Supplementary Material (ESI)

One single catalyst, $Pd(OAc)_2$, for two sequential very different steps : allylic alcohol oxidation/Heck reaction. Access to functionalised α,β-unsaturated ketones.

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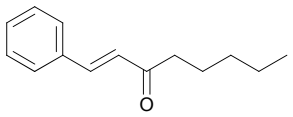
Fax: 33472431669; Tel: 33472431826 ; E-mail:gozzi@cpe.fr

Supplementary informations

^1H and ^{13}C NMR spectra were measured in $CDCl_3$ on a Bruker AC 300 spectrometer. Mass spectra were recorded on a Finigan-MAT 95 XL instrument; IR spectra were recorded on a Nicolet IR100.

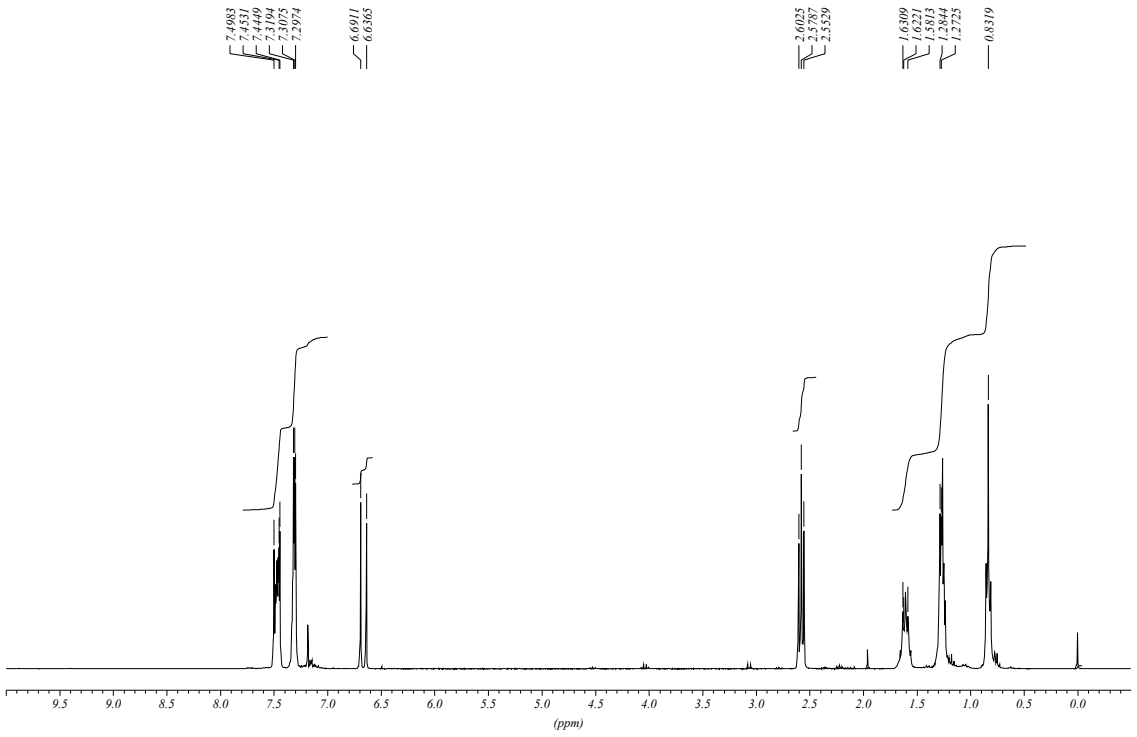
Column chromatography was carried out with silica gel 60A 40-63 μm (SDS). All the commercially available products were used as received, without purification or distillation. All the reaction were performed either under oxygen pressure (1 atm) for the oxidation reaction) or under air for the Heck reactions.

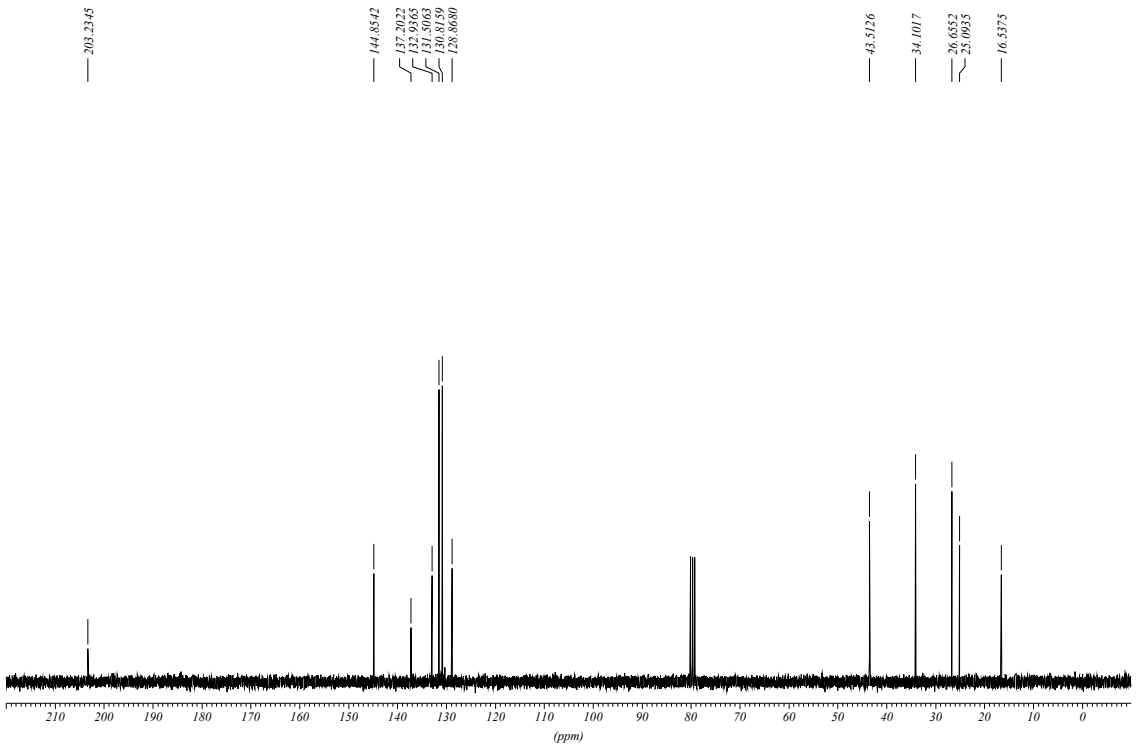
General procedure: 3% $Pd(OAc)_2$ and 6% Et_3N were added to a 1M solution of alcohol **1** in DMA and heated under stiring at 70°C for the appropriate amount of time (generally 4h) under an atmosphere of O_2. The reaction was monitored by TLC. When all the alcohol was oxidized, the O_2 balloon was removed and 1.1 eq of Et_3N and 1.1 eq of the iodoaryl compound were added. The reaction mixture was allowed to stir at 70°C under air atmosphere without special cautions until completion. After diethyl ether-water extraction, column chromatography on silica allowed to obtain the product with good isolated yields.



(*E*)-1-phenyloct-1-en-3-one

3a : CAS: 29478-67-4 ; ^{1}H NMR $CDCl_3$ δ 0.90 (t, *J* = 6.8Hz, 3H), 1.35 (m, 4H), 1.69 (m, 2H), 2.65 (t, *J* = 7.2Hz, 2H), 6.74 (d, *J* = 16.4Hz, 1H), 7.38 (m, 3H), 7.52 (m, 3H); ^{13}C NMR 14.2, 22.8, 24.3, 31.8, 41.2, 126.6, 128.5, 129.2, 130.6, 134.9, 142.5, 200.9; IR (KBr) ν_{max}: 3060, 2951, 2929, 2862, 1690, 1663, 1622, 1178, 983, 739, 689 cm^{-1}.

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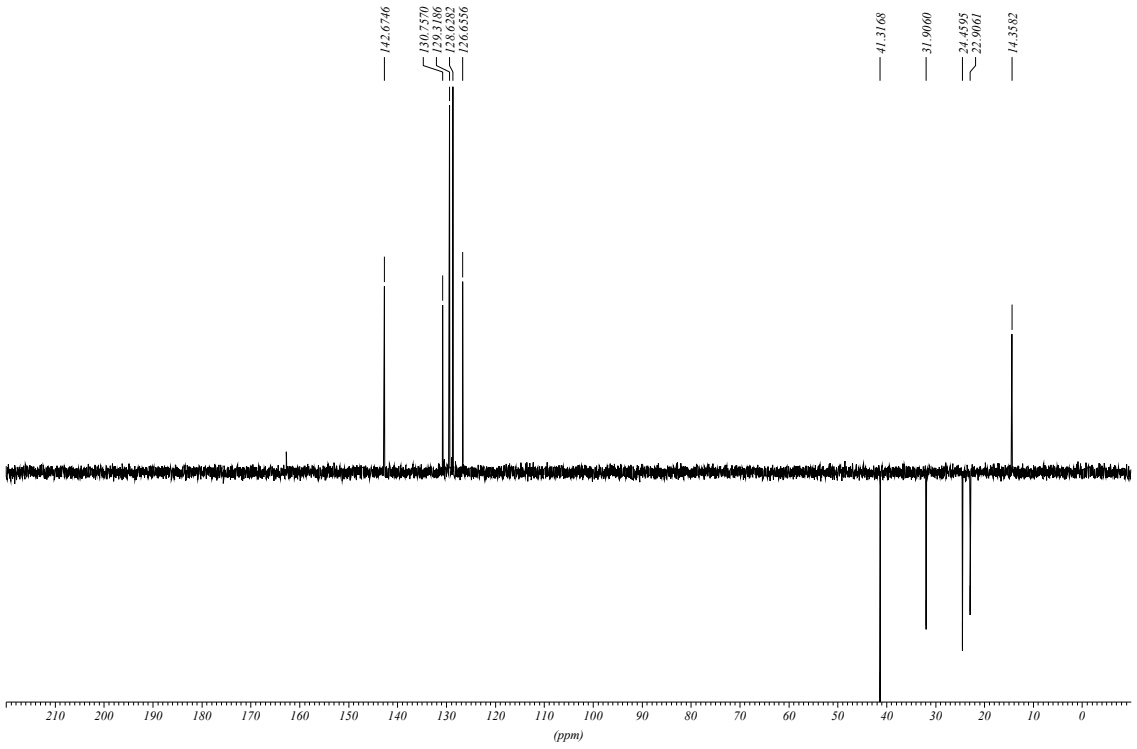
16.5375
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)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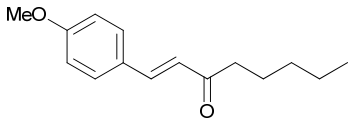
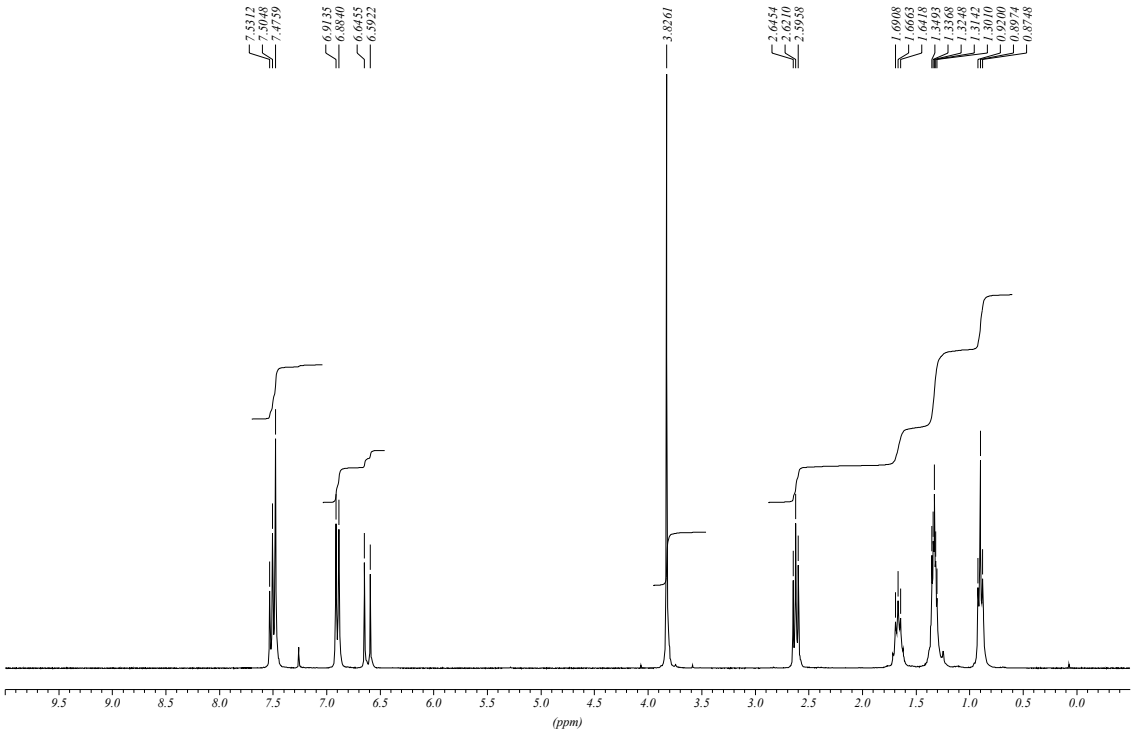
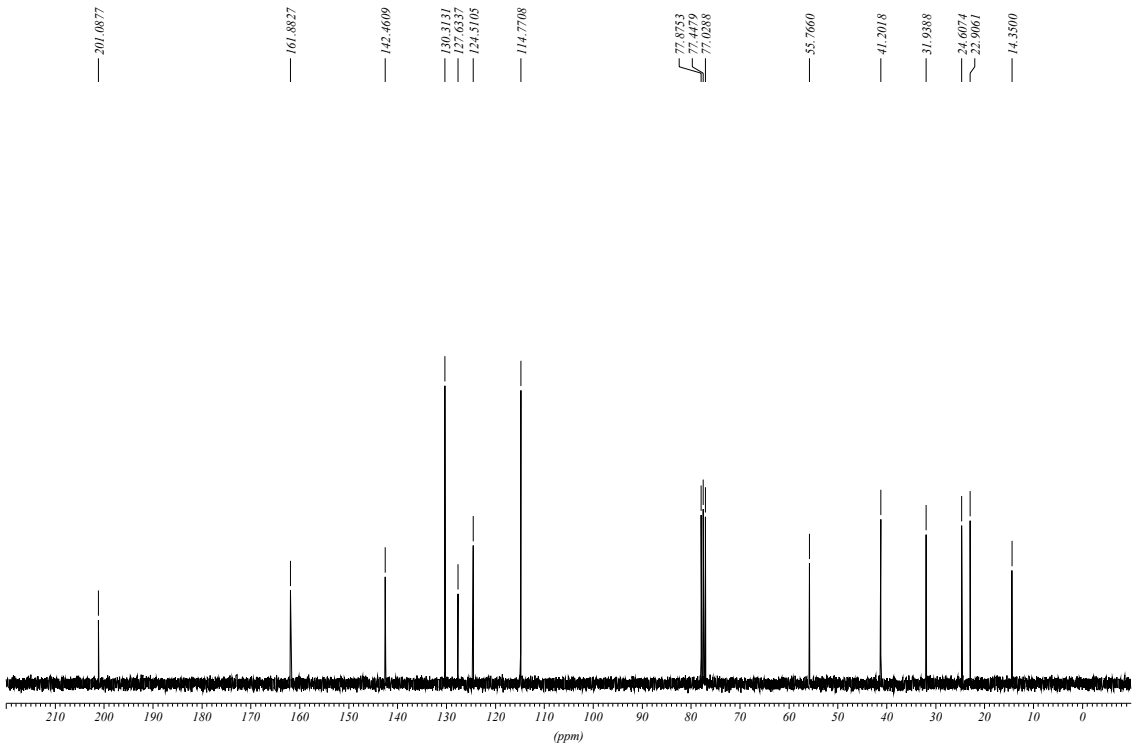
(ppm)



(*E*)-1-(4-methoxyphenyl)oct-1-en-3-one

3b : CAS: 82297-67-4 ; ^{1}H NMR $CDCl_3$ δ 0.89 (t, *J* = 6.8Hz, 3H), 1.33 (m, 4H), 1.66 (m, 2H), 2.62 (t, *J* = 7.4Hz, 2H), 3.83 (s, 3H), 6.62 (d, *J* = 16Hz, 1H), 6.90 (d, *J* = 8.9Hz, 2H), 7.50 (m, 3H); ^{13}C NMR 14.3, 22.9, 24.6, 31.9, 41.2, 55.7, 114.7, 124.5, 127.6, 130.3, 142.4, 161.8, 201.1 ; IR (film) ν_{max}: 3039, 3005, 2931, 2860, 1651, 1600, 1512, 1251, 1033, 734 cm^{-1}.

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77.0288
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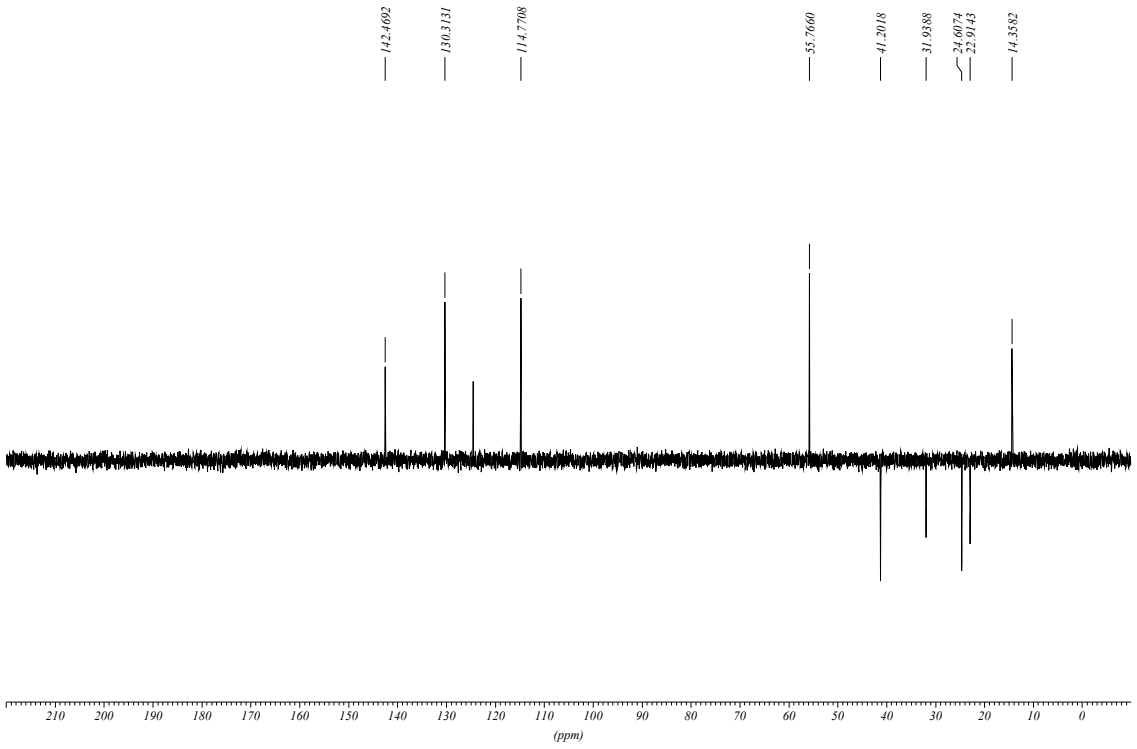
(ppm)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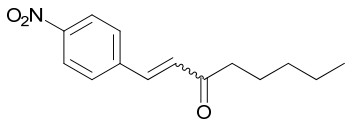
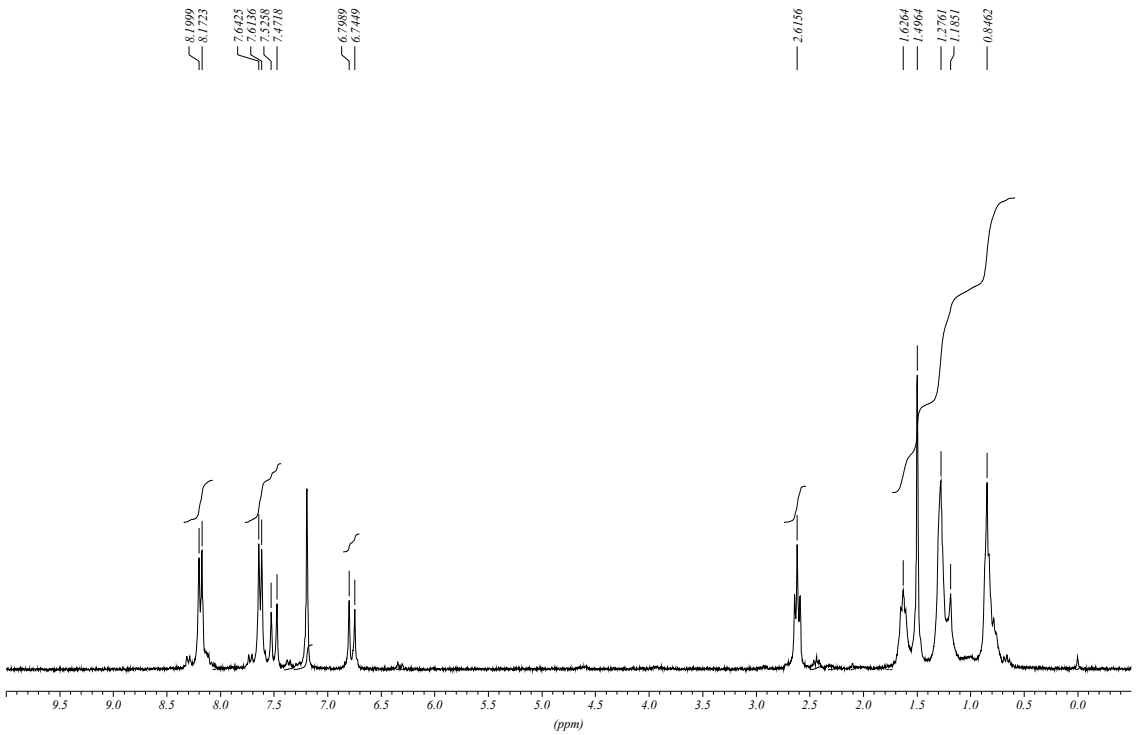
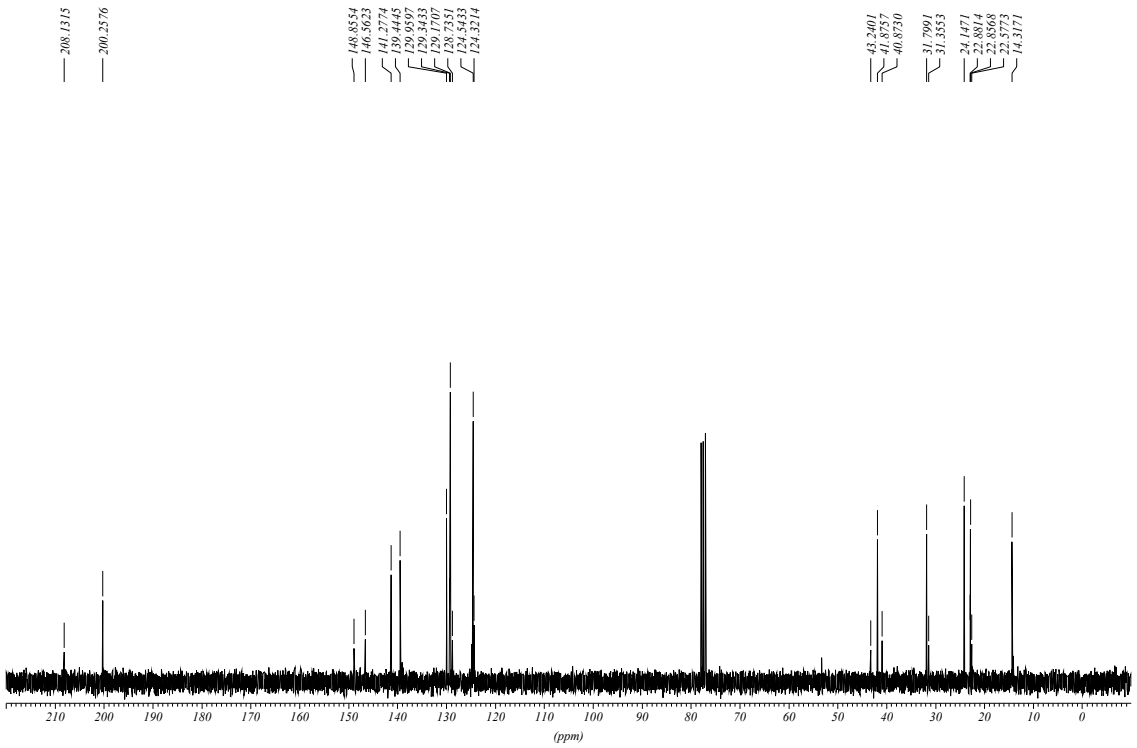
(ppm)



1-(4-nitrophenyl)oct-1-en-3-one

3c : CAS: 929719-02-8 ; ^{1}H NMR $CDCl_3$ δ 0.75 (m, 3H, *cis*) and 0.91 (m, 3H, *trans*), 1.30 (m, 4H, *cis* + *trans*), 1.62 (m, 2H, *cis* + *trans*), 2.43 (t, *J* = 7.5Hz, 2H, *cis*) and 2.62 (t, *J* = 7.4Hz, 2H, *trans*), 6.40 (d, *J* = , 1H, *cis*) and 6.83 (d, *J* = 16.2, 1H, *trans*), 7.36 (d, *J* = 8.8Hz , 1H, *cis*) and 7.50 (d, *J* = 16.2Hz, 1H, *trans*), 7.62 (d, *J* = 8.6Hz, 2H, *trans*) and 7.71 (d, *J* = 8.8Hz, 1H, *cis*), 8.18 (d, *J* = 8.6Hz, 2H, *trans*) and 8.29 (d, *J* = 7.9Hz, 2H, *cis*), *cis/trans* = 8%; ^{13}C NMR: 14.1 (*cis*), 14.3 (*trans*), 22.5 (*cis*), 22.8 (*trans*), 24.1, 31.3 (*cis*), 31.8 (*trans*), 70.8 (*trans*), 43.2 (*cis*), 124.5, 129.1, 129.9, 139.3, 141.1, 146.4, 148.7, 200.1, 208.0; IR (KBr) ν_{max}: 2956, 2931, 2857, 1706, 1596, 1514, 1343, 855 cm^{-1}.

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43.2401
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31.7991
31.3553
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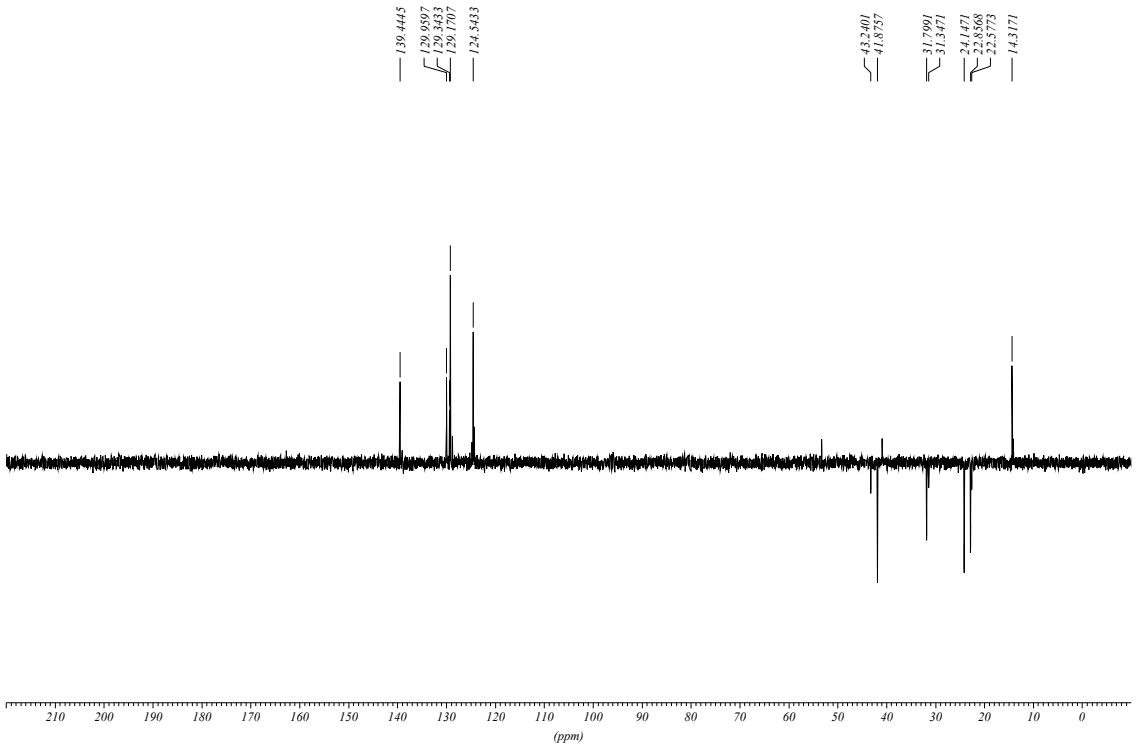
(ppm)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14.3171
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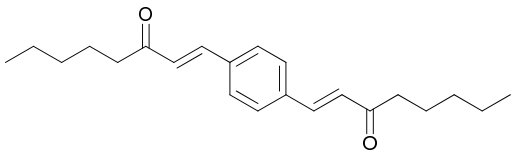
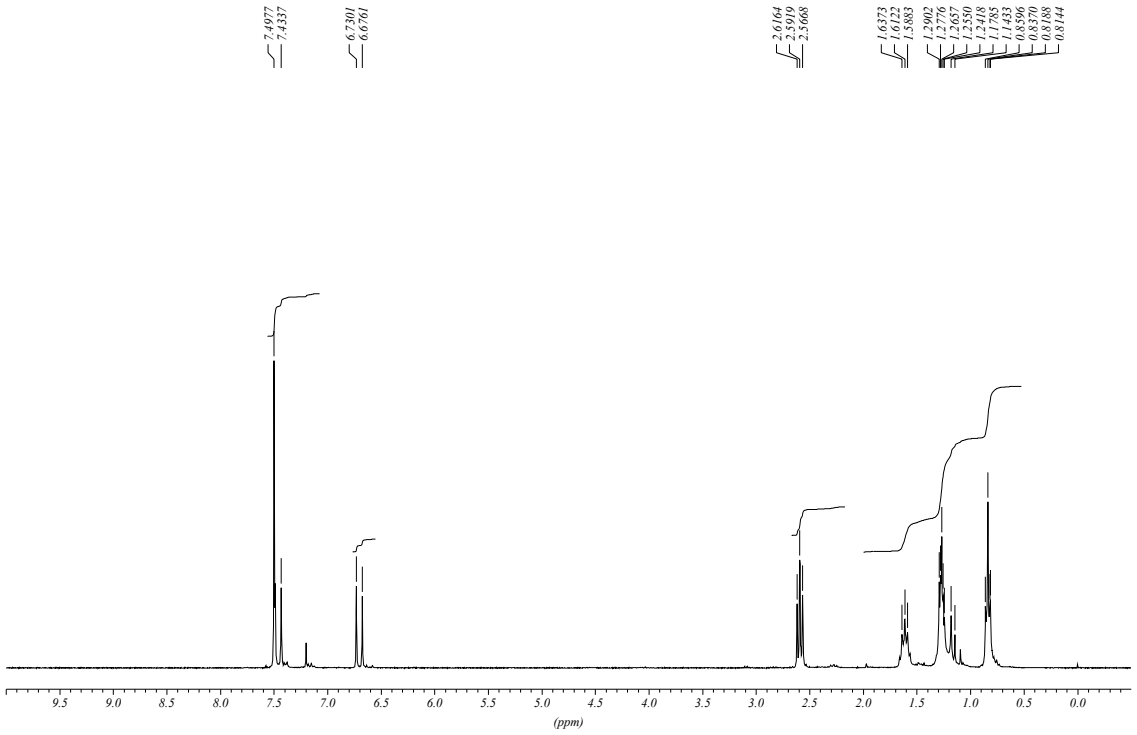
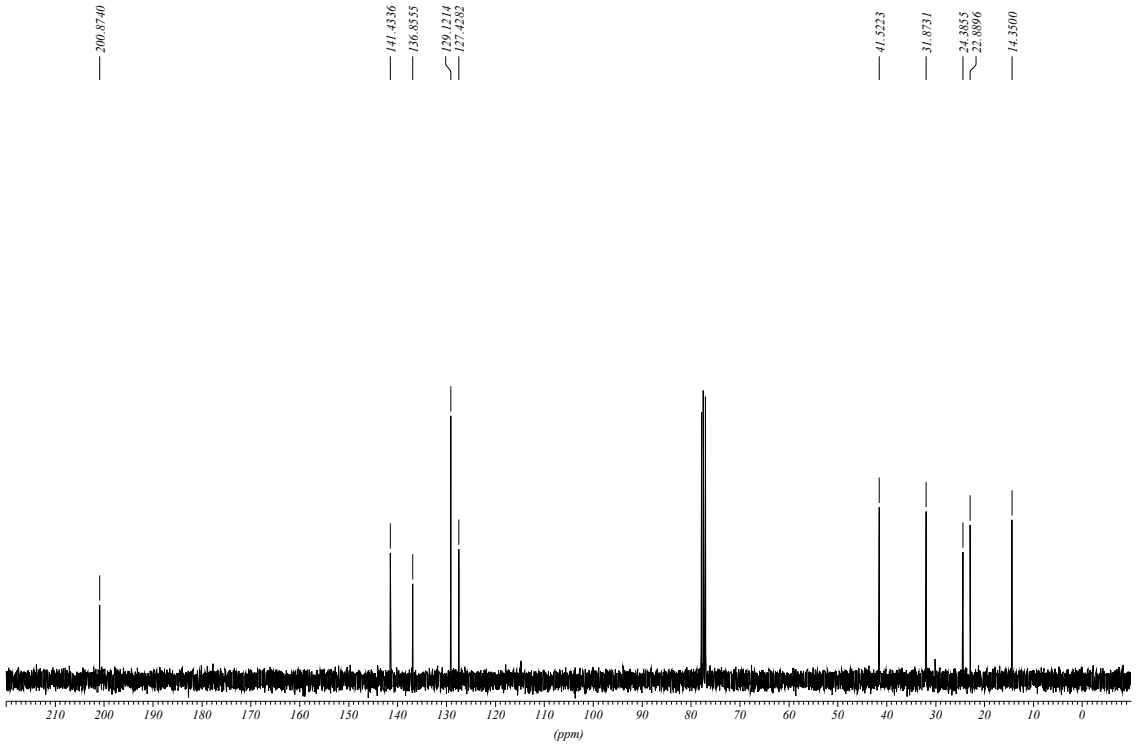
(ppm)



(1*E*,1'*E*)-1,1'-(1,4-phenylene)dioct-1-en-3-one

3d : ^{1}H NMR $CDCl_3$ δ 0.89 (t, *J* = 6.8Hz, 6H), 1.34 (m, 8H), 1.67 (m, 4H), 2.65 (t, *J* = 7.5Hz, 4H), 6.76 (d, *J* = 16Hz, 2H), 7.52 (d, *J* = 16Hz, 2H), 7.56 (s, 4H); ^{13}C NMR 14.2, 22.8, 24.31, 31.7, 41.4, 127.3, 129.0, 136.7, 141.3, 200.7; HRMS calcd for: $C_{22}H_{31}O_2$ (MH^+) 327.2324 ; found 327.2321 ; IR (KBr) ν_{max} : 2927, 2862, 1688, 1615, 1071 cm^{-1}.

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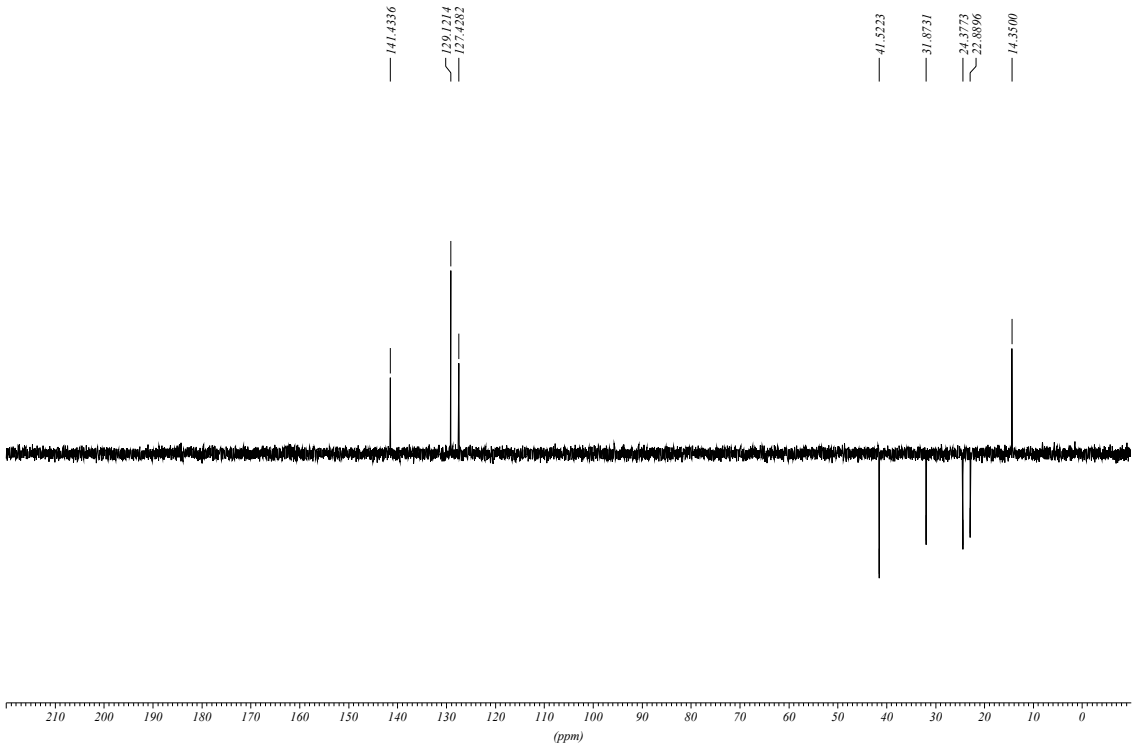
(ppm)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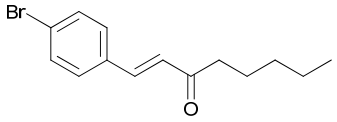
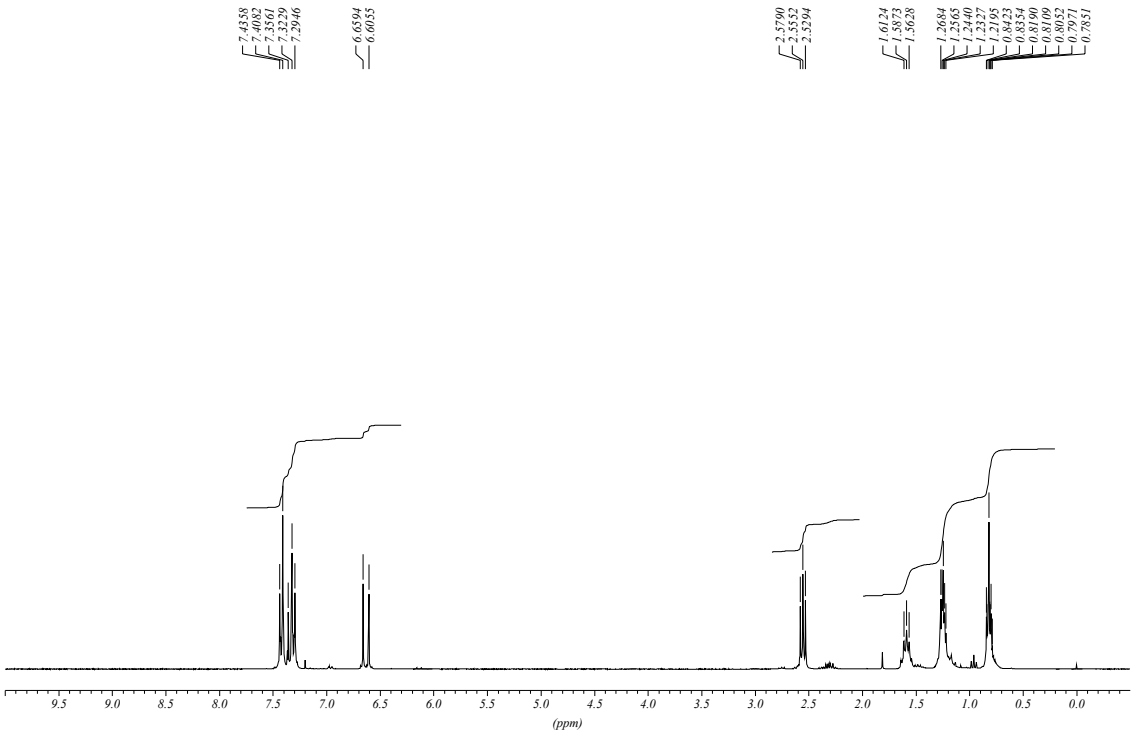
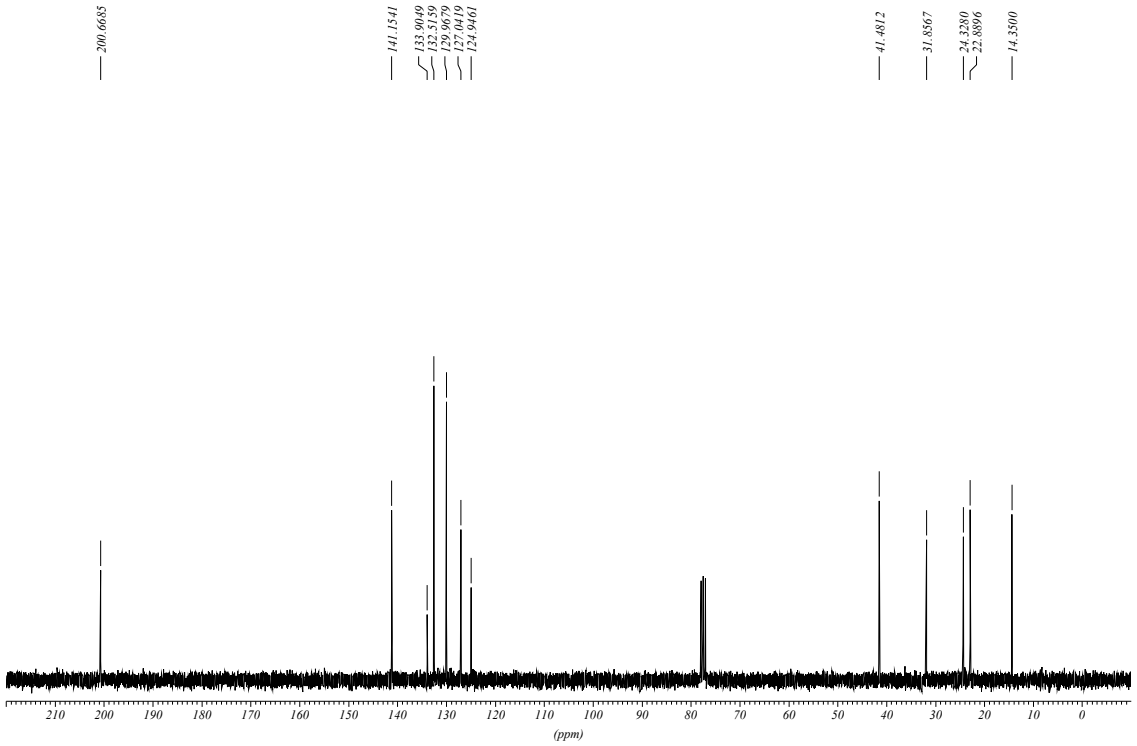
(ppm)



(*E*)-1-(4-bromophenyl)oct-1-en-3-one

3e : CAS: 97109-53-0 ; ^{1}H NMR $CDCl_3$ δ 0.88 (t, *J* = 7Hz, 3H), 1.30 (m, 4H), 1.65 (m, 2H), 2.61 (t, *J* = 7Hz, 2H), 6.69 (d, *J* = 16.2Hz, 1H), 7.41 (m, 5H); ^{13}C NMR 14.2, 22.7, 24.1, 31.7, 41.3, 124.8, 126.8, 129.8, 132.3, 133.7, 141.0, 200.5; HRMS calcd for: $C_{14}H_{17}BrO$ ($M^{+\cdot}$) 280.0463 ; found 280.0462; IR (KBr) ν_{max}: 3060, 2952, 2929, 2862, 1938, 1691, 1664, 1616, 984, 739, 689 cm^{-1}.

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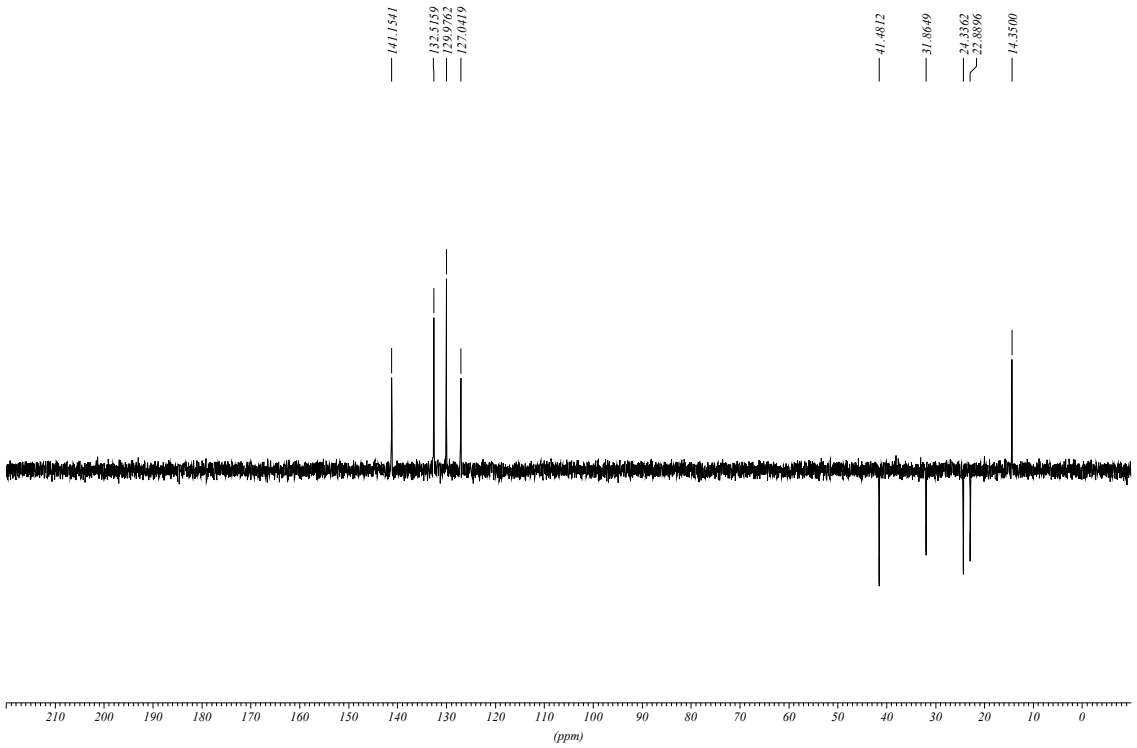
(ppm)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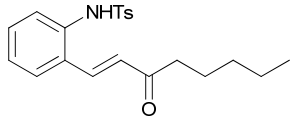
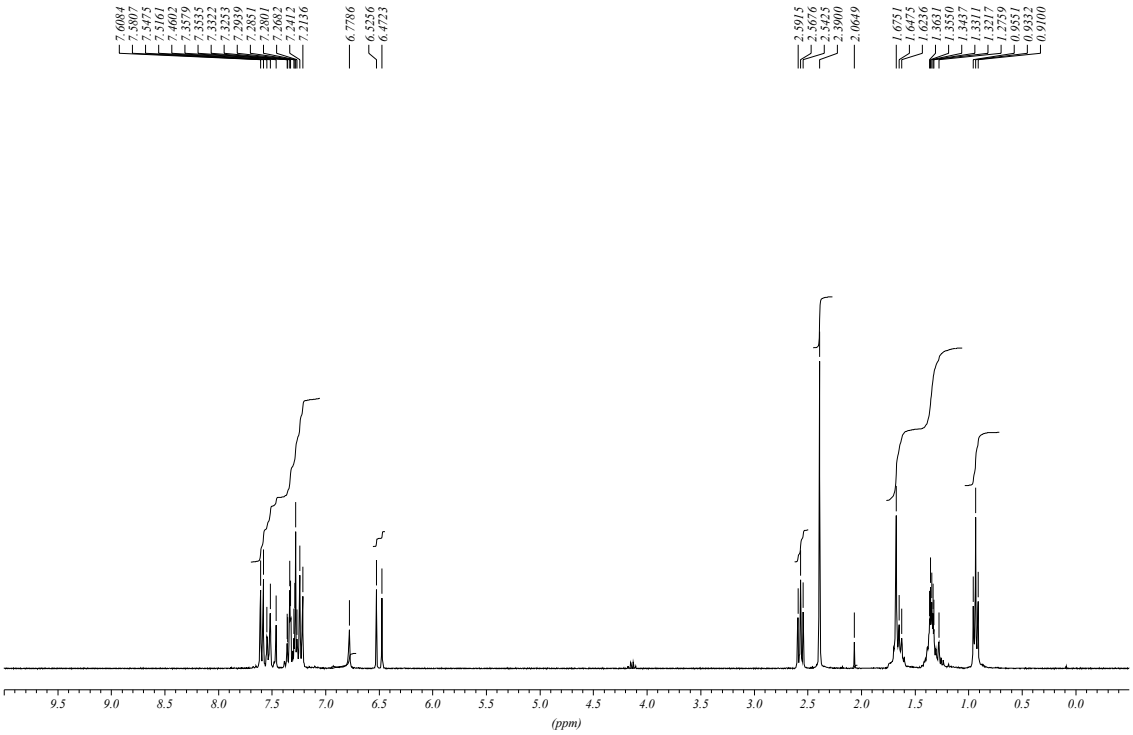
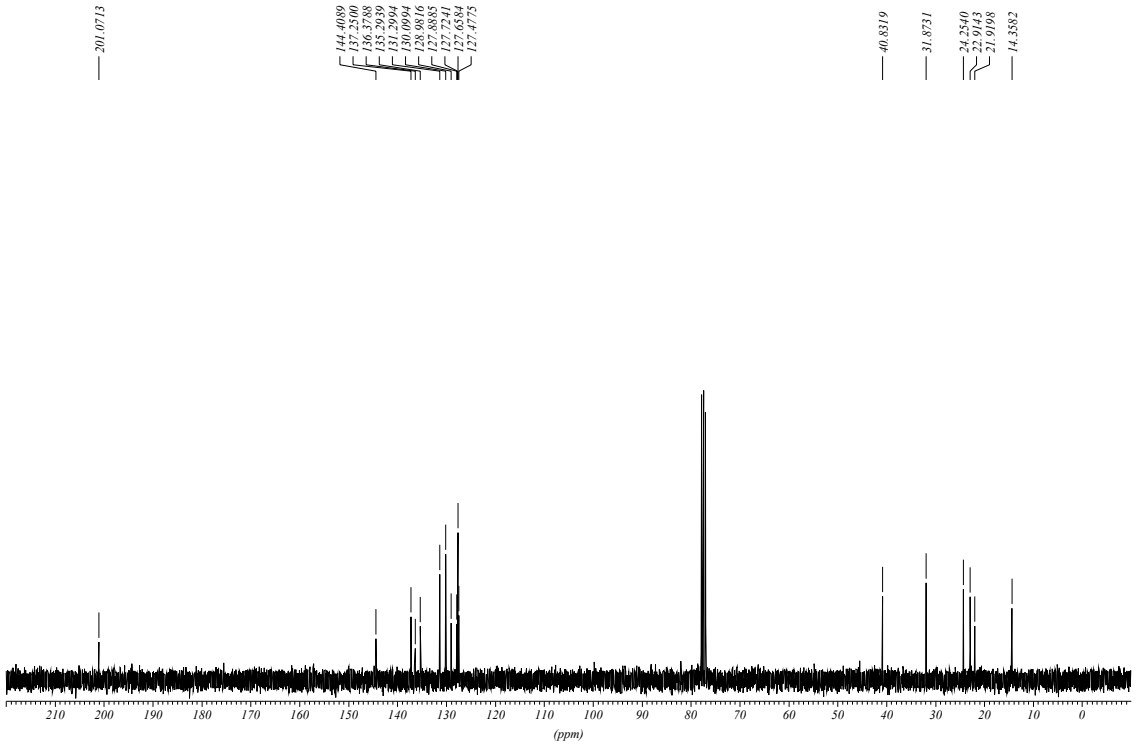
(ppm)



(*E*)-4-methyl-*N*-(2-(3-oxooct-1-enyl)phenyl)benzenesulfonamide

3f: ^{1}H NMR δ 0.93 (t, *J* = 6.6Hz, 3H), 1.32 (m, 4H), 1.65 (m, 2H), 2.07 (s, 3H), 2.57 (t, *J* = 7.5Hz, 2H), 6.50 (d, *J* = 16.6Hz, 1H), 7.41 (m, 9H); ^{13}C NMR 14.2, 21.8, 22.8, 24.1, 31.8, 40.7, 127.4, 127.5, 127.6, 127.8, 128.9, 130.0, 131.2, 136.3, 137.1, 144.3, 201.0; HRMS calcd for: $C_{21}H_{26}NSO_3$ (MH^+) 372.1633 ; found 372.1628 ; IR (KBr) ν_{max}: 3183, 2955, 2925, 2851, 1679, 1601, 1337, 1163 cm^{-1}.

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127.6534
127.4775
40.8319
31.8731
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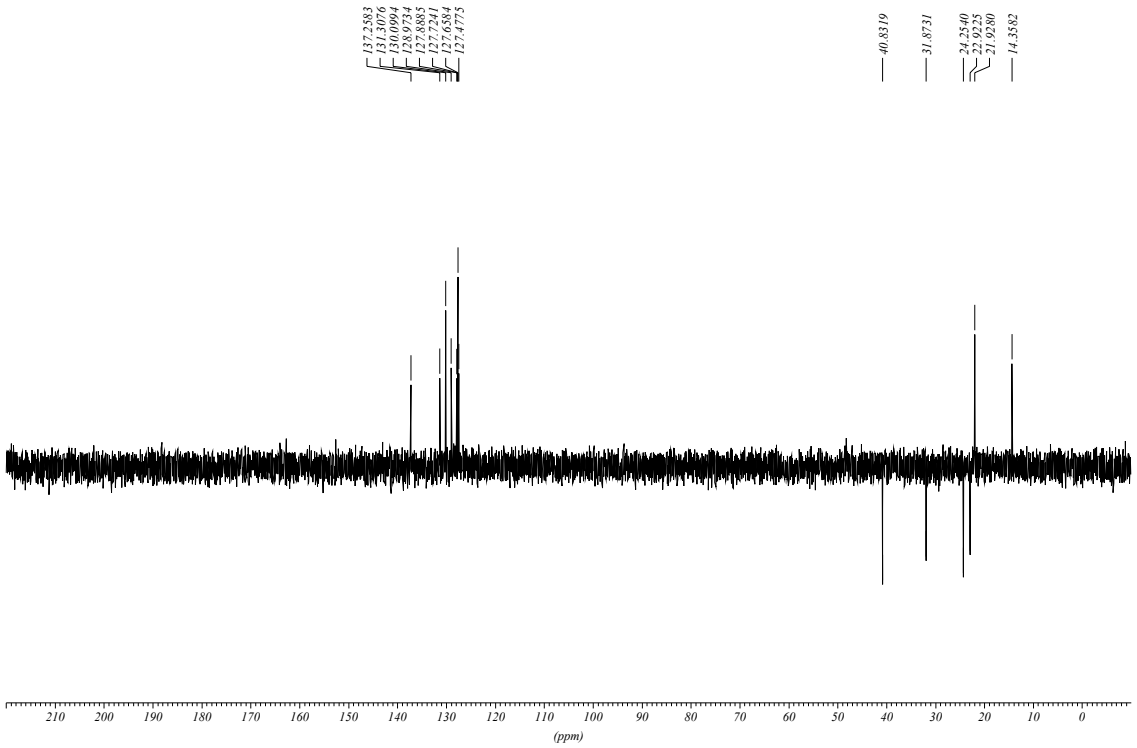
22.9143
21.9198
14.3582
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)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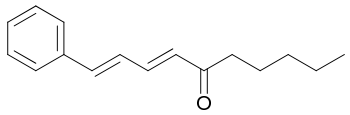
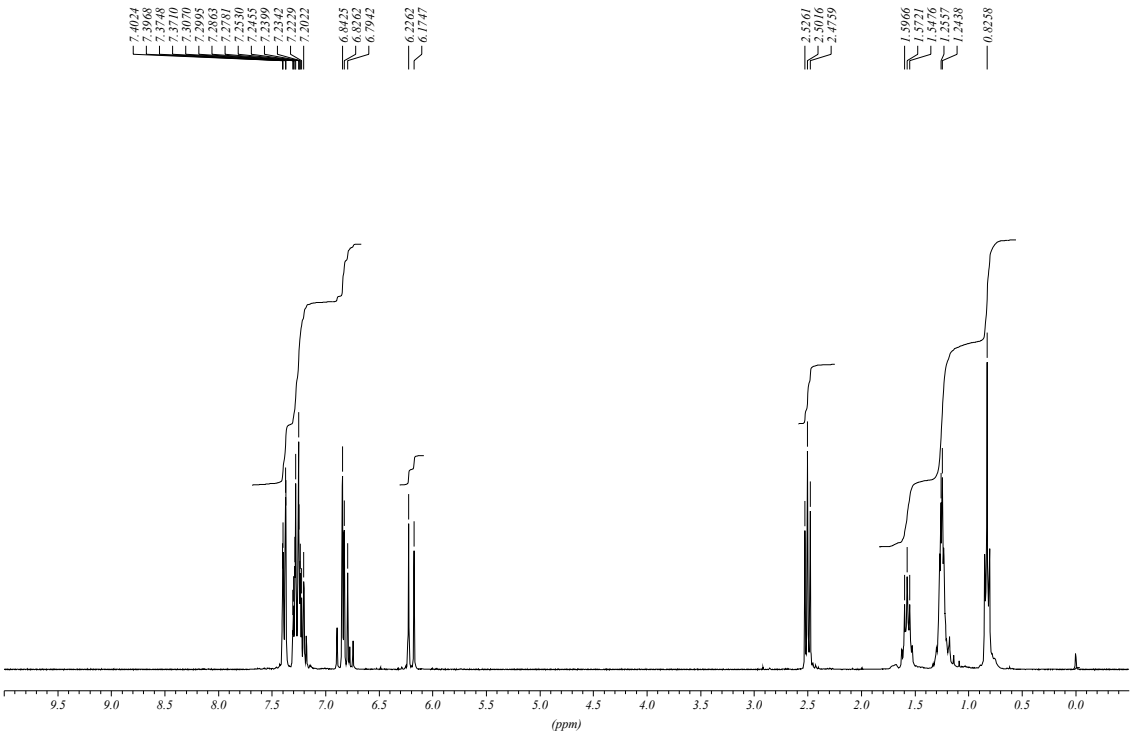
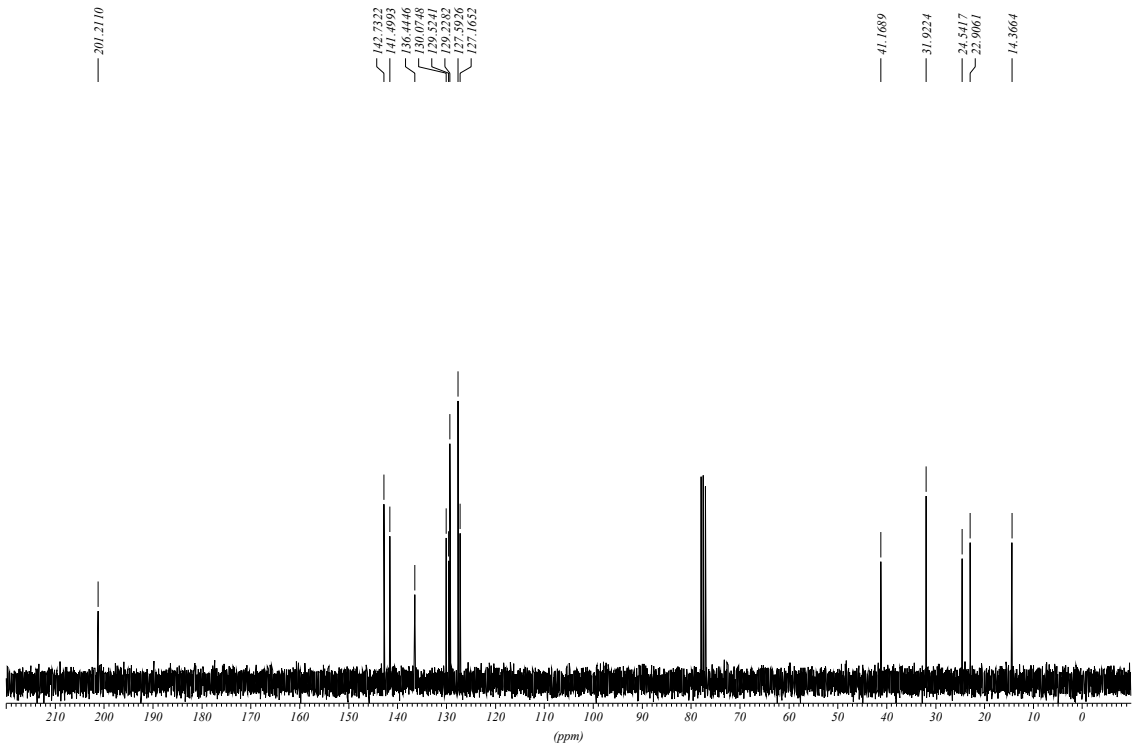
(ppm)



(1*E*,3*E*)-1-phenyldeca-1,3-dien-5-one

3g : CAS: 121077-67-6 ; ^{1}H NMR δ 0.82 (t, *J* = 6.6 Hz, 3H), 1.25 (m, 4H), 1.57 (m, 2H), 2.50 (t, *J* = 7.3Hz, 2H), 6.19 (d, *J* = 15.4Hz, 1H), 6.82 (m, 3H), 7.28 (m, 5H); ^{13}C NMR 14.2, 22.8, 24.4, 31.8, 41.0, 127.0, 127.4, 127.6, 129.1, 129.4, 129.9, 136.3, 141.3, 142.6, 201.1; IR (KBr) ν_{max}: 2958, 2854, 1680, 1588, 1073, 1005 cm^{-1}.

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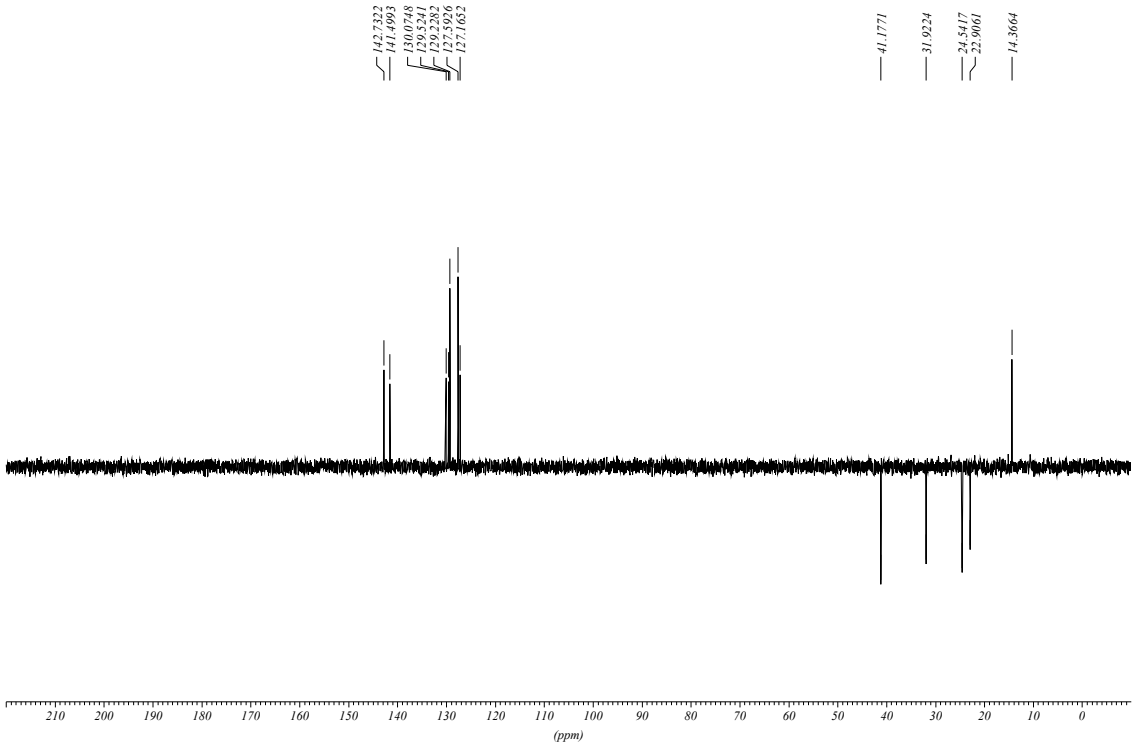
24.5417
22.9061
14.3664
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)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14.3664
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
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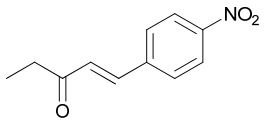
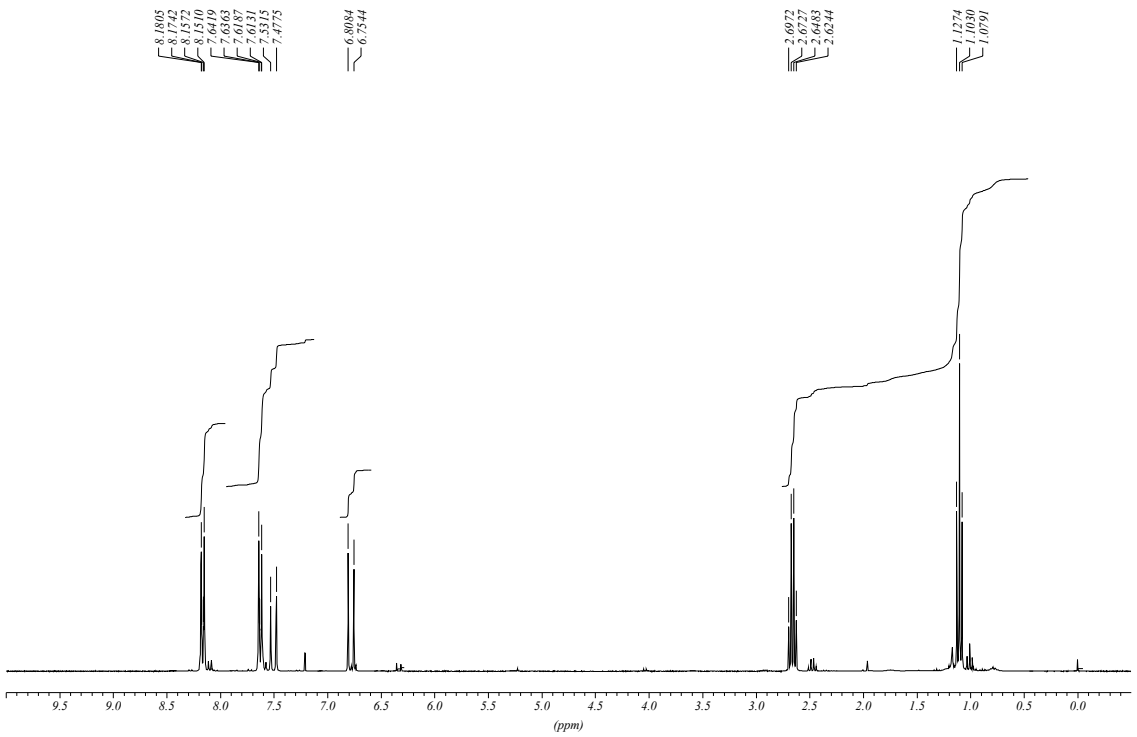
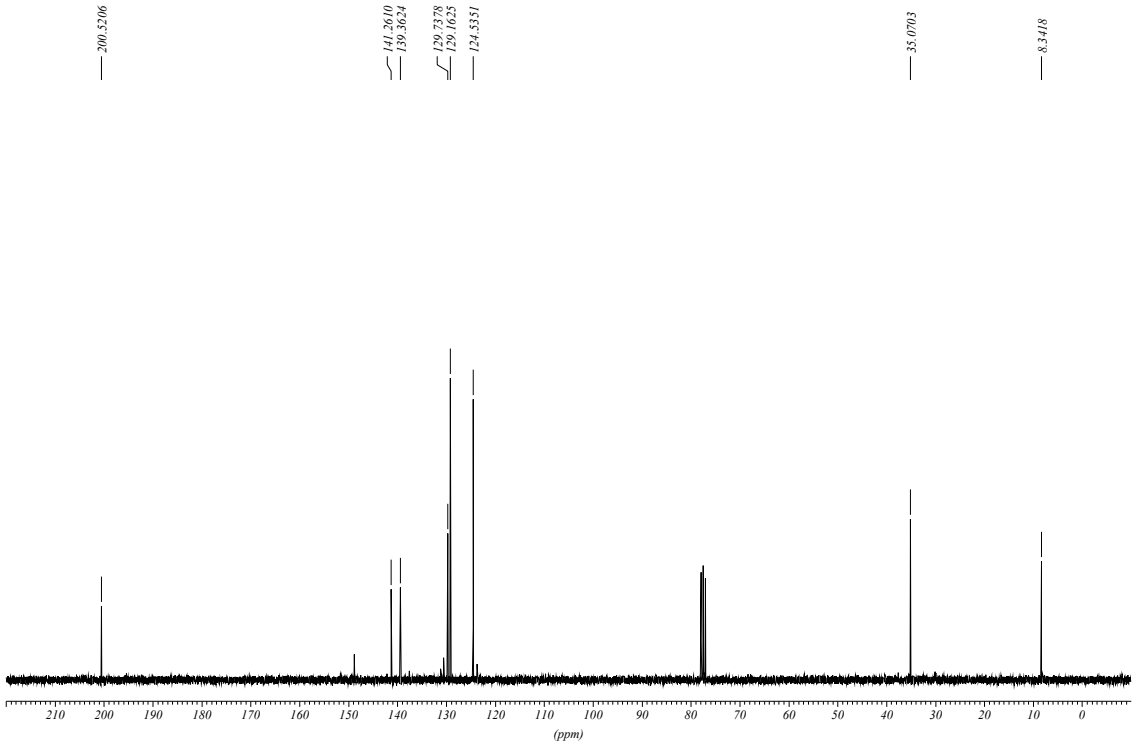
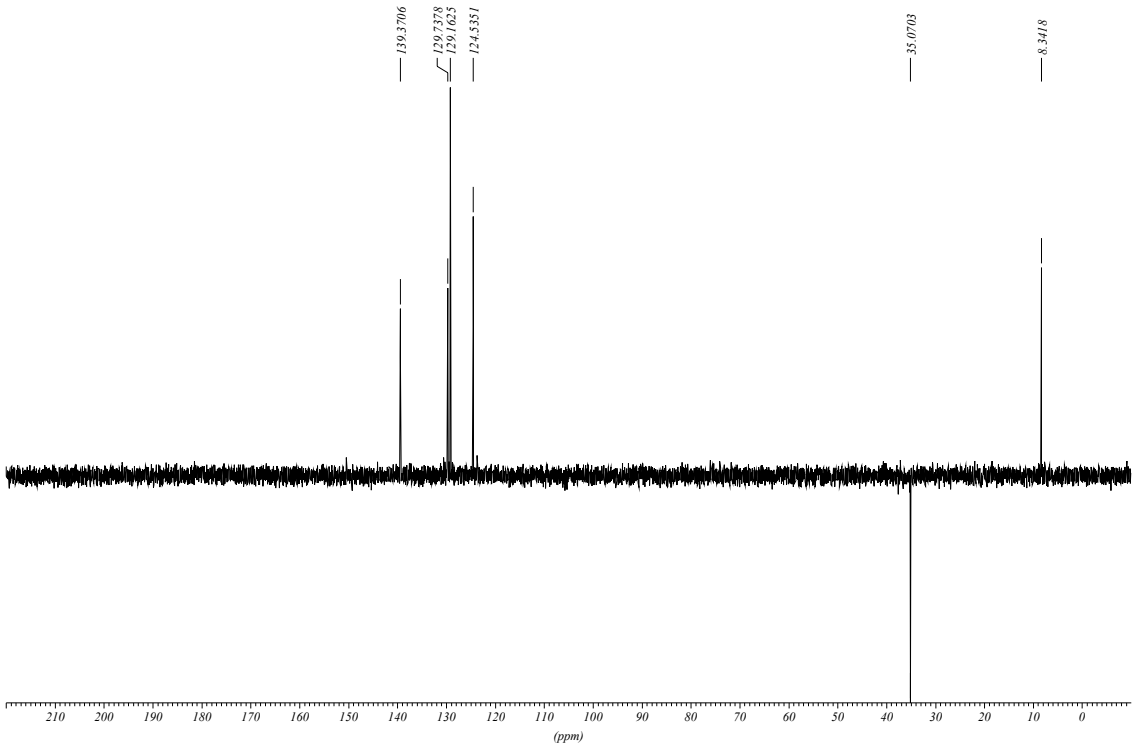


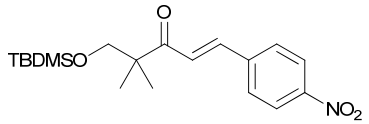
(*E*)-1-(4-nitrophenyl)pent-1-en-3-one

3h : CAS: 54951-55-2 ; ^{1}H NMR δ 1.10 (t, *J* = 7.2 Hz, 3H), 2.65 (q, *J* = 7.2Hz, 2H), 6.78 (d, *J* = 16.2Hz, 1H), 7.50 (d, *J* = 16.2Hz, 1H), 7.62 (dd, *J* = 7Hz, 1.7Hz, 2H), 8.17 (dd, *J* = 7Hz, 1.7Hz, 2H); ^{13}C NMR 8.1, 35.0, 124.5, 129.1, 129.7,139.3, 141.2, 200.5; IR (KBr) ν_{max}: 3110, 2981, 1693, 1667, 1616, 1591, 1510, 1338, 113, 839, 743 cm^{-1}.



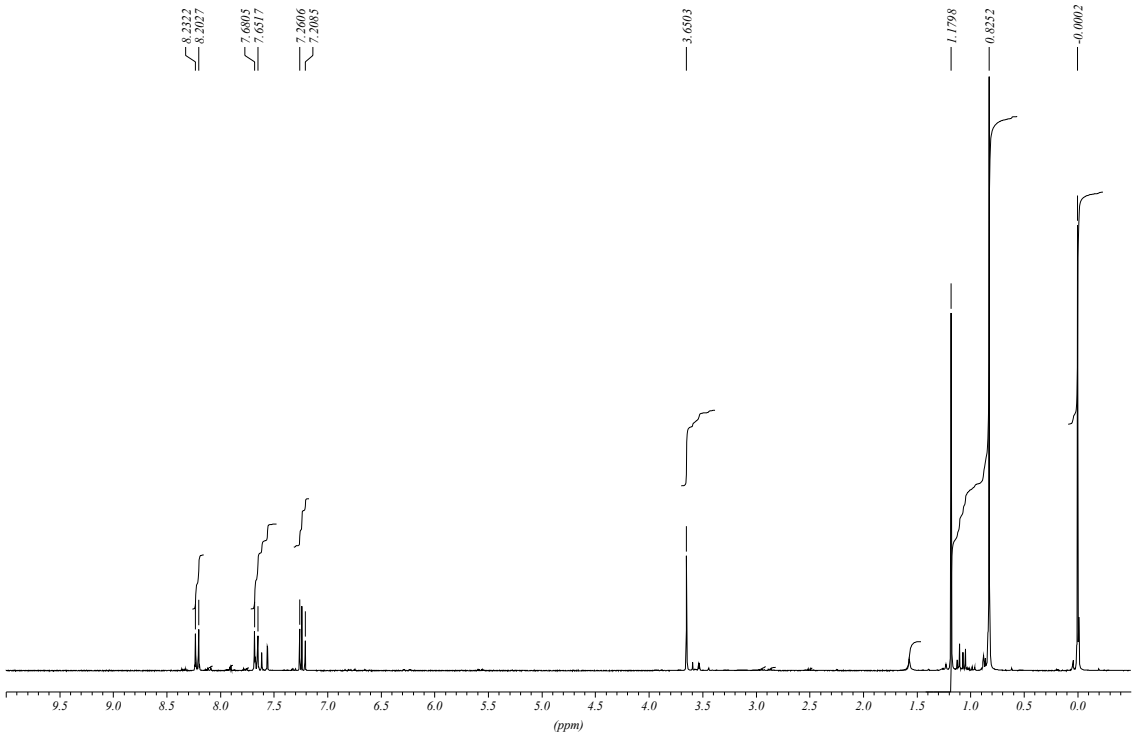

200.5206
141.2610
139.3624
129.7378
129.1625
124.5351
35.0703
8.3418
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

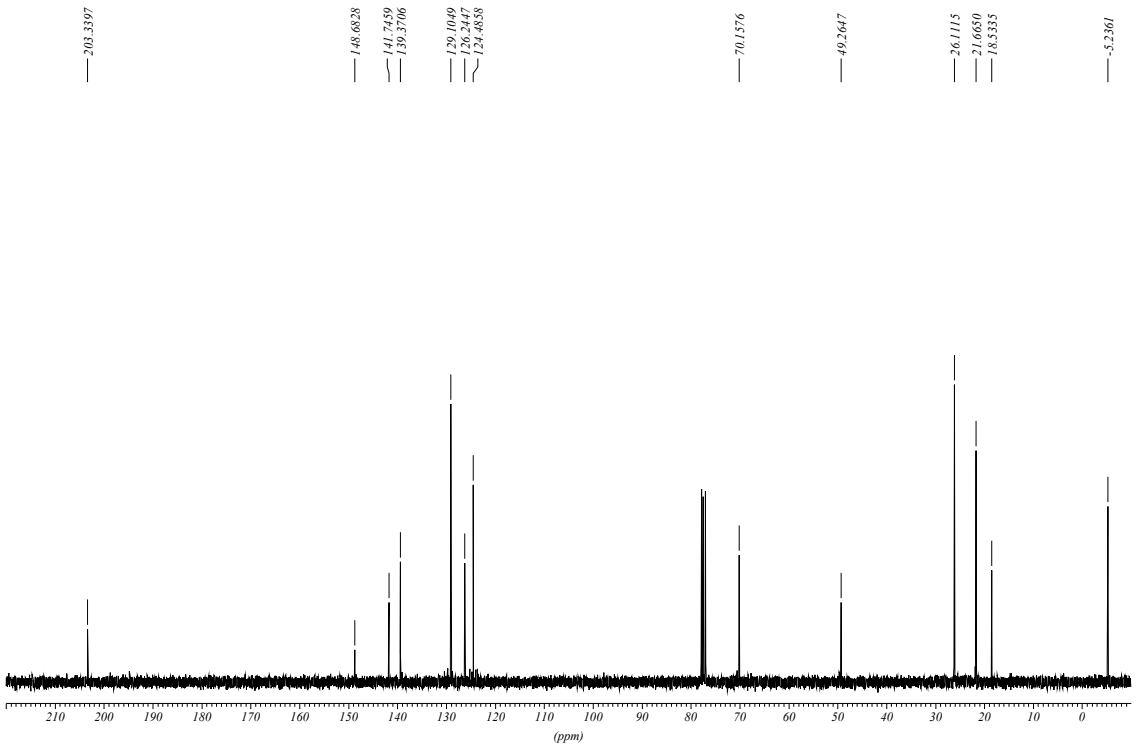

139.3706
129.7378
129.1625
124.5351
35.0703
8.3418
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

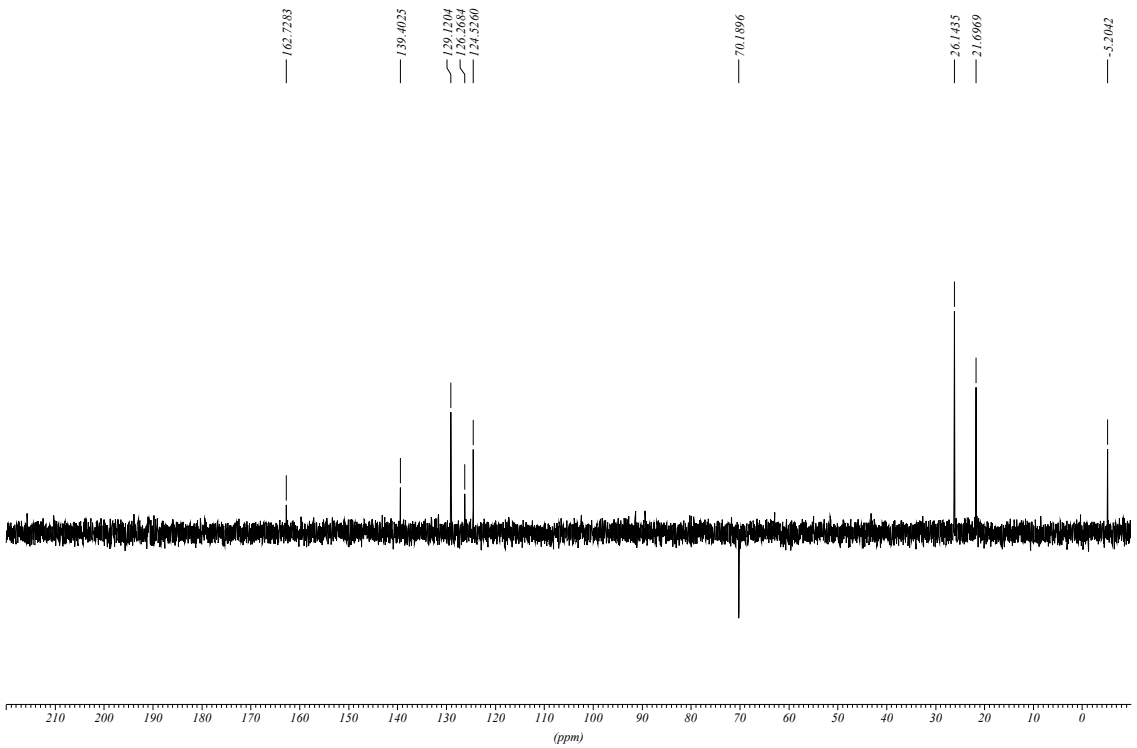


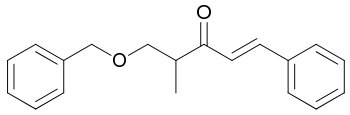
(*E*)-5-(*tert*-butyldimethylsilyloxy)-4,4-dimethyl-1-(4-nitrophenyl)pent-1-en-3-one

3i: ^{1}H NMR δ 0.02 (s, 6H), 0.84 (s, 9H), 1.19 (s, 6H), 3.67 (s, 2H), 7.26 (d, *J* = 18.6Hz, 1H), 7.62 (d, *J* = 18.6Hz, 1H), 7.89 (d, *J* = 8.7Hz, 2H), 8.24 (d, *J* = 8.7Hz, 2H); ^{13}C NMR -5.3, 18.4, 21.5, 26.0, 49.1, 70.0, 124.4, 126.1, 129.0, 139.2, 141.6, 148.6, 203.2; HRMS calcd for: $C_{19}H_{30}NSiO_4$ (MH^+) 364.1944; found 364.1942; IR ν_{max} : 3113, 2955, 2931, 2857, 1682, 1613, 1518, 1345, 1110, 1042, 866, 838, 774 cm^{-1}.



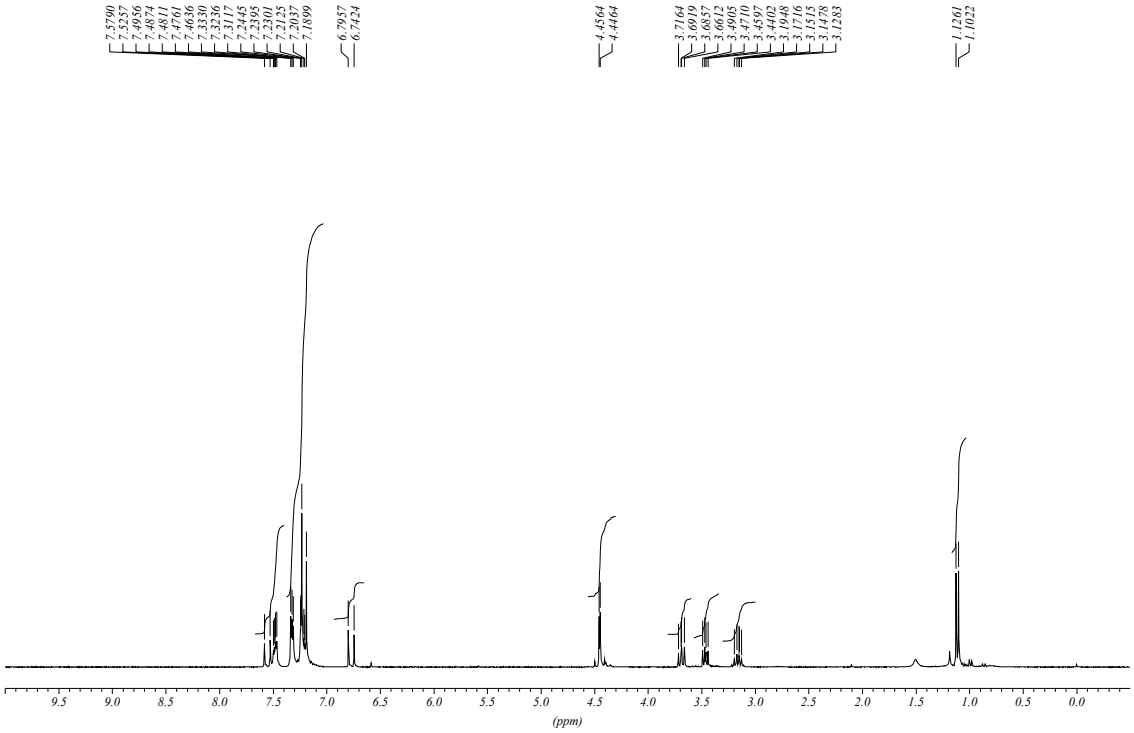

203.3397
148.6828
141.7459
139.3706
129.1049
126.2447
124.4858
70.1576
49.2647
26.1115
21.6650
18.5335
-5.2361
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

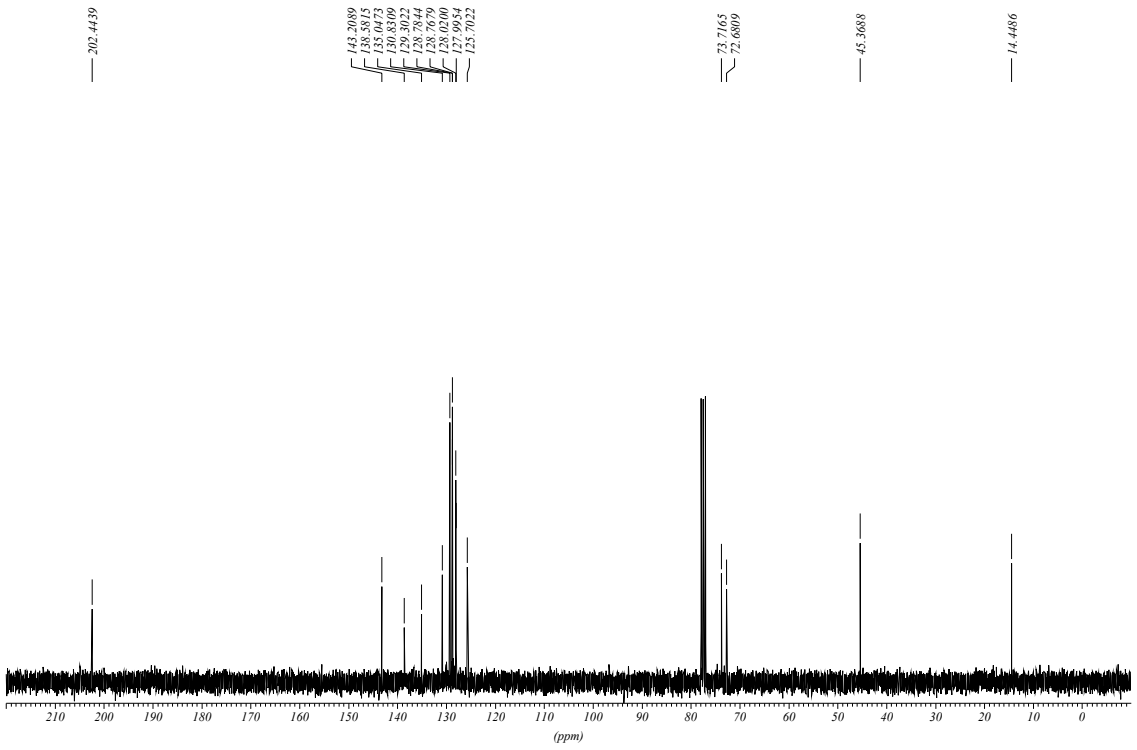

162.7283
139.4025
129.1204
126.2684
124.3260
70.1896
26.1435
21.6969
-5.2042
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)

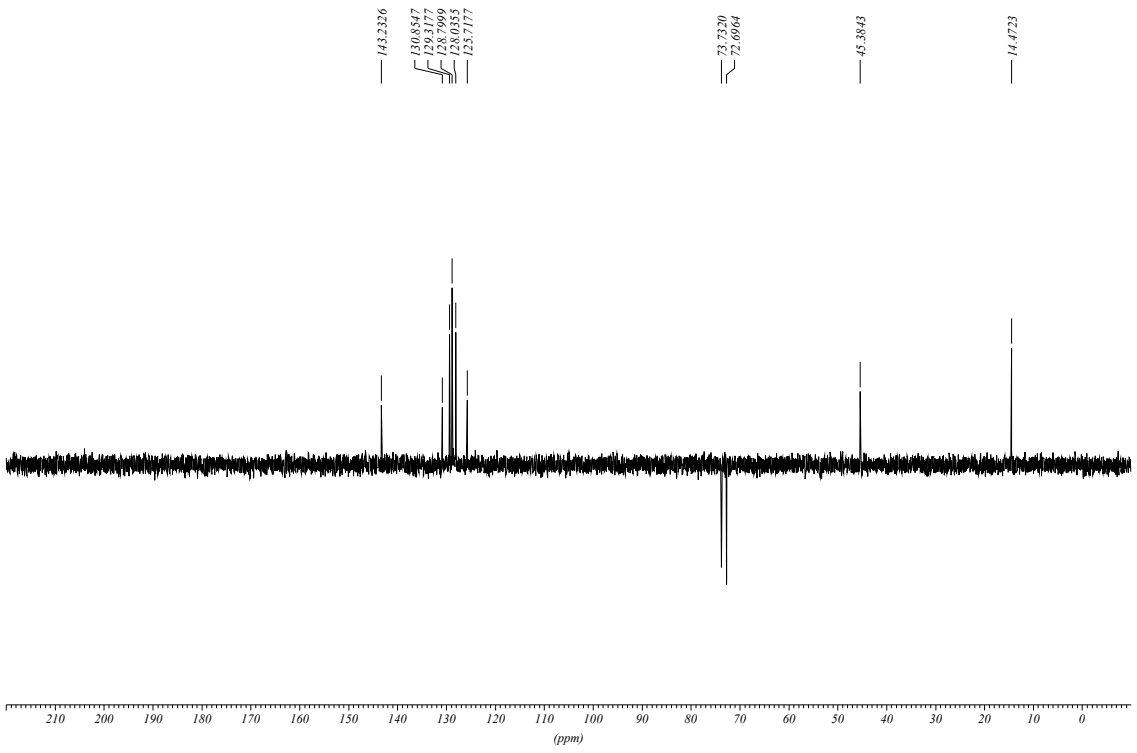


(*E*)-5-(benzyloxy)-4-methyl-1-phenylpent-1-en-3-one

3j: ^{1}H NMR δ 1.11 (d, *J* = 7.2Hz, 3H), 3.16 (m, 1H), 3.47 (dd, *J* = 9.2Hz, 5.9 Hz, 1H), 3.68 (dd, *J* = 9.2Hz, 7.3Hz, 1H), 4.45 (d, *J* = 3Hz, 2H), 6.77 (d, *J* = 16Hz, 1H), 7.22 (m, 5H), 7.32 (m, 3H), 7.48 (m, 2H), 7.56 (d, *J* = 16Hz, 1H); ^{13}C NMR 14.4, 45.4, 72.7, 73.7, 125.7, 128.0, 128.8, 128.9, 130.8, 135.0, 138.6, 143.2, 202.4 ; IR (film) ν_{max}: 3060, 3029, 2970, 1686, 1658, 1610, 1099, 1054, 739, 698 cm^{-1}.




202.4439
143.2089
138.5815
135.0473
130.8309
129.3122
128.7944
128.7679
128.0200
127.9954
125.7022
73.7165
72.6809
45.3688
14.4486
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)


143.2326
130.8547
129.3177
128.7999
128.0355
125.7177
73.7320
72.6964
45.3843
14.4723
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
(ppm)