Electronic Supplementary Material (ESI) for ChemComm.

Metal-free nitro-carbocyclization of 1,6−enyne with ^{t}BuONO and TEMPO

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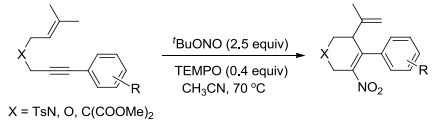
1. General remarks

For product purification by flash column chromatography, silica gel (200−300 mesh). ^{1}H NMR spectra were recorded on 400 MHz in $CDCl_3$ and ^{13}C NMR spectra were recorded on 100 MHz in $CDCl_3$. Chemical shifts (ppm) were recorded with tetramethylsilane (TMS) as the internal reference standard. Multiplicities are given as: s (singlet), d (doublet), t (triplet), dd (doublet of doublets), q (quartet) or m (multiplet). IR spectra were recorded on a FT-IR spectrometer and only major peaks are reported in cm^{-1}. HR-MS was obtained using a Q-TOF instrument equipped with ESI source. Copies of their ^{1}H NMR and ^{13}C NMR spectra are provided in the Supporting Information. Commercially available reagents were used without further purification. All solvents were dried under standard method.

2. General Procedure for the nitration/cyclization of 1,6-enynes with ^{t}BuONO and TEMPO



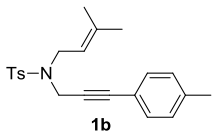
To a 10 mL dried tube were successively added 1,6-enynes **1a** (0.2 mmol, 1.0 equiv) ,TEMPO (0.08 mmol, 0.4 equiv), MeCN(2.0 mL) and *tert*-butyl nitrite (0.50 mmol, 2.5 equiv). The reaction mixture was stirring at 70 ^{o}C for 12 h under air. The solution was extracted with EtOAc and brine, then purified by column chromatography (silica gel, appropriate mixture of *n*-hexane/ethyl acetate) to afford **2a**.

3. Prepartion of Starting Materials

All of 1,6-enynes 1 were synthesized according to the previous literature.[1]

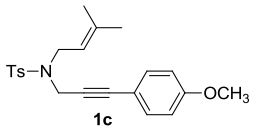
4. Characterization data of 1,6-enyne 1a-1y

Enynes 1a, 1t, 1u, 1v, 1w, 1x, and 1y were synthesized according to the previous literature[1], and the NMR spectroscopies were in full accordance with the data in the literature[1].



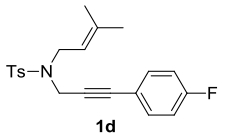
1b

4-methyl-N-(3-methylbut-2-en-1-yl)-N-(3-(p-tolyl)prop-2-yn-1-yl)benzenesulfonamide: 1b ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 2 H), 7.24 (d, J = 8.4 Hz, 2 H), 7.03 (d, J = 8.0 Hz, 2 H), 6.94 (d, J = 8.0 Hz, 2 H), 5.15−5.19 (m, 1 H), 4.27 (s, 2 H), 3.87 (d, J = 7.6 Hz, 2 H), 2.33 (s, 3 H), 2.32 (s, 3 H), 1.74 (s, 3 H), 1.69 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 138.9, 138.4, 136.0, 131.3, 129.4, 128.8, 127.8, 119.2, 118.1, 85.4, 81.4, 44.1, 36.3, 25.9, 21.4, 17.9.



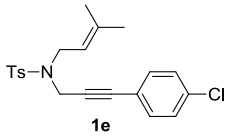
1c

N-(3-(4-methoxyphenyl)prop-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide: 1c ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 2 H), 7.24 (d, J = 8.0 Hz, 2 H), 7.00 (d, J = 8.4 Hz, 2 H), 6.75 (d, J = 8.8 Hz, 2 H), 5.17 (t, J = 7.2 Hz, 1 H), 4.26 (s, 2 H), 3.87 (d, J = 7.6 Hz, 2 H), 3.78 (s, 3 H), 2.33 (s, 3 H), 1.74 (s, 3 H), 1.69 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.5, 143.1, 138.8, 136.0, 132.8, 129.3, 127.7, 118.0, 114.3, 113.6, 85.2, 80.6, 55.2, 44.0, 36.3, 25.8, 21.3, 17.8.



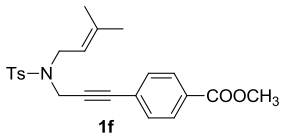
1d

N-(3-(4-fluorophenyl)prop-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide: 1d ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 2 H), 7.25 (d, J = 8.0 Hz, 2 H), 7.02−7.05 (m, 2 H), 6.93 (t, J = 8.4 Hz, 2 H), 5.16 (d, J = 6.4 Hz, 1 H), 4.26 (s, 2 H), 3.87 (d, J = 7.2 Hz, 2 H), 2.34 (s, 3 H),1.74 (s, 3 H), 1.69 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 161.2, 143.2, 139.0, 136.1, 133.3, 133.2, 129.4, 127.8, 118.4, 118.0, 115.5, 115.3, 84.2, 82.0, 44.1, 36.2, 25.9, 21.4, 17.9.



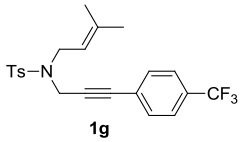
1e

N-(3-(4-chlorophenyl)prop-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide: 1e ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.4 Hz, 2 H), 7.20−7.25 (m, 4 H), 6.97 (d, J = 8.8 Hz, 2 H), 5.14−5.18 (m, 1 H), 4.26 (s, 2 H), 3.86 (d, J = 7.2 Hz, 2 H), 2.34 (s, 3 H), 1.74 (s, 3 H), 1.68 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.5, 139.3, 136.3, 134.6, 132.9, 129.7, 128.7, 128.1, 121.0, 118.2, 84.4, 83.6, 44.4, 36.5, 26.1, 21.6, 18.1.



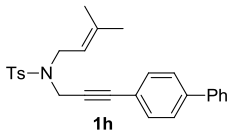
1f

Methyl 4-(3-(4-methyl-N-(3-methylbut-2-en-1-yl)phenylsulfonamido)prop-1-yn-1-yl)benzoate: 1f ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.91 (d, J = 8.4 Hz, 2 H), 7.87 (d, J = 8.0 Hz, 2 H), 7.24 (d, J = 8.0 Hz, 2 H), 7.10 (d, J = 8.4 Hz, 2 H), 5.17 (t, J = 7.2 Hz, 1 H), 4.29 (s, 2 H), 3.91 (s, 3 H), 3.88 (d, J = 7.2 Hz, 2 H), 2.32 (s, 3 H), 1.74 (s, 3 H), 1.69 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.2, 143.3, 139.1, 135.9, 131.2, 129.6, 129.4, 129.2, 127.8, 126.8, 117.8, 85.4, 84.5, 52.1, 44.2, 36.2, 25.8, 21.3, 17.8.



1g

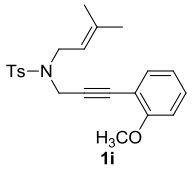
4-methyl-N-(3-methylbut-2-en-1-yl)-N-(3-(4-(trifluoromethyl)phenyl)prop-2-yn-1-yl)benzenesulfonamide: 1g ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.4 Hz, 2 H), 7.50 (d, J = 8.0 Hz, 2 H), 7.25 (d, J = 8.0 Hz, 2 H), 7.15 (d, J = 8.0 Hz, 2 H), 5.15−5.19 (m, 1 H), 4.29 (s, 2 H), 3.88 (d, J = 7.2 Hz, 2 H), 2.33 (s, 3 H), 1.75 (s, 3 H), 1.68 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.4, 139.2, 136.0, 131.6, 129.9, 129.4, 127.9, 126.1, 125.1, 125.1, 125.0, 125.0, 122.4, 117.9, 85.0, 84.0, 44.3, 36.2, 25.9, 21.4, 17.9.



1h

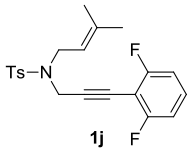
N-(3-([1,1'-biphenyl]-4-yl)prop-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide: 1h ^{1}H NMR

(400 MHz, $CDCl_3$): δ 7.79 (d, J = 8.4 Hz, 2 H), 7.54−7.56 (m, 2 H), 7.42−7.48 (m, 4 H), 7.34−7.38 (m, 1 H), 7.26 (d, J = 7.6 Hz, 2 H), 7.12 (d, J = 8.4 Hz, 2 H), 5.17−5.21 (m, 1 H), 4.30 (s, 2 H), 3.89 (d, J = 7.2 Hz, 2 H), 2.34 (s, 3 H), 1,76 (s, 3 H), 1.71 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 141.1, 140.2, 139.0, 136.1, 131.8, 129.4, 128.9, 127.9, 127.7, 127.0, 126.8, 121.2, 118.1, 85.2, 82.9, 44.2, 36.4, 25.9, 21.4, 17.9.



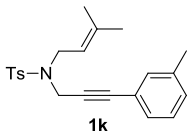
1i

N-(3-(2-methoxyphenyl)prop-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide: 1i ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.4 Hz, 2 H), 7.24−7.26 (m, 1 H), 7.18−7.23 (m, 2 H), 6.90−6.93 (m, 1 H), 6.79−6.83 (m, 2 H), 5.16−5.21 (m, 1 H), 4.33 (s, 2 H), 3.89 (d, J = 7.6 Hz, 2 H), 3.79 (s, 3 H), 2.28 (s, 3 H), 1.73 (s, 3 H), 1.70 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 143.1, 138.9, 136.1, 133.4, 129.7, 129.3, 127.8, 120.1, 118.2, 111.6, 110.4, 86.3, 81.9, 55.5, 44.1, 36.6, 25.9, 21.4, 17.8.



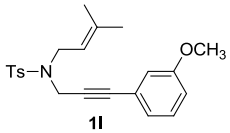
1j

N-(3-(2,6-difluorophenyl)prop-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide: 1j ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 2 H), 7.29 (d, J = 8.0 Hz, 2 H), 6.72−6.78 (m, 1 H), 6.50 (dd , J = 2.0 Hz, 7.6 Hz, 2 H), 5.15−5.18 (m, 1 H), 4.26 (s, 2 H), 3.87 (d, J = 7.2 Hz, 2 H), 2.38 (s, 3 H), 1.75(s, 3 H), 1.68(s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.0, 163.9, 161.5, 161.4, 143.8, 140.0, 136.2, 129.8, 128.1, 125.2, 125.1, 125.0, 118.0, 114.8, 114.7, 114.6, 114.5, 105.0, 104.8, 104.5, 84.7, 83.4, 83.4, 83.4, 44.5, 36.3, 26.1, 21.5, 18.1.



1k

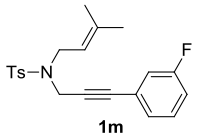
4-methyl-N-(3-methylbut-2-en-1-yl)-N-(3-(m-tolyl)prop-2-yn-1-yl)benzenesulfonamide: 1k ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.78 (d, J = 8.4 Hz, 2 H), 7.25 (d, J = 6.4 Hz, 2 H), 7.07−7.14 (m, 2 H), 6.85−6.87 (m, 2 H), 5.15−5.20 (m, 1 H), 4.27 (s, 2 H), 3.87 (d, J = 7.2 Hz, 2 H), 2.34 (s, 3 H), 2.23 (s, 3 H), 1.74 (s, 3 H), 1.69 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.2, 139.0, 137.7, 136.1, 132.0, 129.4, 129.2, 128.5, 128.0, 127.9, 122.1, 118.1, 85.5, 81.8, 44.1, 36.3, 25.9, 21.4, 21.2, 17.9.



1l

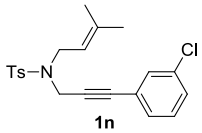
N-(3-(3-methoxyphenyl)prop-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide:1l ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.4 Hz, 2 H), 7.25 (d, J = 8.0 Hz, 2 H), 7.14 (t, J = 8.0 Hz, 1 H), 6.81−6.84 (m, 1 H), 6.64 (d, J = 7.6 Hz, 1 H), 6.59 (dd, J = 1.2 Hz, 2.4 Hz, 1 H), 5.15−5.19 (m, 1 H), 4.27 (s, 2 H), 3.87 (d, J = 7.2 Hz, 2 H), 3.77 (s, 3 H), 2.34 (s, 3 H), 1.74 (s, 3 H), 1.69 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 159.1, 143.3,

139.0, 136.0, 129.4, 129.1, 127.8, 123.9, 123.3, 118.0, 116.9, 114.2, 85.2, 82.1, 55.2, 44.1, 36.3, 25.9, 21.4, 17.9.



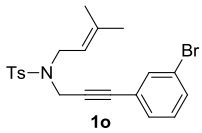
1m

N-(3-(3-fluorophenyl)prop-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide: 1m ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 2 H), 7.26 (d, J = 8.0 Hz, 2 H), 7.17−7.23 (m, 1 H), 6.95−7.00 (m, 1 H), 6.85 (dd, J =1.2 Hz, 7.6 Hz, 1 H), 6.64−6.67 (m, 1 H), 5.15−5.19 (m, 1 H), 4.27 (s, 2 H), 3.87 (d, J = 7.2 Hz, 2 H), 2.35 (s, 3 H), 1.75 (s, 3 H), 1.69 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 163.6, 161.1, 143.7, 139.4, 136.2, 130.0, 129.9, 129.7, 128.1, 127.5, 127.4, 124.4, 124.3, 118.6, 118.4, 118.2, 116.0, 115.8, 84.4, 84.3, 83.5, 44.4, 36.4, 26.1, 21.6, 18.1.



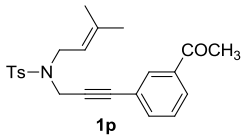
1n

N-(3-(3-chlorophenyl)prop-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide: 1n ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 2 H), 7.24−7.28 (m, 3 H), 7.16 (t, J = 8.0 Hz, 1 H), 6.92−6.98 (m, 2 H), 5.15−5.19 (m, 1 H), 4.27 (s, 2 H), 3.87 (d, J = 7.6 Hz, 2 H), 2.37 (s, 3 H), 1.75 (s, 3 H), 1.68 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 139.4, 136.3, 134.1, 131.2, 129.7, 129.6, 128.8, 128.1, 124.2, 118.2, 84.2, 83.8, 44.5, 36.4, 26.1, 21.7, 18.1.



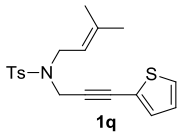
1o

N-(3-(3-bromophenyl)prop-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide: 1o ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.77 (d, J = 8.0 Hz, 2 H), 7.40 (d, J = 8.0 Hz, 1 H), 7.27 (d, J = 8.0 Hz, 2 H), 7.10 (m, 2 H), 7.01 (d, J= 7.6 Hz, 1 H), 5.15−5.19 (m, 1 H), 4.27 (s, 2 H), 3.87 (d, J = 7.2 Hz, 2 H), 2.38 (s, 3 H), 1.75 (s, 3 H), 1.68 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 139.4, 136.2, 134.4, 131.7, 130.1, 129.8, 129.7, 128.1, 124.5, 122.1, 118.2, 84.0, 83.9, 44.5, 36.4, 26.1, 21.7, 18.1.



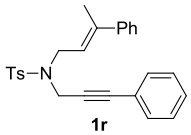
1p

N-(3-(3-acetylphenyl)prop-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide: 1p ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.85 (d, J = 7.6 Hz, 1 H), 7.78 (d, J = 8.0 Hz, 2 H), 7.68 (s, 1 H), 7.36 (t, J = 8.0 Hz, 1 H), 7.23−7. 28 (m, 3 H), 5.16−5.19 (m, 1 H), 4.30 (s, 2 H), 3.88 (d, J = 7.2 Hz, 2 H), 2.58 (s, 3 H), 2.32 (s, 3 H), 1.75 (s, 3 H), 1.70 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.3, 143.7, 139.4, 137.2, 136.1, 135.8, 131.3, 129.7, 128.7, 128.3, 128.0, 123.2, 118.1, 84.5, 83.6, 44.4, 36.4, 26.8, 26.1, 21.6, 18.1.



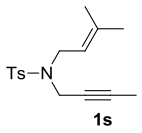
1q

4-methyl-N-(3-methylbut-2-en-1-yl)-N-(3-(thiophen-2-yl)prop-2-yn-1-yl)benzenesulfonamide: 1q ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.76 (d, J = 8.4 Hz, 2 H), 7.27 (d, J = 8.0 Hz, 2 H), 7.19 (dd, J = 2.0 Hz, 4.4 Hz, 1 H), 6.88−6.90 (m, 2 H), 5.13−5.18 (m,1 H), 4.28 (s, 2 H), 3.85 (d, J = 7.2 Hz, 2 H), 2.34 (s, 3 H), 1.74 (s, 3 H), 1.69 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 139.4, 136.1, 132.3, 129.8, 128.0, 127.4, 127.0, 122.5, 118.2, 86.5, 78.9, 44.5, 36.7, 26.1, 21.7, 18.1.



1r

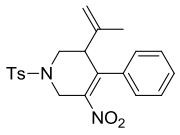
(E)-4-methyl-N-(3-phenylbut-2-en-1-yl)-N-(3-phenylprop-2-yn-1-yl)benzenesulfonamide: 1r ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.81 (d, J = 8.0 Hz, 2 H), 7.21−7.36 (m, 10 H), 7.06−7.08 (m, 2 H), 5.75−5.79 (m, 1 H), 4.34 (s, 2 H), 4.11 (d, J = 7.2 Hz, 2 H), 2.34 (s, 3 H), 2.11 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.7, 142.8, 141.1, 136.3, 131.7, 129.8, 128.6, 128.5, 128.4, 128.1, 127.7, 126.0, 122.5, 121.3, 85.9, 82.4, 45.1, 37.2, 21.7, 16.3.



1s

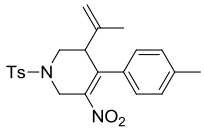
N-(but-2-yn-1-yl)-4-methyl-N-(3-methylbut-2-en-1-yl)benzenesulfonamide: 1s ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.74 (d, J = 8.4 Hz, 2 H), 7.29 (d, J = 8.0 Hz, 2 H), 5.08−5.12 (m, 1 H), 3.99 (d, J = 2.4 Hz, 2 H), 3.77 (d, J = 7.2 Hz, 2 H), 2.43 (s, 3 H), 1.72 (s, 3 H), 1.66 (s, 3 H), 1.53 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.3, 138.9, 136.5, 129.4, 128.2, 118.4, 81.4, 72.3, 44.1, 36.2, 26.1, 21.7, 18.0, 3.4.

5. Characterization data of Products 2a-2aa



2a

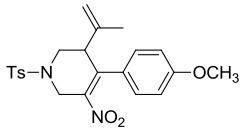
5-nitro-4-phenyl-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine: 2a ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.0 Hz, 2 H), 7.38 (d, J = 8.0 Hz, 2 H), 7.30−7. 32 (m, 3 H), 7.02−7.04 (m, 2 H), 4.92 (s, 1 H), 4.77 (s, 1 H), 4.54 (d, J = 16.0 Hz, 1 H), 3.80 (dd, J = 2.0 Hz, 16.4 Hz, 1 H), 3.62−3.66 (m, 1 H), 3.33 (s, 1 H), 3.05 (dd, J = 4.4 Hz, 12 Hz, 1 H), 2.46 (s, 3 H), 1.71 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.4, 142.7, 141.3, 141.2, 135.8, 132.7, 130.0, 128.6, 128.4, 127.7, 126.7, 116.9, 48.8, 46.8, 44.8, 21.6. HRMS (ESI, m/z): calcd for $C_{21}H_{22}N_2O_4S$: $[M+Na]^+$ = 421.1192, found: 421.1185. IR (neat, cm^{-1}): 3350, 3063, 2923, 2374, 1802, 1597, 1526, 1459, 1345, 1258, 1167, 1021, 947, 857, 813, 737, 700, 658, 549.



2b

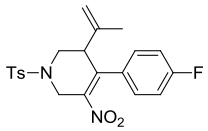
5-nitro-3-(prop-1-en-2-yl)-4-(p-tolyl)-1-tosyl-1,2,3,6-tetrahydropyridine: 2b Yellow solid; mp: 112−114 ^{o}C. ^{1}H

NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 2 H), 7.37 (d, J = 8.0 Hz, 2 H), 7.10 (d, J = 8.0 Hz, 2 H), 6.92 (d, J = 8.0 Hz, 2 H), 4.91 (t, J = 1.2 Hz, 1 H), 4.77 (s, 1 H), 4.53 (d, J = 16.0 Hz, 1 H), 3.75−3.80 (m, 1 H), 3.64 (dd, J = 3.6 Hz, 12 Hz, 1 H), 3.32 (s, 1 H), 3.02−3.06 (m, 1 H), 2.45 (s, 3 H), 2.32 (s, 3 H), 1.71 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.3, 142.6, 141.4, 141.1, 138.7, 132.9, 132.7, 130.0, 129.2, 127.7, 126.6, 116.7, 48.7, 46.8, 44.9, 21.5, 21.2. HRMS (ESI, m/z): calcd for $C_{22}H_{24}N_2O_4S$: $[M+Na]^+$ = 435.1349, found: 435.1360. IR (neat, cm^{-1}): 3345, 3030, 2924, 2857, 2737, 2587, 1918, 1776, 1722, 1642, 1598, 1526, 1454, 1403, 1346, 1266, 1229, 1167, 1113, 1021, 979, 947, 904, 857, 819, 737, 659, 622, 560, 551, 518, 482.



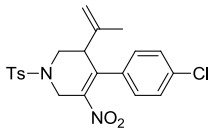
2c

4-(4-methoxyphenyl)-5-nitro-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine: 2c ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 2 H), 7.37 (d, J = 8.0 Hz, 2 H), 6.98 (d, J = 8.8 Hz, 2 H), 6.82 (d, J = 8.4 Hz, 2 H), 4.92 (s, 1 H), 4.77 (s, 1 H), 4.53 (d, J =15.2 Hz, 1 H), 3.74−3.78 (m, 4 H), 3.62−3.66 (m, 1 H), 3.32 (s, 1 H), 3.01−3.05 (m, 1 H), 2.46 (s, 3 H), 1.71 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.2, 144.6, 142.7, 141.8, 140.9, 133.1, 130.3, 128.5, 128.0, 128.0, 117.0, 114.3, 55.4, 48.9, 47.2, 45.3, 21.8, 21.8. HRMS (ESI, m/z): calcd for $C_{22}H_{24}N_2O_5S$: $[M+Na]^+$ = 451.1298, found: 451.1309. IR (neat, cm^{-1}): 3393, 3061, 2926, 2854, 2374, 2052, 1921, 1778, 1720, 1650, 1603, 1523, 1460, 1344, 1295, 1256, 1167, 1114, 1031, 978, 947, 906, 812, 736, 660, 551.



2d

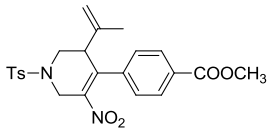
4-(4-fluorophenyl)-5-nitro-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine: 2d Yellow solid; mp: 156−158 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2 H), 7.38 (d, J = 8.4 Hz, 2 H), 6.99−7.02 (m, 4 H), 4.93 (s, 1 H), 4.76 (s, 1 H), 4.51 (d, J = 16.4 Hz, 1 H), 3.81 (dd, J = 2.0 Hz, 16.4 Hz, 1 H), 3.61−3.65 (m, 1 H), 3.28 (s, 1 H), 3.03−3.08 (m, 1 H), 2.46 (s, 3 H), 1.71 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.2, 161.7, 144.7, 143.4, 141.4, 140.5, 133.0, 131.9, 131.9, 130.3, 129.0, 128.9, 128.0, 117.3, 116.0, 115.8, 49.2, 47.0, 45.1, 21.8, 21.8. HRMS (ESI, m/z): calcd for $C_{21}H_{21}FN_2O_4S$: $[M+Na]^+$ = 439.1098, found: 439.1111. IR (neat, cm^{-1}): 3333, 3073, 2924, 2853, 2511, 2375, 1973, 1923, 1899, 1781, 1721, 1640, 1597, 1526, 1453, 1406, 1379, 1345, 1306, 1262, 1226, 11164, 1117, 1041, 979, 948, 889, 856, 834, 814, 741, 659, 617, 551, 548, 527, 491.



2e

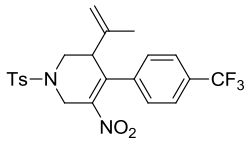
4-(4-chlorophenyl)-5-nitro-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine: 2e Yellow solid; mp: 164−166 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2 H), 7.38 (d, J = 8.0 Hz, 2 H), 7.26−7.29 (m, 2 H), 6.97 (d, J = 8.8 Hz, 2 H), 4.93 (s, 1 H), 4.75 (s, 1 H), 4.51 (dd, J = 1.2 Hz, 16.4 Hz, 1 H), 3.81 (dd, J = 2.4 Hz, 16.4 Hz, 1 H), 3.62 (dd, J = 3.6 Hz, 12.4 Hz, 1 H), 3.27 (s, 1 H), 3.04−3.08 (m, 1 H), 2.46 (s, 3 H), 1.70 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.5, 143.1, 141.0, 140.3, 134.7, 134.2, 132.8, 130.0, 128.8, 128.2, 127.7, 117.1, 48.9, 46.8, 44.8, 21.6, 21.5. HRMS (ESI, m/z): calcd for $C_{21}H_{21}C_{11}N_2O_4S$: $[M+Na]^+$ = 455.0803, found: 455.0817. IR (neat,

cm^{-1}):3372, 3066, 2924, 2854, 2739, 1914, 1736, 1644, 1596, 1527, 1491, 1457, 1344, 1266, 1228, 1167, 1091, 1017, 947, 858, 829, 736, 658, 605, 550, 515.



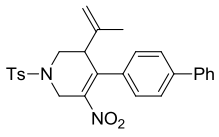
2f

4-(5-nitro-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridin-4-yl) benzoate : 2f Yellow solid; mp: 168−170 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.98 (d, J = 8.4 Hz, 2 H), 7.73 (d, J = 8.0 Hz, 2 H), 7.39 (d, J = 8.4 Hz, 2 H), 7.09 (d, J = 8.4 Hz, 2 H), 4.92 (s, 1 H), 4.75 (s, 1 H), 4.51−4.55 (m, 1 H), 3.90 (s, 3 H), 3.84 (dd, J = 2.0 Hz, 16.4 Hz, 1 H), 3.62 (dd, J = 3.6 Hz, 12 Hz, 1 H), 3.31 (s, 1 H), 3.07−3.11 (m, 1 H), 2.47 (s, 3 H), 1.70 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.6, 144.8, 143.4, 141.3, 141.1, 140.9, 133.1, 130.5, 130.3, 130.0, 128.0, 127.1, 117.5, 52.5, 49.2, 47.0, 45.0, 21.8, 21.8. HRMS (ESI, m/z): calcd for $C_{23}H_{24}N_2O_6S$: $[M+Na]^+$ = 479.1247, found: 479.1261. IR (neat, cm^{-1}): 3422, 3062, 2925, 2854, 2372, 1929, 1809, 1722, 1644, 1608, 1528, 1437, 1405, 1344, 1279, 1167, 1111, 1021, 947, 861, 817, 775, 737, 708, 658, 550, 489.



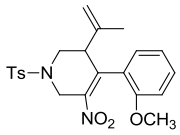
2g

5-nitro-3-(prop-1-en-2-yl)-1-tosyl-4-(4-(trifluoromethyl)phenyl)-1,2,3,6-tetrahydropyridine: 2g ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.4 Hz, 2 H), 7.58 (d, J = 8.4 Hz, 2 H), 7.39 (d, J = 8.0 Hz, 2 H), 7.15 (d, J = 8.0 Hz, 2 H), 4.95 (s, 1 H), 4.77 (s, 1 H), 4.55 (d, J = 16.4 Hz, 1 H), 3.84 (dd, J = 2.0 Hz, 16.4 Hz, 1 H), 3.62−3.66 (m, 1 H), 3.29 (S, 1 H), 3.05−3.10 (m, 1 H), 2.47 (s, 3 H), 1.72 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 143.4, 140.7, 140.5, 139.8, 132.7, 130.1, 127.8, 127.3, 125.5, 125.5, 117.4, 49.0, 46.7, 44.7, 21.6, 21.6. HRMS (ESI, m/z): calcd for $C_{22}H_{21}F_3N_2O_4S$: $[M+Na]^+$ = 489.1066, found: 489.1078. IR (neat, cm^{-1}): 3404, 3060, 2926, 2856, 2307, 1923, 1722, 1642, 1617, 1598, 1529, 1458, 1407, 1325, 1266, 1229, 1167, 1128, 1069, 1019, 947, 908, 842, 816, 739, 660, 578, 550, 515.



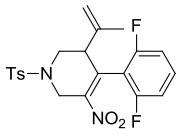
2h

4-([1,1'-biphenyl]-4-yl)-5-nitro-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine: 2h Yellow solid; mp: 92−94 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.4 Hz, 2 H), 7.52−7.57 (m, 4 H), 7.31−7.43 (m, 5 H), 7.11 (d, J = 8.4 Hz, 2 H), 4.94 (s, 1 H), 4.81 (s, 1 H), 4.54−4.59 (m, 1 H), 3.79−3.83 (m, 1 H), 3.67 (dd, J = 3.2 Hz, 12.4 Hz, 1 H), 3.36 (s, 1 H), 3.06 (dd, J = 4.4 Hz, 12 Hz, 1 H), 2.45 (s, 3 H), 1.74 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 143.1, 141.7, 141.5, 141.2, 140.3, 134.9, 133.0, 130.3, 129.0, 128.0, 127.5, 127.3, 127.2, 117.2, 49.0, 47.1, 45.1, 21.9, 21.8. HRMS (ESI, m/z): calcd for $C_{27}H_{25}N_2O_4S$: $[M+Na]^+$ = 497.1505, found: 497.1519. IR (neat, cm^{-1}): 3306, 3058, 2924, 2856, 2587, 2368, 1921, 1807, 1720, 1644, 1599, 1527, 1488, 1457, 1345, 1266, 1229, 1168, 1113, 1019, 1009, 979, 947, 906, 840, 816, 737, 701, 661, 549, 506.



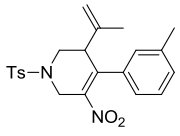
2i

4-(2-methoxyphenyl)-5-nitro-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine: 2i Yellow solid; mp: 166−168 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.73 (d, J = 8.4 Hz, 2 H), 7.37 (d, J = 8.0 Hz, 2 H), 7.25−7.30 (m, 1 H), 6.92−6.94 (m, 2 H), 6.82−6.90 (m, 1 H), 4.83 (s, 1 H), 4.75 (s, 1 H), 4.58 (d, J = 16.0 Hz, 1 H), 3.78 (dd, J = 2.0 Hz, 16.4 Hz, 1 H), 3.70 (s, 3 H), 3.56−3.59 (m, 1 H), 3.45−3.46 (m, 1 H), 3.08 (d, J = 10.0 Hz, 1 H), 2.46 (s, 3 H), 1.68 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 156.2, 144.7, 143.5, 141.9, 133.1, 130.2, 130.1, 128.0, 125.3, 120.7, 116.5, 111.1, 55.5, 47.0, 47.0, 44.9, 21.8, 21.7. HRMS (ESI, m/z): calcd for $C_{22}H_{24}N_2O_5S$: $[M+Na]^+$ = 451.1298, found: 451.1310. IR (neat, cm^{-1}): 3392, 3066, 2925, 2851, 2375, 1923, 1737, 1598, 1526, 1492, 1344, 1290, 1254, 1167, 1117, 1023, 980, 947, 906, 859, 813, 752, 737, 704, 658, 550.



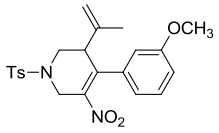
2j

4-(2,6-difluorophenyl)-5-nitro-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine: 2j Yellow solid; mp: 170−172 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 2 H), 7.39 (d, J = 8.0 Hz, 2 H), 6.74−6.79 (m, 1 H), 6.53 (d, J = 6.0 Hz, 2 H), 4.97 (s, 1 H), 4.76 (s, 1 H), 4.51 (d, J = 16.8 Hz, 1 H), 3.82−3.87 (m, 1 H), 3.62 (dd, J = 3.6 Hz, 12.4 Hz, 1 H), 3.21 (s, 1 H), 3.08 (dd, J = 4.8 Hz, 12.4 Hz, 1 H), 2.47 (s, 3 H), 1.73 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 164.4, 164.2, 161.9, 161.7, 144.8, 143.9, 140.9, 139.5, 139.2, 139.1, 133.2, 130.4, 128.0, 117.6, 110.6, 110.5, 110.4, 110.3, 104.7, 104.4, 104.2, 49.0, 46.9, 44.9, 21.8, 21.8. HRMS (ESI, m/z): calcd for $C_{21}H_{20}F_2N_2O_4S$: $[M+Na]^+$ = 457.1004, found: 457.1015. IR (neat, cm^{-1}): 3302, 3058, 2927, 2853, 2686, 2306, 2110, 1919, 1802, 1722, 1621, 1591, 1529, 1494, 1432, 1401, 1346, 1320, 1265, 1228, 1165, 1118, 1090, 1036, 987, 938, 899, 862, 837, 812, 738, 705, 658, 587, 547, 511, 482.



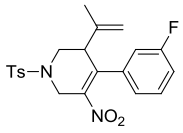
2k

5-nitro-3-(prop-1-en-2-yl)-4-(m-tolyl)-1-tosyl-1,2,3,6-tetrahydropyridine: 2k ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 2 H), 7.38 (d, J = 8.0 Hz, 2 H), 7.17−7.21 (m, 1 H), 7.11 (d, J = 7.6 Hz, 1 H), 6.83 (d, J = 7.6 Hz, 2 H), 4.92 (s, 1 H), 4.77 (s, 1 H), 4.54 (d, J = 16.4 Hz, 1 H), 3.76−3.80 (m, 1 H), 3.63−3.67 (m, 1 H), 3.31 (s, 1 H), 3.01−3.05 (m, 1 H), 2.46 (s, 3 H), 2.30 (s, 3 H), 1.72 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.6, 142.9, 141.6, 141.5, 138.4, 136.0, 133.1, 130.3, 129.7, 128.6, 128.0, 127.5, 124.1, 117.0, 49.0, 47.1, 45.1, 21.8, 21.8, 21.6. HRMS (ESI, m/z): calcd for $C_{22}H_{24}N_2O_4S$: $[M+Na]^+$ = 435.1349, found: 435.1358. IR (neat, cm^{-1}): 3343, 3048, 2923, 2859, 2373, 1926, 1711, 1645, 1599, 1526, 1492, 1457, 1345, 1266, 1229, 1167, 1115, 1091, 1020, 954, 904, 857, 836, 791, 737, 705, 658, 575, 550, 442..



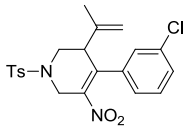
2l

4-(3-methoxyphenyl)-5-nitro-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine: 2l Yellow solid; mp: 140−142 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 2 H), 7.37 (d, J = 8.4 Hz, 2 H), 7.21 (t, J = 8.0 Hz, 1 H), 6.82−6.85 (m, 1 H), 6.56−6.61 (m, 1 H), 6.56 (s, 1 H), 4.93 (s, 1 H), 4.78 (s, 1 H), 4.52 (d, J = 16.0 Hz, 1 H), 3.78 (dd, J = 2.0 Hz, 16.4 Hz, 1 H), 3.75 (s, 3 H), 3.63 (dd, J = 3.2 Hz, 12 Hz, 1 H), 3.30 (s, 1 H), 3.04 (dd, J = 4.4 Hz, 12 Hz, 1 H), 2.50 (s, 3 H), 1.72 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 160.0, 144.6, 143.0, 141.5, 141.0, 137.3, 133.1, 130.2, 129.8, 127.9, 119.3, 117.0, 114.0, 113.1, 55.4, 48.9, 47.1, 45.0, 21.8, 21.8. HRMS (ESI, m/z): calcd for $C_{22}H_{24}FN_2O_5S$: $[M+Na]^+$ = 451.1298, found: 451.1312. IR (neat, cm^{-1}): 3305, 3059, 2926, 2856, 2740, 2585, 2307, 1924, 1721, 1646, 1599, 1580, 1527, 1489, 1459, 1431, 1378, 1345, 1290, 1267, 1209, 1168, 1114, 1019, 1048, 1019, 954, 905, 857, 835, 787, 737, 704, 659, 549, 463.



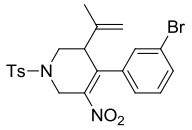
2m

4-(3-fluorophenyl)-5-nitro-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine: 2m Yellow solid, mp: 140−142 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 2 H), 7.38 (d, J = 8.0 Hz, 2 H), 7.24−7.30 (m, 1 H), 7.00 (dt, J = 2.0 Hz, 8.4 Hz, 1 H), 6.80 (d, J = 8.0 Hz, 1 H), 6.71−6.74 (m, 2 H), 4.94 (s, 1 H), 4.77 (s, 1 H), 4.50−4.54 (m, 1 H), 3.81−3.85 (m, 1 H), 3.63 (dd, J = 3.6 Hz, 12 Hz, 1 H), 3.26 (s, 1 H), 3.05−3.09 (m, 1 H), 2.46 (s, 3 H), 1.72 (s, 3 H).^{13}C NMR (100 MHz, $CDCl_3$): δ 163.9, 161.5, 144.8, 143.5, 140.3, 138.2, 138.1, 133.1, 130.5, 130.4, 130.3, 128.0, 122.9, 122.9, 117.4, 116.0, 115.8, 114.4, 114.2, 49.0, 47.0, 45.0, 21.8, 21.8. HRMS (ESI, m/z): calcd for $C_{21}H_{21}FN_2O_4S$: $[M+Na]^+$ = 439.1098, found: 439.1109. IR (neat, cm^{-1}): 3338, 3071, 2923, 2856, 2370, 1922, 1801, 1721, 1641, 1583, 1527, 1485, 1452, 1380, 1344, 1264, 1229, 1164, 1114, 1039, 956, 897, 874, 846, 811, 787, 744, 703, 656, 637, 573, 545, 486.



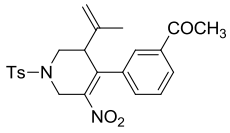
2n

4-(3-chlorophenyl)-5-nitro-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine: 2n Yellow solid, mp: 116−118 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.0 Hz, 2 H), 7.38 (d, J = 8.0 Hz, 2 H), 7.22−7.30 (m, 2 H), 6.98 (s, 1 H), 6.91 (d, J = 7.6 Hz, 1 H), 4.95 (s, 1 H), 4.76 (s, 1 H), 4.52 (d, J = 16.4 Hz, 1 H), 3.81−3.86 (m, 1 H), 3.61−3.65 (m, 1 H), 3.25 (s, 1 H), 3.07 (dd, J = 4.4 Hz, 12.4 Hz), 2.47 (s, 3 H), 1.71 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 143.5, 141.1, 140.4, 137.9, 134.7, 133.2, 130.3, 130.0, 129.0, 128.0, 127.0, 125.4, 117.5, 49.1, 47.0, 45.0, 21.8, 21.8. HRMS (ESI, m/z): calcd for $C_{21}H_{21}ClN_2O_4S$: $[M+Na]^+$ = 455.0803, found: 455.0816. IR (neat, cm^{-1}): 3300, 3058, 2924, 2854, 2584, 2306, 1919, 1803, 1722, 1641, 1596, 1527, 1453, 1414, 1346, 1265, 1229, 1167, 1115, 1013, 951, 891, 856, 813, 734, 657, 549, 483, 443.



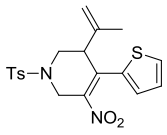
2o

4-(3-bromophenyl)-5-nitro-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine: 2o Yellow solid, mp: 102−104 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.72 (d, J = 8.4 Hz, 2 H), 7.44 (dd, J = 0.8 Hz, 8 Hz, 1 H), 7.38 (d, J = 8.4 Hz, 2 H), 7.13−7.19 (m, 2 H), 6.96 (d, J = 7.6 Hz, 2 H), 4.95 (s, 1 H), , 4.76 (s, 1 H), 4.49−4.54 (m, 1 H), 3.84 (dd, J = 2.0 Hz, 16.4 Hz, 1 H), 3.64 (dd, J = 3.6 Hz, 12 Hz, 1 H), 3.24 (s, 1 H), 3.04−3.09 (m, 1 H), 2.47 (s, 3 H), 1.71 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.8, 143.5, 141.0, 140.3, 138.1, 133.2, 131.9, 130.3, 130.2, 129.8, 128.0, 125.9, 122.6, 117.5, 49.1, 47.0, 45.0, 21.8, 21.8. HRMS (ESI, m/z): calcd for $C_{21}H_{21}BrN_2O_4S$: $[M+Na]^+$ = 499.0298, found: 499.0313. IR (neat, cm^{-1}): 3341, 3067, 2924, 2857, 2585, 2369, 1924, 1808, 1720, 1644, 1595, 1527, 1458, 1406, 1344, 1292, 1263, 1227, 1166, 1117, 1042, 950, 905, 858, 787, 723, 658, 550, 486, 435.



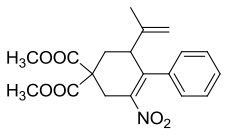
2p

1-(3-(5-nitro-3-(prop-1-en-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridin-4-yl)phenyl)ethanone: 2p ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.89 (d, J = 8.0 Hz, 2 H), 7.63−7.74 (m, 2 H), 7.38−7.44 (m, 3 H), 7.23−7.26 (m, 2 H), 4.93 (s, 1 H), 4.77 (s, 1 H), 4.55 (d, J = 16.8 Hz, 1 H), 3.81−3.86 (m, 1 H), 3.64−3.68 (m, 1 H), 3.32 (s, 1 H), 3.05−3.10 (m, 1 H), 2.56 (s, 3 H), 2.47 (s, 3 H), 1.71 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 197.4, 144.8, 143.5, 141.2, 137.4, 136.9, 133.1, 131.9, 130.3, 129.0, 128.9, 128.0, 126.5, 117.4, 49.3, 47.0, 45.0, 26.8, 21.9, 21.8. HRMS (ESI, m/z): calcd for $C_{23}H_{24}N_2O_5S$: $[M+Na]^+$ = 463.1298, found: 463.1308. IR (neat, cm^{-1}): 3357, 3058, 2925, 2857, 2373, 2307, 1923, 1810, 1687, 1646, 1598, 1528, 1494, 1426, 1358, 1346, 1267, 1221, 1168, 1116, 1019, 953, 907, 857, 816, 740, 703, 670, 574, 550, 481.



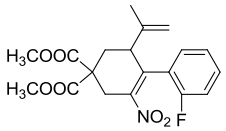
2q

5-nitro-3-(prop-1-en-2-yl)-4-(thiophen-2-yl)-1-tosyl-1,2,3,6-tetrahydropyridine: 2q Yellow solid, mp: 126−128 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 8.4 Hz, 2 H), 7.34−7.38 (m, 3 H), 6.95−6.97 (m, 2 H), 5.02 (s, 1 H), 4.86 (s, 1 H), 4.50 (d, J = 16.4 Hz, 1 H), 3.70−3.80 (m, 2 H), 3.29 (d, J = 1.6 Hz, 1 H), 2,95 (dd, J = 4.4 Hz, 12 Hz, 1 H), 2.45 (s, 3 H), 1.82 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 144.7, 143.2, 141.7, 136.0, 133.1, 131.8, 130.3, 128.0, 128.0, 127.8, 127.6, 117.2, 49.0, 46.9, 45.5, 21.9, 21.8. HRMS (ESI, m/z): calcd for $C_{19}H_{20}FN_2O_4S_2$: $[M+Na]^+$ = 427.0757, found: 427.0771. IR (neat, cm^{-1}): 3391, 3085, 2923, 2857, 2374, 1782, 1707, 1645, 1597, 1528, 1458, 1348, 1230, 1166, 1111, 1019, 969, 906, 850, 816, 716, 658, 549.



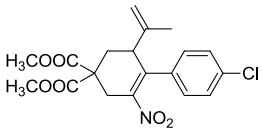
2u

Dimethyl 2-nitro-6-(prop-1-en-2-yl)-5,6-dihydro-[1,1'-biphenyl]-4,4(3H)-dicarboxylate: 2u Yellow solid, mp: 90−92 ℃. 1H NMR (400 MHz, $CDCl_3$): δ 7.26−7.28 (m, 3 H), 7.02−7.05 (m, 2 H), 4.73 (d, J = 10.8 Hz, 2 H), 3.81 (s, 3 H), 3.76 (s, 3 H), 3.56 (d, J = 6.8 Hz, 1 H), 3.20−3.33 (m, 2 H), 2.55−2.61 (m, 1 H), 2.10−2.16 (m, 1 H), 1.55 (s, 3 H). 13C NMR (100 MHz, $CDCl_3$): δ 170.6, 170.2, 145.2, 142.9, 139.1, 136.0, 128.5, 127.2, 116.5, 53.5, 53.4, 53.3, 47.5, 33.0, 32.3, 19.7. HRMS (ESI, m/z): calcd for $C_{19}H_{21}NO_6$: $[M+Na]^+$ = 382.1261, found: 382.1271. IR (neat, cm^{-1}): 3570, 3469, 3058, 3026, 2955, 2854, 2373, 1952, 1735, 1646, 1599, 1525, 1436, 1359, 1298, 1262, 1201, 1099, 1049, 957, 905, 846, 769, 737, 702, 609, 534.



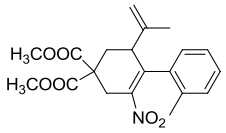
2v

Dimethyl 2'-fluoro-2-nitro-6-(prop-1-en-2-yl)-5,6-dihydro-[1,1'-biphenyl]-4,4(3 H)-dicarboxylate: 2v ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.24−7.32 (m, 2 H), 7.05−7.09 (m, 1 H), 6.96−7.03 (m, 2 H), 4.71−4.73 (m, 2 H), 3.82 (s, 3 H), 3.78 (s, 3 H), 3.56−3.61 (m, 1 H), 3.28−3.31 (m, 2 H), 2.57−2.62 (m, 1 H), 2.10−2.16 (m, 1 H), 1.56 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.6, 170.1, 160.1, 157.7, 146.3, 142.8, 135.3, 130.3, 130.3,129.5, 129.0, 128.8, 124.2, 124.2, 116.4, 115.9, 115.7, 53.6, 53.5, 53.4, 33.0, 32.3, 19.5. HRMS (ESI, m/z): calcd for $C_{19}H_{20}FNO_6$: $[M+Na]^+$ = 400.1067, found: 400.1179. IR (neat, cm^{-1}): 3456, 3076, 2956, 2854, 2374, 1920, 1737, 1646, 1613, 1579, 1528, 1491, 1449, 1352, 1299, 1261, 1204, 1104, 1050, 958, 907, 847, 819, 762, 702, 610, 568, 513, 471.



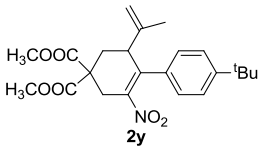
2w

Dimethyl 4'-chloro-2-nitro-6-(prop-1-en-2-yl)-5,6-dihydro-[1,1'-biphenyl]-4,4(3H)-dicarboxylate: 2w ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, *J* = 8.4 Hz, 2 H), 6.96−6.98 (m, 2 H), 4.71−4.76 (m, 2 H), 3.81 (s, 3 H), 3.77 (s, 3 H), 3.50−3.54 (m, 1 H), 3.20−3.31 (m, 2 H), 2.54−2.60 (m, 1 H), 2.09−2.14 (m, 1 H), 1.56 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.2, 169.8, 145.3, 142.3, 137.8, 134.2, 128.5, 128.3, 116.5, 53.2, 53.1, 53.1, 47.2, 32.6, 32.0, 19.4. HRMS (ESI, m/z): calcd for $C_{19}H_{21}NO_6Cl$: $[M+Na]^+$ = 416.0872, found: 416.0867. IR (neat, cm^{-1}): 3366, 2956, 2372, 1737, 1647, 1594, 1526, 1491, 1435, 1352, 1297, 1261, 1200, 1095, 1015, 906, 829, 734, 612, 526.



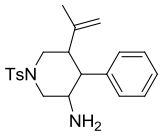
2x

Dimethyl 2'-methyl-2-nitro-6-(prop-1-en-2-yl)-5,6-dihydro-[1,1'-biphenyl]-4,4(3H)-dicarboxylate 2x ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.12−7.18 (m, 2 H), 7.02−7.06 (m, 1 H), 6.82 (d, *J* = 7.6 Hz, 1 H), 4.68−4.73 (m, 2 H), 3.82 (s, 3 H), 3.79 (s, 3 H), 3.41−3.46 (m, 1 H), 3.21−3.37 (m, 2 H), 2.55−2.61 (m, 1 H), 2.14−2.20 (m, 1 H), 2.16 (s, 3 H), 1.56 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.5, 170.1, 145.1, 142.5, 139.8, 134.9, 134.3, 130.0, 128.0, 127.7, 125.3, 116.0, 53.3, 53.2, 45.9, 32,6, 31.8, 20.0, 19.3. HRMS (ESI, m/z): calcd for $C_{20}H_{23}NO_6$: $[M+Na]^+$ = 396.1418, found: 396.1410. IR (neat, cm^{-1}): 3339, 2955, 2372, 1737, 1646, 1526, 1435, 1356, 1262, 1200, 1097, 1051, 956, 902, 847, 735, 703, 613.



2y

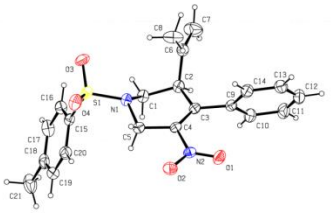
Dimethyl 4'-(tert-butyl)-2-nitro-6-(prop-1-en-2-yl)-5,6-dihydro-[1,1'-biphenyl]-4,4(3H)-dicarboxylate 2y ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26 (d, J = 8.0 Hz, 2 H), 6.97(d, J = 8.4 Hz, 2 H), 4.74 (d, J = 10 Hz, 2 H), 3.81 (s, 3 H), 3.76 (s, 3 H), 3.55−3.60 (m, 1 H), 3.17−3.34 (m, 2 H), 2.54−2.60 (m, 1 H), 2.11−2.17 (m, 1 H), 1.57 (s, 3 H), 1.28 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.3, 169.9, 151.1, 144.7, 142.7, 138.4, 132.5, 126.5, 125.0, 116.0, 53.2, 53.1, 53.0, 46.8, 34.4, 32.7, 32.1, 31.1, 19.4. HRMS (ESI, m/z): calcd for $C_{23}H_{29}NO_6$: $[M+Na]^+$ = 438.1887, found: 438.1879. IR (neat, cm^{-1}): 3371, 2959, 2370, 1738, 1647, 1608, 1527, 1435, 1363, 1262, 1200, 1110, 1048, 901, 835, 769, 739, 617, 569.

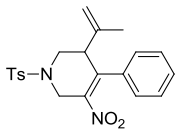


2aa

4-phenyl-5-(prop-1-en-2-yl)-1-tosylpiperidin-3-amine: 2aa ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.75 (d, J = 8 Hz, 2 H), 7.39 (d, J = 8 Hz, 2 H), 7.12 – 7.18 (m, 3 H), 6.99 (d, J = 6.8 Hz, 2 H), 4.58 (s, 1 H), 4.34 (s, 1 H), 3.77 (dd, J = 4.4 Hz, 12 Hz, 1 H),3.66-3.70 (m, 1 H), 3.31 – 3.38 (m, 2H), 2.96-3.02 (m, 1 H), 2.70-2.74 (m, 1 H), 2.55-2.61 (m, 1 H), 2.49 (s, 3 H), 1.54 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.6, 143.5, 136.8, 133.6, 130.6, 129.7, 128.0, 127.5, 126.9, 111.0, 51.0, 48.8, 48.2, 45.4, 44.5, 22.3, 21.5. HRMS (ESI, m/z): calcd for $C_{21}H_{26}N_2O_2S$: $[M+H]^+$ = 371.1783, found: 371.1788. IR (neat, cm^{-1}): 3375, 2924, 1725, 1599, 1452, 1345, 1167, 1093, 982, 910, 816, 770, 734, 704, 659, 580, 550, 516.

6. The Crystal Structure of Product 2a





2a

Data Block:

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Cell: a=13.1530(8) b=17.8912(8) c=9.1269(6)
alpha=90 beta=109.860(7) gamma=90

Temperature: 295 K

	Calculated	Reported
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Space group	P 21/c	P 1 21/c 1
Hall group	-P 2ybc	-P 2ybc
Moiety formula	C21 H22 N2 O4 S	C21 H22 N2 O4 S

Sum formula	C21 H22 N2 O4 S	C21 H22 N2 O4 S
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Dx,g cm-3	1.310	1.310
Z	4	4
Mu (mm-1)	0.189	0.189
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F000'	840.87	
h,k,lmax	16,22,11	16,22,11
Nref	3979	3862
Tmin,Tmax	0.956,0.978	0.865,1.000
Tmin'	0.950	

Correction method= MULTI-SCAN

Data completeness= 0.971 Theta(max)= 25.990

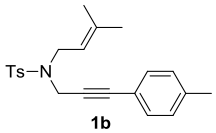
R(reflections)= 0.0547(2574) wR2(reflections)= 0.1455(3862)

S = 1.059 Npar= 255

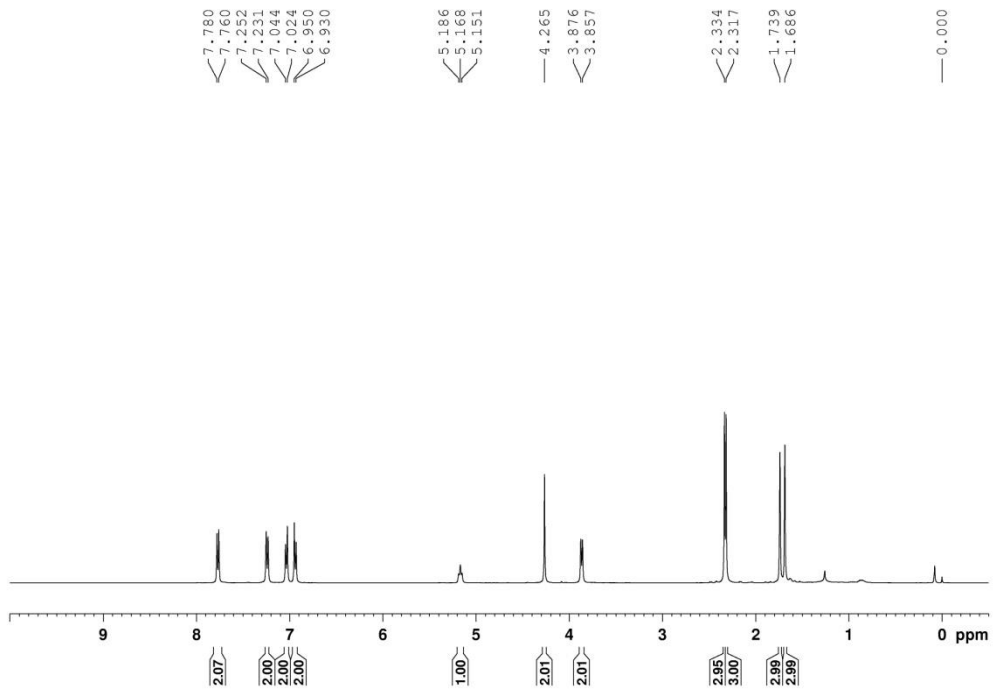
7. References

1. (a) T. Kataoka, M. Yoshimatsu, Y. Noda, T. Sato, H. Shimizu, M. Hori, *J. Chem. Soc. Perkin Trans.*, 1 1993, **1**, 121; (b) A. Gansauer, M. Otte, L. Shi, *J. Am. Chem. Soc*., 2011, **133**, 416; (c) N. Dieltiens, K. Moonen, C. V. Stevens, *Chem. Eur. J*., 2007, **13**, 203.

^{1}H NMR and ^{13}C NMR Spectra of the 1,6-Enynes



1b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3.857
2.334
2.317
1.739
1.686
0.000
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8
7
6
5
4
3
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1.00
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2.01
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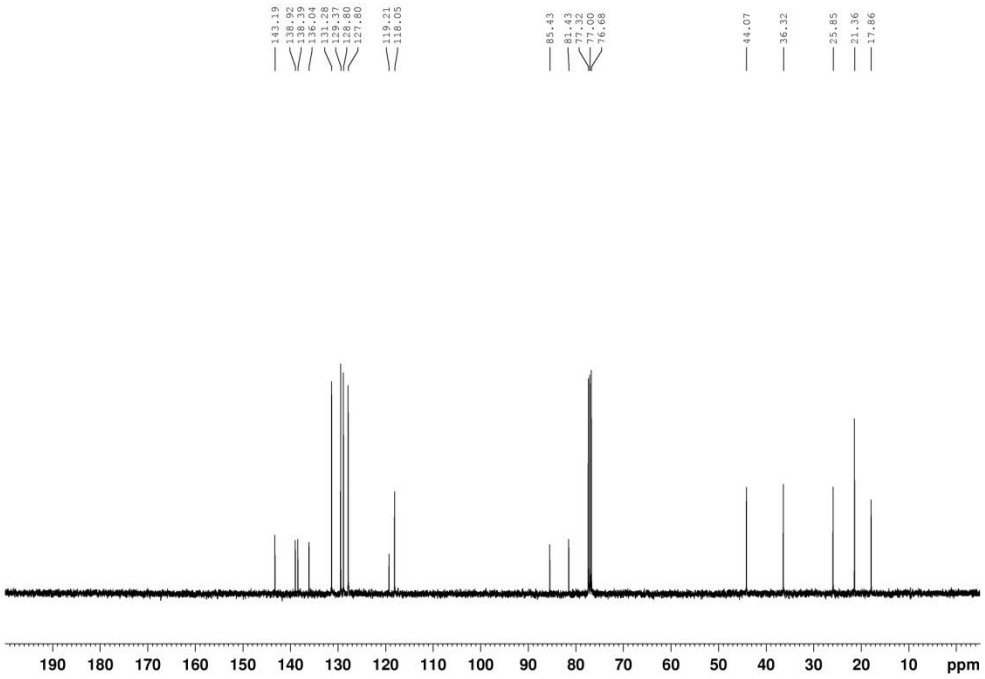
3.00
2.99
2.99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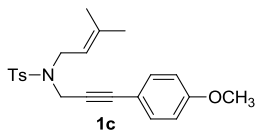
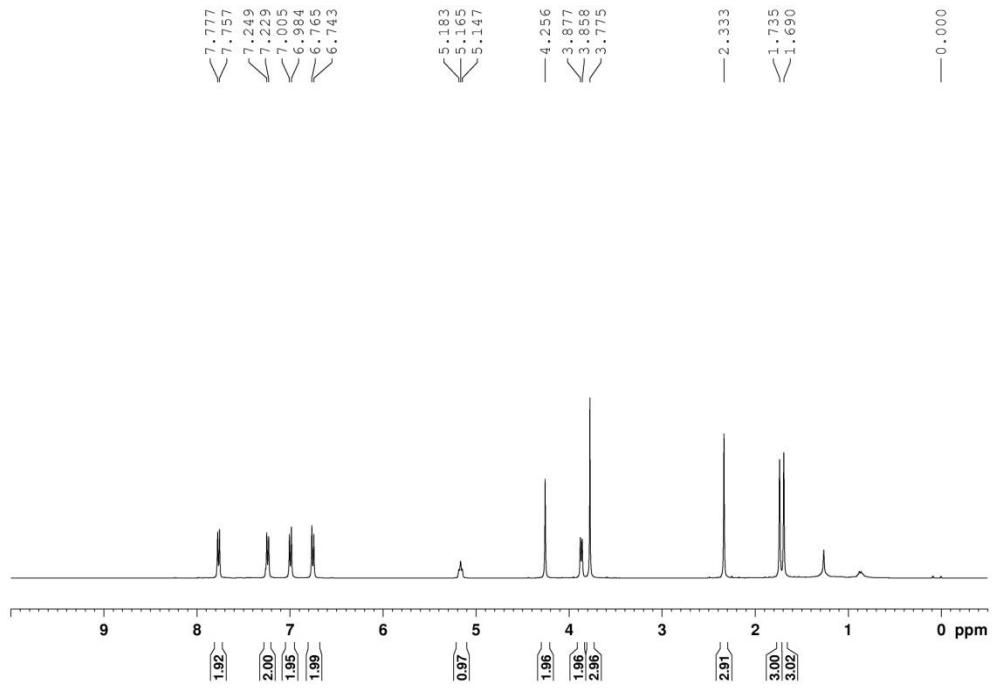
138.92
138.39
136.04
131.28
129.37
128.80
127.80
119.21
116.05
85.43
81.43
77.32
77.00
76.68
44.07
36.32
25.85
21.36
17.86
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts–N
OCH3

1c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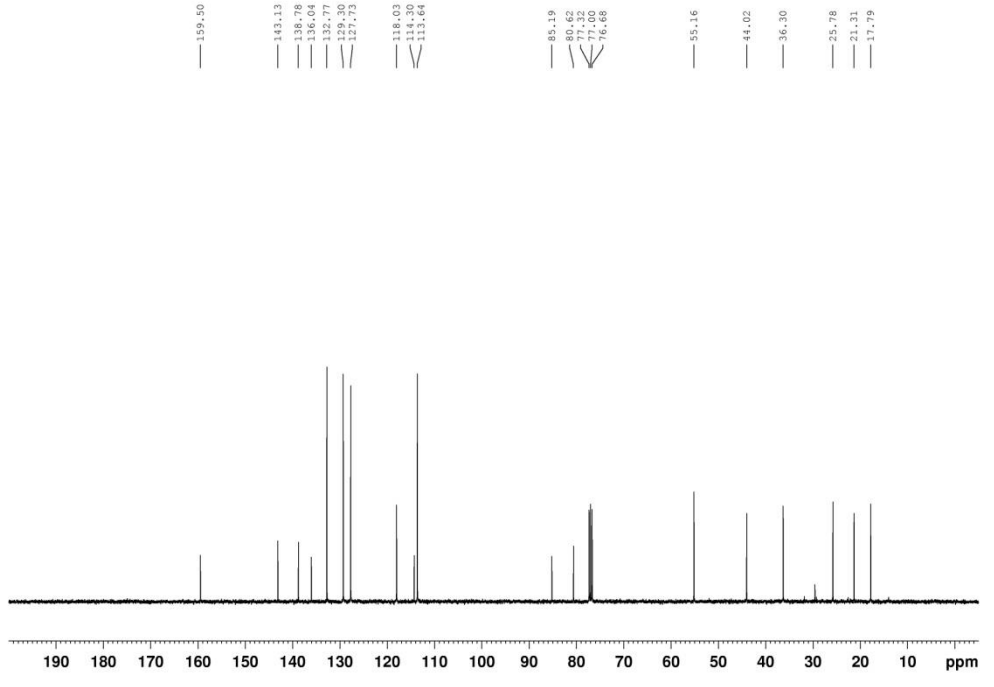
7.757
7.249
7.229
7.005
6.984
6.765
6.743
5.183
5.165
5.147
4.256
3.877
3.858
3.775
2.333
1.735
1.690
0.000
9
8
7
6
5
4
3
2
1
0 ppm
1.92
2.00
1.95
1.99
0.97
1.96
1.96
2.96
2.91
3.00
3.02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132.77
129.30
127.73
118.03
114.30
113.64
85.19
80.62
77.32
77.00
76.68
55.16
44.02
36.30
25.78
21.31
17.79
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70
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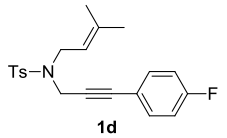
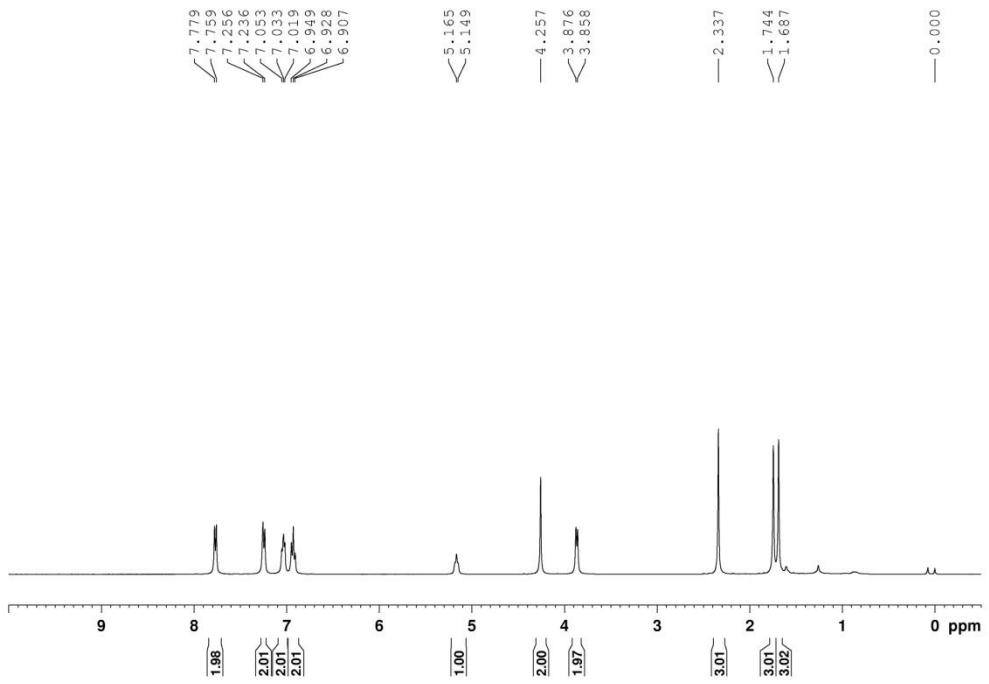
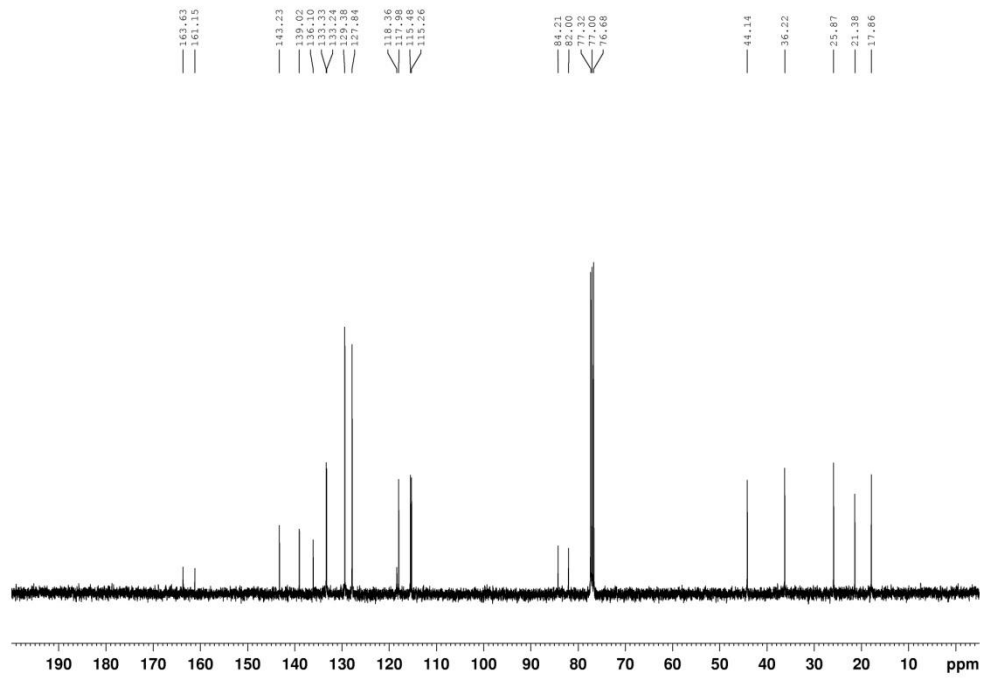
30
20
10
ppm


Ts–N
F

1d


7.779
7.759
7.256
7.236
7.053
7.033
7.019
6.949
6.928
6.907
5.165
5.149
4.257
3.876
3.858
2.337
1.744
1.687
0.000
9
8
7
6
5
4
3
2
1
0 ppm
1.98
2.01
2.01
2.01
1.00
2.00
1.97
3.01
3.01
3.02


163.63
161.15
143.23
139.02
136.10
133.33
133.24
129.38
127.84
118.36
116.88
115.48
115.26
84.21
82.00
77.32
77.00
76.68
44.14
36.22
25.87
21.38
17.86
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180
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150
140
130
120
110
100
90
80
70
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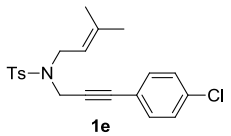
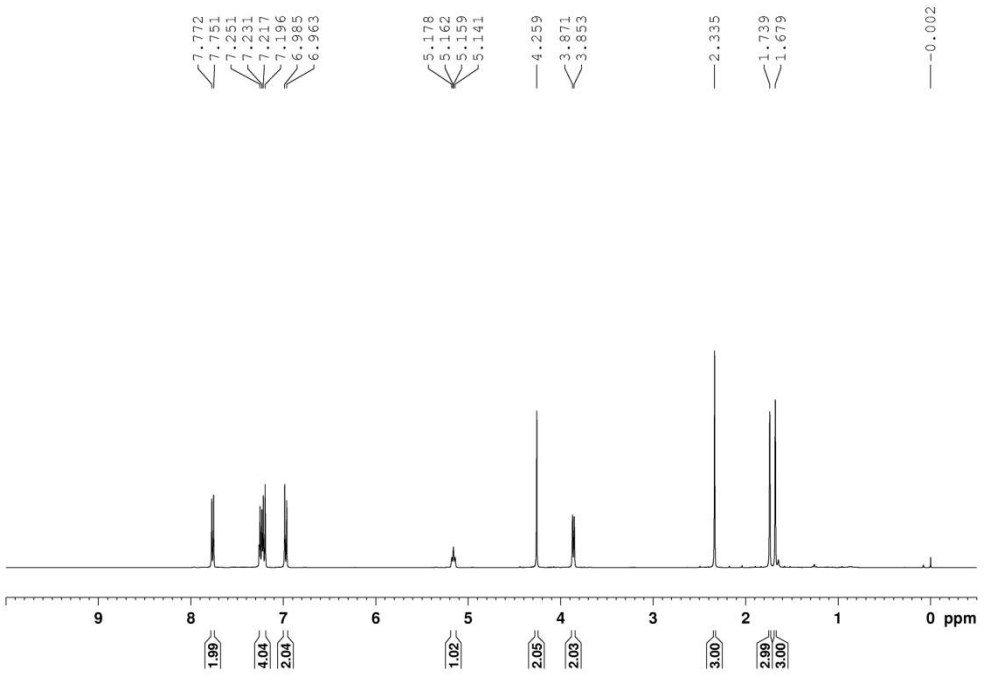
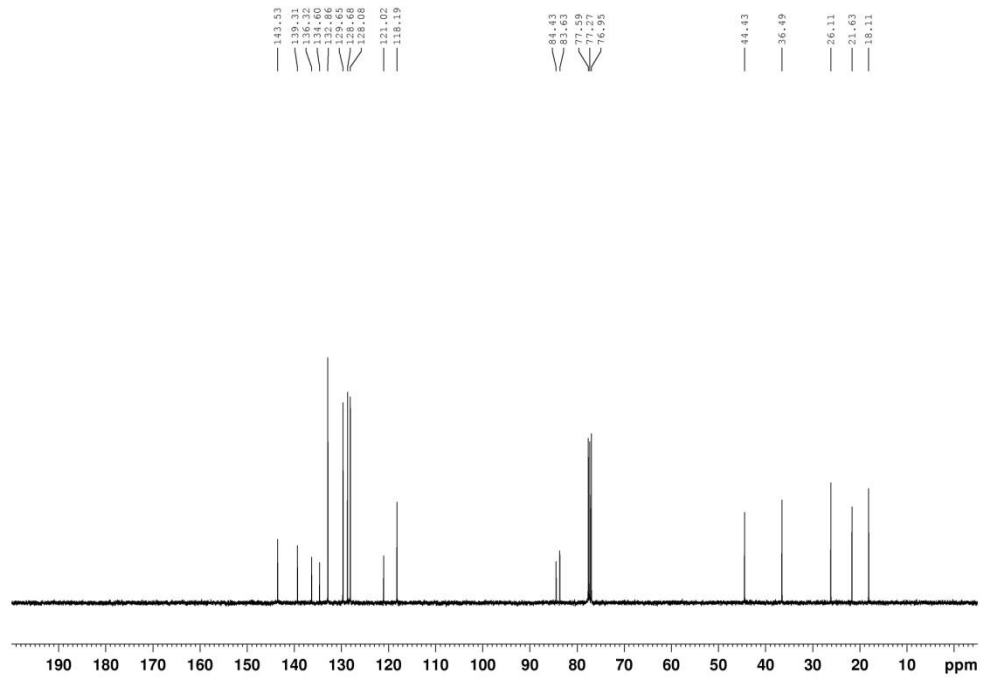
30
20
10
ppm


Ts–N
Cl

1e


7.772
7.751
7.251
7.231
7.217
7.196
6.985
6.963
5.178
5.162
5.159
5.141
4.259
3.871
3.853
2.335
1.739
1.679
0.002
9
8
7
6
5
4
3
2
1
0 ppm
1.99
4.04
2.04
1.02
2.05
2.03
3.00
2.99
3.00


143.53
139.31
136.32
134.60
132.66
129.65
128.68
128.08
121.02
118.19
84.43
83.63
77.59
77.27
76.95
44.43
36.49
26.11
21.63
18.11
190
180
170
160
150
140
130
120
110
100
90
80
70
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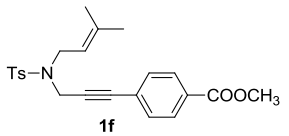
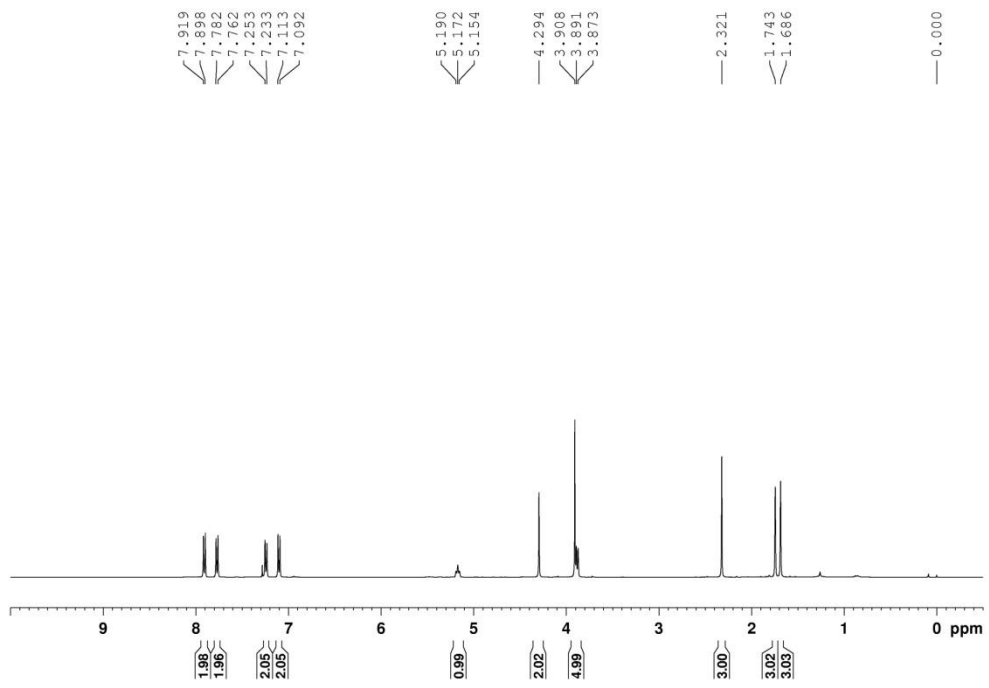
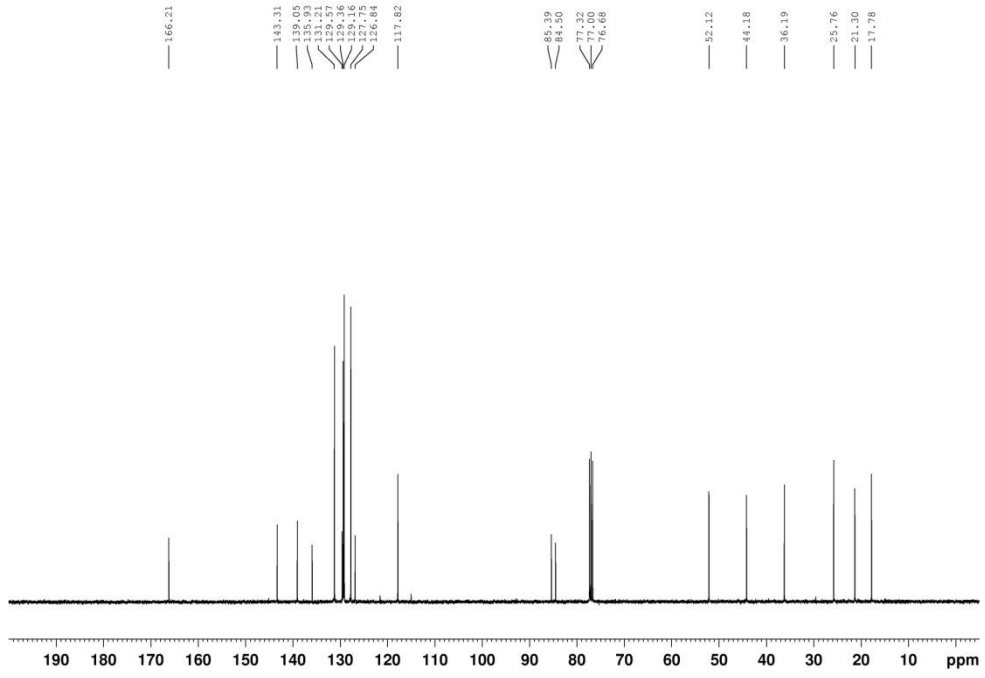
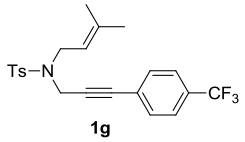
50
40
30
20
10
ppm


Ts–N
COOCH3

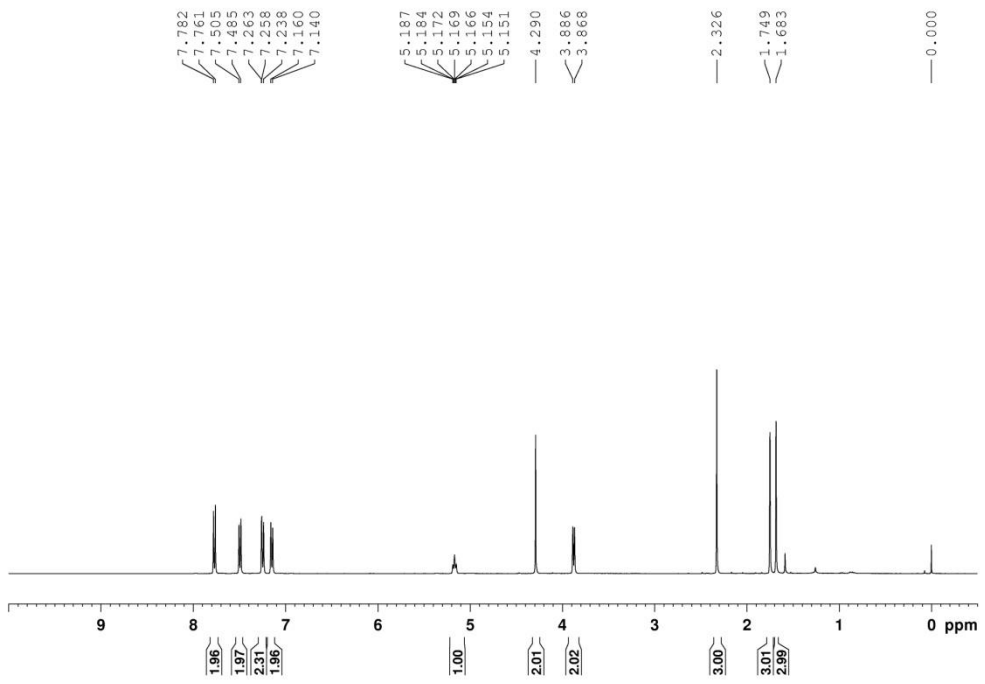
1f

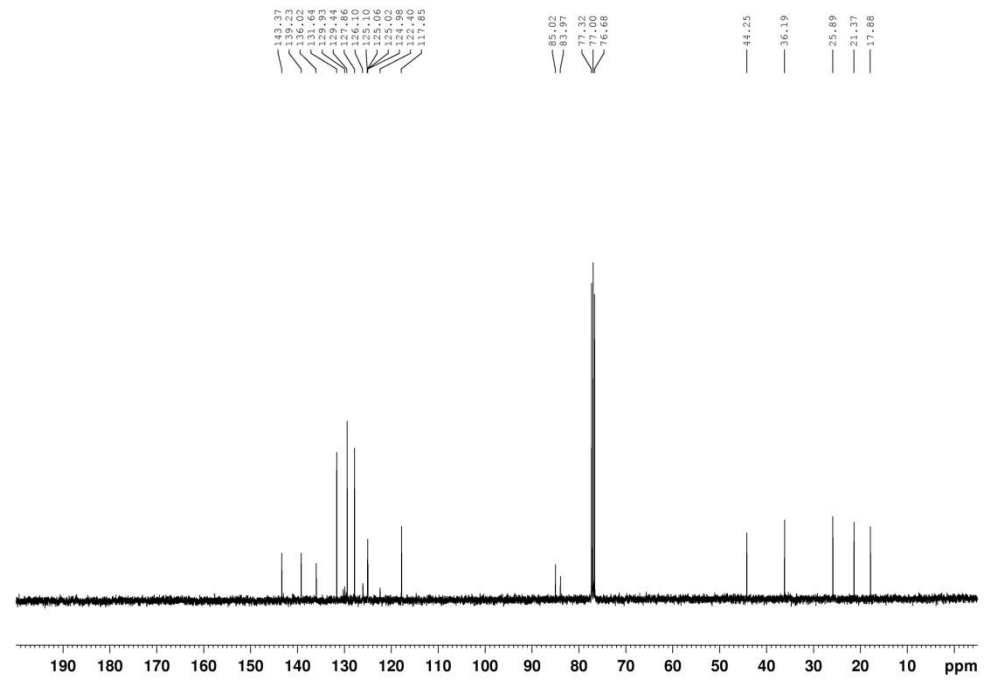

7.919
7.898
7.782
7.762
7.253
7.233
7.113
7.092
5.190
5.172
5.154
4.294
3.908
3.891
3.873
2.321
1.743
1.686
0.000
9
8
7
6
5
4
3
2
1
0 ppm
1.98
1.96
2.05
2.05
0.99
2.02
4.99
3.00
3.02
3.03

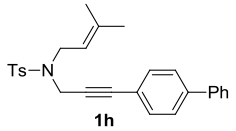

166.21
143.31
139.05
135.93
131.21
129.57
129.36
129.16
127.75
126.84
117.82
85.39
84.50
77.32
77.00
76.68
52.12
44.18
36.19
25.76
21.30
17.78
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts–N
CF3

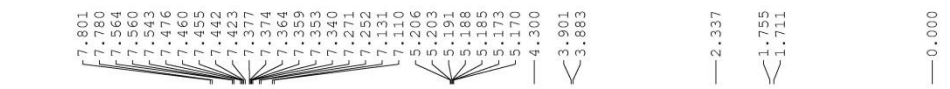
1g


7.782
7.761
7.505
7.485
7.263
7.258
7.238
7.160
7.140
5.187
5.184
5.172
5.169
5.166
5.154
5.151
4.290
3.886
3.868
2.326
1.749
1.683
0.000
9
8
7
6
5
4
3
2
1
0 ppm
1.96
1.97
2.31
1.96
1.00
2.01
2.02
3.00
3.01
2.99


143.37
138.23
136.02
131.64
129.93
129.44
128.86
126.10
125.10
125.06
125.02
123.98
122.40
117.85
85.02
83.97
77.32
77.00
76.68
44.25
36.19
25.89
21.37
17.88
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts–N
Ph

1h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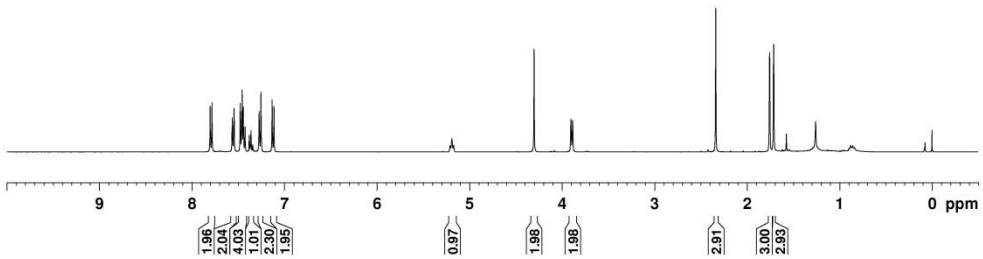
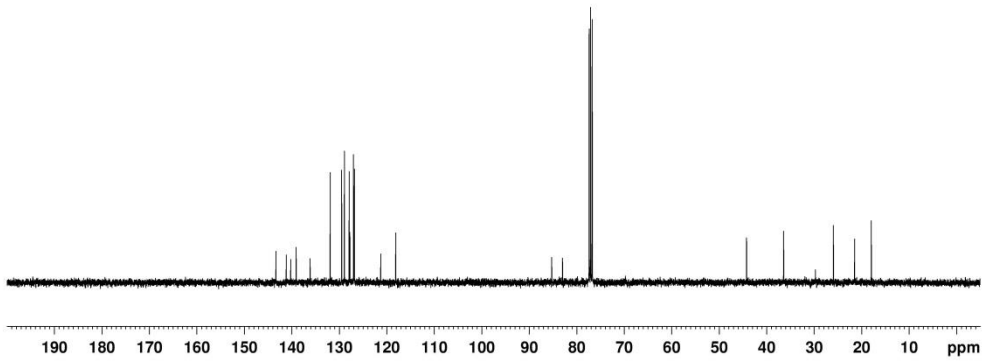
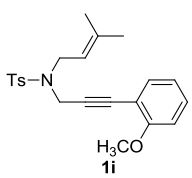
7.476
7.460
7.455
7.442
7.423
7.377
7.374
7.364
7.359
7.353
7.340
7.271
7.252
7.131
7.110
5.206
5.203
5.191
5.188
5.185
5.173
5.170
4.300
3.901
3.883
2.337
1.755
1.711
0.000

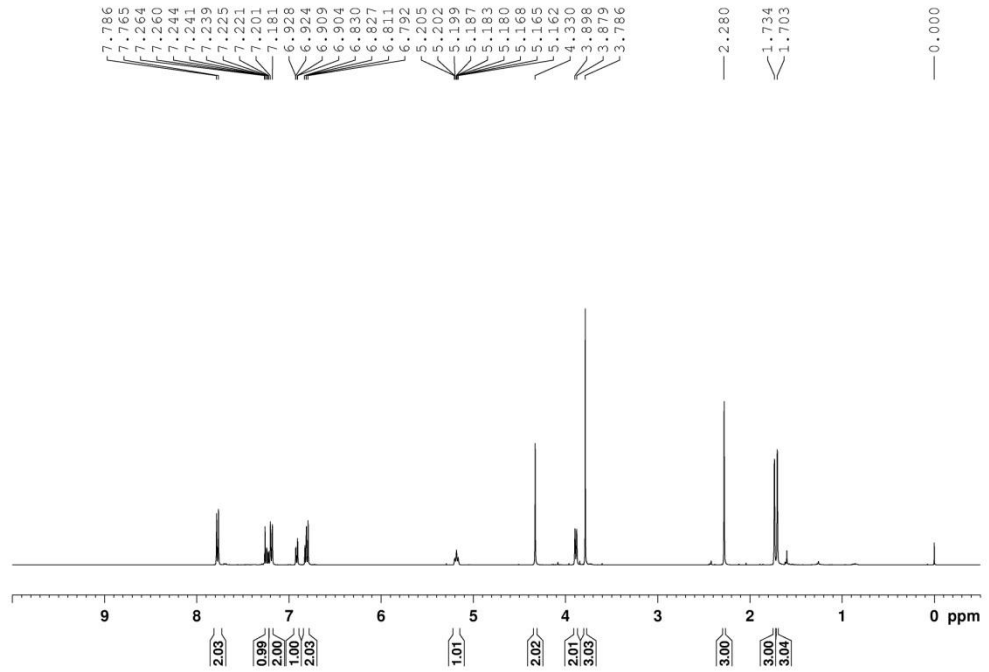

9
8
7
6
5
4
3
2
1
0 ppm
1.96
2.04
4.03
1.01
2.30
1.95
0.97
1.98
1.98
2.91
3.00
2.93


143.26
141.10
140.17
139.03
136.11
131.84
129.44
128.87
127.87
127.72
126.65
126.76
121.21
118.06
85.21
82.92
77.32
77.00
76.68
44.17
36.38
25.89
21.42
17.92


190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts–N
H3CO

1i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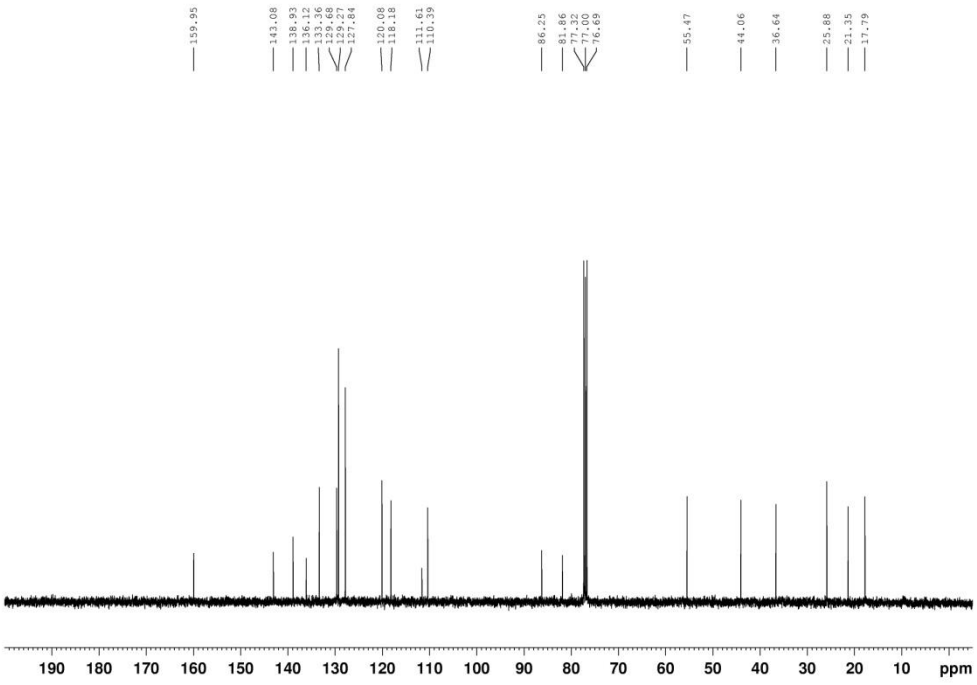
7.264
7.260
7.244
7.241
7.239
7.225
7.221
7.201
7.181
6.928
6.924
6.909
6.904
6.830
6.827
6.811
6.792
5.205
5.202
5.199
5.187
5.183
5.180
5.168
5.165
5.162
4.330
3.898
3.879
3.786
2.280
1.734
1.703
0.000
9
8
7
6
5
4
3
2
1
0 ppm
2.03
0.99
2.00
1.00
2.03
1.01
2.02
2.01
3.03
3.00
3.00
3.04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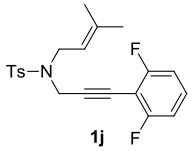
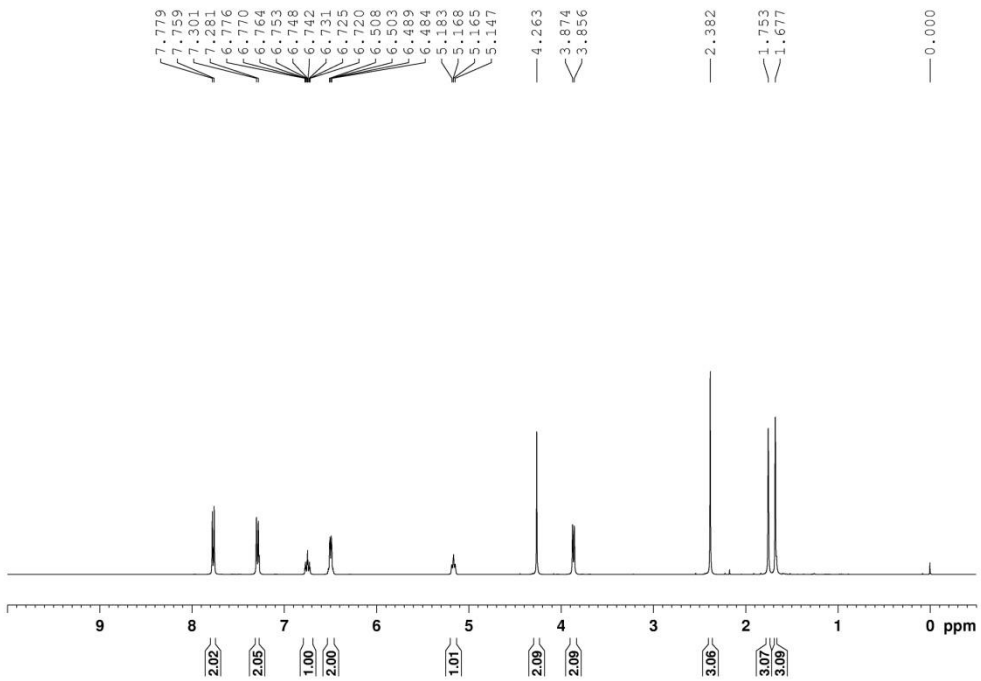
136.12
133.36
129.68
129.27
127.84
120.08
118.18
111.61
110.39
86.25
81.86
77.32
77.00
76.69
55.47
44.06
36.64
25.88
21.35
17.79
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts–N
F
F

1j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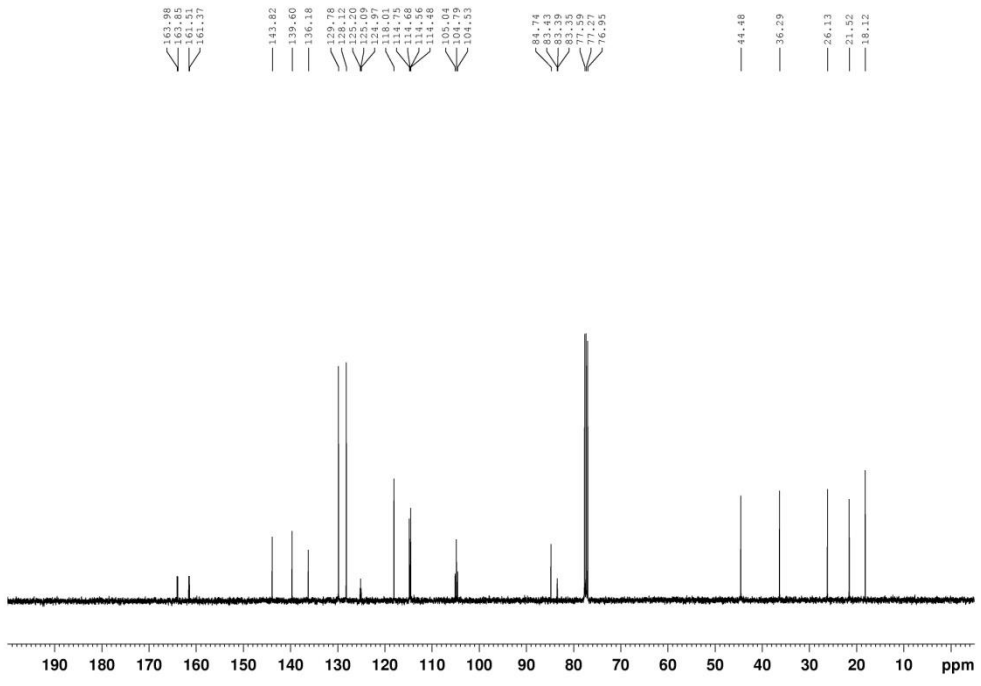
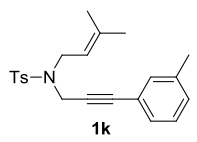
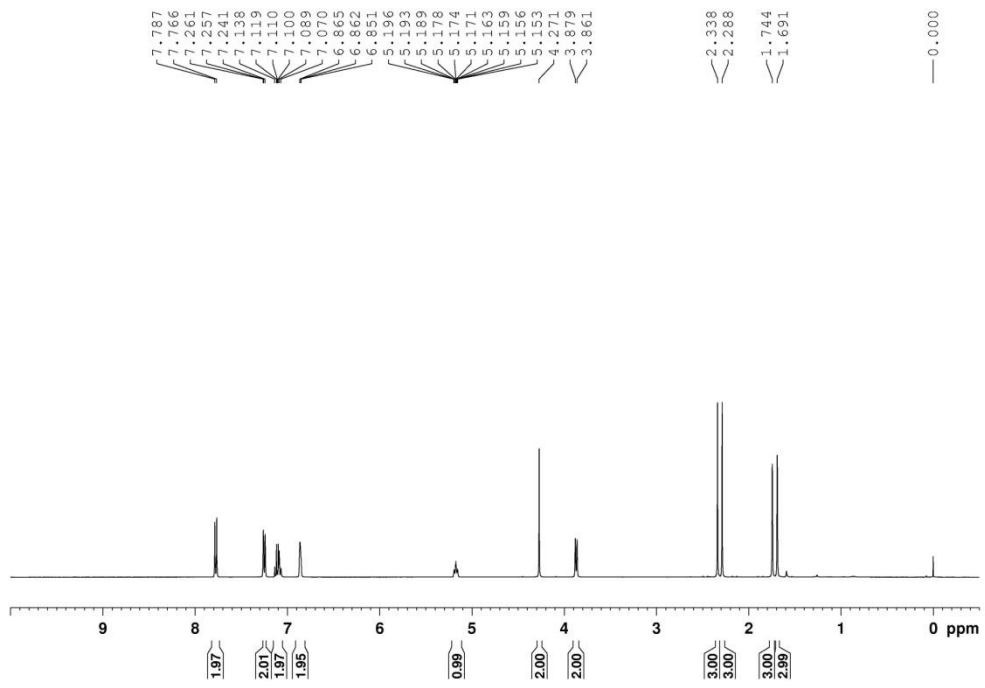
7.759
7.301
7.281
6.776
6.770
6.764
6.753
6.748
6.742
6.731
6.725
6.720
6.508
6.503
6.489
6.484
5.183
5.168
5.165
5.147
4.263
3.874
3.856
2.382
1.753
1.677
0.000
9 8 7 6 5 4 3 2 1 0 ppm
2.02 2.05 1.00 2.00 1.01 2.09 2.09 3.06 3.07 3.09


163.98
163.85
161.51
161.37
143.82
139.60
136.18
129.78
128.12
125.20
125.09
124.97
118.01
114.75
114.68
114.56
114.48
105.04
104.79
104.53
84.74
83.43
83.39
83.35
77.59
77.27
76.95
44.48
36.29
26.13
21.52
18.12
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ts–N

1k


7.787
7.766
7.261
7.257
7.241
7.138
7.119
7.110
7.100
7.089
7.070
6.865
6.862
6.851
5.196
5.193
5.189
5.178
5.174
5.171
5.163
5.159
5.156
5.153
4.271
3.879
3.861
2.338
2.288
1.744
1.691
0.000
9
8
7
6
5
4
3
2
1
0 ppm
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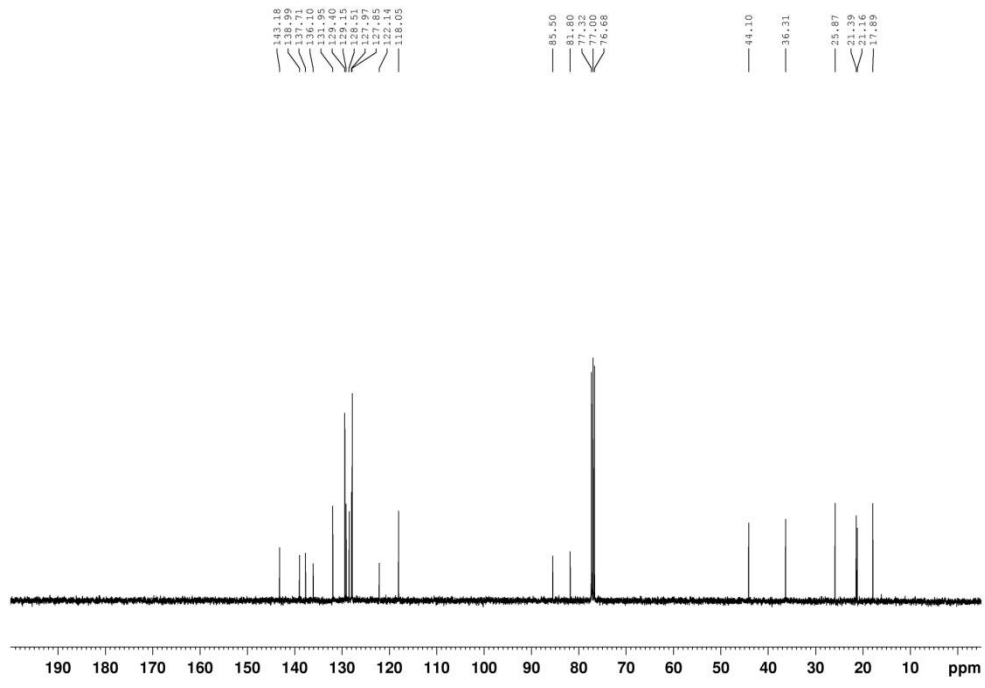
2.01
1.97
1.95
0.99
2.00
2.00
3.00
3.00
3.00
2.99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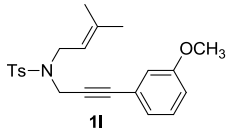
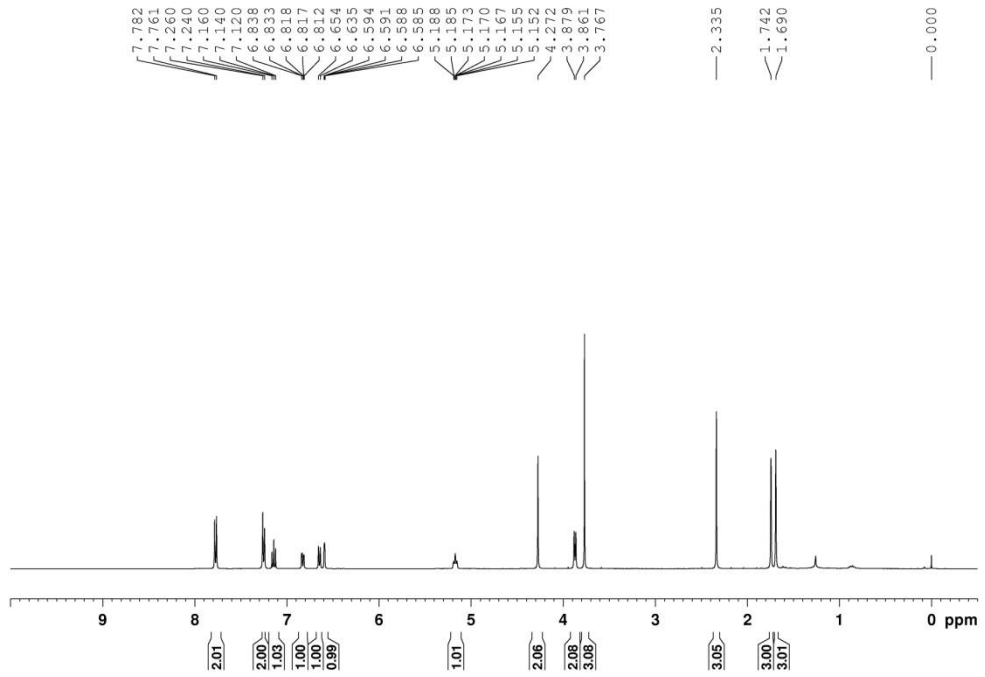
139.69
137.71
136.10
131.95
129.40
128.55
128.51
127.97
127.85
122.14
118.05
85.50
81.80
77.32
77.00
76.68
44.10
36.31
25.87
21.39
21.16
17.89
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts–N
OCH3

1l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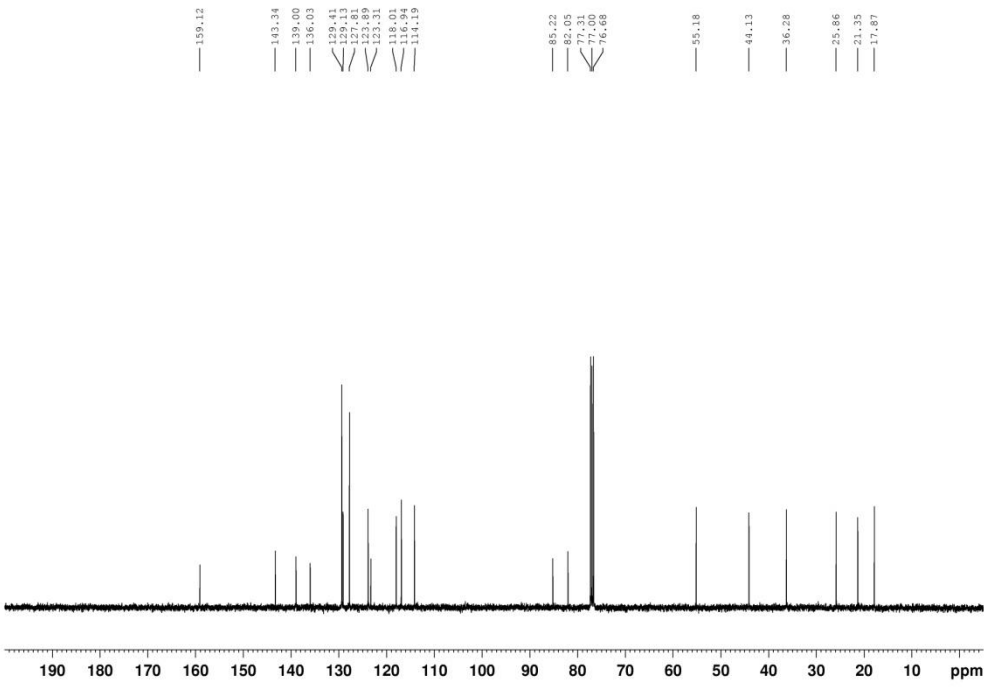
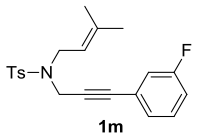
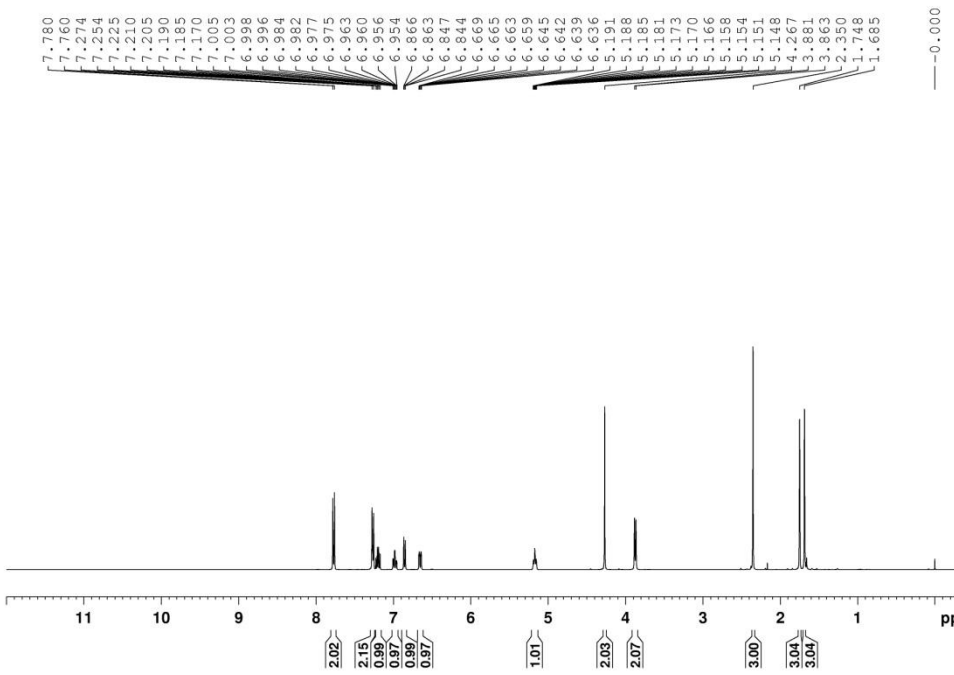
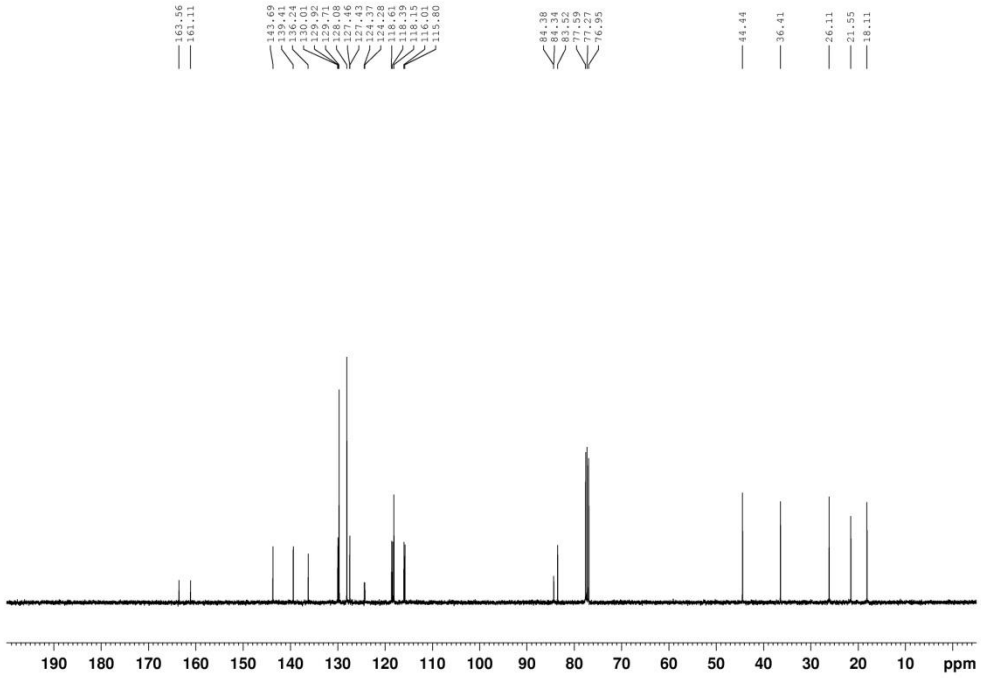
7.761
7.260
7.240
7.160
7.140
7.120
6.838
6.833
6.818
6.817
6.812
6.654
6.635
6.594
6.591
6.588
6.585
5.188
5.185
5.173
5.170
5.167
5.155
5.152
4.272
3.879
3.861
3.767
2.335
1.742
1.690
0.000
9
8
7
6
5
4
3
2
1
0 ppm
2.01
2.00
1.03
1.00
1.00
0.99
1.01
2.06
2.08
3.08
3.05
3.00
3.01

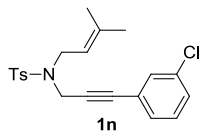

159.12
143.34
139.00
136.03
129.41
129.13
127.81
123.89
123.31
118.01
116.84
114.19
85.22
82.05
77.31
77.00
76.68
55.18
44.13
36.28
25.86
21.35
17.87
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts–N
F

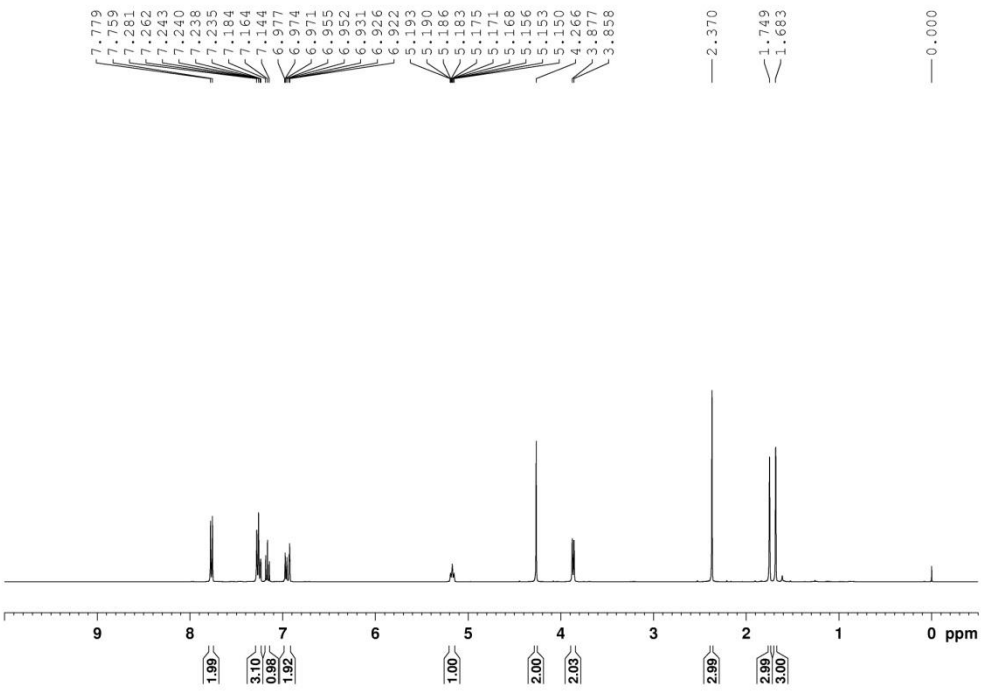
1m

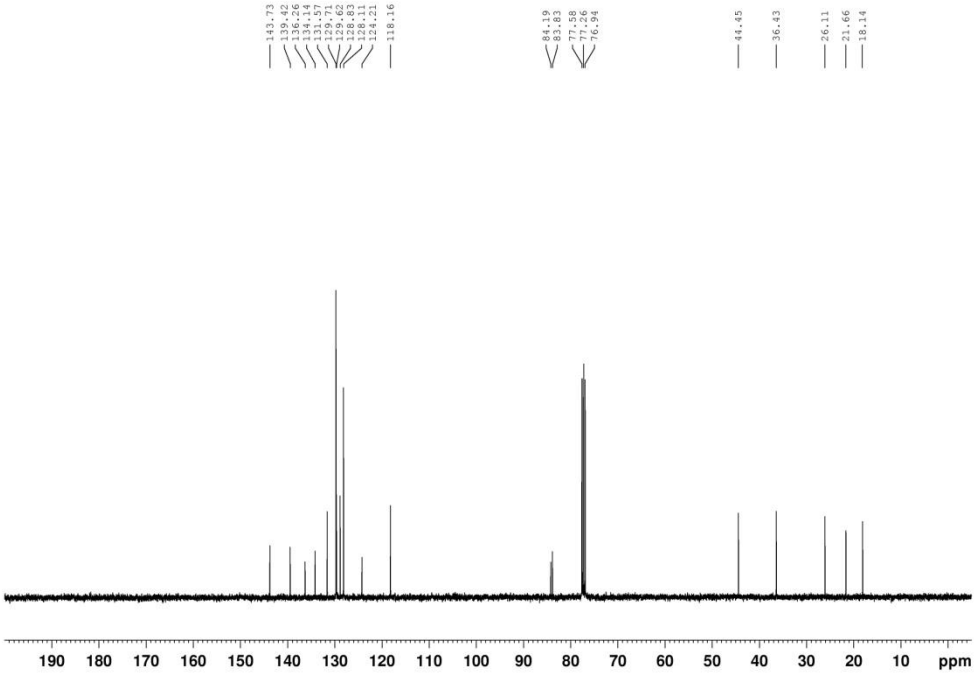

7.780
7.760
7.274
7.254
7.225
7.210
7.205
7.190
7.185
7.170
7.005
7.003
6.998
6.996
6.984
6.982
6.977
6.975
6.963
6.960
6.956
6.954
6.866
6.863
6.847
6.844
6.669
6.665
6.663
6.659
6.645
6.642
6.639
6.636
5.191
5.188
5.185
5.181
5.173
5.170
5.166
5.158
5.154
5.151
5.148
4.267
3.881
3.863
2.350
1.748
1.685
0.000
11 10 9 8 7 6 5 4 3 2 1 ppm
2.02 2.15 0.99 0.97 0.99 0.97 1.01 2.03 2.07 3.00 3.04 3.04

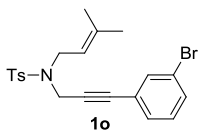

163.56
161.11
143.69
139.41
136.24
130.01
129.92
129.71
128.08
127.46
127.43
124.37
124.28
118.61
118.39
118.15
116.01
115.80
84.38
84.34
83.52
77.59
77.27
76.95
44.44
36.41
26.11
21.55
18.11
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ts–N
Cl

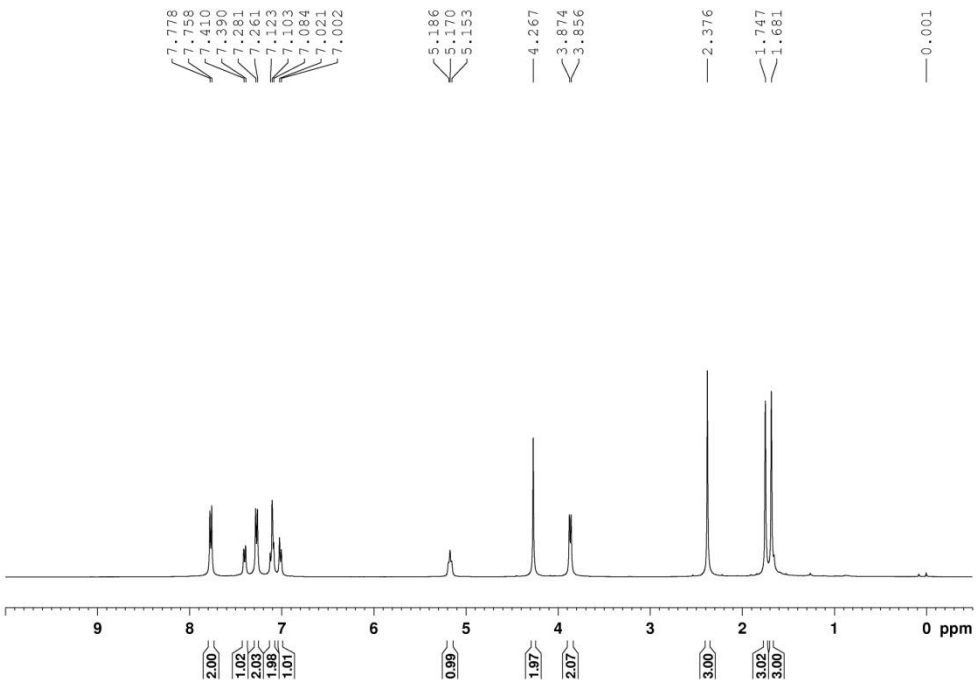
1n

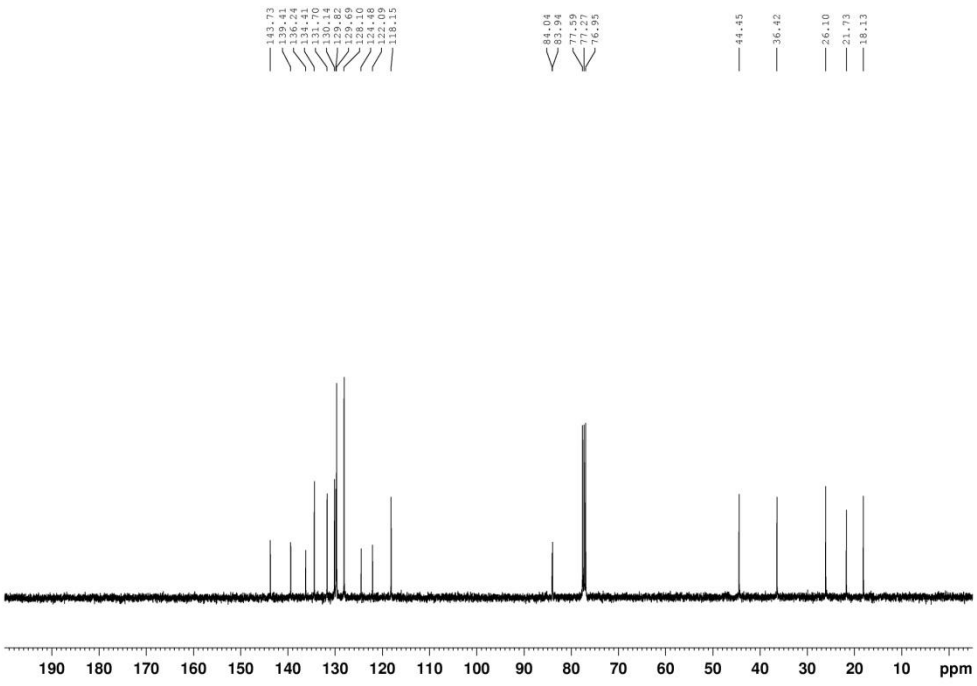

7.779
7.759
7.281
7.262
7.243
7.240
7.238
7.235
7.184
7.164
7.144
6.977
6.974
6.971
6.955
6.952
6.931
6.926
6.922
5.193
5.190
5.186
5.183
5.175
5.171
5.168
5.156
5.153
5.150
4.266
3.877
3.858
2.370
1.749
1.683
0.000
9
8
7
6
5
4
3
2
1
0 ppm
1.99
3.10
0.98
1.92
1.00
2.00
2.03
2.99
2.99
3.00

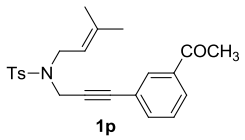

143.73
139.42
137.66
134.14
131.57
129.71
129.62
128.83
128.11
124.21
118.16
84.19
83.83
77.58
77.26
76.94
44.45
36.43
26.11
21.66
18.14
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts–N
Br

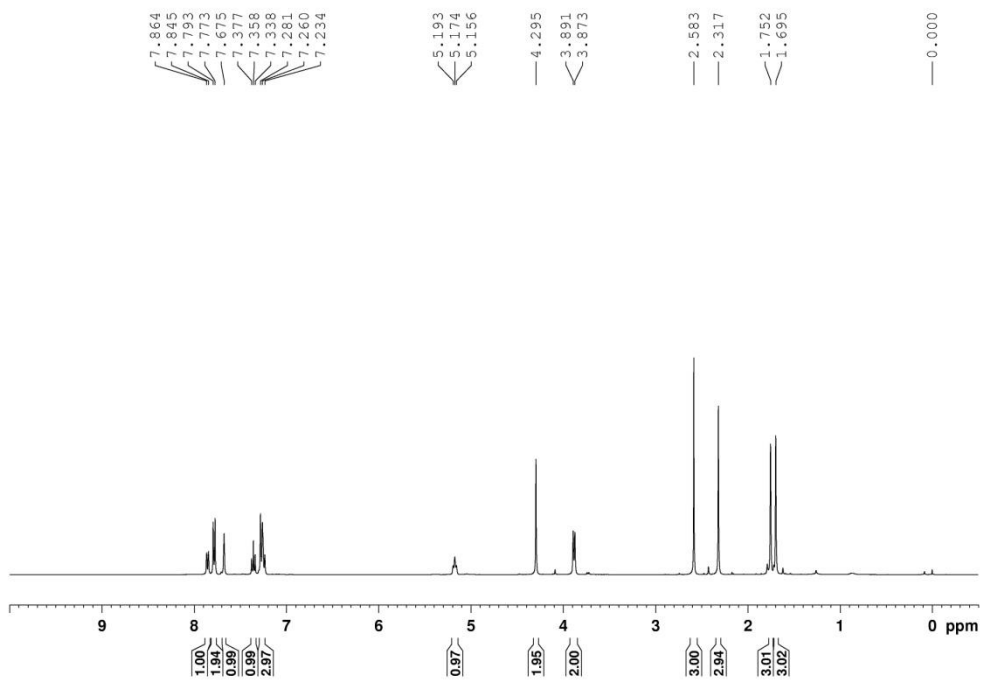
1o

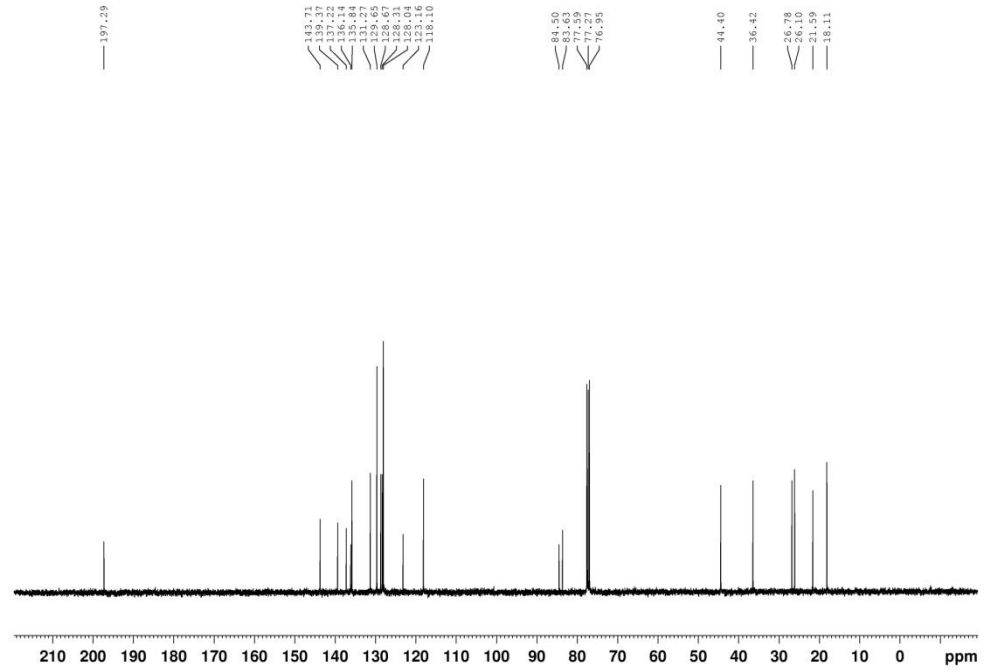

7.778
7.758
7.410
7.390
7.281
7.261
7.123
7.103
7.084
7.021
7.002
5.186
5.170
5.153
4.267
3.874
3.856
2.376
1.747
1.681
0.001
9 8 7 6 5 4 3 2 1 0 ppm
2.00
1.02
2.03
1.98
1.01
0.99
1.97
2.07
3.00
3.02
3.00

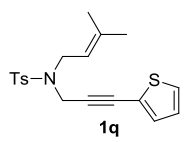

143.73
139.11
136.24
134.41
131.70
130.14
129.82
129.69
128.10
124.48
122.09
118.15
84.04
83.94
77.59
77.27
76.95
44.45
36.42
26.10
21.73
18.13
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ts–N
COCH3

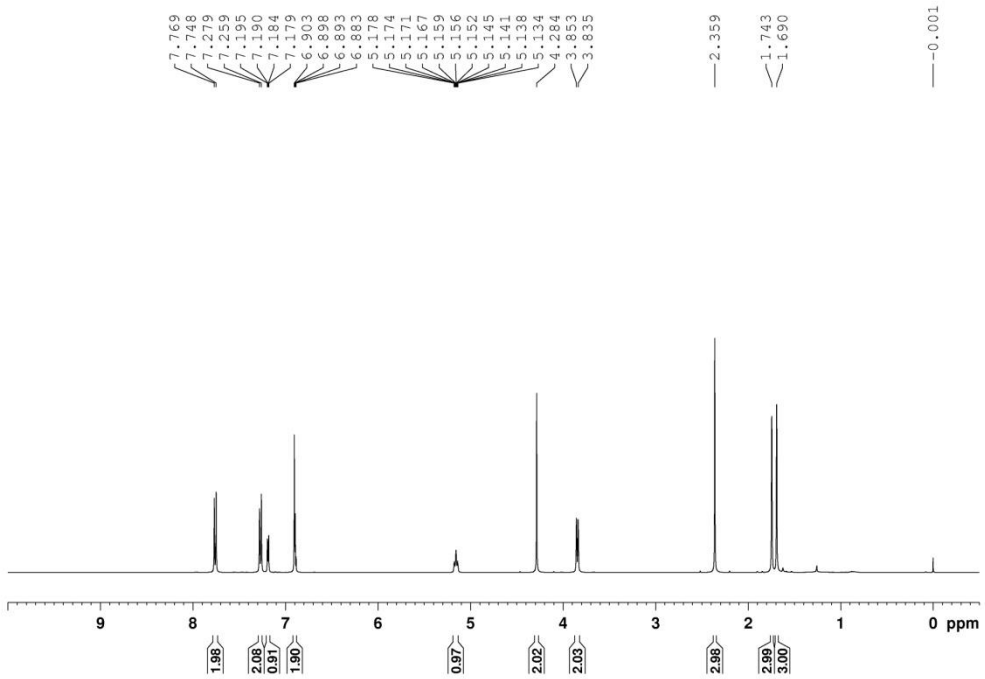
1p

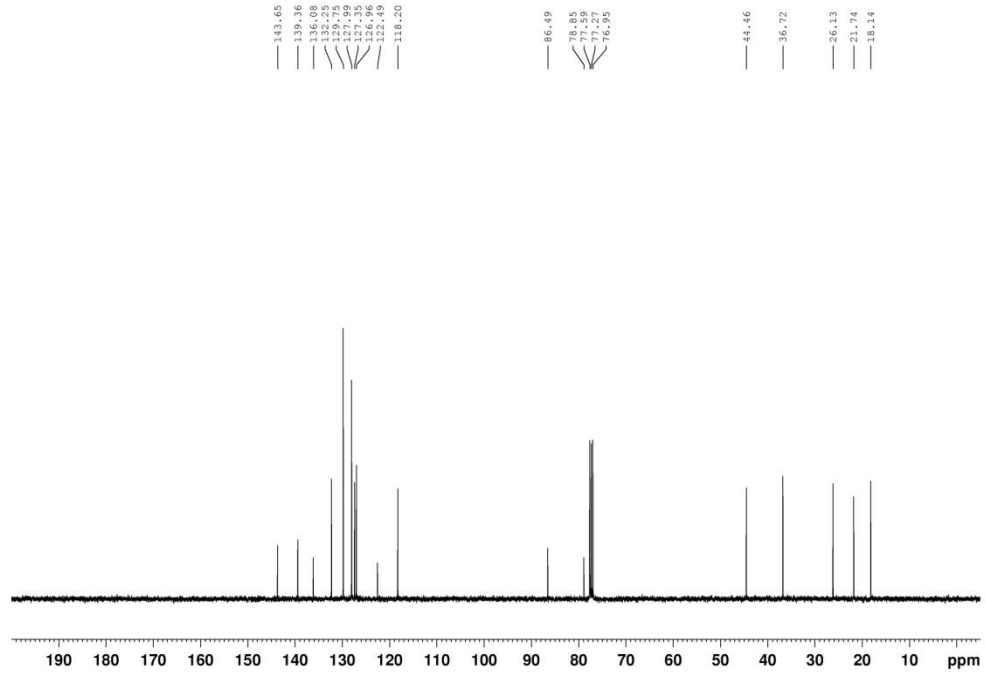

7.864
7.845
7.793
7.773
7.675
7.377
7.358
7.338
7.281
7.260
7.234
5.193
5.174
5.156
4.295
3.891
3.873
2.583
2.317
1.752
1.695
0.000
9 8 7 6 5 4 3 2 1 0 ppm
1.00 1.94 0.99 0.99 2.97 0.97 1.95 2.00 3.00 2.94 3.01 3.02

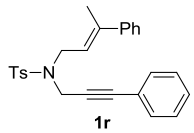

197.29
143.71
139.37
137.22
136.14
135.84
131.27
129.65
128.67
128.31
128.04
123.16
118.10
84.50
83.63
77.59
77.27
76.95
44.40
36.42
26.78
26.10
21.59
18.11
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 ppm


Ts–N
S

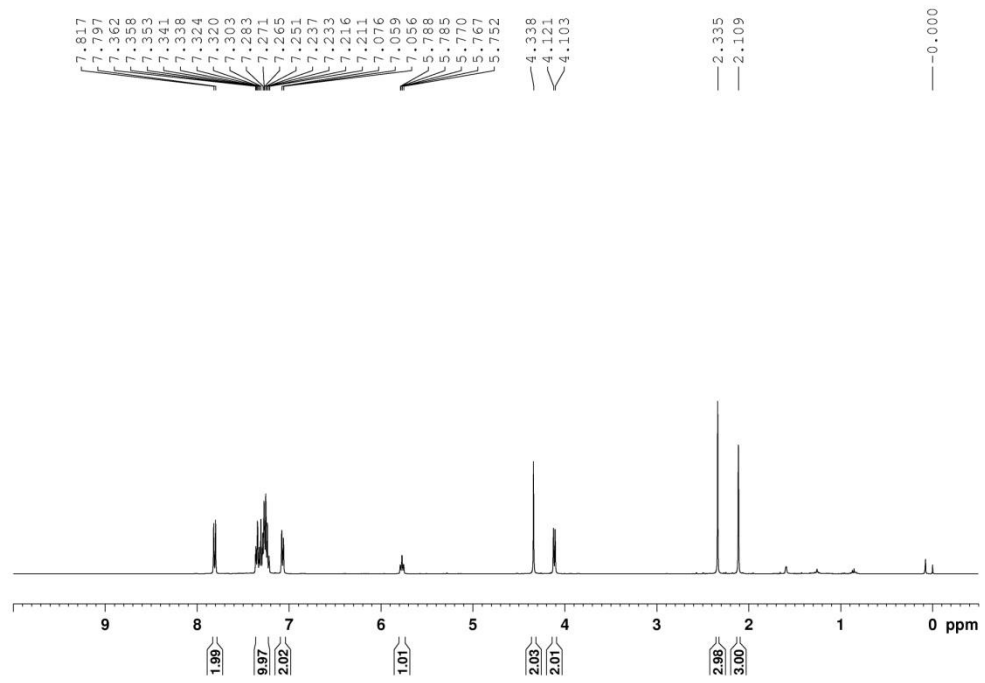
1q

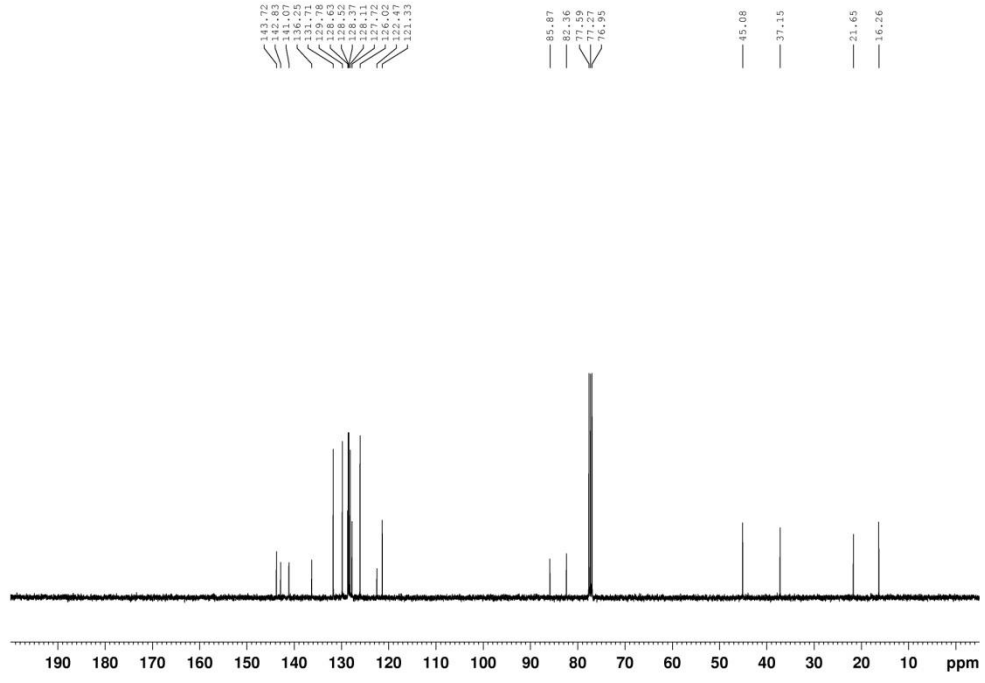

7.769
7.748
7.279
7.259
7.195
7.190
7.184
7.179
6.903
6.898
6.893
6.883
5.178
5.174
5.171
5.167
5.159
5.156
5.152
5.145
5.141
5.138
5.134
4.284
3.853
3.835
2.359
1.743
1.690
0.001
9
8
7
6
5
4
3
2
1
0 ppm
1.98
2.08
0.91
1.90
0.97
2.02
2.03
2.98
2.99
3.00

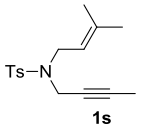

143.65
139.36
136.08
132.25
129.75
127.99
127.55
126.96
122.49
118.20
86.49
78.85
77.59
77.27
76.95
44.46
36.72
26.13
21.74
18.14
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ph
Ts–N

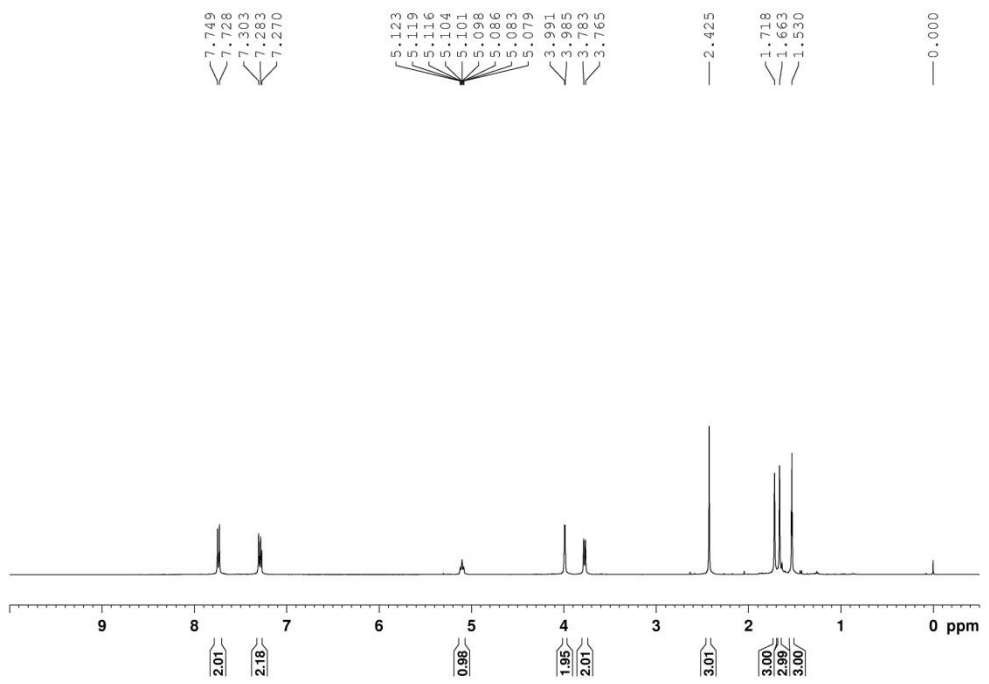
1r

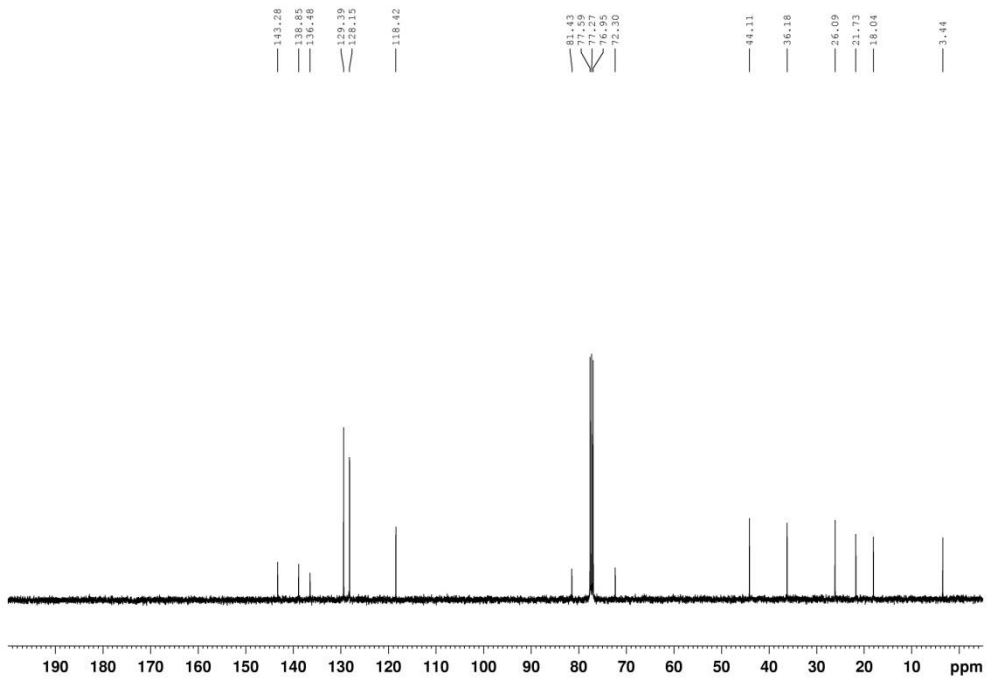

7.817
7.797
7.362
7.358
7.353
7.341
7.338
7.324
7.320
7.303
7.283
7.271
7.265
7.251
7.237
7.233
7.216
7.211
7.076
7.059
7.056
5.788
5.785
5.770
5.767
5.752
4.338
4.121
4.103
2.335
2.109
0.000
9
8
7
6
5
4
3
2
1
0 ppm
1.99
9.97
2.02
1.01
2.03
2.01
2.98
3.00


143.72
142.83
140.07
136.25
131.71
129.78
128.63
128.52
128.37
128.11
127.72
127.02
122.47
121.33
85.87
82.36
77.59
77.27
76.95
45.08
37.15
21.65
16.26
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm

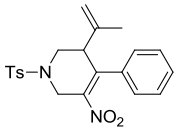

Ts–N

1s

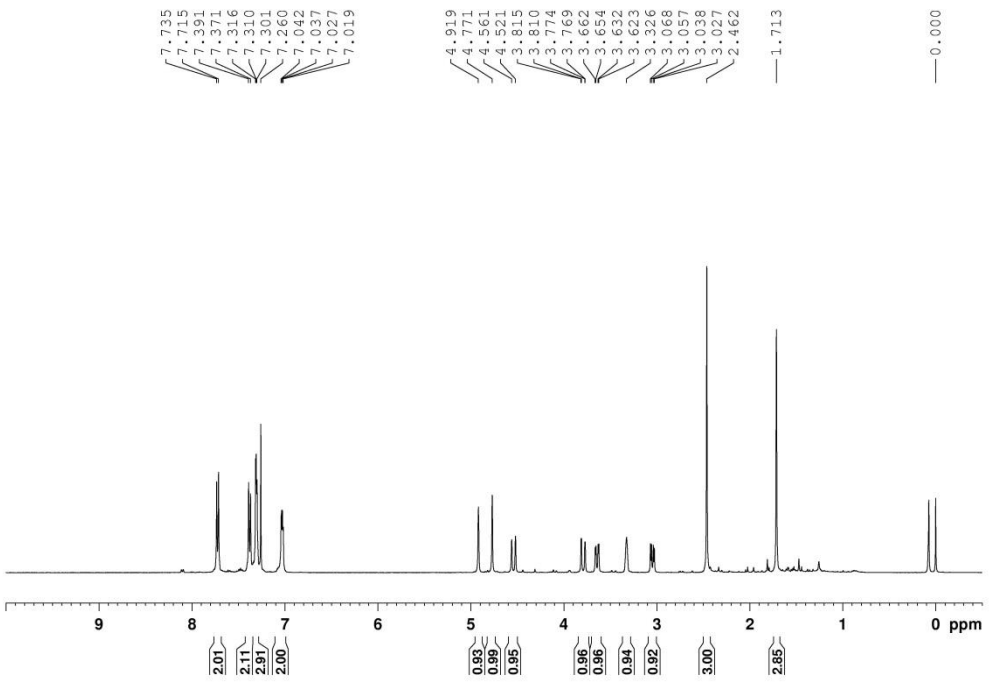


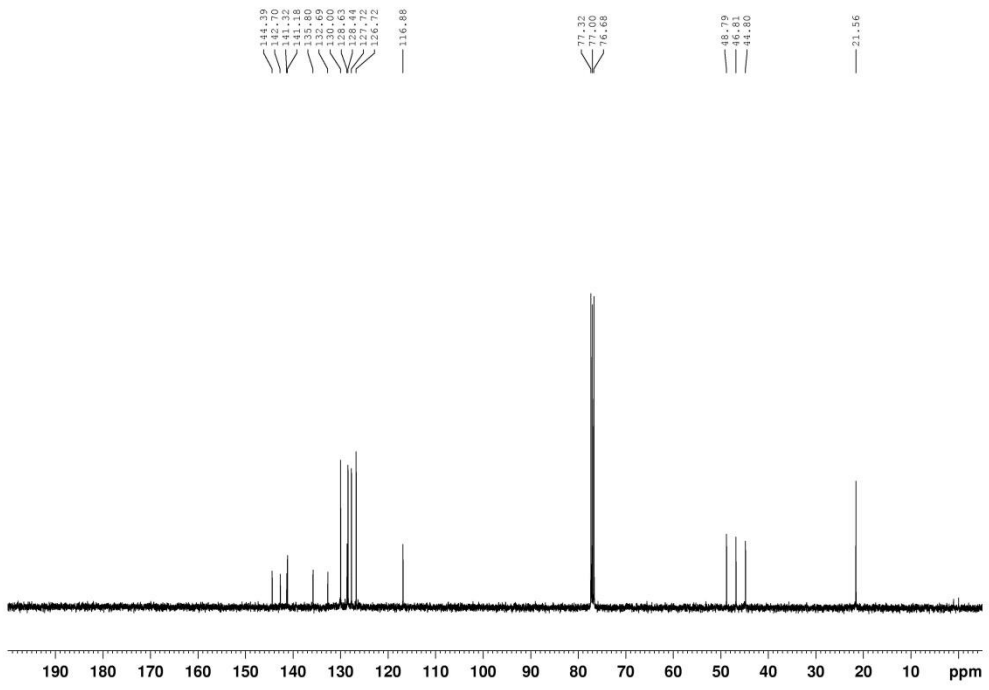


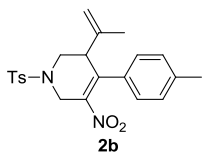
^{1}H NMR and ^{13}C NMR Spectra of the Products



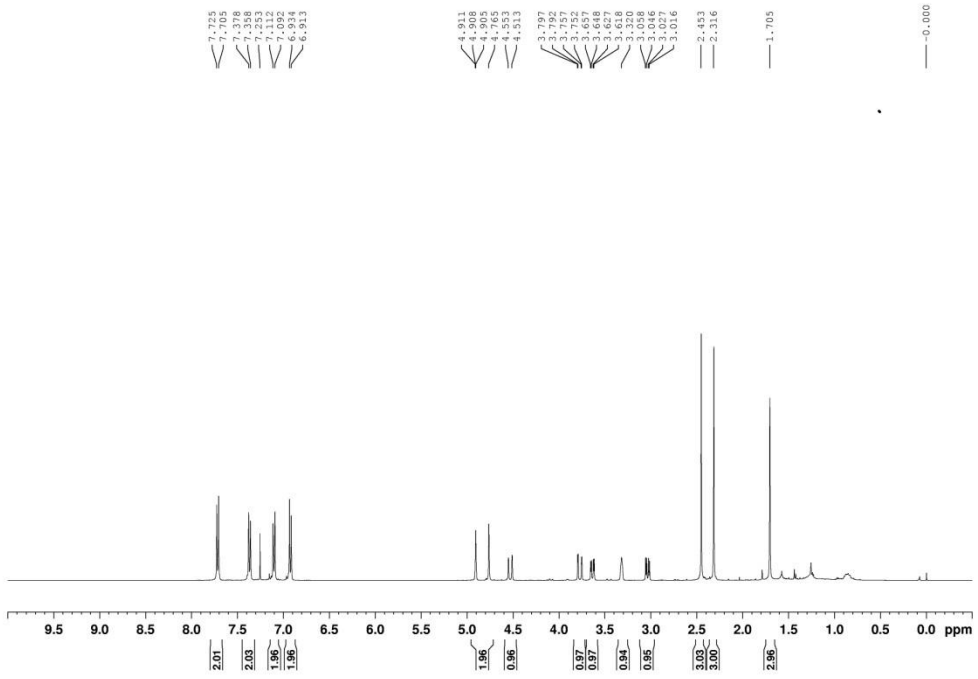
2a

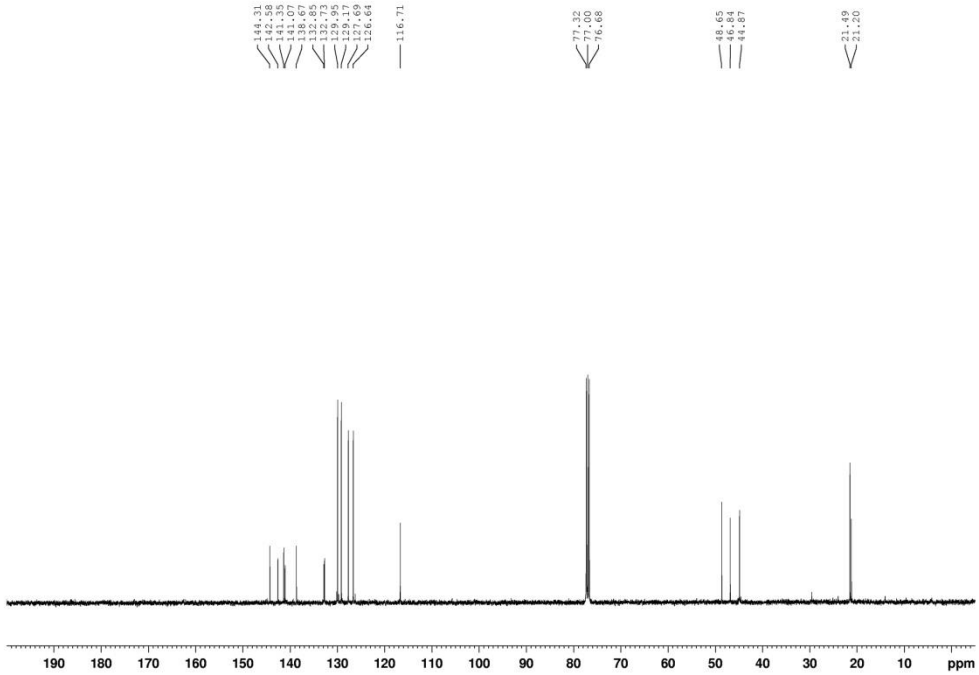

7.735
7.715
7.391
7.371
7.316
7.310
7.301
7.260
7.042
7.037
7.027
7.019
4.919
4.771
4.561
4.521
3.815
3.810
3.774
3.769
3.662
3.654
3.632
3.623
3.326
3.068
3.057
3.038
3.027
2.462
1.713
0.000
9
8
7
6
5
4
3
2
1
0 ppm
2.01
2.11
2.91
2.00
0.93
0.99
0.95
0.96
0.96
0.94
0.92
3.00
2.85

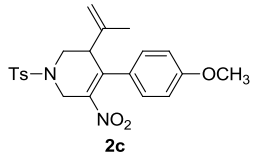

144.39
142.70
142.32
141.18
135.80
132.69
130.60
128.63
128.44
127.72
126.72
116.88
77.32
77.00
76.68
48.79
46.81
44.80
21.56
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts–N
NO2

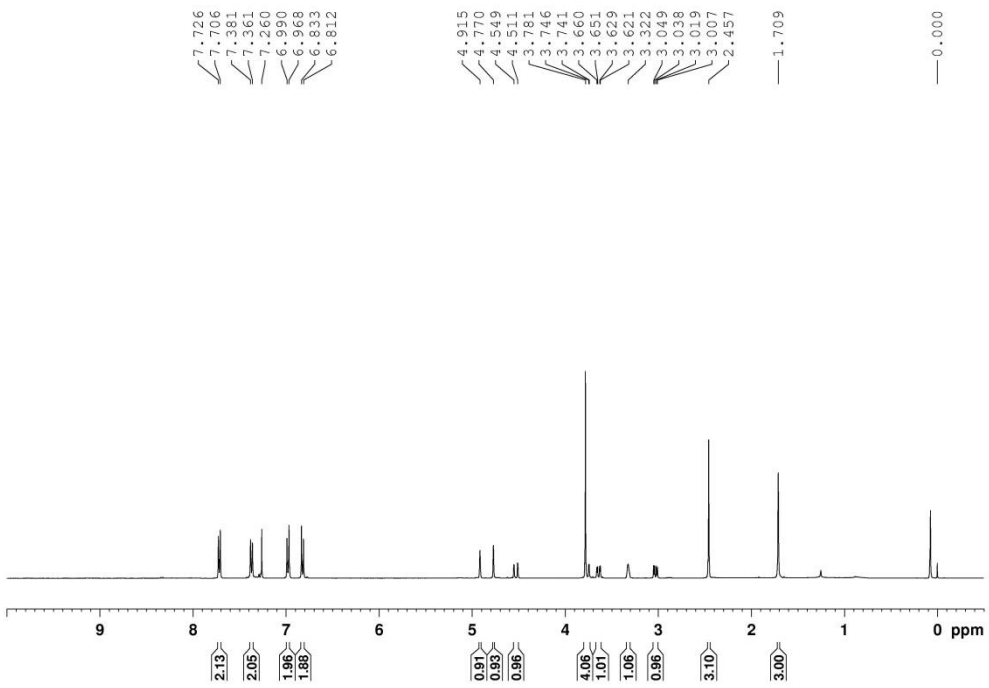
2b

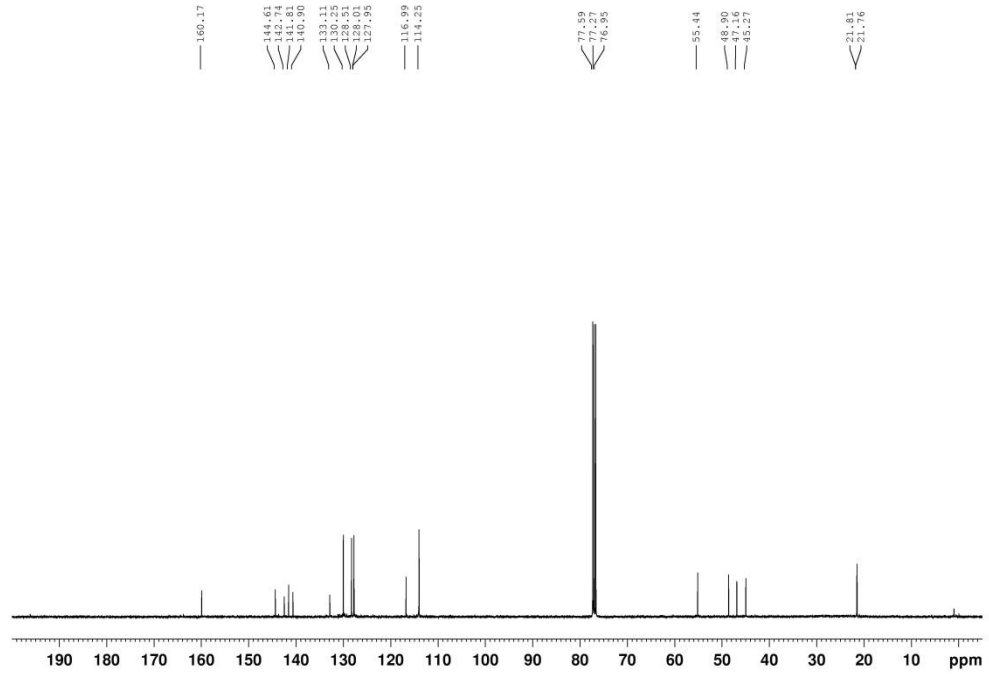


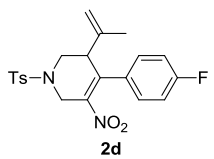




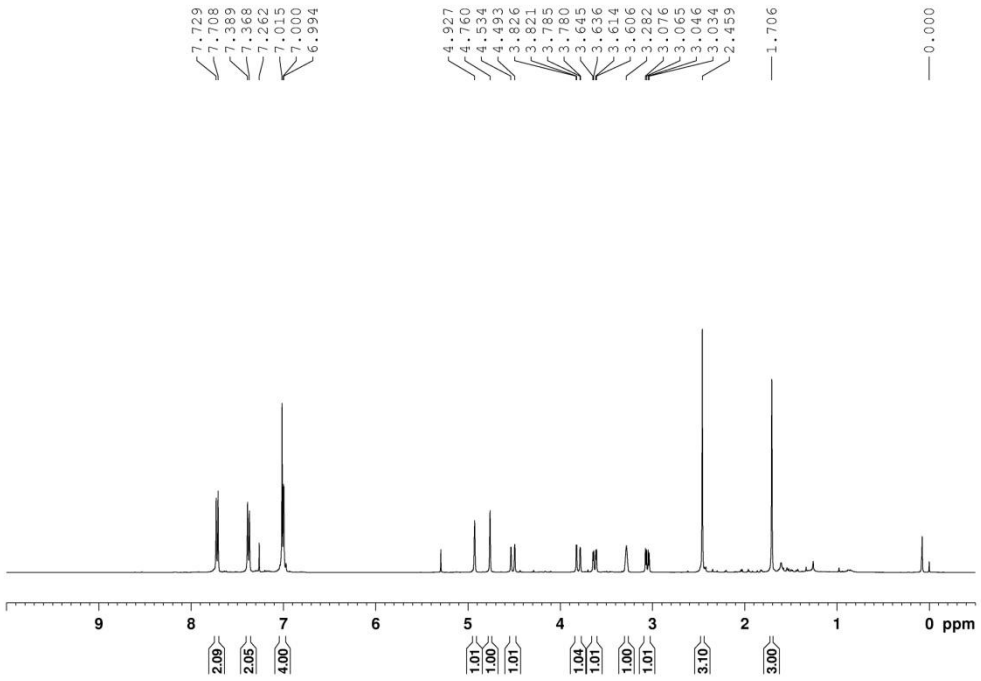
2c

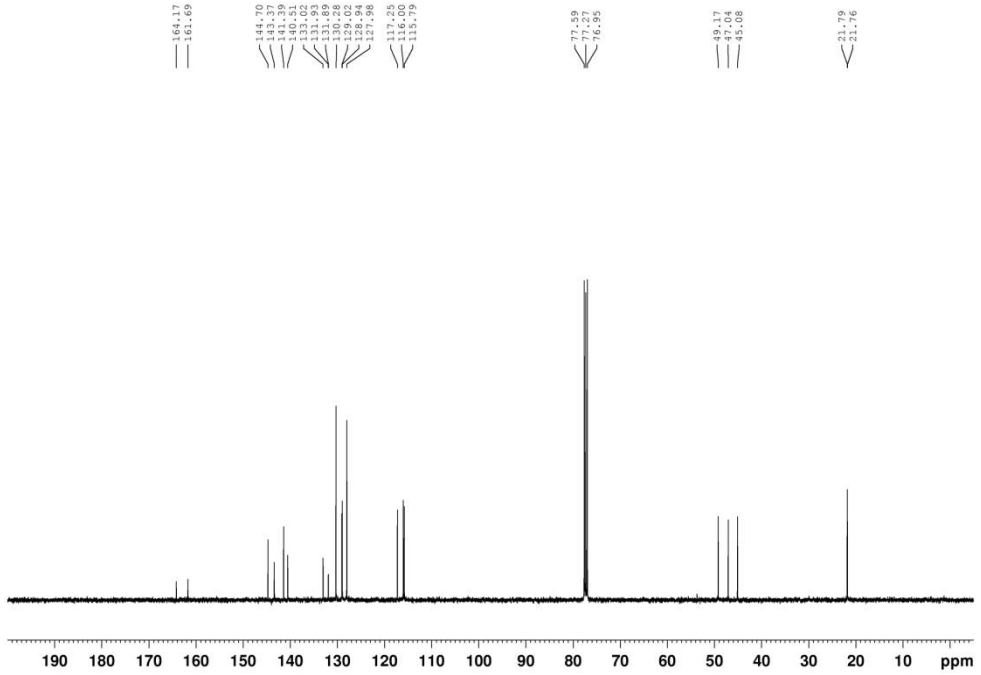

7.726
7.706
7.381
7.361
7.260
6.990
6.968
6.833
6.812
4.915
4.770
4.549
4.511
3.781
3.746
3.741
3.660
3.651
3.629
3.621
3.322
3.049
3.038
3.019
3.007
2.457
1.709
0.000
9
8
7
6
5
4
3
2
1
0 ppm
2.13
2.05
1.96
1.88
0.91
0.93
0.96
4.06
1.01
1.06
0.96
3.10
3.00

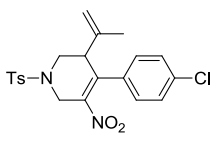

160.17
144.61
142.74
141.81
140.90
133.11
130.25
128.51
128.01
127.95
116.99
114.25
77.59
77.27
76.95
55.44
48.90
47.66
45.27
21.81
21.76
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts–N
F
NO2

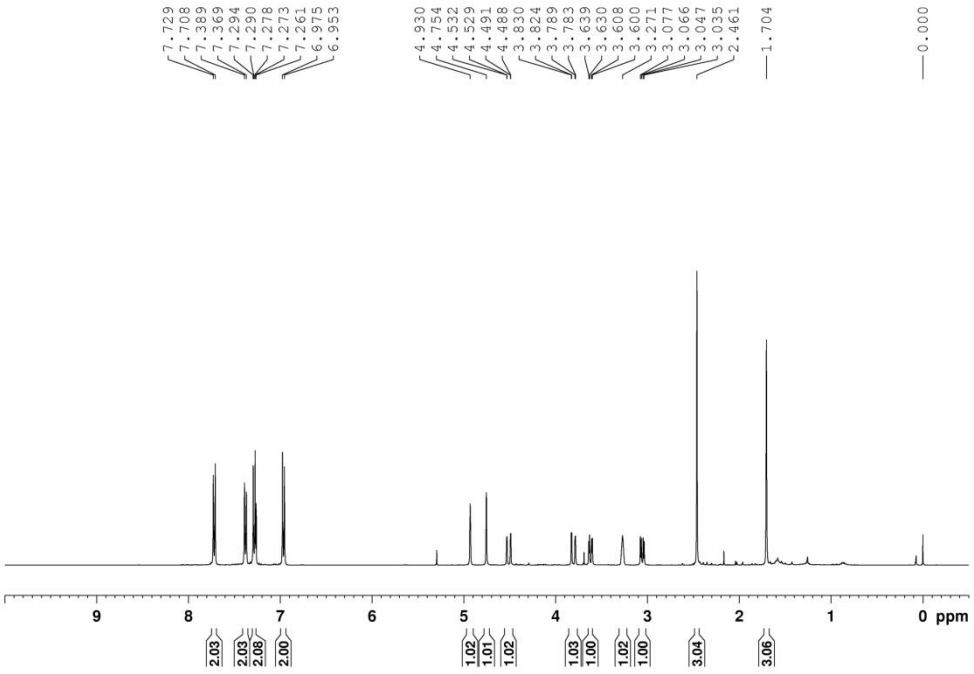
2d


7.729
7.708
7.389
7.368
7.262
7.015
7.000
6.994
4.927
4.760
4.534
4.493
3.826
3.821
3.785
3.780
3.645
3.636
3.614
3.606
3.282
3.076
3.065
3.046
3.034
2.459
1.706
0.000
9
8
7
6
5
4
3
2
1
0 ppm
2.09
2.05
4.00
1.01
1.00
1.01
1.04
1.01
1.00
1.01
3.10
3.00


164.17
161.69
144.70
143.37
141.39
140.51
133.02
131.93
131.89
130.28
129.02
128.94
127.98
117.25
116.00
115.79
77.59
77.27
76.95
49.17
47.04
45.08
21.79
21.76
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts–N
Cl
NO2

2e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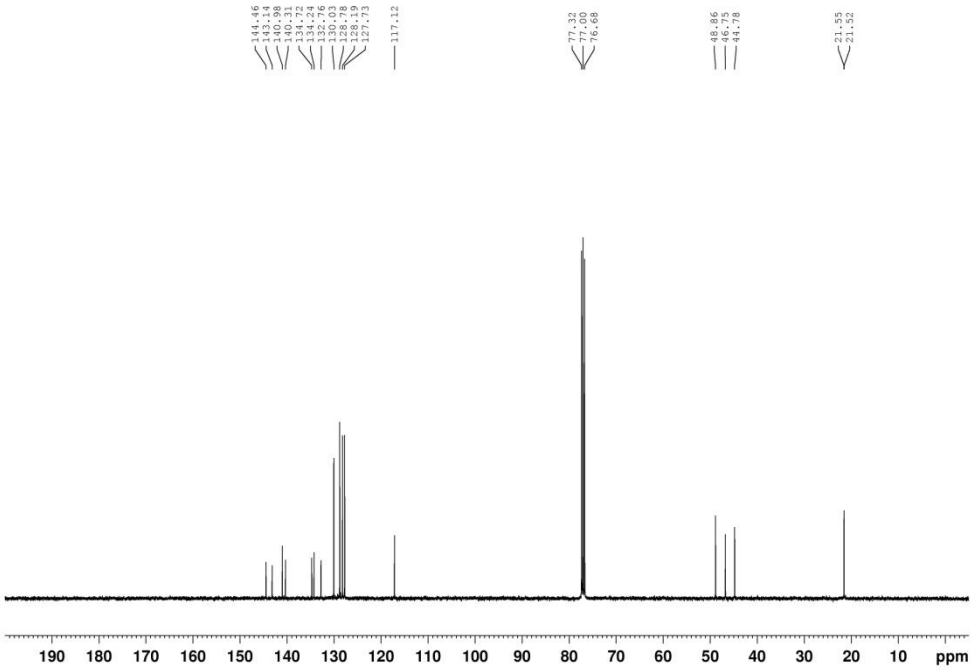
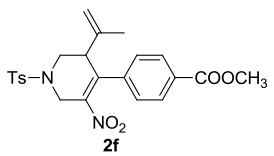
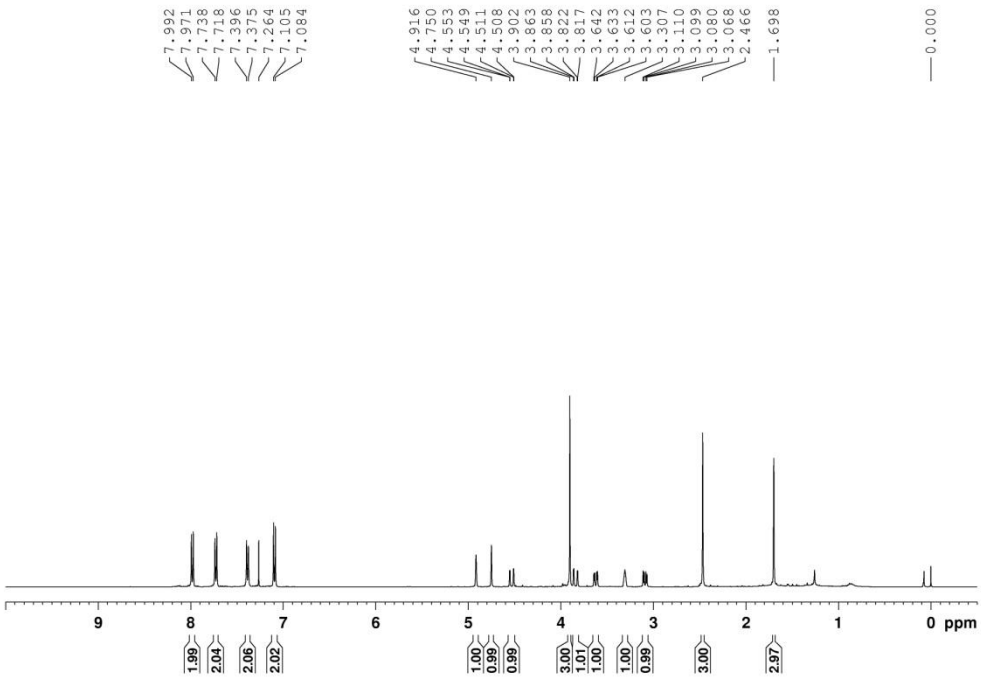
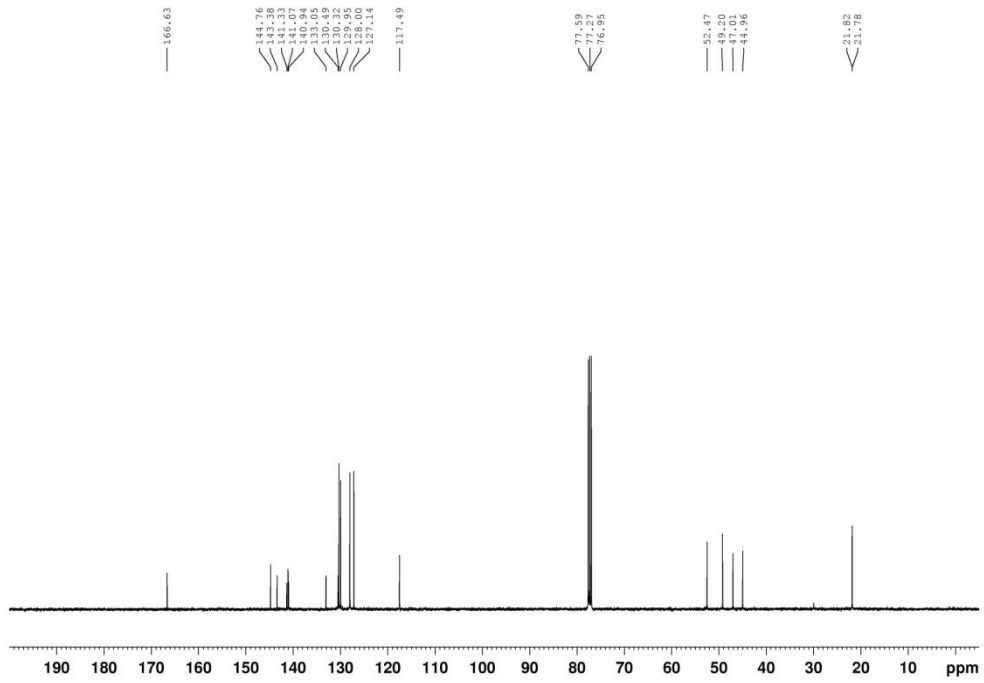
7.708
7.389
7.369
7.294
7.290
7.278
7.273
7.261
6.975
6.953
4.930
4.754
4.532
4.529
4.491
4.488
3.830
3.824
3.789
3.783
3.639
3.630
3.608
3.600
3.271
3.077
3.066
3.047
3.035
2.461
1.704
0.000
9
8
7
6
5
4
3
2
1
0 ppm
2.03
2.03
2.08
2.00
1.02
1.01
1.02
1.03
1.00
1.02
1.00
3.04
3.06

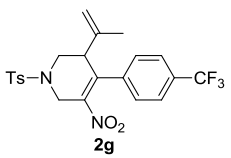

144.46
143.14
140.98
140.31
134.72
134.24
133.76
130.03
128.78
128.19
127.73
117.12
77.32
77.00
76.68
48.06
46.75
44.78
21.55
21.52
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts–N
COOCH3
NO2

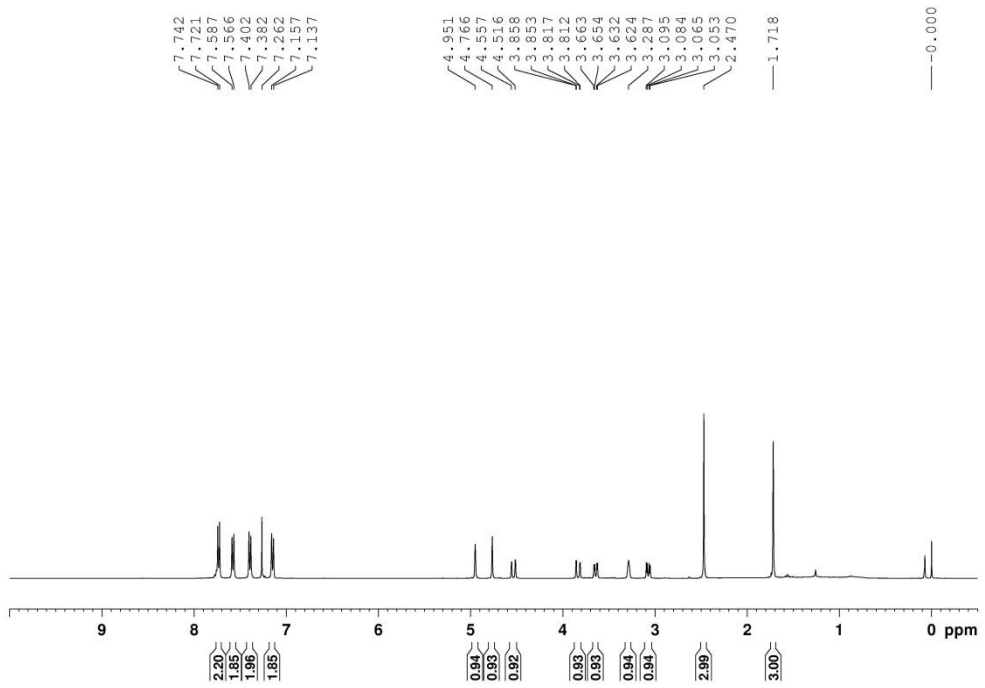
2f

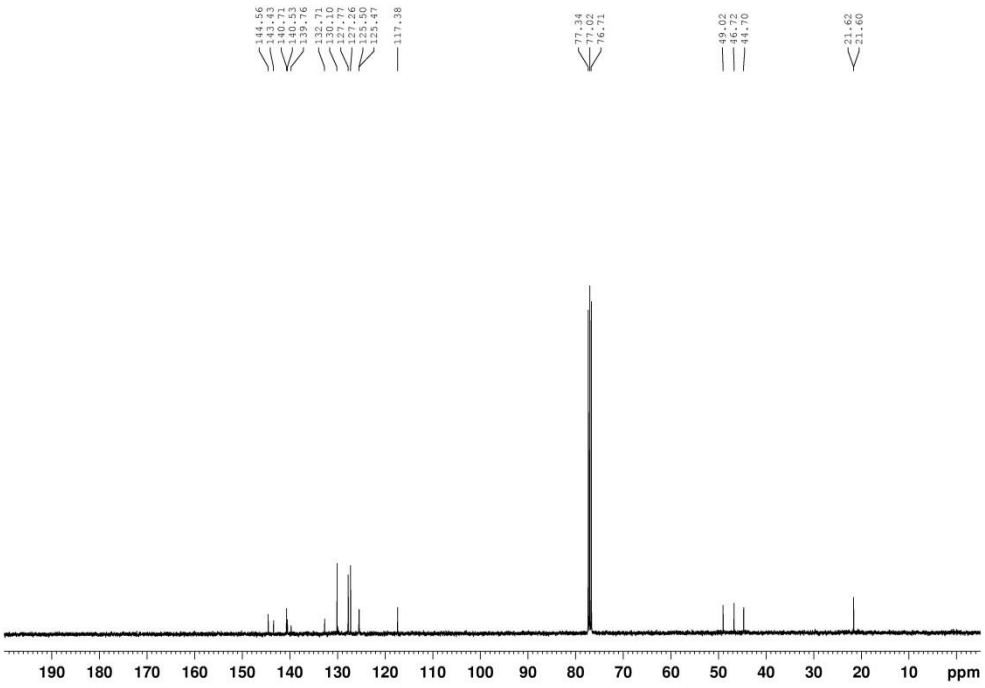

7.992
7.971
7.738
7.718
7.396
7.375
7.264
7.105
7.084
4.916
4.750
4.553
4.549
4.511
4.508
3.902
3.863
3.858
3.822
3.817
3.642
3.633
3.612
3.603
3.307
3.110
3.099
3.080
3.068
2.466
1.698
0.000
9
8
7
6
5
4
3
2
1
0 ppm
1.99
2.04
2.06
2.02
1.00
0.99
0.99
3.00
1.01
1.00
1.00
0.99
3.00
2.97

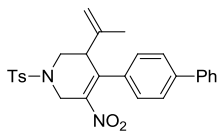

166.63
144.76
143.38
141.33
141.07
140.94
133.05
130.49
130.32
129.95
128.00
127.14
117.49
77.59
77.27
76.95
52.47
49.20
47.01
44.96
21.82
21.78
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts—N
CF3
NO2

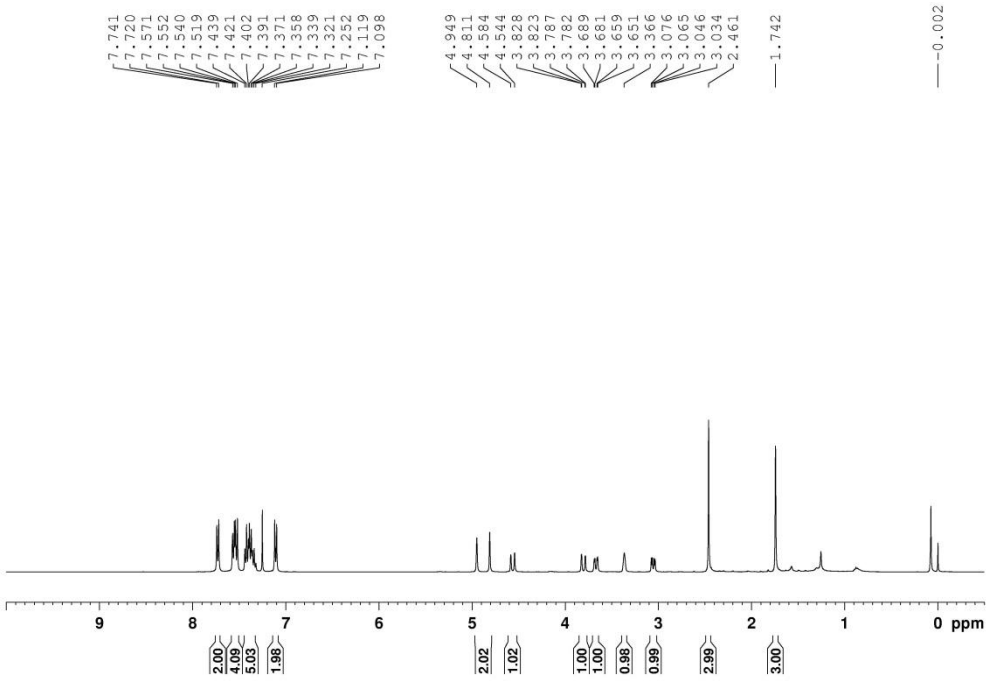
2g

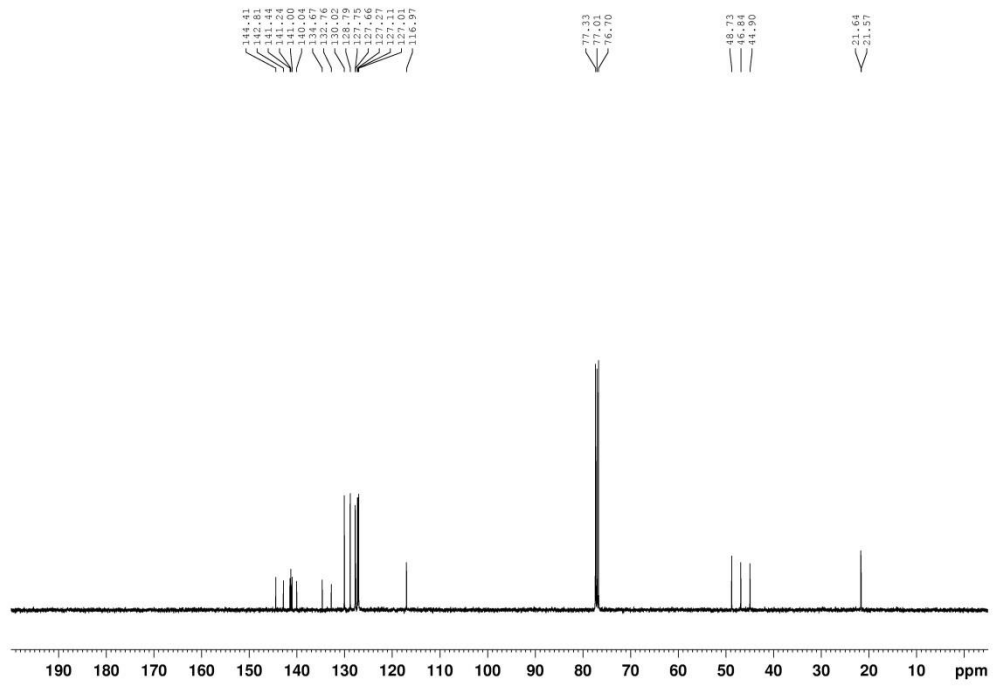

7.742
7.721
7.587
7.566
7.402
7.382
7.262
7.157
7.137
4.951
4.766
4.557
4.516
3.858
3.853
3.817
3.812
3.663
3.654
3.632
3.624
3.287
3.095
3.084
3.065
3.053
2.470
1.718
0.000
9 8 7 6 5 4 3 2 1 0 ppm
2.20 1.85 1.96 1.85 0.94 0.93 0.92 0.93 0.93 0.94 0.94 2.99 3.00

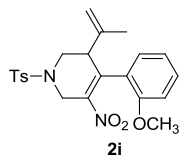

144.56
143.43
140.71
140.53
139.76
132.71
131.10
127.77
127.26
125.50
125.47
117.38
77.34
77.02
76.71
49.02
46.72
44.70
21.62
21.60
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Ts–N
Ph
NO2

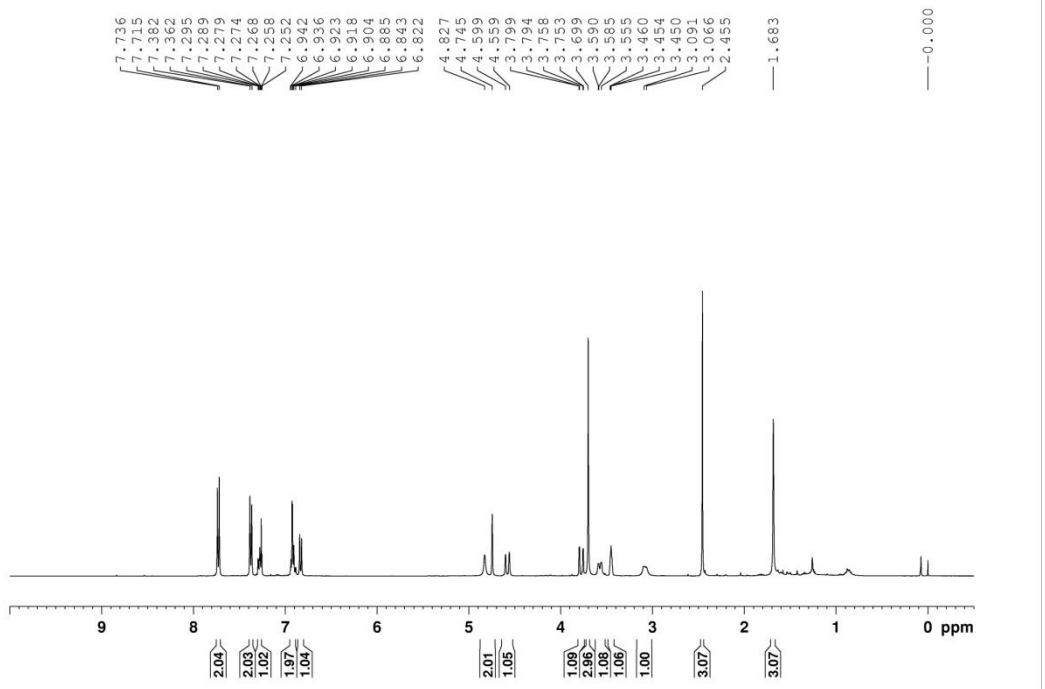
2h


7.741
7.720
7.571
7.552
7.540
7.519
7.439
7.421
7.402
7.391
7.371
7.358
7.339
7.321
7.252
7.119
7.098
4.949
4.811
4.584
4.544
3.828
3.823
3.787
3.782
3.689
3.681
3.659
3.651
3.366
3.076
3.065
3.046
3.034
2.461
1.742
0.002
9
8
7
6
5
4
3
2
1
0 ppm
2.00
4.09
5.03
1.98
2.02
1.02
1.00
1.00
0.98
0.99
2.99
3.00


144.41
142.81
141.44
141.24
141.00
140.04
134.67
132.76
130.08
128.59
127.75
127.66
127.27
127.11
127.01
116.97
77.33
77.01
76.70
48.73
46.84
44.90
21.64
21.57
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts
N
NO2
OCH3

2i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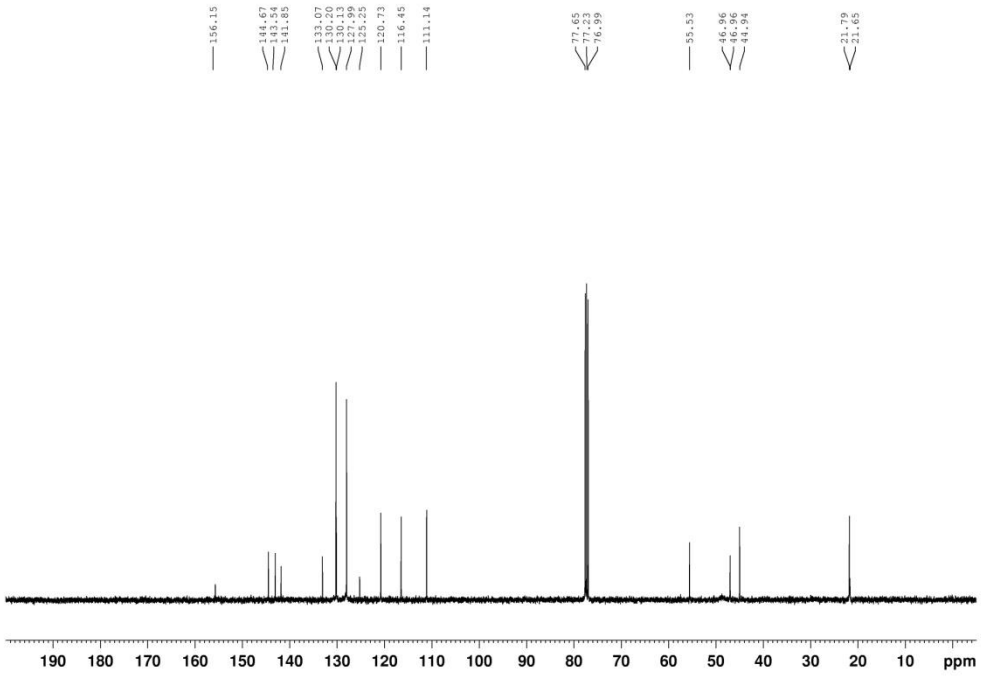
7.715
7.382
7.362
7.295
7.289
7.279
7.274
7.268
7.258
7.252
6.942
6.936
6.923
6.918
6.904
6.885
6.843
6.822
4.827
4.745
4.599
4.559
3.799
3.794
3.758
3.753
3.699
3.590
3.585
3.555
3.460
3.454
3.450
3.091
3.066
2.455
1.683
0.000
9
8
7
6
5
4
3
2
1
0 ppm
2.04
2.03
1.02
1.97
1.04
2.01
1.05
1.09
2.96
1.08
1.06
1.00
3.07
3.07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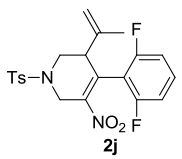
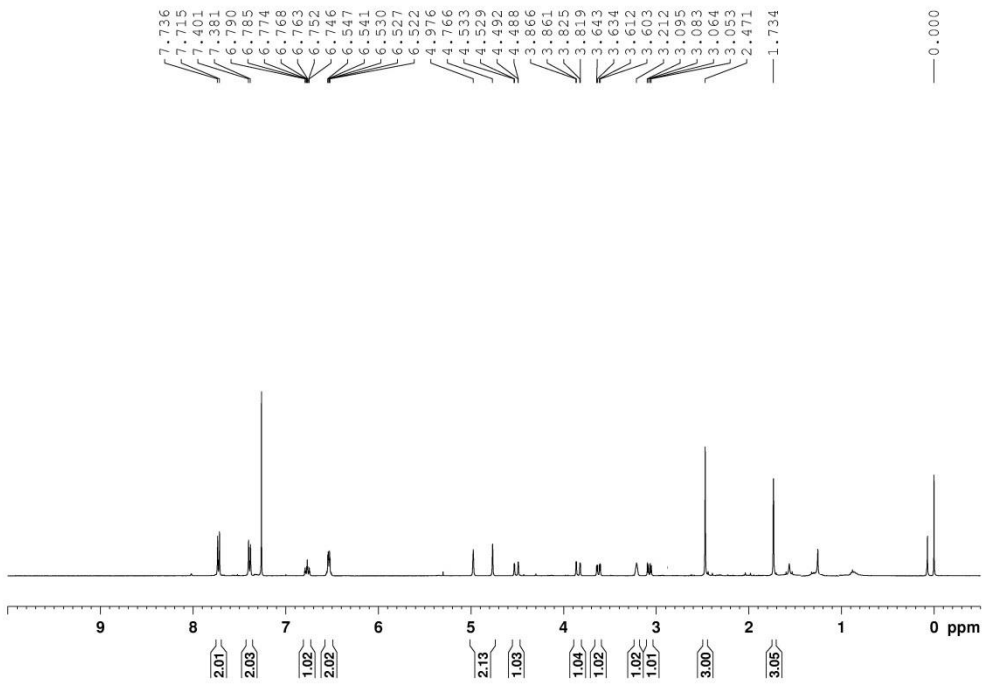
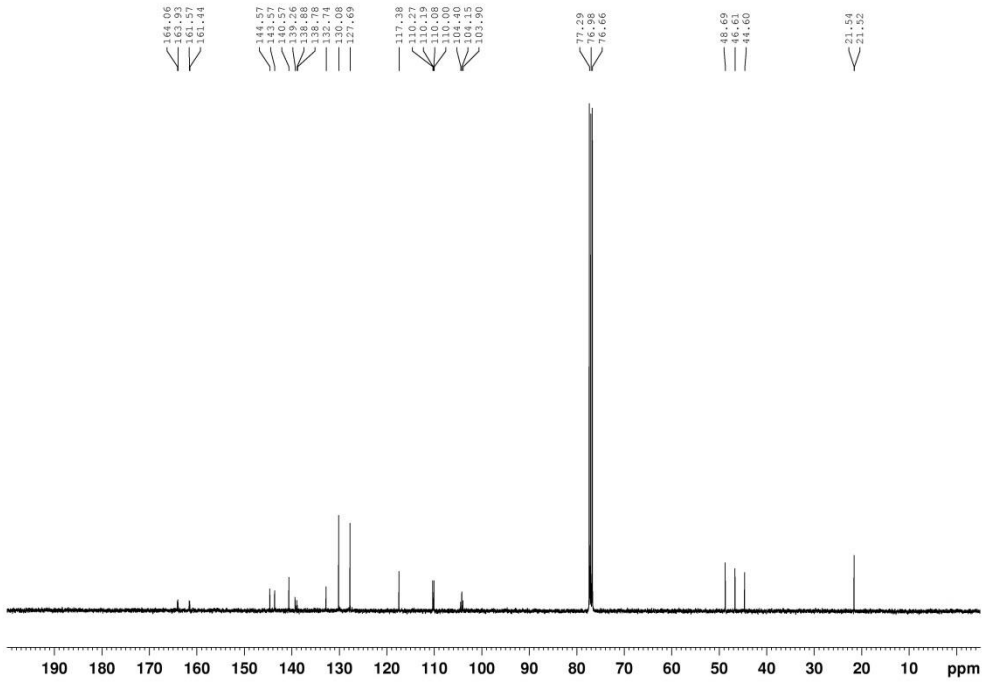
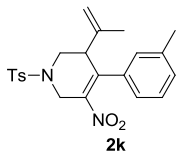
144.67
143.54
141.85
133.07
130.20
130.13
127.99
125.25
120.73
116.45
111.14
77.65
77.23
76.99
55.53
46.96
46.96
44.94
21.79
21.65
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


F
Ts–N
NO2
F

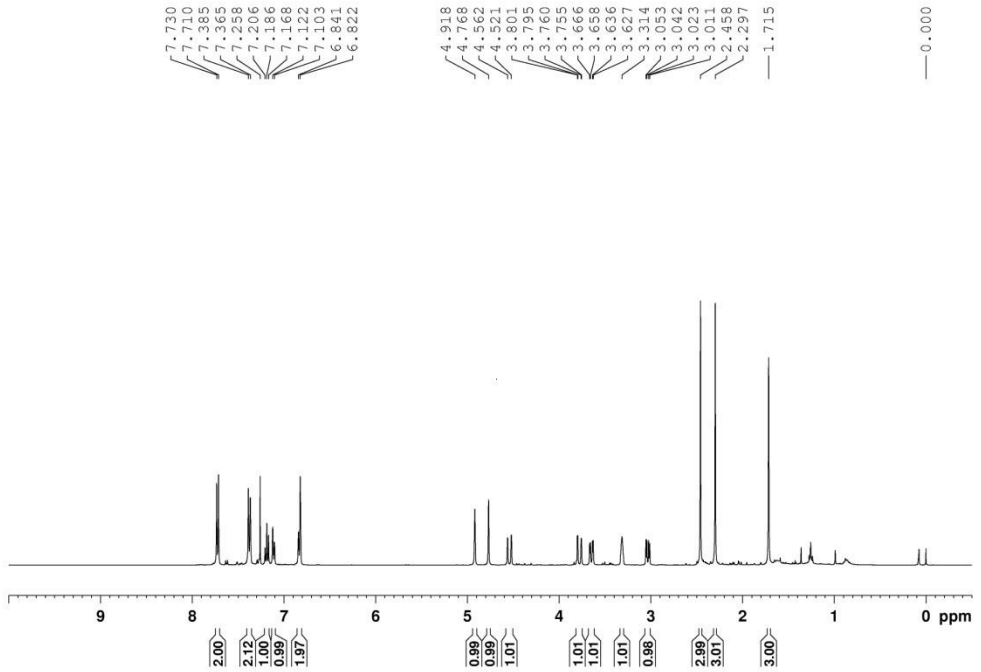
2j


7.736
7.715
7.401
7.381
6.790
6.785
6.774
6.768
6.763
6.752
6.746
6.547
6.541
6.530
6.527
6.522
4.976
4.766
4.533
4.529
4.492
4.488
3.866
3.861
3.825
3.819
3.643
3.634
3.612
3.603
3.212
3.095
3.083
3.064
3.053
2.471
1.734
0.000
9
8
7
6
5
4
3
2
1
0 ppm
2.01
2.03
1.02
2.02
2.13
1.03
1.04
1.02
1.02
1.01
3.00
3.05


164.06
163.93
163.57
161.44
144.57
143.57
140.57
139.26
138.88
138.78
132.74
130.08
127.69
117.38
110.27
110.19
110.08
110.00
104.40
104.15
103.90
77.29
76.98
76.66
48.69
46.61
44.60
21.54
21.52
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts–N
NO2

2k


7.730
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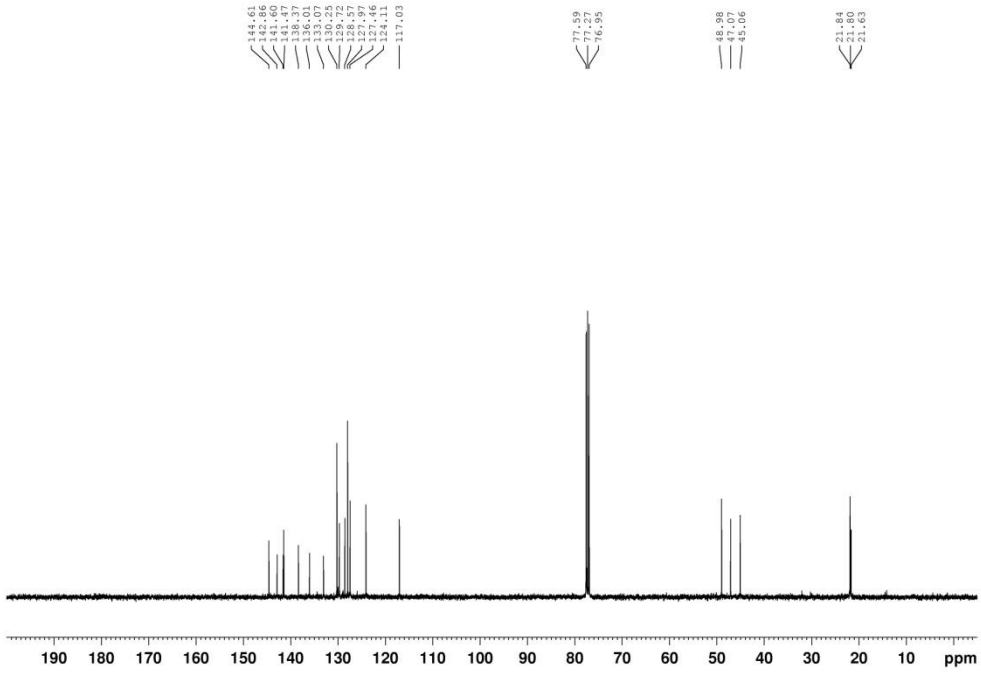
7.385
7.365
7.258
7.206
7.186
7.168
7.122
7.103
6.841
6.822
4.918
4.768
4.562
4.521
3.801
3.795
3.760
3.755
3.666
3.658
3.636
3.627
3.314
3.053
3.042
3.023
3.011
2.458
2.297
1.715
0.000
9
8
7
6
5
4
3
2
1
0 ppm
2.00
2.12
1.00
0.99
1.97
0.99
0.99
1.01
1.01
1.01
1.01
0.98
2.99
3.01
3.00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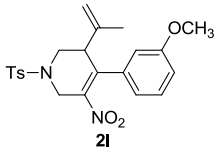
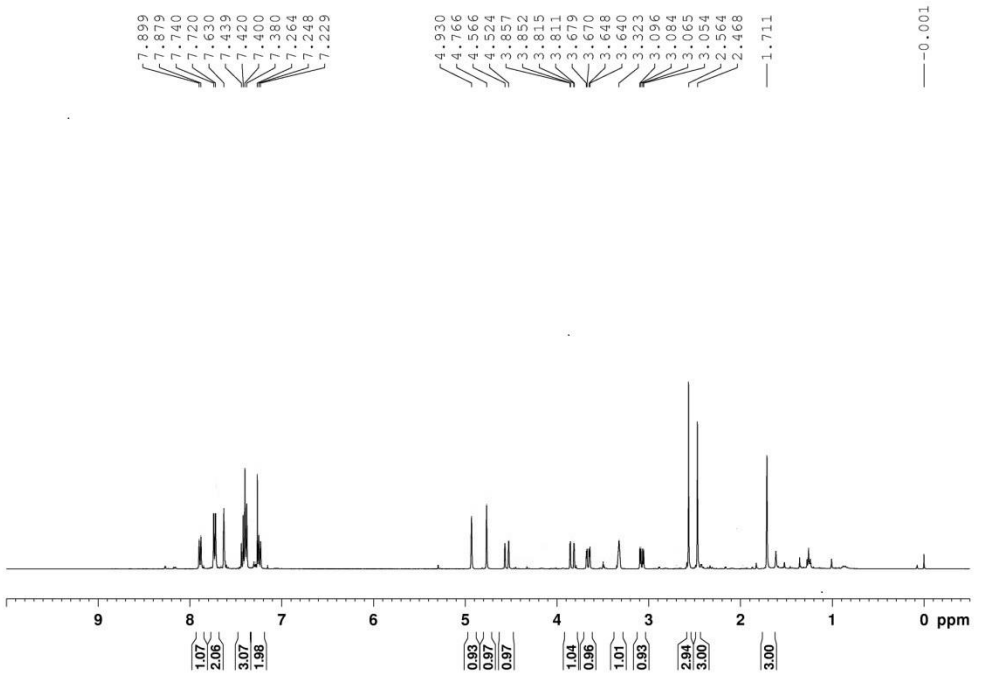
142.86
141.60
138.47
136.37
136.01
133.07
130.25
129.72
128.57
127.97
127.46
124.11
117.03
77.59
77.27
76.95
48.98
47.07
45.06
21.84
21.80
21.63
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


OCH3
Ts–N
NO2

2l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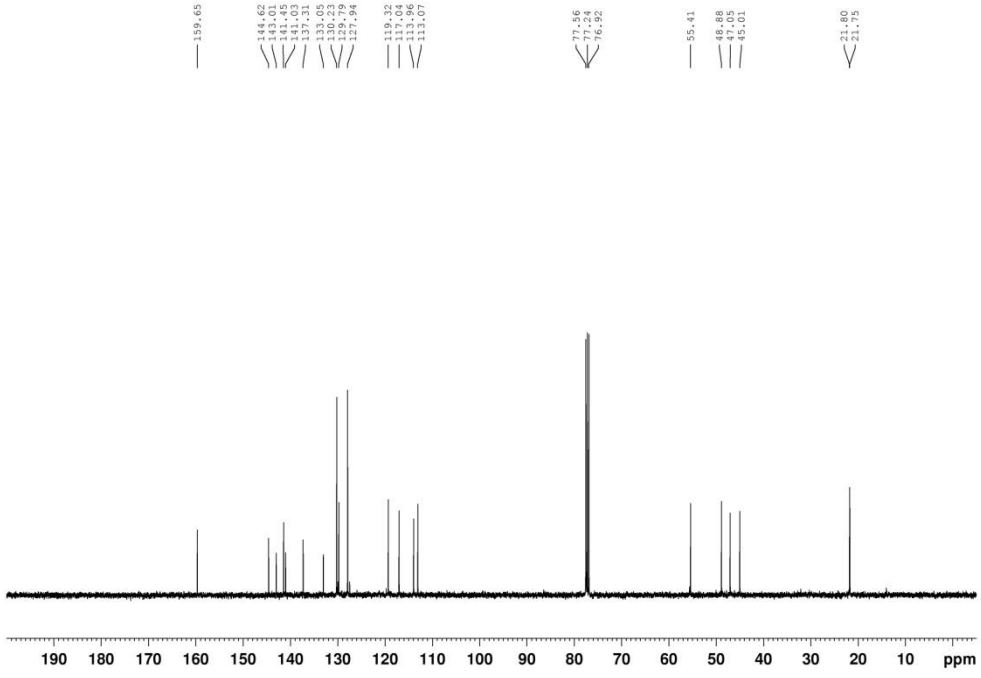
7.740
7.720
7.630
7.439
7.420
7.400
7.380
7.264
7.248
7.229
4.930
4.766
4.566
4.524
3.857
3.852
3.815
3.811
3.679
3.670
3.648
3.640
3.323
3.096
3.084
3.065
3.054
2.564
2.468
1.711
0.001
9
8
7
6
5
4
3
2
1
0 ppm
1.07
2.06
3.07
1.98
0.93
0.97
0.97
1.04
0.96
1.01
0.93
2.94
3.00
3.00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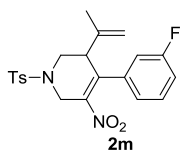
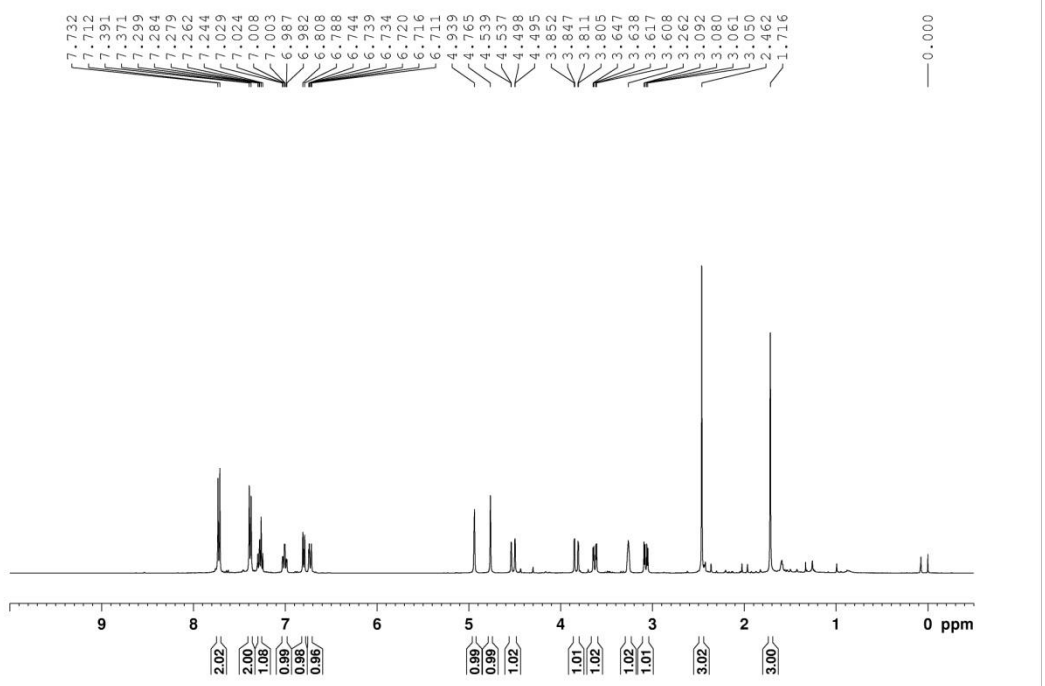
144.62
143.01
141.65
141.03
137.31
133.05
130.23
129.79
127.94
119.32
117.04
113.96
113.07
77.56
77.24
76.92
55.41
48.88
47.05
45.01
21.80
21.75
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


F
Ts–N
NO2

2m


7.732
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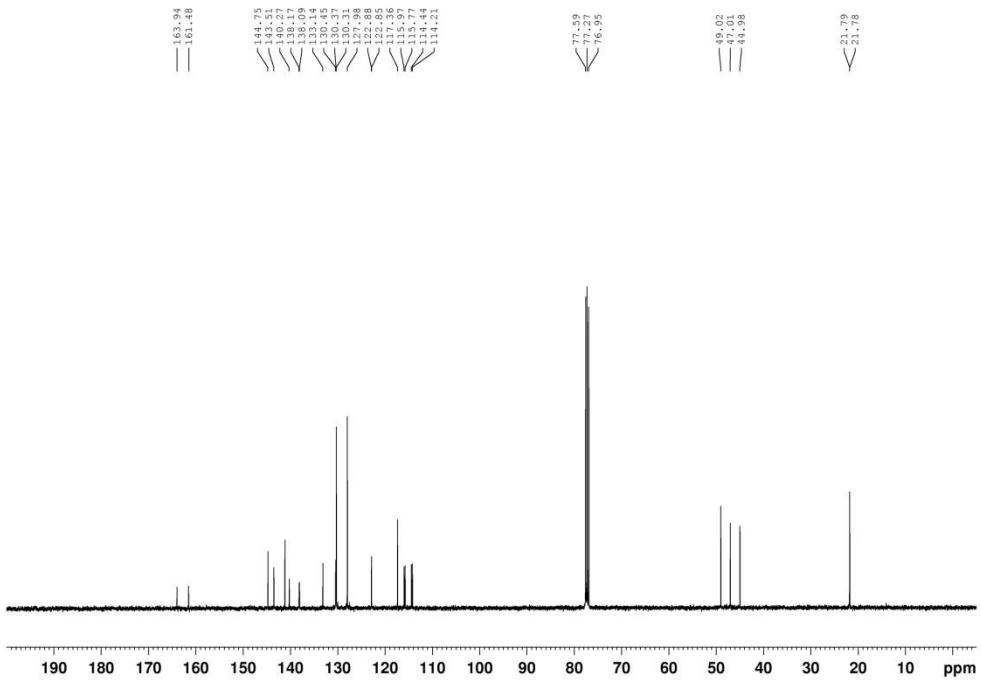
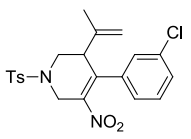
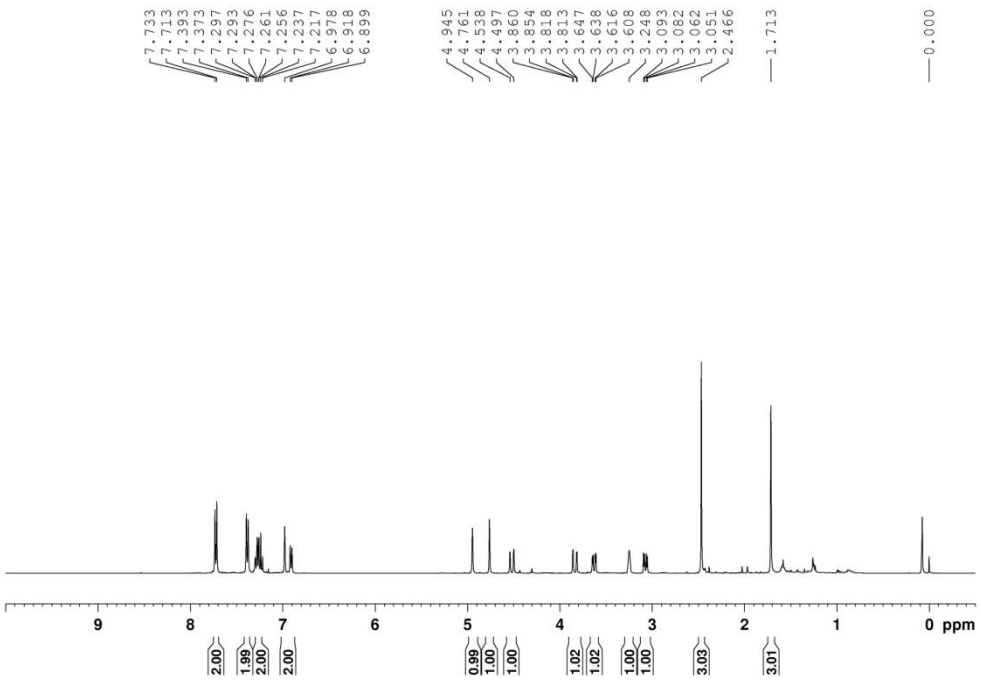
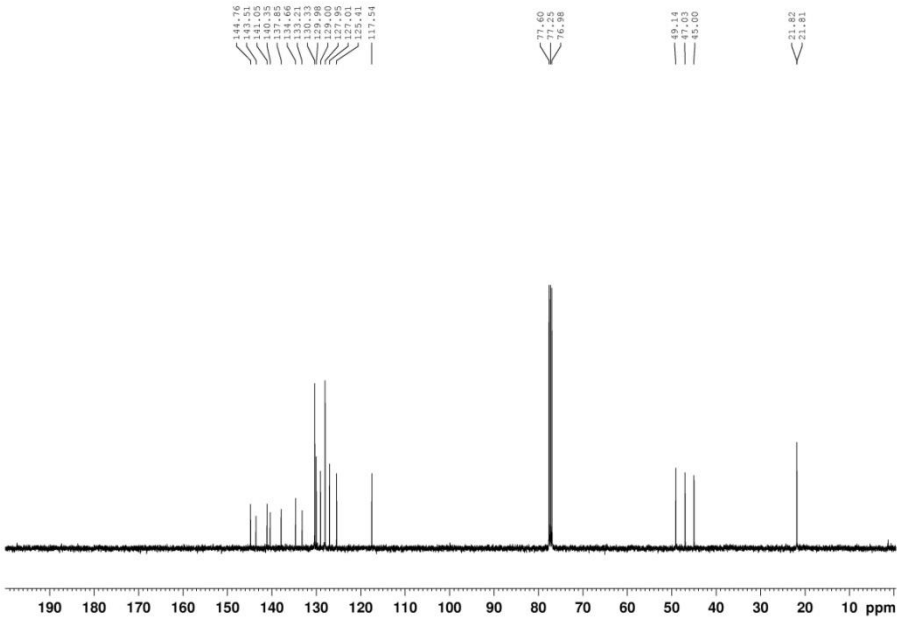
7.391
7.371
7.299
7.284
7.279
7.262
7.244
7.029
7.024
7.008
7.003
6.987
6.982
6.808
6.788
6.744
6.739
6.734
6.720
6.716
6.711
4.939
4.765
4.539
4.537
4.498
4.495
3.852
3.847
3.811
3.805
3.647
3.638
3.617
3.608
3.262
3.092
3.080
3.061
3.050
2.462
1.716
0.000
9 8 7 6 5 4 3 2 1 0 ppm
2.02 2.00 1.08 0.99 0.98 0.96 0.99 0.99 1.02 1.01 1.02 1.02 1.01 3.02 3.00


163.94
161.48
144.75
143.51
140.27
138.17
138.09
133.14
130.45
130.37
130.31
127.98
127.88
122.85
117.36
115.97
115.77
114.44
114.21
77.59
77.27
76.95
49.02
47.01
44.98
21.79
21.78
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 ppm


Cl
Ts–N
NO2

2n


7.733
7.713
7.393
7.373
7.297
7.293
7.276
7.261
7.256
7.237
7.217
6.978
6.918
6.899
4.945
4.761
4.538
4.497
3.860
3.854
3.818
3.813
3.647
3.638
3.616
3.608
3.248
3.093
3.082
3.062
3.051
2.466
1.713
0.000
9
8
7
6
5
4
3
2
1
0 ppm
2.00
1.99
2.00
2.00
0.99
1.00
1.00
1.02
1.02
1.00
1.00
3.03
3.01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143.51
141.05
140.35
137.85
134.66
133.21
130.33
129.98
129.00
127.99
127.01
125.41
117.54
77.60
77.25
76.98
49.14
47.03
45.00
21.82
21.61
190
180
170
160
150
140
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120
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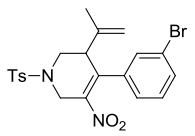
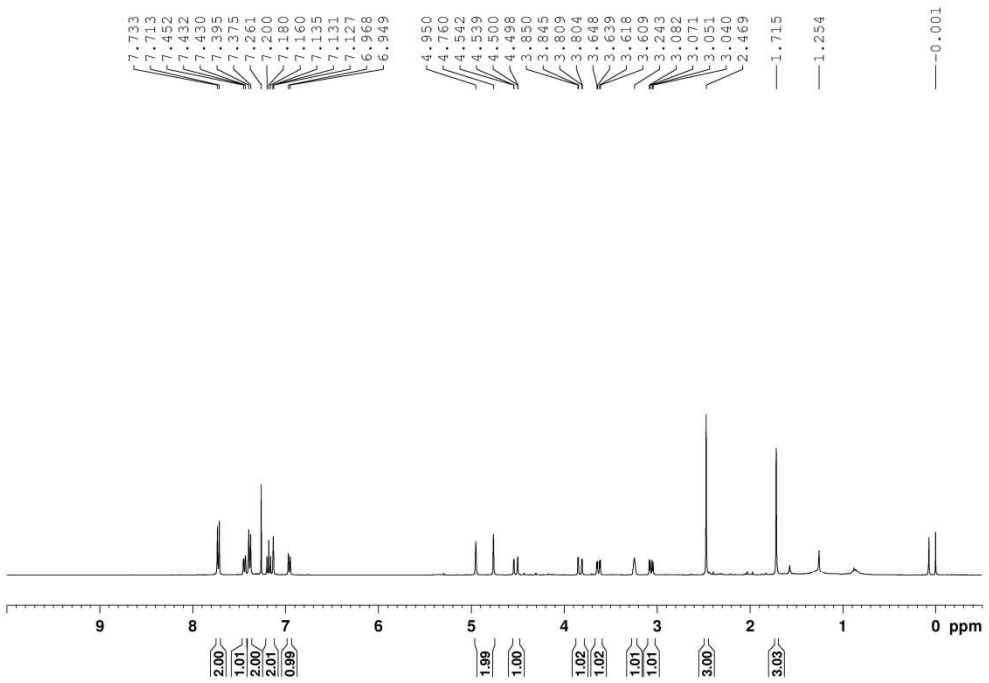
90
80
70
60
50
40
30
20
10 ppm


Br
Ts–N
NO2

2o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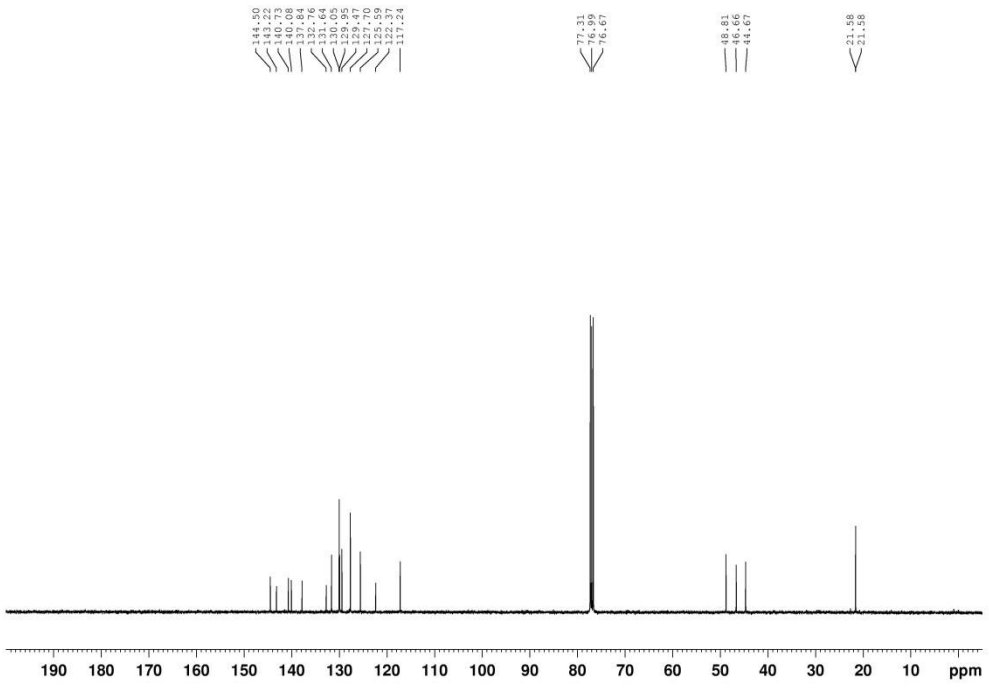
7.713
7.452
7.432
7.430
7.395
7.375
7.261
7.200
7.180
7.160
7.135
7.131
7.127
6.968
6.949
4.950
4.760
4.542
4.539
4.500
4.498
3.850
3.845
3.809
3.804
3.648
3.639
3.618
3.609
3.243
3.082
3.071
3.051
3.040
2.469
1.715
1.254
0.001
9
8
7
6
5
4
3
2
1
0 ppm
2.00
1.01
2.00
2.01
0.99
1.99
1.00
1.02
1.02
1.01
1.01
3.00
3.03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143.22
140.73
140.08
137.84
132.76
131.64
130.05
129.95
129.77
127.70
125.59
122.37
117.24
77.31
76.99
76.67
48.81
46.66
44.67
21.58
21.58
190
180
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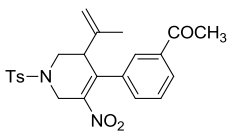
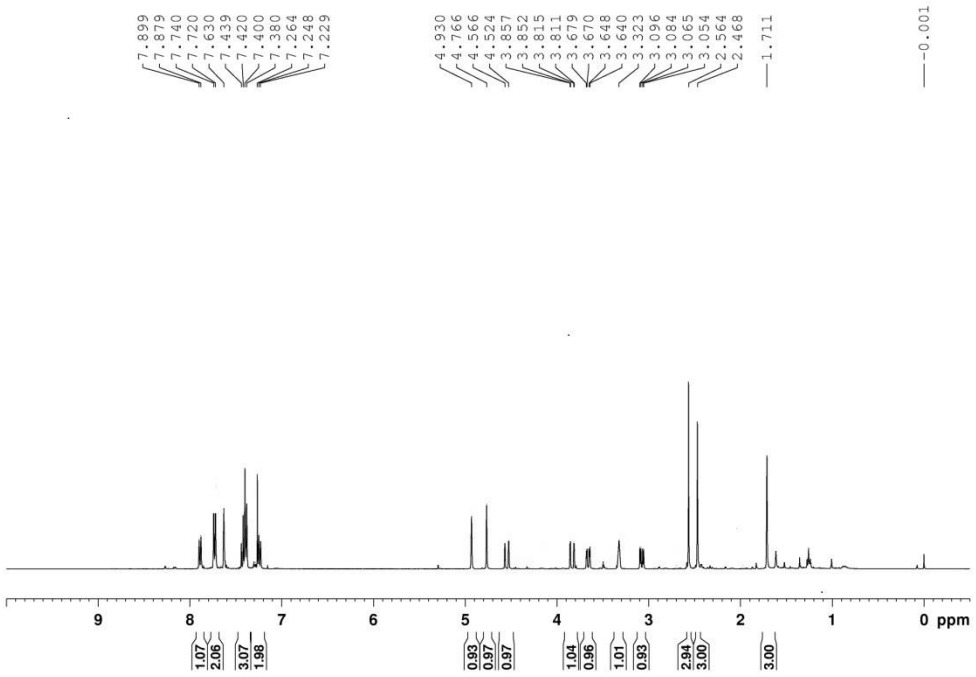
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


COCH3
Ts–N
NO2

2p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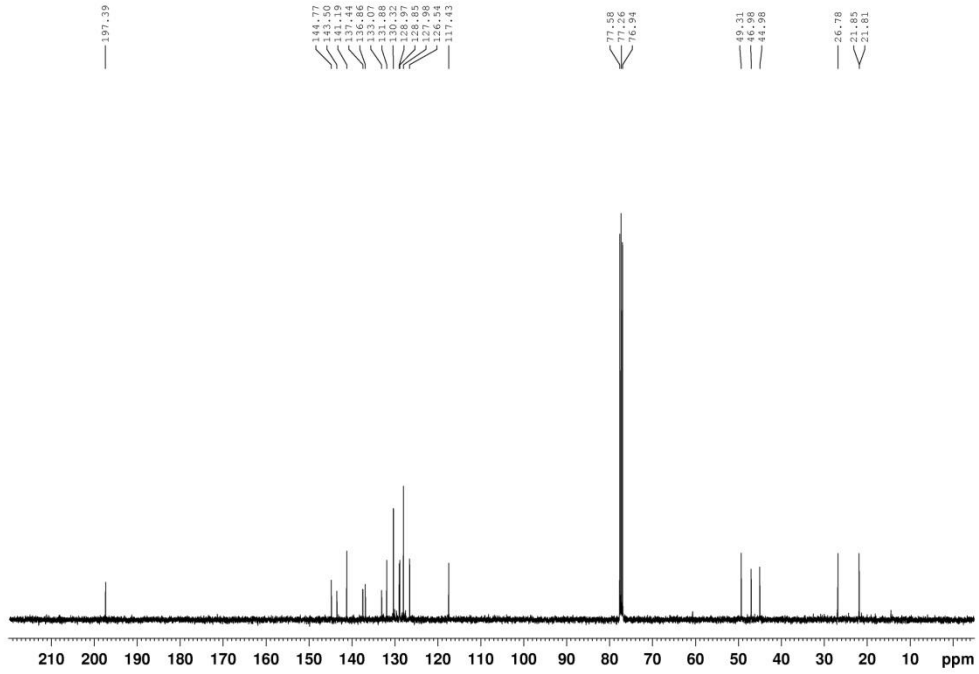
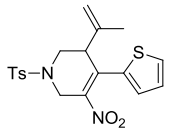
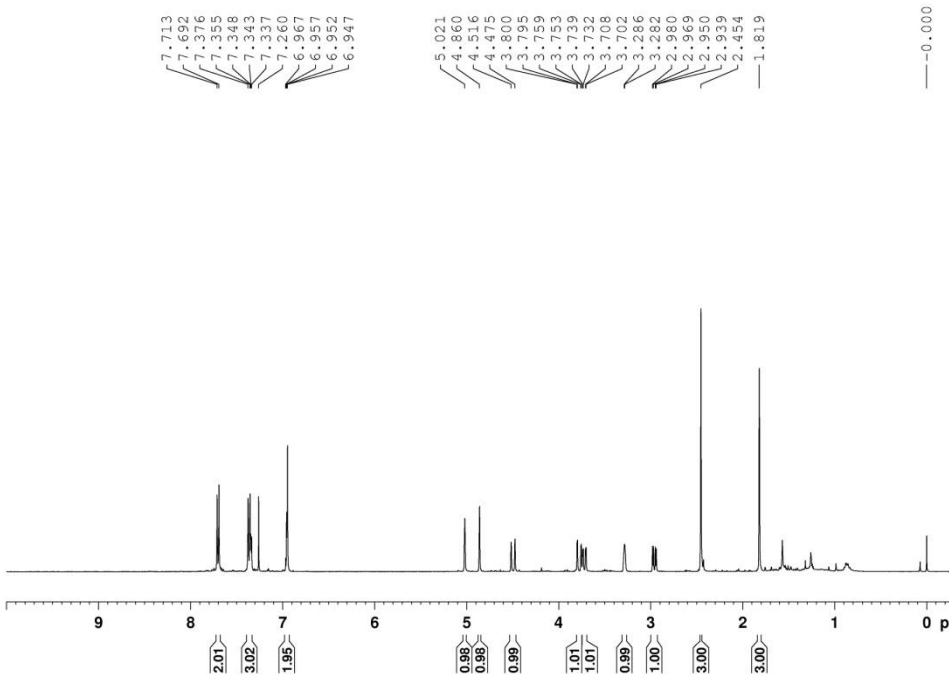
7.740
7.720
7.630
7.439
7.420
7.400
7.380
7.264
7.248
7.229
4.930
4.766
4.566
4.524
3.857
3.852
3.815
3.811
3.679
3.670
3.648
3.640
3.323
3.096
3.084
3.065
3.054
2.564
2.468
1.711
0.001
9
8
7
6
5
4
3
2
1
0 ppm
1.07
2.06
3.07
1.98
0.93
0.97
0.97
1.04
0.96
1.01
0.93
2.94
3.00
3.00


197.39
144.77
143.50
140.19
137.44
136.86
133.07
131.88
130.32
128.97
128.85
127.98
120.54
117.43
77.58
77.16
76.94
49.31
46.98
44.98
26.78
21.85
21.81
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


Ts–N
S
NO2

2q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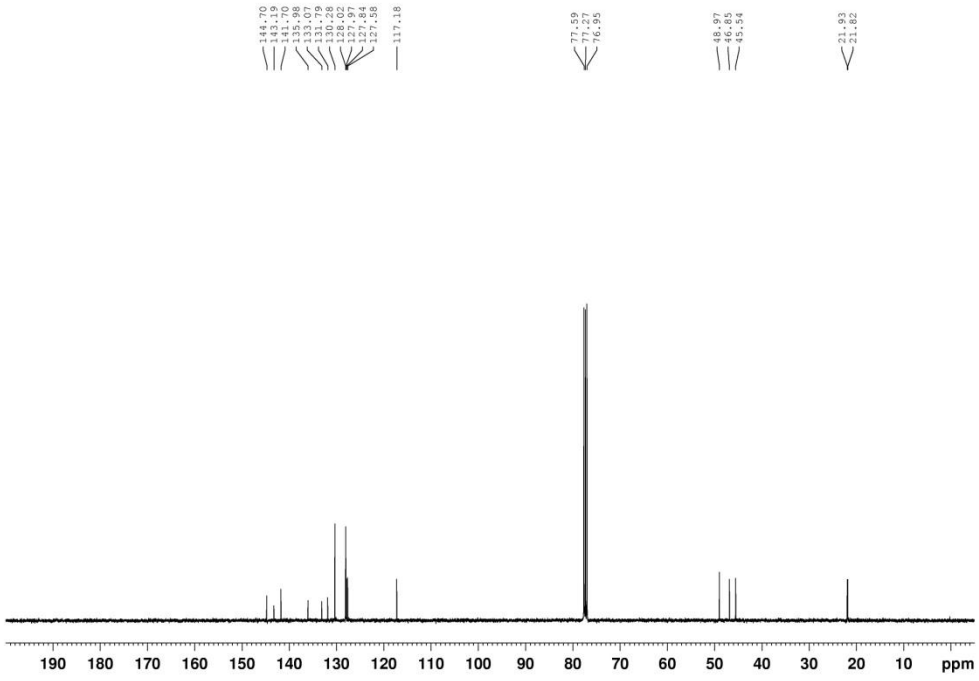
7.692
7.376
7.355
7.348
7.343
7.337
7.260
6.967
6.957
6.952
6.947
5.021
4.860
4.516
4.475
3.800
3.795
3.759
3.753
3.739
3.732
3.708
3.702
3.286
3.282
2.980
2.969
2.950
2.939
2.454
1.819
0.000
9
8
7
6
5
4
3
2
1
0 ppm
2.01
3.02
1.95
0.98
0.98
0.99
1.01
1.01
0.99
1.00
3.00
3.00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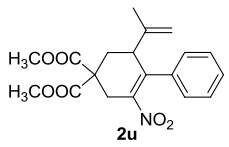
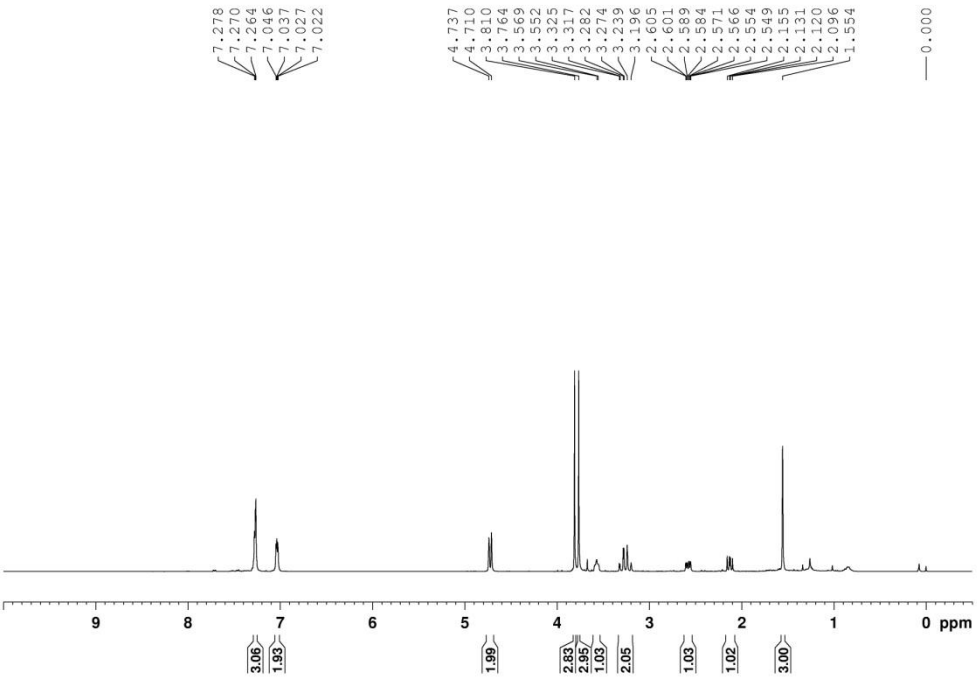
143.19
141.90
135.88
133.07
131.79
130.28
129.82
129.47
127.84
127.58
117.18
77.59
77.27
76.95
48.97
46.85
45.54
21.93
21.82
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


H3COOC
H3COOC
NO2

2u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7.270
7.264
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7.037
7.027
7.022
4.737
4.710
3.810
3.764
3.569
3.552
3.325
3.317
3.282
3.274
3.239
3.196
2.605
2.601
2.589
2.584
2.571
2.566
2.554
2.549
2.155
2.131
2.120
2.096
1.554
0.000
9
8
7
6
5
4
3
2
1
0 ppm
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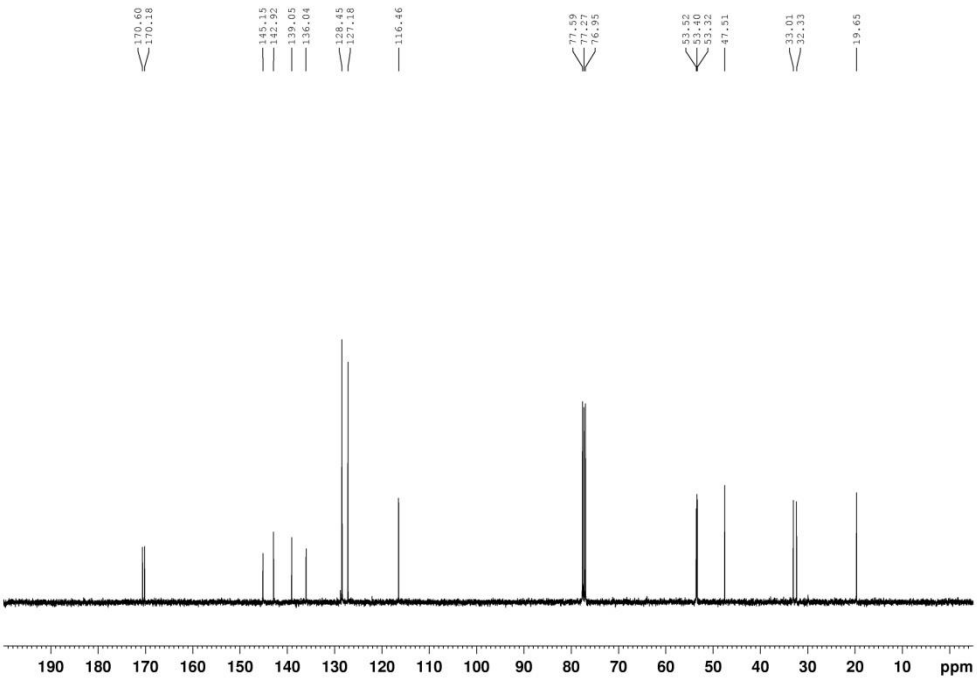
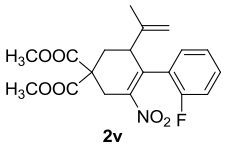
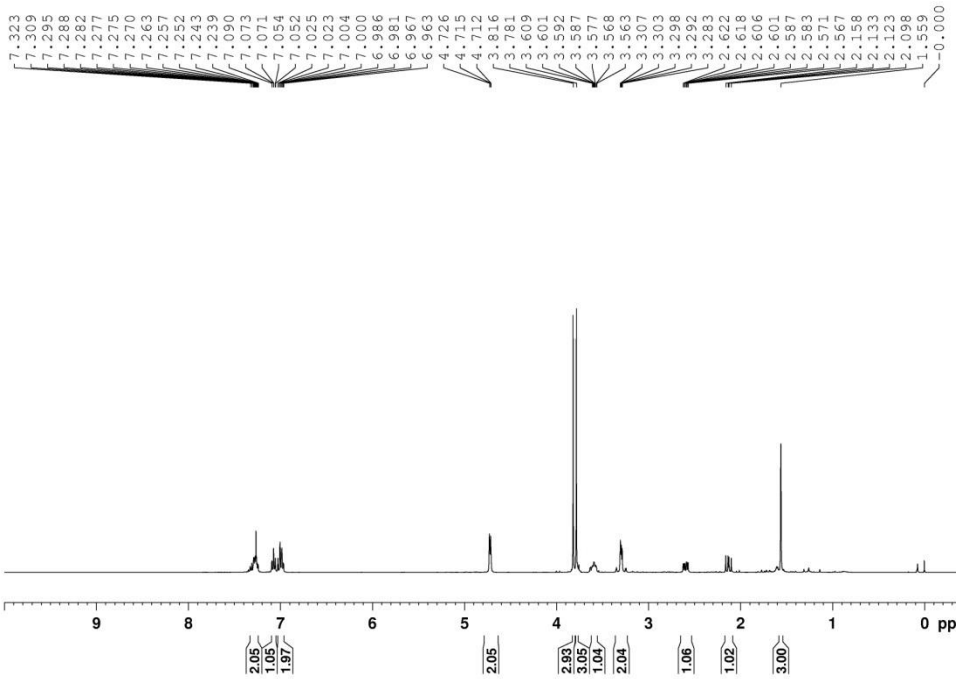
1.93
1.99
2.83
2.95
1.03
2.05
1.03
1.02
3.00


170.60
170.18
145.15
142.92
139.05
136.04
128.45
127.18
116.46
77.59
77.27
76.95
53.52
53.40
53.32
47.51
33.01
32.33
19.65
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


H3COOC
H3COOC
NO2
F

2v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7.295
7.288
7.282
7.277
7.275
7.270
7.263
7.257
7.252
7.243
7.239
7.090
7.073
7.071
7.054
7.052
7.025
7.023
7.004
7.000
6.986
6.981
6.967
6.963
4.726
4.715
4.712
3.816
3.781
3.609
3.601
3.592
3.587
3.577
3.568
3.563
3.307
3.303
3.298
3.292
3.283
2.622
2.618
2.606
2.601
2.587
2.583
2.571
2.567
2.158
2.133
2.123
2.098
1.559
0.000
9
8
7
6
5
4
3
2
1
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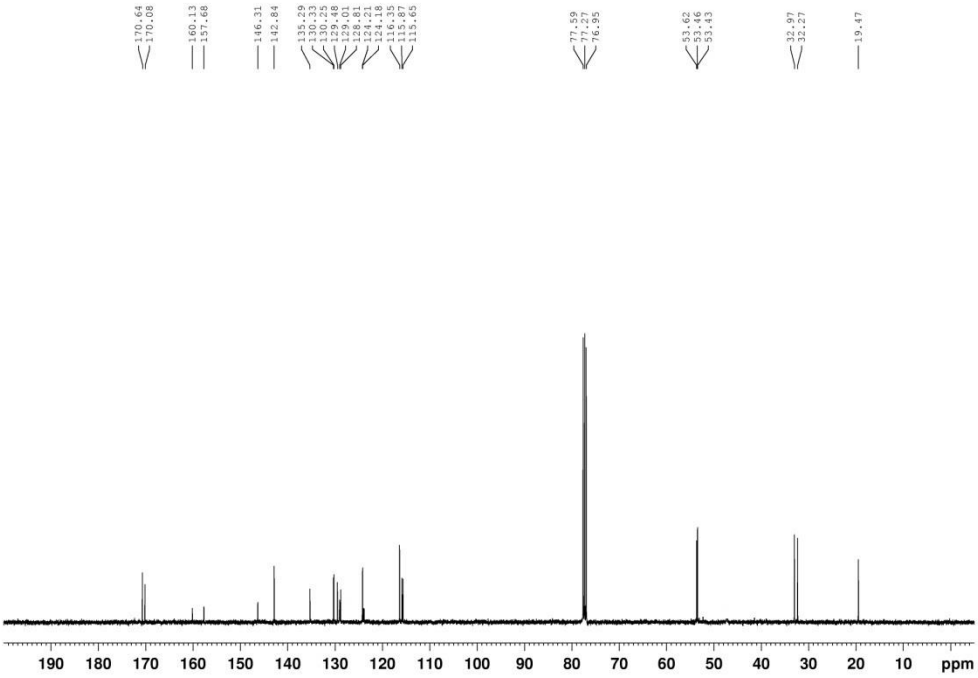
1.05
1.97
2.05
2.93
3.05
1.04
2.04
1.06
1.02
3.00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157.68
146.31
142.84
135.29
130.33
130.25
129.48
129.01
128.81
124.21
124.18
116.35
115.87
115.65
77.59
77.27
76.95
53.62
53.46
53.43
32.97
32.27
19.47
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160
150
140
130
120
110
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90
80
70
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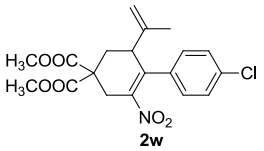
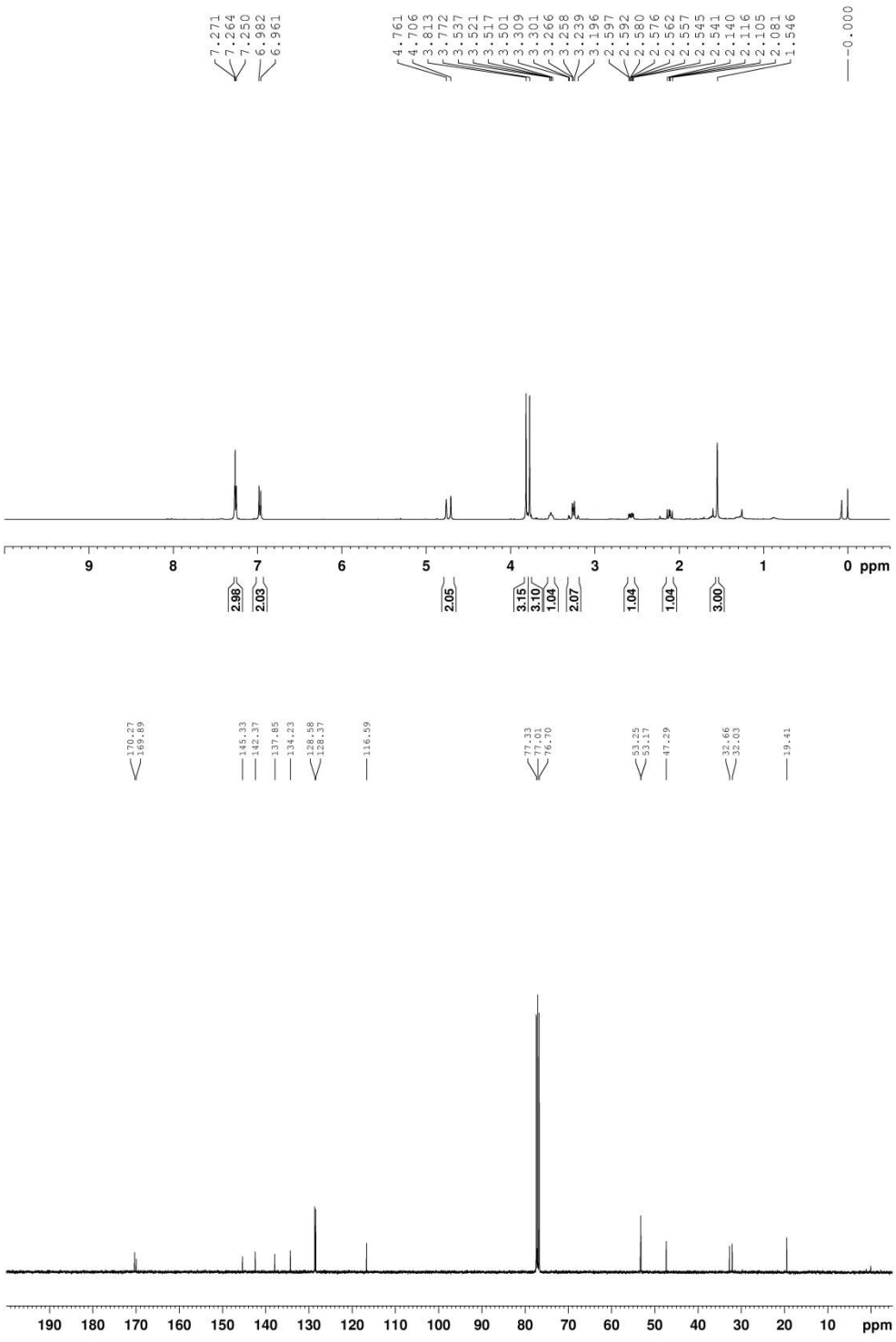
40
30
20
10
ppm


H3COOC
H3COOC
Cl
NO2

2w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7.250
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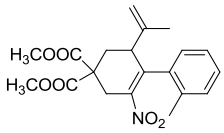
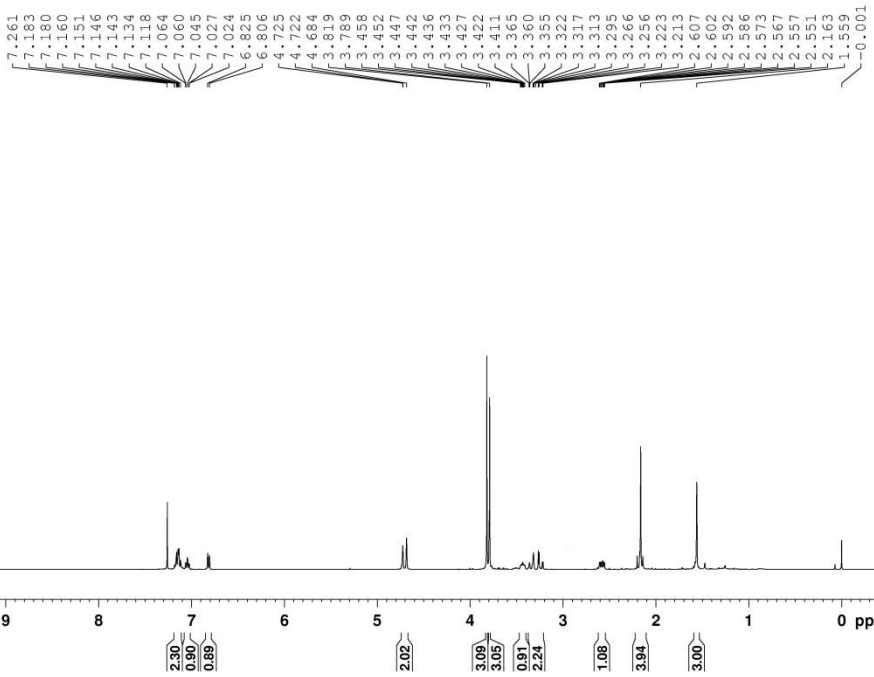
6.961
4.761
4.706
3.813
3.772
3.537
3.521
3.517
3.501
3.309
3.301
3.266
3.258
3.239
3.196
2.597
2.592
2.580
2.576
2.562
2.557
2.545
2.541
2.140
2.116
2.105
2.081
1.546
0.000
9
8
7
6
5
4
3
2
1
0 ppm
2.98
2.03
2.05
3.15
3.10
1.04
2.07
1.04
1.04
3.00
170.27
169.89
145.33
142.37
137.85
134.23
128.58
128.37
116.59
77.33
77.01
76.70
53.25
53.17
47.29
32.66
32.03
19.41
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


H3COOC
H3COOC
NO2

2x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7.183
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7.160
7.151
7.146
7.143
7.134
7.118
7.064
7.060
7.045
7.027
7.024
6.825
6.806
4.725
4.722
4.684
3.819
3.789
3.458
3.452
3.447
3.442
3.436
3.433
3.427
3.422
3.411
3.365
3.360
3.355
3.322
3.317
3.313
3.295
3.266
3.256
3.223
3.213
2.607
2.602
2.592
2.586
2.573
2.567
2.557
2.551
2.163
1.559
-0.001
9
8
7
6
5
4
3
2
1
0 ppm
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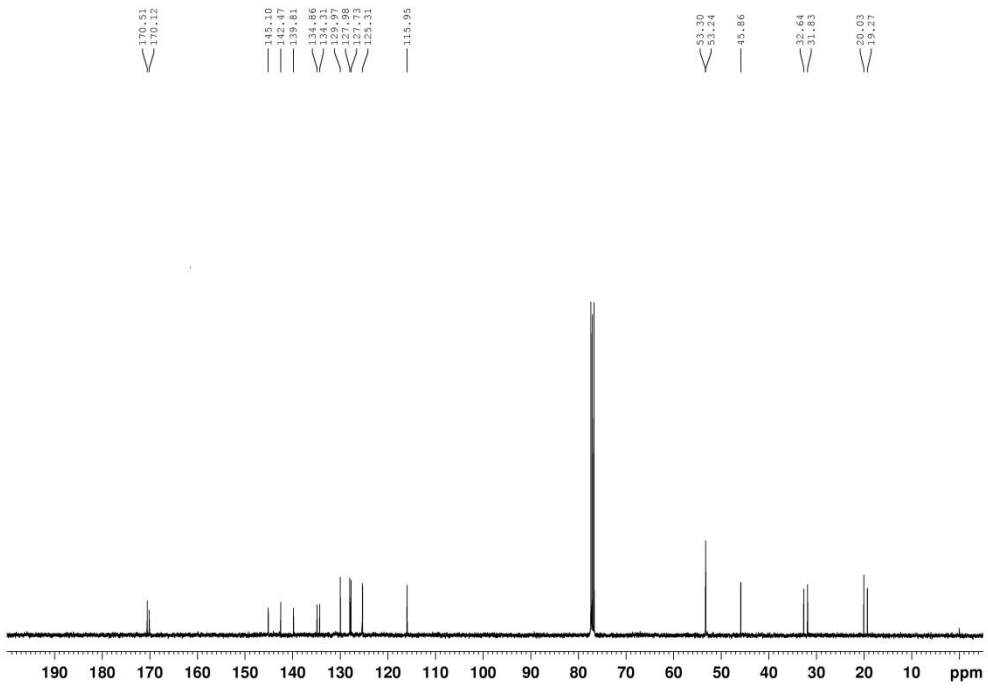
0.89
2.02
3.09
3.05
0.91
2.24
1.08
3.94
3.00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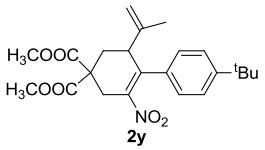
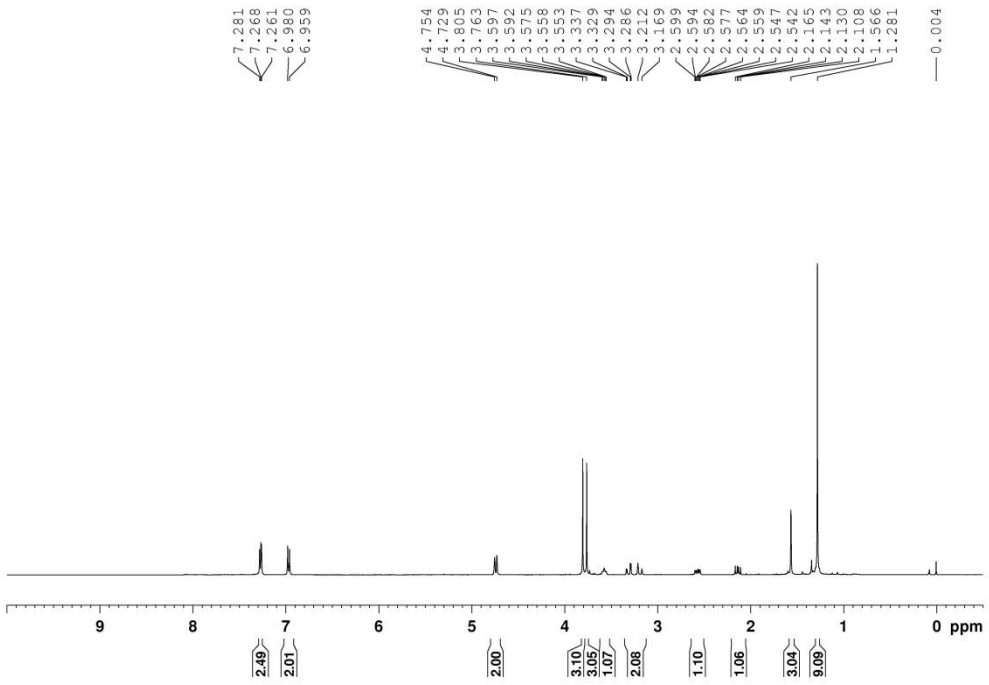
142.47
139.81
134.86
134.31
129.97
127.98
127.32
125.31
115.95
53.30
53.24
45.86
32.64
31.83
20.03
19.27
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


H3COOC
H3COOC
tBu
NO2

2y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7.261
6.980
6.959
4.754
4.729
3.805
3.763
3.597
3.592
3.575
3.558
3.553
3.337
3.329
3.294
3.286
3.212
3.169
2.599
2.594
2.582
2.577
2.564
2.559
2.547
2.542
2.165
2.143
2.130
2.108
1.566
1.281
0.004
9
8
7
6
5
4
3
2
1
0 ppm
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2.00
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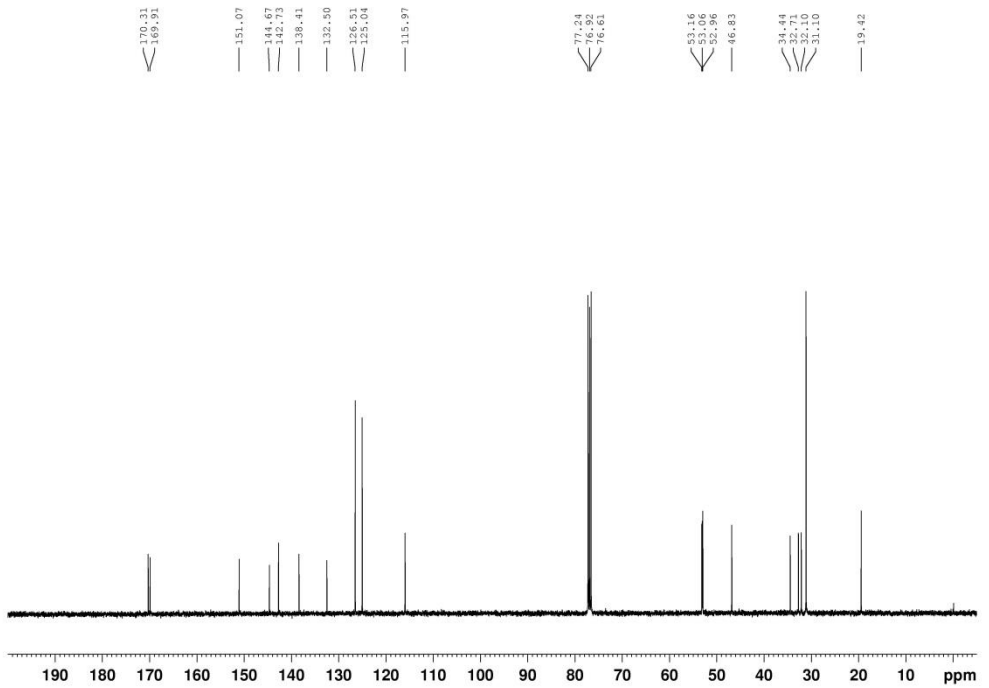
1.07
2.08
1.10
1.06
3.04
9.09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169.91
151.07
144.67
142.73
138.41
132.50
126.51
125.04
115.97
77.24
76.92
76.61
53.16
53.06
52.96
46.83
34.44
32.71
32.10
31.10
19.42
190
180
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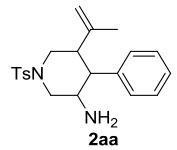
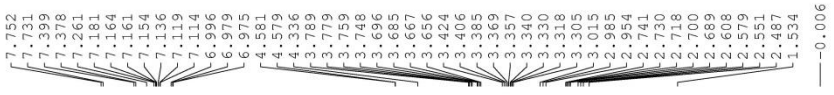
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm


TsN
NH2

2aa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7.378
7.261
7.181
7.164
7.161
7.154
7.136
7.119
7.114
6.996
6.979
6.975
4.581
4.579
4.336
3.789
3.779
3.759
3.748
3.696
3.685
3.667
3.656
3.424
3.406
3.385
3.369
3.357
3.340
3.330
3.318
3.305
3.015
2.985
2.954
2.741
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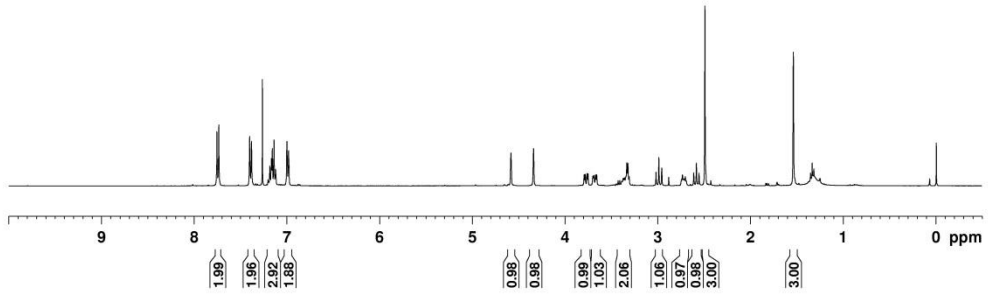
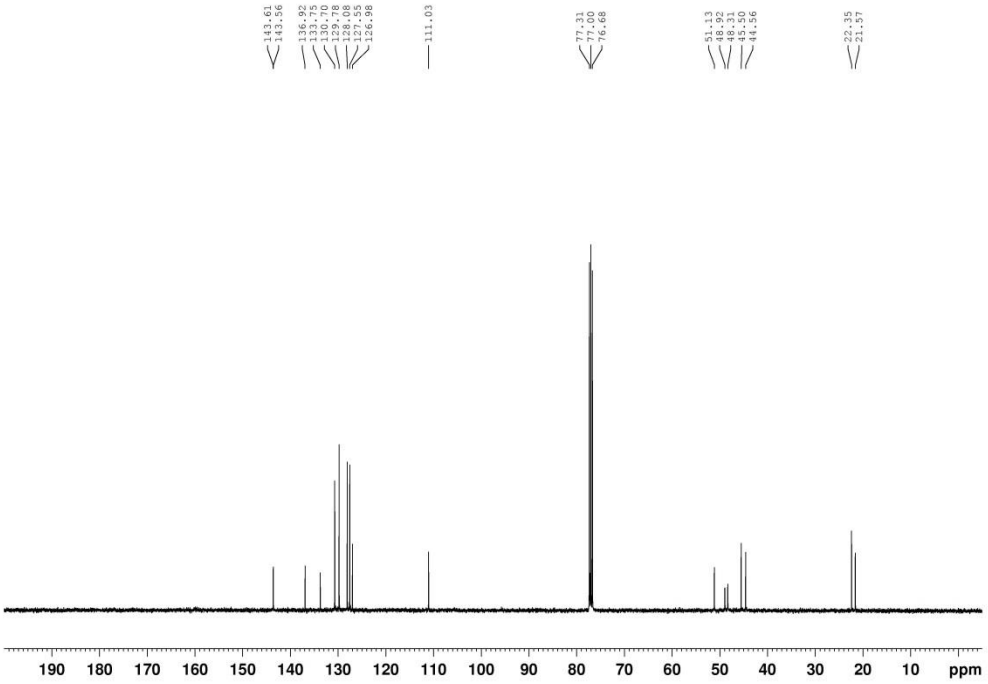
2.718
2.700
2.689
2.608
2.579
2.551
2.487
1.534
-0.006


9
8
7
6
5
4
3
2
1
0 ppm
1.99
1.96
2.92
1.88
0.98
0.98
0.99
1.03
2.06
1.06
0.97
0.98
3.00
3.00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128.08
127.55
126.98
111.03
77.31
77.00
76.68
51.13
48.92
48.31
45.50
44.56
22.35
21.57
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
ppm