Supporting Information

A highly efficient cycloaddition of vinylarenes with electron-deficient alkynes affording 1,2-disubstituted-3,4-dihydronaphthalenes catalysed by *N*,*N*-dimethylformamide dimethyl acetal

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Contents:

1. Experimental general method and characterization of products

(1) General method

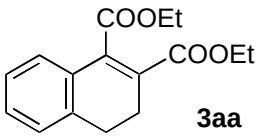
All organic starting materials are analytically pure and used without further purification. ^{1}H and ^{13}C NMR spectra were recorded on a JOEL JNM-ECA300 spectrometer at 300 MHz and 75 MHz, respectively. ^{1}H chemical shifts (δ) were referenced to TMS, and ^{13}C NMR chemical shifts (δ) were referenced to internal solvent resonance. GC analyses of organic compounds were performed on an Agilent Technologies 1790 GC (with a TC-WAX capillary 25m column) instrument. Mass spectra were obtained on a HEWLETT 5890 PACKARD SERIES II GC/MS spectrometer with a PEG-25M column. High-resolution mass spectra were obtained with a ZAB-HS mass spectrometer in the Department of Chemistry of Peking University. Element analyses were obtained with a Flash EA 1112 Element Analyzer in the Institute of Chemistry, Chinese Academy of Sciences.

(2) Typical experimental procedure for cyclic addition of styrene 1a with diethyl acetylenedicarboxylate 2a (Table 1, entry 4): A mixture of styrene (1.0 mL, 8.6 mmol), diethyl acetylenedicarboxylate **2a** (170.0 mg, 1.0 mmol), and N,N-dimethylformamide dimethyl acetal (DMF-DMA, 12.0 mg, 0.1 mmol) under air in a sealed tube was heated with stirring at 110 ^{o}C for 5 h. After cooling, the reaction mixture was diluted with dichloromethane (5.0 mL), and then octadecane (127.0 mg, 0.5 mmol) was added as internal standard for GC analysis. After GC and GCMS analyses, the mixture was concentrated under a reduced pressure. **3aa** (224.0 mg, 0.82 mmol) was isolated as white solid in 82% yield by column chromatography (silica gel, eluted with cyclohexane). The results of GC analysis of the crude reaction mixture revealed that **3aa** was formed in 93% GC yield.

All known products were characterized by their ^{1}H, ^{13}C NMR and GC-MS, and new products were characterized by their ^{1}H, ^{13}C NMR, GC-MS and elemental analyses or high resolution MS.

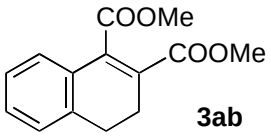
(3) Characterization of products

3aa, **3ab** and **3j** are known compounds, their structures are characterized by ^{1}H, ^{13}C-NMR, mass spectra. Other products are new compounds, and their structures are characterized by ^{1}H, ^{13}C-NMR, mass spectra, elemental analyses and/or high resolution MS.



3aa

1,2-Diethoxycarbonyl-3,4-dihydronaphalene[1] **3aa**: White solid, m.p. 73~74 ^{o}C (recrystallization with CH_2Cl_2/cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.17-7.28 (m, 4H), 4.41 (q, 2H, *J* = 7.2 Hz), 4.26 (q, 2H, *J* = 7.2 Hz), 2.90-2.84 (m, 2H), 2.68-2.63 (m, 2H), 1.38 (t, 3H, *J* = 7.2 Hz), 1.31 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 166.2, 140.4, 136.8, 130.3, 129.9, 127.9, 127.0, 126.0, 61.5, 61.2, 27.3, 22.8, 14.2. GCMS *m/z* (% relative intensity): 274(M^+, 29), 246(2), 228(35), 200(70), 199(27), 172(36), 155(92), 128(100), 115(58), 102(16), 89(4), 77(12).



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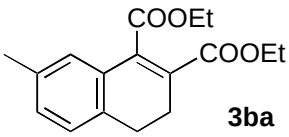
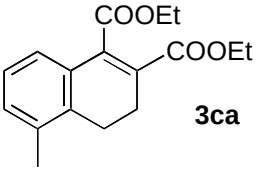
1,2-Dimethoxycarbonyl-3,4-dihydronaphalene[2] **3ab**: White solid, m.p. 55~56 ^{o}C (recrystallization with CH_2Cl_2/cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15-7.28 (m, 4H), 3.94 (s, 3H), 3.80 (s, 3H), 2.89-2.84 (m, 2H), 2.68-2.63 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.1, 166.6, 140.7, 136.8, 130.1, 127.9, 127.0, 126.8, 126.1, 52.5, 52.3, 27.3, 22.7. GCMS *m/z* (% relative intensity): 246(M^+, 54), 214(65), 186(32), 171(4), 155(100), 129(19), 128(84), 115(28), 102(11), 77(10), 59(14).



3ba

1,2-Diethoxycarbonyl-7-methyl-3,4-dihydronaphalene 3ba: White solid, m.p. 54~55 ^{o}C (recrystallization with CH_2Cl_2/cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10 (s, 2H), 7.01 (s, 1H), 4.46 (q, 2H, *J* = 7.2 Hz), 4.29 (q, 2H, *J* = 7.2Hz), 2.87-2.82 (m, 2H), 2.69-2.64 (m, 2H), 2.33 (s, 3H), 1.43 (t, 3H, *J* = 7.2 Hz), 1.35 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 166.3, 140.7, 136.5, 133.9, 130.7, 130.2, 127.8, 126.9, 126.6, 61.5, 61.2, 26.9, 23.0, 21.2, 14.3, 14.2. GCMS *m/z* (% relative intensity): 288(M^+, 73), 260(2), 242(50), 214(71), 199(10), 186(27), 169(100), 159(5), 141(51), 128(38), 115(24), 101(3), 91(7), 77(3), 63(3). Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.83; H, 6.94. Found: C, 72.79; H, 7.01. HRMS: calcd for $C_{17}H_{20}O_4$ 288.1362; found 288.1362.



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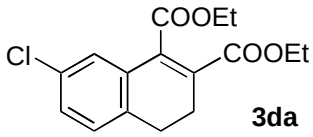
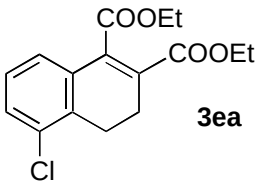
1,2-Diethoxycarbonyl-5-methyl-3,4-dihydronaphalene 3ca: White solid, m.p. 56~57 ^{o}C (recrystallization with CH_2Cl_2/cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.02-7.17 (m, 3H), 4.40 (q, 2H, *J* = 7.2 Hz), 4.26 (q, 2H, *J* = 7.2 Hz), 2.83-2.77 (m, 2H), 2.66-2.62 (m, 2H), 2.29 (s, 3H), 1.37 (t, 3H, *J* = 7.2 Hz), 1.32 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.8, 166.2, 140.9, 135.4, 135.2, 132.0, 130.2, 126.3, 126.1, 124.1, 61.5, 61.2, 23.4, 22.5, 19.6, 14.2. GCMS *m/z* (% relative intensity): 288(M^+, 32), 242(30), 215(43), 214(73), 199(17), 186(26), 169(90), 141(100), 128(61), 115(72), 91(14), 77(7). HRMS: calcd for $C_{17}H_{20}O_4$ 288.1362; found 288.1360.



3da

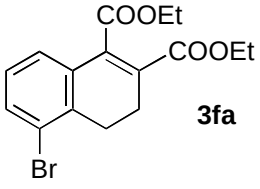
7-Chloro-1,2-diethoxycarbonyl-3,4-dihydronaphalene 3da: White solid, m.p. 93~94

^{o}C (recrystallization with CH_2Cl_2/cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11-7.25 (m, 3H), 4.42 (q, 2H, *J* = 7.2 Hz), 4.26 (q, 2H, *J* = 7.2 Hz), 2.86-2.79 (m, 2H), 2.67-2.62 (m, 2H), 1.39 (t, 3H, *J* = 7.2 Hz), 1.31 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0, 165.9, 139.1, 135.0, 132.7, 131.8, 129.6, 129.1, 128.6, 125.9, 61.8, 61.4, 26.7, 22.8, 14.2, 14.1. GCMS *m/z* (% relative intensity): 308(M^+, 36), 280(1), 262(43), 234(89), 206(27), 189(100), 163(35), 149(23), 128(57), 127(75), 115(39), 101(8), 99(6), 89(11), 77(11). Anal. Calcd for $C_{16}H_{17}ClO_4$: C, 62.33; H, 5.52. Found: C, 62.50; H, 5.62. HRMS: calcd for $C_{16}H_{17}ClO_4$ 308.0815, found 308.0812



3ea

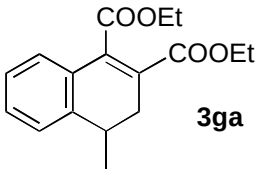
5-Chloro-1,2-diethoxycarbonyl-3,4-dihydronaphalene 3ea: White solid, m.p. 95~96 ^{o}C (recrystallization with CH_2Cl_2/cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11-7.35 (m, 3H), 4.40 (q, 2H, *J* = 7.2 Hz), 4.26 (q, 2H, *J* = 7.2 Hz), 3.06-2.96 (m, 2H), 2.70-2.64 (m, 2H), 1.37 (t, 3H, *J* = 7.2 Hz), 1.32 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.4, 165.9, 143.9, 141.4, 139.7, 134.4, 133.5, 130.8, 126.4, 124.6, 61.7, 61.4, 23.9, 22.2, 14.1. GCMS *m/z* (% relative intensity): 308(M^+, 33), 280(1), 262(45), 234(100), 206(29), 189(90), 163(39), 162(40), 151(13), 149(26), 128(52), 127(75), 126(41), 116(15), 115(36), 77(10). HRMS: calcd for $C_{16}H_{17}ClO_4$ 308.0815, found 308.0817



3fa

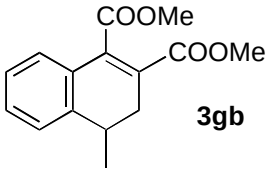
5-Bromo-1,2-diethoxycarbonyl-3,4-dihydronaphalene 3fa: White solid, m.p. 120~122 ^{o}C (recrystallization with CH_2Cl_2/cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.10-7.54 (m, 3H), 4.44 (q, 2H, *J* = 7.2 Hz), 4.30 (q, 2H, *J* = 7.2 Hz), 3.06-3.00 (m, 2H), 2.73-2.68 (m, 2H), 1.41 (t, 3H, *J* = 7.2 Hz), 1.36 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$)

δ 168.2, 165.9, 139.7, 136.3, 134.0, 132.4, 128.0, 127.9, 125.3, 124.2, 61.8, 61.5, 27.0, 22.5, 14.2, 14.1. GCMS *m/z* (% relative intensity): 352(M^+, 47), 308(68), 280(100), 252(19), 235(65), 207(13), 199(17), 72(12), 156(20), 142(15), 128(78), 115(36), 101(8), 89(3), 77(11). HRMS: calcd for $C_{16}H_{17}BrO_4$ 352.0310, found 352.0310



3ga

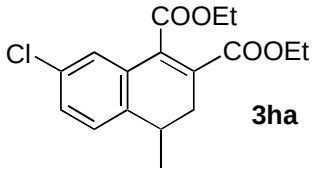
1,2-Diethoxycarbonyl-4-methyl-3,4-dihydronaphalene 3ga: White solid, m.p. 68~69 ^oC (recrystallization with CH_2Cl_2/cyclohexane). ^1H NMR (300 MHz, $CDCl_3$) δ 7.17-7.32 (m, 4H), 4.39 (q, 2H, *J* = 7.2 Hz), 4.23 (q, 2H, *J* = 7.2 Hz), 2.99 (m, 1H), 2.72 (dd, 1H, *J* = 17.1, 6.5 Hz), 2.47 (dd, 1H, J = 17.1, 8.1 Hz), 1.36 (t, 3H, *J* = 7.2 Hz), 1.29 (t, 3H, *J* = 7.2 Hz), 1.25 (d, 3H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.6, 166.3, 141.8, 140.0, 130.2, 129.5, 126.8, 126.4, 126.2, 125.6, 61.5, 61.2, 31.6, 30.5, 19.8, 14.2. GCMS *m*/*z* (% rel. inten.) 288(M^+, 21), 265(3), 243(12), 227(64), 15(26), 199(100), 186(6), 169(30), 155(32), 143(46), 128(65), 115(69), 91(8), 77(6). Anal. Calcd for $C_{17}H_{20}O_4$: C, 70.83; H, 6.94. Found: C, 72.53; H, 6.97. HRMS calcd for $C_{17}H_{20}O_4$ 288.1362, found 288.1362.



3gb

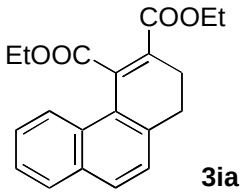
1,2-Dimethoxycarbonyl-4-methyl-3,4-dihydronaphalene 3gb: White solid, m.p. 49~50 ^oC (recrystallization with CH_2Cl_2/cyclohexane). ^1H NMR (300 MHz, $CDCl_3$) δ 7.18-7.32 (m, 4H), 3.93 (s, 3H), 3.80 (s, 3H), 3.01 (m, 1H), 2.74 (dd, 1H, *J* = 17.0, 6.7 Hz), 2.51 (dd, 1H, *J* = 17.0, 7.7 Hz), 1.26 (d, 3H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.0, 166.8, 141.8, 140.2, 130.4, 129.2, 126.9, 126.5, 126.3, 125.5, 52.5, 52.3, 31.6, 30.3, 19.8. GCMS *m*/*z* (% rel. inten.) 260(M^+, 18), 229(15), 213(100), 200(12), 185(2), 169(27),

155(12), 142(39), 141(44), 128(17), 127(20), 115(37), 89(4), 77(4), 59(9). HRMS calcd for $C_{15}H_{16}O_4$ 260.1049, found 260.1048.



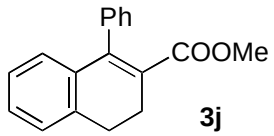
3ha

7-Chloro-1,2-diethoxycarbonyl-4-methyl-3,4-dihydronaphalene 3ha: White solid, m.p. 89~90 ^{o}C (recrystallization with CH_2Cl_2/cyclohexane). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.15-7.28 (m, 3H), 4.42 (q, 2H, *J* = 7.2 Hz), 4.26 (q, 2H, *J* = 7.2 Hz), 2.99 (m, 1H), 2.74 (dd, 1H, *J* = 17.1, 6.6 Hz), 2.48 (dd, 1H, *J* = 16.8, 7.9 Hz), 1.39 (t, 3H, *J* = 7.2 Hz), 1.31 (t, 3H, *J* = 7.2 Hz), 1.25 (d, 3H, *J* = 6.8 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0, 166.1, 140.0, 138.6, 132.6, 131.1, 129.9, 127.7, 127.3, 126.1, 61.8, 61.4, 31.1, 30.5, 19.6, 14.2, 14.1. GCMS *m/z* (% relative intensity): 322(M^+, 27), 294(0.7), 277(14), 261(68), 249(29), 233(100), 221(5), 203(20), 189(25), 177(22), 163(17), 149(18), 141(35), 128(18), 115(25), 89(3), 77(2). Anal. Calcd for $C_{17}H_{19}ClO_4$: C, 63.33; H, 5.90. Found: C, 62.95; H, 5.59. HRMS: calcd for $C_{17}H_{19}ClO_4$ 322.0972, found 322.0970



3ia

1,2-Diethoxycarbonyl-3,4-dihydrophenanthrene 3ia: White solid, m.p. 115~116 ^{o}C (recrystallization with CH_2Cl_2/cyclohexane).^{1}H NMR (300 MHz, $CDCl_3$) δ 7.25-7.96 (m, 6H), 4.38 (q, 2H, *J* = 7.2 Hz), 4.30 (q, 2H, *J* = 7.2 Hz), 2.97-2.91 (m, 2H), 2.63-2.58 (m, 2H), 1.36 (t, 3H, *J* = 7.2 Hz), 1.31 (t, 3H, *J* = 7.2 Hz). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.7, 167.7, 138.2, 136.6, 133.3, 132.6, 130.4, 129.0, 127.8, 127.4, 126.6, 126.1, 125.2, 123.7, 61.7, 61.3, 29.5, 24.6, 14.2, 13.9. GCMS *m/z* (% rel. inten.) 324(M^+, 61), 296(4), 279(12), 250(33), 222(22), 205(70), 178(100), 165(38), 152(29), 139(4), 115(2), 77(1). HRMS calcd for $C_{20}H_{20}O_4$ 324.1362, found 324.1360.



3j

2-Methoxycarbonyl-1-phenyl-3,4-dihydronaphalene[3] **3j**: Pale-yellow viscous oil. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.74-7.39 (m, 9H), 3.50 (s, 3H), 2.95-2.89 (m, 2H), 2.74-2.70 (m, 2H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 169.4, 145.1, 139.2, 137.1, 135.3, 128.7, 128.6, 128.0, 127.7, 127.4, 127.3, 127.2, 126.4, 119.8, 51.2, 27.9, 25.3. GCMS *m*/*z* (% rel. inten.) 264(M^+, 88), 249(1), 231(100), 215(15), 205(79), 204(66), 203(94), 202(70), 190(19), 189(18), 178(21), 165(10), 152(5), 139(2), 127(12), 115(5), 101(26), 89(9), 77(6), 63(3), 51(3).

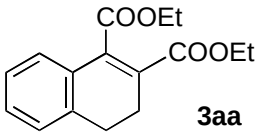
References

(1) Bailey, W. J.; Quigley, S. T. *J. Am. Chem. Soc*. **1959**, *81*, 5598-5601.

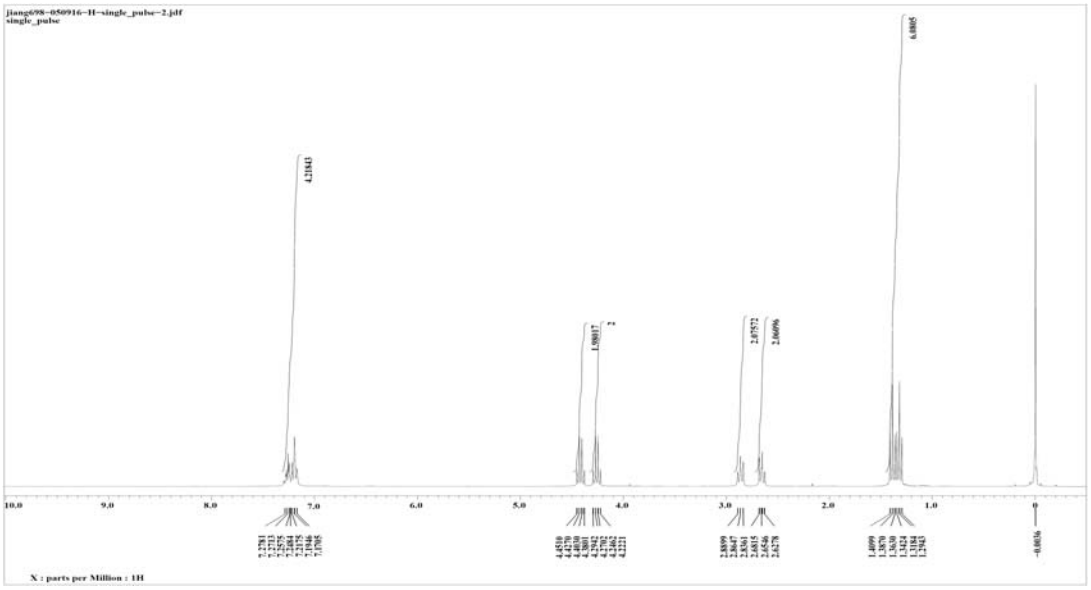
(2) Lyssy, T. M. *J. Org. Chem.* **1962**, *27*, 5-13.

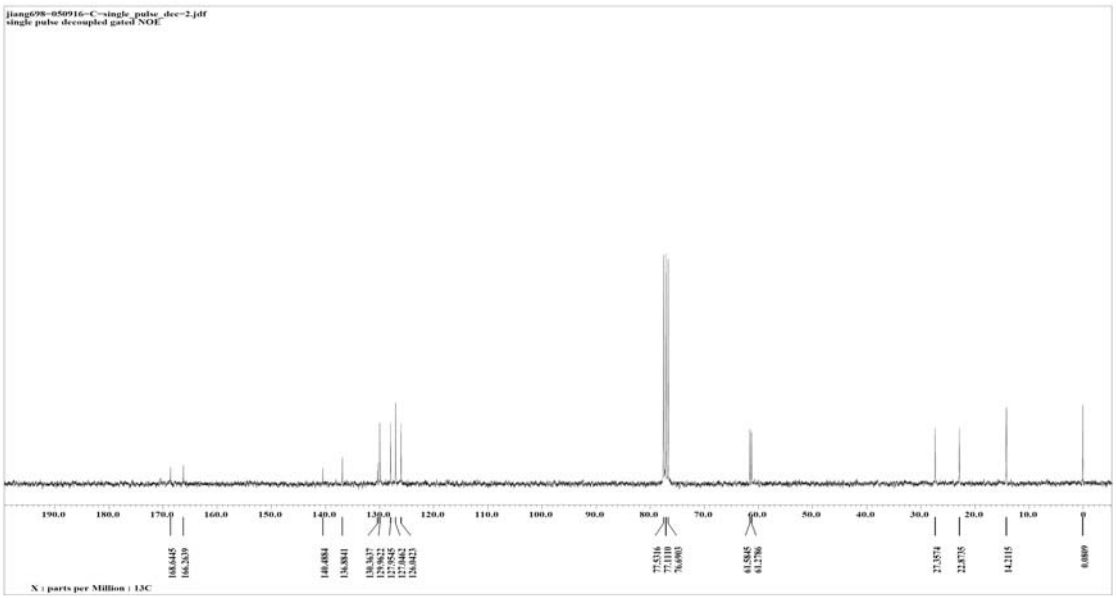
(3) Pfau, M.; Combrisson, S.; RoweJr. J. E.; Heindel, N. D. *Tetrahedron* **1978**, *34*, 3459-3468.

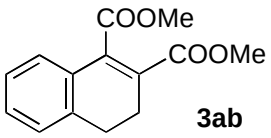
2. Copies of ^{1}H NMR and ^{13}C NMR spectra for compounds 3aa~ 3j



3aa



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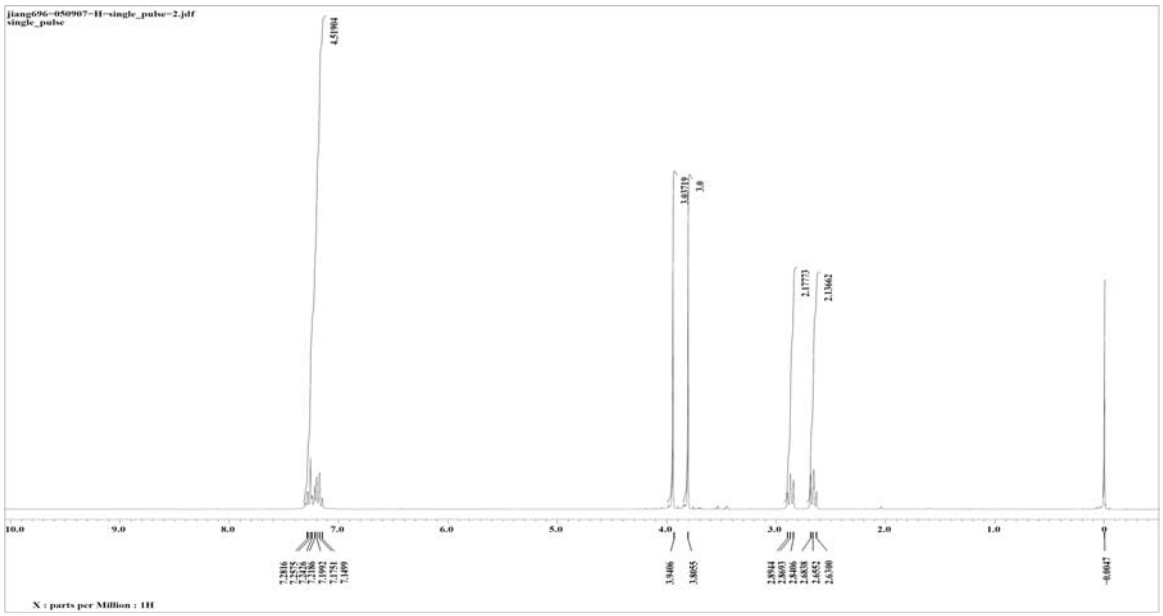
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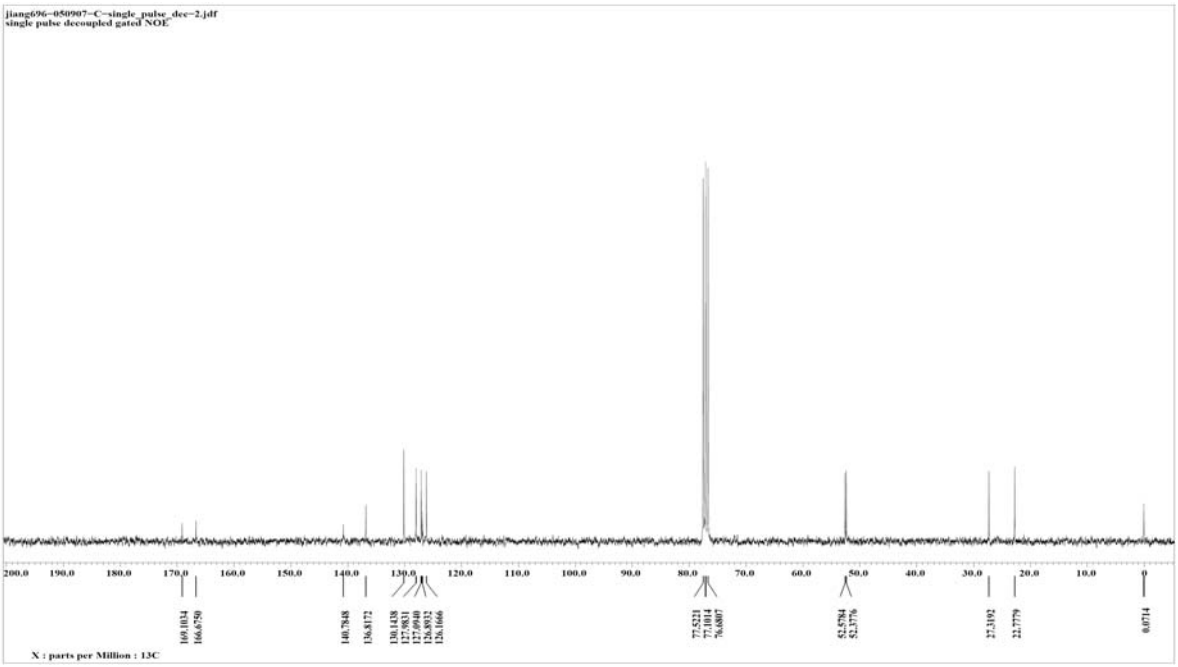
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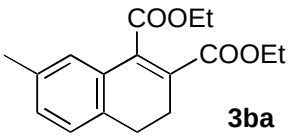
X : parts per Million : 13C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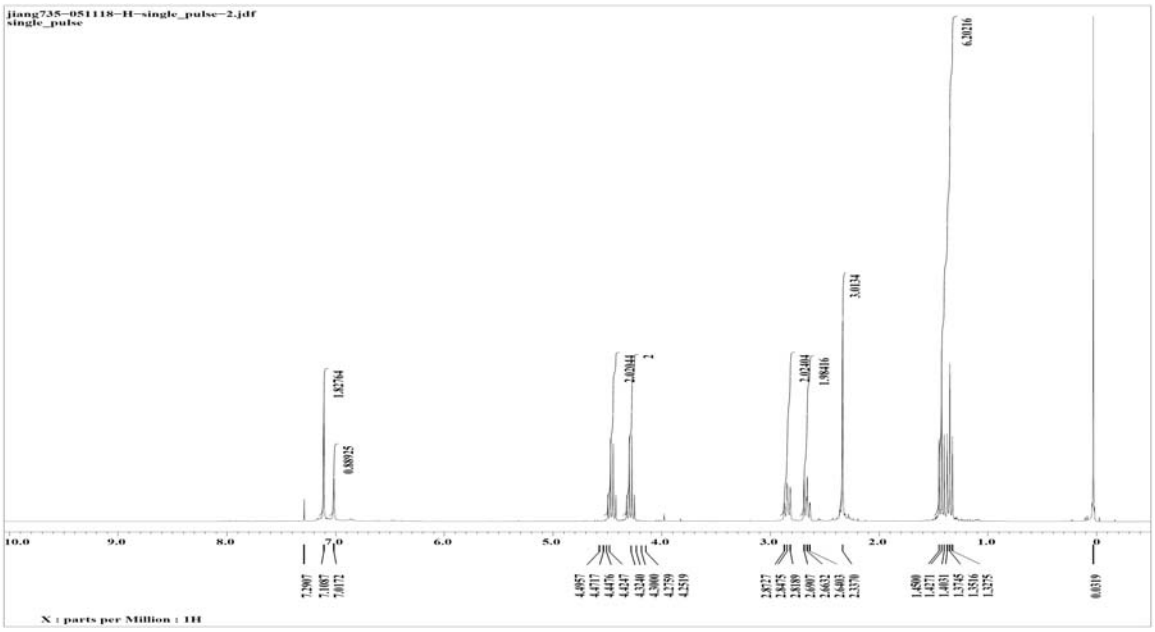
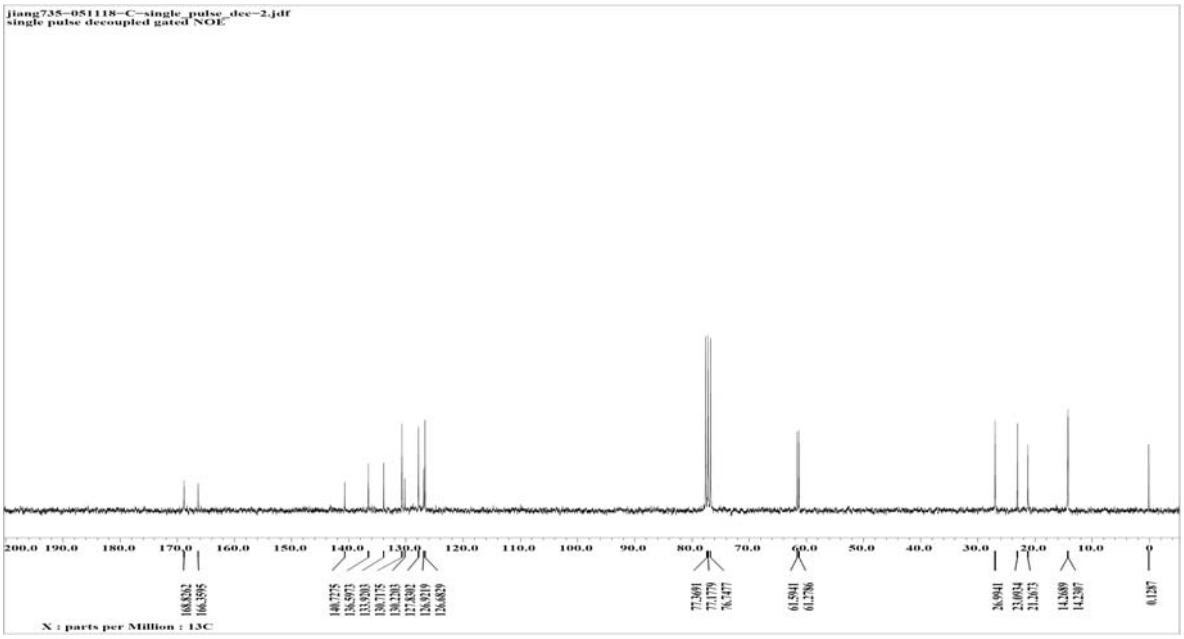
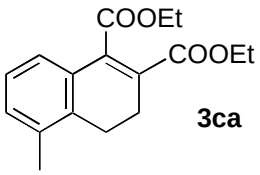
COOEt

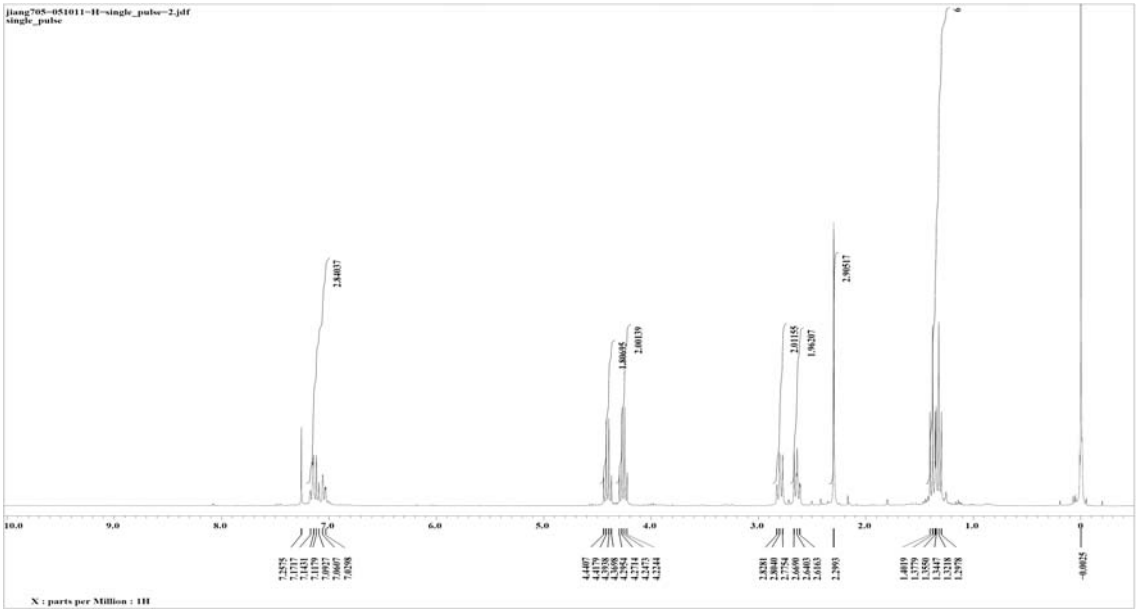
3ba

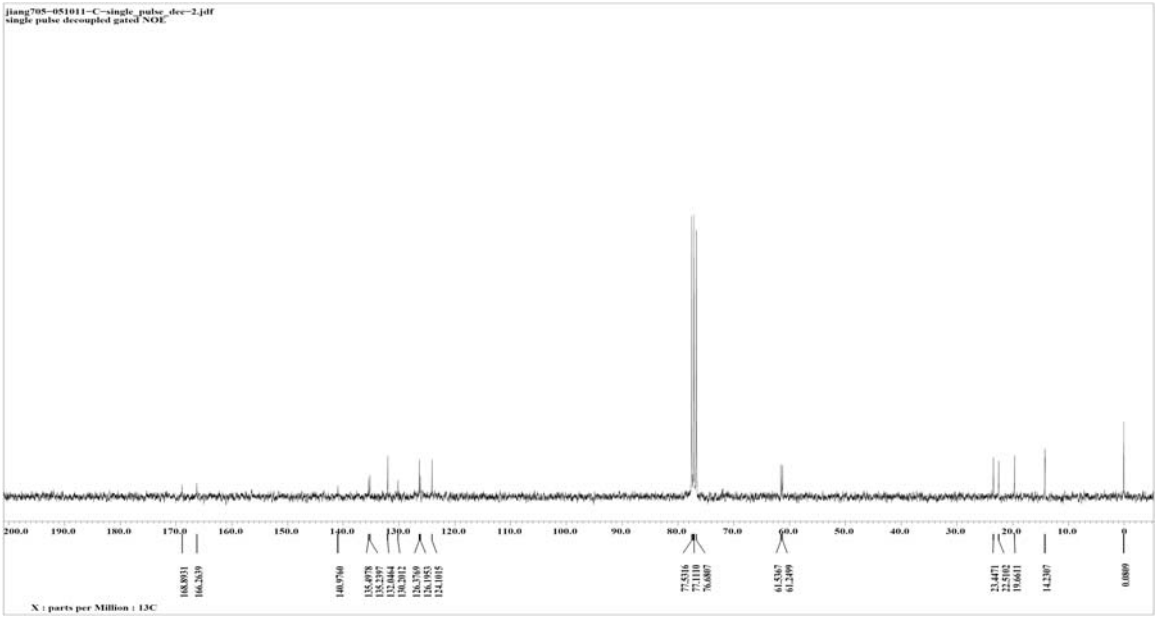

jiang735-051118-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H


jiang735-051118-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C


COOEt
COOEt

3ca


jiang705-051011-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H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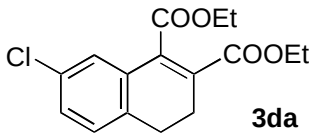
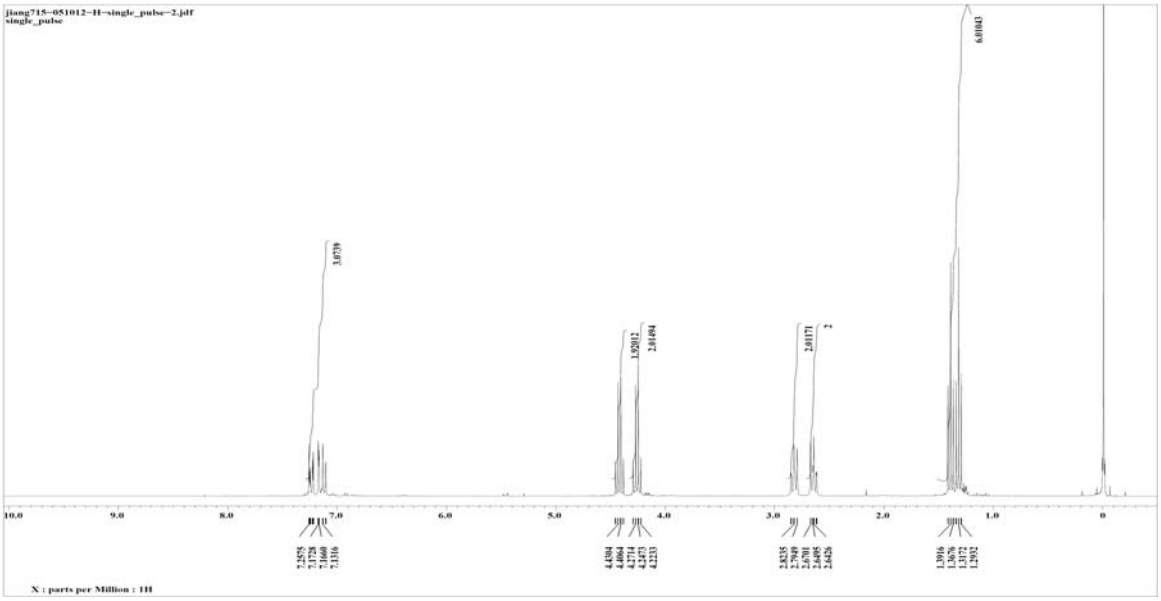
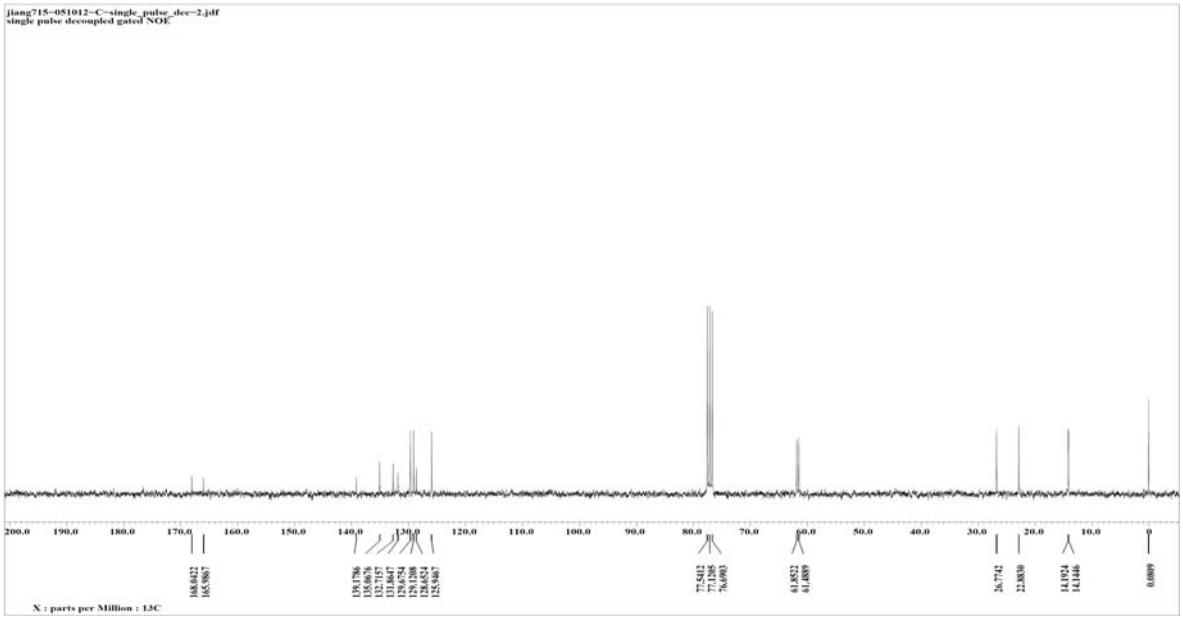
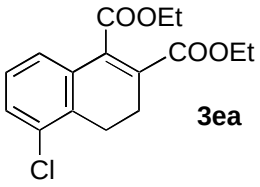
single pulse decoupled gated NOE
X : parts per Million : 13C


COOEt
Cl
COOEt

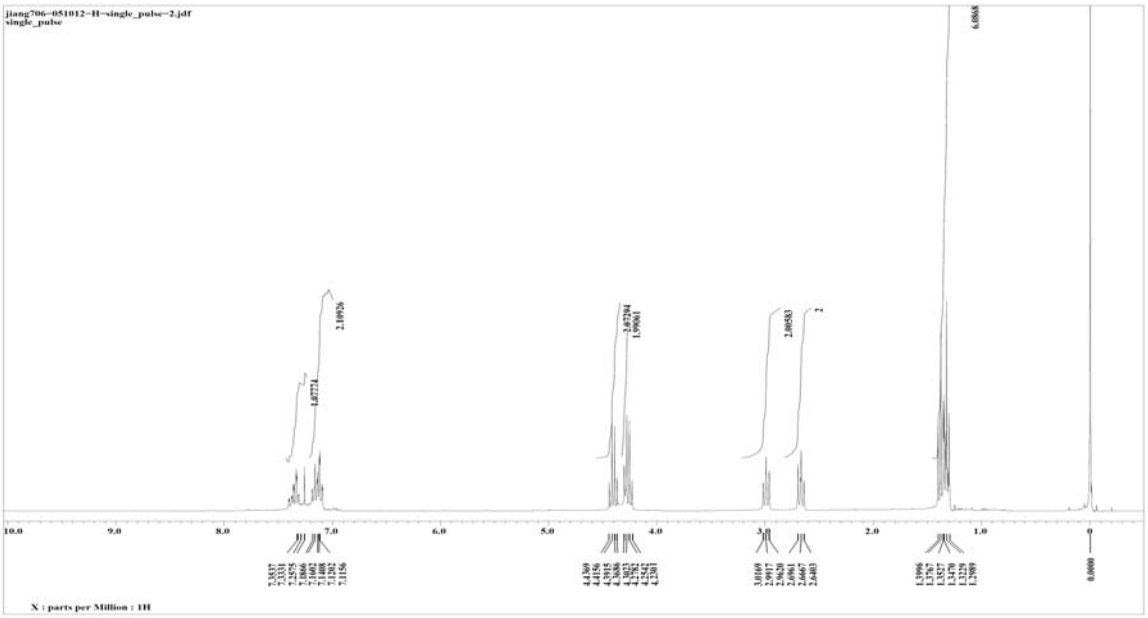
3da

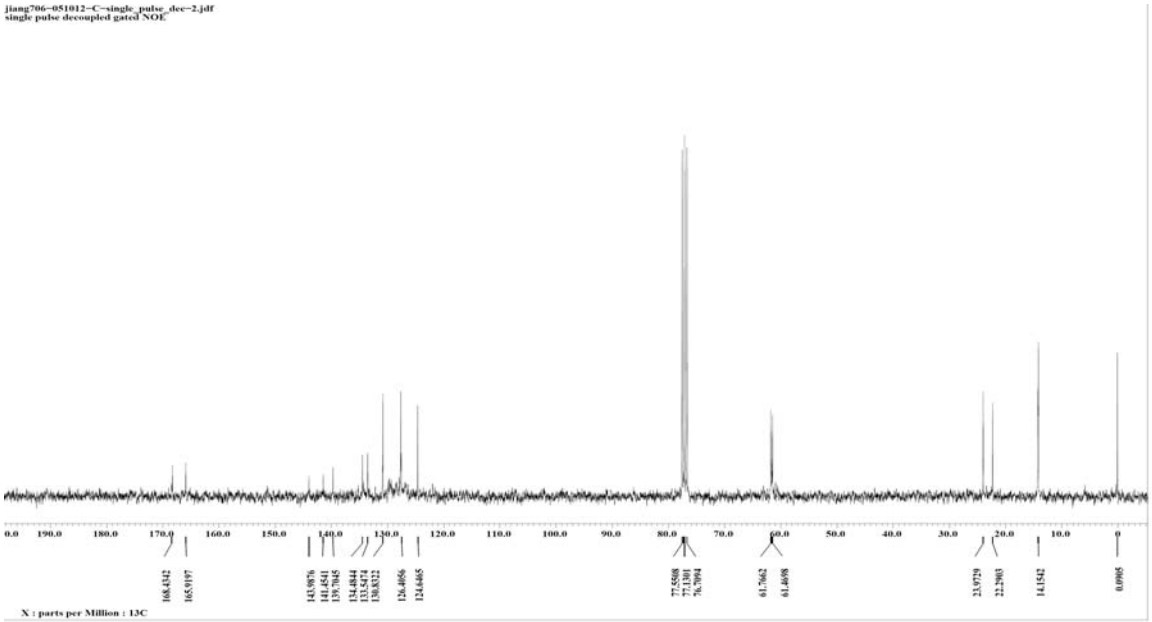

jiang715-051012-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H

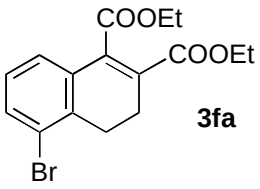

jiang715-051012-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C


COOEt
COOEt
Cl

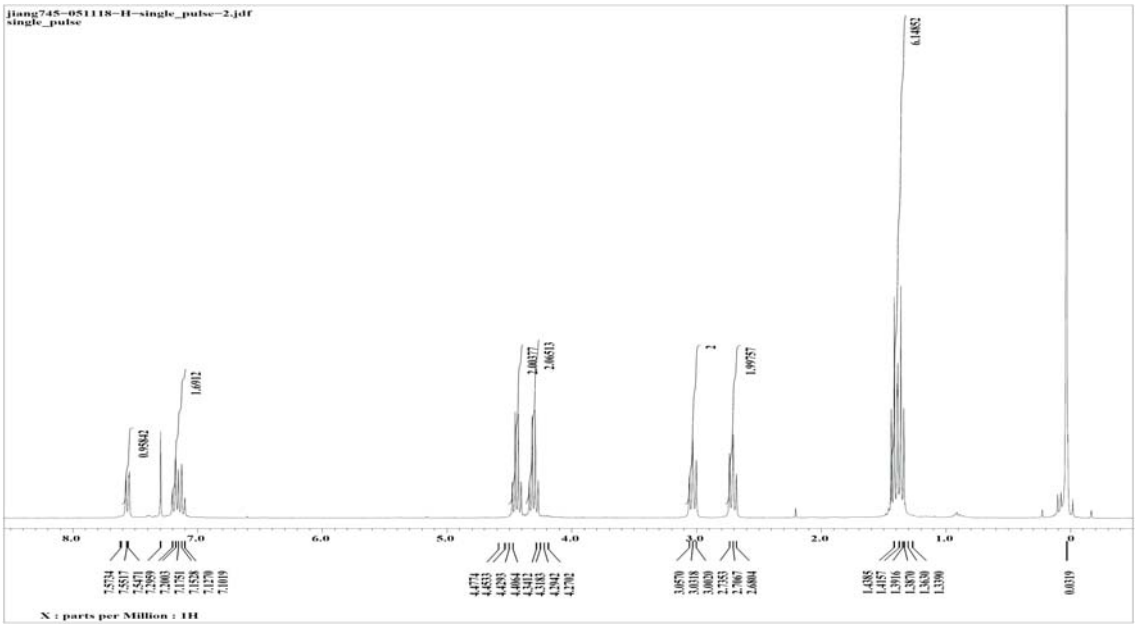
3ea

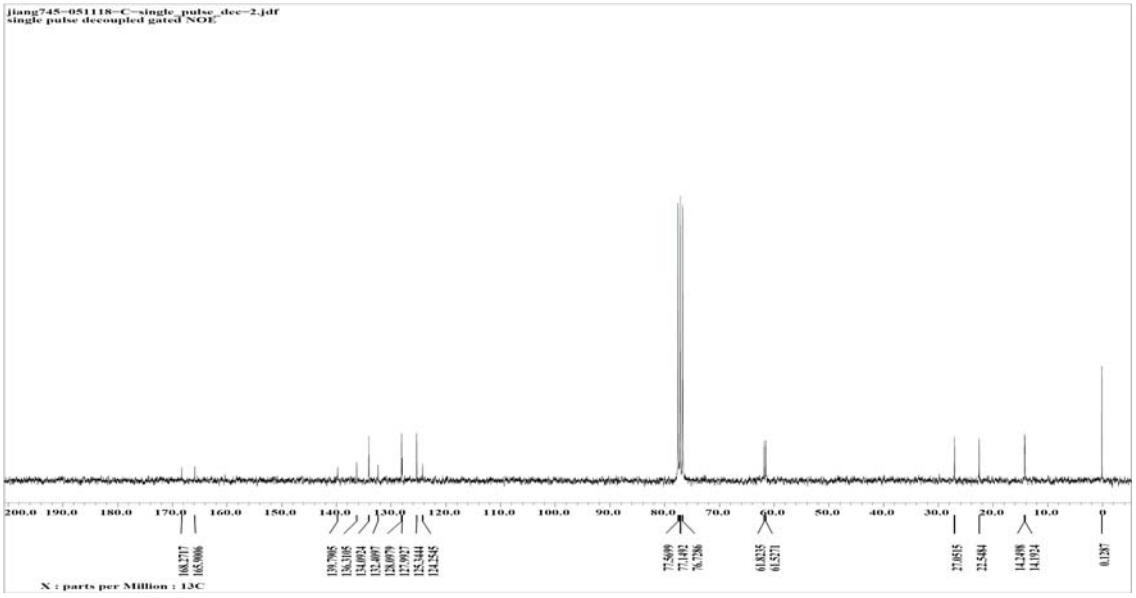

jiang706-051012-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H

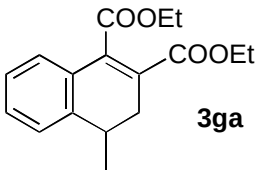

jiang706-051012-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C


COOEt
COOEt
Br

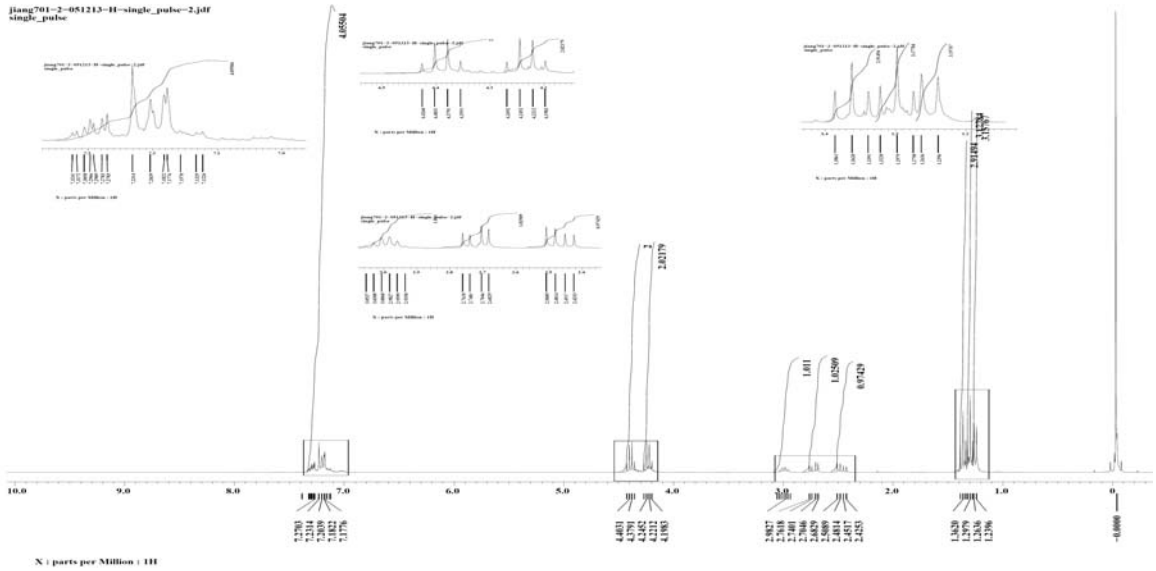
3fa

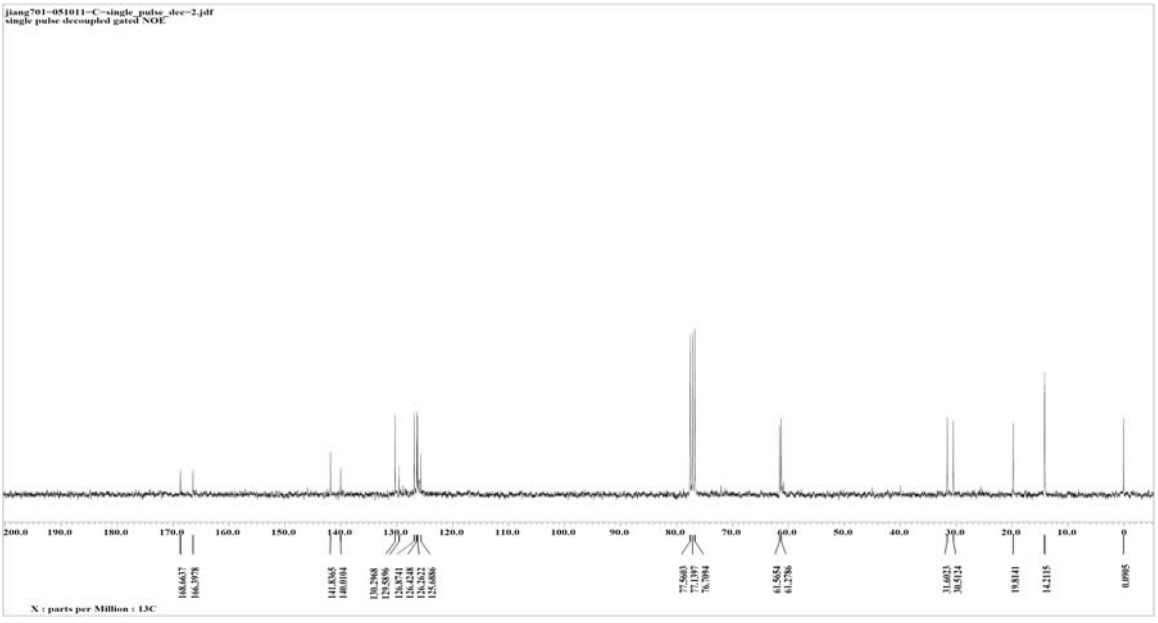

jiang745-051118-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H

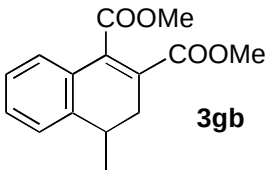

jiang745-051118-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C


COOEt
COOEt

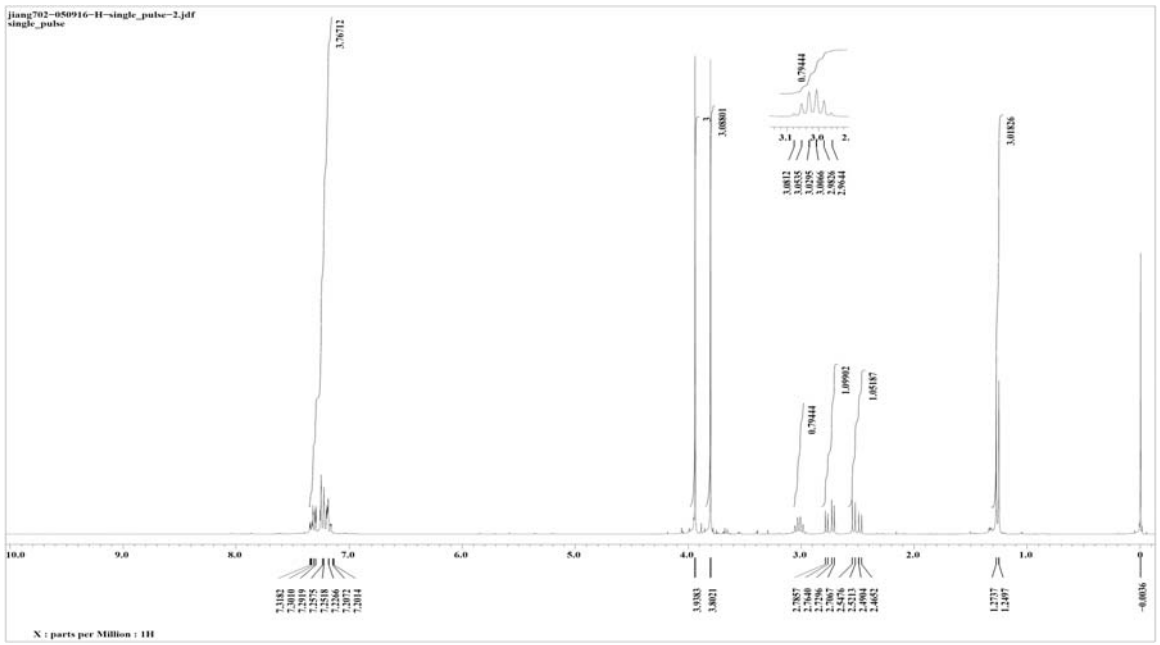
3ga

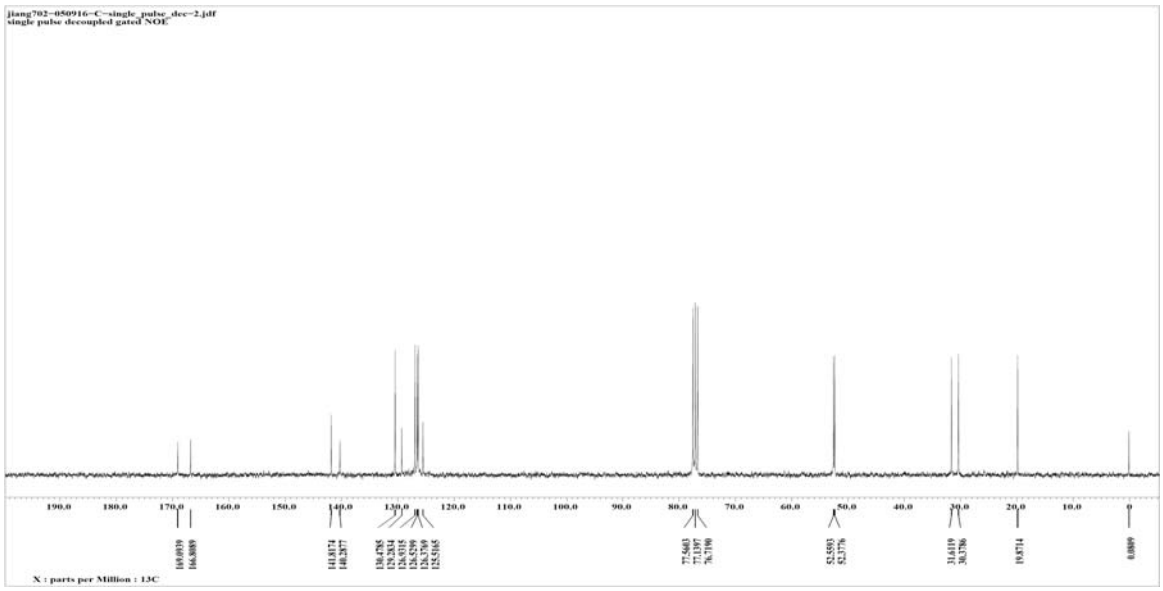

jiang701-2-051213-H-single_pulse-2.jdf
single_pulse
4.05504
2.02179
1.011
1.02589
0.97429
2.91494
3.13979
X : parts per Million : 1H

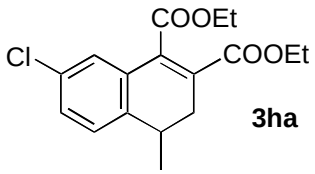

jiang701-051011-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C


COOMe
COOMe

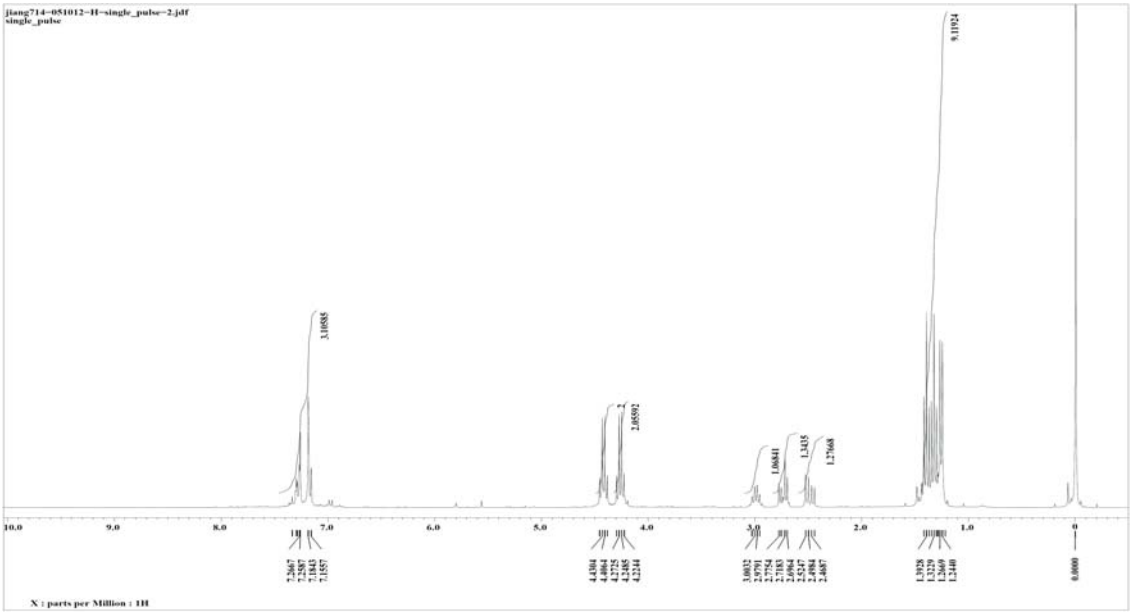
3gb

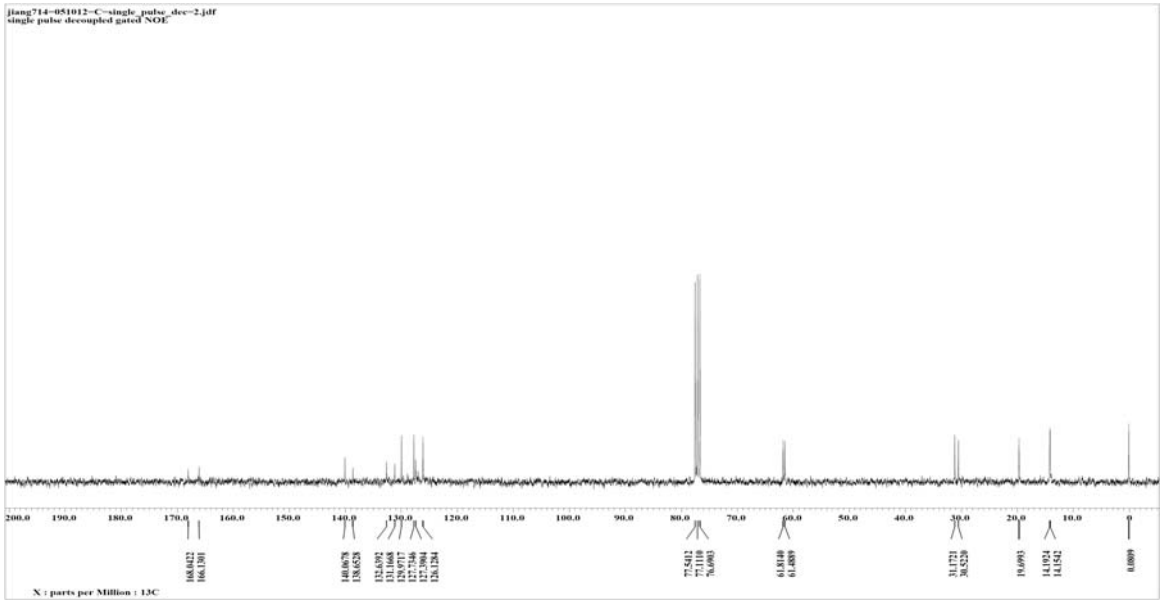

jiang702-050916-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H

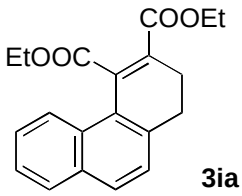

jiang702-050916-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C


COOEt
Cl
COOEt

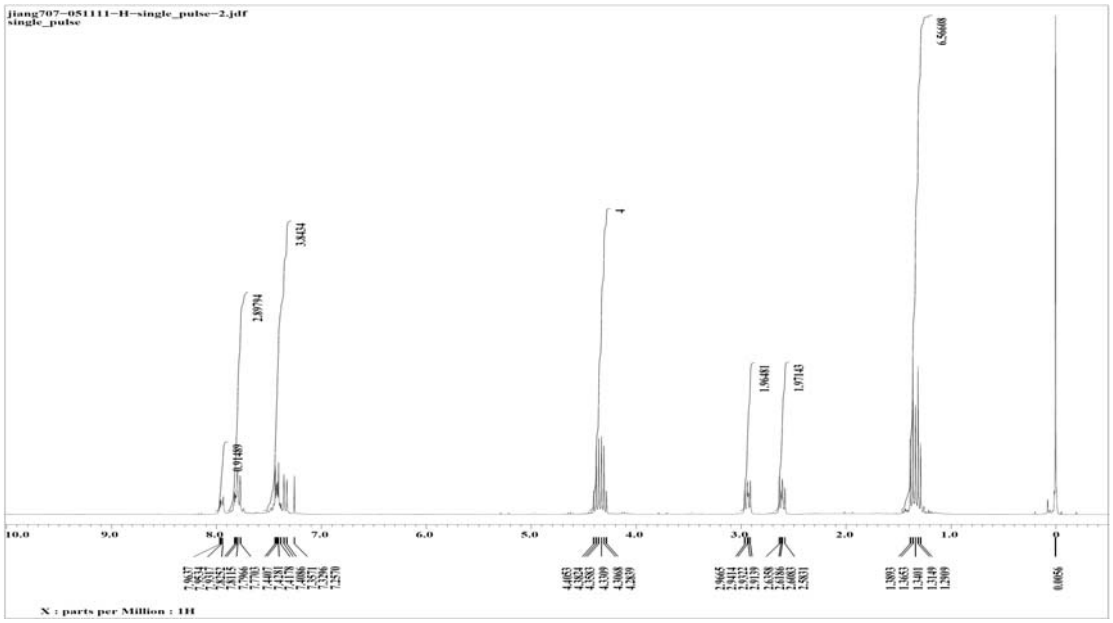
3ha

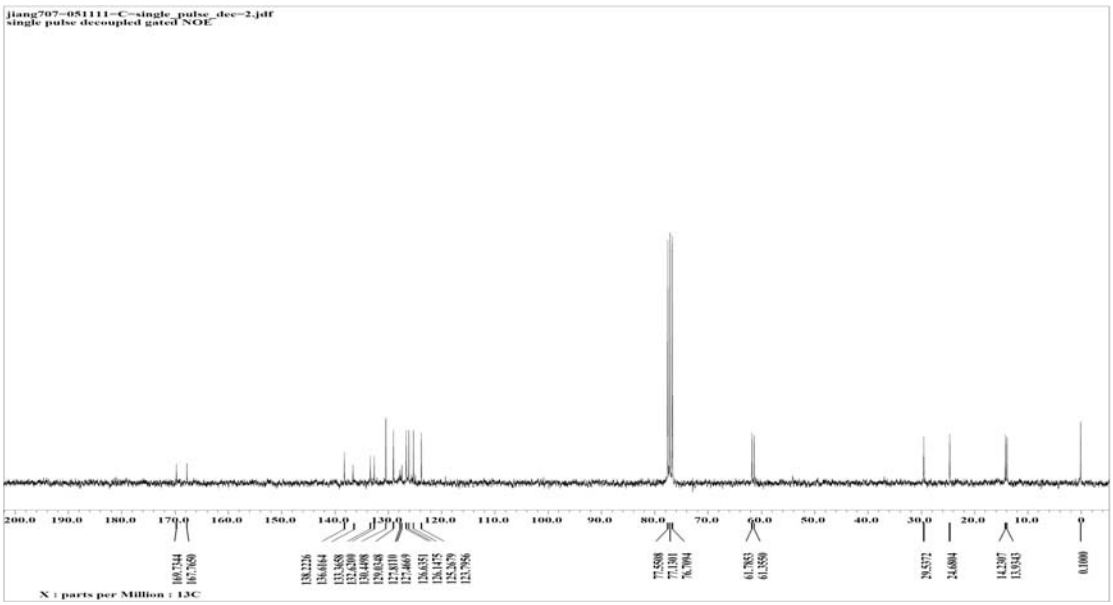

jiang714-051012-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H

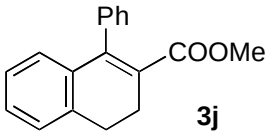

jiang714-051012-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C


COOEt
EtOOC

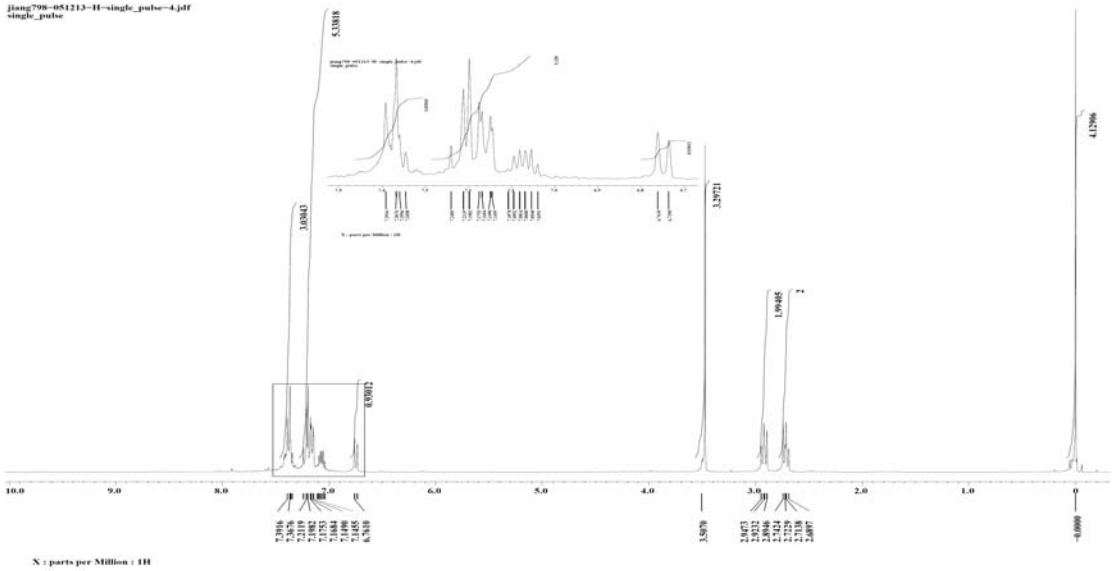
3ia

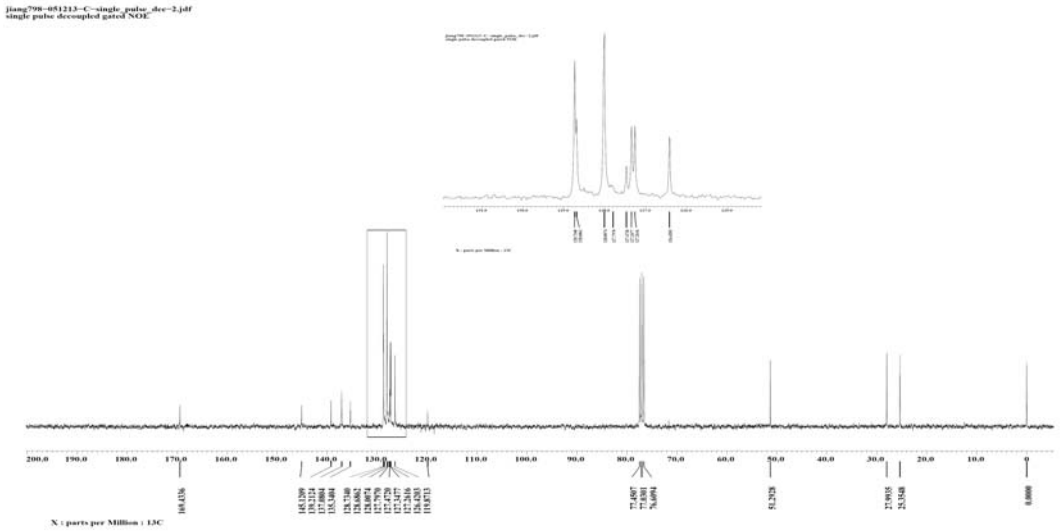

jiang707-051111-H-single_pulse-2.jdf
single_pulse
X : parts per Million : 1H


jiang707-051111-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C


Ph
COOMe

3j


jiang798-051213-H-single_pulse-4.jdf
single_pulse
5.3318
3.0843
3.2972
1.9948
4.1296
0.9302
X : parts per Million : 1H


jiang798-051213-C-single_pulse_dec-2.jdf
single pulse decoupled gated NOE
X : parts per Million : 13C