Supporting Information

For the article entitled

Additive- and Ligand-Free Cross-Coupling Reactions between Alkenes and Alkynes by Iridium Catalysis

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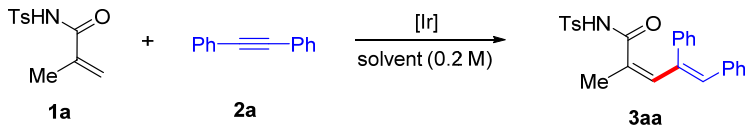
General Methods

Analytical thin layer chromatography (TLC) was performed using Merck 60 F254 precoated silica gel plate (0.2 mm thickness). Subsequent to elution, plates were visualized using UV radiation (254 nm) on Spectroline Model ENF-24061/F254 nm. Further visualization was possible by staining with basic solution of potassium permanganate or acidic solution of ceric molybdate. Flash column chromatography was performed using Merck aluminium oxide 90 active neutral with freshly distilled solvents. Columns were typically packed as slurry and equilibrated with the appropriate solvent system prior to use. Proton nuclear magnetic resonance spectra (^{1}H NMR) were recorded on Bruker AMX400 and 500 MHz spectrophotometer ($CDCl_3$ as solvent). Chemical shifts for ^{1}H NMR spectra are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 7.26, singlet). Multiplicities were given as: s (singlet), d (doublet), t (triplet), dd (doublets of doublet) or m (multiplets). The number of protons (n) for a given resonance is indicated by nH. Coupling constants are reported as a *J* value in Hz. Carbon nuclear magnetic resonance spectra (^{13}C NMR) are reported as δ in units of parts per million (ppm) downfield from $SiMe_4$ (δ 0.0) and relative to the signal of chloroform-*d* (δ 77.0, triplet). Mass spectrometry was performed by Waters Q-Tof Premier Micromass instrument, using Electro Spray Ionization (ESI) mode. IR spectra were recorded as thin films on KBr or NaCl plates on a Bio-Rad FTS 165 FTIR spectrometer and are reported in frequency of absorption (cm^{-1}). $[IrCp^*Cl_2]_2$, $[Ir(cod)Cl]_2$ and $AgBF_4$ were purchased from Energy and used directly. Other reagents, unless otherwise noted below, are commercially available from Alfa Aesar (China) Chemical Co., Ltd. and used without further purification. Acrylamides were prepared by reported methods.[1-2]

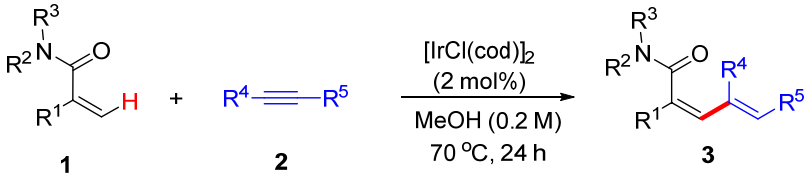
Table 1. Optimization Conditions for Alkene-Alkyne Coupling [a]



Entry	Catalyst	Solvent	Temperature (℃)	Time (h)	Yield (%)[b]
1	$[IrCl(cod)]_2$	Toluene	70	1.5	21
2	$[IrCl(cod)]_2$	Toluene	70	12	85
3	$[IrCl(cod)]_2$	Toluene	50	12	50
4	$[IrCl(cod)]_2$	Toluene	60	12	67
5	$[IrCl(cod)]_2$	Toluene	70	24	88
6	$[IrOMe(cod)]_2$	Toluene	70	24	74
7	$[IrCl(cod)]_2$	1,4-Dioxane	70	24	86
8	$[IrCl(cod)]_2$	DCE	70	24	83
9	$[IrCl(cod)]_2$	DME	70	24	71
10	$[IrCl(cod)]_2$	MeOH	70	24	96
11	$[IrCl(cod)]_2$	EtOH	70	24	72
12	$[IrCl(cod)]_2$	*i*-PrOH	70	24	76
13	$[IrCl(cod)]_2$	CH_3CH_2OH	70	24	91
14	$[IrCl(cod)]_2$	HFIP	70	24	67

[a] Conditions: **1a** (0.2 mmol, 1.0 equiv), **2a** (0.3 mmol, 1.5 equiv), [Ir] (4 mol%) in a solvent (0.2 M) at 70 ℃ for 24 h. [b] Isolated yield.

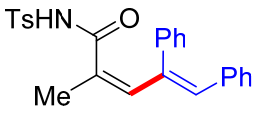
General Procedure for Ir-Catalyzed Alkene-Alkyne Coupling Reaction



1 2 3

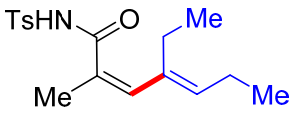
An oven-dried vial was charged with $[Ir(cod)Cl]_2$ (2.7 mg, 2 mol%), and MeOH (1 mL). Then, alkyne **2** (0.3 mmol, 1.5 equiv) and acrylamide **1** (0.2 mmol, 1.0 equiv) were added into the solution in sequence. The vial was sealed under argon and heated to 70 ℃ with stirring for 24 hours. After cooling down, the mixture was concentrated to give the crude product which was directly applied to a flash column chromatography for purification (EtOAc/Petroleum ether mixtures).

Characterization of Butadienes



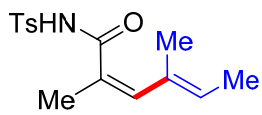
(2*Z*, 4*Z*)-2-Methyl-4,5-diphenyl-*N*-tosylpenta-2,4-dienamide (3aa)

Following the general experiment procedure, **3aa** was obtained as a yellow solid (96%, 38 mg). M. p. = 146 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.41 (s, 1H), 7.60 (d, *J* = 8.5 Hz, 2H), 7.17-7.16 (m, 3H), 7.08-7.02 (m, 5H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.79 (d, *J* = 7.0 Hz, 2H), 6.32 (s, 1H), 6.25(t, *J* = 1.5 Hz, 1H), 2.20 (s, 3H), 1.93 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.02, 143.66, 136.71, 135.77, 135.36, 134.82, 133.84, 131.20, 131.05, 128.65, 128.25, 128.12, 127.78, 127.38, 127.16, 126.99, 126.59, 20.61, 20.09. HR-MS (ESI): m/z calculated for $C_{25}H_{23}NO_3S$: $[M+H]^+$: 418.1471, found: 418.1475. FTIR (KBr, cm^{-1}): 3685.35, 3419.37, 2974.61, 2899.50, 1651.53, 1384.18, 1087.13, 1048.10.



(2*Z*, 4*E*)-4-Ethyl-2-methyl-*N*-tosylhepta-2,4-dienamide (3ab)

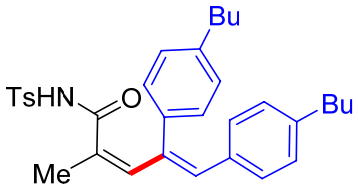
Following the general experiment procedure, **3ab** was obtained as a yellow liquid (69%, 44 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.61 (s, 1H), 7.95 (d, *J* = 8.5 Hz, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 6.31 (s, 1H), 5.40 (t, *J* = 7.0 Hz, 1H), 2.44 (s, 3H), 2.17-2.05 (m, 4H), 1.88 (d, *J* = 1.5 Hz, 3H), 1.00 (td, *J* = 7.5, 4.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.06, 143.88, 137.64, 136.42, 134.82, 133.74, 128.66, 128.47, 127.47, 22.52, 20.64, 20.29, 19.55, 12.67, 12.35. HR-MS (ESI): m/z calculated for $C_{17}H_{23}NO_3S$: $[M+H]^+$: 322.1471, found: 322.1473. FTIR (KBr, cm^{-1}): 3850.93, 3646.34, 3500.35, 3444.47, 1633.98, 1384.26, 1164.90, 1083.37.



(2*Z*, 4*E*)-2, 4-Dimethyl-*N*-tosylhexa-2,4-dienamide (3ac)

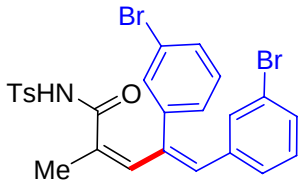
Following the general experiment procedure, **3ac** was obtained as a yellow liquid (77%, 45 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.24 (s, 1H), 7.88 (d, *J* = 8.5 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 6.12 (s, 1H), 5.43 (d, *J* = 6.5 Hz, 1H), 2.37 (s, 3H), 1.80 (d, *J* = 1.5 Hz, 3H), 1.57 (s, 3H), 1.56 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.95, 144.01,

137.62, 134.52, 131.23, 128.49, 127.99, 127.54, 127.07, 20.60, 19.74, 14.42, 12.90. HR-MS (ESI): m/z calculated for $C_{15}H_{19}NO_3S$: $[M+H]^+$: 294.1158, found: 294.1157. FTIR (KBr, cm^{-1}): 3627.22, 3444.29, 2980.82, 1668.18, 1557.87, 1384.26, 1164.45, 1082.29.



(2*Z*,4*Z*)-4,5-*bis*(4-Butylphenyl)-2-methyl-*N*-tosylpenta-2,4-dienamide (3ad).

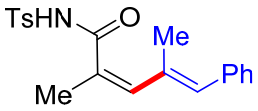
Following the general experiment procedure, **3ad** was obtained as a yellow solid (84%, 89 mg). M. p. = 92 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.5 Hz, 2H), 7.05-7.09 (m, 4H), 6.96-6.92 (dd, *J* = 12.0, 8.5 Hz, 4H), 6.83 (d, *J* = 8.0 Hz, 2H), 6.36 (d , *J* = 1.5 Hz, 1H), 6.33 (s, 1H), 2.61-2.55 (m, 4H), 2.29 (s, 3H), 1.99 (d, *J* = 1.5 Hz, 3H), 1.62-1.56 (m, 4H), 1.39-1.34 (m, 4H), 0.94 (td, *J* = 7.5, 2.5 Hz, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.03, 143.48, 142.04, 141.60, 136.22, 134.82, 134.00, 133.97, 132.31, 130.83, 130.67, 128.62, 128.18, 127.93, 127.83, 127.44, 127.03, 34.42, 34.38, 32.45, 32.39, 21.42, 21.33, 20.59, 19.98, 12.94, 12.93. HR-MS (ESI): m/z calculated for $C_{33}H_{39}NO_3S$: $[M+H]^+$: 530.2723, found: 530.2731. FTIR (KBr, cm^{-1}): 3646.52, 3444.43, 2956.09, 2923.57, 1651.68, 1384.19, 1163.79, 1082.07.



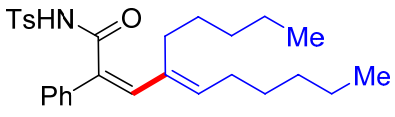
(2*Z*,4*Z*)-4,5-*bis*(3-Bromophenyl)-2-methyl-*N*-tosylpenta-2,4-dienamide (3ae).

Following the general experiment procedure, **3ae** was obtained as a white solid (90%, 83 mg). M. p. = 206 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.45 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.36 (ddd, *J* = 3.0, 1.5, 1.0 Hz, 1H), 7.31-7.29 (m, 1H), 7.26 (s, 1H), 7.09 (t, *J* = 7.5 Hz, 1H), 7.01-7.03 (m, 3H), 6.99-6.96 (m, 2H), 6.75 (d, *J* = 7.5 Hz, 1H), 6.31 (s, 1H), 6.20 (t, *J* = 1.5 Hz ,1H), 2.31 (s, 3H), 2.05-2.04 (t, *J* = 1.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.97, 144.03, 138.49, 136.58, 135.82, 133.69, 133.44, 132.65, 131.54, 130.92, 130.39, 129.62, 129.60, 129.23, 128.48, 128.32, 127.31, 126.94, 126.91, 121.78, 121.14, 20.68, 20.21. HR-MS (ESI): m/z calculated for $C_{25}H_{23}Br_2NO_3S$: $[M+H]^+$: 575.9838, found: 575.9843. FTIR (KBr, cm^{-1}): 3626.43, 3564.48, 3472.97, 3287.26, 2932.48, 1651.80, 1384.21, 480.23.

(2*Z*, 4*Z*)-2-Methyl-4-phenyl-*N*-tosylhexa-2,4-dienamide (3af)



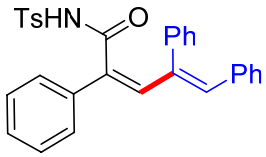
Following the general experiment procedure, **3af** was obtained as a white solid (51%, 38 mg). M. p. = 153 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.31 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.27 (t, *J* = 7.5 Hz, 2H), 7.21-7.19 (m, 1H), 7.08 (d, *J* = 7.5 Hz, 2H), 6.99 (d, *J* = 8.0 Hz, 2H), 6.21 (s, 1H), 6.17 (s, 1H), 2.25 (s, 3H), 1.90 (d, *J* = 1.0 Hz, 3H), 1.82 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.36, 143.89, 137.07, 135.54, 133.87, 131.99, 131.62, 129.05, 128.34, 128.25, 127.47, 127.18, 126.28, 20.63, 20.15, 16.69. HR-MS (ESI): m/z calculated for $C_{20}H_{21}NO_3S$: $[M+H]^+$: 356.1315, found: 356.1314. FTIR (KBr, cm^{-1}): 3626.10, 3573.43, 3450.95, 1645.11, 1557.59, 1384.17, 1163.73, 1083.16.



(2*Z*,4*E*)-4-Pentyl-2-phenyl-*N*-tosyldeca-2,4-dienamide (3bg).

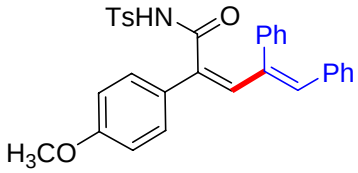
Following the general experiment procedure, **3bg** was obtained as a yellow solid (93%, 88 mg). M. p. = 237 °C. ^{1}H NMR (500

MHz, $CDCl_3$): δ = 8.17 (s, 1H), 7.87 (d, *J* = 8.0 Hz, 2H), 7.25 (d, *J* = 8.0 Hz, 2H), 7.18-7.16 (m, 3H), 7.11-7.09 (m, 2H), 6.38 (s, 1H), 5.47 (t, *J* = 7.5 Hz, 1H), 2.37 (s, 3H), 2.00 ((t, *J* =8.0 Hz, 2H), 1.84-1.79 (m, 2H), 1.23-1.12 (m, 12H), 0.83-0.79 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.68, 144.02, 135.35, 135.28, 134.97, 134.54, 134.44, 132.27, 128.49, 127.70, 127.63, 127.21, 125.43, 35.75, 30.67, 30.66, 28.86, 27.86, 27.84, 27.34, 21.49, 21.47, 20.67, 13.02. HR-MS (ESI): m/z calculated for $C_{28}H_{37}NO_3S$: $[M+H]^+$: 468.2567, found: 468.2562. FTIR (KBr, cm^{-1}): 3850.92, 3534.17, 3444.62, 2923.03, 2330.28, 1644.97, 1455.37, 1384.19.



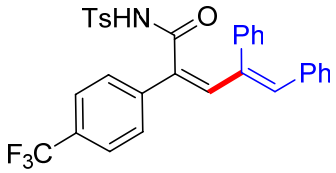
(2*Z*, 4*Z*)-2, 4, 5-Triphenyl-*N*-tosylpenta-2, 4-dienamide (3ba).

Following the general experiment procedure, **3ba** was obtained as a yellow solid (84%, 80 mg). M. p. = 221 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.0 Hz, 2H), 7.30-7.27 (m, 5H), 7.22-7.20 (m, 3H), 7.17-7.15 (m, 2H), 7.13-7.10 (dt, *J* = 7.0, 2.5 Hz, 1H), 7.08-7.05 (m, 2H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.80 (d, *J* = 7.0 Hz, 2H), 6.67 (d, *J* = 1.0 Hz, 1H), 6.62 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.38, 143.67, 137.13, 136.60, 134.97, 134.92, 134.83, 133.82, 133.78, 131.51, 128.75, 128.39, 128.24, 127.83, 127.66, 127.28, 126.97, 126.82, 126.40, 125.54, 20.63. HR-MS (ESI): m/z calculated for $C_{30}H_{25}NO_3S$: $[M+H]^+$: 480.1628, found: 480.1623. FTIR (KBr, cm^{-1}): 3850.98, 3626.64, 3444.57, 2930.42, 2357.26, 1651.64, 1384.28, 683.22.



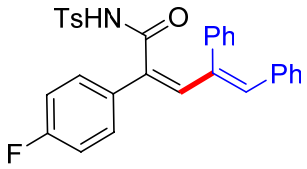
(2*Z*,4*Z*)-2-(4-Methoxylphenyl)-4,5-diphenyl-*N*-tosylpenta-2,4-di enamide (3ca).

Following the general experiment procedure, **3ca** was obtained as a yellow solid (74%, 75 mg). M. p. = 225 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.62 (s, 1H), 7.61 (d, *J* = 8.5 Hz, 2H), 7.15-7.11 (m, 5H), 7.07 (dd, *J* = 7.5, 3.5 Hz, 2H), 7.02 (d, *J* = 7.5 Hz, 1H), 6.97 (t, *J* = 7.5 Hz, 2H), 6.82 (d, *J* = 8.5 Hz, 2H), 6.70 (t, *J* = 8.5 Hz, 4H), 6.49 (s, 1H), 6.47 (d, *J* = 1.5 Hz, 1H), 3.68 (s, 3H), 2.15 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.63, 159.01, 143.63, 137.35, 136.74, 135.11, 134.57, 133.79, 131.95, 130.88, 128.71, 128.41, 128.22, 127.61, 127.34, 127.26, 126.93, 126.90, 126.79, 126.26, 113.26, 54.31, 20.62. HR-MS (ESI): m/z calculated for $C_{31}H_{27}NO_4S$: $[M+H]^+$: 510.1734, found: 510.1731. FTIR (KBr, cm^{-1}): 3876.56, 3564.33, 3444.34, 2382.40, 1714.31, 1633.92, 1434.65, 1360.44.



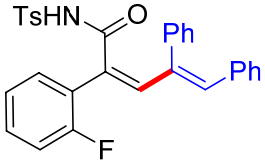
(2*Z*,4*Z*)-2-(4-Trifluoromethylphenyl)-4,5-diphenyl-*N*-tosylpenta-2,4-dienamide (3da).

Following the general experiment procedure, **3da** was obtained as a yellow solid (86%, 94 mg). M. p. = 215 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.65 (s, 1H), 7.67 (d, *J* = 8.0 Hz, 2H), 7.52 (d, *J* = 8.0 Hz, 2H), 7.39 (d, *J* = 8.0 Hz, 2H), 7.25-7.23 (m, 3H), 7.18-7.15 (m, 3H), 7.09 (t, *J* = 7.5 Hz, 2H), 6.95 (d, *J* = 8.0 Hz, 2H), 6.81 (d, *J* = 7.5 Hz, 2H), 6.77 (d, *J* = 1.0 Hz, 1H), 6.68 (s, 1H), 2.27 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.78, 143.97, 138.37, 136.66, 136.21, 135.81, 134.66, 133.56, 133.40, 132.89, 128.82, 128.38, 128.32, 127.81, 127.24, 126.93, 126.79, 126.52, 126.33, 125.78, 124.74 (J_{C-F} = 3.8 Hz), 122.86 (J_{C-F} = 270.4 Hz), 20.61. HR-MS (ESI): m/z calculated for $C_{31}H_{24}FNO_3S$: $[M+H]^+$: 548.1502, found: 548.1496. FTIR (KBr, cm^{-1}): 3850.02, 3507.34, 3444.48, 2956.12, 1651.57, 1463.05, 1123.78, 1083.92.



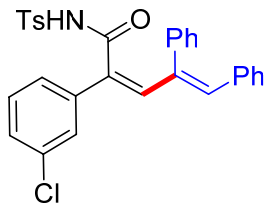
(2*Z*,4*Z*)-2-(4-Fluorophenyl)-4,5-diphenyl-*N*-tosylpenta-2,4-dienamide (3ea).

Following the general experiment procedure, **3ea** was obtained as a yellow solid (98%, 98 mg). M. p. = 180 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.49 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.29-7.23(m, 5H), 7.17-7.12 (m, 3H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.99-6.93 (m, 4H), 6.80 (d, *J* = 7.5 Hz, 2H), 6.62 (d, *J* = 13.0 Hz, 2H), 2.26 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.15, 161.92 ($J_{C\text{-}F}$ = 248.0 Hz), 160.93, 143.84, 136.97, 136.38, 134.84, 133.87 ($J_{C\text{-}F}$ = 4.6 Hz), 133.63, 131.04 ($J_{C\text{-}F}$ = 3.3 Hz), 128.75, 128.35, 128.28, 127.74, 127.48, 127.42, 127.29, 127.09, 126.87, 126.54, 114.86 ($J_{C\text{-}F}$ = 21.6 Hz), 20.63. HR-MS (ESI): m/z calculated for $C_{30}H_{24}FNO_3S$: $[M+H]^+$: 498.1534, found: 498.1531. FTIR (KBr, cm^{-1}): 3654.91, 3550.29, 3444.57, 2983.70, 1651.68, 1538.91, 1384.31, 470.37.



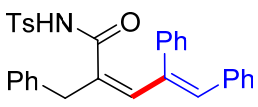
(2*Z*,4*Z*)-2-(2-Fluorophenyl)-4,5-diphenyl-*N*-tosylpenta-2,4-dienamide (3fa).

Following the general experiment procedure, **3fa** was obtained as a yellow solid (75%, 76 mg). M. p. = 230 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.71 (s, 1H), 7.73 (d, *J* = 8.0 Hz, 2H), 7.29-7.26 (m, 2H), 7.23-7.20 (m, 5H), 7.14 (d, *J* = 7.0 Hz, 1H), 7.10-7.06 (m, 3H), 7.00 (td, *J* = 8.5 ,0.5 Hz, 1H), 6.94 (d, *J* = 8.0 Hz, 2H), 6.87 (d, *J* = 7.5 Hz, 2H), 6.69 (d, *J* = 1.5 Hz, 1H), 6.63 (s, 1H), 2.25 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.58, 158.91 ($J_{C\text{-}F}$ = 248.0 Hz), 143.56, 138.24 ($J_{C\text{-}F}$ = 2.8 Hz), 136.85, 136.02, 134.84, 133.82, 132.05, 130.01, 129.55 ($J_{C\text{-}F}$ = 8.4 Hz), 129.33 ($J_{C\text{-}F}$ = 2.7 Hz), 128.83, 128.32, 128.17, 127.70, 127.33, 127.04, 126.88, 126.62, 123.86 ($J_{C\text{-}F}$ = 13.2 Hz), 123.51 ($J_{C\text{-}F}$ = 3.5 Hz), 114.98 ($J_{C\text{-}F}$ = 21.8 Hz), 20.61. HR-MS (ESI): m/z calculated for $C_{30}H_{24}FNO_3S$: $[M+H]^+$: 498.1534, found: 498.1538. FTIR (KBr, cm^{-1}): 3829.87, 3520.45, 3444.99, 2980.17, 1698.65, 1682.47, 1384.44, 1084.11.



(2*Z*,4*Z*)-2-(2-Chlorophenyl)-4,5-diphenyl-*N*-tosylpenta-2,4-dienamide (3ga)

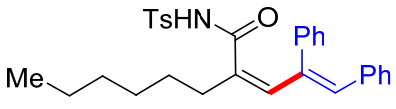
Following the general experiment procedure, **3ga** was obtained as a yellow solid (67%, 69 mg). M. p. = 171 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.60 (s, 1H), 7.70 (d, *J* = 8.0 Hz, 2H), 7.25-7.23 (m, 4H), 7.20-7.12 (m, 6H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.98 (d, *J* = 8.5 Hz, 2H), 6.82 (d, *J* = 7.5 Hz, 2H), 6.70 (d, *J* = 1.0 Hz, 1H), 6.66 (s, 1H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 164.75, 143.91, 136.73, 136.72, 136.32, 135.10, 134.76, 133.73, 133.59, 133.38, 132.62, 129.03, 128.79, 128.38, 128.37, 127.80, 127.63, 127.23, 127.18, 126.90, 126.66, 125.39, 123.74, 20.66. HR-MS (ESI): m/z calculated for $C_{30}H_{24}ClNO_3S$: $[M+H]^+$: 514.1238, found: 514.1239. FTIR (KBr, cm^{-1}): 3813.80, 3616.82, 3444.55, 2980.34, 2330.23, 1694.40, 1557.40, 1384.28.



(2*Z*, 4*Z*)-2-Benzyl-4,5-diphenyl-*N*-tosylpenta-2,4-dienamide (3ha).

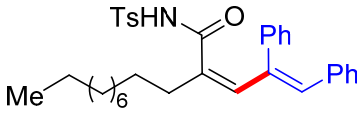
Following the general experiment procedure, **3ha** was obtained as a yellow solid (81%, 80 mg). M. p. = 176 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.40 (s, 1H), 7.59 (d, *J* = 8.5 Hz, 2H), 7.28 (s, 1H), 7.22-7.19 (m, 5H), 7.13-7.08 (m, 7H), 6.93 (d, *J* = 8.0 Hz, 2H), 6.86 (d, *J* =

7.0 Hz, 2H), 6.49 (s, 1H), 6.25 (s, 1H), 3.61 (s, 2H), 2.28 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.84, 143.47, 136.76, 136.16, 135.72, 135.11, 135.05, 134.92, 133.88, 131.32, 128.63, 128.19, 128.16, 127.91, 127.75, 127.72, 127.21, 127.06, 126.91, 126.48, 125.77, 40.15, 20.59. HR-MS (ESI): m/z calculated for $C_{31}H_{27}NO_3S$: $[M+H]^+$: 494.1784, found: 494.1777. FTIR (KBr, cm^{-1}): 3851.07, 3606.10, 3472.55, 2922.66, 1698.63, 1574.44, 1384.20, 1157.74.



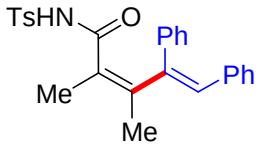
(2*Z*, 4*Z*)-2-Hexyl-4,5-diphenyl-*N*-tosylpenta-2,4-dienamide (3ia).

Following the general experiment procedure, **3ia** was obtained as a yellow solid (88%, 89 mg). M. p. = 146 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.53 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.22 (dd, *J* = 6.0, 2.5 Hz, 3H), 7.15-7.12 (m, 3H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.91 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 7.5 Hz, 2H), 6.39 (s, 1H), 6.22 (s, 1H), 2.34-2.29 (t, *J* = 7.0 Hz, 2H), 2.26 (s, 3H), 1.45-1.39 (m, 2H), 1.28-1.23 (m, 6H), 0.86 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.47, 143.57, 137.06, 136.20, 135.90, 135.04, 133.82, 133.71, 130.56, 128.65, 128.20, 127.70, 127.32, 127.01, 126.88, 126.37, 125.76, 34.40, 30.45, 27.76, 27.01, 21.50, 20.59, 13.03. HR-MS (ESI): m/z calculated for $C_{30}H_{34}NO_3S$: $[M+H]^+$: 488.2254, found: 488.2247. FTIR (KBr, cm^{-1}): 3667.30, 3605.72, 3450.97, 2950.32, 1651.72, 1505.05, 1384.23, 449.35.

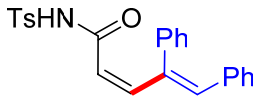


(2*Z*,4*Z*)-2-Decyl-4,5-diphenyl-*N*-tosylpenta-2,4-dienamide (3ja).

Following the general experiment procedure, **3ja** was obtained as a yellow solid (89%, 97 mg). M. p. = 180 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.61 (s, 1H), 7.69 (d, *J* = 8.0 Hz, 2H), 7.21 (dd, *J* = 6.0, 2.5 Hz, 3H), 7.14-7.12 (m, 3H), 7.08 (t, *J* = 7.5 Hz, 2H), 6.90 (d, *J* = 8.0 Hz, 2H), 6.83 (d, *J* = 7.5 Hz, 2H), 6.39 (s, 1H), 6.20 (s, 1H), 2.31 (t, *J* = 7.5 Hz, 2H), 2.25 (s, 3H), 1.45-1.39 (m, 2H), 1.23 (s, 14H), 0.88 (t, *J* = 6.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.53, 143.54, 137.09, 136.21, 135.94, 135.07, 133.83, 133.65, 130.49, 128.66, 128.22, 128.21, 127.67, 127.31, 126.98, 126.87, 126.34, 34.40, 30.88, 28.56, 28.53, 28.29, 28.11, 27.06, 21.66, 20.59, 13.11. HR-MS (ESI): m/z calculated for $C_{34}H_{41}NO_3S$: $[M+H]^+$: 544.2880, found: 544.2880. FTIR (KBr, cm^{-1}): 3626.13, 3444.44, 2922.75, 1694.37, 1384.25, 1159.81, 1083.89, 459.45.

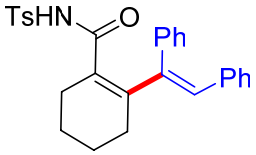


(2*Z*,4*Z*)-2,3-Mimethyl-4,5-diphenyl-*N*-tosylpenta-2,4-dienamide (3ka). Following the general experiment procedure, **3ka** was obtained as a yellow solid (30%, 25 mg). M. p. = 169 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.65 (d, *J* = 8.5 Hz, 2H), 7.26 (dd, *J* = 4.0, 2.5 Hz, 3H), 7.15-7.09 (m, 5H), 6.85 (d, *J* = 8.5 Hz, 4H), 6.30 (s, 1H), 2.20 (s, 3H), 1.98 (d, *J* = 1.0 Hz, 3H), 1.67 (d, *J* = 1.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.89, 143.95, 143.39, 141.56, 136.19, 134.91, 134.09, 128.63, 128.53, 128.49, 128.07, 127.80, 127.51, 127.18, 127.05, 126.89, 126.25, 20.57, 17.95, 15.39. HR-MS (ESI): m/z calculated for $C_{26}H_{25}NO_3S$: $[M+H]^+$: 432.1628, found: 432.1626. FTIR (KBr, cm^{-1}): 3882.07, 3500.66, 3363.34, 2358.43, 1651.52, 1557.50, 1384.19.



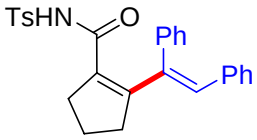
(2*Z*, 4*Z*)-4, 5-Diphenyl-*N*-tosylpenta-2,4-dienamide (3la).

Following the general experiment procedure, **3la** was obtained as a yellow solid (40%, 32 mg). M. p. = 216 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.35 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 2H), 7.41-7.32 (m, 7H), 7.29-7.26 (m, 3H), 7.17 (d, *J* = 8.5 Hz, 2H), 7.04 (dd, *J* = 9.5, 2.0 Hz, 2H), 6.08 (d, *J* = 13.0 Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 161.12, 143.60, 140.36, 138.84, 134.90, 134.82, 134.39, 132.81, 128.74, 128.30, 127.89, 127.56, 127.52, 127.32, 127.26, 125.79, 124.06, 20.63. HR-MS (ESI): m/z calculated for $C_{24}H_{21}NO_3S$: $[M+H]^+$: 404.1315, found: 404.1319. FTIR (KBr, cm^{-1}): 3850.93, 3450.69, 3416.32, 2338.40, 1651.59, 1633.83, 1557.17, 1384.19.

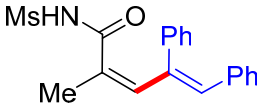


(*E*)-2-(1,2-Diphenylvinyl)-*N*-tosylcyclohex-1-ene-1-carboxamide (3ma).

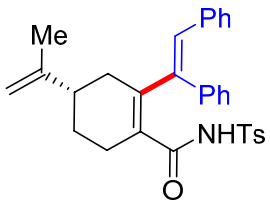
Following the general experiment procedure, **3ma** was obtained as a yellow solid (87%, 80 mg). M. p. = 168 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.74 (s, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.25 (dd, *J* = 5.5, 2.5 Hz, 3H), 7.15-7.09 (m, 5H), 6.87 (d, *J* = 8.0 Hz, 4H), 6.34 (s, 1H), 2.42-2.39 (m, 2H), 2.21 (s, 3H), 1.99-1.96 (m, 2H), 1.64-1.60 (m, 2H), 1.54-1.51 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 166.57, 145.89, 143.40, 140.98, 136.32, 134.92, 134.16, 129.19, 128.61, 128.58, 128.34, 128.09, 127.79, 127.21, 126.97, 126.92, 126.26, 28.72, 25.82, 20.93, 20.83, 20.56. HR-MS (ESI): m/z calculated for $C_{28}H_{27}NO_3S$: $[M+H]^+$: 458.1784, found: 458.1784. FTIR (KBr, cm^{-1}): 3850.08, 3444.39, 2923.28, 1682.54, 1538.71, 1545.50, 1384.23, 1164.59.



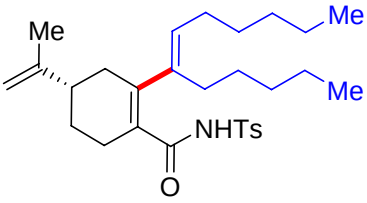
(*E*)-2-(1,2-Diphenylvinyl)-*N*-tosylcyclopent-1-ene-1-carboxamide (3na). Following the general experiment procedure, **3na** was obtained as a yellow solid (72%, 64 mg). M. p. = 225 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.69 (d, *J* = 8.5 Hz, 2H), 7.30-7.27 (m, 3H), 7.21 (dd, *J* = 5.5, 2.5 Hz, 3H), 7.16 (dd, *J* = 5.5, 2.0 Hz, 2H), 7.13 (d, *J* = 8.0 Hz, 2H), 7.05 (dd, *J* = 5.5, 2.0 Hz, 2H), 6.57 (s, 1H), 2.75 (t, *J* = 7.5 Hz, 2H), 2.51 (t, *J* = 7.5 Hz, 2H), 2.37 (s, 3H), 1.86-1.80 (m, 2H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 162.20, 153.52, 143.51, 136.77, 135.48, 134.75, 134.27, 131.86, 130.43, 128.53, 128.29, 128.01, 127.95, 127.41, 127.38, 127.31, 127.00, 38.17, 33.34, 20.58, 20.55. HR-MS (ESI): m/z calculated for $C_{27}H_{25}NO_3S$: $[M+H]^+$: 444.1628, found: 444.1631. FTIR (KBr, cm^{-1}): 3819.04, 3556.93, 3406.63, 2980.82, 1682.37, 1651.53, 1384.22.



(2*Z*,4*Z*)-2-methyl-*N*-(methylsulfonyl)-4,5-diphenylpenta-2,4-dienamide (3oa). Following the general experiment procedure, **3oa** was obtained as a colorless liquid (87%, 59 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.23-7.22 (m, 3H), 7.16-7.14 (m, 2H), 7.05 (dd, *J* = 5.0, 2.0 Hz, 3H), 6.88 (dd, *J* = 6.0, 2.0 Hz, 2H), 6.67 (s, 1H), 6.43(t, *J* = 1.0 Hz, 1H), 2.77 (s, 3H), 2.01 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 168.29, 137.66, 137.21, 136.70, 135.89, 133.53, 131.85, 129.67, 129.44, 128.90, 128.23, 128.21, 127.75, 41.17, 21.45. HR-MS (ESI): m/z calculated for $C_{19}H_{19}NO_3S$: $[M+H]^+$: 342.1158, found: 342.1157. FTIR (KBr, cm^{-1}): 3851.09, 3673.66, 3520.95, 3444.80, 2980.82, 2340.50, 1651.72, 1384.28.

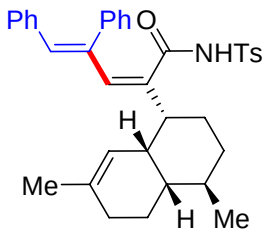


(*S*,*E*)-2-(1,2-Diphenylvinyl)-4-(prop-1-en-2-yl)-*N*-tosylcyclohex-1-ene-1-carboxamide (3pa). Following the general experiment procedure, **3pa** was obtained as a yellow solid (96%, 95 mg). M. p. = 145 °C. ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.52 (s, 1H), 7.64 (d, *J* = 8.5 Hz, 2H), 7.28-7.29 (m, 3H), 7.13-7.18 (m, 5H), 6.90-6.93 (m, 4H), 6.36 (s, 1H), 4.68 (s, 1H), 4.60 (s, 1H), 2.59-2.63 (m, 1H), 2.37-2.43 (m, 1H), 2.24 (s, 3H), 2.08-2.14 (m, 2H), 1.93-1.98 (m, 1H), 1.86-1.89 (m, 1H), 1.63 (s, 3H), 1.43-1.46 (m, 1H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.87, 147.01, 146.00, 143.47, 140.42, 135.82, 134.66, 134.08, 129.35, 128.76, 128.59, 128.23, 128.10, 127.99, 127.37, 127.27, 127.07, 126.55, 108.59, 39.39, 34.19, 26.12, 25.76, 20.58, 19.63. HR-MS (ESI): m/z calculated for $C_{31}H_{31}NO_3S$: $[M+H]^+$: 498.2097, found: 498.2103. FTIR (KBr, cm^{-1}): 3850.91, 3742.22, 3646.11, 3626.54, 2358.43, 2340.31, 1651.53, 1402.76, 1385.09.



(*S*,*E*)-2-(Dodec-6-en-6-yl)-4-(prop-1-en-2-yl)-*N*-tosylcyclohex-1-ene-1-carboxamide (3pg).

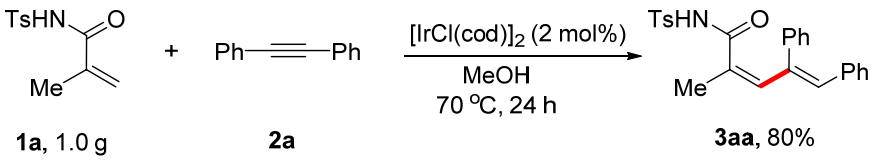
Following the general experiment procedure, **3pg** was obtained as a yellow liquid (71%, 69 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.81 (s, 1H), 7.93-7.95 (m, 2H), 7.31 (d, *J* = 8.0 Hz, 2H), 5.40 (t, *J* = 7.5 Hz, 1H), 4.75 (t, *J* = 1.5 Hz, 1H), 4.69 (s, 1H), 2.47-2.51 (m, 1H), 2.43 (s, 3H), 2.21-2.27 (m, 1H), 2.05-2.12 (m, 5H), 1.96-2.02 (m, 1H), 1.81-1.85 (m, 1H), 1.72 (s, 3H), 1.20-1.45 (m, 14H), 0.92 (t, *J* = 7.0 Hz, 3H), 0.87 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 165.14, 148.13, 147.31, 143.71, 140.91, 134.89, 130.47, 128.35, 127.53, 125.74, 108.43, 39.69, 37.49, 30.99, 30.69, 30.38, 27.92, 27.21, 26.96, 25.80, 25.16, 21.50, 21.27, 20.62, 19.67, 13.01, 12.97. HR-MS (ESI): m/z calculated for $C_{29}H_{43}NO_3S$: $[M+H]^+$: 486.3036, found: 486.3041. FTIR (KBr, cm^{-1}): 3626.50, 3564.48, 3175.23, 2358.03, 1651.51, 1557.22, 1455.26, 1402.64, 1385.10.



(2*E*,4*Z*)-2-((1R,4R,4aS,8aR)-4,7-Dimethyl-1,2,3,4,4a,5,6,8a-octahydronaphthalen-1-yl)-4,5-diphenyl-*N*-tosylpenta-2,4-dienamide (3qa).

Following the general experiment procedure, **3qa** was obtained as a yellow liquid (86%, 97 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.43 (s, 1H), 7.67 (d, *J* = 8.5 Hz, 2H), 7.24-7.26 (m, 3H), 7.12-7.18 (m, 3H), 7.07 (t, *J* = 7.5 Hz, 2H), 6.81-6.86 (dd, *J* = 8.5 Hz, *J* = 19.0 Hz, 4H), 6.38 (s, 1H), 6.05 (s, 1H), 5.10 (s, 1H), 2.66 (d, *J* = 12.5 Hz, 1H), 2.38 (s, 1H), 2.24 (s, 3H), 1.82-1.89 (m, 2H), 1.71-1.75 (m, 1H), 1.64-1.67 (m, 1H), 1.59 (s, 3H), 1.41-1.47 (m, 2H), 1.33-1.37 (m, 1H), 1.24-1.31 (m, 2H), 0.98-1.03 (m, 1H), 0.85 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 167.09, 143.49, 139.14, 137.35, 136.08, 135.13, 134.86, 133.67, 132.61, 130.21, 128.67, 128.31, 128.08, 127.72, 127.37, 127.02, 126.84, 126.27, 118.44, 44.47, 40.21, 36.84, 34.00, 26.43, 25.32, 24.50, 24.19, 22.90, 20.59, 18.61. HR-MS (ESI): m/z calculated for $C_{36}H_{39}NO_3S$: $[M+H]^+$: 566.2723, found: 566.2715. FTIR (KBr, cm^{-1}): 3850.91, 3646.03, 3224.94, 1682.37, 1667.42, 1422.72, 1403.10, 1345.58, 1156.85, 1120.77, 1087.78.

Gram-Scale Synthesis of 3aa

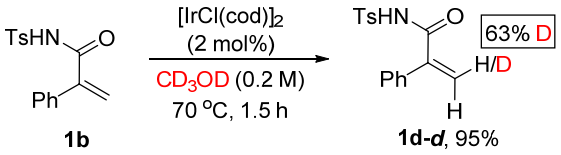


1a, 1.0 g **2a** **3aa**, 80%

An oven-dried vial was charged with $[Ir(cod)Cl]_2$ (56.2 mg, 2 mol%), MeOH (21 mL). Then, alkyne **2a** (1.12 g, 6.27 mmol) and acrylamide **1a** (1.00 g, 4.18 mmol) were added into the solution in sequence. The vial was sealed under argon and heated to 70 ℃ with stirring for 24 hours. After cooling down, the mixture was directly applied to a flash column chromatography (EtOAc/petroleum ether mixtures). The desires product **3aa** was obtained as a yellow solid (1.40 g, 80%).

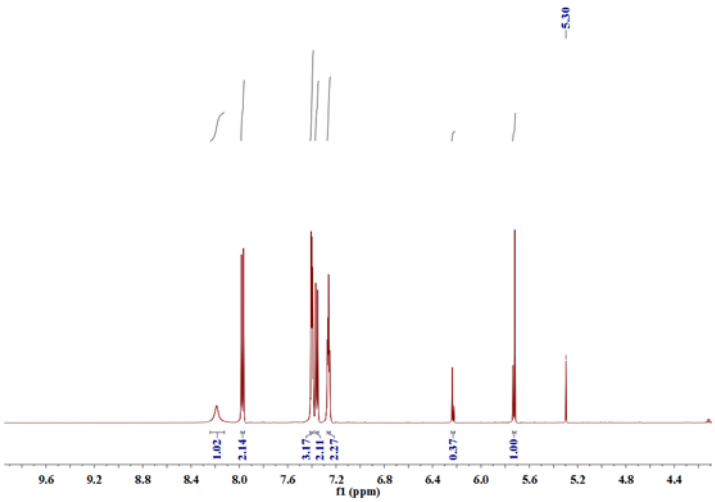
Deuterium-Labeled Experiments

H/D Exchange in 1b

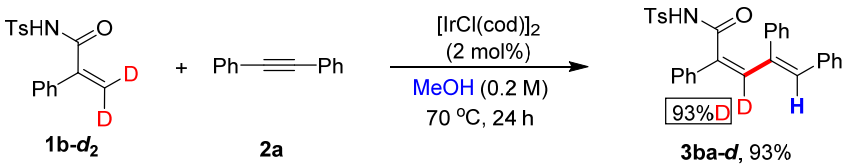


1b **1d-*d***, 95%

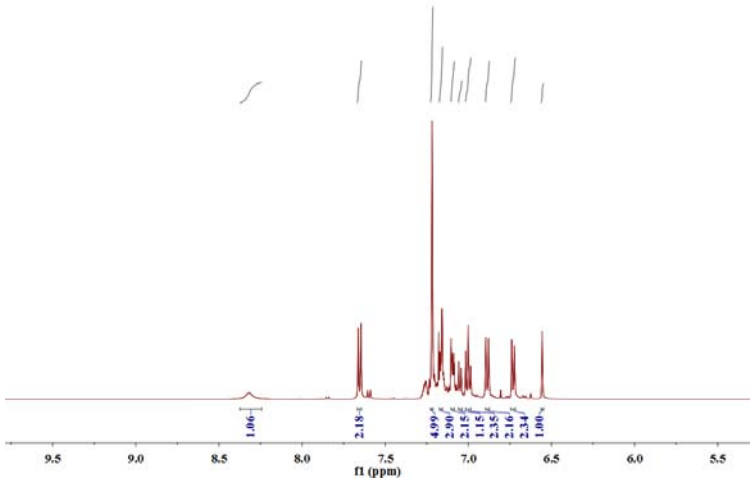
An oven-dried vial was charged with $[Ir(cod)Cl]_2$ (1.3 mg, 2 mol%), acrylamide **1b** (60.3 mg, 0.2 mmol) and CD_3OD (1 mL). The vial was sealed under argon and heated to 70 ℃ with stirring for 1.5 hours. After cooling down, the mixture was directly applied to a flash column chromatography (EtOAc/petroleum ether mixtures) on silica gel to afford acrylamide **1d-*d*** (57.3 mg, 95% recovered). The D % of **1b-*d*** was estimated by ^1H NMR.

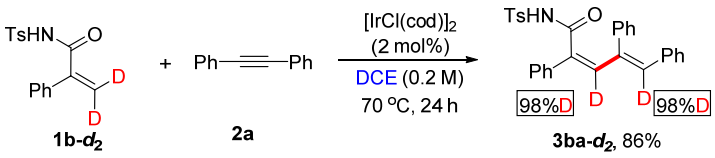


Selective Deuterium-Labeled Synthesis

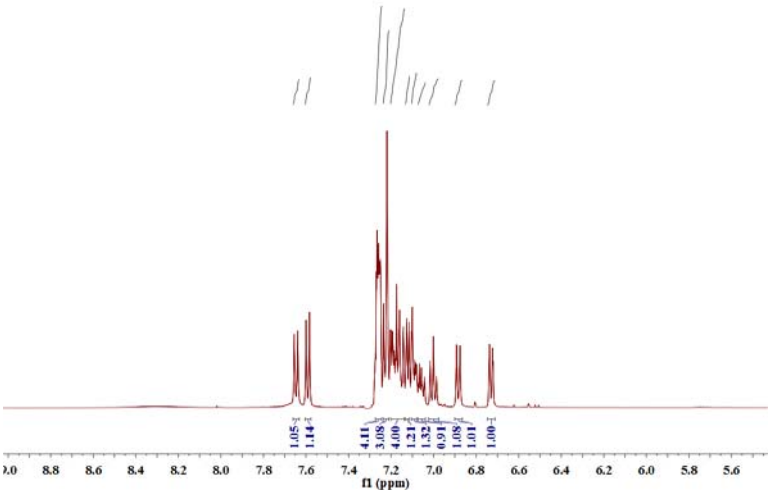


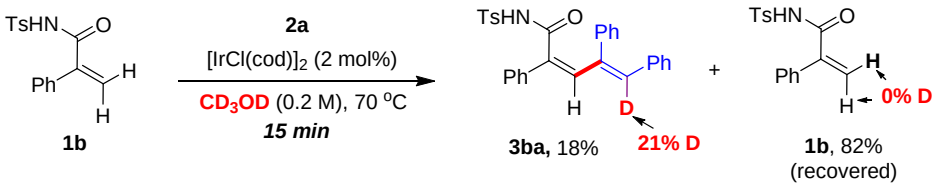
A 10 mL vial was charged with $[Ir(cod)Cl]_2$ (1.4 mg, 2 mol%), MeOH (1 mL). Then, alkyne **2a** (26.8 mg, 0.3 mmol**)** and acrylamide **1b-*d*$_2$** (30.4 mg, 0.1 mmol) were added into the solution in sequence. The vial was sealed under Ar and heated to 70 ℃ with stirring for 24 h. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography, affording the product **3ba-*d*** as a yellow solid (44.9 mg, 93%).



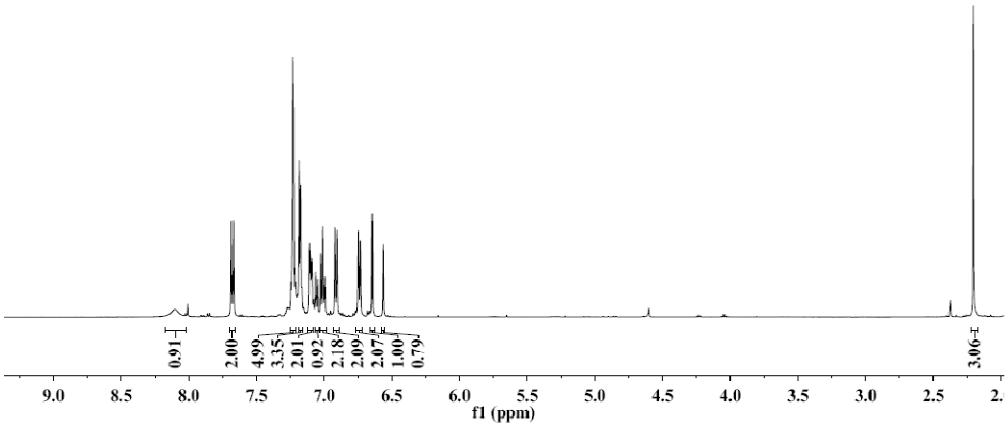


A 10 mL vial was charged with $[Ir(cod)Cl]_2$ (1.4 mg, 2 mol%), DCE (1 mL). Then, alkyne **2a** (26.8 mg, 0.15 mmol**)** and acrylamide **1b-*d*$_2$** (30.4 mg, 0.1 mmol) were added into the solution in sequence. The vial was sealed under Ar and heated to 70 ℃ with stirring for 24 hours. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography, affording the product **3ba-*d*$_2$** as a yellow solid (41.4 mg, 86%).

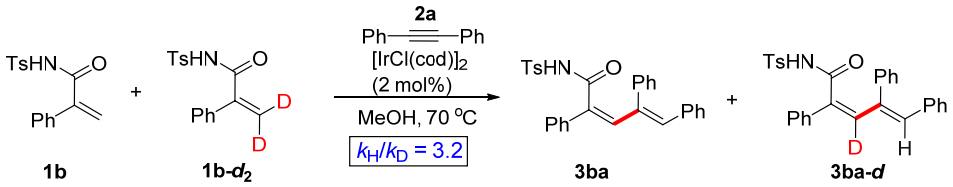




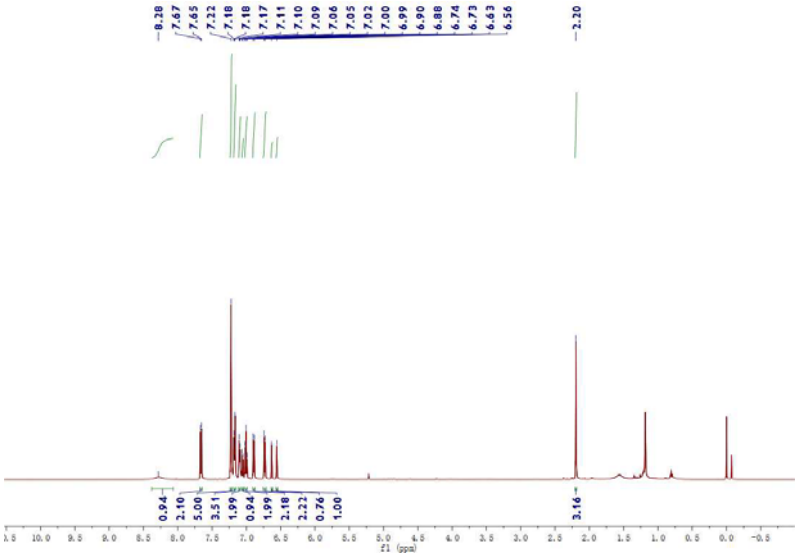
A 10 mL vial was charged with $[Ir(cod)Cl]_2$ (2.8 mg, 2 mol%), alkyne **2a** (107.0 mg, 0.3 mmol**)**, MeOH (1.0 mL). Then, acrylamide **1b** (60.4 mg, 0.2 mmol) awere added into the solution in sequence. The vial was sealed under Ar and heated to 70 ℃ with stirring for 15 min. After cooling down, the mixture was directly applied to column chromatography for separation. The D% incorporation of product and recovered starting material were determined by ^{1}H NMR.



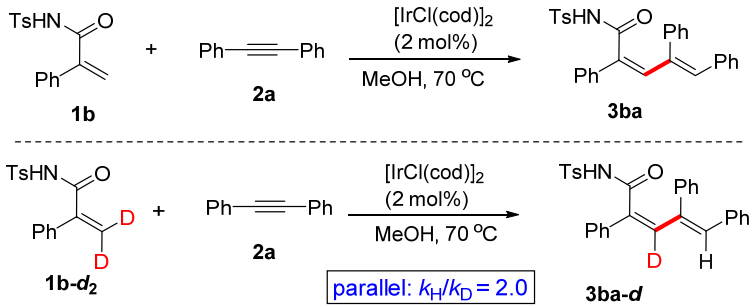
Competitive KIE Experiments with 1b and 1b-d_2



A 10 mL vial was charged with $[Ir(cod)Cl]_2$ (1.4 mg, 2 mol%), alkyne **2a** (53.5 mg, 0.15 mmol**)**, MeOH (1.0 mL). Then, acrylamide **1b** (30.2 mg, 0.1 mmol) and **1b-*d*$_2$** (30.4 mg, 0.1 mmol) were added into the solution in sequence. The vial was sealed under Ar and heated to 70 ℃ with stirring for 0.5 hours. After cooling down, the mixture was directly applied to column chromatography for separation. The ratio of **3ba**/**3ba-*d*** (22.5 mg, 23% yield) was determined to be 3.2 by ^{1}H NMR.



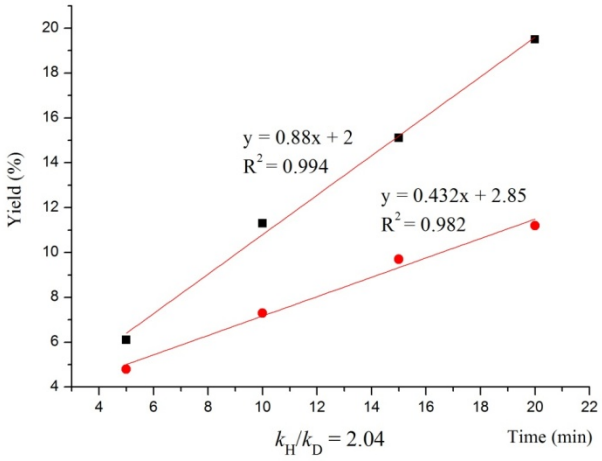
Parallel KIE Experiments with 1b and 1b-d_2



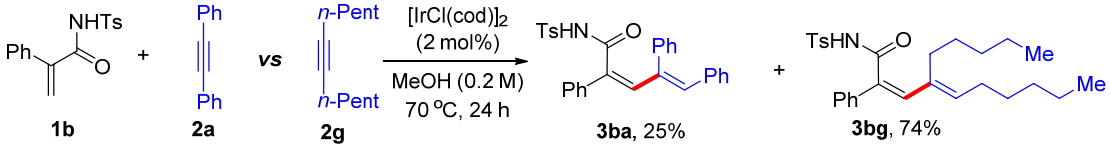
Parallel independent reactions of **1b**/**1b-d$_2$** with **2a** were performed to determine the corresponding KIE value. Each 10 mL vials was charged with $[Ir(cod)Cl]_2$ (1.4 mg, 2.0 mol %), MeOH (1 mL). Then, alkyne **2a** (26.8 mg, 0.15 mmol**)** and acrylamide **1b** (30.2 mg, 0.1 mmol) or **1b-*d*$_2$** (30.4 mg, 0.1 mmol) were added into the solution in sequence. The vial was sealed under Ar and heated to 70 ℃ with stirring for 5, 10, 15 or 20 minutes. After cooling down, the mixture was concentrated in vacuo and

purified by column chromatography, affording the product **3ba** or **3ba-d_2**. The KIE value was determined to be 2.0.

t/min. / yield	5	10	15	20
3ba	6.1%	11.3%	15.1%	19.5%
3ba-d_2	4.8%	7.3%	9.7%	11.2%

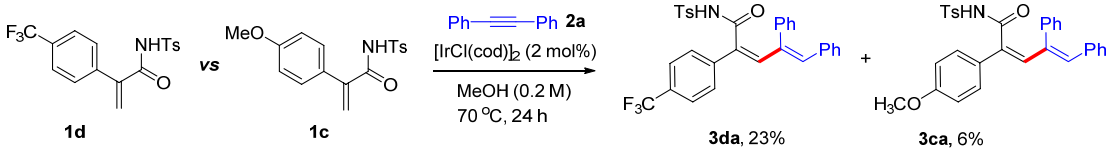


Competitive Reaction of Different Alkynes 2



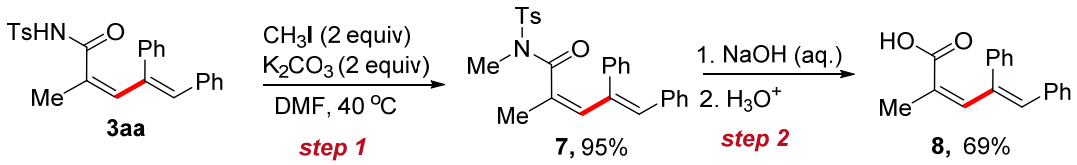
A 10 mL vial was charged with $[Ir(cod)Cl]_2$ (2.7 mg, 2 mol%), MeOH (1 mL). Then, diphenylacetylene **2a** (35.6mg, 0.2 mmol**)**, dodec-6-yne **2g** (33.3mg, 0.2 mmol) and acrylamide **1b** (60.3mg, 0.2 mmol) were added into the solution in sequence. The vial was sealed under Ar and heated to 70 ℃ with stirring for 24 hour. After cooling down, the mixture was separated by column chromatography to afford the product **3ba** (23.9 mg, 25%) and **3bg** (68.8 mg, 74%).

Competitive Reaction of Different Acrylamides 1



A 10 mL vial was charged with $[Ir(cod)Cl]_2$ (2.7 mg, 2 mol%), MeOH (1 mL). Then, alkyne **2a** (53.5 mg, 0.3 mmol**)**, acrylamide **1d** (73.9 mg, 0.2 mmol) and **1c** (66.2 mg, 0.2 mmol) were added into the solution in sequence. The vial was sealed under Ar and heated to 70 ℃ with stirring for 24 hours. After cooling down, the mixture was concentrated in vacuo and purified by column chromatography to afford the product **3da** (24.4 mg, 23%) and **3ca** (7.2 mg, 6%).

Amide Group Removal



Step 1: K_2CO_3 (27.7 mg, 0.2 mmol) and iodomethane (28.4 mg, 0.2 mmol) were added to a stirred solution of diene **3aa** (0.1 mmol) in DMF (1.0 ml). After stirring at 40 ℃ for 3 hours, the solution was evaporated, diluted with water (10 mL) and the resulting mixture was extracted with ethyl acetate (3 x 20 mL). The combined organic layers were dried over Na_2SO_4, filtrated and evaporated. The crude product was purified by flash column chromatography using petroleum ether/ethyl acetate = 30:1 as the eluent to give product **7** as a yellow oil (95%, 41 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.71 (d, *J* = 8.5 Hz, 2H), 7.22-7.19 (m, 3H), 7.08 – 7.03 (m, 7H), 6.77 – 6.76 (m, 2H), 6.45 (s, 1H), 6.17 (s, 1H), 3.11 (s, 3H), 2.31 (s, 3H), 2.05 (d, *J* = 1.5 Hz, 3H).

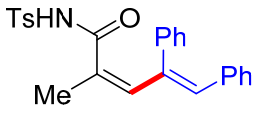
Step 2: To a solution of compound **7** (41 mg, 0.095 mmol) in 1,4-dioxane (2.5 mL) was added NaOH (6 M, 2.5 mL). The mixture was heated to 60 ℃ with stirring for 16 hours. After cooling to room temperature, the solution was concentrated, diluted with water (10 mL), acidified with HCl (3 M) and extracted with ethyl acetate (2 x10 mL). The combined organic layers were dried over Na_2SO_4, filtrated and evaporated. The crude product was purified by flash column chromatography using petroleum ether/ethyl acetate = 10:1 as the eluent to give the product **8** as a colorless oil (69%, 17.3 mg). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.11-7.08 (m, 5H), 7.02-7.00 (m, 3H), 6.89-6.87 (m, 2H), 6.54 (s, 1H), 6.37 (t, *J* = 1.5 Hz, 1H), 1.94 (d, *J* = 1.5 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$): δ = 173.63, 137.72, 137.56, 137.08, 135.61, 130.31, 128.66, 128.46, 128.18, 127.27, 126.90, 126.46, 126.05, 20.13. HR-MS (ESI): m/z calculated for $C_{18}H_{16}NO_2S$: $[M+H]^+$: 265.1223, found: 265.1221. FTIR (KBr, cm^{-1}): 3794.03, 3500.17, 3444.85, 2922.17, 1621.50, 1384.30, 1258.86, 1026.75.

References

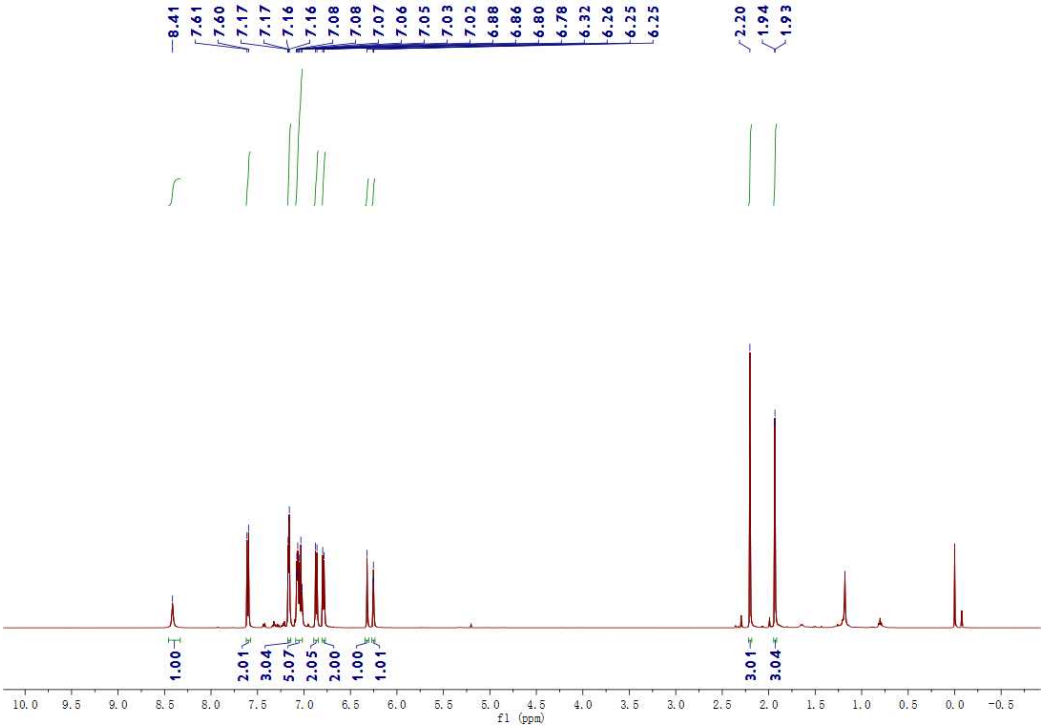
1. K. Meng, J. Zhang, F. Li, Z. Lin, K. Zhang, G. Zhong, *Org. Lett*. **2017**, *19*, 2498.

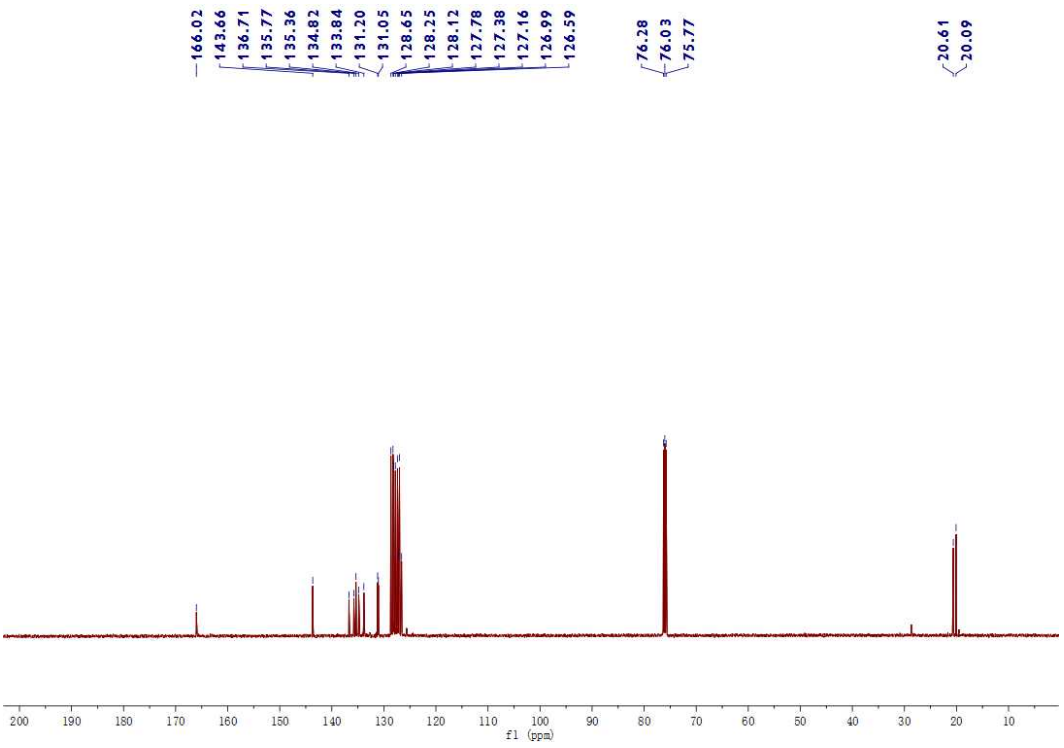
2. C. Feng, D. Feng, T. P. Loh, *Chem. Commun*. **2015**, *51*, 342.

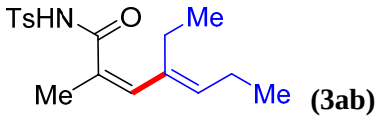
NMR Spectra



(3aa)



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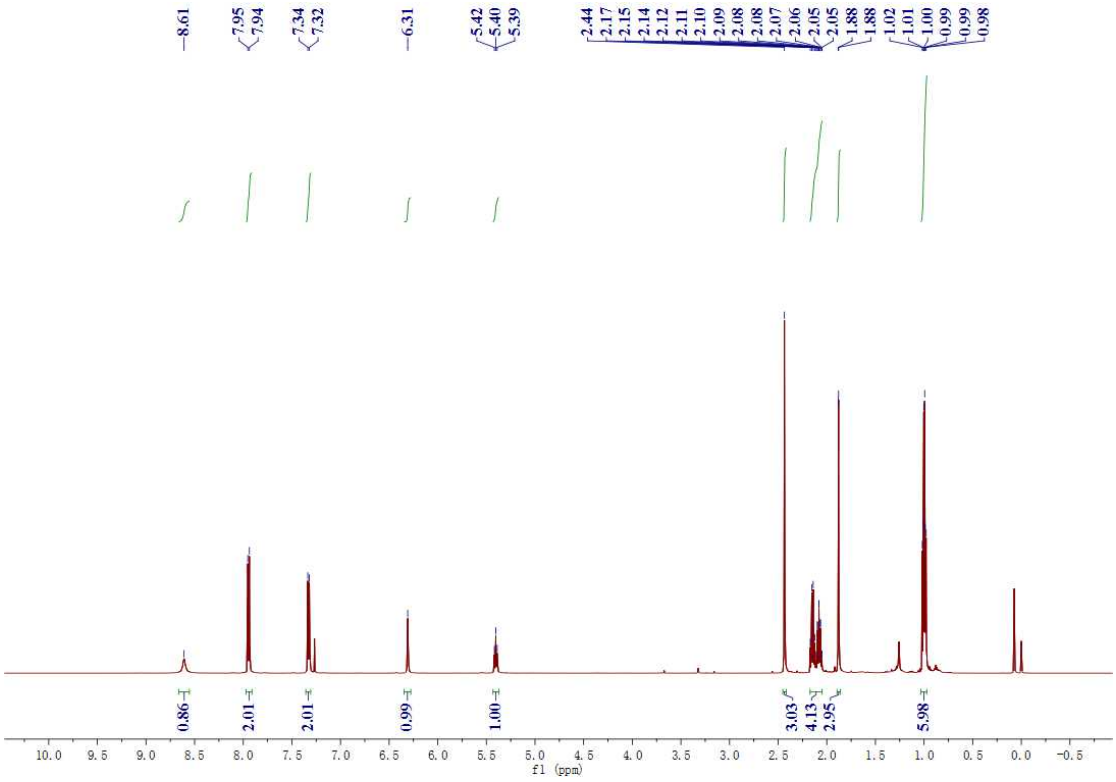
Me
Me
Me

(3ab)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2.08
2.08
2.07
2.06
2.05
2.05
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1.88
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1.01
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0.99
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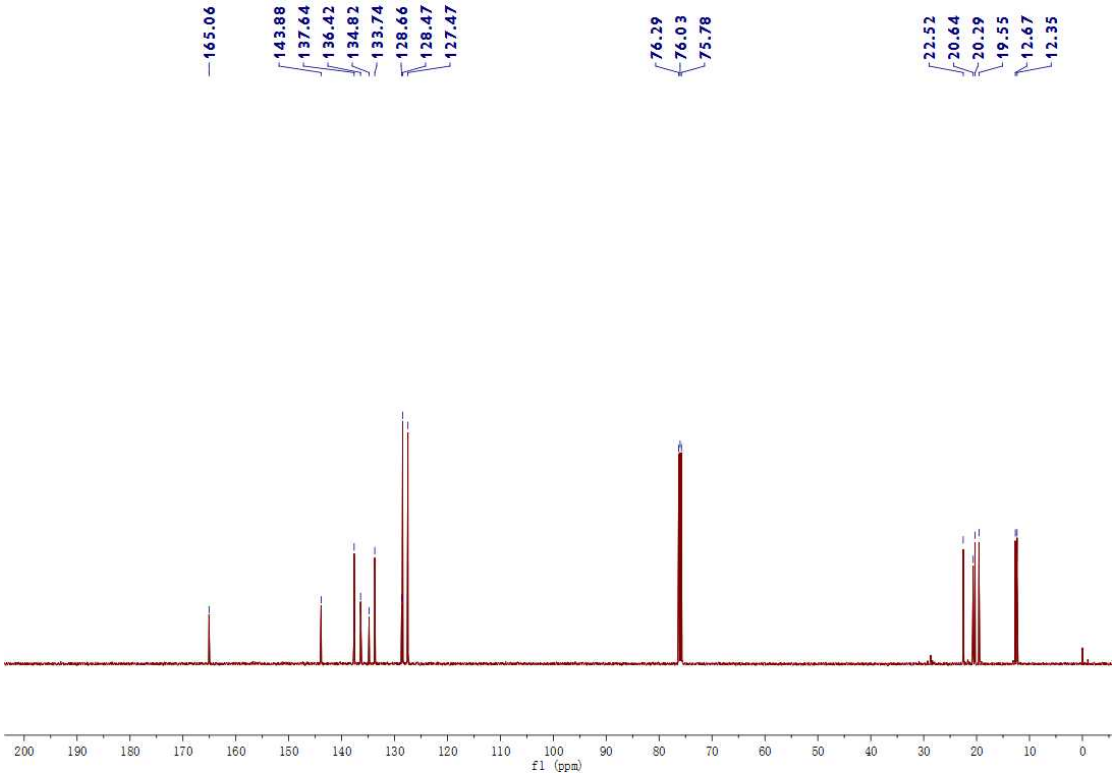
f1 (ppm)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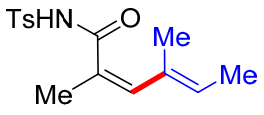
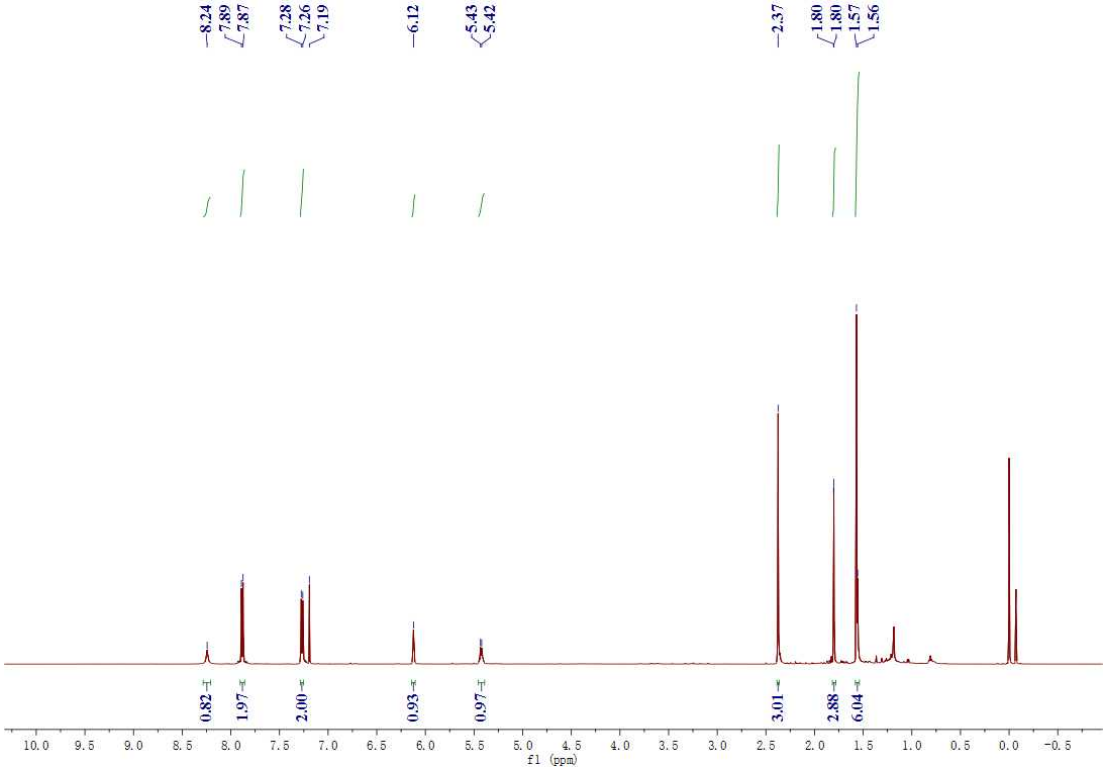
12.35
f1 (ppm)


TsHN
O
Me
Me
Me

(3ac)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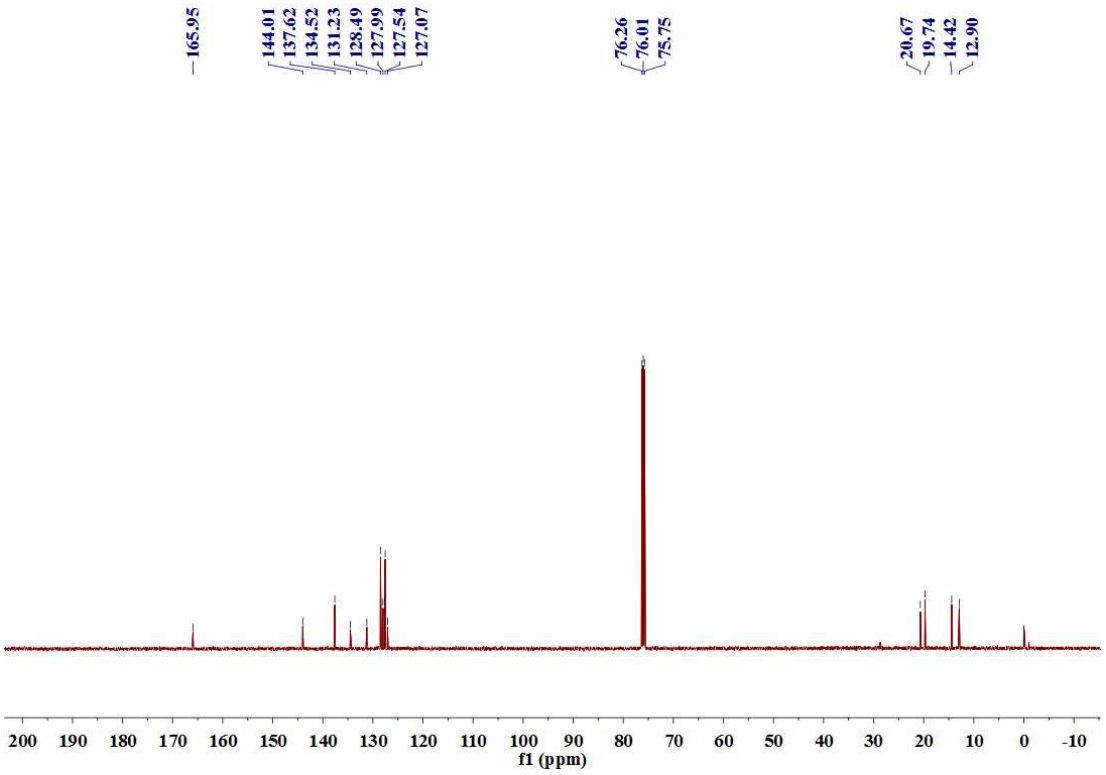
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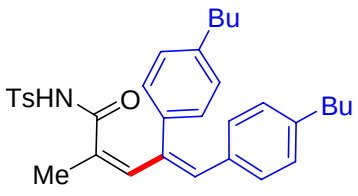
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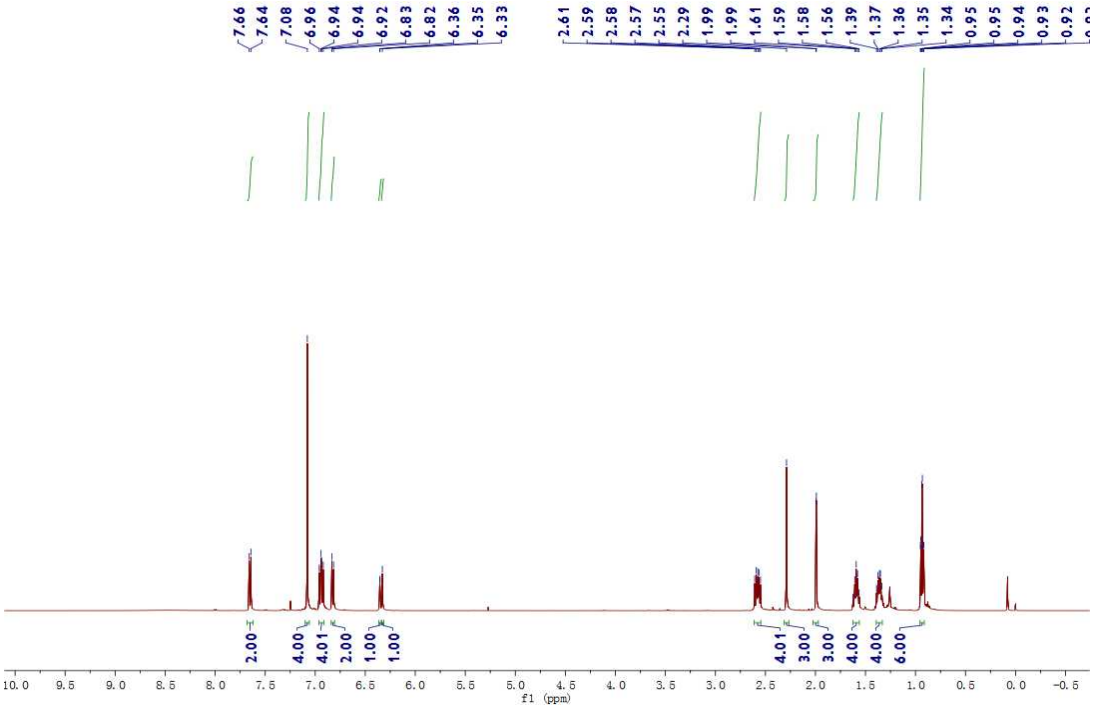
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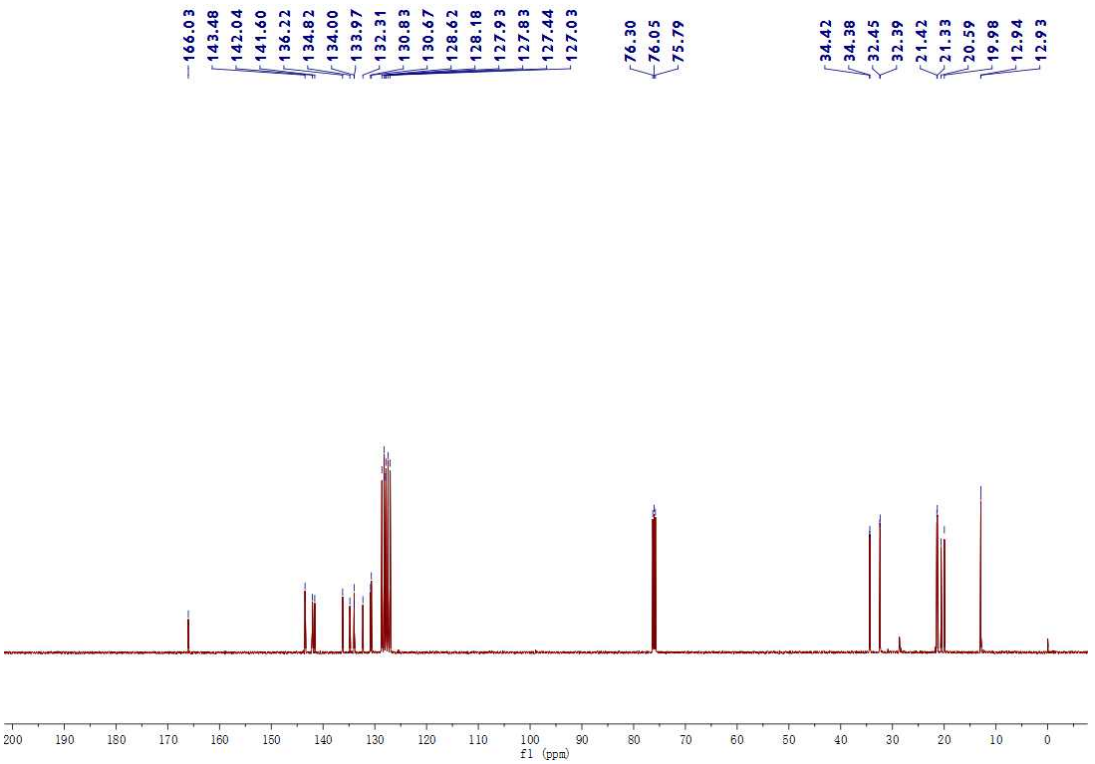
f1 (ppm)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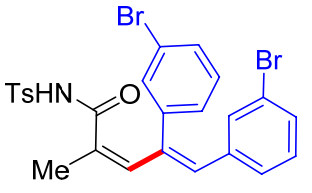
f1 (ppm)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Br
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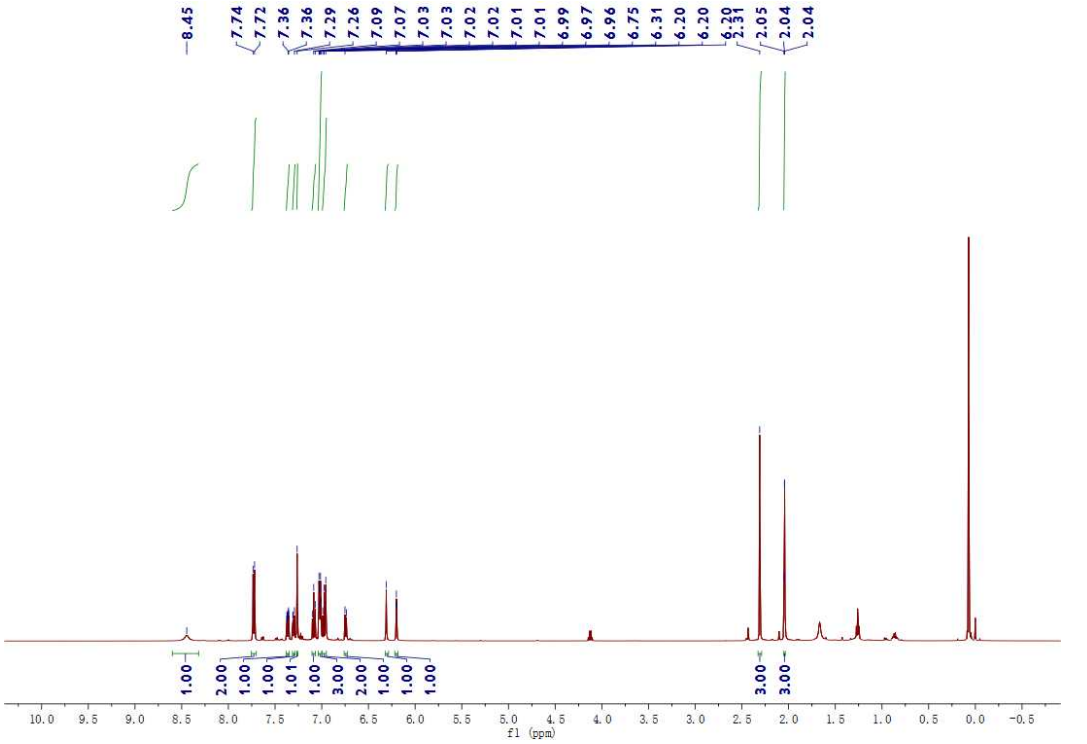
O
Me

(3ae)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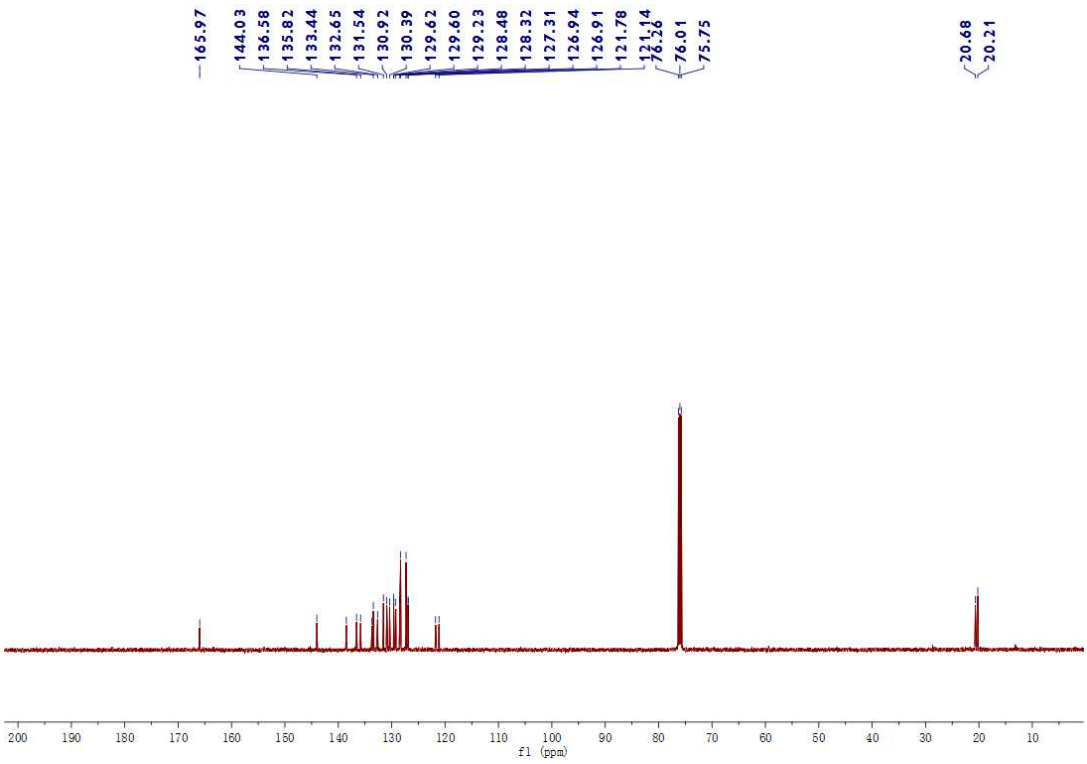
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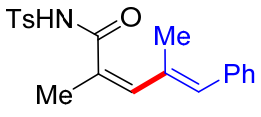
TsHN
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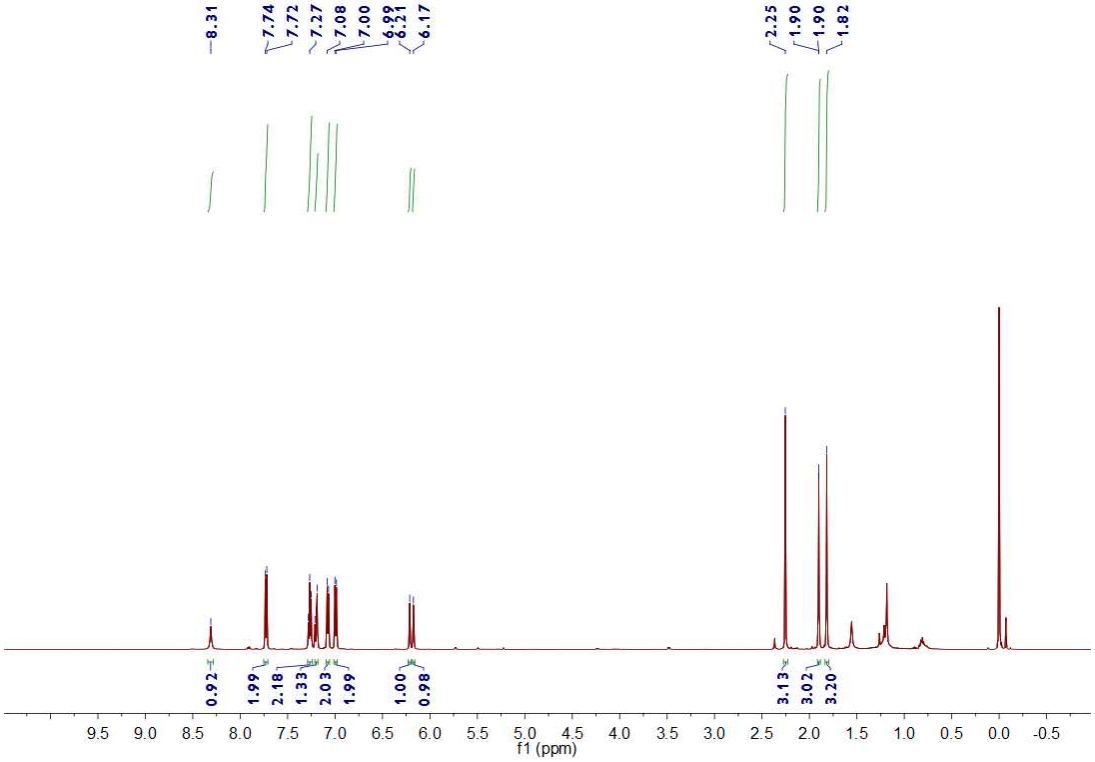
Ph
Me

(3af)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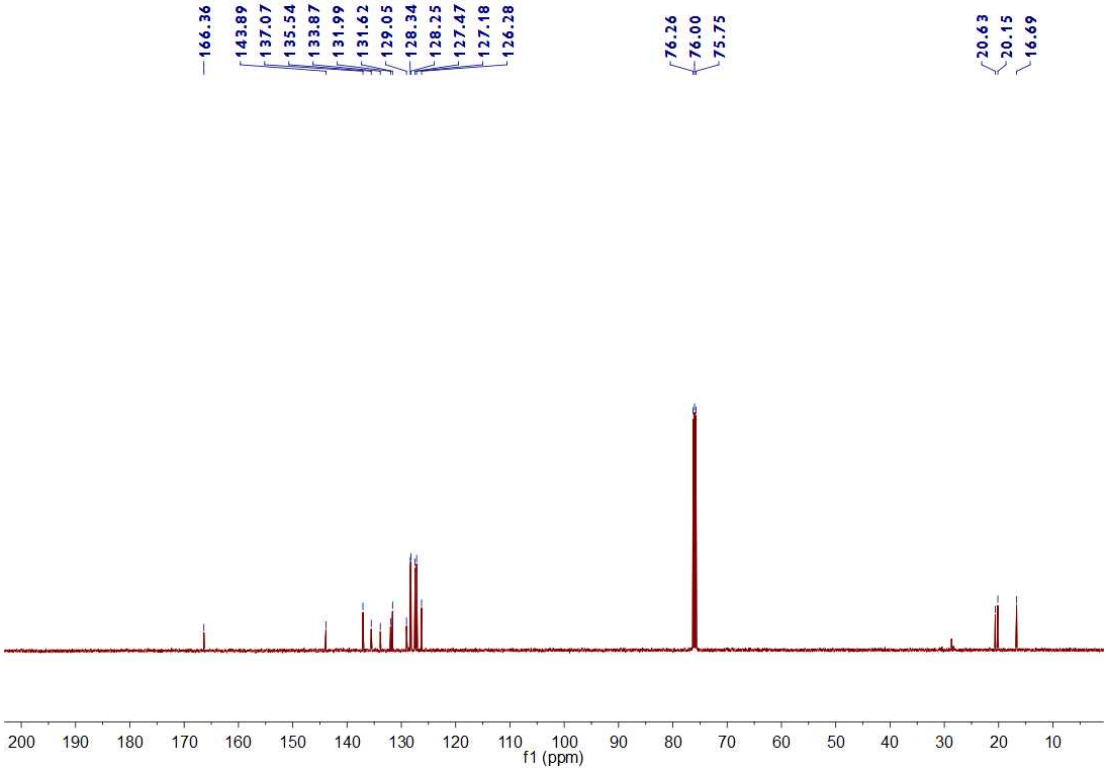
3.13
3.02
3.20
f1 (ppm)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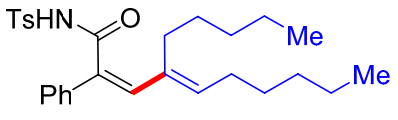
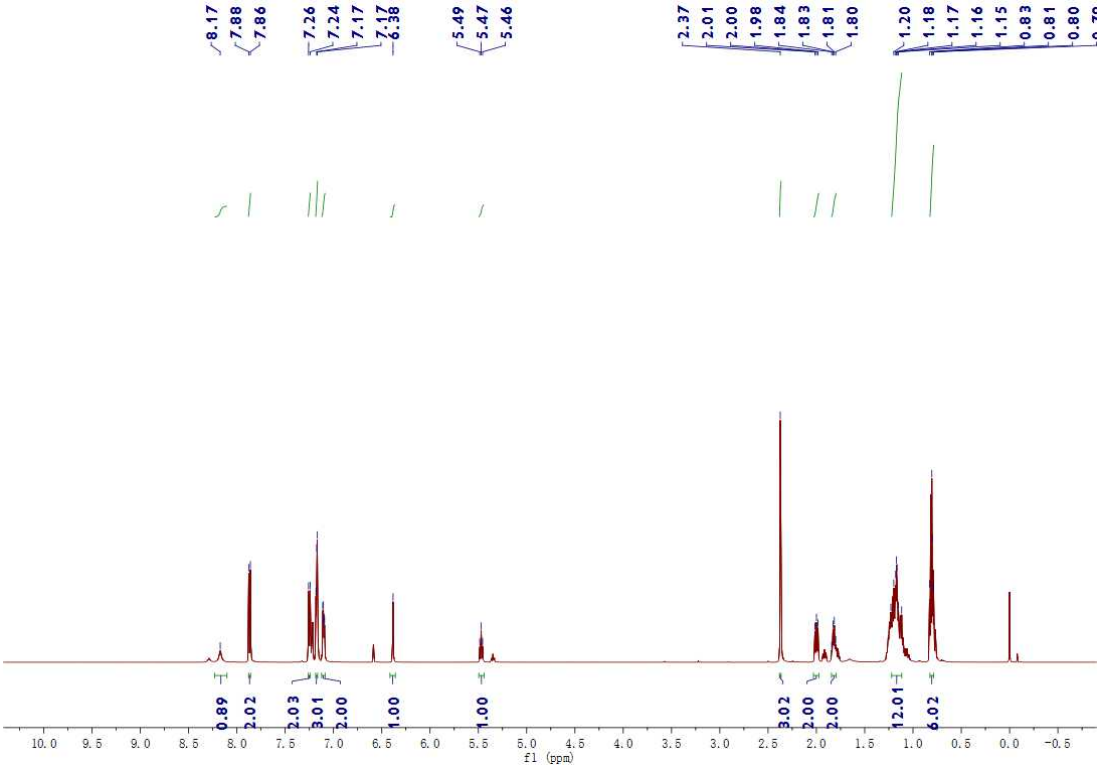
143.89
137.07
135.54
133.87
131.99
131.62
129.05
128.34
128.25
127.47
127.18
126.28
76.26
76.00
75.75
20.63
20.15
16.69
f1 (ppm)


TsHN
O
Me
Me
Ph

(3bg)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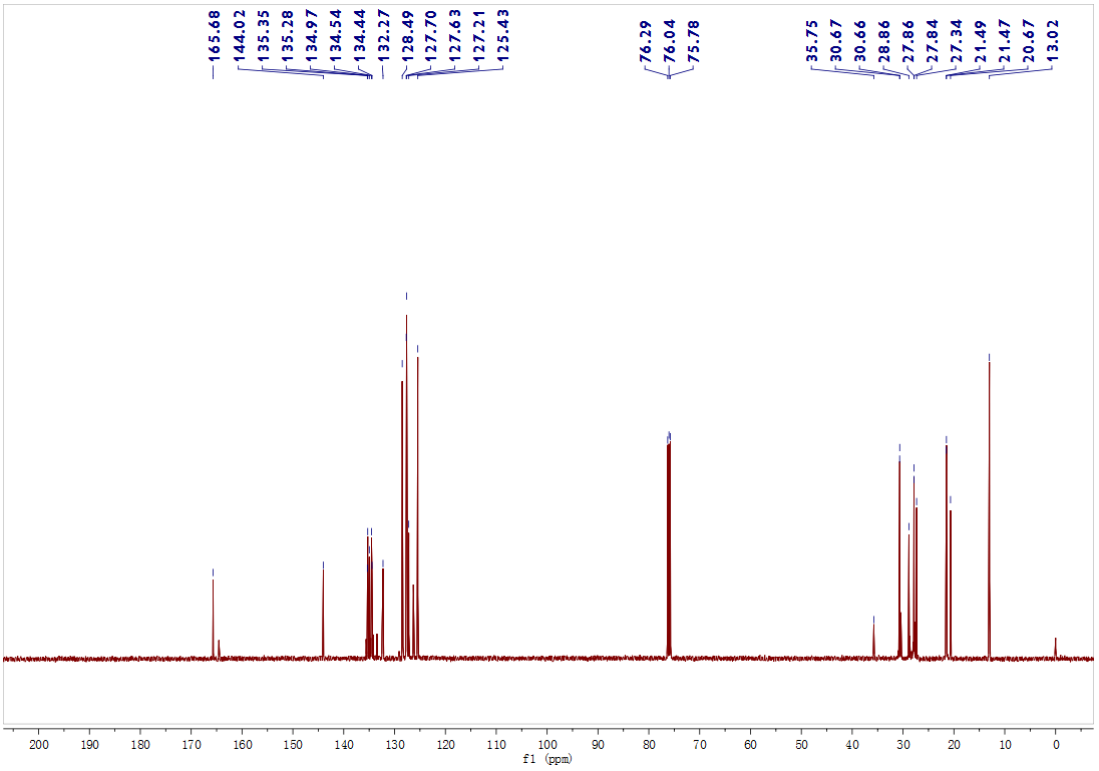
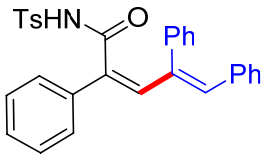
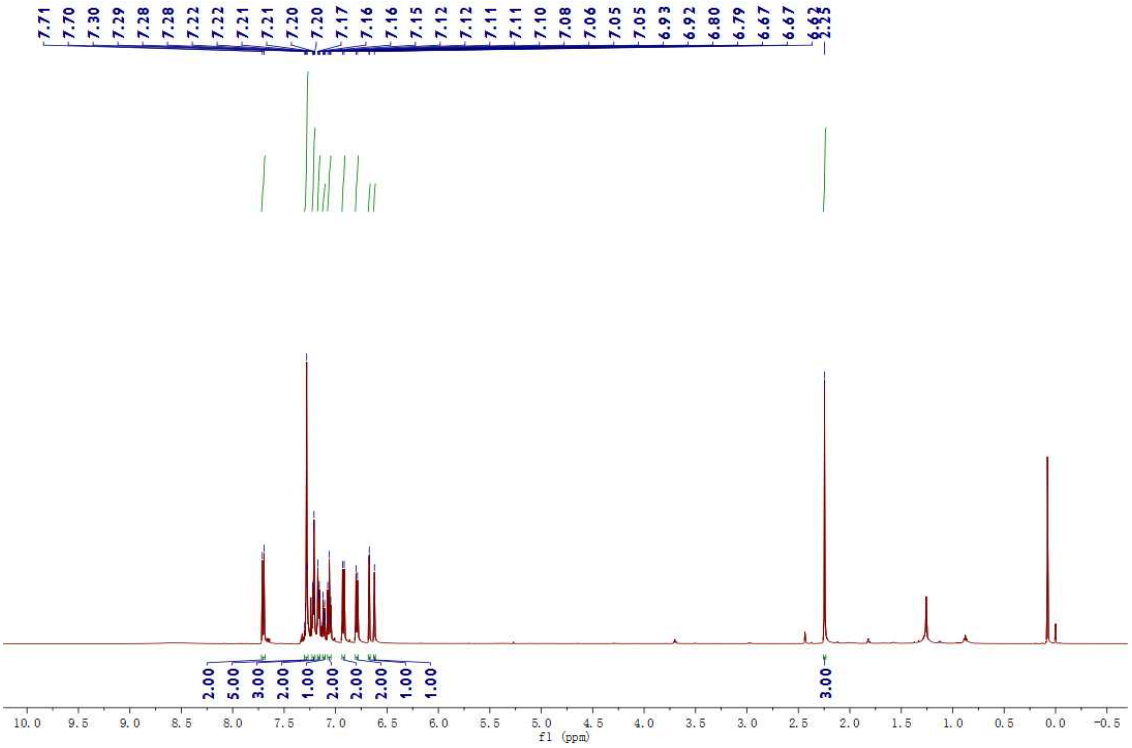
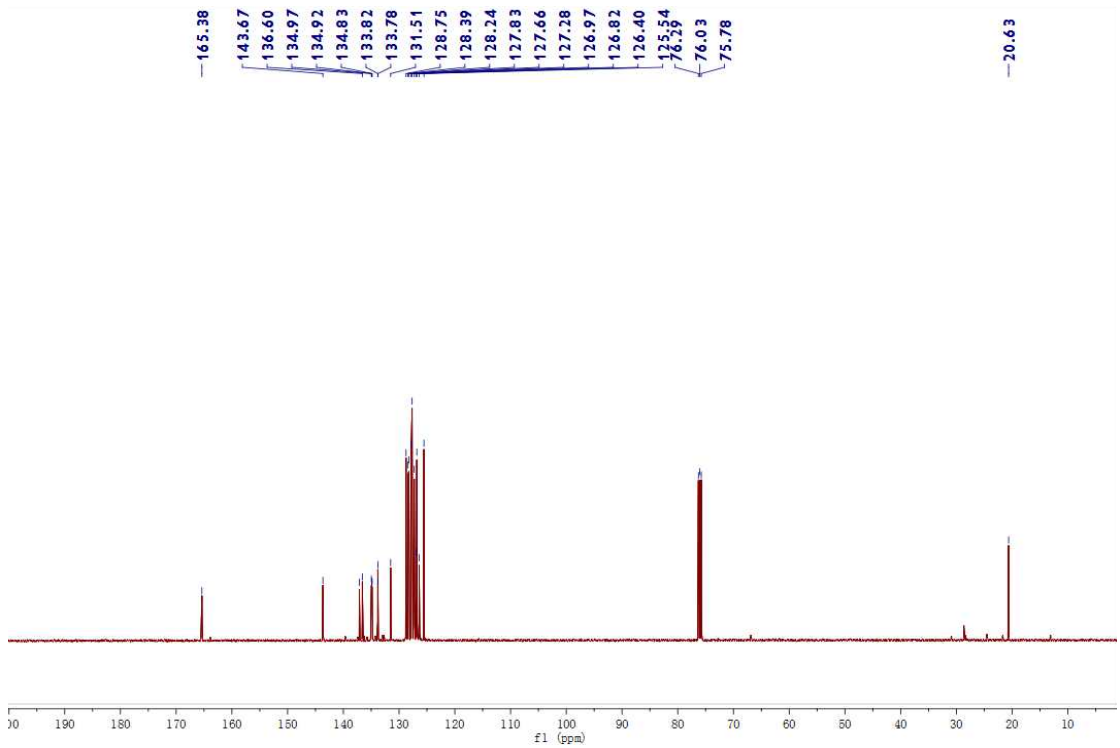
7.86
7.26
7.24
7.17
7.17
6.38
5.49
5.47
5.46
2.37
2.01
2.00
1.98
1.84
1.83
1.81
1.80
1.20
1.18
1.17
1.16
1.15
0.83
0.81
0.80
0.89
2.02
2.03
3.01
2.00
1.00
1.00
3.02
2.00
2.00
12.01
6.02
f1 (ppm)

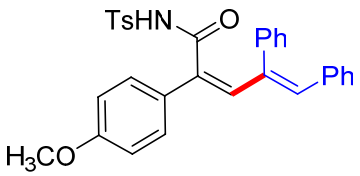

165.68
144.02
135.35
135.28
134.97
134.54
134.44
132.27
128.49
127.70
127.63
127.21
125.43
76.29
76.04
75.78
35.75
30.67
30.66
28.86
27.86
27.84
27.34
21.49
21.47
20.67
13.02
f1 (ppm)


TsHN
O
Ph
Ph

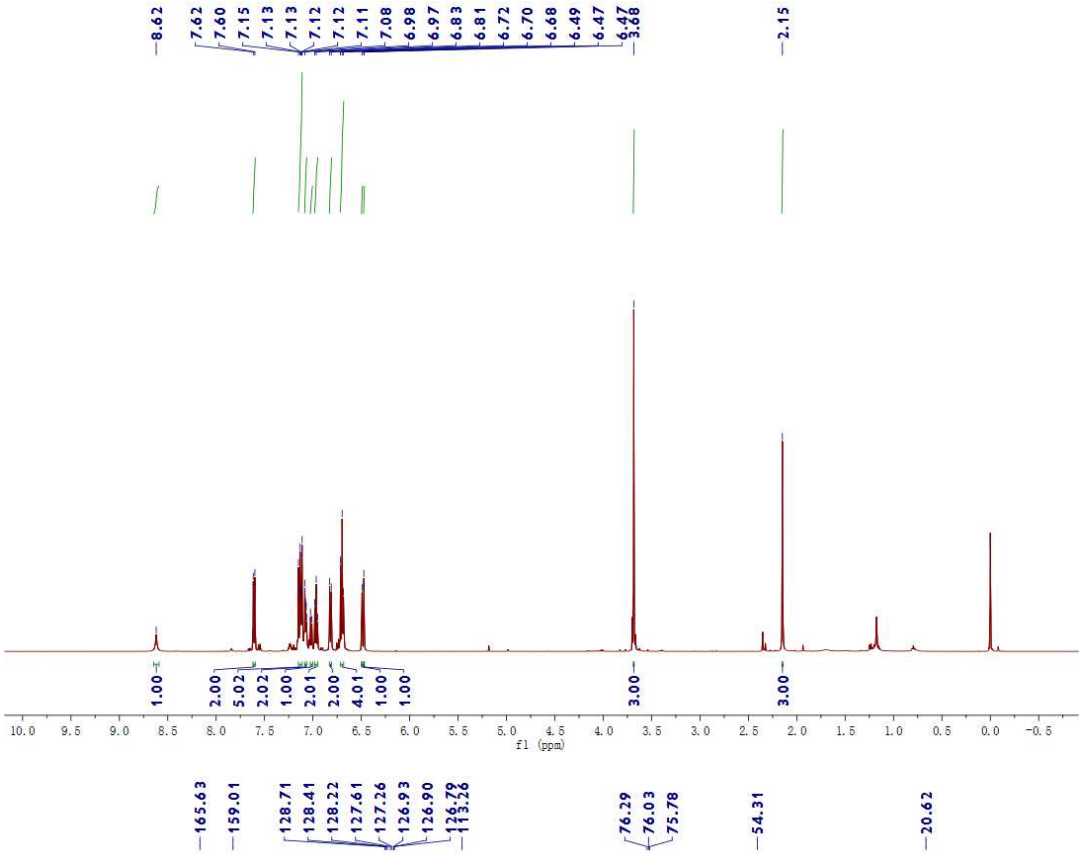
(3ba)


7.71 7.70 7.30 7.29 7.28 7.28 7.22 7.22 7.21 7.21 7.20 7.20 7.17 7.16 7.16 7.15 7.12 7.12 7.11 7.11 7.10 7.08 7.06 7.05 7.05 6.93 6.92 6.80 6.79 6.67 6.67 6.62 2.25
2.00 5.00 3.00 2.00 1.00 2.00 2.00 2.00 1.00 1.00 3.00
f1 (ppm)


165.38 143.67 136.60 134.97 134.92 134.83 133.82 133.78 131.51 128.75 128.39 128.24 127.83 127.66 127.28 126.97 126.82 126.40 125.54 76.29 76.03 75.78 20.63
f1 (ppm)


TsHN
O
Ph
Ph
H3CO

(3ca)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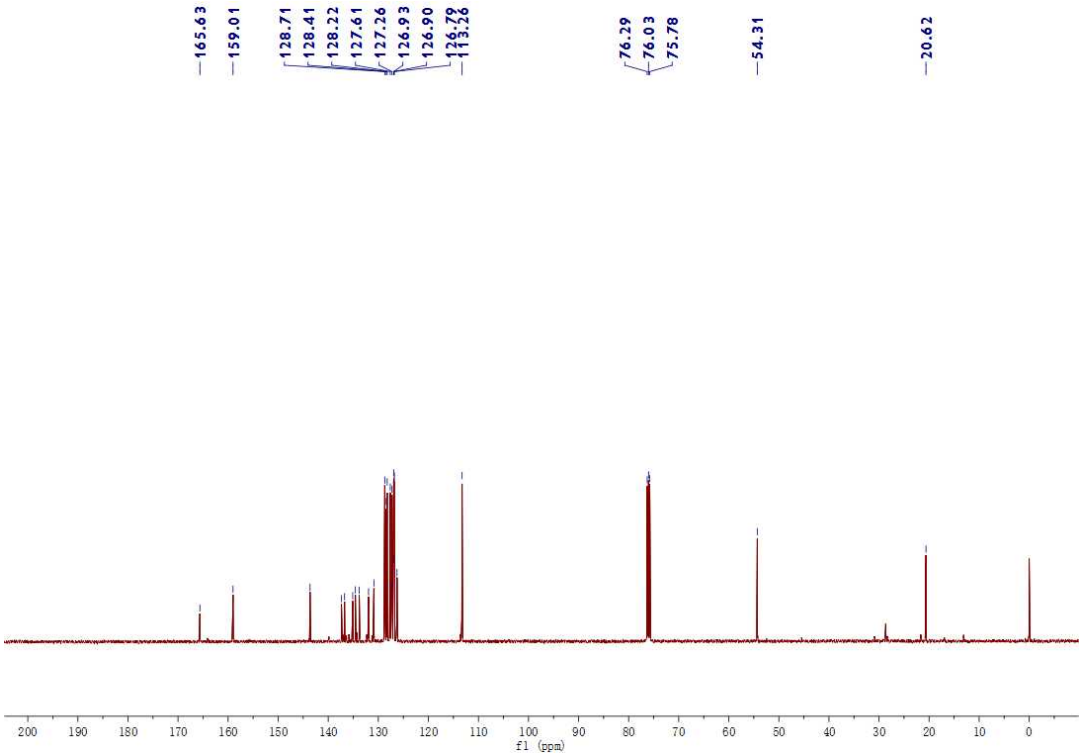
7.13
7.12
7.12
7.11
7.08
6.98
6.97
6.83
6.81
6.72
6.70
6.68
6.49
6.47
6.47
3.68
2.15
1.00
2.00
5.02
2.02
1.00
2.01
2.00
4.01
1.00
1.00
3.00
3.00
f1 (ppm)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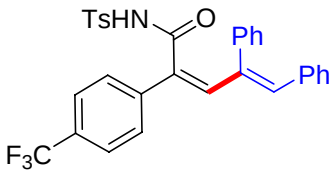
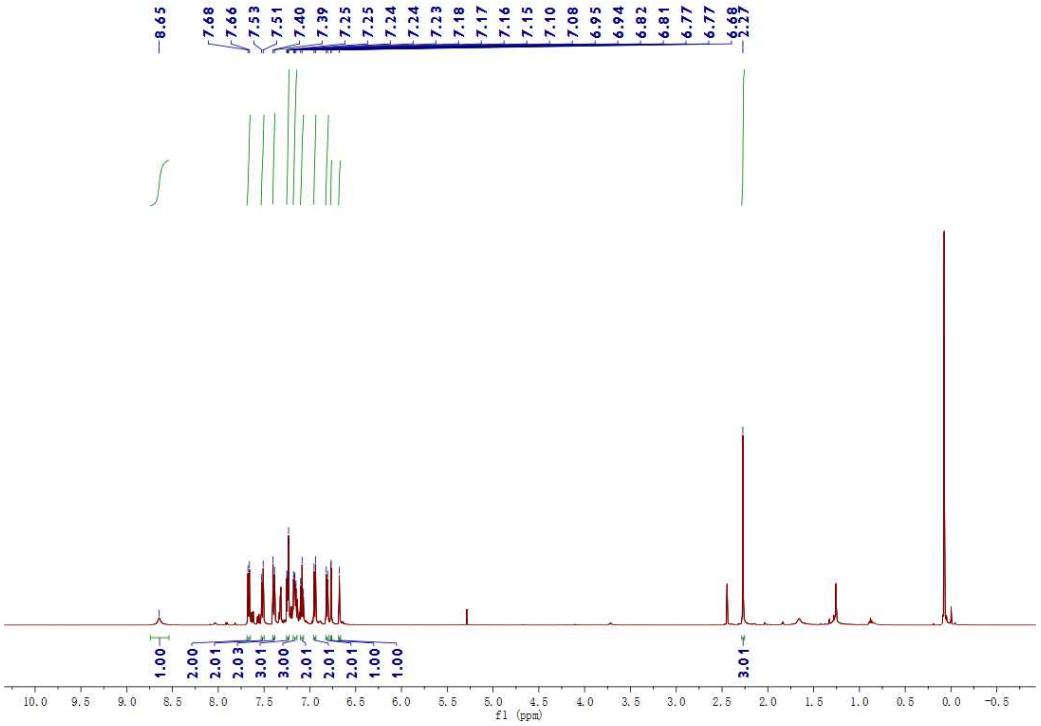
159.01
128.71
128.41
128.22
127.61
127.26
126.93
126.90
126.79
113.26
76.29
76.03
75.78
54.31
20.62
f1 (ppm)


TsHN
O
Ph
Ph
F3C

(3da)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7.40
7.39
7.25
7.25
7.24
7.24
7.23
7.18
7.17
7.16
7.15
7.10
7.08
6.95
6.94
6.82
6.81
6.77
6.77
6.68
2.27
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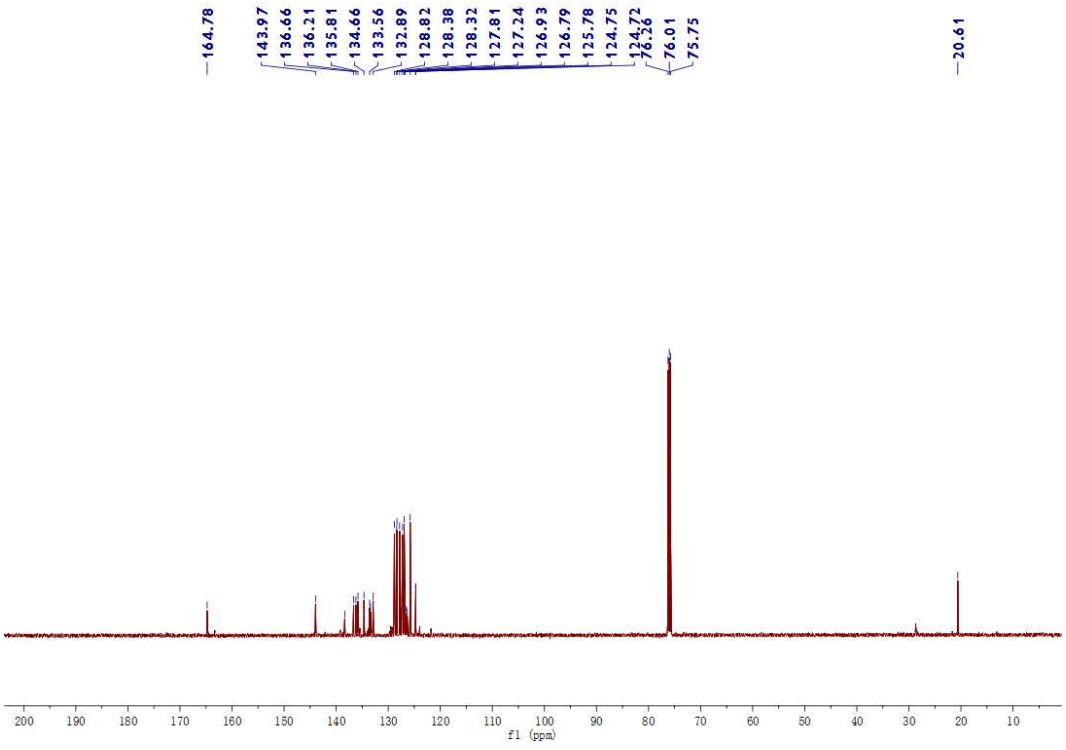
2.01
1.00
1.00
3.01
f1 (ppm)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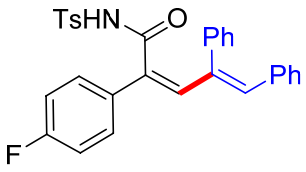
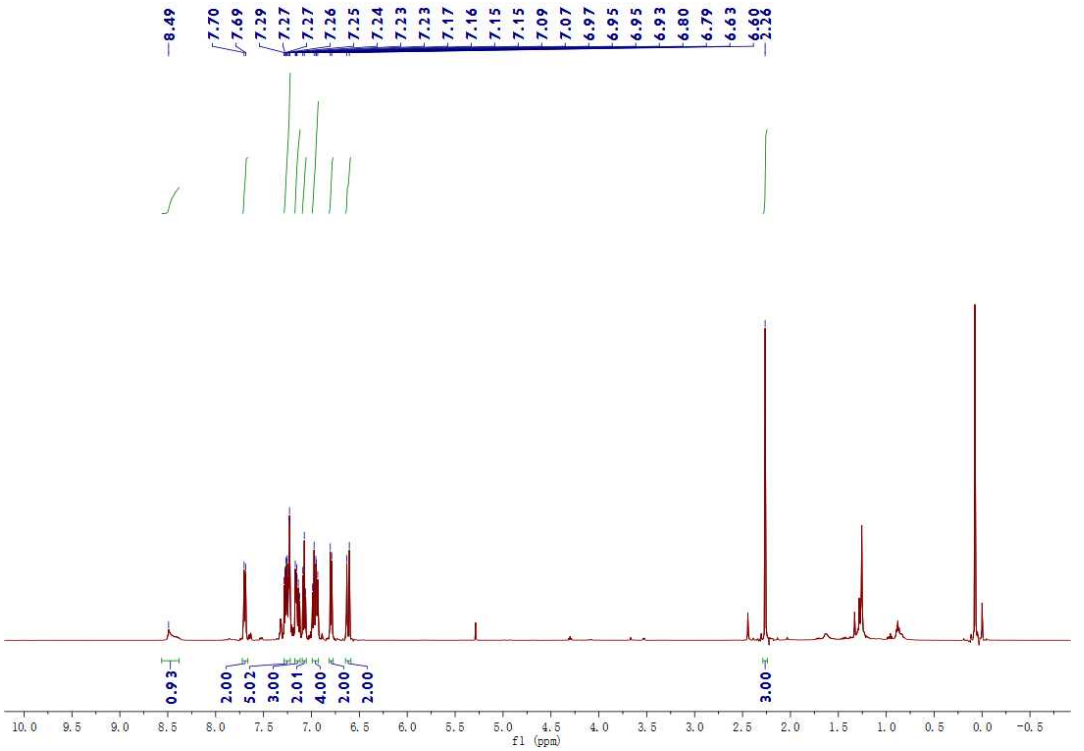
134.66
133.56
132.89
128.82
128.38
128.32
127.81
127.24
126.93
126.79
125.78
124.75
124.72
76.26
76.01
75.75
20.61
f1 (ppm)


TsHN
O
Ph
Ph
F

(3ea)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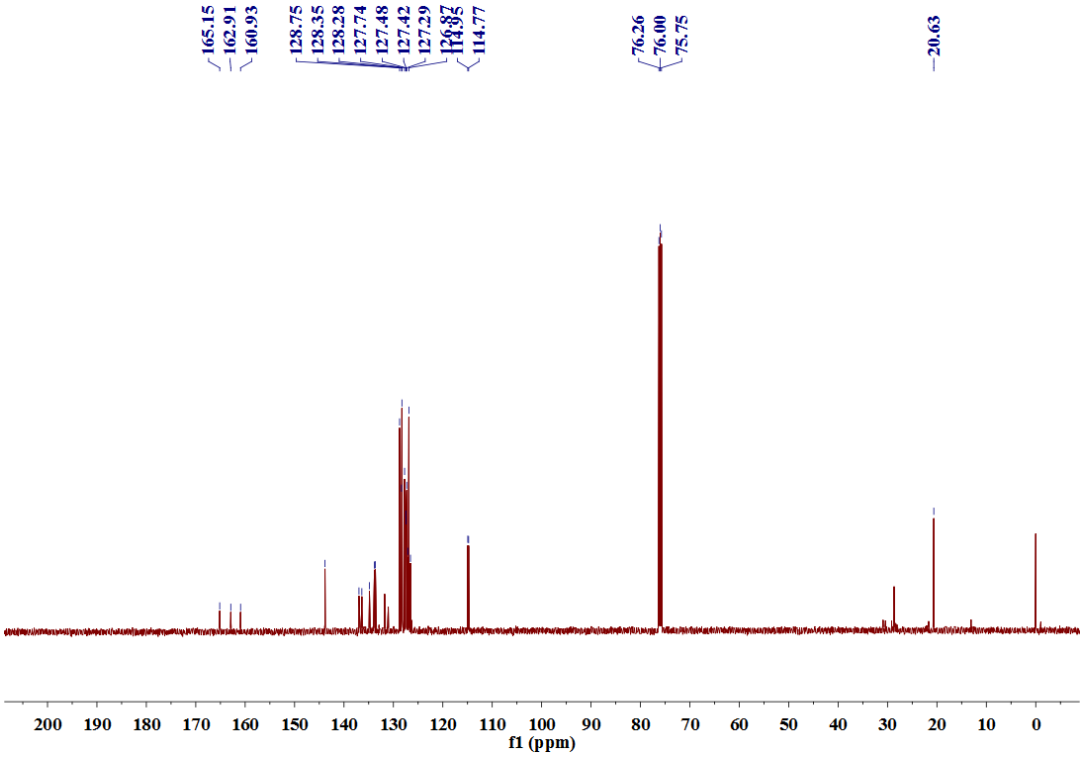
7.29
7.27
7.27
7.26
7.25
7.24
7.23
7.23
7.17
7.16
7.15
7.15
7.09
7.07
6.97
6.95
6.95
6.93
6.80
6.79
6.63
6.60
2.26
0.93
2.00
5.02
3.00
2.01
4.00
2.00
2.00
3.00
f1 (ppm)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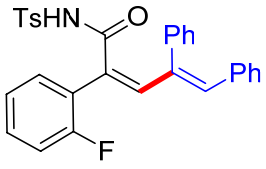
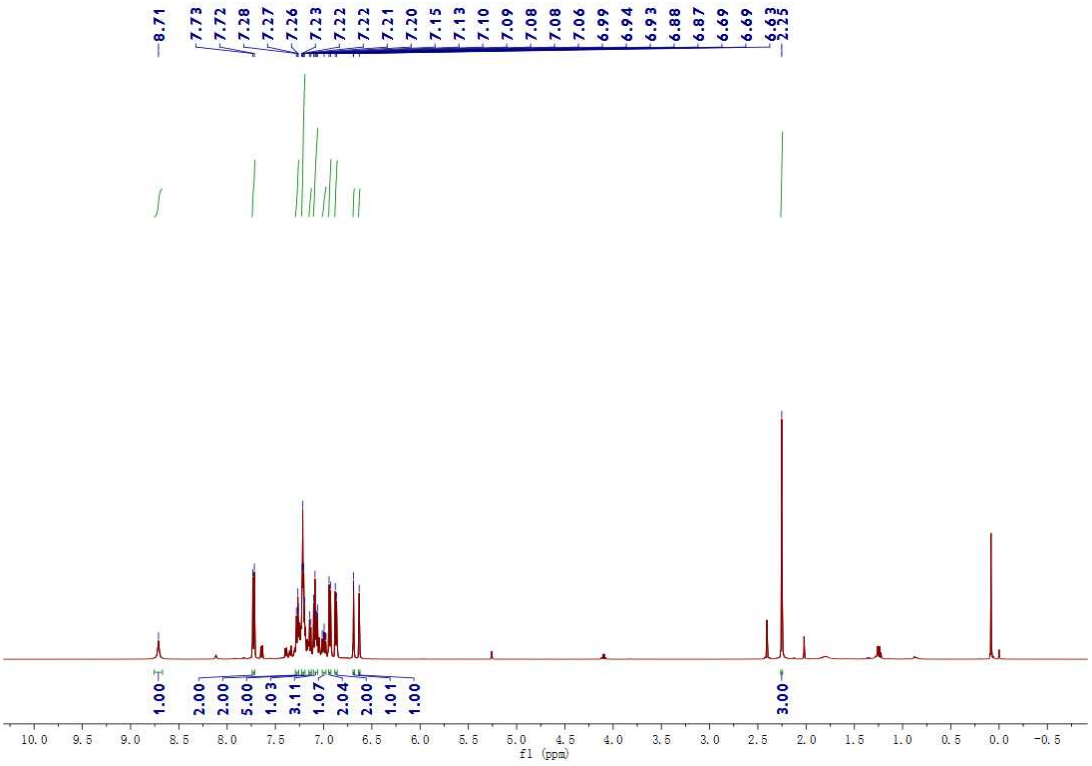
162.91
160.93
128.75
128.35
128.28
127.74
127.48
127.42
127.29
114.77
76.26
76.00
75.75
20.63
f1 (ppm)


TsHN
O
Ph
Ph
F

(3fa)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7.23
7.22
7.22
7.21
7.20
7.15
7.13
7.10
7.09
7.08
7.08
7.06
6.99
6.94
6.93
6.88
6.87
6.69
6.69
6.63
2.25
1.00
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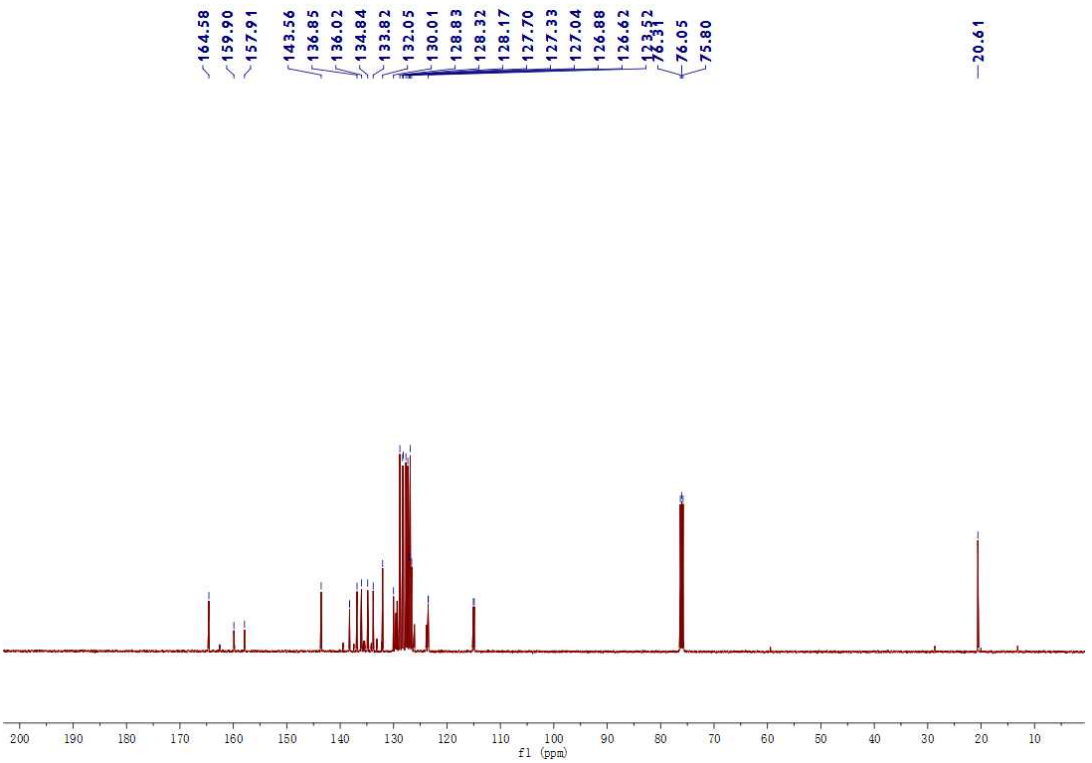
2.04
2.00
1.01
1.00
3.00
f1 (ppm)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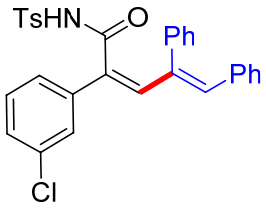
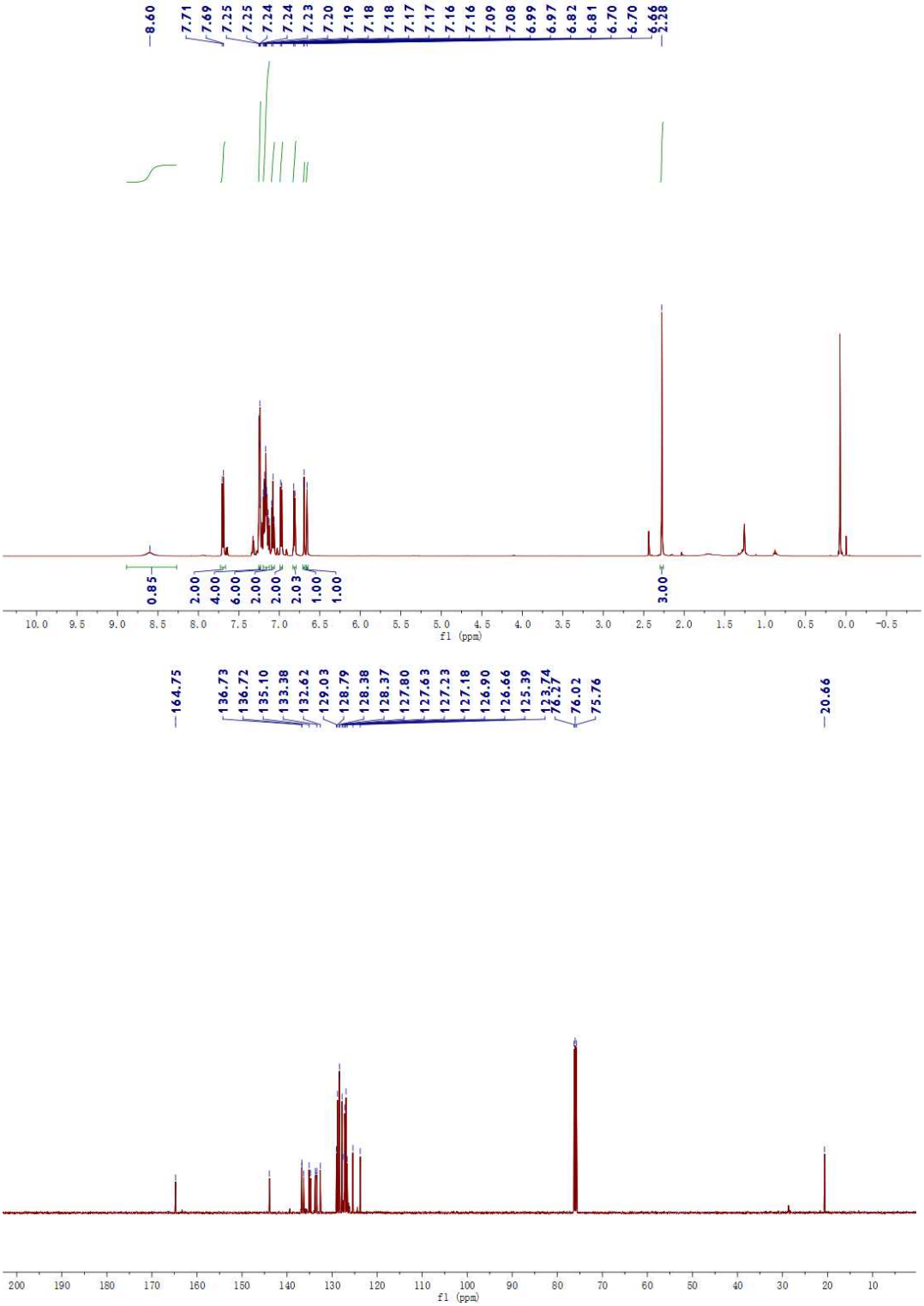
159.90
157.91
143.56
136.85
136.02
134.84
133.82
132.05
130.01
128.83
128.32
128.17
127.70
127.33
127.04
126.88
126.62
123.52
78.31
76.05
75.80
20.61
f1 (ppm)


TsHN
O
Ph
Ph
Cl

(3ga)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7.23
7.20
7.19
7.18
7.18
7.17
7.17
7.16
7.16
7.09
7.08
6.99
6.97
6.82
6.81
6.70
6.70
6.66
2.28
0.85
2.00
4.00
6.00
2.00
2.00
2.03
1.00
1.00
3.00
f1 (ppm)
164.75
136.73
136.72
135.10
133.38
132.62
129.03
128.79
128.38
128.37
127.80
127.63
127.23
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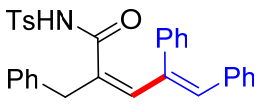
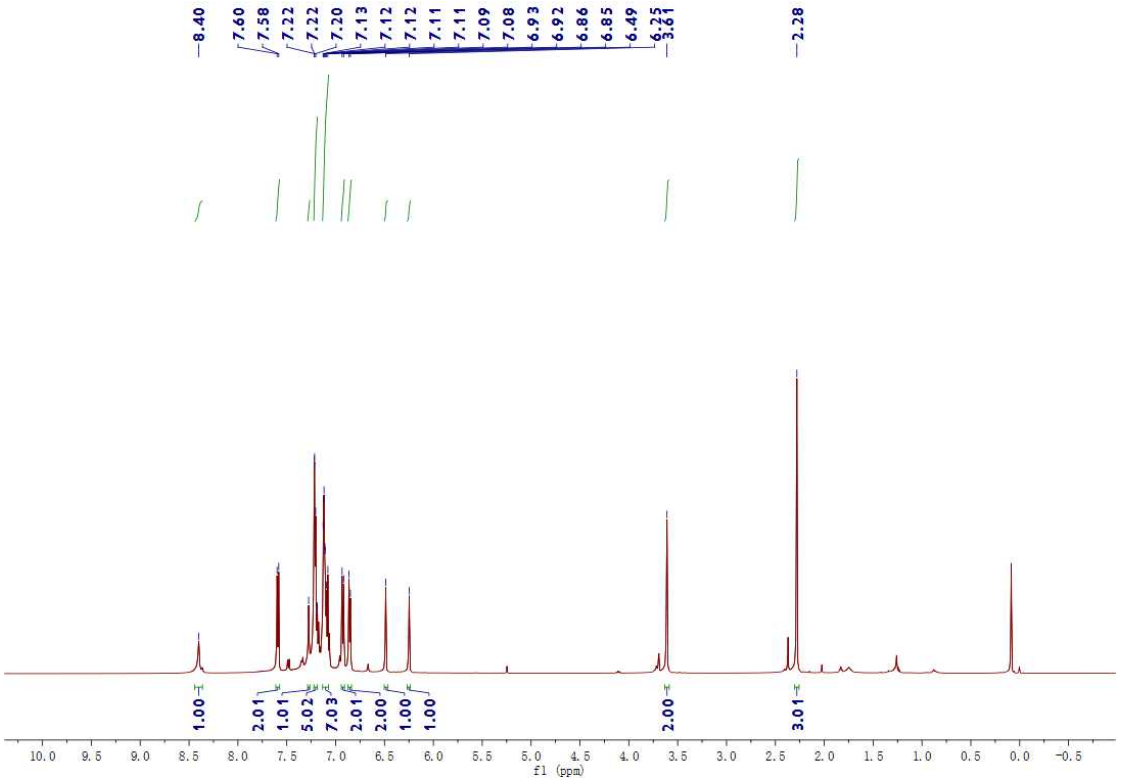
126.90
126.66
125.39
123.74
76.27
76.02
75.76
20.66
f1 (ppm)


TsHN
O
Ph
Ph
Ph

(3ha)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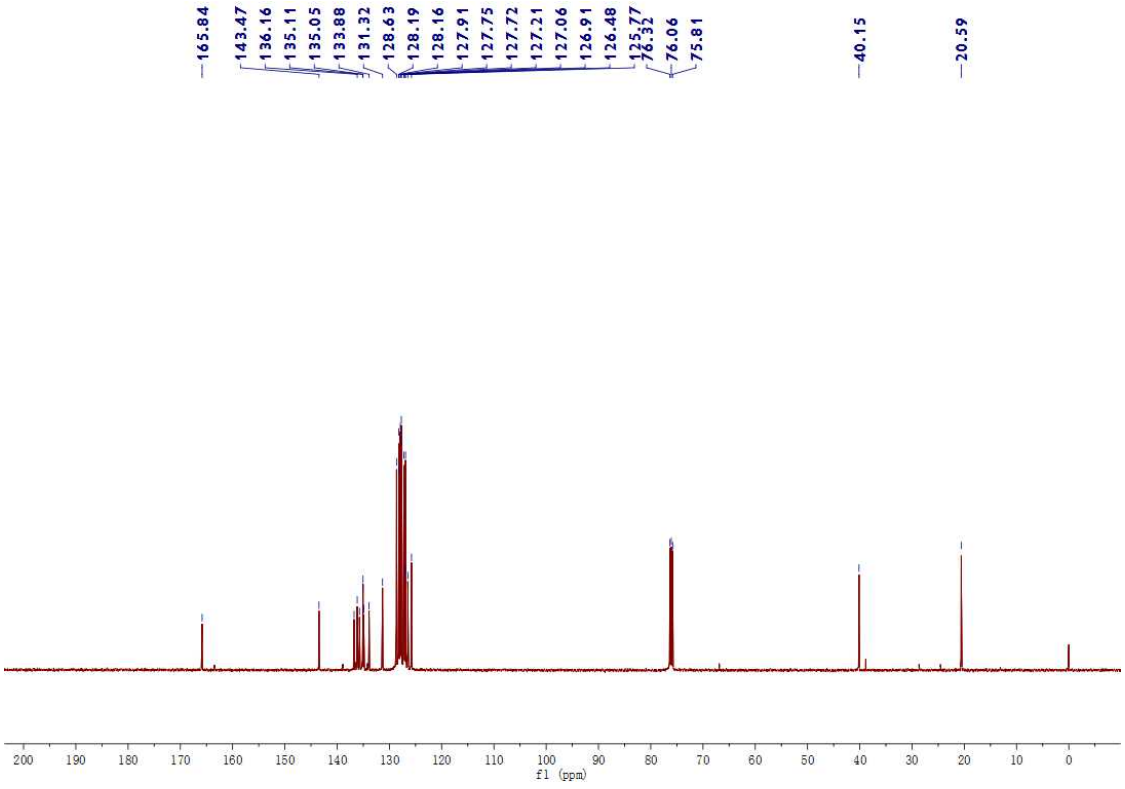
7.12
7.11
7.11
7.09
7.08
6.93
6.92
6.86
6.85
6.49
6.25
3.01
2.28
1.00
2.01
1.01
5.02
7.03
2.01
2.00
1.00
1.00
2.00
3.01
f1 (ppm)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128.16
127.91
127.75
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127.21
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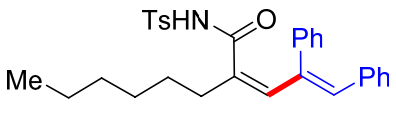
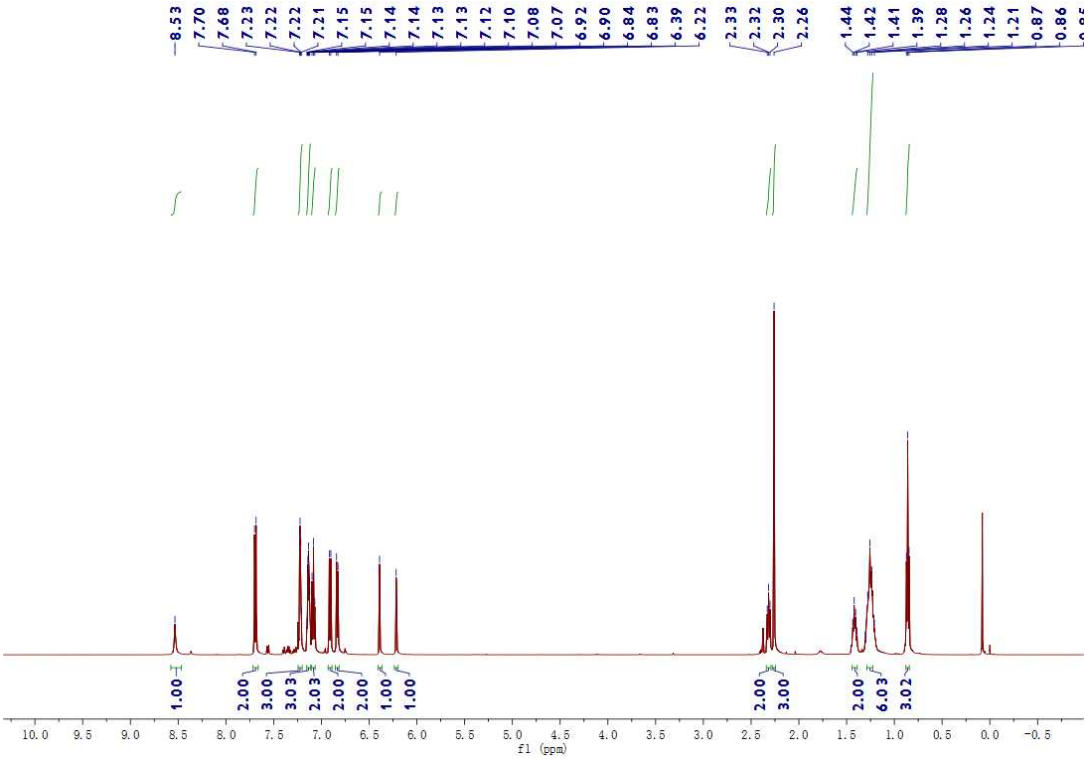
126.91
126.48
125.77
78.32
76.06
75.81
40.15
20.59
f1 (ppm)


TsHN
O
Ph
Ph
Me

(3ia)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7.14
7.14
7.13
7.13
7.12
7.10
7.08
7.07
6.92
6.90
6.84
6.83
6.39
6.22
2.33
2.32
2.30
2.26
1.44
1.42
1.41
1.39
1.28
1.26
1.24
1.21
0.87
0.86
1.00
2.00
3.00
3.03
2.03
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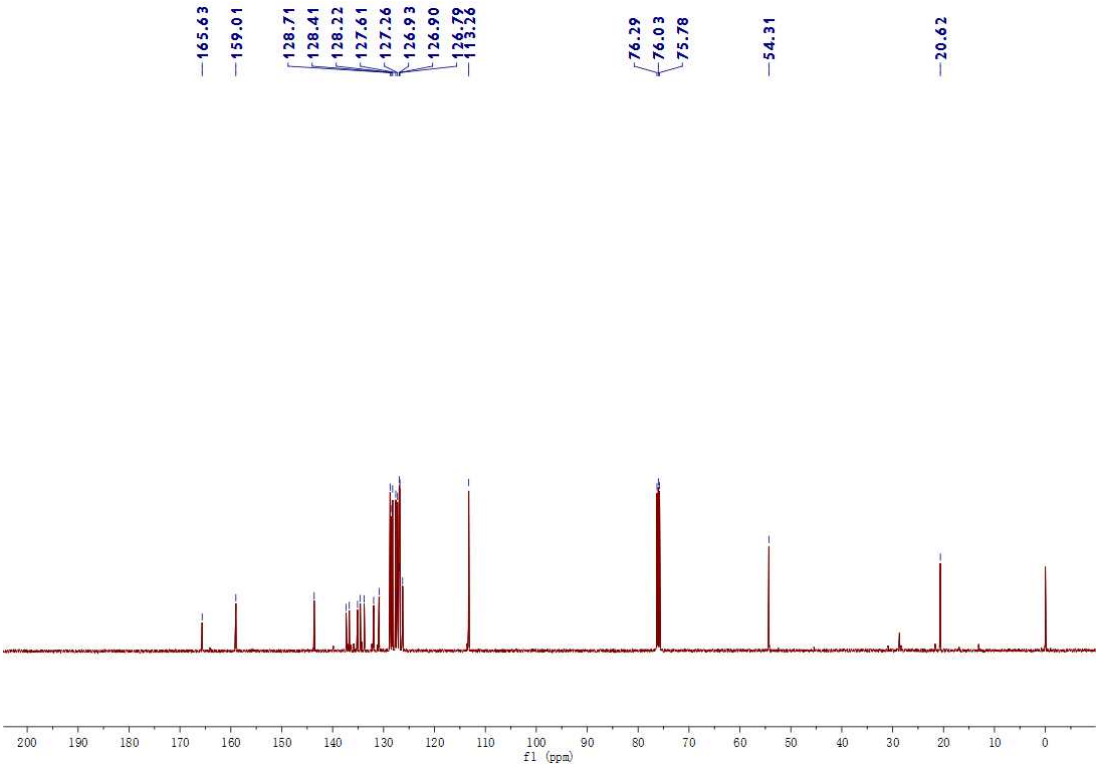
2.00
1.00
1.00
2.00
3.00
2.00
6.03
3.02
f1 (ppm)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128.41
128.22
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127.26
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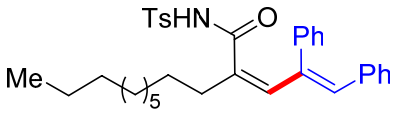
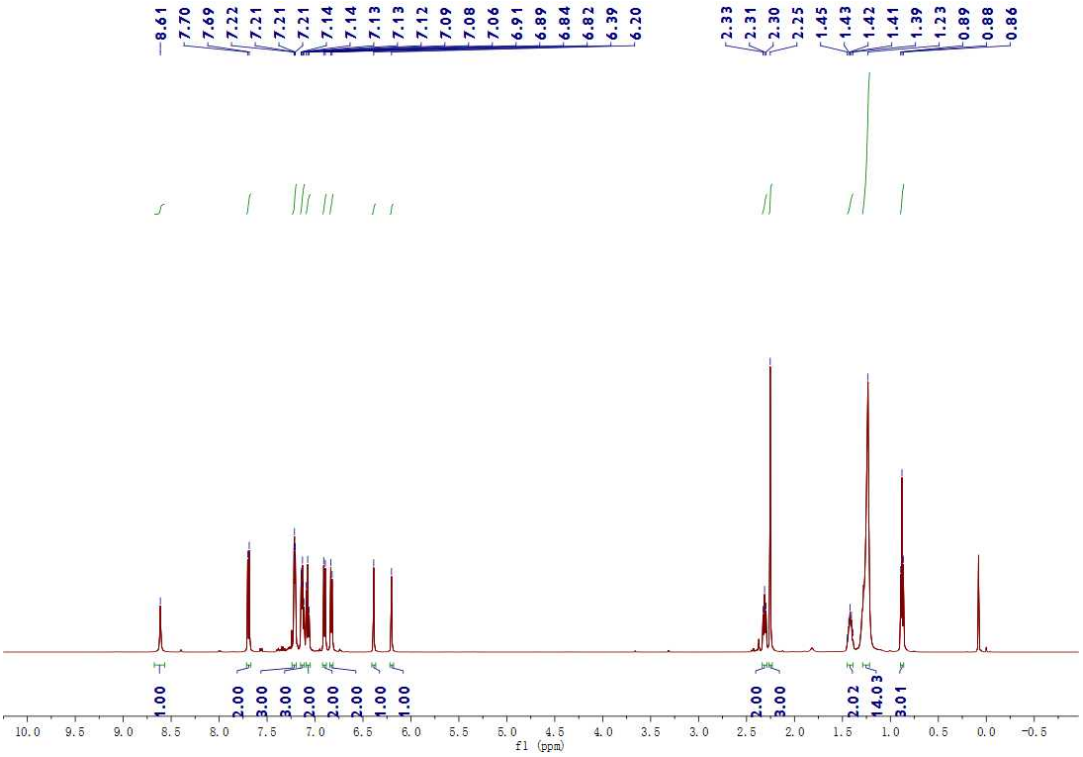
126.79
113.26
76.29
76.03
75.78
54.31
20.62
f1 (ppm)


TsHN
O
Ph
Ph
Me
5

(3ja)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7.13
7.13
7.12
7.09
7.08
7.06
6.91
6.89
6.84
6.82
6.39
6.20
2.33
2.31
2.30
2.25
1.45
1.43
1.42
1.41
1.39
1.23
0.89
0.88
0.86
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2.00
3.00
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2.00
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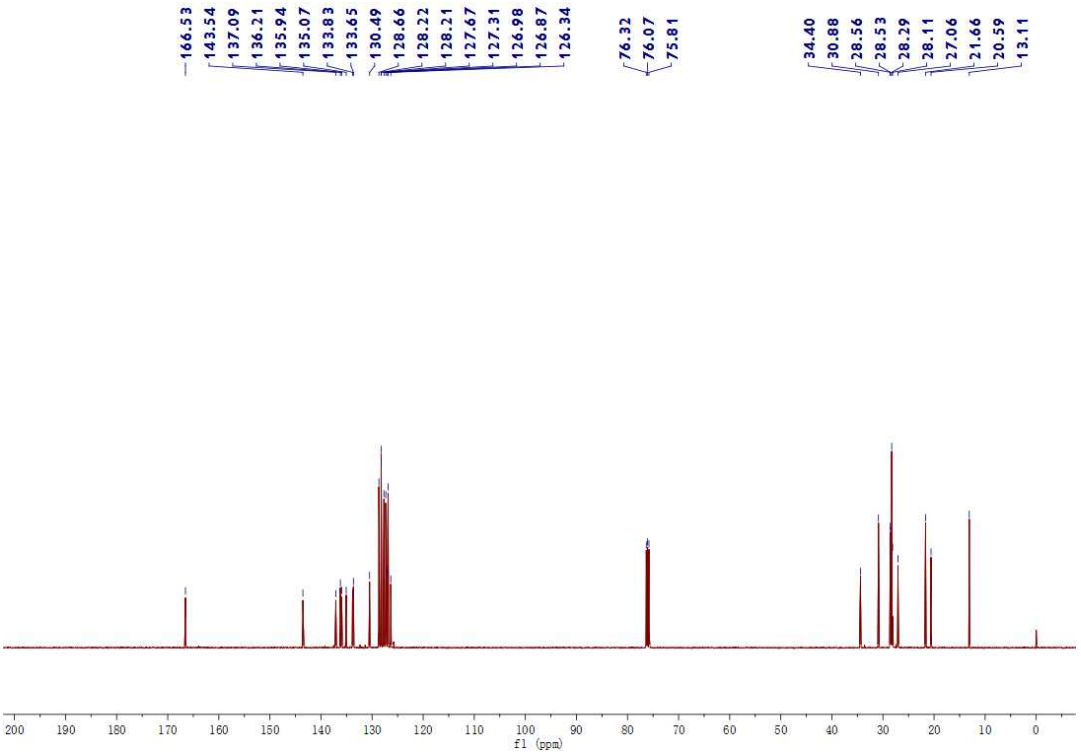
1.00
1.00
2.00
3.00
2.02
14.03
3.01
f1 (ppm)


166.53
143.54
137.09
136.21
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135.07
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133.65
130.49
128.66
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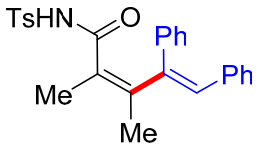
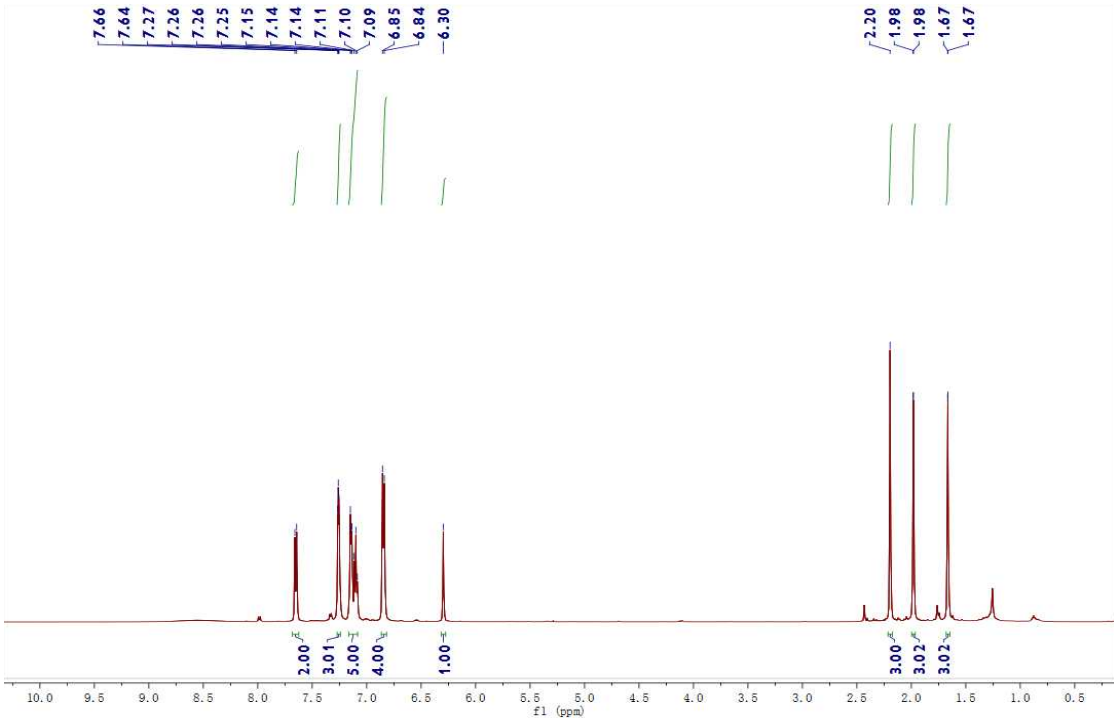
127.67
127.31
126.98
126.87
126.34
76.32
76.07
75.81
34.40
30.88
28.56
28.53
28.29
28.11
27.06
21.66
20.59
13.11
f1 (ppm)


TsHN
O
Ph
Ph
Me
Me

(3ka)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7.14
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7.11
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7.09
6.85
6.84
6.30
2.20
1.98
1.98
1.67
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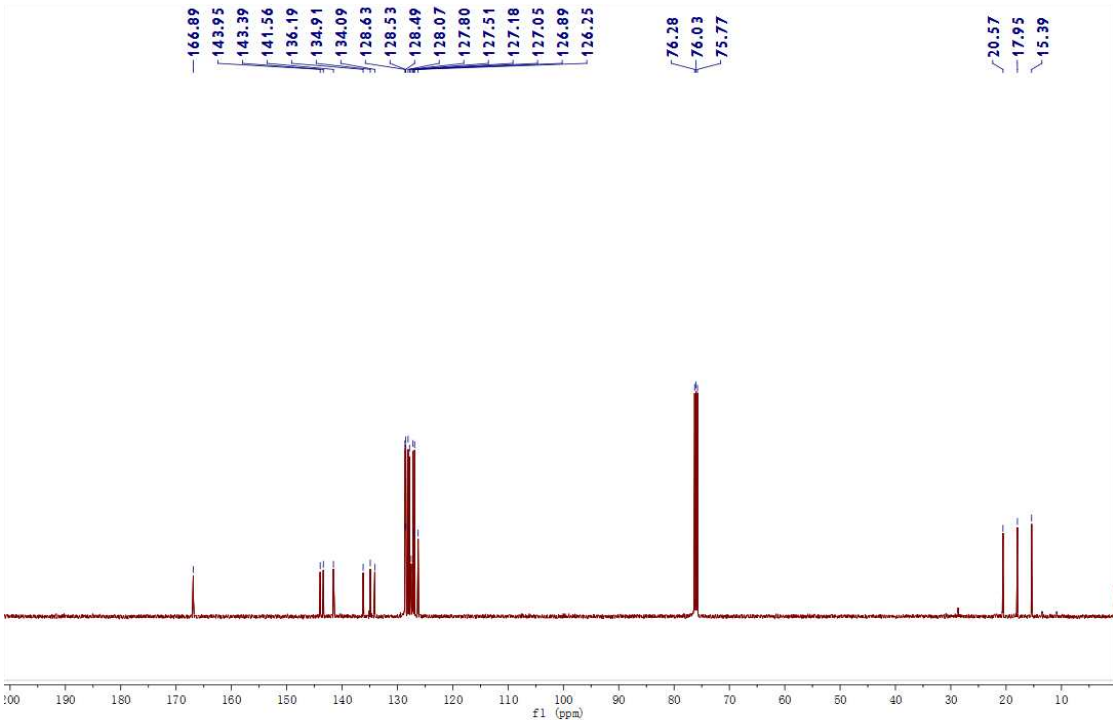
2.00
3.01
5.00
4.00
1.00
3.00
3.02
3.02
f1 (ppm)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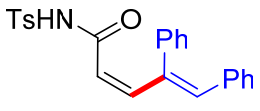
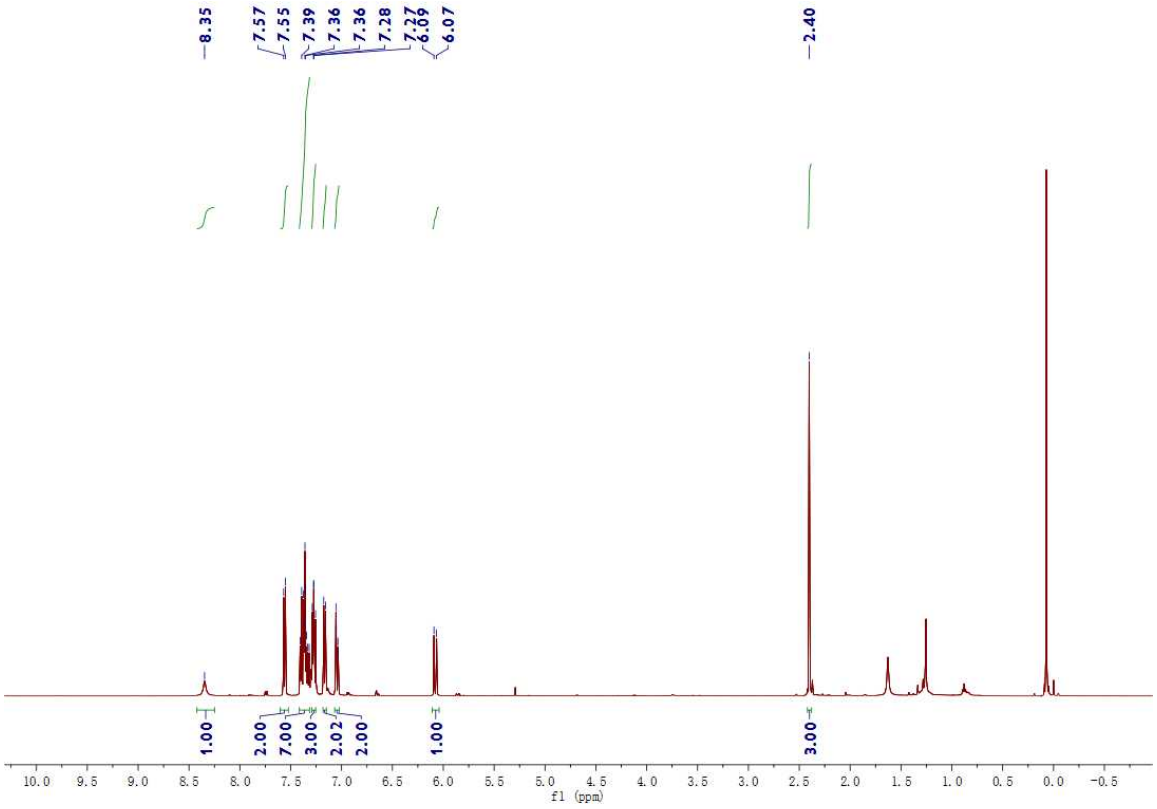
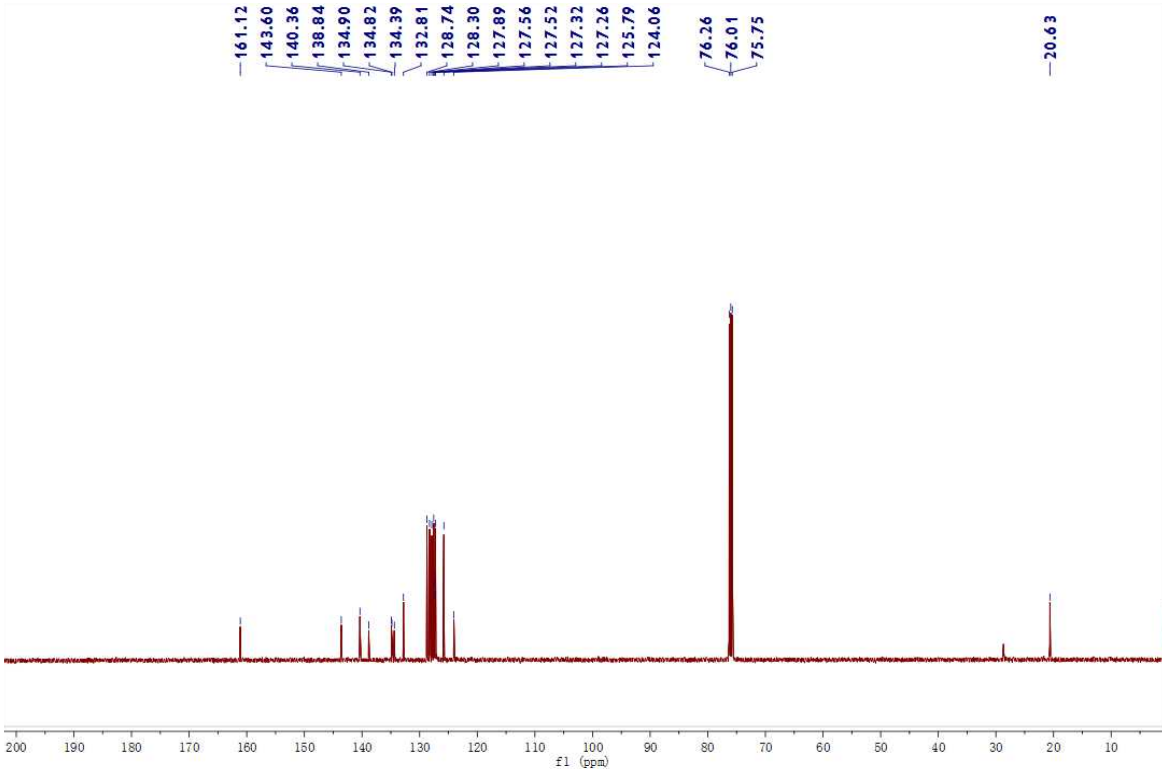
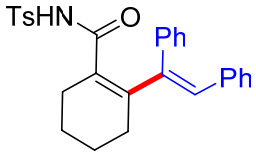
134.91
134.09
128.63
128.53
128.49
128.07
127.80
127.51
127.18
127.05
126.89
126.25
76.28
76.03
75.77
20.57
17.95
15.39
f1 (ppm)


TsHN
O
Ph
Ph

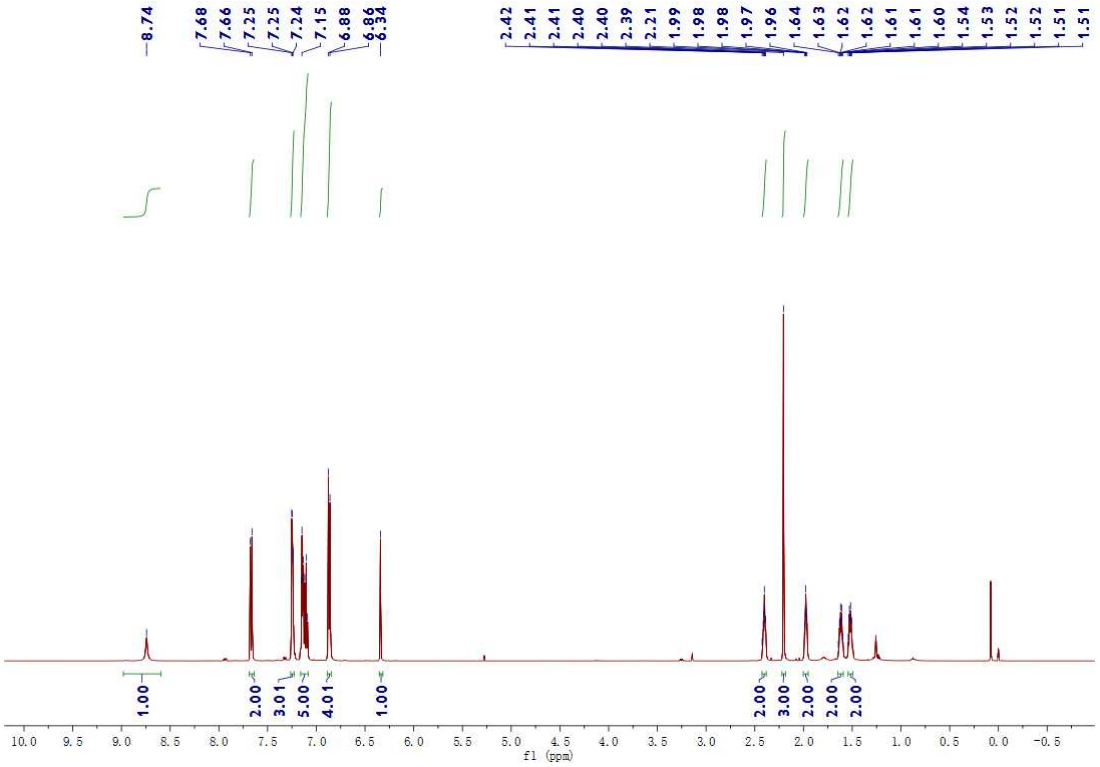
(3la)

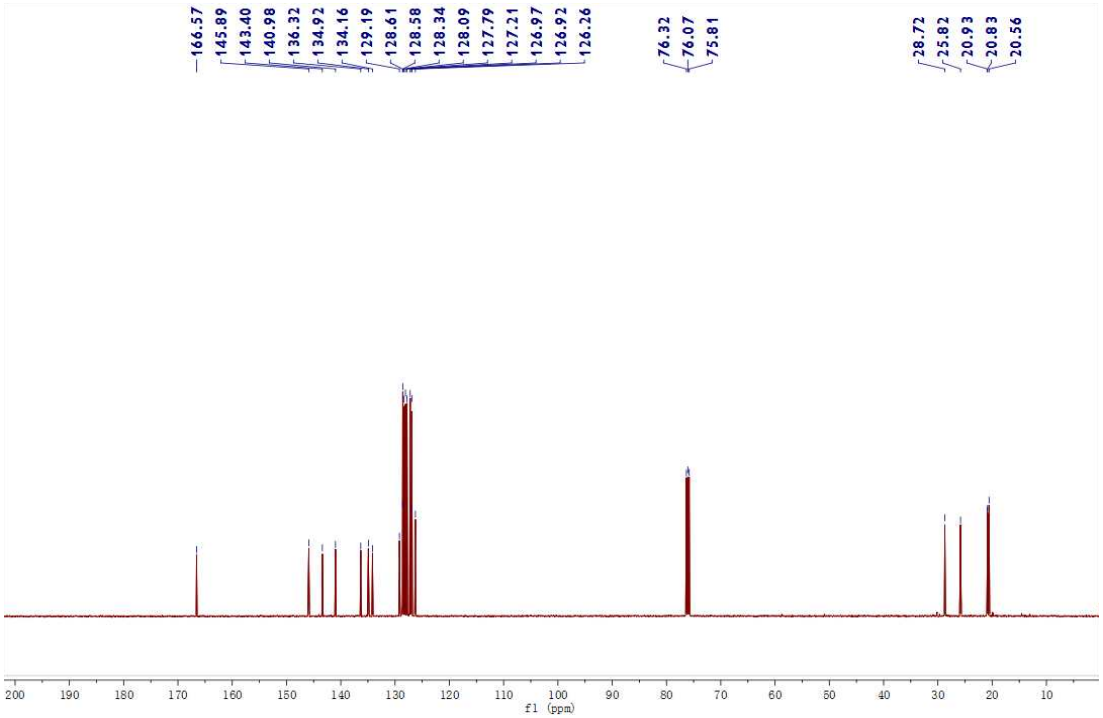

8.35
7.57
7.55
7.39
7.36
7.36
7.28
7.27
6.09
6.07
2.40
1.00
2.00
7.00
3.00
2.02
2.00
1.00
3.00
f1 (ppm)


161.12
143.60
140.36
138.84
134.90
134.82
134.39
132.81
128.74
128.30
127.89
127.56
127.52
127.32
127.26
125.79
124.06
76.26
76.01
75.75
20.63
f1 (ppm)


TsHN
O
Ph
Ph

(3ma)


8.74
7.68
7.66
7.25
7.25
7.24
7.15
6.88
6.86
6.34
2.42
2.41
2.41
2.40
2.40
2.39
2.21
1.99
1.98
1.98
1.97
1.96
1.64
1.63
1.62
1.62
1.61
1.61
1.60
1.54
1.53
1.52
1.52
1.51
1.51
1.00
2.00
3.01
5.00
4.01
1.00
2.00
3.00
2.00
2.00
2.00
f1 (ppm)


166.57
145.89
143.40
140.98
136.32
134.92
134.16
129.19
128.61
128.58
128.34
128.09
127.79
127.21
126.97
126.92
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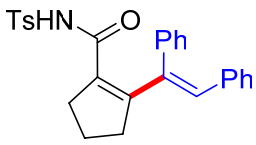
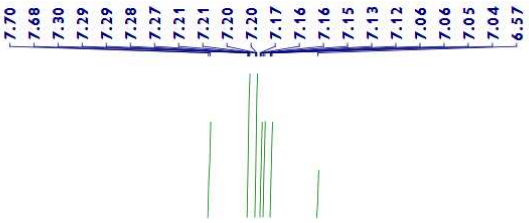
76.32
76.07
75.81
28.72
25.82
20.93
20.83
20.56
f1 (ppm)


TsHN
O
Ph
Ph

(3na)


7.70
7.68
7.30
7.29
7.29
7.28
7.27
7.21
7.21
7.20
7.20
7.17
7.16
7.16
7.15
7.13
7.12
7.06
7.06
7.05
7.04
6.57
2.77
2.75
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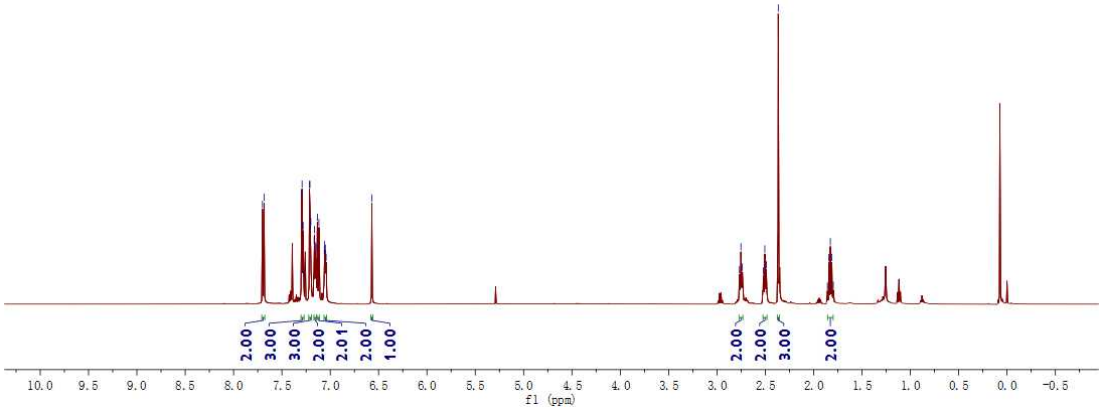
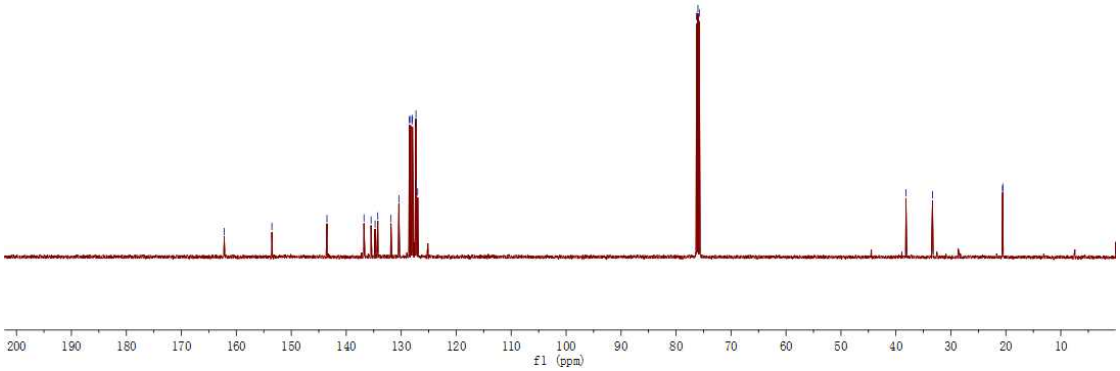
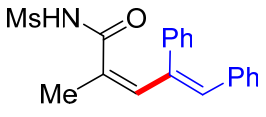
2.37
1.86
1.84
1.83
1.81
1.80

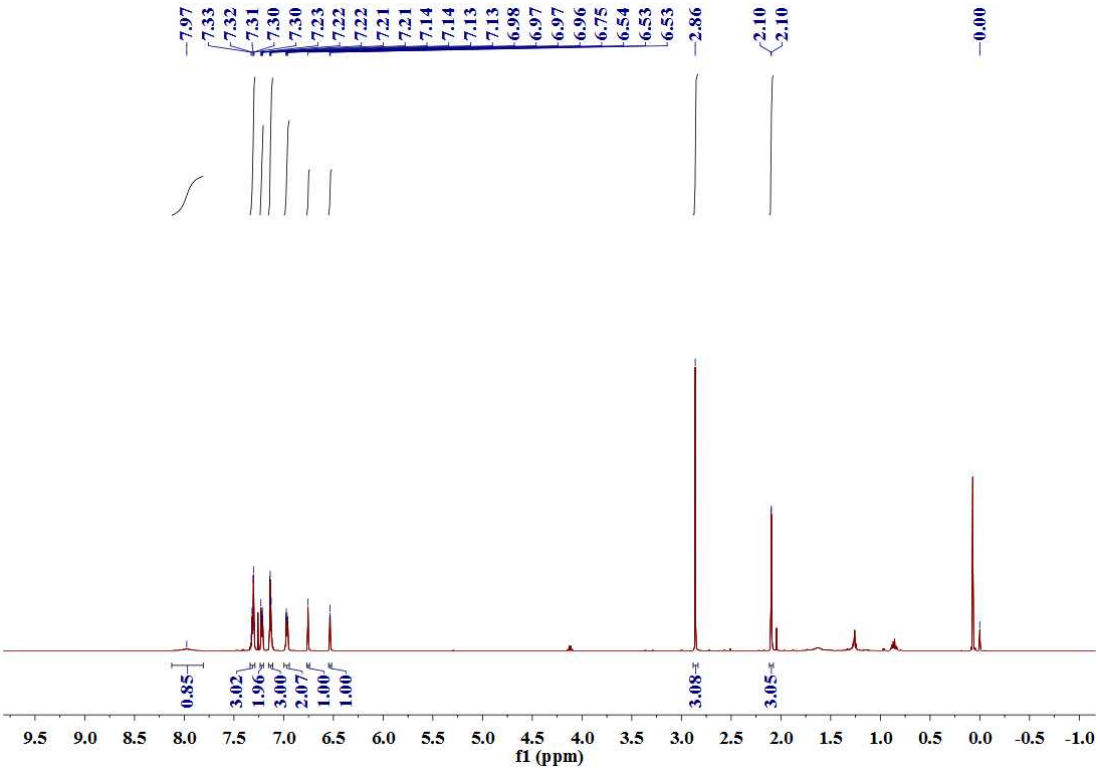

2.00
3.00
3.00
2.00
2.01
2.00
1.00
2.00
2.00
3.00
2.00
f1 (ppm)

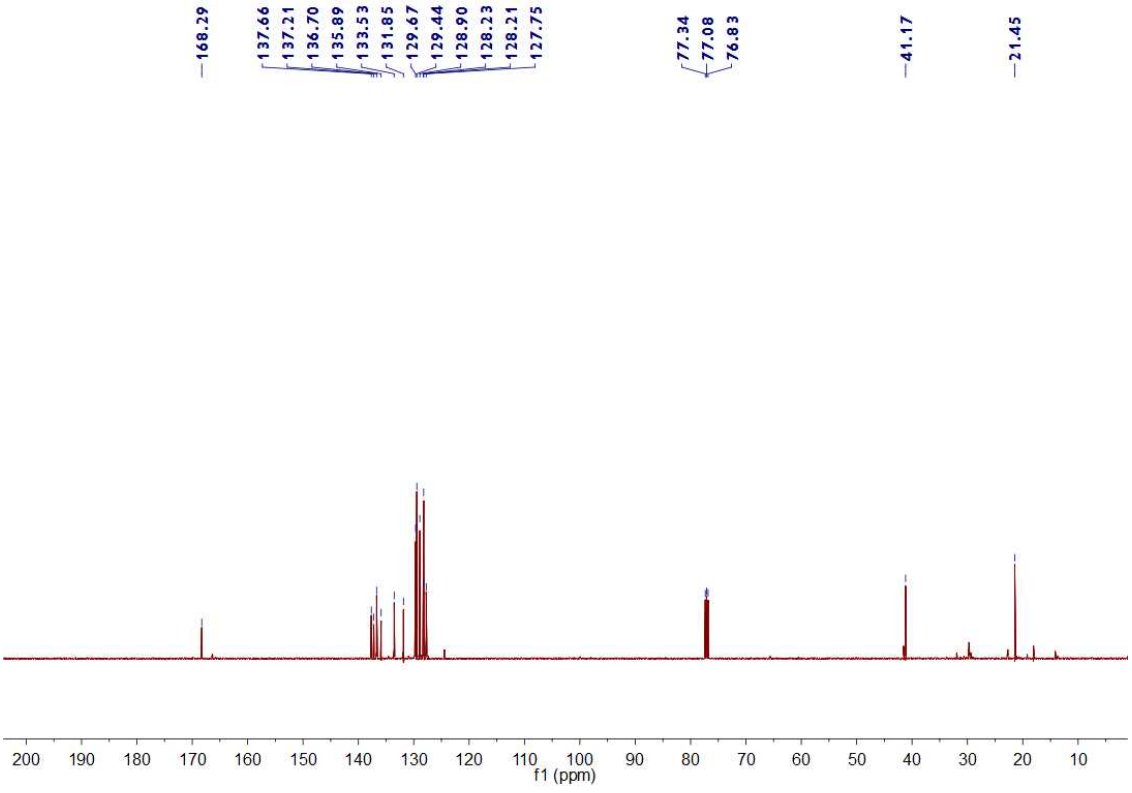

162.20
153.52
143.51
136.77
135.48
134.75
134.27
131.86
130.43
128.53
128.29
128.01
127.95
127.41
127.38
127.31
127.00
76.28
76.02
75.77
38.17
33.34
20.61
20.55

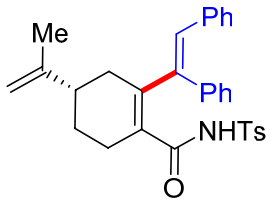

f1 (ppm)


MsHN
O
Ph
Ph
Me

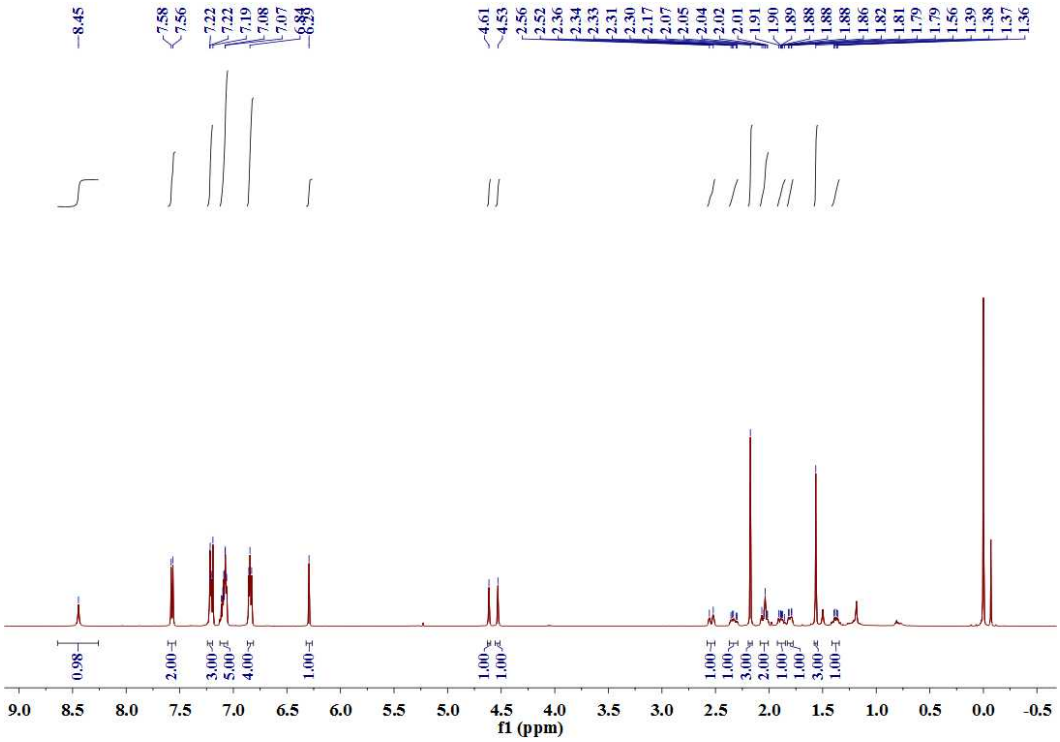
(3oa)

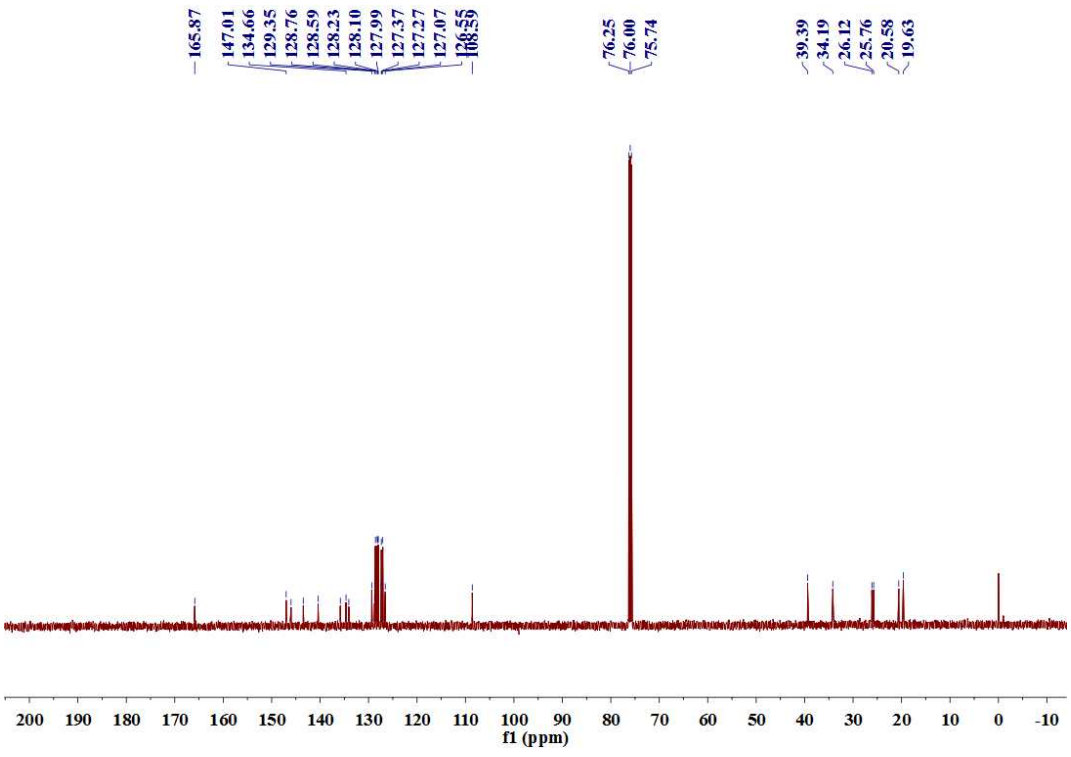

7.97
7.33
7.32
7.31
7.30
7.30
7.23
7.22
7.22
7.21
7.21
7.14
7.14
7.13
7.13
6.98
6.97
6.97
6.96
6.75
6.54
6.53
6.53
2.86
2.10
2.10
0.00
0.85
3.02
1.96
3.00
2.07
1.00
1.00
3.08
3.05
f1 (ppm)

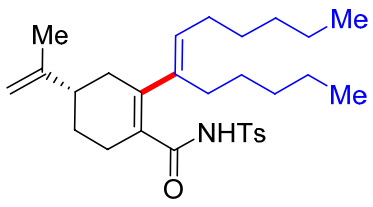

168.29
137.66
137.21
136.70
135.89
133.53
131.85
129.67
129.44
128.90
128.23
128.21
127.75
77.34
77.08
76.83
41.17
21.45
f1 (ppm)


Me
Ph
Ph
NHTs
O

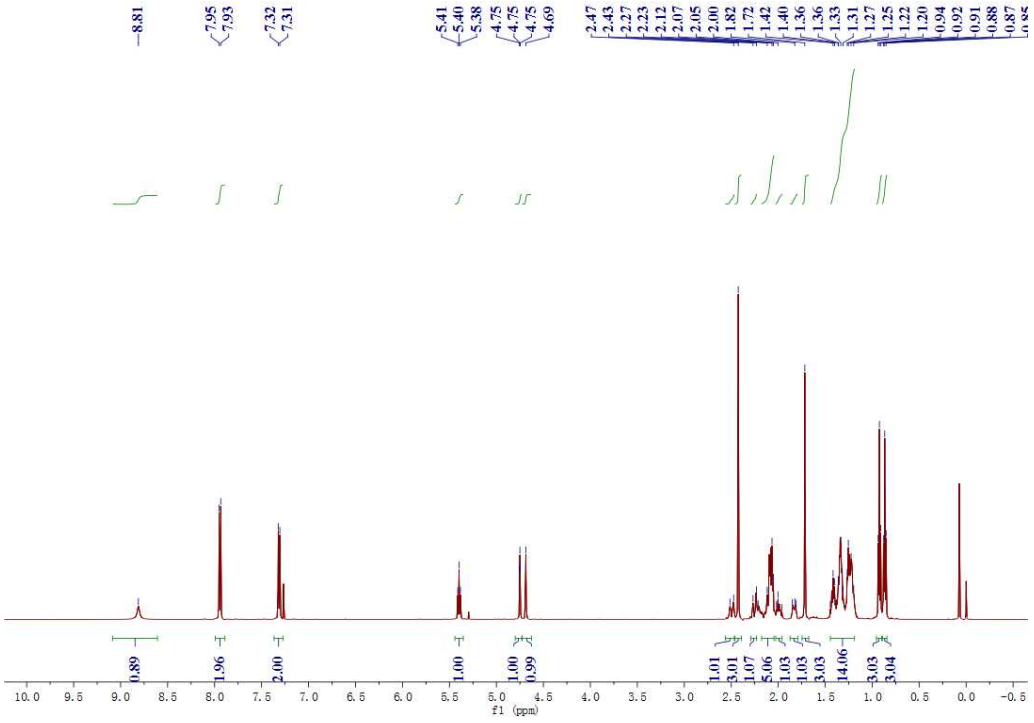
(3pa)

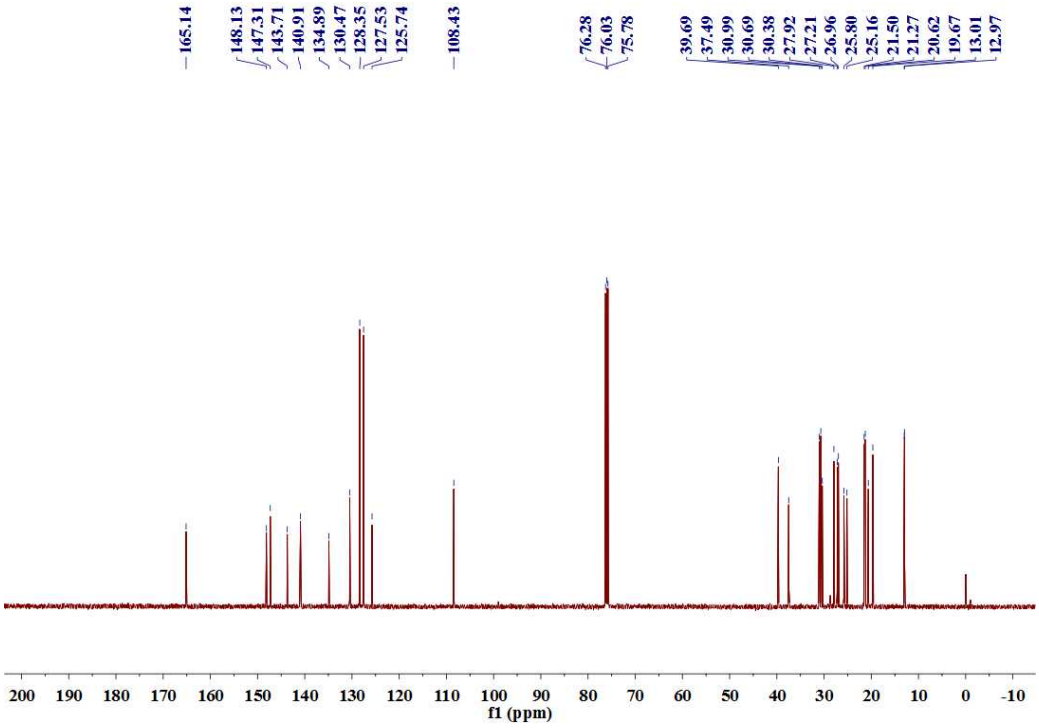

8.45
7.58
7.56
7.22
7.22
7.19
7.08
7.07
6.84
6.83
4.61
4.53
2.56
2.52
2.36
2.34
2.33
2.31
2.30
2.17
2.07
2.05
2.04
2.02
2.01
1.91
1.90
1.89
1.88
1.88
1.88
1.86
1.82
1.81
1.79
1.79
1.56
1.39
1.38
1.37
1.36
0.98
2.00
3.00
5.00
4.00
1.00
1.00
1.00
1.00
3.00
2.00
1.00
1.00
3.00
1.00
9.0 8.5 8.0 7.5 7.0 6.5 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 -0.5
f1 (ppm)

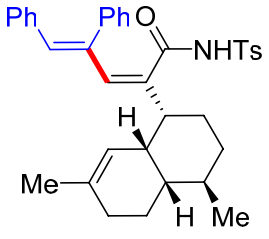

165.87
147.01
134.66
129.35
128.76
128.59
128.23
128.10
127.99
127.37
127.27
127.07
126.55
126.29
76.25
76.00
75.74
39.39
34.19
26.12
25.76
20.58
19.63
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


Me
Me
Me
NHTs
O

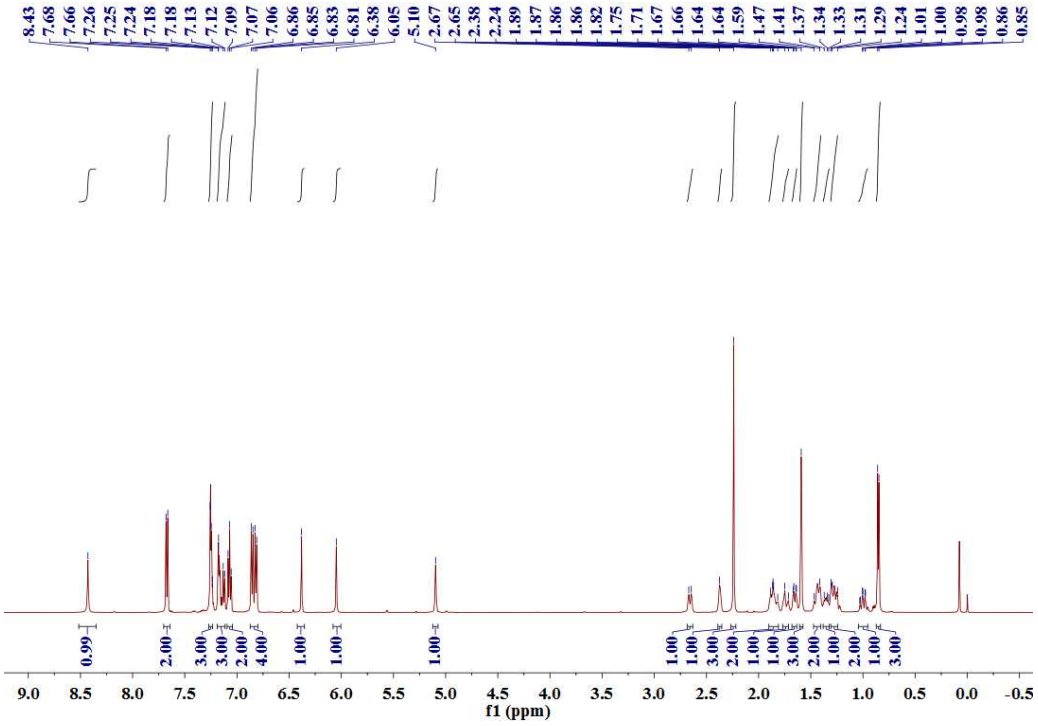
(3pg)

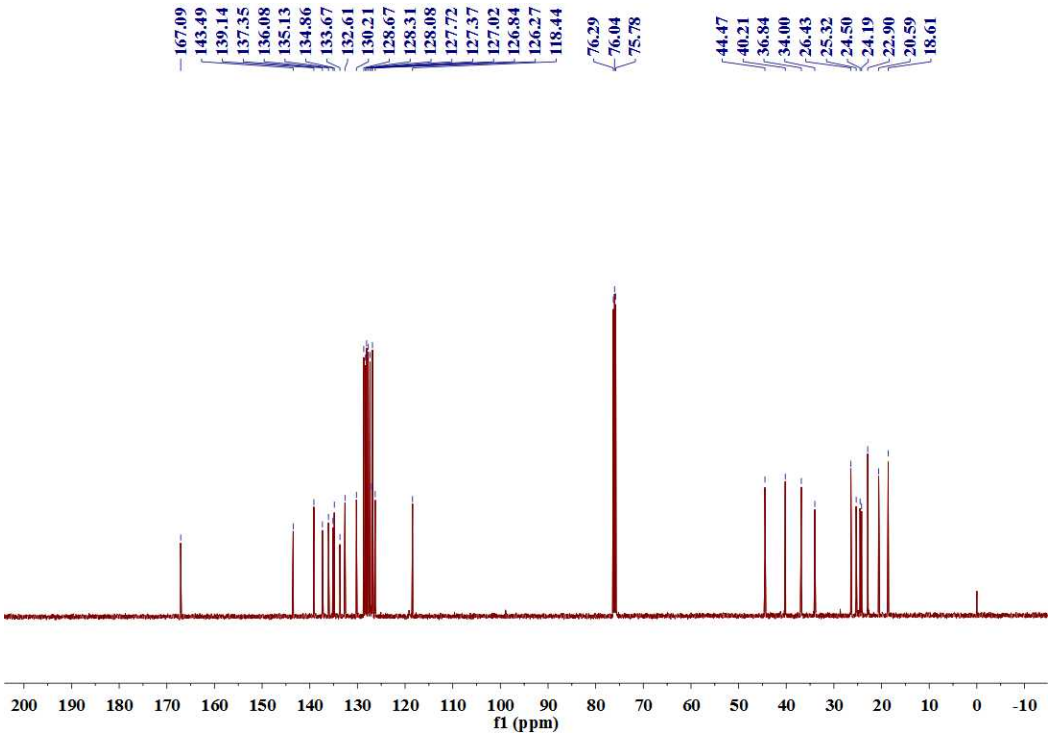

8.81
7.95
7.93
7.32
7.31
5.41
5.40
5.38
4.75
4.75
4.75
4.69
2.47
2.43
2.27
2.23
2.12
2.07
2.05
2.00
1.82
1.72
1.42
1.40
1.36
1.36
1.33
1.31
1.27
1.25
1.22
1.20
0.94
0.92
0.91
0.88
0.87
0.89
1.96
2.00
1.00
1.00
0.99
1.01
3.01
1.07
5.06
1.03
1.03
3.03
14.06
3.03
3.04
f1 (ppm)

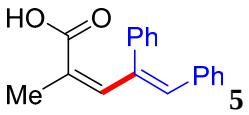

165.14
148.13
147.31
143.71
140.91
134.89
130.47
128.35
127.53
125.74
108.43
76.28
76.03
75.78
39.69
37.49
30.99
30.69
30.38
27.92
27.21
26.96
25.80
25.16
21.50
21.27
20.62
19.67
13.01
12.97
f1 (ppm)


Ph
Ph
O
NHTs
H
Me
H
Me

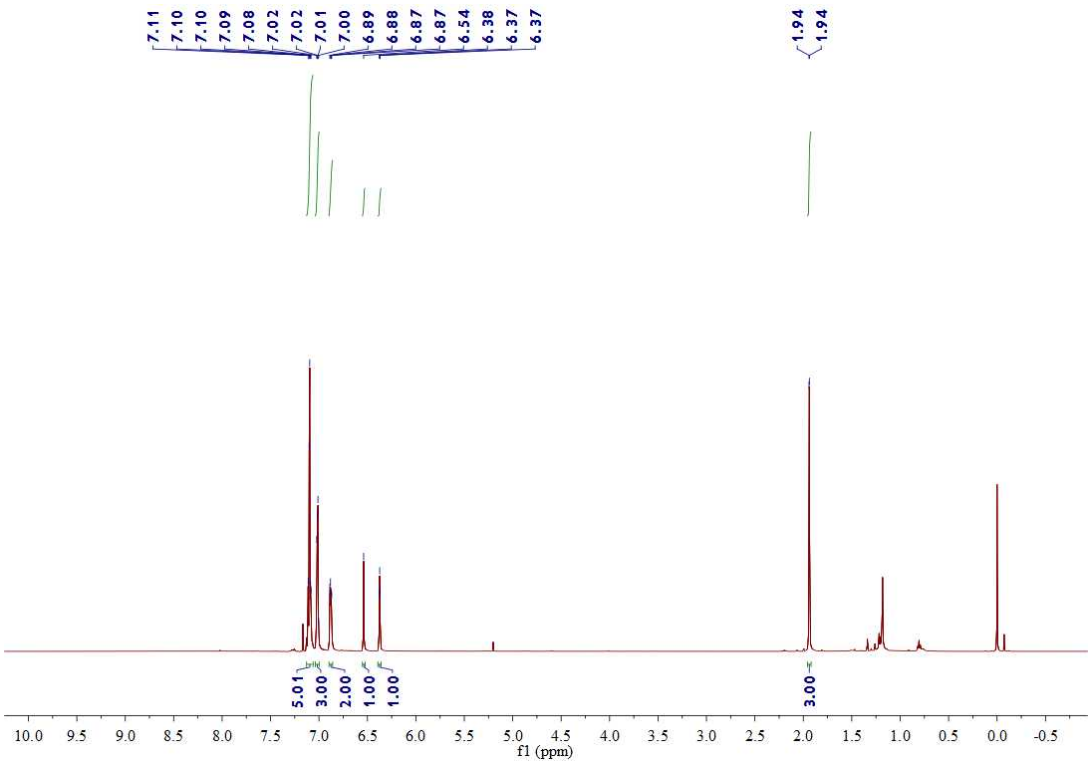
(3qa)

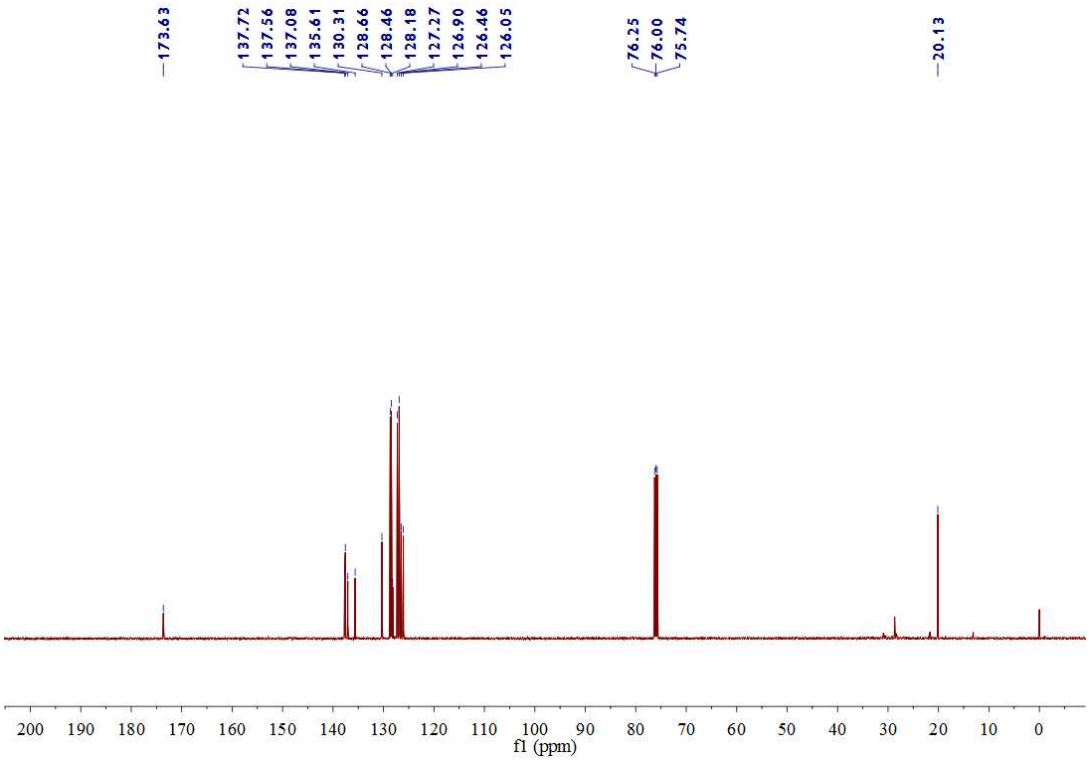

8.43 7.68 7.66 7.26 7.25 7.24 7.18 7.18 7.13 7.12 7.09 7.07 7.06 6.86 6.85 6.83 6.81 6.38 6.05 5.10 2.67 2.65 2.38 2.24 1.89 1.87 1.86 1.86 1.82 1.75 1.71 1.67 1.66 1.64 1.64 1.59 1.47 1.41 1.37 1.34 1.33 1.31 1.29 1.24 1.01 1.00 0.98 0.98 0.86 0.85
0.99 2.00 3.00 3.00 2.00 4.00 1.00 1.00 1.00 1.00 1.00 3.00 2.00 1.00 1.00 3.00 2.00 1.00 2.00 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 -0.5
f1 (ppm)

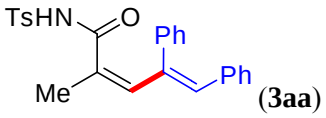

167.09 143.49 139.14 137.35 136.08 135.13 134.86 133.67 132.61 130.21 128.67 128.31 128.08 127.72 127.37 127.02 126.84 126.27 118.44
76.29 76.04 75.78
44.47 40.21 36.84 34.00 26.43 25.32 24.50 24.19 22.90 20.59 18.61
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


HO
O
Ph
Ph
Me

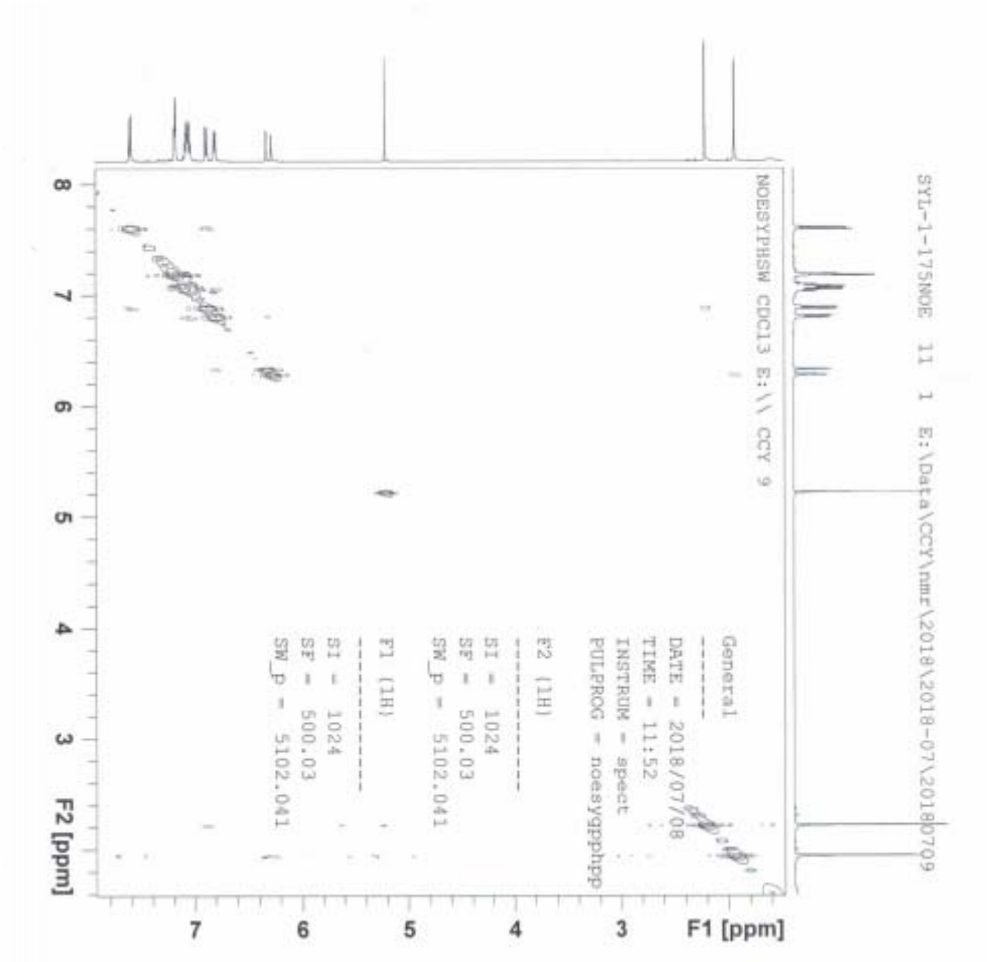
5


7.11
7.10
7.10
7.09
7.08
7.02
7.02
7.01
7.00
6.89
6.88
6.87
6.87
6.54
6.38
6.37
6.37
1.94
1.94
5.01
3.00
2.00
1.00
1.00
3.00
f1 (ppm)


173.63
137.72
137.56
137.08
135.61
130.31
128.66
128.46
128.18
127.27
126.90
126.46
126.05
76.25
76.00
75.74
20.13
f1 (ppm)


TsHN
O
Ph
Ph
Me

(**3aa**)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NOESYPHSW CDCl3 E:\\ CCY 9
General
DATE = 2018/07/08
TIME = 11:52
INSTRUM = spect
PULPROG = noesygpphpp
F2 (1H)
SI = 1024
SF = 500.03
SW_p = 5102.041
F1 (1H)
SI = 1024
SF = 500.03
SW_p = 5102.041
F1 [ppm]
F2 [ppm]