Supporting Information

Rational Synthesis of Pd Nanoparticles-Embedded Reduced Graphene Oxide Frameworks with Enhanced Selective Catalysis in Water

Jian Liu, Guowen Hu, Yanmei Yang, Haoli Zhang, Wei Zuo, and Baodui Wang*

Jian Liu, Guowen Hu, Yanmei Yang, Haoli Zhang, Wei Zuo, Weisheng Liu, and Baodui Wang*

Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, State Key Laboratory of Applied Organic Chemistry, and Key Laboratory of Special Function Materials and Structure Design, Ministry of Education, Lanzhou University Gansu, Lanzhou, 730000, P. R. China.

E-mail: wangbd@lzu.edu.cn.

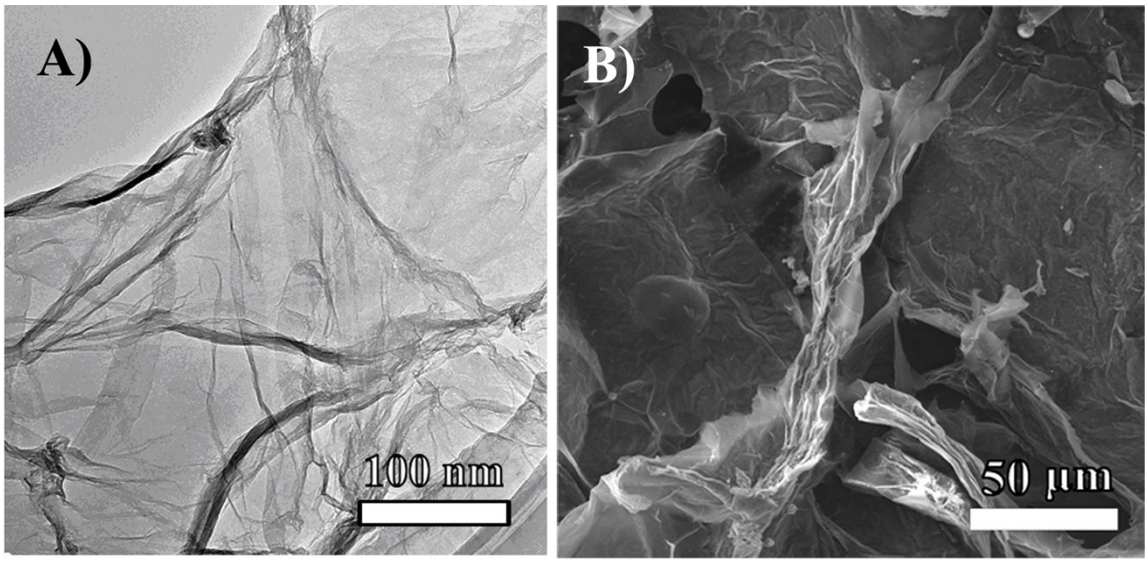


Figure S1. TEM (A) and SEM (B) images of GO-GOOH.

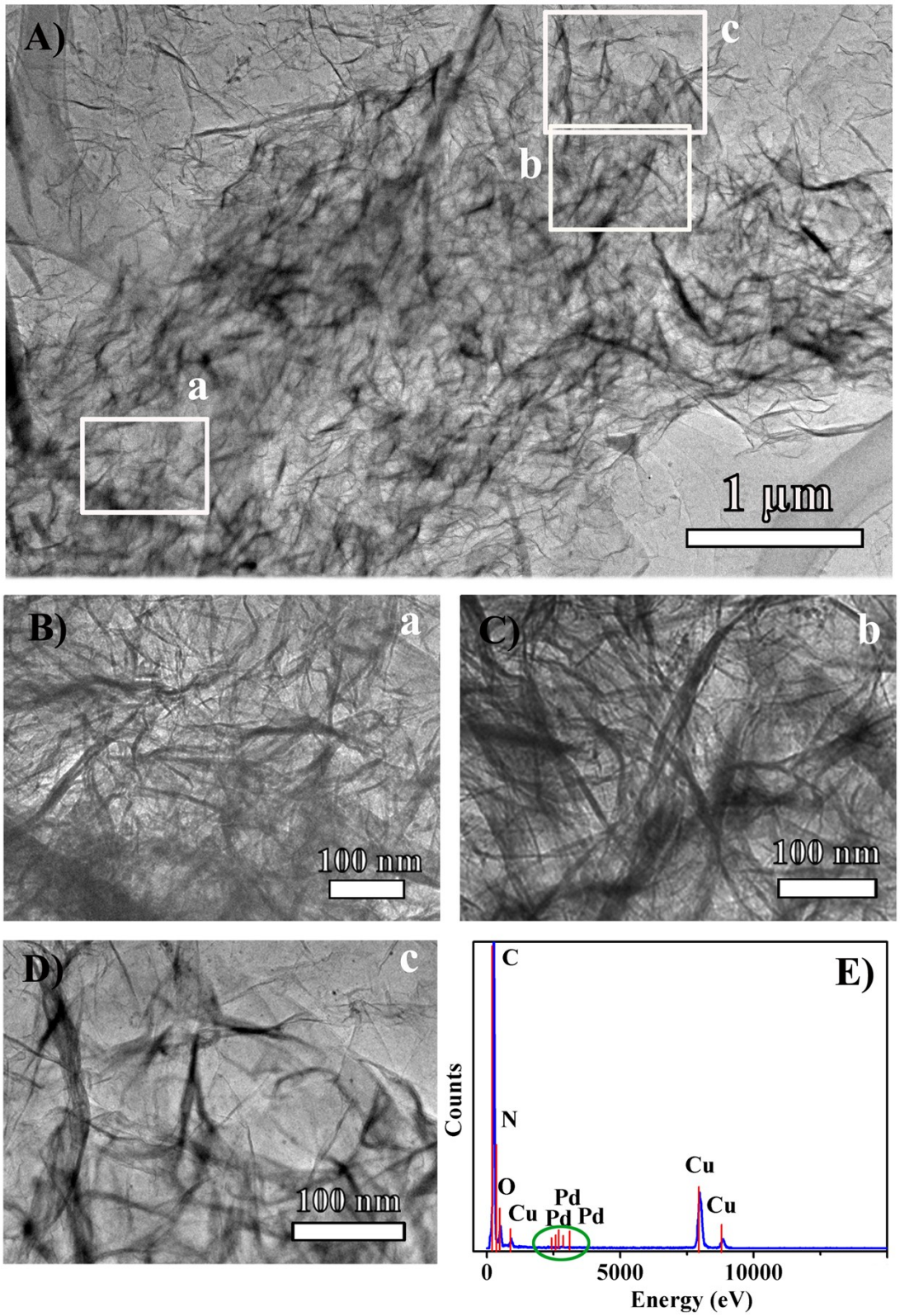


Figure S2. (A~D) TEM images of GOF; (E) the typical EDX pattern of GOF.

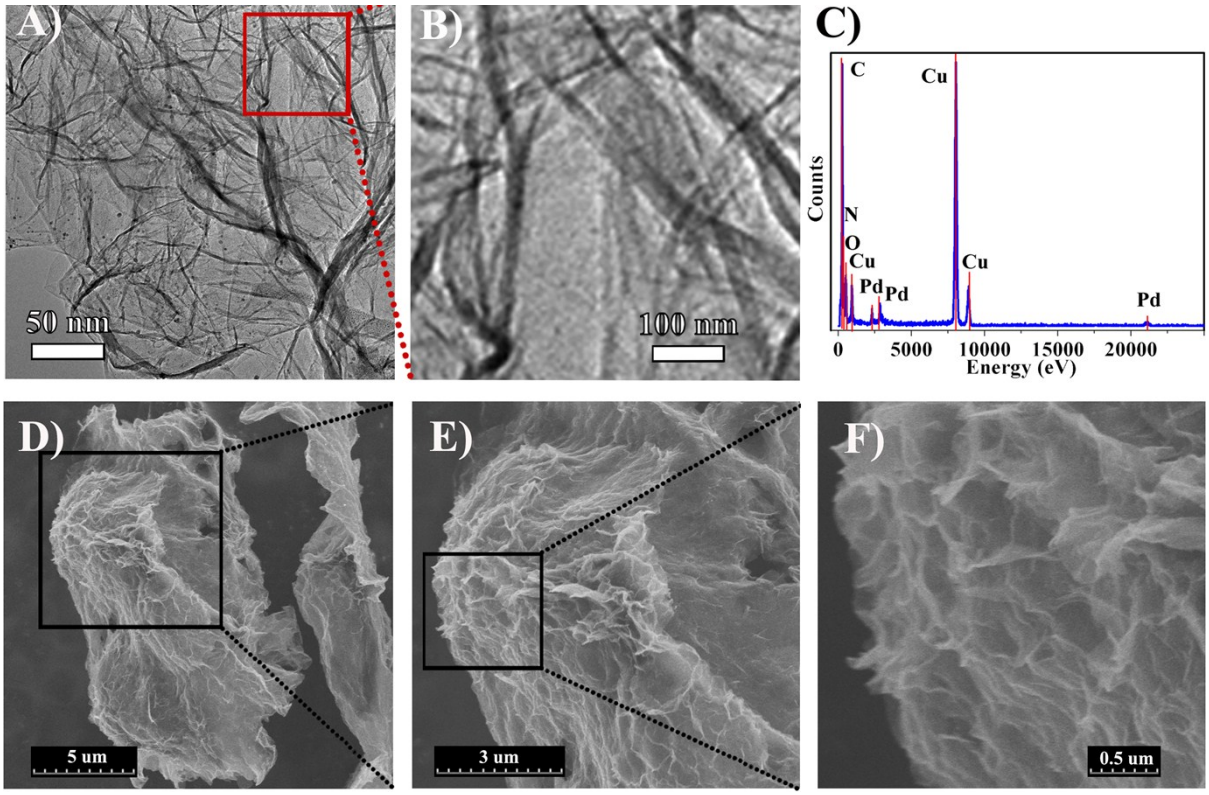


Figure S3. (A, B) TEM images, (C) the typical EDX pattern, and (D~F) SEM images of Pd^{2+}-GOF.

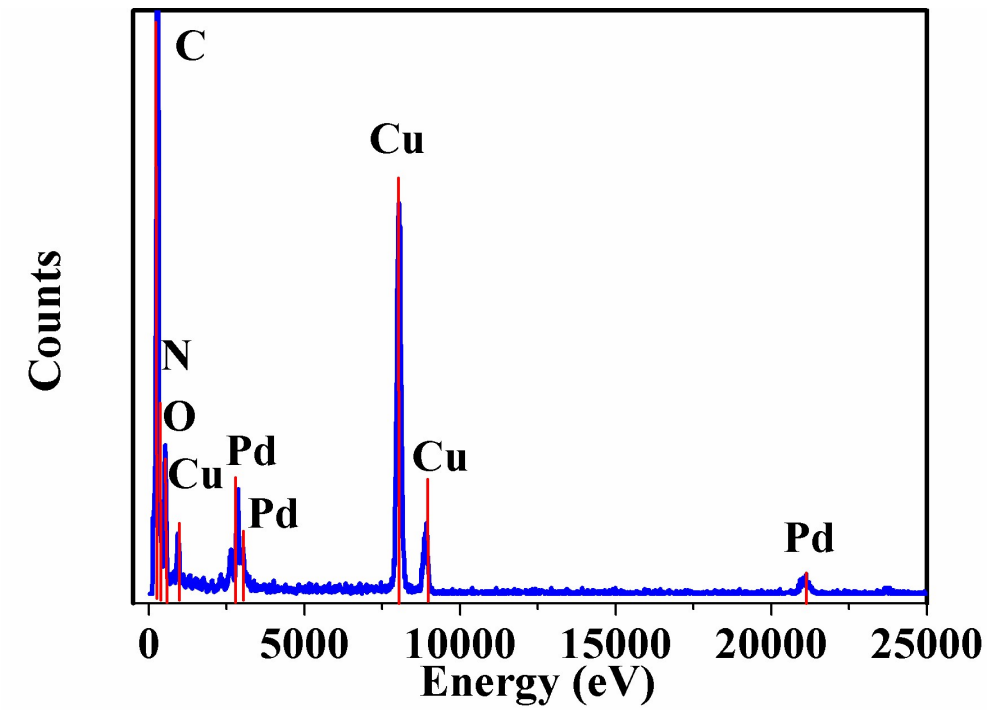


Figure S4. The typical EDX pattern of Pd-rGOF.

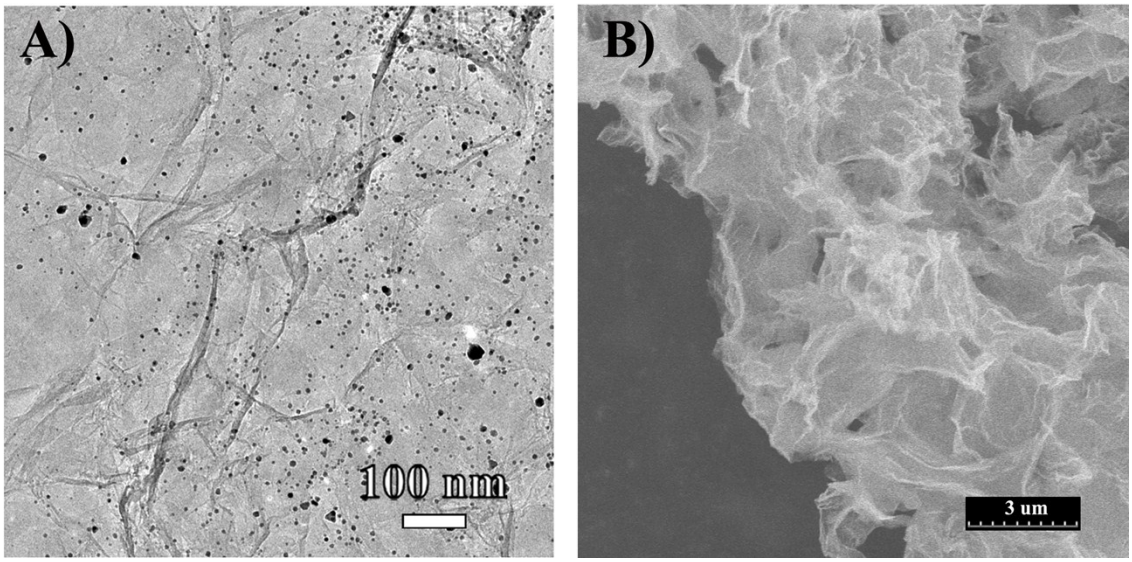


Figure S5. (A) TEM images and (B) SEM images of Pd-rGOF after 10 th cycles.

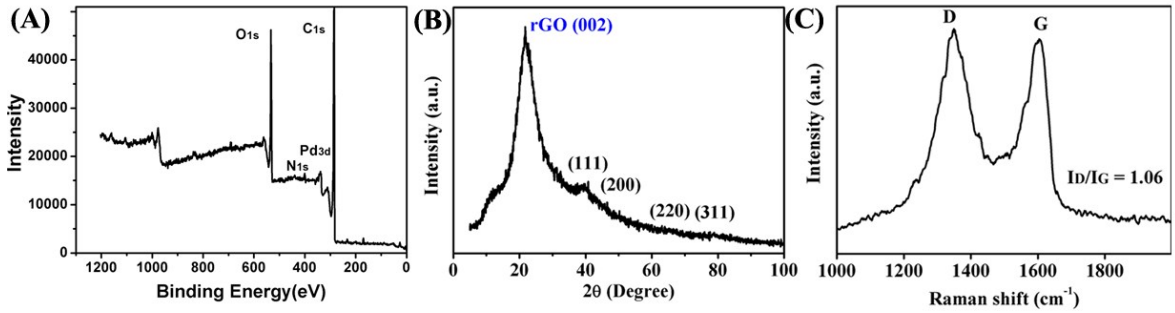
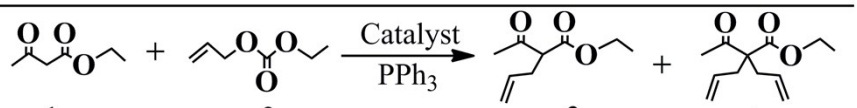


Figure S6. (A) XPS spectrum wide scan, (B) XRD pattern, and (C) Raman spectrum of Pd-rGOF of the 3D Pd-rGOF after 10 th cycles. Inset of D shows the pore size distribution of the 3D Pd-rGOF.

Table S1 The optimal condition choice of Tsuji-Trost reaction using Pd/TETA/CGO catalyst in H_2O and air.[a]

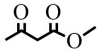
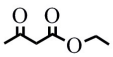
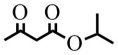
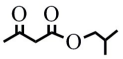
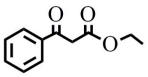
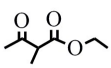
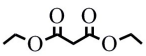


1 **2** **3** **4**

Entry	$Pd_{(\mu mol)}$	$PPh_{3(\mu mol)}$	T(^oC)	Yield (%)[b]	**3 : 4** (%)[b]
1	1.4	0	100	21	100:0
2	1.4	3.5	100	38	75:25
3	1.4	7.0	100	>99	0:100
4	1.4	10.5	100	63	70:30
5	0	7.0	100	0	-
6	1.4	7.0	90	>99	20:80
7	1.4	7.0	80	70	80:20
8	1.4	7.0	70	50	80:20
9[c]	1.4	0	70	63	100:0
10[d]	1.4	7.0	70	70	80:20
11[e]	1.4	7.0	100	0	-

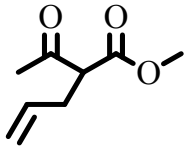
[a] Reaction condition: **1**(2.0 mmol), **2** (5.0 mmol), H_2O (3.0 mL), 0.5 h.
[b] Yields of isolated products and determined by ^{1}H-NMR,^{13}C-NMR. Tetramethylsilane was used as an internal standard. [c, d] K_2CO_3 (2.5 mmol) was added. [e] **2** was blank.

Table S2 Tsuji-Trost reaction of various 1,3-dicarbonyl compounds with allyl ethyl carbonate in H_2O and air.[a]

Entry	1,3-Dicarbonyl	Catalyst	Time (h)	Mono-:Di-	Yield (%)[b]
1		Pd-GOF	0.5	0:100	>99
2		Pd/C	0.5	35:65	60
3		Pd-GOF	0.5	0:100	>99
4		Pd/C	0.5	20:80	61
5		Pd-GOF	1.0	0:100	>99
6		Pd/C	1.0	45:55	58
7		Pd-GOF	1.0	0:100	>99
8		Pd/C	1.0	41:59	67
9		Pd-GOF	1.5	0:100	90
10		Pd/C	1.5	0:100	64
11		Pd-GOF	1.0	100:0	90
12		Pd/C	1.0	100:0	40
13		Pd-GOF	1.5	100:0	90
14		Pd/C	1.5	100:0	60
15		Pd-GOF	2.0	100:0	60
16		Pd/C	2.0	100:0	35

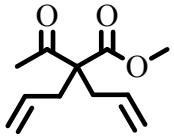
[a] Reaction condition: Pd-rGOF (Pd: 1.4 μmol), Pd/C (Pd: 1.4 μmol), PPh_3 (7.0 μmol)), **1** (2.0 mmol), **2** (5.0 mmol), H_2O (3.0 mL), 100 ^{o}C.
[b] Yields of isolated products and determined by ^{1}H-NMR and^{13}C-NMR.

1. Methyl 2-acetylpent-4-enoate



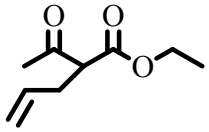
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.18 (s, 3H), 2.51-2.56 (m, 2H), 3.50 (t, 1H), 3.68 (s, 3H), 4.97-5.07 (m, 2H), 5.63-5.73 (m, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 29.3, 32.3, 52.5, 59.1, 117.6, 134.2, 169.8, 202.9
MS (EI) m/z (%): 113 (M^+-CH_3CO), 97, 81, 71, 55, 43 (100)

Methyl 2-acetyl-2-allylpent-4-enoate



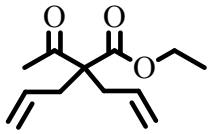
^{1}H NMR (400 MHz, $CDCl_3$) δ 2.14 (s, 3H), 2.56-2.67 (m, 4H), 3.74 (s, 3H), 5.09-5.14 (m, 4H), 5.54-5.65 (m, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 27.0, 36.0, 52.4, 63.4, 119.3, 132.2, 171.9, 202.9
MS (EI) m/z (%): 154 (M^+-CH_3CO), 149, 137, 123, 111, 95, 81, 71, 57, 43 (100)

2. Ethyl 2-acetylpent-4-enoate



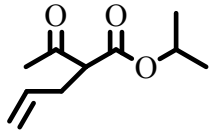
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.22 (t, J = 7.1Hz, 3H), 2.18 (s, 3H), 2.54 (quint, 2H), 3.46 (t, J = 7.4Hz, 1H), 4.15 (q, J = 7.1Hz, 2H), 4.97-5.06 (m, 2H), 5.63-5.74 (m, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 29.0, 32.0, 59.1, 61.3, 117.3, 134.1, 169.1, 202.3
MS (EI) m/z (%): 127 (M^+ -CH_3CO), 99, 81, 55, 43 (100)

Ethyl 2-acetyl-2-allylpent-4-enoate



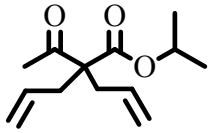
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.27 (t, J = 7.1Hz, 3H), 2.14 (s, 3H), 2.61 (quint, 4H), 4.20 (q, J = 7.1Hz, 2H), 5.08-5.13 (m, 4H), 5.55-5.65 (m, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 26.9, 35.9, 61.4, 63.2, 118.2, 132.2, 172.1, 203.8
MS (EI) m/z (%): 168 (M^+ -CH_3CO), 123, 95, 79, 67, 43 (100)

3. Isopropyl 2-acetylpent-4-enoate



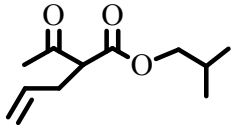
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (d, 6H), 2.24 (s, 3H), 2.59 (quint, 2H), 2.47-2.51 (m, 1H), 5.04-5.13 (m, 3H), 5.70-5.80 (m, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 29.1, 32.2, 59.5, 69.2, 117.5, 134.3, 168.9, 202.4
MS (EI) m/z (%): 141 (M^+-CH_3CO), 124, 99, 92, 82, 71, 57, 43 (100)

Isopropyl 2-acetyl-2-allylpent-4-enoate



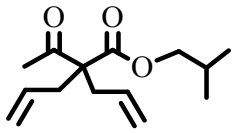
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.25 (d, 6H), 2.13 (s, 3H), 2.55-2.67 (m, 4H), 5.05-5.13 (m, 5H), 5.55-5.65 (m, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 21.7, 26.9, 35.9, 63.1, 69.1, 119.3, 132.3, 171.6, 204.0
MS (EI) m/z (%): 180 (M^+-CH_3CO), 178, 169, 149, 123, 95, 79, 57, 44 (100)

4. Isobutyl 2-acetylpent-4-enoate



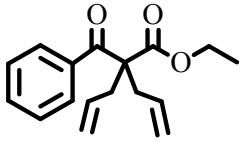
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (d, 6H), 1.90-2.00 (m, 1H), 2.25 (s, 3H), 2.55-2.66 (m, 2H), 3.55 (t, 2H), 3.92 (d, 2H), 5.04-5.13 (m, 2H), 5.70-5.80 (m, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 27.8, 29.3, 32.2, 59.3, 71.6, 117.6, 134.3, 169.4, 202.5
MS (EI) m/z (%):155 (M^+-CH_3CO), 142, 124, 109, 99, 82, 57, 43 (100)

Isobutyl 2-acetyl-2-allylpent-4-enoate



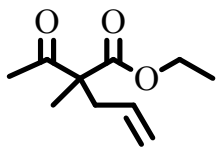
^{1}H NMR (400 MHz, $CDCl_3$) δ 0.93 (d, 6H), 1.88-1.98(m, 1H), 2.14 (s, 3H), 2.56-2.69 (m, 4H), 3.90 (d, 2H),5.08-5.13 (m, 4H), 5.54-5.65 (m, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 19.3, 26.9, 27.6, 36.0, 63.4, 71.7, 119.3, 132.1, 173.3, 203.8
MS (EI) m/z (%): 141 (M^+-CH_3CO), 123, 95, 79, 57, 43 (100)

5. Ethyl 2-allyl-2-benzoylpent-4-enoate



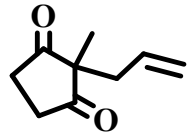
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.08 (t, J = 7.1Hz, 3H), 2.81 (m, 4H), 4.13 (q, J = 7.1Hz, 2H), 5.00-5.09 (m, 4H), 5.53-5.64 (m, 2H), 7.40-7.54 (m, 3H), 7.83-7.85 (m, 2H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 37.2, 60.6, 61.5, 119.1, 128.5 ,128.6, 132.0, 132.8, 136.0, 172.7, 196.2
MS (EI) m/z (%): 272 (M^+), 198, 159, 105 (100), 77

6. Ethyl 2-acetyl-2-methylpent-4-enoate



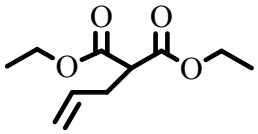
^{1}H NMR (400 MHz, $CDCl_3$) δ 1.20 (t, J = 7.1Hz, 3H), 1.26 (s, 3H), 2.08 (s, 3H), 2.41-2.60 (m, 2H), 4.13(q, J = 7.1Hz, 2H), 4.97-5.09 (m, 2H), 5.53-5.64 (m, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 18.9, 26.2, 39.4, 59.4, 61.4, 119.0, 132.7, 172.5, 204.8
MS (EI) m/z (%): 142, 114, 97, 69, 43 (100)

7. 2-allyl-2-methylcyclopentane-1, 3-dione



^{1}H NMR (400 MHz, $CDCl_3$) δ 1.11 (s, 3H), 2.33-2.05 (m, 2H), 2.65-2.82 (m, 4H), 5.04-5.08 (m, 2H), 5.54-5.65 (m, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 19.2, 36.8, 40.4, 57.1, 120.2, 131.9, 289.1
MS (EI) m/z (%): 152 (M^+), 124, 111, 97 (100), 55, 41

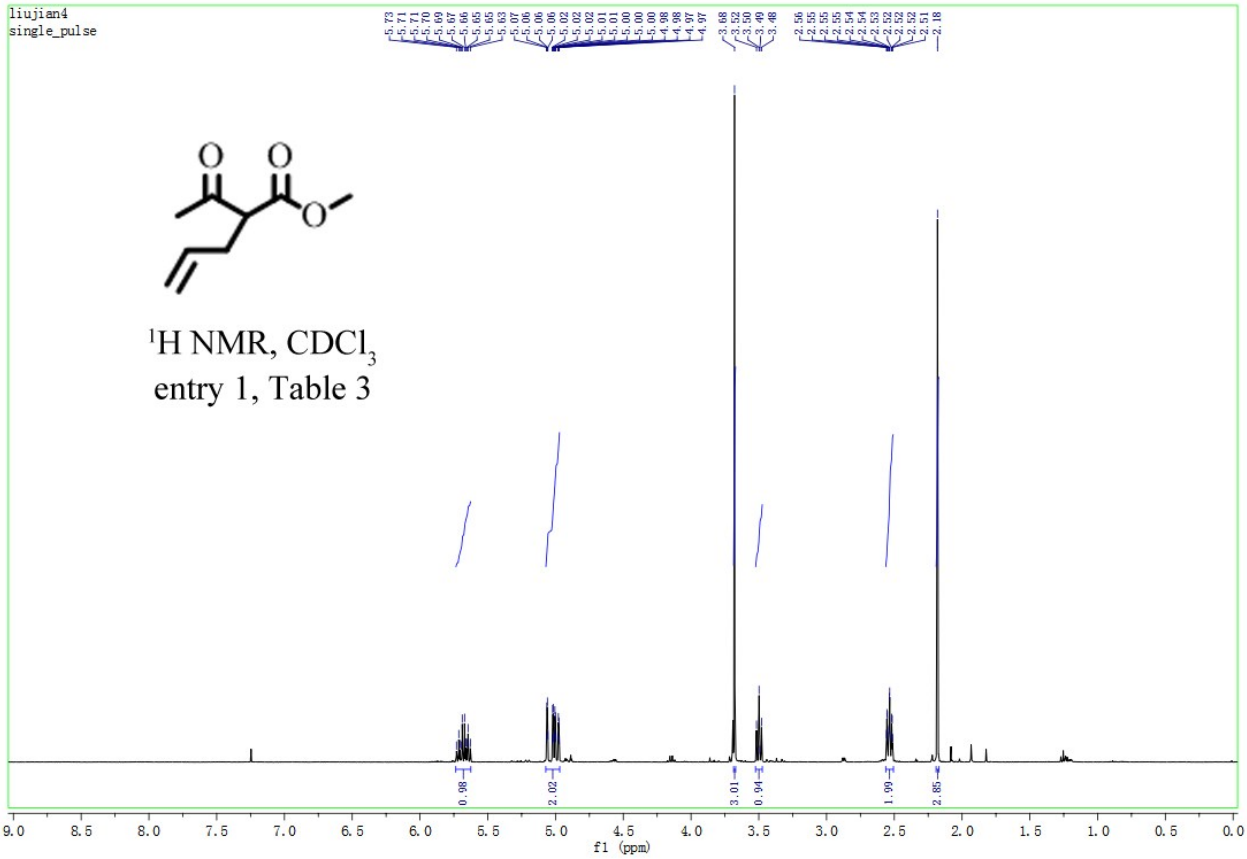
8. Table 2 entry 21 (Mono-)

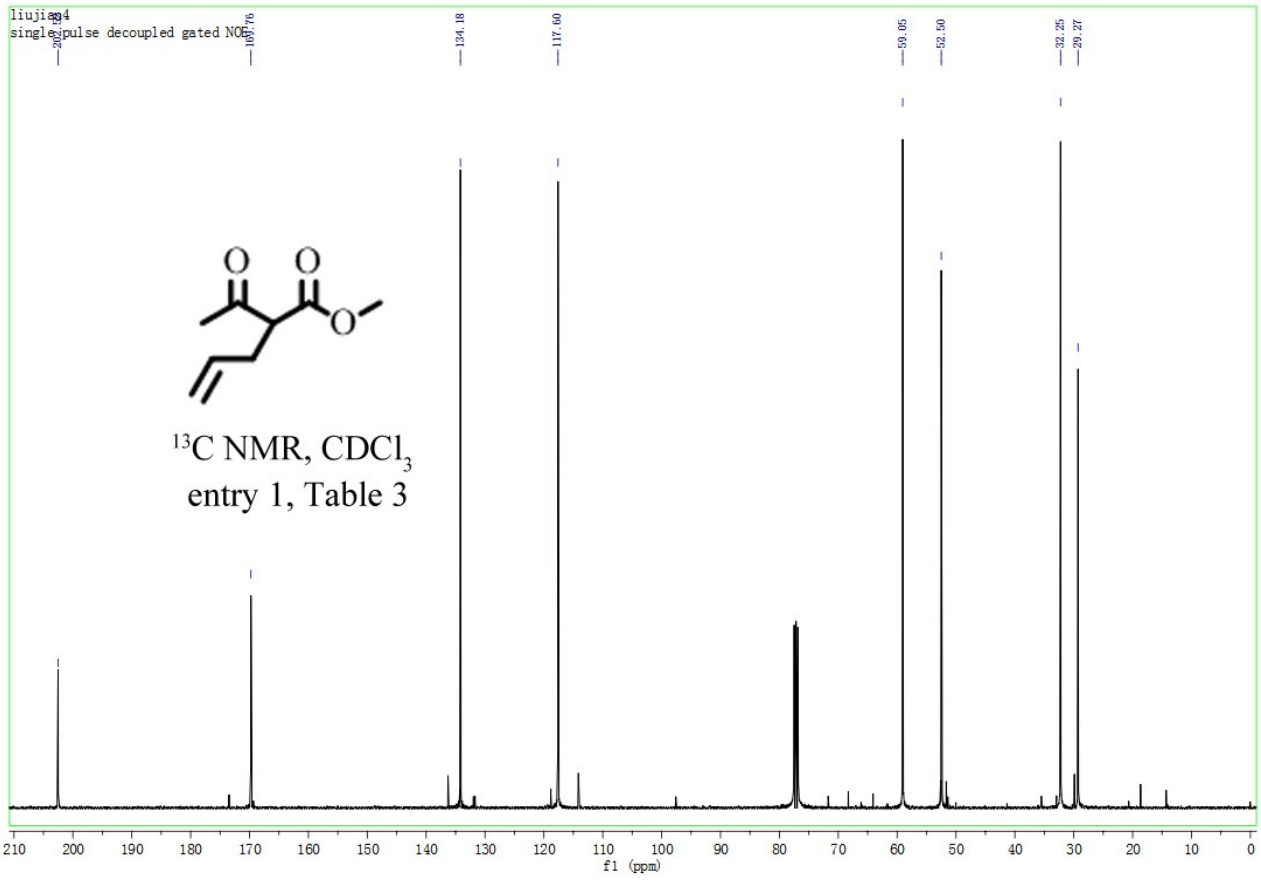


^{1}H NMR (400 MHz, $CDCl_3$) δ 1.19 (t, 6H), 2.56 (m, J = 7.2Hz, 2H), 3.35 (t, J = 7.5Hz, 1H), 4.12 (quint, J = 3.9Hz, 4H), 4.93-5.10 (m, 2H), 5.66-5.76 (m, 1H)
^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 32.8, 51.6, 61.3, 117.4, 134.1, 168.9
MS (EI) m/z (%): 155 (M^+-OCH_2CH_3), 149, 127, 109, 98 (100), 81, 67, 55, 44

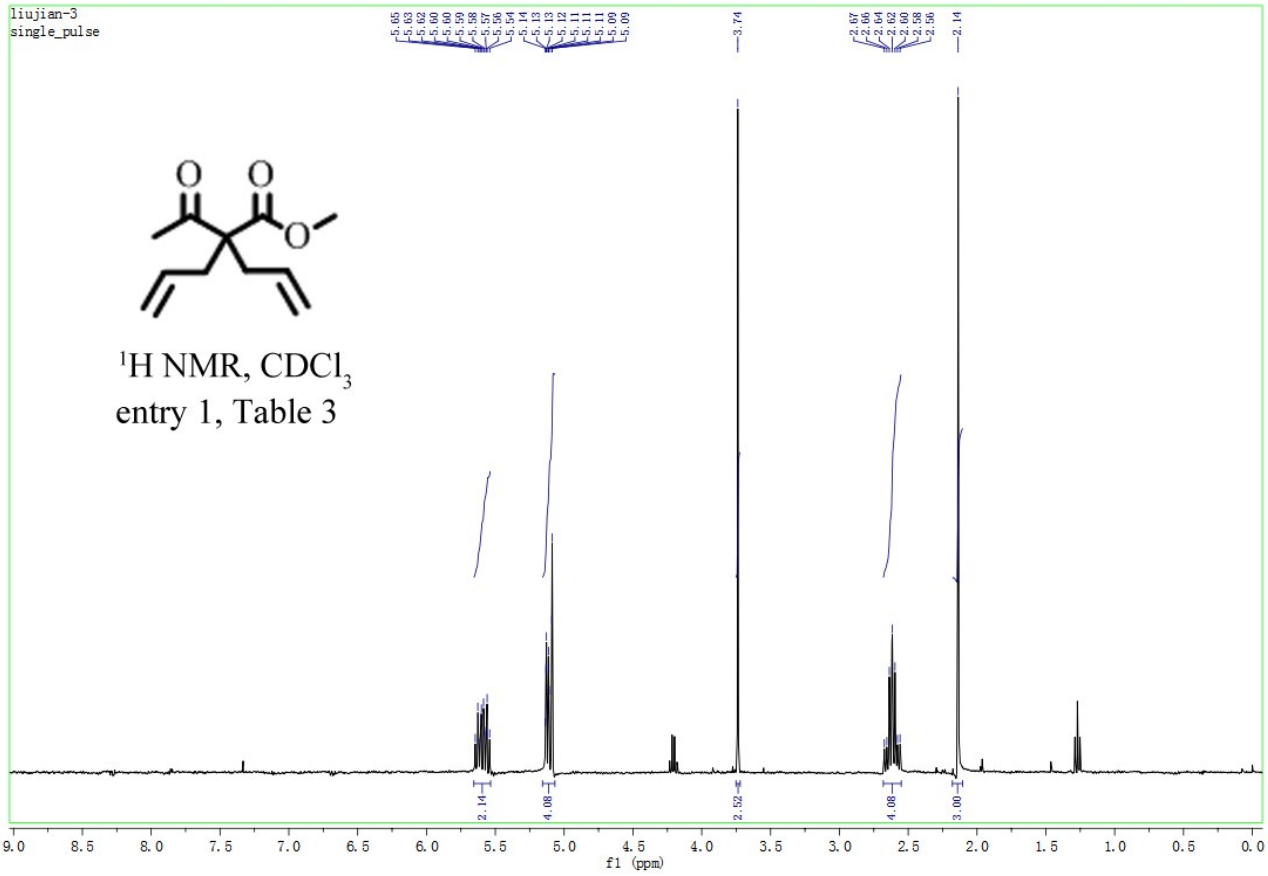
Copies of ^{1}H-NMR, ^{13}C-NMR

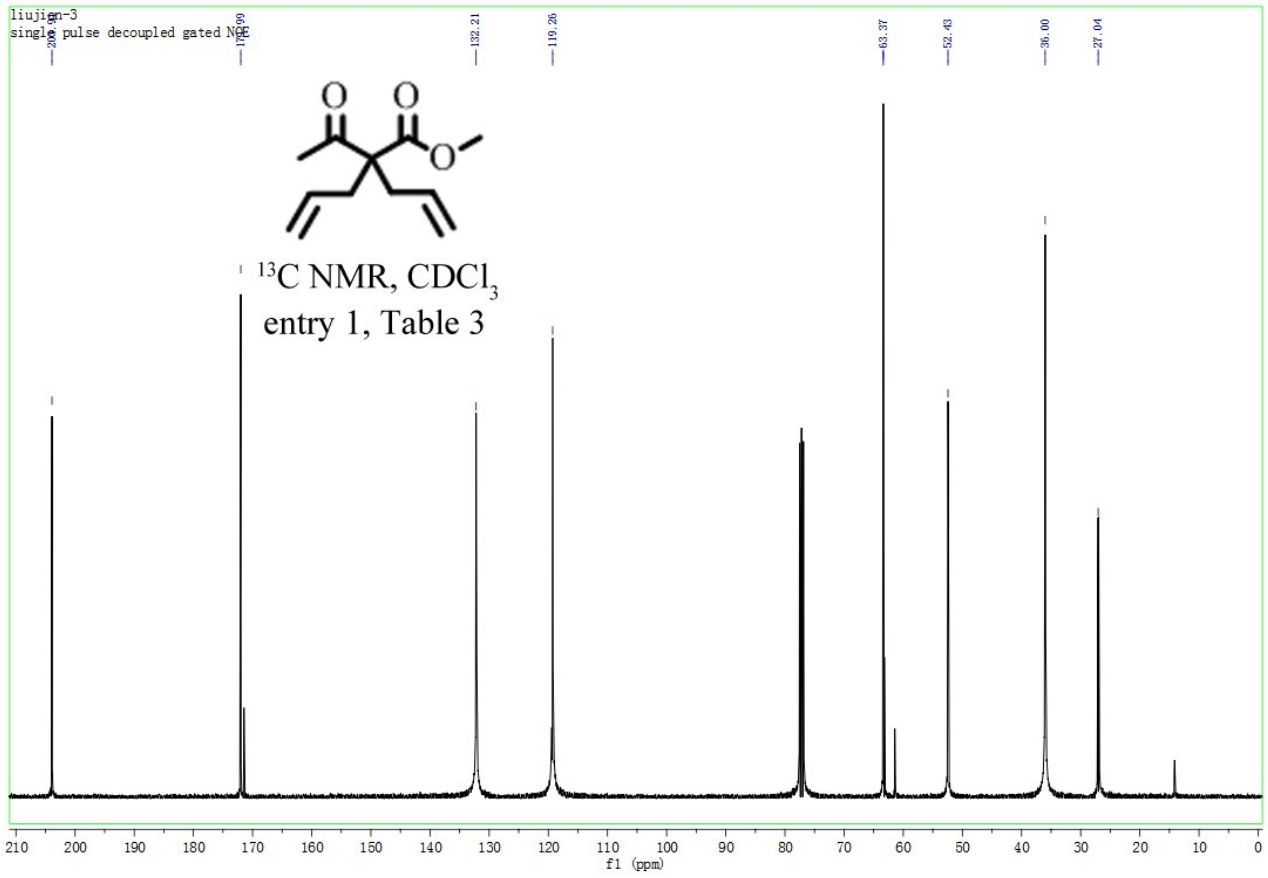
Methyl 2-acetylpent-4-enoate



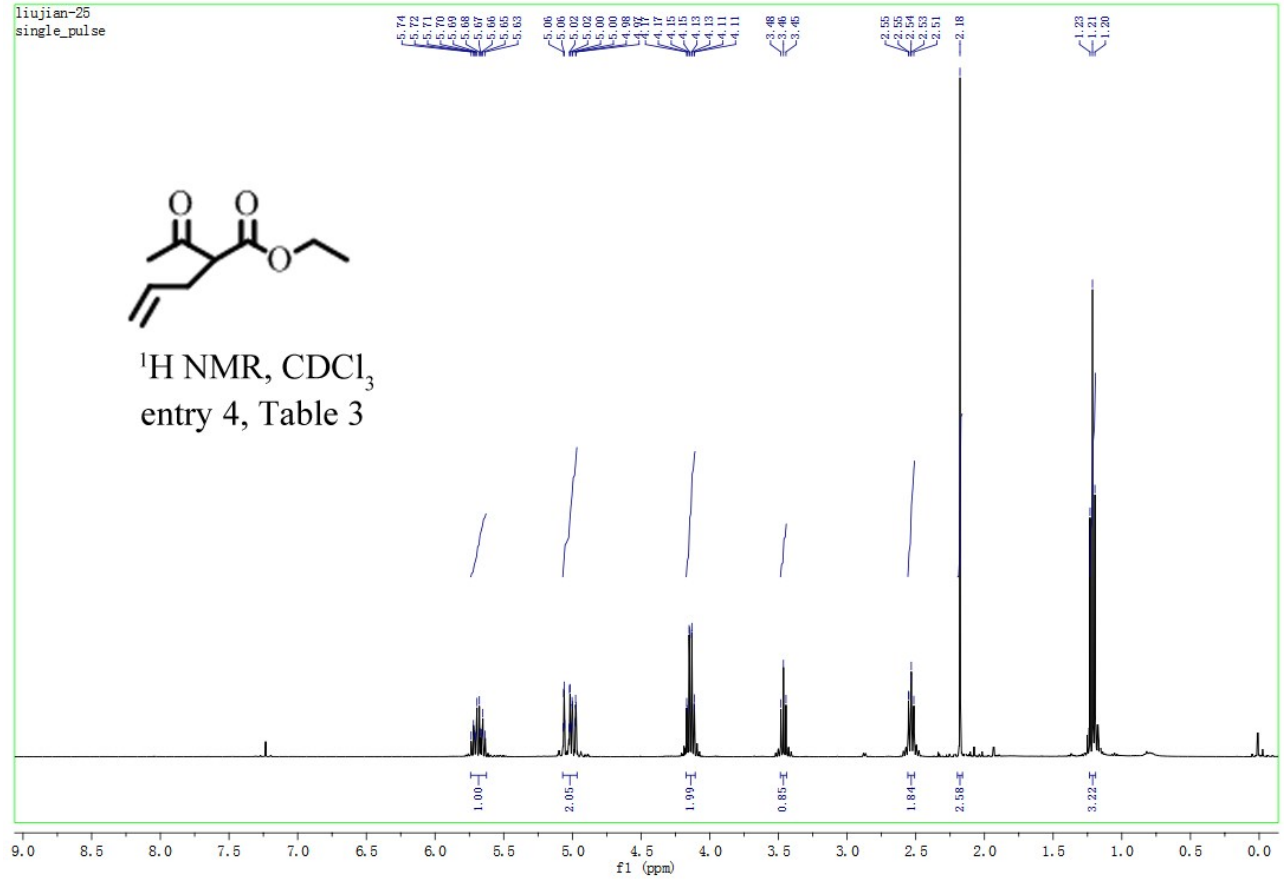


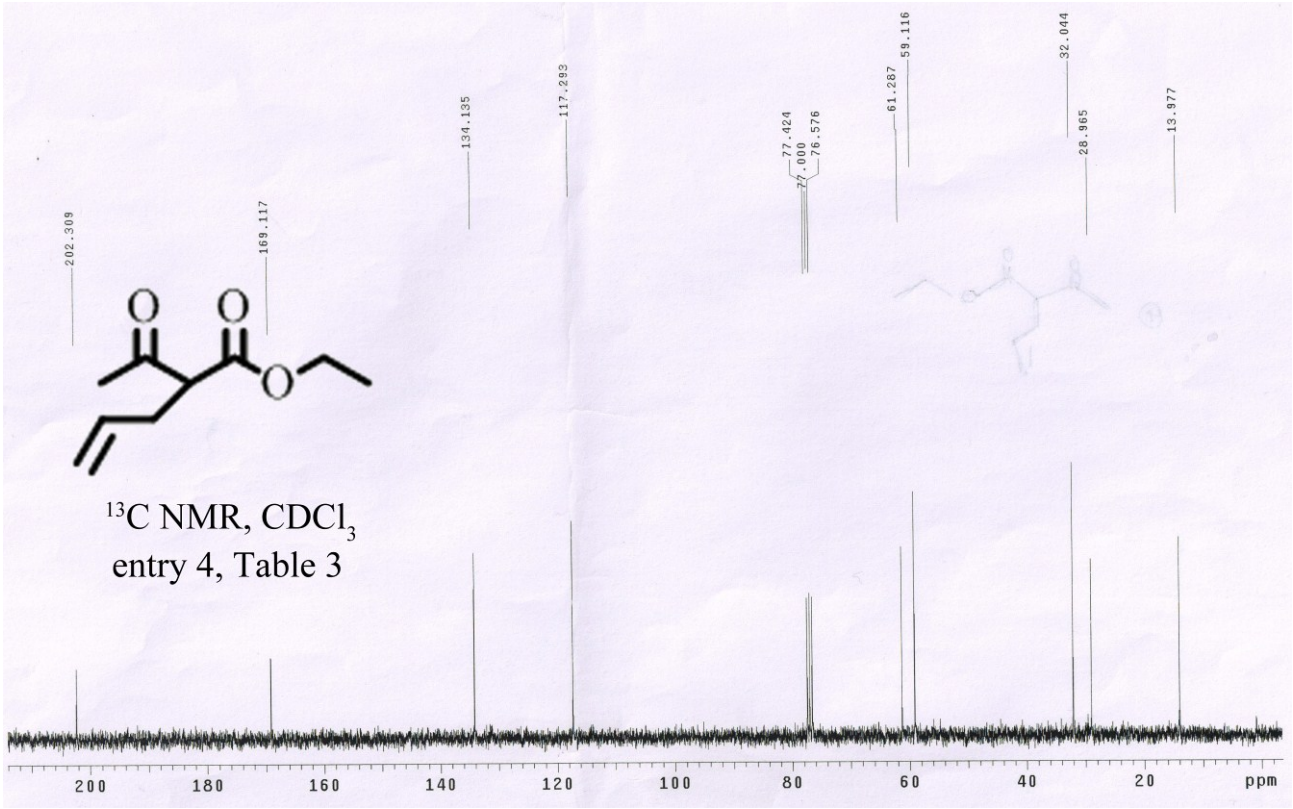
Methyl 2-acetyl-2-allylpent-4-enoate



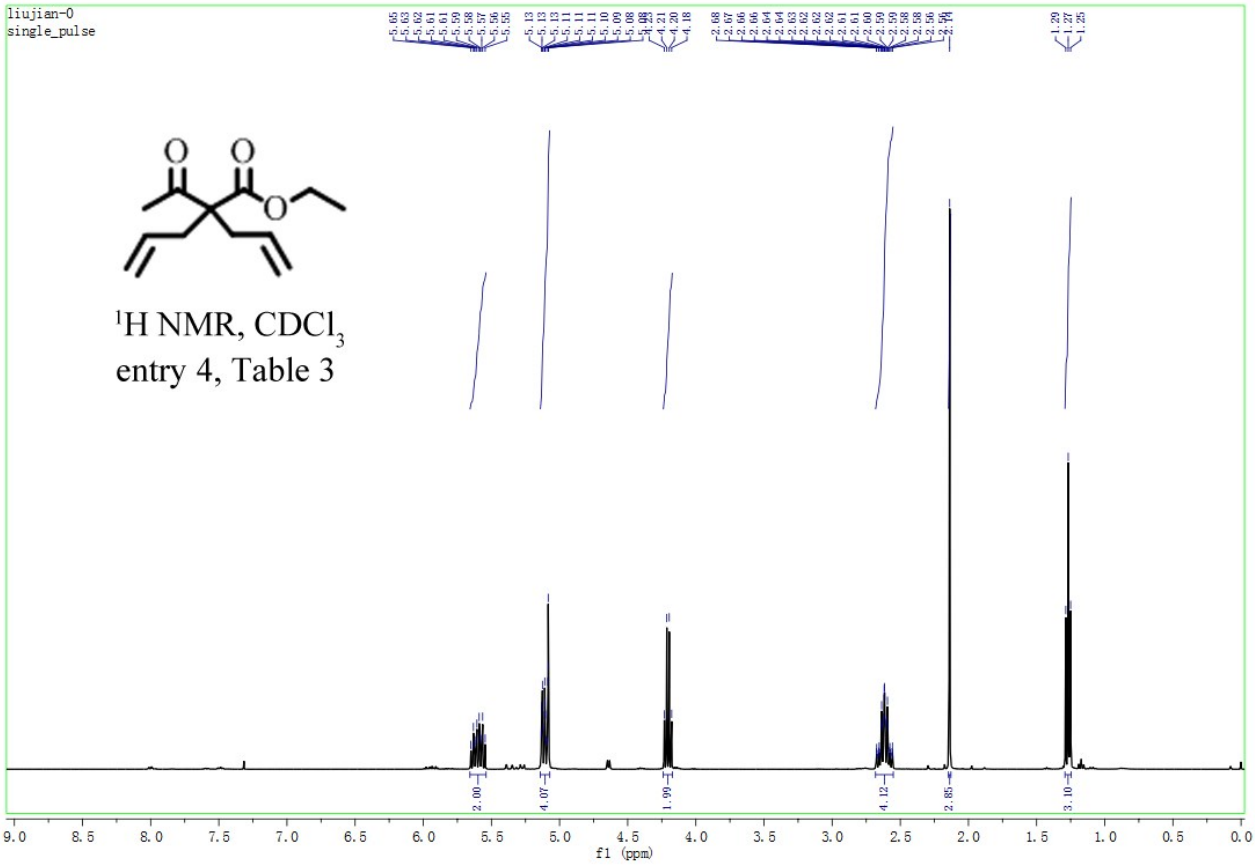


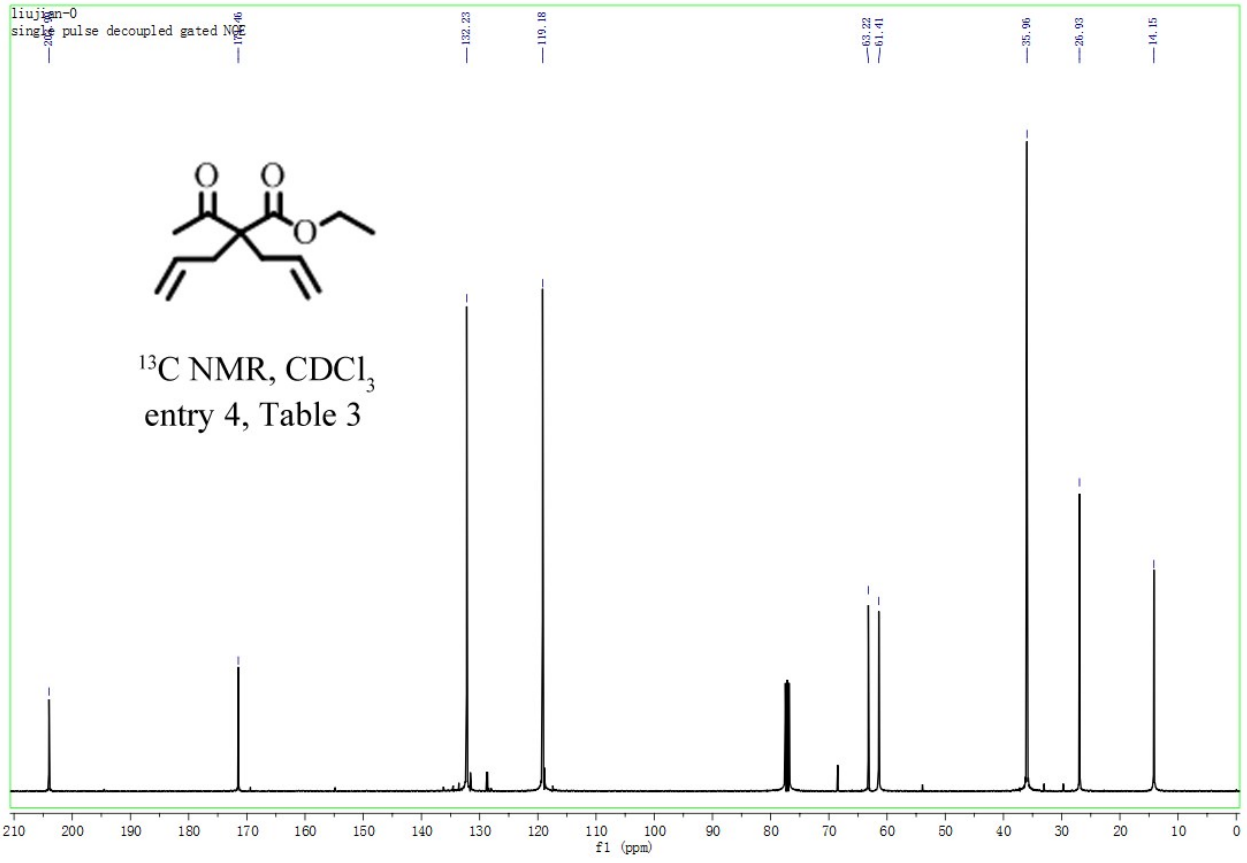
Ethyl 2-acetylpent-4-enoate



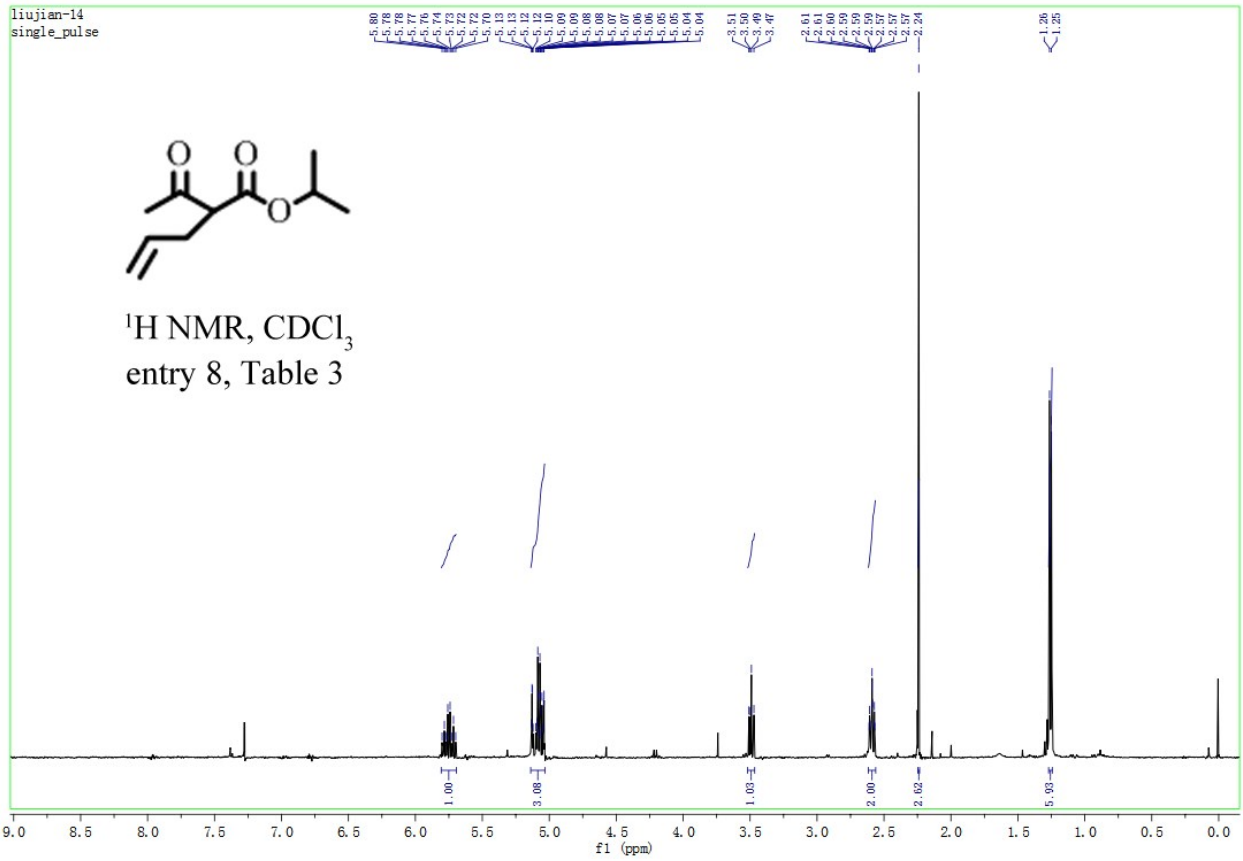


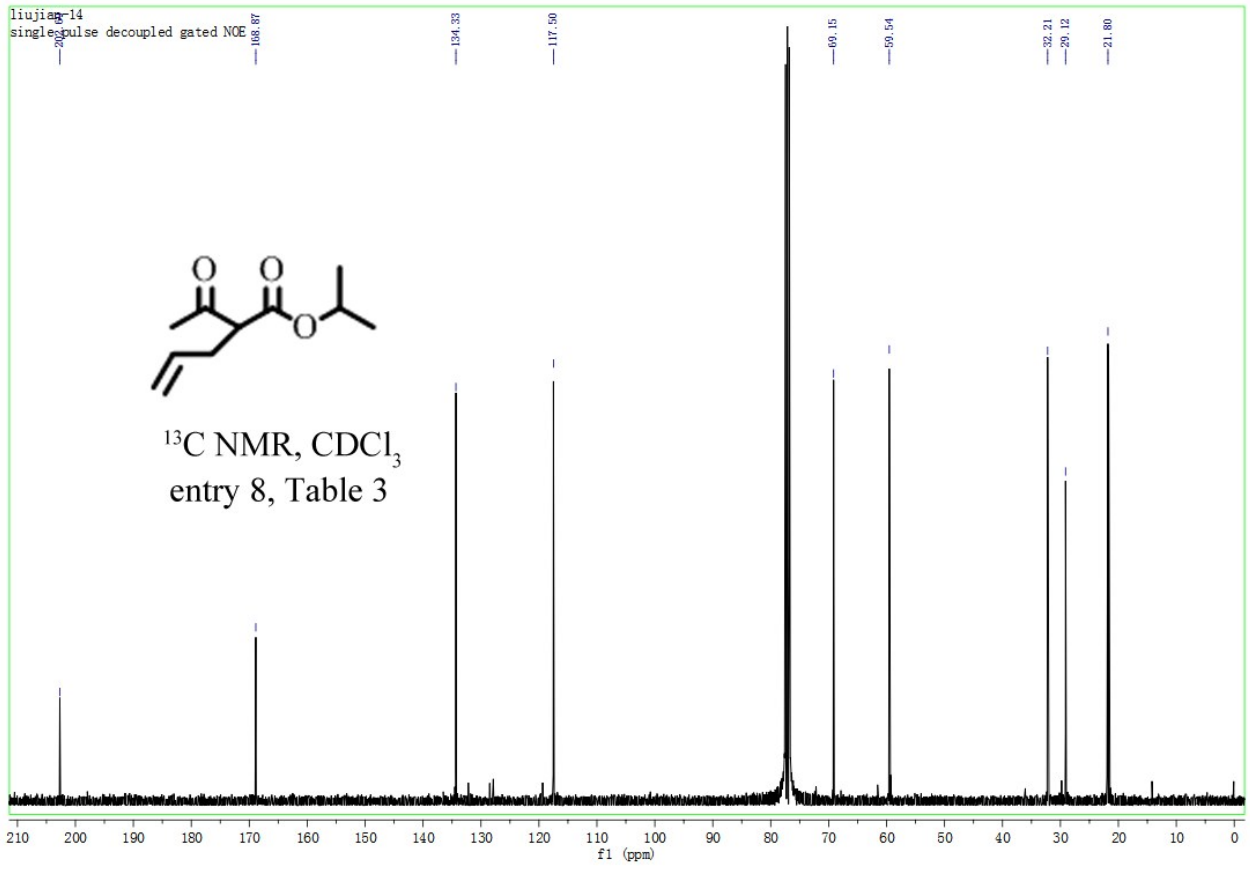
Ethyl 2-acetyl-2-allylpent-4-enoate





Isopropyl 2-acetylpent-4-enoate





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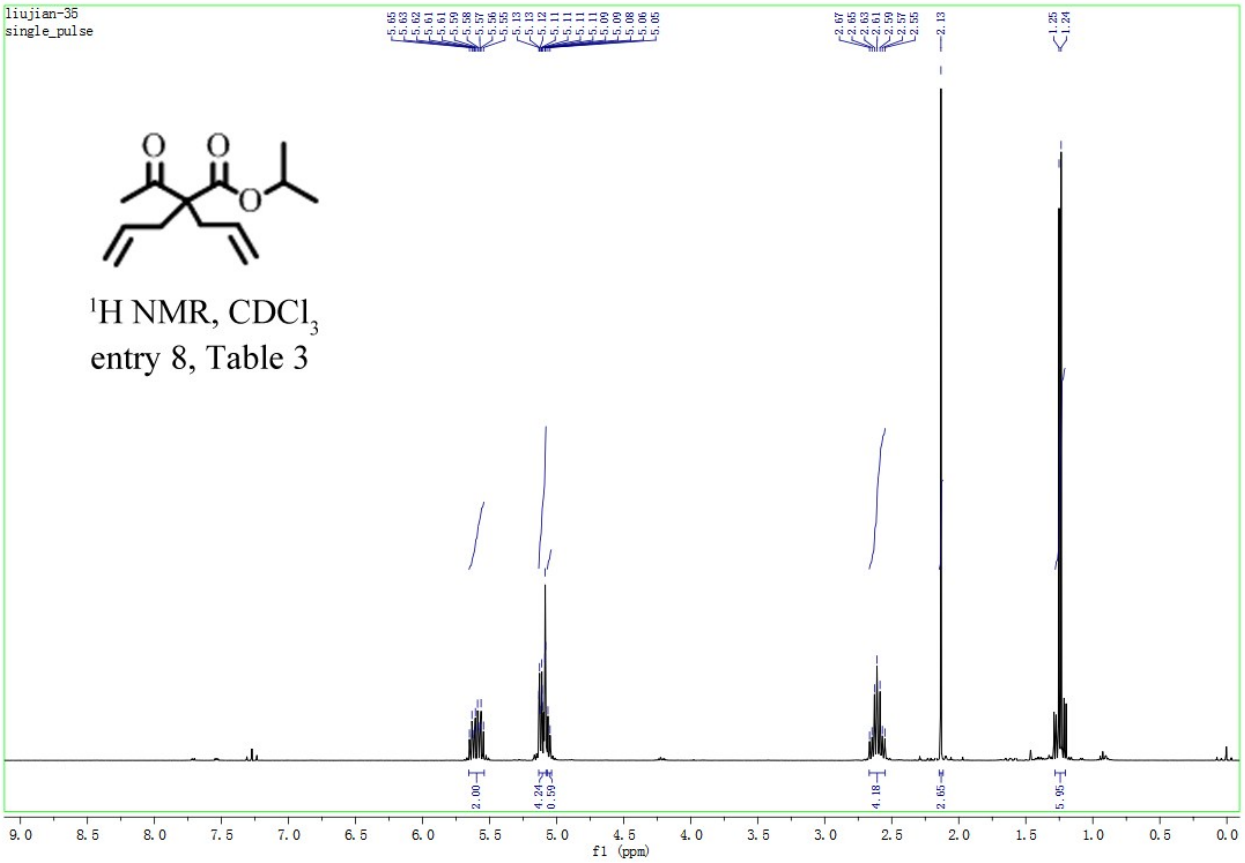
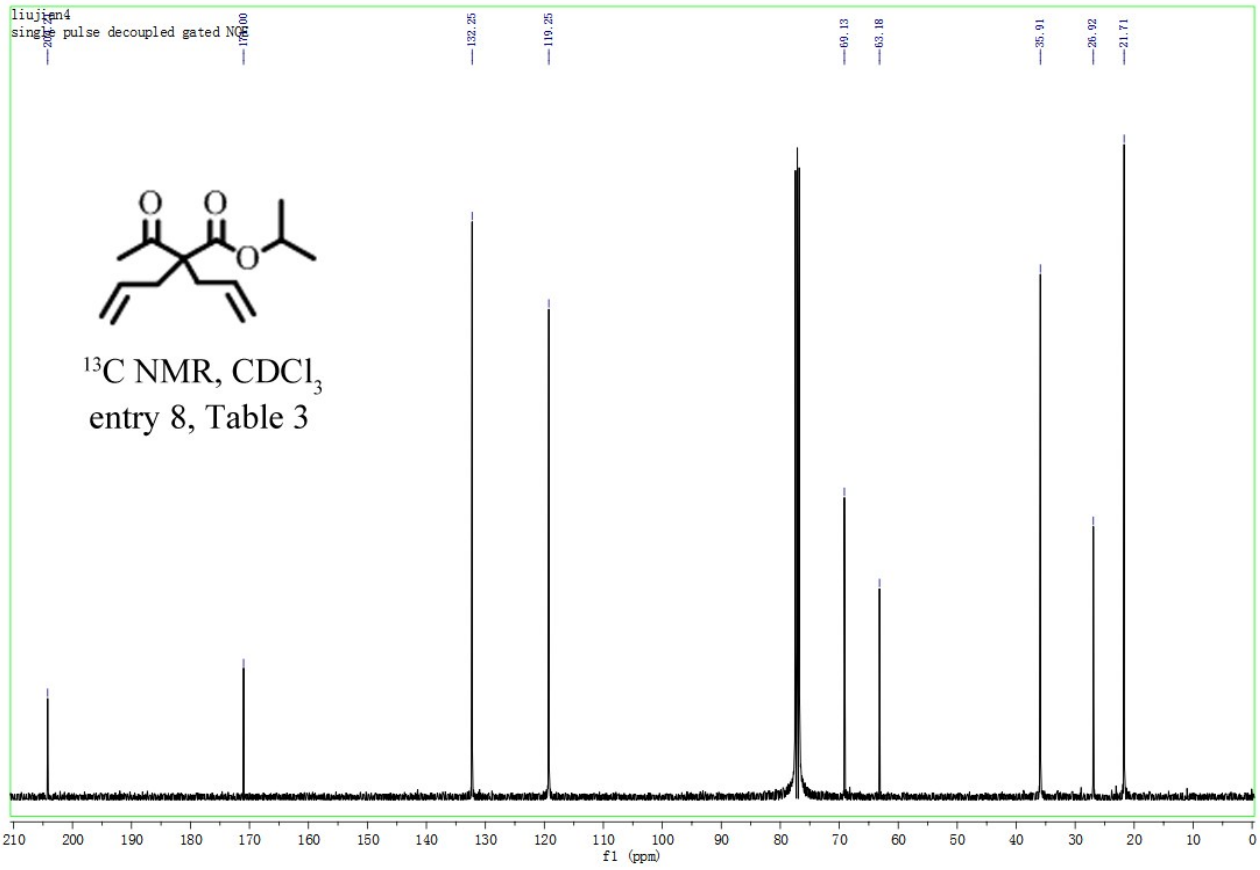
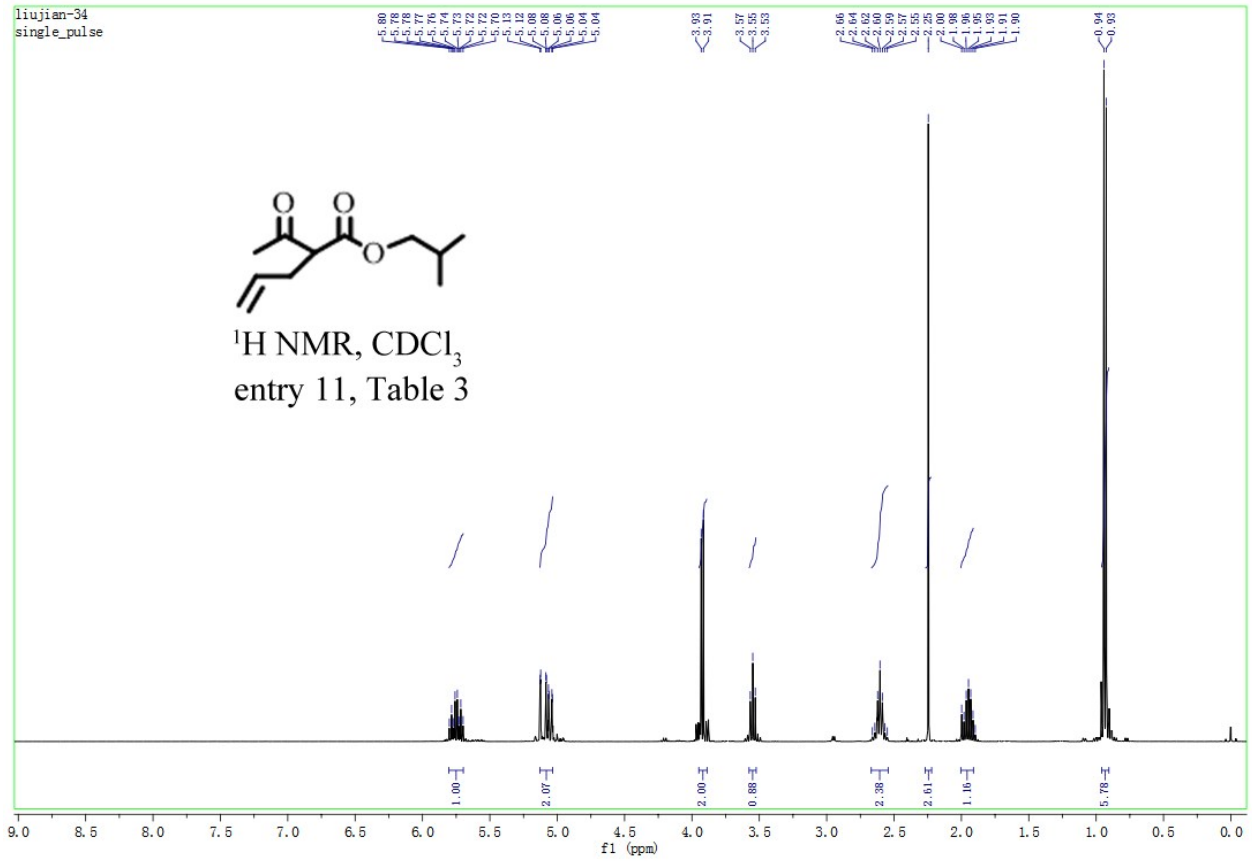
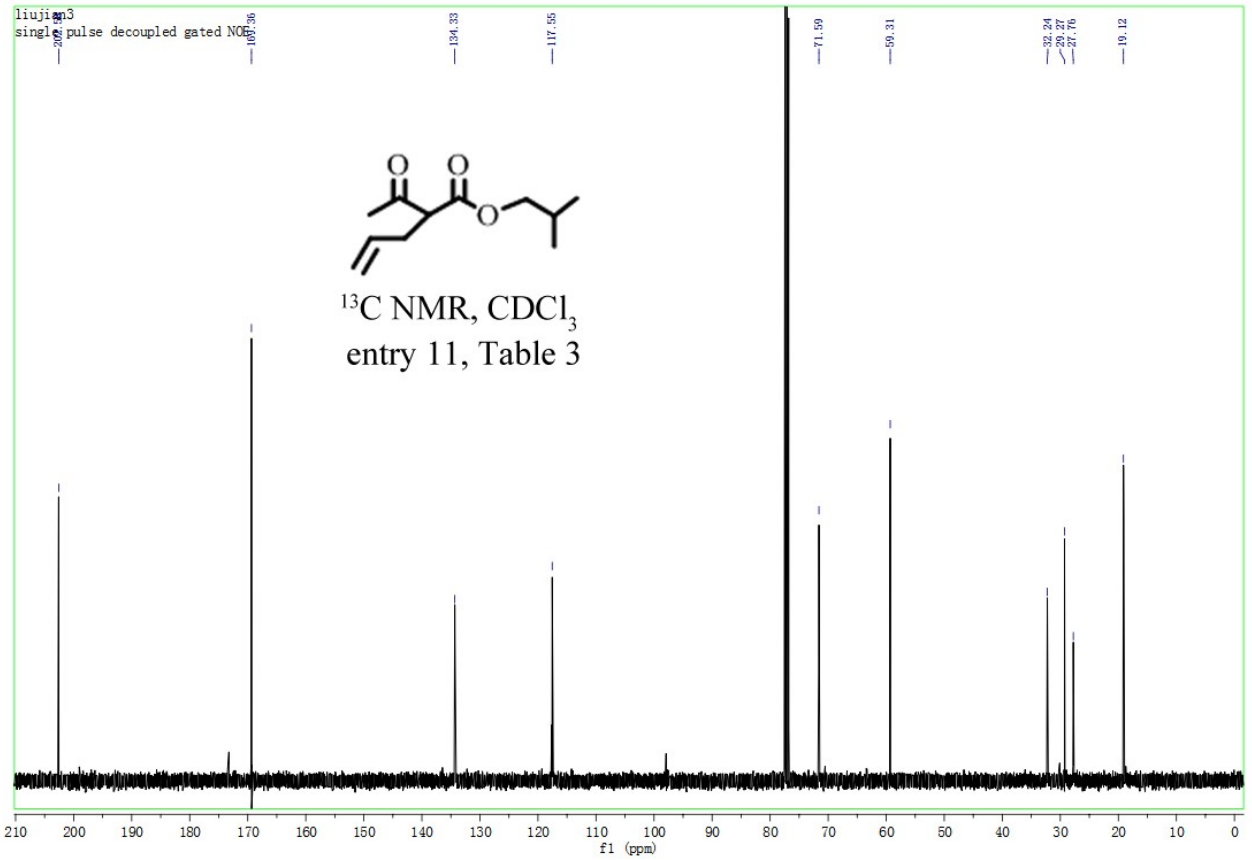


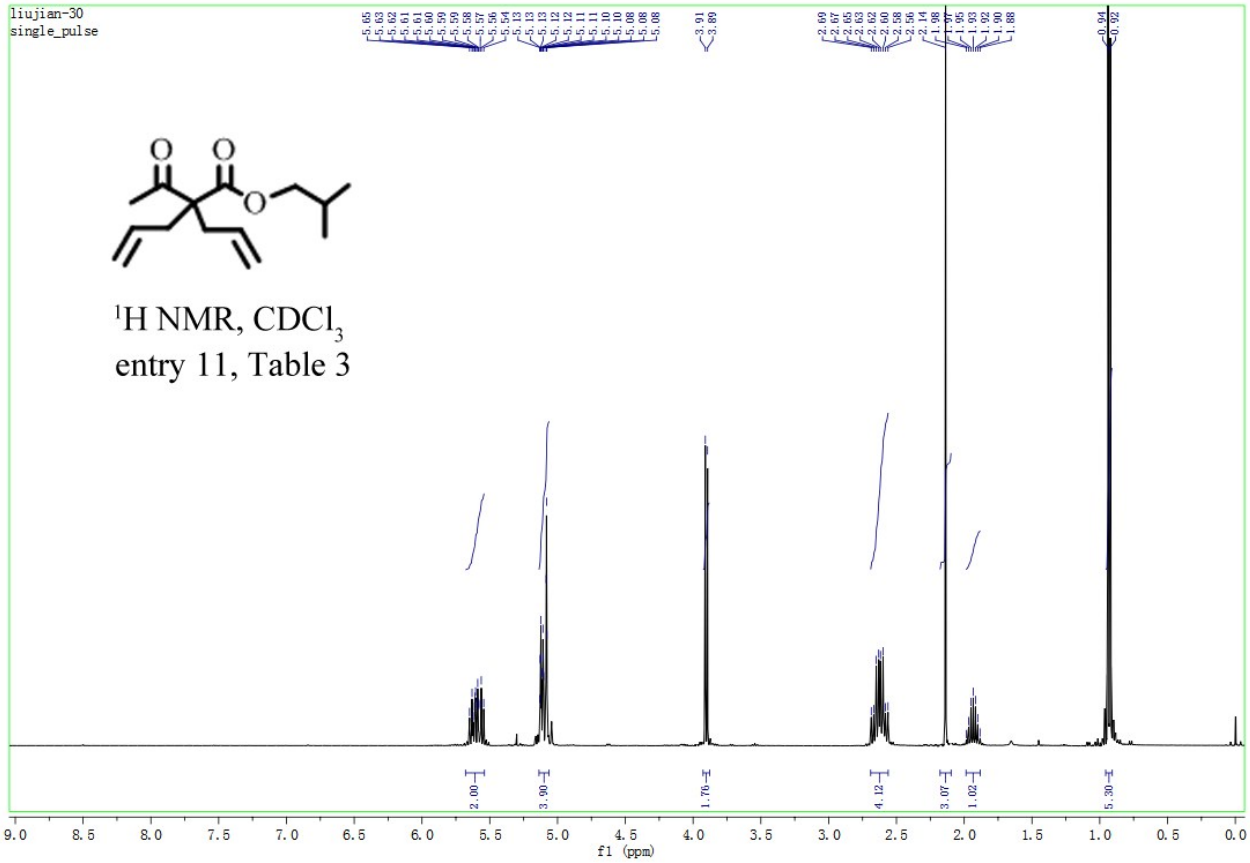


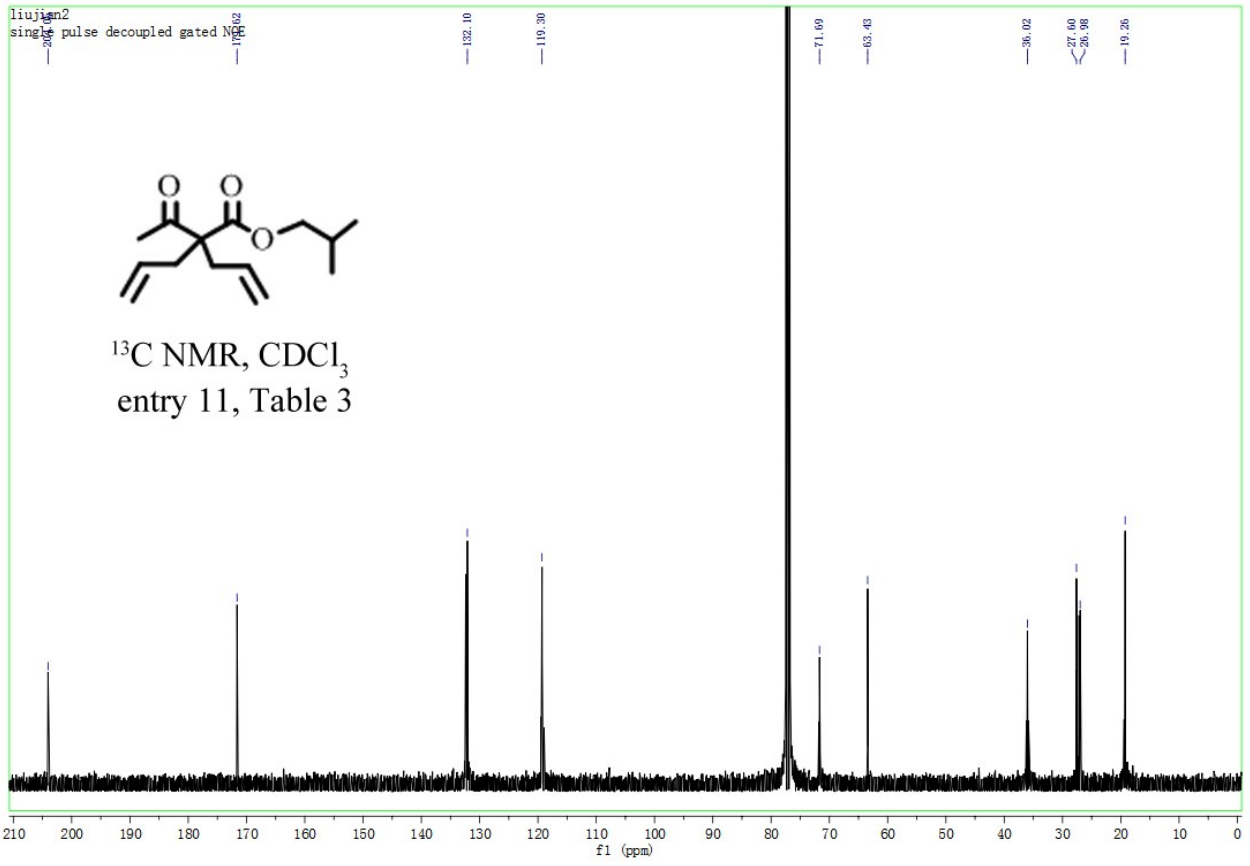
Isobutyl 2-acetylpent-4-enoate



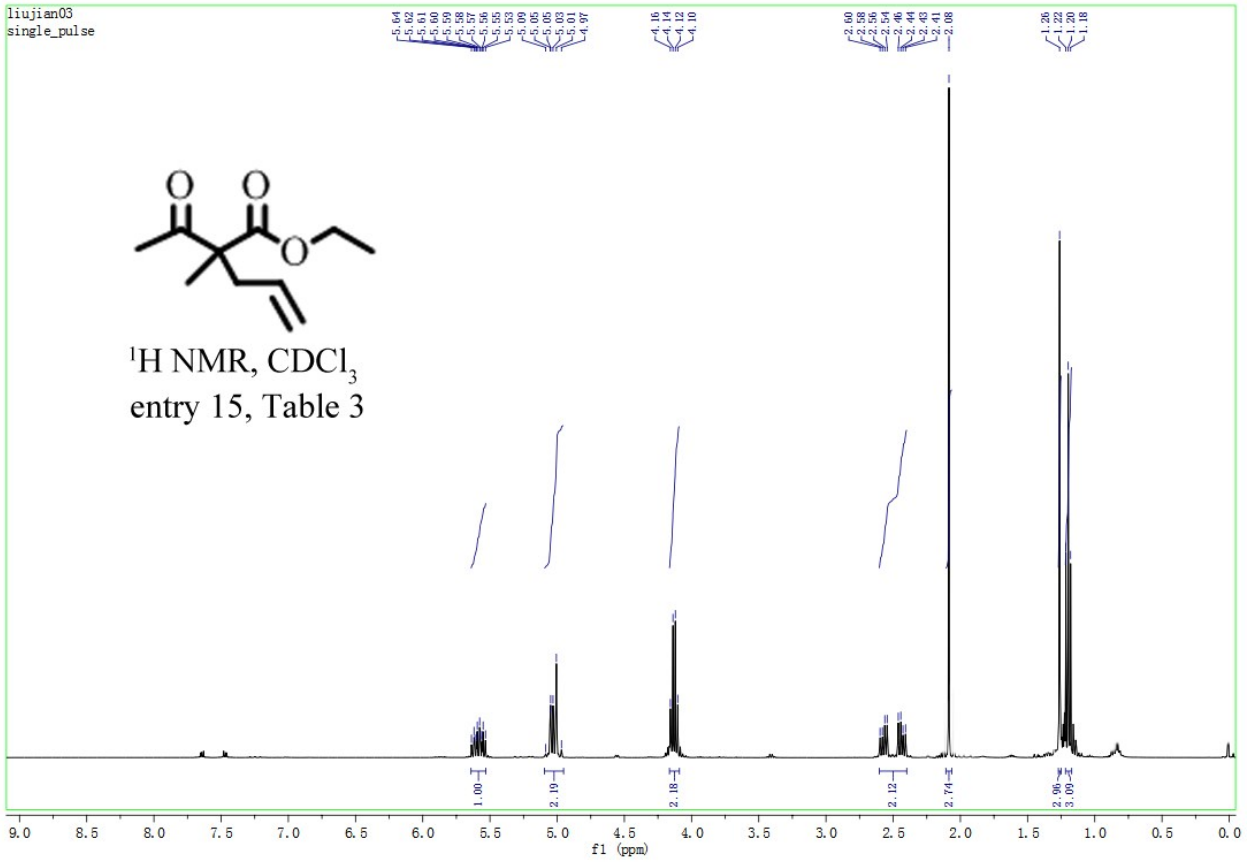


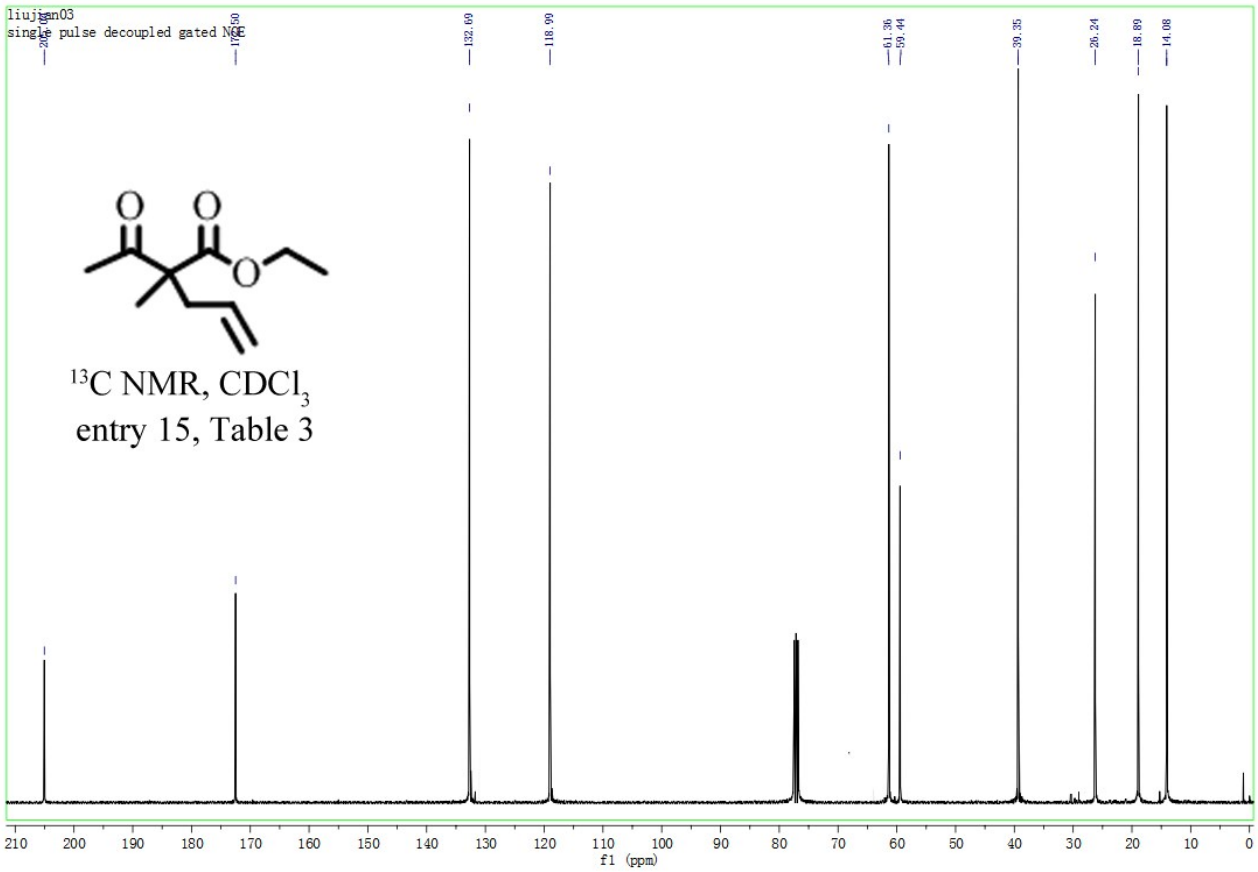
Isobutyl 2-acetyl-2-allylpent-4-enoate



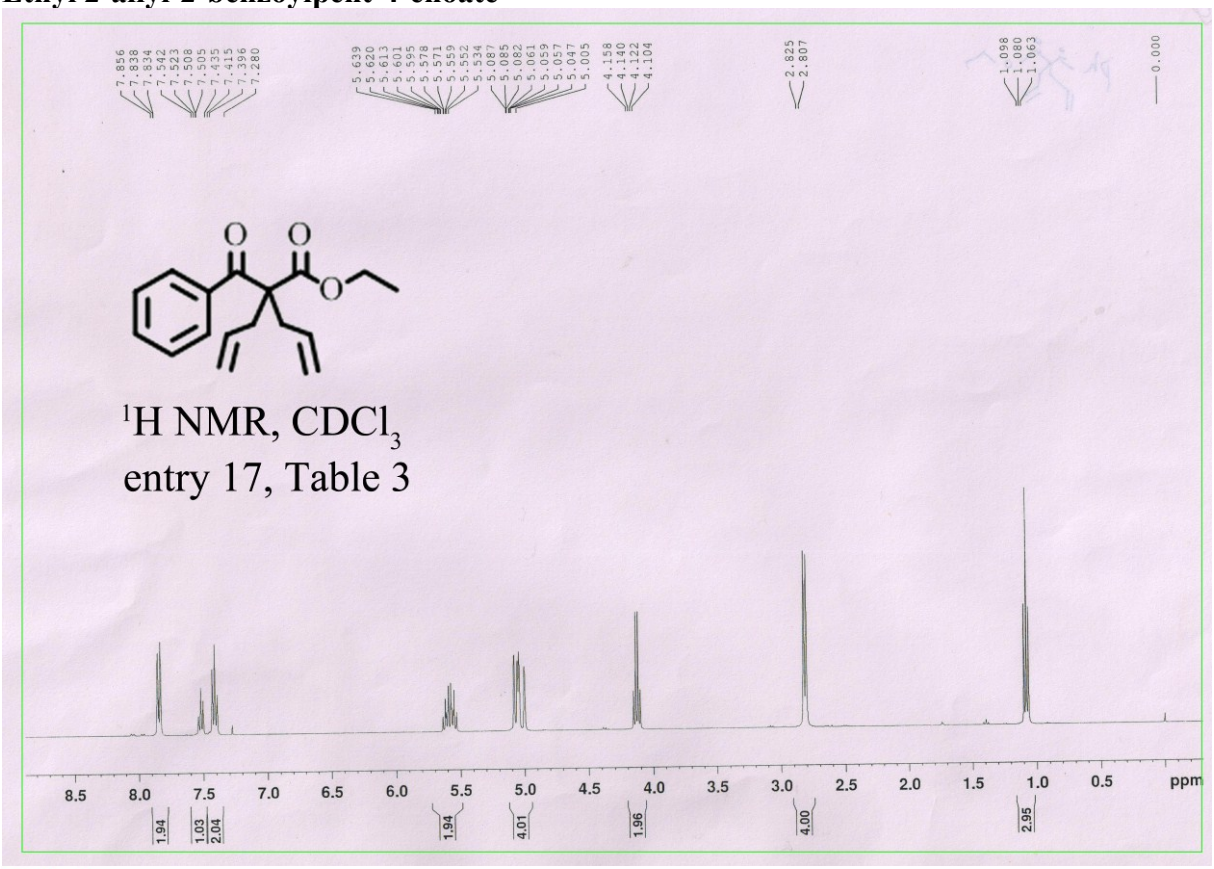


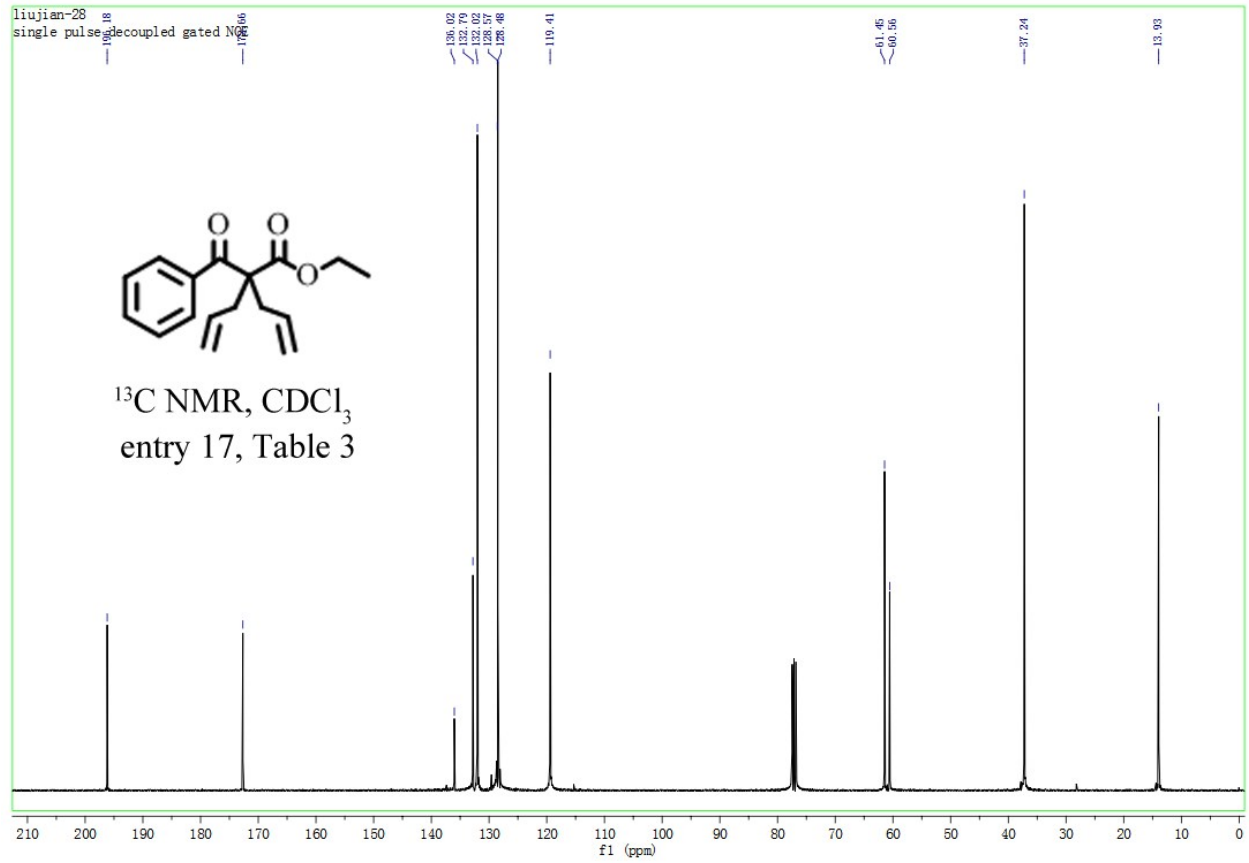
Ethyl 2-acetyl-2-methylpent-4-enoate



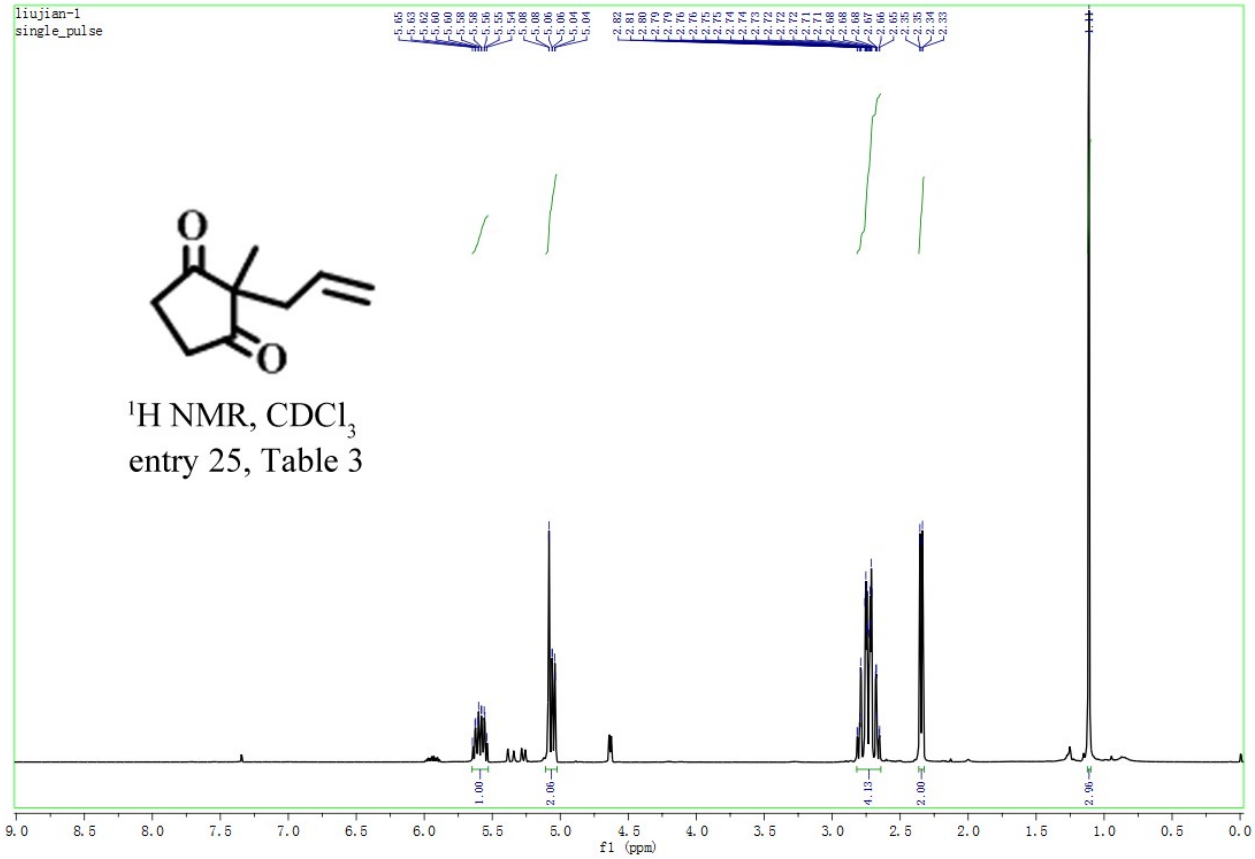


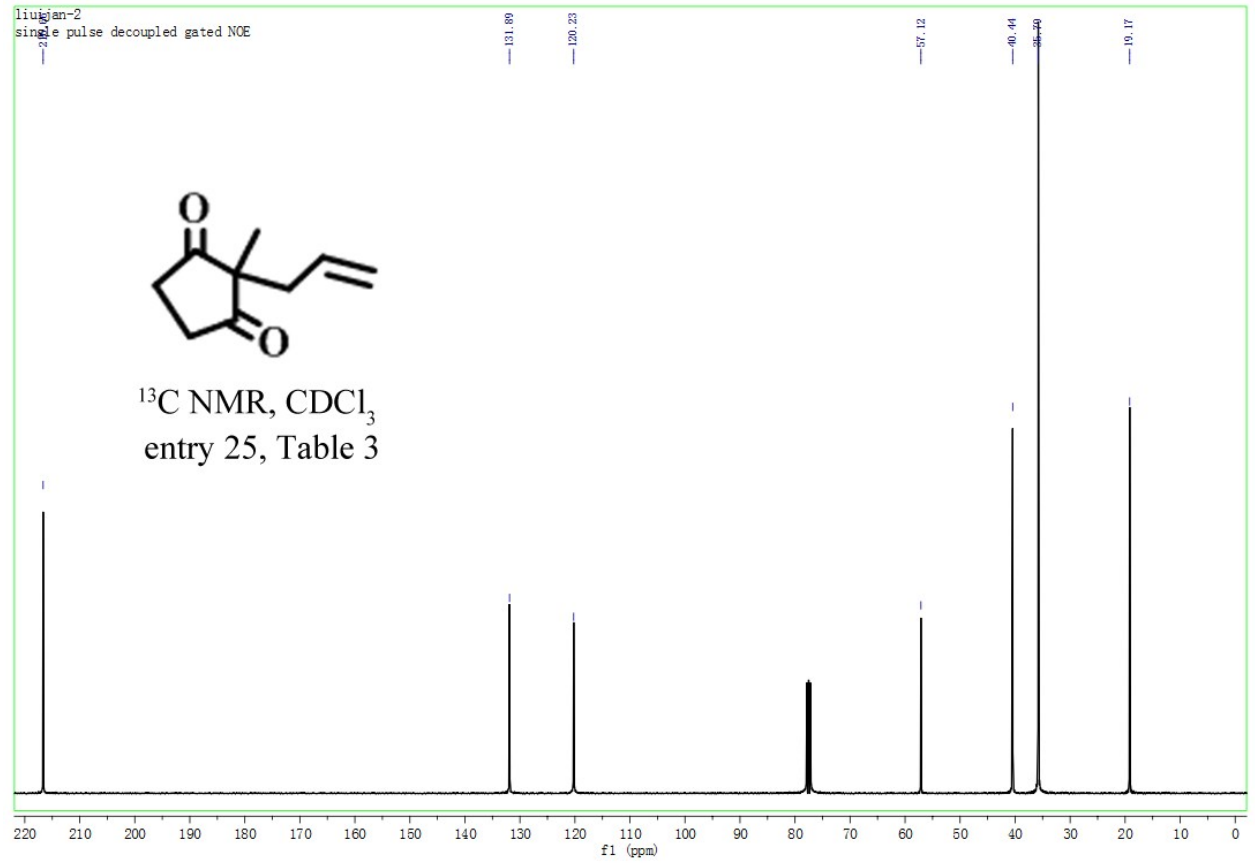
Ethyl 2-allyl-2-benzoylpent-4-enoate





2-allyl-2-methylcyclopentane-1, 3-dione





Diethyl 2-allylmalonate