$Sc(OTf)_3$-Catalyzed Transfer Diazenylation of 1,3-Dicarbonyls with Triazenes *via* N-N Bond Cleavage

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Supporting Information

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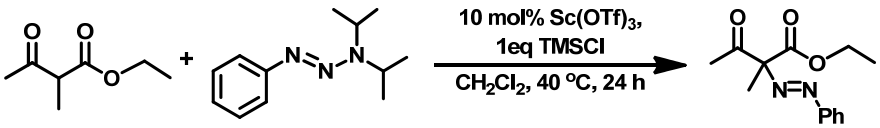
General Information: Commercial reagents were used as received, unless otherwise stated. ^{1}H and ^{13}C NMR were recorded on Bruker UltraShield 300 MHz spectrometer spectrometer, and ^{19}F and ^{31}P NMR were recorded on Bruker Avance 500 MHz spectrometer spectrometer. ^{1}H NMR and ^{13}C NMR chemical shifts were determined relative to internal standard TMS at δ 0.0 and ^{19}F NMR and ^{31}PNMR chemical shifts were determined relative to $CFCl_3$ and 85% H_3PO_4 aqueous solution as internal standard. Chemical shifts (δ) are reported in ppm, and coupling constants (J) are in Hertz (Hz). The following abbreviations were used to designate chemical shift mutiplicities: s= singlet, d= doublet, t= triplet, q= quartet, m= multiplet. All first-order splitting patterns were assigned on the basis of the appearance of the multiplet. Splitting patterns that could not be easily interpreted are designated as multiplet (m). Infrared Spectroscopy was conducted on Thermo Fisher Nicolet 6700. High resolution mass spectra were obtained using electrospray ionization (ESI) mass spectrometer. HPLC analysis was performed using Chiralcel columns purchased.

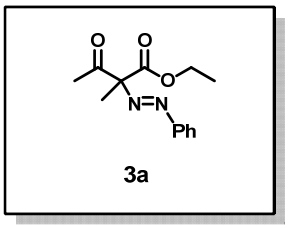
Materials: β-Keto esters **1a**-**1g**, **1i**, malonic ester **1o** and ethyl cyanacetate **1p** were prepared by alkylation of the corresponding α-unsubstituted β-keto esters with alkyl iodide or bromide.[1] 1,3-diketones **3m** and **3n** were prepared using standard literature procedures.[2] β-Keto esters **3j**-**3l** and β-keto amide **1q** were prepared according to standard literature procedures.[3] β-keto phosphonate **1r**[4] and α-(Phenylsulfonyl)acetophenone **1s**[5] were prepared using standard literature procedures. All triazenes were prepared according to standard literature procedures.[6] All other reagents were received from commercial sources without further purification. Solvents were freshly dried according to *the purification handbook Purification of Laboratory Chemicals* before using.

Experimental Section



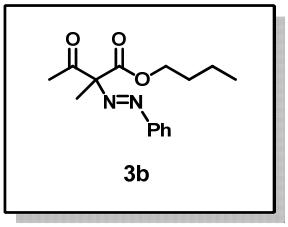
2-methyl acetoacetate **1a** (0.12 mmol, 17.3 mg), 3,3-diisopropyl-1-phenyltriazene **2a** (0.10 mmol, 20.5 mg), and $Sc(OTf)_3$ (0.01 mmol, 4.9 mg) were added to a 10 mL flame-dried Schlenk tube under argon, followed by addition of anhydrous CH_2Cl_2 (0.3 mL). After TMSCl (0.1 mmol ,13μL) in CH_2Cl_2 (0.1 mL) was added, the resulting mixture was stirred at 40 ^{o}C for 24 h. After monitored by TLC, the crude product was purified by flash column chromatography on silica gel to afford the desired product (21.1 mg, 85% yield) as light yellow oil.

Characterization of new compounds



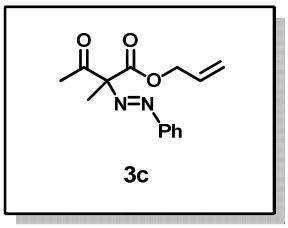
3a

The azo product was synthesized according to the general procedure as yellow oil in 85% overall yield (21.1 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79–7.72 (m, 2H), 7.50–7.48 (m, 3H), 4.27 (qd, *J* = 7.2, 4.7 Hz, 2H), 2.36 (s, 3H), 1.66 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.4, 169.2, 151.7, 131.8, 129.2, 122.8, 88.0, 62.0, 28.3, 19.0, 14.2. IR (thin film, cm^{-1}): 2984, 2940, 1724, 1453, 1368, 1258, 1139, 1020. HRMS (ESI^+): calcd. for $[C_{13}H_{16}N_2O_3+Na]^+$ 271.1053, found 271.1047.For chiral product: 24% *ee*: the enantiomeric excess was determined by HPLC with an OJ-H column at 254 nm (2-propanol: hexane=3:97), 1.0 mL/min; t_R= 18.5 min(major), 22.4 min (minor).



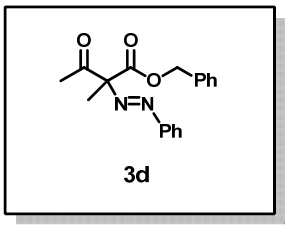
3b

The azo product was synthesized according to the general procedure as yellow oil in 80% overall yield (22.1 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.72 (m, 2H), 7.50–7.48 (m, 3H), 4.22 (td, *J* = 6.6, 3.5 Hz, 2H), 2.35 (s, 3H), 1.66 (s, 3H), 1.65–1.58 (m, 2H), 1.38–1.28 (m, 2H), 0.90 (t, *J* = 7.4 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.3, 169.2, 151.6, 131.8, 129.2, 122.7, 88.1, 65.7, 30.6, 28.3, 19.1, 19.0, 13.7. IR (thin film, cm^{-1}):2961, 2936, 2874, 1748, 1724, 1454, 1355, 1260, 1119. HRMS (ESI^+): calcd. for $[C_{15}H_{20}N_2O_3+Na]^+$ 299.1366, found 299.1366.



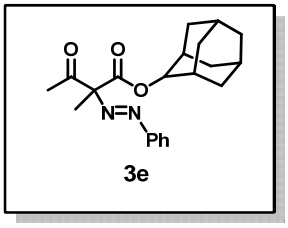
3c

The azo product was synthesized according to the general procedure as yellow oil in 86% overall yield (22.4 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.73 (m, 2H), 7.51–7.47 (m, 3H), 5.90 (ddt, *J* = 16.0, 11.4, 5.7 Hz, 1H), 5.35–5.22 (m, 2H), 4.71 (d, *J* = 5.8Hz, 2H), 2.36 (s, 3H), 1.68 (s, 3H);^{13}C NMR (75 MHz, $CDCl_3$) δ 203.2, 168.9, 151.6, 131.9, 131.5, 129.2, 122.8, 118.9, 88.1, 66.3, 28.3, 19.1. IR (thin film, cm^{-1}): 3067, 2993, 2940, 1748, 1724, 1453, 1356, 1254, 1120, 928. HRMS (ESI^+): calcd. for $[C_{14}H_{16}N_2O_3+Na]^+$ 283.1053, found 283.1055.



3d

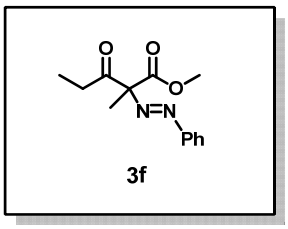
The azo product was synthesized according to the general procedure as yellow oil in 90% overall yield (27.9 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.64–7.61 (m, 2H), 7.43–7.38 (m, 3H), 7.25 (s, 4H), 7.19 (s, 1H), 5.18 (q, *J* = 12.4 Hz, 2H), 2.25 (s, 3H), 1.61 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.3, 169.1, 151.6, 135.4, 131.9, 129.2, 128.7, 128.5, 128.3, 122.8, 88.1, 67.5, 28.4, 19.1. IR (thin film, cm^{-1}): 3445, 1722, 1635, 1454, 1260, 1115. HRMS (ESI^+): calcd. for $[C_{18}H_{18}N_2O_3+Na]^+$ 333.1210, found 333.1208.



3e

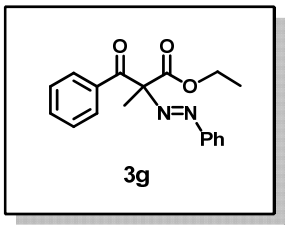
The azo product was synthesized according to the general procedure as yellow oil in 75% overall yield (26.6 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ

7.76–7.73 (m, 2H), 7.51–7.46 (m, 3H), 2.33 (s, 3H), 2.17 (s, 3H), 2.13 (s, 6H), 1.65 (s, 6H), 1.60 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.4, 167.7, 151.8, 131.6, 129.2, 122.6, 88.4, 83.0, 41.3, 36.2, 31.0, 28.3, 18.8. IR (thin film, cm^{-1}): 3447, 2912, 2853, 1744, 1721, 1455, 1354, 1258, 1143, 1052, 966. HRMS (ESI^+): calcd. for $[C_{21}H_{26}N_2O_3+Na]^+$ 377.1836, found 377.1834.



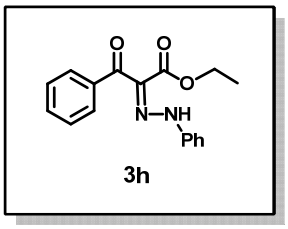
3f

The azo product was synthesized according to the general procedure as yellow oil in 97% overall yield (24.1 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.78–7.72 (m, 2H), 7.50–7.48 (m, 3H), 3.78 (s, 3H), 2.69 (q, *J* = 7.1 Hz, 2H), 1.68 (s, 3H), 1.12 (t, *J* = 7.16 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.2, 169.9, 151.7, 131.8, 129.2, 122.8, 88.1, 52.8, 34.3, 19.3, 7.8. IR (thin film, cm^{-1}): 3445, 1755, 1724, 1646, 1453, 1266, 1124. HRMS (ESI^+): calcd. for $[C_{13}H_{16}N_2O_3+Na]^+$ 271.1053, found 271.1055.



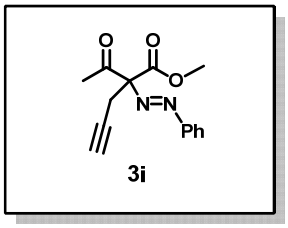
3g

The azo product was synthesized according to the general procedure as yellow oil in 91% overall yield (28.2 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86–7.83 (m, 2H), 7.72–7.68 (m, 2H), 7.50–7.36 (m, 6H), 4.25 (qd, *J* = 7.1, 4.5 Hz, 2H), 1.82 (s, 3H), 1.11 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.2, 171.0, 151.9, 134.7, 133.0, 131.7, 129.9, 129.1, 128.6, 122.8, 85.4, 62.0, 21.1, 14.0. IR (thin film, cm^{-1}): 3369, 3064, 2980, 2938, 1748, 1694, 1600, 1449, 1369, 1263, 1118. HRMS (ESI^+): calcd. for $[C_{18}H_{18}N_2O_3+Na]^+$ 333.1210, found 333.1207.



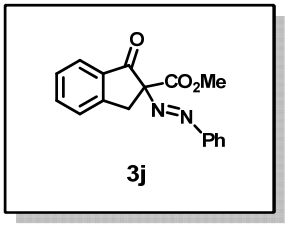
3h

The azo product was synthesized according to the general procedure as yellow oil in 95% overall yield (28.2 mg, keto : enol ≈ 7:1). NMR data for major keto isomer: ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.74 (s, 1H), 7.93 (d, *J* = 7.5 Hz, 2H), 7.56 (d, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.8 Hz, 2H), 7.29 (q, *J* = 7.6 Hz, 2H), 7.17 (d, *J* = 8.0 Hz, 2H), 7.08 (t, *J* = 7.4 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.36 (t, *J* = 7.2 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 189.7, 164.2, 142.0, 138.0, 132.5, 130.5, 129.7, 128.1, 124.6, 115.5, 61.5, 14.2. IR (thin film, cm^{-1}): 3446, 1660, 1601, 1526, 1472, 1304, 1225, 1189, 903. HRMS (ESI^+): calcd. for $[C_{17}H_{16}N_2O_3+Na]^+$ 319.1053, found 319.1055.



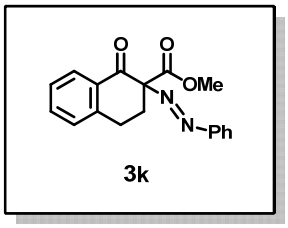
3i

The azo product was synthesized according to the general procedure as yellow oil in 88% overall yield (22.7 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82–7.78 (m, 2H), 7.53–7.50 (m, 3H), 3.81 (s, 3H), 3.17–3.02 (m, 2H), 2.44 (s, 3H), 1.99 (s, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 201.9, 168.0, 151.6, 132.2, 129.5, 129.3, 123.1, 114.5, 89.0, 78.3, 71.5, 53.1, 29.4, 23.8. IR (thin film, cm^{-1}): 3446, 3293, 1722, 1646, 1435, 1355, 1239, 1207. HRMS (ESI^+): calcd. for $[C_{14}H_{14}N_2O_3+Na]^+$ 281.0897, found 281.0895.



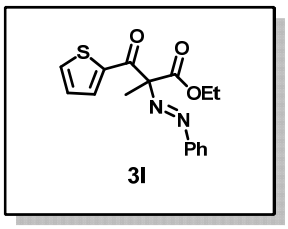
3j

The azo product was synthesized according to the general procedure as yellow oil in 79% overall yield (21.5 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, *J* = 7.8 Hz, 1H), 7.77–7.71 (m, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.53 (d, *J* = 7.8 Hz, 1H), 7.46–7.42 (m, 4H), 3.98–3.84 (m, 5H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 196.6, 169.0, 152.3, 151.5, 136.0, 134.5, 131.7, 129.1, 128.3, 126.6, 125.3, 123.0, 87.8, 53.3, 36.0. IR (thin film, cm^{-1}): 3446, 1748, 1716, 1646, 1607, 1434, 1272, 1212, 1154, 960. HRMS (ESI^+): calcd. for $[C_{17}H_{14}N_2O_3+Na]^+$ 317.0897, found 317.0893.



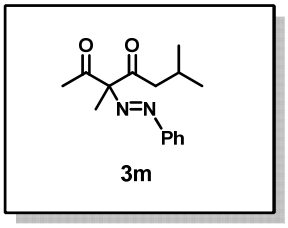
3k

The azo product was synthesized according to the general procedure as yellow oil in 71% overall yield (21.9 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.10 (d, *J* = 7.7 Hz, 1H), 7.71–7.68 (m, 2H), 7.50 (t, *J* = 7.4 Hz, 1H), 7.45–7.42 (m, 3H), 7.34 (t, *J* = 7.5 Hz, 1H), 7.23 (d, *J* = 7.6 Hz, 1H), 3.80 (s, 3H), 3.13–3.07 (m, 2H), 2.98–2.92 (m, 2H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 191.6, 168.7, 151.5, 142.9, 134.0, 131.6, 129.0, 128.9, 128.1, 127.2, 122.9, 85.2, 53.0, 31.1, 25.1. IR (thin film, cm^{-1}): 3446, 1743, 1688, 1646, 1602, 1455, 1301, 1263, 1225, 905. HRMS (ESI^+): calcd. for $[C_{18}H_{16}N_2O_3+Na]^+$ 331.1053, found 331.1056.



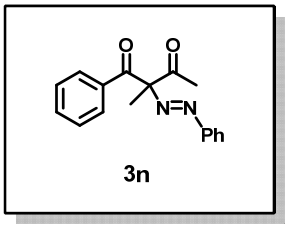
3l

The azo product was synthesized according to the general procedure as yellow oil in 75% overall yield (23.7 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.79–7.74 (m, 3H), 7.63 (d, *J* = 4.92 Hz, 1H), 7.48–7.46 (m, 3H), 7.10–7.07 (m, 1H), 4.35–4.18 (m, 2H), 1.81 (s, 3H), 1.18 (t, *J*= 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.7, 170.1, 151.8, 141.6, 134.7, 134.5, 131.8, 129.2, 128.1, 123.0, 86.6, 62.1, 20.4, 14.1. IR (thin film, cm^{-1}): 3100, 2985, 2938, 1748, 1670, 1515, 1445, 1411, 1355, 1266, 1116, 1018, 851. HRMS (ESI^+): calcd. for $[C_{16}H_{16}N_2O_3S+Na]^+$ 339.0774, found 339.0773.



3m

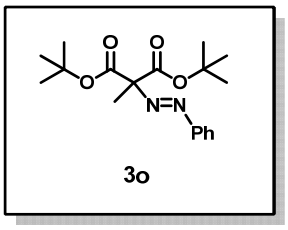
The azo product was synthesized according to the general procedure as yellow oil in 94% overall yield (24.5 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80–7.75 (m, 2H), 7.53–7.50 (m, 3H), 2.58–2.41 (m, 2H), 2.28–2.19 (m, 4H), 1.56 (s, 3H), 0.91 (dd, *J* = 11.8, 6.7 Hz, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.8, 204.0, 151.9, 131.9, 129.4, 122.7, 93.8, 49.6, 28.5, 24.0, 22.7, 22.6, 18.4. IR (thin film, cm^{-1}): 3361, 2958, 2922, 1732, 1712, 1469, 1454, 1355, 1036. HRMS (ESI^+): calcd. for $[C_{15}H_{20}N_2O_2+Na]^+$ 283.1417, found 283.1417.



3n

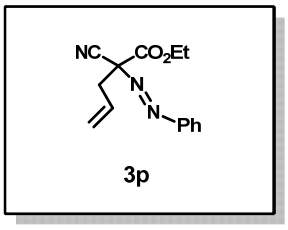
The azo product was synthesized according to the general procedure as yellow oil in 91% overall yield (25.5 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74–7.67 (m, 4H), 7.49–7.43 (m, 4H), 7.38 (t, *J* = 7.4 Hz, 2H), 2.56 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.9, 195.4, 151.9,

134.4, 133.0, 131.9, 130.0, 129.2, 128.7, 122.6, 91.9, 27.6, 20.9. IR (thin film, cm^{-1}): 3446, 1716, 1693, 1597, 1449, 1358, 1241, 1102. HRMS (ESI^+): calcd. for $[C_{17}H_{16}N_2O_2+Na]^+$ 303.1104, found 303.1103.



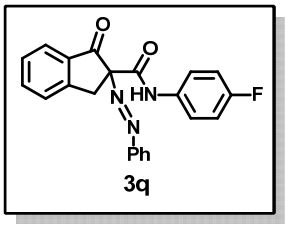
3o

The azo product was synthesized according to the general procedure as yellow oil in 70% overall yield (23.4 mg). ^1H NMR (300 MHz, $CDCl_3$) δ 7.76–7.70 (m, 2H), 7.46–7.44 (m, 3H), 1.70 (s, 3H), 1.50 (s, 18H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 168.0, 151.7, 131.4, 129.1, 122.7, 83.1, 82.4, 28.1, 20.2. IR (thin film, cm^{-1}): 3470, 2979, 2936, 1739, 1478, 1455, 1393, 1369, 1286, 1255, 1127, 845, 751. HRMS (ESI^+): calcd. for $[C_{18}H_{26}N_2O_4+Na]^+$ 357.1785, found 357.1784.



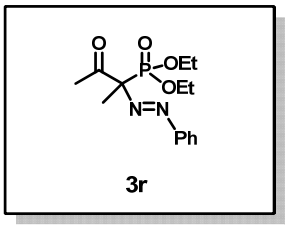
3p

The azo product was synthesized according to the general procedure as yellow oil in 83% overall yield (21.4 mg). ^1H NMR (300 MHz, $CDCl_3$) δ 7.82–7.79 (m, 2H), 7.54–7.47 (m, 3H), 5.83 (ddt, *J* = 17.3, 10.1, 7.2 Hz, 1H), 5.37–5.28 (m, 2H), 4.36 (q, *J* = 7.1 Hz, 2H), 3.22 (dd, *J* = 14.0, 7.2 Hz, 1H), 3.08 (dd, *J* = 13.9, 7.3 Hz, 1H), 1.34 (t, *J* = 7.1 Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 164.3, 150.7, 132.7, 129.4, 129.1, 123.5, 122.2, 114.9, 79.4, 63.7, 40.3, 14.2. IR (thin film, cm^{-1}): 3480, 3089, 1748, 1644, 1455, 1227, 1150, 1096, 992, 929. HRMS (ESI^+): calcd. for $[C_{14}H_{15}N_3O_2+Na]^+$ 280.1056, found 280.1059.



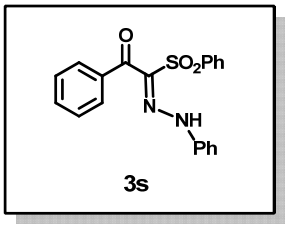
3q

The azo product was synthesized according to the general procedure as yellow solid in 76% overall yield (28.3 mg). ^1H NMR (300 MHz, $CDCl_3$) δ 9.41 (s, 1H), 7.78–7.58 (m, 7H), 7.48–7.38 (m, 4H), 7.05 (t, *J* = 8.4 Hz, 2H), 4.19 (d, *J* = 17.6 Hz, 1H), 3.96 (d, *J*= 17.6Hz, 1H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 198.1, 164.3, 161.4, 158.1, 154.1, 151.2, 136.5, 133.8, 133.7, 133.4, 132.1, 129.3, 128.1, 126.7, 125.5, 123.0, 122.2, 122.1, 115.9, 115.6, 89.8, 33.4; ^{19}F NMR (471 MHz, $CDCl_3$) δ -117.5. IR (thin film, cm^{-1}): 3354, 1716, 1682, 1608, 1589, 1508, 1476, 1408, 1302, 1272, 1212, 1156, 912, 833. HRMS (ESI^+): calcd. for $[C_{22}H_{16}FN_3O_2+Na]^+$ 396.1119, found 396.1118.



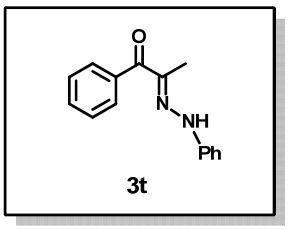
3r

The azo product was synthesized according to the general procedure as yellow oil in 65% overall yield (20.3 mg). ^1H NMR (300 MHz, $CDCl_3$) δ 7.81–7.75 (m, 2H), 7.50–7.48 (m, 3H), 4.25–4.12 (m, 4H), 2.47 (s, 3H), 1.67 (d, *J* = 15.1 Hz, 3H), 1.35–1.26 (m, 6H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 203.2, 152.0, 151.9, 131.7, 129.5, 129.3, 122.8, 118.0, 89.5, 87.6, 63.9, 63.8, 63.7, 29.5, 16.6, 16.5, 16.1; ^{31}P NMR (202 MHz, $CDCl_3$) δ 17.0. IR (thin film, cm^{-1}): 2985, 2930, 1719, 1444, 1392, 1355, 1257, 1162, 1098, 1047, 1020. HRMS (ESI^+): calcd. for $[C_{14}H_{21}N_2O_4P+Na]^+$ 335.1131, found 335.1128.



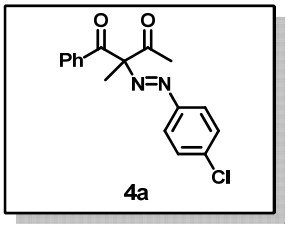
3s

The azo product was synthesized according to the general procedure as yellow solid in 53% overall yield (19.3 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 12.44 (s, 1H), 8.18 (d, *J* = 7.2Hz, 2H), 7.80 (d, *J* = 6.9Hz, 2H), 7.69–7.52 (m, 4H), 7.45–7.34 (m, 4H), 7.20–7.14 (m, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 186.6, 141.4, 140.5, 137.2, 134.3, 132.4, 130.3, 129.9, 129.2, 128.7, 128.0, 125.5, 115.7. IR (thin film, cm^{-1}): 3446, 3228, 1647, 1600, 1522, 1479, 1447, 1307, 1281, 1255, 1134, 1069, 878. HRMS (ESI^+): calcd. for $[C_{20}H_{16}N_2O_3S+Na]^+$ 387.0774, found 387.0769.



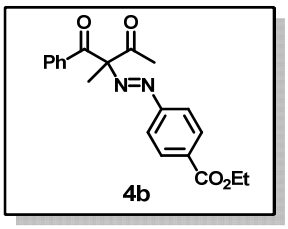
3t

The azo product was synthesized according to the general procedure as yellow solid in 40% overall yield (9.5 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (d, *J* = 7.4Hz, 3H), 7.53 (t, *J* = 7.2 Hz, 1H), 7.45 (t, *J* = 7.4 Hz, 2H), 7.28 (t, *J* = 8.0 Hz, 2H), 7.09 (d, *J* = 8.0 Hz, 2H), 6.97 (t, *J* = 7.3Hz, 1H), 2.20 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 192.0, 143.2, 140.6, 138.1, 131.5, 130.7, 129.6, 127.8, 122.4, 114.3, 9.0. IR (thin film, cm^{-1}): 3446, 1633, 1603, 1555, 1496, 1346, 1242, 1169, 1013, 914. HRMS (ESI^+): calcd. for $[C_{15}H_{14}N_2O+H]^+$ 239.1179, found 239.1179.



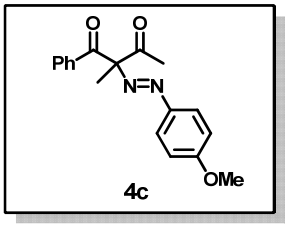
4a

The azo product was synthesized according to the general procedure as yellow solid in 79% overall yield (24.9 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.66 (dd, *J* = 15.8, 8.0Hz, 4H), 7.50–7.35 (m, 5H), 2.53 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.5, 195.1, 150.2, 138.1, 134.3, 133.2, 130.0, 129.6, 128.7, 123.9, 91.9, 27.6, 20.8. IR (thin film, cm^{-1}): 3446, 1712,1690, 1594, 1580, 1504, 1448, 1367, 1240, 1087, 1011, 834. HRMS (ESI^+): calcd. for $[C_{17}H_{15}ClN_2O_2+Na]^+$ 337.0714, found 337.0713.



4b

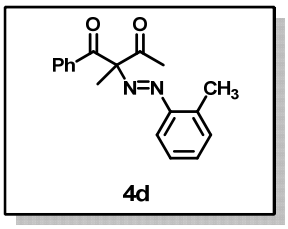
The azo product was synthesized according to the general procedure as yellow oil in 87% overall yield (30.6 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (d, *J* = 8.5Hz, 2H), 7.70 (d, *J* = 8.1 Hz, 4H), 7.48 (t, *J* = 7.3Hz, 1H), 7.38 (t, *J* = 7.5 Hz, 2H), 4.39 (q, *J* = 7.2 Hz, 2H), 2.55 (s, 3H), 1.76 (s, 3H), 1.40 (t, *J* = 7.1Hz, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 205.3, 194.9, 165.8, 154.2, 134.2, 133.2, 133.1, 130.7, 130.0, 128.7, 122.4, 92.4, 61.5, 27.6, 20.8, 14.4. IR (thin film, cm^{-1}): 3446, 1717, 1694, 1597, 1448, 1410, 1366, 1277, 1106, 1015, 864. HRMS (ESI^+): calcd. for $[C_{20}H_{20}N_2O_4+Na]^+$ 375.1315, found 375.1312.



4c

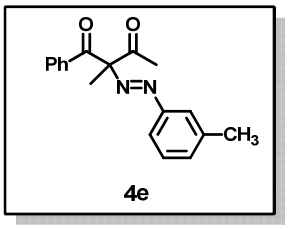
The azo product was synthesized according to the general procedure as yellow solid in 67% overall yield (20.8 mg). ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.7Hz, 4H), 7.45 (t, *J* = 7.3 Hz, 1H), 7.36 (t, *J* = 7.6 Hz, 2H), 6.93 (d, *J* = 8.6Hz, 2H), 3.85 (s, 3H), 2.54 (s, 3H), 1.73 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.4, 195.8, 162.7, 146.3, 134.5, 132.9, 130.1, 128.6,

124.6, 114.3, 91.2, 55.7, 27.6, 20.9. IR (thin film, cm^{-1}): 3446, 1714, 1691, 1602, 1585, 1507, 1448, 1358, 1255, 1149, 1105, 1028, 839. HRMS (ESI^+): calcd. for $[C_{18}H_{18}N_2O_3+Na]^+$ 333.1210, found 333.1205.



4d

The azo product was synthesized according to the general procedure as yellow oil in 84% overall yield (24.7 mg). ^1H NMR (300 MHz, $CDCl_3$) δ 7.68 (d, *J* = 7.2 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 1H), 7.40–7.32 (m, 4H), 7.24–7.19 (m, 2H), 2.61 (s, 3H), 2.25 (s, 3H), 1.75 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.3, 195.8, 150.2, 138.1, 134.2, 132.9, 131.7, 131.4, 130.1, 128.6, 126.5, 115.1, 92.1, 27.6, 21.3, 17.0. IR (thin film, cm^{-1}): 3446, 1716, 1693, 1598, 1448, 1358, 1241, 1100. HRMS (ESI^+): calcd. for $[C_{18}H_{18}N_2O_2+Na]^+$ 317.1260, found 317.1259.



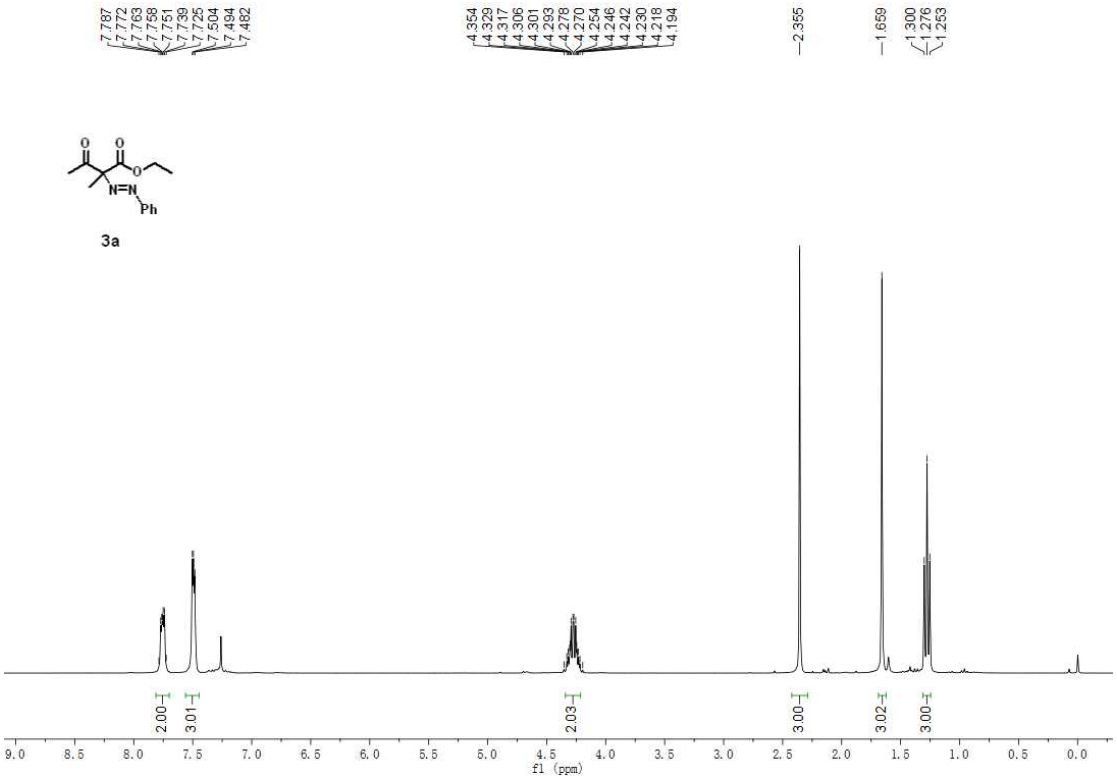
4e

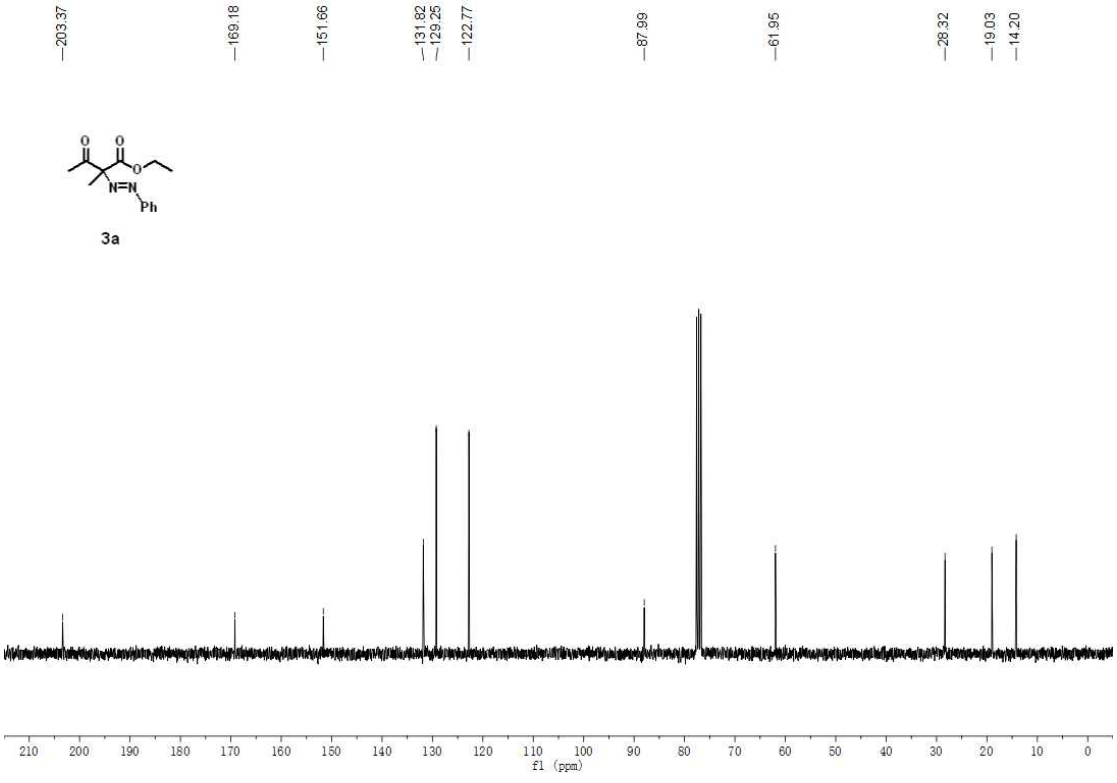
The azo product was synthesized according to the general procedure as yellow oil in 85% overall yield (25.0 mg). ^1H NMR (300 MHz, $CDCl_3$) δ 7.70 (d, *J* = 7.76 Hz, 2H), 7.50-7.44 (m, 3H), 7.40–7.26 (m, 4H), 2.56 (s, 3H), 2.40 (s, 3H), 1.74 (s, 3H); ^{13}C NMR (75 MHz, $CDCl_3$) δ 206.1, 195.5, 152.0, 139.3, 134.4, 133.0, 132.6, 130.0, 129.0, 128.7, 123.2, 119.7, 91.7, 27.6, 21.4, 21.0. IR (thin film, cm^{-1}): 3445, 2065, 1645, 1448, 1356, 1238, 1100. HRMS (ESI^+): calcd. for $[C_{18}H_{18}N_2O_2+Na]^+$ 317.1260, found 317.1260.

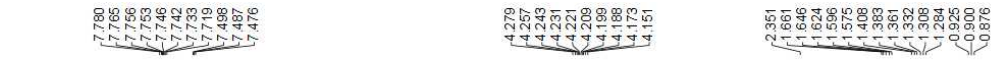
References:

1. (a) Kalaitzakis, D.; Kambourakis, S.; Rozzell, J. D.; Smonou, I. *Tetrahedron: Asymmetry* **2007**, *18*, 2418; (b) Gao, L.; Kang, B. C.; Hwang, G.-S.; Ryu, D. H. *Angew. Chem. Int. Ed.* **2012**, *51*, 8322.
2. Kalaitzakis, E. D.; Rozzell, D. J.; Kambourakis, S.; Smonou, I. *Adv. Synth. Catal.* **2006**, *348*, 1958.
3. González, D. F.; Brand, J. P.; Mondière, R.; Waser, J. *Adv. Synth. Catal.* **2013**, *355*, 1631.
4. Akula, R.; Galligan, M.; Ibrahim, H. *Chem. Commun.* **2009**, 6991.
5. Suryakiran, N.; Reddy, T. S.; Ashalatha, K.; Lakshman M.; Venkateswarlu, Y. *Tetrahedron Lett.* **2006**, *47*, 3853.
6. (a) Yang, W.; Zhou, J.; Wang, B.; Ren, H. *Chem. Eur. J.* **2011**, *17*, 13665; (b) Hafner, A.; Bräse, S. *Angew. Chem. Int. Ed.* **2012**, *51*, 3713; (c) Wang, C.; Chen, H.; Wang, Z.; Chen, J.; Huang, Y. *Angew. Chem. Int. Ed.* **2012**, *51*, 7242.

NMR spectrum:



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7.476
4.279
4.257
4.243
4.231
4.221
4.209
4.199
4.188
4.173
4.151
2.351
1.661
1.646
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1.596
1.575
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1.308
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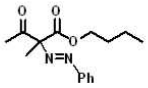
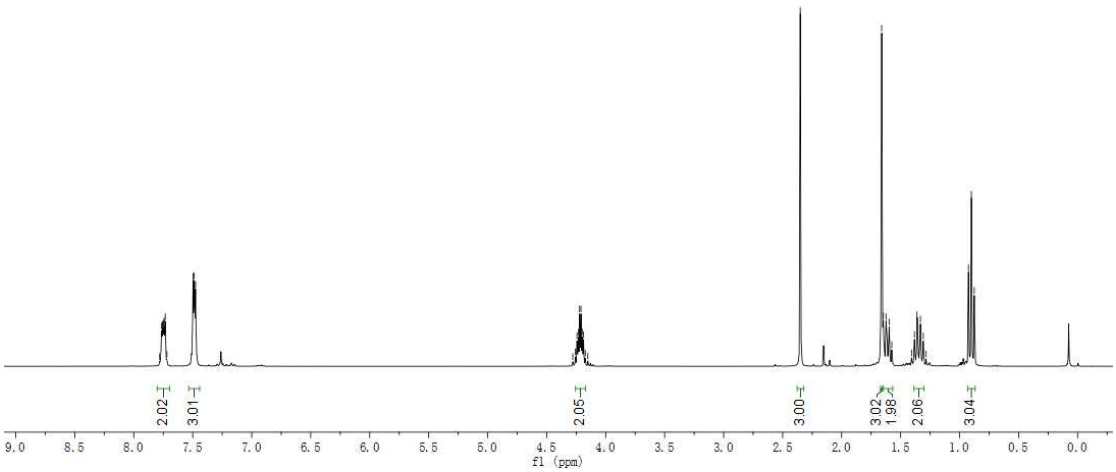
0.900
0.876



3b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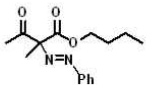
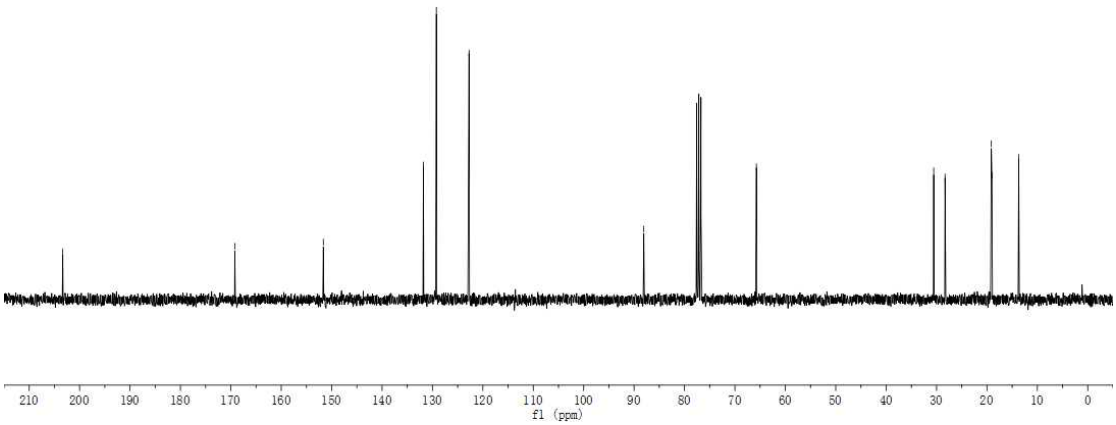
3.01
2.05
3.00
3.02
1.98
2.06
3.04
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


203.34
169.21
151.65
131.80
129.23
122.74
88.08
65.73
30.56
28.31
19.14
19.00
13.69



3b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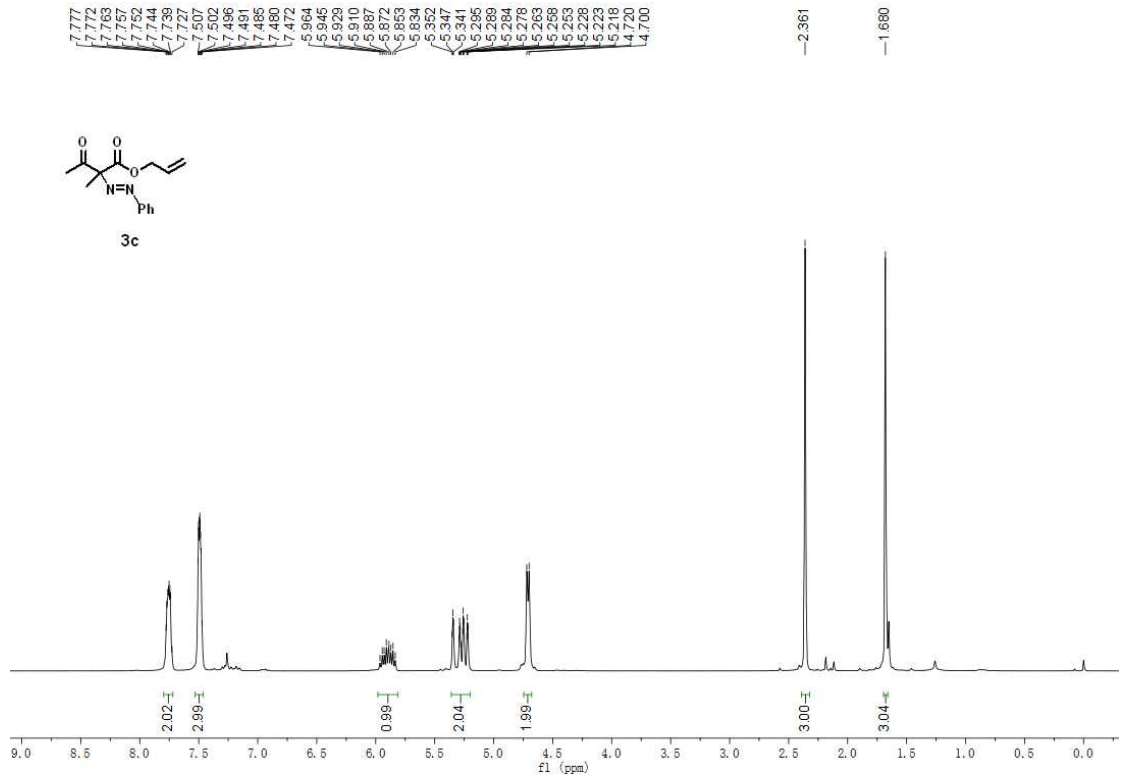
f1 (ppm)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7.485
7.480
7.472
5.964
5.945
5.929
5.910
5.887
5.872
5.853
5.834
5.352
5.347
5.341
5.295
5.289
5.284
5.278
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5.258
5.253
5.228
5.223
5.218
4.720
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3c
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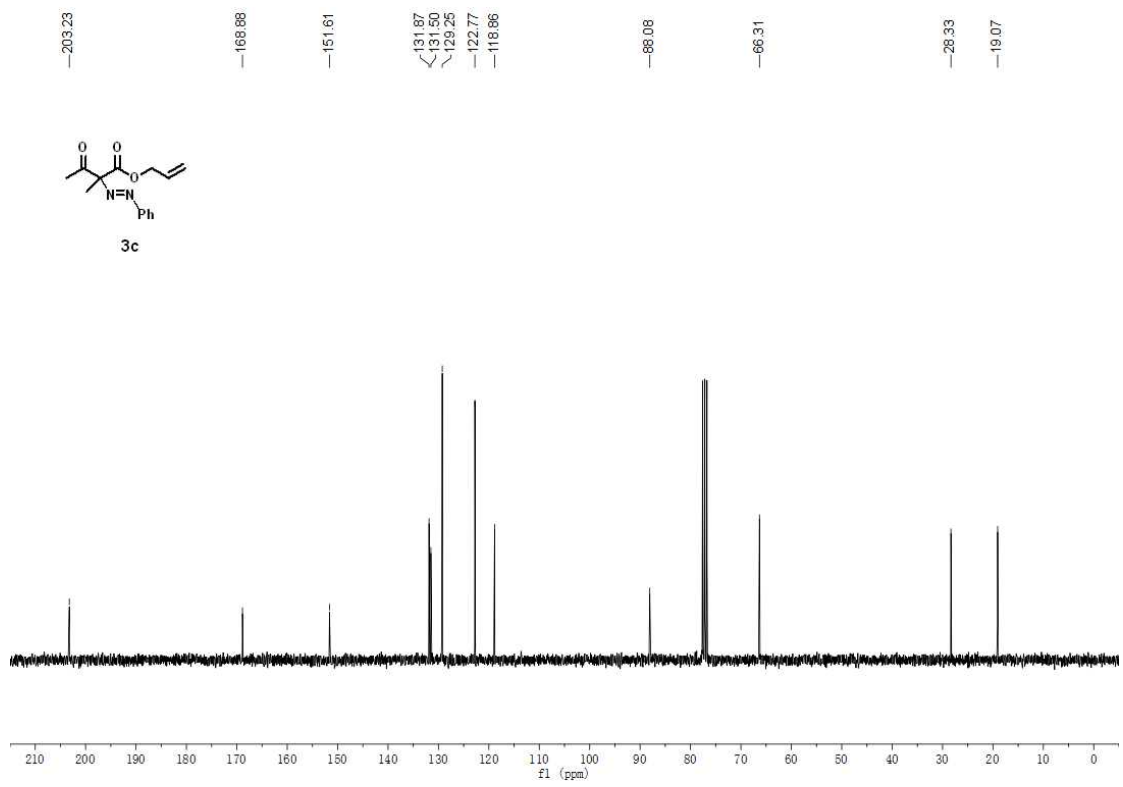
2.99
0.99
2.04
1.99
3.00
3.04
f1 (ppm)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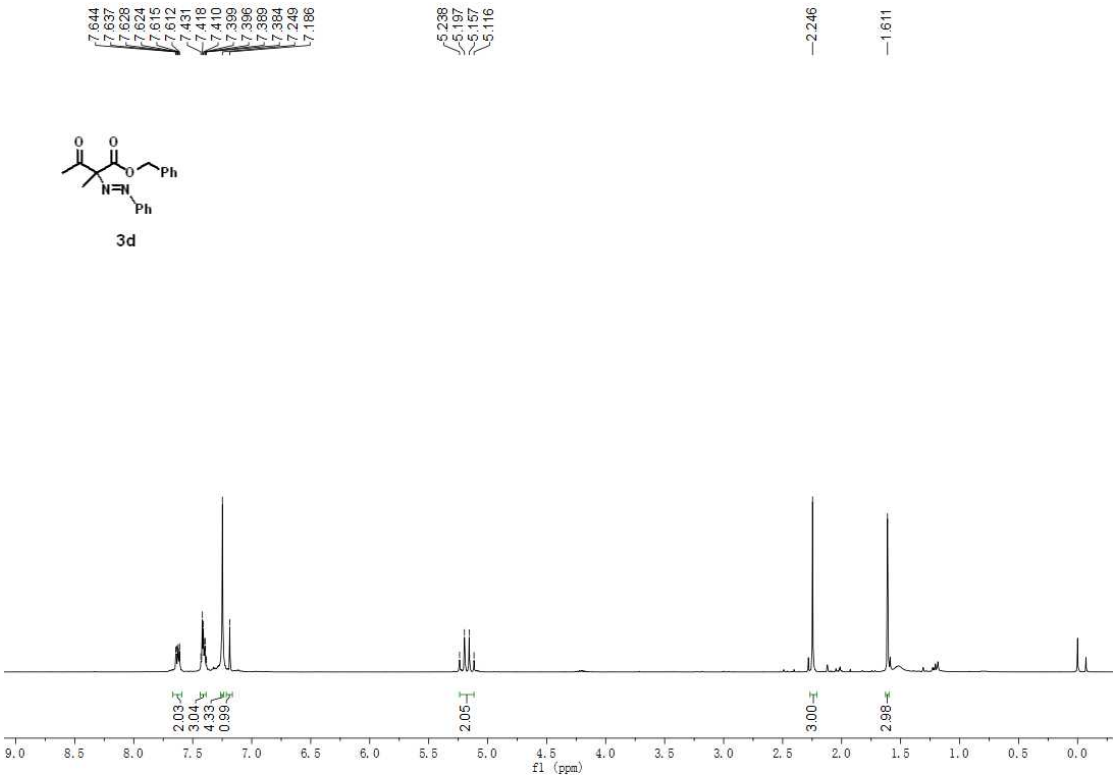
3c
f1 (ppm)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7.418
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7.399
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5.238
5.197
5.157
5.116
2.246
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Ph
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Ph
3d
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4.33
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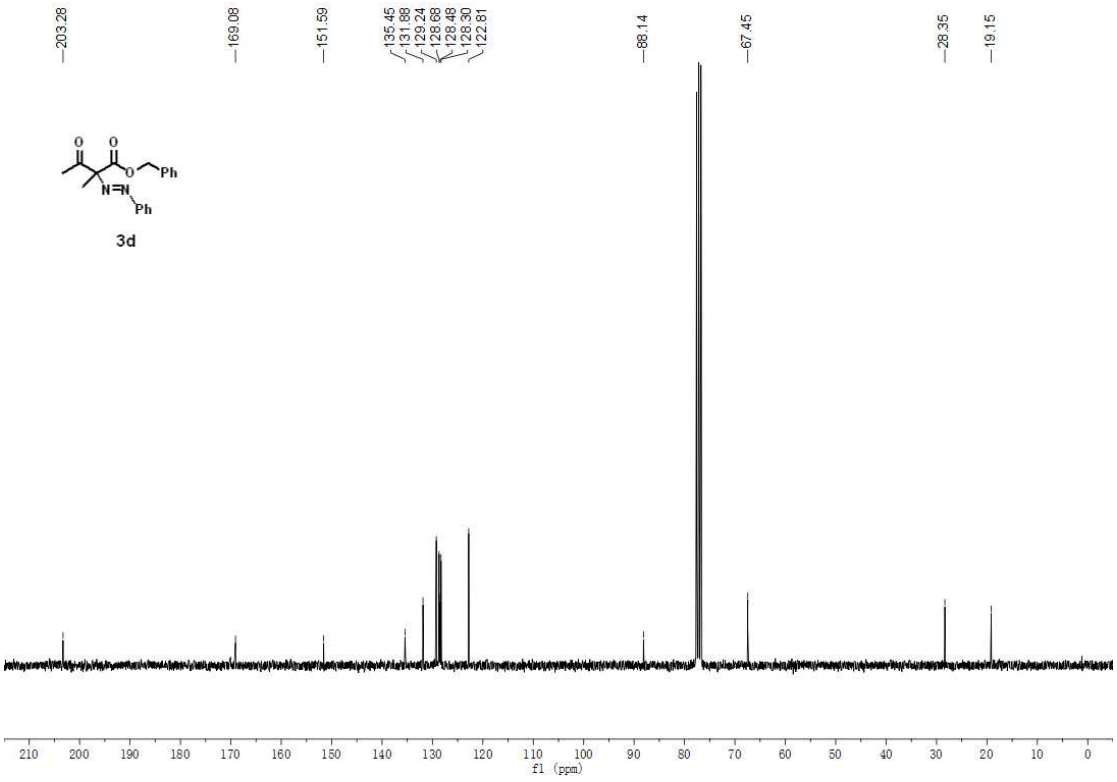
2.98
f1 (ppm)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19.15
Ph
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Ph
3d
f1 (ppm)


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7.752
7.747
7.739
7.731
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7.457


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2.166
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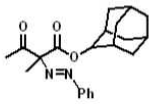
1.602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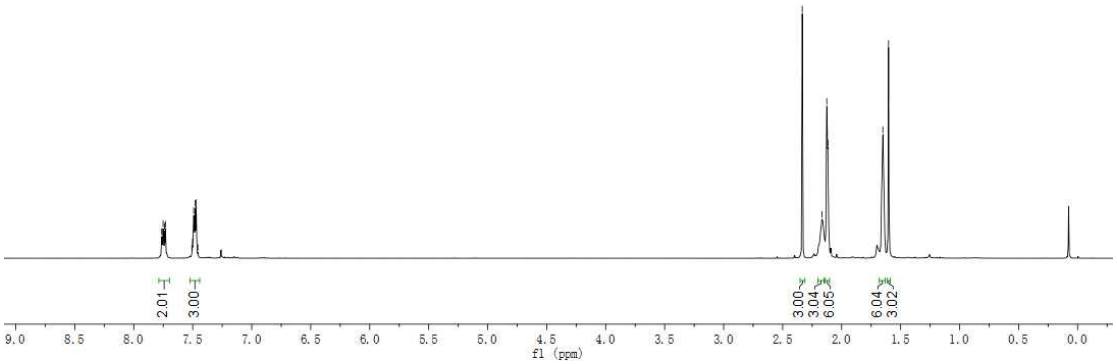
O
O
N=N
Ph

3e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6.04
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8.0
7.5
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6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


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41.29
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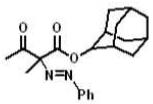
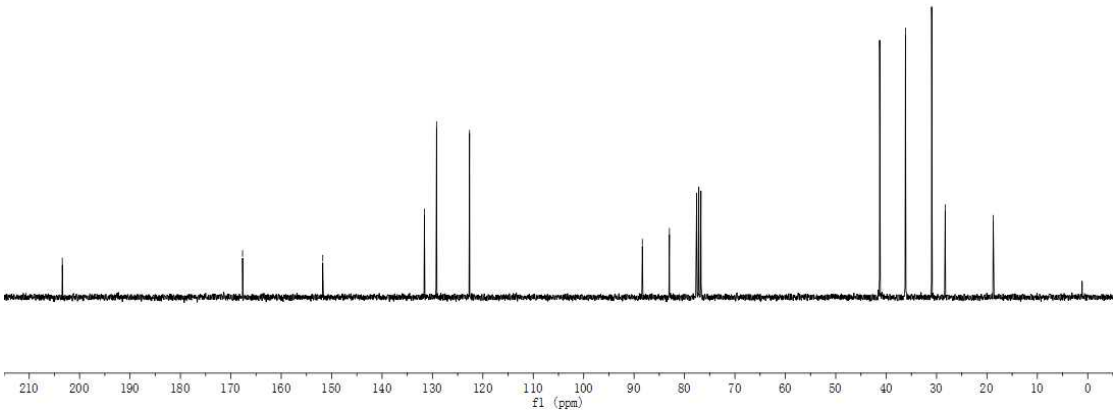
18.75


O
O
O
N=N
Ph

3e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140
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110
100
90
80
70
60
50
40
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20
10
0
f1 (ppm)


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7.754
7.751
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7.718
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7.495
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2.656


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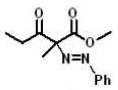
O
O
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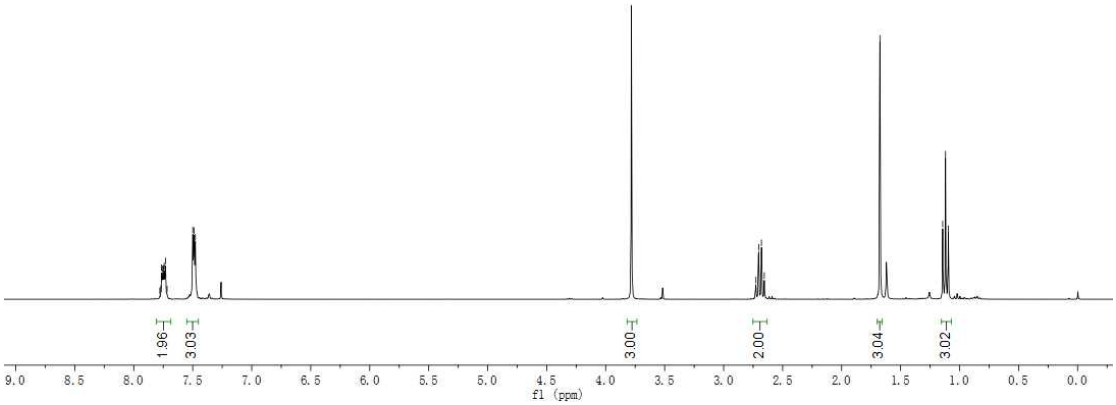
Ph

3f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5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


206.24


169.89


151.67


131.81
129.25
122.80

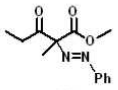

88.12


52.78

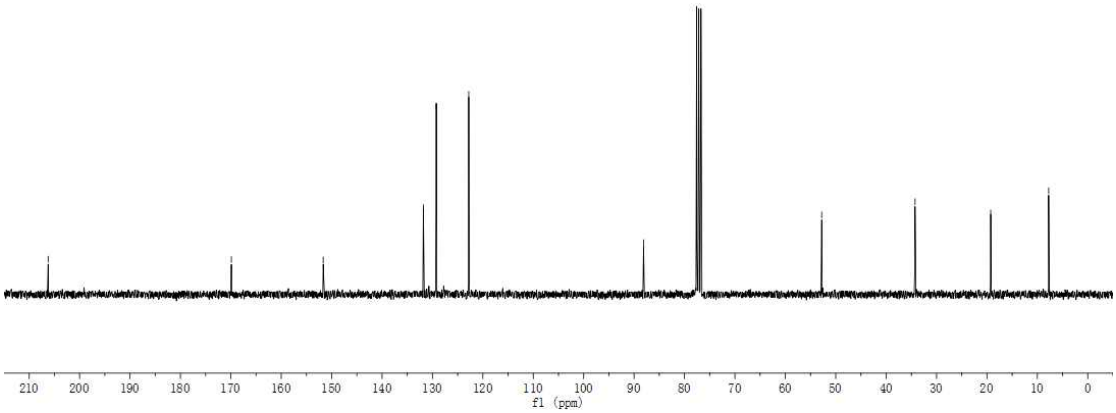

34.27

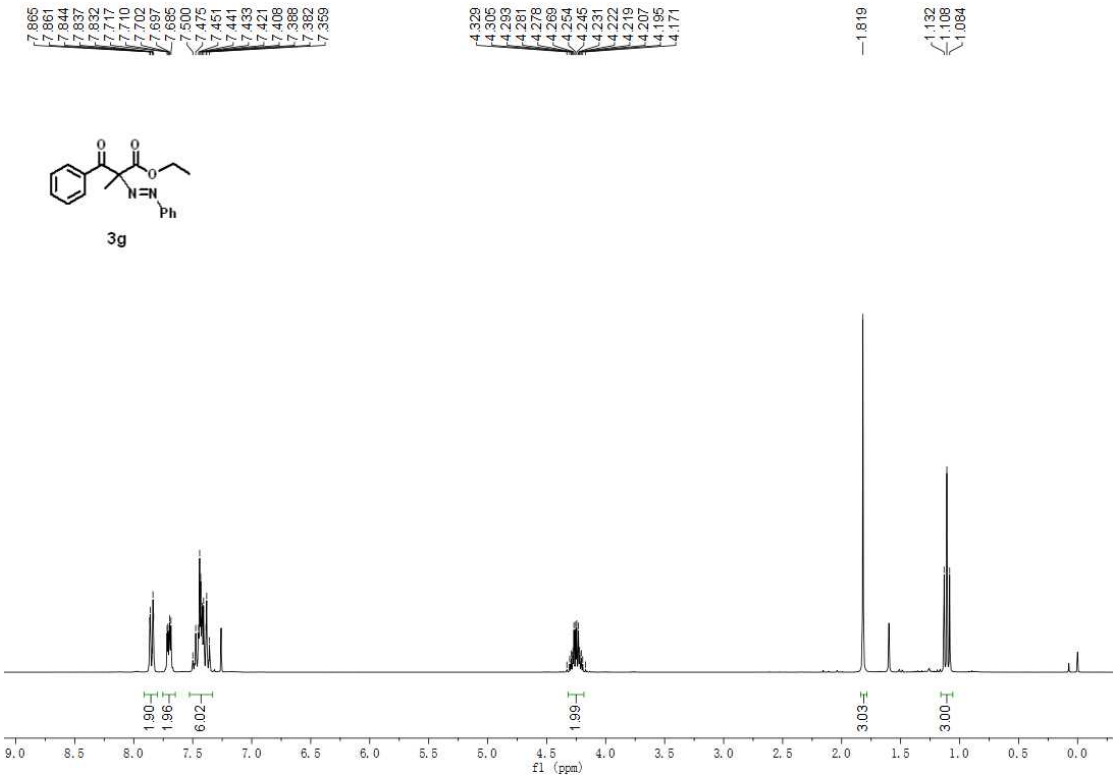

19.26

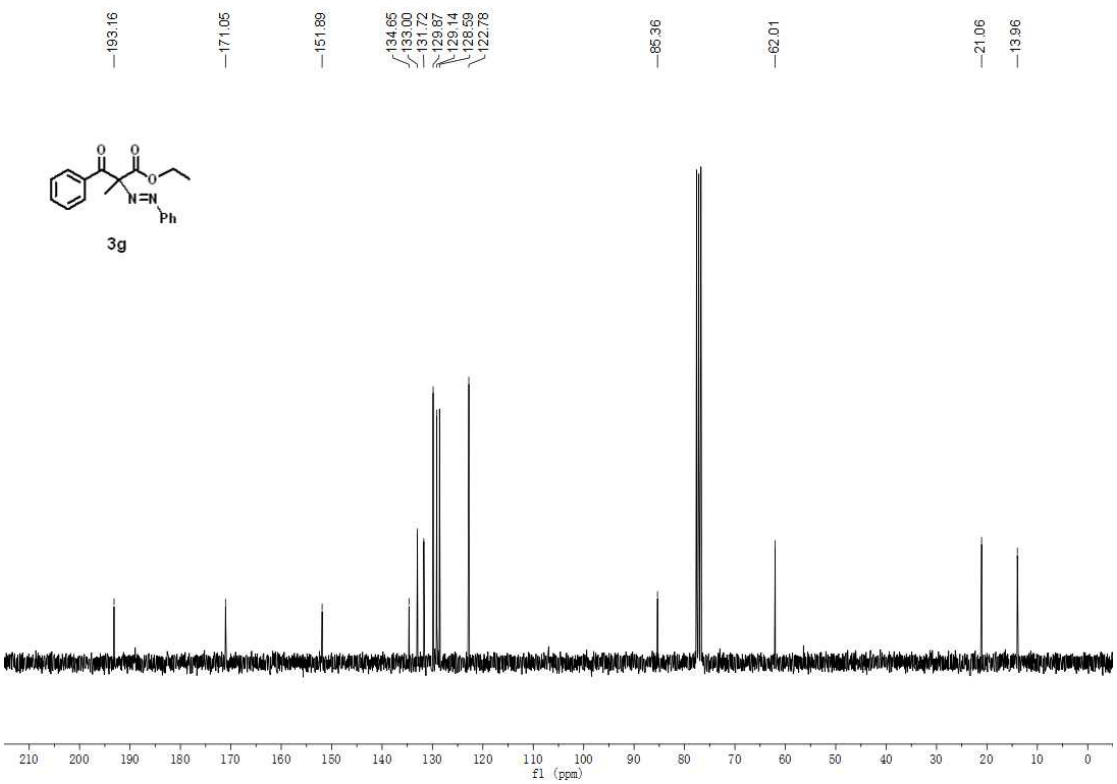

7.76

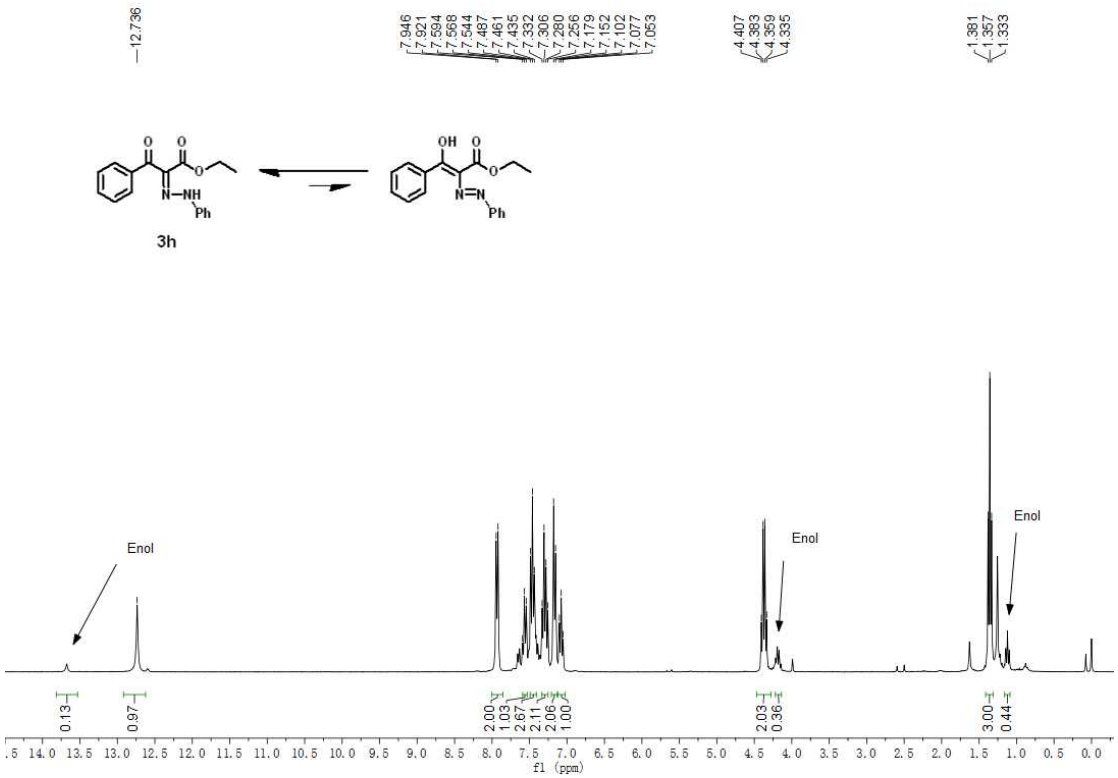

O
O
O
N=N
Ph

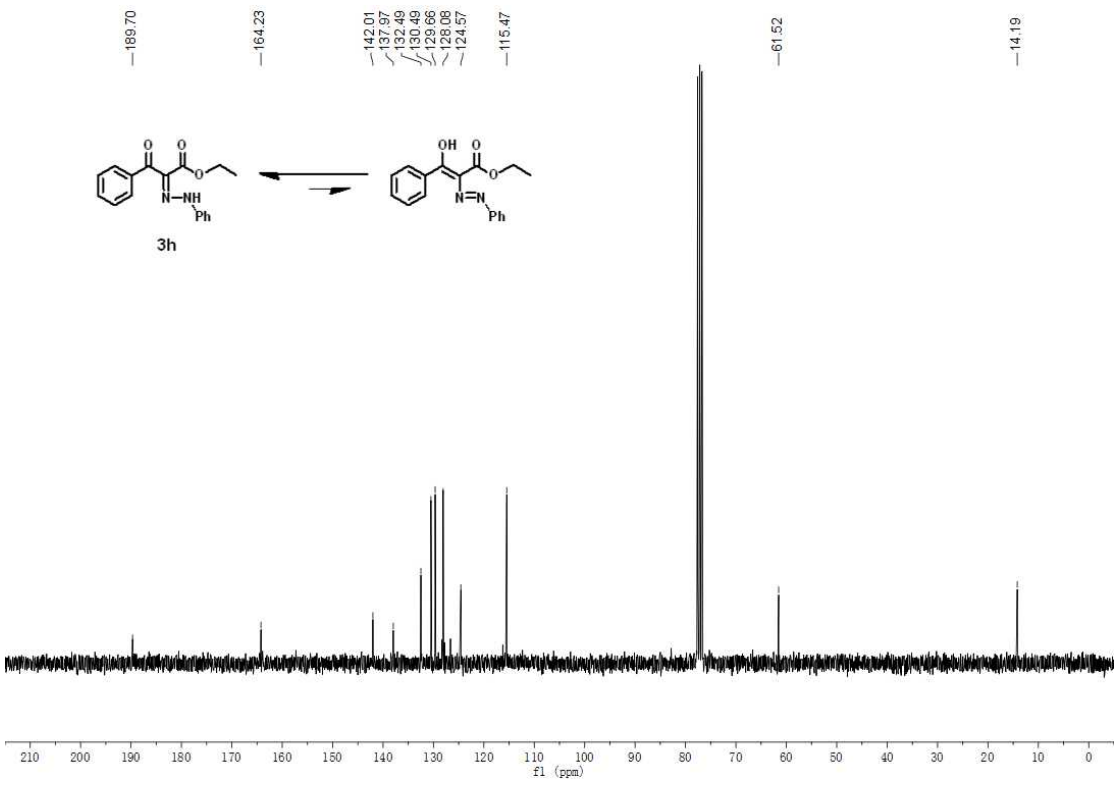
3f

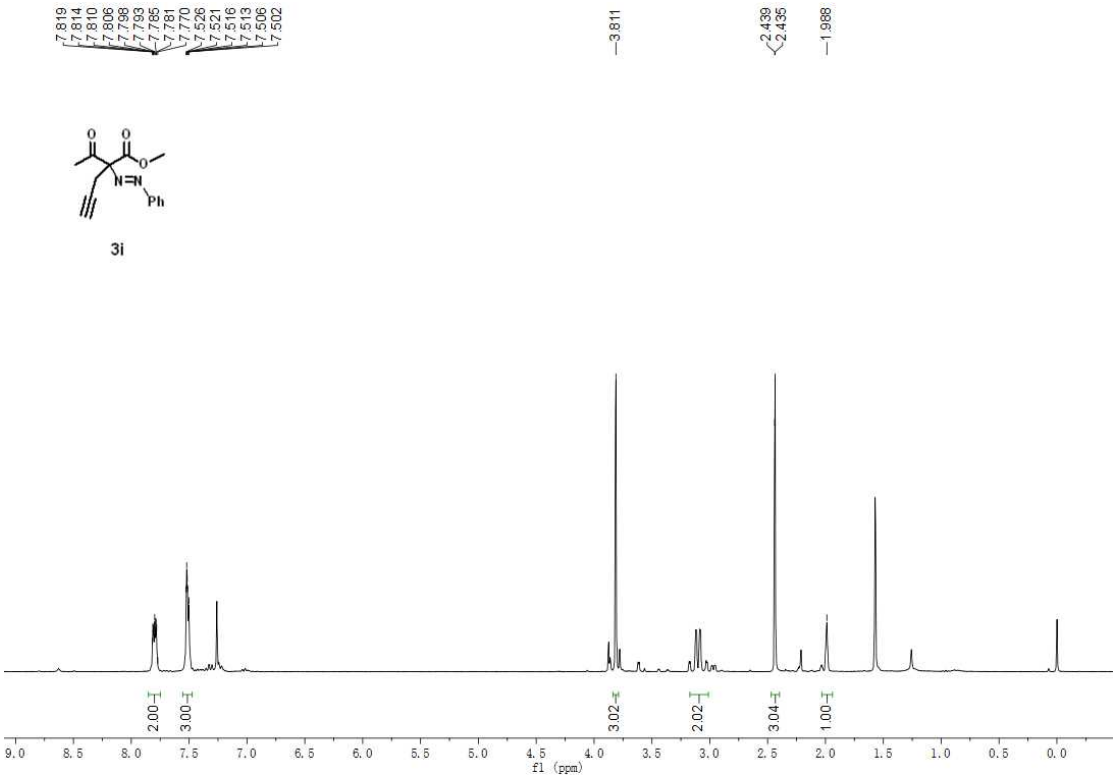

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

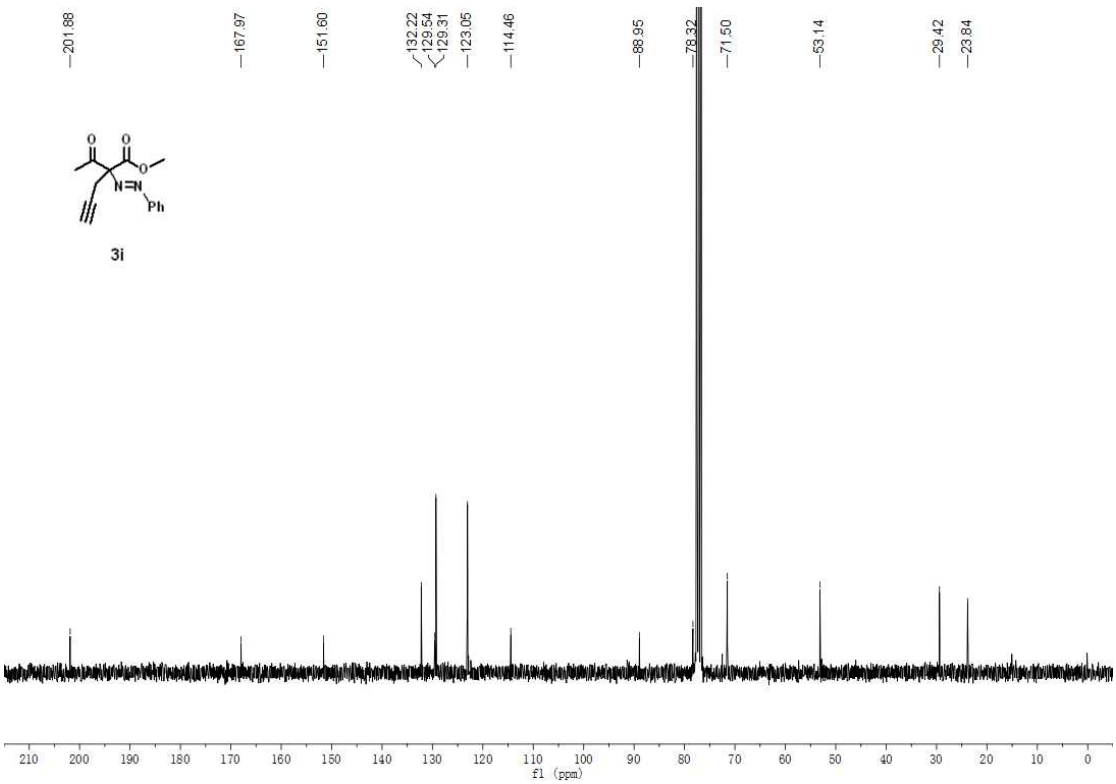

7.865
7.861
7.844
7.837
7.832
7.717
7.710
7.702
7.697
7.685
7.500
7.475
7.451
7.441
7.433
7.421
7.408
7.388
7.382
7.359
4.329
4.305
4.293
4.281
4.278
4.269
4.254
4.245
4.231
4.222
4.219
4.207
4.196
4.171
1.819
1.132
1.108
1.084
3g
1.90
1.96
6.02
1.99
3.03
3.00
f1 (ppm)


193.16
171.05
151.89
134.65
133.00
131.72
129.87
129.14
128.59
122.78
85.36
62.01
21.06
13.96
3g
f1 (ppm)


12.736
7.946
7.921
7.594
7.568
7.544
7.487
7.461
7.435
7.332
7.306
7.280
7.256
7.179
7.152
7.102
7.077
7.053
4.407
4.383
4.359
4.335
1.381
1.357
1.333
3h
Enol
Enol
Enol
0.13
0.97
2.00
1.03
2.67
2.11
2.06
1.00
2.03
0.36
3.00
0.44
f1 (ppm)

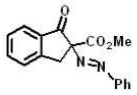

189.70
164.23
142.01
137.97
132.49
130.49
129.66
128.08
124.57
115.47
61.52
14.19
3h
f1 (ppm)


7.819
7.814
7.810
7.806
7.798
7.793
7.785
7.781
7.770
7.526
7.521
7.516
7.513
7.506
7.502
3.811
2.439
2.435
1.988
3i
2.00
3.00
3.02
2.02
3.04
1.00
f1 (ppm)

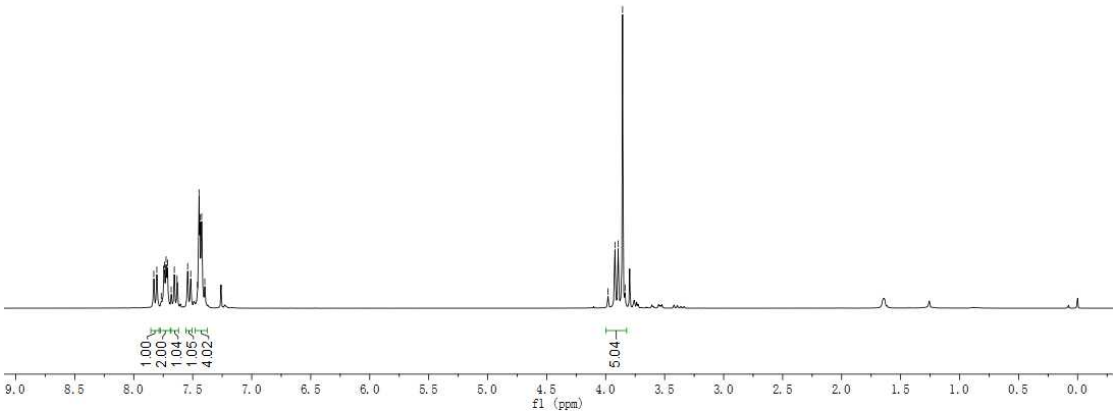

201.88
167.97
151.60
132.22
129.54
129.31
123.05
114.46
88.95
78.32
71.50
53.14
29.42
23.84
3i
f1 (ppm)

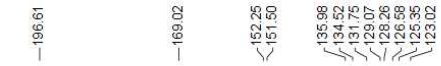

7.830
7.804
7.767
7.746
7.739
7.726
7.714
7.683
7.656
7.633
7.543
7.517
7.460
7.447
7.438
7.425
7.398

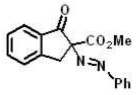

3.980
3.922
3.894
3.857
3.836


O
CO2Me
N
N
Ph

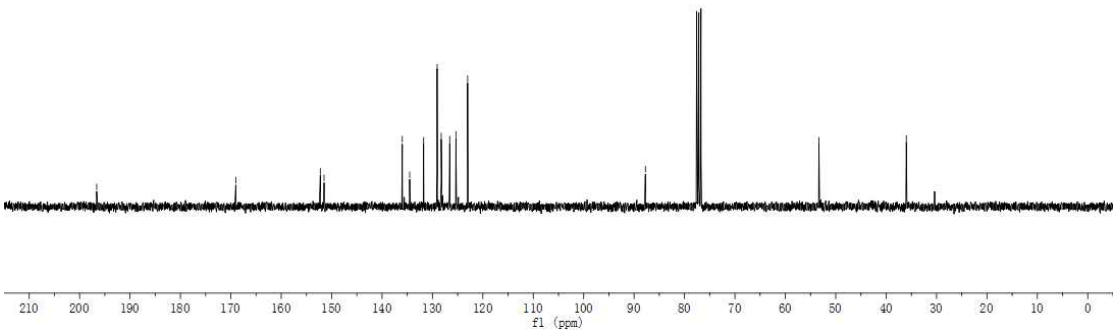
3j


1.00
2.00
1.04
1.05
4.02
5.04
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

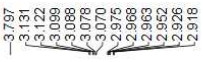

196.61
169.02
152.25
151.50
135.98
134.52
131.75
129.07
128.26
126.58
125.35
123.02
87.76
53.34
36.00

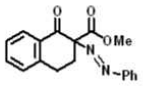

O
CO2Me
N
N
Ph

3j

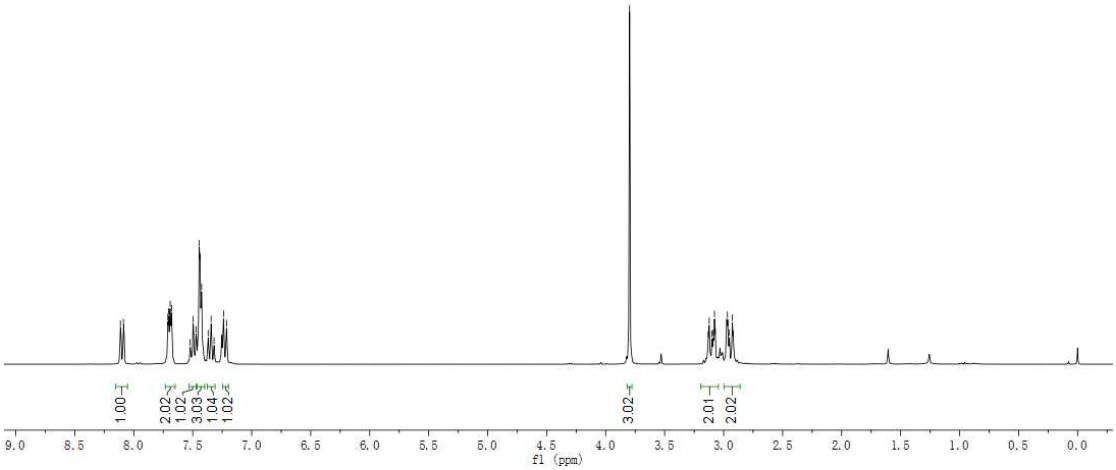

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


8.113
8.088
7.711
7.704
7.691
7.679
7.522
7.498
7.473
7.446
7.437
7.425
7.369
7.344
7.319
7.239
7.214

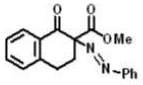

3.797
3.131
3.122
3.099
3.088
3.078
3.070
2.975
2.968
2.963
2.952
2.926
2.918


O
O
OMe
N
N
Ph

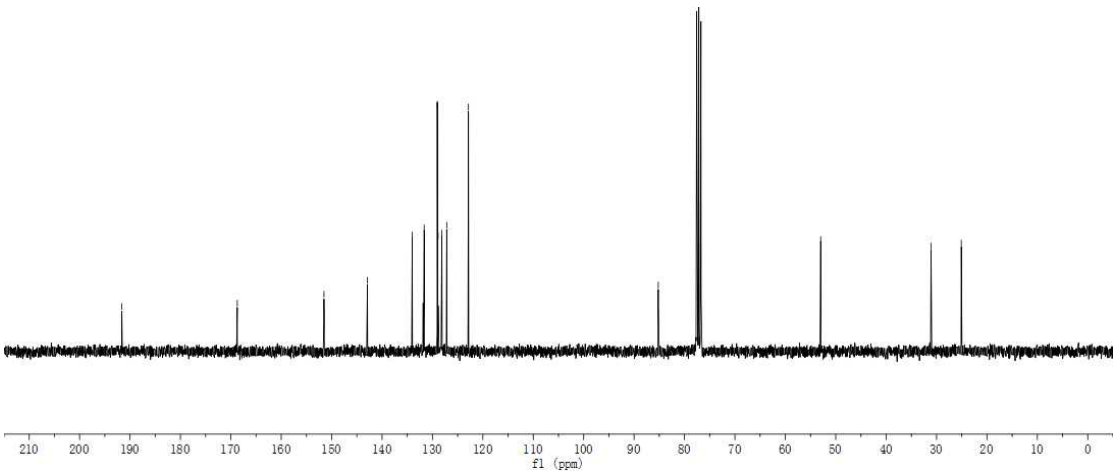
3k

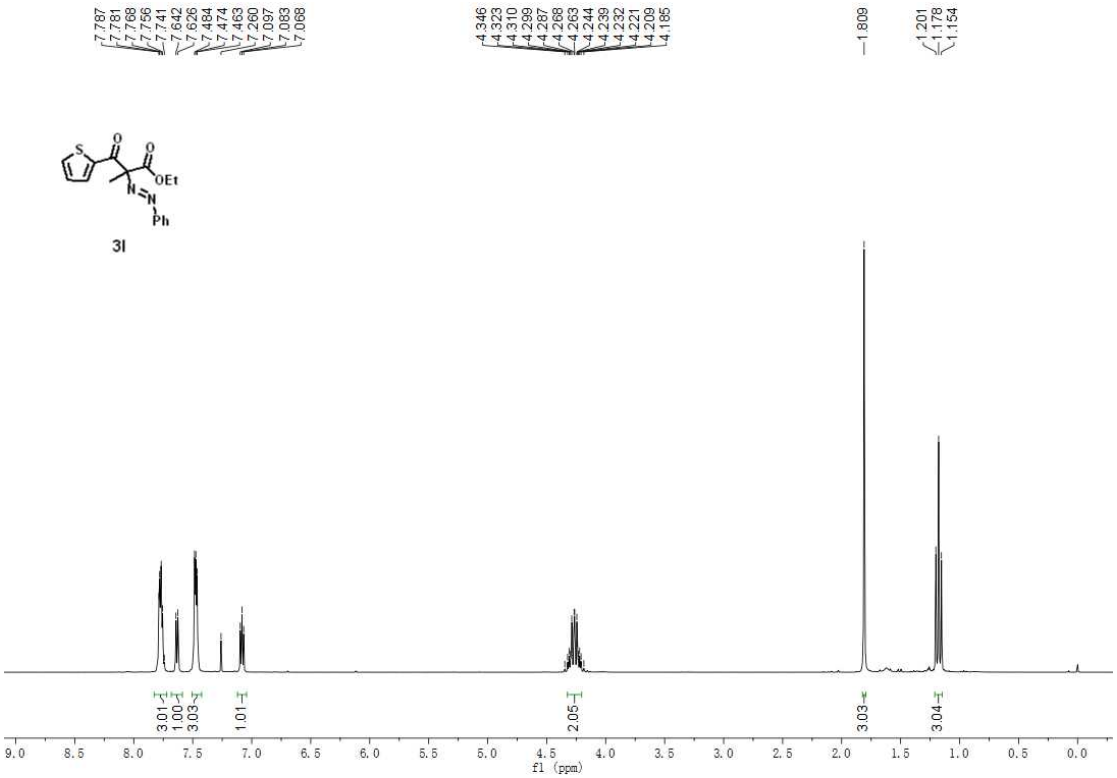

1.00
2.02
1.02
3.03
1.04
1.02
3.02
2.01
2.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

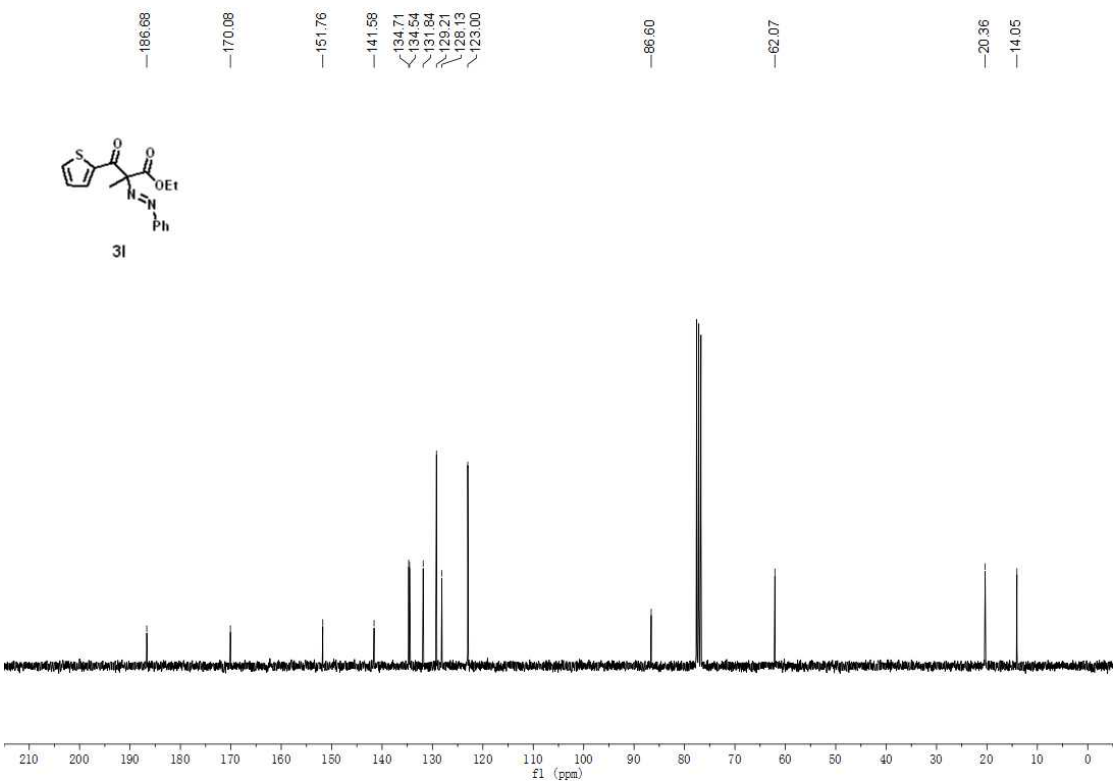

191.62
168.72
151.52
142.91
134.01
131.64
129.05
128.88
128.14
127.17
122.86
86.20
52.99
31.10
25.09

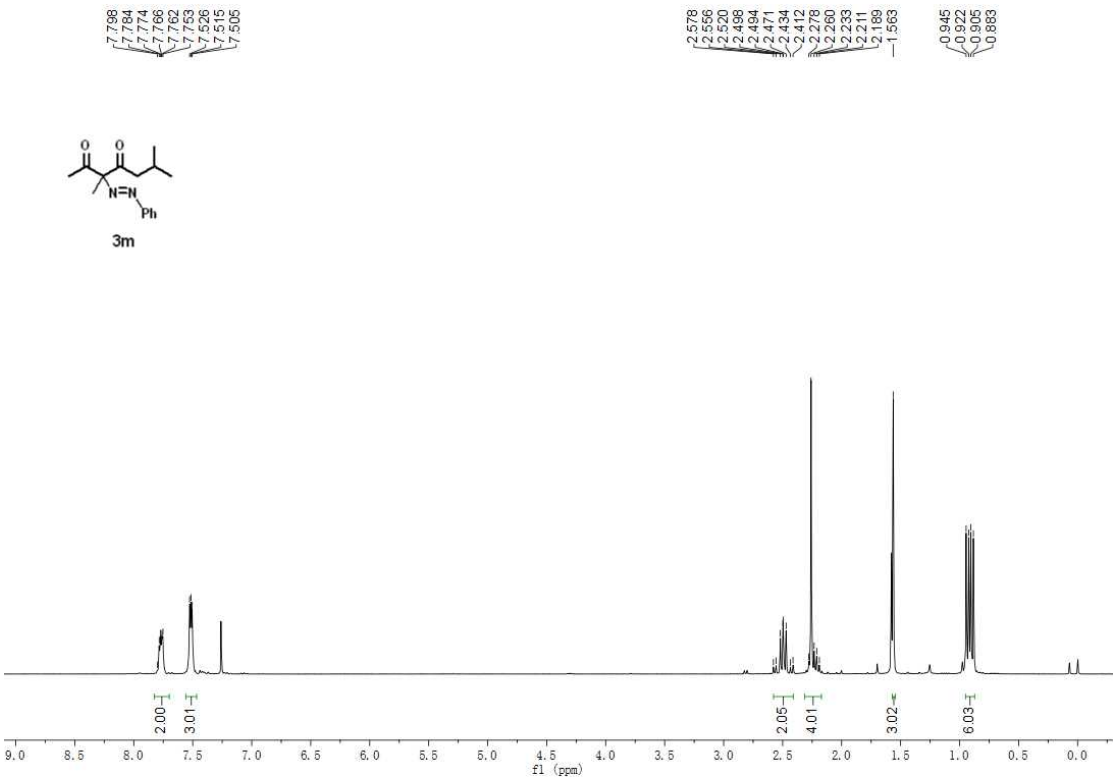

O
O
OMe
N
N
Ph

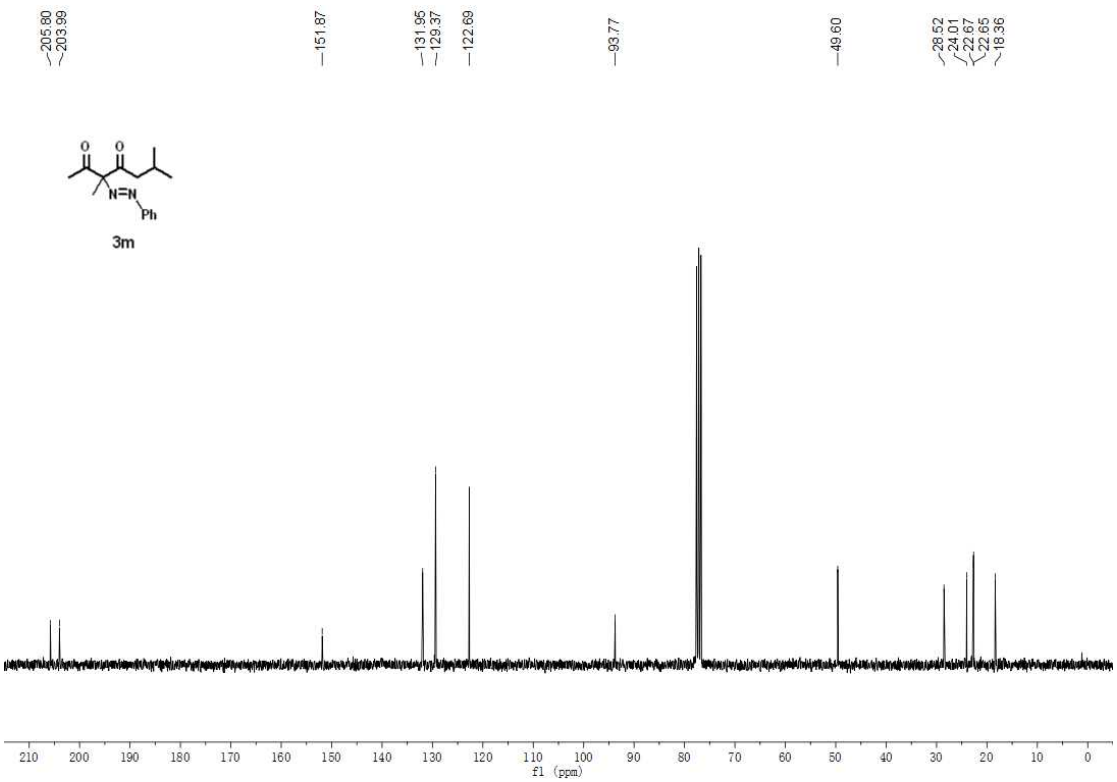
3k

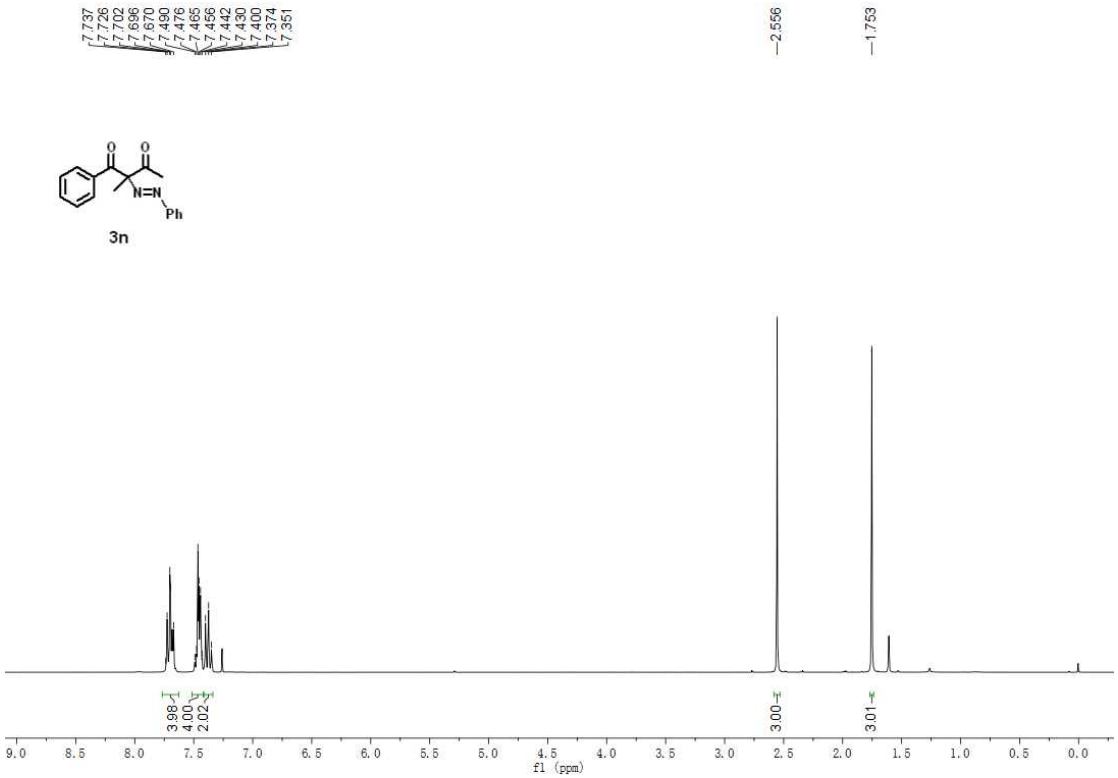

210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

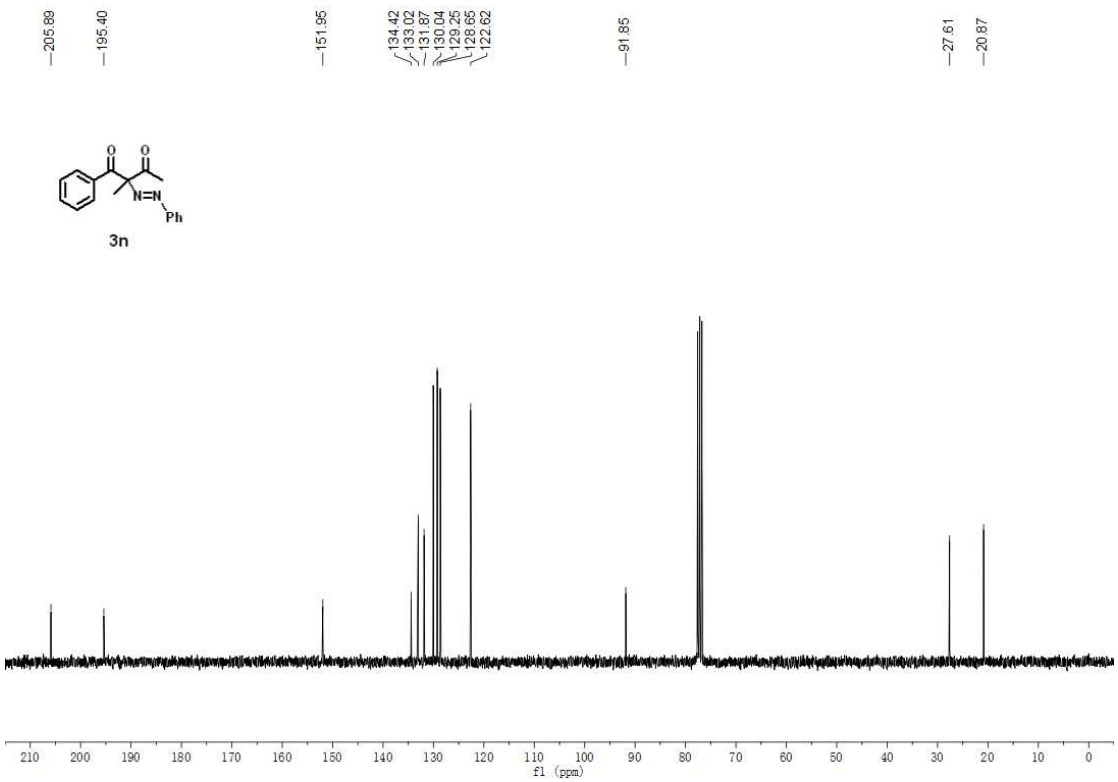

7.787
7.781
7.768
7.756
7.741
7.642
7.626
7.484
7.474
7.463
7.260
7.097
7.083
7.068
4.346
4.323
4.310
4.299
4.287
4.268
4.263
4.244
4.239
4.232
4.221
4.209
4.185
1.809
1.201
1.178
1.154
O
S
O
OEt
N
N
Ph
3l
3.01
1.00
3.03
1.01
2.05
3.03
3.04
f1 (ppm)

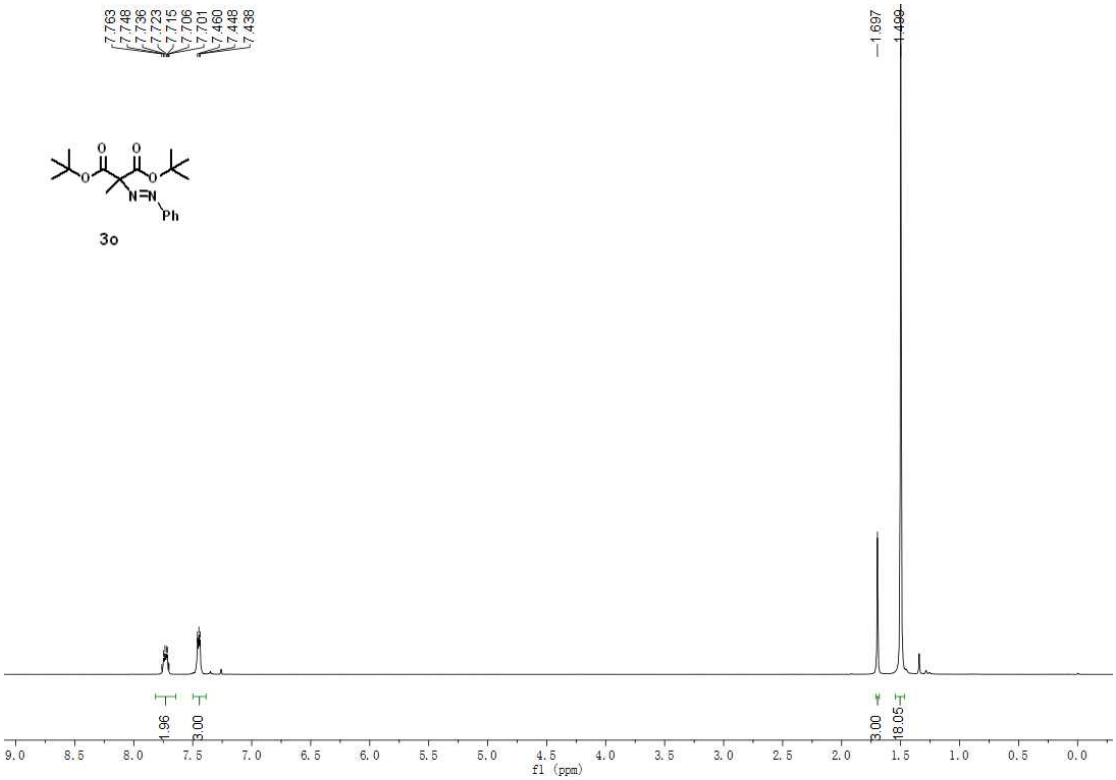

186.68
170.08
151.76
141.58
134.71
134.54
131.84
129.21
128.13
123.00
86.60
62.07
20.36
14.05
O
S
O
OEt
N
N
Ph
3l
f1 (ppm)

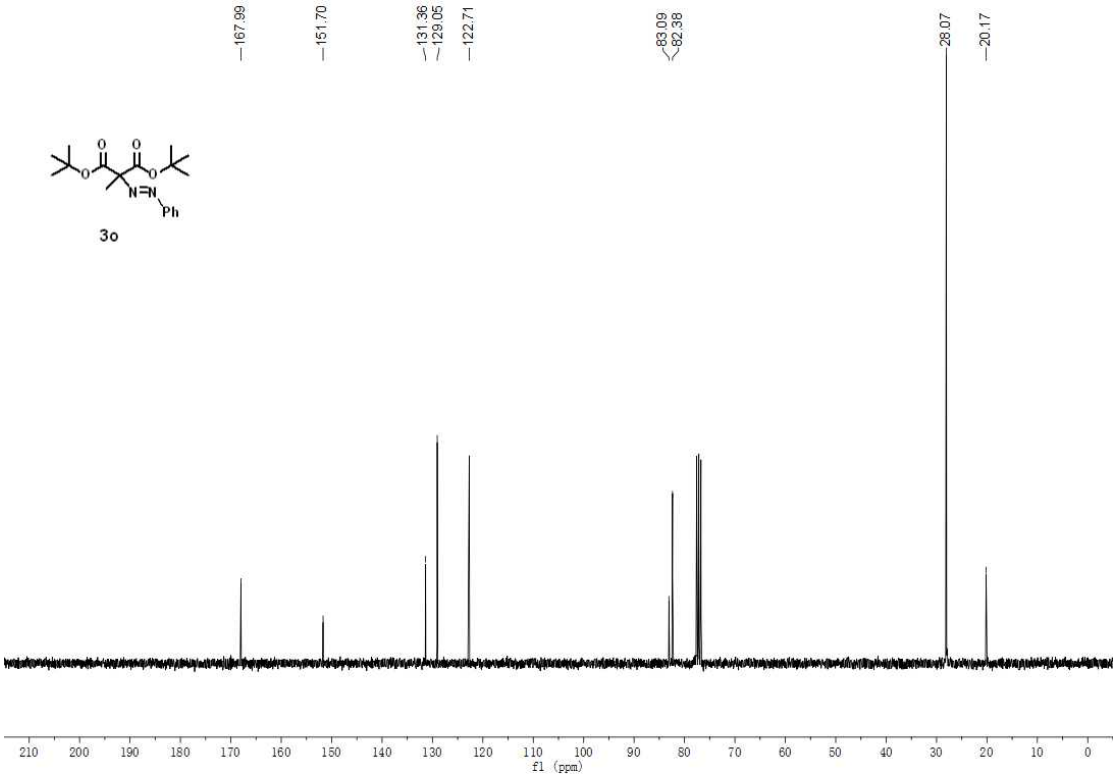

7.798
7.784
7.774
7.766
7.762
7.753
7.526
7.515
7.505
2.578
2.556
2.520
2.498
2.494
2.471
2.434
2.412
2.278
2.260
2.233
2.211
2.189
1.563
0.945
0.922
0.905
0.883
3m
2.00
3.01
2.05
4.01
3.02
6.03
f1 (ppm)

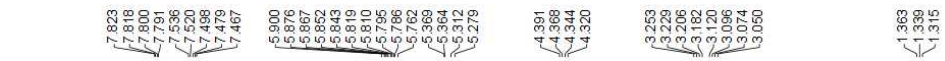

205.80
203.99
151.87
131.95
129.37
122.69
93.77
49.60
28.52
24.01
22.67
22.65
18.36
3m
f1 (ppm)

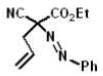

7.737
7.726
7.702
7.696
7.670
7.490
7.476
7.465
7.456
7.442
7.430
7.400
7.374
7.351
2.556
1.753
3n
3.98
4.00
2.02
3.00
3.01
f1 (ppm)


205.89
195.40
151.95
134.42
133.02
131.87
130.04
129.25
128.65
122.62
91.85
27.61
20.87
3n
f1 (ppm)

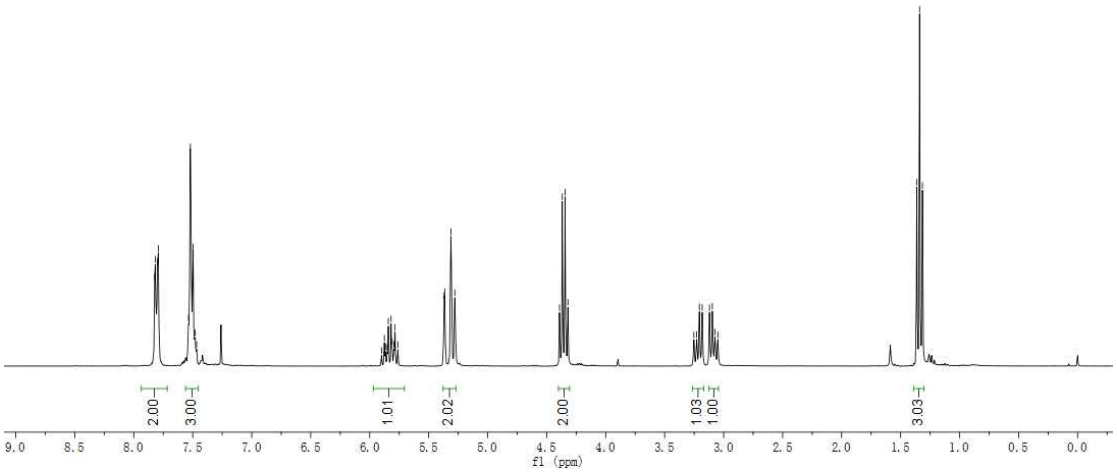

7.763
7.748
7.736
7.723
7.715
7.706
7.701
7.460
7.448
7.438
1.697
1.499
3o
1.96
3.00
3.00
18.05
f1 (ppm)


167.99
151.70
131.36
129.05
122.71
83.09
82.38
28.07
20.17
3o
f1 (ppm)

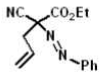

7.823
7.818
7.800
7.791
7.536
7.520
7.498
7.479
7.467
5.900
5.876
5.867
5.852
5.843
5.819
5.810
5.795
5.786
5.762
5.369
5.364
5.312
5.279
4.391
4.368
4.344
4.320
3.253
3.229
3.206
3.182
3.120
3.096
3.074
3.050
1.363
1.339
1.315


NC
CO2Et
N
N
Ph

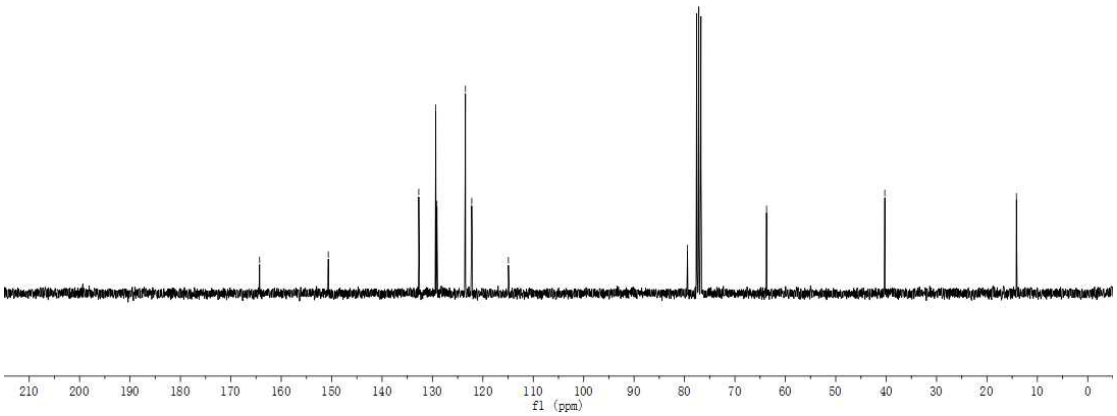
3p

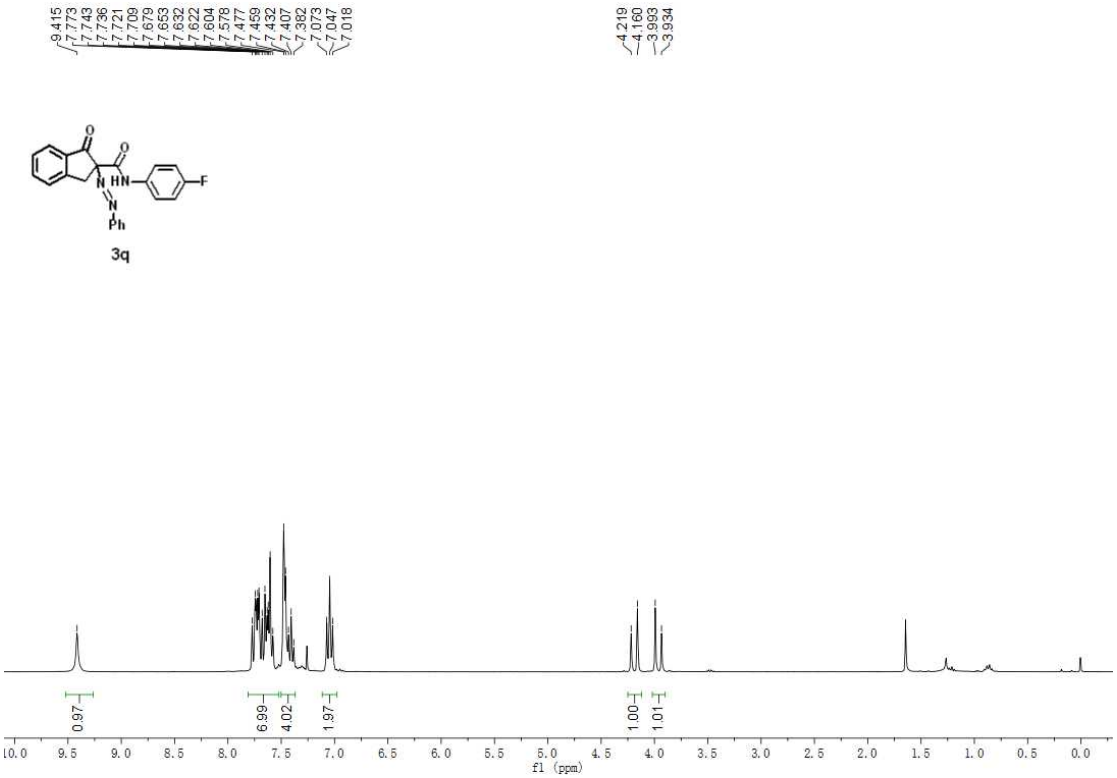

2.00
3.00
1.01
2.02
2.00
1.03
1.00
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

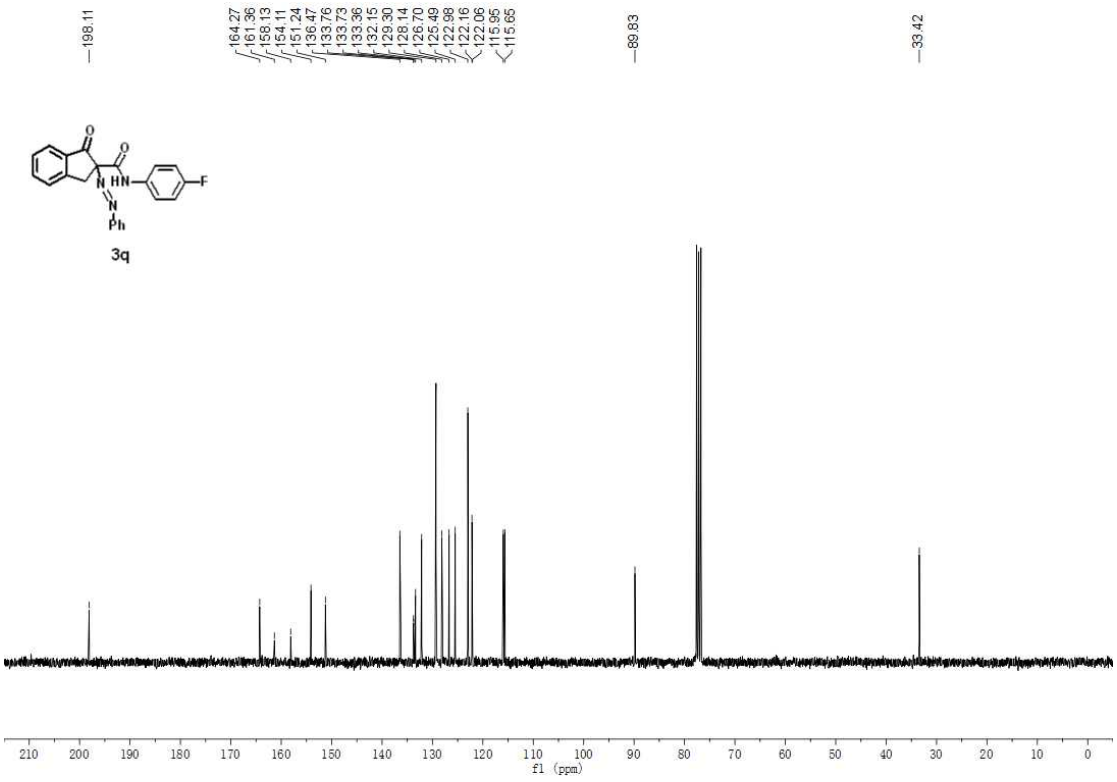

164.29
150.67
132.72
129.35
129.12
123.45
122.21
114.93
79.41
63.73
40.26
14.16

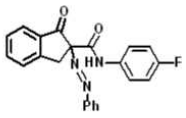

NC
CO2Et
N
N
Ph

3p


210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


9.415
7.773
7.743
7.736
7.721
7.709
7.679
7.653
7.632
7.622
7.604
7.578
7.477
7.459
7.432
7.407
7.382
7.073
7.047
7.018
4.219
4.160
3.993
3.934
O
O
HN
F
N
Ph
3q
0.97
6.99
4.02
1.97
1.00
1.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


198.11
164.27
161.36
158.13
154.11
151.24
136.47
133.76
133.73
133.36
132.15
129.30
128.14
126.70
125.49
122.98
122.16
122.06
115.95
115.65
89.83
33.42
O
O
HN
F
N
Ph
3q
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

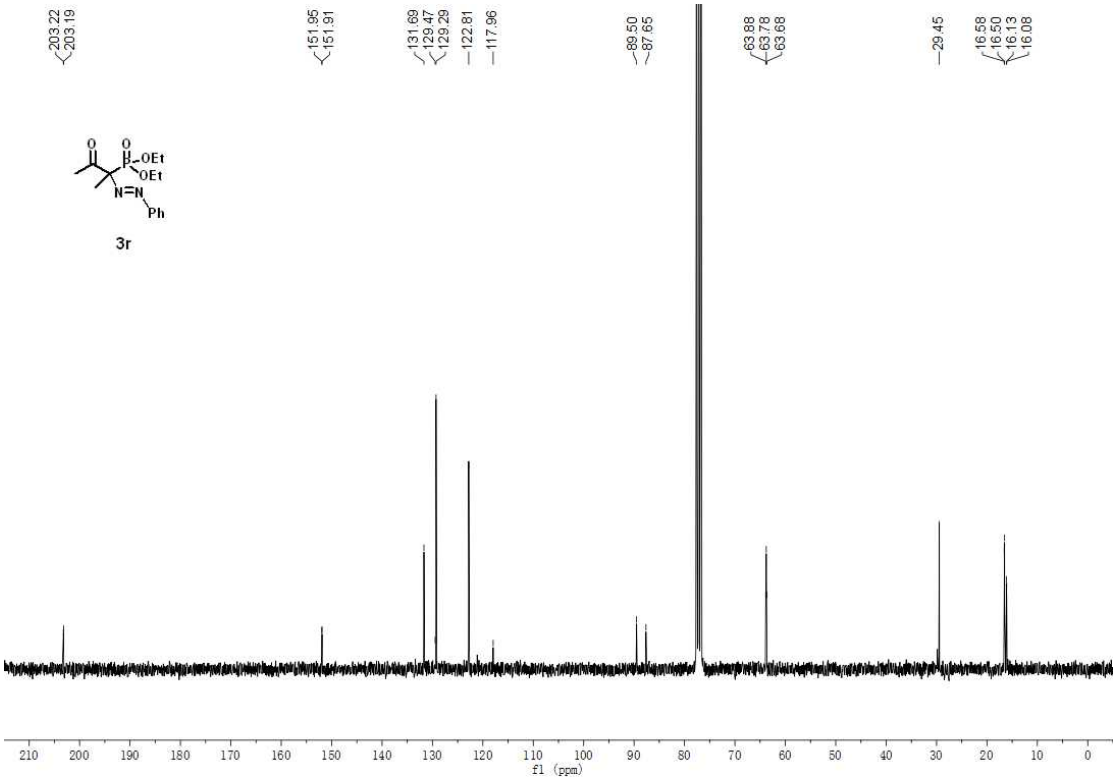


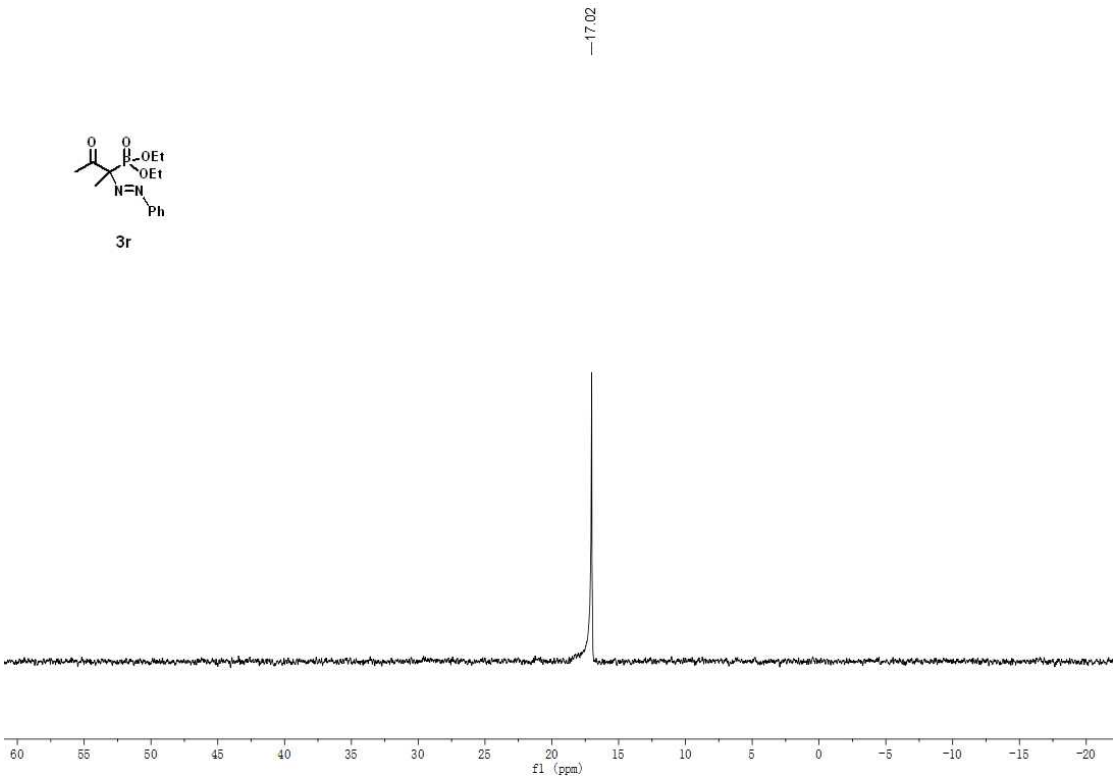
3q

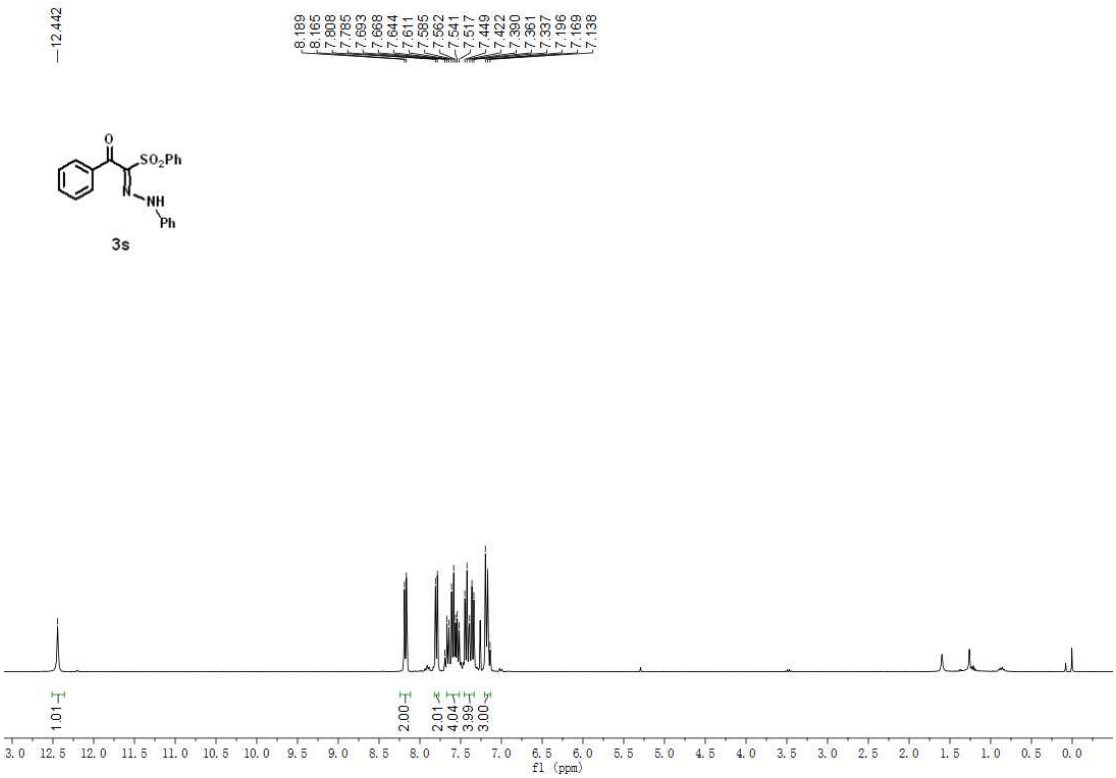
117.45
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
f1 (ppm)

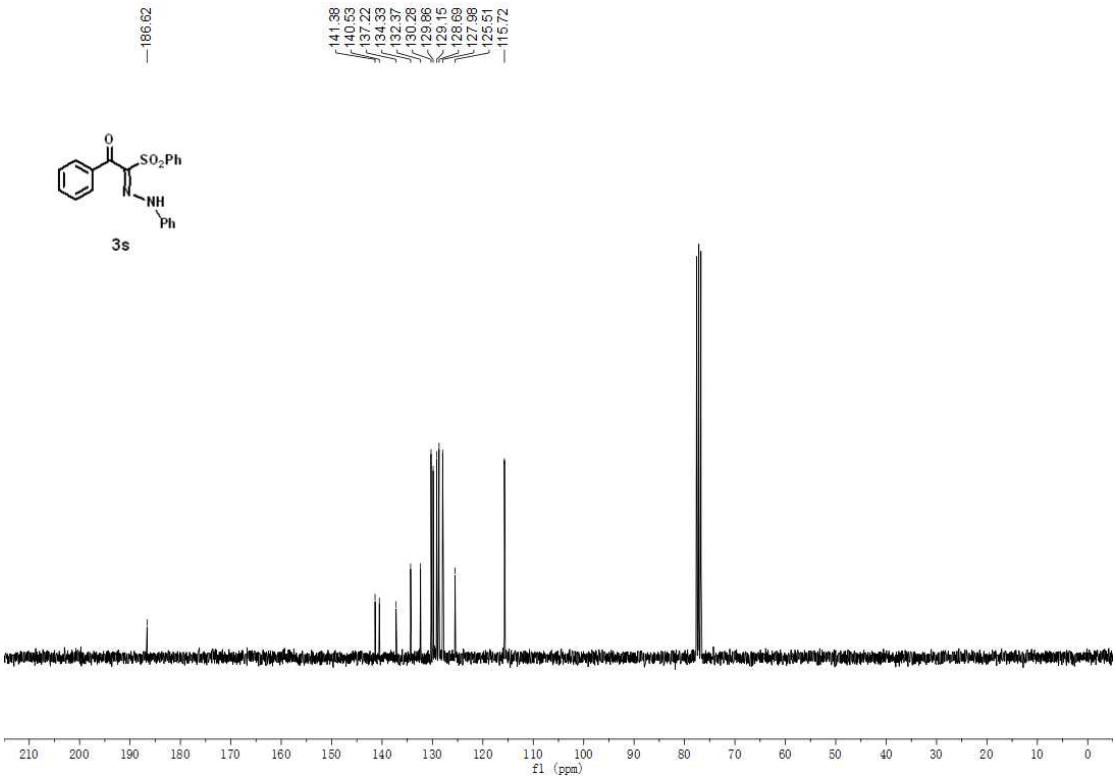
3r

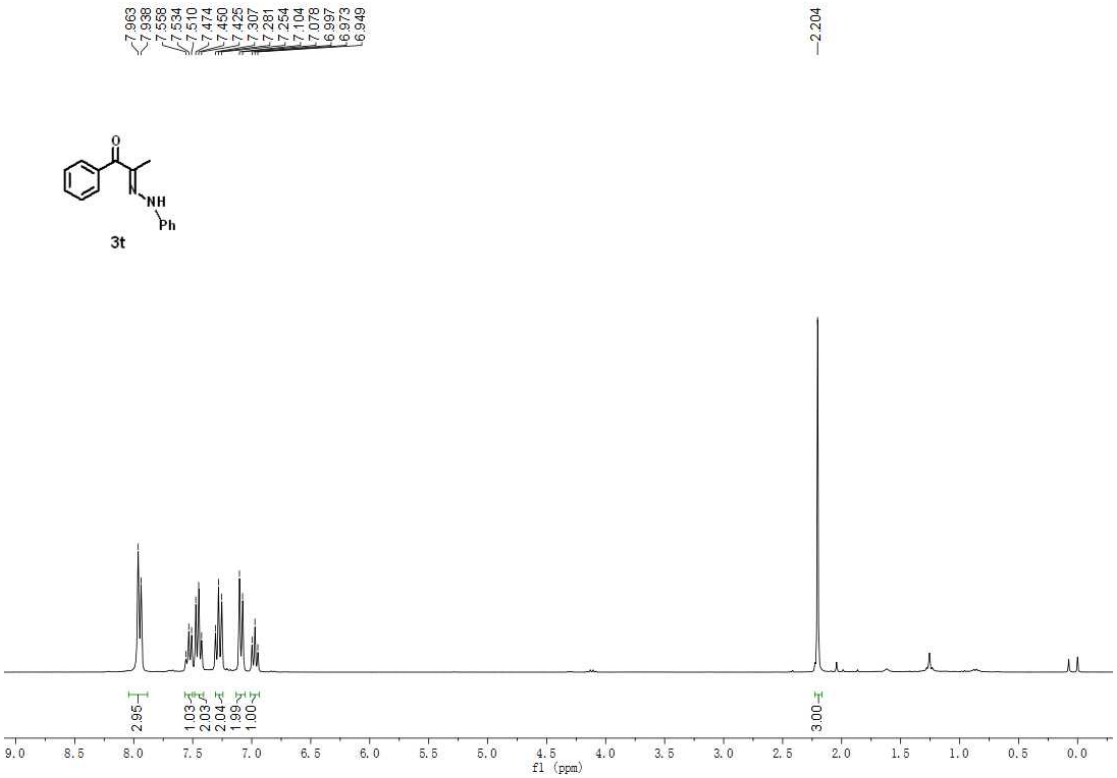
7.807
7.792
7.780
7.766
7.759
7.746
7.501
7.489
7.480
4.251
4.227
4.203
4.180
4.173
4.146
4.138
4.122
4.115
2.466
1.692
1.641
1.350
1.326
1.305
1.283
1.259
2.00
2.99
4.03
3.00
3.04
6.08
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

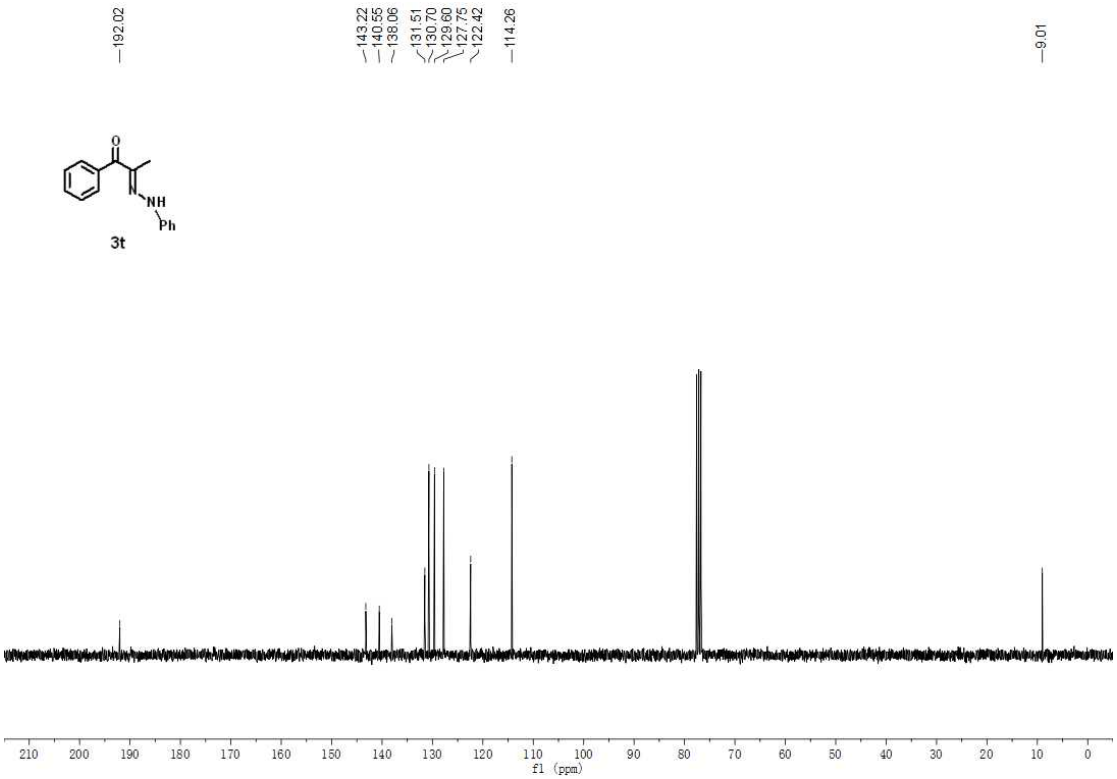

203.22
203.19
151.95
151.91
131.69
129.47
129.29
122.81
117.96
89.50
87.65
63.88
63.78
63.68
29.45
16.58
16.50
16.13
16.08
3r
f1 (ppm)

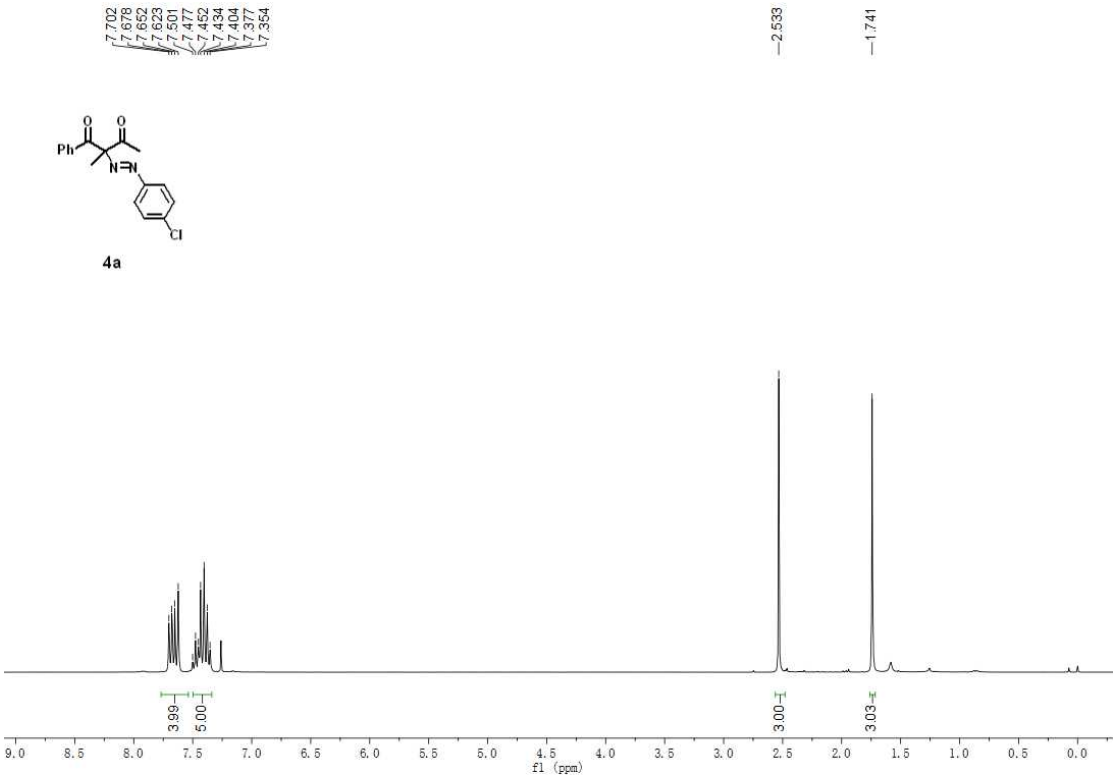

17.02
3r
f1 (ppm)

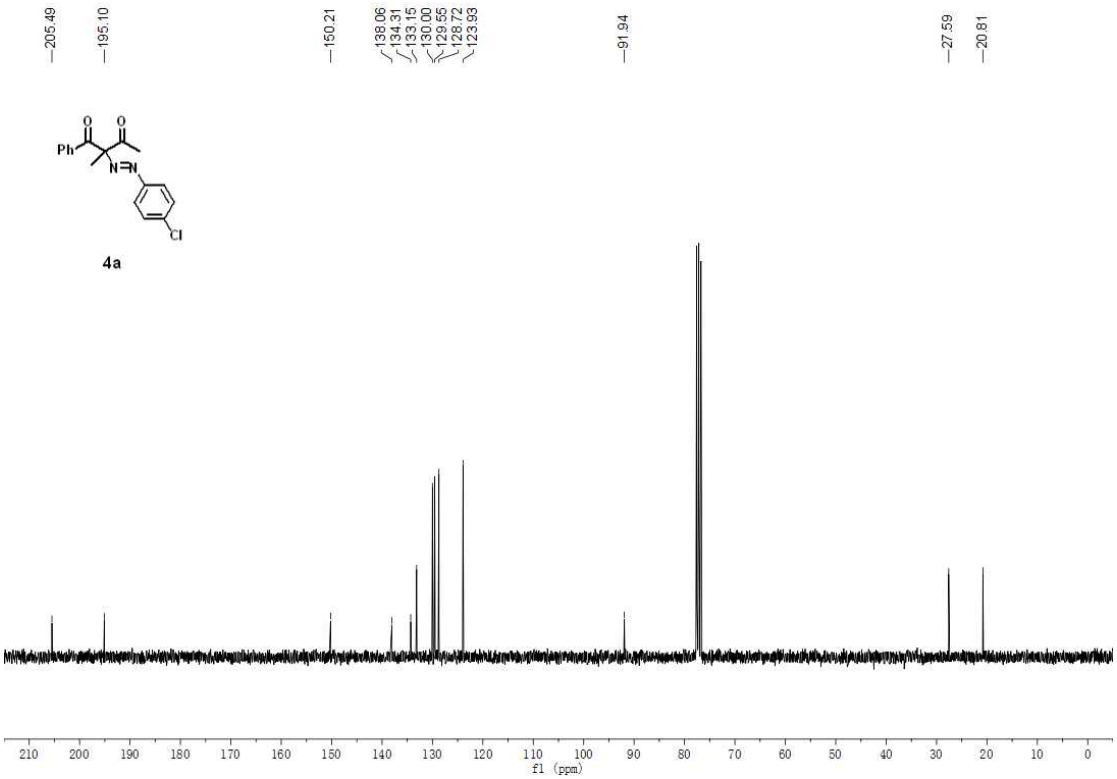

12.442
8.189
8.165
7.808
7.785
7.693
7.668
7.644
7.611
7.585
7.562
7.541
7.517
7.449
7.422
7.390
7.361
7.337
7.196
7.169
7.138
SO2Ph
NH
Ph
3s
1.01
2.00
2.01
4.04
3.99
3.00
f1 (ppm)

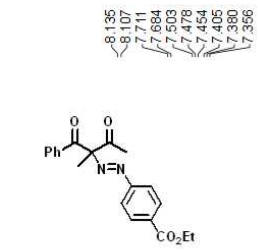

186.62
141.38
140.53
137.22
134.33
132.37
130.28
129.86
129.15
128.69
127.98
125.51
115.72
SO2Ph
NH
Ph
3s
f1 (ppm)


7.963
7.938
7.558
7.534
7.510
7.474
7.450
7.425
7.307
7.281
7.254
7.104
7.078
6.997
6.973
6.949
2.204
O
NH
Ph
3t
2.95
1.03
2.03
2.04
1.99
1.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

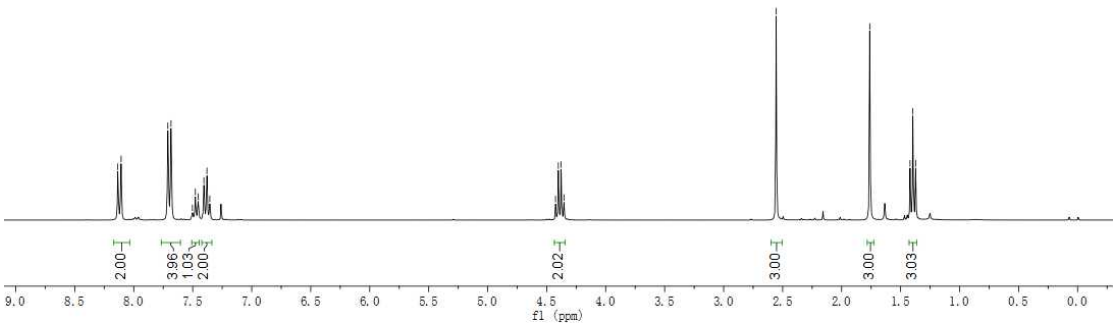

192.02
143.22
140.55
138.06
131.51
130.70
129.60
127.75
122.42
114.26
9.01
O
NH
Ph
3t
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

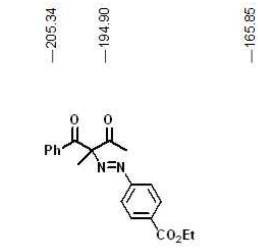

7.702
7.678
7.652
7.623
7.501
7.477
7.452
7.434
7.404
7.377
7.354
2.533
1.741
Ph
N
Cl
4a
3.99
5.00
3.00
3.03
f1 (ppm)


205.49
195.10
150.21
138.06
134.31
133.15
130.00
129.55
128.72
123.93
91.94
27.59
20.81
Ph
N
Cl
4a
f1 (ppm)

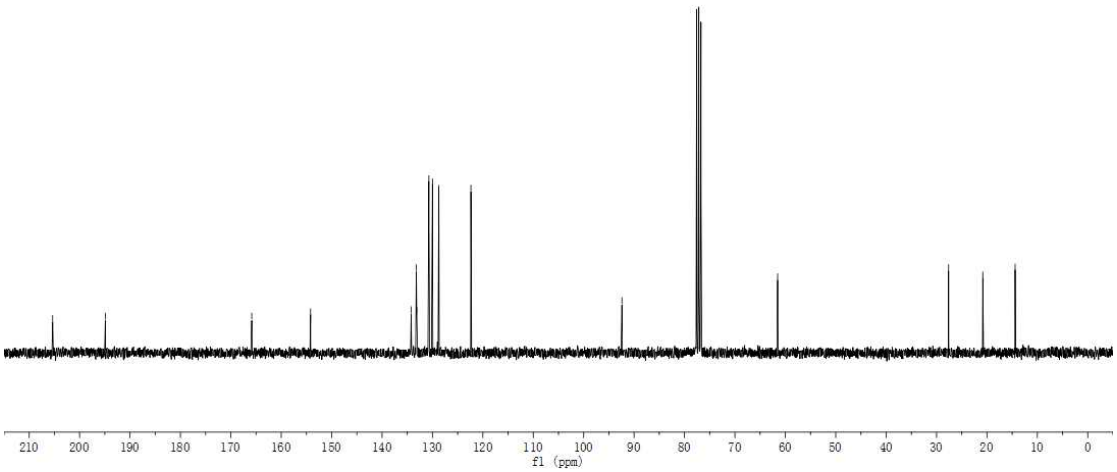

8.135
8.107
7.711
7.684
7.503
7.478
7.454
7.405
7.380
7.356
4.425
4.401
4.377
4.353
2.555
1.762
1.420
1.396
1.373
Ph
N=N
CO2Et

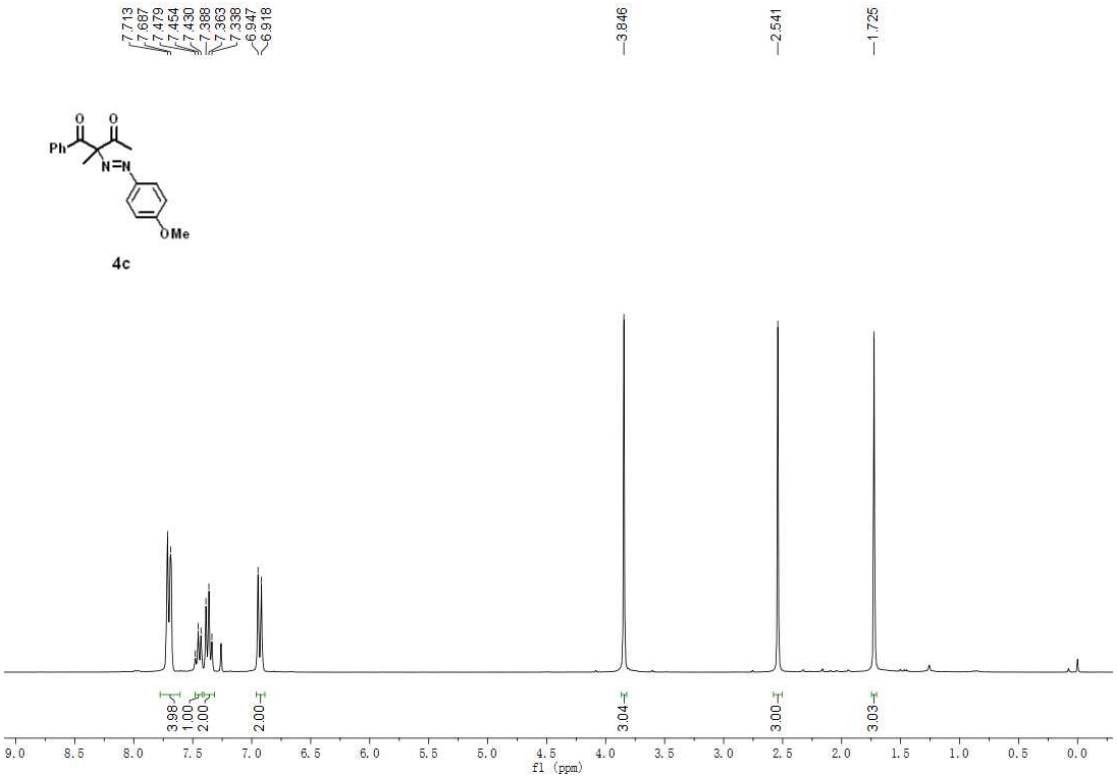
4b

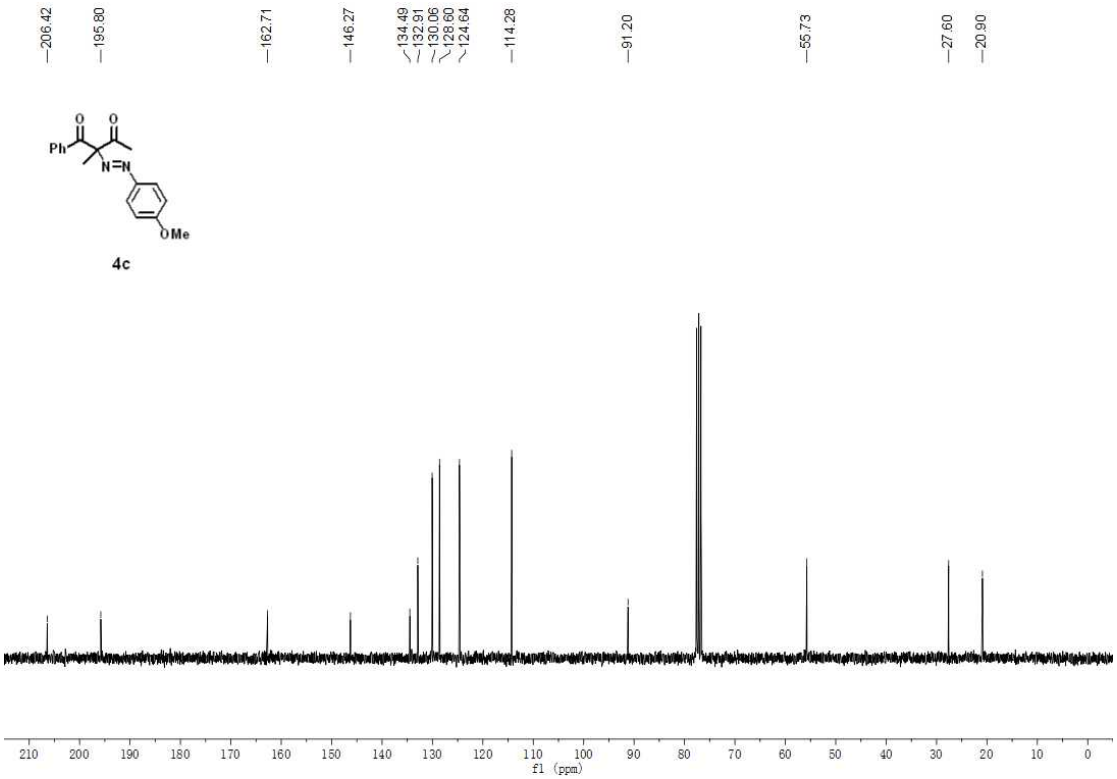

2.00
3.96
1.03
2.00
2.02
3.00
3.00
3.03
f1 (ppm)

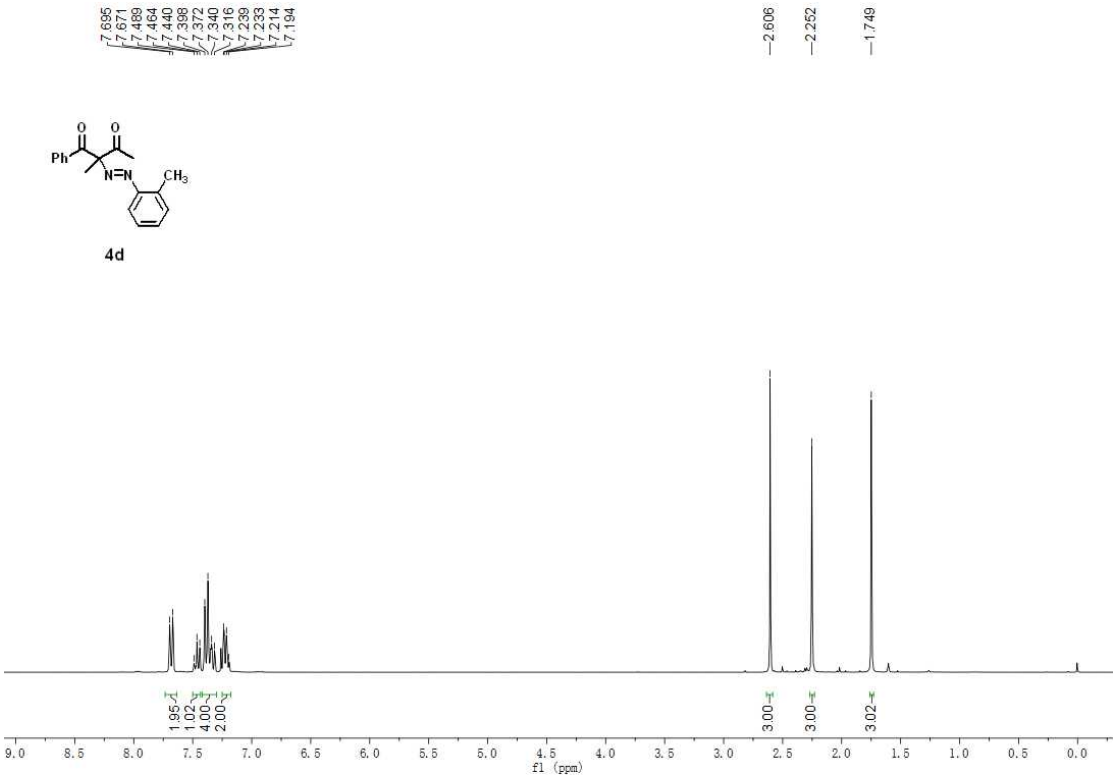

205.34
194.90
165.85
154.18
134.22
133.21
133.11
130.71
130.00
128.74
122.37
92.41
61.52
27.61
20.83
14.41
Ph
N=N
CO2Et

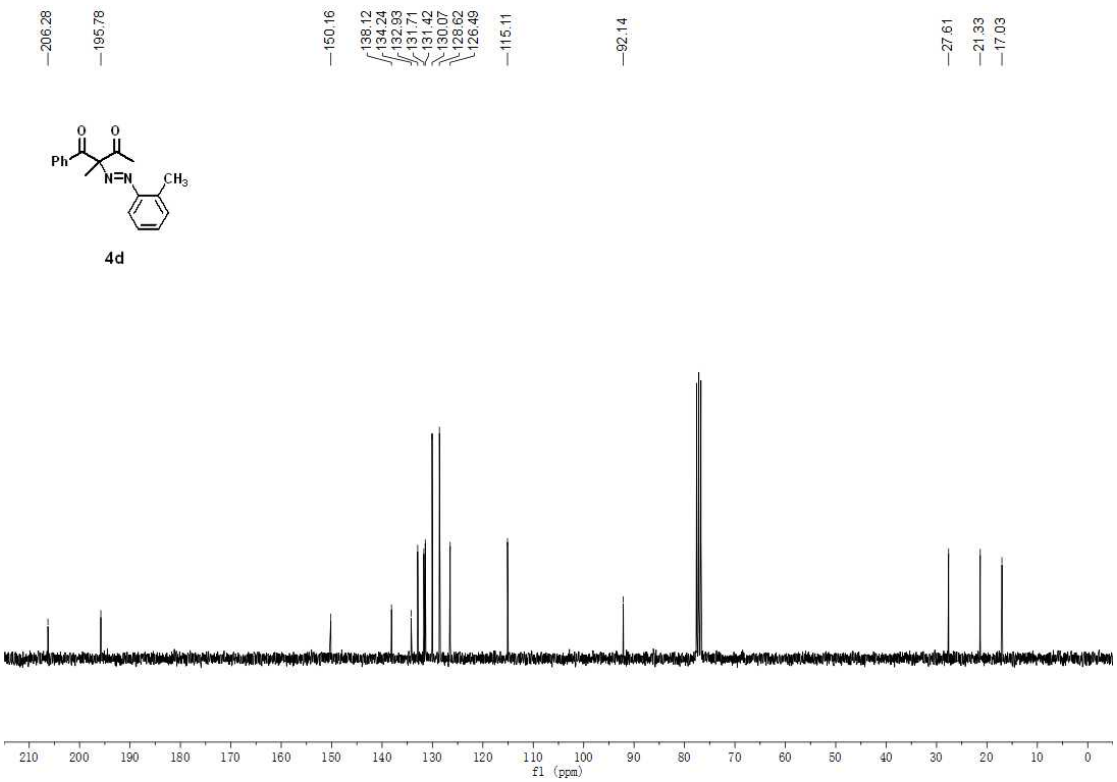
4b

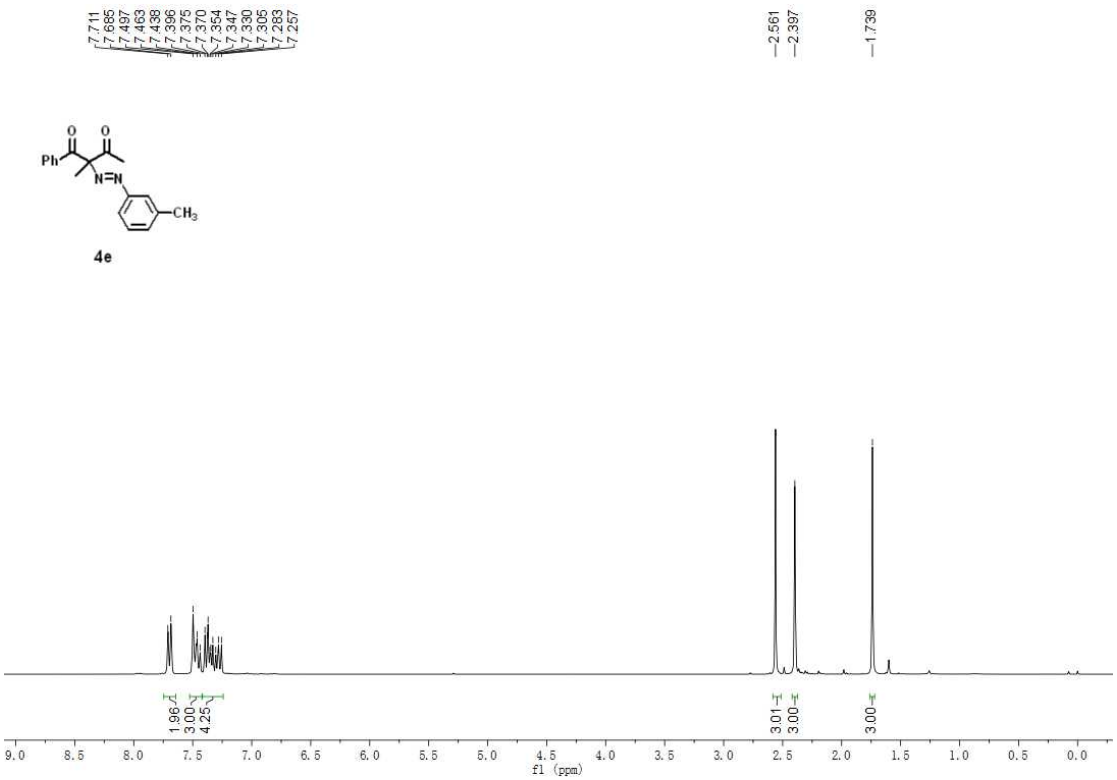

f1 (ppm)

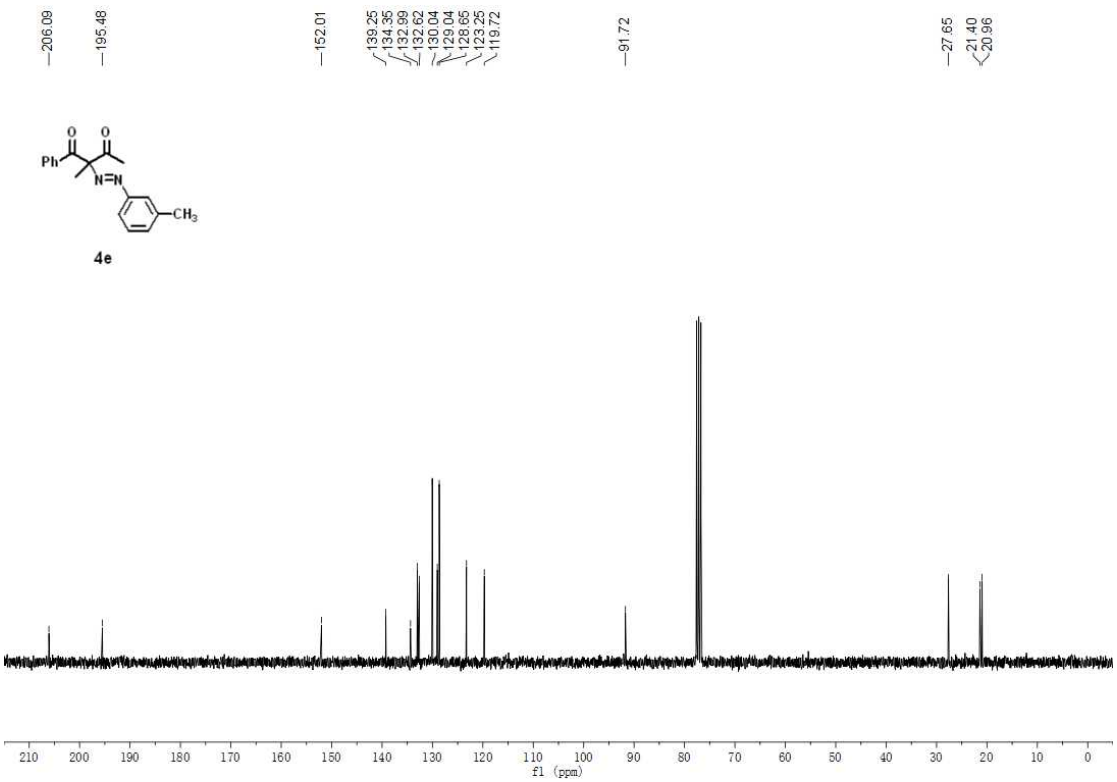

7.713
7.687
7.479
7.454
7.430
7.388
7.363
7.338
6.947
6.918
3.846
2.541
1.725
O
O
Ph
N=N
OMe
4c
3.98
1.00
2.00
2.00
3.04
3.00
3.03
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


206.42
195.80
162.71
146.27
134.49
132.91
130.06
128.60
124.64
114.28
91.20
55.73
27.60
20.90
O
O
Ph
N=N
OMe
4c
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

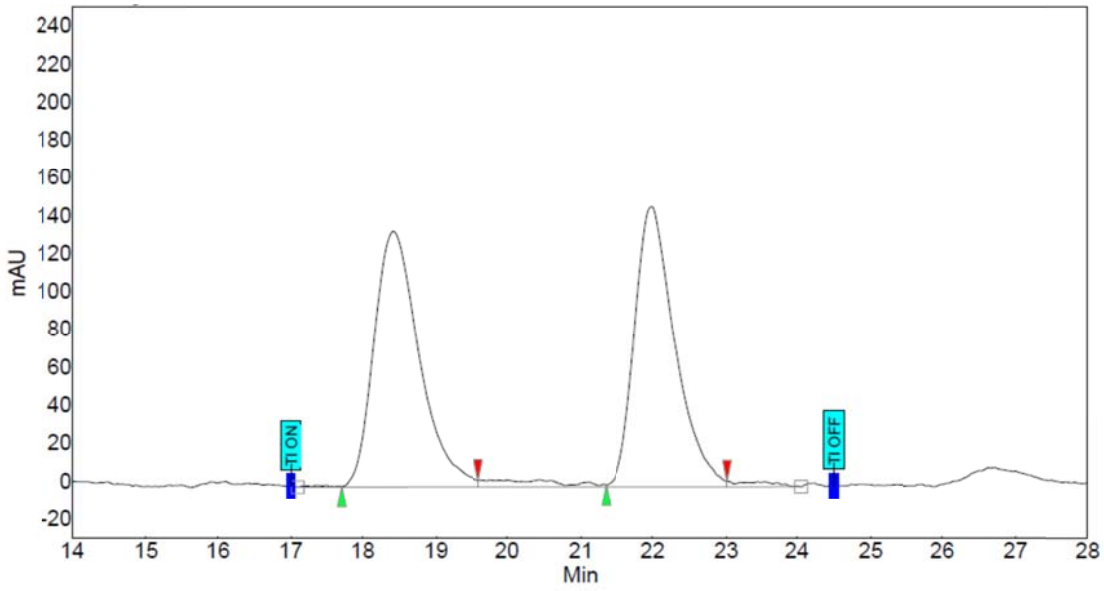

7.695
7.671
7.489
7.464
7.440
7.398
7.372
7.340
7.316
7.239
7.233
7.214
7.194
2.606
2.252
1.749
Ph
O
O
N=N
CH3
4d
1.95
1.02
4.00
2.00
3.00
3.00
3.02
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)


206.28
195.78
150.16
138.12
134.24
132.93
131.71
131.42
130.07
128.62
126.49
115.11
92.14
27.61
21.33
17.03
Ph
O
O
N=N
CH3
4d
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.711
7.685
7.497
7.463
7.438
7.396
7.375
7.370
7.354
7.347
7.330
7.305
7.283
7.257
2.561
2.397
1.739
Ph
O
O
N=N
CH3
4e
1.96
3.00
4.25
3.01
3.00
3.00
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

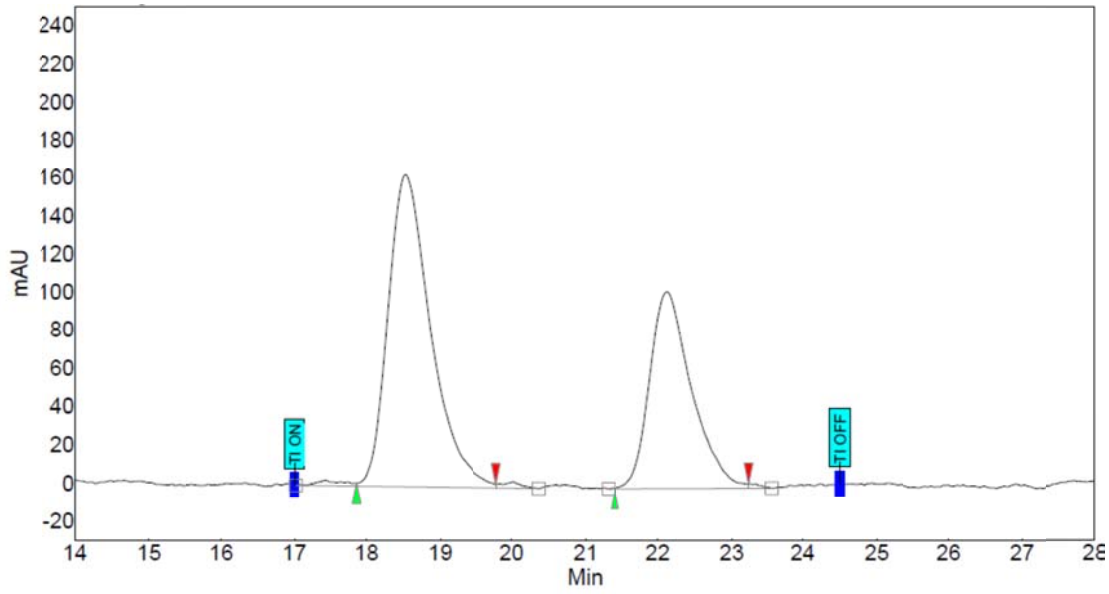

206.09
195.48
152.01
139.25
134.35
132.99
132.62
130.04
129.04
128.65
123.25
119.72
91.72
27.65
21.40
20.96
Ph
O
O
N=N
CH3
4e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)

HPLC spectrum for 3a:



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.42	50.46	134.6	95.8	50.462
2	UNKNOWN	21.99	49.54	147.6	94.1	49.538
Total			100.00	282.2	189.9	100.000



Peak results :

Index	Name	Time [Min]	Quantity [% Area]	Height [mAU]	Area [mAU.Min]	Area % [%]
1	UNKNOWN	18.53	61.81	163.3	109.2	61.813
2	UNKNOWN	22.13	38.19	103.0	67.4	38.187
Total			100.00	266.3	176.6	100.000