1-(m-tolyl)hex-2-en-1-one (2g)



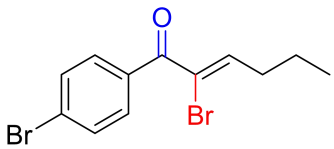
Rf 0.29 (PE/EA = 40/1). 69%, 18.3 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.45 (s, 1H), 7.41 (d, J = 7.2 Hz, 1H), 7.29-7.26 (m, 2H), 6.75 (t, J = 7.2 Hz, 1H), 2.39 (dd, J_1 = 8.0 Hz; J_2 = 16.8 Hz, 2H), 2.34 (s, 3H), 1.51-1.45 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.7, 147.8, 138.3, 136.8, 133.2, 130.0, 128.1, 126.7, 126.3, 34.5, 21.3, 21.1, 13.8. HRMS (EI-TOF) calcd for $C_{13}H_{15}BrO$ (M^+): 266.0306, found: 266.0307.

6-(4-chlorophenyl)-3-morpholino-*N*-(quinolin-8-yl)hex-5-ynamide (2h)



Rf 0.31 (PE/EA = 40/1). 71%, 18.9 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.28 (s, 1H), 7.181 (d, J = 10.0 Hz, 3H), 6.71 (t, J = 7.2 Hz, 1H), 2.39-2.33 (m, 2H), 2.23 (s, 3H), 1.46-1.38 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.2, 151.0, 137.9, 136.3, 130.9, 130.2, 129.1, 127.7, 125.3, 34.7, 20.1, 19.5, 13.8. HRMS (EI-TOF) calcd for $C_{13}H_{15}BrO$ (M^+): 266.0306, found: 266.0309.

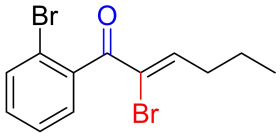
(Z)-2-bromo-1-(4-bromophenyl)hex-2-en-1-one (2i)



Rf 0.39 (PE/EA = 40/1). 50%, 16.5 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.58-7.45 (m, 4H), 6.73 (t, J = 6.8 Hz, 1H), 2.38 (dd, J_1 = 6.8 Hz; J_2 = 14.0 Hz, 2H),

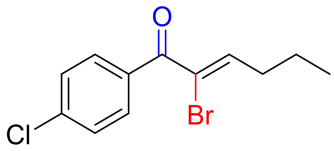
1.49 (dd, J_1 = 7.2 Hz; J_2 = 14.8 Hz, 2H), 0.91 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.5, 148.1, 135.4, 131.7, 131.0, 127.5, 125.7, 34.5, 21.1, 13.9. HRMS (EI-TOF) calcd for $C_{12}H_{12}Br_2O$ (M^+): 329.9255, found: 329.9259.

(Z)-2-bromo-1-(2-bromophenyl)hex-2-en-1-one (2j)



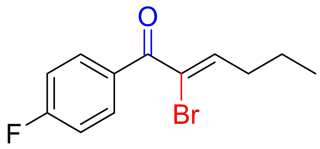
Rf 0.25 (PE/EA = 40/1). 65%, 21.4 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.53 (d, J = 7.6 Hz, 1H), 7.34-7.20 (m, 2H), 7.18 (d, J = 1.6 Hz, 1H), 6.72 (t, J = 7.2 Hz, 1H), 2.37 (dd, J_1 = 6.8 Hz; J_2 = 14.4 Hz, 2H), 1.48-1.37 (m, 2H), 0.87 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.7, 152.4, 139.9, 133.2, 131.3, 138.7, 127.7, 127.2, 119.4, 34.8, 20.8, 13.8. HRMS (EI-TOF) calcd for $C_{12}H_{12}Br_2O$ (M^+): 329.9255, found: 329.9256.

(Z)-2-bromo-1-(4-chlorophenyl)hex-2-en-1-one (2k)



Rf = 0.31 (PE/EA = 40/1). 66%, 18.8 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.59 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 6.73 (t, J = 7.2 Hz, 1H), 2.38 (t, J = 7.2 Hz, 2H), 1.51-1.46 (m, 2H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.4, 147.8, 139.0, 134.9, 130.9, 128.7, 125.6, 34.5, 21,1, 13.8. HRMS (EI-TOF) calcd for $C_{12}H_{12}BrClO$ (M^+): 285.9760, found: 285.9767.

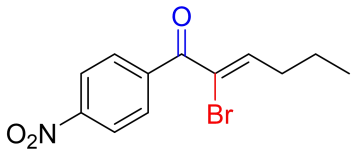
(Z)-2-bromo-1-(4-fluorophenyl)hex-2-en-1-one (2l)



Rf 0.36 (PE/EA = 40/1). 70%, 18.9 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.70-7.67 (m, 2H), 7.07 (t, J = 8.4 Hz, 2H), 6.71 (t, J = 7.2 Hz, 1H), 2.39 (dd, J_1 = 6.8

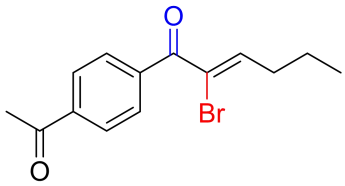
Hz; J_2 = 14.4 Hz, 2H), 1.49 (dd, J_1 = 7.2 Hz; J_2 = 14.8 Hz, 2H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 189.2, 165.4 (d, $J_{C\text{-}F}$ = 253.2 Hz), 147.2, 132.4 (d, $J_{C\text{-}F}$ = 62.4 Hz), 125.4, 124.2 (d, $J_{C\text{-}F}$ = 49.3 Hz), 115.6 (d, $J_{C\text{-}F}$ = 22.0 Hz), 34.4, 21.1, 13.9. HRMS (EI-TOF) calcd for $C_{12}H_{12}BrFO$ (M^+): 270.0056, found: 270.0058.

(Z)-2-bromo-1-(4-nitrophenyl)hex-2-en-1-one (2m)



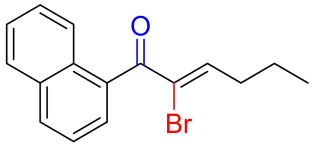
Rf = 0.18 (PE/EA = 40/1). 61%, 18.1 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 8.25 (d, J = 8.0 Hz, 2H), 7.76 (d, J = 8.0 Hz, 2H), 6.79 (t, J = 6.8 Hz, 1H), 2.42 (dd, J_1 = 7.2 Hz; J_2 = 14.4 Hz, 2H), 1.49 (dd, J_1 = 7.2 Hz; J_2 = 14.4 Hz, 2H), 0.92 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 188.8, 150.3, 149.9, 142.2, 130.1, 125.8, 123.6, 34.7, 21.0, 13.9. HRMS (EI-TOF) calcd for $C_{12}H_{12}BrNO_3$ (M^+): 297.0001, found: 297.0001.

(Z)-1-(4-acetylphenyl)-2-bromohex-2-en-1-one (2n)



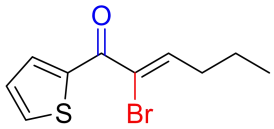
Rf 0.23 (PE/EA = 10/1). 63%, 18.5 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.96 (d, J = 7.6 Hz, 2H), 7.69 (d, J = 7.2 Hz, 2H), 6.77 (s, 1H), 2.59 (s, 3H), 2.40 (d, J = 5.6 Hz, 2H), 1.48 (d, J = 6.0 Hz, 2H), 0.92 (t, J = 5.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 197.2, 189.8, 149.3, 140.6, 139.7, 129.5, 128.2, 126.1, 34.6, 26.7, 21.0, 13.8. HRMS (EI-TOF) calcd for $C_{14}H_{15}BrO_2$ (M^+): 294.0255, found: 294.0259.

(Z)-2-bromo-1-(naphthalen-1-yl)hex-2-en-1-one (2o)



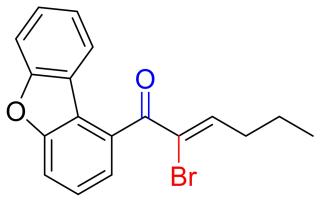
Rf 0.30 (PE/EA = 40/1). 49%, 14.8 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.91-7.82 (m, 3H), 7.48-7.41 (m, 4H), 6.78 (t, J = 6.8 Hz, 1H), 2.36 (dd, J_1 = 7.6 Hz; J_2 = 14.4 Hz, 2H), 1.38 (dd, J_1 = 7.2 Hz; J_2 = 14.4 Hz, 2H), 0.83 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.6, 151.6, 135.6, 133.6, 131.2, 130.8, 129.4, 128.4, 127.4, 126.7, 126.6, 125.3, 124.3, 34.8, 20.9, 13.8. HRMS(EI-TOF) calcd for $C_{16}H_{15}BrO$ (M^+): 302.0306, found: 302.0310.

(Z)-2-bromo-1-(thiophen-2-yl)hex-2-en-1-one (2p)



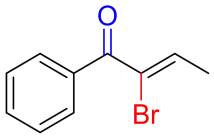
Rf 0.23 (PE/EA = 40/1). 58%, 14.9 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (s, 1H), 7.42 (d, J = 4.8 Hz, 1H), 7.29 (d, J = 2.8 Hz, 1H), 6.88 (t, J = 6.8 Hz, 1H), 2.39 (dd, J_1 = 7.2 Hz; J_2 = 14.4 Hz, 2H), 1.51 (dd, J_1 = 7.2 Hz; J_2 = 14.4 Hz, 2H), 0.94 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 194.9, 145.8, 133.0, 131.5, 128.4, 127.0, 126.2, 31.5, 22.5, 13.9. HRMS (EI-TOF) calcd for $C_{10}H_{11}BrOS$ (M^+): 257.9714, found: 257.9719.

(Z)-2-bromo-1-(dibenzo[b,d]furan-1-yl)hex-2-en-1-one (2q)



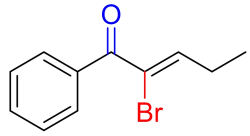
Rf 0.25 (PE/EA = 40/1). 47%, 16.1 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.85 (d, J = 8.0 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.50 (d, J = 8.4 Hz, 1H), 7.42 (d, J = 7.2 Hz, 2H), 7.36 (t, J = 7.2 Hz, 1H), 7.23 (t, J = 7.2 Hz, 1H), 6.86 (t, J = 7.2 Hz, 1H), 2.36 (dd, J_1 = 7.2 Hz; J_2 = 14.4 Hz, 2H), 1.37 (dd, J_1 = 7.2 Hz; J_2 = 14.4 Hz, 2H), 0.81 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.2, 156.7, 156.4, 151.5, 131.9, 128.2, 128.0, 126.3, 123.9, 123.8, 123.0, 122.9, 122.3, 114.7, 111.6, 34.9, 20.9, 13.8. HRMS (EI-TOF) calcd for $C_{18}H_{15}BrO_2$ (M^+): 342.0255, found: 342.0256.

(Z)-2-bromo-1-phenylbut-2-en-1-one (2r)



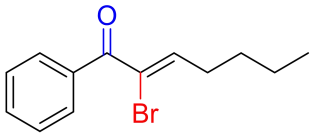
Rf 0.28 (PE/EA = 4/1). 85%, 19.0 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.62 (d, *J* = 7.2 Hz, 2H), 7.51-7.47 (m, 1H), 7.38 (t, *J* = 7.6 Hz, 2H), 6.88-6.83 (m, 1H), 2.00 (d, *J* = 6.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.5, 143.3, 136.7, 132.3, 129.4, 128.4, 127.7, 18.3. HRMS (EI-TOF) calcd for $C_{10}H_9BrO$ (M^+): 223.9837, found: 223.9842.

(Z)-2-bromo-1-phenylpent-2-en-1-one (2s)



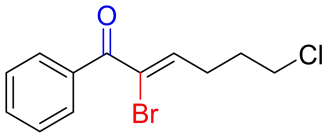
Rf 0.32 (PE/EA = 40/1). 75%, 17.8 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.63 (d, *J* = 7.2 Hz, 2H), 7.52-7.48 (m, 1H), 7.41-7.37 (m, 2H), 6.76 (d, *J* = 6.8 Hz, 1H), 2.44-2.40 (m, 2H), 1.05 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.6, 149.3, 136.7, 132.4, 129.5, 128.4, 125.6, 26.1, 12.0. HRMS (EI-TOF) calcd for $C_{11}H_{11}BrO$ (M^+): 237.9993, found: 237.9998.

(Z)-2-bromo-1-phenylhept-2-en-1-one (2t)



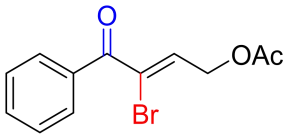
Rf 0.32 (PE/EA = 40/1). 70%, 18.6 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.69 (d, *J* = 7.2 Hz, 2H), 7.58-7.54 (m, 1H), 7.45 (t, *J* = 7.2 Hz, 2H), 6.82 (d, *J* = 7.2 Hz, 1H), 2.48 (dd, J_1 = 7.2 Hz; J_2 = 14.0 Hz, 2H), 1.49 (dd, J_1 = 7.2 Hz; J_2 = 14.0 Hz, 2H), 1.41-1.33 (m, 2H), 0.93 (t, *J* = 7.2 HZ, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.5, 148.2, 136.8, 132.4, 129.5, 128.4, 126.1, 32.3, 29.8, 22.4, 13.8. HRMS (EI-TOF) calcd for $C_{13}H_{15}BrO$ (M^+): 266.0306, found: 266.0306.

(Z)-2-bromo-6-chloro-1-phenylhex-2-en-1-one (2u)



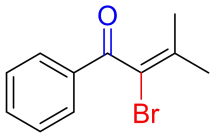
Rf 0.21 (PE/EA = 40/1). 72%, 20.6 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.64 (d, *J* = 7.2 Hz, 2H), 7.50 (d, *J* = 6.8 Hz, 1H), 7.41 (d, *J* = 6.8 Hz, 2H), 6.75 (t, *J* = 6.4 Hz, 1H), 3.52 (s, 2H), 2.58 (d, *J* = 6.8 Hz, 2H), 1.93 (t, *J* = 6.0 Hz, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.4, 145.5, 136.4, 132.6, 131.6, 129.6, 128.5, 44.1, 30.5, 30.0. HRMS (EI-TOF) calcd for $C_{12}H_{12}BrClO$ (M^+): 285.9760, found: 285.9766.

(Z)-3-bromo-4-oxo-4-phenylbut-2-en-1-yl acetate (2v)



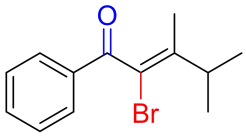
Rf 0.25 (PE/EtOAc = 10/1). 66%, 18.6 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.79 (d, *J* = 7.6 Hz, 2H), 7.58-7.52 (m, 1H), 7.46-7.40 (m, 2H), 6.81 (t, *J* = 4.8 Hz, 1H), 4.86 (d, *J* = 4.8 Hz, 2H), 2.03 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 192.4, 170.8, 140.6, 138.8, 133.8, 129.7, 128.6, 125.6, 61.8, 20.6. HRMS (EI-TOF) calcd for $C_{12}H_{11}BrO_3$ (M^+): 281.9892, found: 281.9892.

2-bromo-3-methyl-1-phenylbut-2-en-1-one (2w)



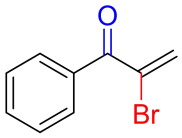
Rf 0.42 (PE/EA = 40/1). 85%, 20.2 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.89 (d, *J* = 7.6 Hz, 2H), 7.55-7.51 (m, 1H), 7.44-7.40 (m, 2H), 2.07 (s, 3H), 1.73 (s, 3H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.8, 138.5, 135.0, 133.7, 129.9, 128.7, 112.1, 23.9, 22.0. HRMS (EI-TOF) calcd for $C_{11}H_{11}BrO$ (M^+): 237.9993, found: 237.9996.

(Z)-2-bromo-3,4-dimethyl-1-phenylpent-2-en-1-one (2x)



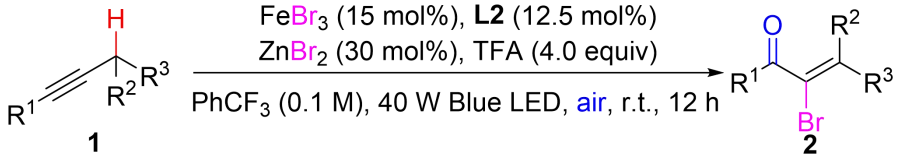
Rf = 0.40 (PE/EA = 40/1). 60%, 15.9 mg. Yellow oil. ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.51 (d, *J* = 6.8 Hz, 2H), 7.42-7.38 (m, 1H), 7.33 (d, *J* = 7.2 Hz, 2H), 2.39 (s, 3H), 1.97-1.92 (m, 1H), 1.24 (d, *J* = 19.2 Hz, 6H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 191.6, 144.2, 134.2, 133.0, 130.7, 128.6, 117.9, 29.7, 22.5, 13.0. HRMS (EI-TOF) calcd for $C_{13}H_{15}BrO(M^+)$: 266.0306, found: 266.0310.

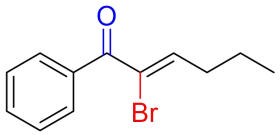
2-bromo-1-phenylprop-2-en-1-one (2y)



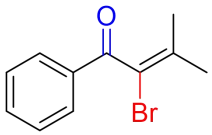
Rf 0.31 (PE/EA = 40/1). 79%, 16.6 mg. Yellow oil; ^{1}H NMR ($CDCl_3$, 400 MHz) δ 7.74 (d, *J* = 6.8 Hz, 2H), 7.55-7.51 (m, 1H), 7.41 (t, *J* = 7.2 Hz, 2H), 6.48 (s, 1H), 6.41 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz) δ 190.2, 135.2, 133.2, 129.9, 129.7, 129.5, 128.7. HRMS (EI-TOF) calcd for C_9H_7BrO (M^+): 209.9680, found: 209.9680.

Large-scale synthesis of 2a and 2w





2a, 72%

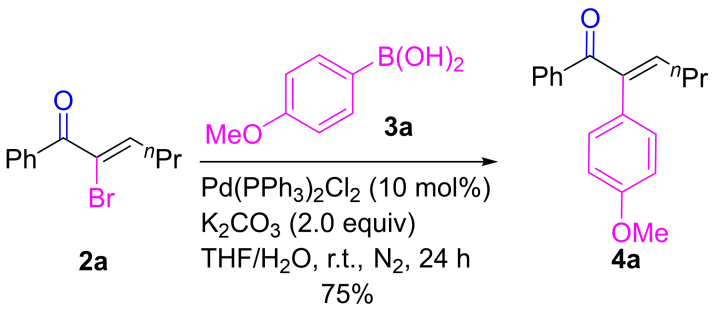


2w, 75%

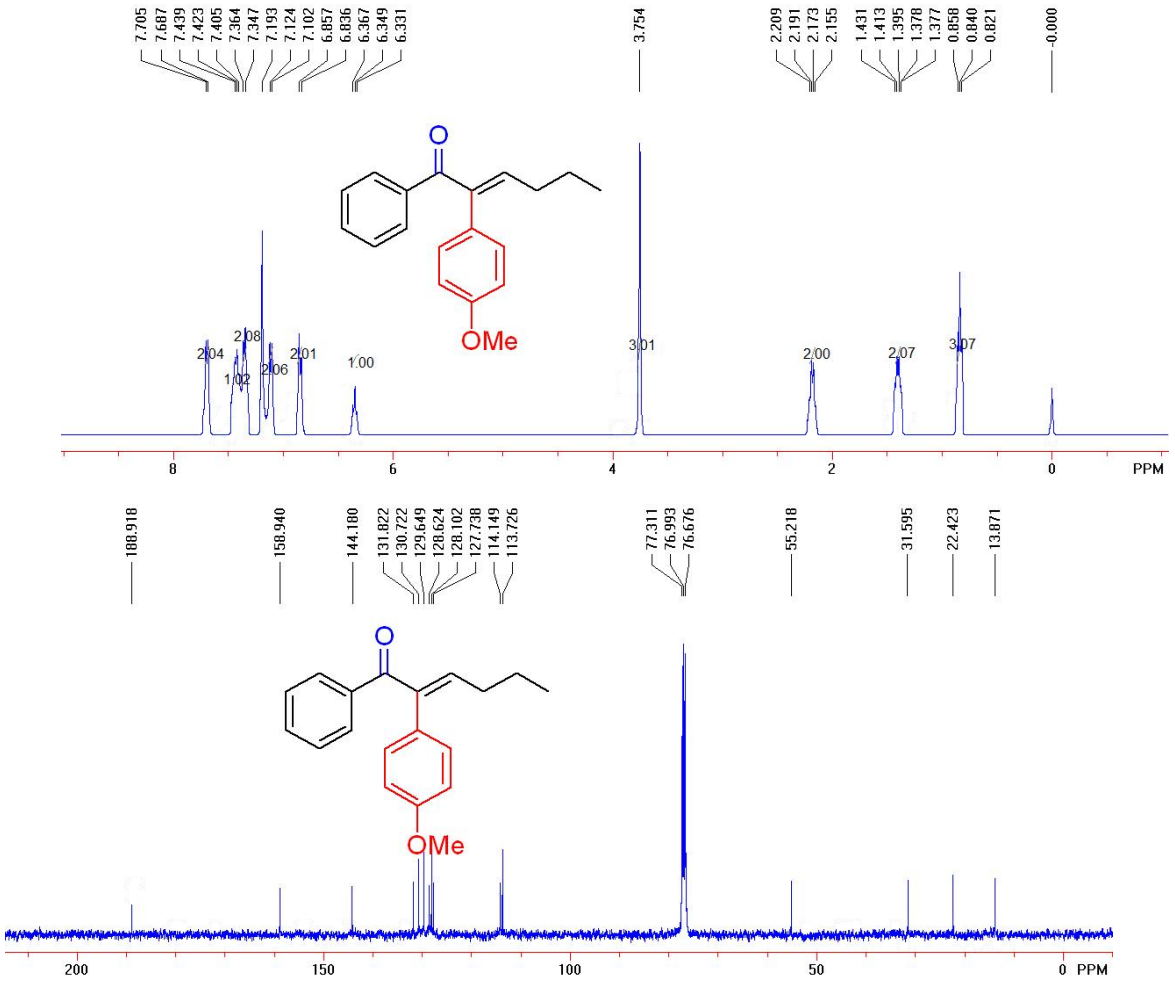
A 25 mL thick wall pressure sealed tube was charged with **1a** (1.0 mmol), $FeBr_3$ (44.0 mg, 0.15 mmol), **L2** (36 mg, 0.125 mmol), $ZnBr_2$ (68 mg, 0.3 mmol), TFA (458 mg, 4.0 mmol), and $PhCF_3$ (10.0 mL) with 40 W blue LED irradiation under air at room temperature for 12 h. The mixture was then cooled to room temperature, diluted with EtOAc, filtered through a celite pad, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/PE (1:40 ~ 1:30, v/v), to give the corresponding product **2a** (72%).

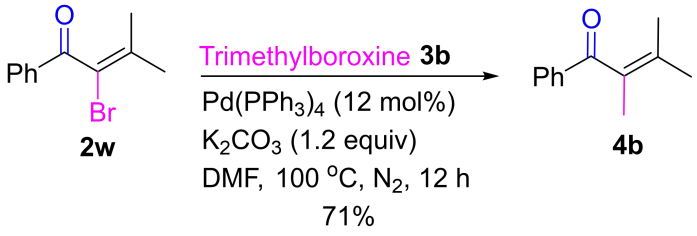
A 25 mL thick wall pressure sealed tube was charged with **1w** (1.0 mmol), $FeBr_3$ (44.0 mg, 0.15 mmol), **L2** (36 mg, 0.125 mmol), $ZnBr_2$ (68 mg, 0.3 mmol), TFA (458 mg, 4.0 mmol), and $PhCF_3$ (10.0 mL) with 40 W blue LED irradiation under air at room temperature for 12 h. The mixture was then cooled to room temperature, diluted with EtOAc, filtered through a celite pad, and concentrated in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/PE (1:40 ~ 1:30, v/v), to give the corresponding product **2w** (75%).

Product diversification



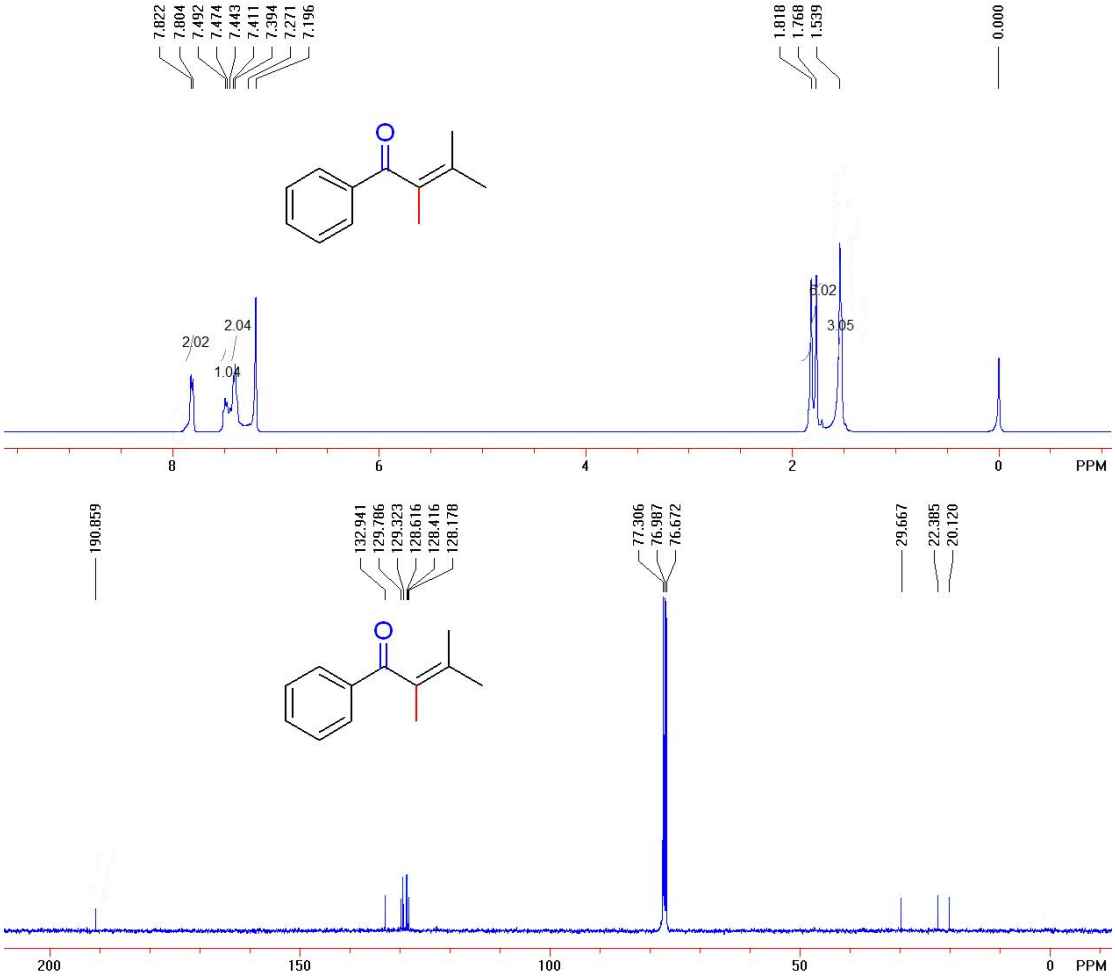
The deprotection was accomplished by adapting a literature procedure.[1] To an oven-dried microwave vial equipped with a magnetic stir bar was added 4-methoxyphenylboronicacid (18.24 mg, 0.12 mmol), K_2CO_3 (22 mg, 0.16 mmol), and $Pd(PPh_3)_2Cl_2$ (5.6 mg, 0.0080 mmol). The vial was placed under an atmosphere of nitrogen and freshly sparged (N_2, 15 minutes), THF (0.05 mL) and H_2O (0.05 mL) was added. To this mixture was added the vinyl bromide (20.14 mg, 0.0799 mmol) in freshly sparged (N_2, 15 minutes), THF (0.2 mL). The reaction was stirred at rt for 23 hr. At that point, the reaction mixture was filtered through a small plug of silica (diethyl ether) and concentrated under reduced pressure. The resulting residue was purified via flash chromatography (Petroleum ether/Et_2O 8:1 to 5:1) to afford the (*E*)-2-(4-methoxyphenyl)-1-phenylhex-2-en-1-one **4a** as a pale yellow oil (16.78 mg, 75%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.2 Hz, 2H), 7.44-7.40 (m, 1H), 7.36 (d, *J* = 7.6 Hz, 2H), 7.11 (d, *J* = 8.8 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.35 (t, *J* = 7.2 Hz, 1H), 3.75 (s, 3H), 2.21-2.16 (m, 2H), 1.43-1.38 (m, 2H), 0.84 (t, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 188.9, 158.9, 144.2, 131.8, 130.7, 129.6, 128.6, 128.1, 127.7, 114.1, 113.7, 55.2, 31.6, 22.4, 13.9. HRMS (EI-TOF) calcd for $C_{19}H_{20}O_4$ (M^+): 280.1463, found: 280.1469.





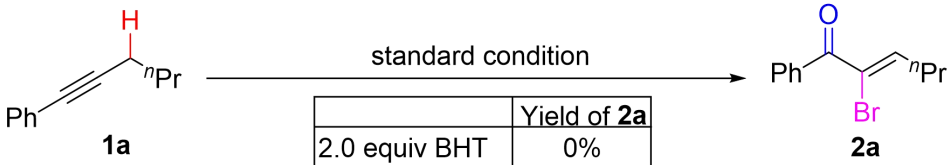
A mixture of 2-bromo-3-methyl-1-phenylbut-2-en-1-one **2w** (42.66 mg, 0.18 mmol, 1.0 equiv.), trimethylboroxine (27.6 mg, 0.22 mmol, 1.2 equiv.), $Pd(PPh_3)_4$ (24.9 mg, 12 mol%), and K_2CO_3 (74.6 mg, 0.54 mmol, 1.2 equiv.) in DMF (3.0 mL) was stirred at 100 °C under an argon atmosphere for 12 h in a sealed tube.[2] After the reaction mixture was cooled to room temperature, water was added and the mixture was extracted with EtOAc (3×10.0 mL). The combined organic phase was washed with water and brine, dried (Na_2SO_4), and concentrated. Evaporation of the solvent followed by purification on silica gel column, eluting with EtOAc/PE (1:10 ~ 1:5,

v/v), to give the product **2,3-dimethyl-1-phenylbut-2-en-1-one 4b** as a pale yellow oil (22.24 mg, 71%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81 (d, *J* = 7.2 Hz, 2H), 7.49-7.44 (m, 1H), 7.40 (d, *J* = 6.8 Hz, 2H), 1.79 (d, *J* = 120.0 Hz, 6H), 1.54 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 190.9, 132.9, 129.8, 129.3, 128.6, 128.4, 128.2, 29.7, 22.4, 20.1. HRMS (EI-TOF) calcd for $C_{12}H_{14}O$ (M^+): 174.1045, found: 174.1048.



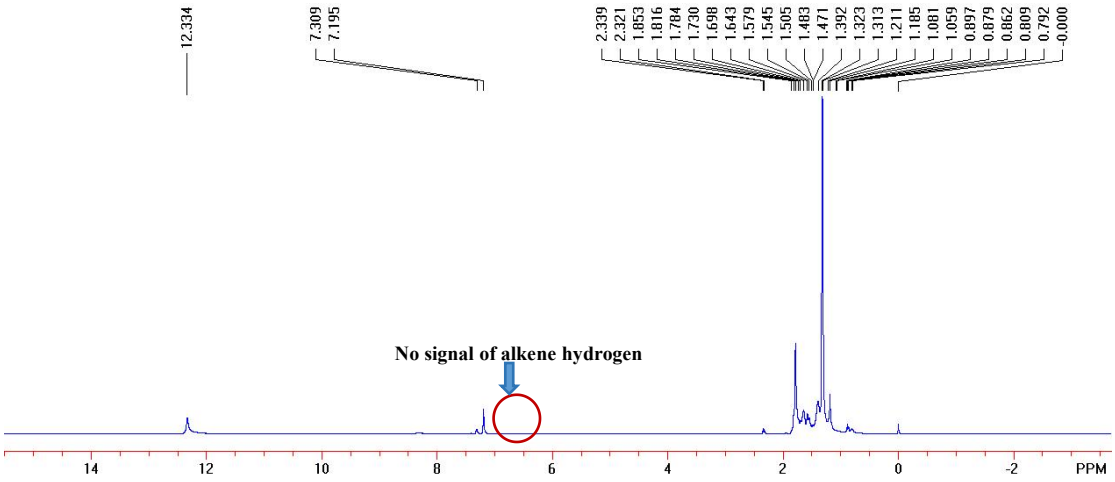
Preliminary Mechanistic Investigations

a) Radical trapping

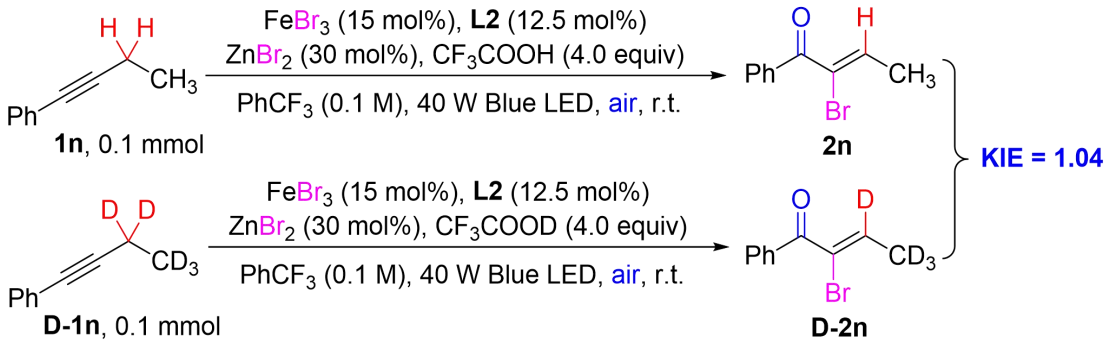


	Yield of **2a**
2.0 equiv BHT	0%
2.0 equiv tempo	0%

A 25 mL thick wall pressure sealed tube was charged with **1a** (0.1 mmol), $FeBr_3$ (4.4 mg, 0.015 mmol), **L2** (3.6 mg, 0.0125 mmol), $ZnBr_2$ (6.8 mg, 0.03 mmol), TFA (45.8 mg, 0.4 mmol), radical scavenger (0.2 mmol), and $PhCF_3$ (1.0 mL) with 40 W blue LED irradiation under air at room temperature for 12 h. The mixture was then cooled to room temperature, diluted with EtOAc. The product **2a** was not observed through TLC. The crude reaction mixture was analyzed by ^1H NMR after filtered through a celite pad, washed with water three times, and concentrated in vacuo.



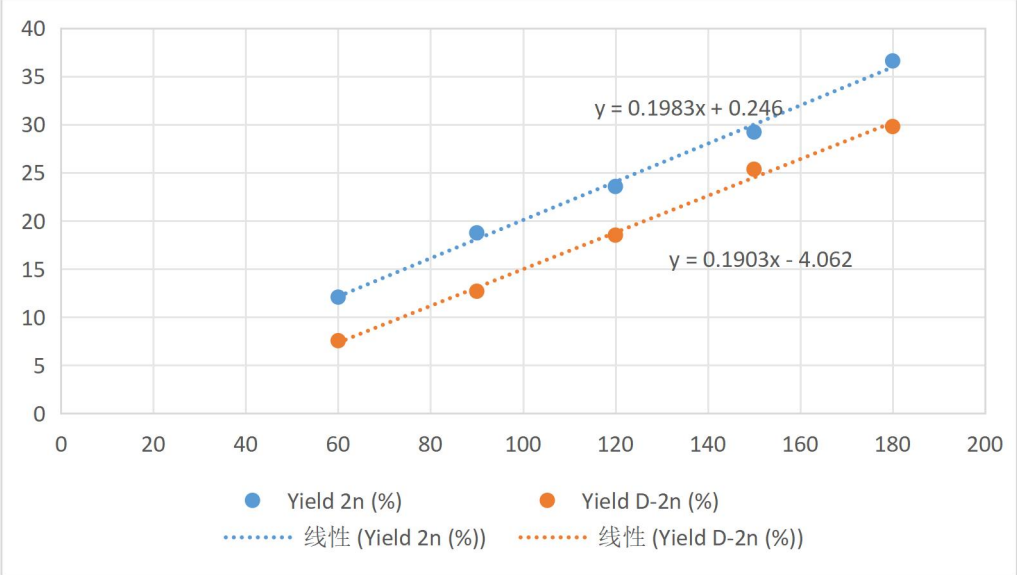
b) Intermoleclar kinetic isotopic effects



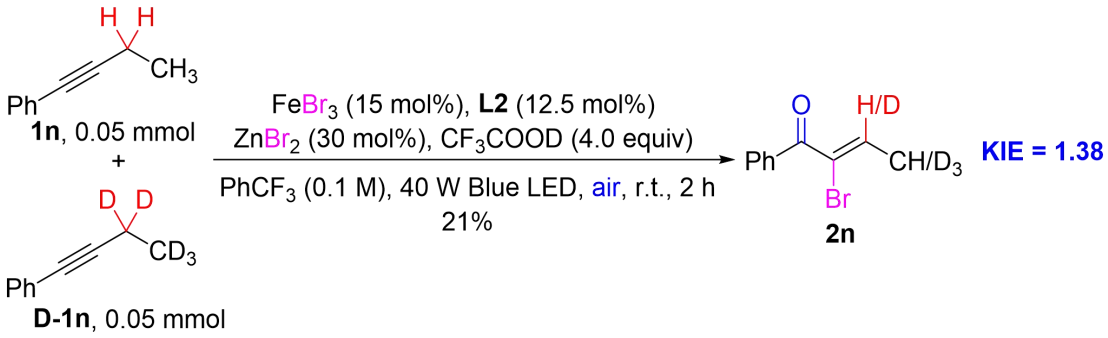
A 25 mL thick wall pressure sealed tube was charged with **1n** or **D-1n** (0.1 mmol), $FeBr_3$ (4.4 mg, 0.015 mmol), **L2** (3.6 mg, 0.0125 mmol), $ZnBr_2$ (6.8 mg, 0.03 mmol), CF_3COOH or CF_3COOD (45.8 mg, 0.4 mmol), and $PhCF_3$ (1.0 mL) with 40 W blue LED irradiation under air at room temperature for 1.0-3.0 h. The mixture was then cooled to room temperature, diluted with EtOAc, filtered through a celite pad, and concentrated in vacuo. The yield of **2n** or **D-2n** was determined on the basis of ^1H

NMR analysis which using dichloromethane (7.0 μL) as the internal standard.

entry	1	2	3	4	5
time/min	60	90	120	150	180
Yield **3n** (%)	12.08	18.75	23.56	29.21	36.59
Yield **D-3n** (%)	7.56	12.69	18.51	25.35	29.78

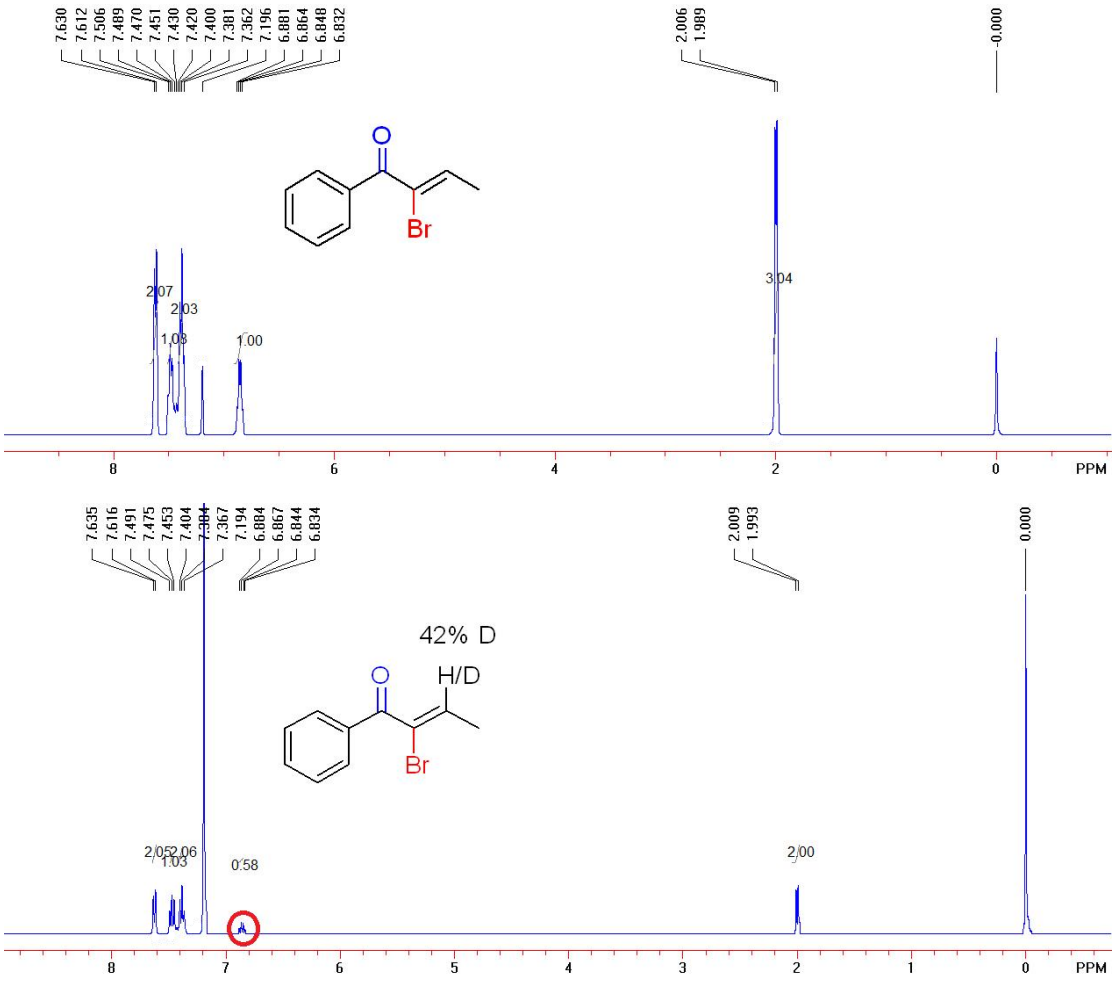


The calculated $k_H/k_D = 0.1983/0.1903 = 1.04$.

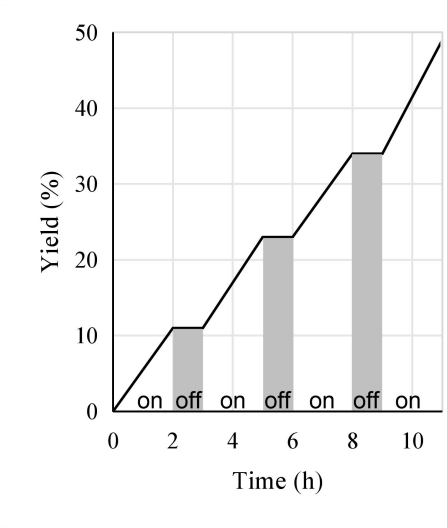


A 25 mL thick wall pressure sealed tube was charged with **1n** (0.05 mmol), **D-1n** (0.05 mmol), $FeBr_3$ (4.4 mg, 0.015 mmol), **L2** (3.6 mg, 0.0125 mmol), $ZnBr_2$ (6.8 mg, 0.03 mmol), CF_3COOD (45.8 mg, 0.4 mmol), and $PhCF_3$ (1.0 mL) with 40 W blue LED irradiation under air at room temperature for 2 h. The mixture was then cooled to room temperature, diluted with EtOAc, filtered through a celite pad, and concentrated

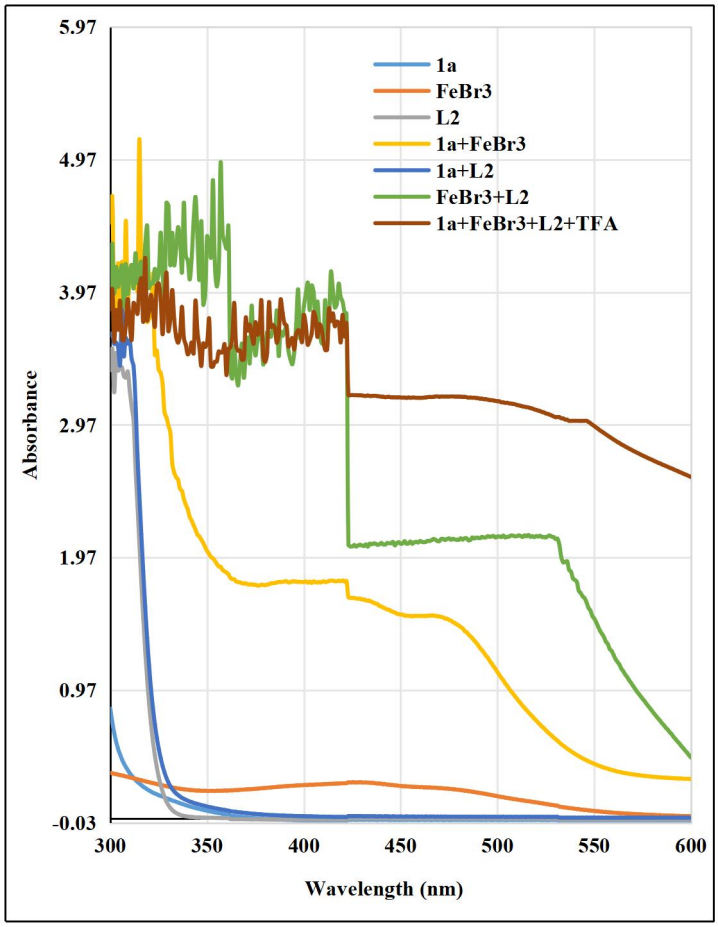
in vacuo. The residue was purified by flash column chromatography on silica gel, eluting with EtOAc/PE (1:40 ~ 1:30, v/v), to give the corresponding product **2n** (23%).



c) Light on/off experiments



A 25 mL thick wall pressure sealed tube was charged with **1a** (15.8 mg, 1.0 mmol), $FeBr_3$ (44 mg, 0.15 mmol), **L2** (36 mg, 0.125 mmol), $ZnBr_2$ (68 mg, 0.3 mmol), TFA (458 mg, 0.4 mmol), and $PhCF_3$ (10 mL) with 40 W blue LED irradiation under air at room temperature for 12 h. After degassing, the reaction mixture was alternately exposed to light and dark conditions, with the irradiation status switched every 3 h to monitor potential photochemical effects. Aliquots (400 μL) were periodically withdrawn from the reaction mixture for quantitative analysis. Upon completion of irradiation, the yield of product **2a** was determined by ^1H NMR spectroscopy using dibromomethane (7.0 μL) as an internal standard.



Ultraviolet-visible (UV-Vis) spectroscopy was performed on individual reaction components and their combinations using a Dual-beam ultraviolet-visible spectrometer UV-VIS (Beijing Pulse, China). The ultraviolet-visible absorption spectra were measured immediately after the preparation of the solutions. The sample for UV-Vis spectroscopic analysis was prepared at concentrations optimized under specific reaction conditions and then diluted 100-fold to acquire the UV-Vis spectrum.

UV-Vis spectrum for the solvents of different combinations with iron salts: A: **1a** (15.8 mg, 0.1 mmol) was dissolved in $PhCF_3$ (100 mL), stirred for 10 min; B: $FeBr_3$ (4.4 mg, 0.015 mmol) was dissolved in $PhCF_3$ (100 mL), stirred for 10 min; C: **L2** (3.6 mg, 0.0125 mmol) was dissolved in $PhCF_3$ (100 mL), stirred for 10 min; D: **1a** (15.8 mg, 0.1 mmol) and $FeBr_3$ (4.4 mg, 0.015 mmol) were dissolved in $PhCF_3$ (100 mL), stirred for 10 min; E: **1a** (15.8 mg, 0.1 mmol) and **L2** (3.6 mg, 0.0125 mmol) were dissolved in $PhCF_3$ (100 mL), stirred for 10 min; F: $FeBr_3$ (4.4 mg, 0.015

mmol) and **L2** (3.6 mg, 0.0125 mmol) were dissolved in $PhCF_3$ (100 mL), F: **1a** (15.8 mg, 0.1 mmol), $FeBr_3$ (4.4 mg, 0.015 mmol), **L2** (3.6 mg, 0.0125 mmol) and TFA (458 mg, 0.4 mmol) were dissolved in $PhCF_3$ (100 mL), stirred for 10 min;each time, 3 mL of the prepared solvent was moved to the cuvette for the measurement.

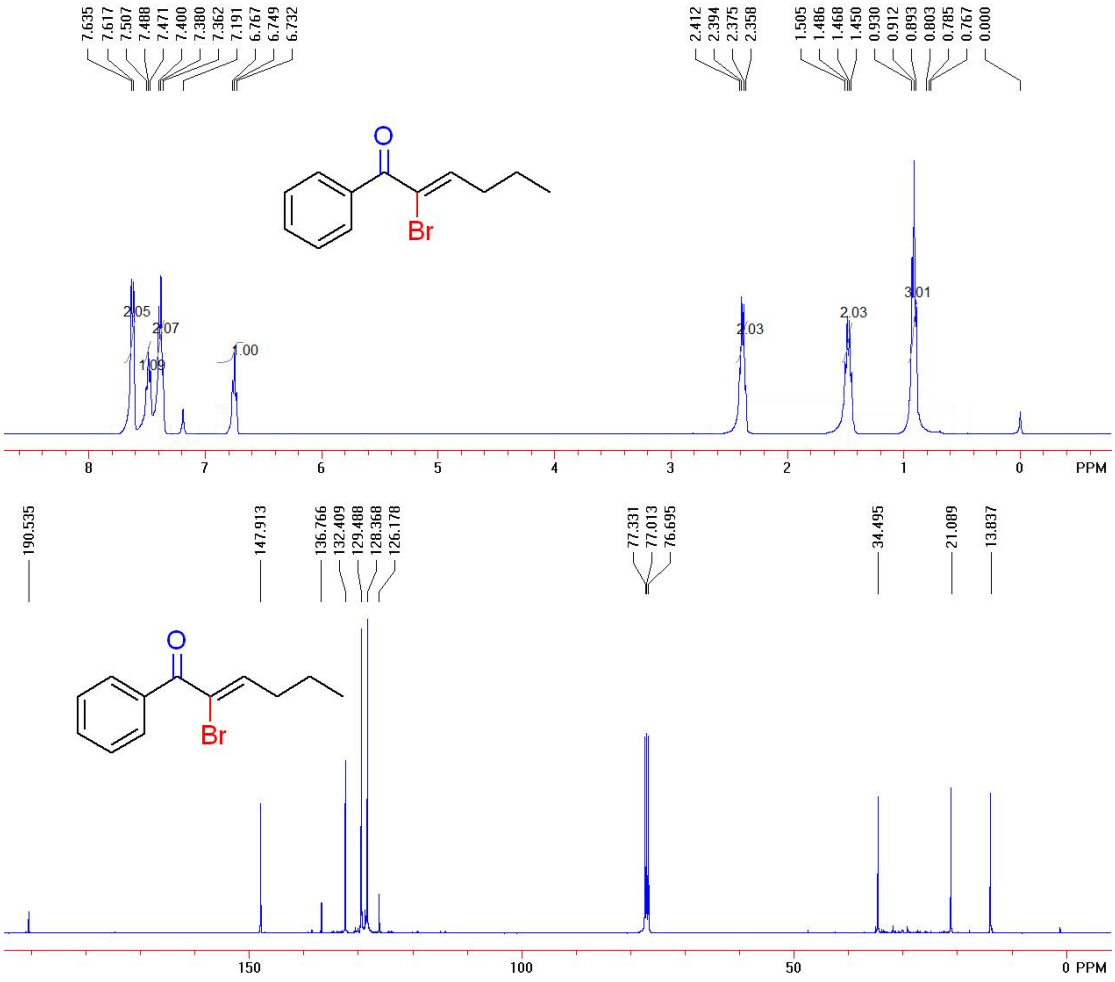
References

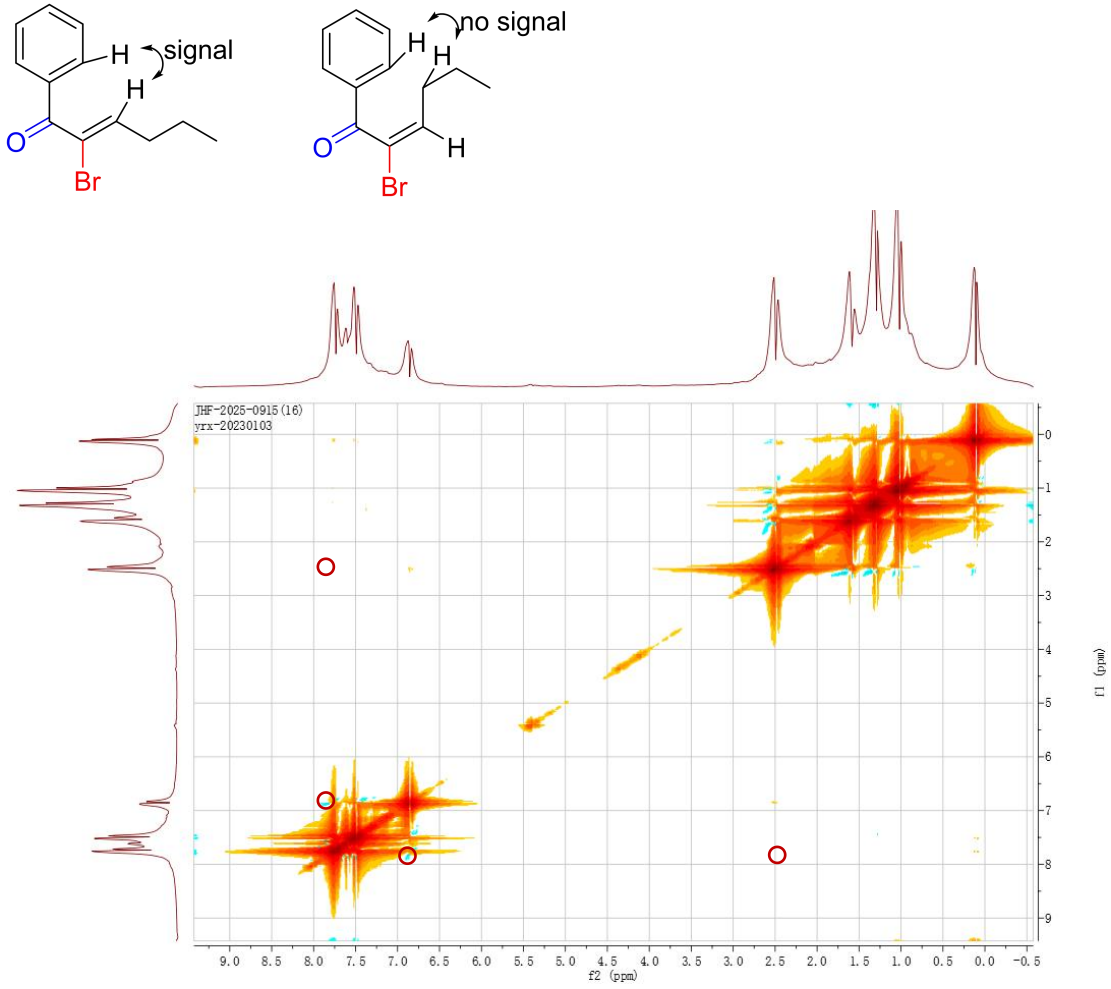
(1) B. M. Trost and J. S. Tracy, Vanadium-Catalyzed Synthesis of Geometrically Defined Acyclic Triand Tetrasubstituted Olefins from Propargyl Alcohols, *ACS Catal.*, 2019, **9**, 1584−1594.

(2) F. Wan, N. Wang, Y. Zhu, C. Tang, J. Claveria and W. Tang, Enantioselective hydrogenation of cyclic tetrasubstituted-olefinic dehydroamino acid derivatives, *Chem. Commun.*, 2021, **57**, 5546-5549.

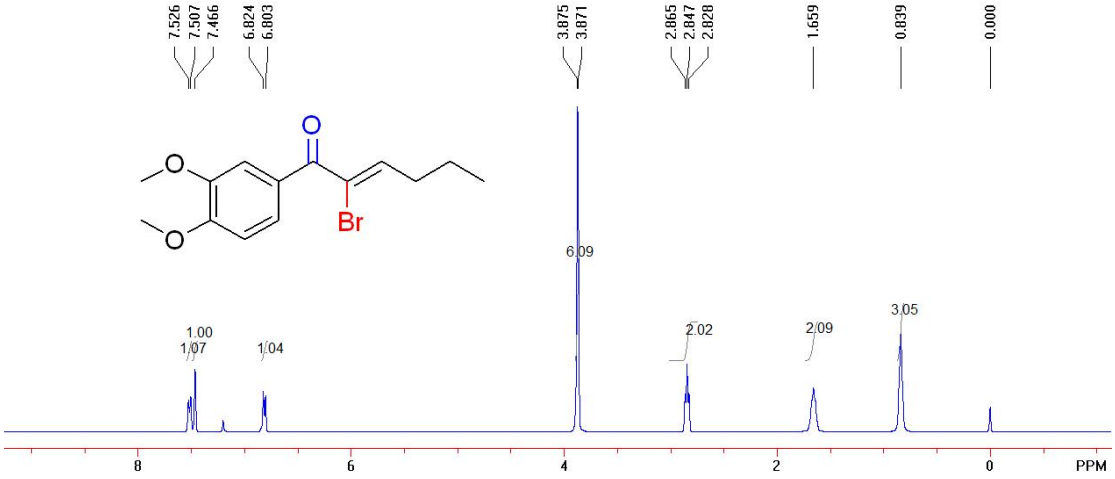
Copies of ^{1}H and ^{13}C NMR Spectra

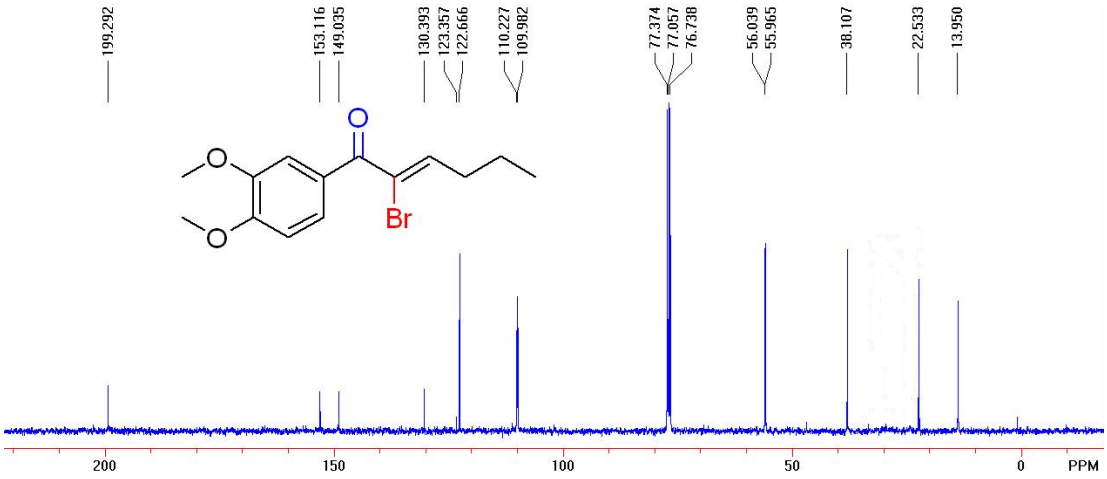
(Z)-2-bromo-1-phenylhex-2-en-1-one (2a)



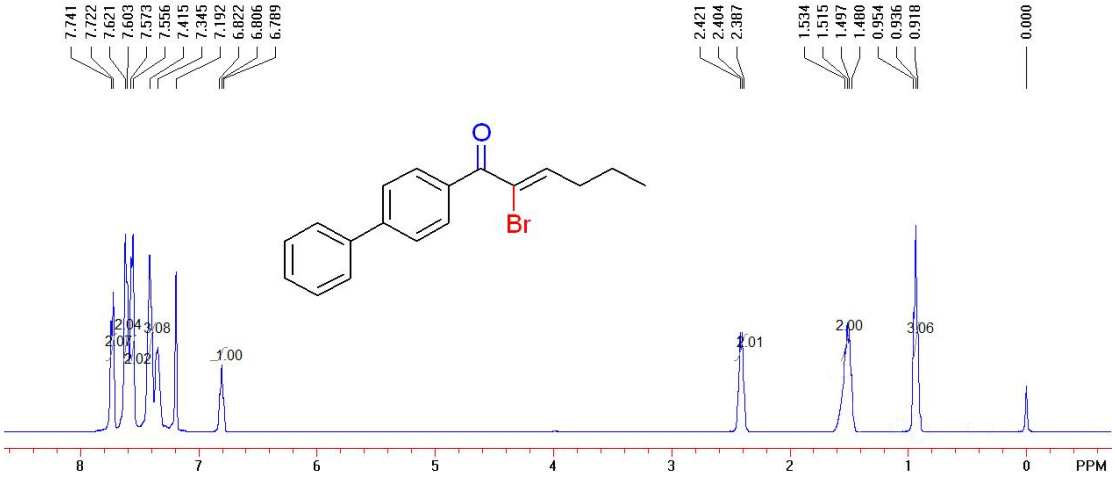

H
signal
H
O
Br
H
no signal
H
O
H
Br
JHF-2025-0915(16)
yrx-20230103
f2 (ppm)
f1 (ppm)

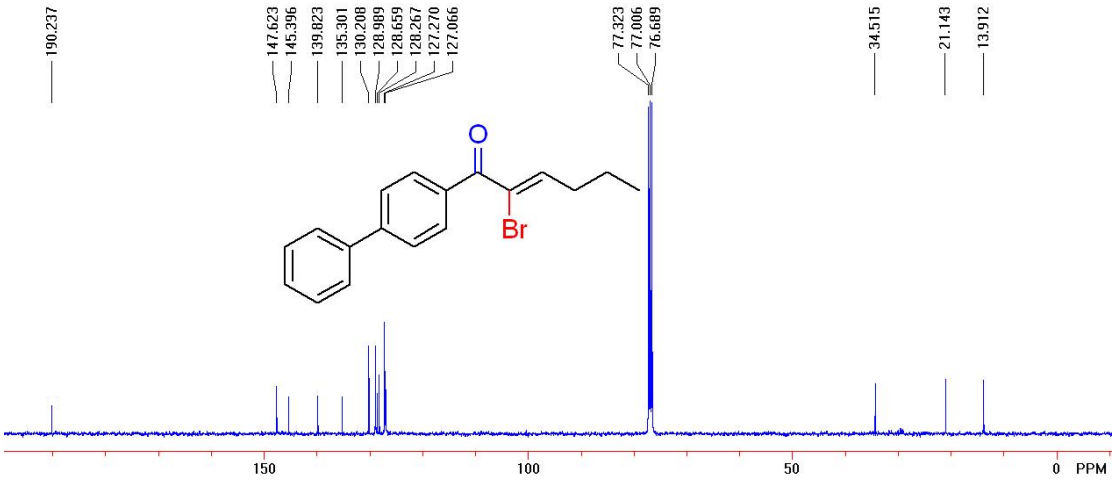
2-(Z)-2-bromo-1-(3,4-dimethoxyphenyl)hex-2-en-1-one (2b)



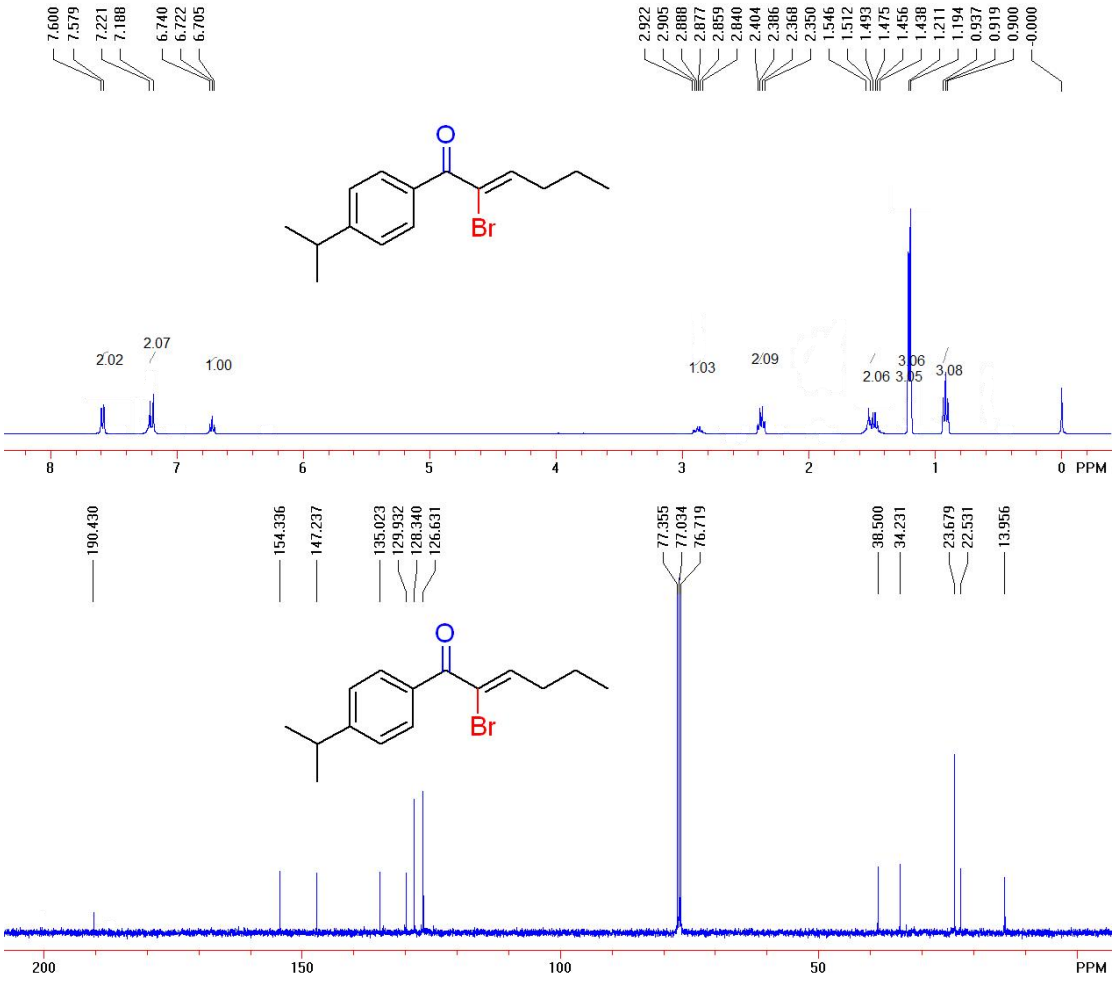


(Z)-1-([1,1'-biphenyl]-4-yl)-2-bromohex-2-en-1-one (2c)

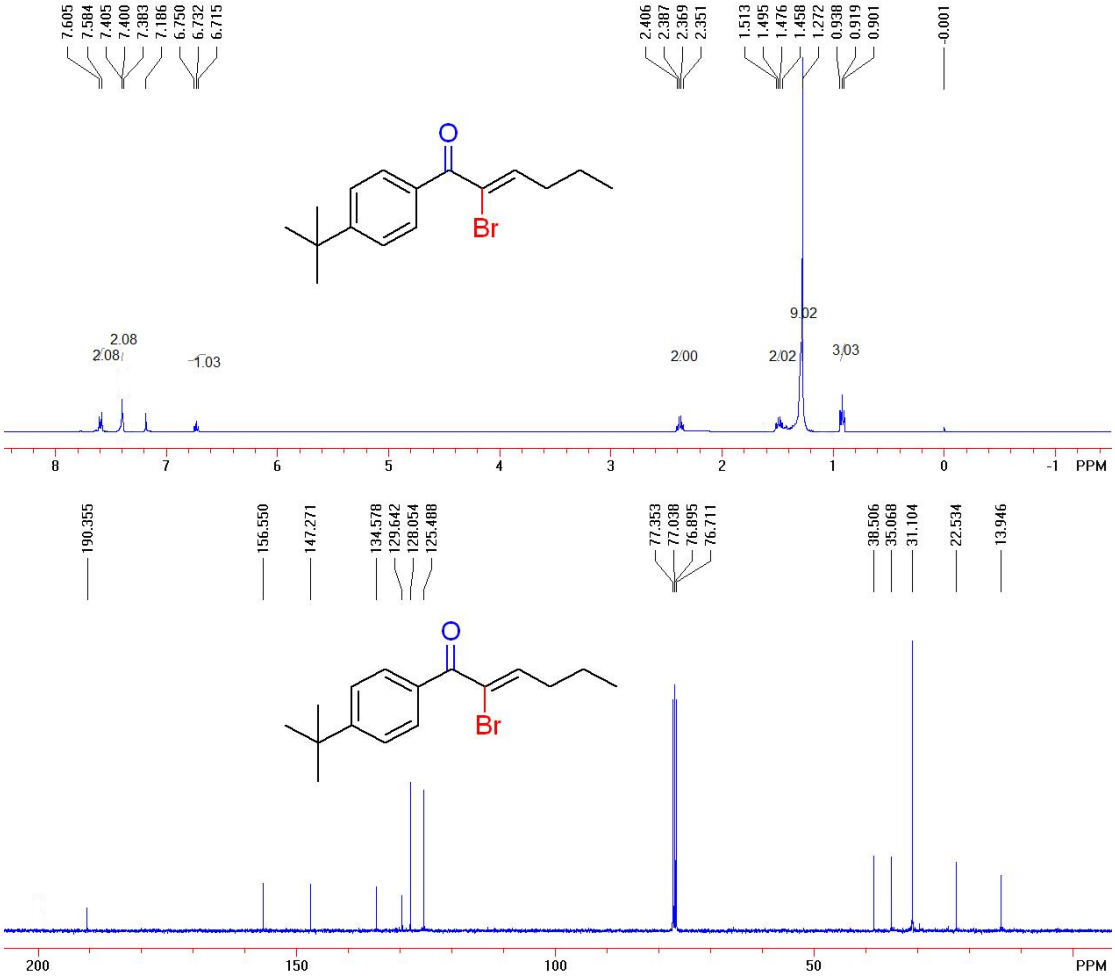




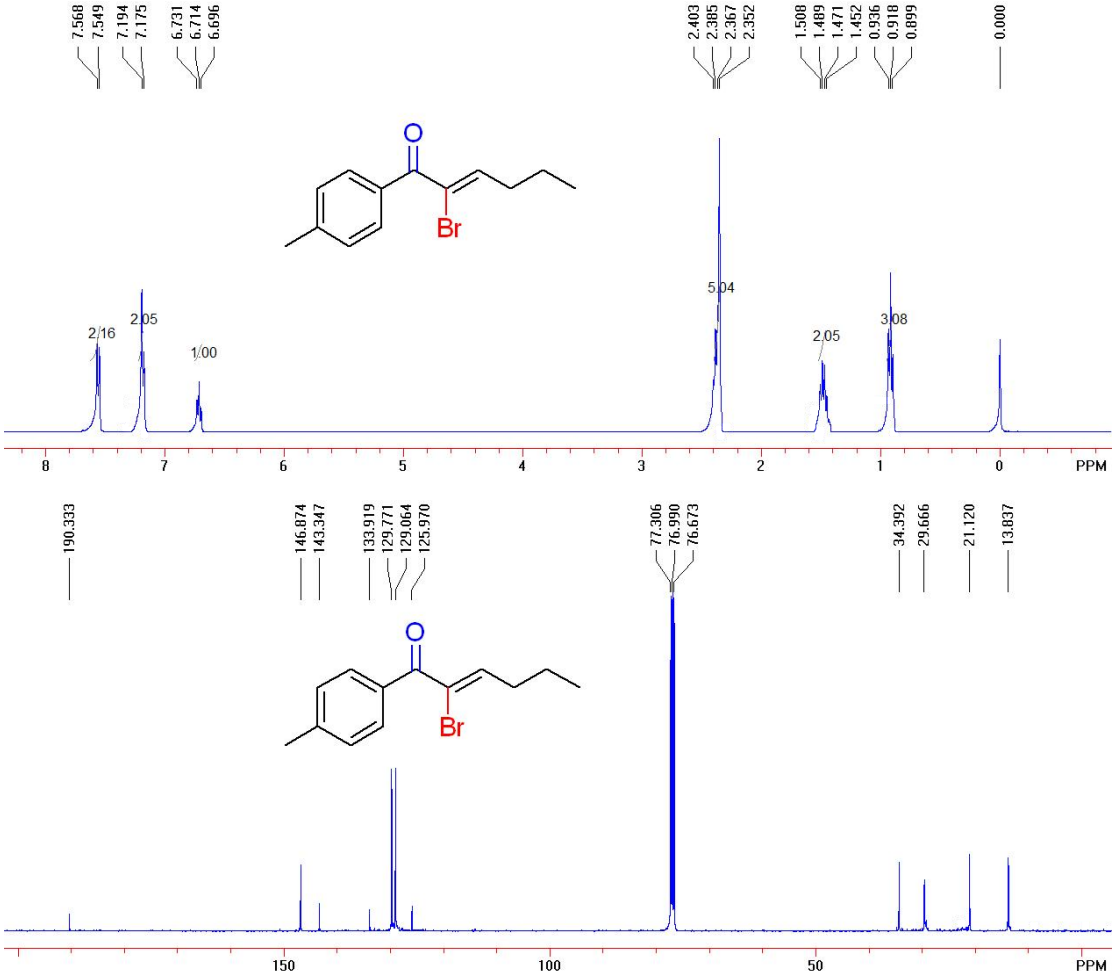
(Z)-2-bromo-1-(4-isopropylphenyl)hex-2-en-1-one (2d)



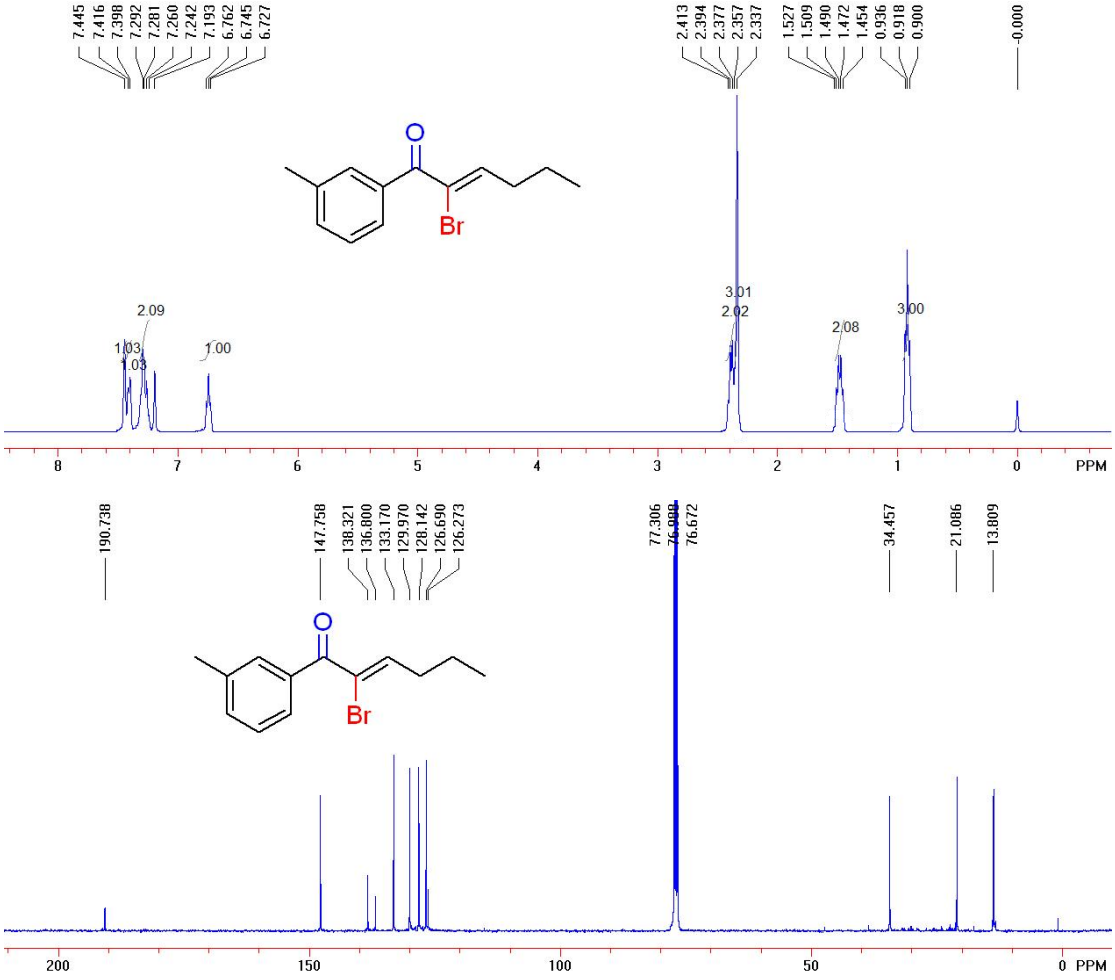
(Z)-2-bromo-1-(4-(tert-butyl)phenyl)hex-2-en-1-one (2e)



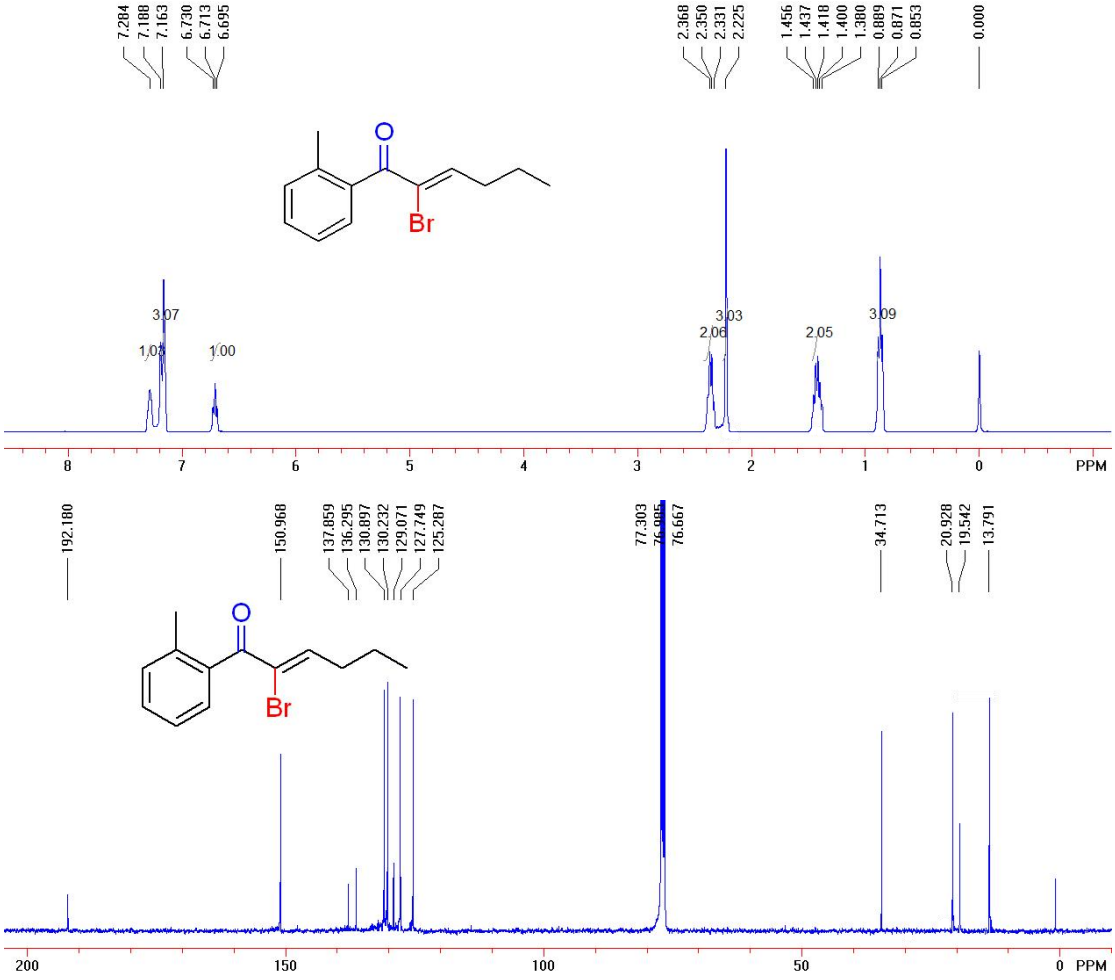
(Z)-2-bromo-1-(p-tolyl)hex-2-en-1-one (2f)



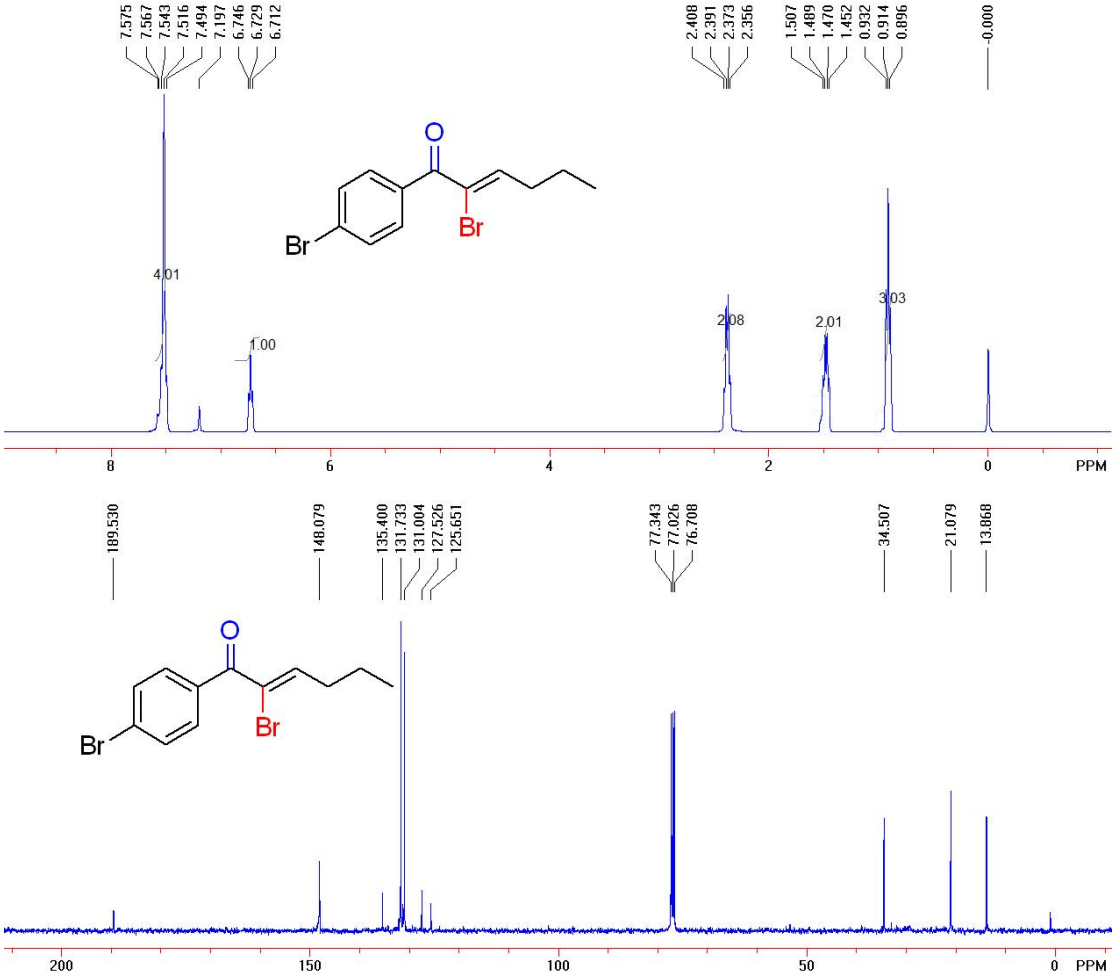
(Z)-2-bromo-1-(m-tolyl)hex-2-en-1-one (2g)



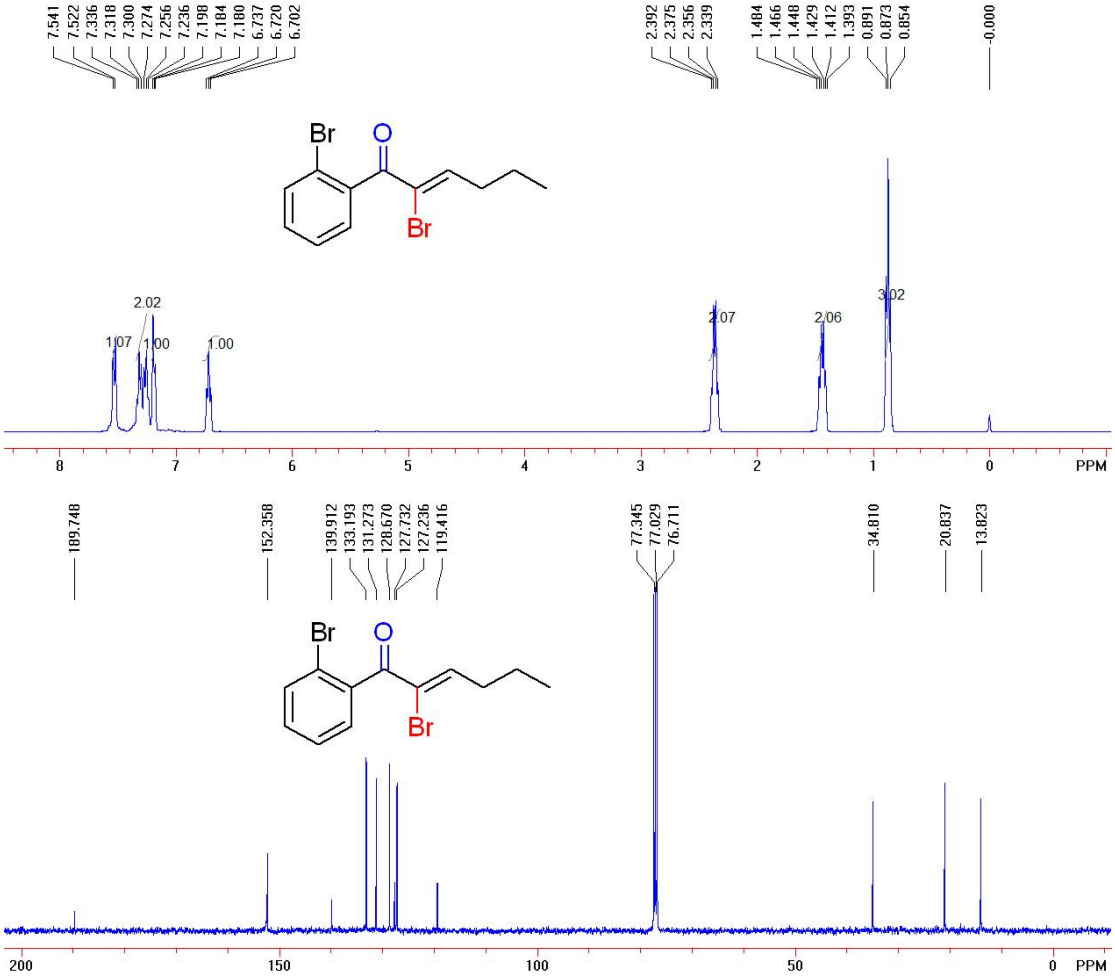
6-(4-chlorophenyl)-3-morpholino-*N*-(quinolin-8-yl)hex-5-ynamide (2h)



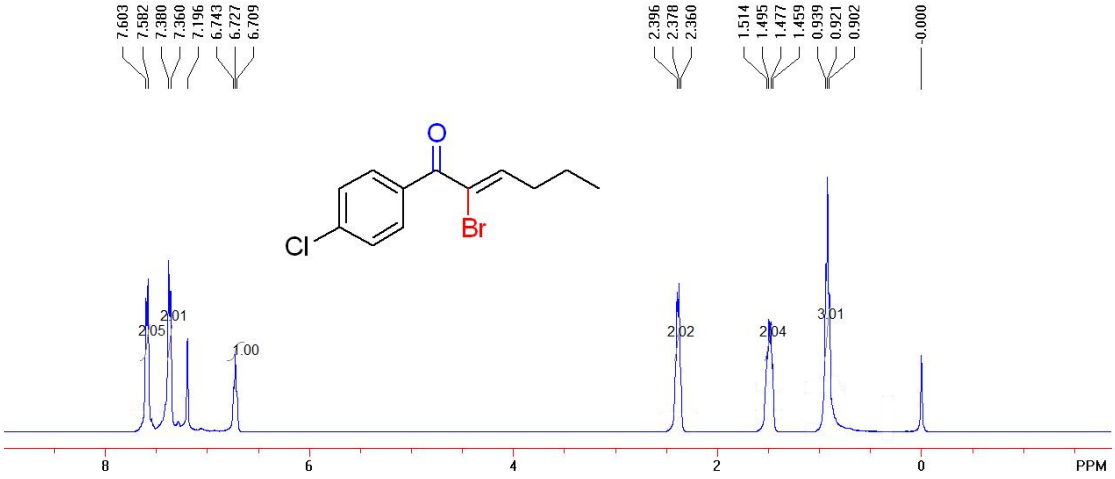
(Z)-2-bromo-1-(4-bromophenyl)hex-2-en-1-one (2i)

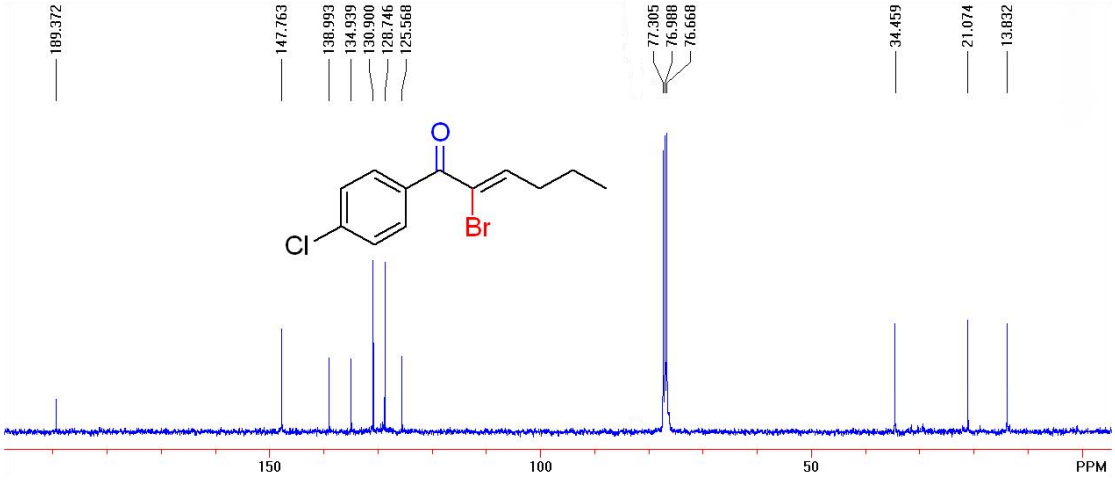


(Z)-2-bromo-1-(2-bromophenyl)hex-2-en-1-one (2j)

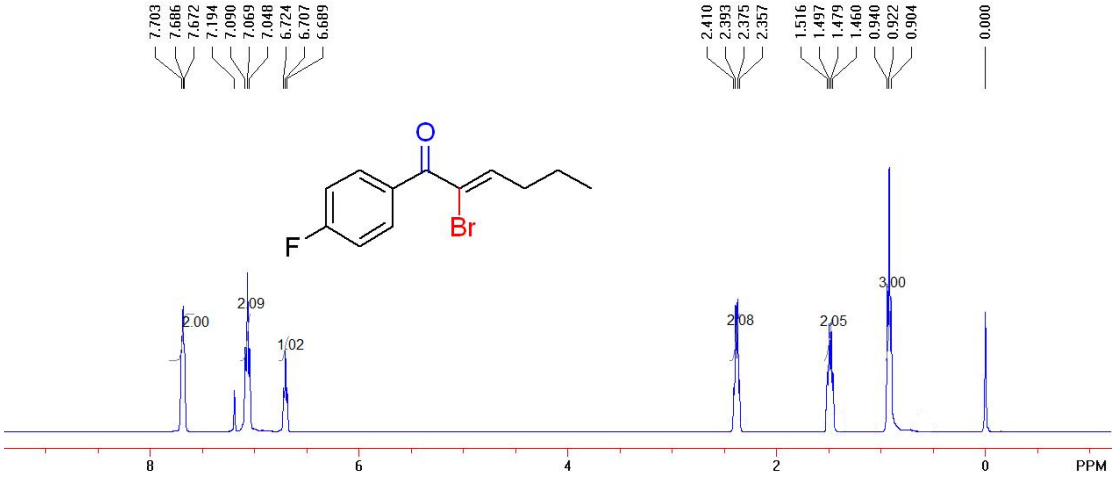


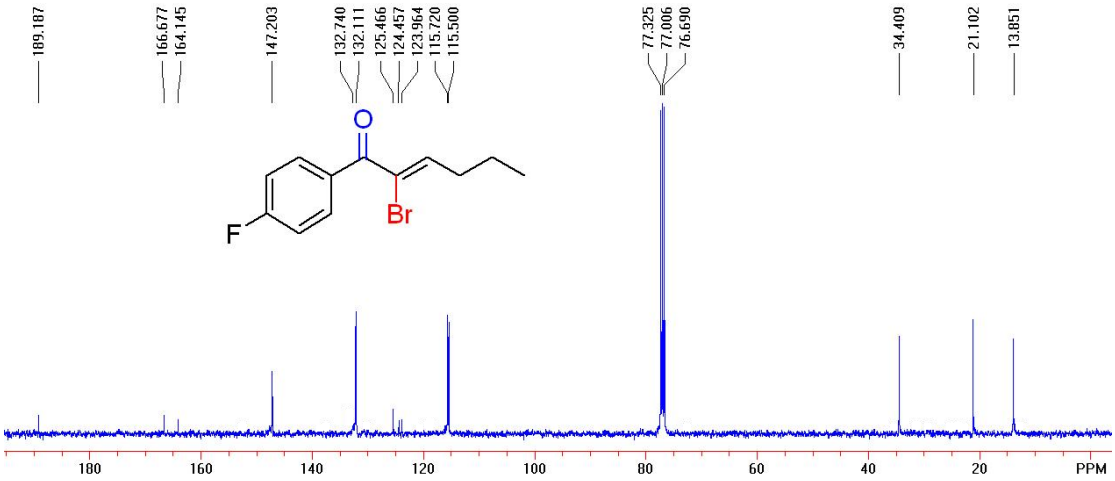
(Z)-2-bromo-1-(4-chlorophenyl)hex-2-en-1-one (2k)



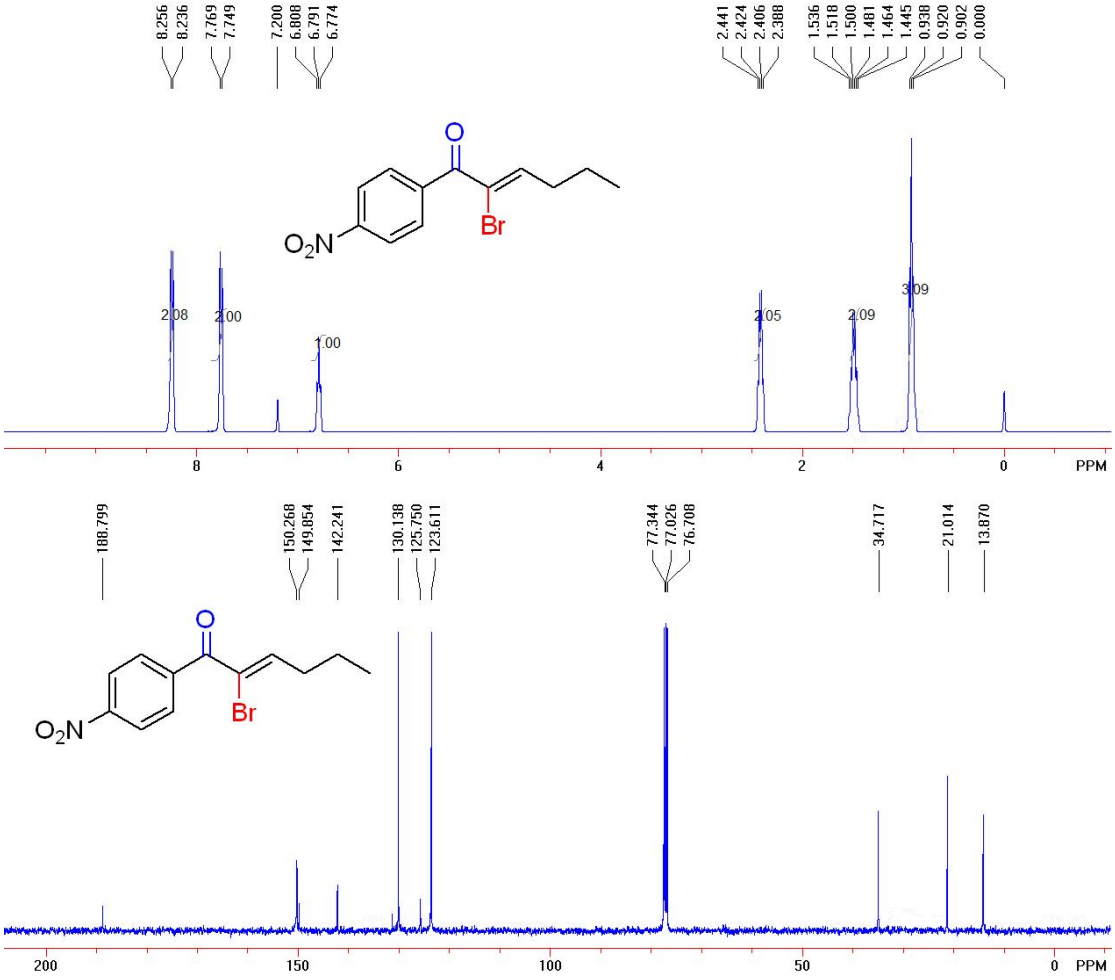


(Z)-2-bromo-1-(4-fluorophenyl)hex-2-en-1-one (2l)

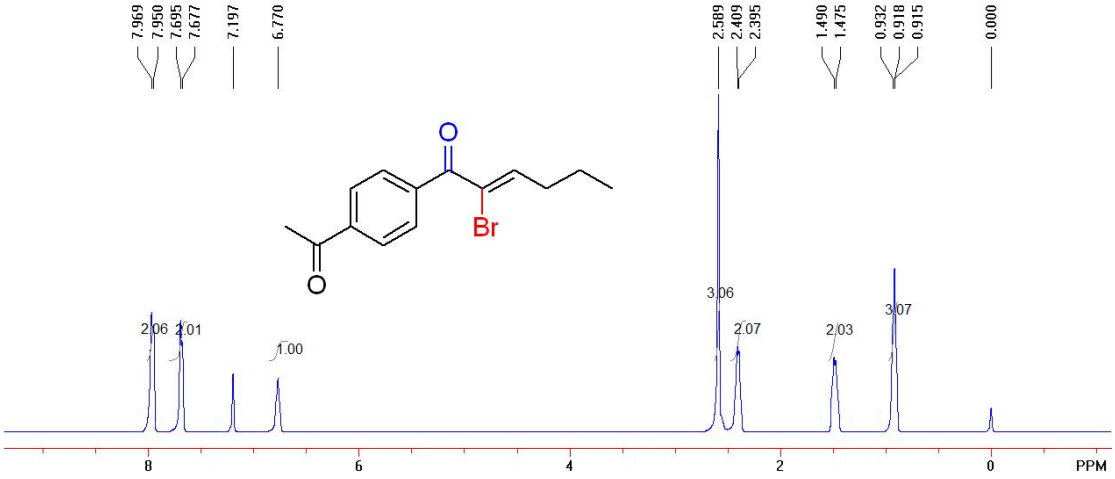


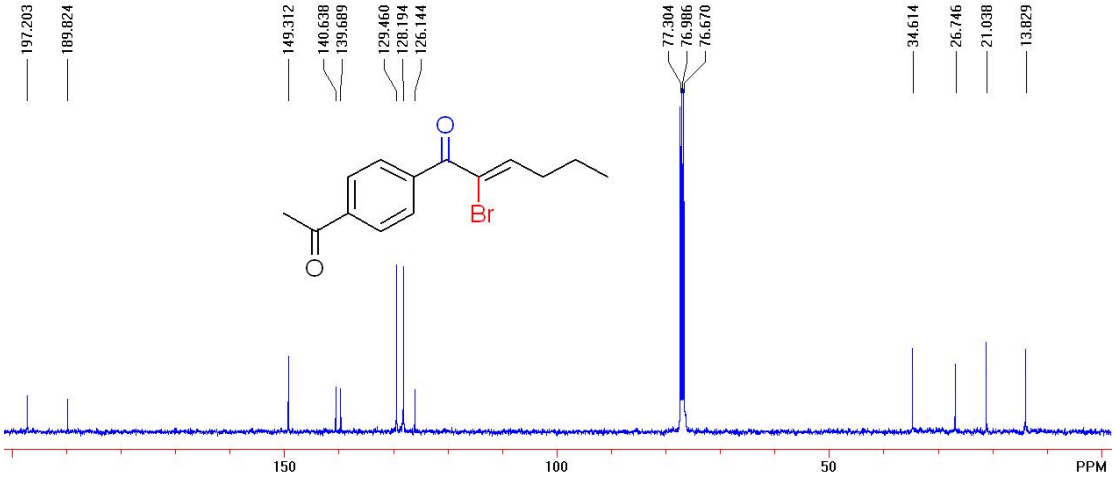


(Z)-2-bromo-1-(4-nitrophenyl)hex-2-en-1-one (2m)

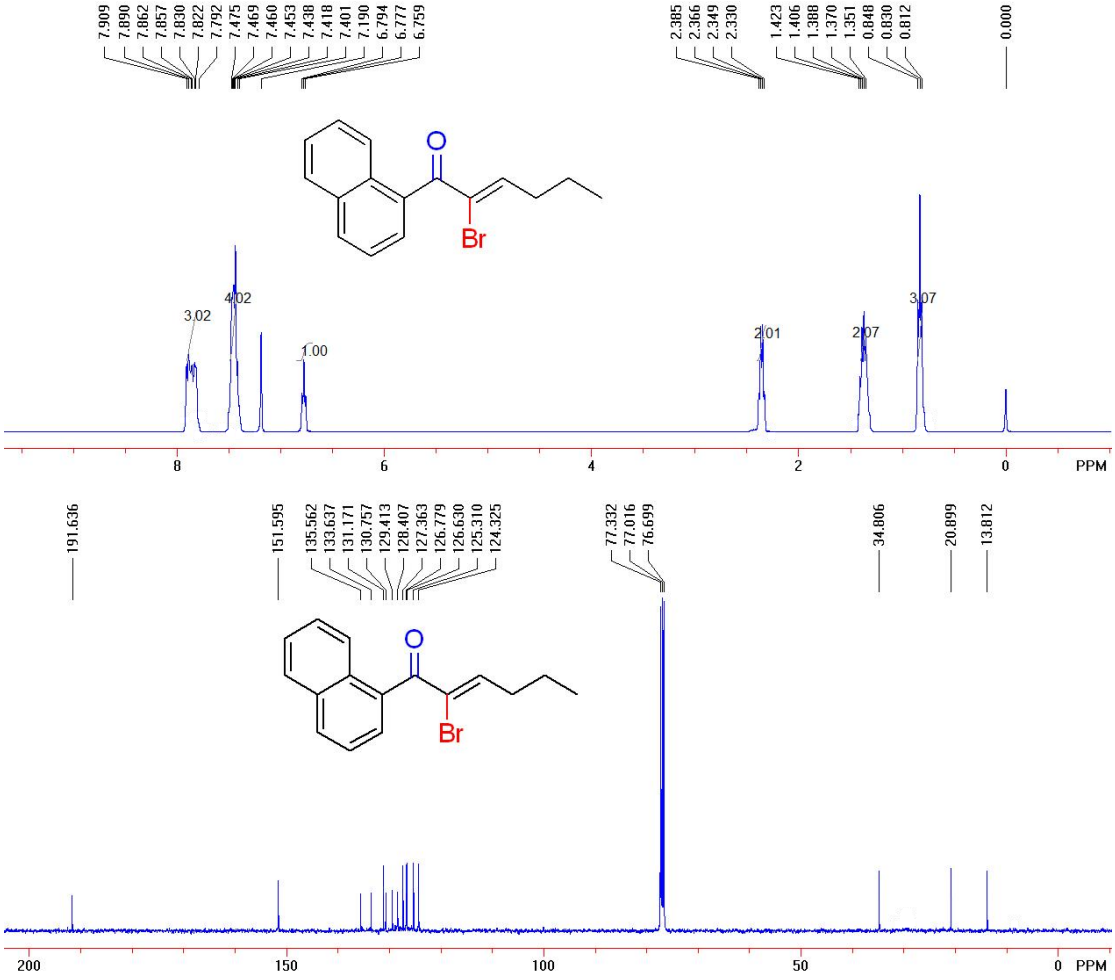


(Z)-1-(4-acetylphenyl)-2-bromohex-2-en-1-one (2n)

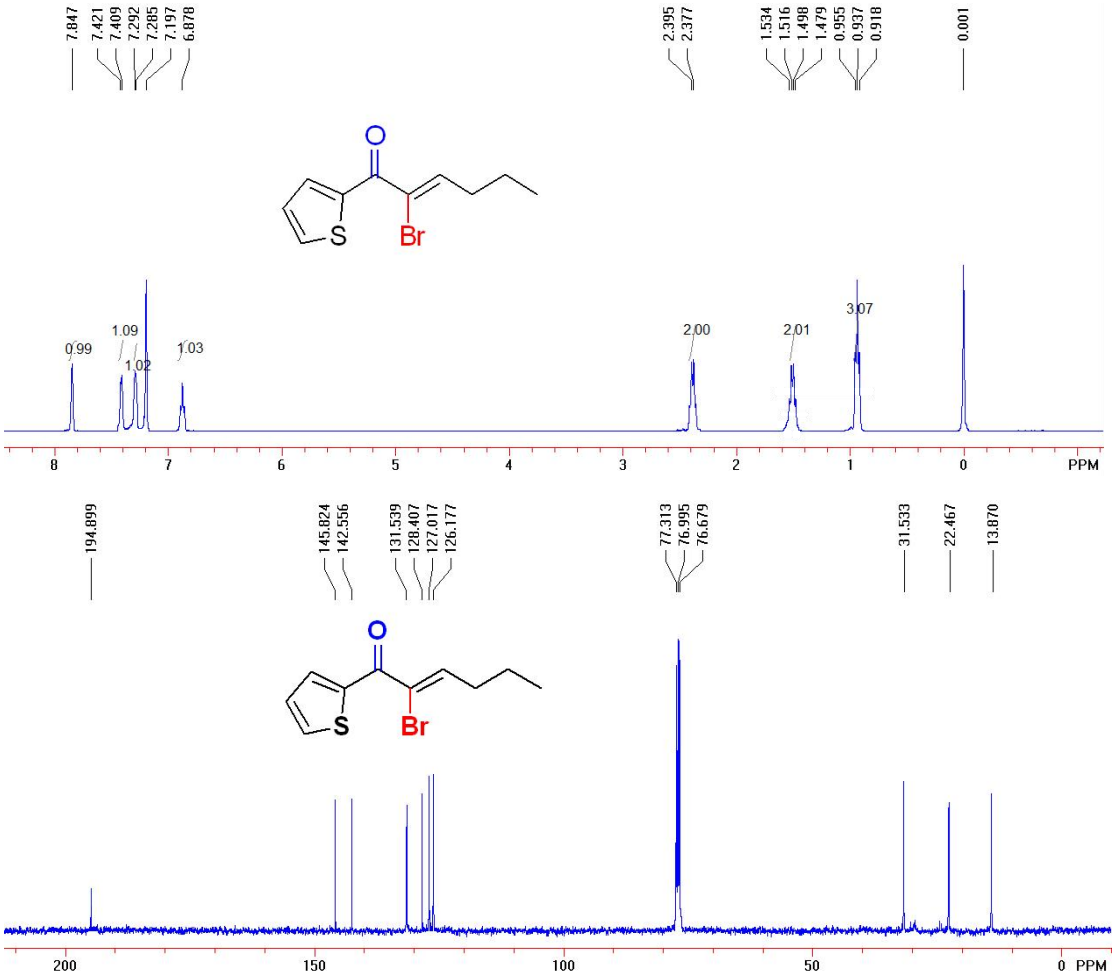




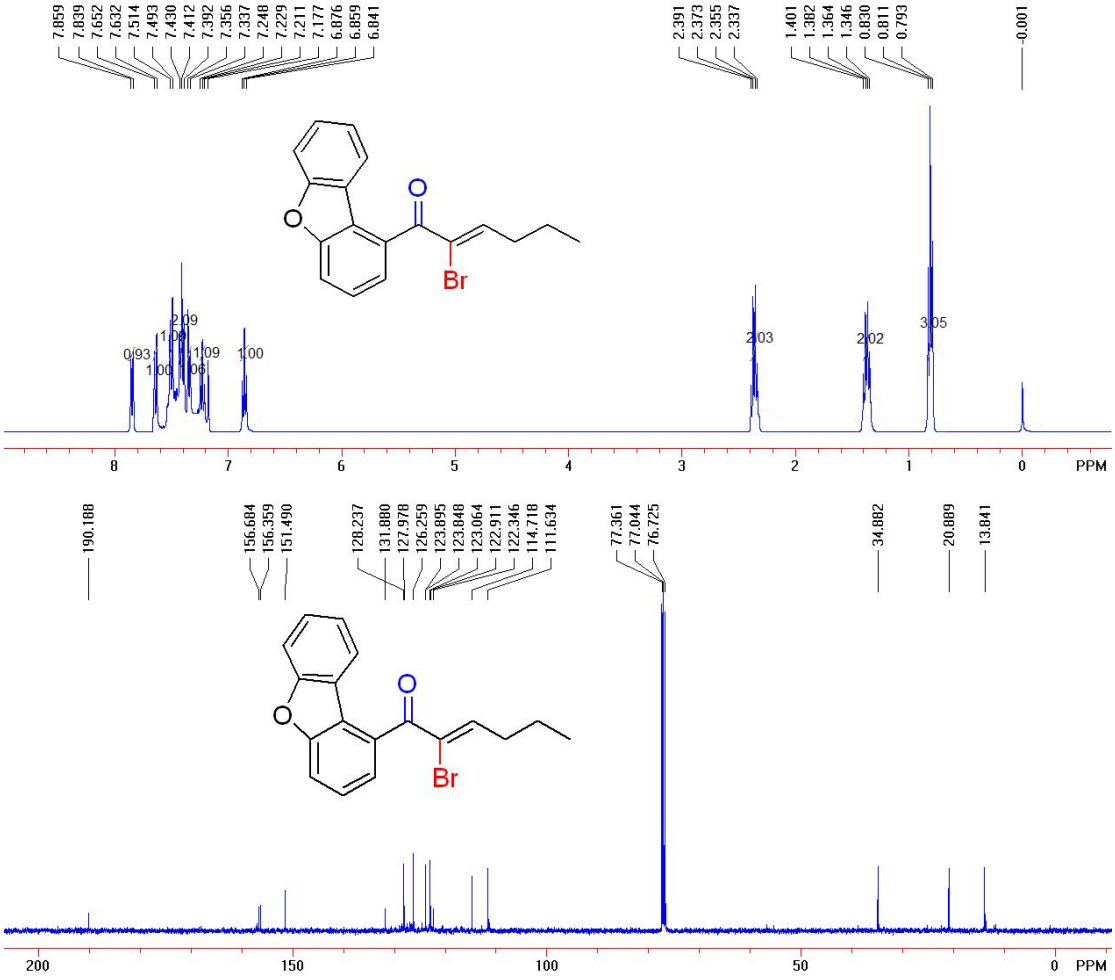
(Z)-2-bromo-1-(naphthalen-1-yl)hex-2-en-1-one (2o)



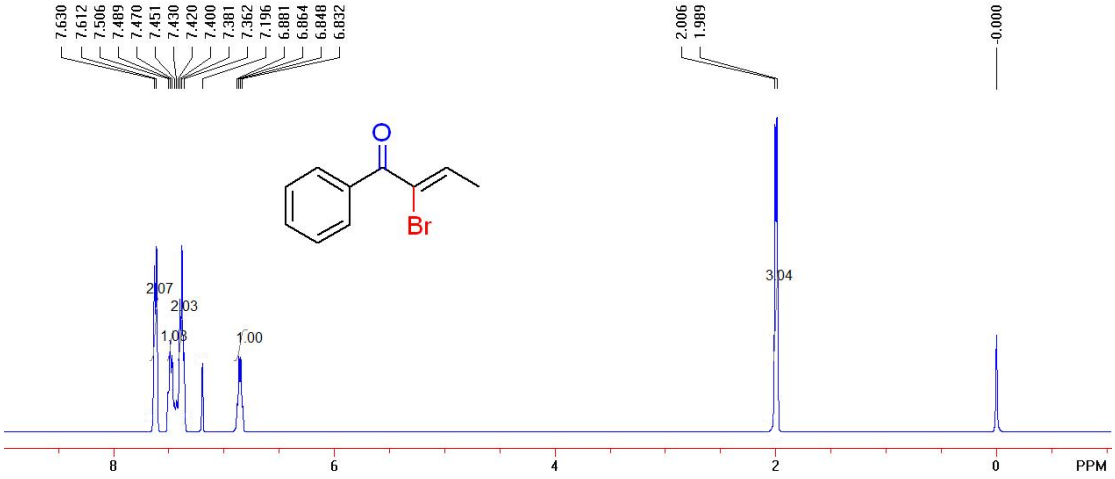
(Z)-2-bromo-1-(thiophen-2-yl)hex-2-en-1-one (2p)

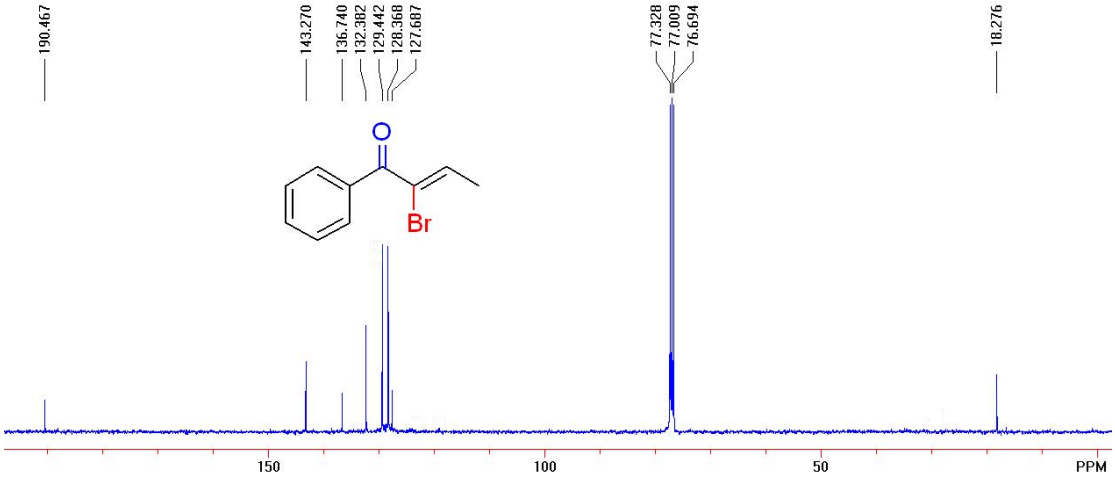


(Z)-2-bromo-1-(dibenzo[b,d]furan-1-yl)hex-2-en-1-one (2q)



(Z)-2-bromo-1-phenylbut-2-en-1-one (2r)





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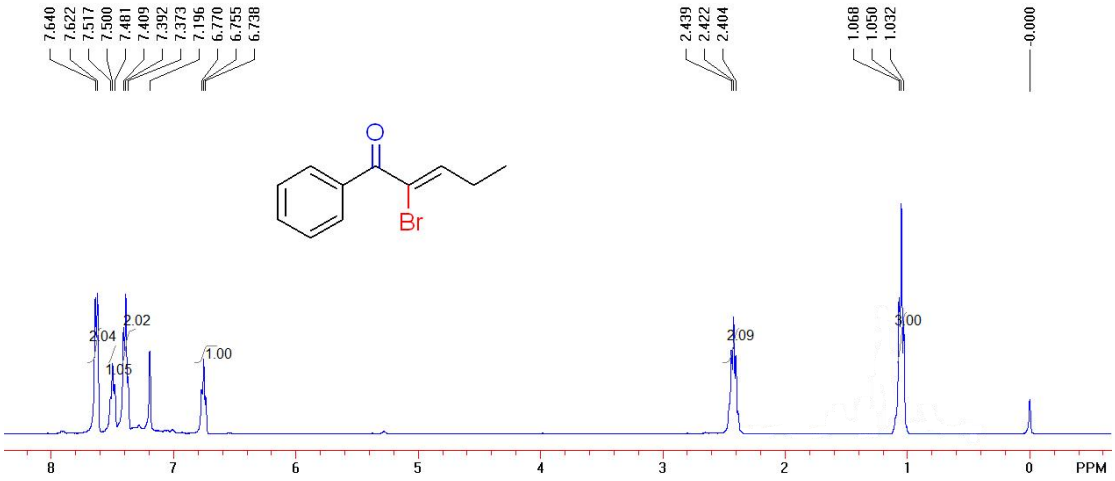

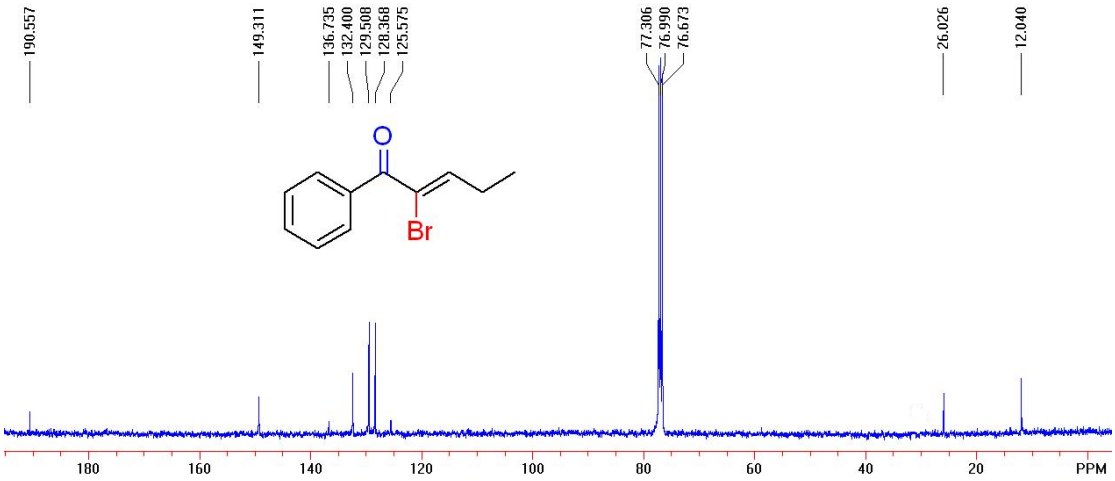

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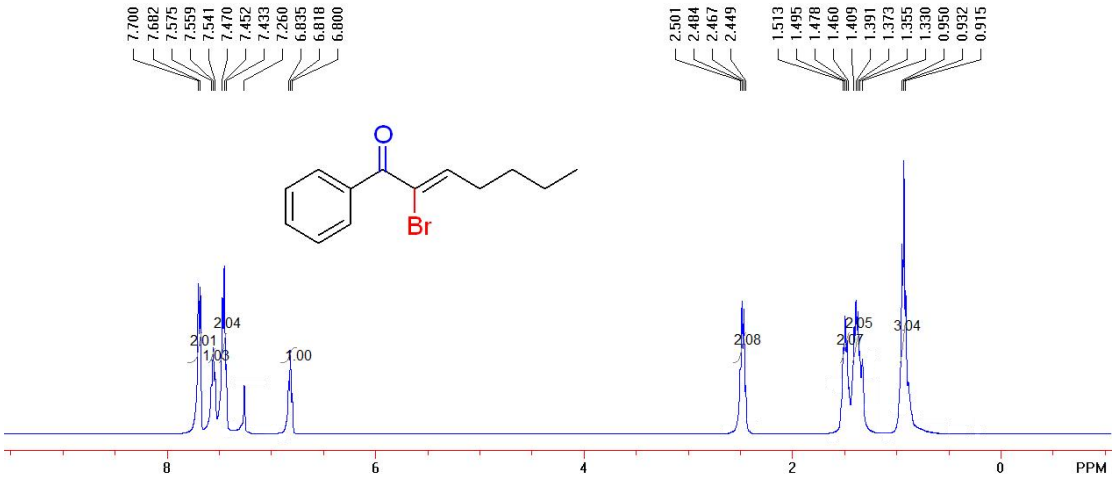
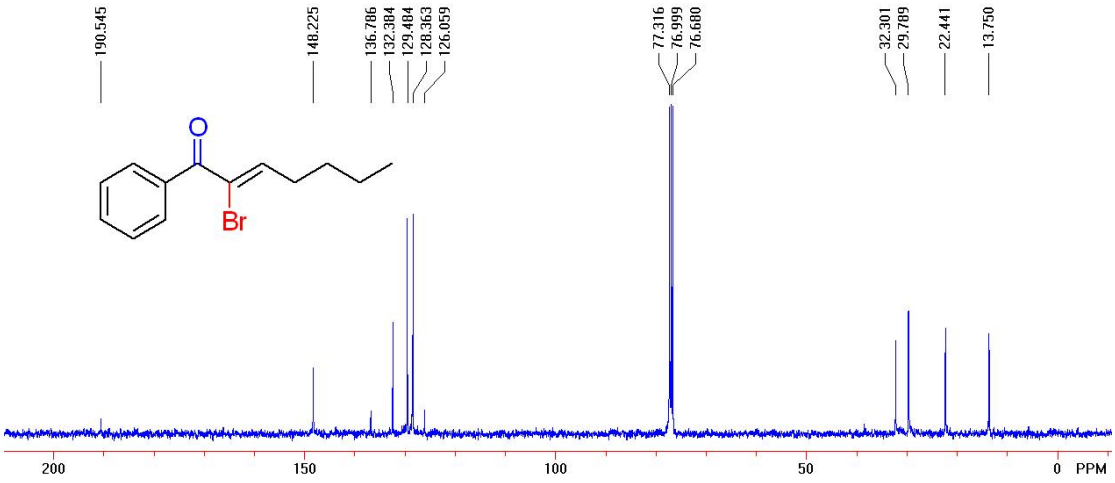
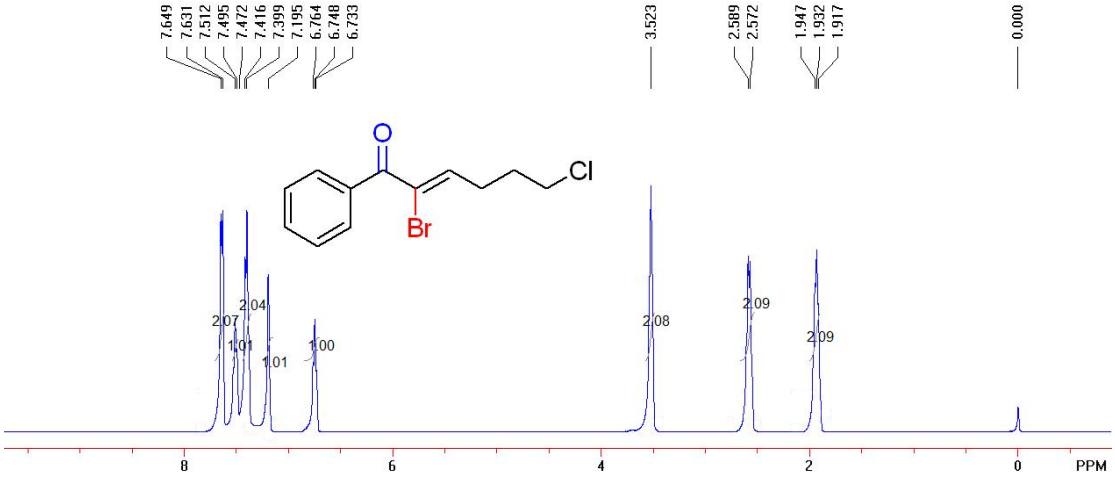
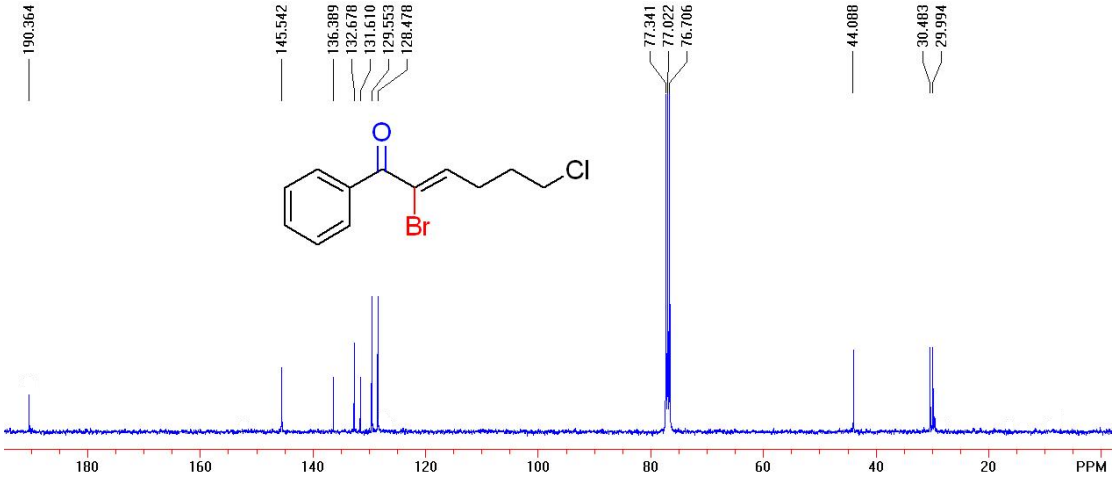


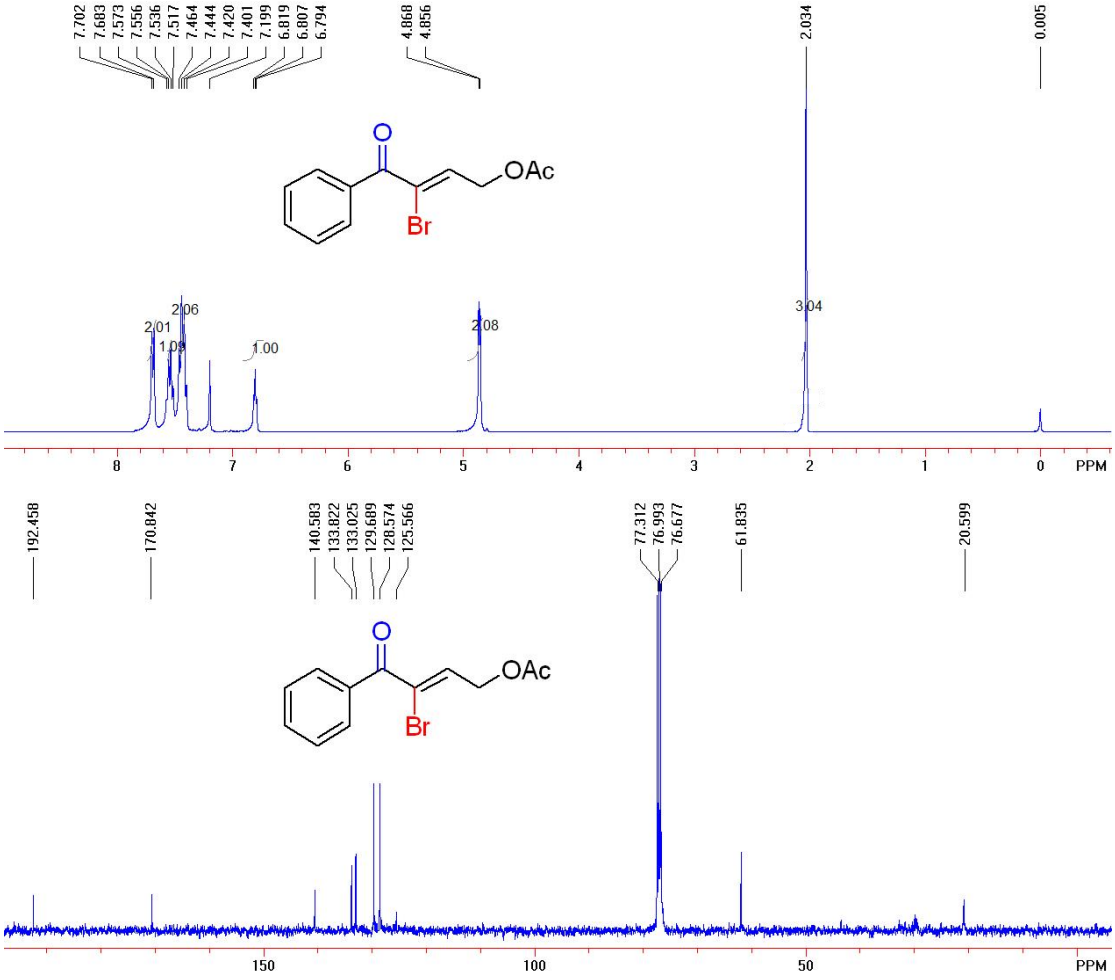


(Z)-2-bromo-6-chloro-1-phenylhex-2-en-1-one (2u)

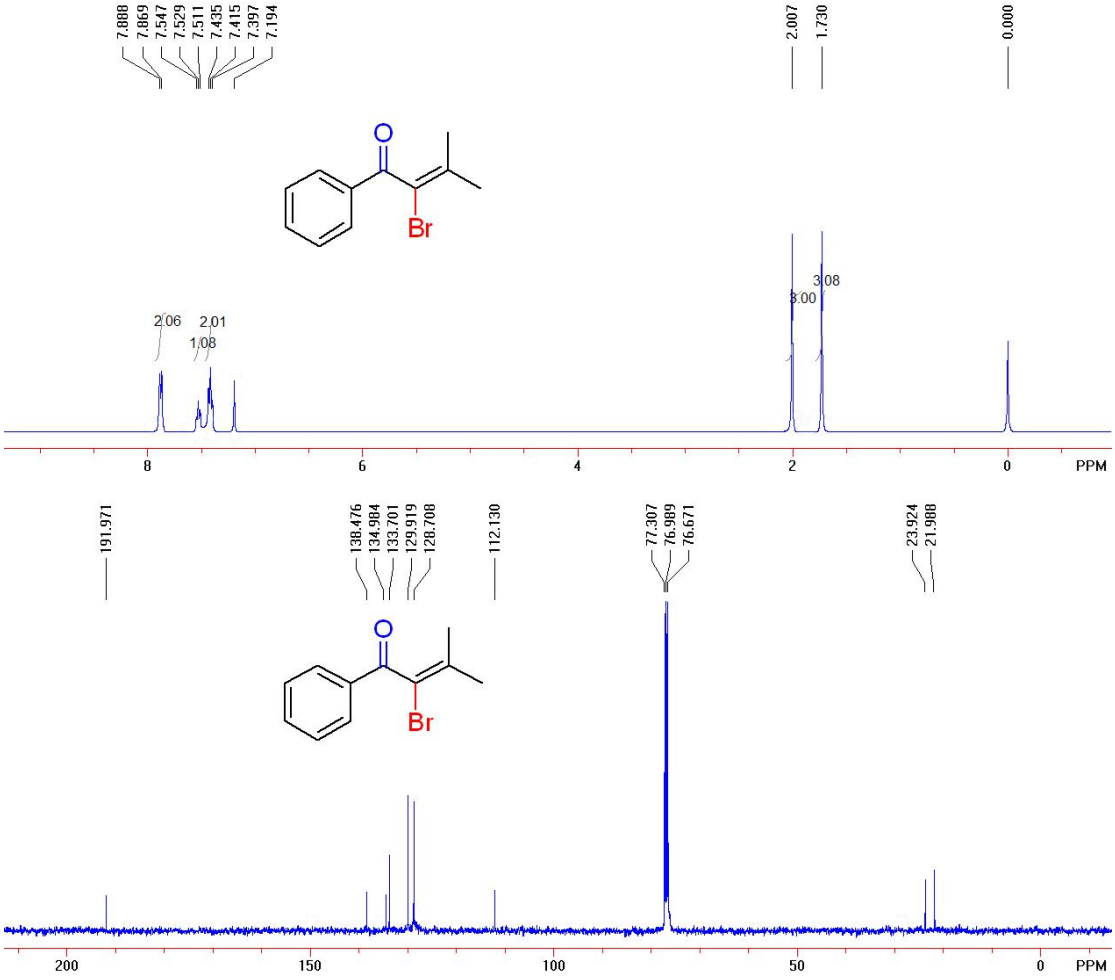




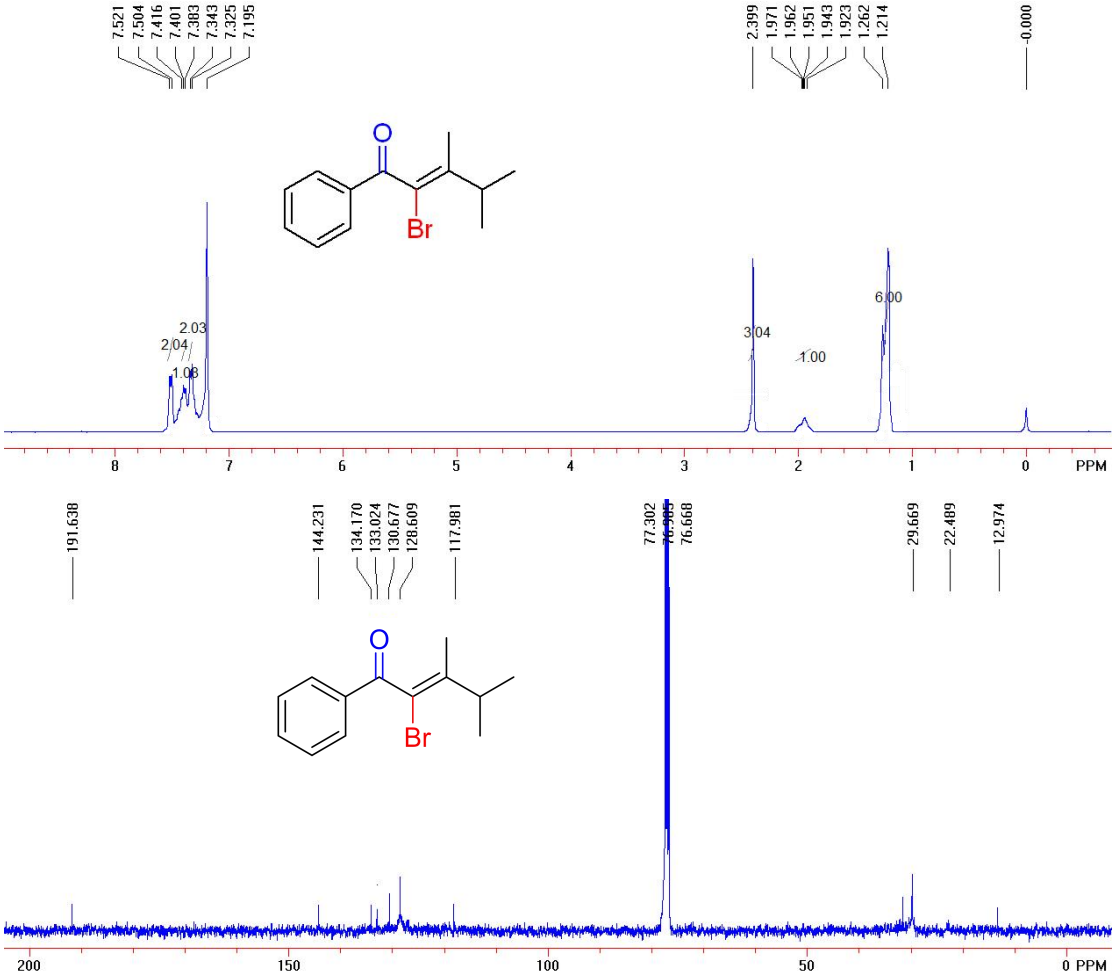
(Z)-3-bromo-4-oxo-4-phenylbut-2-en-1-yl acetate (2v)



2-bromo-3-methyl-1-phenylbut-2-en-1-one (2w)



(Z)-2-bromo-3,4-dimethyl-1-phenylpent-2-en-1-one (2x)



2-bromo-1-phenylprop-2-en-1-one (2y)