

Supplementary Information

1. X-ray Crystallography

The major product of dimethyl 2-phenylsuccinate was isolated by column chromatography which was characterization by means of the single crystal X-ray diffraction method (Figure S1).

Table S1 The crystal data and structure refinement for dimethyl 2-phenylsuccinate

	Dimethyl 2-phenylsuccinate
Empirical formula	C ₁₂ H ₁₄ O ₄
Formula weight	222.23
Crystal system	Monoclinic
Space group	P2(1)/n
<i>a</i> (Å)	5.8802(4)
<i>b</i> (Å)	25.3608(19)
<i>c</i> (Å)	8.2156(6)
α (°)	90
β (°)	109.663(2)
γ (°)	90
<i>V</i> (Å ³)	1153.72(14)
<i>Z</i>	4
<i>d</i> _{calc} (g cm ⁻³)	1.279
μ (Mo-K α) (mm ⁻¹)	0.096
<i>T</i> (K)	296(2)
λ	0.71073
Total reflections	13133
Unique reflections (<i>R</i> _{int})	0.0265
<i>R</i> ₁ [<i>I</i> > 2 σ (<i>I</i>)]	0.0514
<i>wR</i> ₂ (all data)	0.1301
<i>F</i> (000)	472

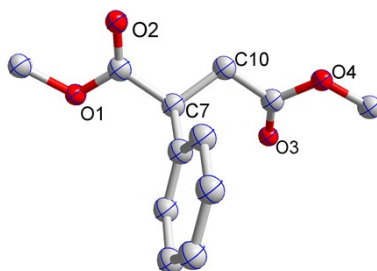


Figure S1 The molecular structures of dimethyl 2-phenylsuccinate (H-atoms and the solvent molecules were omitted for clarity).

2. IR spectral characterization

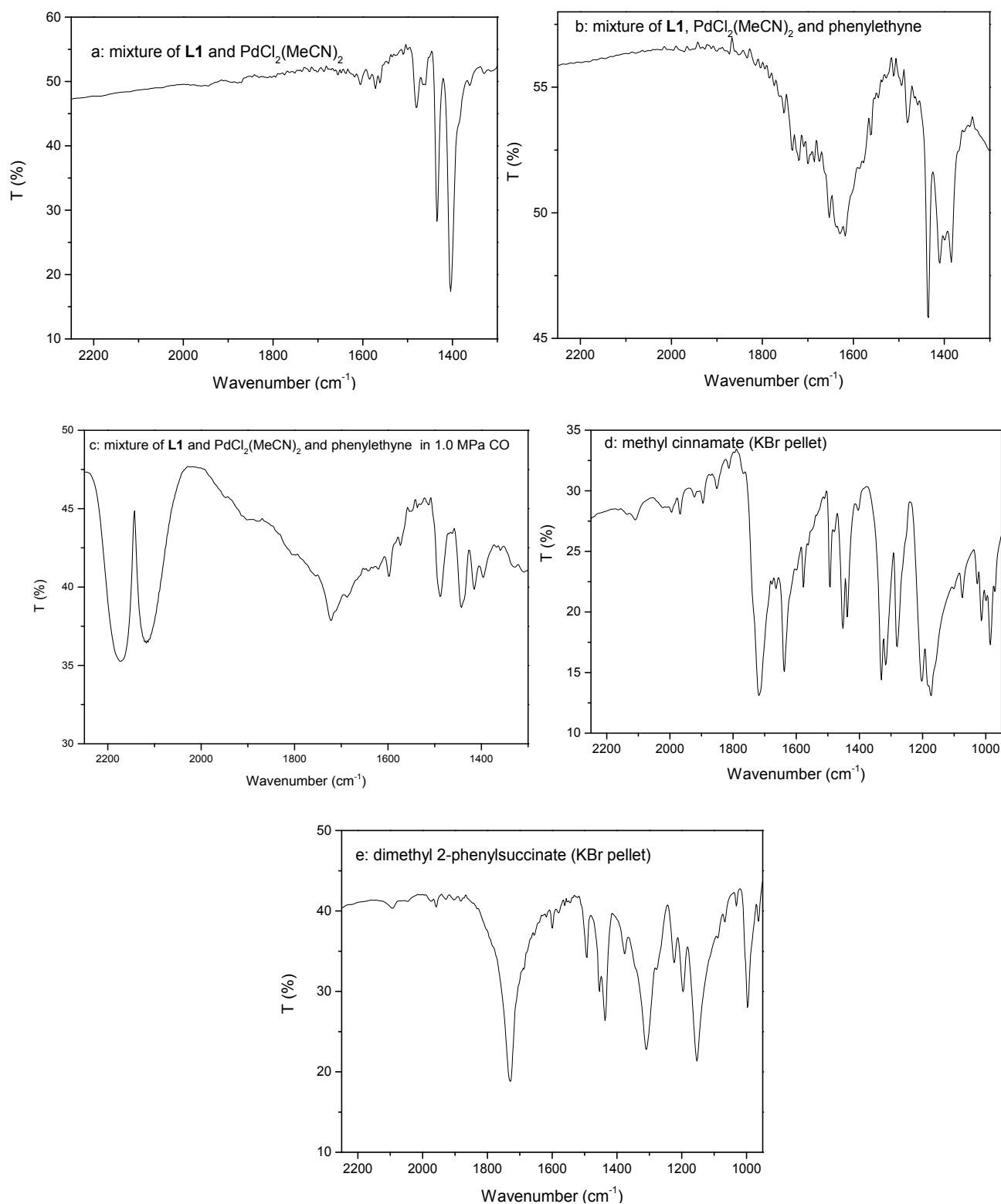
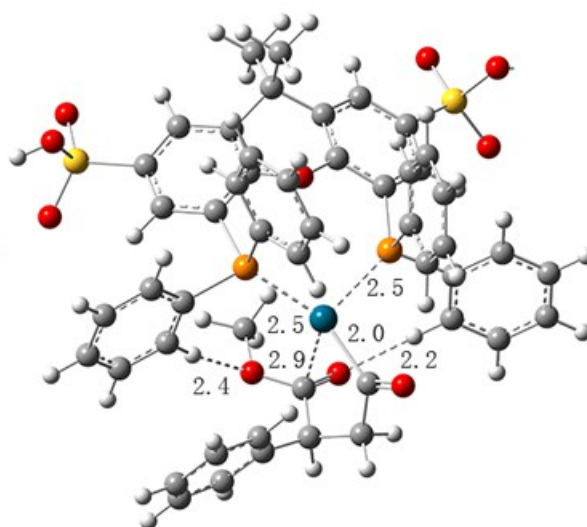


Figure S2 The FT-IR spectra of (a) **L1** and $\text{PdCl}_2(\text{MeCN})_2$ recorded at room temperature in air atmosphere (KBr pellet); (b) **L1** and $\text{PdCl}_2(\text{MeCN})_2$ mixed with phenylacetylene recorded at room temperature in air atmosphere (KBr pellet); (c) **L1** and $\text{PdCl}_2(\text{MeCN})_2$ mixed with phenylacetylene recorded in 1.0 MPa CO at 30 °C in high pressure IR cell; (d) methyl cinnamate recorded at room temperature in air atmosphere (KBr pellet); (e) dimethyl 2-phenylsuccinate recorded at room temperature in air atmosphere (KBr pellet).

3. Computational data



F

Table S2 The Cartesian coordinates of the optimized structure of **F**

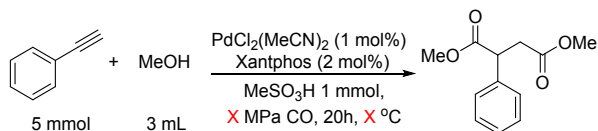
C	-5.48317200	-1.50075300	1.11095500
C	-4.10895900	-1.59145300	0.84642100
C	-3.43111800	-0.39979300	0.55787600
C	-4.03074100	0.86295400	0.86295400
C	-5.40272700	0.92040200	0.80631400
C	-6.10299600	-0.24934000	1.07870100
C	-3.19070900	2.06540200	0.10860500
C	-1.75872300	1.85061000	0.58986200
C	-1.23778100	0.54203800	0.57230700
C	0.10597500	0.22649700	0.84514400
C	0.97058000	1.26998100	1.18273700
C	0.44203900	2.56168600	1.23214200
C	-0.88394900	2.88187400	0.93965200
H	-6.07595500	-2.38346600	1.34470200
H	-5.97041000	1.84965800	0.80436700
H	2.01721600	1.08393700	1.42023600
H	-1.21391200	3.91625400	0.99243900
S	1.56132500	3.92892900	1.67861000
O	2.36585200	4.10027000	0.10298600
O	2.69545800	3.47414200	2.70530000
O	0.73029000	5.25859400	1.95715700
C	-3.77865400	3.38386000	0.61805200
H	-3.83622500	3.40348800	1.71254600
H	-3.17895200	4.23704200	0.27737400
H	-4.78847200	3.52864200	0.22107400
C	-3.15152500	2.09353600	-1.44452200
H	-2.54575400	2.94087500	-1.79358200
H	-2.72332900	1.16713500	-1.85158400
H	-4.17223300	2.20046900	-1.83174300
O	-2.05391100	-0.52319500	0.27020400
S	-7.95763400	-0.13209400	1.38181200
O	-8.58166400	-1.09088000	0.23757700
O	-8.22798600	1.45458900	1.18092200
O	-8.15045500	-0.68215900	2.88922100

P	0.59967200	-1.58871100	0.76686500
P	-3.14207300	-3.20109100	0.91237900
C	2.39735800	-1.43443800	1.26377900
C	2.69204700	-1.54691900	2.63531100
C	3.42231300	-1.15510100	0.34535300
C	4.00297000	-1.33428900	3.08451000
H	1.90243700	-1.80457000	3.34493900
C	4.73703000	-0.97187100	0.79653600
H	3.19277700	-1.08354900	-0.71632500
C	5.02489200	-1.04742400	2.16782000
H	4.22145300	-1.39553400	4.14634700
H	5.52835200	-0.75906700	0.08314900
H	6.03989600	-0.88509200	2.51990800
C	0.65438000	-1.84367500	-1.08970200
C	0.50123200	-3.15841500	-1.56140600
C	0.79577700	-0.78851500	-2.00646500
C	0.50106400	-3.41724300	-2.93830000
H	0.36052600	-3.97318600	-0.84971000
C	0.78921900	-1.04822900	-3.38383200
H	0.89881500	0.23593000	-1.65062200
C	0.64466900	-2.36301800	-3.85110400
H	0.35957300	-4.43488400	-3.29161500
H	0.89090400	-0.22666800	-4.08751300
H	0.62787700	-2.56240400	-4.91909000
C	-4.43340900	-4.37203500	1.58309500
C	-5.39037700	-4.99226400	0.76440800
C	-4.46628700	-4.56645000	2.97464600
C	-6.37323000	-5.81158300	1.33486900
H	-5.38116800	-4.82334900	-0.31054700
C	-5.45447500	-5.38281200	3.54140800
H	-3.74035100	-4.06554500	3.61529700
C	-6.40613800	-6.00745400	2.72305700
H	-7.12295600	-6.27434500	0.70014500
H	-5.48908200	-5.51344800	4.61900700
H	-7.17987400	-6.62914300	3.16483800
Pd	-0.79083700	-3.41630600	1.80053400
C	-3.02716300	-3.69380300	-0.89235400
C	-2.49430600	-4.96648000	-1.17988400
C	-3.42805100	-2.85190400	-1.94060500
C	-2.39383900	-5.39555100	-2.50922600
H	-2.16200700	-5.61400000	-0.36702300
C	-3.31295700	-3.28197800	-3.27116800
H	-3.84978100	-1.87196600	-1.72462600
C	-2.80192100	-4.55506500	-3.55800700
H	-1.99942300	-6.38549900	-2.72333800
H	-3.63299600	-2.62681100	-4.07648700
H	-2.72660900	-4.89204200	-4.58875500
C	-0.95804200	-5.34833100	2.43408100
H	3.17810300	4.65057800	0.20109200
C	-0.87392800	-5.68399500	3.93547200
H	-0.40286400	-6.67141500	4.04246400
H	-1.91852700	-5.77496300	4.26877700
C	-0.16589400	-4.65037800	4.82478400
H	-0.36509000	-4.97106500	5.86124700
C	1.34149000	-4.56889100	4.67553700
C	2.03135200	-5.02202300	3.53902800
C	2.08783700	-4.06735900	5.75829300
C	3.43252100	-4.97457900	3.48967100
H	1.48614700	-5.41099100	2.68304900

C	3.48562200	-4.02618800	5.71742000
H	1.56071800	-3.71081500	6.64259000
C	4.16538400	-4.48673800	4.57879400
H	3.94799100	-5.31698600	2.59703900
H	4.04232500	-3.64442900	6.56918500
H	5.25089400	-4.45726300	4.53808400
C	-0.91475200	-3.32258300	4.73728400
O	-0.12188800	-2.22019900	4.56357700
C	-0.82892000	-0.94504300	4.44597500
H	-0.05379900	-0.19769500	4.27096200
H	-1.53060300	-0.99452200	3.60418000
H	-1.38388000	-0.73265200	5.36377600
O	-2.13657400	-3.23445100	4.93097900
O	-1.11015700	-6.28458600	1.62427300

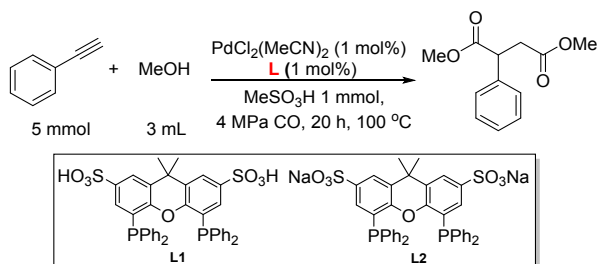
4. The selected screening data

Table S3 The effects of pressure and temperature on Pd-catalyzed bis-methoxycarbonylation of phenylacetylene with MeOH^[a]



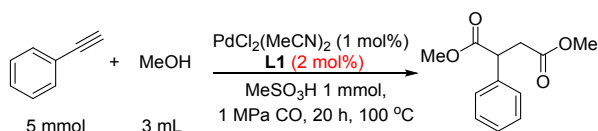
Entry	Temperature Pressure	Conv. (%) ^[a]	Sel. L-ester (%) ^[a]	Sel. B-ester (%) ^[a]	Sel. diester (%) ^[a]
1	100°C 4MPa	100	5	9	86
2	100°C 2MPa	100	14	2	84
3	100°C 1MPa	100	14	-	86
4	120°C 1MPa	100	13	-	87

[a] Determined by GC. Sel._{L-ester} represents selectivity to linear methyl cinnamate. Sel._{B-ester} represents selectivity to branched methyl 2-phenylacrylate. Sel._{diester} represents selectivity to dimethyl 2-phenylsuccinate.

Table S4 The effect of ligand on Pd-catalyzed bis-methoxycarbonylation of phenylacetylene with MeOH^[a]

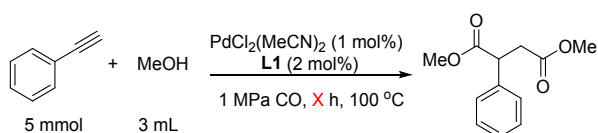
Entry	Ligand	Conv. (%) ^[a]	Sel. L-ester (%) ^[a]	Sel. B-ester (%) ^[a]	Sel. diester (%) ^[a]
1	DPPF	100	28	2	70
2	BINAP	100	12	28	60
3	Xantphos	100	18	-	82
4	L1	100	12	8	80
5	L2	100	14	8	78

[a] Determined by GC. Sel._{L-ester} represents selectivity to linear methyl cinnamate. Sel._{B-ester} represents selectivity to branched methyl 2-phenylacrylate. Sel._{diester} represents selectivity to dimethyl 2-phenylsuccinate.

Table S5 The effect of the amount of **L1** on Pd-catalyzed bis-methoxycarbonylation of phenylacetylene with MeOH^[a]

Entry	Ligand Amount	Conv. (%) ^[a]	Sel. L-ester (%) ^[a]	Sel. B-ester (%) ^[a]	Sel. diester (%) ^[a]
1	0.5 mol%	100	12	14	74
2	1 mol%	100	12	8	80
3	2 mol%	100	10	-	90
4	4 mol%	100	10	-	90

[a] Determined by GC. Sel._{L-ester} represents selectivity to linear methyl cinnamate. Sel._{B-ester} represents selectivity to branched methyl 2-phenylacrylate. Sel._{diester} represents selectivity to dimethyl 2-phenylsuccinate.

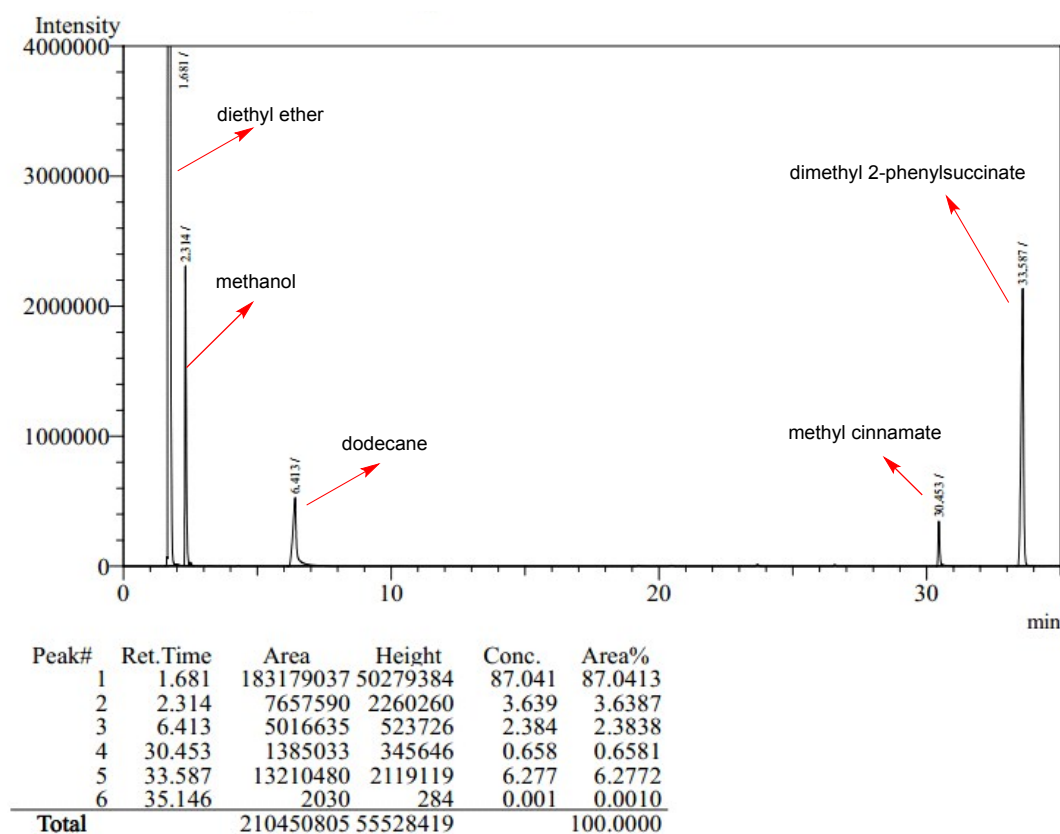
Table S6 The effect of reaction time on Pd-catalyzed bis-methoxycarbonylation of phenylacetylene with MeOH^[a]

Entry	Time (h)	Conv. (%) ^[a]	Sel. _{L-ester} (%) ^[a]	Sel. _{B-ester} (%) ^[a]	Sel. _{diester} (%) ^[a]
1	0.5	100	15	79	5
2	2	100	15	56	29
3	4	100	15	29	56
4	8	100	14	10	76
5	12	100	13	1	86
6	20	100	10	-	90

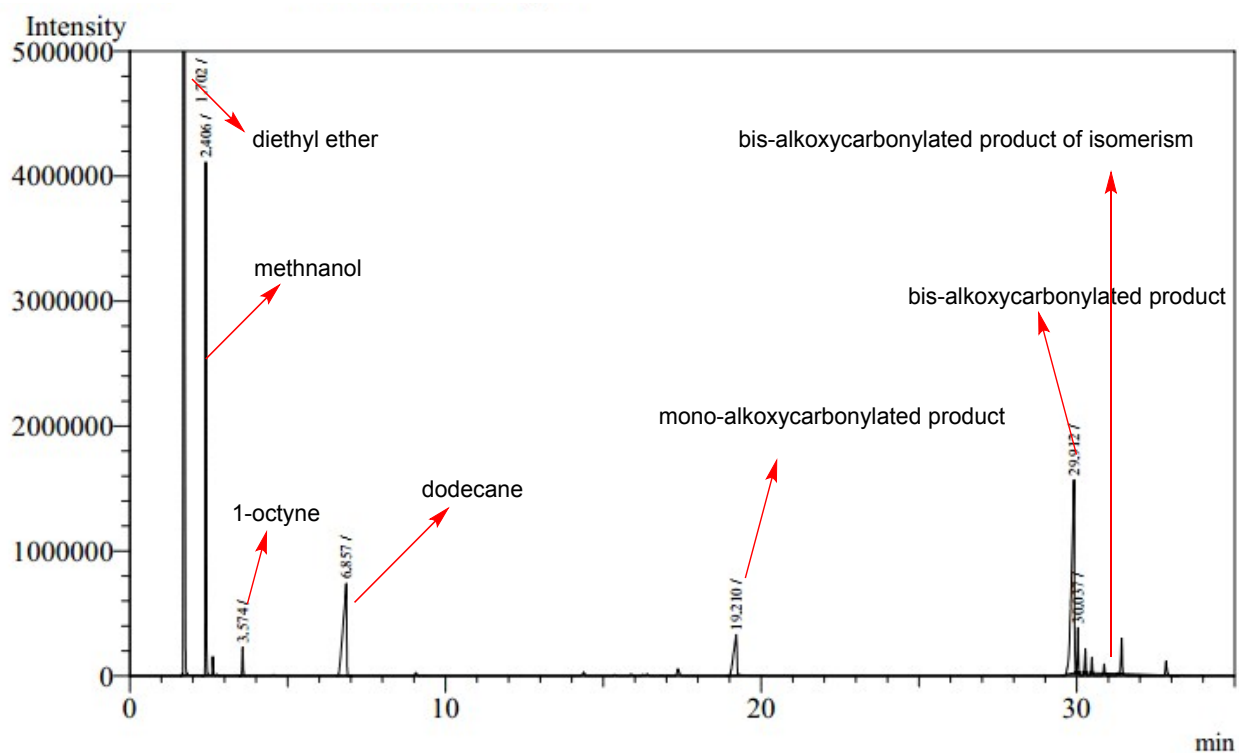
[a] Determined by GC. Sel._{L-ester} represents selectivity to linear methyl cinnamate. Sel._{B-ester} represents selectivity to branched methyl 2-phenylacrylate. Sel._{diester} represents selectivity to dimethyl 2-phenylsuccinate.

5. Gas chromatographic data

The standard GC data of phenylacetylene



The standard GC data of 1-octyne



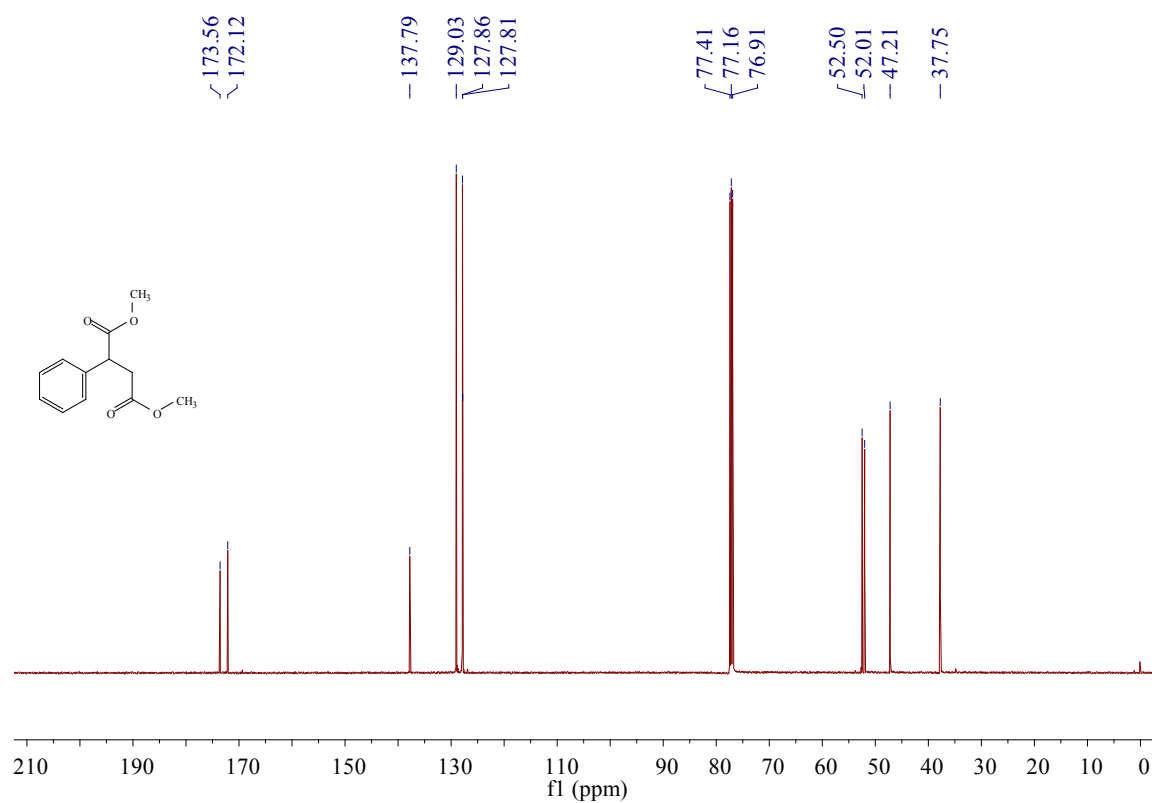
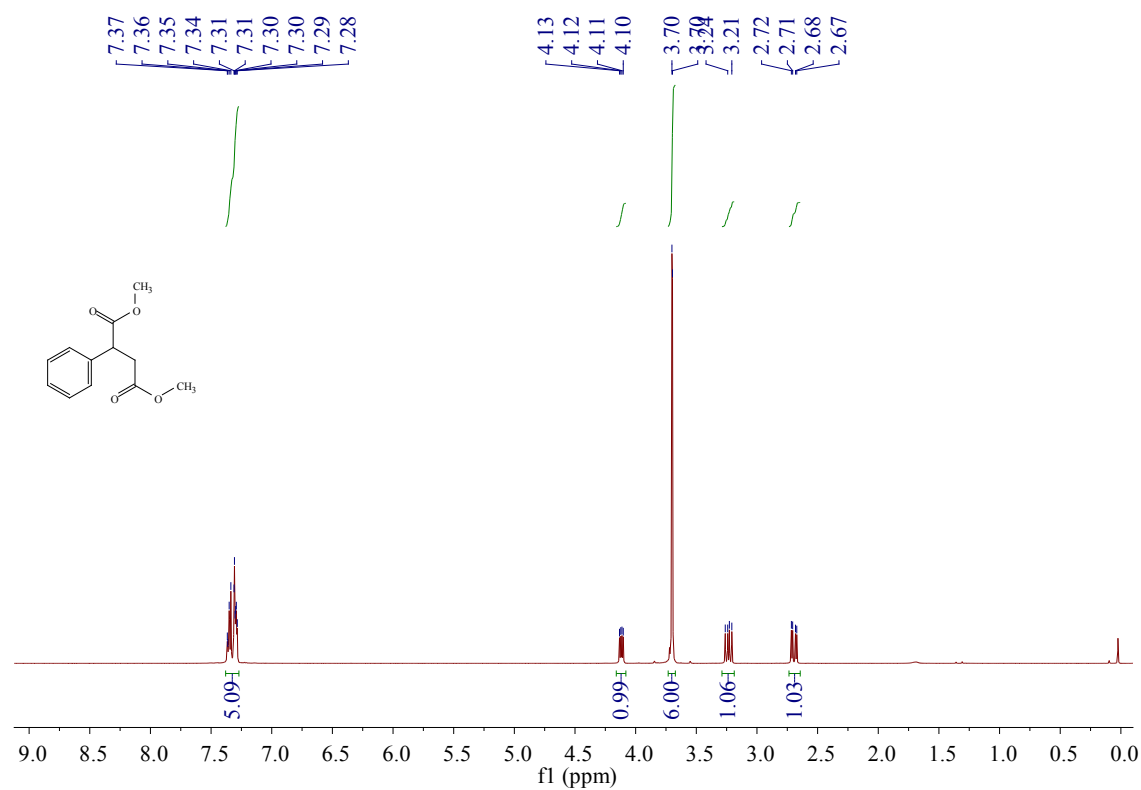
Peak#	Ret.Time	Area	Height	Conc.	Area%
1	1.702	139863328	66284251	84.428	84.4281
2	2.406	6936483	4066519	4.187	4.1872
3	3.574	492341	220464	0.297	0.2972
4	6.857	5786858	739182	3.493	3.4932
5	19.210	2398250	327410	1.448	1.4477
6	29.912	9423805	1497623	5.689	5.6887
7	30.037	758695	357843	0.458	0.4580
Total		165659760	73493292		100.0000

6. Characterization of the products

Dimethyl 2-phenylsuccinate

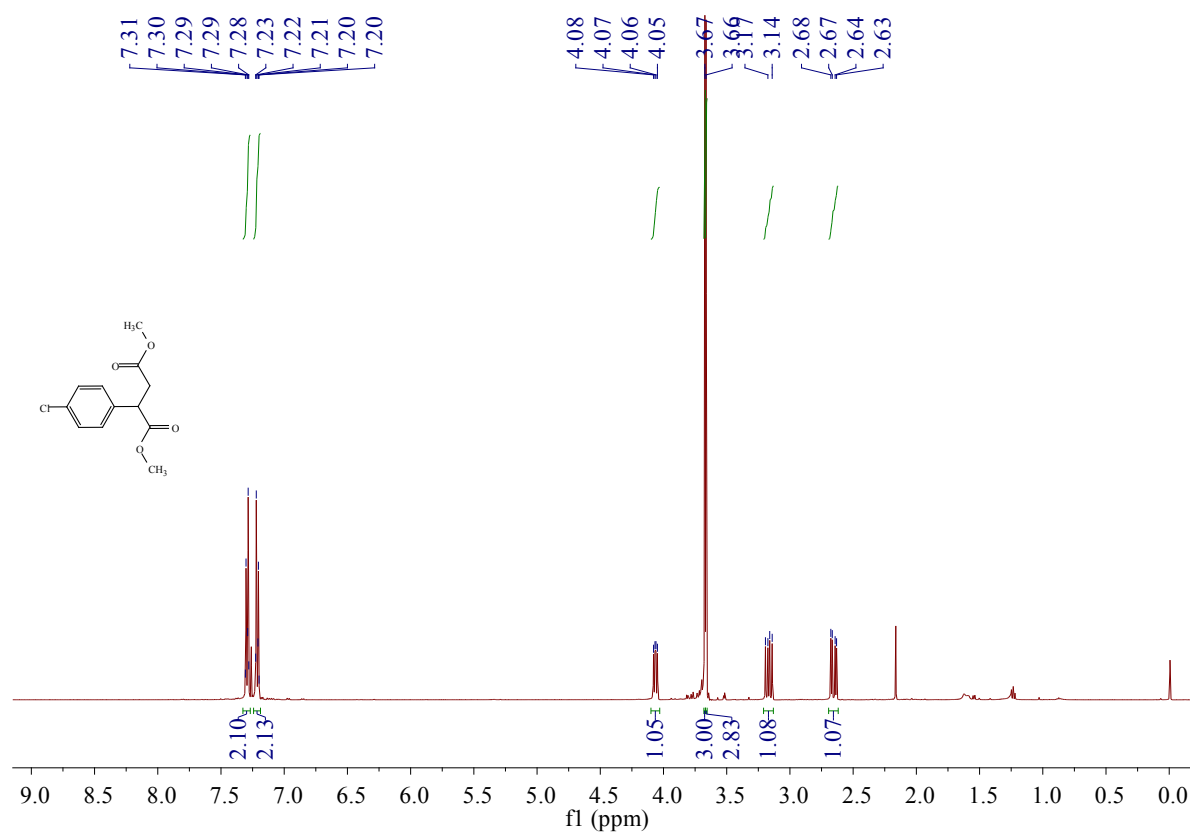
^1H NMR (500 MHz, CDCl_3): δ = 7.28-7.37 (m, 5H, C_6H_5), 4.10-4.13 (m, 1H, PhCHCH_2), 3.70 (s, 6H, 2OCH_3), 3.21-3.26 (m, 1H, CHCH_2), 2.67-2.72 (m, 1H, CHCH_2).

^{13}C NMR (125 MHz, CDCl_3): δ = 173.56, 172.12, 137.79, 129.03, 127.86, 127.81, 52.50, 52.01, 47.21, 37.75.

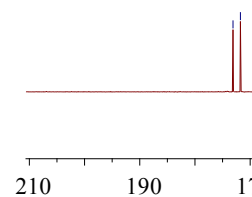
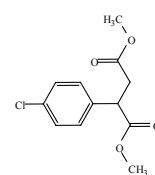


Dimethyl 2-(4-chlorophenyl)succinate

^1H NMR (500 MHz, CDCl_3): δ = 7.20-7.31 (m, 4H, C_6H_4), 4.05-4.08 (t, 1H, J = 5.0 Hz, PhCHCH_2), 3.67 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 3.14-3.18 (m, 1H, CHCH_2), 2.63-2.68 (m, 1H, CHCH_2).



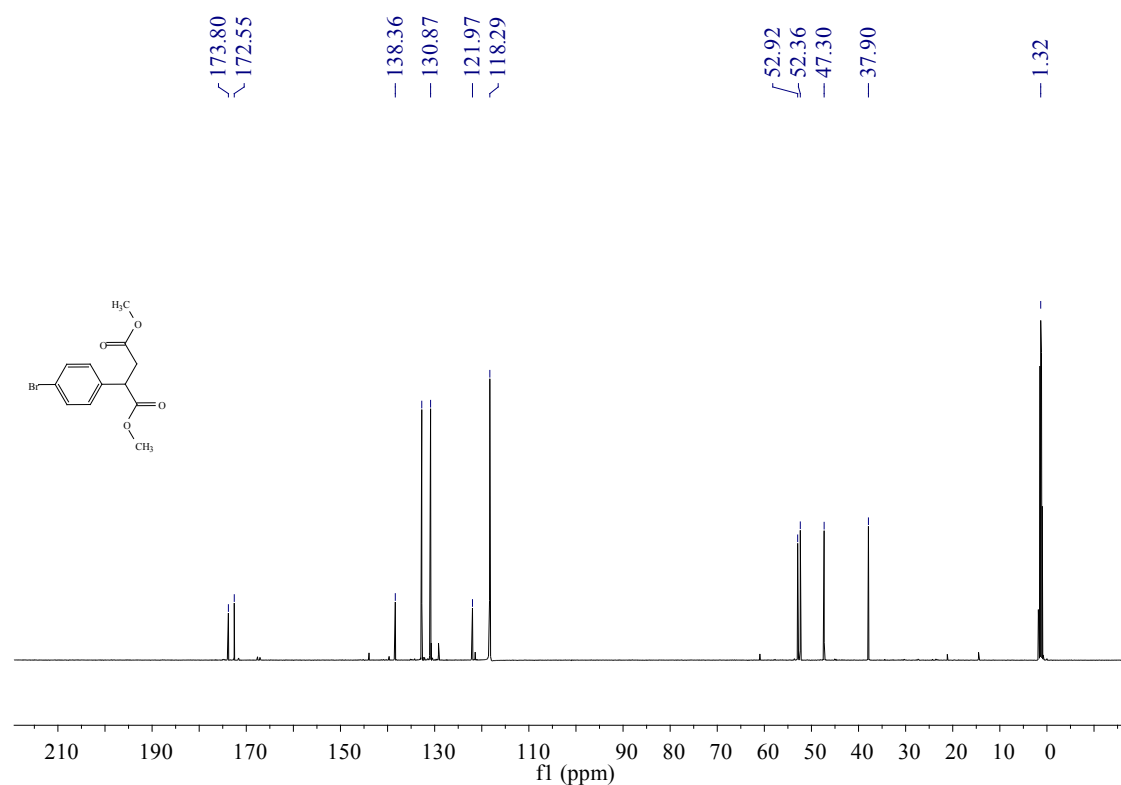
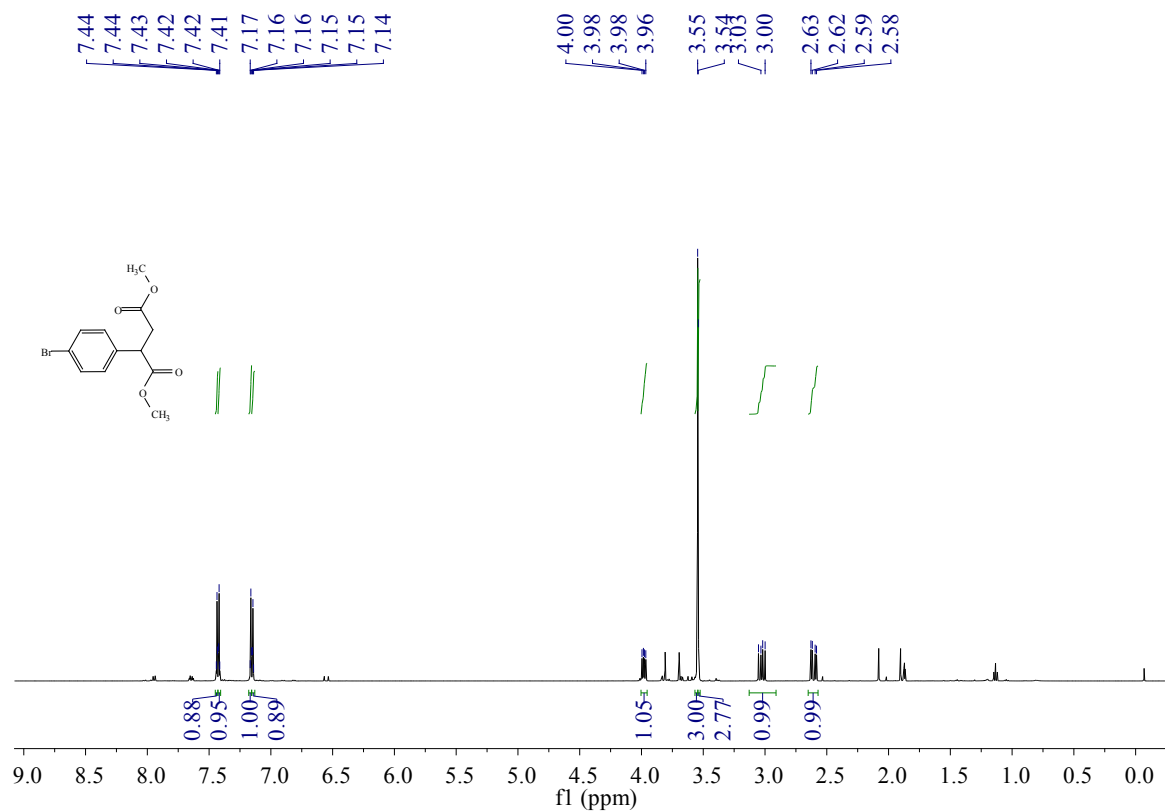
^{13}C NMR
(125
MHz,
 CDCl_3): δ
= 173.11,
171.77,
136.20,
135.95,
133.72,
129.24,
129.14,
52.56,
52.02,
46.54,
37.51.



Dimethyl 2-(4-bromophenyl)succinate

^1H NMR (500 MHz, CD_3CN): δ = 7.41-7.44 (m, 2H, C_6H_4), 7.14-7.17 (m, 2H, C_6H_4), 3.96-4.00 (t, 1H, J = 5.0 Hz, PhCHCH_2), 3.55 (s, 3H, OCH_3), 3.54 (s, 3H, OCH_3), 3.00-3.05 (m, 1H, CHCH_2), 2.58-2.63 (m, 1H, CHCH_2).

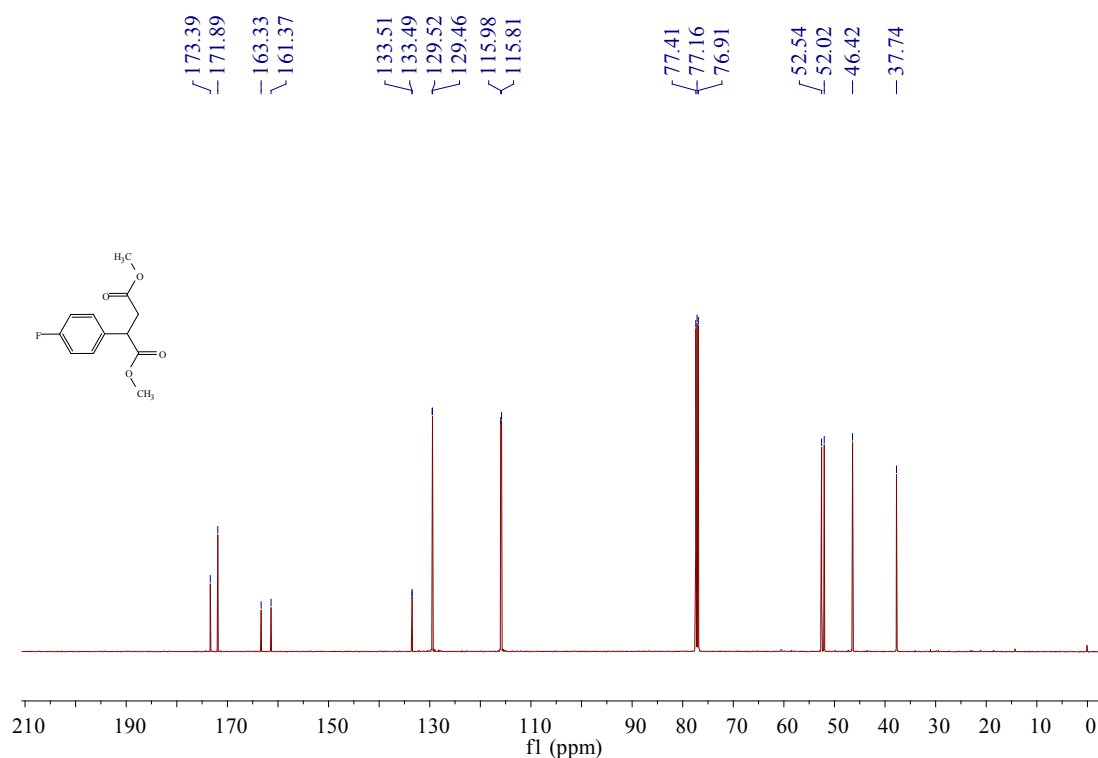
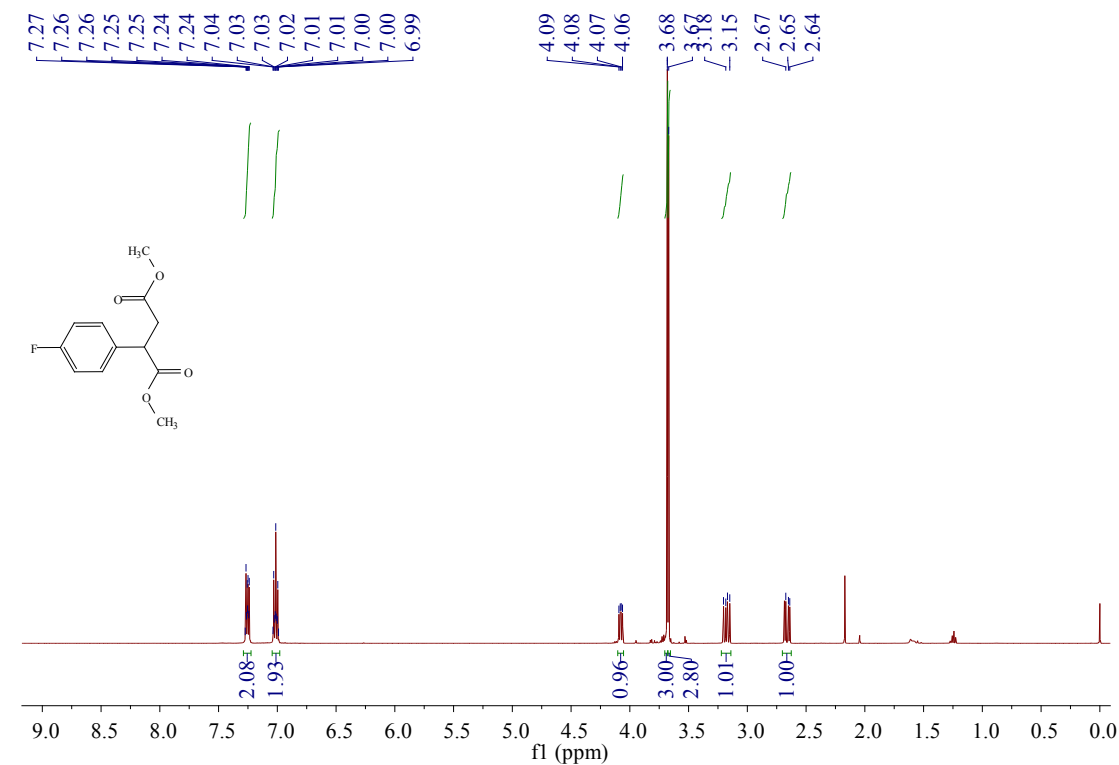
^{13}C NMR (125 MHz, CD_3CN): δ = 173.80, 172.55, 138.36, 130.87, 121.97, 118.29, 52.92, 52.36, 47.30, 37.90.



Dimethyl 2-(4-fluorophenyl)succinate

^1H NMR (500 MHz, CDCl_3): δ = 7.24-7.27 (m, 2H, C_6H_4), 6.99-7.04 (m, 2H, C_6H_4), 4.06-4.09 (t, 1H, J = 5.0 Hz, PhCHCH_2), 3.68 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.15-3.20 (m, 1H, CHCH_2), 2.64-2.67 (m, 1H, CHCH_2).

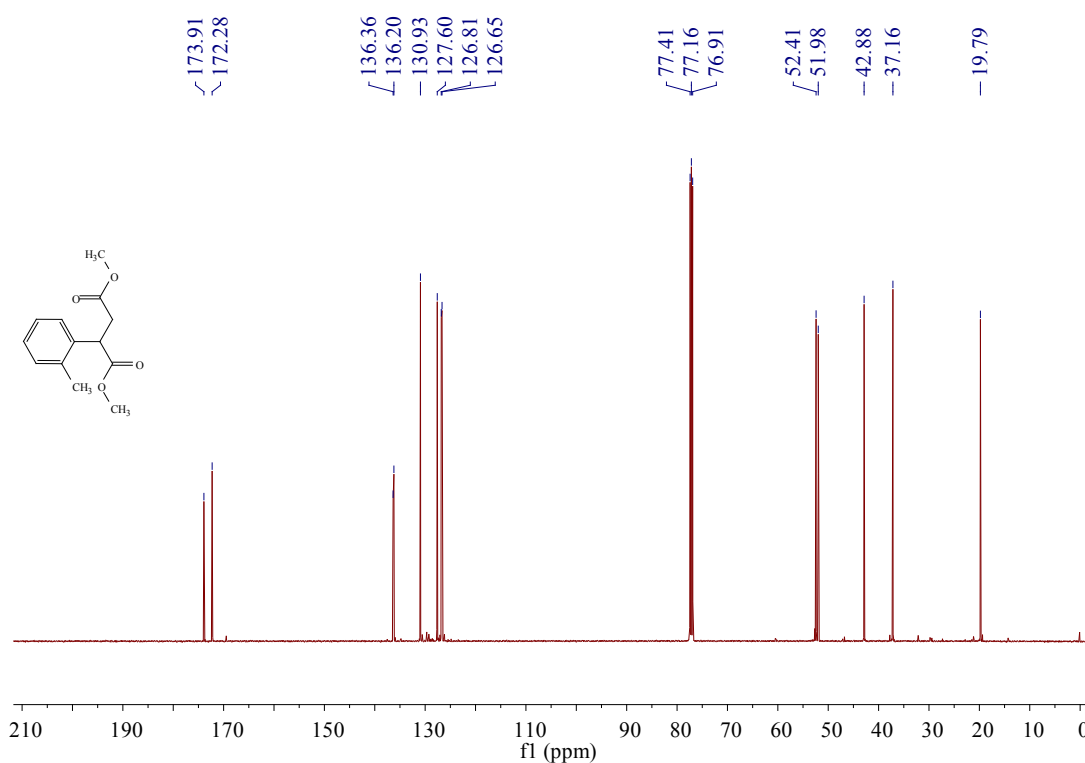
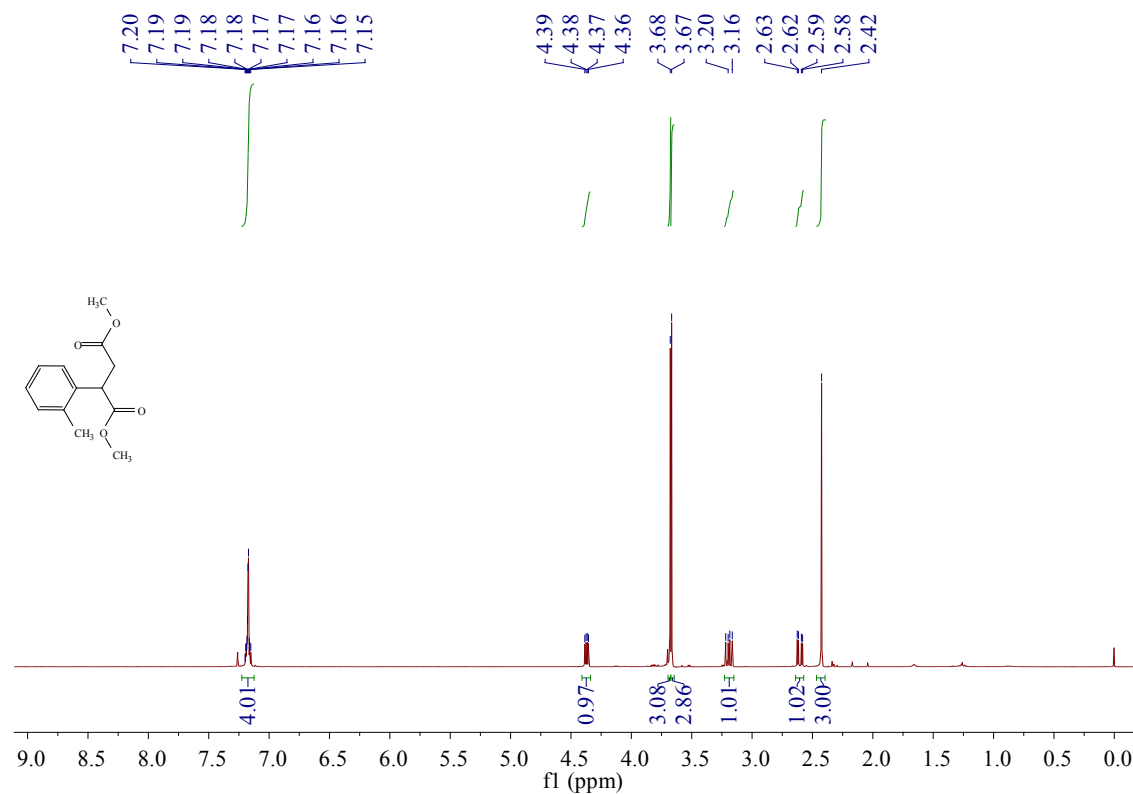
^{13}C NMR (125 MHz, CDCl_3): δ = 173.39, 171.89, 163.33, 161.37, 133.51, 133.49, 129.52, 129.46, 115.98, 115.81, 52.54, 52.02, 46.42, 37.74.



Dimethyl 2-(*o*-tolyl)succinate

^1H NMR (500 MHz, CDCl_3): δ = 7.15-7.20 (m, 4H, C_6H_4), 4.36-4.39 (t, 1H, J = 5.0 Hz, PhCHCH_2), 3.68 (s, 3H, OCH_3), 3.67 (s, 3H, OCH_3), 3.16-3.22 (m, 1H, CHCH_2), 2.58-2.63 (m, 1H, CHCH_2).

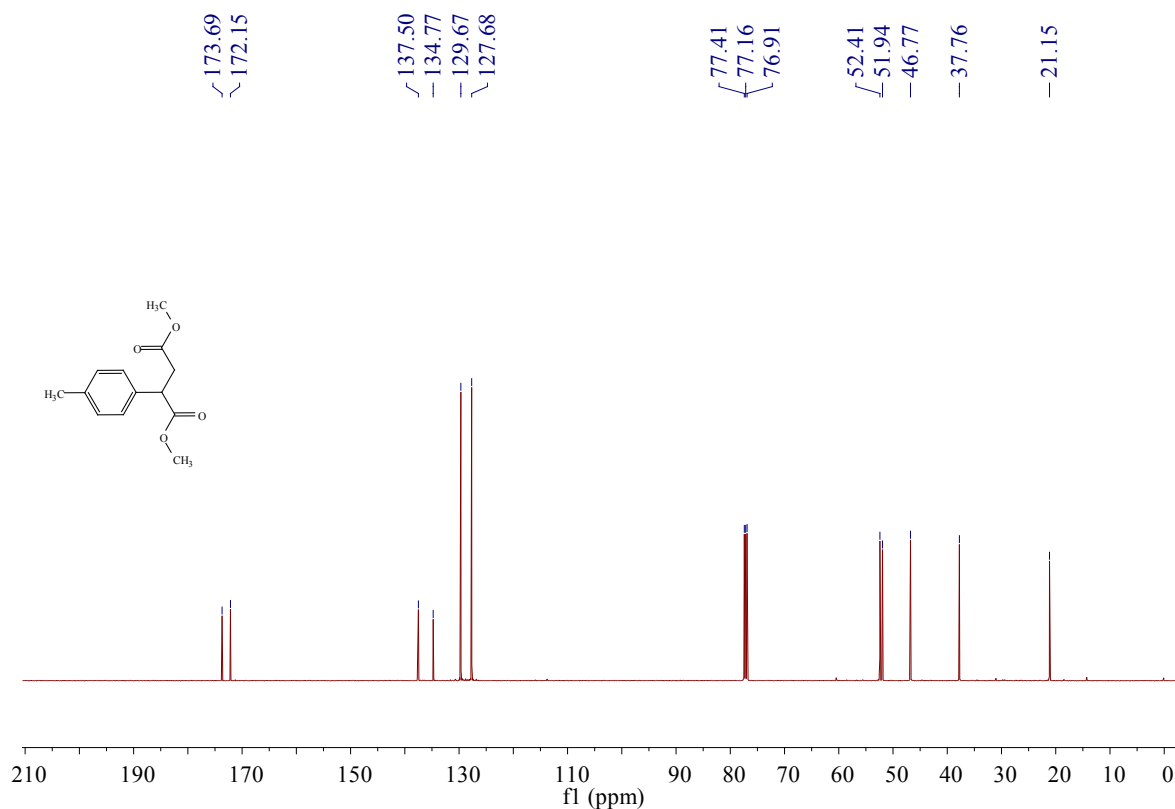
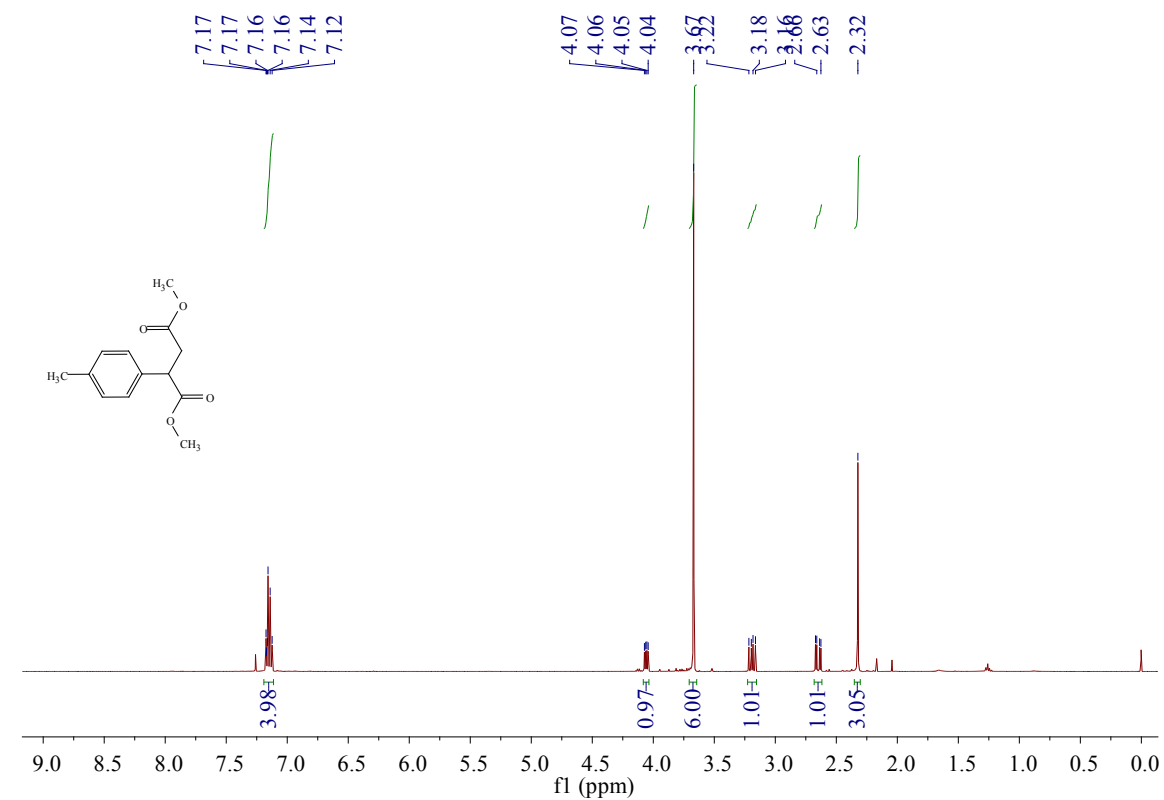
^{13}C NMR (125 MHz, CDCl_3): δ = 173.91, 172.28, 136.36, 136.20, 130.93, 127.60, 126.81, 126.65, 52.41, 51.98, 42.88, 37.16, 19.79.



Dimethyl 2-(*p*-tolyl)succinate

^1H NMR (500 MHz, CDCl_3): δ = 7.12-7.17 (m, 4H, C_6H_4), 4.04-4.07 (t, 1H, J = 5.0 Hz, PhCHCH_2), 3.67 (s, 6H, 2OCH_3), 3.16-3.22 (m, 1H, CHCH_2), 2.63-2.67 (m, 1H, CHCH_2).

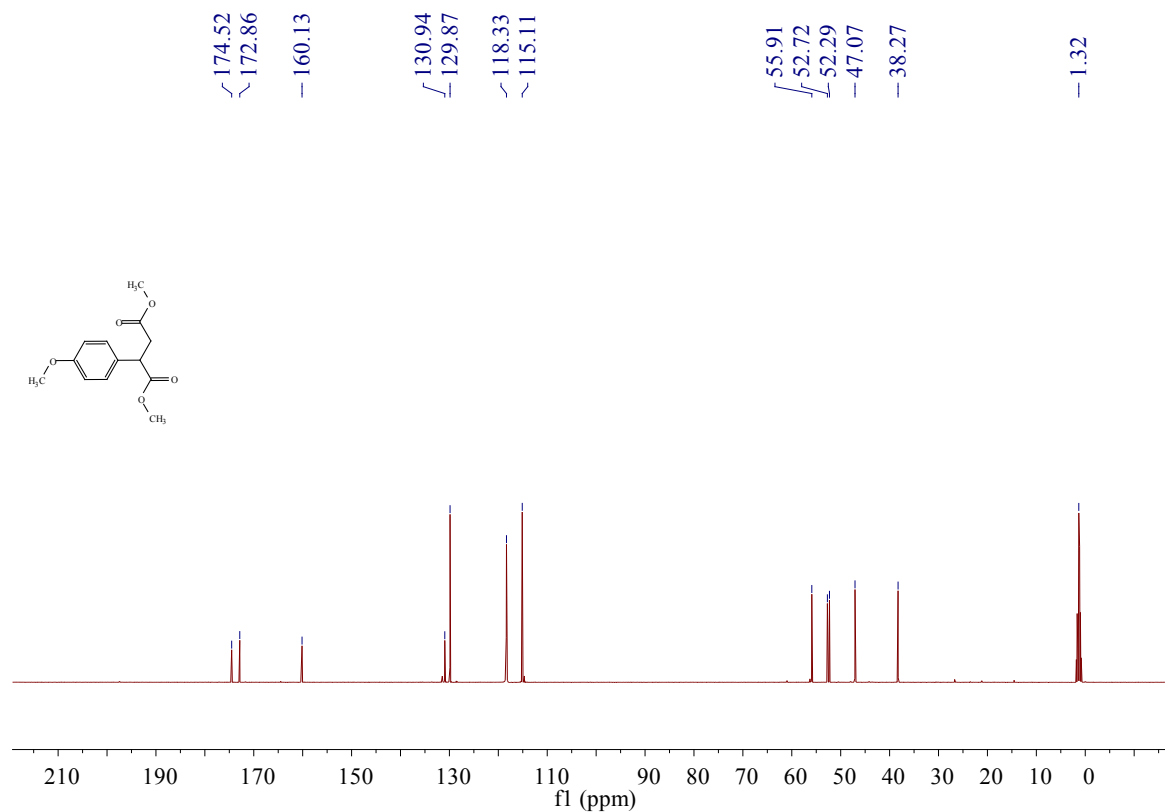
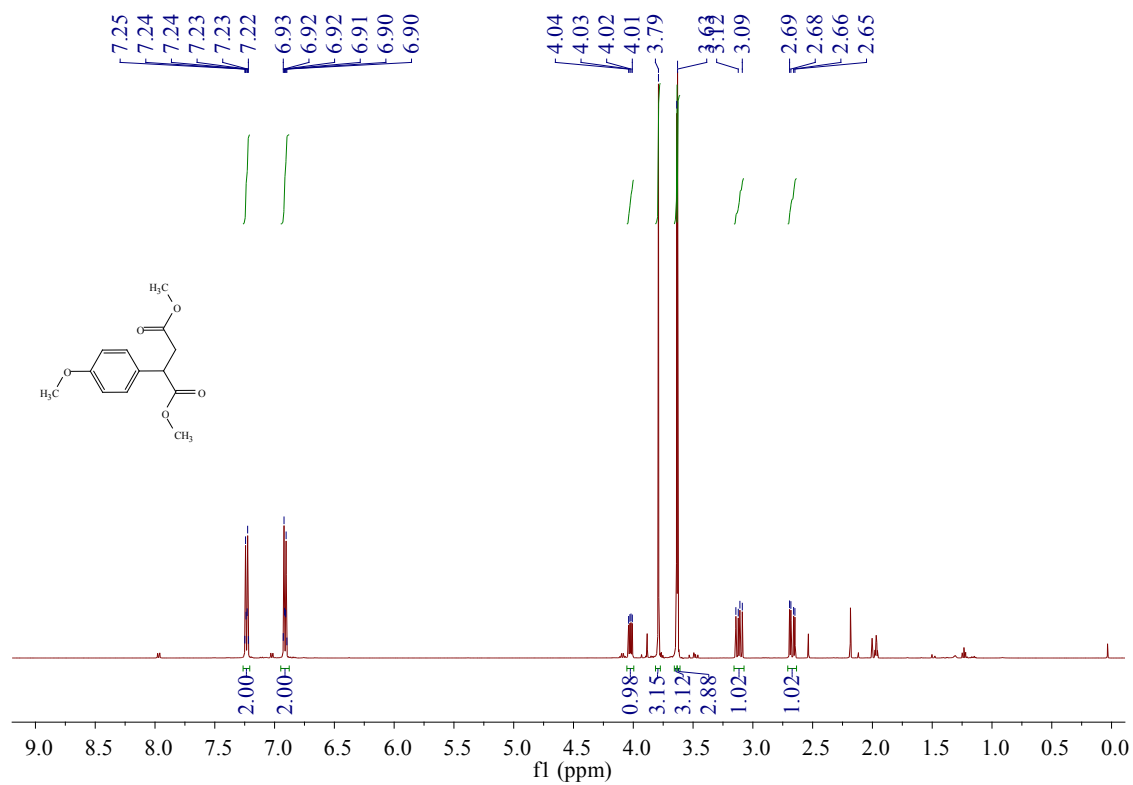
^{13}C NMR (125 MHz, CDCl_3): δ = 173.69, 172.15, 137.50, 134.77, 129.67, 127.68, 52.41, 51.94, 46.77, 37.76, 21.15.



Dimethyl 2-(4-methoxyphenyl)succinate

^1H NMR (500 MHz, CD_3CN): δ = 7.22-7.25 (m, 2H, C_6H_4), 6.90-6.93 (m, 2H, C_6H_4), 4.01-4.04 (t, 1H, J = 5.0 Hz, PhCHCH_2), 3.79 (s, 3H, PhOCH_3), 3.64 (s, 3H, OCH_3), 3.63 (s, 3H, OCH_3), 3.09-3.14 (m, 1H, CHCH_2), 2.65-2.69 (m, 1H, CHCH_2).

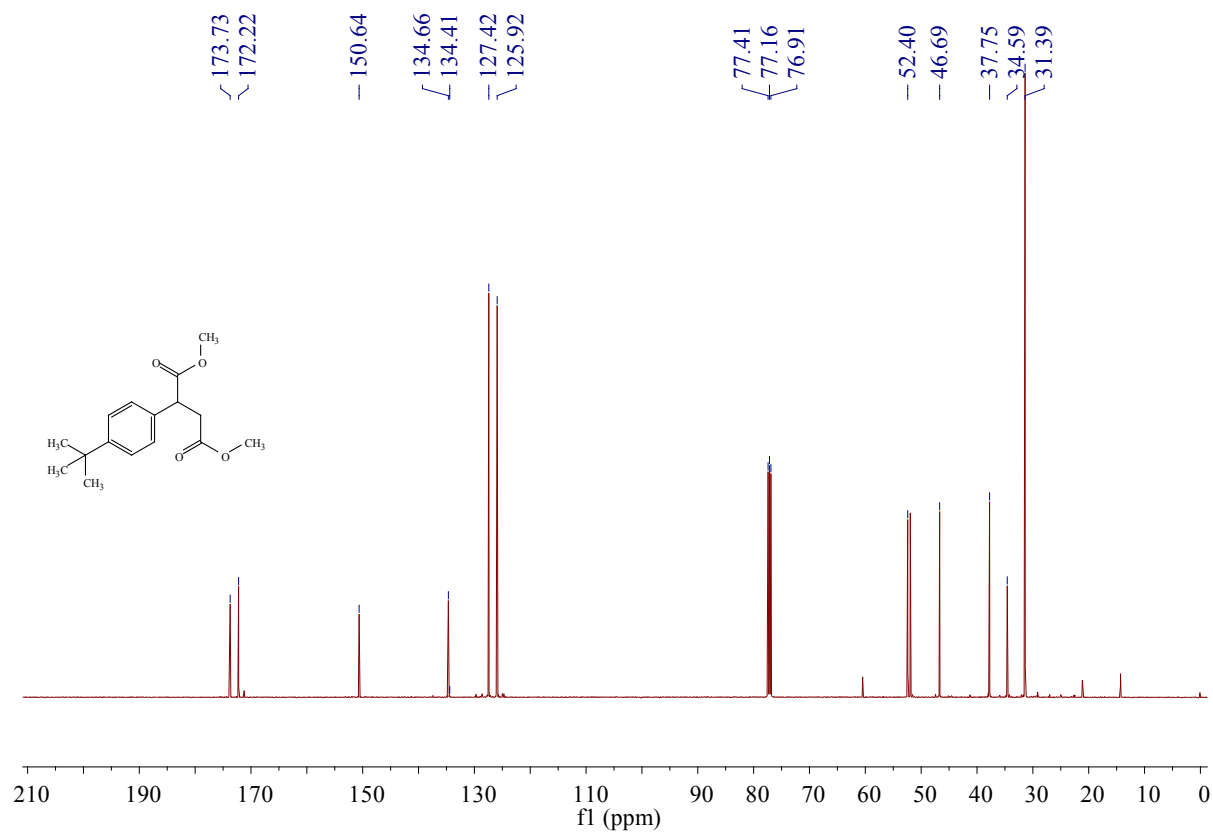
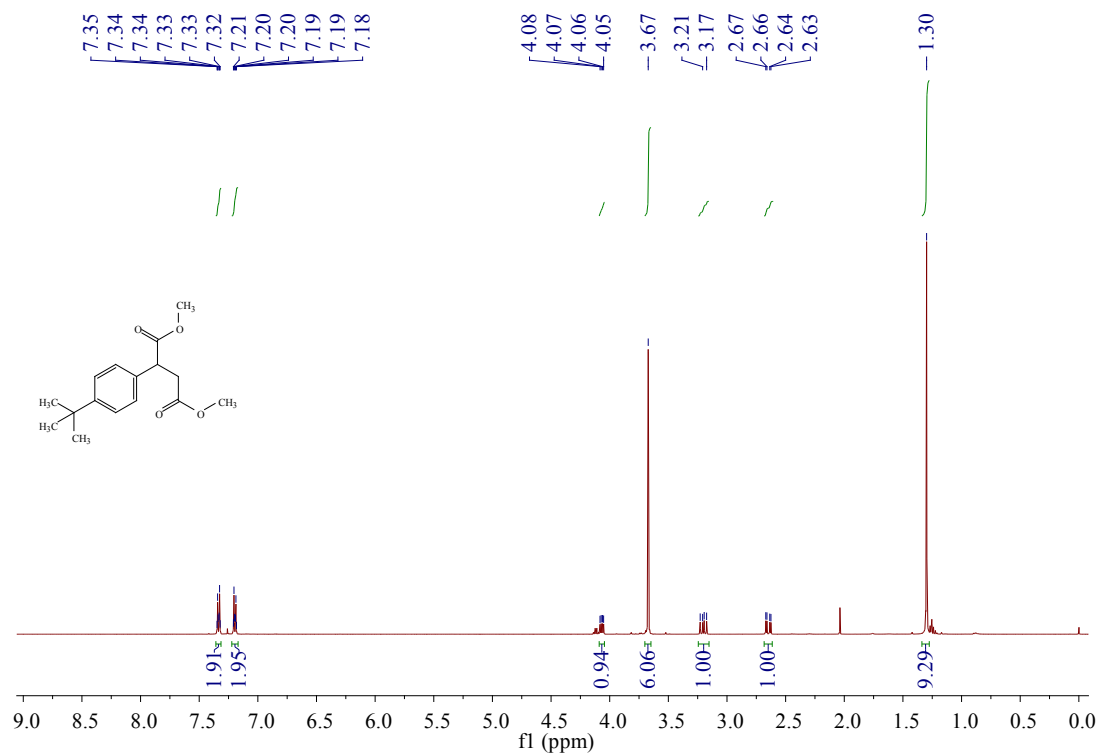
^{13}C NMR (125MHz, CD_3CN): δ = 174.52, 172.86, 160.13, 130.94, 129.87, 129.87, 115.11, 55.91, 52.72, 52.29, 47.07, 38.27.



Dimethyl 2-(4-(*tert*-butyl)phenyl)succinate

^1H NMR (500 MHz, CDCl_3): δ = 7.32-7.35 (m, 2H, C_6H_2), 7.18-7.21 (m, 2H, C_6H_2), 4.05-4.08 (m, 1H, PhCHCH_2), 3.17-3.23 (m, 1H, CHCH_2), 2.63-2.67 (m, 1H, CHCH_2), 1.30 (s, 9H, $\text{C}(\text{CH}_3)_3$).

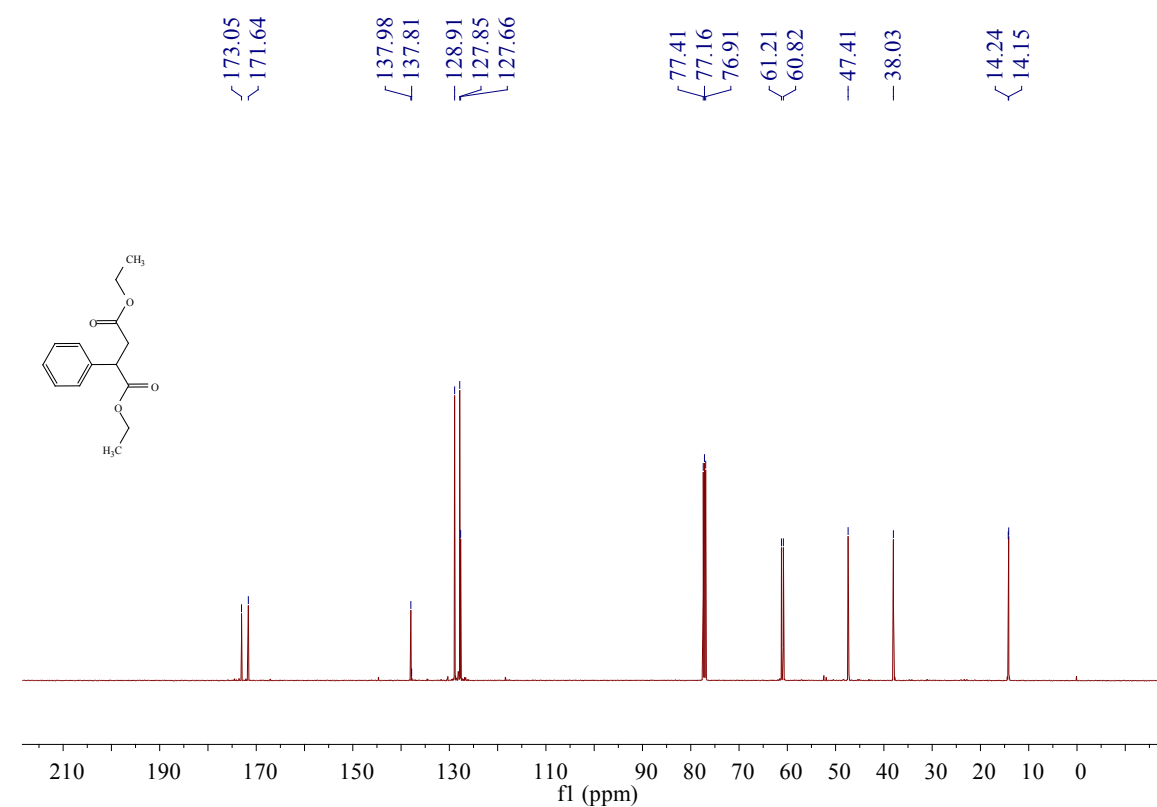
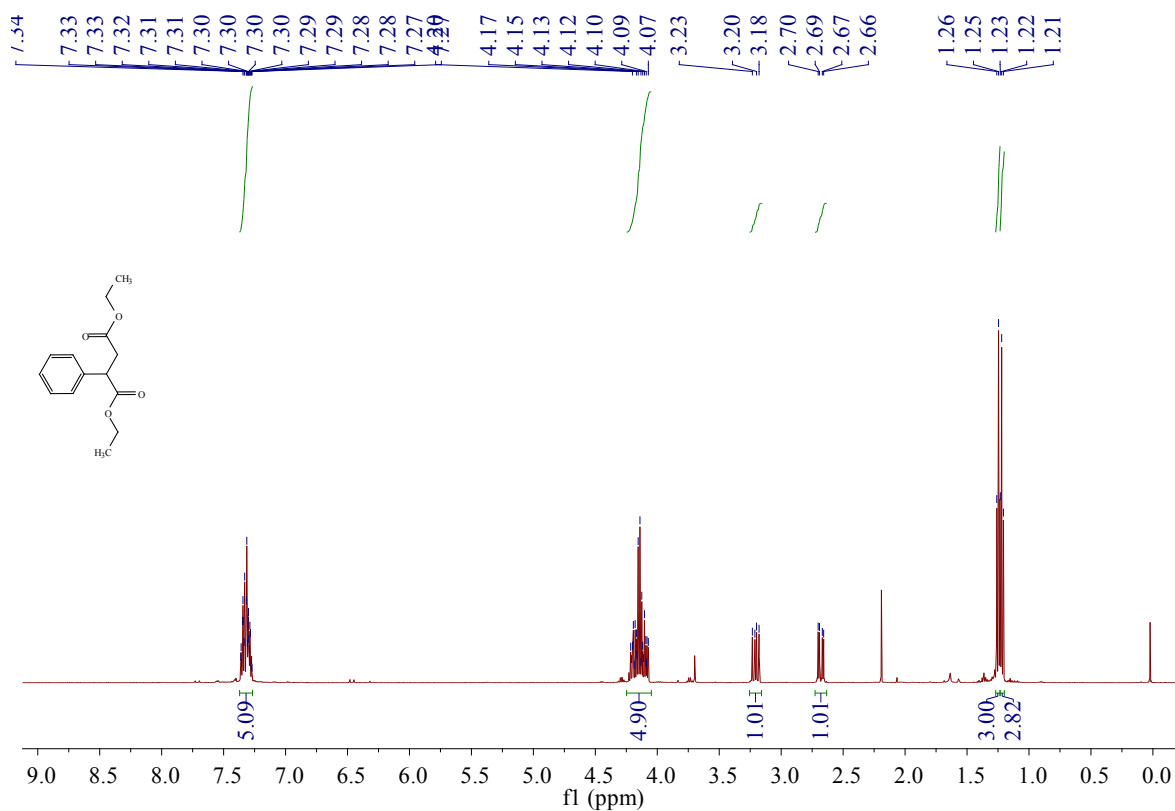
^{13}C NMR (125 MHz, CDCl_3): δ = 173.73, 172.22, 150.64, 134.66, 134.41, 127.42, 125.92, 52.40, 46.69, 37.75, 34.59, 31.39.



Diethyl 2-phenylsuccinate

^1H NMR (500 MHz, CDCl_3): δ = 7.27-7.36 (m, 4H, C_6H_4), 4.07-4.21 (m, 1H, $\text{PhCHCH}_2/2\text{OCH}_2\text{CH}_3$), 3.18-3.23 (m, 1H, CHCH_2), 2.66-2.70 (m, 1H, CHCH_2), 1.24-1.26 (m, 3H, OCH_2CH_3), 1.21-1.23 (m, 3H, OCH_2CH_3).

^{13}C NMR (125 MHz, CDCl_3): δ = 173.05, 171.64, 137.98, 137.81, 128.91, 127.85, 127.66, 61.21, 60.82, 47.41, 38.03, 14.24, 14.15.



Dimethyl 2-hexylsuccinate

^1H NMR (500 MHz, CDCl_3): δ = 3.68 (s, 3H, OCH_3), 3.66 (s, 3H, OCH_3), 2.80-2.83 (m, 1H, $\text{C}_6\text{H}_{13}\text{CHCH}_2$), 2.68-2.71 (m, 1H, $\text{C}_6\text{H}_{13}\text{CHCH}_2$), 2.40-2.44 (m, 1H, $\text{C}_6\text{H}_{13}\text{CHCH}_2$), 1.22-1.28 (m, 10H, $\text{C}_5\text{H}_{10}\text{CH}_3$), 0.84-0.87 (t, 3H, J = 5.0 Hz, CH_2CH_3).

^{13}C NMR (125 MHz, CDCl_3): δ = 175.67, 172.63, 51.90, 51.86, 41.29, 32.08, 29.15, 22.66, 14.15.

