Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

MeOTf-catalyzed Annulation of Aldehydes and Arylalkynes Leading to 2, 3-Disubstituted Indanones

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1. General Comments

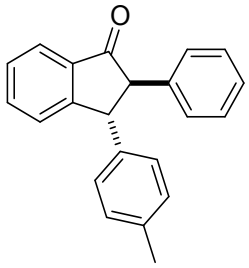
All the reactions were carried out in oven-dried sealed tube with Teflon-lined septum under N_2 atmosphere. Unless indicated, all materials were obtained from commercial sources and used as received. DCE was dried by activated 4Å molecular sieve. Column chromatography was performed on silica gel (particle size 200-300 mesh). ^{1}H NMR and ^{13}C NMR spectra were recorded on 300 MHz or 400 MHz at ambient temperature with $CDCl_3$ as the solvent. Chemical shifts (δ) were given in ppm, referenced to the residual proton resonance of $CDCl_3$ (7.26), to the carbon resonance of $CDCl_3$ (77.16). Coupling constants (*J*) were given in Hertz (Hz). The term m, q, t, d, and s referred to multiplet, quartet, triplet, doublet, and singlet. The reaction progress was monitored by GC-MS or NMR if applicable.

1,2-Di-*p*-tolylethyne, 1,2-bis(4-methoxyphenyl)ethyne, and 1,2-bis(4-fluorophenyl)-ethyne were prepared according to literature reported.[1] 1,2-bis(4-(Trifluoromethyl)phenyl)ethyne were obtained according to literature reported.[2] 1-Methoxy-4-(phenylethynyl)benzene, 1-(phenylethynyl)-4-(*p*-tolyl)benzene, and 1-(p-tolylphenylethynyl)-4-fluorobenzene were obtained according to literature reported.[3]

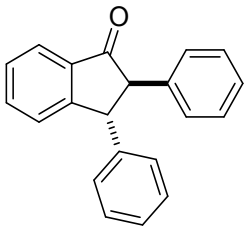
2. Experimental Section

2.1 General procedure for the synthesis of product 4

An oven-dried sealed tube was charged with a mixture of alkyne **1** (0.22 mmol), aromatic aldehyde **2** (0.2 mmol), MeOTf **3** (0.04 mmol, 4.7 μL), then stirred in dichloroethane (0.5 mL) at 50 ^{o}C under nitrogen atmosphere for 24 h. After completion, the crude product was subjected to silica gel column chromatography (petroleum ether/ethyl acetate: 20/1) to provide the corresponding product.

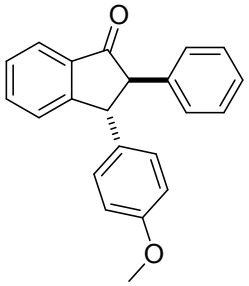


2-Phenyl-3-(*p*-tolyl)-2,3-dihydro-1*H*-inden-1-one (4aa): Yellow liquid, 35 mg (58% yield); ^{1}H NMR($CDCl_3$, 301 MHz): δ 7.88 (d, *J* = 7.6 Hz, 1H), 7.65 - 7.57 (m, 1H), 7.50 - 7.43 (m, 1H), 7.32 - 7.22 (m, 4H), 7.14 - 7.06 (m, 4H), 6.97 (m, 1.8 Hz, 2H), 4.53 (d, *J* = 4.8 Hz, 1H), 3.79 (d, *J* = 4.8 Hz, 1H), 2.33 (s, 3H); ^{13}C NMR ($CDCl_3$, 76 MHz): δ205.9, 156.9, 140.1, 139.2, 137.4, 136.7, 135.9, 130.2, 129.4, 128.8, 128.7,128.4, 127.7, 127.2, 124.5, 65.3, 55.1, 21.6. IR (neat) ν_{max} cm^{-1} 1714 (C=O); GC-MS: 298. HRMS (ESI positive mode) calcd for $C_{22}H_{19}O^{+}$ 299.1430, found 299.1433.

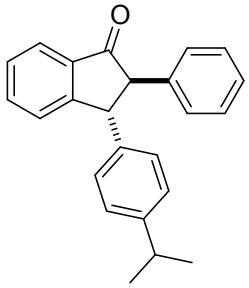


2,3-Diphenyl-2,3-dihydro-1*H*-inden-1-one (4ab)[4]: Yellow liquid, 37 mg (65% yield); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, *J* = 7.6 Hz, 1H), 7.63 (t, *J* = 7.5 Hz, 1H), 7.48

(t, J = 7.4 Hz, 1H), 7.33–7.24 (m, 7H), 7.09 (m, 4H), 4.57 (d, J = 4.8 Hz, 1H), 3.81 (d, J = 4.8 Hz,1H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 205.5, 156.4, 142.8, 138.9, 136.5, 135.7, 19.2, 129.1, 128.7, 128.6, 128.2, 127.5, 127.0, 124.4, 64.9, 55.2. IR (neat) ν_{max} cm^{-1} 1715 (C=O); GC-MS: 284.

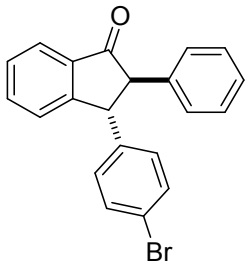


3-(4-Methoxyphenyl)-2-phenyl-2,3-dihydro-1*H*-inden-1-one(4ac): Yellow liquid, 38 mg (60% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.88 (d, J = 7.6 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.4 Hz, 1H), 7.33-7.29 (m, 4H), 7.11 - 7.08 (m, 2H), 7.01 (d, J = 8.6 Hz, 2H), 6.84 (d, J = 8.6 Hz, 2H), 4.52 (d, J = 4.8 Hz, 1H), 3.79 (s, 3H), 3.77 (d, J = 4.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 205.7, 159.1, 156.7, 138.9, 136.5, 135.7, 134.8, 129.3, 129.1, 128.7, 128.5, 127.5, 126.9, 124.3, 114.6, 65.1, 55.6, 54.5. IR (neat) ν_{max} cm^{-1} 1713 (C=O); GC-MS: 314. HRMS (ESI positive mode) calcd for $C_{22}H_{19}O_2^+$ 315.1380, found 315.1378.

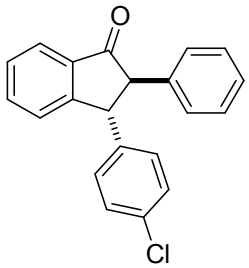


3-(4-Isopropylphenyl)-2-phenyl-2,3-dihydro-1*H*-inden-1-one(4ad): Yellow liquid, 29 mg(45% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.88 (d, J = 7.6 Hz, 1H), 7.63 (t, J = 7.5 Hz, 1H), 7.47 (t, J = 7.5 Hz, 1H), 7.33-7.28 (m, 4H), 7.17-7.11 (m, 4H), 7.00 (d,

J = 8.0 Hz, 2H), 4.56 (d, *J* = 4.6 Hz, 1H), 3.80 (d, *J* = 4.7 Hz, 1H), 2.95 – 2.81 (m, 1H), 1.24 (d, *J* = 6.9 Hz, 6H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 205.8, 156.8, 148.0, 140.2, 139.1, 136.5, 135.7, 129.2, 128.7, 128.5, 128.1, 127.5, 127.3, 127.2, 124.3, 64.8, 54.8, 34.1, 24.3. IR (neat) ν_{max} cm^{-1} 1714 (C=O); GC-MS: 326. HRMS (ESI positive mode) calcd for $C_{24}H_{23}O^+$ 327.1743, found 327.1748.

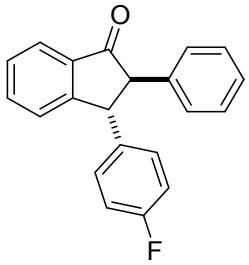


3-(4-Bromophenyl)-2-phenyl-2,3-dihydro-1*H*-inden-1-one(4ae): Yellow liquid, 56 mg (78% yield); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.89 (d, *J* = 7.7 Hz, 1H), 7.65 (t, *J* = 7.7Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.46 – 7.41 (m, 2H), 7.35 – 7.23 (m, 4H), 7.10 – 7.05 (m, 2H), 6.99 – 6.94 (m, 2H), 4.53 (d, *J* = 5.0 Hz, 1H), 3.74 (d, *J* = 5.0 Hz, 1H) ; ^{13}C NMR ($CDCl_3$, 101 MHz): δ205.0, 141.8, 138.4, 136.5, 135.9, 132.4, 129.9, 129.3, 128.9, 128.7, 127.7,126.8, 124.5, 121.5, 64.9, 54.7. IR (neat) ν_{max} cm^{-1} 1716 (C=O); GC-MS: 362. HRMS (ESI positive mode) calcd for $C_{21}H_{16}BrO^+$ 363.0379, found 363.0377.

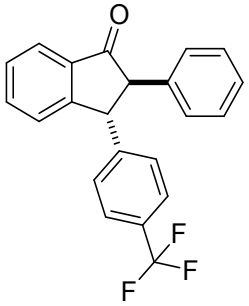


3-(4-Chlorophenyl)-2-phenyl-2,3-dihydro-1*H*-inden-1-one(4af): Yellow liquid, 51 mg (80% yield); ^{1}H NMR ($CDCl_3$, 400 MHz) : δ 7.89 (d, J = 7.7 Hz, 1H), 7.65 (t, *J* =

7.5 Hz, 1H), 7.50 (t, *J* = 7.5 Hz, 1H), 7.35 – 7.25 (m, 6H), 7.08 (d, J = 6.9 Hz, 2H), 7.02 (d, J = 8.4 Hz, 2H), 4.54 (d, *J* = 5.0 Hz, 1H), 3.74 (d, J = 5.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 205.0, 155.7, 141.3, 138.5, 136.5, 135.8, 133.4, 129.6, 129.4, 129.2, 128.8, 128.7, 127.7, 126.8, 124.5, 65.0, 54.6. IR (neat) ν_{max} cm^{-1} 1716 (C=O); GC-MS: 318. HRMS (ESI positive mode) calcd for $C_{21}H_{16}ClO^+$ 319.0884, found 319.0888.

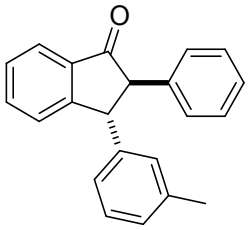


3-(4-Fluorophenyl)-2-phenyl-2,3-dihydro-1*H*-inden-1-one(4ag): Yellow liquid, 42 mg(70% yield); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.64 (t, *J* = 7.5 Hz, 1H), 7.49 (t, *J* = 7.5 Hz, 1H), 7.33 – 7.26 (m, 4H), 7.10 – 6.97 (m, 6H), 4.55 (d, *J* = 4.9 Hz, 1H), 3.74 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 205.2, 163.5, 161.1, 156.1, 138.6, 136.5, 135.8, 129.7 (d, *J* = 7.9 Hz), 129.2, 128.7 (d, *J* = 9.3 Hz), 127.6, 126.9, 124.4, 116.2, 116.0, 65.1, 54.5. IR (neat) ν_{max} cm^{-1} 1715 (C=O); GC-MS: 302. HRMS (ESI positive mode) calcd for $C_{21}H_{16}FO^+$ 303.1180, found 303.1185.

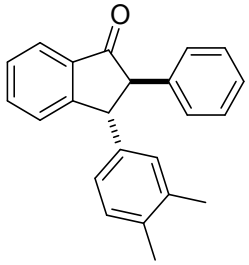


2-Phenyl-3-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-inden-1-one(4ah): Yellow liquid, 51 mg (73% yield); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.91 (d, *J* = 7.7 Hz, 1H), 7.67 (m, 1H), 7.60 – 7.49 (m, 3H), 7.36 – 7.26 (m, 4H), 7.21 (m, 2H), 7.11 – 7.07 (m,

2H), 4.64 (d, *J* = 4.9 Hz, 1H), 3.77 (d, *J* = 5.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ204.5, 155.1, 146.6, 138.1, 136.3, 135.7, 129.1, 128.8, 128.5, 128.4, 127.6, 126.6, 126.0, 124.4, 64.6, 54.7. IR (neat) ν_{max} cm^{-1} 1716 (C=O); GC-MS: 352. HRMS (ESI positive mode) calcd for $C_{22}H_{16}F_3O^+$ 353.1148, found 353.1146.

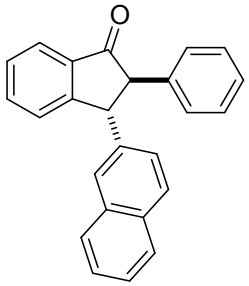


2-Phenyl-3-(*m*-tolyl)-2,3-dihydro-1*H*-inden-1-one(4ai): Yellow liquid, 36 mg(60% yield); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.63 (t, J = 7.4 Hz, 1H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.34 – 7.26 (m, 4H), 7.19 (m, 1H), 7.12– 7.07 (m, 3H), 6.88 (d, *J* = 7.8 Hz, 2H), 4.54 (d, *J* = 4.7 Hz, 1H), 3.82 (d, *J* = 4.7 Hz, 1H), 2.30 (s, 3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 205.6, 156.6, 142.8, 138.9, 138.8, 136.4, 135.7, 129.1, 129.0, 128.6, 128.5, 128.2, 127.4, 126.9, 125.3, 124.3, 64.7, 55.1, 21.7. IR (neat) ν_{max} cm^{-1} 1718 (C=O); GC-MS: 298. HRMS (ESI positive mode) calcd for $C_{22}H_{19}O^+$ 299.1430, found 299.1429.

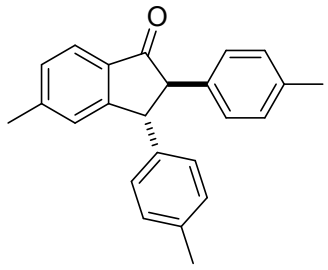


3-(3,4-Dimethylphenyl)-2-phenyl-2,3-dihydro-1*H*-inden-1-one(4aj): Yellow solid, 39 mg(62% yield); 1H NMR ($CDCl_3$, 400 MHz): δ 7.88 (d, *J* = 7.7 Hz, 1H), 7.62 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.4 Hz, 1H), 7.33 – 7.25 (m, 4H), 7.13 – 7.05 (m, 3H), 6.86 – 6.80 (m, 2H), 4.51 (d, *J* = 4.6 Hz, 1H), 3.81 (d, *J* = 4.7 Hz, 1H), 2.24 (s, 3H), 2.20 (s,

3H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 205.9, 156.9, 140.3, 139.1, 137.5, 135.8, 135.7, 130.4, 129.4, 129.2, 128.7, 128.5, 127.4, 127.0, 125.7, 124.3, 64.9, 54.8, 20.1, 19.7. IR (neat) ν_{max} cm^{-1} 1708 (C=O); GC-MS: 312. HRMS (ESI positive mode) calcd for $C_{23}H_{21}O^+$ 313.1587, found 313.1590.

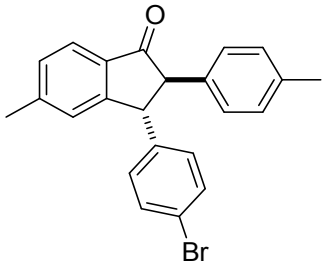


3-(Naphthalen-2-yl)-2-phenyl-2,3-dihydro-1*H*-inden-1-one(4ak): Red liquid, 28 mg(42% yield); ^1H NMR ($CDCl_3$, 400 MHz): δ 7.93 (d, *J* = 7.7 Hz, 1H), 7.84 – 7.78 (m, 2H), 7.76 – 7.72 (m, 1H), 7.66 – 7.58 (m, 2H), 7.51 (d, *J* = 7.3 Hz, 1H), 7.48 – 7.45 (m, 2H), 7.32 – 7.24 (m, 4H), 7.16 – 7.10 (m, 3H), 4.73 (d, *J* = 4.8 Hz, 1H), 3.91 (d, J = 4.9 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 205.4, 156.2, 139.8, 138.6, 136.3, 135.6, 133.5, 132.7, 129.1, 129.0, 128.5, 127.8, 127.4, 127.0, 126.9, 126.5, 126.1, 125.7, 124.2, 64.6, 55.3. IR (neat) ν_{max} cm^{-1} 1713 (C=O); GC-MS: 334. HRMS (ESI positive mode) calcd for $C_{25}H_{19}O^+$ 335.1430, found 335.1433.



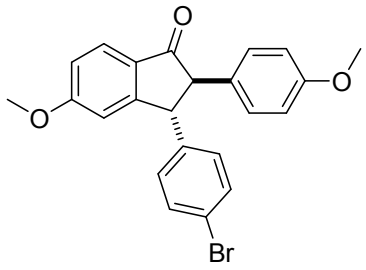
5-Methyl-2,3-di-p-tolyl-2,3-dihydro-1*H*-inden-1-one(4ba): Yellow liquid, 49 mg(75% yield): ^1H NMR ($CDCl_3$, 400 MHz): δ 7.76 (d, *J* = 7.9 Hz, 1H), 7.28 – 7.23 (m, 1H), 7.26–7.10 (m, 5H), 6.99–6.97 (m, 4H), 4.45 (d, *J* = 4.7 Hz, 1H), 3.73 (d, *J* =

4.7 Hz, 1H), 2.40 (s, 3H), 2.34 (s, 3H), 2.31 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 205. 4, 157.2, 146.9, 140.0, 136.9, 136.1, 134.2, 129.8, 129.7, 128.0, 127.1, 124.1, 64.7, 54.7, 22.4, 21.3. IR (neat) ν_{max} cm^{-1} 1712 (C=O); GC-MS: 326. HRMS (ESI positive mode) calcd for $C_{24}H_{23}O^+$ 327.1743, found 327.1747.



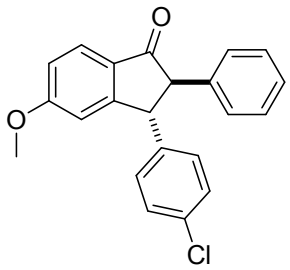
3-(4-Bromophenyl)-5-methyl-2-(p-tolyl)-2,3-dihydro-1*H*-inden-1-one(4be):

Yellow solid, 74 mg(94% yield) , mp: 158-160 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.77 (d, *J* = 7.9 Hz, 1H), 7.45 – 7.41 (m, 2H), 7.31 – 7.24 (m, 1H), 7.13 – 7.09 (m, 2H), 7.05 (s, 1H), 6.96 (m, 4H), 4.44 (d, J = 4.9 Hz, 1H), 3.68 (d, J = 4.9 Hz, 1H), 2.41 (s, 3H), 2.32 (s, 3H). 13C NMR ($CDCl_3$, 101MHz): δ204.62, 156.1, 147.1, 141.9, 137.1, 135.6, 134.2, 132.2, 130.0, 129.9, 129.8, 128.4, 126.9, 124.2, 121.2, 64.6, 54.5, 22.4, 21.3. IR (neat) ν_{max} cm^{-1} 1711 (C=O); GC-MS: 390. HRMS (ESI positive mode) calcd for $C_{23}H_{20}BrO^+$ 391.0692, found 391.0691.



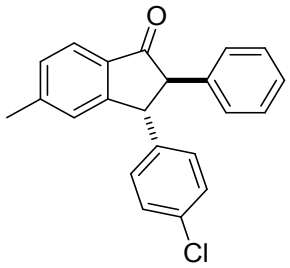
3-(4-Bromophenyl)-5-methoxy-2-(4-methoxyphenyl)-2,3-dihydro-1*H*-inden-1-one(4ce): Yellow solid, 46 mg(65% yield),mp: 52-54 ^{o}C; ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.81 (d, J = 8.5 Hz, 1H), 7.12 (d, J = 8.0 Hz, 2H), 7.03 – 6.95 (m, 5H), 6.85 – 6.83

(m, 2H), 6.68 (d, *J* = 1.8 Hz, 1H), 4.41 (d, J = 4.6 Hz, 1H), 3.81 (s, 3H), 3.78 (s, 3H), 3.70 (d, *J* = 4.7 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101MHz): δ 204.1, 166.1, 159.5, 158.9, 139.8, 136.9, 131.4, 129.8, 129.6, 128.0, 125.9, 116.6, 114.5, 109.8, 64.4, 55.9, 55.5, 55.0, 21.3. IR (neat) ν_{max} cm^{-1} 1707 (C=O); HRMS (ESI positive mode) calcd for $C_{23}H_{20}BrO_3^+$ 423.0590, found 423.0595.



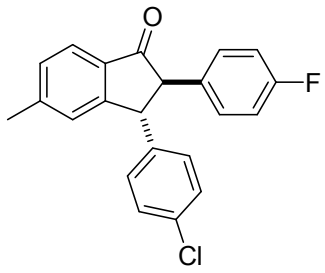
3-(4-Chlorophenyl)-5-methoxy-2-phenyl-2,3-dihydro-1*H*-inden-1-one(4gf):

Yellow solid, 28 mg(40% yield), mp: 42-44 ^{o}C; ^{1}H NMR ($CDCl_3$,400 MHz): δ 7.83 (d, *J* = 8.5 Hz, 1H), 7.35 – 7.26 (m, 5H), 7.08 (m, 2H), 7.05 – 7.00 (m, 3H), 6.66 (d, *J* = 1.7 Hz, 1H), 4.46 (d, *J* = 4.7 Hz, 1H), 3.83 (s, 3H), 3.72 (d, *J* = 4.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 203.1, 166.1, 158.6, 141.1, 138.8, 133.2, 129.7, 129.4, 129.3, 129.0, 128.4, 127.4, 126.1, 116.7, 109.6, 64.9, 55.9, 54.6. IR (neat) ν_{max} cm^{-1} 1705 (C=O); GC-MS: 348. HRMS (ESI positive mode) calcd for $C_{22}H_{18}ClO_2^+$ 349.0990, found 349.0992.

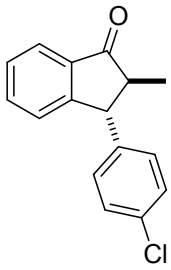


3-(4-Chlorophenyl)-5-methyl-2-phenyl-2,3-dihydro-1*H*-inden-1-one(4hf): Orange liquid, 54 mg(82% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.80 (d, *J* = 7.9 Hz, 1H), 7.36

– 7.27 (m, 6H), 7.11 – 7.06 (m, 3H), 7.06 – 7.01 (m, 2H), 4.50 (d, *J* = 4.8 Hz, 1H), 3.74 (d, *J* = 4.9 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 204.4, 156.1, 147.1, 141.2, 138.6, 134.1, 133.1, 129.9, 129.4, 129. 2, 129.1, 128.4, 127.4, 126.9, 124.1, 64.9, 54.4, 22.3. IR (neat) ν_{max} cm^{-1} 1710 (C=O); GC-MS: 332. HRMS (ESI positive mode) calcd for $C_{22}H_{18}ClO^+$ 333.1041, found 333.1046.

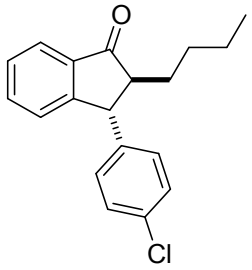


3-(4-Chlorophenyl)-2-(4-fluorophenyl)-5-methyl-2,3-dihydro-1*H*-inden-1-one(4if): Yellow liquid, 49 mg(70% yield); ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, *J* = 7.9 Hz, 1H), 7.34 – 7.28 (m, 3H), 7.06 – 6.98 (m, 7H), 4.41 (d, *J* = 5.0 Hz, 1H), 3.71 (d, *J* = 5.1 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 204.1, 155.9, 147.3, 141.0, 133.9, 133.3, 130.1, 130.0, 129.4, 129.3, 126.9, 124.2, 116.1, 115.8, 64.2, 54.5, 22.4. IR (neat) ν_{max} cm^{-1} 1715 (C=O); GC-MS: 350. HRMS (ESI positive mode) calcd for $C_{22}H_{17}ClFO^+$ 351.0946, found 351.0945.

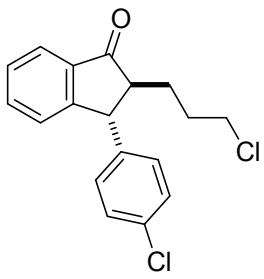


3-(4-Chlorophenyl)-2-methyl-2,3-dihydro-1*H*-inden-1-one(4jf): Yellow liquid,36 mg(70% yield); ^{1}H NMR ($CDCl_3$, 400 MHz)：δ 7.82 (d, *J* = 7.7 Hz, 1H), 7.59 (t, J = 7.4 Hz, 1H), 7.44 (t, *J* = 7.2 Hz, 1H), 7.32 (d, J = 8.1 Hz, 2H), 7.20 (d, *J* = 7.7 Hz, 1H),

7.11 (d, J = 8.1 Hz, 2H), 4.02 (d, J = 5.0 Hz, 1H), 2.67 – 2.52 (m, 1H), 1.37 (d, J = 7.3 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 207.4, 155.5, 141.4, 136.4, 135.3, 133.1, 129.5, 129.2, 128.3, 126.5, 123.8, 53.7, 53.3, 14.2. IR (neat) ν_{max} cm^{-1} 1714 (C=O); GC-MS: 256. HRMS (ESI positive mode) calcd for $C_{16}H_{14}ClO^+$ 257.0728, found 257.0729.

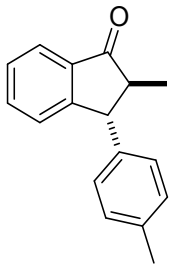


2-Butyl-3-(4-chlorophenyl)-2,3-dihydro-1*H*-inden-1-one(4kf): Yellow liquid, 39 mg (65% yield); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, J = 7.6 Hz, 1H), 7.59 – 7.53 (m, 1H), 7.42 (t, J = 7.4 Hz, 1H), 7.31 – 7.27 (m, 2H), 7.16 (d, J = 7.8 Hz, 1H), 7.10 – 7.04 (m, 2H), 4.18 (d, J = 4.2 Hz, 1H), 2.68 – 2.58 (m, 1H), 2.03 – 1.90 (m, 1H), 1.74 – 1.62 (m, 1H), 1.44 – 1.35 (m, 2H), 1.33 – 1.23 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 207.7, 156.4, 142.4, 136.4, 135.3, 132.8, 129.4, 129.1, 128.2, 126.6, 123.7, 58.1, 51.1, 30.59, 29.4, 22.8, 14.0. IR (neat) ν_{max} cm^{-1} 1711 (C=O); GC-MS: 298. HRMS (ESI positive mode) calcd for $C_{19}H_{20}ClO^+$ 299.1197, found 299.1195.

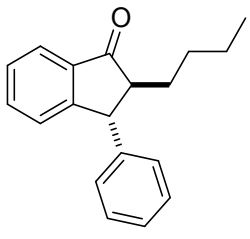


3-(4-Chlorophenyl)-2-(3-chloropropyl)-2,3-dihydro-1*H*-inden-1-one(4lf): Yellow

liquid,26 mg(40% yield); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, *J* = 7.7 Hz, 1H), 7.58 (m, 1H), 7.43 (m, 1H), 7.34 – 7.29 (m, 2H), 7.19 – 7.15 (m, 1H), 7.12 – 7.07 (m, 2H), 4.17 (d, *J* = 4.6 Hz, 1H), 3.56 – 3.47 (m, 2H), 2.67 – 2.60 (m, 1H), 2.15 – 2.04 (m, 1H), 1.97 – 1.84 (m, 3H).^{13}C NMR ($CDCl_3$, 101 MHz): δ 206.8, 156.0, 141.79 (s), 136.2, 135.5, 133.1, 129.4,129.3, 128.4, 126.6, 123.8, 57.3, 51.2, 44.9, 30.2, 27.9. IR (neat) ν_{max} cm^{-1} 1709 (C=O); GC-MS: 318. HRMS (ESI positive mode) calcd for $C_{18}H_{17}Cl_2O^+$ 319.0651, found 319.0649.



2-Methyl-3-(*p*-tolyl)-2,3-dihydro-1*H*-inden-1-one(4ja): Yellow liquid, 22 mg(45% yield); ^{1}H NMR ($CDCl_3$,400 MHz): δ 7.81 (d, *J* = 7.6 Hz, 1H), 7.56 (t, *J* = 7.5 Hz, 1H), 7.42 (t, *J* = 7.4 Hz, 1H), 7.22 (d, *J* = 7.7 Hz, 1H), 7.16 (d, *J* = 7.7 Hz, 2H), 7.06 (d, *J* = 7.7 Hz, 2H), 4.00 (d, *J* = 5.0 Hz, 1H), 2.67 – 2.58 (m, 1H), 2.36 (s, 3H), 1.37 (dd, *J* = 7.3, 0.6 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 208.1, 156.4, 139.6, 136.9, 136.4, 135.1, 129.7, 128.0, 126.6, 123.6, 53.7, 53.5, 21.2, 14.2. IR (neat) ν_{max} cm^{-1} 1714 (C=O); GC-MS: 236. HRMS (ESI positive mode) calcd for $C_{17}H_{17}O^+$ 237.1274, found 237.1277.

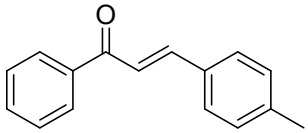


2-Butyl-3-phenyl-2,3-dihydro-1*H*-inden-1-one(4kb)[4]: Yellow liquid, 32 mg(60%

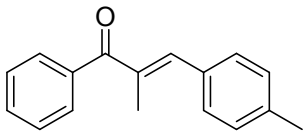
yield); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.80 (d, *J* = 7.6 Hz, 1H), 7.55 (m, 1H), 7.40 (t, *J* = 7.4 Hz, 1H), 7.35 – 7.29 (m, 2H), 7.28 – 7.25 (m, 1H), 7.20 – 7.17 (m, 1H), 7.16 – 7.11 (m, 2H), 4.20 (d, *J* = 4.2 Hz, 1H), 2.72 – 2.66 (m, 1H), 2.02 – 1.90 (m, 1H), 1.77 – 1.65 (m, 1H), 1.41 (m, 2H), 1.31 – 1.24 (m, 2H), 0.86 (m, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 208.3, 157.0, 143.8, 136.4, 135.2, 128.9, 128.1, 128.0, 127.0, 126.8, 123.6, 58.1, 51.7, 30.6, 29.4, 22.9, 14.03. IR (neat) ν_{max} cm^{-1} 1713 (C=O); GC-MS: 264.

2.2 General procedure for the synthesis of compound 5

An oven-dried sealed tube was charged with the mixture of alkyne **1** (0.22 mmol), aromatic aldehyde **2** (0.2 mmol), MeOTf **3** (0.04 mmol, 4.7 μL), then stirred in dichloroethane (0.5 mL) at 40 °C under nitrogen atmosphere for 5 h. After completion, the crude product was subjected to silica gel column chromatography (petroleum ether/ethyl acetate: 20/1) to provide the corresponding product.



(*E*)-1-Phenyl-3-(*p*-tolyl)prop-2-en-1-one(5ma)[5]: Yellow solid, 28 mg(62% yield); ^{1}H NMR ($CDCl_3$, 400 MHz,): δ 8.04 – 7.99 (m, 2H), 7.79 (d, *J* = 15.7 Hz, 1H), 7.60 – 7.47 (m, 6H), 7.25-7.21 (m, 2H), 2.39 (s, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 191.0, 145.3, 141.4, 138.7, 133.0, 132.5, 130.0, 128.9, 128.8, 121.4, 21.9. GC-MS: 222.



(*E*)-2-Methyl-1-phenyl-3-(*p*-tolyl)prop-2-en-1-one (5ja)[6]: Yellow solid, 28 mg(59% yield); ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.75 – 7.70 (m, 2H), 7.54 – 7.50 (m, 1H), 7.45

(t, J = 7.4 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H), 7.16 (s, 1H), 2.38 (s, 3H), 2.27 (d, J = 0.8 Hz, 3H). ^{13}C NMR ($CDCl_3$, 101 MHz): δ 199.9, 142.9, 139.2, 139.1, 136.4, 133.3, 131.8, 130.1, 129.8, 129.5, 128.5, 21.7, 14.8. GC-MS: 236.

3. References

[1] Xu, Y.; Zhao, J.; Chen, H.; Wu, W.; Jiang, H. *Chem. Commun.* **2014,** *50*, 2488.

[2] Mio, M. J.; Kopel, L. C.; Braun, J. B.; Gadzikwa, T. L.; Hull, K. L.; Brisbois, R. G.; Markworth, C. J.; Grieco, P. A. *Org. Lett.* **2002,** *4*, 3199.

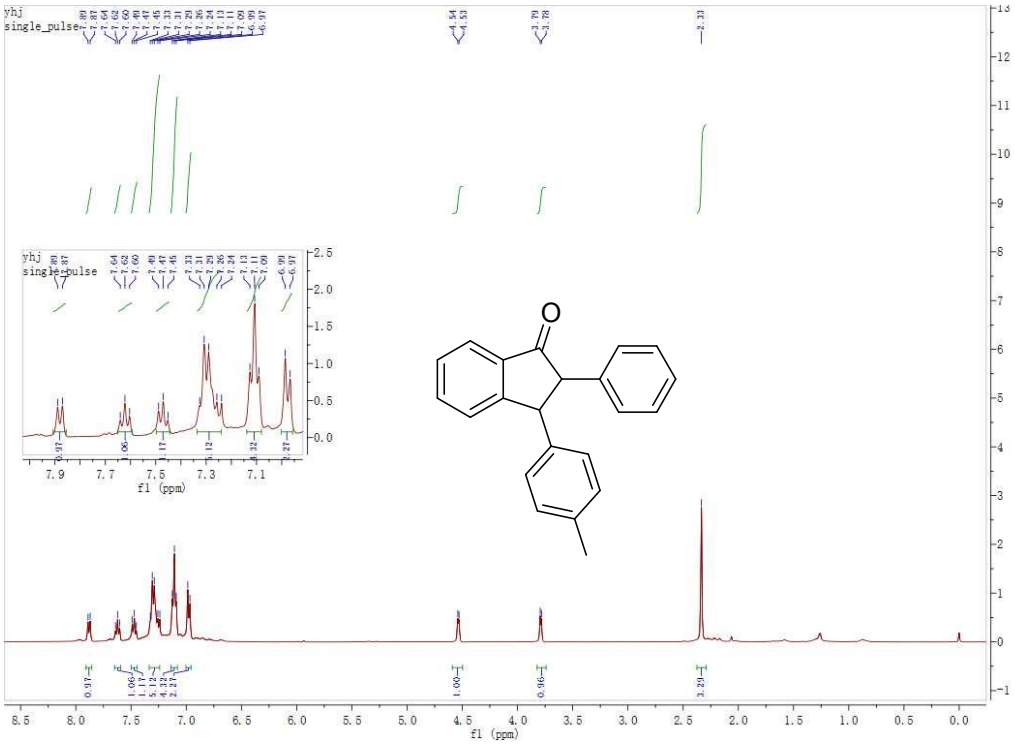
[3] Belger, C.; Plietker, B. *Chem. Commun.* **2012,** *48*, 5419.

[4] A, Saito, A.; Umakoshi, M.; Yagyu, N.; Hanzawa, Y. *Org. Lett.* **2008,** *10,* 1783.

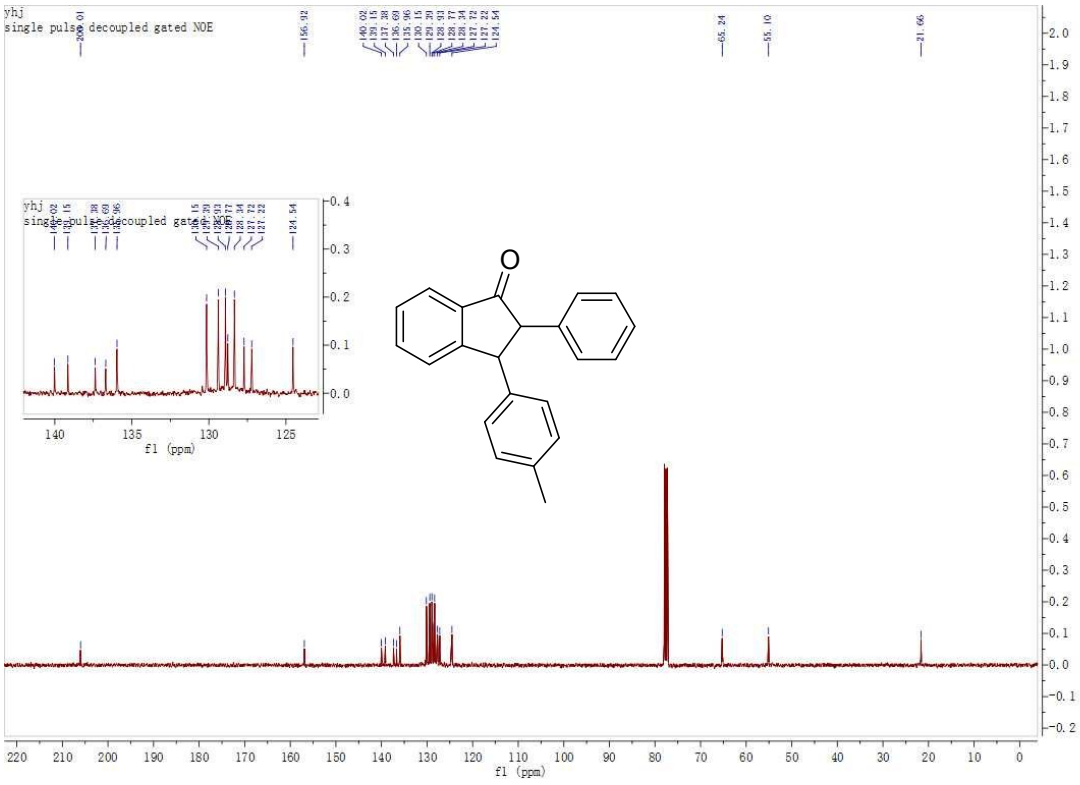
[5] Zhang, L.; Wang, A.; Wang, W.; Huang, Y.; Liu, X.; Miao, S.; Liu, J.; Zhang, T. *ACS. Catal.* **2015,** *11,* 6563.

[6] Wei, Y.; Tang, J.; Cong, X.; Zeng, X. *Green. Chem.* **2013,** *15,* 3165.

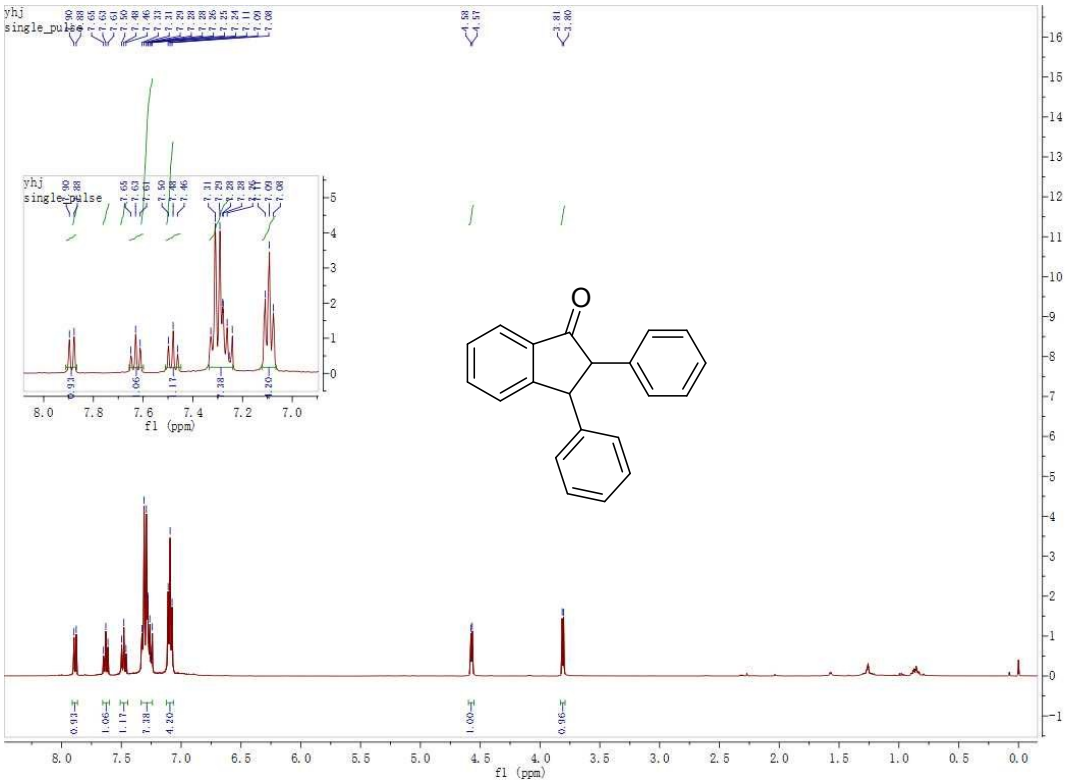
4. Copies of ^{1}H and ^{13}C NMR Spectra



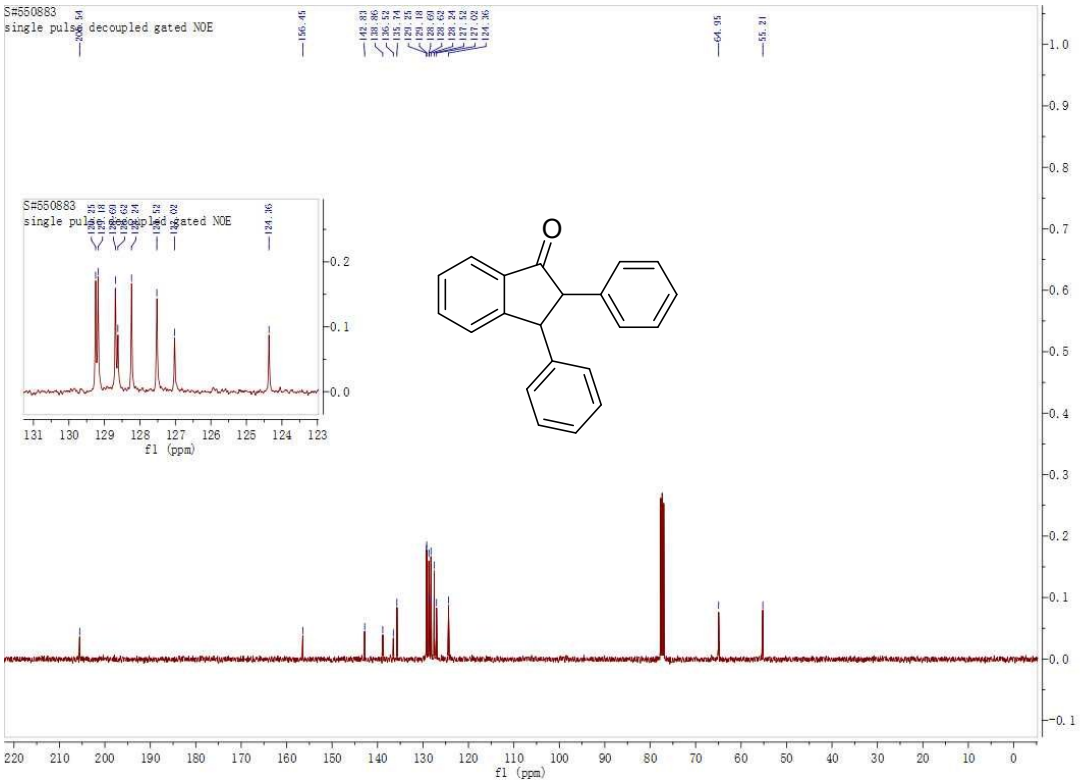
^{1}H NMR of **4aa**



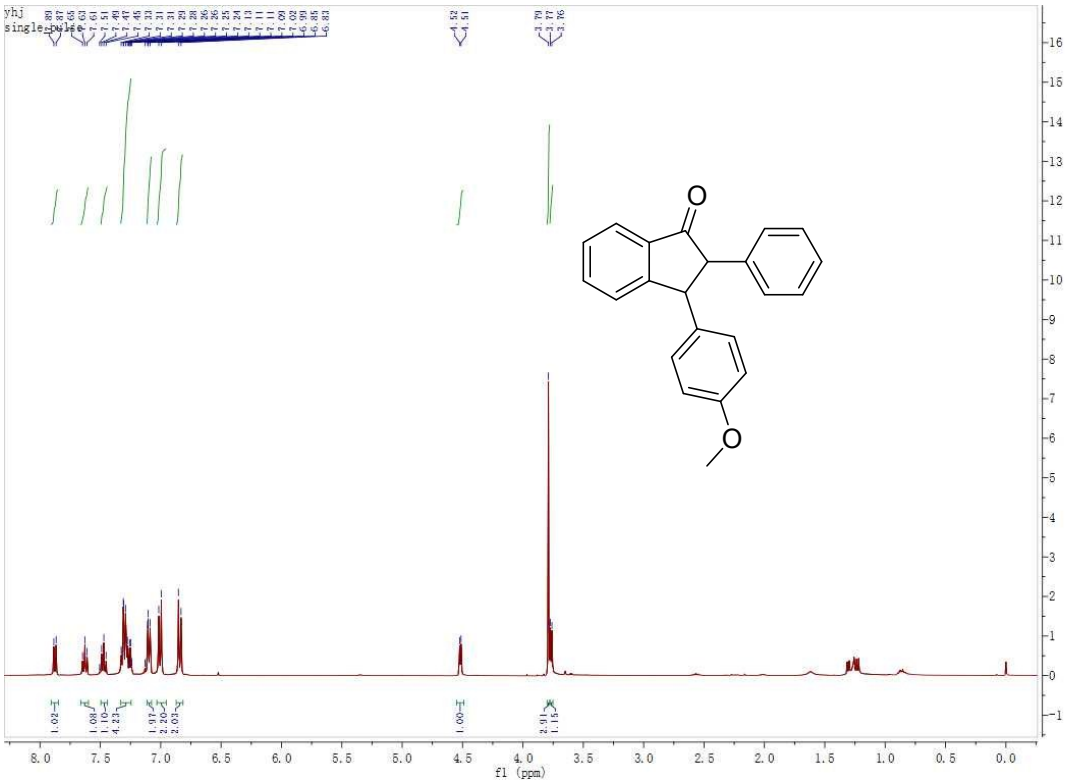
^{13}C NMR of **4aa**



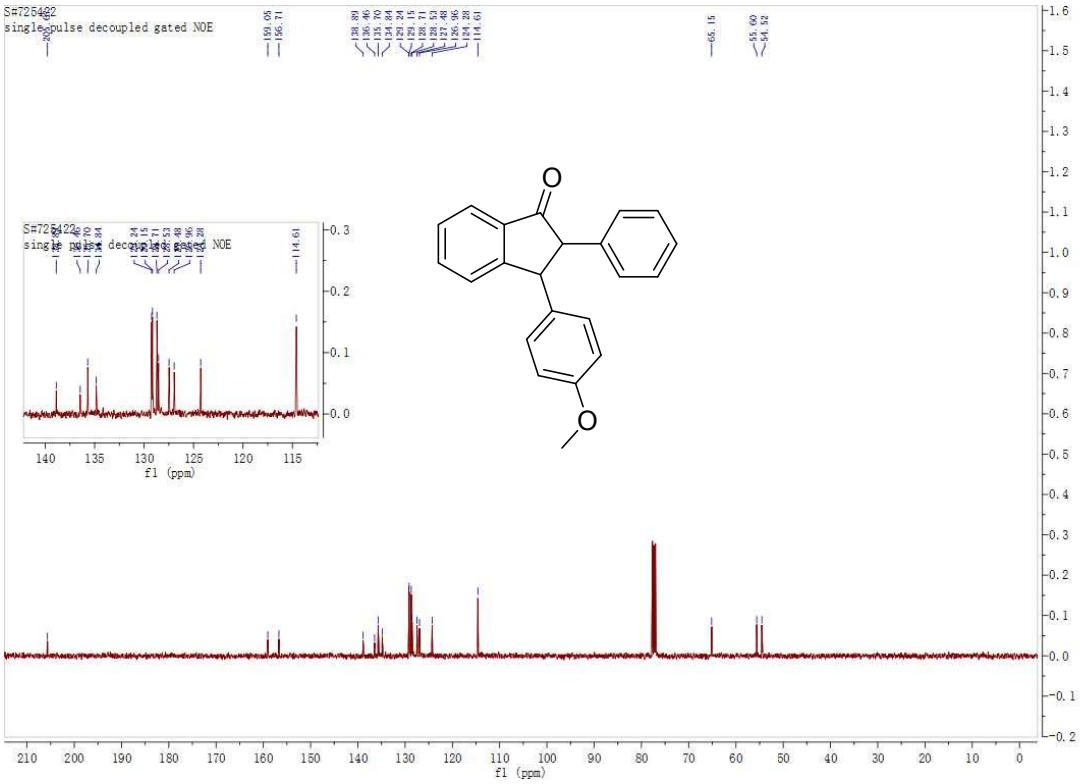
^{1}H NMR of **4ab**



^{13}C NMR of **4ab**



^{1}H NMR of **4ac**



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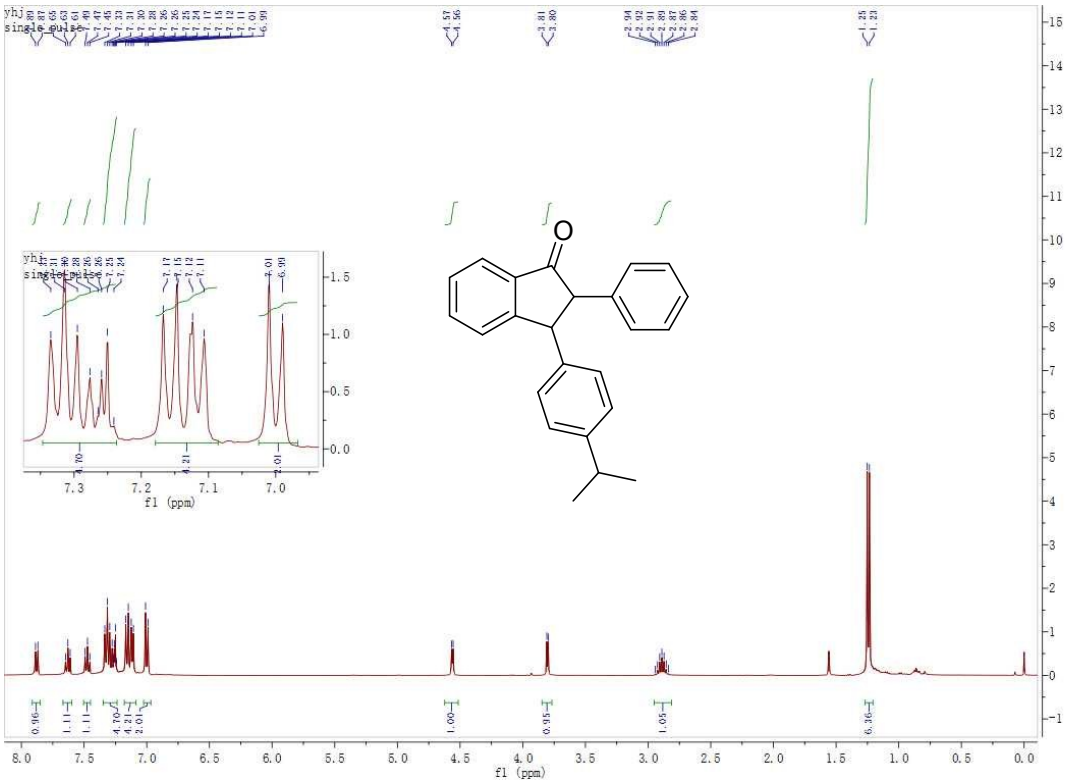

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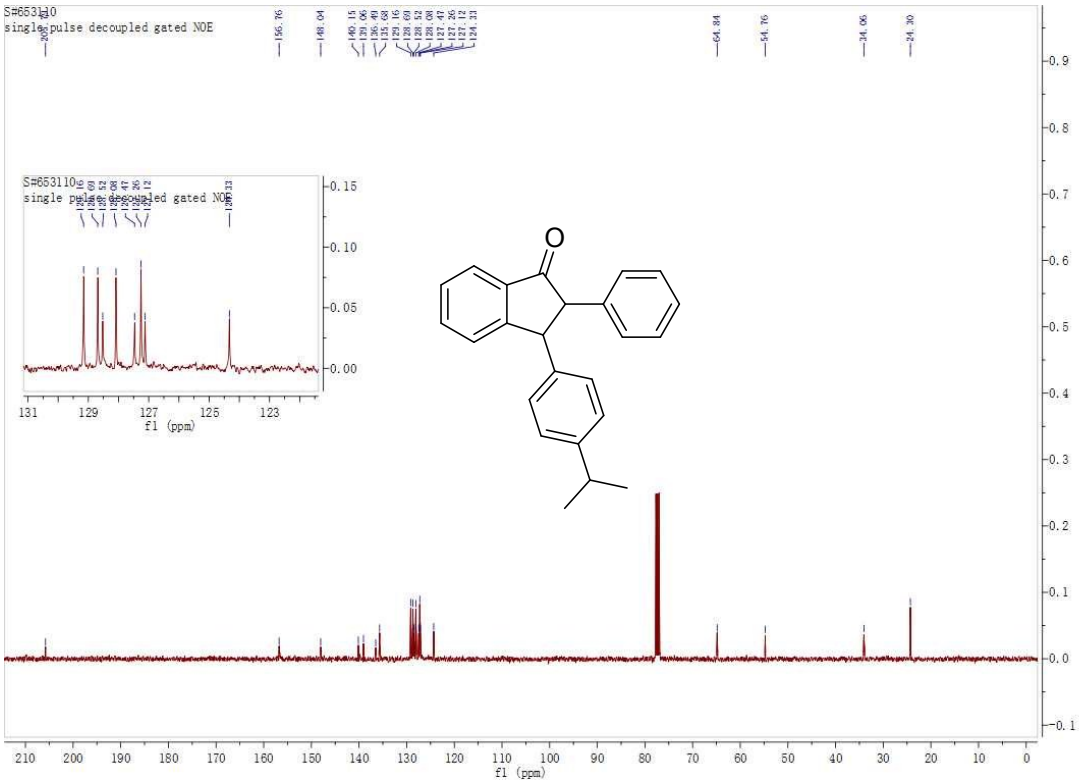
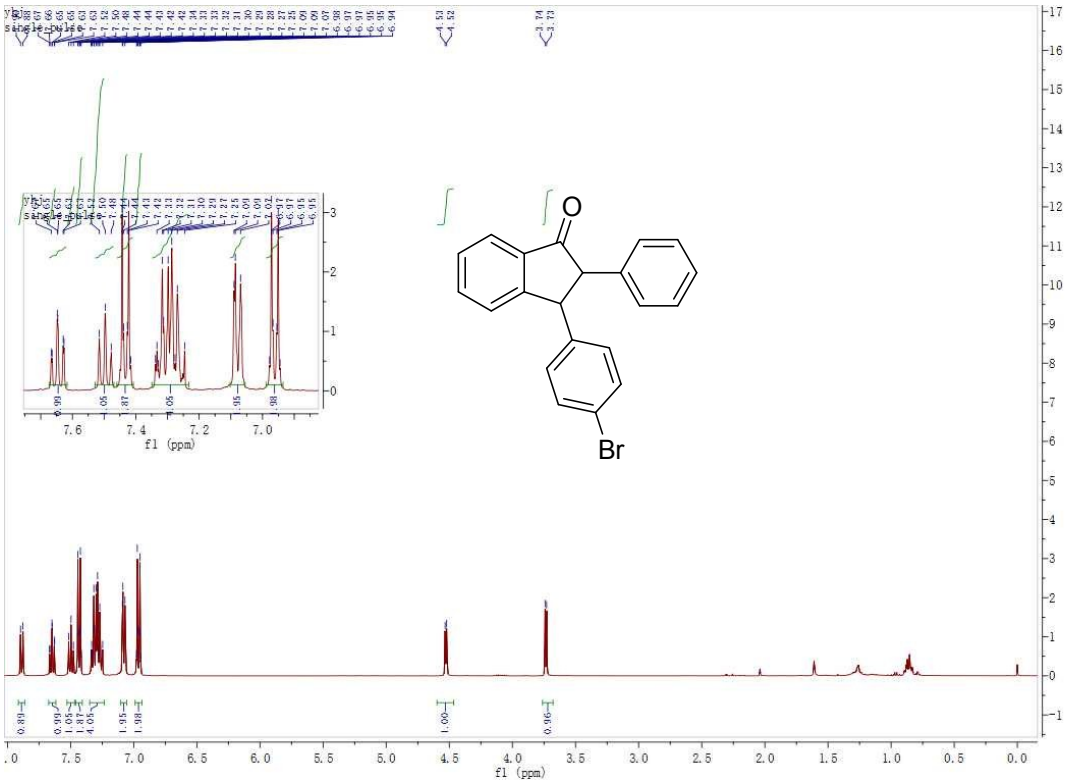
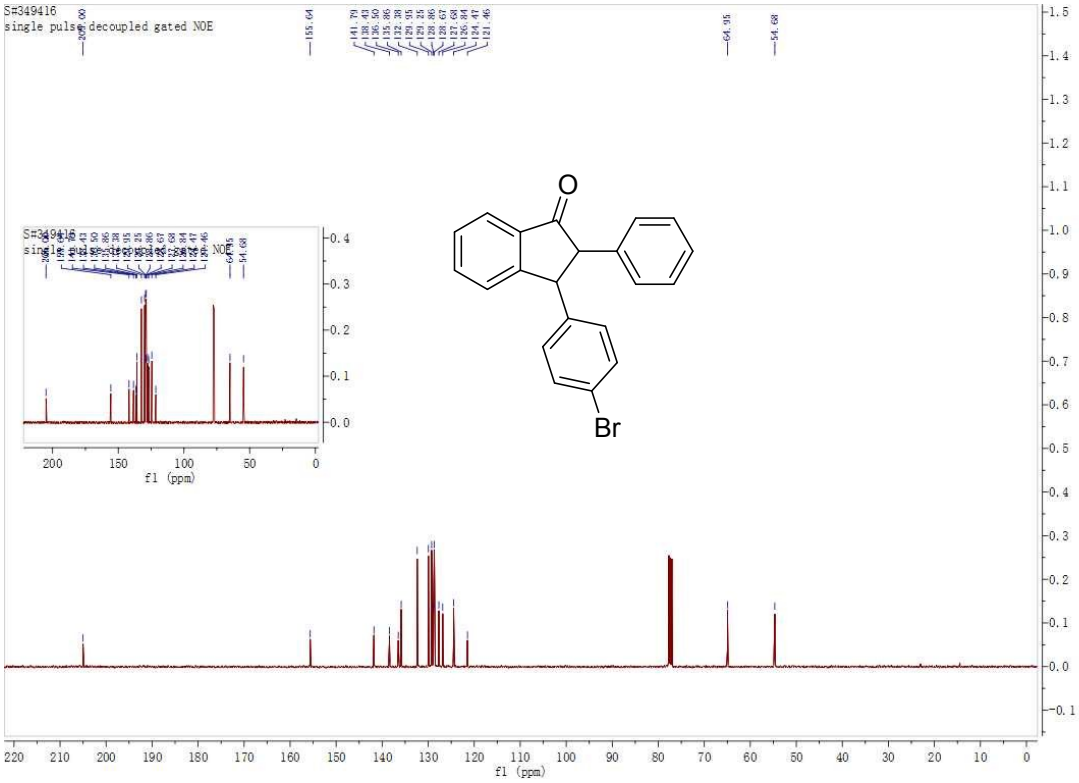


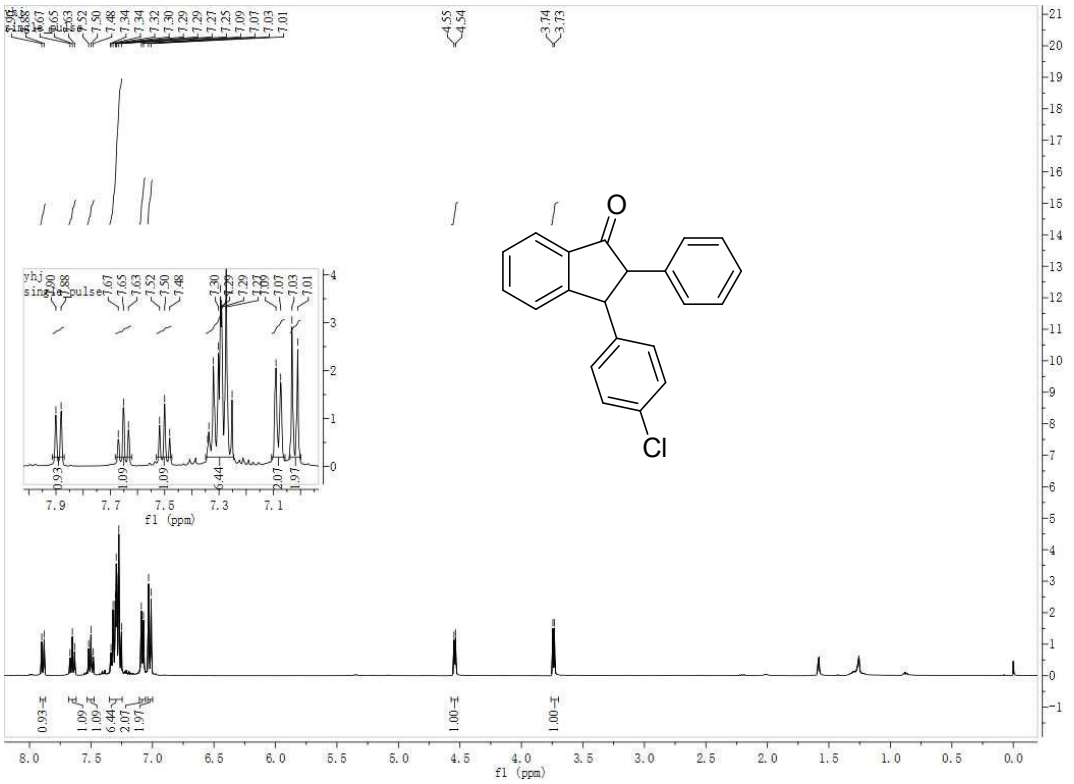
^{13}C NMR of **4ad**



^{1}H NMR of **4ae**



^{13}C NMR of **4ae**



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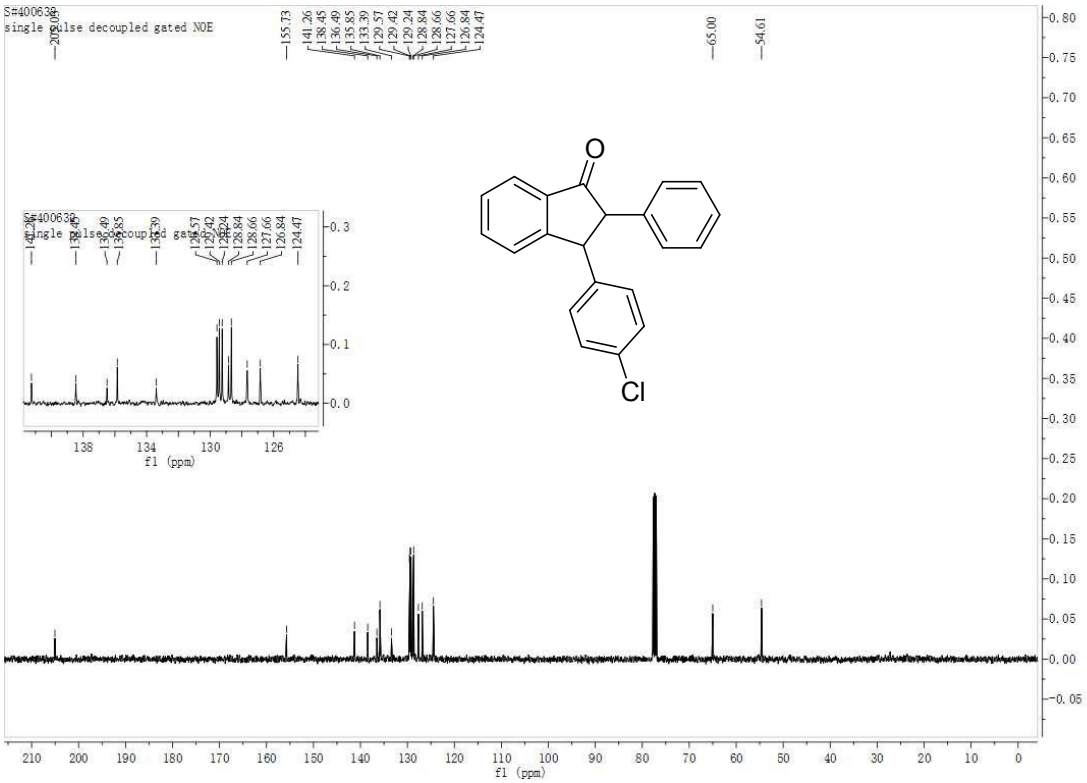
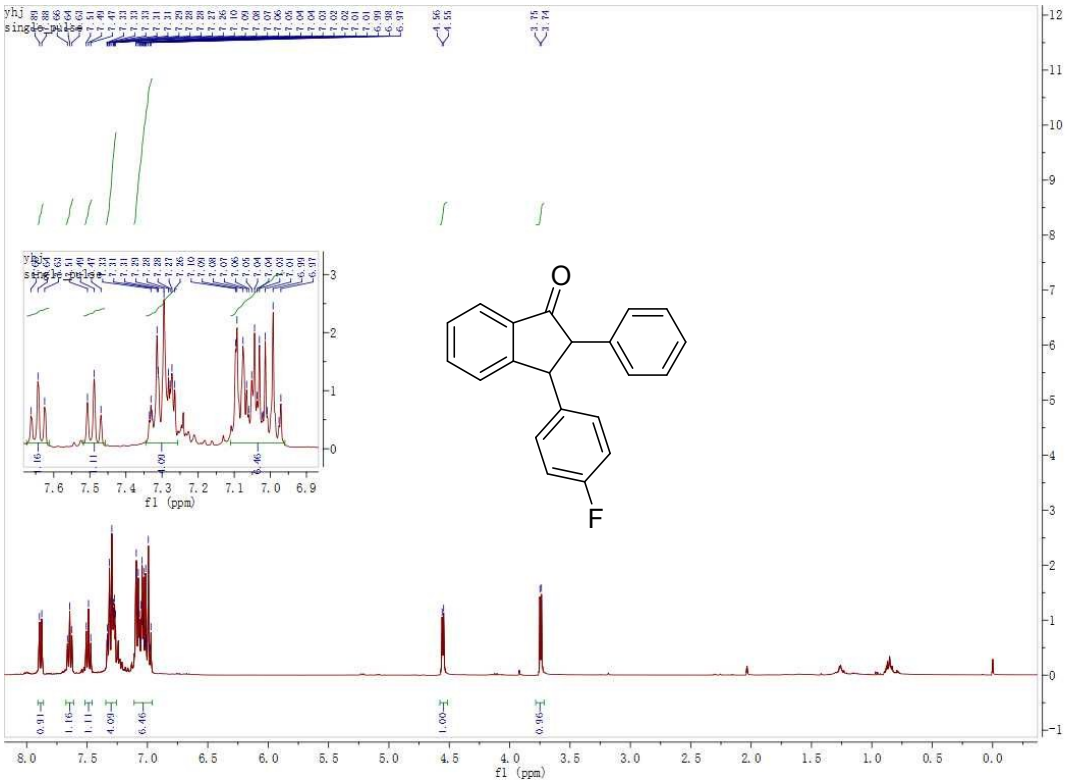
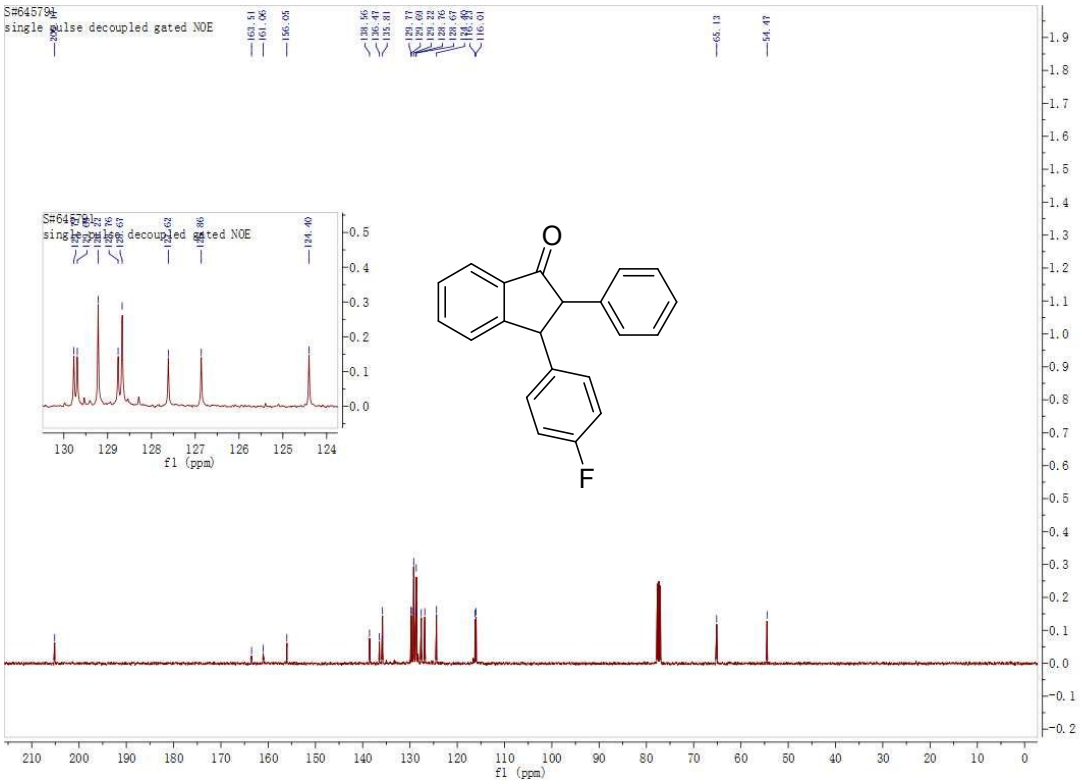


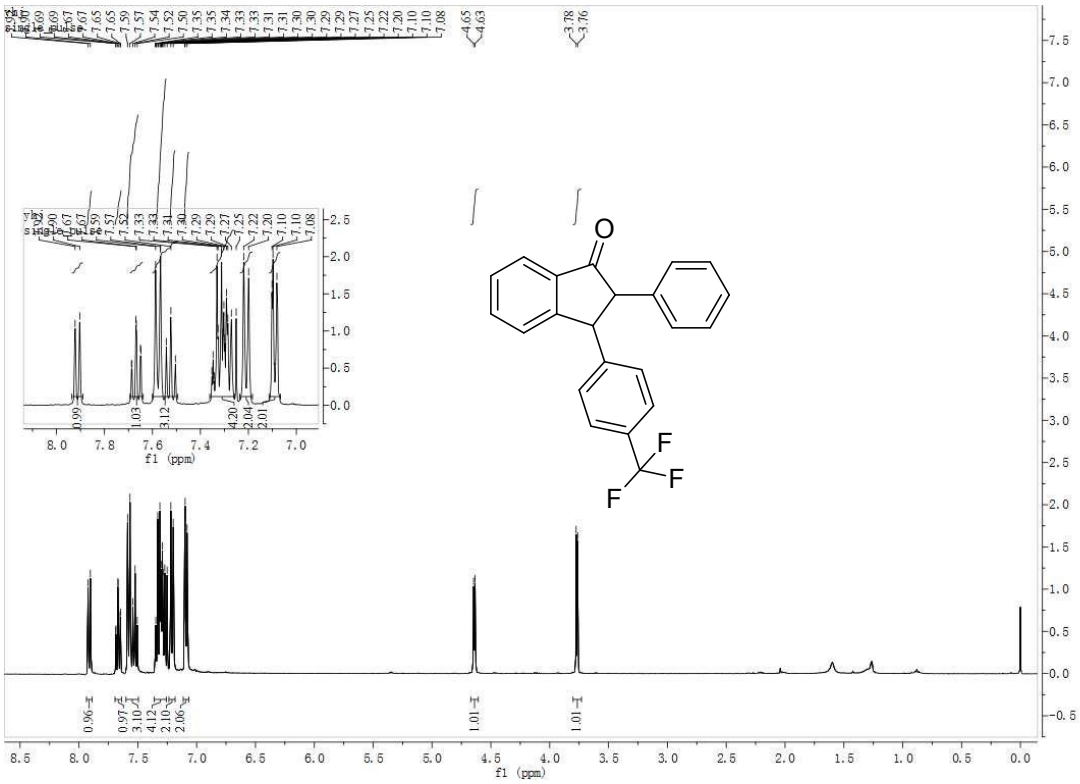
^{13}C NMR of **4af**



^{1}H NMR of **4ag**



^{13}C NMR of **4ag**



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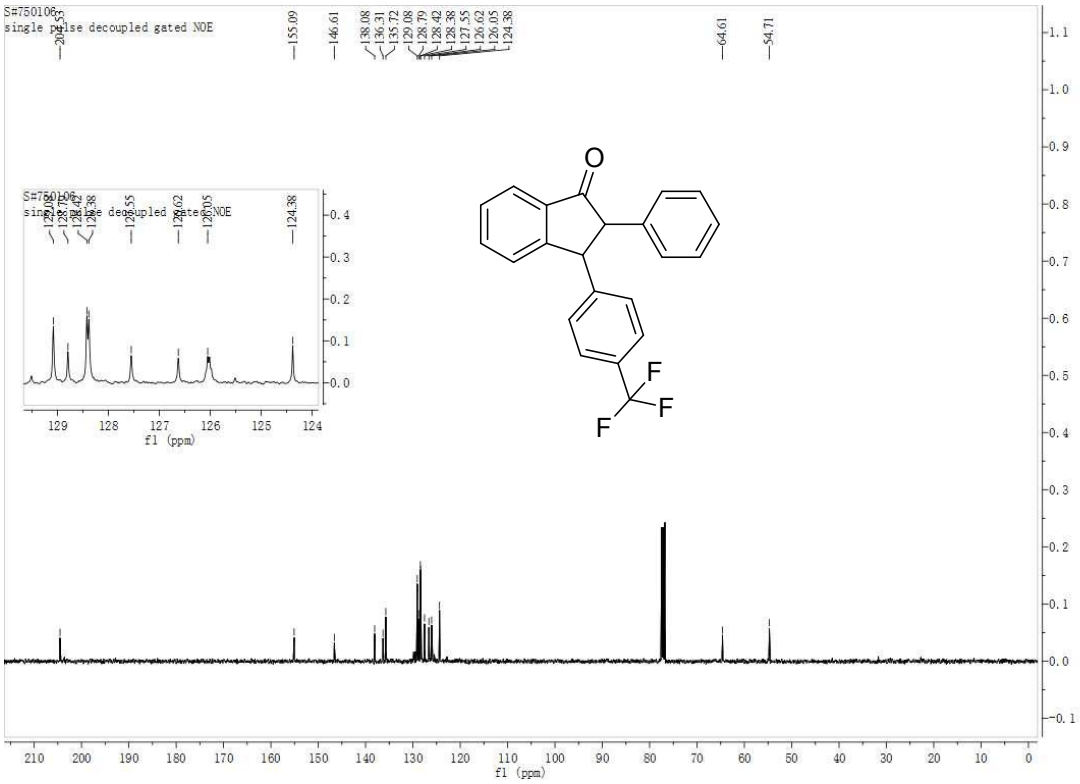

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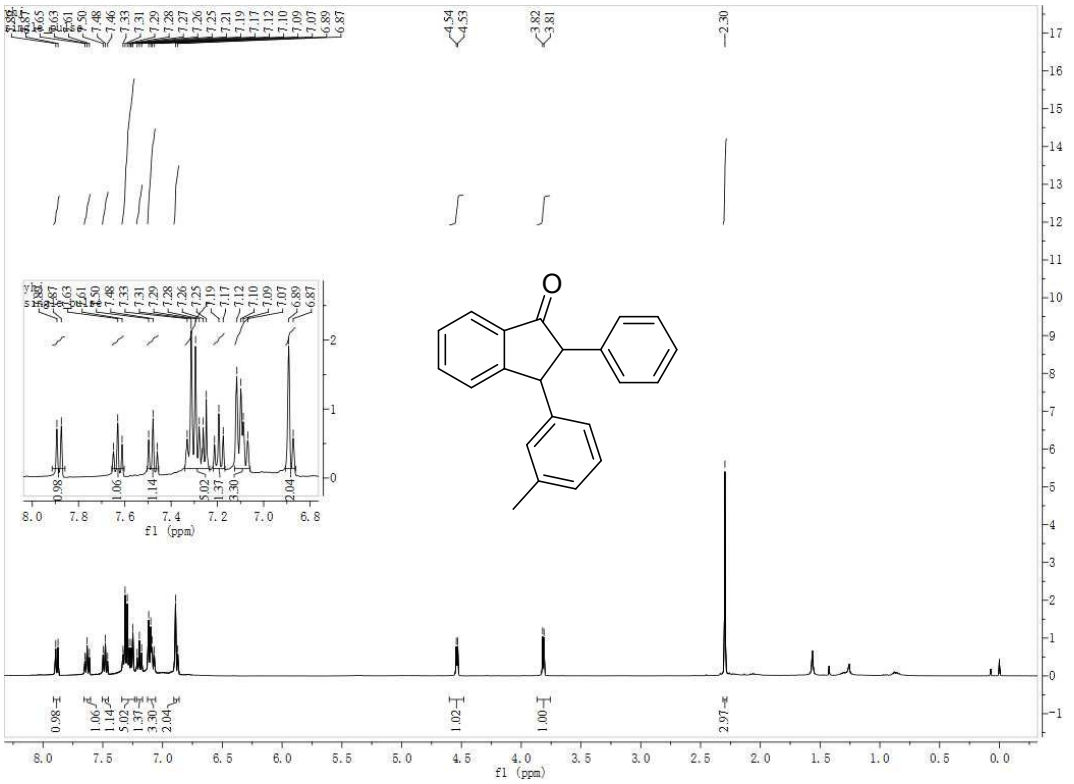
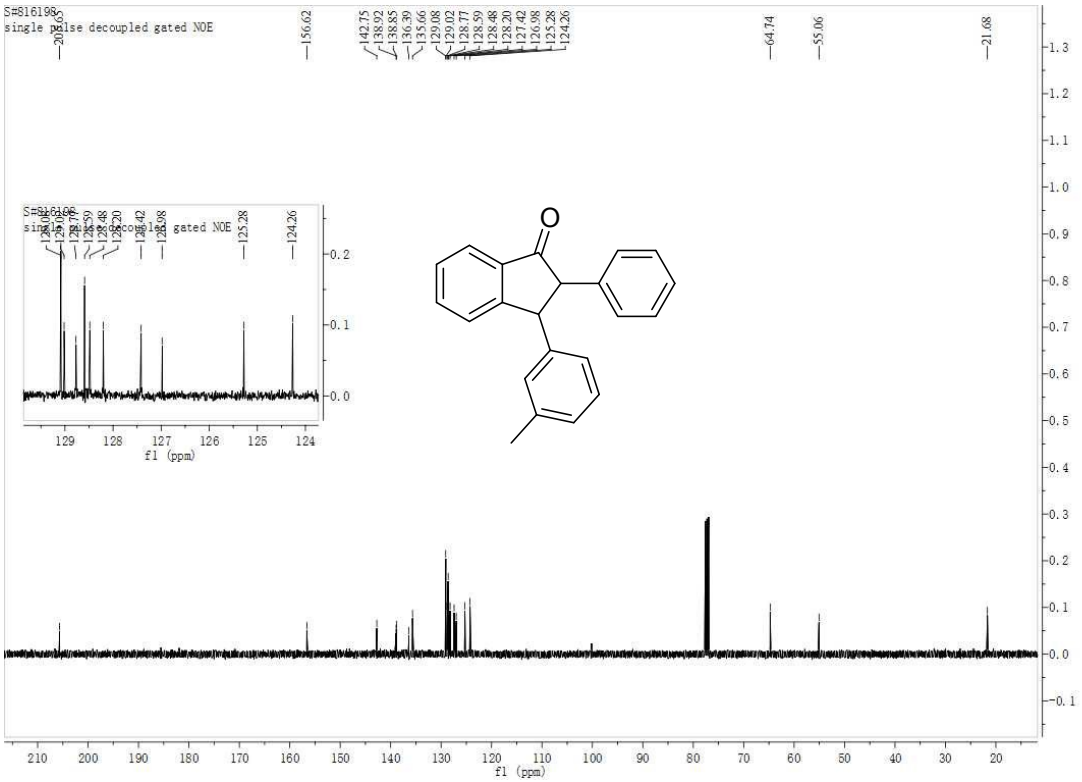


^{1}H NMR of **4ai**



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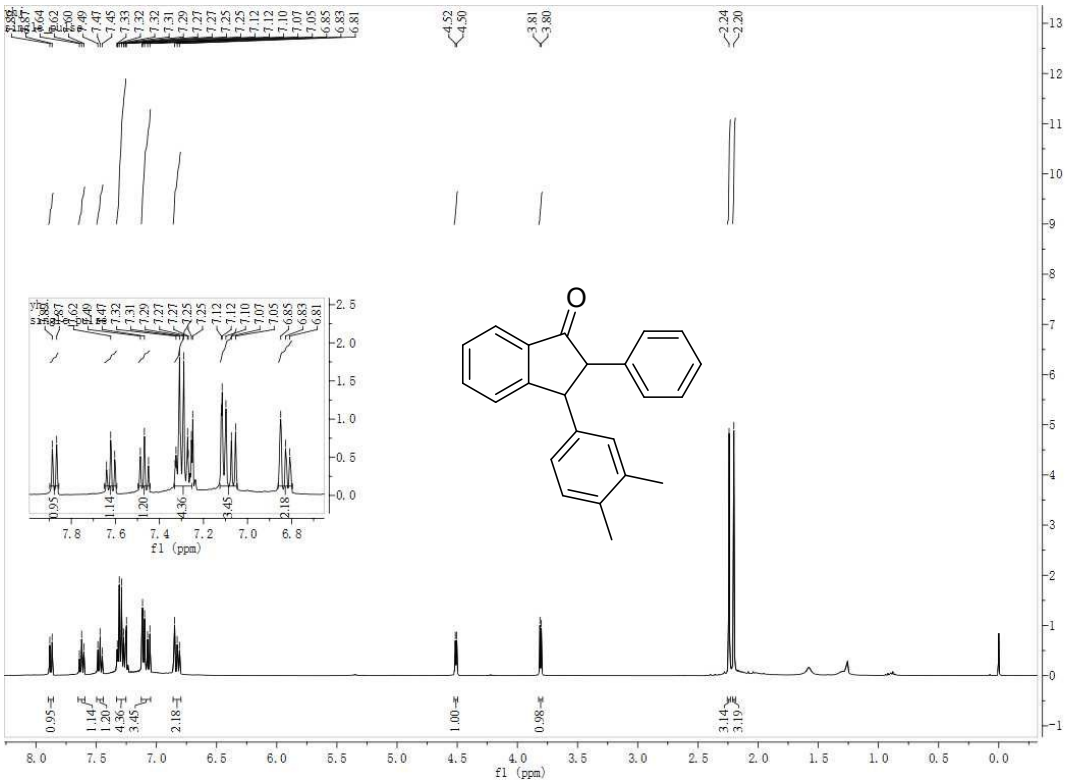

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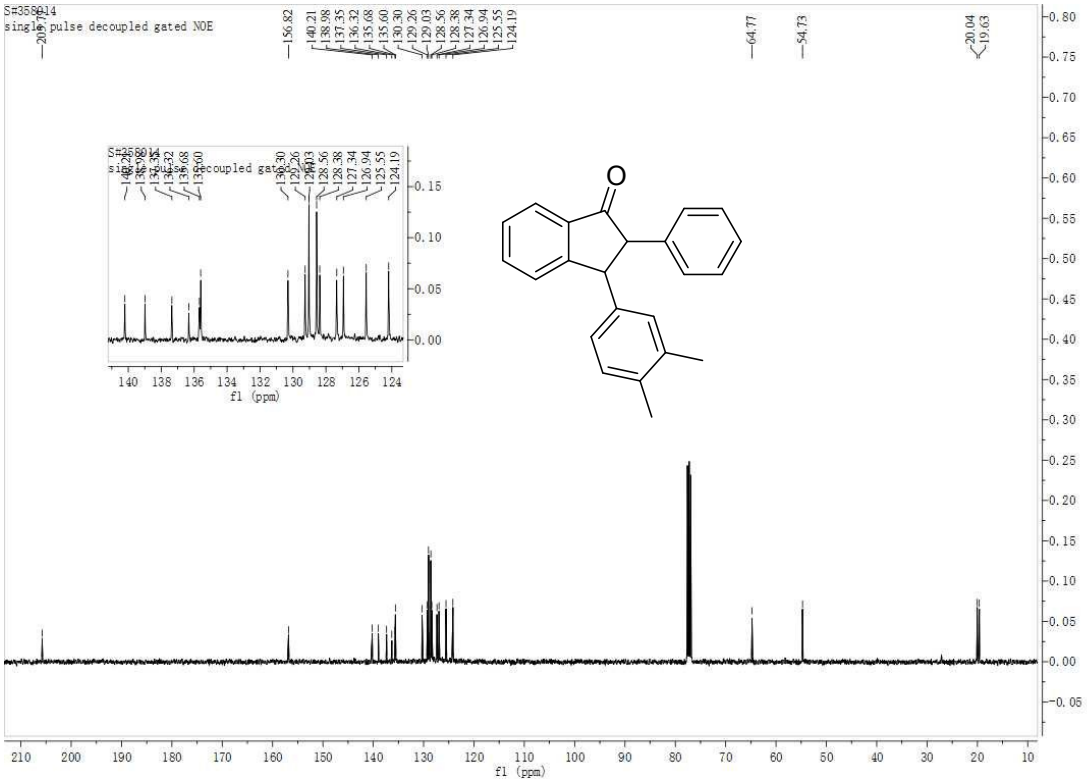

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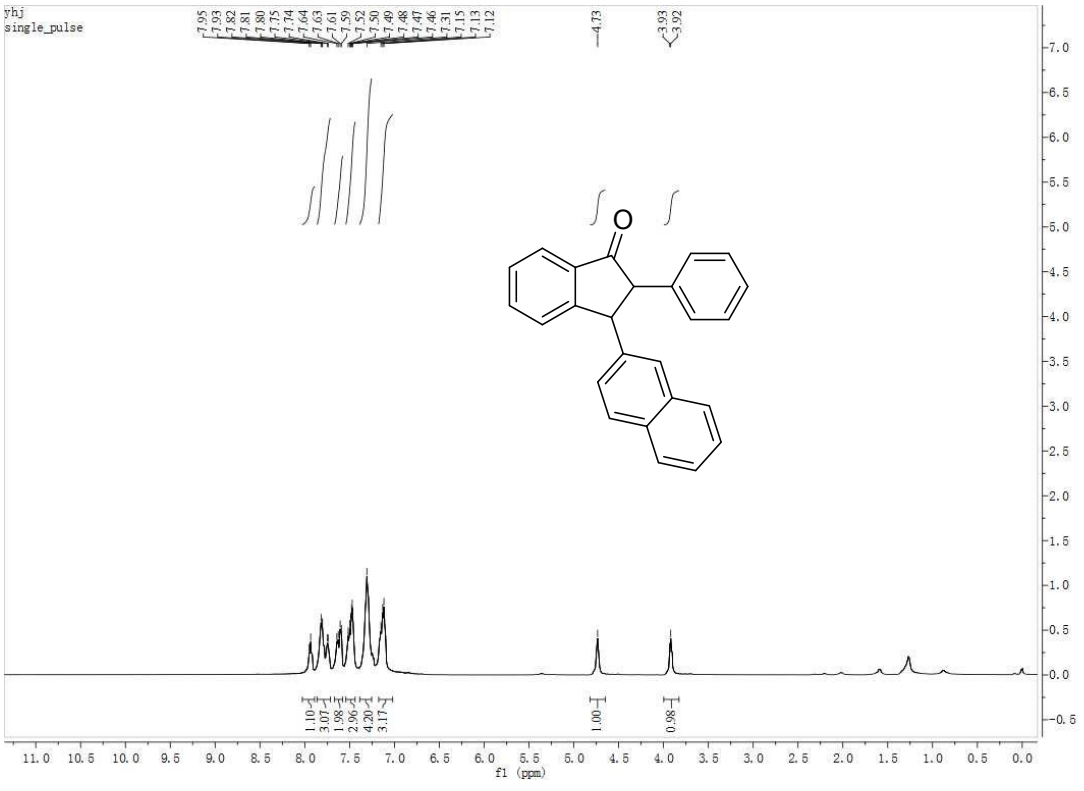

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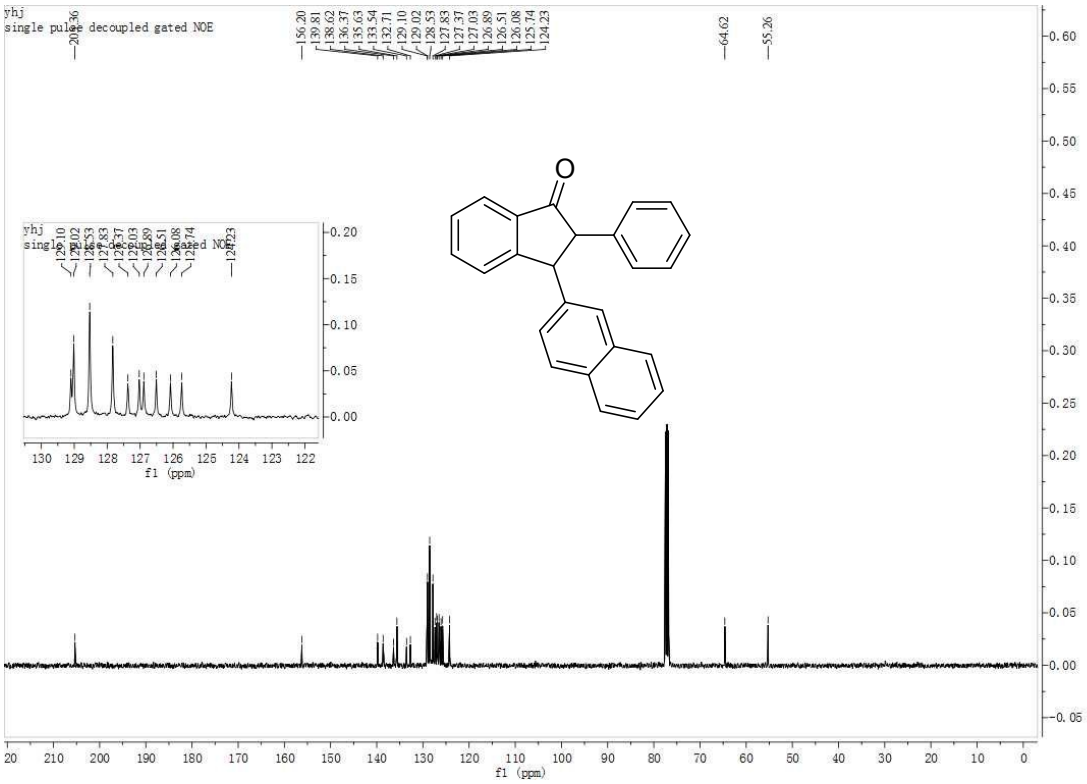

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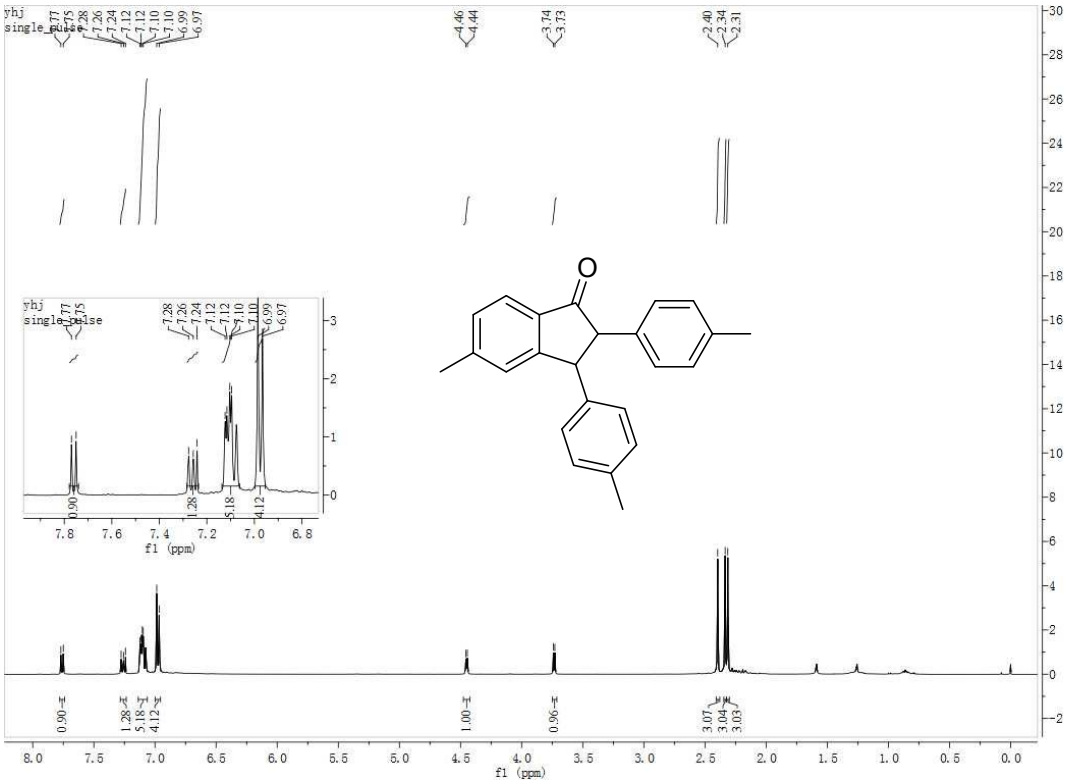

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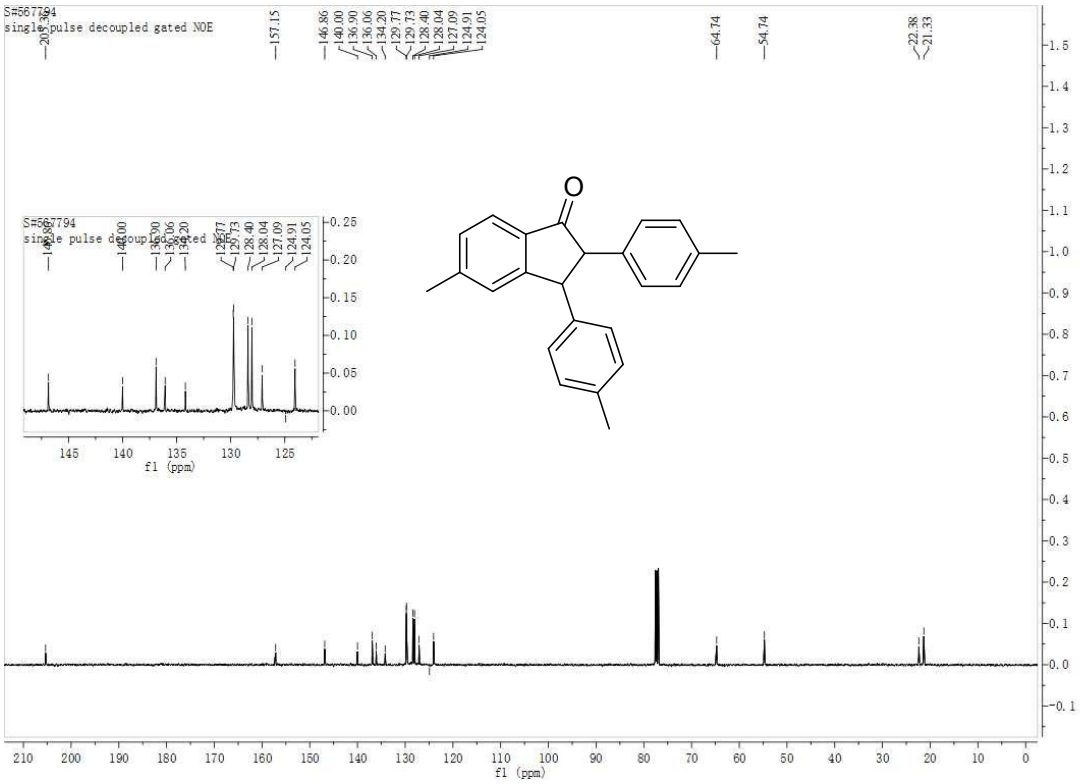

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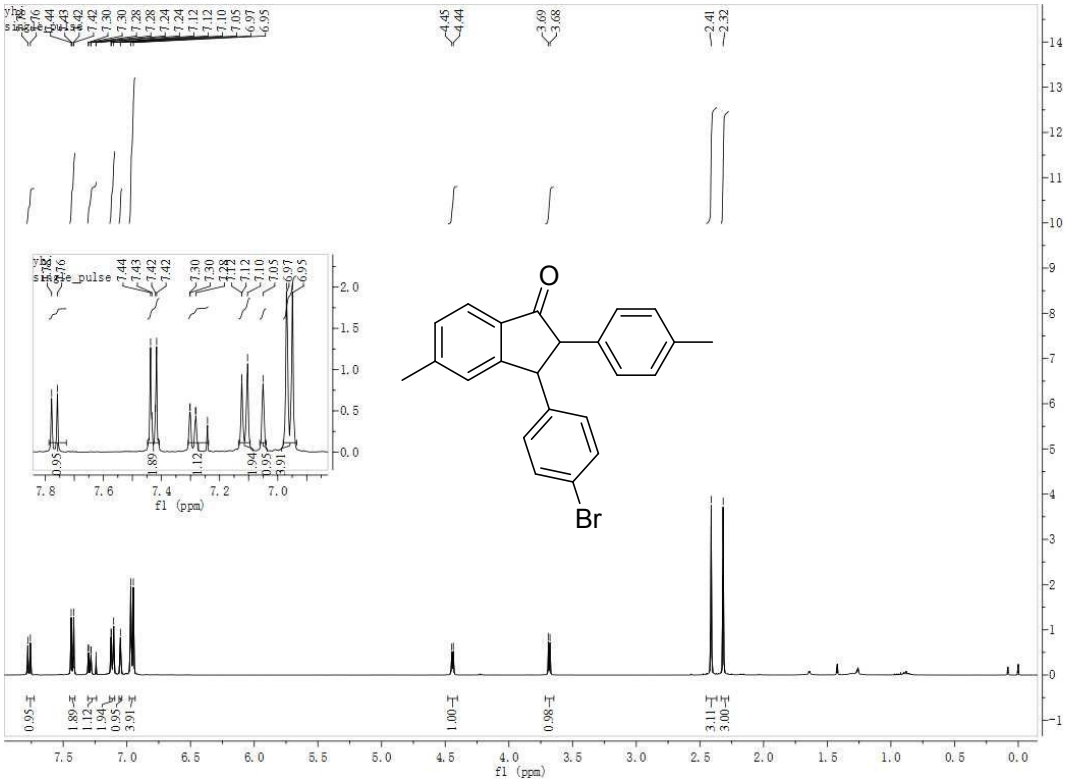
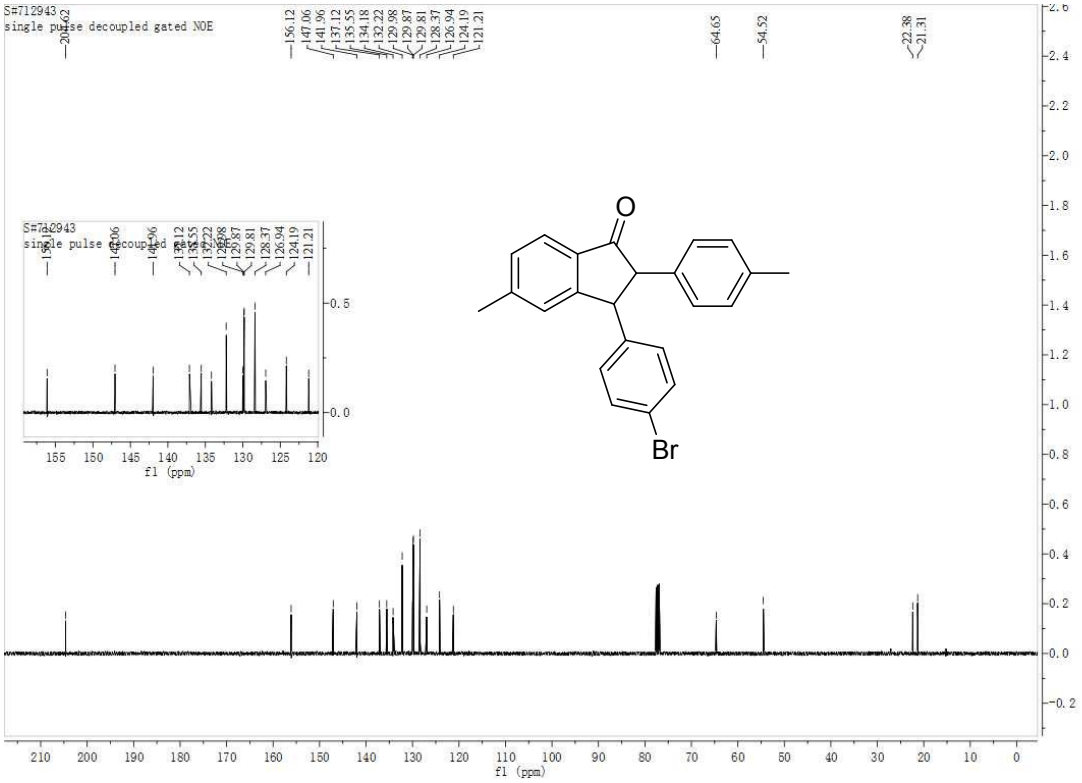
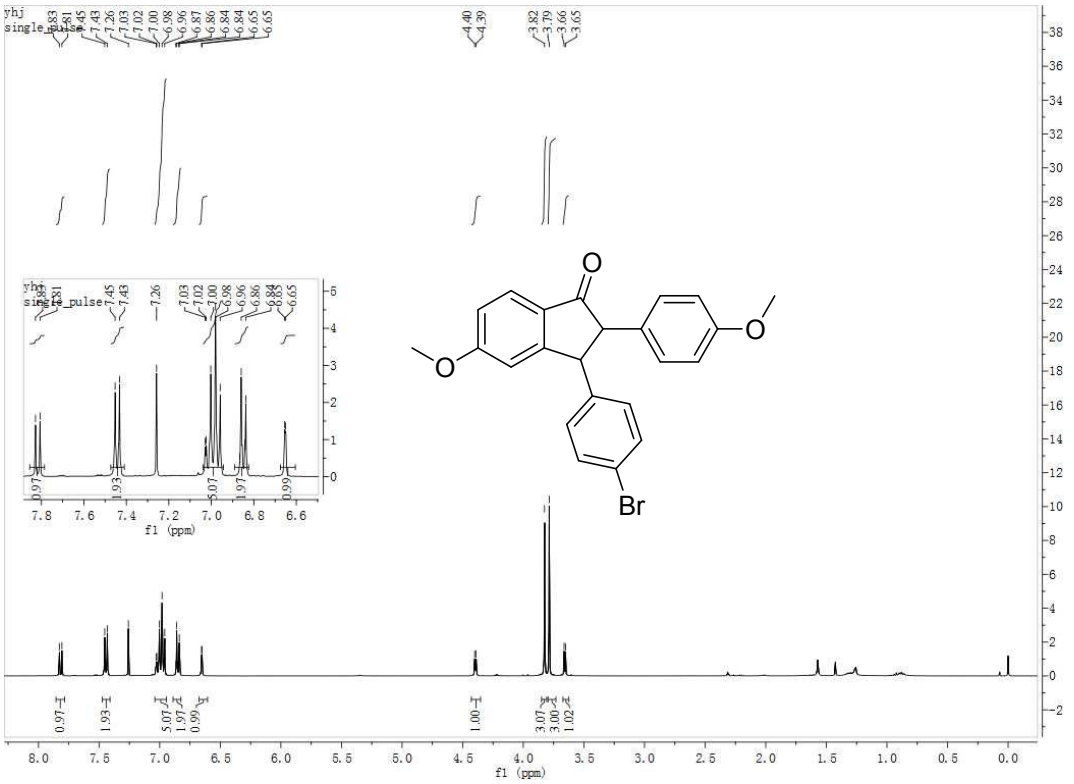


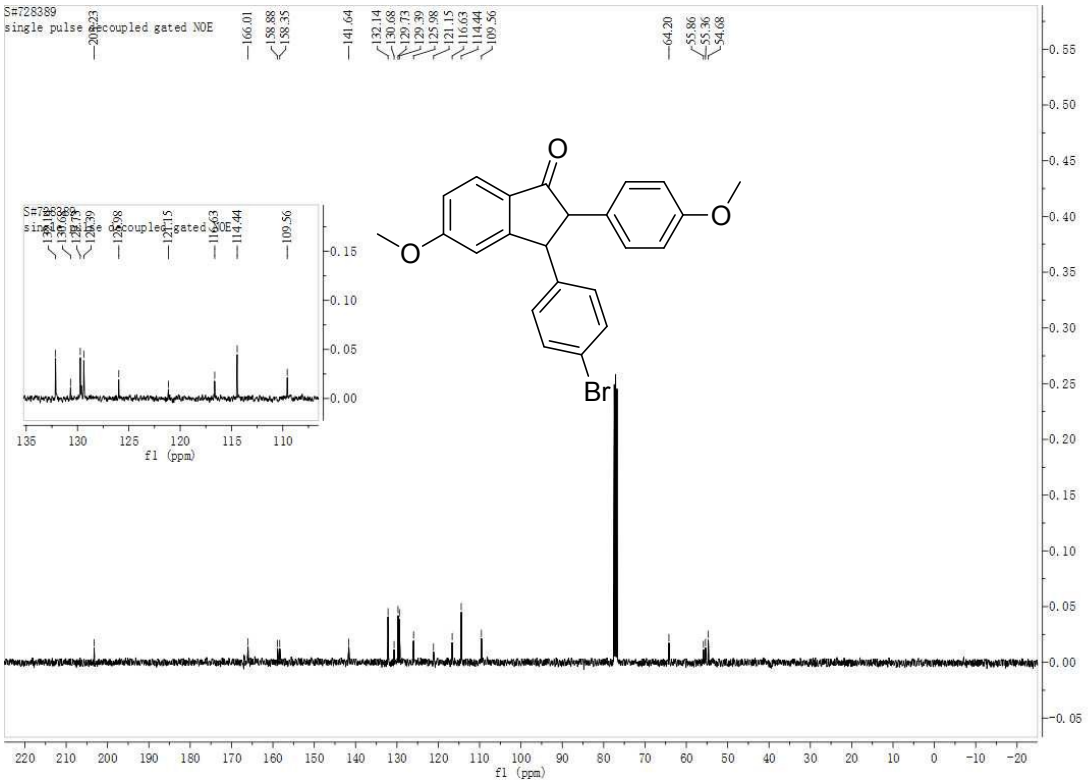
^{1}H NMR of **4be**



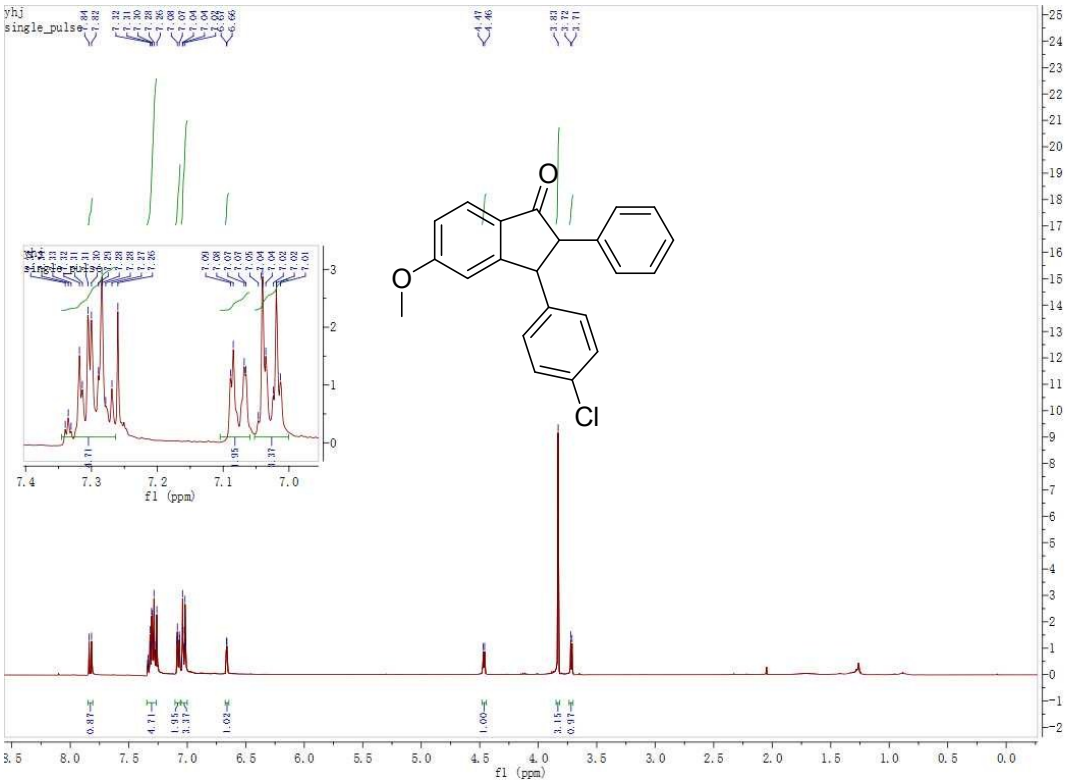
^{13}C NMR of **4be**



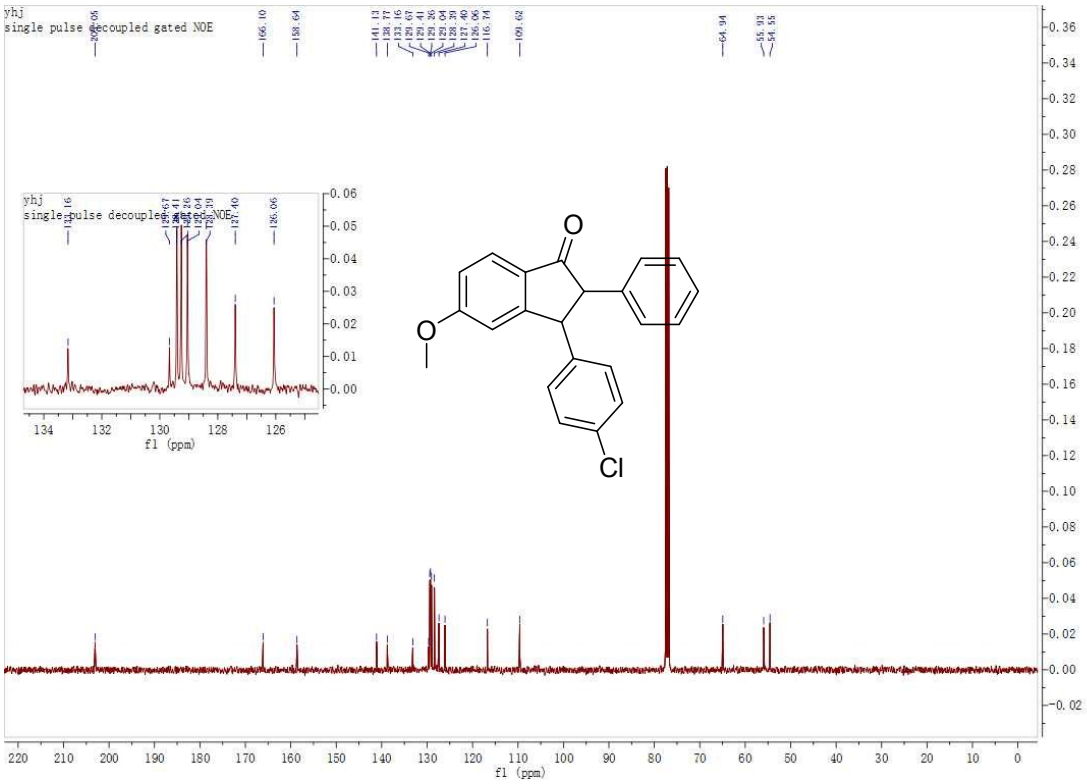
^{1}H NMR of **4ce**



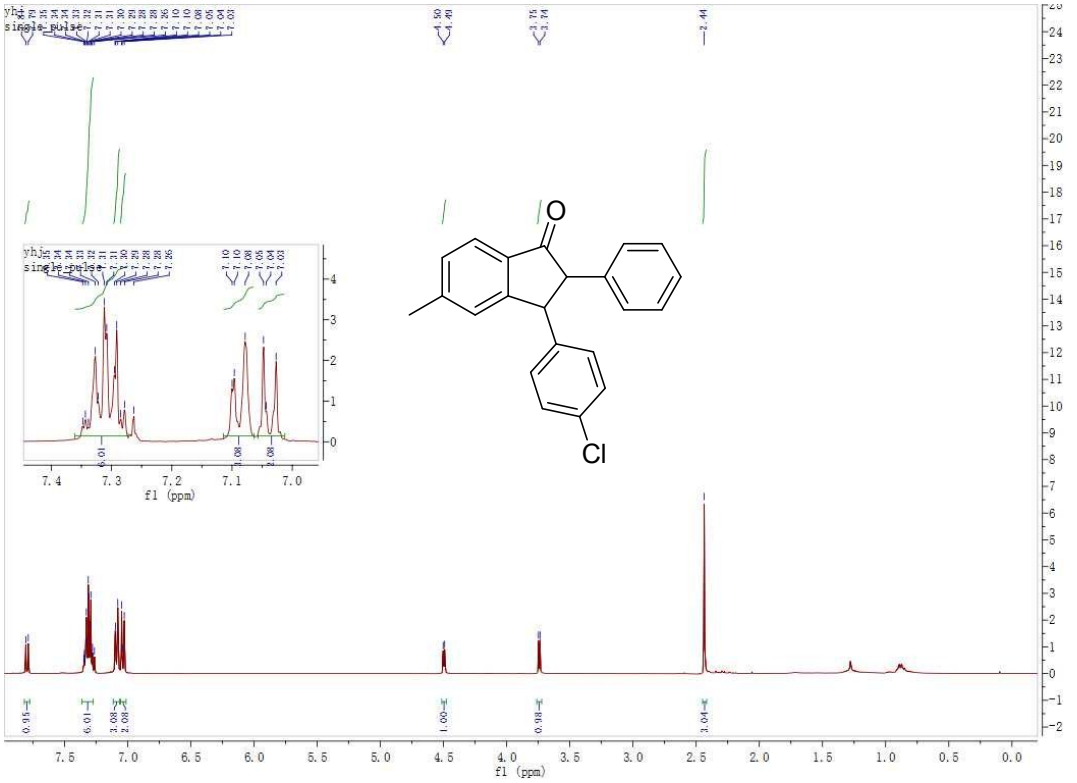
^{13}C NMR of **4ce**



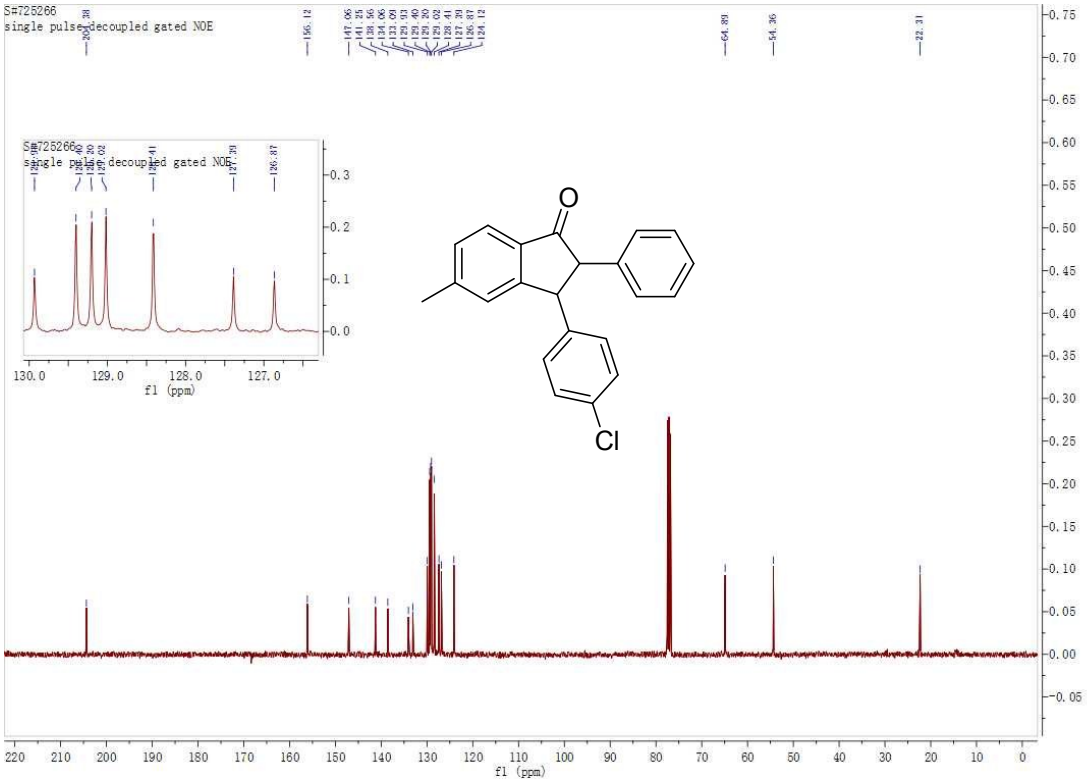
^{1}H NMR of **4gf**



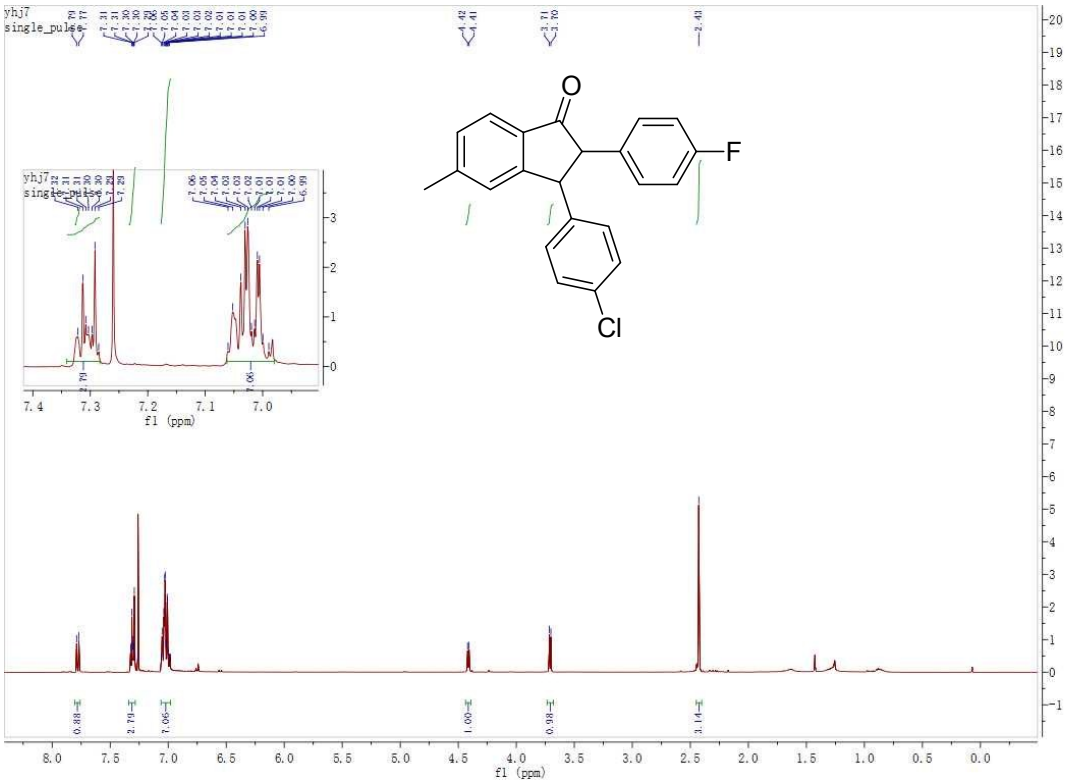
^{13}C NMR of **4gf**



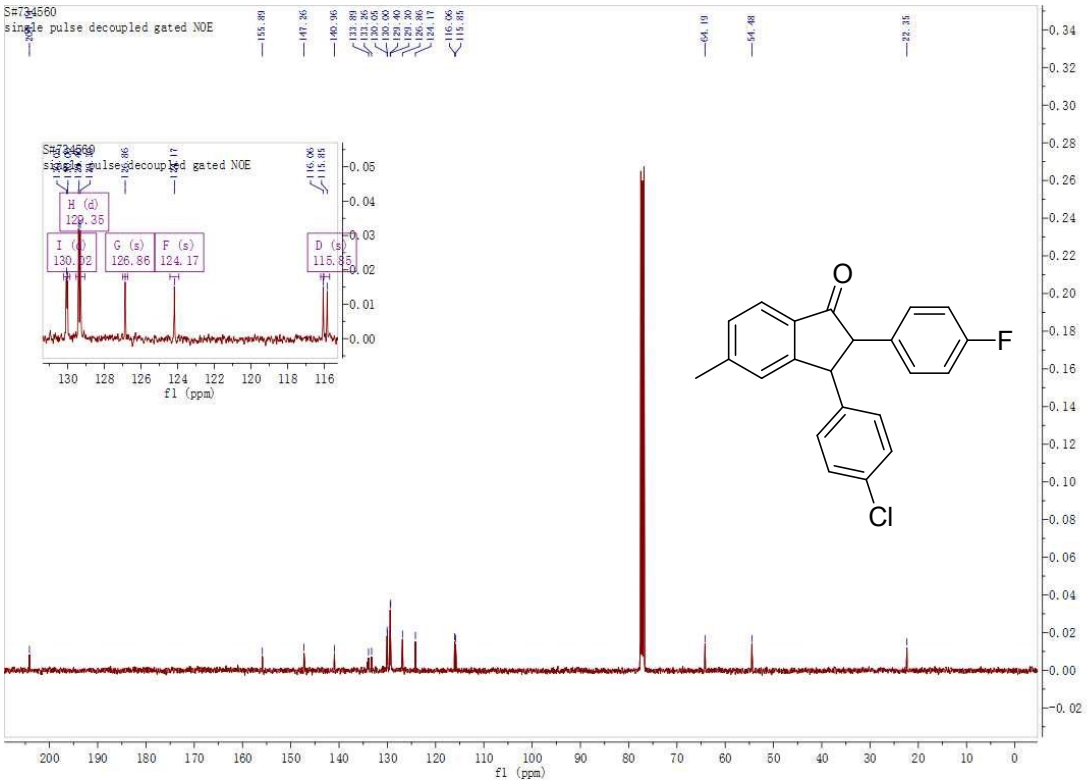
^{1}H NMR of **4hf**



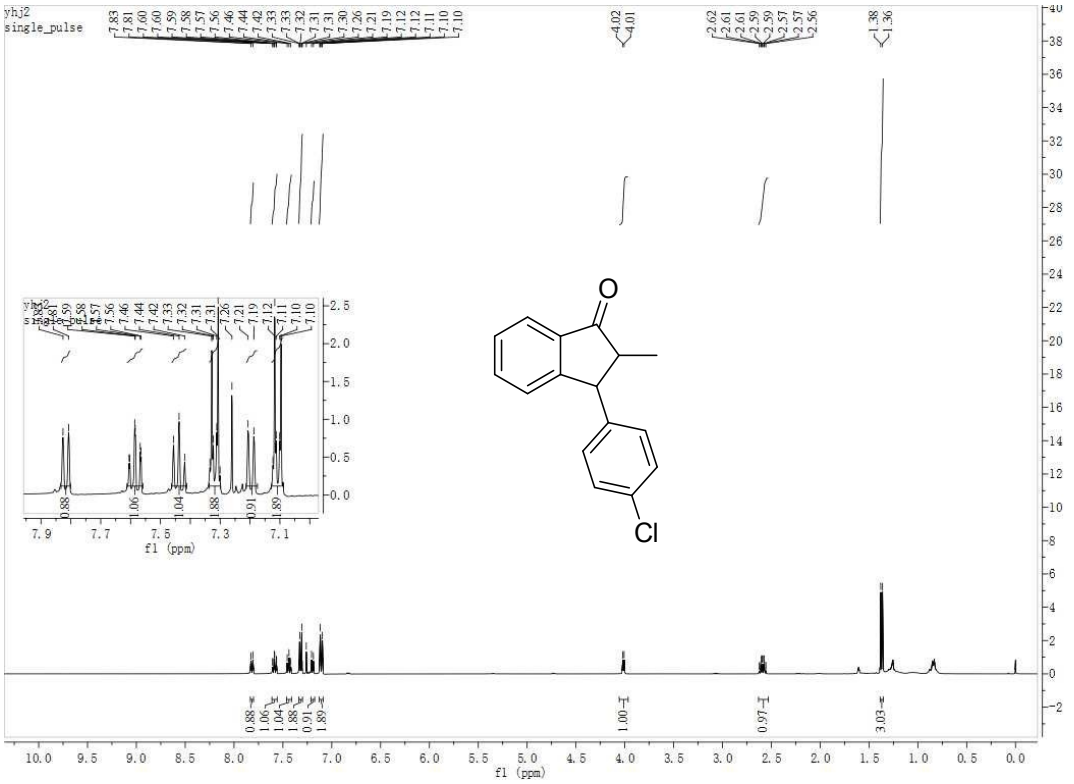
^{13}C NMR of **4hf**



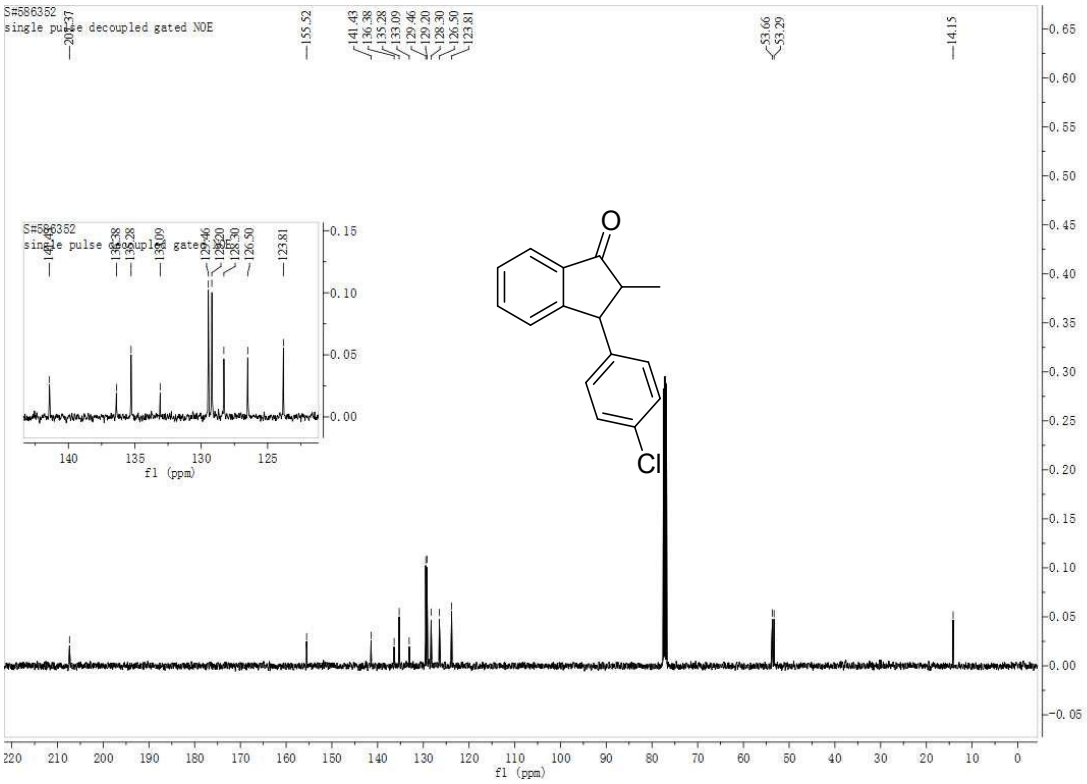
^{1}H NMR of **4if**



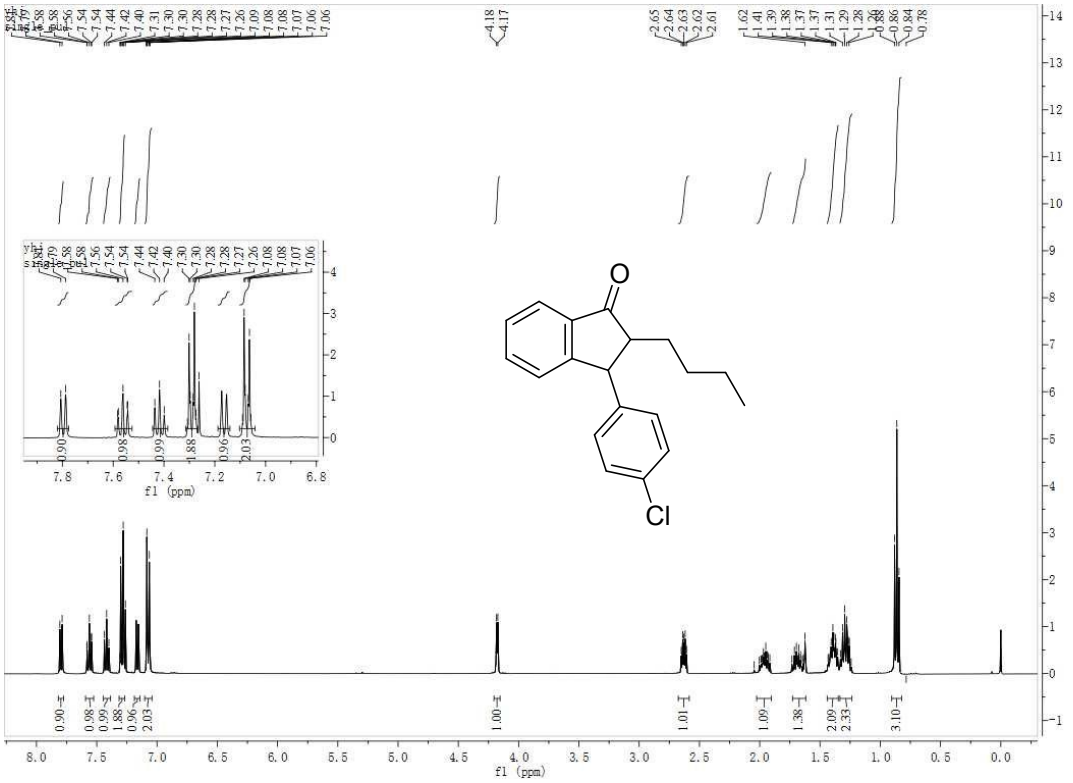
^{13}C NMR of **4if**



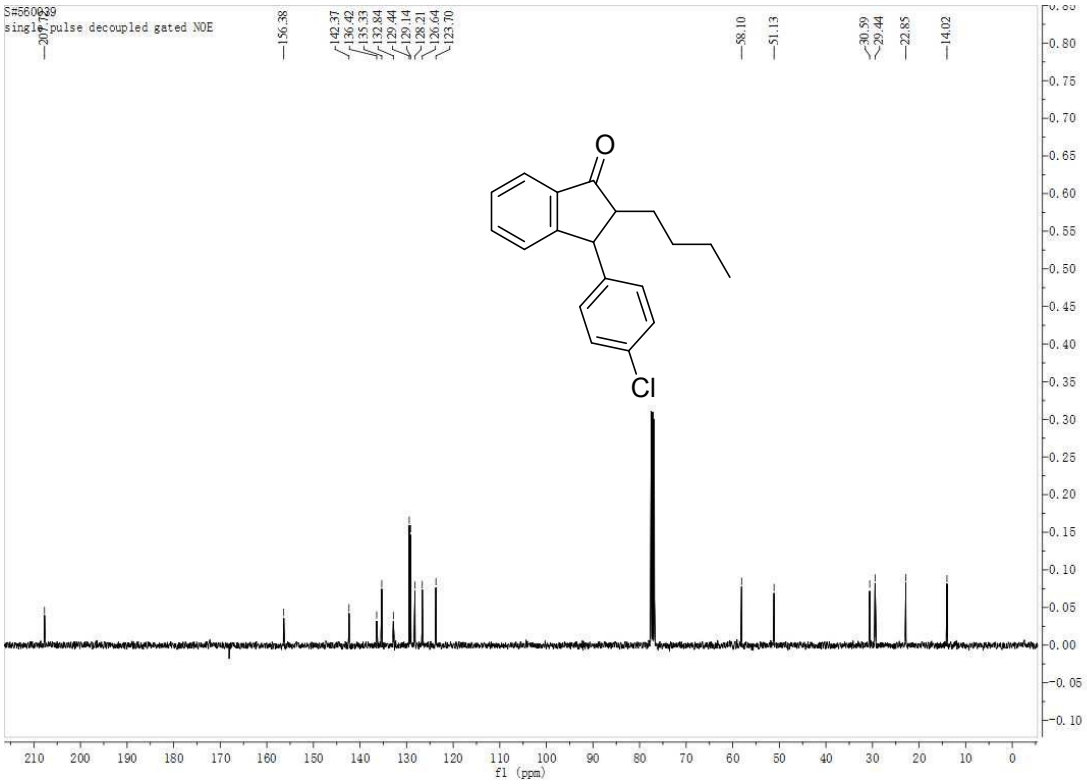
^{1}H NMR of **4jf**



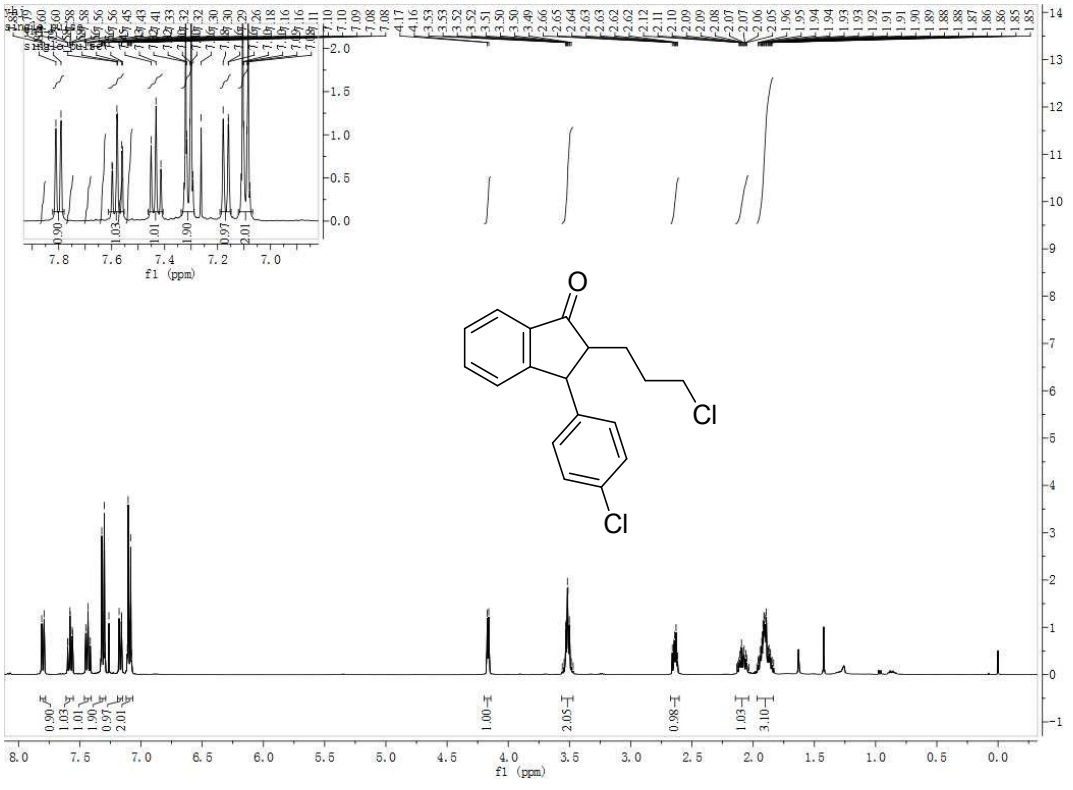
^{13}C NMR of **4jf**



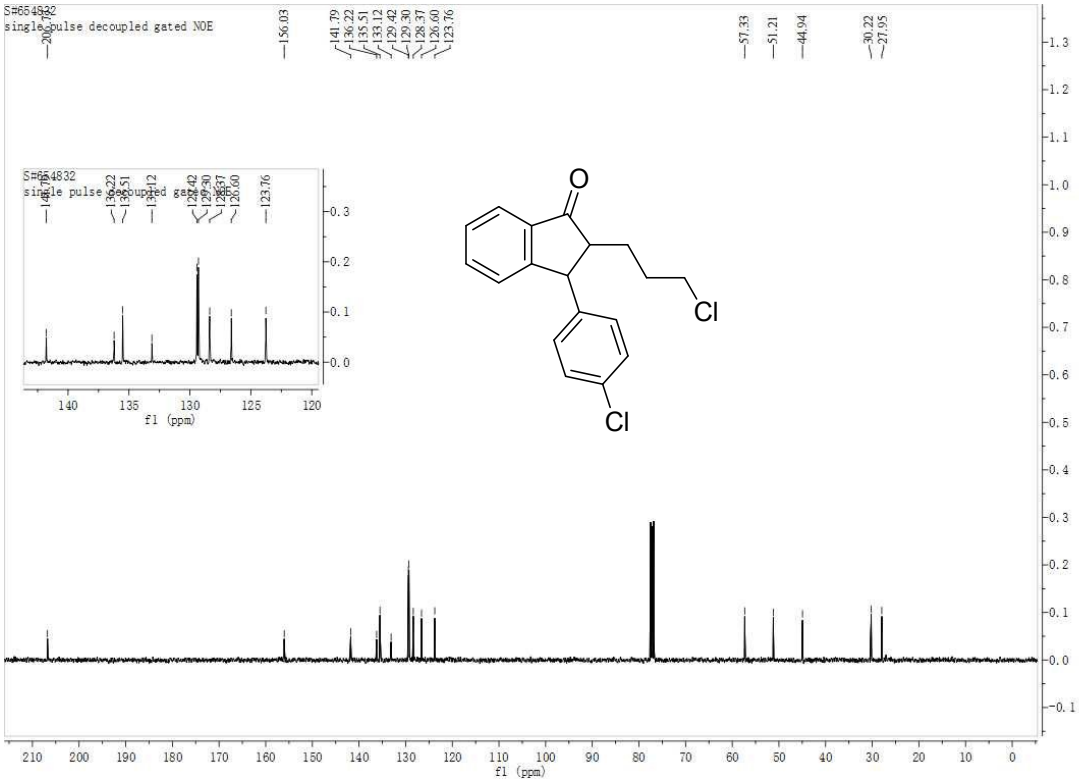
^{1}H NMR of **4kf**



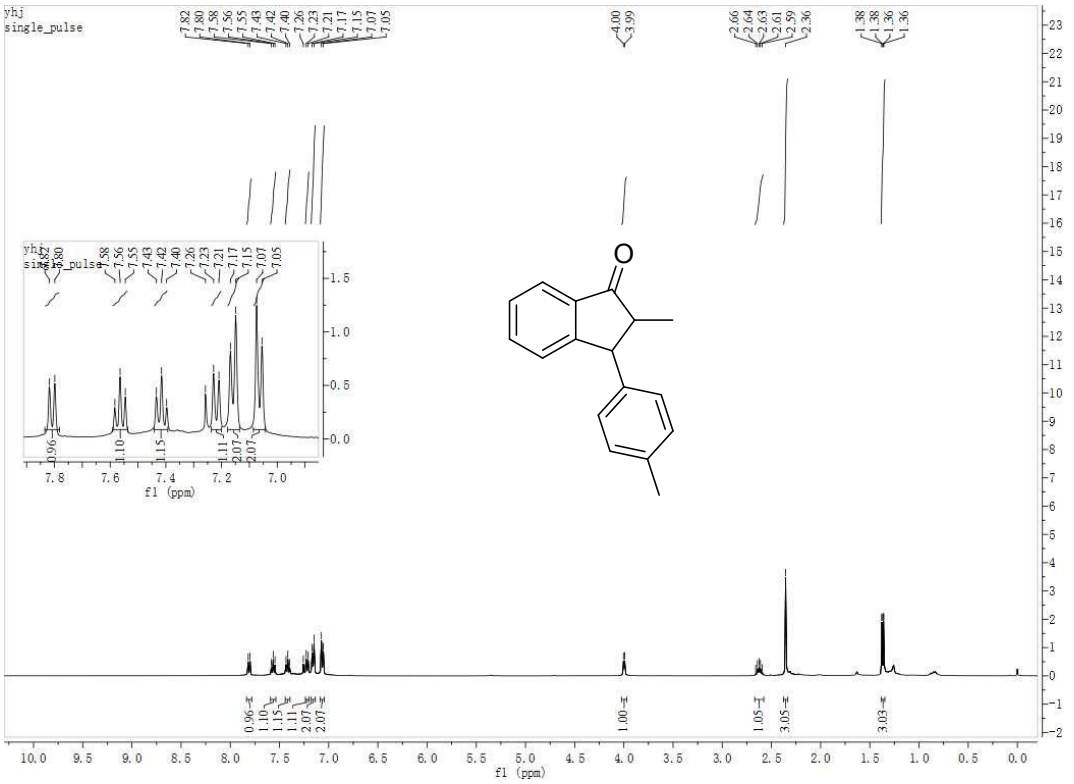
^{13}C NMR of **4kf**



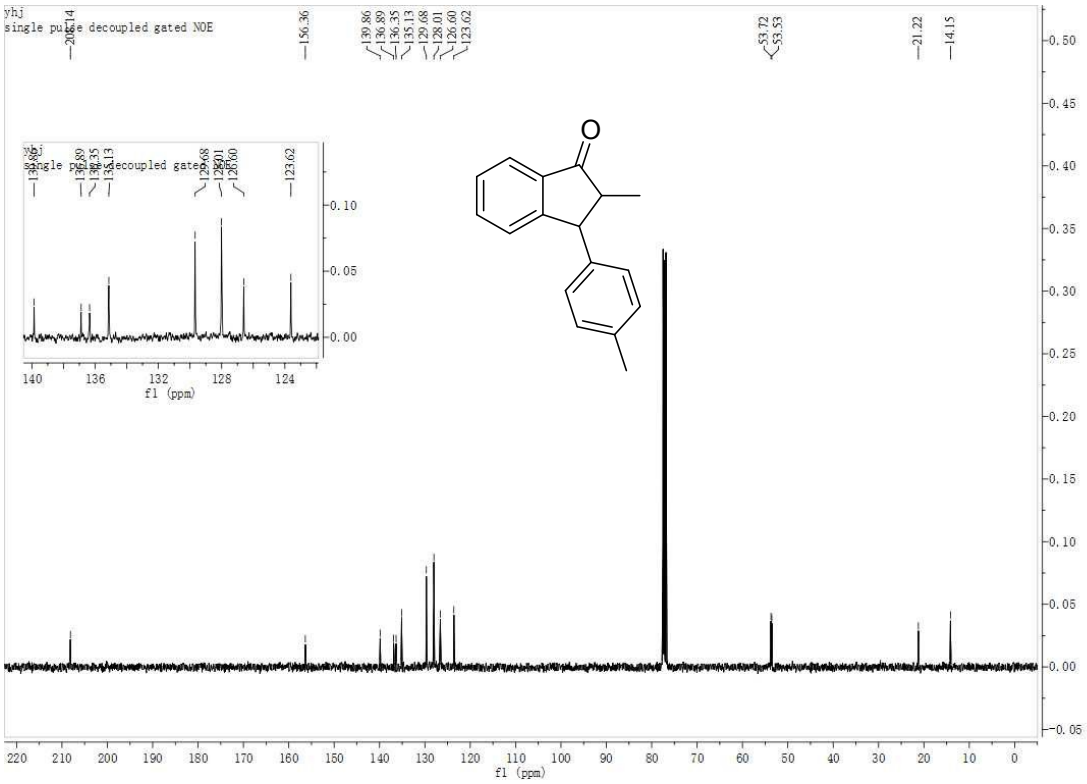
^{1}H NMR of **4lf**



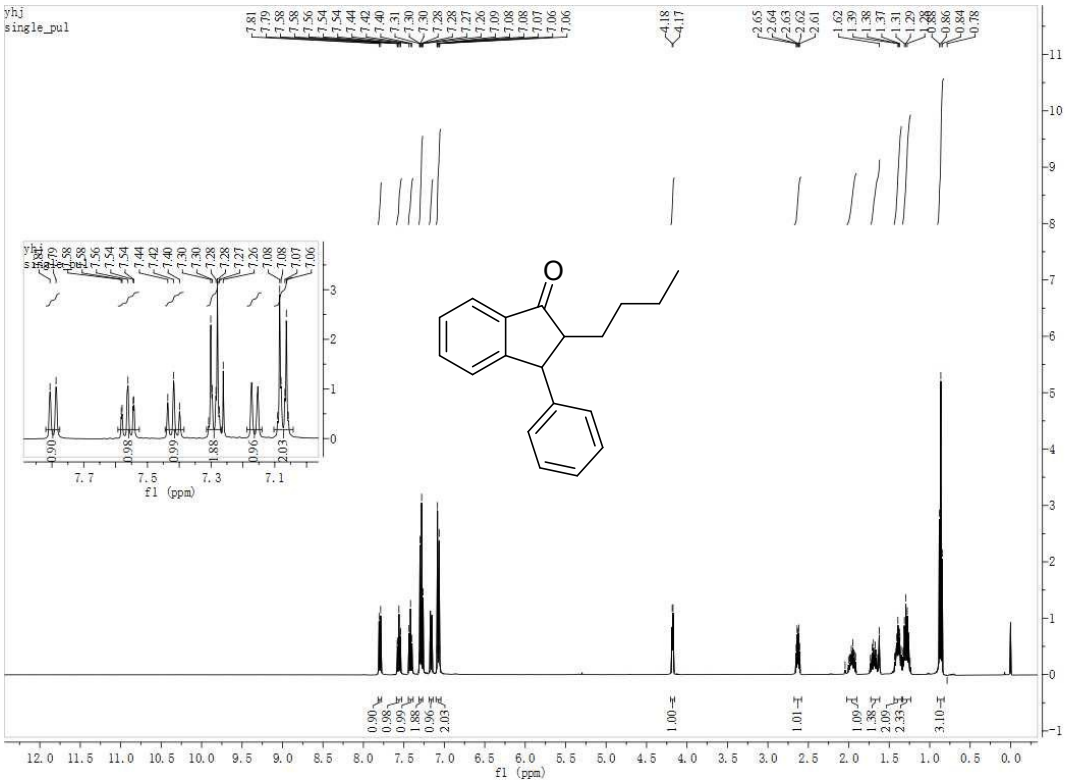
^{13}C NMR of **4lf**



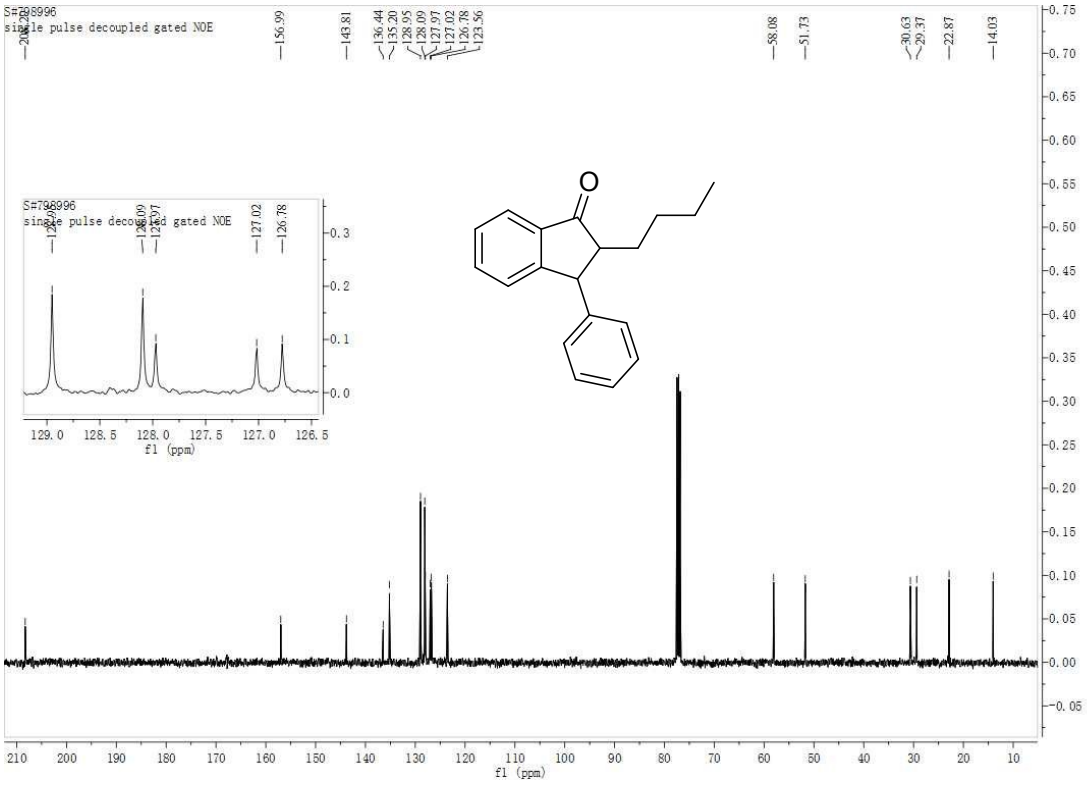
^{1}H NMR of **4ja**



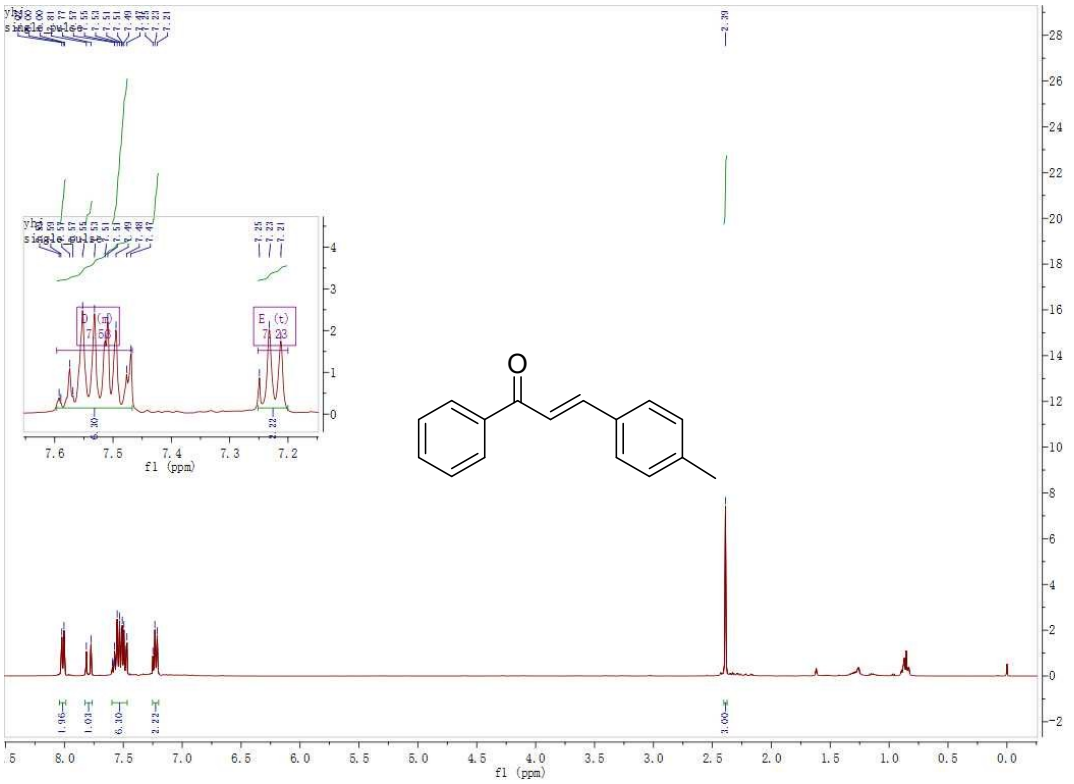
^{13}C NMR of **4ja**



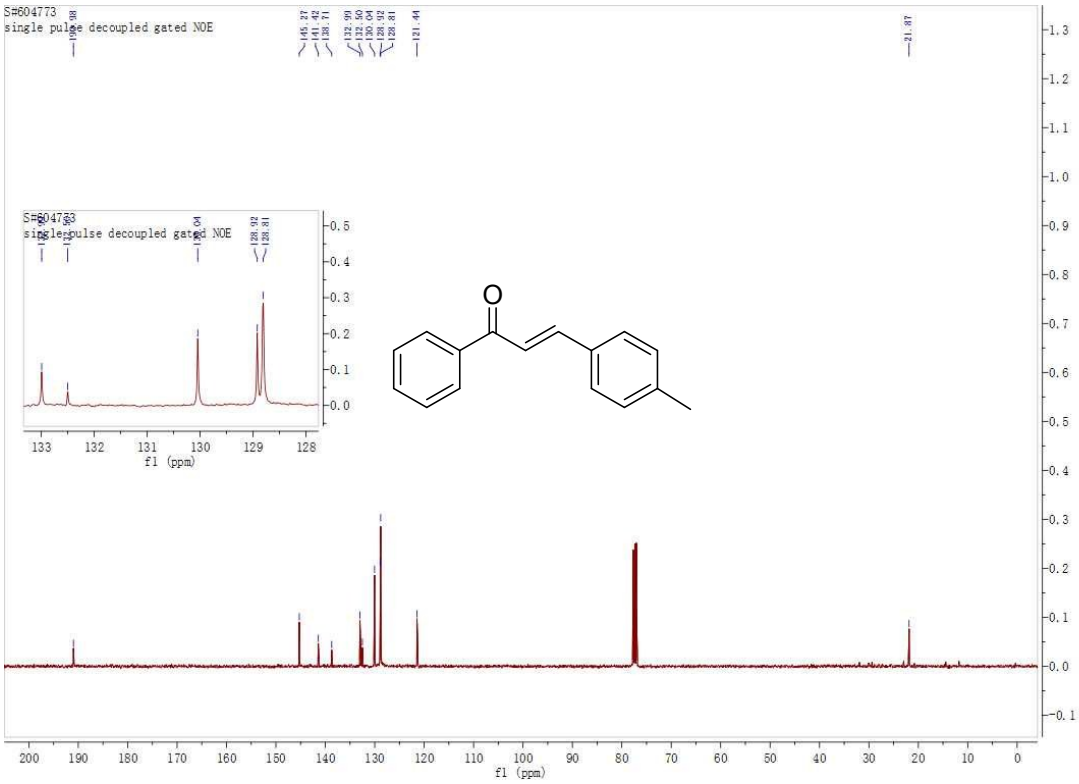
^{1}H NMR of **4kb**



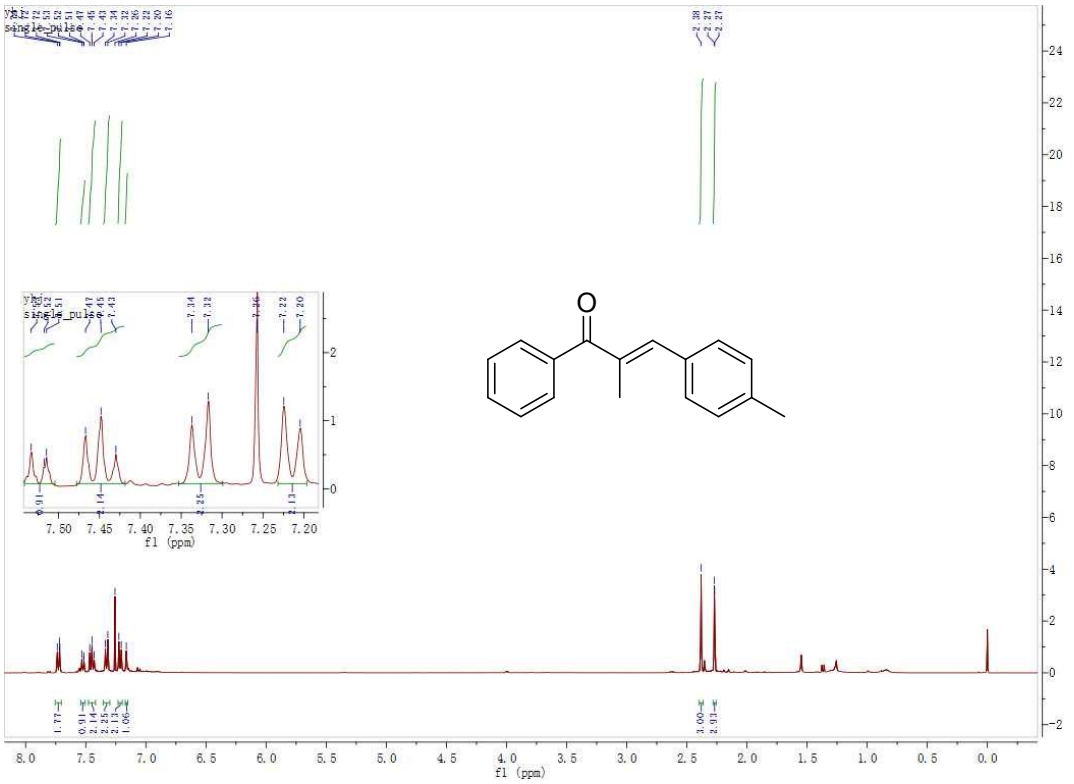
^{13}C NMR of **4kb**



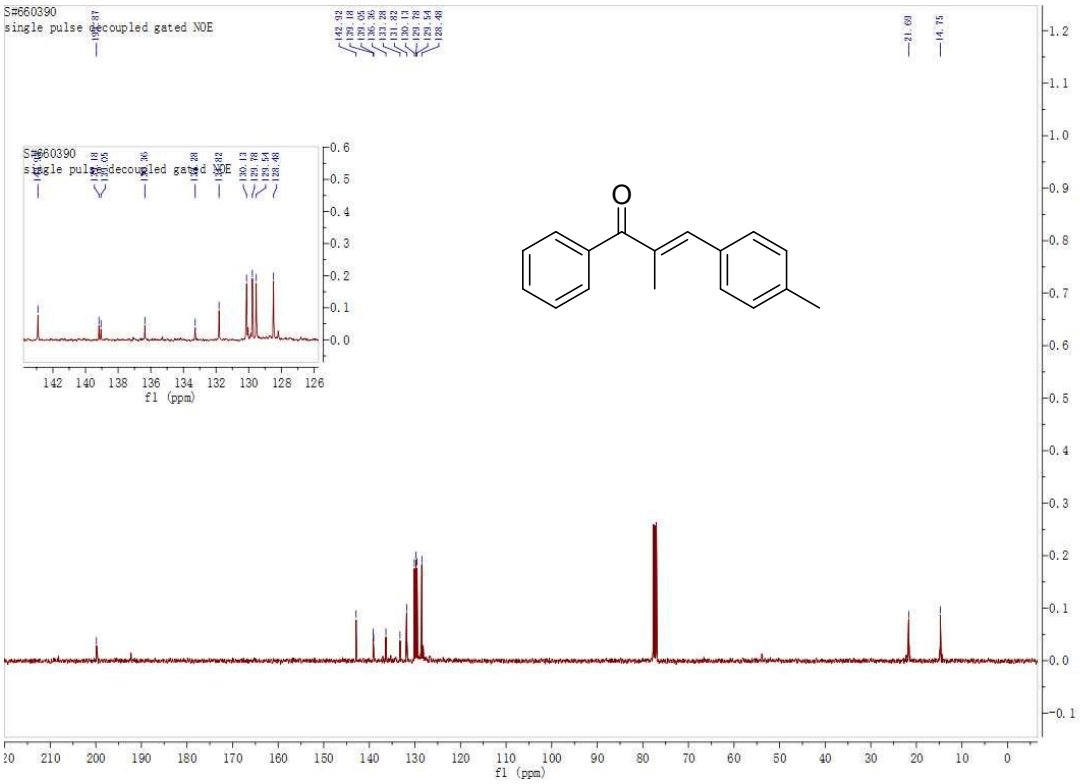
^{1}H NMR of **5ma**



^{13}C NMR of **5ma**



^{1}H NMR of **5ja**



^{13}C NMR of **5ja**