

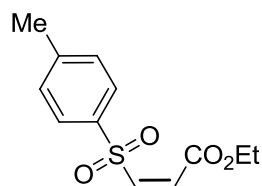
Supporting Information

Regioselective and Stereoselective Sulfonylation of Alkynylcarbonyl Compounds in Water

Wenyi Li, Guoxing Yin, Lei Huang, Yan Xiao, Zhimin Fu, Xiu Xin, Fang Liu,
Zhizhang Li and Weimin He*

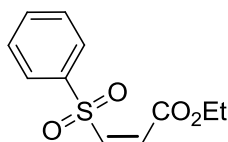
Content	Page number
Characterization Data	2
^1H and ^{13}C NMR Spectra	17

(Z)-ethyl 3-tosylacrylate (3aa)¹



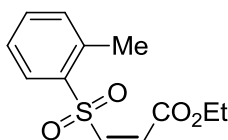
¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.0 Hz, 2H), 7.36 (d, *J* = 8.0 Hz, 2H), 6.52 (d, *J* = 11.6 Hz, 1H), 6.27 (d, *J* = 11.6 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 2.45 (s, 3H), 1.35 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.1, 145.2, 136.5, 135.4, 131.4, 130.0, 128.3, 62.2, 21.7, 14.0.

(Z)-ethyl 3-(phenylsulfonyl)acrylate (3ba)¹



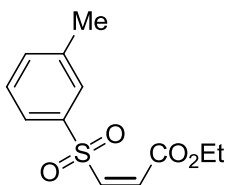
¹H NMR (400 MHz, CDCl₃) δ 8.02 (d, *J* = 8.0 Hz, 2H), 7.70 – 7.66 (m, 1H), 7.62 – 7.57 (m, 2H), 6.56 (d, *J* = 11.6 Hz, 1H), 6.53 (d, *J* = 11.2 Hz, 1H), 4.38 (q, *J* = 6.8 Hz, 2H), 1.41 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.1, 139.6, 135.3, 134.2, 132.1, 129.5, 128.4, 62.3, 14.1.

(Z)-ethyl 3-(phenylsulfonyl)acrylate (3ca)



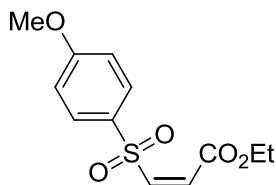
¹H NMR (400 MHz, CDCl₃) δ 8.05 (d, *J* = 7.6 Hz, 1H), 7.52 (t, *J* = 7.2 Hz, 1H), 7.38 (t, *J* = 7.6 Hz, 1H), 7.32 (d, *J* = 7.6 Hz, 1H), 6.61 (d, *J* = 12.0 Hz, 1H), 6.51 (d, *J* = 11.6 Hz, 1H), 4.28 (q, *J* = 6.8 Hz, 2H), 2.65 (s, 3H), 1.33 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.6, 138.4, 137.8, 135.6, 134.0, 132.6, 131.6, 129.7, 126.5, 62.1, 20.3, 13.9. IR: 2971, 1730, 1336, 1144, 730, 705. MS (ESI, *m/z*) 277 (M + Na⁺); HRESIMS Calcd for [C₁₂H₁₄NaO₄S]⁺ (M + Na⁺) 277.0505, found 277.0501.

(Z)-ethyl 3-(m-tolylsulfonyl)acrylate (3da)



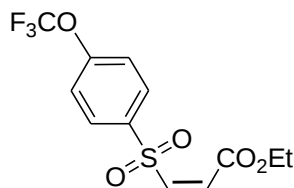
^1H NMR (400 MHz, CDCl_3) δ 7.83 – 7.77 (m, 2H), 7.46 – 7.2 (m, 2H), 6.52 (d, J = 11.2 Hz, 1H), 6.48 (d, J = 11.6 Hz, 1H), 4.35 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.38 (t, J = 7.1 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.0, 138.6, 138.3, 134.1, 133.8, 130.7, 128.2, 127.4, 124.3, 61.1, 20.3, 13.0. IR: 2978, 1723, 1344, 1142, 732, 702. MS (ESI, m/z) 277 ($\text{M} + \text{Na}^+$); HRESIMS Calcd for $[\text{C}_{12}\text{H}_{14}\text{NaO}_4\text{S}]^+$ ($\text{M} + \text{Na}^+$) 277.0505, found 277.0511.

(Z)-ethyl 3-(4-methoxyphenylsulfonyl)acrylate (3ea)¹



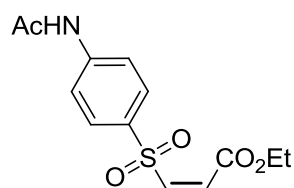
^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, J = 9.2 Hz, 2H), 6.95 (d, J = 8.8 Hz, 2H), 6.44 (d, J = 11.6 Hz, 1H), 6.37 (d, J = 11.6 Hz, 1H), 4.29 (q, J = 7.2 Hz, 2H), 3.81 (s, 3H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 164.1, 135.7, 130.9, 130.6, 114.6, 62.1, 55.7, 14.0.

(Z)-ethyl 3-(4-(trifluoromethoxy)phenylsulfonyl)acrylate (3fa)



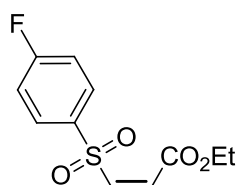
^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 6.62 (d, J = 11.6 Hz, 1H), 6.57 (d, J = 11.6 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 142.9, 135.6 (d, J = 32.6 Hz), 134.5, 133.5, 128.9, 126.4 (q, J = 3.8 Hz), 123.0 (d, J = 271.8 Hz), 62.3, 13.9. IR: 2986, 1734, 1322, 1152, 733, 701. MS (ESI, m/z) 347 ($\text{M} + \text{Na}^+$); HRESIMS Calcd for $[\text{C}_{12}\text{H}_{11}\text{NaF}_3\text{O}_5\text{S}]^+$ ($\text{M} + \text{Na}^+$) 347.0171, found 347.0177.

(Z)-ethyl 3-(4-acetamidophenylsulfonyl)acrylate (3ga)²



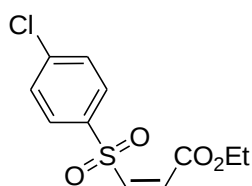
¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, *J* = 8.4 Hz, 2H), 7.70 (d, *J* = 8.8 Hz, 2H), 7.57 (s, 1H), 6.45 (d, *J* = 11.2 Hz, 1H), 6.41 (d, *J* = 11.6 Hz, 1H), 4.29 (q, *J* = 6.8 Hz, 2H), 2.15 (s, 3H), 1.31 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 168.7, 164.1, 143.3, 135.4, 133.9, 131.6, 129.7, 119.4, 62.1, 24.7, 13.9.

(Z)-ethyl 3-(4-fluorophenylsulfonyl)acrylate (3ha)¹



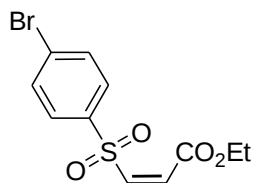
¹H NMR (400 MHz, CDCl₃) δ 8.01 – 7.93 (m, 2H), 7.18 (d, *J* = 8.0 Hz 2H), 6.45 (s, 2H), 4.30 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.1 (d, *J* = 271.2 Hz), 163.9, 135.5 (d, *J* = 3.7 Hz), 135.2, 132.2, 131.3 (d, *J* = 9.4 Hz), 116.7 (d, *J* = 22.6 Hz), 62.3, 14.0.

(Z)-ethyl 3-(4-chlorophenylsulfonyl)acrylate (3ia)²



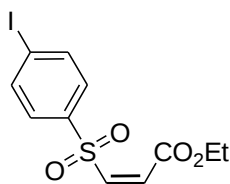
¹H NMR (400 MHz, CDCl₃) δ 7.88 (d, *J* = 8.4 Hz, 2H), 7.48 (d, *J* = 8.8 Hz 2H), 6.46 (s, 2H), 4.29 (q, *J* = 7.2 Hz, 2H), 1.32 (t, *J* = 6.8 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.9, 140.9, 138.0, 135.0, 132.5, 129.8, 129.7, 62.3, 14.0.

(Z)-ethyl 3-(4-bromophenylsulfonyl)acrylate (3ja)¹



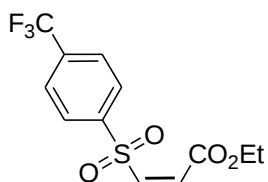
^1H NMR (400 MHz, CDCl_3) δ 7.80 (d, J = 8.4 Hz, 2H), 7.64 (d, J = 8.4 Hz, 2H), 6.46 (s, 2H), 4.29 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.3 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.8, 138.5, 135.0, 132.6, 132.5, 129.8, 129.5, 62.3, 14.0.

(Z)-ethyl 3-(4-iodophenylsulfonyl)acrylate (3ka)



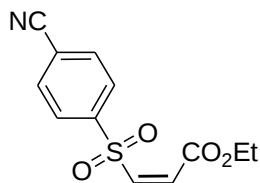
^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, J = 8.8 Hz, 2H), 7.71 (d, J = 8.4 Hz, 2H), 6.56 (d, J = 11.2 Hz, 1H), 6.52 (d, J = 11.6 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.8, 139.0, 138.6, 134.8, 132.5, 129.5, 102.2, 62.2, 13.9. MS (ESI, m/z) 367 ($\text{M} + \text{H}^+$); HRESIMS Calcd for $[\text{C}_{11}\text{H}_{12}\text{IO}_4\text{S}]^+$ ($\text{M} + \text{H}^+$) 366.9495, found 366.9494.

(Z)-ethyl 3-(4-(trifluoromethyl)phenylsulfonyl)acrylate (3la)



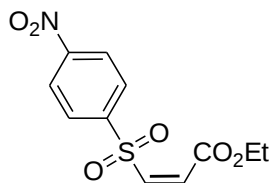
^1H NMR (400 MHz, CDCl_3) δ 8.16 (d, J = 8.4 Hz, 2H), 7.85 (d, J = 8.4 Hz, 2H), 6.63 (d, J = 11.6 Hz, 1H), 6.58 (d, J = 11.6 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.8, 142.9, 135.5 (t, J = 32.7 Hz), 134.5, 133.5, 128.8, 126.4 (d, J = 3.8 Hz), 123.0 (d, J = 271.8 Hz), 62.3, 13.9. IR: 2956, 1733, 1322, 1151, 735, 701. MS (ESI, m/z) 331 ($\text{M} + \text{Na}^+$); HRESIMS Calcd for $[\text{C}_{12}\text{H}_{11}\text{NaF}_3\text{O}_4\text{S}]^+$ ($\text{M} + \text{Na}^+$) 331.0222, found 331.0228.

(Z)-ethyl 3-(4-cyanophenylsulfonyl)acrylate (3ma)



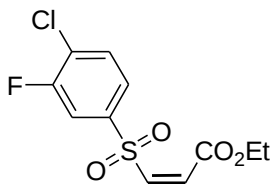
^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, J = 8.8 Hz, 2H), 7.80 (d, J = 8.8 Hz, 2H), 6.56 (d, J = 11.2 Hz, 1H), 6.49 (d, J = 11.6 Hz, 1H), 4.30 (q, J = 7.2 Hz, 2H), 1.31 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.5, 143.6, 134.5, 134.0, 133.0, 128.9, 117.7, 117.0, 62.4, 13.9. IR: 2987, 1735, 1326, 1150, 740, 702. MS (ESI, m/z) 288 ($\text{M} + \text{Na}^+$); HRESIMS Calcd for $[\text{C}_{12}\text{H}_{11}\text{NaNO}_4\text{S}]^+$ ($\text{M} + \text{Na}^+$) 288.0301, found 288.0309.

(Z)-ethyl 3-(4-nitrophenylsulfonyl)acrylate (3na)³



^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, J = 8.8 Hz, 2H), 8.16 (d, J = 8.8 Hz, 2H), 6.57 (d, J = 11.6 Hz, 1H), 6.51 (d, J = 11.2 Hz, 1H), 4.31 (q, J = 7.2 Hz, 2H), 1.32 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.4, 151.0, 145.2, 134.5, 134.3, 129.8, 124.4, 62.5, 13.8. IR: 2983, 1734, 1325, 1153, 742, 704.

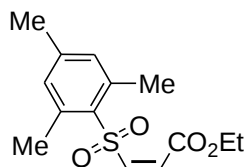
(Z)-ethyl 3-(4-chloro-3-fluorophenylsulfonyl)acrylate (3oa)



^1H NMR (400 MHz, CDCl_3) δ 8.12 – 8.10 (m, 1H), 7.96 – 7.92 (m, 1H), 7.35 (t, J = 8.4 Hz, 1H), 6.60 (d, J = 11.6 Hz, 1H), 6.55 (d, J = 11.6 Hz, 1H), 4.37 (q, J = 7.2 Hz, 2H), 1.40 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 161.6 (d, J = 1032.4 Hz), 136.5 (d, J = 15.2 Hz), 134.7, 133.2, 131.4, 129.1 (d, J = 36.4 Hz), 122.8 (d, J = 72.8 Hz), 117.7 (d, J = 91.2 Hz), 62.3, 14.0. δ IR: 2985, 1733, 1322, 1152, 740,

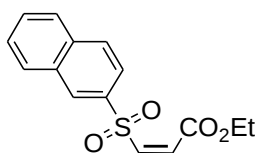
705. MS (ESI, m/z) 315 (M + Na⁺); HRESIMS Calcd for [C₁₁H₁₀NaClFO₄S]⁺ (M + Na⁺) 314.9865, found 314.9866.

(Z)-ethyl 3-(mesitylsulfonyl)acrylate (3pa)



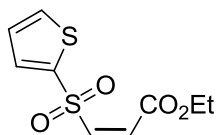
¹H NMR (400 MHz, CDCl₃) δ 6.89 (s, 2H), 6.59 (d, *J* = 12.0 Hz, 1H), 6.35 (d, *J* = 12.0 Hz, 1H), 4.14 (q, *J* = 7.2 Hz, 2H), 2.57 (s, 6H), 2.23 (s, 3H), 1.22 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 143.9, 140.4, 138.4, 133.8, 132.3, 129.7, 62.1, 22.8, 21.2, 14.1. IR: 2925, 1724, 1305, 1146, 732, 704. MS (ESI, m/z) 305 (M + Na⁺); HRESIMS Calcd for [C₁₄H₁₈NaO₄S]⁺ (M + Na⁺) 305.0818, found 305.0825.

(Z)-ethyl 3-(naphthalen-2-ylsulfonyl)acrylate (3qa)¹



¹H NMR (400 MHz, CDCl₃) δ 8.50 (s, 1H), 7.95 – 7.85 (m, 4H), 7.63 – 7.55 (m, 2H), 6.52 (d, *J* = 11.6 Hz, 1H), 6.45 (d, *J* = 11.6 Hz, 1H), 4.32 (q, *J* = 7.2 Hz, 2H), 1.34 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 164.0, 136.3, 135.5, 135.2, 132.2, 131.9, 130.2, 129.7, 129.6, 129.5, 128.0, 127.7, 122.7, 62.2, 13.9.

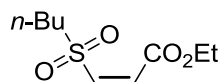
(Z)-ethyl 3-(thiophen-2-ylsulfonyl)acrylate (3ra)



¹H NMR (400 MHz, CDCl₃) δ 7.82 (d, *J* = 3.6 Hz, 1H), 7.74 (d, *J* = 5.6 Hz, 1H), 7.17 (t, *J* = 4.4 Hz, 1H), 6.64 (d, *J* = 11.6 Hz, 1H), 6.48 (d, *J* = 11.2 Hz, 1H), 4.37 (q, *J* = 7.2 Hz, 2H), 1.39 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.8, 140.7,

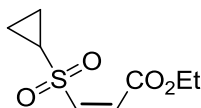
135.9, 135.2, 135.2, 131.6, 128.3, 62.4, 14.1. IR: 2924, 1726, 1319, 1144, 734, 701. MS (ESI, m/z) 269 (M + Na⁺); HRESIMS Calcd for [C₉H₁₀NaO₄S₂]⁺ (M + Na⁺) 268.9913, found 268.9916.

(Z)-ethyl 3-(butylsulfonyl)acrylate (3sa)



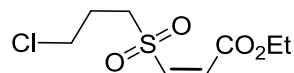
¹H NMR (400 MHz, CDCl₃) δ 6.59 (d, *J* = 11.2 Hz, 1H), 6.54 (d, *J* = 11.6 Hz, 1H), 4.26 (q, *J* = 7.6 Hz, 2H), 3.18 (t, *J* = 8.0 Hz, 2H), 1.81 – 1.73 (m, 2H), 1.48 – 1.39 (m, 2H), 1.30 (t, *J* = 7.2 Hz, 3H), 0.92 (t, *J* = 7.2 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 163.4, 135.9, 134.1, 62.1, 55.1, 23.8, 21.6, 13.8, 13.4. IR: 2972, 1647, 1304, 1153, 739, 702. MS (ESI, m/z) 243 (M + Na⁺); HRESIMS Calcd for [C₉H₁₆NaO₄S]⁺ (M + Na⁺) 243.0662, found 243.0672.

(Z)-ethyl 3-(cyclopropylsulfonyl)acrylate (3ta)



¹H NMR (400 MHz, CDCl₃) δ 6.54(d, *J* = 11.6 Hz, 1H), 6.49(d, *J* = 11.6 Hz, 1H), 4.24(q, *J* = 7.2 Hz, 2H), 2.70 – 2.62 (m, 1H), 1.32 – 1.18 (m, 5H), 1.04 – 0.97 (m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 163.7, 135.9, 132.6, 62.2, 31.4, 13.9, 5.3. IR: 2924, 1726, 1319, 1144, 736, 701. MS (ESI, m/z) 227 (M + Na⁺); HRESIMS Calcd for [C₈H₁₂NaO₄S]⁺ (M + Na⁺) 227.0349, found 227.0357.

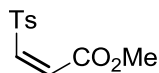
(Z)-ethyl 3-(3-chloropropylsulfonyl)acrylate (3ua)



¹H NMR (400 MHz, CDCl₃) δ 6.65(d, *J* = 12.0 Hz, 1H), 6.59(d, *J* = 11.6 Hz, 1H), 4.32(q, *J* = 7.2 Hz, 2H), 3.69(t, *J* = 6.4 Hz, 2H), 3.43(t, *J* = 7.6 Hz, 2H), 1.35(t, *J* = 7.2 Hz, 3H), 1.31 – 1.24(m, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 163.3, 135.7, 134.8, 62.4, 52.7, 42.7, 25.2, 13.9. IR: 2964, 1733, 1316, 112

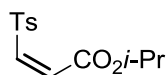
9, 735, 702. MS (ESI, m/z) 263 ($M + Na^+$); HRESIMS Calcd for $[C_8H_{13}NaClO_4S]^+$ ($M + Na^+$) 263.0115, found 263.0123.

(Z)-methyl 3-tosylacrylate (3ab)²



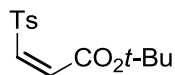
1H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, $J = 8.0$ Hz, 2H), 7.35 (d, $J = 8.0$ Hz, 2H), 6.53 (d, $J = 11.6$ Hz, 1H), 6.47 (d, $J = 11.6$ Hz, 1H), 3.88 (d, $J = 1.7$ Hz, 3H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 145.4, 136.5, 136.0, 131.1, 130.1, 128.4, 52.9, 21.8.

(Z)-isopropyl 3-tosylacrylate (3ac)



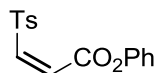
1H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, $J = 8.4$ Hz, 2H), 7.36 (d, $J = 8.0$ Hz, 2H), 6.48 (d, $J = 11.6$ Hz, 1H), 6.44 (d, $J = 11.6$ Hz, 1H), 5.28 – 5.19 (m, 1H), 2.45 (s, 3H), 1.38 (s, 3H), 1.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.6, 145.1, 136.6, 134.9, 131.8, 129.9, 128.3, 70.3, 21.7, 21.6. IR: 2924, 1722, 1308, 1142, 738, 706. MS (ESI, m/z) 291 ($M + Na^+$); HRESIMS Calcd for $[C_{13}H_{16}NaO_4S]^+$ ($M + Na^+$) 291.0662, found 291.0667.

(Z)-tert-butyl 3-tosylacrylate (3ad)



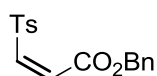
1H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, $J = 8.0$ Hz, 2H), 7.28 (d, $J = 8.4$ Hz, 2H), 6.34 (s, 2H), 2.37 (s, 3H), 1.52 (s, 9H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 145.0, 136.7, 133.6, 132.5, 129.9, 128.1, 83.9, 28.0, 21.83. IR: 2925, 1724, 1307, 1147, 731, 701. MS (ESI, m/z) 305 ($M + Na^+$); HRESIMS Calcd for $[C_{14}H_{18}NaO_4S]^+$ ($M + Na^+$) 305.0818, found 305.0825.

(Z)-phenyl 3-tosylacrylate (3ae)



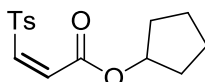
^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 8.4 Hz, 2H), 7.46-7.42 (m, 2H), 7.38 – 7.28 (m, 5H), 6.68 (d, J = 11.6 Hz, 1H), 6.65 (d, J = 11.6 Hz, 1H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.0, 150.2, 145.6, 136.4, 130.7, 130.2, 129.8, 129.6, 128.6, 126.6, 121.7, 21.9. IR: 2923, 1731, 1307, 1141, 733, 710. MS (ESI, m/z) 325 ($\text{M} + \text{Na}^+$); HRESIMS Calcd for $[\text{C}_{16}\text{H}_{14}\text{NaO}_4\text{S}]^+$ ($\text{M} + \text{Na}^+$) 325.0505, found 325.0511.

(Z)-benzyl 3-tosylacrylate (3af)



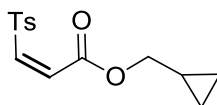
^1H NMR (400 MHz, CDCl_3) δ 7.74 (d, J = 8.4 Hz, 2H), 7.39 – 7.28 (m, 5H), 7.20 (d, J = 6.8 Hz, 2H), 6.47 (d, J = 11.2 Hz, 1H), 6.42 (d, J = 11.6 Hz, 1H), 5.25 (s, 2H), 2.36 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.9, 145.2, 136.4, 135.9, 134.8, 131.0, 129.9, 128.9, 128.7, 128.6, 128.3, 68.0, 21.7. IR: 2920, 1732, 1305, 1143, 734, 713. MS (ESI, m/z) 362 ($\text{M} + \text{Na}^+$); HRESIMS Calcd for $[\text{C}_{17}\text{H}_{16}\text{NaO}_4\text{S}]^+$ ($\text{M} + \text{Na}^+$) 362.0662, found 362.0668.

(Z)-cyclopentyl 3-tosylacrylate (3ag)



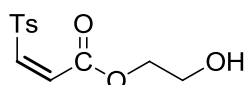
^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.0 Hz, 2H), 7.35 (d, J = 8.4 Hz, 2H), 6.47 (d, J = 11.6 Hz, 1H), 6.44 (d, J = 11.2 Hz, 1H), 5.40 – 5.35 (m, 1H), 2.45 (s, 3H), 1.95 – 1.90 (m, 4H), 1.82 – 1.77 (m, 2H), 1.68 – 1.61 (m, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.9, 145.1, 136.6, 134.9, 131.8, 129.9, 128.3, 79.6, 32.4, 23.7, 21.7. IR: 2973, 1742, 1319, 1149, 738, 702. MS (ESI, m/z) 317 ($\text{M} + \text{Na}^+$); HRESIMS Calcd for $[\text{C}_{15}\text{H}_{18}\text{NaO}_4\text{S}]^+$ ($\text{M} + \text{Na}^+$) 317.0818, found 317.0820.

(Z)-cyclopropylmethyl 3-tosylacrylate (3ah)



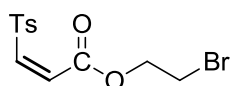
^1H NMR (400 MHz, CDCl_3) δ 7.90 (d, J = 8.0 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 6.52 (d, J = 11.2 Hz, 1H), 6.49 (d, J = 11.6 Hz, 1H), 4.13 (d, J = 7.6 Hz, 2H), 2.45 (s, 3H), 1.30 – 1.20 (m, 1H), 0.65 (q, J = 5.6 Hz, 2H), 0.37 (q, J = 4.8 Hz, 2H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 145.2, 136.6, 135.4, 131.4, 139.9, 128.4, 71.1, 21.7, 9.52, 3.53. IR: 2924, 1726, 1319, 1144, 701. MS (ESI, m/z) 303 ($\text{M} + \text{Na}^+$); HRESIMS Calcd for $[\text{C}_{14}\text{H}_{16}\text{NaO}_4\text{S}]^+$ ($\text{M} + \text{Na}^+$) 303.0662, found 303.0670.

(Z)-2-hydroxyethyl 3-tosylacrylate (3ai)



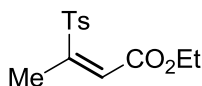
^1H NMR (400 MHz, CDCl_3) δ 7.86 (d, J = 8.4 Hz, 2H), 7.38 (d, J = 8.0 Hz, 2H), 6.54 (d, J = 11.6 Hz, 1H), 6.50 (d, J = 11.6 Hz, 1H), 4.47 (t, J = 4.4 Hz, 2H), 3.95 (t, J = 4.0 Hz, 2H), 2.87 (s, 1H), 2.46 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.2, 145.6, 136.0, 135.3, 130.8, 130.1, 128.2, 68.1, 60.7, 21.7. IR: 2971, 1749, 1312, 1145, 735, 706. MS (ESI, m/z) 293 ($\text{M} + \text{Na}^+$); HRESIMS Calcd for $[\text{C}_{12}\text{H}_{14}\text{NaO}_5\text{S}]^+$ ($\text{M} + \text{Na}^+$) 293.0454, found 293.0458.

(Z)-2-bromoethyl 3-tosylacrylate (3aj)



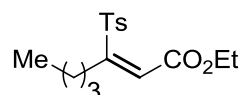
^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, J = 8.4 Hz, 2H), 7.37 (d, J = 8.0 Hz, 2H), 6.55 (d, J = 11.6 Hz, 1H), 6.50 (d, J = 11.6 Hz, 1H), 4.61 (t, J = 6.4 Hz, 2H), 3.63 (t, J = 6.4 Hz, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 163.7, 145.4, 136.2, 135.9, 130.4, 130.1, 128.3, 65.1, 27.9, 21.7. IR: 2971, 1740, 1312, 1147, 738, 704. MS (ESI, m/z) 355 ($\text{M} + \text{Na}^+$); HRESIMS Calcd for $[\text{C}_{12}\text{H}_{13}\text{NaBrO}_4\text{S}]^+$ ($\text{M} + \text{Na}^+$) 354.9610, found 354.9618.

(Z)-ethyl 3-tosylbut-2-enoate (3al)



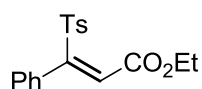
^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, J = 8.4 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 6.26 (s, 1H), 4.35 (q, J = 7.2 Hz, 2H), 2.44 (s, 3H), 1.96 (s, 3H), 1.38 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.1, 145.1, 142.4, 135.3, 129.9, 128.8, 128.6, 61.9, 21.7, 17.9, 14.0. IR: 2977, 1720, 1344, 1145, 733, 707. MS (ESI, m/z) 291 ($\text{M} + \text{Na}^+$); HRESIMS Calcd for $[\text{C}_{13}\text{H}_{16}\text{NaO}_4\text{S}]^+$ ($\text{M} + \text{Na}^+$) 291.0662, found 291.0665.

(Z)-ethyl 3-tosylhept-2-enoate (3am)



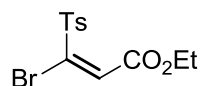
^1H NMR (400 MHz, CDCl_3) δ 7.87 (d, J = 7.6 Hz, 2H), 7.35 (d, J = 8.0 Hz, 2H), 6.25 (s, 1H), 3.89 (s, 3H), 2.45 (s, 3H), 2.24 (t, J = 7.6 Hz, 2H), 1.45-1.38 (m, 2H), 1.25-1.21 (m, 4H), 0.83 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 166.3, 147.1, 145.0, 135.7, 129.9, 128.5, 127.4, 52.7, 30.9, 30.2, 27.3, 22.2, 21.7, 13.8. IR: 2978, 1721, 1343, 1143, 735, 709. MS (ESI, m/z) 305 ($\text{M} + \text{Na}^+$); HRESIMS Calcd for $[\text{C}_{16}\text{H}_{22}\text{NaO}_4\text{S}]^+$ ($\text{M} + \text{Na}^+$) 305.0818, found 305.0810.

(Z)-ethyl 3-phenyl-3-tosylacrylate (3an)⁴



^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, J = 8.4 Hz, 2H), 7.36-7.31 (m, 1H), 7.27-7.26 (m, 4H), 7.20 (d, J = 8.0 Hz, 2H), 6.39 (s, 1H), 4.42 (q, J = 7.2 Hz, 2H), 2.37 (s, 3H), 1.44 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 165.1, 146.2, 144.8, 135.5, 132.3, 130.4, 129.6, 129.6, 129.5, 128.7, 128.2, 62.1, 21.6, 14.0.

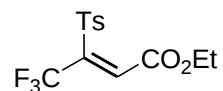
(E)-ethyl 3-bromo-3-tosylacrylate (3ao)



^1H NMR (400 MHz, CDCl_3) δ 7.76 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 6.72 (s, 1H), 4.35 (q, J = 7.2 Hz, 2H), 2.38 (s, 3H), 1.35 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 161.6, 144.6, 135.1, 132.5, 129.2, 127.2, 124.7, 62.5, 20.7, 12.8. IR: 2973, 1720, 1343, 1146, 738, 702. MS (ESI,

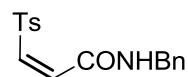
m/z) 355 ($M + Na^+$); HRESIMS Calcd for $[C_{12}H_{13}NaBrO_4S]^+$ ($M + Na^+$) 354.9610, found 354.9613.

(Z)-ethyl 4,4,4-trifluoro-3-tosylbut-2-enoate (3ap)



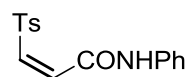
1H NMR (500 MHz, $CDCl_3$) δ 7.93 (d, $J = 8.0$ Hz, 2H), 7.38 (d, $J = 7.5$ Hz, 2H), 7.05 (s, 1H), 4.45 (q, $J = 7.5$ Hz, 2H), 2.47 (s, 3H), 1.43 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 162.8, 146.1, 136.1, 135.4, 135.3, 129.9, 128.9, 119.1, 62.8, 21.7, 13.8. IR: 2973, 1722, 1345, 1143, 734, 705. MS (ESI, m/z) 345 ($M + Na^+$); HRESIMS Calcd for $[C_{13}H_{13}F_3NaO_4S]^+$ ($M + Na^+$) 345.0379, found 345.0381.

(Z)-N-benzyl-3-tosylacrylamide (3ar)



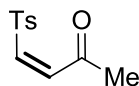
1H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, $J = 8.4$ Hz, 2H), 7.33 – 7.24 (m, 7H), 6.80 (s, 1H), 6.46 (d, $J = 12.0$ Hz, 1H), 6.43 (d, $J = 12.0$ Hz, 1H), 4.49 (d, $J = 5.6$ Hz, 2H), 2.37 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.0, 145.4, 137.1, 136.4, 134.8, 130.1, 128.9, 128.8, 128.2, 128.0, 127.8, 44.13, 21.72. IR: 2978, 1721, 1343, 1143, 709. MS (ESI, m/z) 338 ($M + Na^+$); HRESIMS Calcd for $[C_{17}H_{17}NaNO_3S]^+$ ($M + Na^+$) 338.0821, found 338.0822.

(Z)-N-phenyl-3-tosylacrylamide (3as)



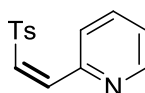
1H NMR (400 MHz, $(CD_3)SO$) δ 10.38 (s, 1H), 7.83 (d, $J = 8.0$ Hz, 2H), 7.60 (d, $J = 8.0$ Hz, 2H), 7.47 (d, $J = 8.0$ Hz, 2H), 7.34 (t, $J = 8.0$ Hz, 2H), 7.09 (t, $J = 8.0$ Hz, 1H), 7.01 (d, $J = 8.0$ Hz, 1H), 6.88 (d, $J = 8.0$ Hz, 1H), 2.40 (s, 3H). ^{13}C NMR (100 MHz, $(CD_3)SO$) δ 162.5, 145.1, 139.0, 137.4, 136.7, 133.5, 130.3, 129.2, 128.3, 124.2, 120.1, 21.6. IR: 2976, 1724, 1344, 1141, 732, 705. MS (ESI, m/z) 324 ($M + Na^+$); HRESIMS Calcd for $[C_{16}H_{15}NaNO_3S]^+$ ($M + Na^+$) 324.0665, found 324.0667.

(Z)-4-tosylbut-3-en-2-one (3at)⁵



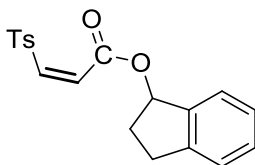
¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.0 Hz, 2H), 7.05 (d, *J* = 15.2 Hz, 1H), 6.90 (d, *J* = 15.6 Hz, 1H), 2.40 (s, 3H), 2.28 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 196.7, 141.3, 137.9, 135.6, 131.8, 130.3, 128.3, 29.0, 26.8.

(Z)-2-(2-tosylvinyl)pyridine (3au)



¹H NMR (400 MHz, CDCl₃) δ 8.59 (d, *J* = 4.8 Hz, 1H), 7.83 (d, *J* = 8.0 Hz, 2H), 7.73 (t, *J* = 7.6 Hz, 1H), 7.62 (d, *J* = 7.6 Hz, 1H), 7.45 – 7.39 (m, 2H), 7.33 (d, *J* = 8.0 Hz, 2H), 7.30 – 7.26 (m, 1H), 2.43 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 151.1, 150.3, 144.6, 139.9, 137.3, 137.0, 132.2, 129.9, 127.9, 125.4, 124.9, 21.6. IR: 2973, 1723, 1343, 1146, 735, 703. MS (ESI, *m/z*) 282 (*M* + Na⁺); HRESIMS Calcd for [C₁₄H₁₃NaNO₂S]⁺ (*M* + Na⁺) 282.0559, found 282.0563.

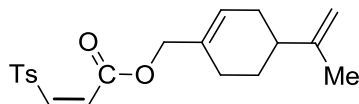
(Z)-2,3-dihydro-1H-inden-1-yl 3-tosylacrylate (4aa)



¹H NMR (400 MHz, CDCl₃) δ 7.80 (d, *J* = 8.4 Hz, 2H), 7.54 (d, *J* = 7.6 Hz, 1H), 7.34-7.33 (m, 2H), 7.29-7.27 (m, 3H), 6.49 (d, *J* = 11.6 Hz, 1H), 6.46 (d, *J* = 11.6 Hz, 1H), 6.42-6.40 (m, 1H), 3.22-3.14 (m, 1H), 3.22-3.14 (m, 1H), 2.97-2.90 (m, 1H), 2.61-2.52 (m, 1H), 2.43 (s, 3H), 2.42-2.34 (m, 1H). ¹³C NMR (100 MHz, CDCl₃) δ 164.1, 145.3, 145.1, 140.2, 136.8, 135.5, 131.6, 130.1, 129.5, 128.5, 127.0, 126.3, 125.0, 80.8, 32.1, 30.5, 21.8. IR: 2975, 1726, 1341, 1142, 739, 701. MS (ESI, *m/z*)

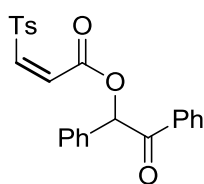
365 (M + Na⁺); HRESIMS Calcd for [C₁₉H₁₈NaO₄S]⁺ (M + Na⁺) 365.0818, found 365.0820.

(Z)-(4-(prop-1-en-2-yl)cyclohex-1-enyl)methyl 3-tosylacrylate (4ab)



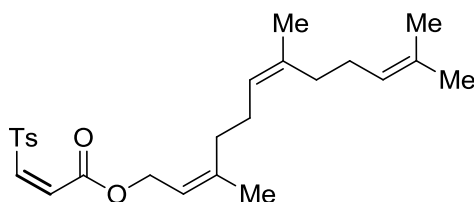
¹H NMR (400 MHz, CDCl₃) δ 7.87 (d, *J* = 8.4 Hz, 2H), 7.35 (d, *J* = 8 Hz, 2H), 6.54 (d, *J* = 11.6 Hz, 1H), 6.49 (d, *J* = 11.6 Hz, 1H), 5.88 (s, 1H), 4.74-4.73 (m, 2H), 4.67 (s, 2H), 2.45 (s, 3H), 2.22-2.16 (m, 4H), 2.04-1.97 (m, 1H), 1.90-1.84 (m, 1H), 1.75 (s, 3H), 1.56-1.46 (m, 1H), 1.26 (s, 2H). ¹³C NMR (100 MHz, CDCl₃) δ 164.2, 149.6, 145.3, 136.5, 135.5, 132.0, 131.4, 130.0, 128.4, 127.6, 108.9, 70.3, 40.8, 30.6, 27.4, 26.5, 21.8, 20.9. IR: 2922, 1733, 1320, 1147, 731, 702. MS (ESI, *m/z*) 383 (M + Na⁺); HRESIMS Calcd for [C₂₀H₂₄NaO₄S]⁺ (M + Na⁺) 383.1288, found 383.1389.

(Z)-2-oxo-1,2-diphenylethyl 3-tosylacrylate (4ac)



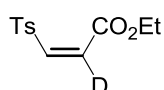
¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, *J* = 8.0 Hz, 2H), 7.61 (d, *J* = 8.0 Hz, 2H), 7.50–7.44 (m, 3H), 7.37–7.30 (m, 5H), 7.09 (d, *J* = 8.0 Hz, 2H), 7.03 (s, 1H), 6.57 (d, *J* = 11.6 Hz, 1H), 7.61 (d, *J* = 11.6 Hz, 1H), 2.32 (s, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 192.9, 163.3, 145.6, 136.1, 134.3, 133.6, 132.8, 130.5, 129.9, 129.7, 129.2, 129.2, 128.9, 128.8, 128.7, 128.3, 79.0, 21.7. IR: 2915, 1603, 1264, 1155, 741, 703. MS (ESI, *m/z*) 443 (M + Na⁺); HRESIMS Calcd for [C₂₄H₂₀NaO₅S]⁺ (M + Na⁺) 443.0924, found 443.0934.

(Z)-((2Z,6Z)-3,7,11-trimethyldodeca-2,6,10-trienyl) 3-tosylacrylate (4ad)



^1H NMR (400 MHz, CDCl_3) δ 7.88 (d, $J = 8.0$ Hz, 2H), 7.34 (d, $J = 8.0$ Hz, 2H), 6.51 (d, $J = 11.2$ Hz, 1H), 6.46 (d, $J = 11.6$ Hz, 1H), 5.45 (t, $J = 7.2$ Hz, 1H), 5.13-5.07 (m, 2H), 4.83-4.79 (m, 2H), 2.45 (s, 3H), 2.17 – 1.95 (m, 8H), 1.76 (s, 3H), 1.68 (s, 6H), 1.57 (s, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.1, 145.2, 143.8, 136.5, 135.7, 135.5, 131.4, 130.0, 128.4, 124.4, 124.3, 123.6, 117.3, 62.9, 39.7, 39.6, 26.6, 26.2, 26.1, 23.3, 17.7, 16.6, 16.0. IR: 2916, 1607, 1265, 1157, 738, 709. MS (ESI, m/z) 453 ($\text{M} + \text{Na}^+$); HRESIMS Calcd for $[\text{C}_{25}\text{H}_{34}\text{NaO}_4\text{S}]^+$ ($\text{M} + \text{Na}^+$) 453.2070, found 453.2077.

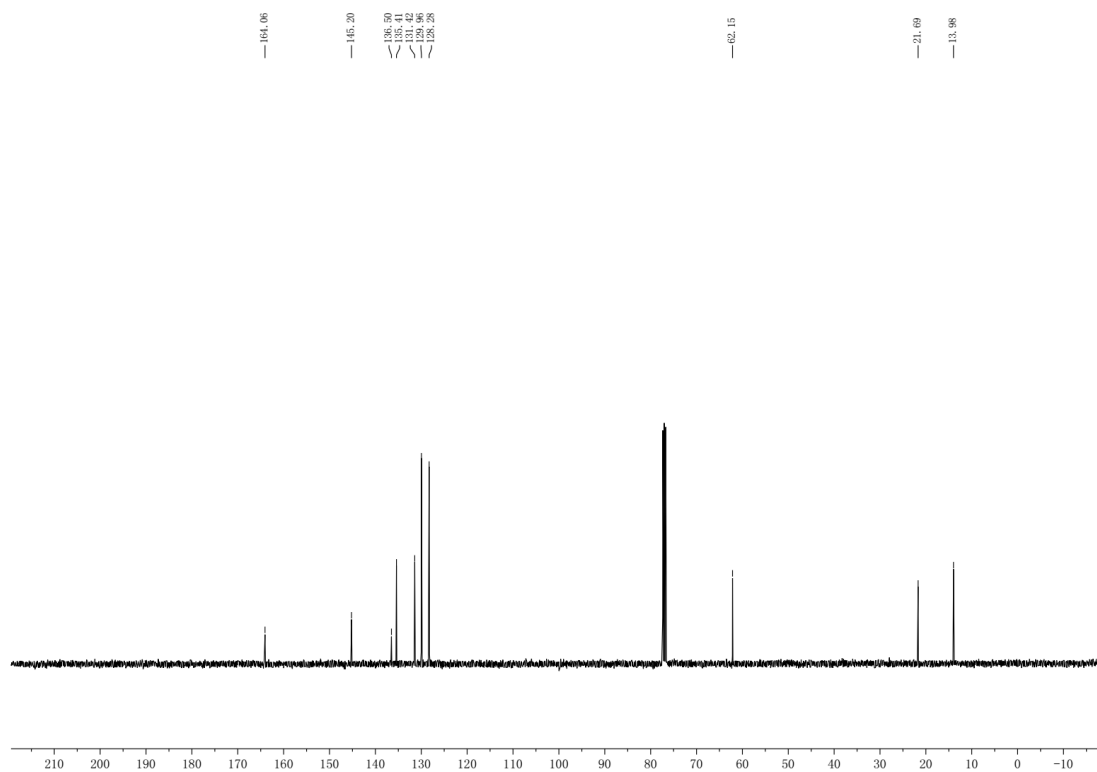
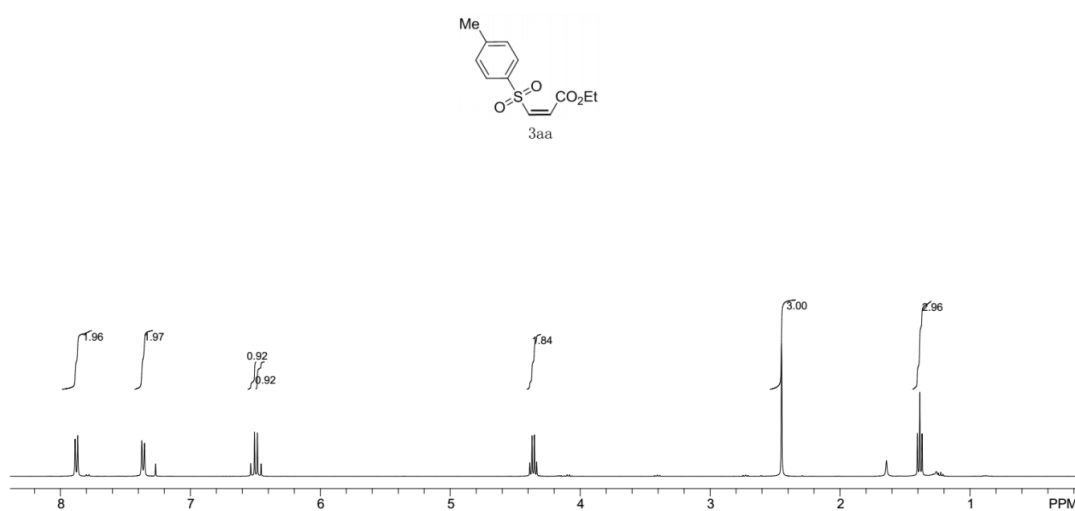
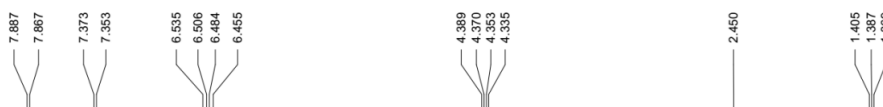
Deuterated -(Z)-ethyl 3-tosylacrylate

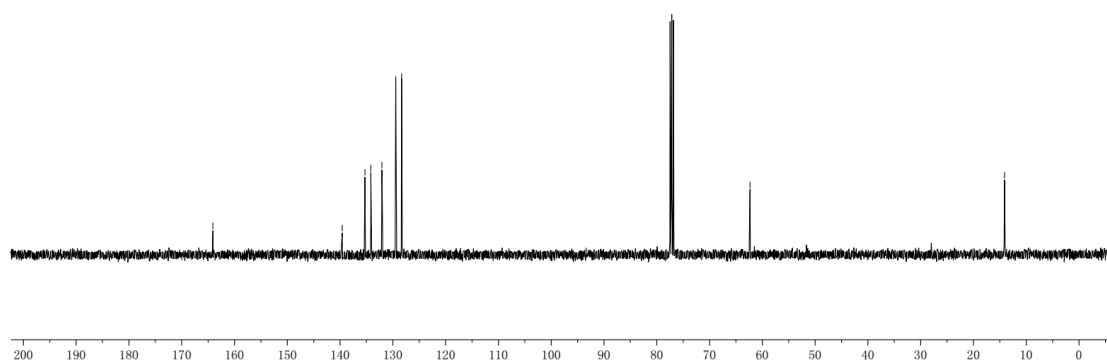
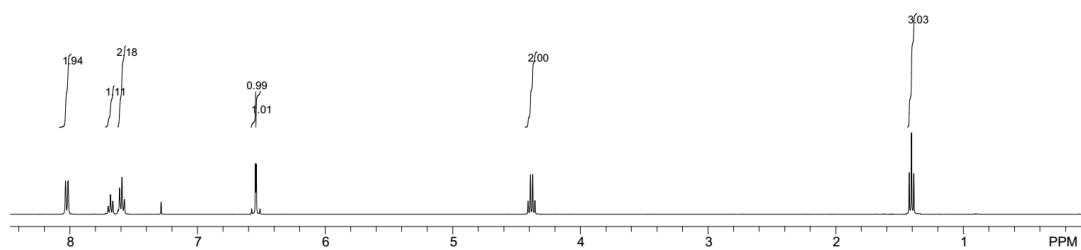
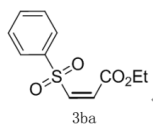
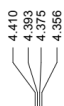
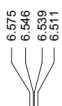
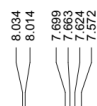


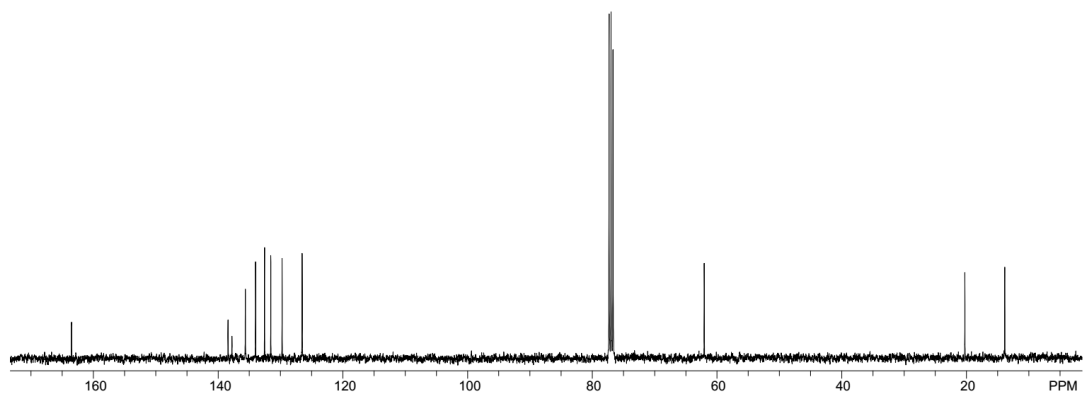
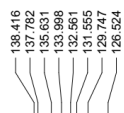
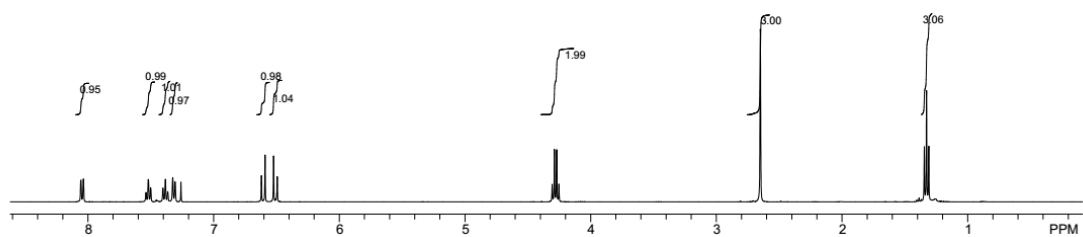
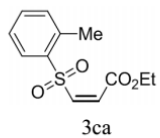
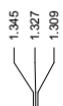
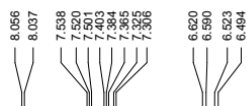
^1H NMR (400 MHz, CDCl_3) δ 7.81 (d, $J = 8.0$ Hz, 2H), 7.30 (d, $J = 8.0$ Hz, 2H), 6.45 (s, 1H), 4.30 (q, $J = 7.2$ Hz, 2H), 2.38 (s, 3H), 1.33 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (100 MHz, CDCl_3) δ 164.0, 145.2, 136.5, 135.4, 130.0, 128.3, 62.1, 21.7, 14.0. IR: 2926, 1725, 1306, 1144, 732, 705. MS (ESI, m/z) 278 ($\text{M} + \text{Na}^+$); HRESIMS Calcd for $[\text{C}_{12}\text{H}_{13}\text{DNaO}_4\text{S}]^+$ ($\text{M} + \text{Na}^+$) 278.0568, found 278.0571.

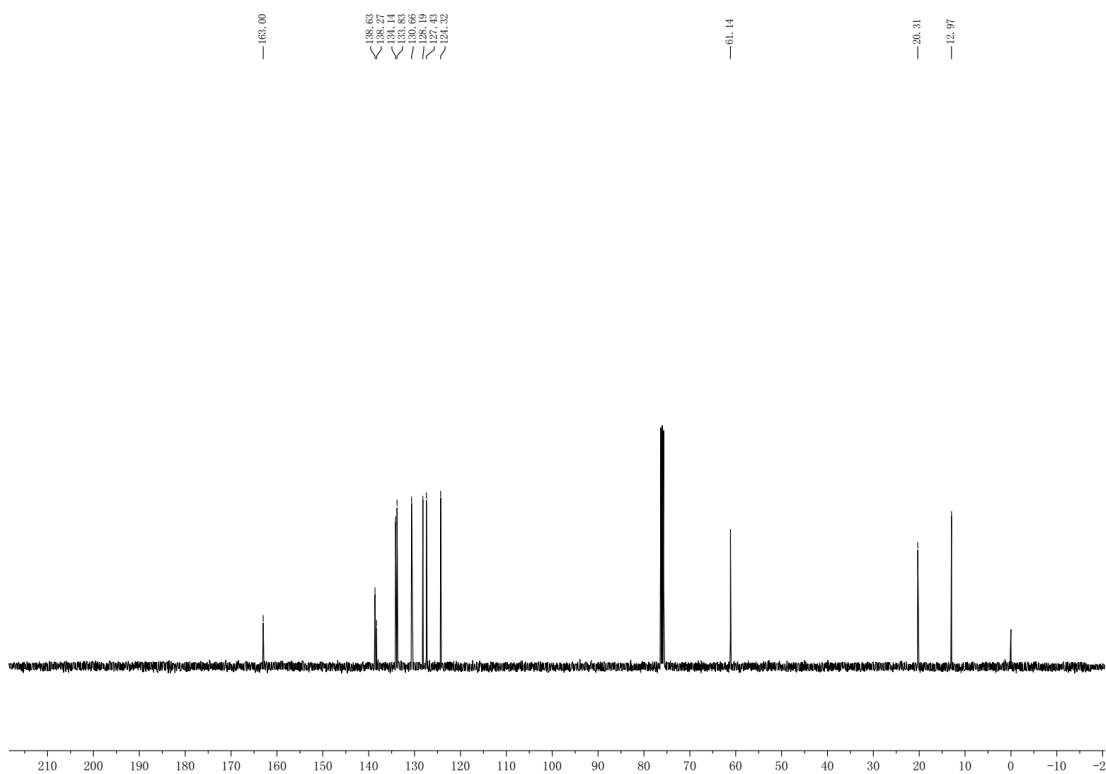
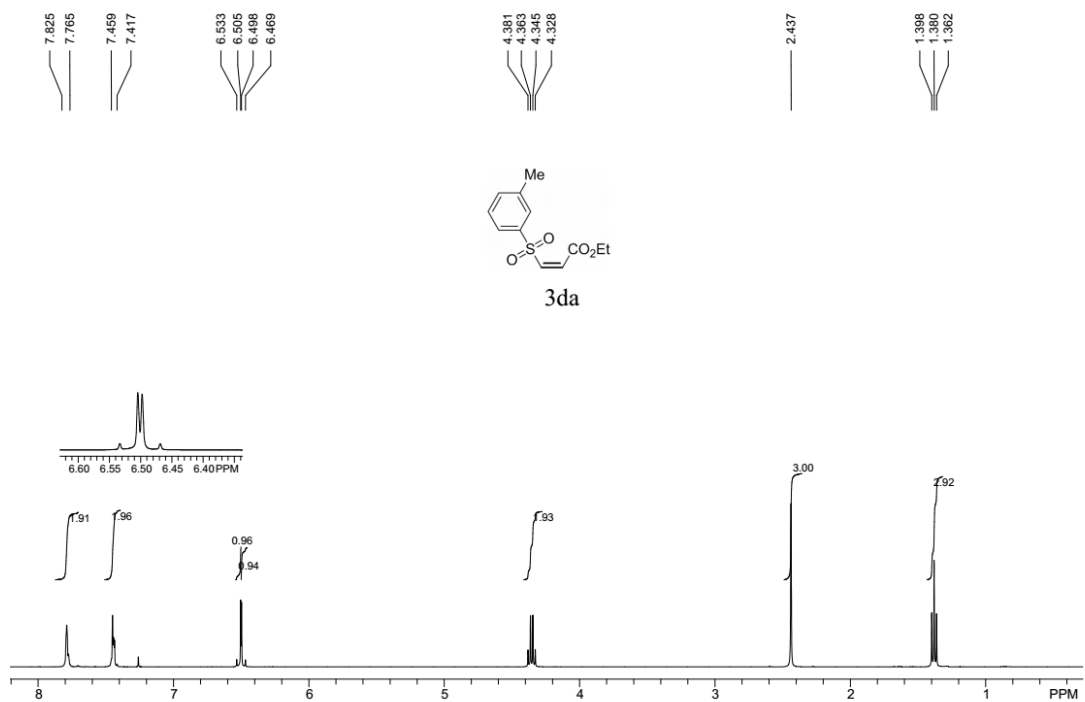
- (1) Downey, C. W.; Craciun, S.; Neferu, A. M.; Vivel, C. A.; Mueller, C. J.; Southall, B. C.; Corsi, S.; Etchill, E. W.; Sault, R. J. *Tetrahedron Lett.* **2012**, 53, 5763-5765.
- (2) Araviiskii, R. A.; Veksler, V. I.; Grinberg, G. E.; Mikhailets, G. A.; Mikhailova, V. N.; Mikhailova, M. A.; Yakovlev, V. V. *Pharm. Chem. J.* **1988**, 22, 53-57.
- (3) Santo, R. D.; Costi, R.; Massa, S.; Artico, M. *Synth. Commun.* **1998**, 28, 1801-1815.
- (4) Shi, W.; Zhang, B.; Liu, B.; Xu, F.; Xiao, F.; Zhang, J.; Zhang, S.; Wang, J. *Tetrahedron Lett.* **2004**, 45, 4563-4566.
- (5) Zoller, T.; Breuilles, P.; Klein, S.; Uguen, D.; De Cian, A.; Fischer, J. *Tetrahedron Lett.* **1999**, 40, 9015-9018.

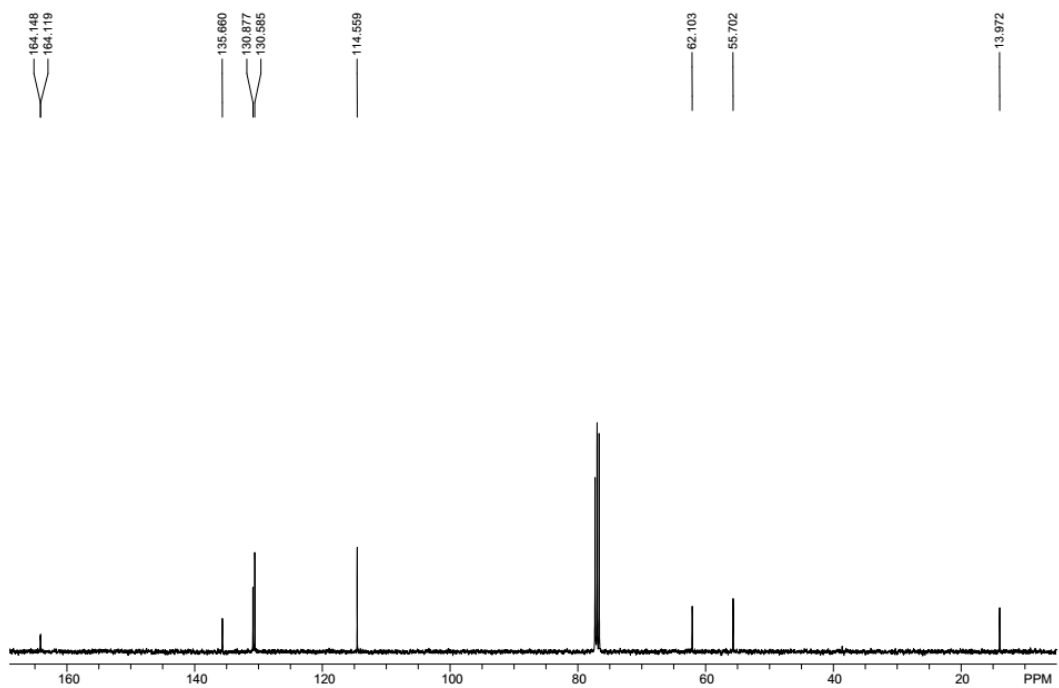
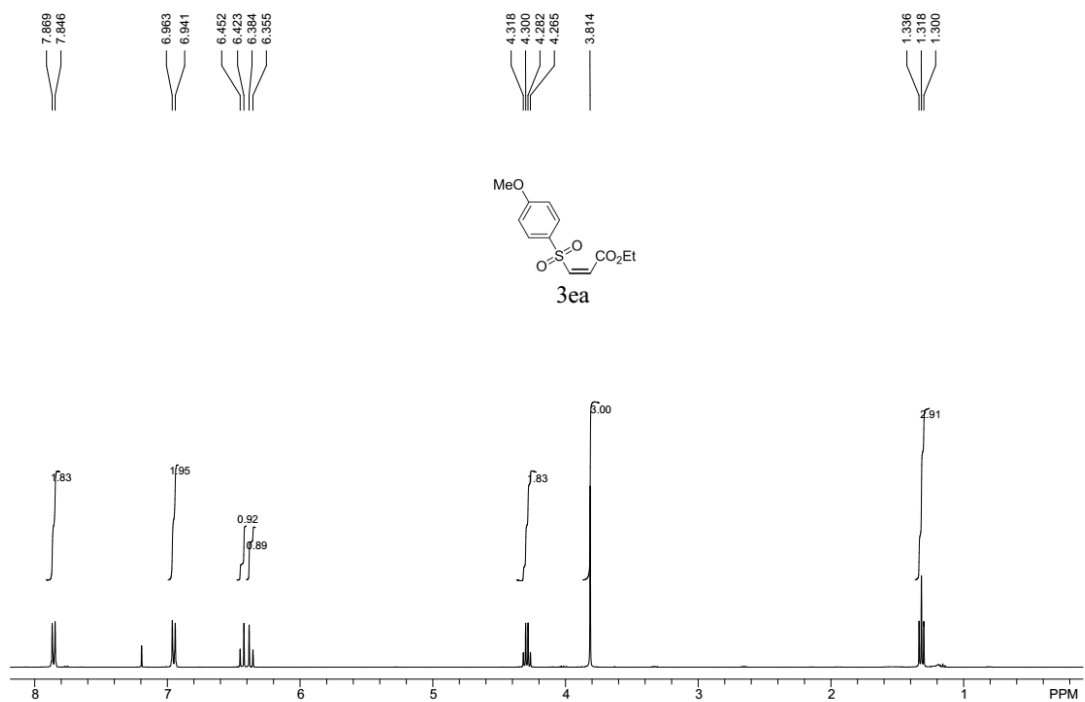
¹H and ¹³C NMR spectra

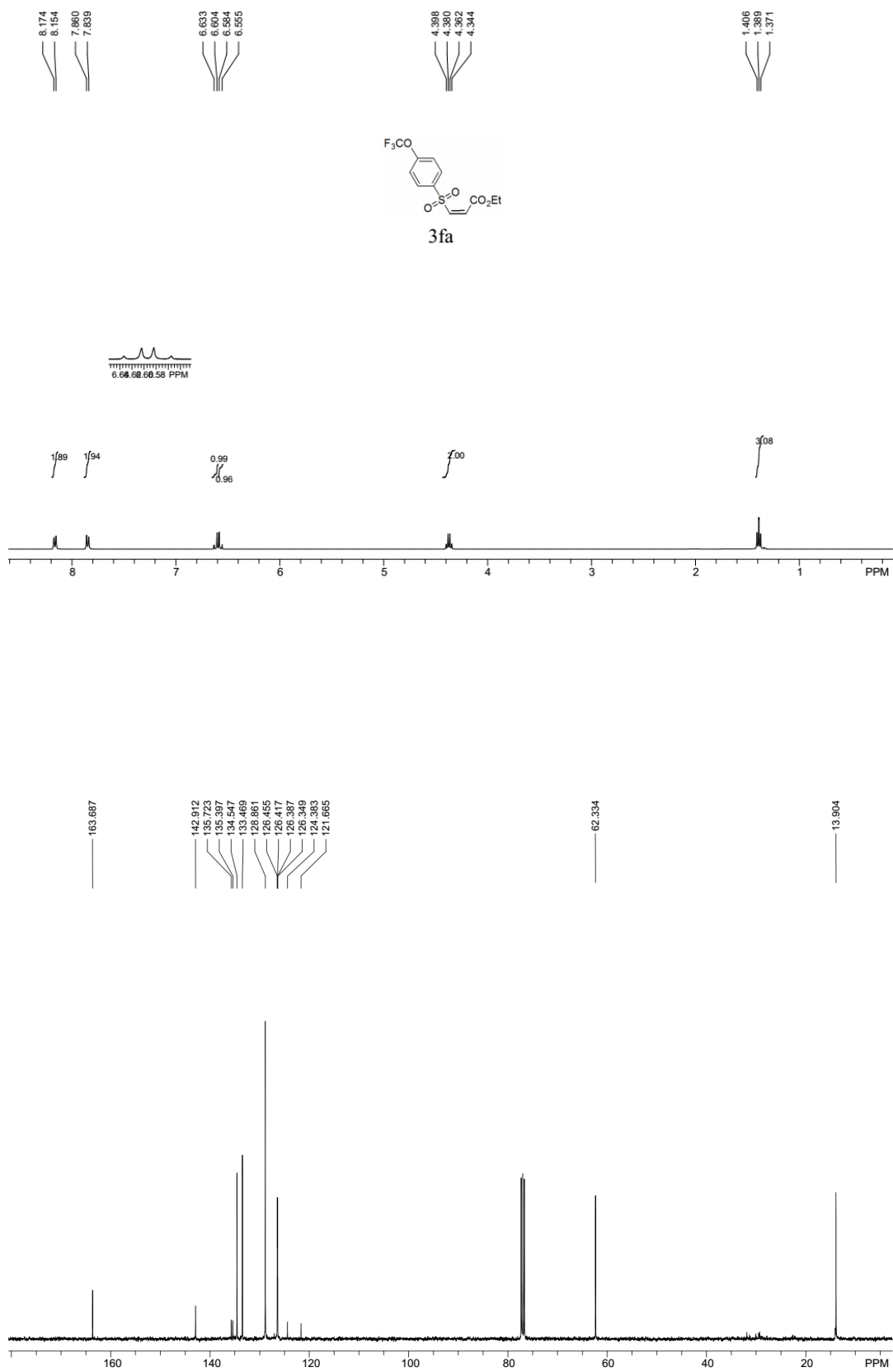


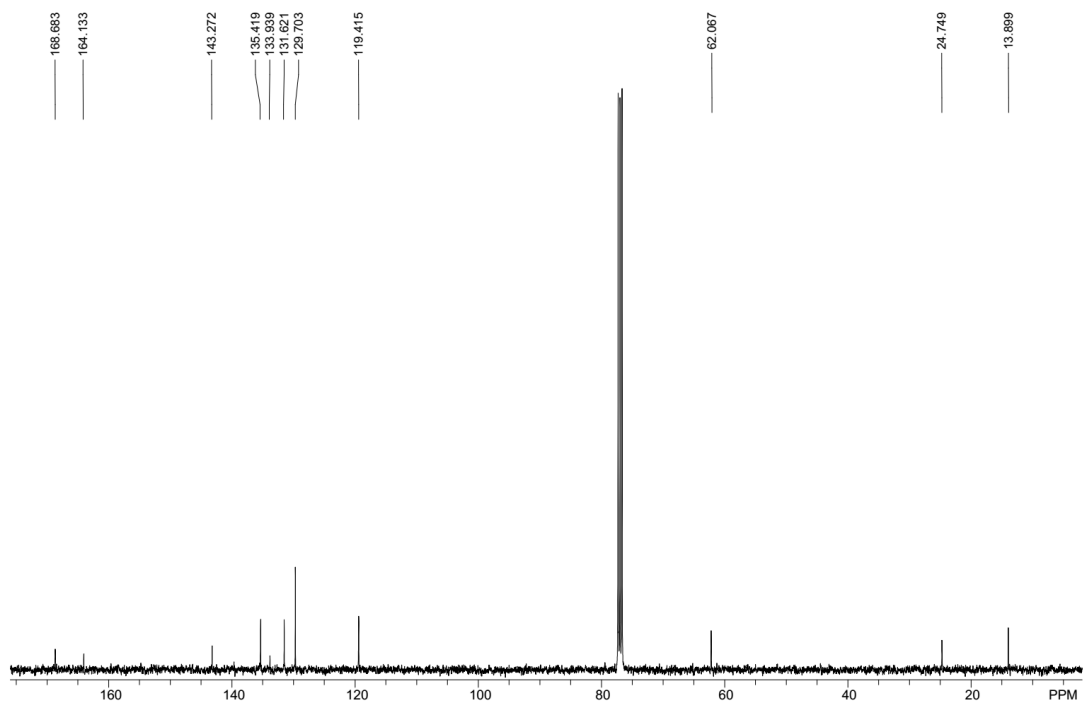
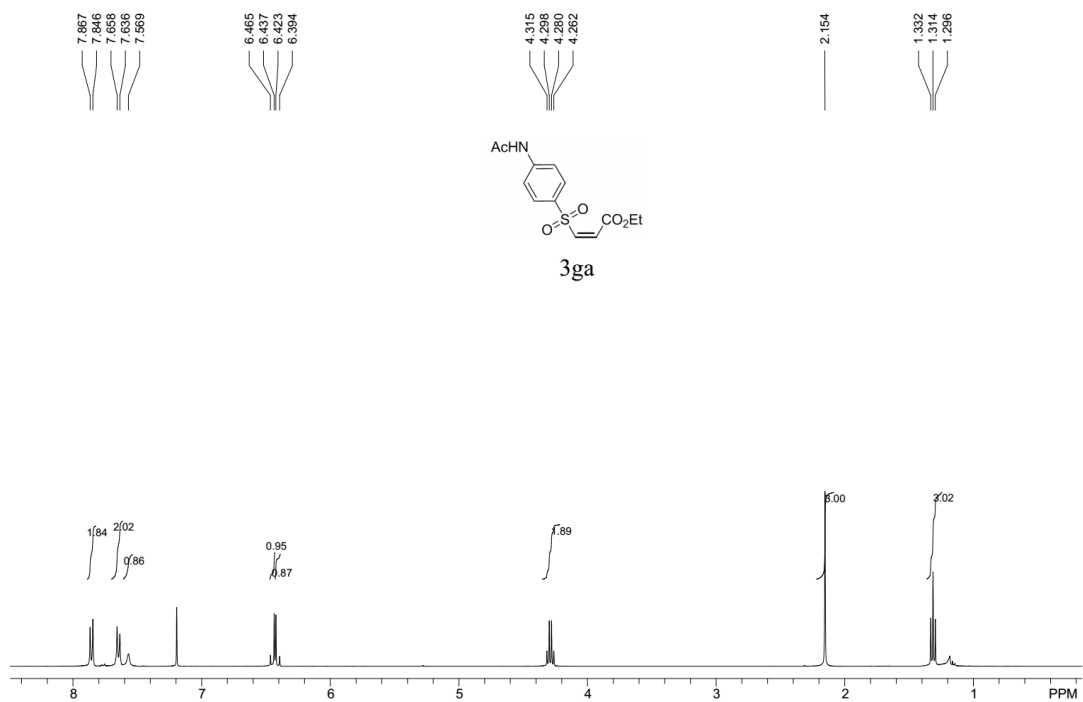


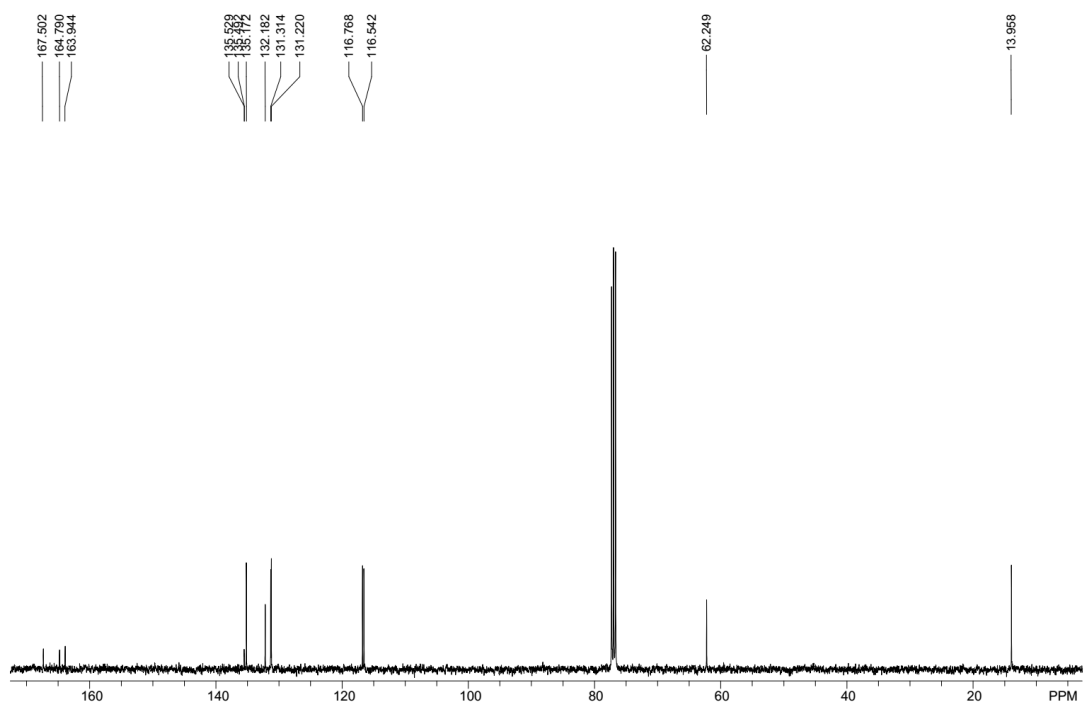
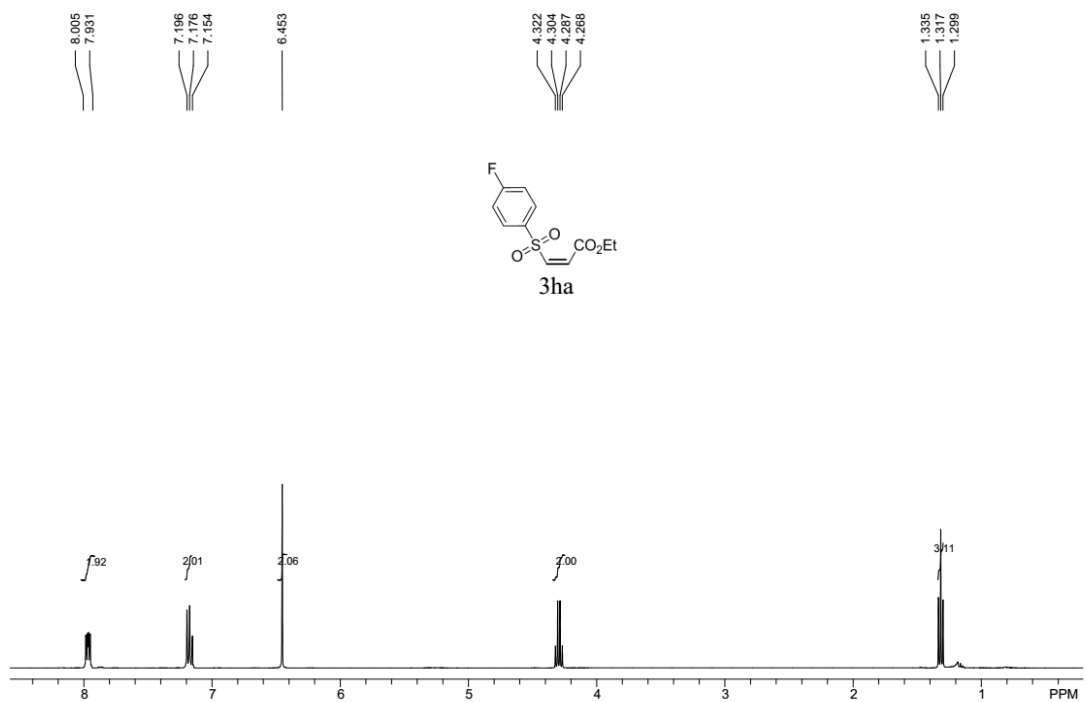


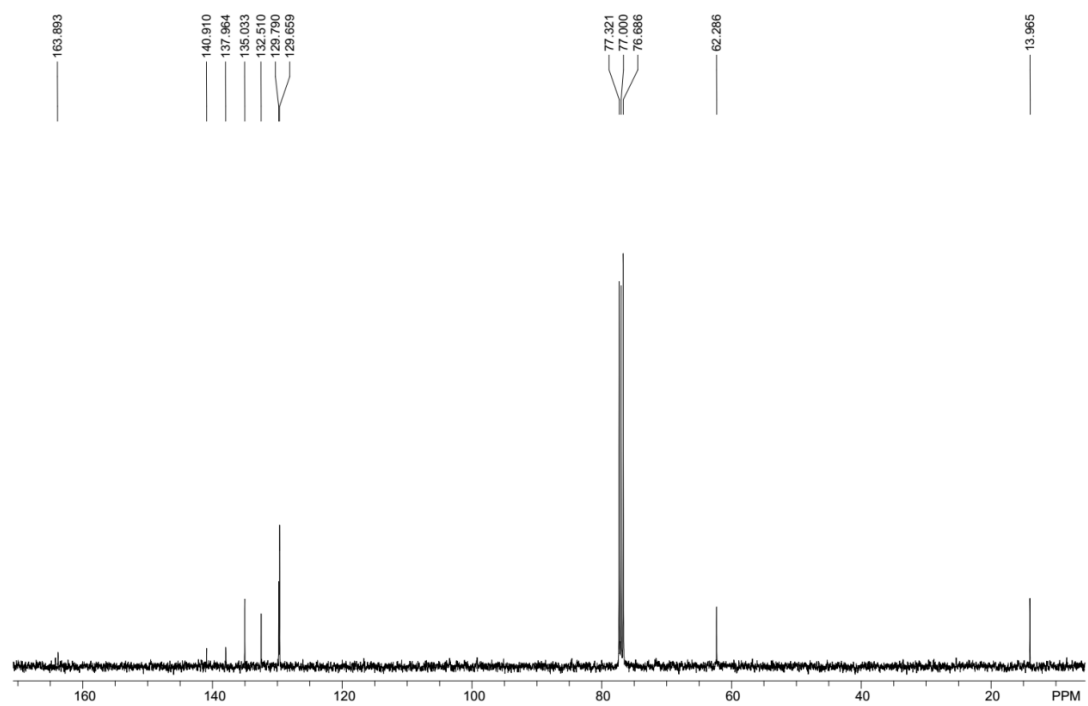
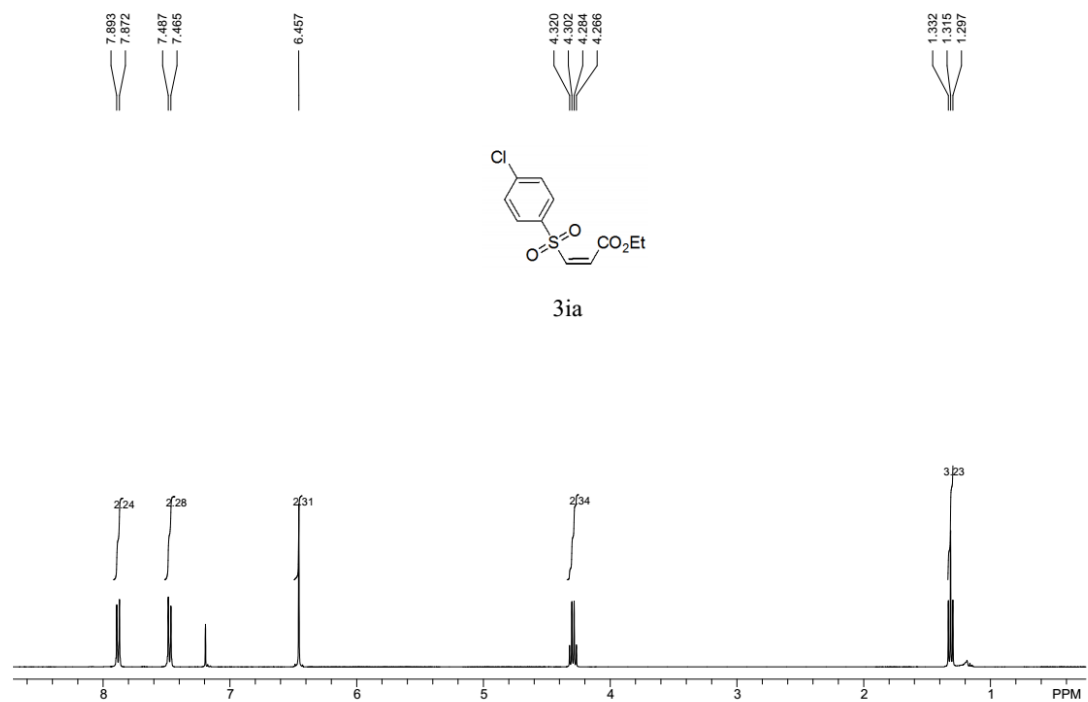


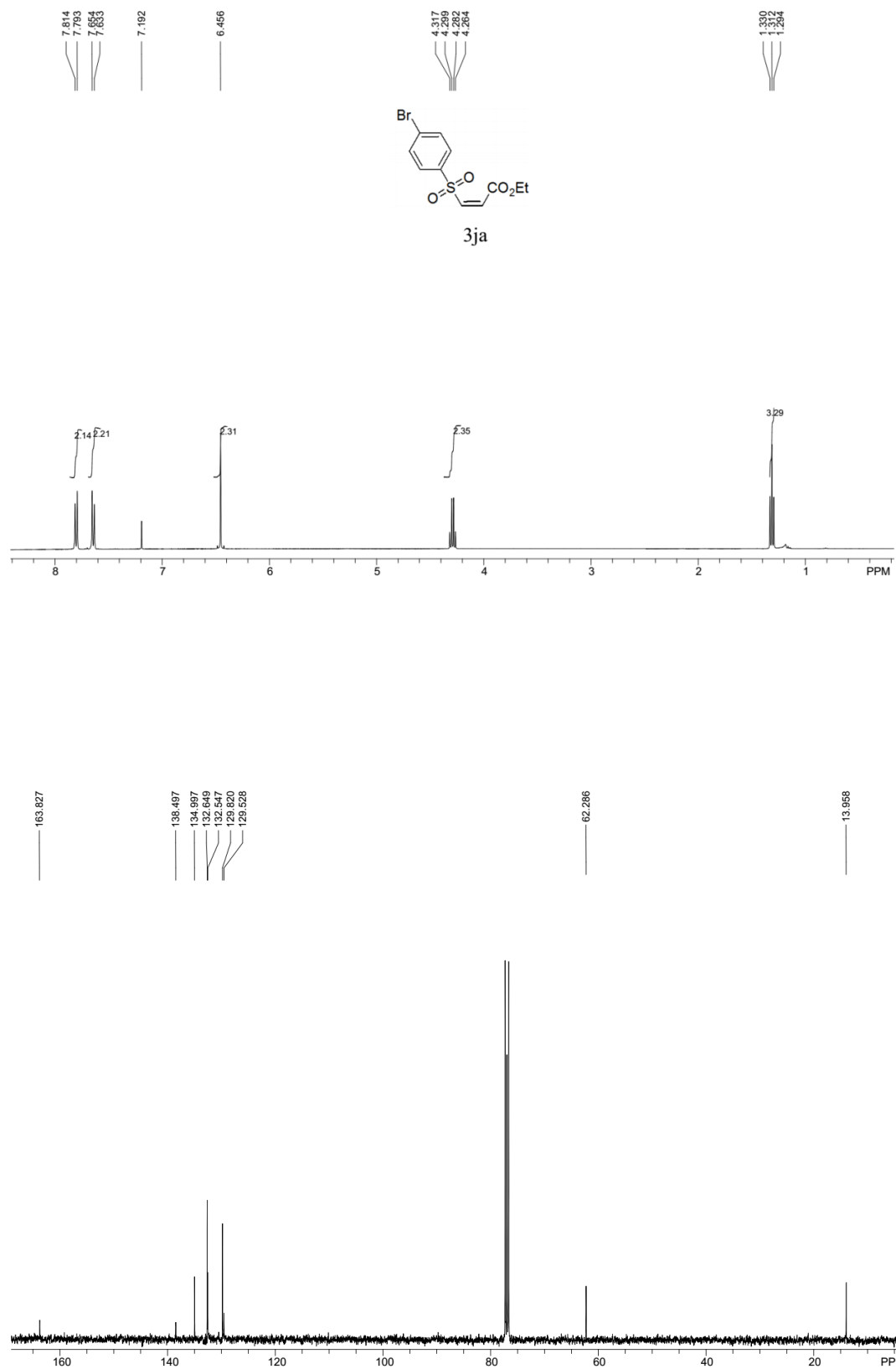


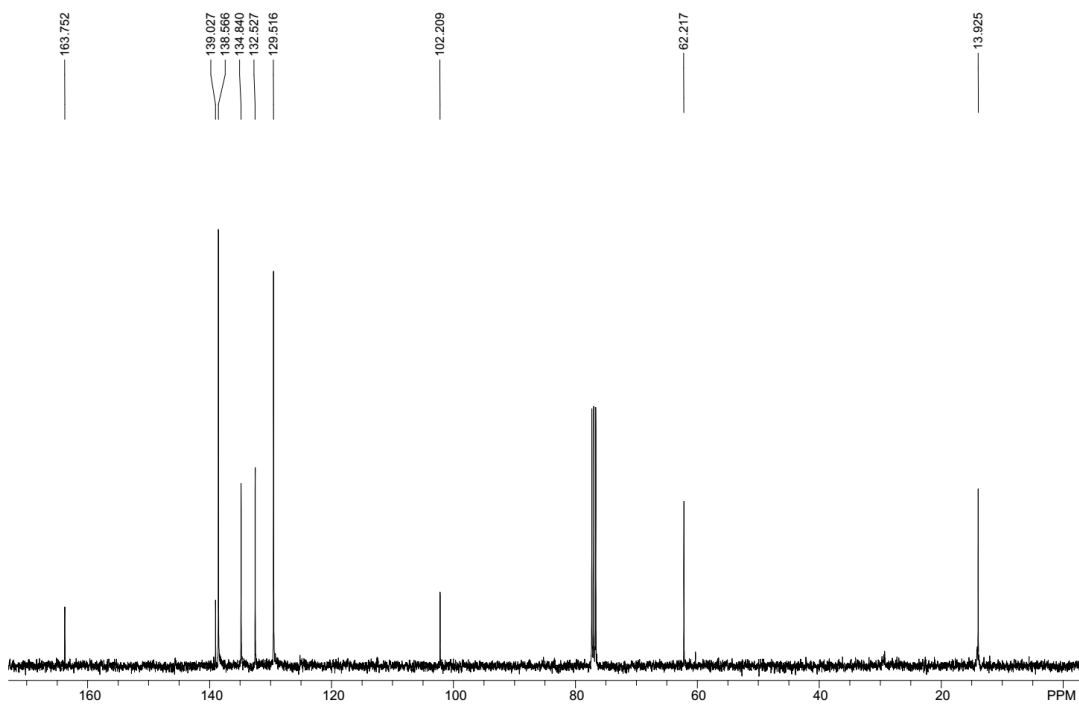
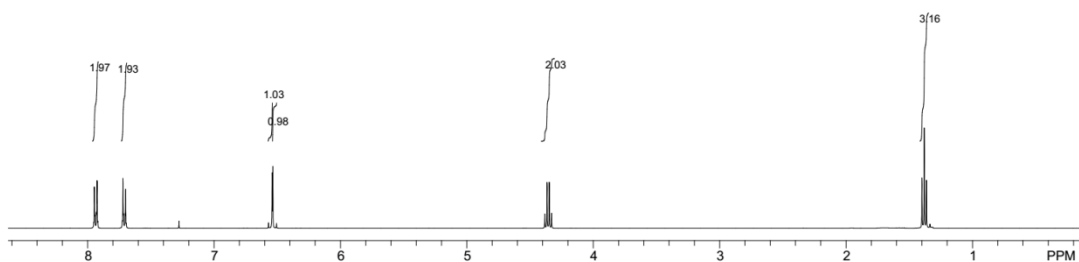
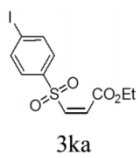
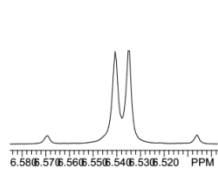
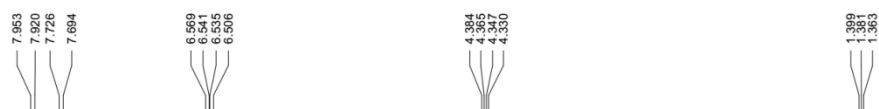


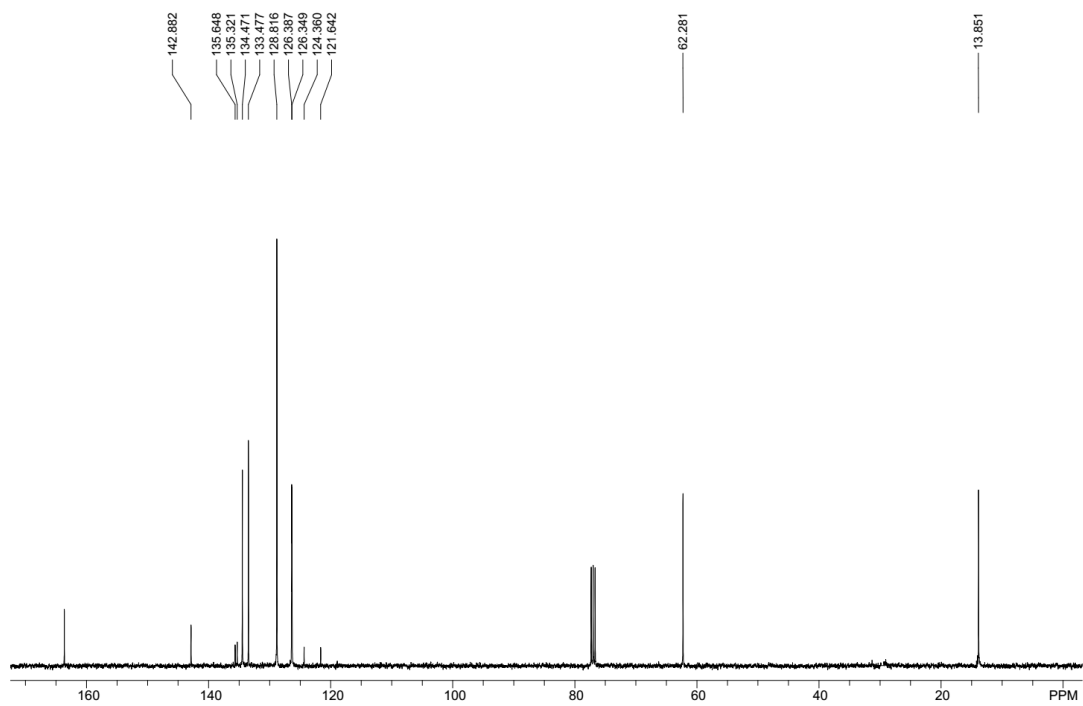
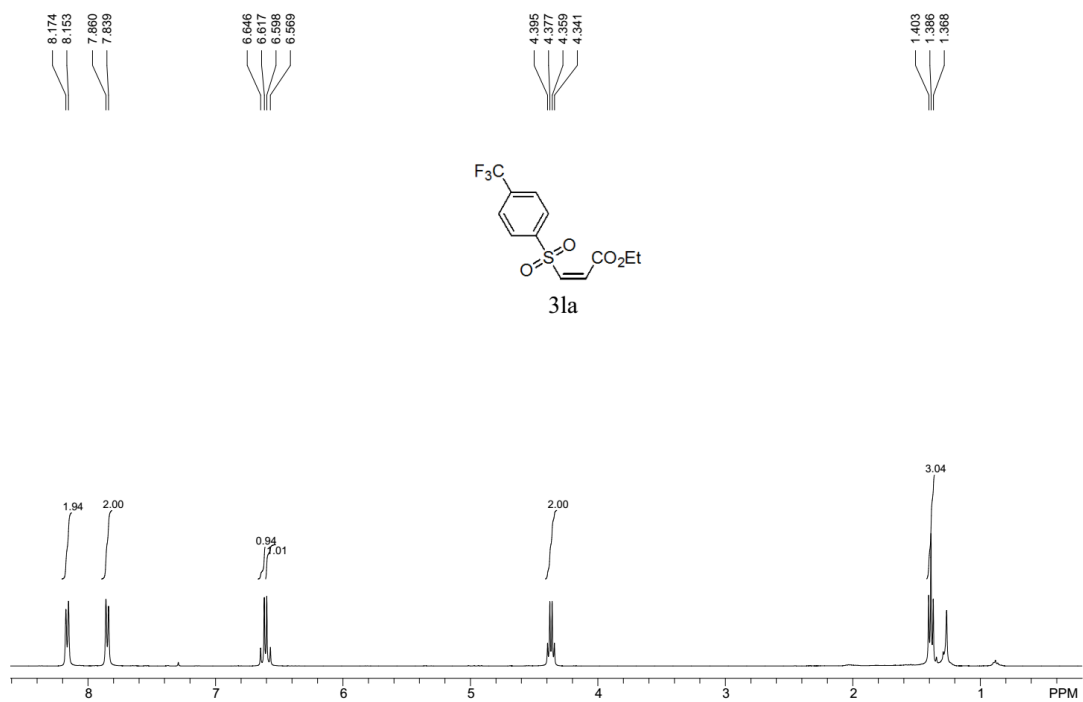


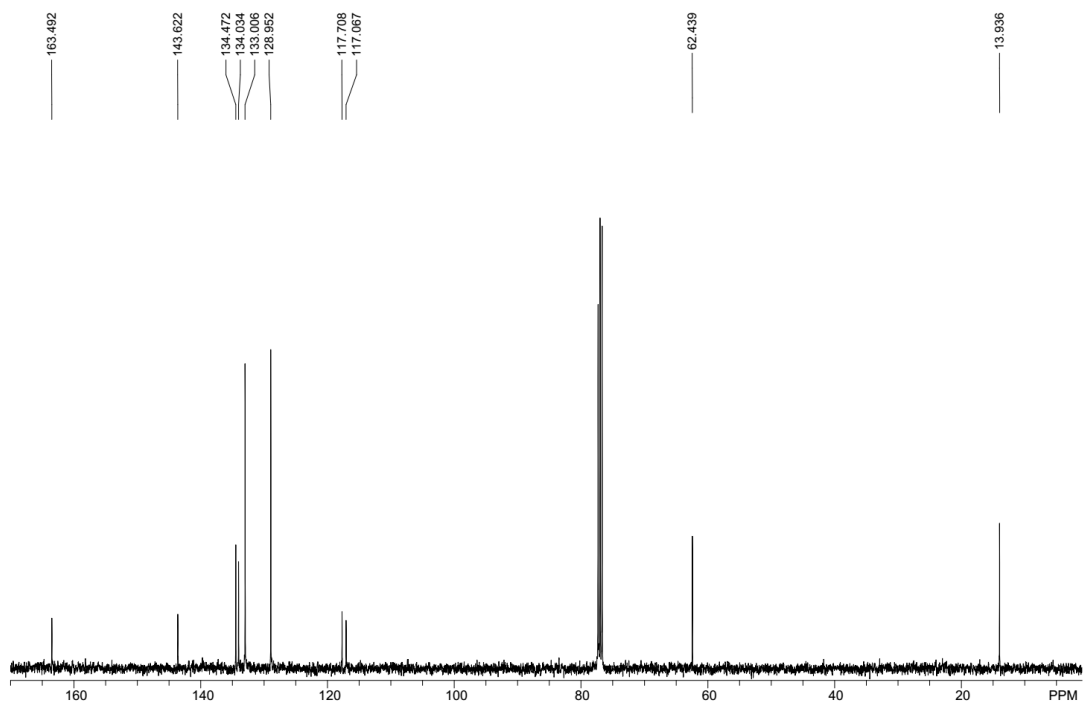
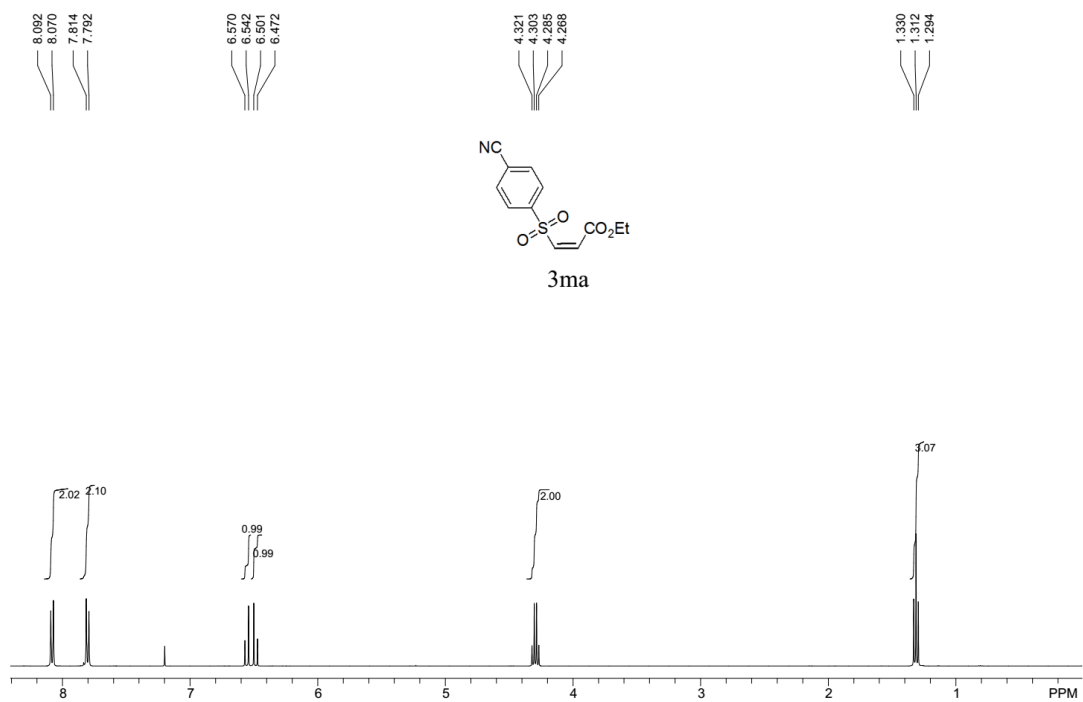










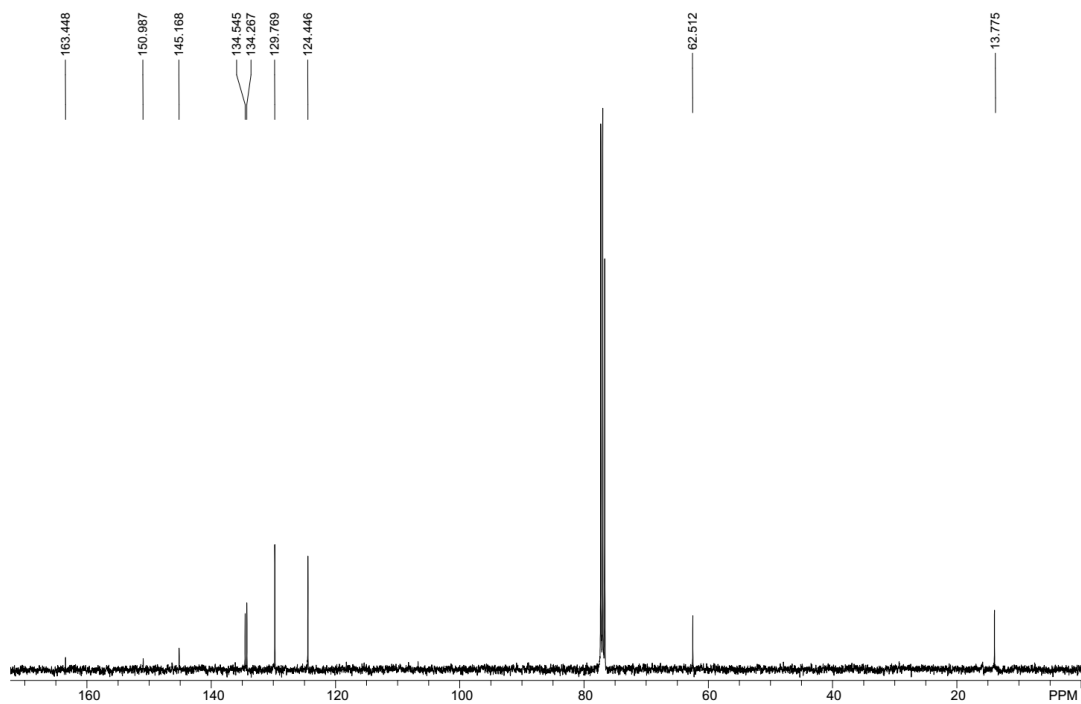
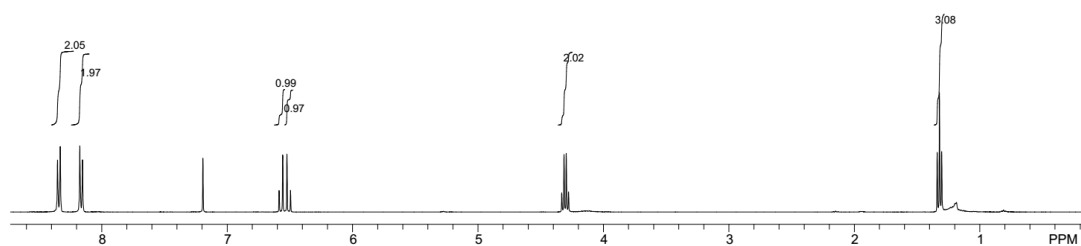
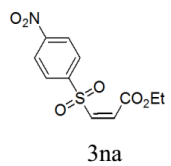


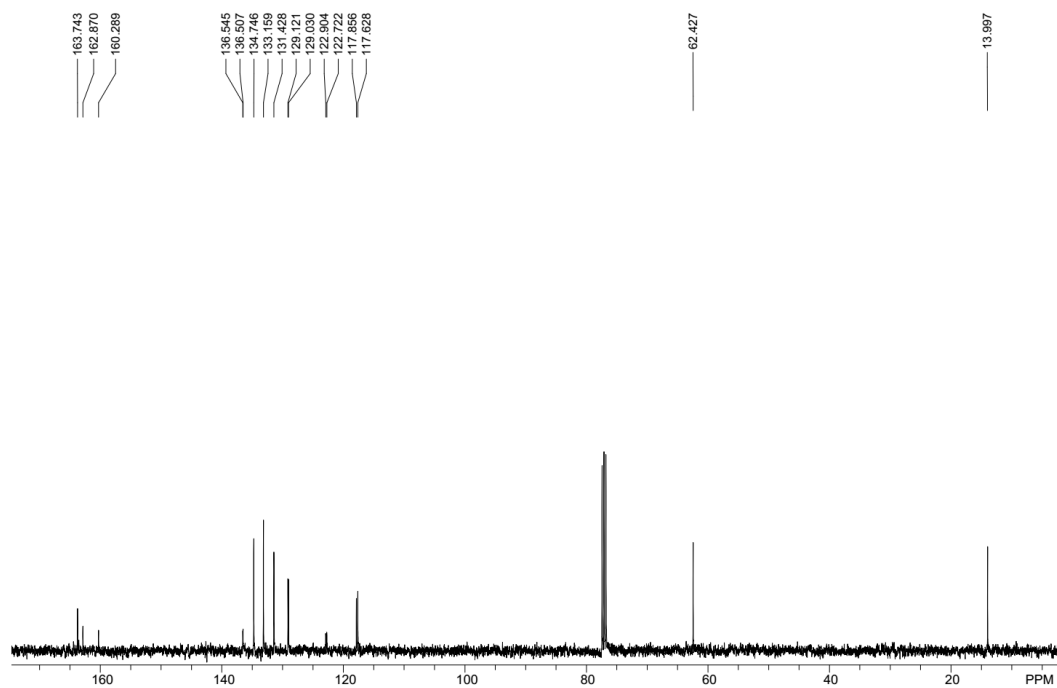
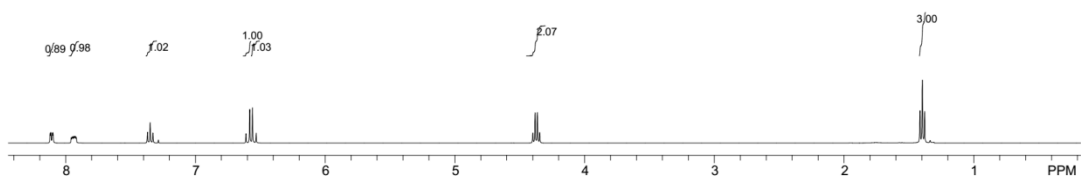
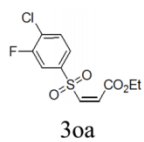
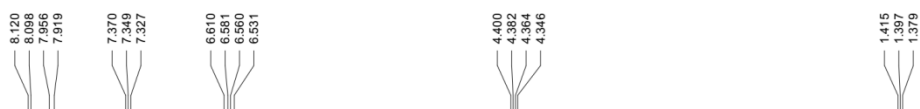
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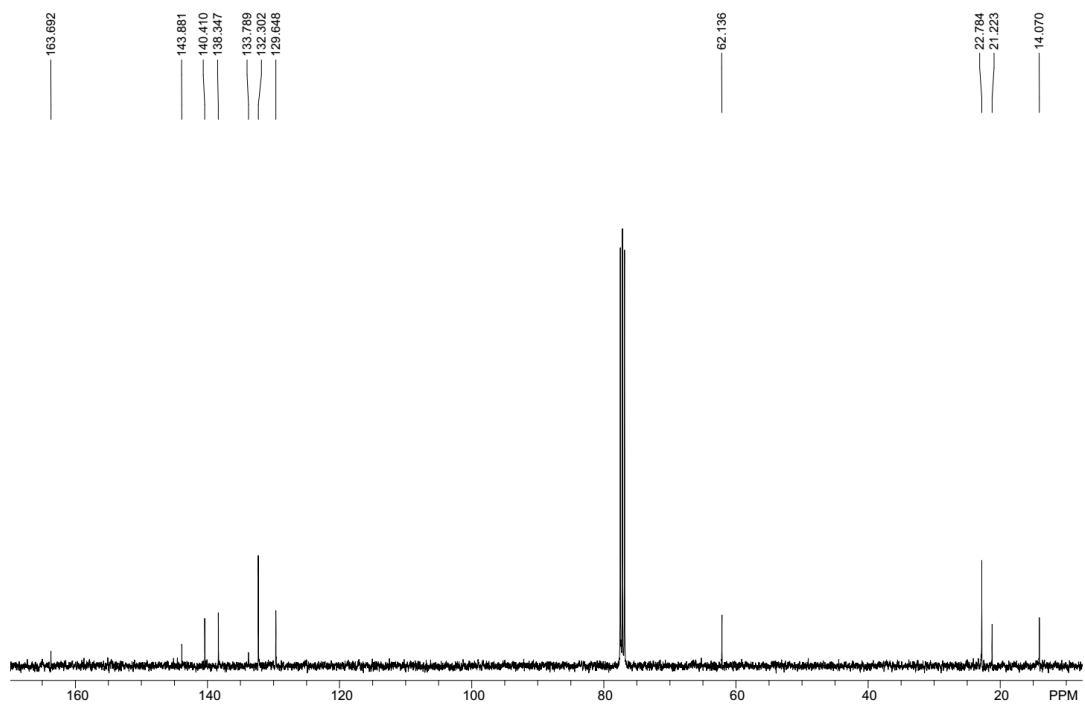
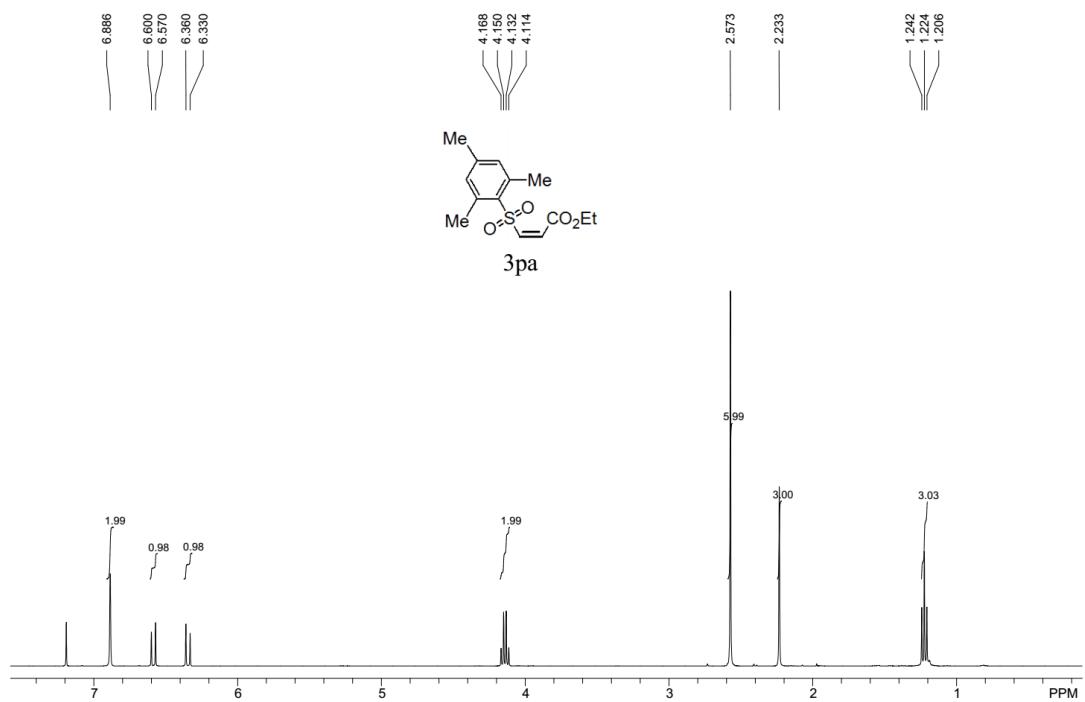
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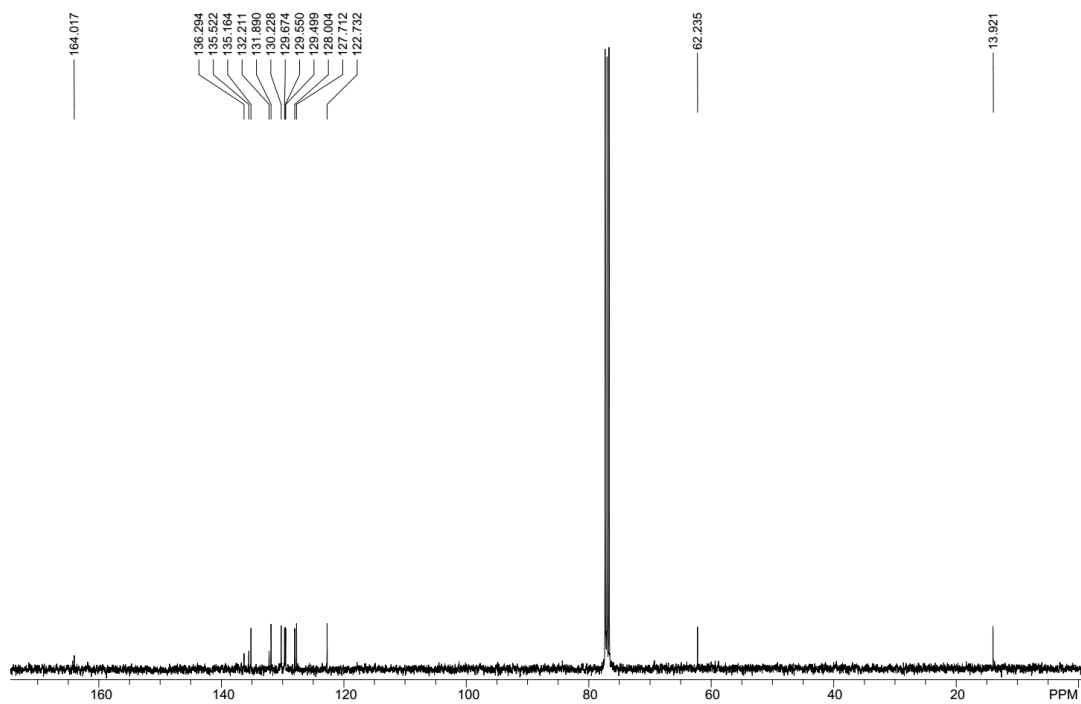
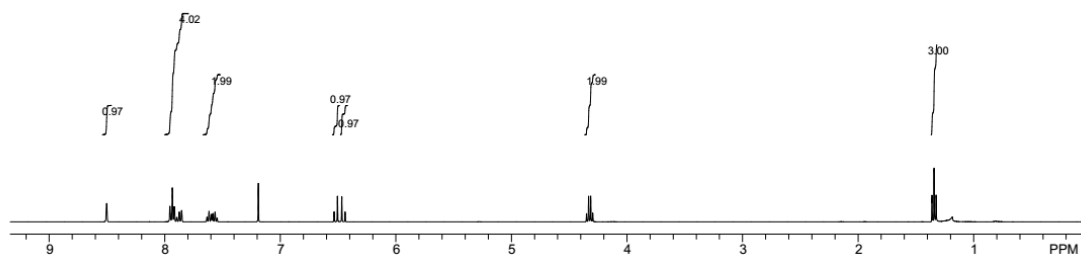
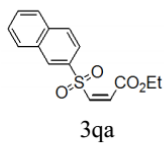
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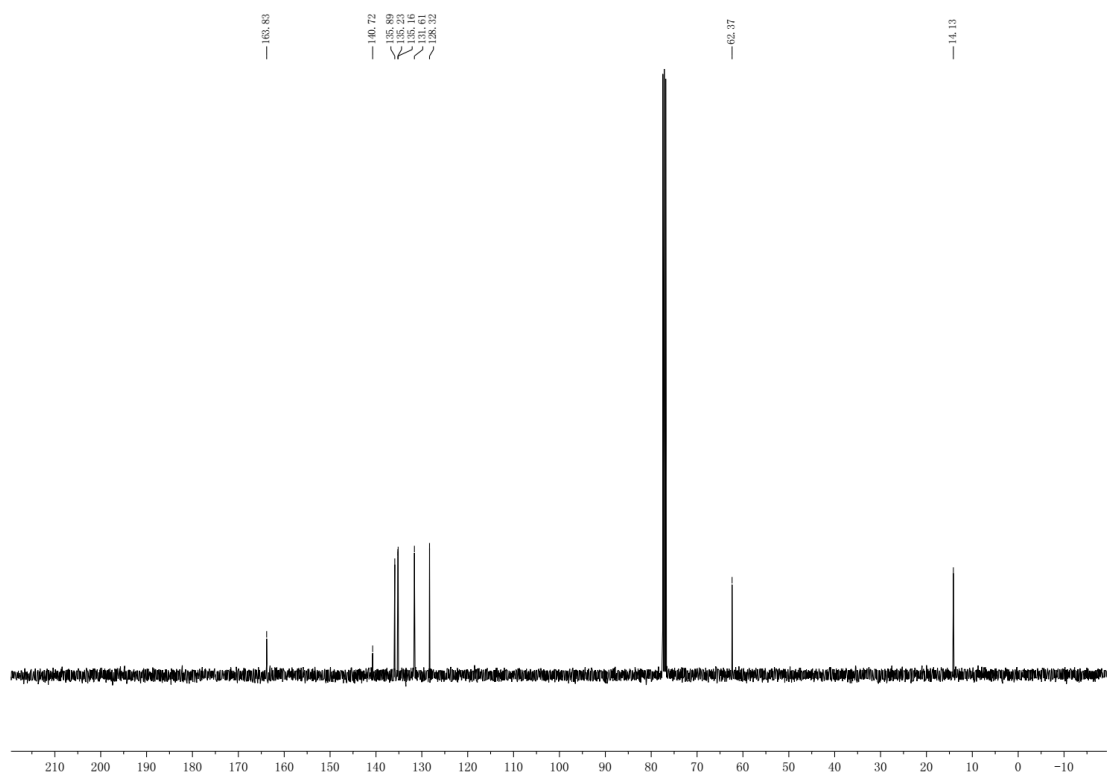
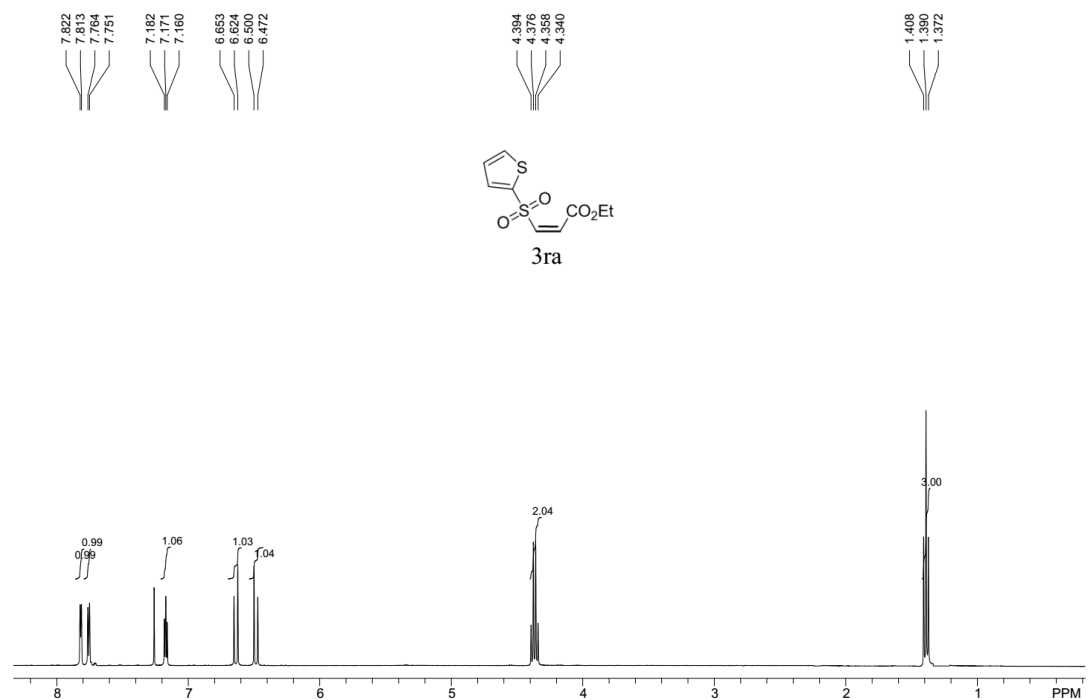
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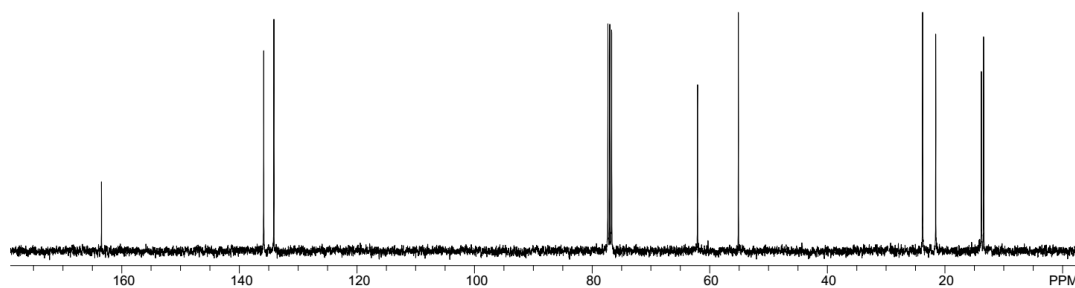
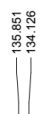
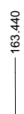
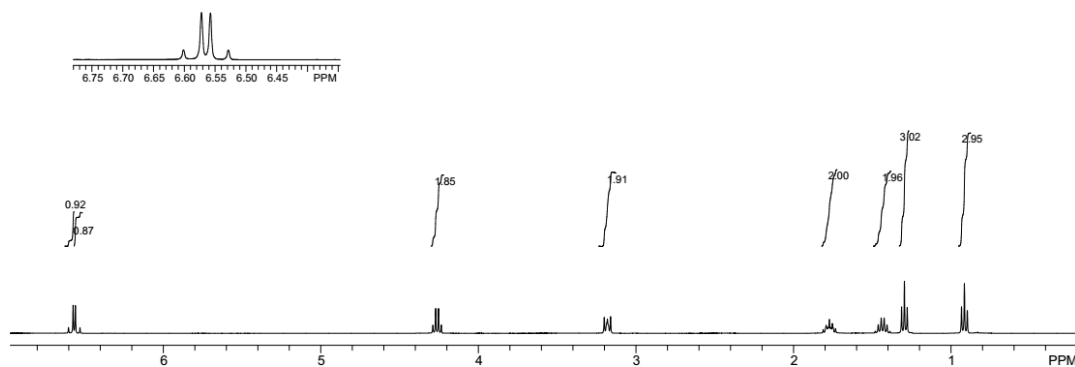
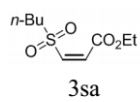
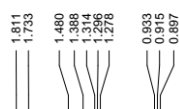
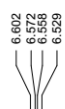










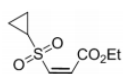


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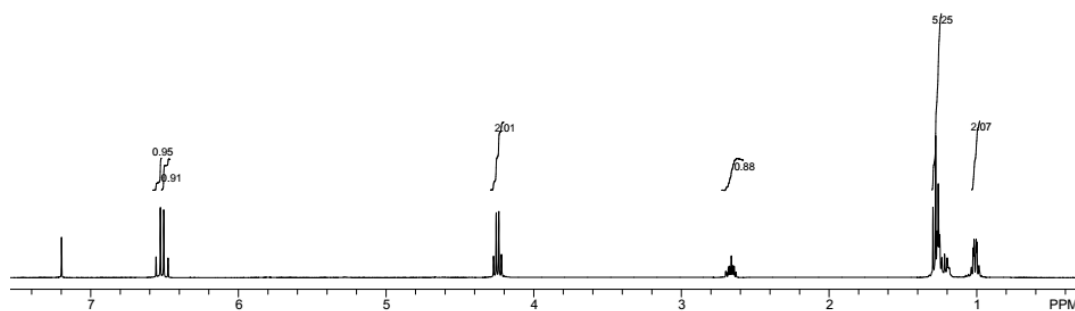
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3ta



163.73

135.88
132.63

62.15

31.39

13.94

5.28

