Electronic Supplementary Material (ESI) for Chemical Communications

Supplementary Information

Phosphine-Catalyzed [3 + 2] Annulation of α-Substituted Allenoates with Ester-Activated α,β-Unsaturated Imines: A Novel Variation of the Lu [3 + 2] Cycloaddition Reaction

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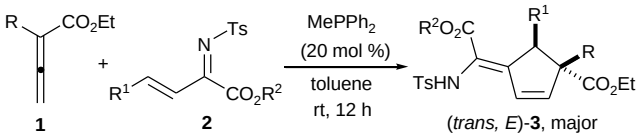
I. General Information

Unless otherwise noted, all reactions were carried out in nitrogen atmosphere under anhydrous conditions. All the solvents were purified according to the standard procedures. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV 400 in $CDCl_3$ with tetramethylsilane (TMS) as the internal standard. Melting points were measured on a RY-I apparatus and uncorrected. High resolution ESI mass spectra were acquired with Varian 7.0T FTMS instrument. X-ray crystal diffraction data were collected on a Nonius Kappa CCD diffractometer with Mo Kα radiation (λ = 0.7107 Å) at room temperature. Column chromatography was performed on silica gel (200-300 mesh) using a mixture of petroleum ether/ethyl acetate as eluant. The unsaturated imines were prepared according the literature procedure from ketones.[1] The α-substituted allenoates were prepared according to the reported procedures.[2]

General procedure for the phosphine-catalyzed [3+2] annulation of α-substituted allenoates and α, β-unstaturated imines

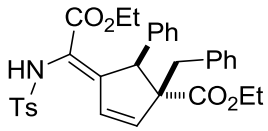


1 **2** (*trans, E*)-**3**, major

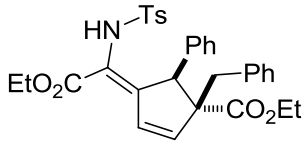
Under N_2 and at room temperature, a mixture of α-substituted allenoates **1** (0.375 mmol), α, β-unstaturated imines **2** (0.25 mmol), and $MePPh_2$ (0.05 mmol) in toluene (2.0 mL) was stirred for 12 h. After the reaction completed, the mixture was concentrated on a rotary evaporator under reduced pressure. The residue was purified by flash chromatography on silica gel eluted with a mixture of petroleum ether/ ethyl acetate (6:1-4:1) to afford the products **3**.

[1] L.-Q. Lu, J.-J. Zhang, F. Li, Y. Cheng, J. An, J.-R. Chen and W.-J. Xiao, *Angew. Chem., Int. Ed.*, 2010, **49**, 4495.
[2] X.-F. Zhu, J. Lan and O. Kwon, *J. Am. Chem. Soc.*, 2003, **125**, 4716;

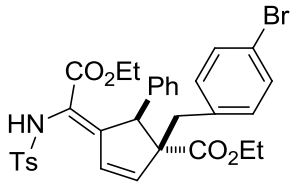
II. Analytical Data for Compounds 3



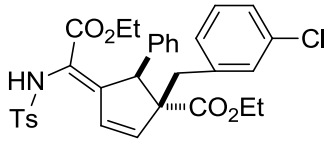
(*trans*, *E*)-3a. Yield 72%; white solid; mp 133-134 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.45 (br s, 1H), 7.38 – 7.30 (m, 3H), 7.29 – 7.24 (m, 2H), 7.23 – 7.14 (m, 3H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.98 (dd, *J* = 7.7, 1.4 Hz, 2H), 6.57 (d, *J* = 5.8 Hz, 1H), 6.12 (s, 1H), 5.04 (s, 1H), 4.12 – 3.98 (m, 2H), 3.62 (dq, *J* = 10.8, 7.1 Hz, 1H), 3.49 (dq, *J* = 10.8, 7.1 Hz, 1H), 2.68 (d, *J* = 13.5 Hz, 1H), 2.31 (s, 3H), 2.20 (d, *J* = 13.4 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.71 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.70, 163.84, 163.20, 146.84, 143.58, 140.41, 137.19, 135.96, 134.23, 131.62, 129.69, 129.22, 128.13, 127.98, 127.56, 126.79, 126.61, 115.55, 64.96, 61.21, 60.82, 56.20, 42.06, 21.40, 13.88, 13.61; MALDI-MS: Calcd for $C_{32}H_{33}NO_6S$ [M +Na]$^+$: *m*/*z* 582.1921, found: 582.1922.



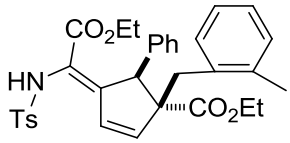
(*trans*, *Z*)-3a. Yield 16%; white solid; mp 138-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.45 (d, *J* = 5.9 Hz, 1H), 7.40 (br s, 1H), 7.32 – 7.23 (m, 5H), 7.22 – 7.15 (m, 3H), 6.98 – 6.91 (m, 3H), 6.54 (d, *J* = 5.9 Hz, 1H), 5.37 (s, 1H), 4.74 (s, 1H), 4.18 – 4.04 (m, 2H), 4.04 – 3.94 (m, 1H), 3.90 – 3.81 (m, 1H), 2.53 (d, *J* = 13.3 Hz, 1H), 2.42 (s, 3H), 2.12 (d, *J* = 13.3 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.09 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.08, 164.30, 162.12, 148.66, 143.70, 137.64, 137.06, 136.95, 131.94, 129.69, 129.40, 128.17, 127.40, 127.27, 126.67, 116.47, 62.73, 61.20, 61.16, 55.89, 42.75, 21.54, 14.02, 13.88; MALDI-MS: Calcd for $C_{32}H_{33}NO_6S$ [M +Na]$^+$: *m*/*z* 582.1921; found: 582.1917.



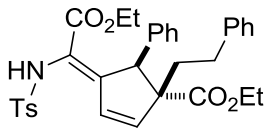
(*trans*, *E*)-3b. In 78% yield; yellow semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.43 (br s, 1H), 7.37 – 7.30 (m, 5H), 7.30 – 7.24 (m, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.85 (d, *J* = 8.4 Hz, 2H), 6.49 (d, *J* = 5.8 Hz, 1H), 6.22 (s, 1H), 5.04 (s, 1H), 4.12 – 4.01 (m, 2H), 3.67 – 3.56 (m, 1H), 3.54 – 3.43 (m, 1H), 2.64 (d, *J* = 13.5 Hz, 1H), 2.31 (s, 3H), 2.18 (d, *J* = 13.5 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.70 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.36, 163.37, 163.06, 146.00, 143.52, 140.14, 136.21, 135.93, 134.59, 131.35, 131.14, 129.16, 127.97, 127.46, 126.83, 120.55, 115.73, 64.65, 61.32, 60.78, 56.05, 41.19, 21.33, 13.89, 13.52; MALDI-MS: Calcd for $C_{32}H_{32}BrNO_6S$ [M +Na]$^+$: *m*/*z* 660.1026, found: 660.1023. **(*trans*, *Z*)-3b** (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 5.9 Hz, 1H), 7.44 – 7.37 (m, 2H), 7.35 – 7.28 (m, 4H), 7.24 (s, 2H), 6.91 (br s, 1H), 6.82 (d, *J* = 8.4 Hz, 2H), 6.48 (d, *J* = 5.9 Hz, 1H), 5.39 (s, 1H), 4.81 (s, 1H), 4.20 – 4.05 (m, 2H), 4.03 – 3.93 (m, 1H), 3.89 – 3.78 (m, 1H), 2.51 (d, *J* = 13.4 Hz, 1H), 2.41 (s, 3H), 2.08 (d, *J* = 13.4 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H).



(*trans, E*)-3c. In 74% yield; white solid; mp 127-129 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.3 Hz, 2H), 7.43 (br s, 1H), 7.38 – 7.31 (m, 3H), 7.30 – 7.23 (m, 2H), 7.18 – 7.11 (m, 2H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.95 (s, 1H), 6.89 – 6.83 (m, 1H), 6.51 (d, *J* = 5.8 Hz, 1H), 6.24 (s, 1H), 5.06 (s, 1H), 4.18 – 4.00 (m, 2H), 3.69 – 3.57 (m, 1H), 3.55 – 3.44 (m, 1H), 2.66 (d, *J* = 13.5 Hz, 1H), 2.31 (s, 3H), 2.21 (d, *J* = 13.5 Hz, 1H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.71 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.35, 163.31, 163.06, 145.94, 143.51, 140.10, 139.22, 135.91, 134.56, 133.82, 131.50, 129.69, 129.29, 129.15, 127.97, 127.79, 127.45, 126.85, 126.73, 115.76, 64.67, 61.37, 60.78, 56.00, 41.45, 21.32, 13.86, 13.51; MALDI-MS: Calcd for $C_{32}H_{32}ClNO_6S$ $[M+Na]^+$: *m/z* 616.1531, found: 616.1533. **(*trans, Z*)-3c** (minor): ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.61 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 5.8 Hz, 1H), 7.37 (br s, 2H), 7.31 – 7.23 (m, 5H), 7.17 – 7.12 (m, 2H), 6.93 (s, 1H), 6.83 (dt, *J* = 6.6, 1.6 Hz, 1H), 6.50 (d, *J* = 5.9 Hz, 1H), 5.39 (s, 1H), 4.79 (s, 1H), 4.22 – 4.06 (m, 2H), 4.04 – 3.94 (m, 1H), 3.90 – 3.80 (m, 1H), 2.52 (d, *J* = 13.4 Hz, 1H), 2.42 (s, 3H), 2.11 (d, *J* = 13.4 Hz, 1H), 1.24 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).

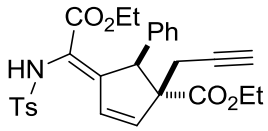


(*trans, E*)-3d. In 75% yield; yellow semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.2 Hz, 2H), 7.44 (br s, 1H), 7.38 – 7.23 (m, 5H), 7.09 – 7.01 (m, 5H), 6.97 (d, *J* = 6.2 Hz, 1H), 6.42 (d, *J* = 5.8 Hz, 1H), 6.24 (s, 1H), 5.12 (s, 1H), 4.14 – 4.03 (m, 2H), 3.69 – 3.58 (m, 1H), 3.56 – 3.45 (m, 1H), 2.64 (d, *J* = 14.2 Hz, 1H), 2.38 (d, *J* = 14.2 Hz, 1H), 2.30 (s, 3H), 2.06 (s, 3H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.72 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 175.04, 163.60, 163.17, 147.00, 143.44, 140.58, 136.56, 135.91, 135.73, 134.13, 131.36, 130.27, 129.36, 129.11, 127.86, 127.46, 126.72, 126.50, 125.54, 115.47, 64.97, 61.28, 60.73, 56.29, 37.81, 21.29, 19.84, 13.78, 13.52; MALDI-MS: Calcd for $C_{33}H_{35}NO_6S$ $[M+Na]^+$ *m/z* 596.2077, found: 596.2073. **(*trans, Z*)-3d** (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.46 – 7.37 (m, 3H), 7.31 – 7.26 (m, 3H), 7.25 (s, 1H), 7.08 – 7.02 (m, 3H), 6.97 – 6.90 (m, 2H), 6.41 (d, *J* = 5.8 Hz, 1H), 5.38 (s, 1H), 4.79 (s, 1H), 4.23 – 4.08 (m, 2H), 4.04 – 3.94 (m, 1H), 3.90 – 3.81 (m, 1H), 2.50 (d, *J* = 14.0 Hz, 1H), 2.42 (s, 3H), 2.29 (d, *J* = 13.8 Hz, 1H), 2.05 (s, 3H), 1.23 (t, *J* = 7.2 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).

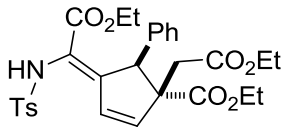


(*trans, E*)-3e. In 74% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.41 (d, *J* = 8.3 Hz, 2H), 7.35 – 7.23 (m, 6H), 7.16 – 7.06 (m, 3H), 7.01 (d, *J* = 8.1 Hz, 2H), 6.70 (d, *J* = 6.9 Hz, 2H), 6.58 (d, *J* = 5.6 Hz, 1H), 6.16 (s, 1H), 5.26 (s, 1H), 4.30 – 4.14 (m, 2H), 3.71 – 3.60 (m, 1H), 3.58 – 3.47 (m, 1H), 2.45 – 2.30 (m, 2H), 2.28 (s, 3H), 1.83 – 1.61 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.76 (d, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.91, 164.04, 163.09, 147.55, 143.42, 141.28, 139.83, 135.68, 134.73, 129.09, 128.15, 128.01, 127.77, 127.50, 126.82, 125.76, 115.65, 64.44, 61.38, 60.75, 54.42, 36.02, 31.74, 21.31, 14.20, 13.61; MALDI-MS: Calcd for $C_{33}H_{35}NO_6S$ $[M+Na]^+$ *m/z* 596.2077, found:

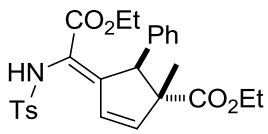
596.2070. **(*trans, Z*)-3e** (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (d, *J* = 8.2 Hz, 2H), 7.43 (d, *J* = 5.8 Hz, 1H), 7.32 – 7.22 (m, 6H), 7.16 – 7.08 (m, 4H), 6.74 (d, *J* = 6.9 Hz, 2H), 6.66 (d, *J* = 5.8 Hz, 1H), 5.37 (s, 1H), 5.01 (s, 1H), 4.34 – 4.18 (m, 2H), 4.00 – 3.91 (m, 1H), 3.87 – 3.76 (m, 1H), 2.42 (s, 3H), 2.38 – 2.16 (m, 3H), 1.58 – 1.54 (m, 1H), 1.36 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H).



(*trans, E*)-3f. In 55% yield; white solid; mp 162-163 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.2 Hz, 2H), 7.37 (d, *J* = 5.7 Hz, 1H), 7.31 (t, *J* = 7.2 Hz, 2H), 7.28 – 7.23 (m, 2H), 7.15 (br s, 1H), 7.07 (d, *J* = 8.2 Hz, 2H), 6.70 (d, *J* = 5.7 Hz, 1H), 6.13 (s, 1H), 5.00 (s, 1H), 4.33 – 4.17 (m, 2H), 3.67 – 3.58 (m, 1H), 3.53 – 3.44 (m, 1H), 2.31 (s, 3H), 2.25 – 2.15 (m, 1H), 2.06 – 1.93 (m, 2H), 1.31 (t, *J* = 7.1 Hz, 3H), 0.71 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.27, 163.26, 163.08, 146.09, 143.61, 139.65, 135.85, 135.64, 129.23, 128.07, 127.55, 127.09, 115.98, 80.18, 71.11, 63.56, 61.76, 60.89, 54.89, 24.53, 21.40, 14.15, 13.60; MALDI-MS: Calcd for $C_{28}H_{29}NO_6S$ $[M+Na]^+$ *m/z* 530.1608, found: 530.1612. **(*trans, Z*)-3f** (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.2 Hz, 2H), 7.52 (d, *J* = 5.9 Hz, 1H), 7.37 – 7.22 (m, 7H), 6.80 (d, *J* = 5.8 Hz, 1H), 5.40 (s, 1H), 4.85 (s, 1H), 4.34 – 4.22 (m, 2H), 4.01 – 3.90 (m, 1H), 3.86 – 3.74 (m, 1H), 2.41 (s, 3H), 2.15 (dd, *J* = 16.6, 2.5 Hz, 1H), 1.97 (t, *J* = 2.5 Hz, 1H), 1.76 (dd, *J* = 16.6, 2.5 Hz, 1H), 1.35 (t, *J* = 7.1 Hz, 3H), 1.06 (t, *J* = 7.1 Hz, 3H).

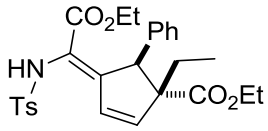


(*trans, E*)-3g. In 65% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.3 Hz, 2H), 7.37 (d, *J* = 5.6 Hz, 1H), 7.34 – 7.15 (m, 5H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.50 (d, *J* = 5.6 Hz, 1H), 6.22 (s, 1H), 5.23 (s, 1H), 4.29 – 4.11 (m, 2H), 3.97 (q, *J* = 7.1 Hz, 2H), 3.72 – 3.60 (m, 1H), 3.59 – 3.47 (m, 1H), 2.65 (d, *J* = 17.4 Hz, 1H), 2.27 (d, *J* = 19.8 Hz, 4H), 1.25 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.1 Hz, 3H), 0.74 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.92, 170.84, 163.47, 163.09, 145.92, 143.43, 139.98, 136.24, 135.63, 131.66, 129.08, 128.22, 127.49, 126.93, 116.07, 62.15, 61.58, 60.81, 60.43, 54.49, 37.91, 21.28, 13.92, 13.89, 13.57; MALDI-MS: Calcd for $C_{29}H_{33}NO_8S$ $[M+Na]^+$ *m/z* 578.1819, found: 578.1812. **(*trans, Z*)-3g** (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 8.3 Hz, 2H), 7.51 (d, *J* = 5.7 Hz, 1H), 7.34 – 7.21 (m, 6H), 6.79 (br s, 1H), 6.71 (d, *J* = 5.7 Hz, 1H), 5.41 (s, 1H), 5.03 (s, 1H), 4.25 (q, *J* = 7.1 Hz, 2H), 4.01 – 3.89 (m, 3H), 3.85 – 3.73 (m, 1H), 2.41 (s, 3H), 2.34 (d, *J* = 17.1 Hz, 1H), 2.23 (d, *J* = 17.1 Hz, 1H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.13 (t, *J* = 7.2 Hz, 3H), 1.05 (t, *J* = 7.1 Hz, 3H).

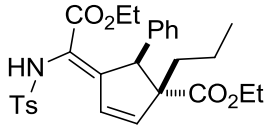


(*trans, E*)-3h. In 68% yield; white solid; mp 85-87 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.54 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.18 (m, 6H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.47 (d, *J* = 5.6 Hz, 1H), 6.19 (s, 1H), 5.12 (s, 1H), 4.24 – 4.13 (m, 2H), 3.63 – 3.46 (m, 2H), 2.31 (s, 3H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.93 (s, 3H), 0.71 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.98, 164.16, 163.29, 148.75, 143.49, 141.12, 135.85, 134.00, 129.14, 127.85, 127.53, 126.47, 115.79, 61.38, 60.73, 60.37, 54.72, 21.34, 20.92, 14.04,

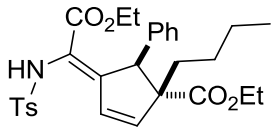
13.54; MALDI-MS: Calcd for $C_{26}H_{29}NO_6S$ [M +Na]$^+$ *m/z* 506.1608, found: 506.1606.



(*trans*, *E*)-3i. In 53% yield; white solid; mp 76-78 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.2 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.27 – 7.21 (m, 2H), 7.05 (d, *J* = 8.1 Hz, 2H), 6.66 (d, *J* = 5.7 Hz, 1H), 6.15 (s, 1H), 5.06 (s, 1H), 4.27 – 4.11 (m, 2H), 3.67 – 3.57 (m, 1H), 3.55 – 3.44 (m, 1H), 2.30 (s, 3H), 1.44 – 1.34 (m, 1H), 1.29 (t, *J* = 7.1 Hz, 3H), 1.26 – 1.18 (m, 1H), 0.78 – 0.69 (m, 6H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.56, 164.19, 163.18, 147.32, 143.44, 140.32, 135.80, 134.46, 129.12, 127.64, 127.50, 126.55, 115.40, 64.86, 61.19, 60.72, 55.08, 27.78, 21.34, 14.16, 13.58, 9.85; MALDI-MS: Calcd for $C_{27}H_{31}NO_6S$ [M +Na]$^+$ m/z 520.1764, found: 520.1766. **(*trans*, *Z*)-3i** (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.2 Hz, 2H), 7.42 (d, *J* = 5.8 Hz, 1H), 7.33 – 7.23 (m, 7H), 6.71 (d, *J* = 5.8 Hz, 1H), 5.34 (s, 1H), 4.77 (s, 1H), 4.31 – 4.14 (m, 2H), 4.02 – 3.92 (m, 1H), 3.88 – 3.77 (m, 1H), 2.41 (s, 3H), 1.33 (t, *J* = 7.1 Hz, 3H), 1.30 – 1.15 (m, 2H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.70 (t, *J* = 7.4 Hz, 3H).

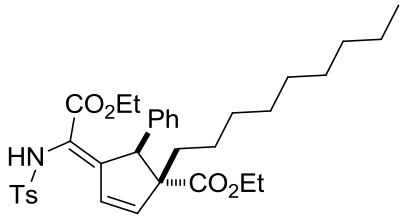


(*trans*, *E*)-3j. In 64% yield; white solid; mp 112-113 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, *J* = 8.0 Hz, 2H), 7.35 – 7.27 (m, 4H), 7.26 – 7.21 (m, 2H), 7.04 (d, *J* = 8.0 Hz, 2H), 6.62 (d, *J* = 5.6 Hz, 1H), 6.21 (s, 1H), 5.08 (s, 1H), 4.25 – 4.10 (m, 2H), 3.68 – 3.57 (m, 1H), 3.56 – 3.45 (m, 1H), 2.30 (s, 3H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.24 – 1.07 (m, 4H), 0.72 (t, *J* = 7.1 Hz, 3H), 0.61 (t, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.52, 164.06, 163.14, 147.65, 143.35, 140.18, 135.77, 134.29, 129.04, 127.54, 127.45, 126.49, 115.41, 64.40, 61.10, 60.64, 54.98, 36.56, 21.27, 18.72, 14.20, 14.08, 13.52; MALDI-MS: Calcd for $C_{28}H_{33}NO_6S$ [M +Na]$^+$ m/z 534.1921, found: 534.1922. **(*trans*, *Z*)-3j** (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.1 Hz, 2H), 7.41 (d, *J* = 5.8 Hz, 1H), 7.34 – 7.21 (m, 7H), 6.68 (d, *J* = 5.8 Hz, 1H), 5.34 (s, 1H), 4.76 (s, 1H), 4.29 – 4.13 (m, 2H), 4.02 – 3.92 (m, 1H), 3.88 – 3.78 (m, 1H), 2.41 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.22 – 1.14 (m, 2H), 1.07 (t, *J* = 7.1 Hz, 3H), 1.03 – 0.97 (m, 2H), 0.62 (t, *J* = 6.0 Hz, 3H).

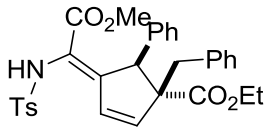


(*trans*, *E*)-3k. In 75% yield; white solid; mp 86-88 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.2 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.26 – 7.20 (m, 2H), 7.04 (d, *J* = 8.1 Hz, 2H), 6.62 (d, *J* = 5.7 Hz, 1H), 6.12 (s, 1H), 5.09 (s, 1H), 4.27 – 4.12 (m, 2H), 3.66 – 3.57 (m, 1H), 3.56 – 3.42 (m, 1H), 2.30 (s, 3H), 1.35 – 1.23 (m, 4H), 1.17 – 0.90 (m, 5H), 0.73 (t, *J* = 7.1 Hz, 3H), 0.66 (t, *J* = 7.0 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.56, 164.25, 163.22, 147.94, 143.45, 140.20, 135.78, 134.38, 129.13, 127.61, 127.55, 126.59, 115.43, 64.44, 61.19, 60.74, 54.95, 34.02, 27.46, 22.76, 21.36, 14.16, 13.63, 13.53; MALDI-MS: Calcd for $C_{29}H_{35}NO_6S$ [M +Na]$^+$ m/z 548.2077, found: 548.2073. **(*trans*, *Z*)-3k** (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 5.8 Hz, 1H), 7.29 – 7.22 (m, 7H), 6.68 (d, *J* = 5.8 Hz, 1H), 5.34 (s, 1H), 4.78 (s, 1H), 4.27 – 4.15 (m, 2H), 4.02 – 3.93 (m, 1H), 3.88 – 3.78 (m, 1H), 2.41 (s, 3H), 1.32 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H), 1.02 – 0.77 (m, 6H), 0.66

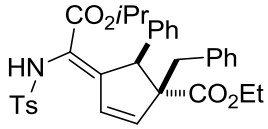
(t, *J* = 7.1 Hz, 3H).



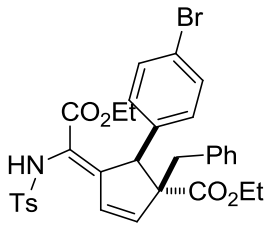
(*trans*, *E*)-3l. In 68% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J* = 8.3 Hz, 2H), 7.33 – 7.26 (m, 4H), 7.26 – 7.21 (m, 2H), 7.03 (d, *J* = 8.1 Hz, 2H), 6.62 (d, *J* = 5.7 Hz, 1H), 6.16 (s, 1H), 5.10 (s, 1H), 4.27 – 4.09 (m, 2H), 3.68 – 3.57 (m, 1H), 3.55 – 3.45 (m, 1H), 2.30 (s, 3H), 1.33 – 1.22 (m, 8H), 1.21 – 1.13 (m, 4H), 1.13 – 0.97 (m, 7H), 0.86 (t, *J* = 7.1 Hz, 3H), 0.73 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.50, 164.22, 163.18, 147.91, 143.39, 140.17, 135.76, 134.33, 129.08, 127.57, 127.51, 126.55, 115.41, 64.47, 61.14, 60.69, 54.87, 34.30, 31.72, 29.62, 29.20, 29.07, 28.99, 25.28, 22.56, 21.32, 14.13, 14.02, 13.59; MALDI-MS: Calcd for $C_{34}H_{45}NO_6S$ [M +Na]$^+$ m/z 618.2860, found: 618.2852.



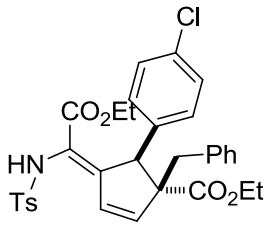
(*trans*, *E*)-3m. In 66% yield; white solid; mp 170-171 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.2 Hz, 2H), 7.44 (br s, 1H), 7.35 (t, *J* = 7.6 Hz, 2H), 7.30 – 7.23 (m, 3H), 7.23 – 7.14 (m, 3H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.97 (dd, *J* = 7.6, 1.3 Hz, 2H), 6.59 (d, *J* = 5.8 Hz, 1H), 6.09 (s, 1H), 5.04 (s, 1H), 4.11 – 3.97 (m, 2H), 3.04 (s, 3H), 2.67 (d, *J* = 13.5 Hz, 1H), 2.32 (s, 3H), 2.23 (d, *J* = 13.5 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.62, 164.47, 163.50, 147.19, 143.57, 140.22, 137.13, 135.85, 134.06, 131.45, 129.65, 129.17, 128.12, 127.98, 127.49, 126.80, 126.59, 115.27, 64.97, 61.23, 56.17, 51.29, 41.95, 21.41, 13.86; MALDI-MS: Calcd for $C_{31}H_{31}NO_6S$ [M +Na]$^+$ m/z 568.1764, found: 568.1770.



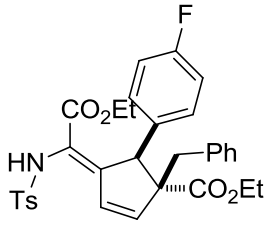
(*trans*, *E*)-3n. In 70% yield; white solid; mp 70-71 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 8.3 Hz, 2H), 7.47 (br s, 1H), 7.39 – 7.30 (m, 4H), 7.29 – 7.24 (m, 1H), 7.23 – 7.15 (m, 3H), 7.08 (d, *J* = 8.1 Hz, 2H), 7.02 – 6.95 (m, 2H), 6.54 (d, *J* = 5.8 Hz, 1H), 6.25 (s, 1H), 5.06 (s, 1H), 4.54 – 4.46 (m, 1H), 4.14 – 3.96 (m, 2H), 2.70 (d, *J* = 13.4 Hz, 1H), 2.30 (s, 3H), 2.16 (d, *J* = 13.4 Hz, 1H), 1.11 (t, *J* = 7.1 Hz, 3H), 0.84 (d, *J* = 6.3 Hz, 3H), 0.60 (d, *J* = 6.2 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.66, 162.99, 162.89, 146.29, 143.48, 140.46, 137.17, 136.08, 134.34, 131.75, 129.64, 129.20, 128.08, 127.89, 127.55, 126.74, 126.55, 115.88, 68.97, 64.85, 61.11, 56.09, 42.09, 21.31, 21.22, 20.80, 13.84; MALDI-MS: Calcd for $C_{33}H_{35}NO_6S$ [M +Na]$^+$ m/z 596.2077, found: 596.2072.



(*trans, E*)-3o. In 69% yield; white solid; mp 141-142 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 8.5 Hz, 2H), 7.35 (br s, 1H), 7.28 (d, *J* = 5.8 Hz, 1H), 7.24 – 7.15 (m, 4H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.96 (dd, *J* = 7.7, 1.5 Hz, 2H), 6.56 (d, *J* = 5.8 Hz, 1H), 6.24 (s, 1H), 5.04 (s, 1H), 4.10 – 3.98 (m, 2H), 3.69 – 3.58 (m, 1H), 3.55 – 3.43 (m, 1H), 2.65 (d, *J* = 13.4 Hz, 1H), 2.33 (s, 3H), 2.22 (d, *J* = 13.4 Hz, 1H), 1.09 (t, *J* = 7.1 Hz, 3H), 0.75 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.34, 163.33, 162.83, 146.68, 143.64, 139.40, 136.75, 135.99, 134.02, 133.21, 130.98, 129.50, 129.22, 128.10, 127.36, 126.63, 120.54, 115.63, 64.73, 61.24, 60.80, 55.36, 42.08, 21.34, 13.77, 13.56; MALDI-MS: Calcd for $C_{32}H_{32}BrNO_6S$ $[M+Na]^+$ m/z 660.1026, found: 660.1032. **(*trans, Z*)-3o** (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.59 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 5.9 Hz, 1H), 7.38 (br s, 2H), 7.27 – 7.16 (m, 6H), 6.94 (dd, *J* = 7.6, 1.6 Hz, 2H), 6.81 (br s, 1H), 6.58 (d, *J* = 5.9 Hz, 1H), 5.45 (s, 1H), 5.02 (s, 1H), 4.22 – 4.06 (m, 2H), 3.99 – 3.88 (m, 1H), 3.81 – 3.70 (m, 1H), 2.55 (d, *J* = 13.3 Hz, 1H), 2.40 (s, 3H), 2.15 (d, *J* = 13.3 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H).

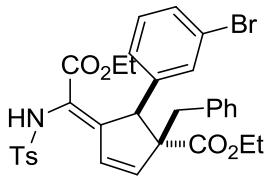


(*trans, E*)-3p. In 60% yield; white solid; mp 138-140 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, *J* = 8.3 Hz, 2H),7.40 (br s, 1H), 7.35 – 7.26 (m, 4H), 7.25 – 7.17 (m, 3H), 7.12 (d, *J* = 8.1 Hz, 2H), 6.96 (dd, *J* = 7.6, 1.5 Hz, 2H), 6.57 (d, *J* = 5.8 Hz, 1H), 6.15 (s, 1H), 5.04 (s, 1H), 4.09 – 3.96 (m, 2H), 3.70 – 3.60 (m, 1H), 3.55 – 3.44 (m, 1H), 2.65 (d, *J* = 13.4 Hz, 1H), 2.34 (s, 3H), 2.21 (d, *J* = 13.4 Hz, 1H), 1.09 (t, *J* = 7.1 Hz, 3H), 0.75 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.47, 163.53, 162.93, 146.82, 143.76, 138.95, 136.84, 136.02, 134.09, 132.54, 129.58, 129.30, 128.18, 128.11, 127.43, 126.71, 115.64, 64.87, 61.32, 60.89, 55.39, 42.13, 21.41, 13.84, 13.63; MALDI-MS: Calcd for $C_{32}H_{32}ClNO_6S$ $[M+Na]^+$ m/z 616.1531, found: 616.1533. **(*trans, Z*)-3p** (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.60 (d, *J* = 8.3 Hz, 2H), 7.48 (d, *J* = 5.9 Hz, 1H), 7.39 (s, 2H), 7.26 – 7.17 (m, 6H), 6.94 (dd, *J* = 7.6, 1.7 Hz, 2H), 6.87 (br s, 1H), 6.58 (d, *J* = 5.9 Hz, 1H), 5.45 (s, 1H), 5.03 (s, 1H), 4.22 – 4.07 (m, 2H), 3.99 – 3.90 (m, 1H), 3.81 – 3.71 (m, 1H), 2.56 (d, *J* = 13.3 Hz, 1H), 2.40 (s, 3H), 2.15 (d, *J* = 13.3 Hz, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.03 (t, *J* = 7.1 Hz, 3H).

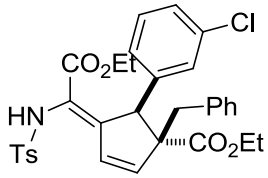


(*trans, E*)-3q. In 49% yield; yellow semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, *J* = 8.1 Hz, 2H), 7.42 (br s, 1H), 7.33 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 7.11 (d, *J* = 8.2 Hz, 2H), 7.04 (t, *J* = 8.4 Hz, 2H), 6.97 (d, *J* = 6.9 Hz, 2H), 6.56 (d, *J* = 5.8 Hz, 1H), 6.28 (s, 1H), 5.07 (s, 1H), 4.13 – 3.96 (m, 2H), 3.70 – 3.58 (m, 1H), 3.56 – 3.43 (m, 1H), 2.66 (d, *J* = 13.4 Hz, 1H), 2.32 (s, 3H), 2.21 (d, *J* = 13.5 Hz, 1H), 1.09 (t, *J* = 7.1 Hz, 3H), 0.74 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.43, 163.68, 162.91, 161.56 (d, *J* = 245.3 Hz), 146.62, 143.56, 136.87, 136.19 (d, *J* = 3.1 Hz), 136.03, 134.00, 133.01, 129.49, 129.15, 128.07, 127.35, 126.57, 115.57, 114.65 (d, *J* = 21.4 Hz), 64.82, 61.17, 60.73, 55.17, 42.03, 21.27, 13.75, 13.52; MALDI-MS: Calcd for $C_{32}H_{32}FNO_6S$ $[M+Na]^+$ m/z 600.1827,

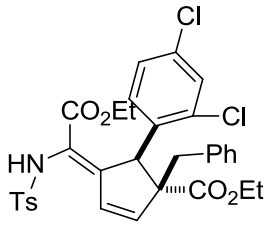
found: 600.1825.



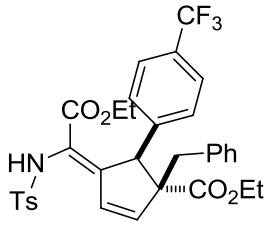
(*trans*, *E*)-3r. In 70% yield; white solid; mp 144-146 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 (d, *J* = 6.8 Hz, 1H), 7.57 (br s, 1H), 7.50 (d, *J* = 5.6 Hz, 1H), 7.42 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 4.6 Hz, 1H), 7.26 – 7.07 (m, 6H), 6.99 (br s, 2H), 6.57 (d, *J* = 5.7 Hz, 1H), 6.18 (br s, 1H), 5.01 (s, 1H), 4.10 – 3.96 (m, 2H), 3.71 – 3.61 (m, 1H), 3.60 – 3.42 (br, 1H), 2.67 (d, *J* = 13.3 Hz, 1H), 2.33 (s, 3H), 2.30 – 2.15 (br, 1H), 1.09 (t, *J* = 6.2 Hz, 3H), 0.82 – 0.64 (br, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 203.04, 174.41, 163.21, 162.79, 146.69, 143.65, 143.02, 136.76, 136.09, 134.40, 134.10, 130.09, 129.91, 129.62, 129.50, 129.28, 128.17, 127.56, 126.73, 126.01, 122.34, 115.87, 64.87, 61.33, 60.83, 55.67, 42.42, 21.40, 13.83, 13.57; MALDI-MS: Calcd for $C_{32}H_{32}BrNO_6S$ [M +Na]$^+$ m/z 660.1026, found: 660.1021.



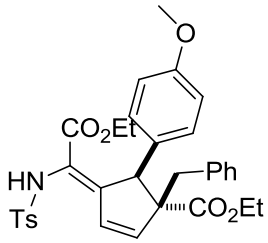
(*trans*, *E*)-3s. In 67% yield; white solid; mp 138-139 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, *J* = 5.6 Hz, 1H), 7.51 (br s, 1H), 7.40 (d, *J* = 16.5 Hz, 1H), 7.33 – 7.23 (m, 4H), 7.23 – 7.07 (m, 5H), 6.99 (br s, 2H), 6.57 (d, *J* = 5.8 Hz, 1H), 6.15 (s, 1H), 5.02 (br s, 1H), 4.11 – 3.97 (m, 2H), 3.73 – 3.61 (m, 1H), 3.50 (br s, 1H), 2.68 (d, *J* = 13.4 Hz, 1H), 2.33 (s, 3H), 2.30 – 2.14 (br, 1H), 1.10 (t, *J* = 7.0 Hz, 3H), 0.81 – 0.66 (br, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.44, 163.22, 162.87, 146.72, 143.69, 142.78, 136.80, 136.04, 134.12, 131.55, 129.65, 129.28, 129.21, 128.19, 127.55, 127.30, 126.98, 126.75, 125.58, 115.86, 64.87, 61.34, 60.86, 55.67, 42.41, 21.42, 13.85, 13.59; MALDI-MS: Calcd for $C_{32}H_{32}ClNO_6S$ [M +Na]$^+$ m/z 616.1531, found: 616.1530.



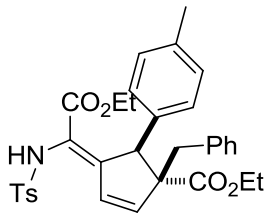
(*trans*, *E*)-3t. In 53% yield; white solid; mp 143-145 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (d, *J* = 8.3 Hz, 2H), 7.46 (d, *J* = 1.8 Hz, 1H), 7.34 (d, *J* = 5.8 Hz, 1H), 7.30 – 7.27 (m, 2H), 7.25 – 7.16 (m, 3H), 7.11 (d, *J* = 8.1 Hz, 2H), 7.02 (dd, *J* = 7.7, 1.4 Hz, 2H), 6.57 (d, *J* = 5.8 Hz, 1H), 6.20 (s, 1H), 5.48 (s, 1H), 4.09 – 4.00 (m, 2H), 3.85 – 3.74 (m, 1H), 3.63 – 3.52 (m, 1H), 2.87 (d, *J* = 13.2 Hz, 1H), 2.33 (s, 3H), 2.17 (d, *J* = 13.2 Hz, 1H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.72 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.60, 163.20, 162.94, 147.08, 143.81, 137.81, 136.68, 136.07, 135.95, 134.42, 133.16, 130.49, 129.90, 129.32, 129.10, 128.18, 127.38, 126.92, 126.76, 115.95, 65.21, 61.37, 61.22, 51.91, 40.13, 21.39, 13.83, 13.67; MALDI-MS: Calcd for $C_{32}H_{31}Cl_2NO_6S$ [M +Na]$^+$ m/z 650.1141, found: 650.1137.



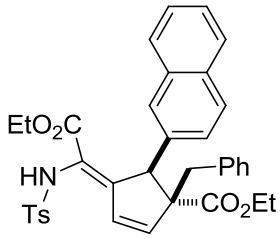
(*trans*, *E*)-3u. In 52% yield; yellow semi-solid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.66 – 7.54 (m, 3H), 7.49 (d, *J* = 8.3 Hz, 2H), 7.42 (br s, 1H), 7.31 (d, *J* = 5.7 Hz, 1H), 7.24 – 7.17 (m, 3H), 7.08 (d, *J* = 8.1 Hz, 2H), 6.95 (dd, *J* = 7.5, 1.7 Hz, 2H), 6.60 (d, *J* = 5.8 Hz, 1H), 6.16 (s, 1H), 5.13 (s, 1H), 4.15 – 3.99 (m, 2H), 3.69 – 3.58 (m, 1H), 3.54 – 3.36 (m, 1H), 2.63 (d, *J* = 13.4 Hz, 1H), 2.32 (s, 3H), 2.24 (d, *J* = 13.4 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.71 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.32, 163.21, 162.79, 146.87, 144.51, 143.84, 136.64, 135.94, 134.13, 131.92, 129.53, 129.25, 129.02 (d, *J* = 32.6 Hz), 128.22, 127.43, 126.78, 124.83, 124.16 (d, *J* = 271.9 Hz),115.81, 64.85, 61.43, 60.91, 55.61, 42.17, 21.37, 13.84, 13.56; MALDI-MS: Calcd for $C_{33}H_{32}F_3NO_6S$ $[M+Na]^+$ m/z 650.1795, found: 650.1797.



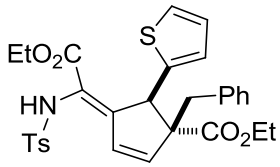
(*trans*, *E*)-3v. In 78% yield; white solid; mp 157-158 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.2 Hz, 2H), 7.35 (br s, 1H), 7.29 (d, *J* = 5.8 Hz, 1H), 7.24 – 7.14 (m, 4H), 7.09 (d, *J* = 8.1 Hz, 2H), 6.98 (d, *J* = 6.5 Hz, 2H), 6.89 (d, *J* = 8.8 Hz, 2H), 6.55 (d, *J* = 5.8 Hz, 1H), 6.12 (s, 1H), 5.01 (s, 1H), 4.10 – 3.97 (m, 2H), 3.82 (s, 3H), 3.69 – 3.58 (m, 1H), 3.56 – 3.45 (m, 1H), 2.68 (d, *J* = 13.5 Hz, 1H), 2.32 (s, 3H), 2.21 (d, *J* = 13.5 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.75 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.74, 164.23, 163.19, 158.35, 146.83, 143.56, 137.29, 136.04, 134.15, 132.65, 129.66, 129.23, 128.11, 127.52, 126.56, 115.37, 113.29, 65.09, 61.16, 60.80, 55.50, 55.25, 41.99, 21.41, 13.87, 13.67; MALDI-MS: Calcd for $C_{33}H_{35}NO_7S$ $[M+Na]^+$ m/z 612.2026, found: 612.2024.



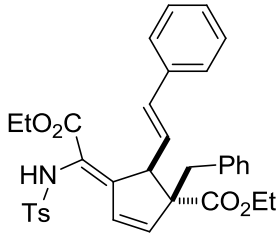
(*trans*, *E*)-3w. In 75% yield; white solid; mp 159-160 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.35 (br s, 1H), 7.29 (d, *J* = 5.8 Hz, 1H), 7.23 – 7.13 (m, 6H), 7.08 (d, *J* = 8.0 Hz, 2H), 7.01 – 6.96 (m, 2H), 6.55 (d, *J* = 5.8 Hz, 1H), 6.17 (s, 1H), 5.01 (s, 1H), 4.09 – 3.98 (m, 2H), 3.66 – 3.57 (m, 1H), 3.56 – 3.45 (m, 1H), 2.68 (d, *J* = 13.5 Hz, 1H), 2.35 (s, 3H), 2.32 (s, 3H), 2.19 (d, *J* = 13.5 Hz, 1H), 1.10 (t, *J* = 7.1 Hz, 3H), 0.74 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.70, 163.95, 163.20, 146.73, 143.46, 137.26, 137.25, 136.19, 136.03, 134.15, 131.32, 129.66, 129.15, 128.58, 128.05, 127.54, 126.51, 115.41, 64.93, 61.10, 60.73, 55.87, 41.96, 21.36, 21.05, 13.83, 13.58; MALDI-MS: Calcd for $C_{33}H_{35}NO_6S$ $[M+Na]^+$ m/z 596.2077, found: 596.2072.



(*trans*, *E*)-3x. In 70% yield; white solid; mp 120-121 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 – 7.75 (m, 4H), 7.65 (d, *J* = 7.9 Hz, 1H), 7.58 – 7.43 (m, 4H), 7.42 – 7.35 (m, 1H), 7.22 – 7.11 (m, 3H), 6.95 (t, *J* = 6.9 Hz, 3H), 6.83 (d, *J* = 7.5 Hz, 1H), 6.62 (t, *J* = 6.3 Hz, 1H), 6.16 (s, 1H), 5.23 (br s, 1H), 4.16 – 3.98 (m, 2H), 3.61 – 3.50 (m, 1H), 3.50 – 3.36 (br, 1H), 2.71 (d, *J* = 13.4 Hz, 1H), 2.20 (d, *J* = 11.8 Hz, 4H), 1.12 (t, *J* = 7.1 Hz, 3H), 0.72 – 0.58 (m, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.79, 164.53, 163.68, 163.04, 146.87, 143.49, 139.12, 137.06, 136.09, 134.15, 133.16, 132.32, 130.16, 129.89, 129.66, 129.15, 128.08, 127.81, 127.61, 127.39, 126.59, 126.08, 125.82, 125.64, 115.48, 65.21, 61.26, 60.81, 56.27, 42.24, 21.29, 13.88, 13.56; MALDI-MS: Calcd for $C_{36}H_{35}NO_6S$ $[M+Na]^+$ m/z 632.2077, found: 632.2078. **(*trans*, *Z*)-3x** (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 – 7.78 (m, 3H), 7.73 (d, *J* = 7.8 Hz, 1H), 7.63 – 7.43 (m, 6H), 7.20 – 7.12 (m, 3H), 7.06 (d, *J* = 8.1 Hz, 1H), 6.92 (d, *J* = 6.3 Hz, 2H), 6.66 – 6.55 (m, 1H), 5.36 (s, 1H), 4.99 (br s, 1H), 4.22 – 4.06 (m, 3H), 4.05 – 3.93 (m, 1H), 3.91 – 3.78 (m, 1H), 2.55 (t, *J* = 12.1 Hz, 1H), 2.41 (s, 3H), 2.23 – 2.09 (m, 1H), 1.23 (t, *J* = 7.1 Hz, 3H), 1.07 (t, *J* = 7.1 Hz, 3H).



(*trans*, *E*)-3y. In 72% yield; white solid; mp 139-141 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.53 (d, *J* = 8.3 Hz, 2H), 7.25 – 7.16 (m, 5H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.03 – 6.95 (m, 4H), 6.52 (d, *J* = 5.8 Hz, 1H), 6.19 (s, 1H), 5.38 (s, 1H), 4.08 – 4.00 (m, 2H), 3.74 – 3.55 (m, 2H), 2.93 (d, *J* = 13.6 Hz, 1H), 2.51 (d, *J* = 13.6 Hz, 1H), 2.34 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H), 0.82 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.04, 163.27, 162.24, 145.93, 143.55, 142.23, 137.01, 135.94, 133.50, 129.59, 129.22, 128.09, 127.54, 126.62, 126.57, 126.16, 123.75, 115.81, 65.12, 61.26, 60.98, 51.17, 40.47, 21.37, 13.79, 13.65; MALDI-MS: Calcd for $C_{30}H_{31}NO_6S_2$ $[M+Na]^+$ m/z 565.1593; found, 565.1486. **(*trans*, *Z*)-3y** (minor): ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, *J* = 8.3 Hz, 2H), 7.40 (d, *J* = 5.9 Hz, 1H), 7.28 – 7.15 (m, 6H), 7.02 – 6.94 (m, 4H), 6.51 (d, *J* = 5.9 Hz, 1H), 5.61 (s, 1H), 5.05 (s, 1H), 4.17 – 4.05 (m, 2H), 4.02 – 3.94 (m, 1H), 3.91 – 3.80 (m, 1H), 2.78 (d, *J* = 13.3 Hz, 1H), 2.41 (s, 3H), 2.34 (d, *J* = 13.3 Hz, 1H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.08 (t, *J* = 7.1 Hz, 3H).



(*trans*, *E*)-3z. In 30% yield; yellow oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 8.2 Hz, 2H), 7.39 (d, *J* = 7.2 Hz, 2H), 7.33 (t, *J* = 7.5 Hz, 2H), 7.29 – 7.19 (m, 4H), 7.14 (t, *J* = 6.6 Hz, 3H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.61 (d, *J* = 15.9 Hz, 1H), 6.55 (d, *J* = 5.7 Hz, 1H), 6.17 – 6.07 (m, 2H), 4.80 (d, *J* = 9.2 Hz,

1H), 4.06 – 3.96 (m, 2H), 3.86 – 3.75 (m, 1H), 3.73 – 3.62 (m, 1H), 3.19 (d, *J* = 13.8 Hz, 1H), 2.97 (d, *J* = 13.8 Hz, 1H), 2.25 (s, 3H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.92 (t, *J* = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.94, 163.32, 162.56, 146.43, 143.66, 137.32, 136.92, 135.74, 133.29, 133.17, 129.64, 129.18, 128.61, 128.22, 127.71, 127.56, 127.16, 126.62, 126.15, 115.54, 64.70, 61.21, 60.98, 53.24, 40.33, 21.37, 13.85, 13.84; MALDI-MS: Calcd for $C_{34}H_{35}NO_6S$ $[M+Na]^+$ m/z 608.2077, found: 608.2072.

III. Crystal Data and ORTEP Drawings for (*trans*, *E*)-3a and (*trans*, *Z*)-3a

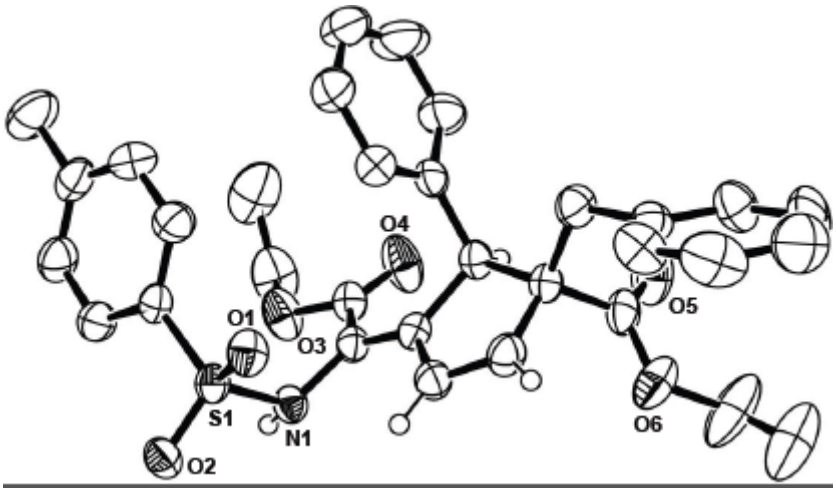


Table 1. Crystal structure data for (*trans*, *E*)-**3a**.

Identification code	(*trans*, *E*)-3a
Empirical formula	C32 H33 N O6 S
Formula weight	559.65
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.2167(16) Å α = 97.25(3)°.
	b = 8.9290(18) Å β = 94.20(3)°.
	c = 21.221(4) Å γ = 107.69(3)°.
Volume	1461.1(5) $Å^3$
Z, Calcd density	2, 1.272 Mg/m^3
Absorption coefficient	0.155 mm^{-1}
F(000)	592
Crystal size	0.20x 0.18x 0.14 mm^3
Theta range for data collection	2.69 to 27.92°
Limiting indices	-10<=h<=10, -11<=k<=11, -24<=l<=27
Reflections collected / unique	14817 / 6863 [R(int) = 0.0517]
Completeness to the θ = 27.92°	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. *trans*mission	0.9786 and 0.9696
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6863 / 7 / 369
Goodness-of-fit on F^2	1.015
Final R indices [I>2σ(I)]	R1 = 0.0510, wR2 = 0.1222
R indices (all data)	R1 = 0.0845, wR2 = 0.1390
Largest diff. peak and hole	0.343 and -0.345 e. $Å^{-3}$

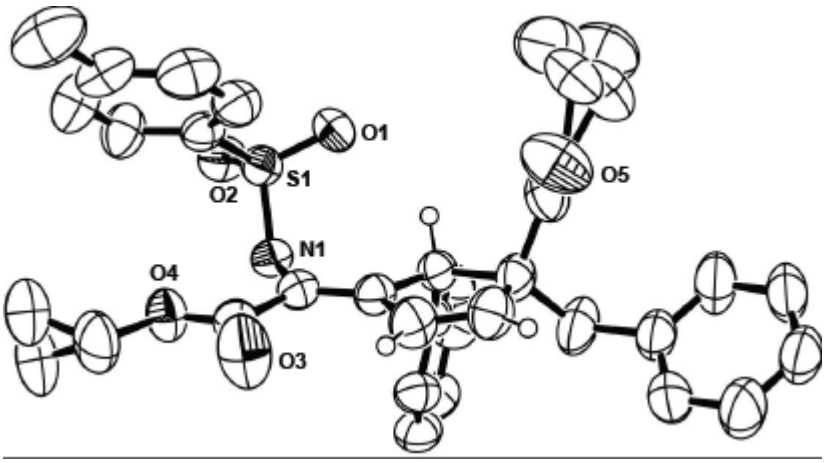
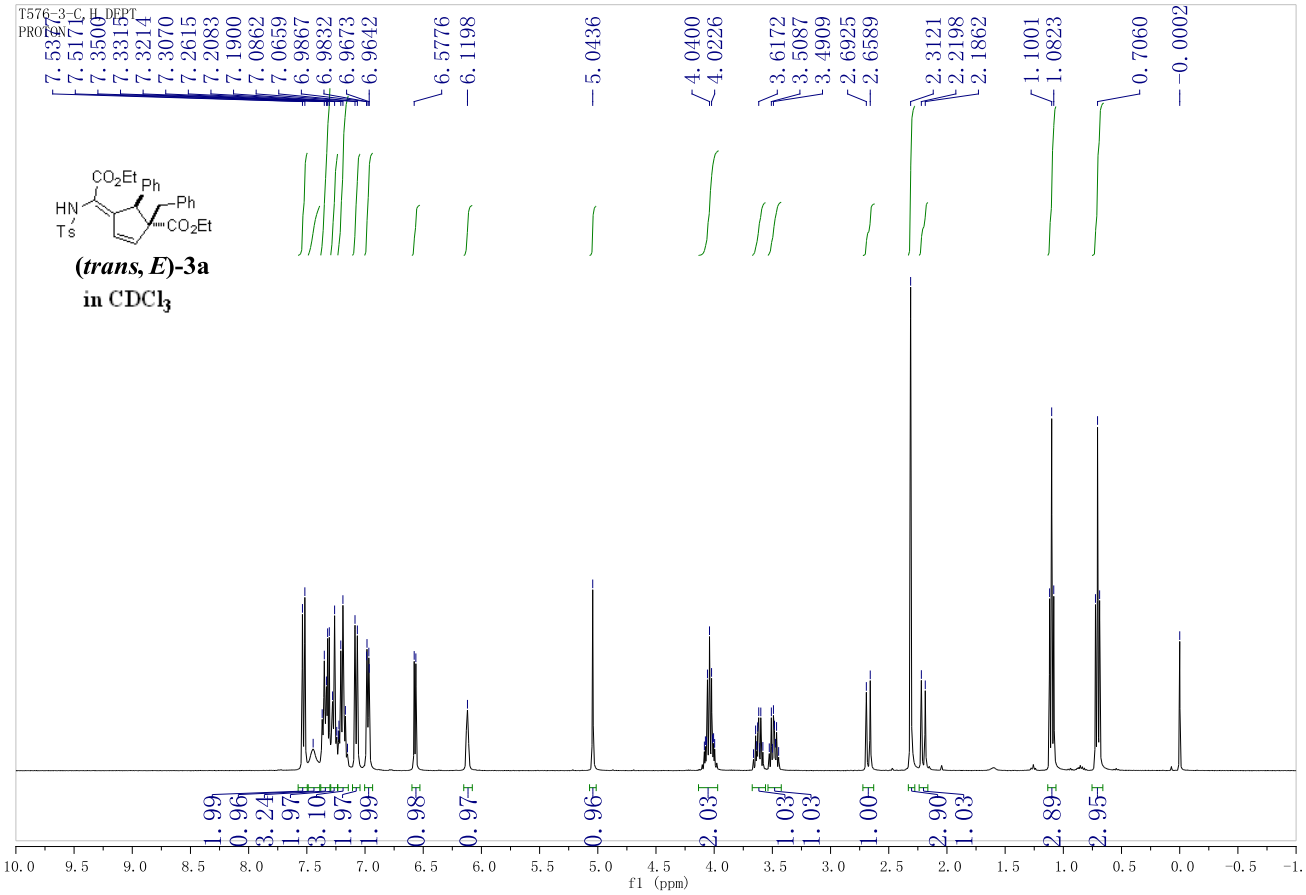
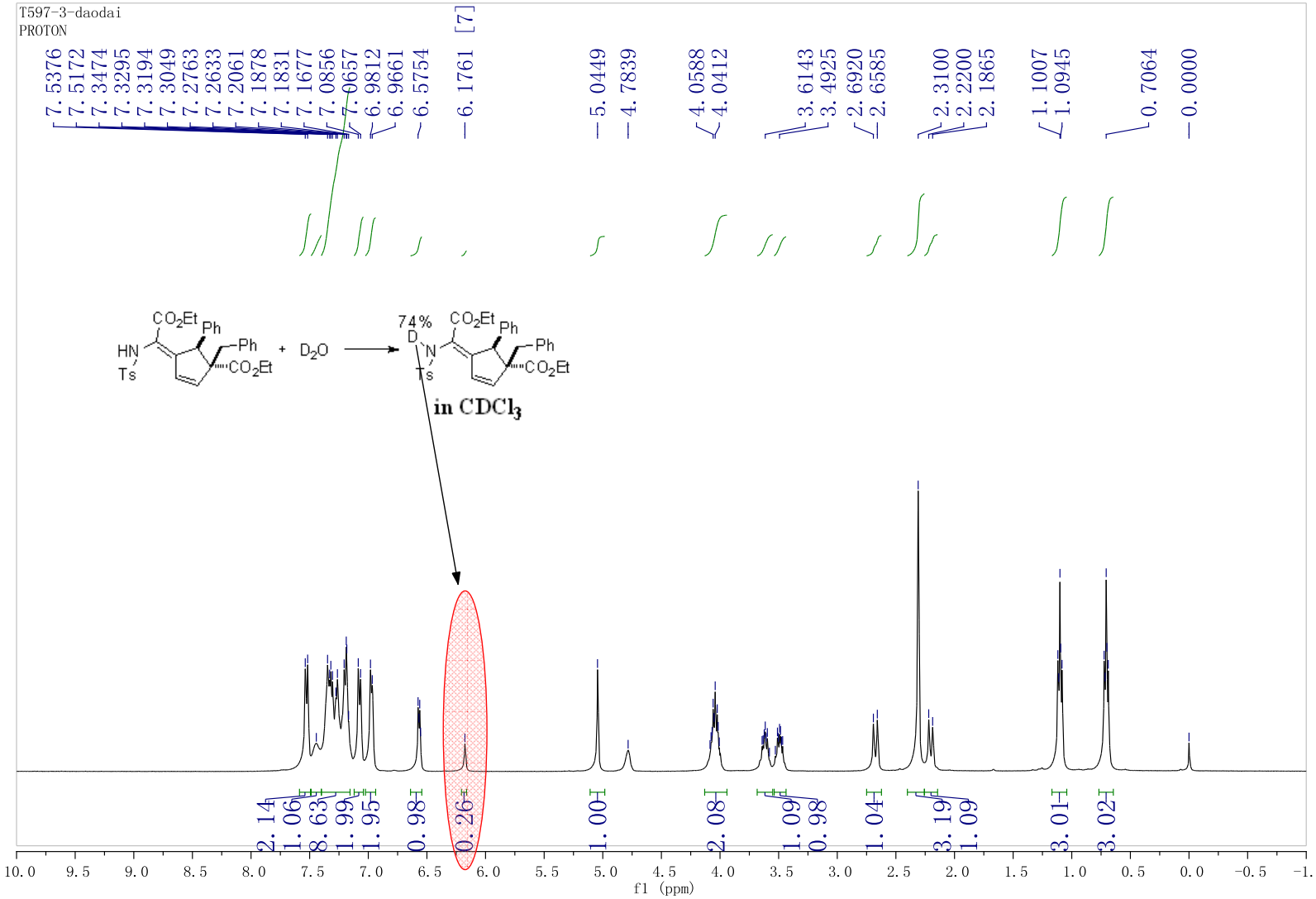


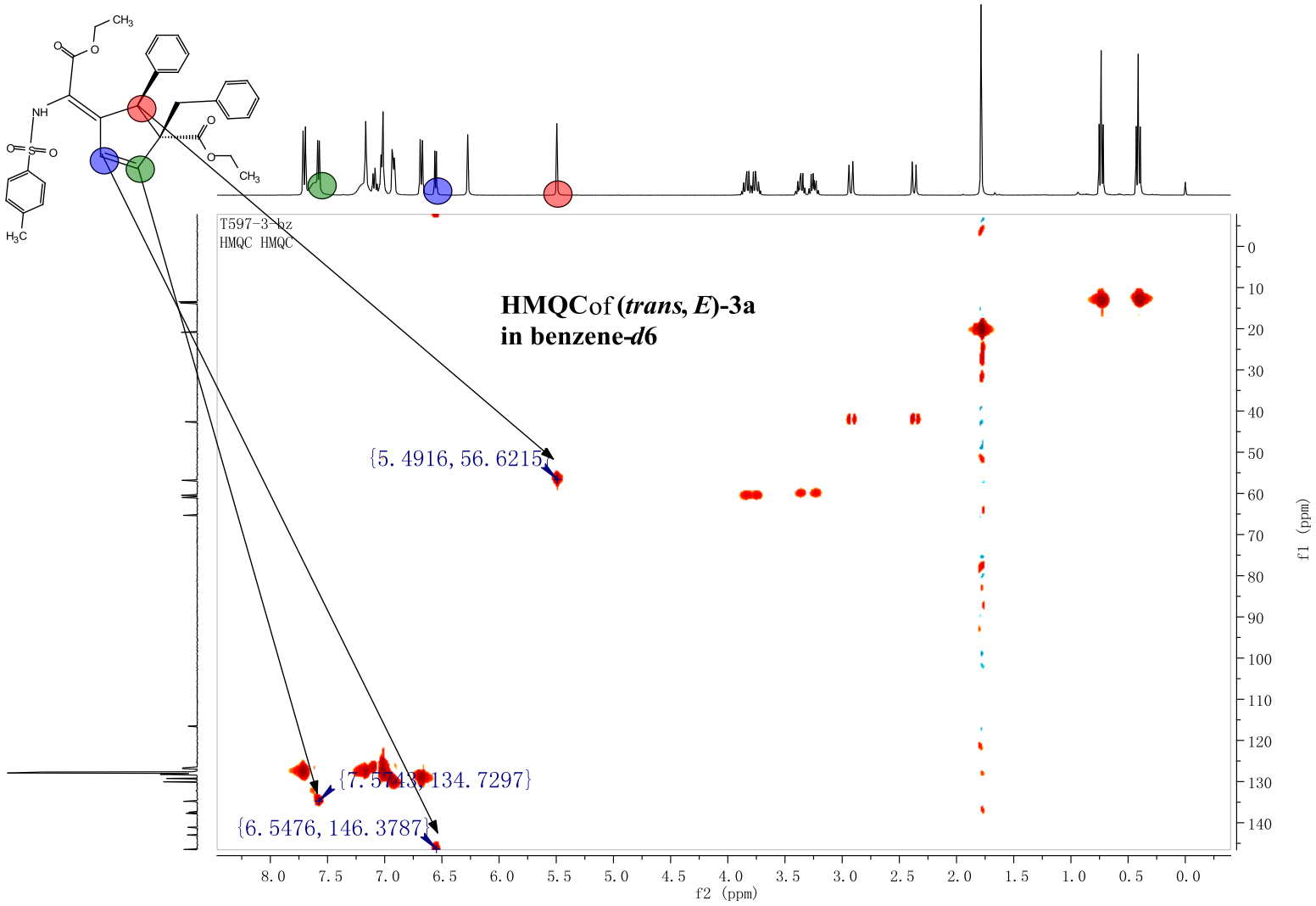
Table 2. Crystal structure data for (*trans*, *Z*)-**3a**.

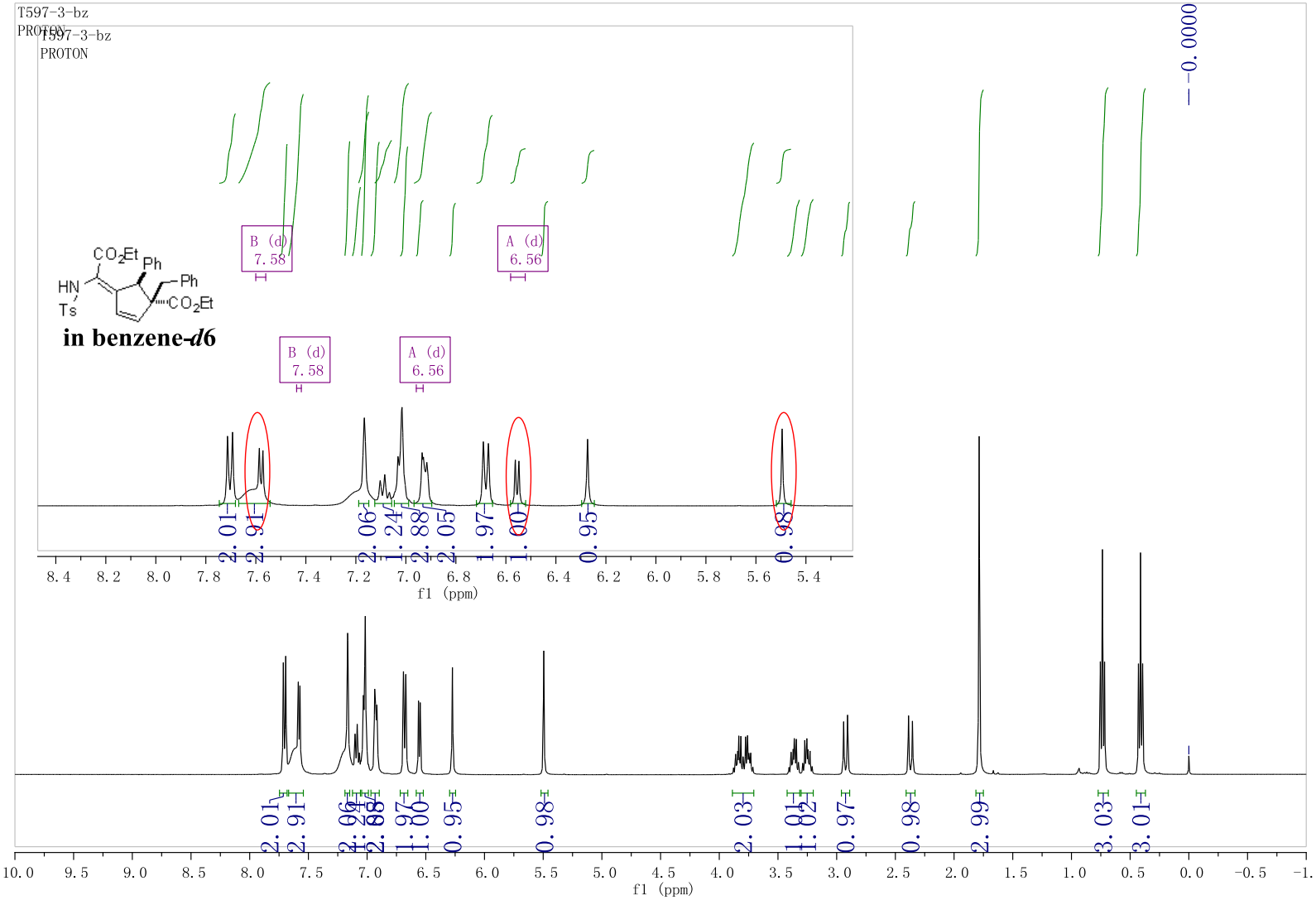
Identification code	(*trans*, *Z*)-3a
Empirical formula	C32 H32 N O6 S
Formula weight	558.65
Temperature	113(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.2454(18) Å α = 69.90(3)°.
	b = 12.053(2) Å β = 86.02(3) °.
	c = 14.310(3) Å γ = 87.63(3)°.
Volume	1493.7(5) $Å^3$
Z, Calcd density	2, 1.242 Mg/m^3
Absorption coefficient	0.152 mm^{-1}
F(000)	590
Crystal size	0.20x 0.18x 0.12 mm^3
Theta range for data collection	2.72 to 27.94°
Limiting indices	-12<=h<=11, -15<=k<=13, -18<=l<=18
Reflections collected / unique	15369 / 7008 [R(int) = 0.0385]
Completeness to the θ = 27.94°	97.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. *trans*mission	0.9820 and 0.9703
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7008 / 124 / 391
Goodness-of-fit on F^2	1.042
Final R indices [I>2σ(I)]	R1 = 0.0564, wR2 = 0.1345
R indices (all data)	R1 = 0.0998, wR2 = 0.1550
Largest diff. peak and hole	0.441 and -0.275 e. $Å^{-3}$

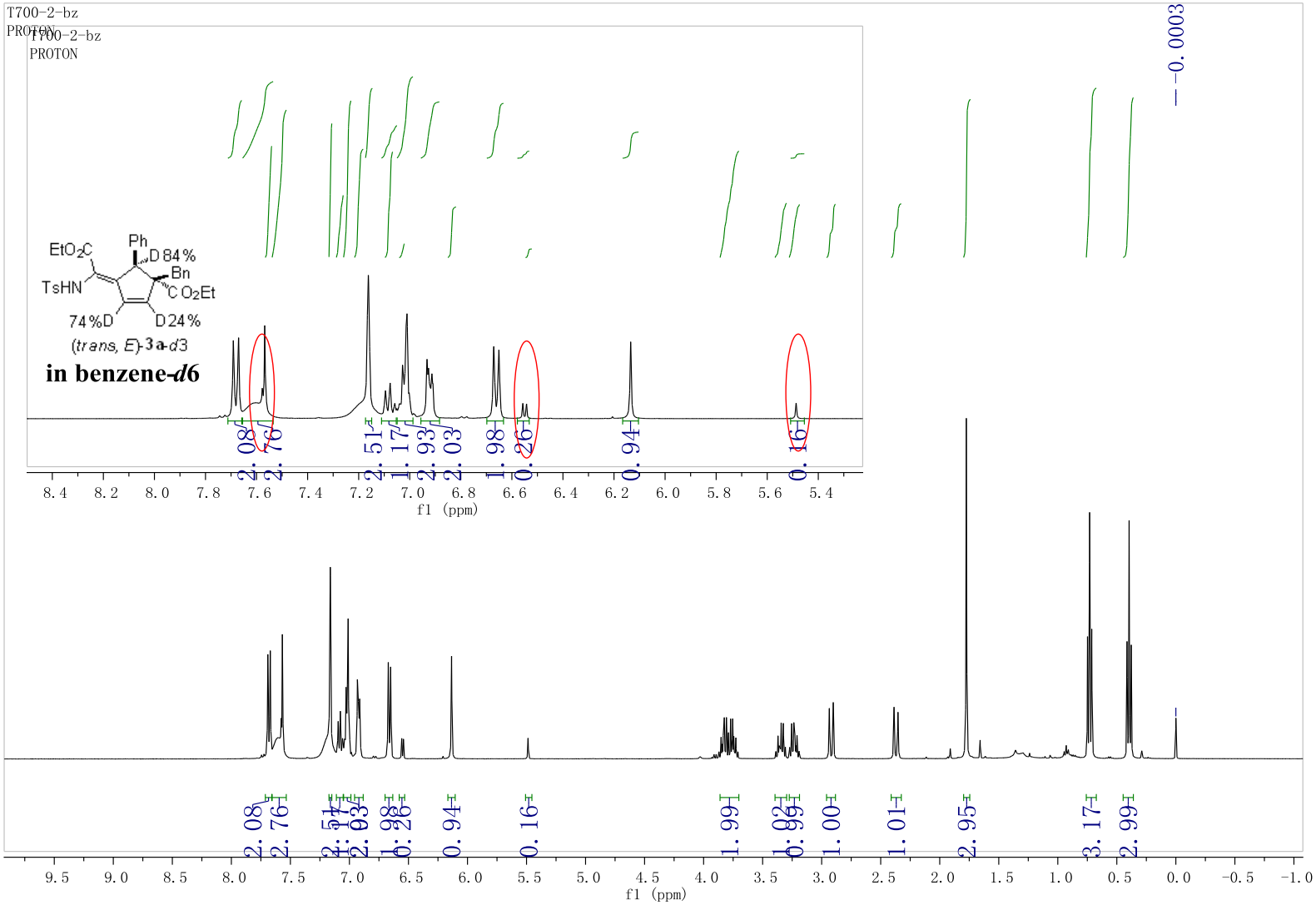
IV. NMR Signals of (*trans, E*)-3a and Deuterium-Labelling Experiment



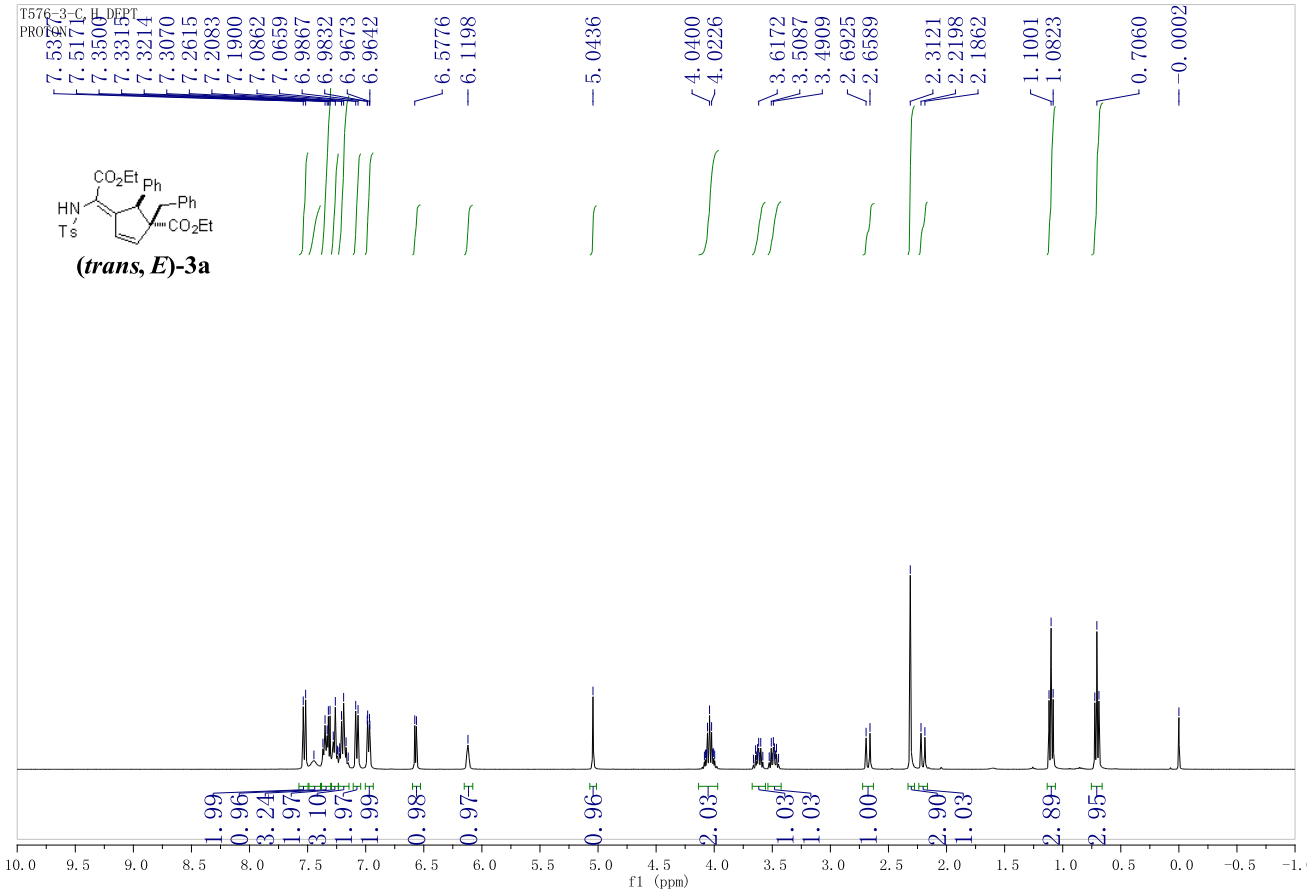

T597-3-daodai
PROTON
7.5376
7.5172
7.3474
7.3295
7.3194
7.3049
7.2763
7.2633
7.2061
7.1878
7.1831
7.1677
7.0856
7.0657
6.9812
6.9661
6.5754
6.1761
5.0449
4.7839
4.0588
4.0412
3.6143
3.4925
2.6920
2.6585
2.3100
2.2200
2.1865
1.1007
1.0945
0.7064
0.0000
CO2Et
Ph
HN
Ts
Ph
CO2Et
+ D2O
74%
D
N
Ts
in CDCl3
2.14
1.06
8.63
1.99
1.95
0.98
0.26
1.00
2.08
1.09
0.98
1.04
3.19
1.09
3.01
3.02
f1 (ppm)

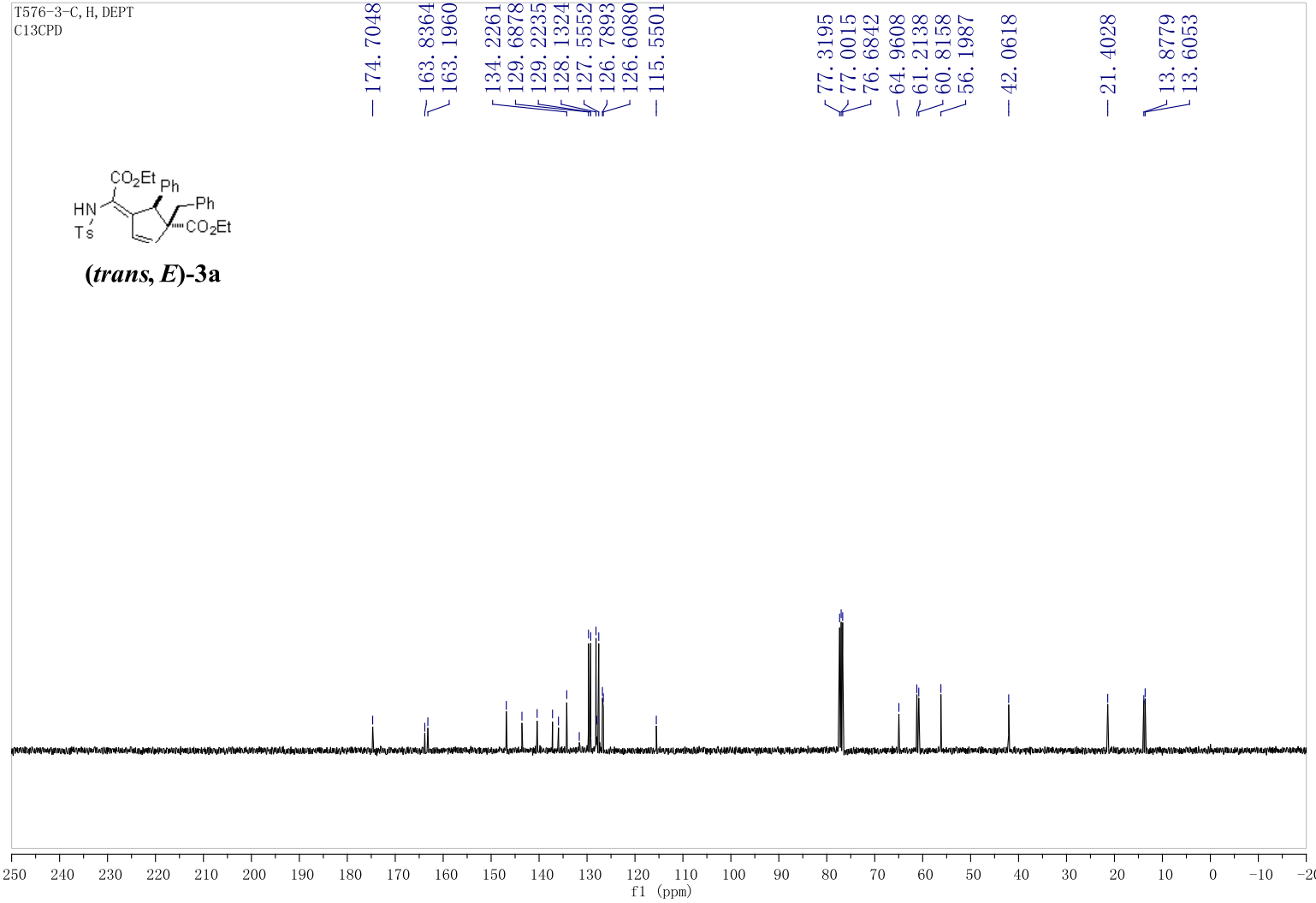

T597-3-bz
HMQC HMQC
HMQC of (trans, E)-3a
in benzene-d6
{5.4916, 56.6215}
{7.5743, 134.7297}
{6.5476, 146.3787}
f2 (ppm)
f1 (ppm)


T597-3-bz
PROTON
T597-3-bz
PROTON
B (d)
7.58
H
A (d)
6.56
H
CO2Et
Ph
HN
Ts
Ph
CO2Et
in benzene-d6
B (d)
7.58
H
A (d)
6.56
H
2.01
2.91
2.06
1.24
2.88
2.05
1.97
1.00
0.95
0.98
8.4 8.2 8.0 7.8 7.6 7.4 7.2 7.0 6.8 6.6 6.4 6.2 6.0 5.8 5.6 5.4
f1 (ppm)
2.01
2.91
2.06
1.24
2.88
2.05
1.97
1.00
0.95
0.98
2.03
1.01
1.02
0.97
0.98
2.99
3.03
3.01
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5 -1.
f1 (ppm)

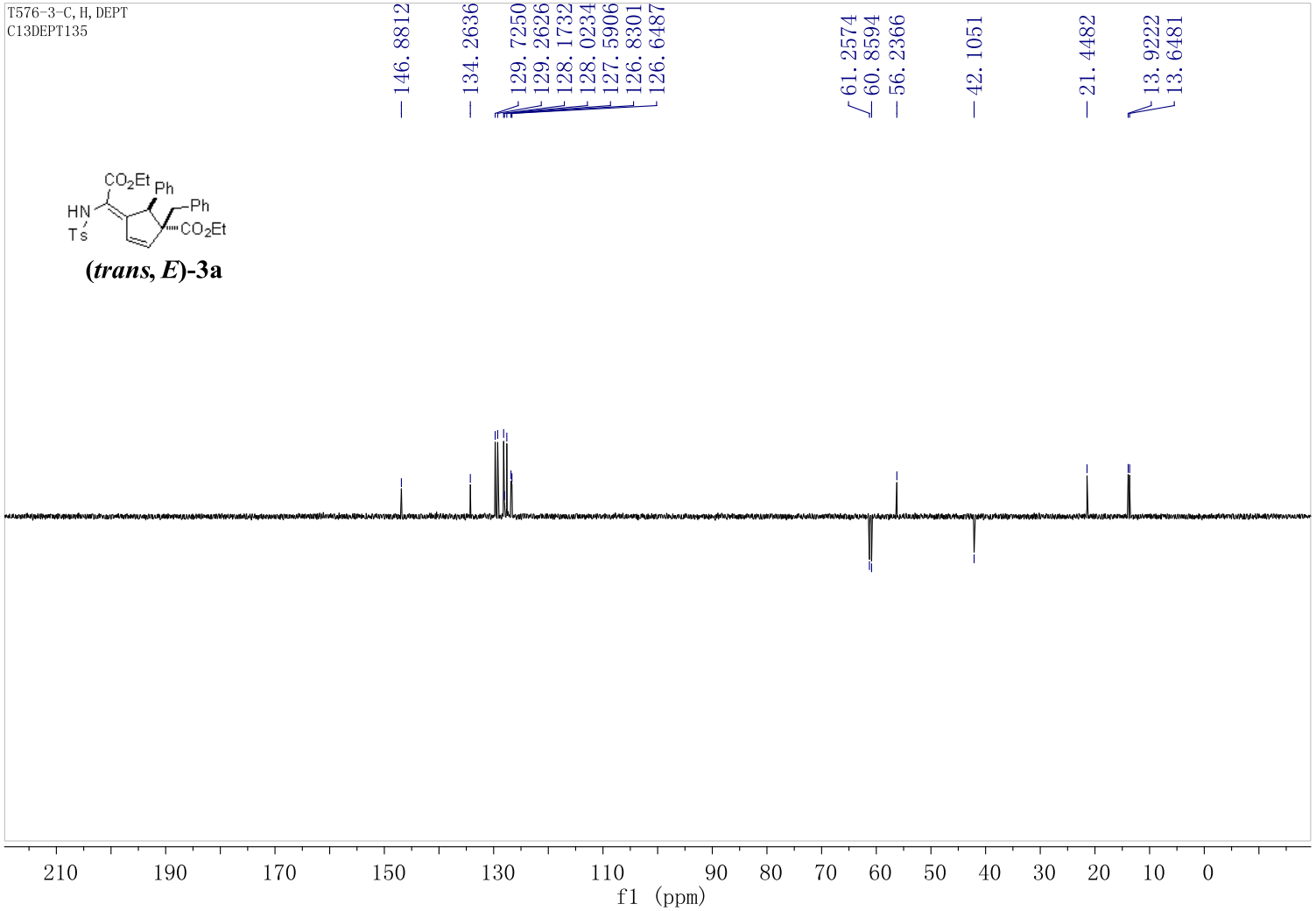

T700-2-bz
PROTON
T700-2-bz
PROTON
EtO2C
Ph
D 84%
TsHN
Bn
CO2Et
74%D
D 24%
(trans, E)-3a-d3
in benzene-d6
-0.0003
2.08
2.76
2.51
2.17
2.03
1.98
0.26
0.94
0.16
1.99
1.02
0.99
1.00
1.01
2.95
3.17
2.99
f1 (ppm)

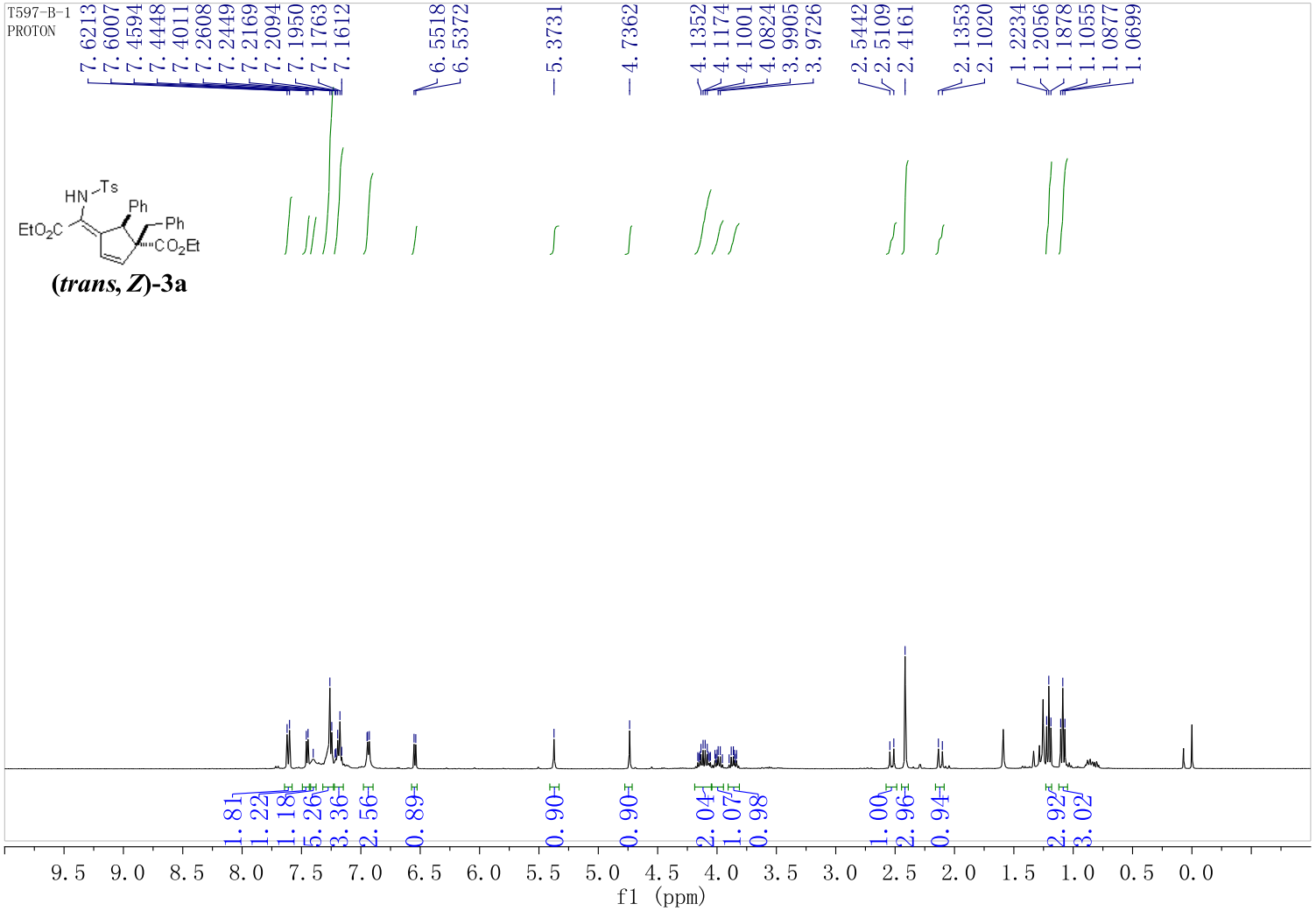
V. ^{1}H and ^{13}C NMR Spectra for Compounds 3



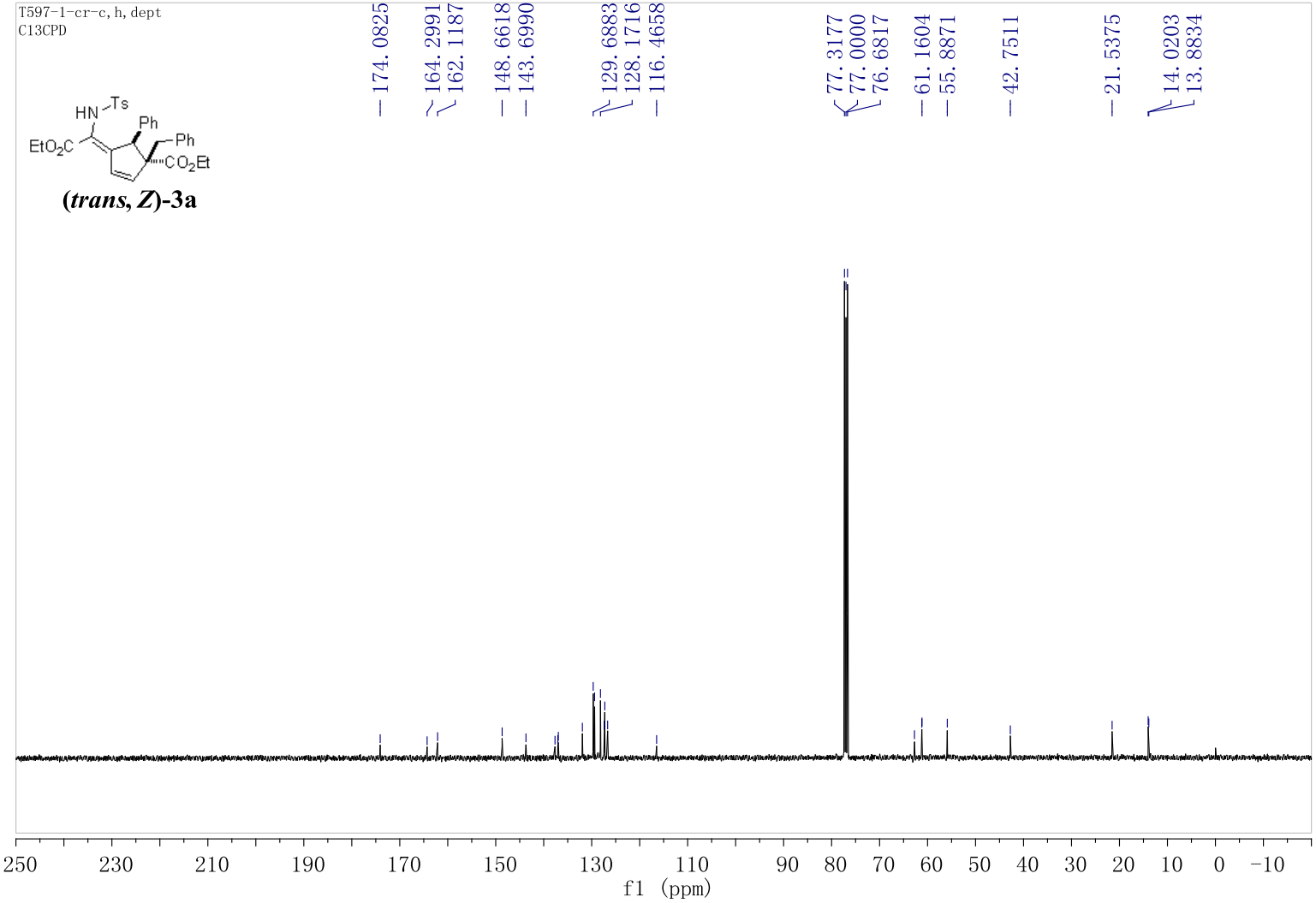

T576-3-C, H, DEPT
C13CPD
174.7048
163.8364
163.1960
134.2261
129.6878
129.2235
128.1324
127.5552
126.7893
126.6080
115.5501
77.3195
77.0015
76.6842
64.9608
61.2138
60.8158
56.1987
42.0618
21.4028
13.8779
13.6053
CO2Et
Ph
HN
Ts
Ph
CO2Et
f1 (ppm)

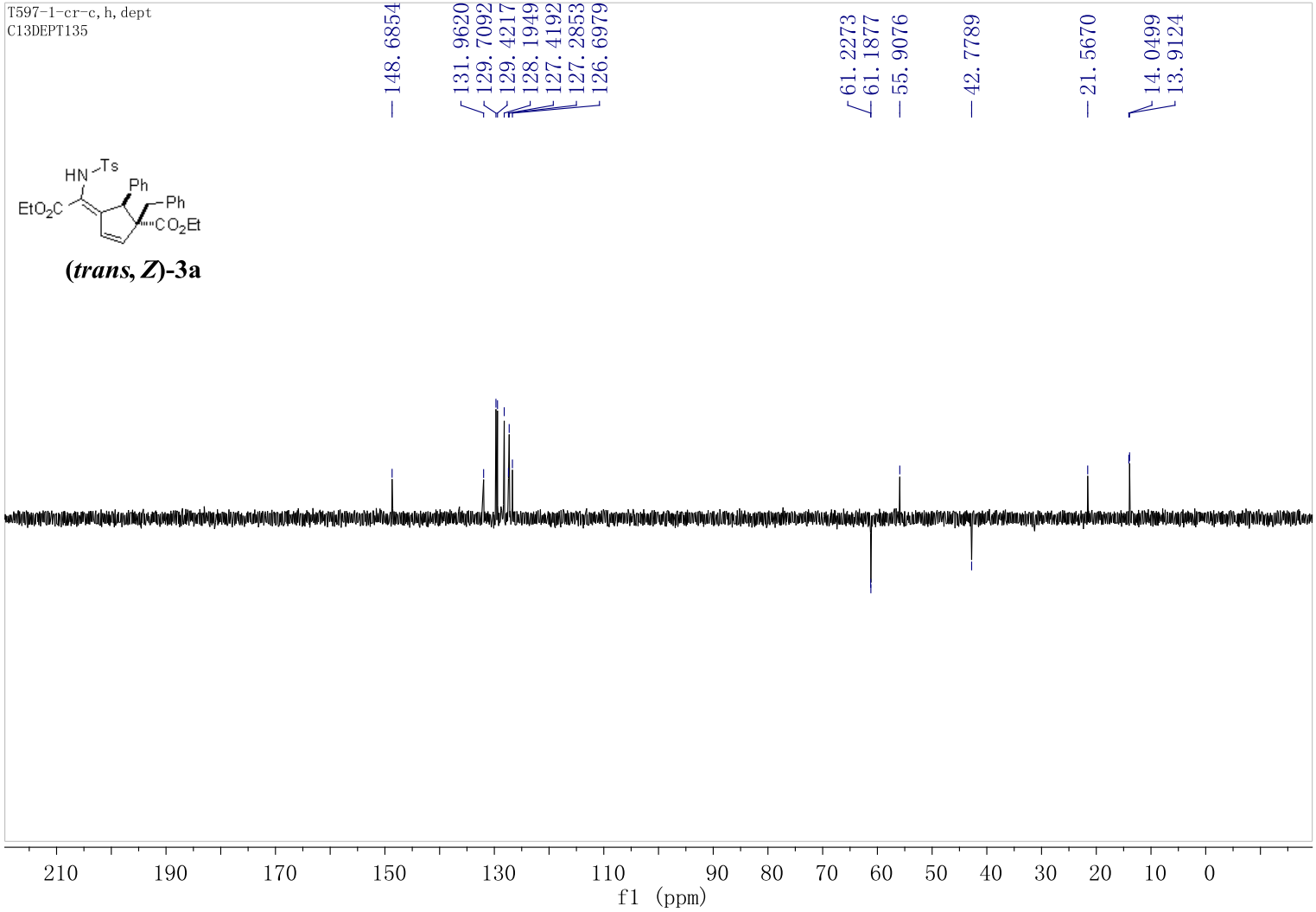
(*trans*, *E*)-3a

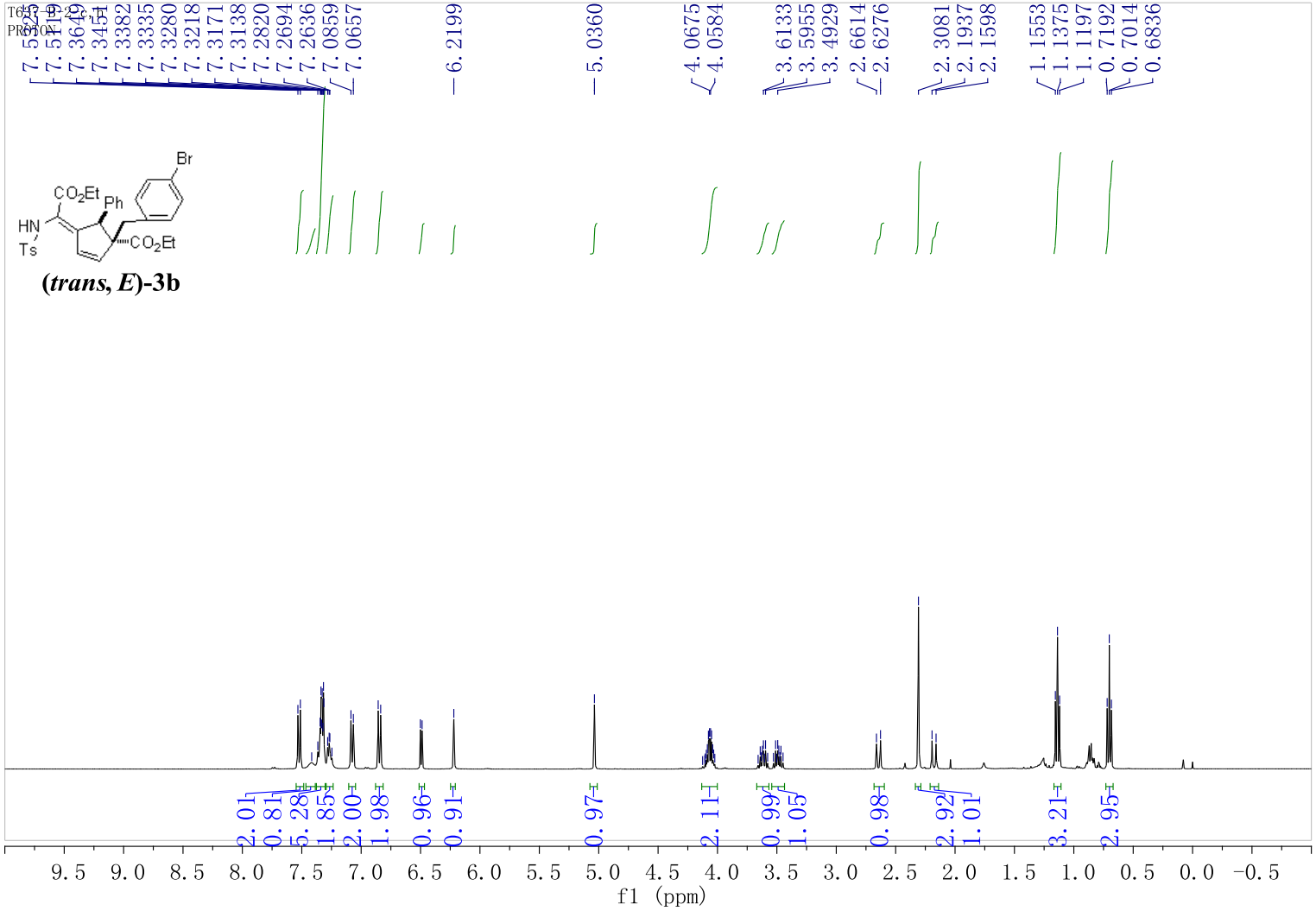

T576-3-C, H, DEPT
C13DEPT135
146.8812
134.2636
129.7250
129.2626
128.1732
128.0234
127.5906
126.8301
126.6487
61.2574
60.8594
56.2366
42.1051
21.4482
13.9222
13.6481
CO2Et
Ph
HN
Ts
Ph
CO2Et
(trans, E)-3a
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

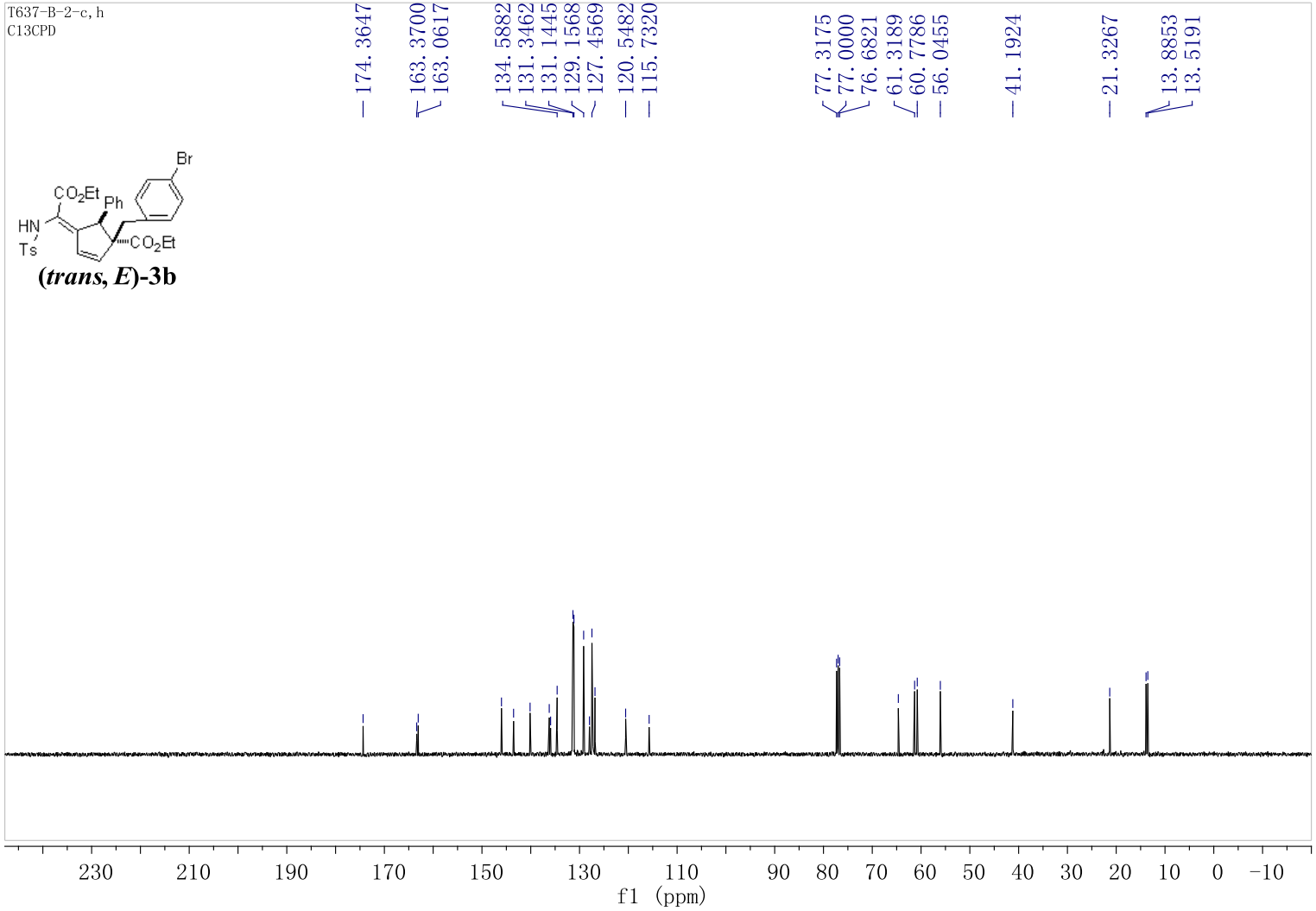

T597-B-1
PROTON
7.6213
7.6007
7.4594
7.4448
7.4011
7.2608
7.2449
7.2169
7.2094
7.1950
7.1763
7.1612
6.5518
6.5372
5.3731
4.7362
4.1352
4.1174
4.1001
4.0824
3.9905
3.9726
2.5442
2.5109
2.4161
2.1353
2.1020
1.2234
1.2056
1.1878
1.1055
1.0877
1.0699
HN
Ts
Ph
Ph
EtO2C
CO2Et
1.81
1.22
1.18
5.26
3.36
2.56
0.89
0.90
0.90
2.04
1.07
0.98
1.00
2.96
0.94
2.92
3.02
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

(*trans*, *Z*)-3a

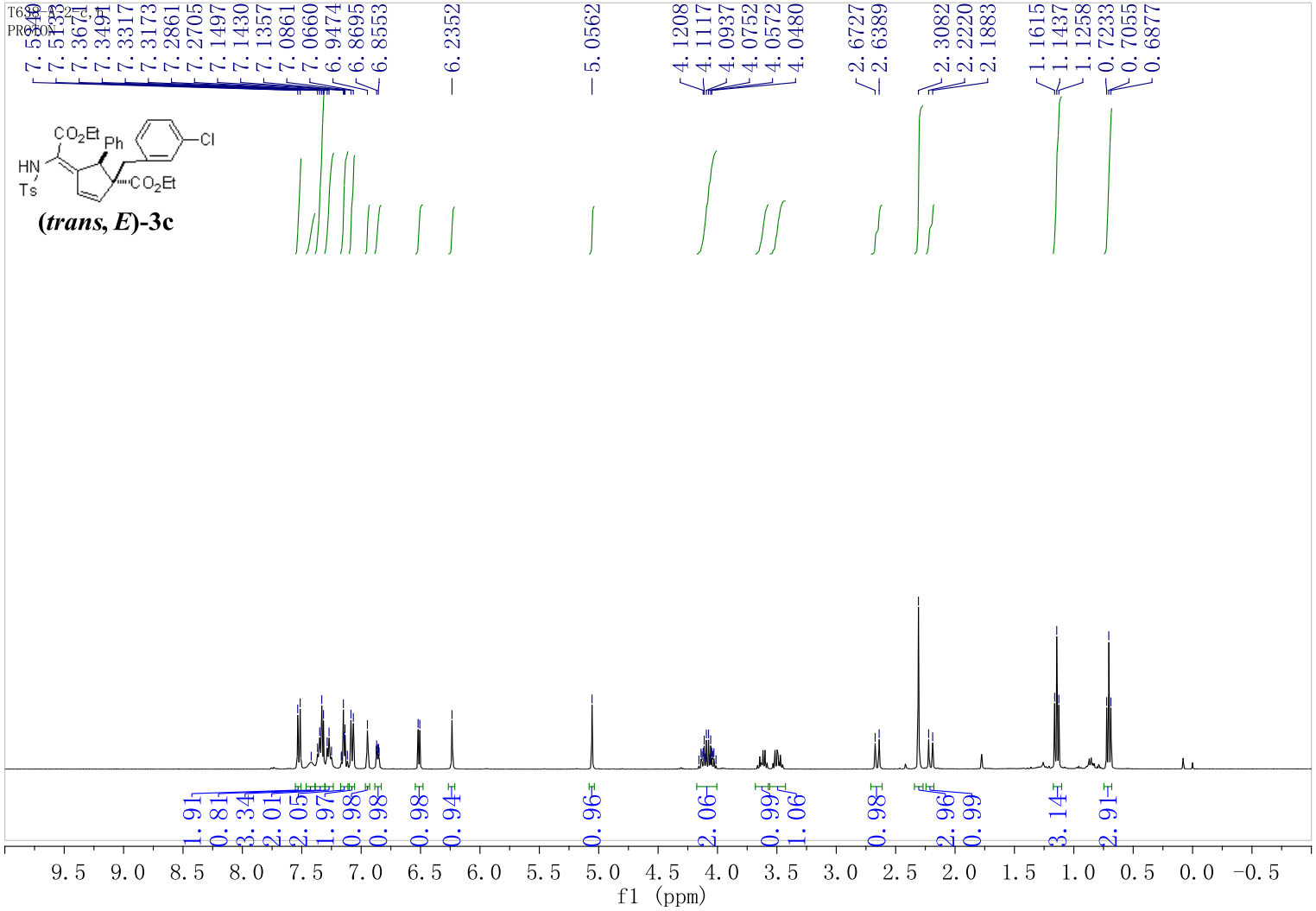

T597-1-cr-c, h, dept
C13CPD
174.0825
164.2991
162.1187
148.6618
143.6990
129.6883
128.1716
116.4658
77.3177
77.0000
76.6817
61.1604
55.8871
42.7511
21.5375
14.0203
13.8834
HN
Ts
Ph
Ph
EtO2C
CO2Et
(trans, Z)-3a
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

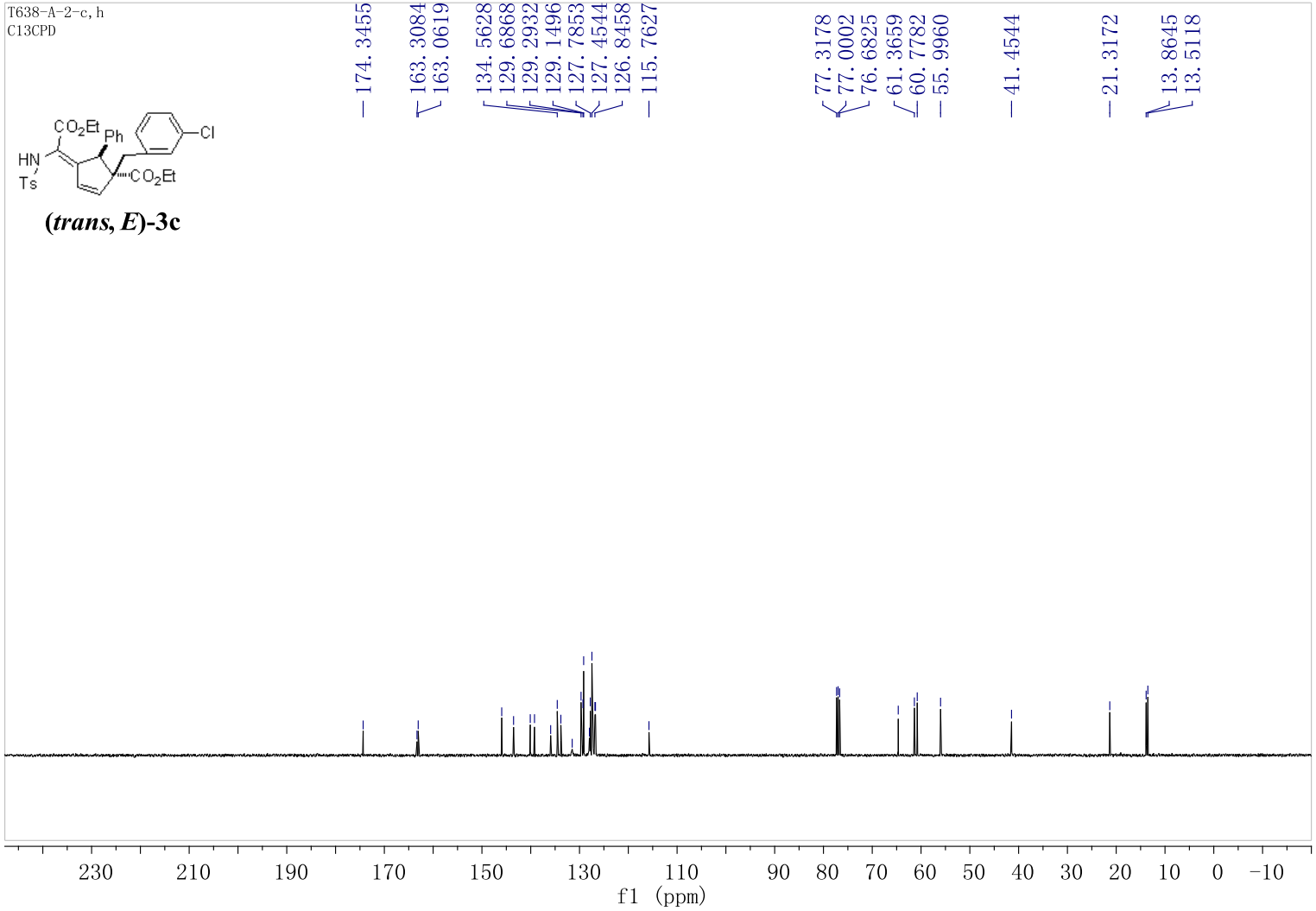

T597-1-cr-c, h, dept
C13DEPT135
148.6854
131.9620
129.7092
129.4217
128.1949
127.4192
127.2853
126.6979
61.2273
61.1877
55.9076
42.7789
21.5670
14.0499
13.9124
HN
Ts
Ph
Ph
EtO2C
CO2Et
(trans, Z)-3a
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


7.5511
7.3645
7.3451
7.3382
7.3335
7.3280
7.3218
7.3171
7.3138
7.2820
7.2694
7.2636
7.0859
7.0657
6.2199
5.0360
4.0675
4.0584
3.6133
3.5955
3.4929
2.6614
2.6276
2.3081
2.1937
2.1598
1.1553
1.1375
1.1197
0.7192
0.7014
0.6836
Br
CO2Et
Ph
HN
Ts
CO2Et
(trans, E)-3b
2.01
0.81
5.28
1.85
2.00
1.98
0.96
0.91
0.97
2.11
0.99
1.05
0.98
2.92
1.01
3.21
2.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

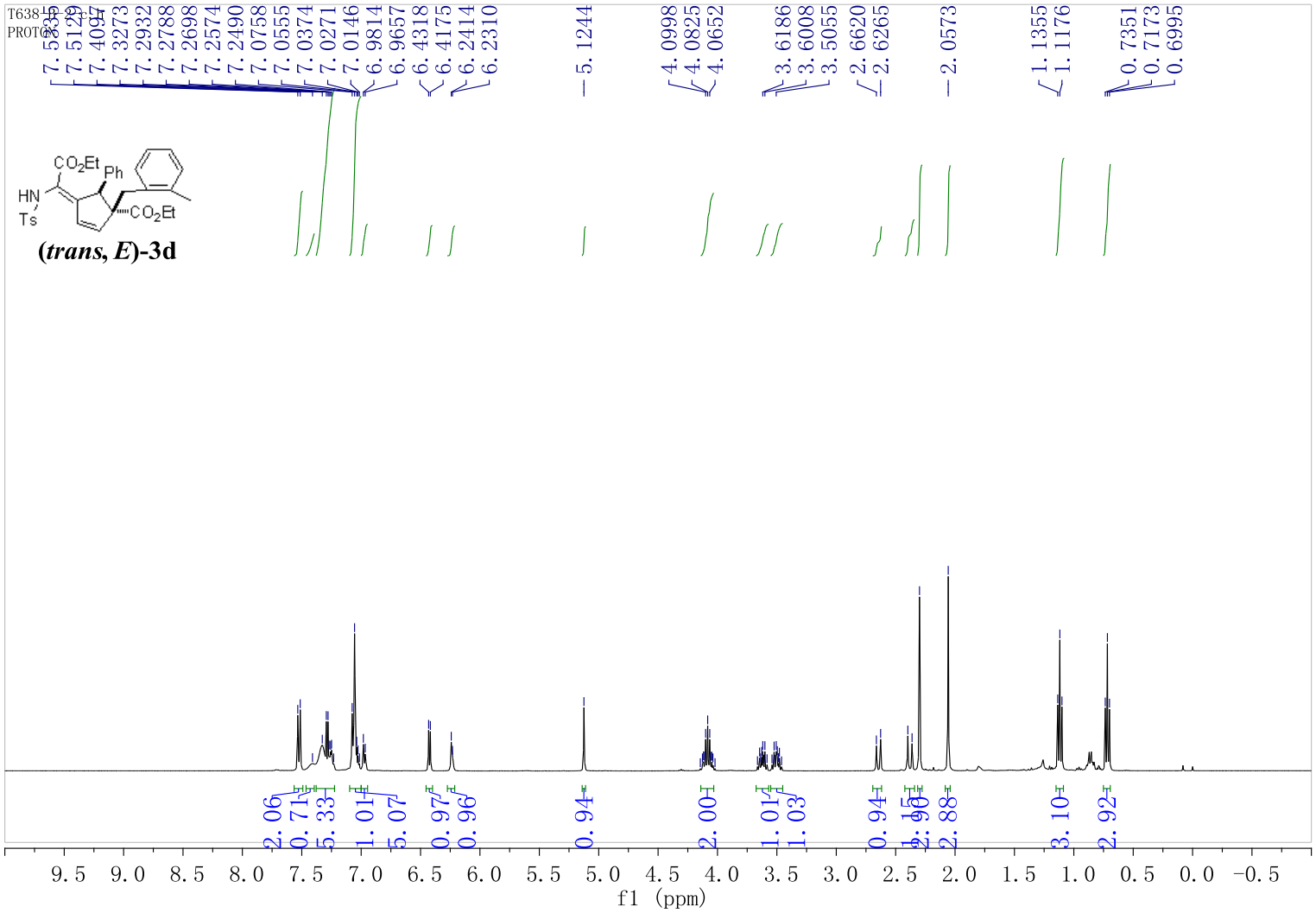


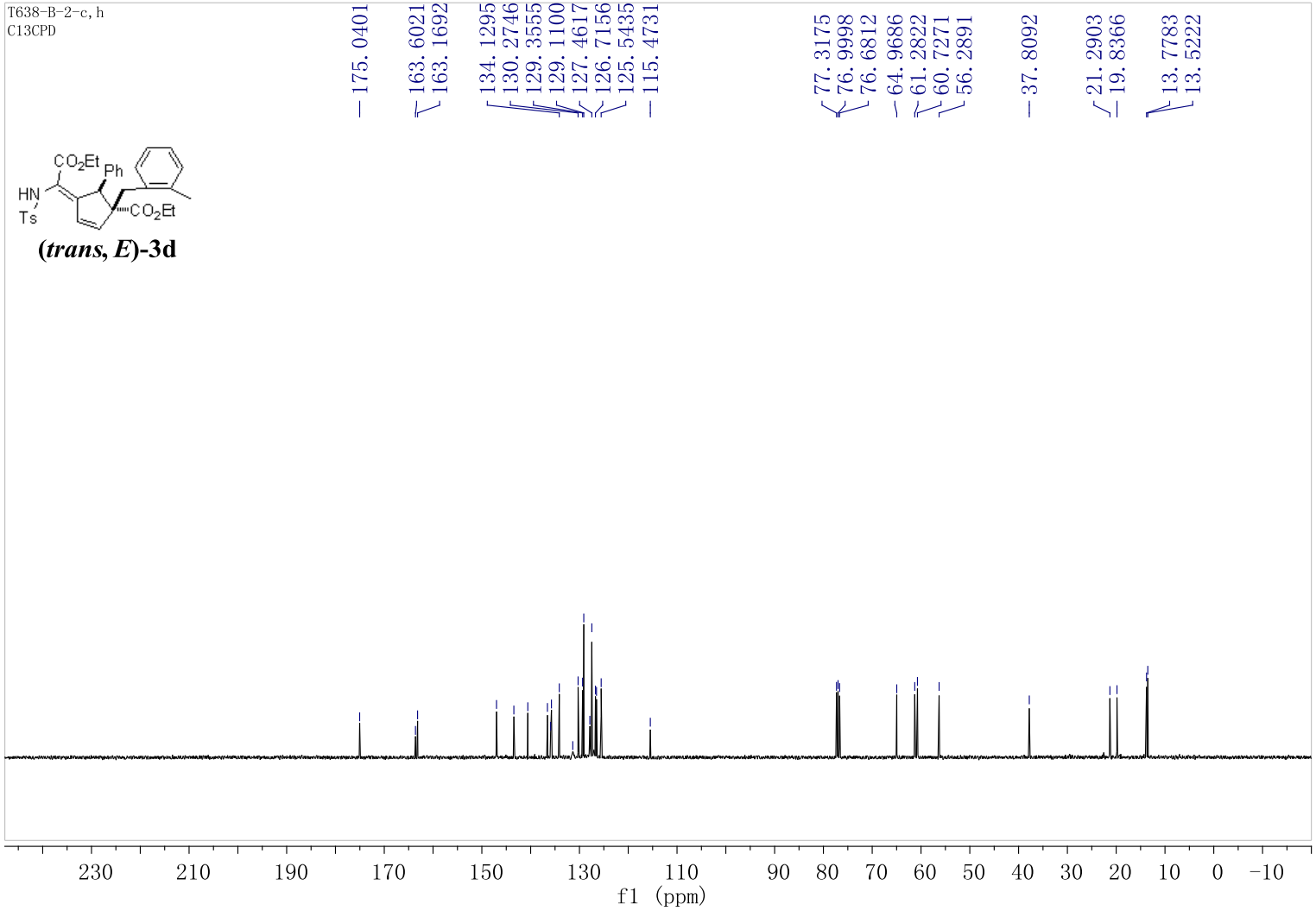
(*trans*, *E*)-3b


7.5633
7.5133
7.3671
7.3491
7.3317
7.3173
7.2861
7.2705
7.1497
7.1430
7.1357
7.0861
7.0660
6.9474
6.8695
6.8553
6.2352
5.0562
4.1208
4.1117
4.0937
4.0752
4.0572
4.0480
2.6727
2.6389
2.3082
2.2220
2.1883
1.1615
1.1437
1.1258
0.7233
0.7055
0.6877
CO2Et
Ph
Cl
HN
Ts
CO2Et
(trans, E)-3c
1.91
0.81
3.34
2.01
2.05
1.97
0.98
0.98
0.98
0.94
0.96
2.06
0.99
1.06
0.98
2.96
0.99
3.14
2.91
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

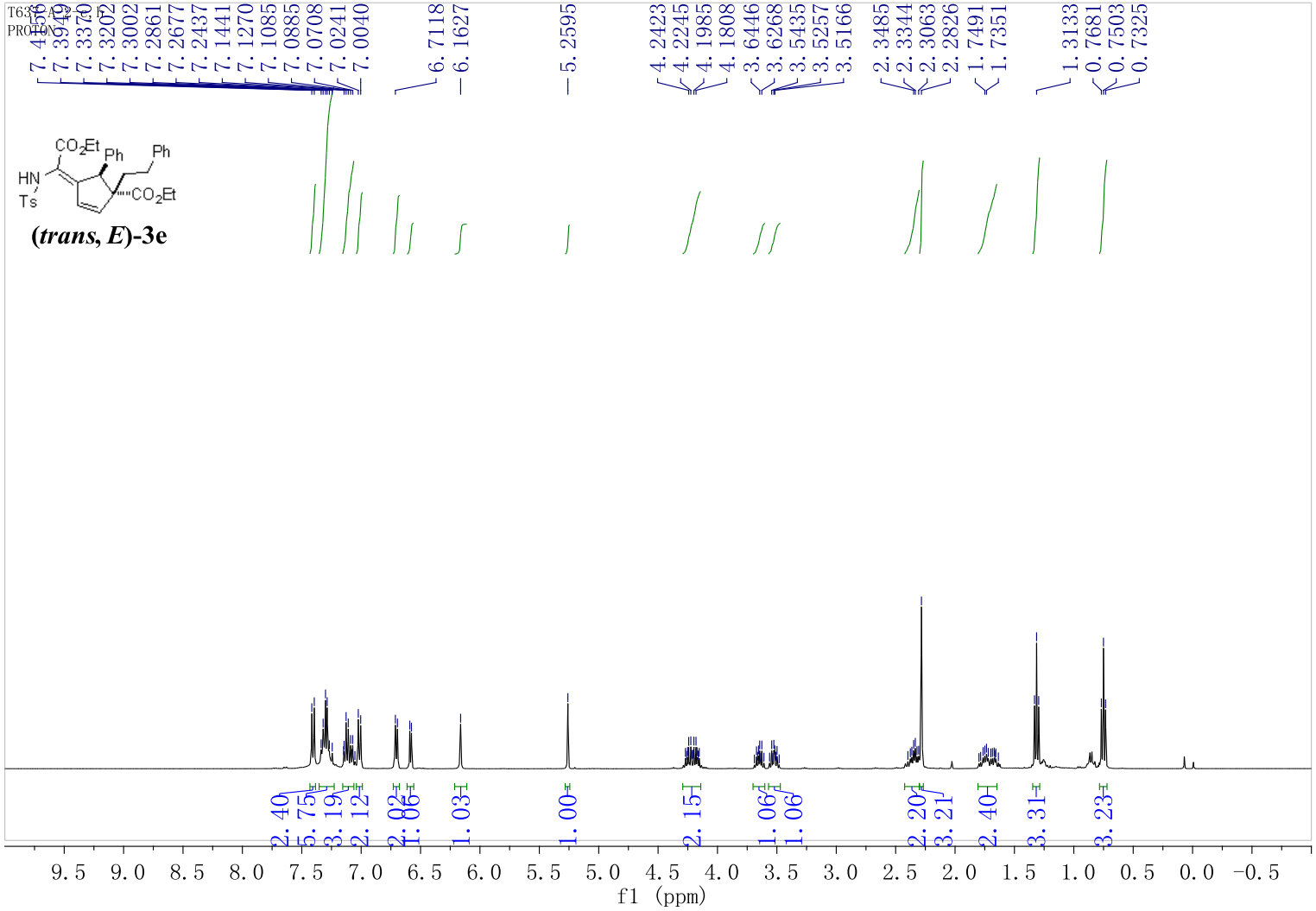

T638-A-2-c, h
C13CPD
174.3455
163.3084
163.0619
134.5628
129.6868
129.2932
129.1496
127.7853
127.4544
126.8458
115.7627
77.3178
77.0002
76.6825
61.3659
60.7782
55.9960
41.4544
21.3172
13.8645
13.5118
CO2Et
Ph
Cl
HN
Ts
CO2Et
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

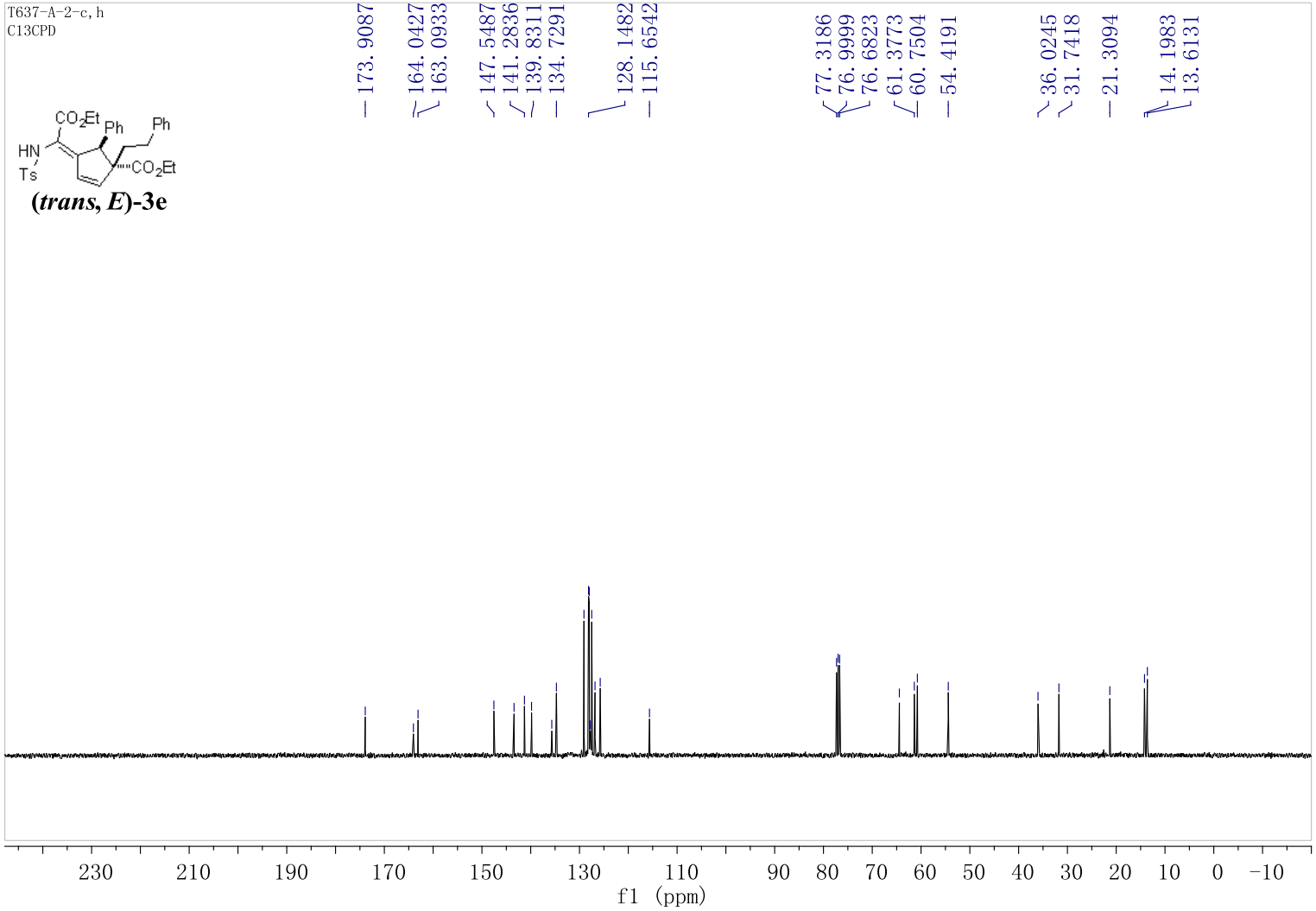
(*trans, E*)-3c


T638
PROTON
7.5335
7.5129
7.4097
7.3273
7.2932
7.2788
7.2698
7.2574
7.2490
7.0758
7.0555
7.0374
7.0271
7.0146
6.9814
6.9657
6.4318
6.4175
6.2414
6.2310
5.1244
4.0998
4.0825
4.0652
3.6186
3.6008
3.5055
2.6620
2.6265
2.0573
1.1355
1.1176
0.7351
0.7173
0.6995
CO2Et
Ph
HN
Ts
CO2Et
(trans, E)-3d
2.06
0.71
5.33
1.01
5.07
0.97
0.96
0.94
2.00
1.01
1.03
0.94
1.15
1.90
2.88
3.10
2.92
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

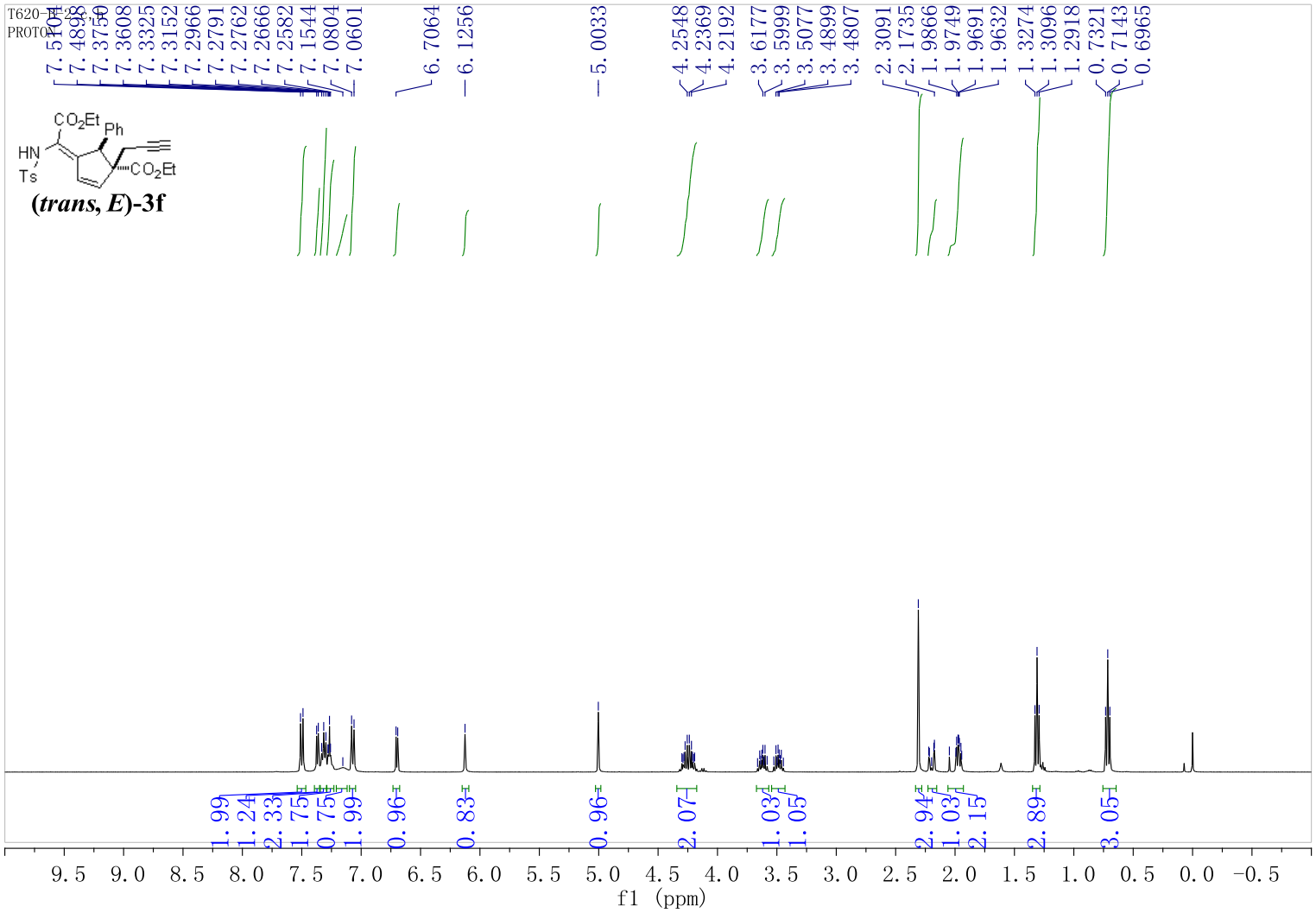


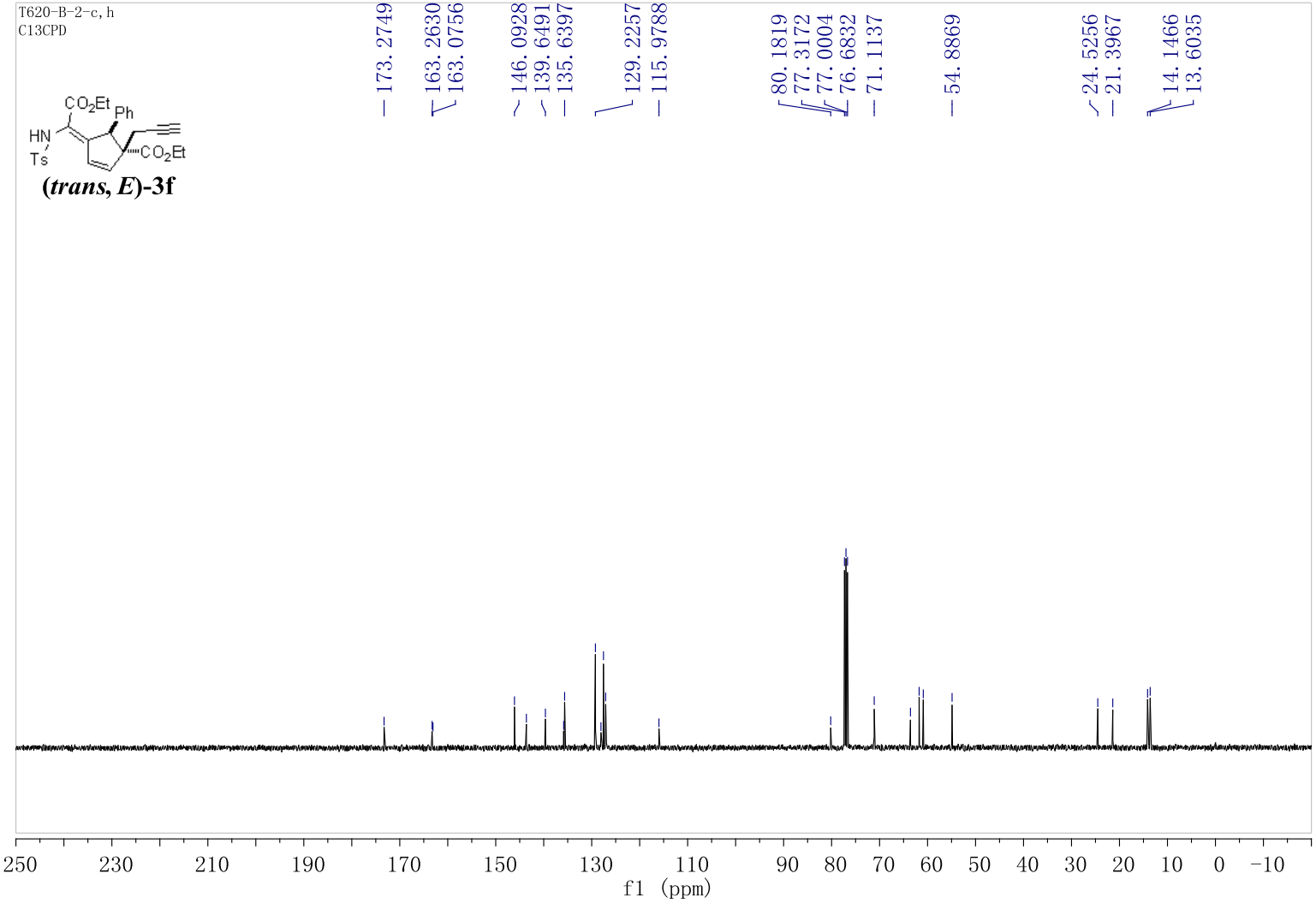
(*trans*, *E*)-3d

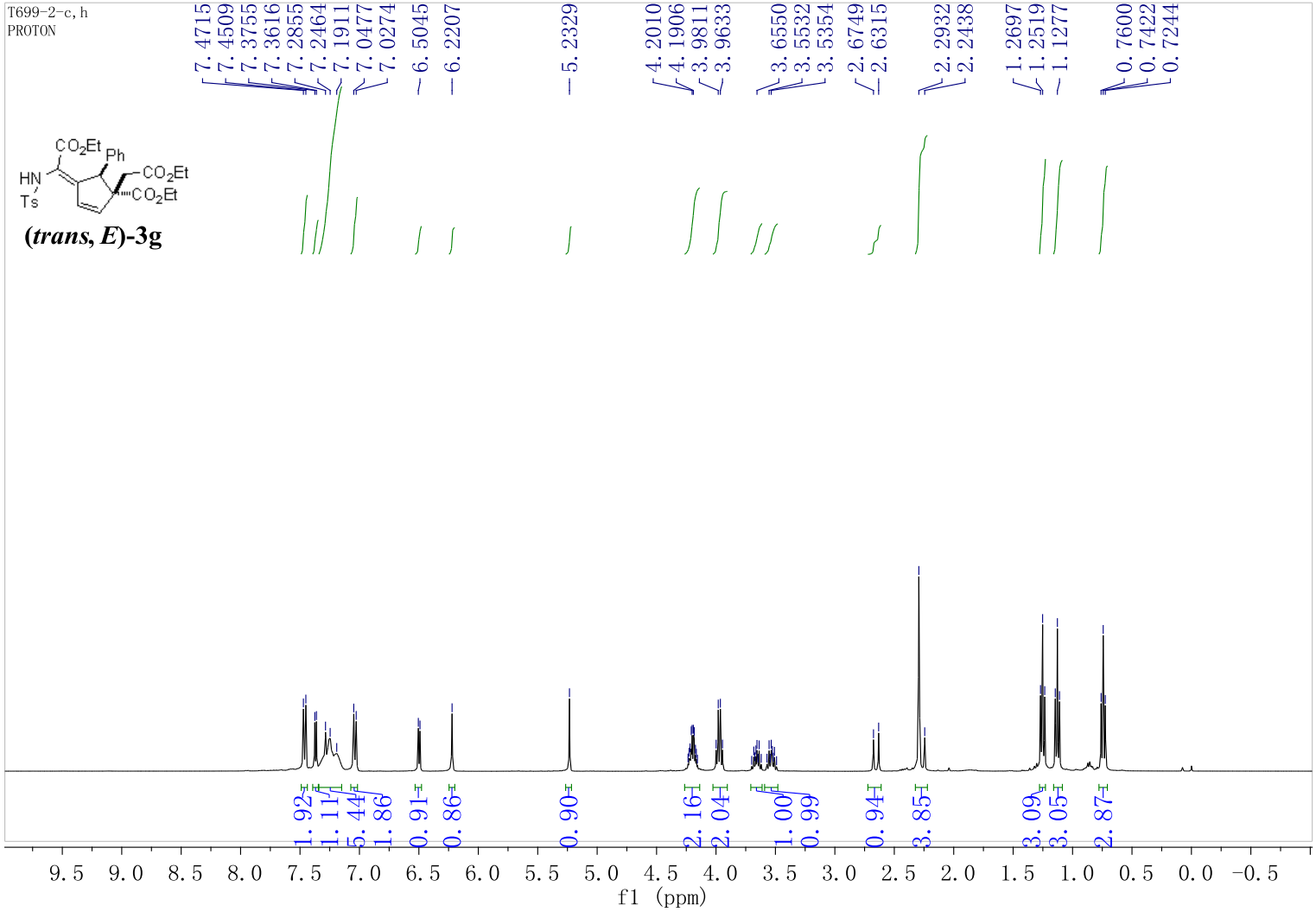

7.4156
7.3940
7.3370
7.3202
7.3002
7.2861
7.2677
7.2437
7.1441
7.1270
7.1085
7.0885
7.0708
7.0241
7.0040
6.7118
6.1627
5.2595
4.2423
4.2245
4.1985
4.1808
3.6446
3.6268
3.5435
3.5257
3.5166
2.3485
2.3344
2.3063
2.2826
1.7491
1.7351
1.3133
0.7681
0.7503
0.7325
CO2Et
Ph
Ph
HN
Ts
CO2Et
(trans, E)-3e
2.40
5.75
3.19
2.12
2.02
1.86
1.03
1.00
2.15
1.06
1.06
2.20
3.21
2.40
3.31
3.23
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



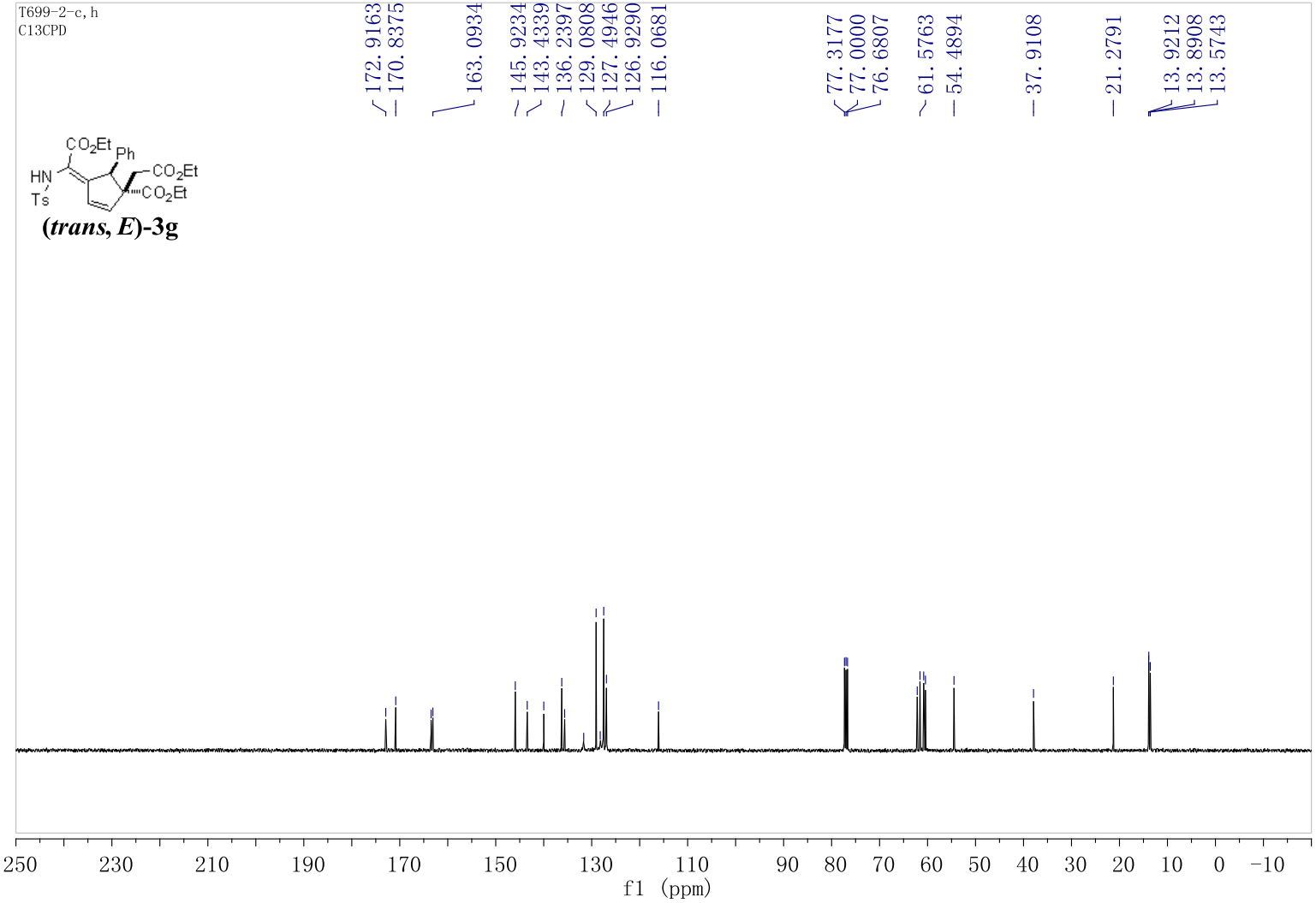
(*trans*, *E*)-3e


T620-1H
PROTON
7.5104
7.4898
7.3750
7.3608
7.3325
7.3152
7.2966
7.2791
7.2762
7.2666
7.2582
7.1544
7.0804
7.0601
6.7064
6.1256
5.0033
4.2548
4.2369
4.2192
3.6177
3.5999
3.5077
3.4899
3.4807
2.3091
2.1735
1.9866
1.9749
1.9691
1.9632
1.3274
1.3096
1.2918
0.7321
0.7143
0.6965
CO2Et
Ph
HN
Ts
CO2Et
(trans, E)-3f
1.99
1.24
2.33
1.75
0.75
1.99
0.96
0.83
0.96
2.07
1.03
1.05
2.94
1.03
2.15
2.89
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

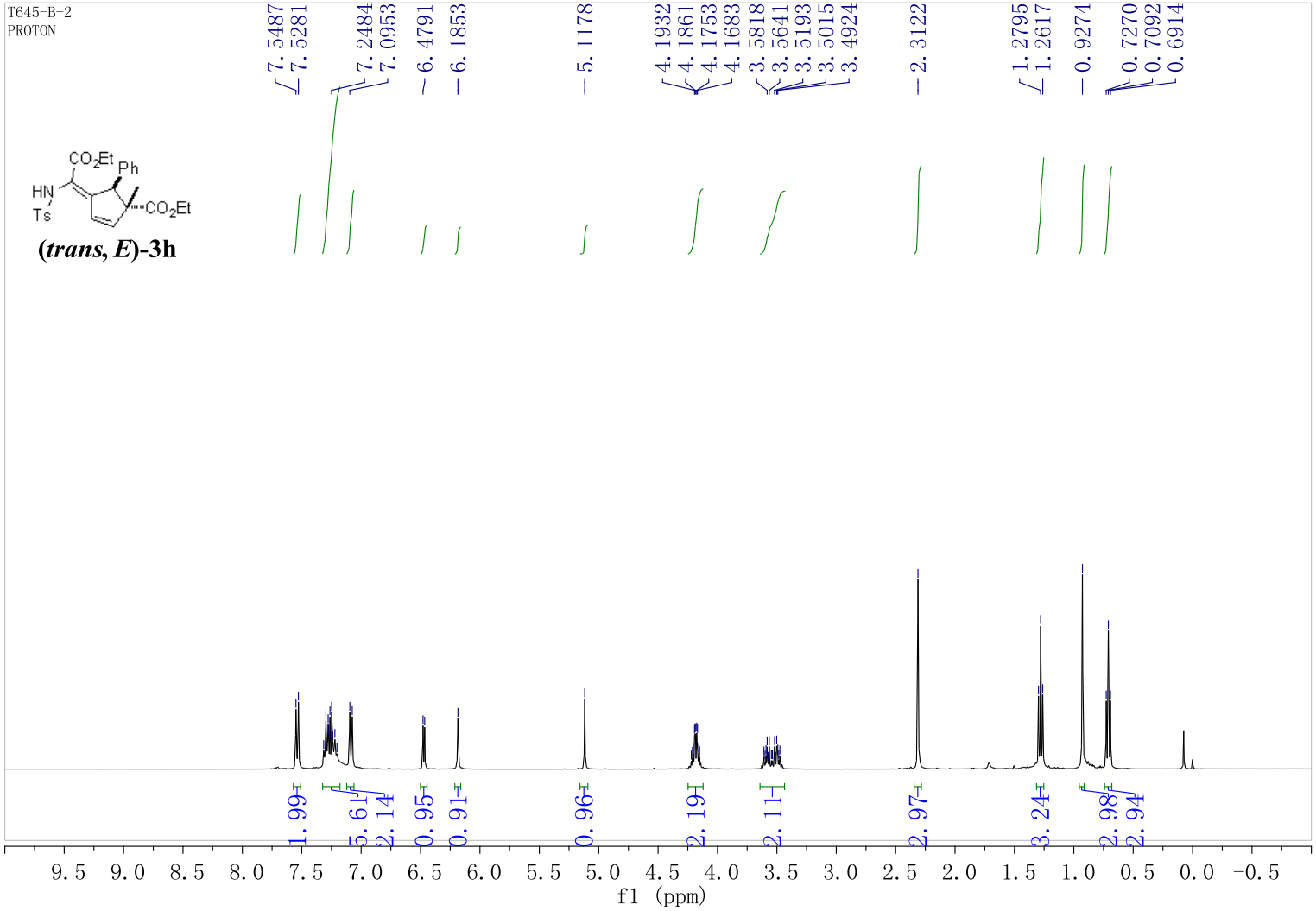


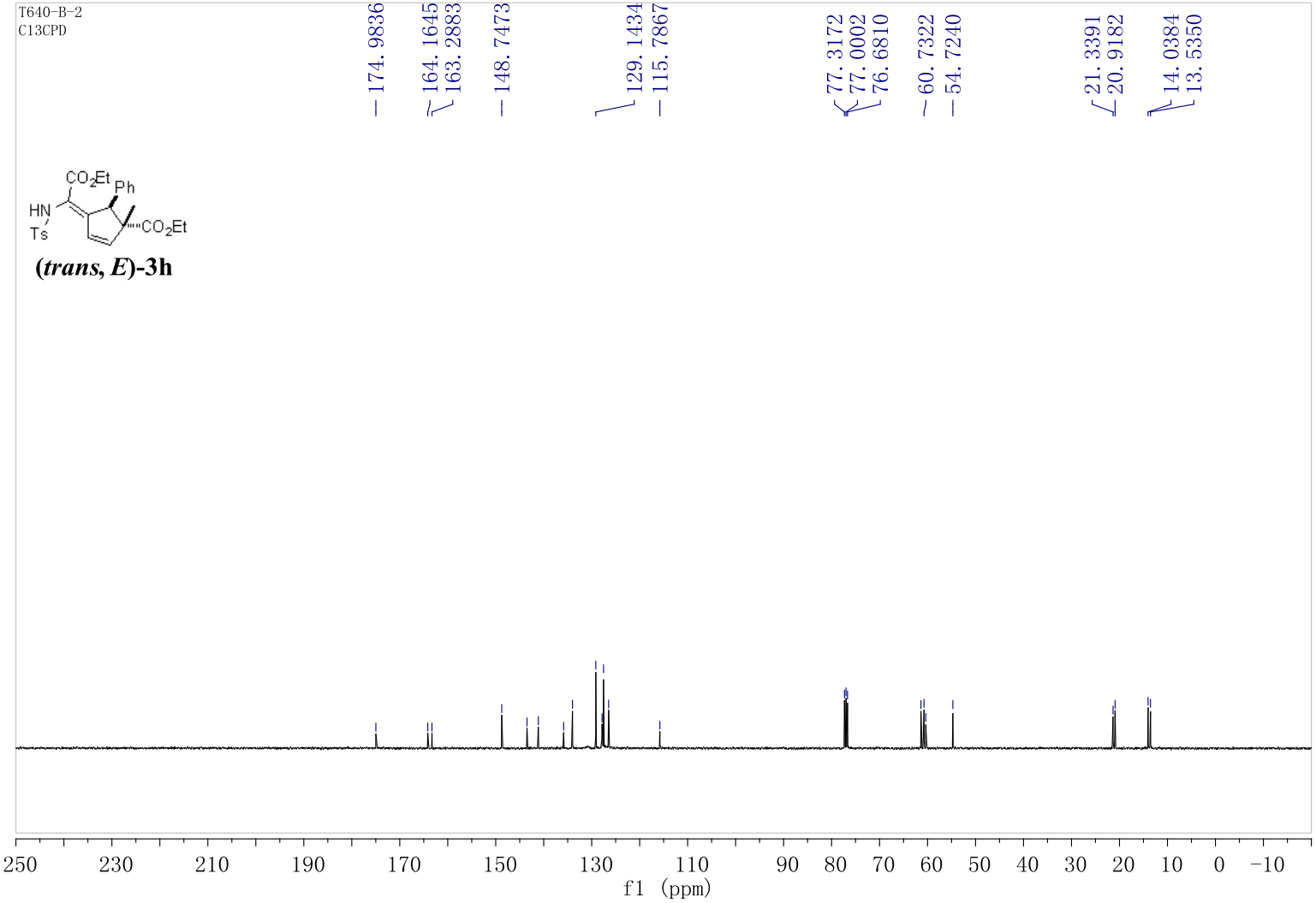

T699-2-c, h
PROTON
7.4715
7.4509
7.3755
7.3616
7.2855
7.2464
7.1911
7.0477
7.0274
6.5045
6.2207
5.2329
4.2010
4.1906
3.9811
3.9633
3.6550
3.5532
3.5354
2.6749
2.6315
2.2932
2.2438
1.2697
1.2519
1.1277
0.7600
0.7422
0.7244
1.92
1.11
5.44
1.86
0.91
0.86
0.90
2.16
2.04
1.00
0.99
0.94
3.85
3.09
3.05
2.87
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

(*trans*, *E*)-3g

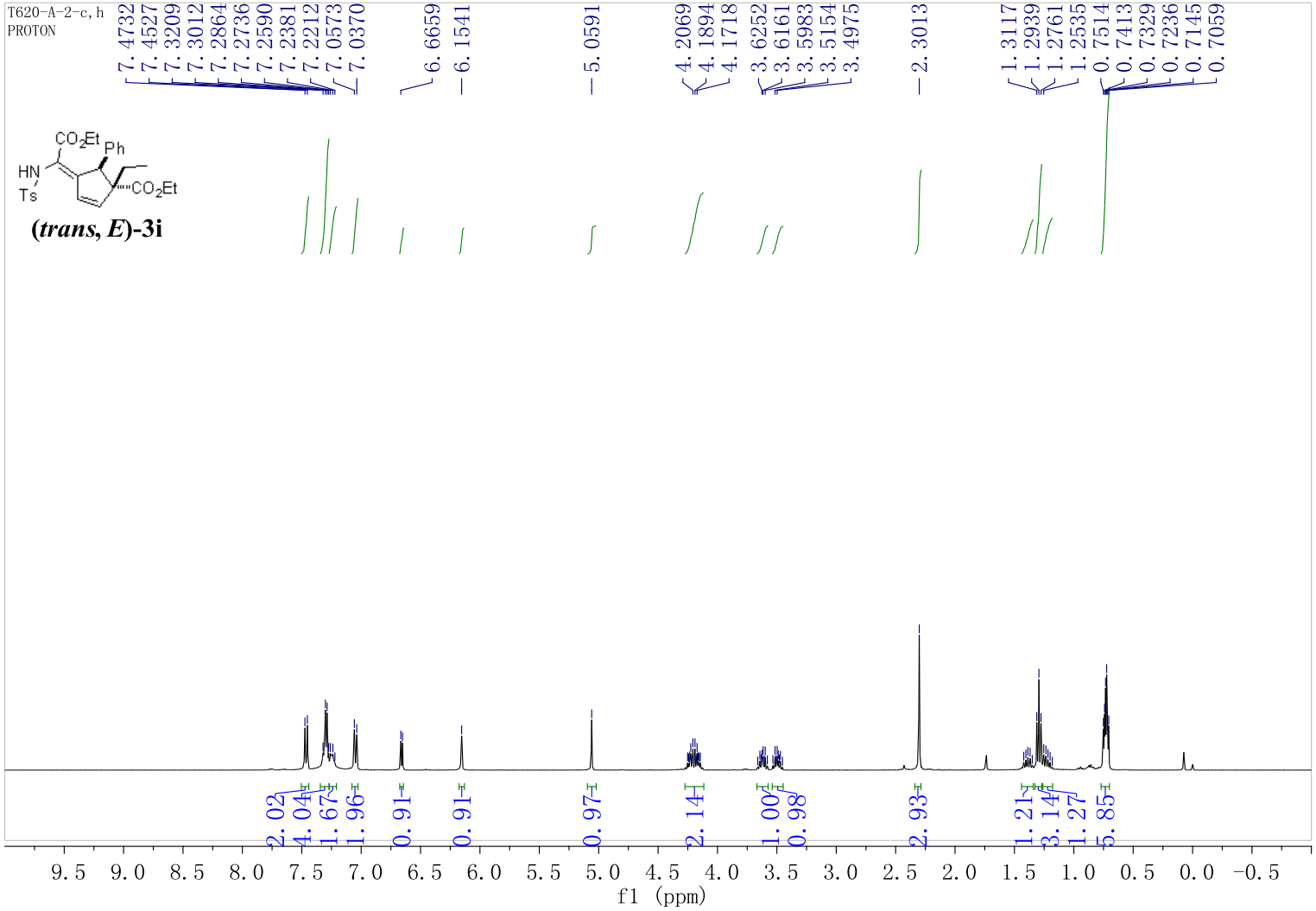

T699-2-c, h
C13CPD
172.9163
170.8375
163.0934
145.9234
143.4339
136.2397
129.0808
127.4946
126.9290
116.0681
77.3177
77.0000
76.6807
61.5763
54.4894
37.9108
21.2791
13.9212
13.8908
13.5743
CO2Et
Ph
HN
Ts
CO2Et
CO2Et
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 −10
f1 (ppm)

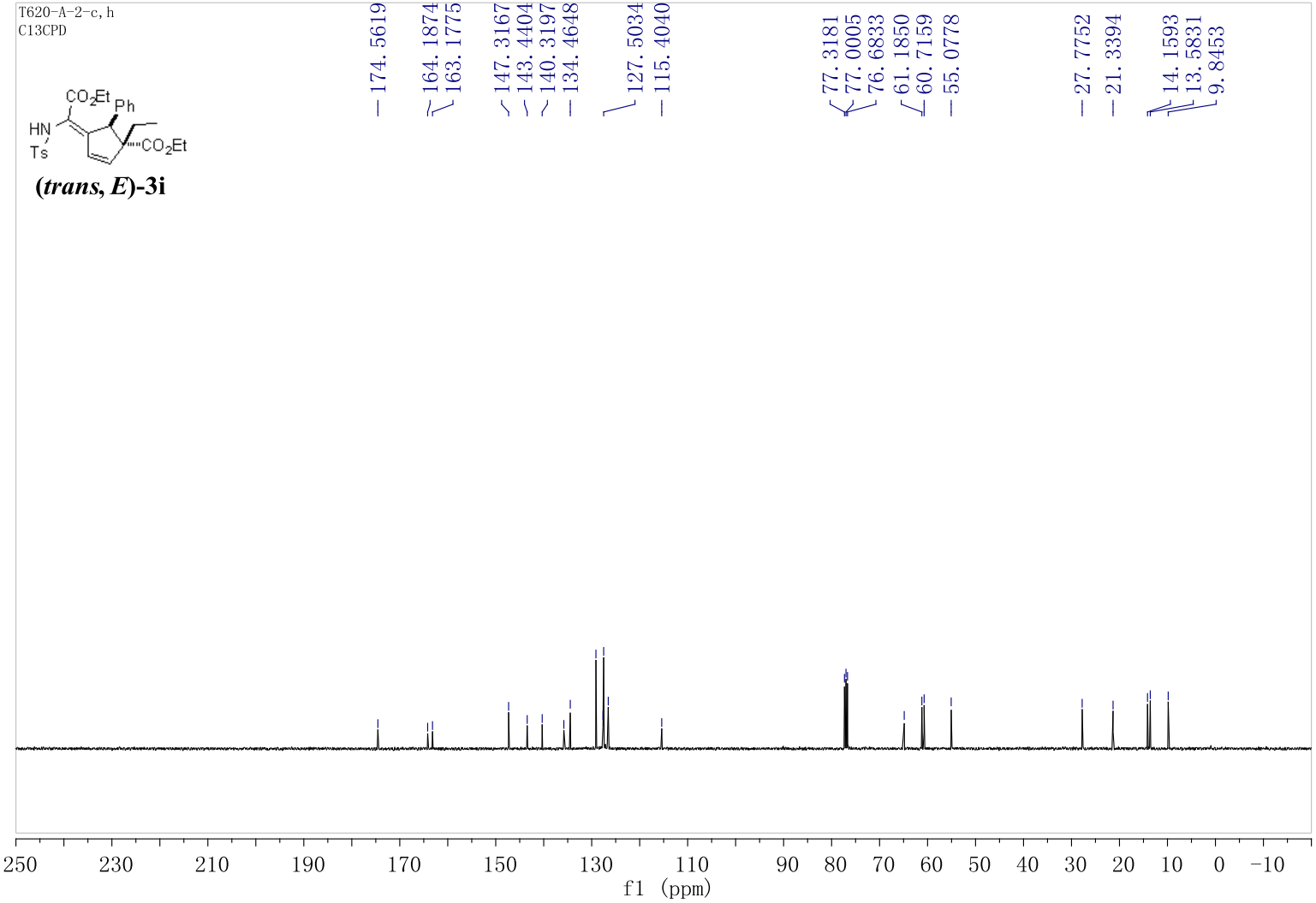
(*trans*, *E*)-3g

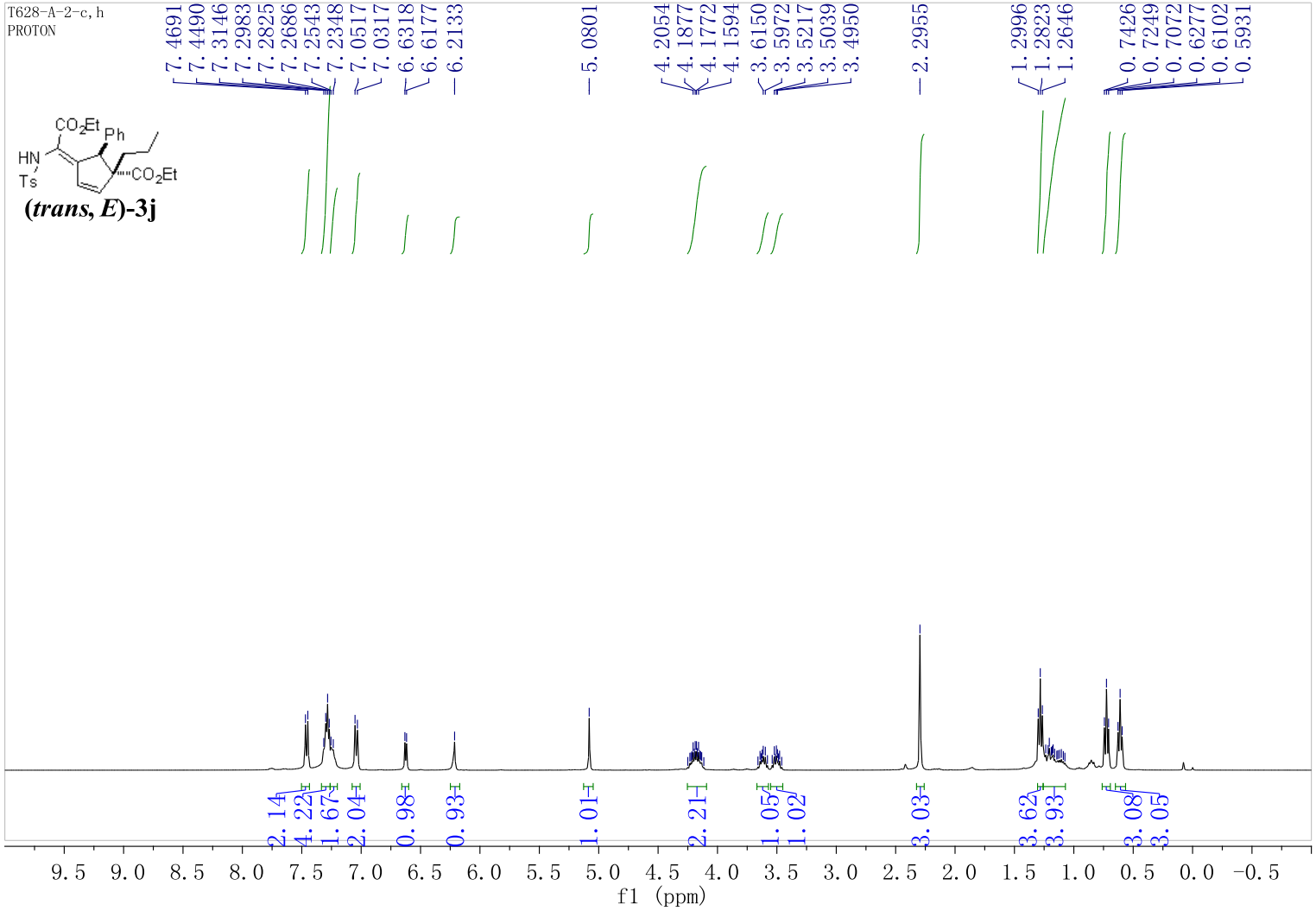


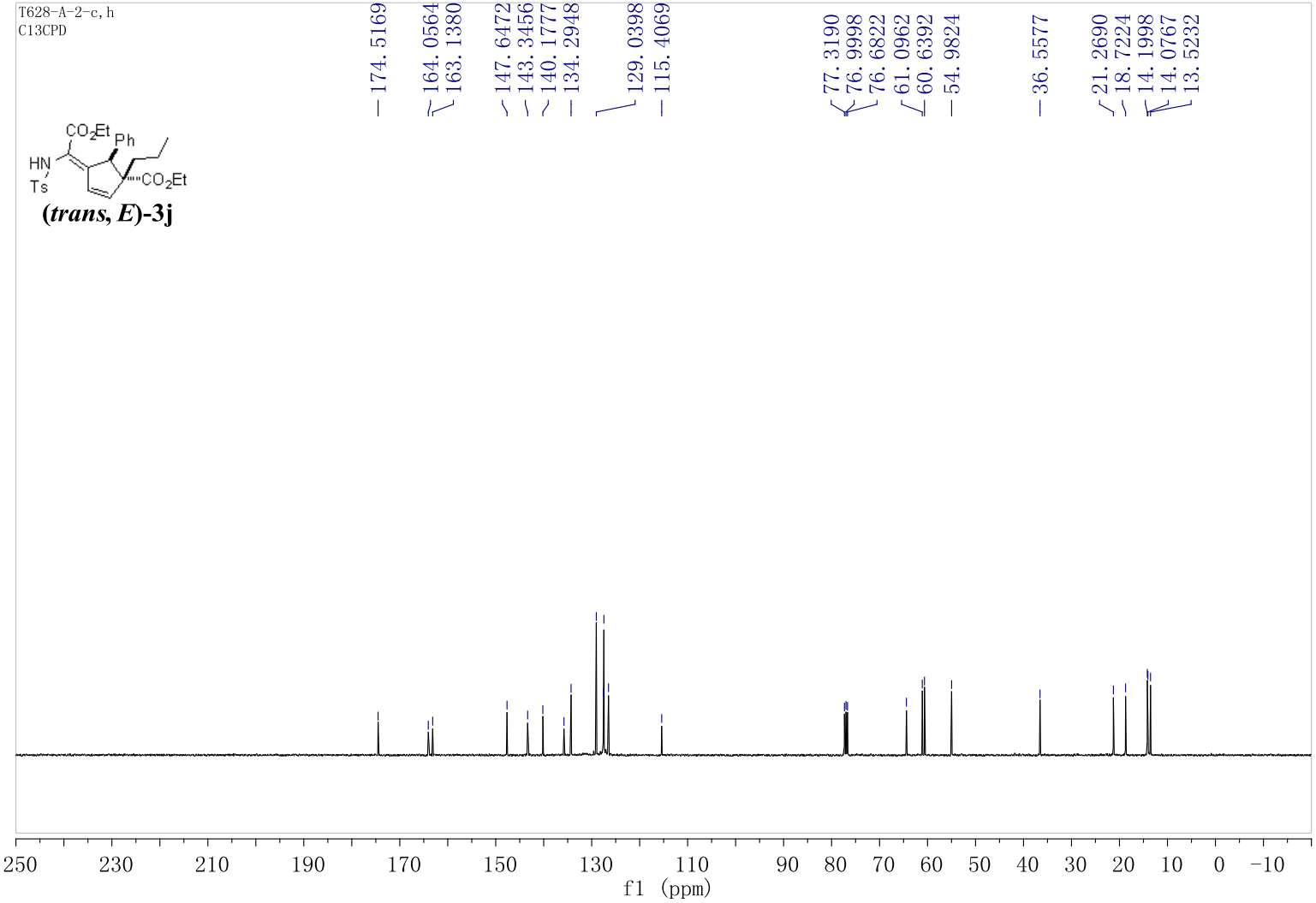


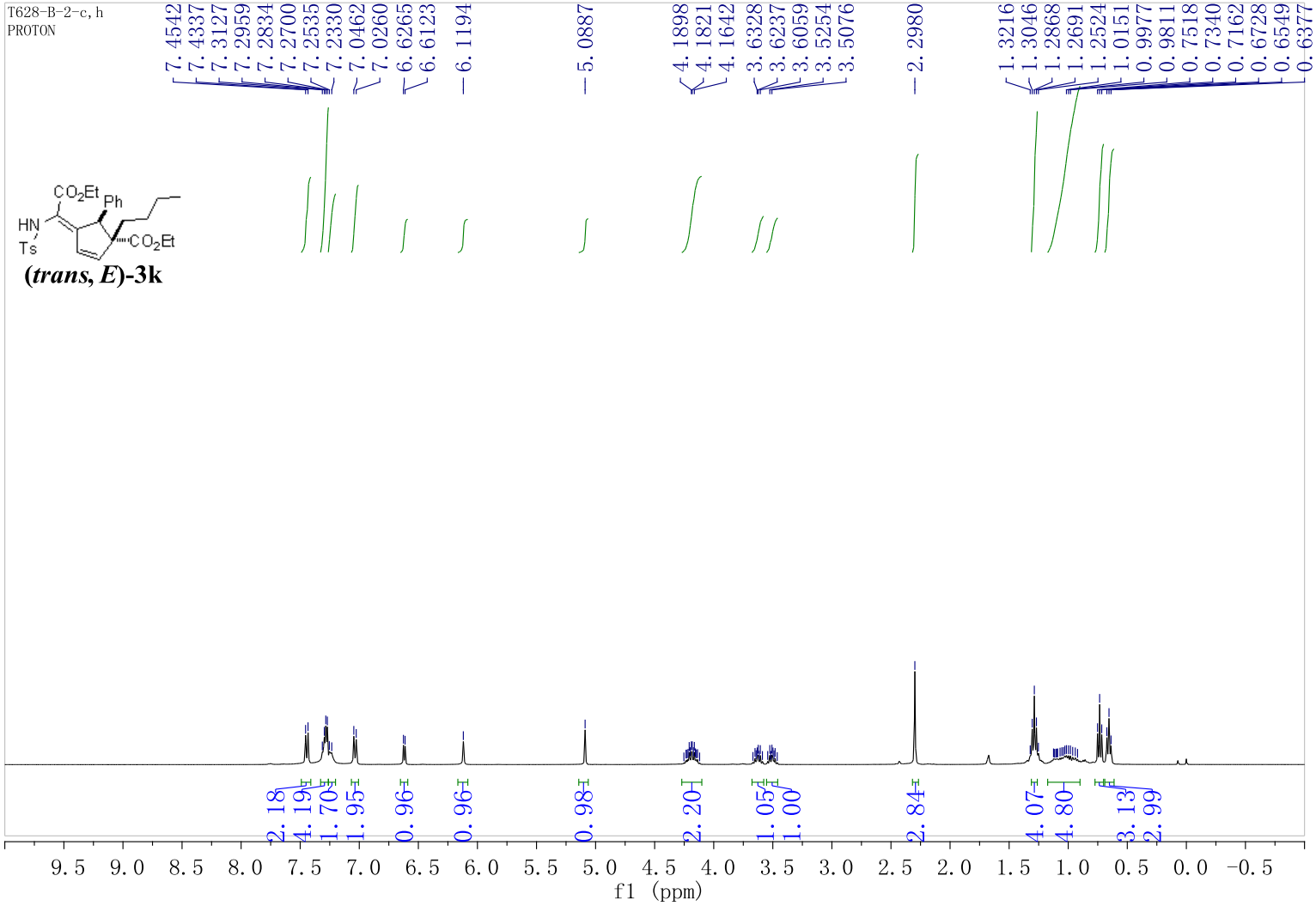
(*trans*, *E*)-3h

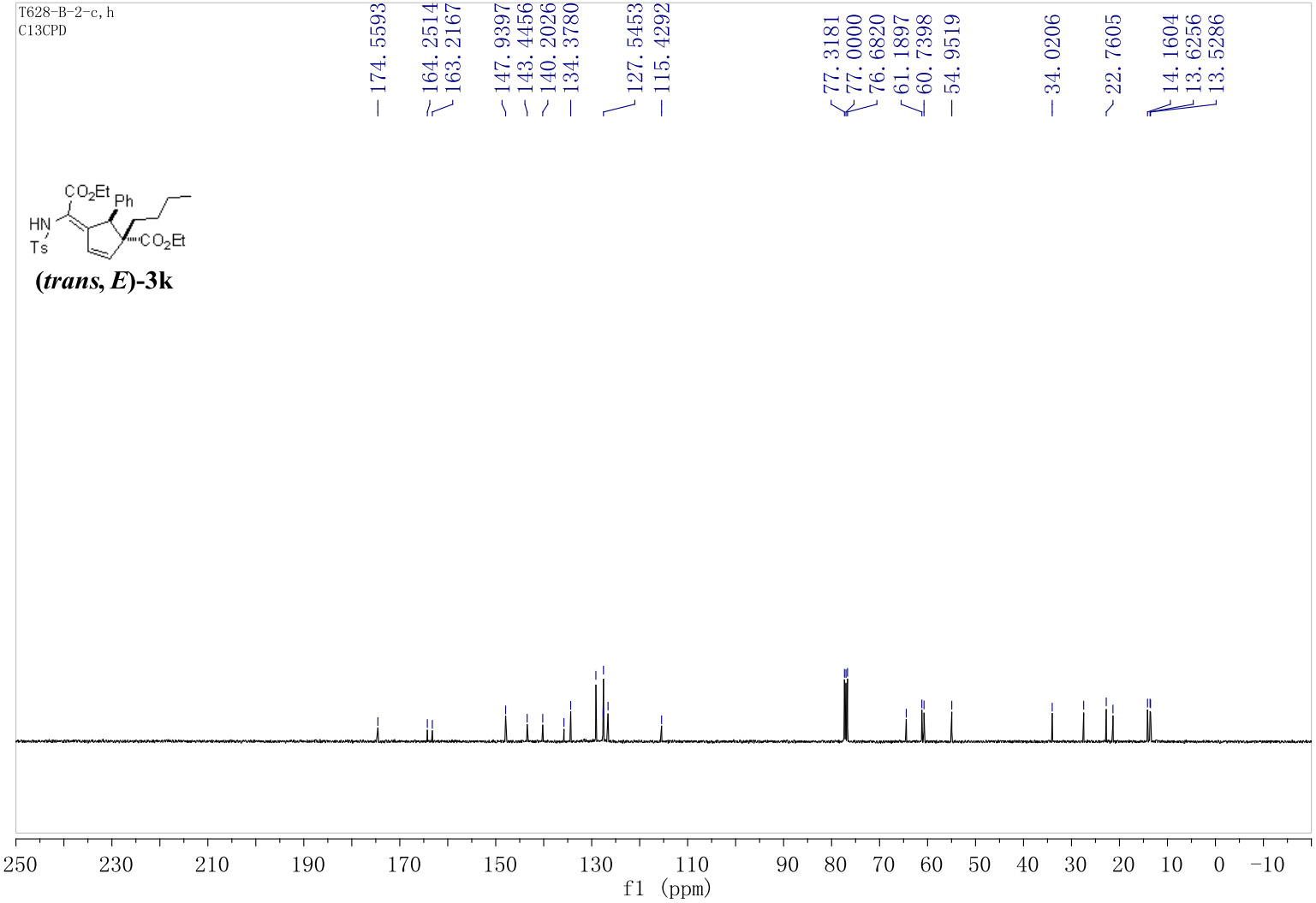

T620-A-2-c, h
PROTON
7.4732
7.4527
7.3209
7.3012
7.2864
7.2736
7.2590
7.2381
7.2212
7.0573
7.0370
6.6659
6.1541
5.0591
4.2069
4.1894
4.1718
3.6252
3.6161
3.5983
3.5154
3.4975
2.3013
1.3117
1.2939
1.2761
1.2535
0.7514
0.7413
0.7329
0.7236
0.7145
0.7059
CO2Et
Ph
HN
Ts
CO2Et
(trans, E)-3i
2.02
4.04
1.67
1.96
0.91
0.91
0.97
2.14
1.00
0.98
2.93
1.21
3.14
1.27
5.85
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)



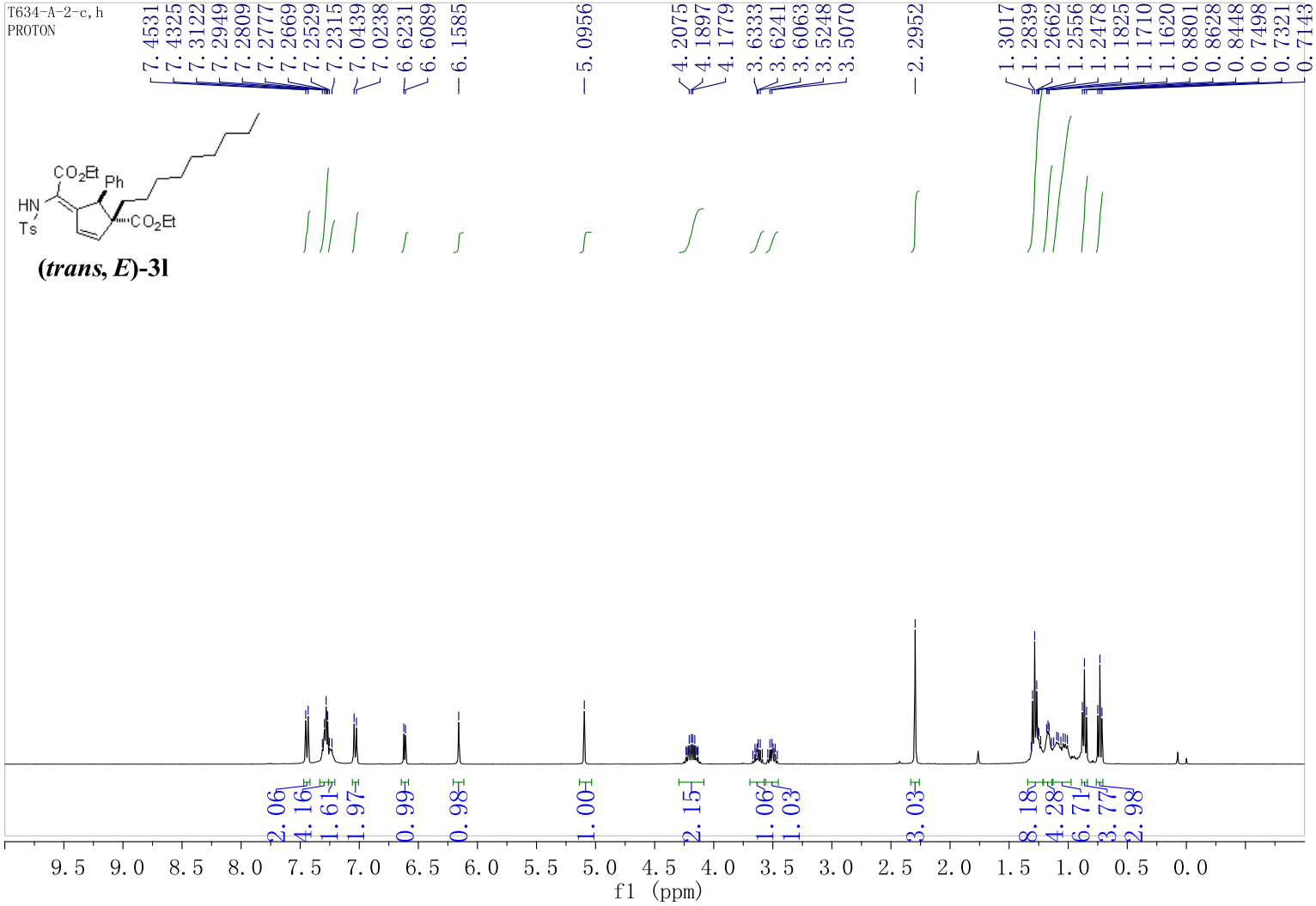

T628-A-2-c, h
PROTON
7.4691
7.4490
7.3146
7.2983
7.2825
7.2686
7.2543
7.2348
7.0517
7.0317
6.6318
6.6177
6.2133
5.0801
4.2054
4.1877
4.1772
4.1594
3.6150
3.5972
3.5217
3.5039
3.4950
2.2955
1.2996
1.2823
1.2646
0.7426
0.7249
0.7072
0.6277
0.6102
0.5931
CO2Et
Ph
HN
Ts
CO2Et
(trans, E)-3j
2.14
4.22
1.67
2.04
0.98
0.93
1.01
2.21
1.05
1.02
3.03
3.62
3.93
3.08
3.05
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

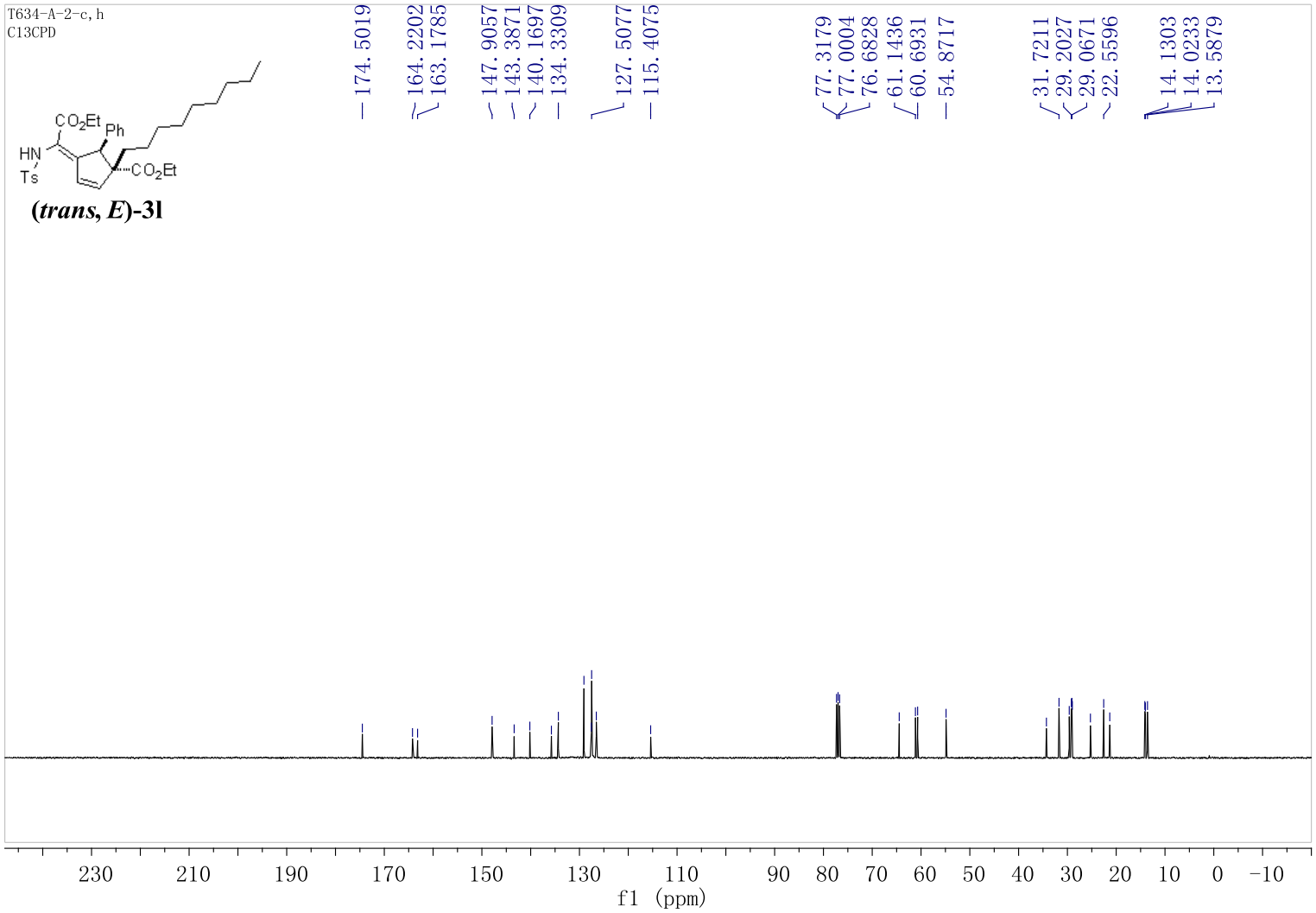



T628-B-2-c, h
PROTON
7.4542
7.4337
7.3127
7.2959
7.2834
7.2700
7.2535
7.2330
7.0462
7.0260
6.6265
6.6123
6.1194
5.0887
4.1898
4.1821
4.1642
3.6328
3.6237
3.6059
3.5254
3.5076
2.2980
1.3216
1.3046
1.2868
1.2691
1.2524
1.0151
0.9977
0.9811
0.7518
0.7340
0.7162
0.6728
0.6549
0.6377
CO2Et
Ph
HN
Ts
CO2Et
(trans, E)-3k
2.18
4.19
1.70
1.95
0.96
0.96
0.98
2.20
1.05
1.00
2.84
4.07
4.80
3.13
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

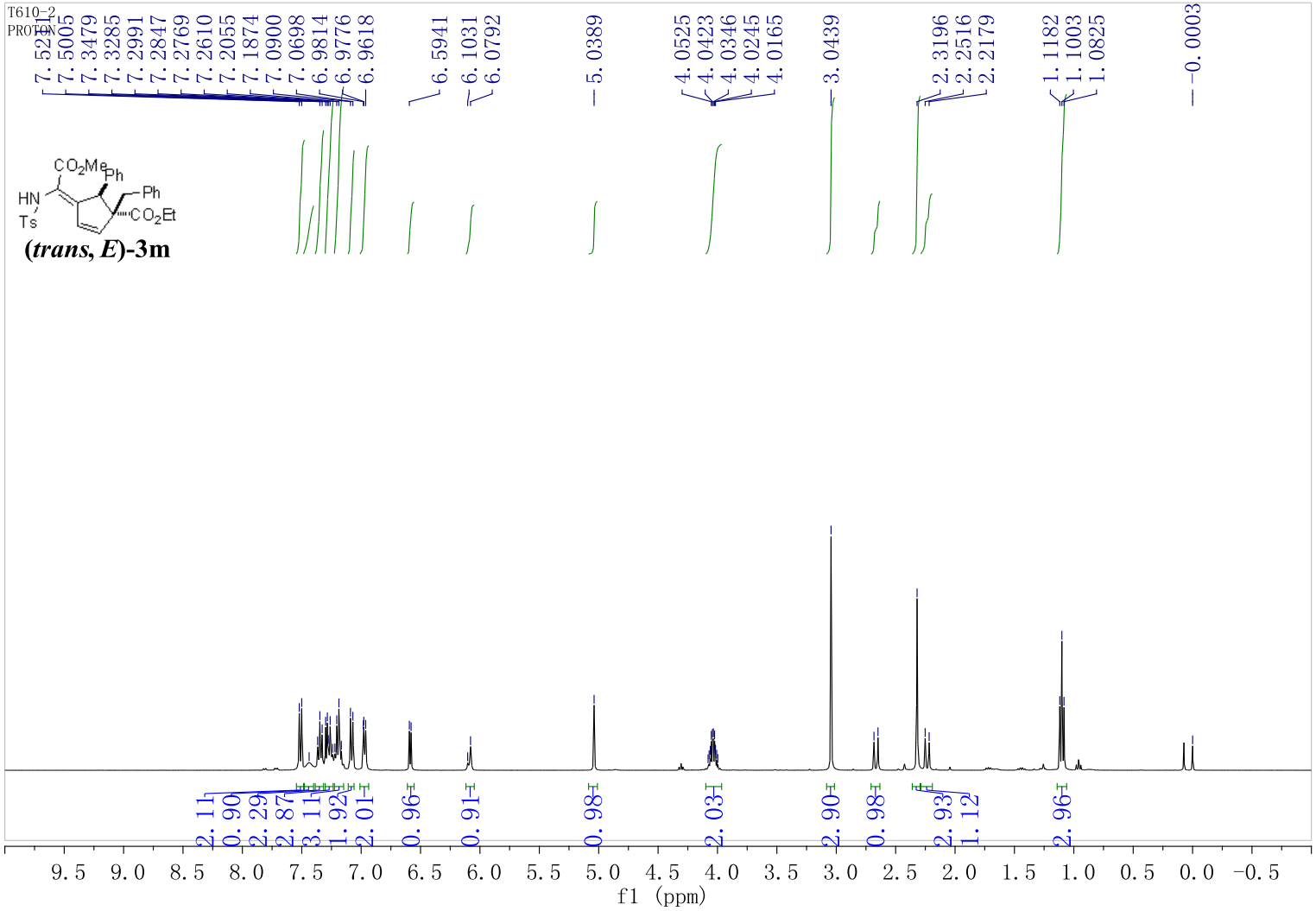


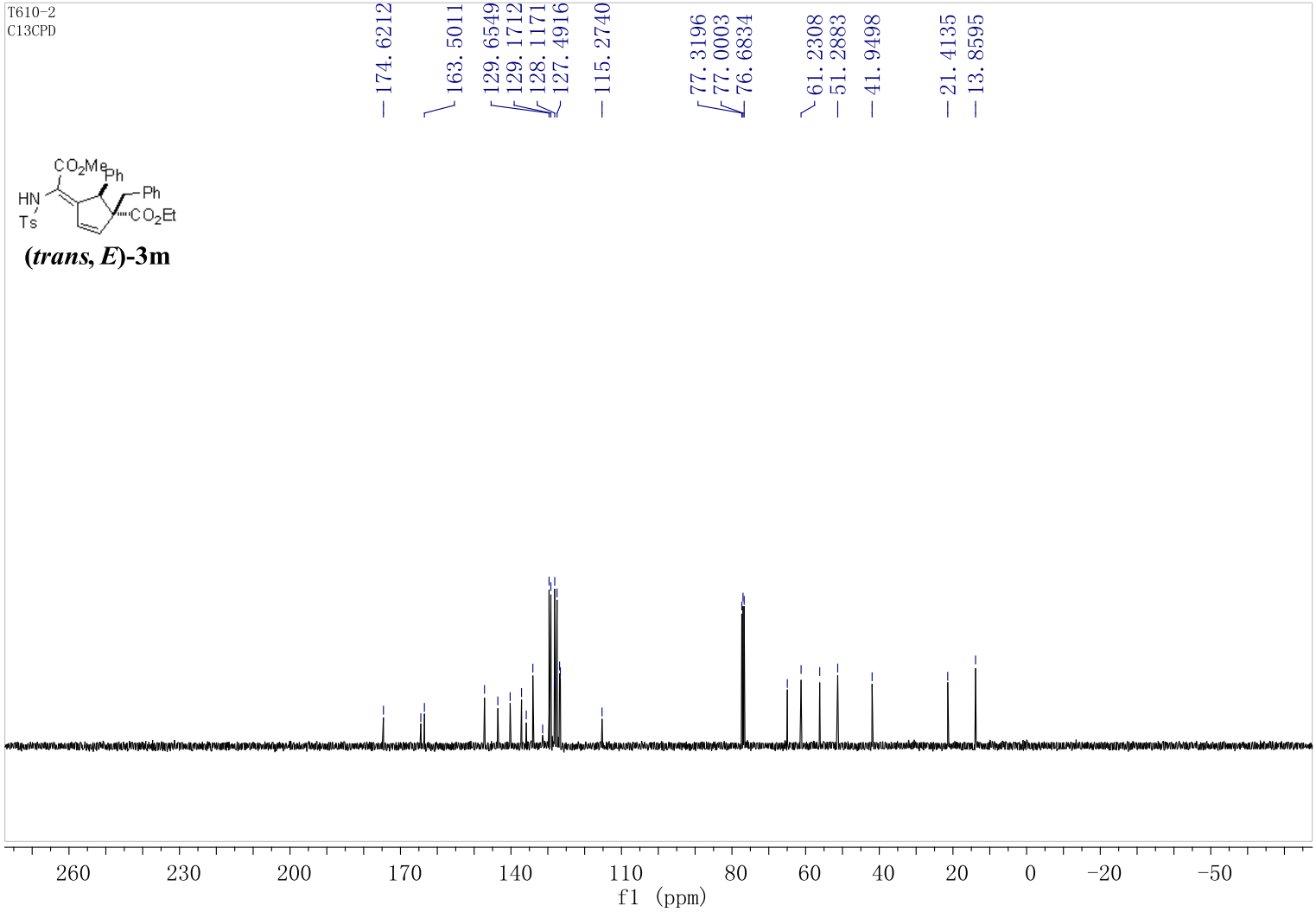
(*trans*, *E*)-3k


T634-A-2-c, h
PROTON
7.4531
7.4325
7.3122
7.2949
7.2809
7.2777
7.2669
7.2529
7.2315
7.0439
7.0238
6.6231
6.6089
6.1585
5.0956
4.2075
4.1897
4.1779
3.6333
3.6241
3.6063
3.5248
3.5070
2.2952
1.3017
1.2839
1.2662
1.2556
1.2478
1.1825
1.1710
1.1620
0.8801
0.8628
0.8448
0.7498
0.7321
0.7143
CO2Et
Ph
HN
Ts
CO2Et
(trans, E)-3l
2.06
4.16
1.61
1.97
0.99
0.98
1.00
2.15
1.06
1.03
3.03
8.18
4.28
6.71
3.77
2.98
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

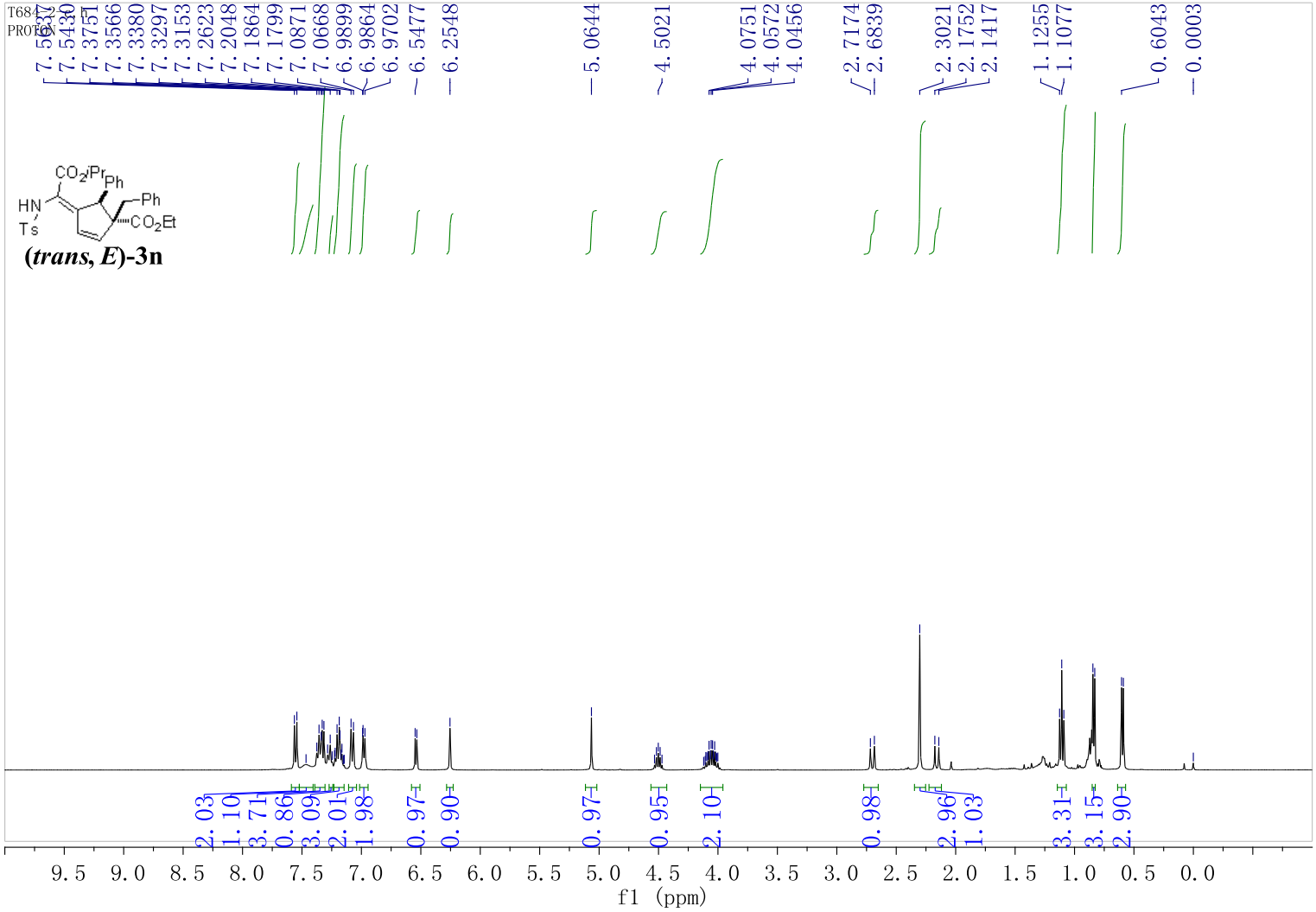


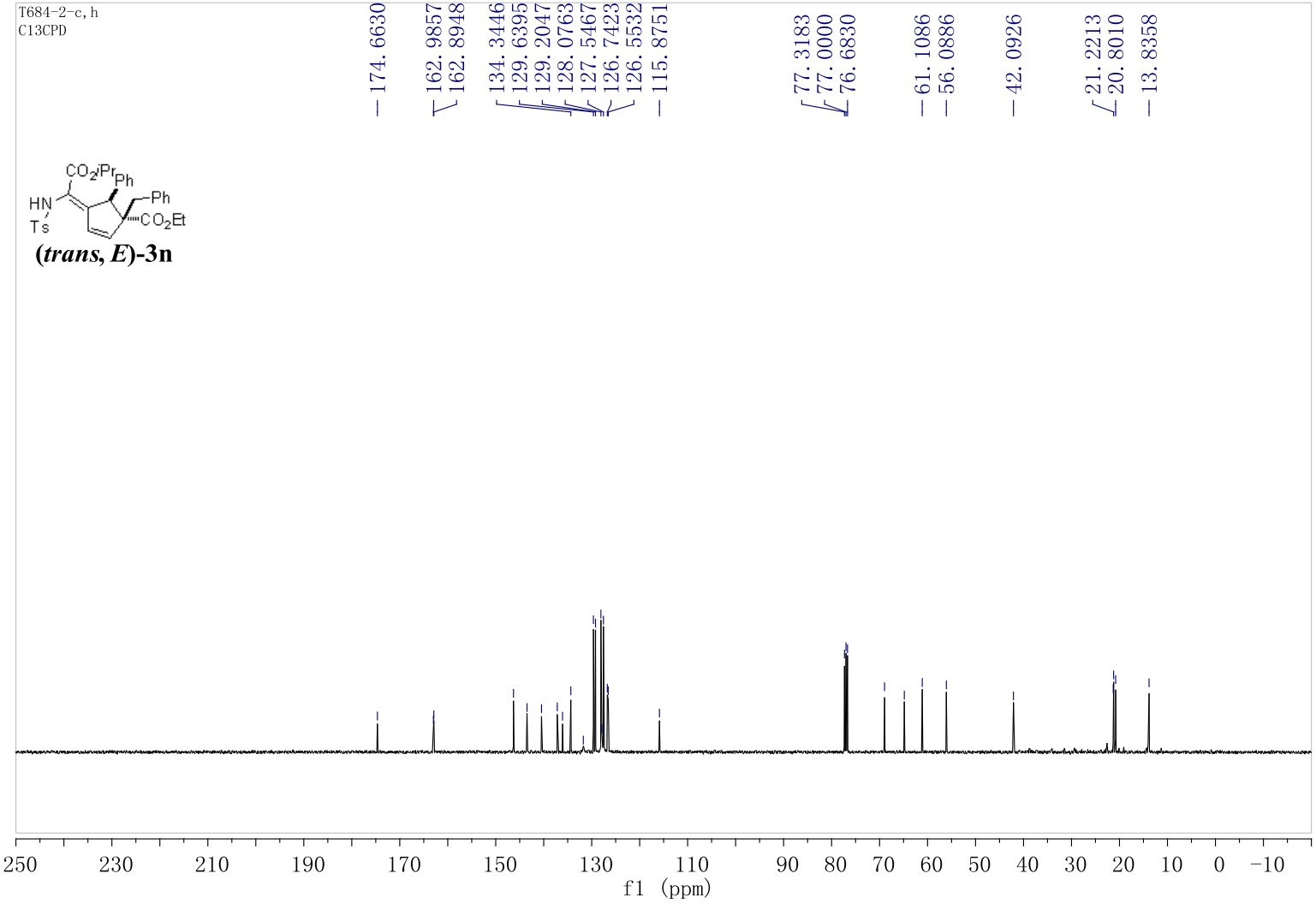
(*trans*, *E*)-3l

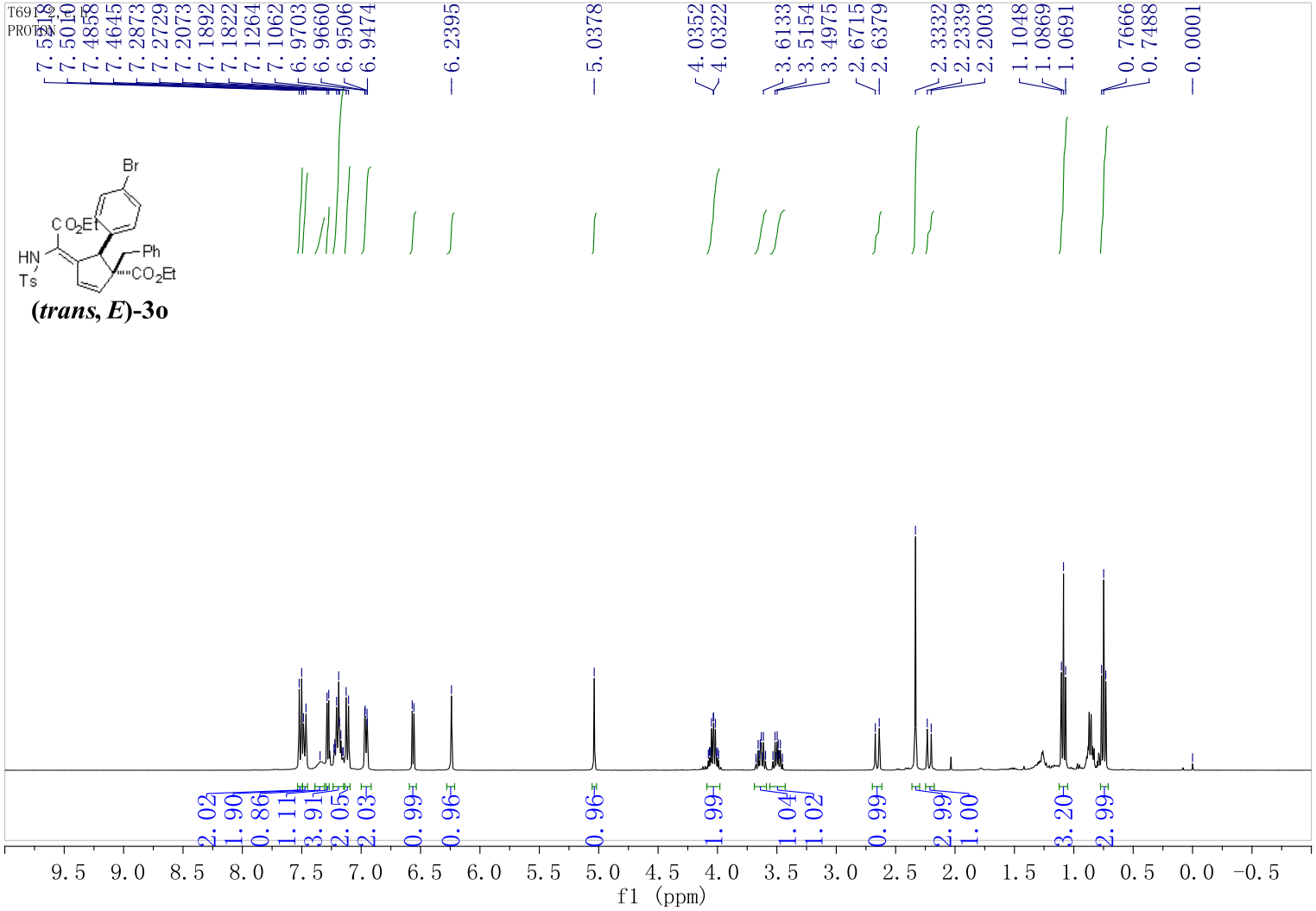

T610-2
PROTON
7.5221
7.5005
7.3479
7.3285
7.2991
7.2847
7.2769
7.2610
7.2055
7.1874
7.0900
7.0698
6.9814
6.9776
6.9618
6.5941
6.1031
6.0792
5.0389
4.0525
4.0423
4.0346
4.0245
4.0165
3.0439
2.3196
2.2516
2.2179
1.1182
1.1003
1.0825
-0.0003
CO2Me
Ph
Ph
HN
Ts
CO2Et
(trans, E)-3m
2.11
0.90
2.29
2.87
3.11
1.92
2.01
0.96
0.91
0.98
2.03
2.90
0.98
2.93
1.12
2.96
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

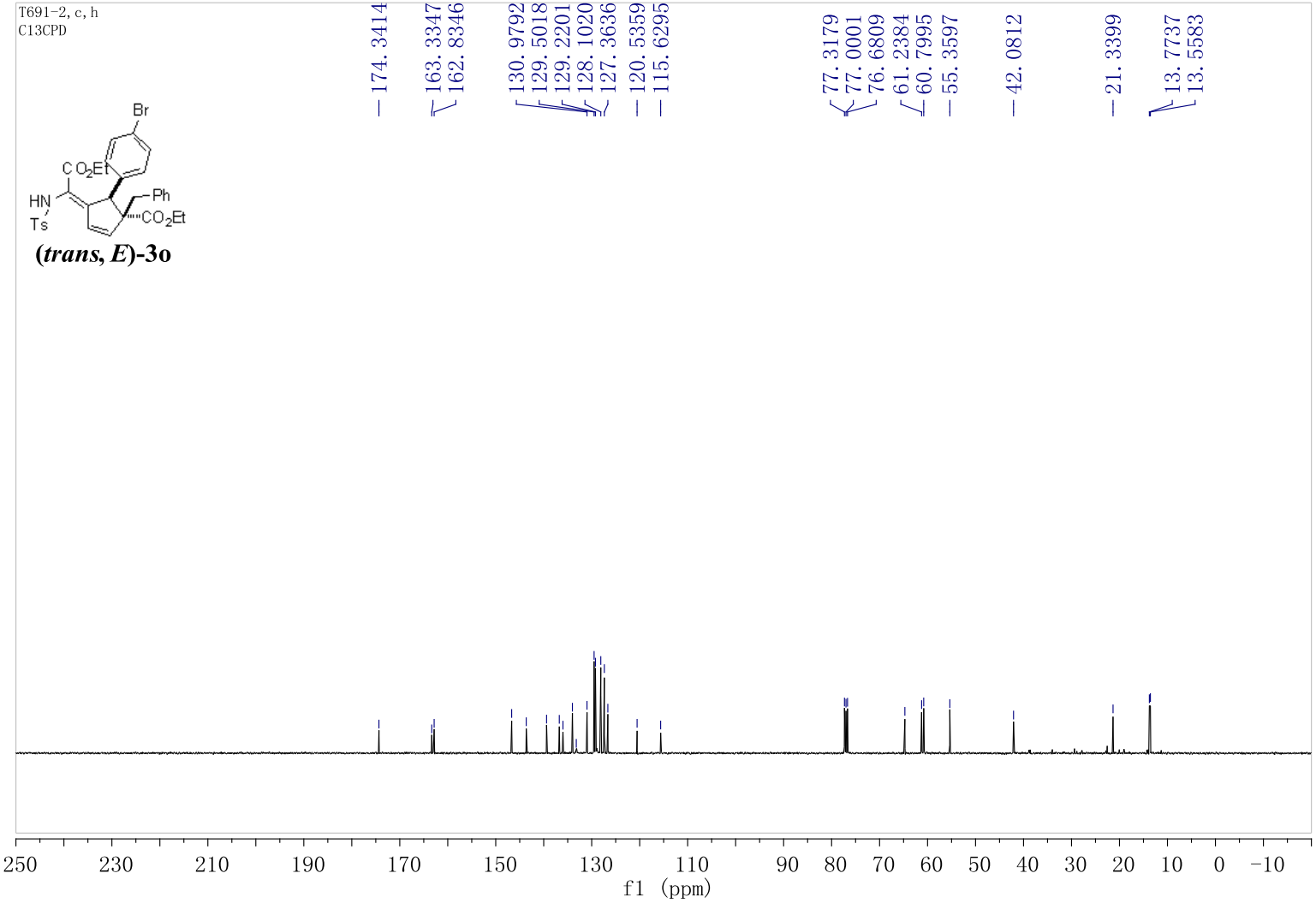


(*trans*, *E*)-3m

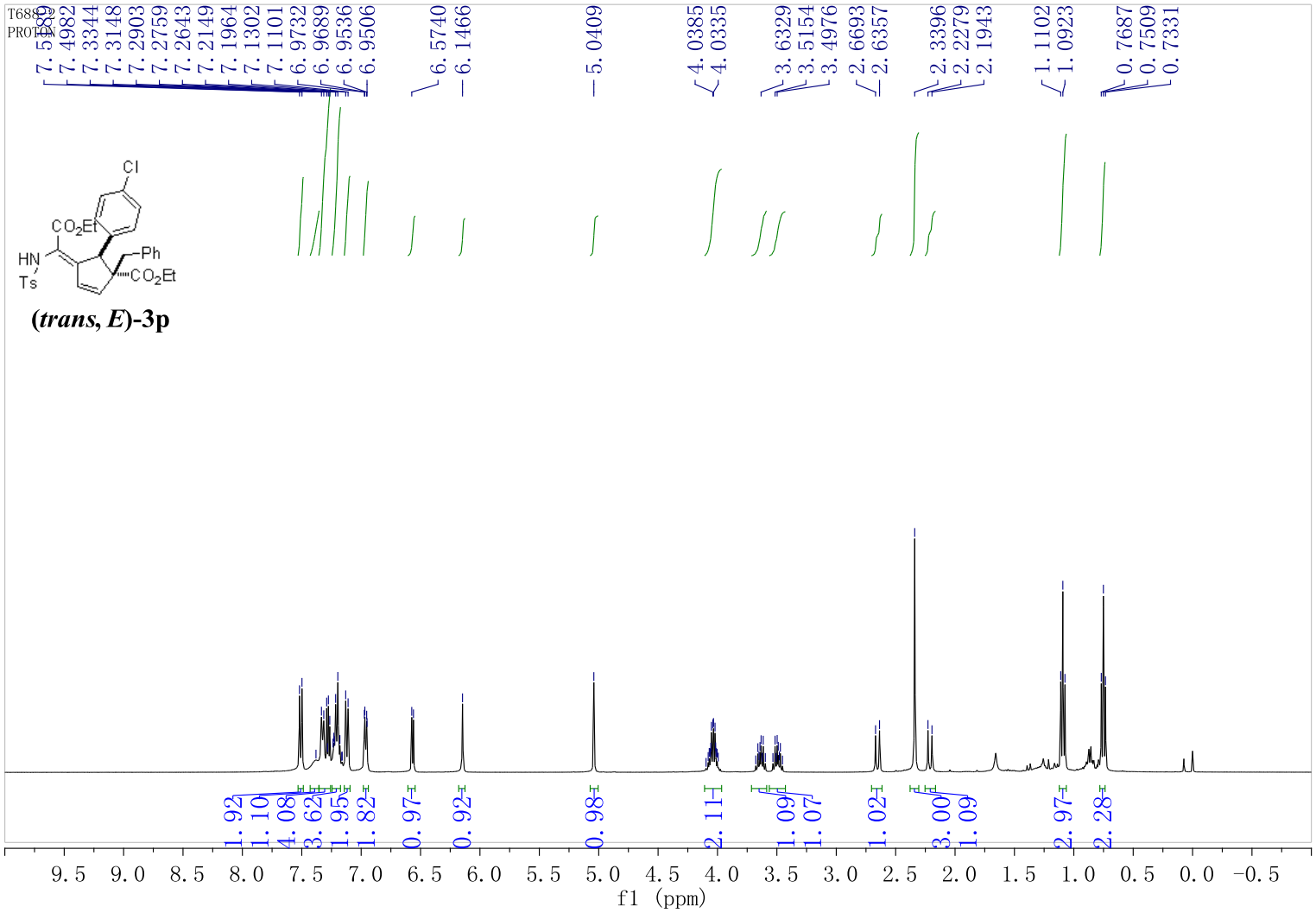

T6847
PROTON
7.5837
7.5430
7.3751
7.3566
7.3380
7.3297
7.3153
7.2623
7.2048
7.1864
7.1799
7.0871
7.0668
6.9899
6.9864
6.9702
6.5477
6.2548
5.0644
4.5021
4.0751
4.0572
4.0456
2.7174
2.6839
2.3021
2.1752
2.1417
1.1255
1.1077
0.6043
0.0003
CO2iPr
Ph
HN
Ts
Ph
CO2Et
(trans, E)-3n
2.03
1.10
3.71
0.86
3.09
2.01
1.98
0.97
0.90
0.97
0.95
2.10
0.98
2.96
1.03
3.31
3.15
2.90
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


T684-2-c, h
C13CPD
174.6630
162.9857
162.8948
134.3446
129.6395
129.2047
128.0763
127.5467
126.7423
126.5532
115.8751
77.3183
77.0000
76.6830
61.1086
56.0886
42.0926
21.2213
20.8010
13.8358
CO2iPr
Ph
HN
Ts
Ph
CO2Et
(trans, E)-3n
250
230
210
190
170
150
130
110
90
80
70
60
50
40
30
20
10
0
−10
f1 (ppm)


T691-8
PROTON
7.5118
7.5010
7.4858
7.4645
7.2873
7.2729
7.2073
7.1892
7.1822
7.1264
7.1062
6.9703
6.9660
6.9506
6.9474
6.2395
5.0378
4.0352
4.0322
3.6133
3.5154
3.4975
2.6715
2.6379
2.3332
2.2339
2.2003
1.1048
1.0869
1.0691
0.7666
0.7488
0.0001
Br
CO2Et
HN
Ts
Ph
CO2Et
(trans, E)-3o
2.02
1.90
0.86
1.11
3.91
2.05
2.03
0.99
0.96
0.96
1.99
1.04
1.02
0.99
2.99
1.00
3.20
2.99
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

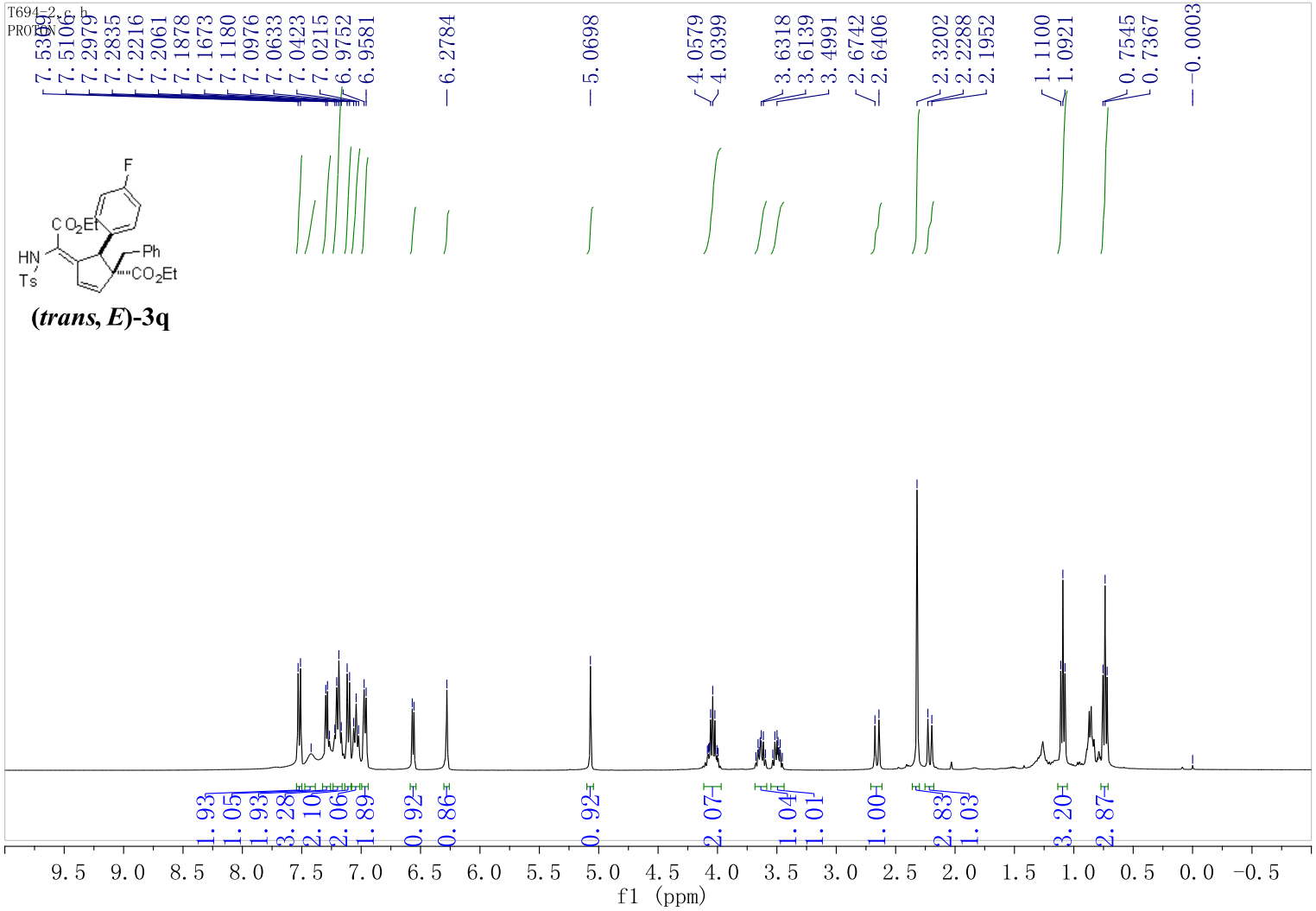

T691-2, c, h
C13CPD
174.3414
163.3347
162.8346
130.9792
129.5018
129.2201
128.1020
127.3636
120.5359
115.6295
77.3179
77.0001
76.6809
61.2384
60.7995
55.3597
42.0812
21.3399
13.7737
13.5583
Br
CO2Et
HN
Ts
Ph
CO2Et
250 230 210 190 170 150 130 110 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

(*trans*, *E*)-3o

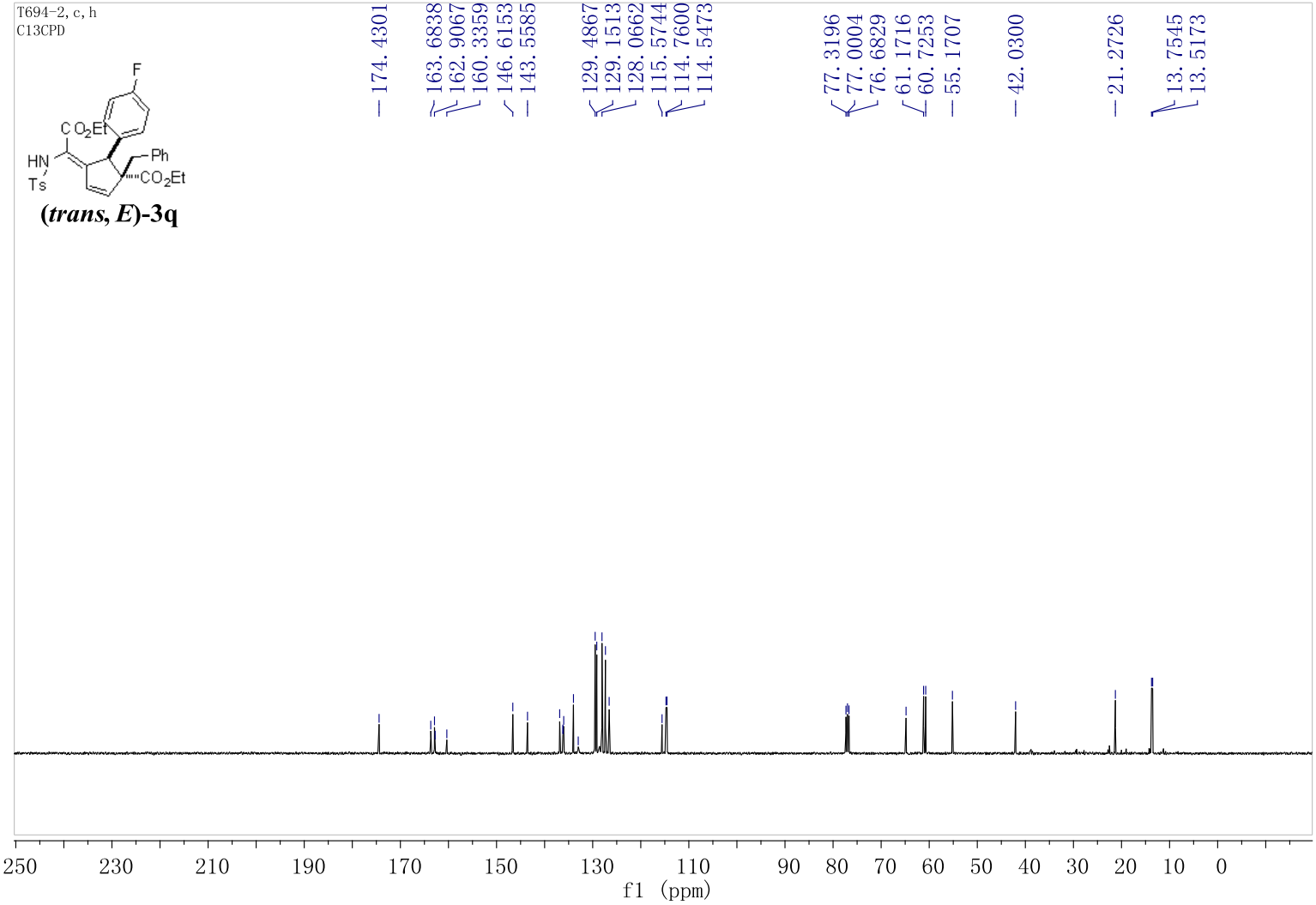

T6888
PROTON
7.5889
7.4982
7.3344
7.3148
7.2903
7.2759
7.2643
7.2149
7.1964
7.1302
7.1101
6.9732
6.9689
6.9536
6.9506
6.5740
6.1466
5.0409
4.0385
4.0335
3.6329
3.5154
3.4976
2.6693
2.6357
2.3396
2.2279
2.1943
1.1102
1.0923
0.7687
0.7509
0.7331
Cl
CO2Et
HN
Ts
Ph
CO2Et
1.92
1.10
4.08
3.62
1.95
1.82
0.97
0.92
0.98
2.11
1.09
1.07
1.02
3.00
1.09
2.97
2.28
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

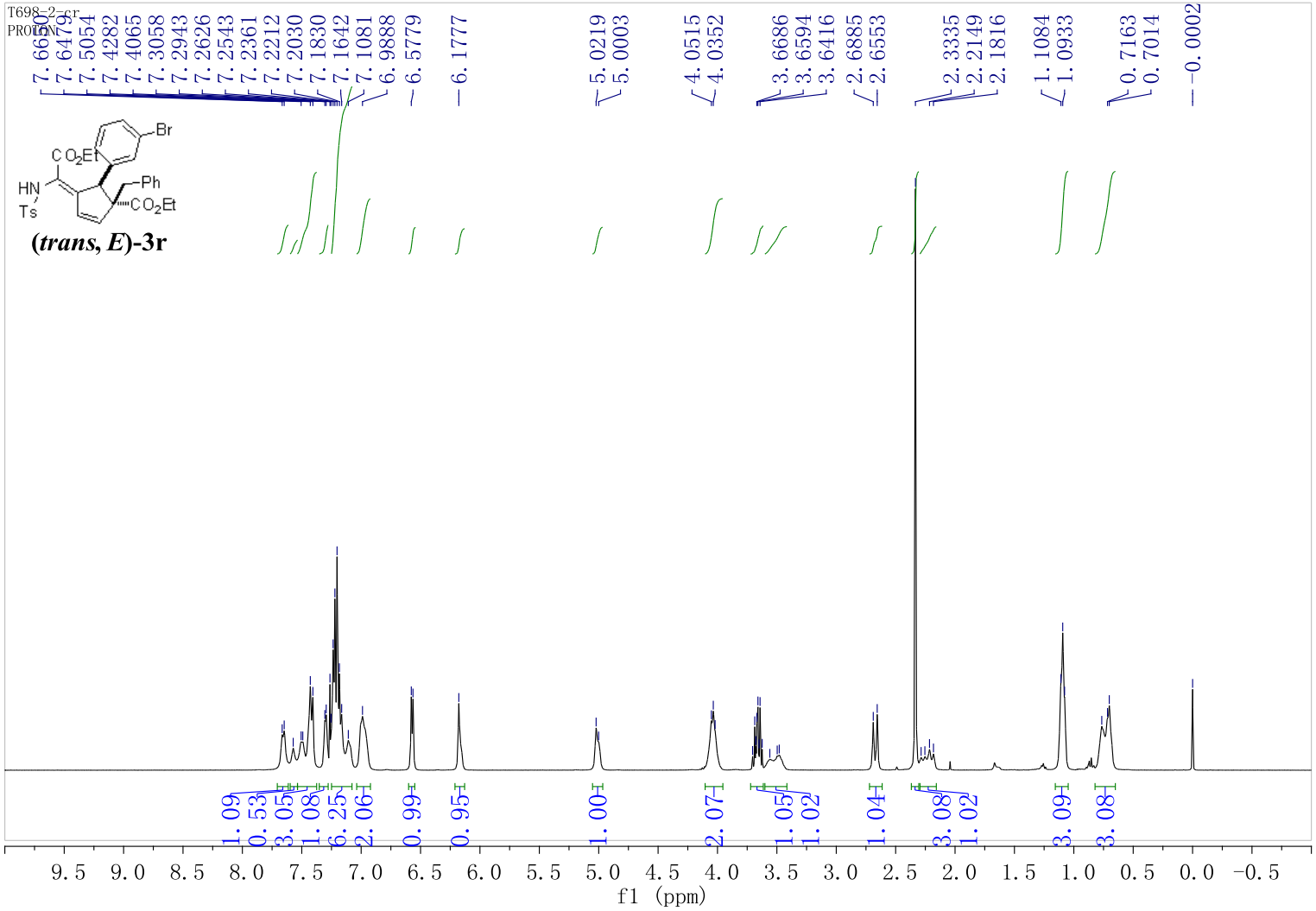
(*trans*, *E*)-3p

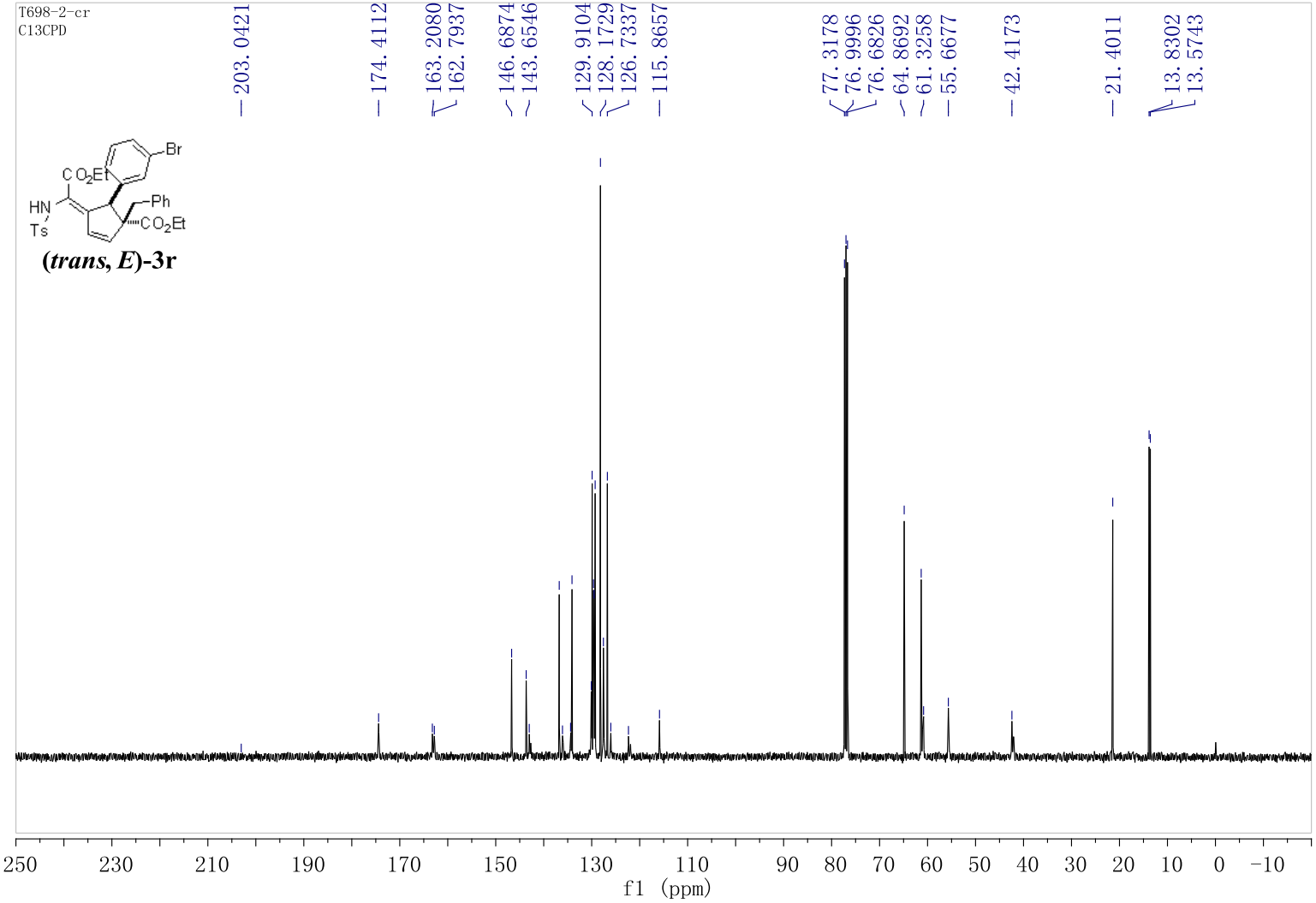
错误！不能通过编辑域代码创建对象。

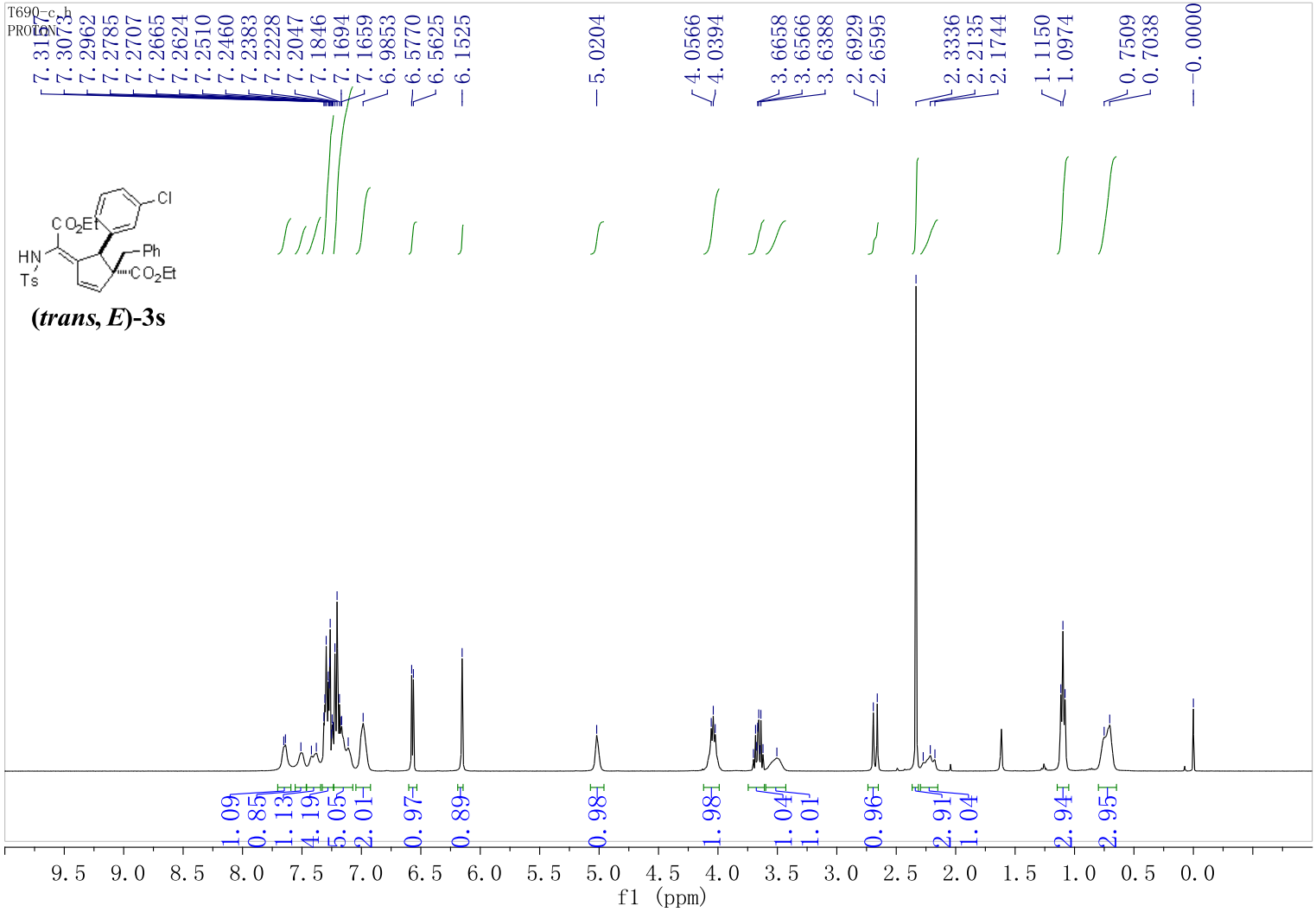

7.5306
7.5106
7.2979
7.2835
7.2216
7.2061
7.1878
7.1673
7.1180
7.0976
7.0633
7.0423
7.0215
6.9752
6.9581
6.2784
5.0698
4.0579
4.0399
3.6318
3.6139
3.4991
2.6742
2.6406
2.3202
2.2288
2.1952
1.1100
1.0921
0.7545
0.7367
-0.0003
F
CO2Et
HN
Ts
Ph
CO2Et
1.93
1.05
1.93
3.28
2.10
2.06
1.89
0.92
0.86
0.92
2.07
1.04
1.01
1.00
2.83
1.03
3.20
2.87
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

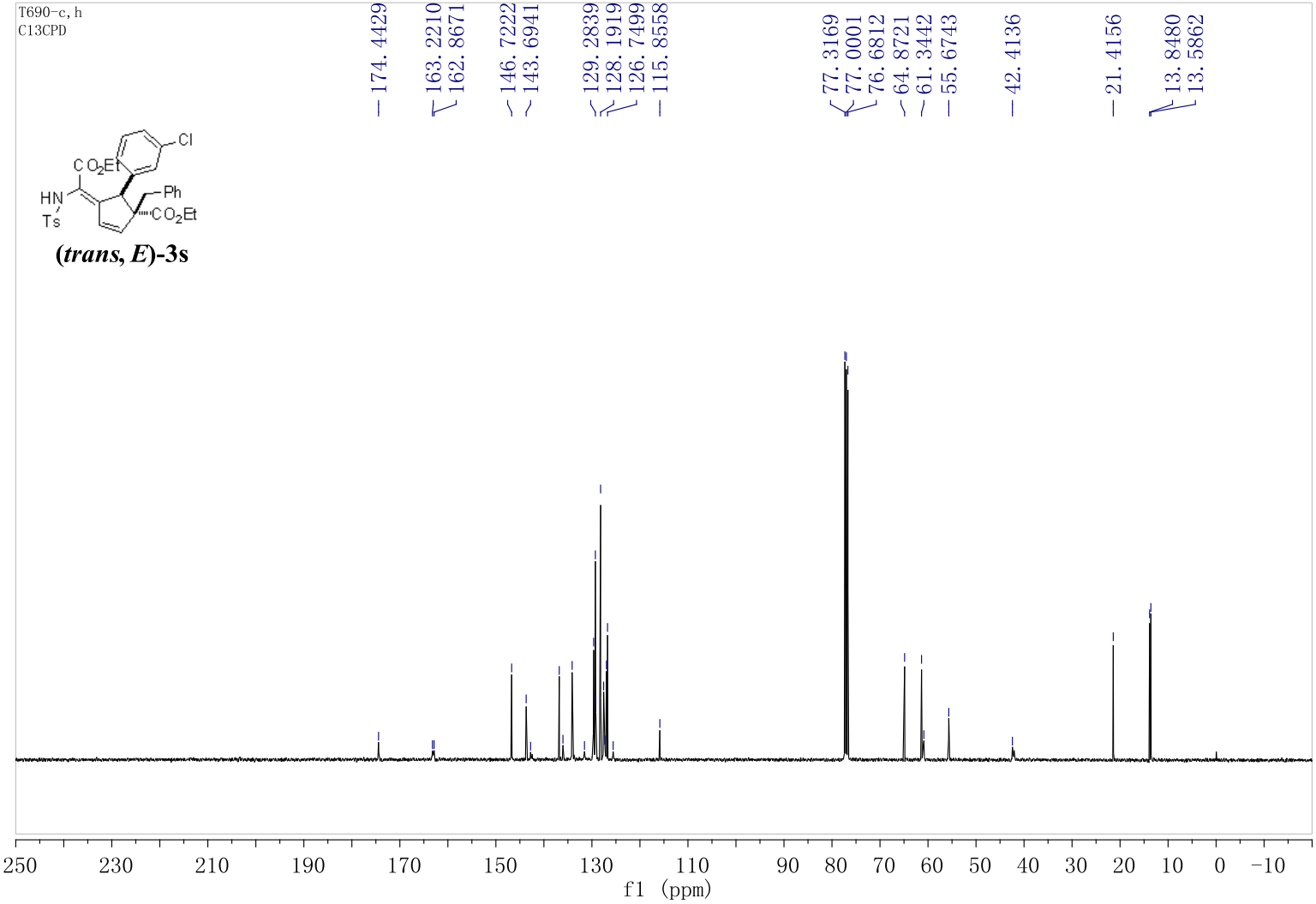
(*trans*, *E*)-3q



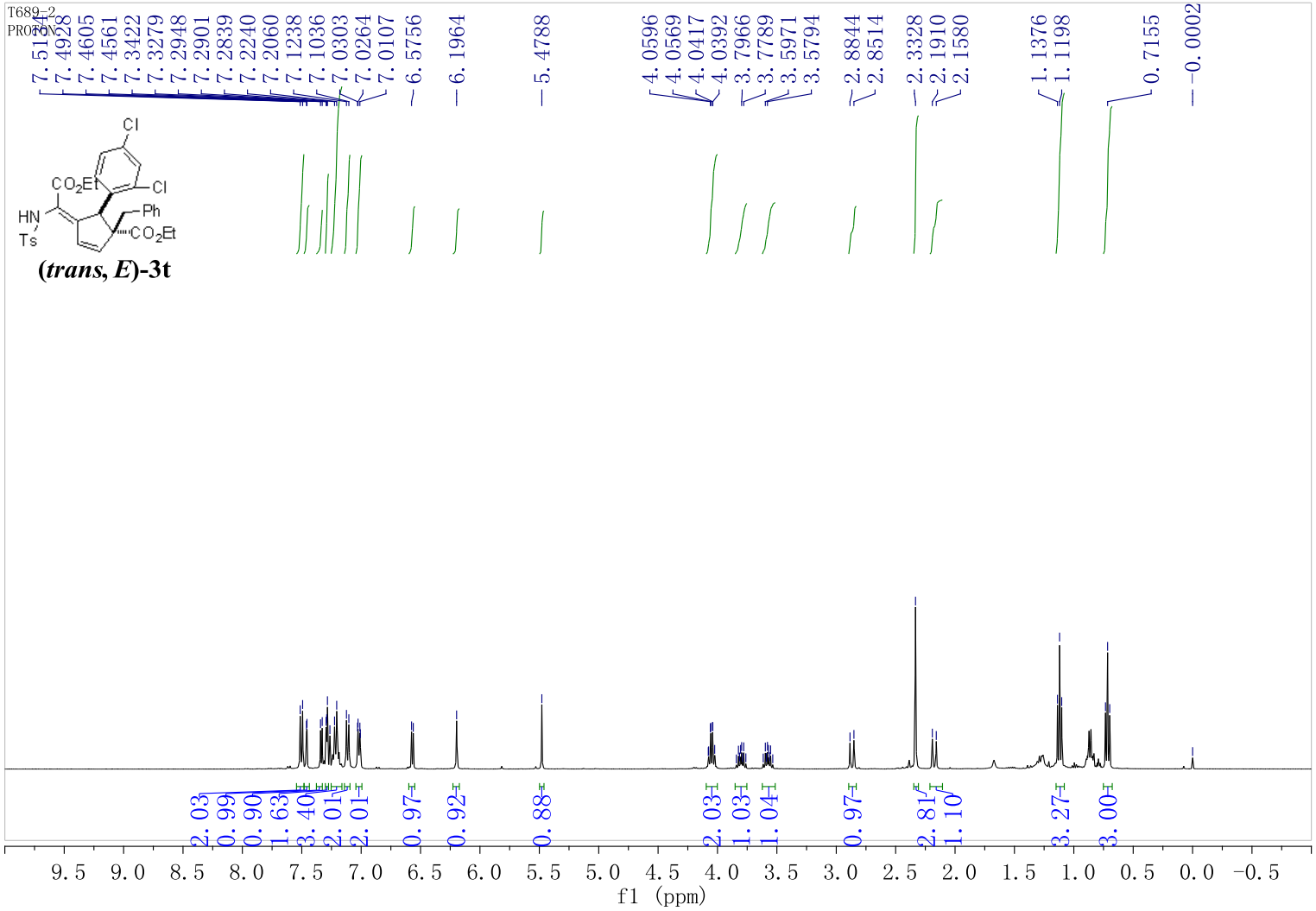

T698-2-cr
PROTON
7.6650
7.6479
7.5054
7.4282
7.4065
7.3058
7.2943
7.2626
7.2543
7.2361
7.2212
7.2030
7.1830
7.1642
7.1081
6.9888
6.5779
6.1777
5.0219
5.0003
4.0515
4.0352
3.6686
3.6594
3.6416
2.6885
2.6553
2.3335
2.2149
2.1816
1.1084
1.0933
0.7163
0.7014
-0.0002
Br
CO2Et
HN
Ts
Ph
CO2Et
(trans, E)-3r
1.09
0.53
3.05
1.08
6.25
2.06
0.99
0.95
1.00
2.07
1.05
1.02
1.04
3.08
1.02
3.09
3.08
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

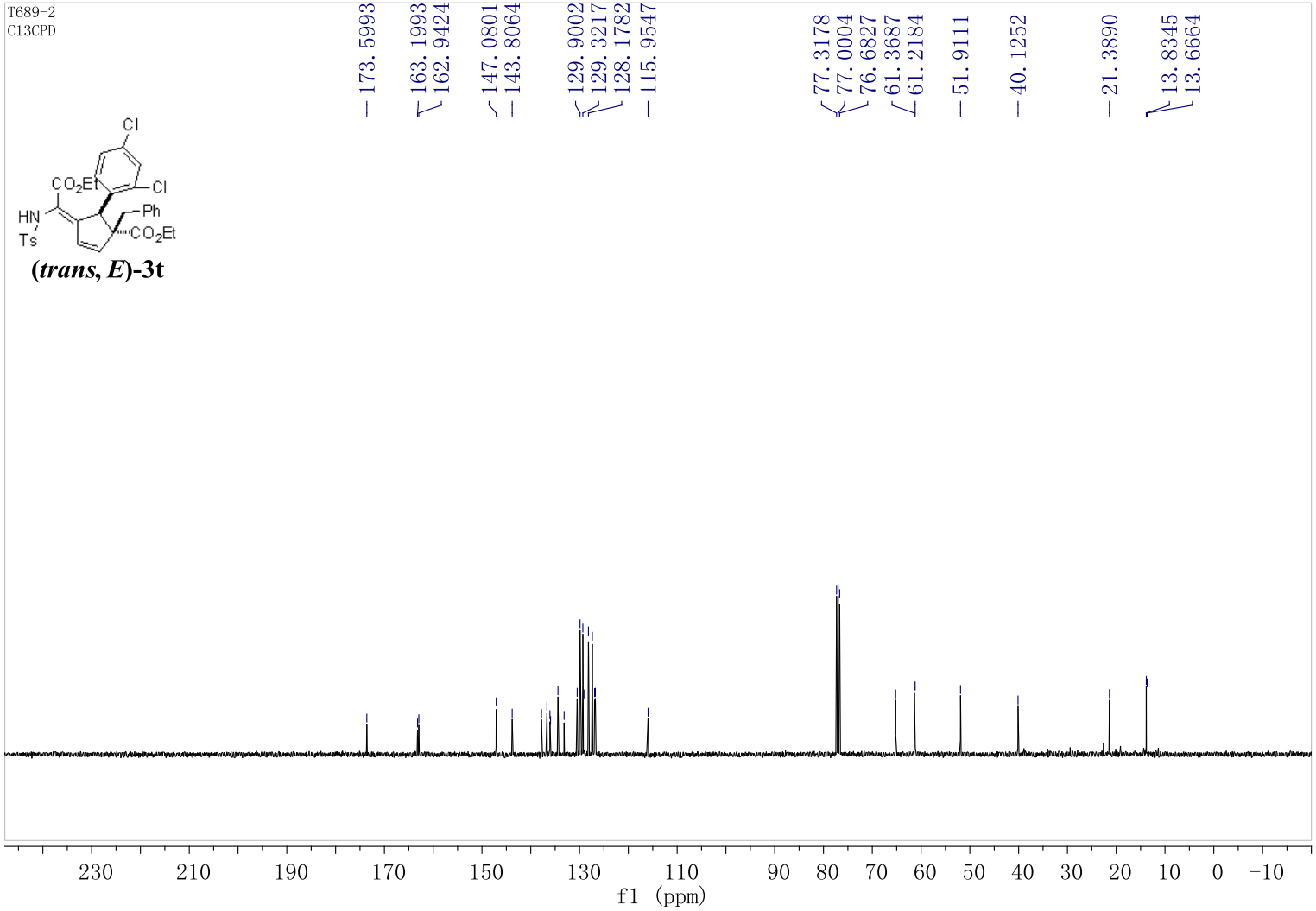



T690-c_h
PROTON
7.3153
7.3073
7.2962
7.2785
7.2707
7.2665
7.2624
7.2510
7.2460
7.2383
7.2228
7.2047
7.1846
7.1694
7.1659
6.9853
6.5770
6.5625
6.1525
5.0204
4.0566
4.0394
3.6658
3.6566
3.6388
2.6929
2.6595
2.3336
2.2135
2.1744
1.1150
1.0974
0.7509
0.7038
-0.0000
Cl
CO2Et
HN
Ts
Ph
CO2Et
(trans, E)-3s
1.09
0.85
1.13
4.19
5.05
2.01
0.97
0.89
0.98
1.98
1.04
1.01
0.96
2.91
1.04
2.94
2.95
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

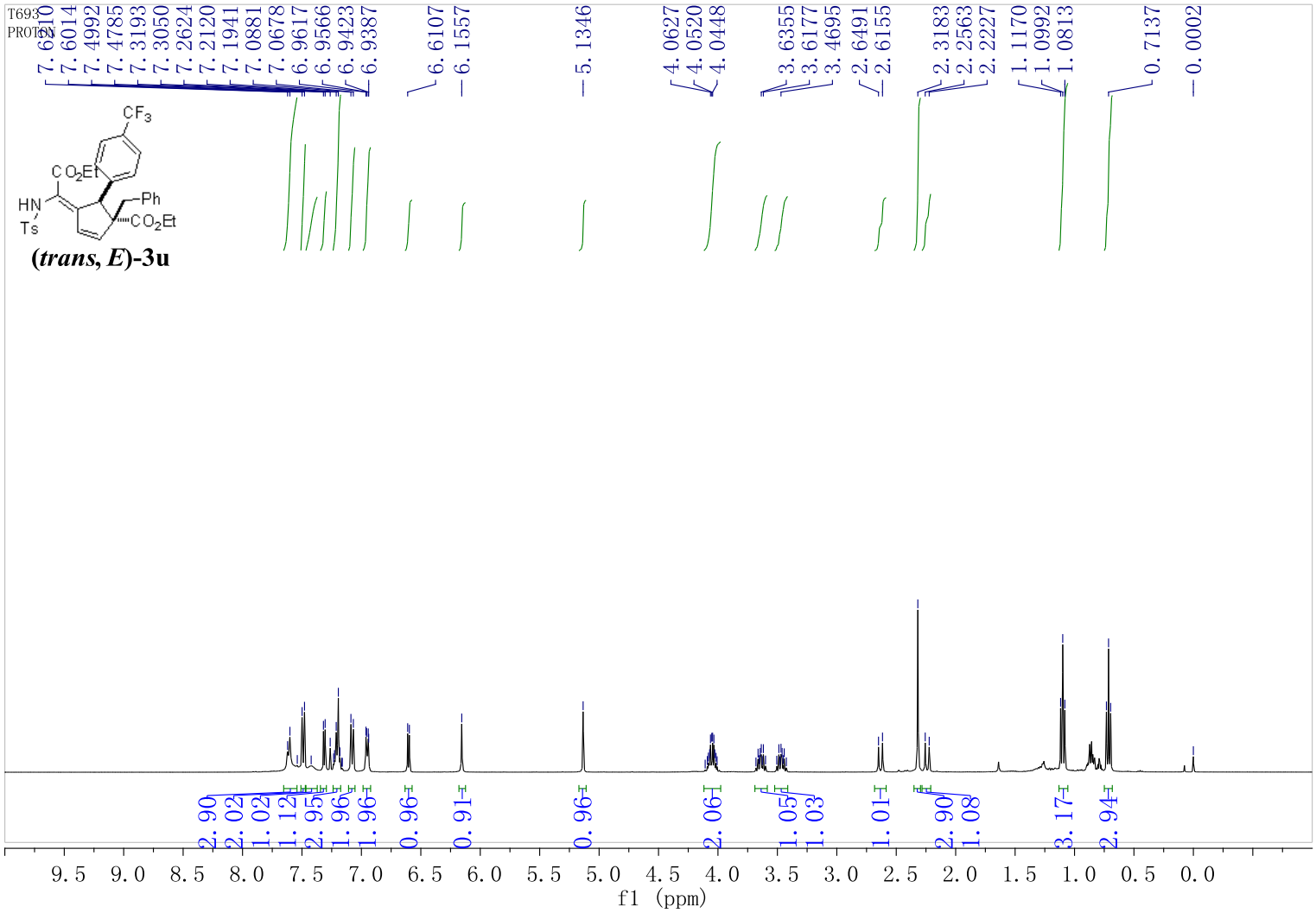


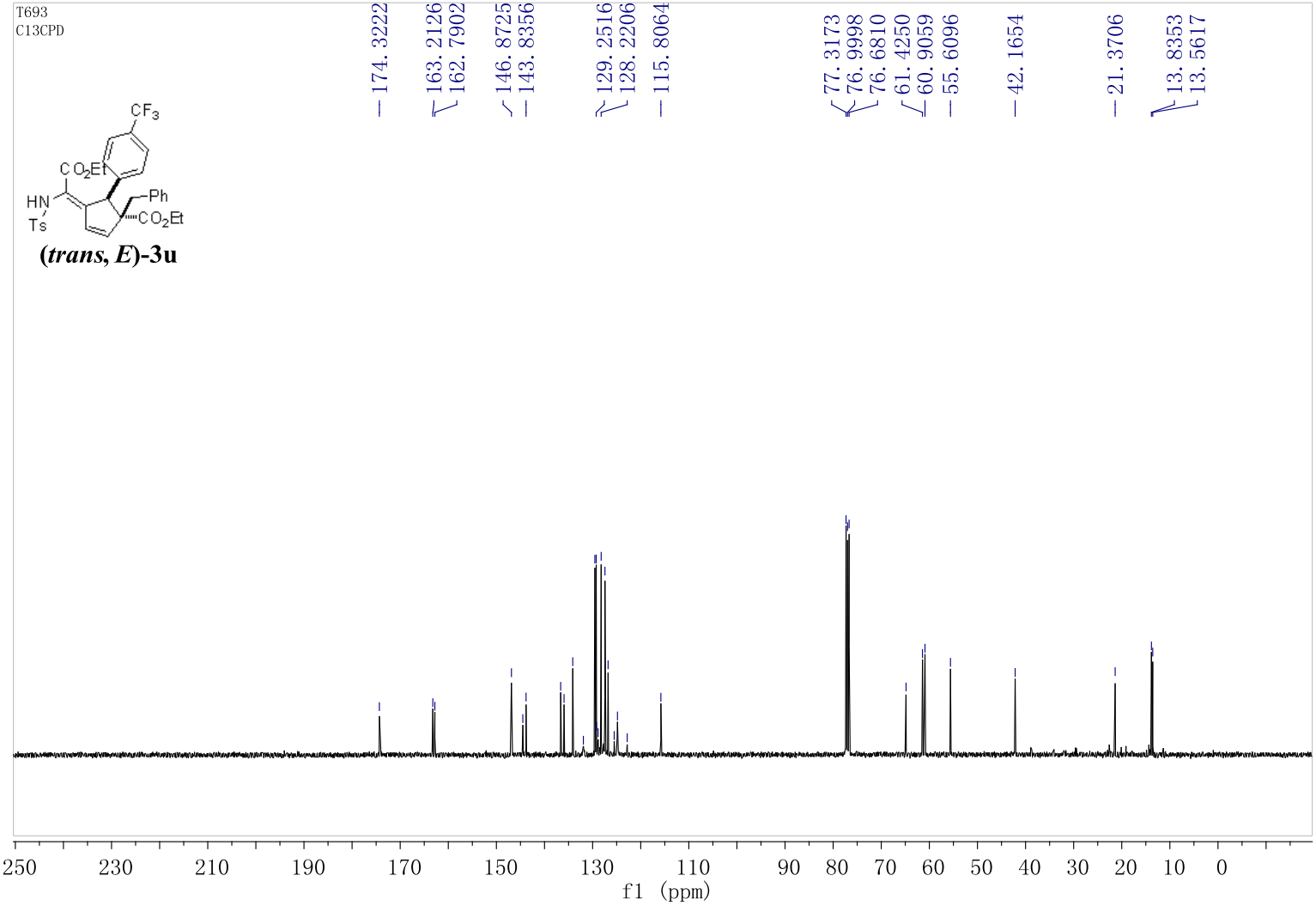
(*trans*, *E*)-3s


T689-2
PROTON
7.5154
7.4928
7.4605
7.4561
7.3422
7.3279
7.2948
7.2901
7.2839
7.2240
7.2060
7.1238
7.1036
7.0303
7.0264
7.0107
6.5756
6.1964
5.4788
4.0596
4.0569
4.0417
4.0392
3.7966
3.7789
3.5971
3.5794
2.8844
2.8514
2.3328
2.1910
2.1580
1.1376
1.1198
0.7155
-0.0002
Cl
CO2Et
Cl
HN
Ts
Ph
CO2Et
(trans, E)-3t
2.03
0.99
0.90
1.63
3.40
2.01
2.01
0.97
0.92
0.88
2.03
1.03
1.04
0.97
2.81
1.10
3.27
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

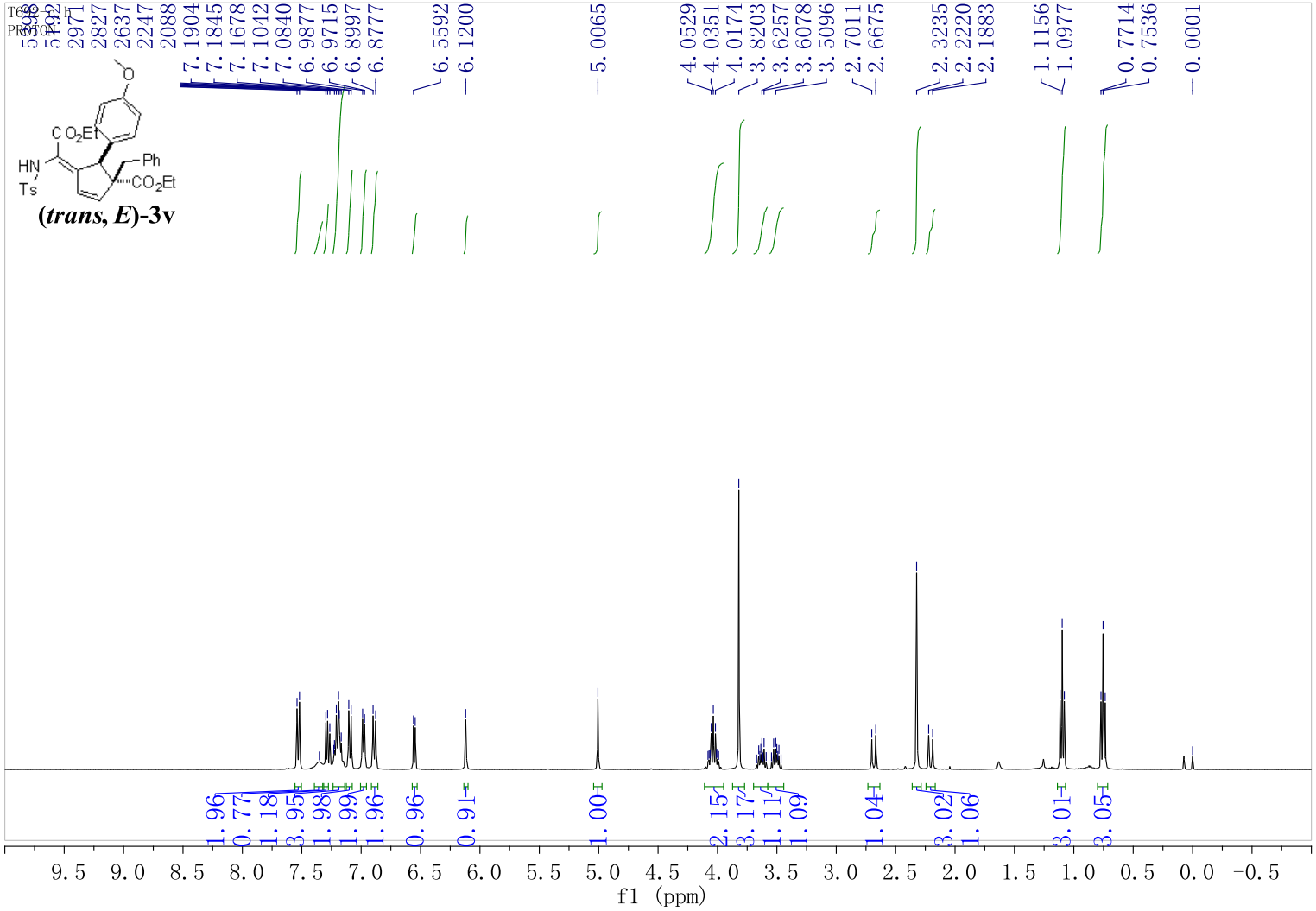


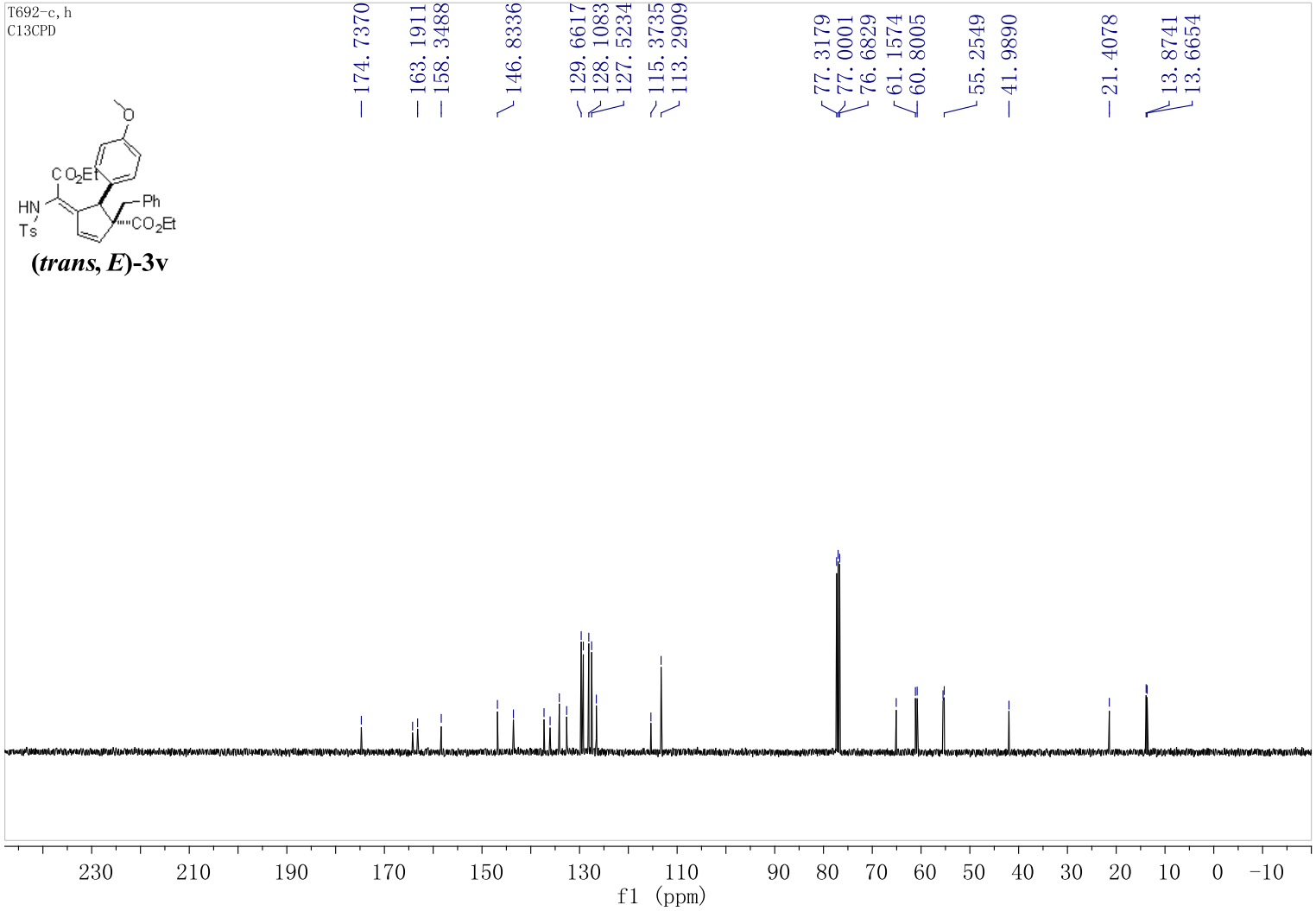
(*trans*, *E*)-3t


T693
PROTON
7.6010
7.6014
7.4992
7.4785
7.3193
7.3050
7.2624
7.2120
7.1941
7.0881
7.0678
6.9617
6.9566
6.9423
6.9387
6.6107
6.1557
5.1346
4.0627
4.0520
4.0448
3.6355
3.6177
3.4695
2.6491
2.6155
2.3183
2.2563
2.2227
1.1170
1.0992
1.0813
0.7137
0.0002
CF3
CO2Et
HN
Ts
Ph
CO2Et
(trans, E)-3u
2.90
2.02
1.02
1.12
2.95
1.96
1.96
0.96
0.91
0.96
2.06
1.05
1.03
1.01
2.90
1.08
3.17
2.94
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

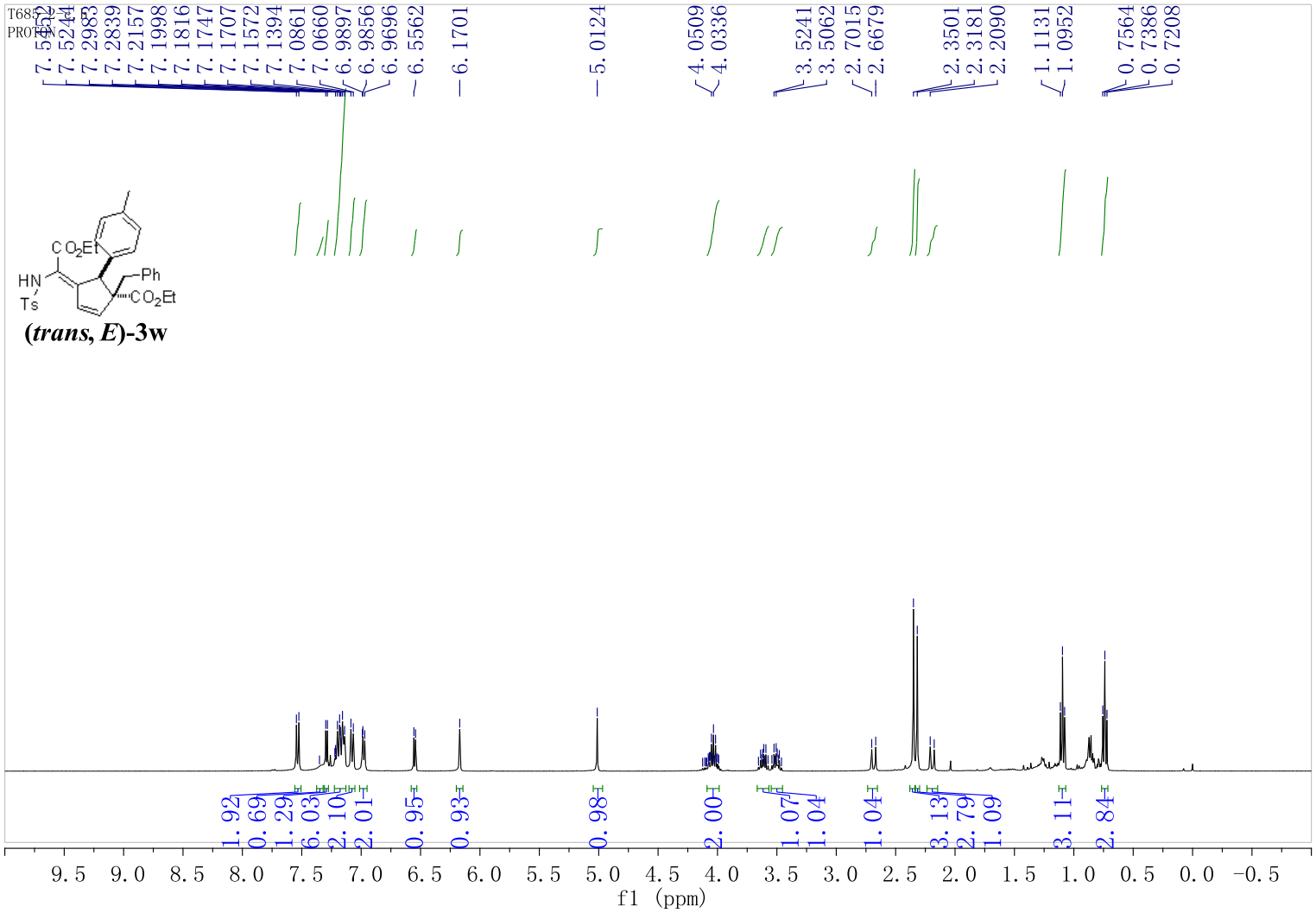


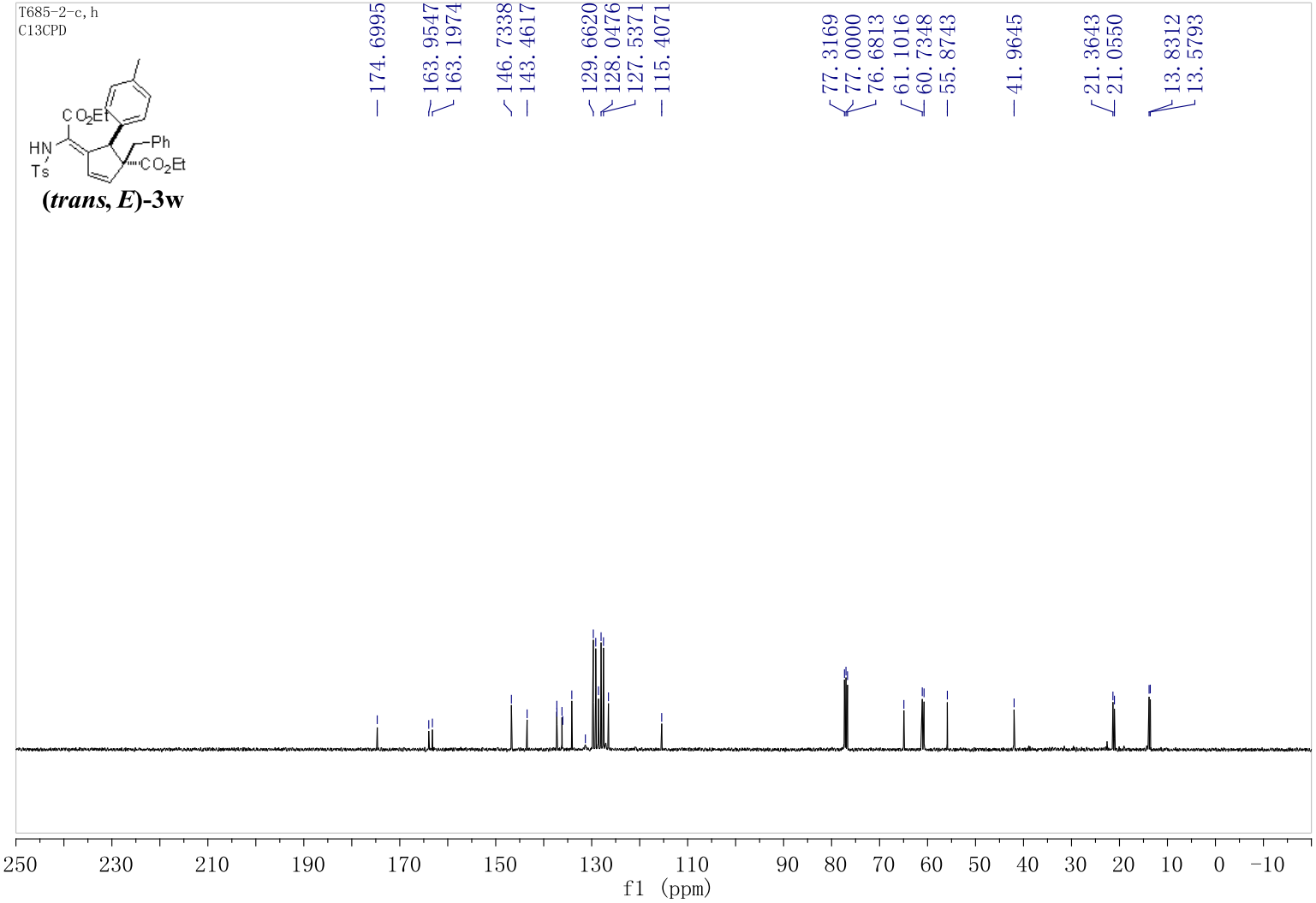
(*trans*, *E*)-3u

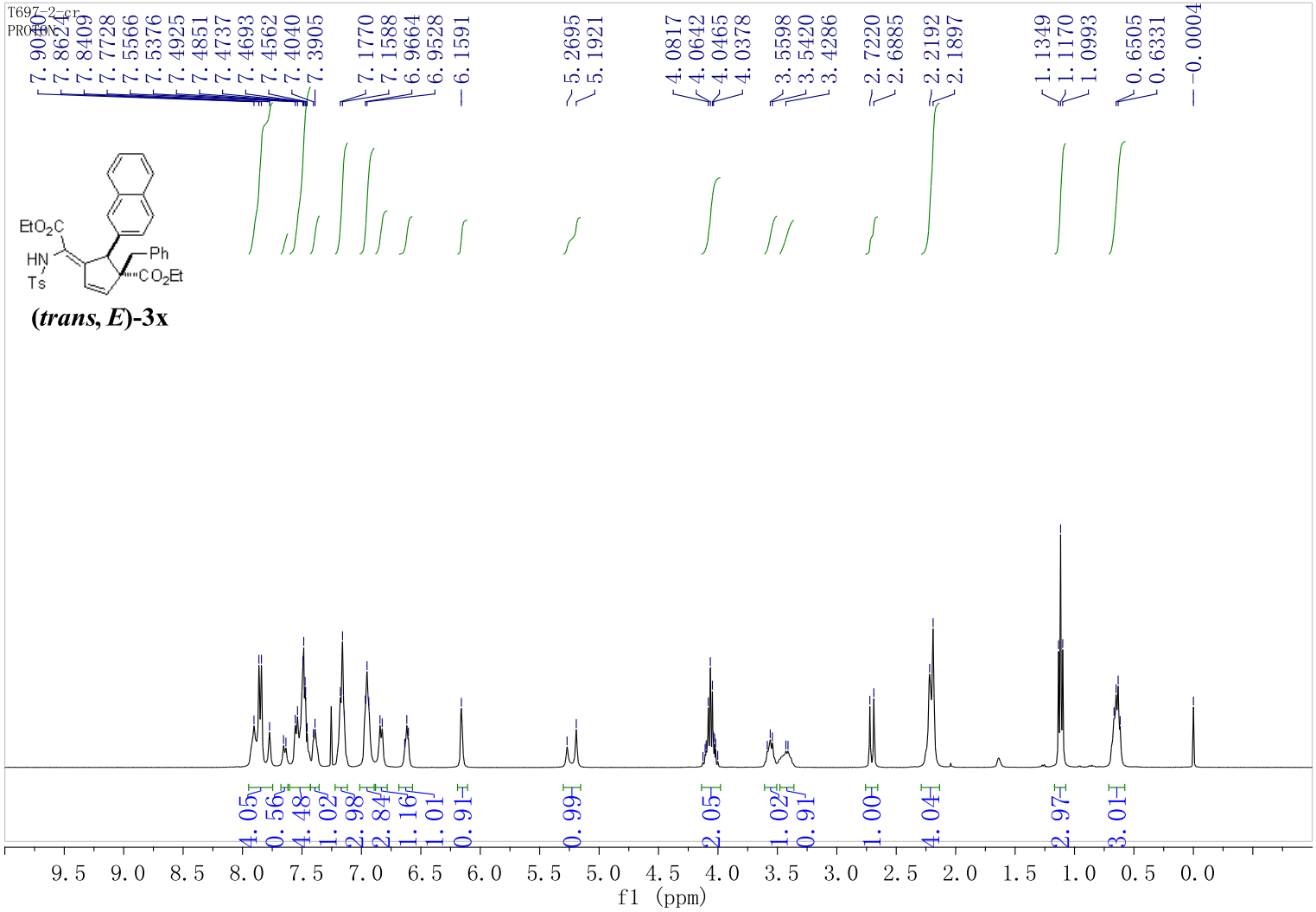

(trans, E)-3v
f1 (ppm)

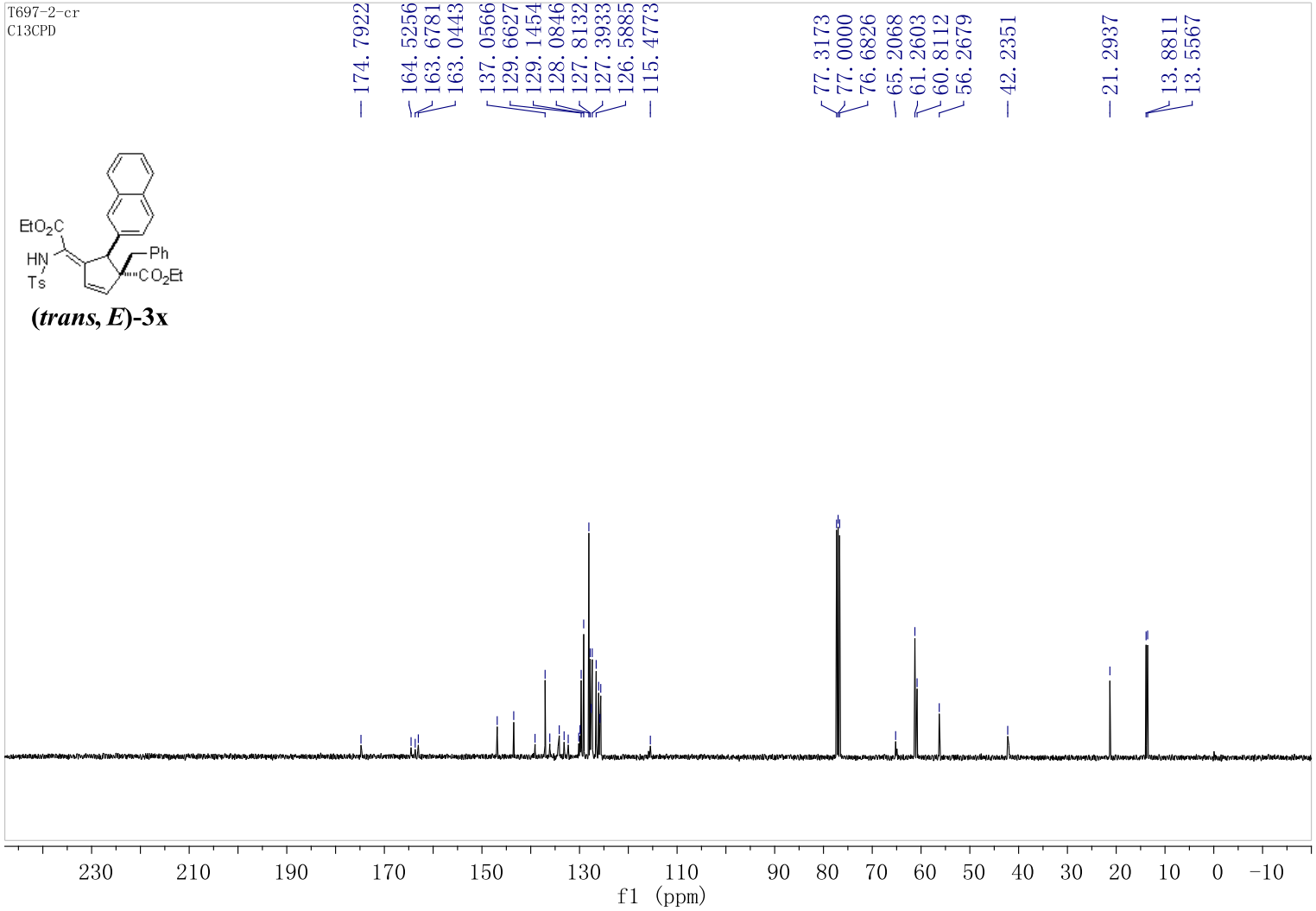


(*trans*, *E*)-3v

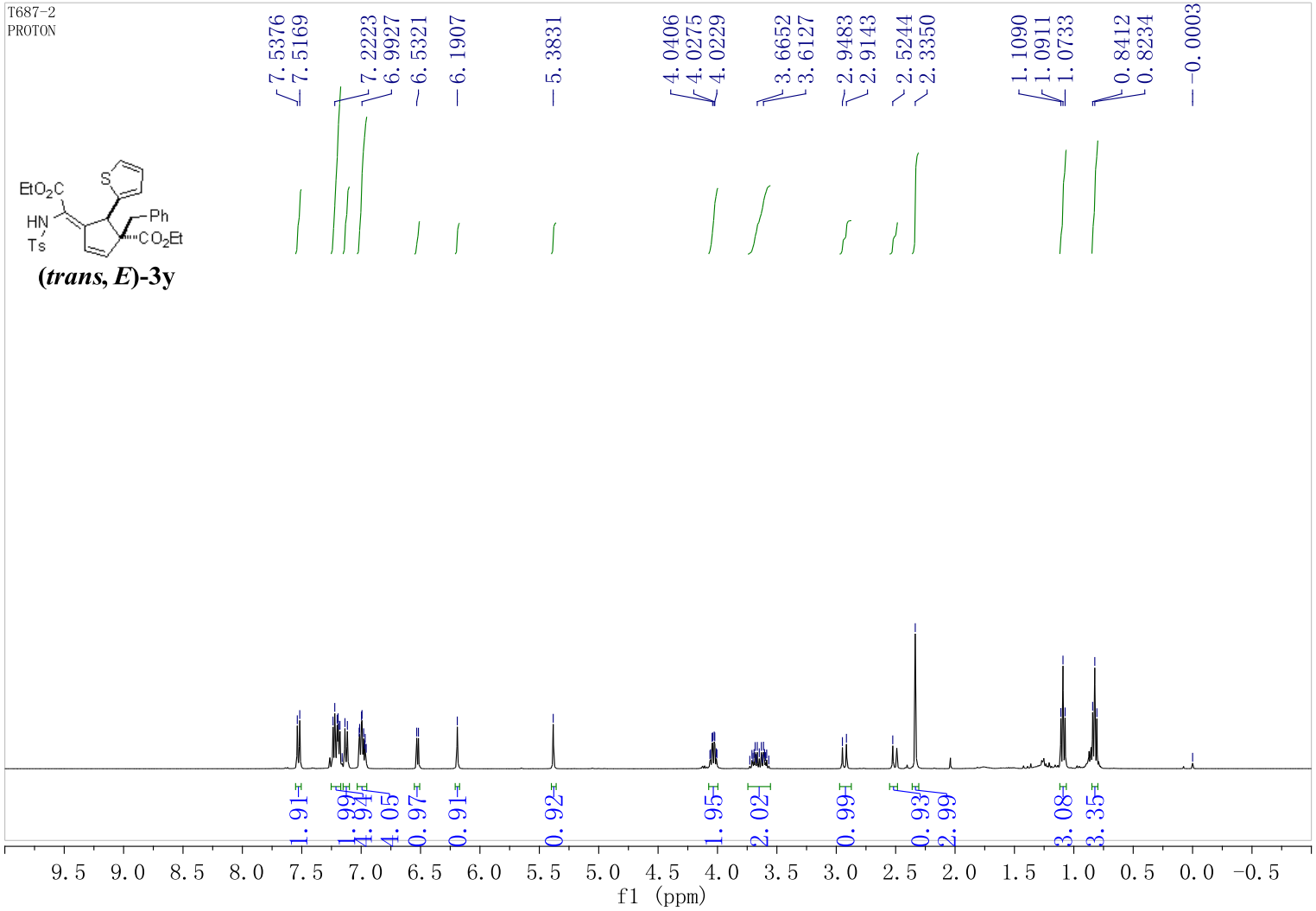

T685-2
PROTON
7.5522
7.5244
7.2983
7.2839
7.2157
7.1998
7.1816
7.1747
7.1707
7.1572
7.1394
7.0861
7.0660
6.9897
6.9856
6.9696
6.5562
6.1701
5.0124
4.0509
4.0336
3.5241
3.5062
2.7015
2.6679
2.3501
2.3181
2.2090
1.1131
1.0952
0.7564
0.7386
0.7208
CO2Et
HN
Ts
Ph
CO2Et
(trans, E)-3w
1.92
0.69
1.29
6.03
2.10
2.01
0.95
0.93
0.98
2.00
1.07
1.04
1.04
3.13
2.79
1.09
3.11
2.84
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

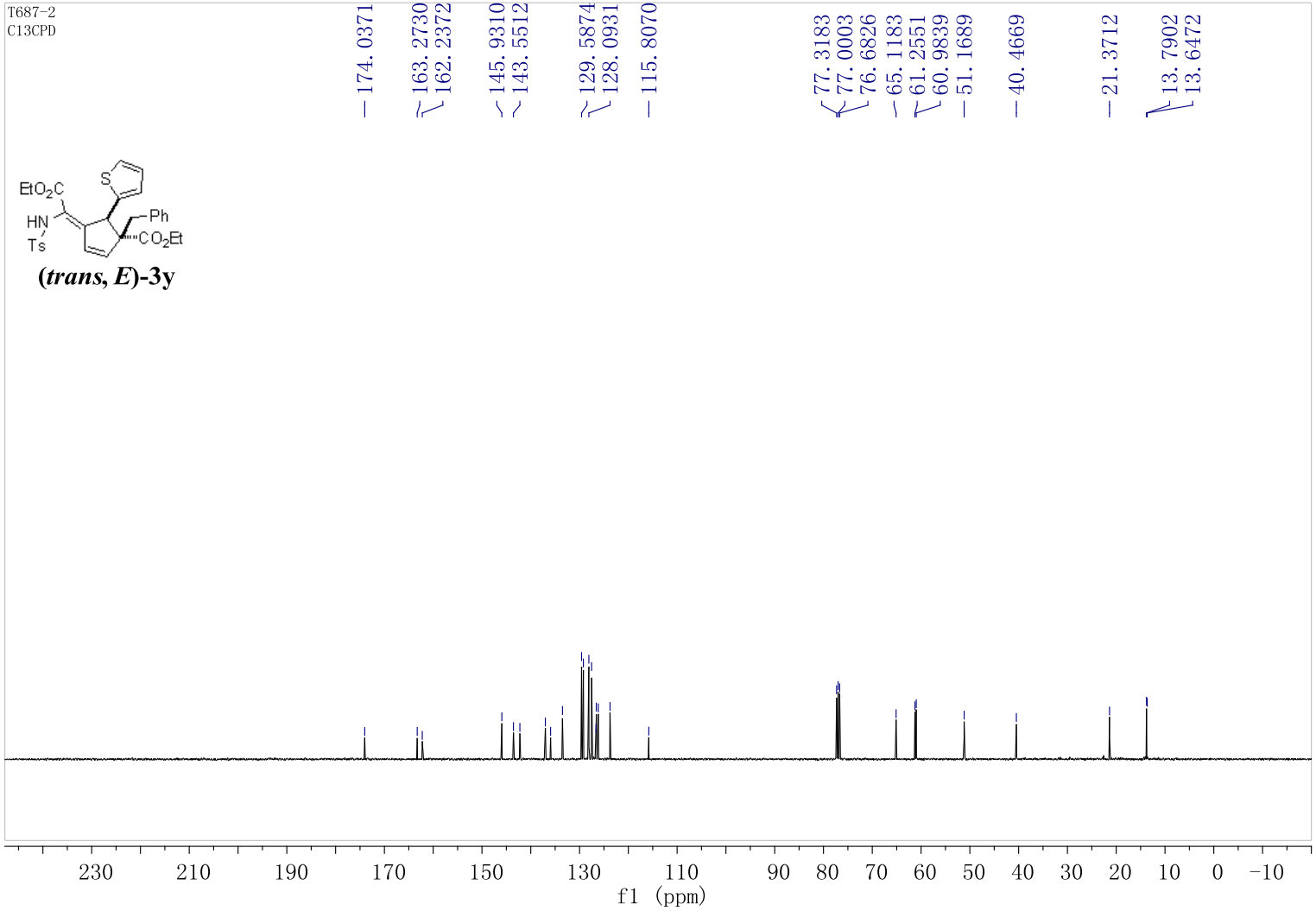


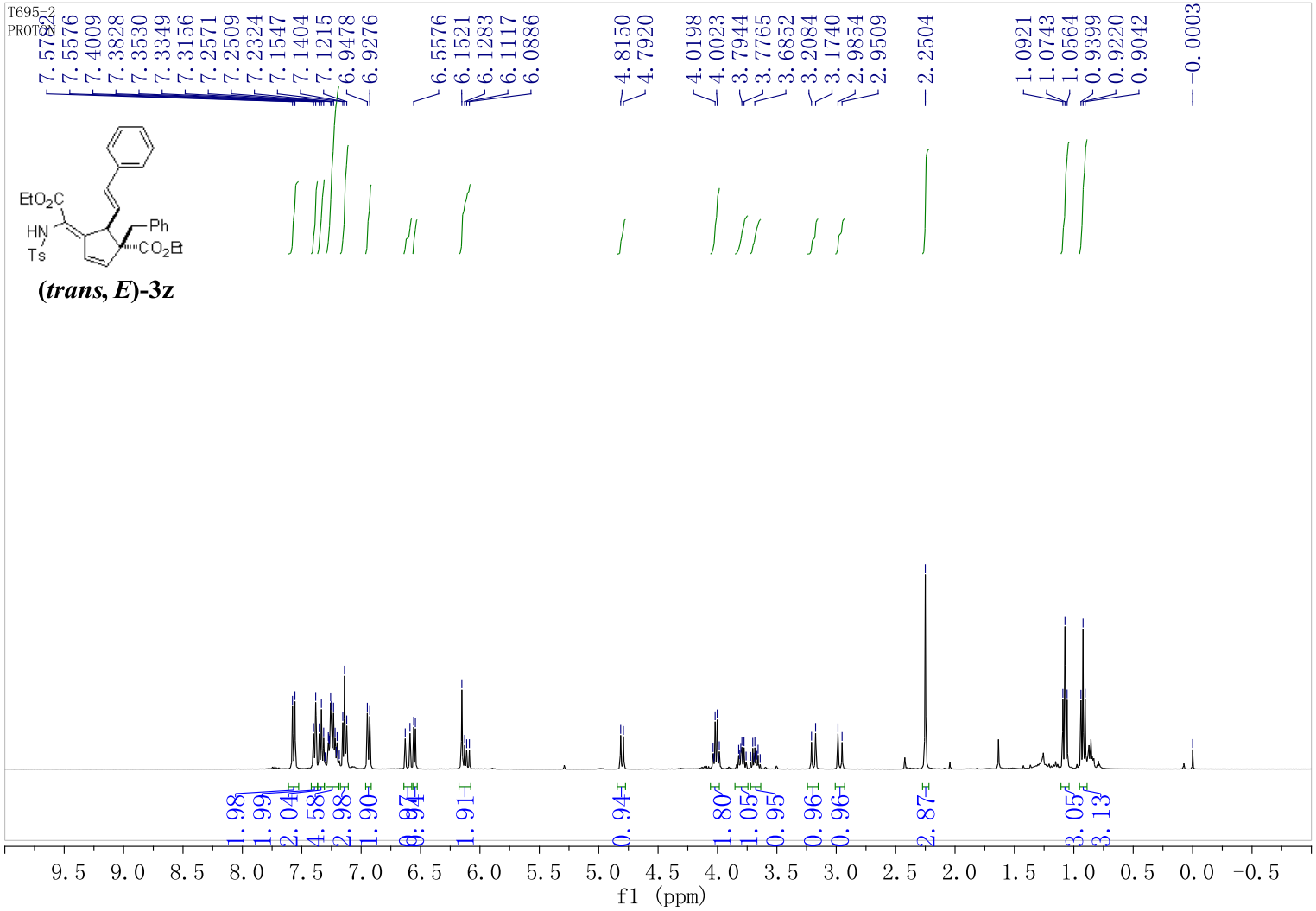

T697-2-cr
PROTON
7.9057
7.8627
7.8409
7.7728
7.5566
7.5376
7.4925
7.4851
7.4737
7.4693
7.4562
7.4040
7.3905
7.1770
7.1588
6.9664
6.9528
6.1591
5.2695
5.1921
4.0817
4.0642
4.0465
4.0378
3.5598
3.5420
3.4286
2.7220
2.6885
2.2192
2.1897
1.1349
1.1170
1.0993
0.6505
0.6331
-0.0004
EtO2C
HN
Ts
Ph
CO2Et
(trans, E)-3x
4.05
0.56
4.48
1.02
2.98
2.84
1.16
1.01
0.91
0.99
2.05
1.02
0.91
1.00
4.04
2.97
3.01
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)



(*trans*, *E*)-3x


T687-2
PROTON
7.5376
7.5169
7.2223
6.9927
6.5321
6.1907
5.3831
4.0406
4.0275
4.0229
3.6652
3.6127
2.9483
2.9143
2.5244
2.3350
1.1090
1.0911
1.0733
0.8412
0.8234
-0.0003
EtO2C
HN
Ts
S
Ph
CO2Et
(trans, E)-3y
1.91
1.99
4.14
4.05
0.97
0.91
0.92
1.95
2.02
0.99
0.93
2.99
3.08
3.35
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)




T695-2
PROTON
7.5782
7.5576
7.4009
7.3828
7.3530
7.3349
7.3156
7.2571
7.2509
7.2324
7.1547
7.1404
7.1215
6.9478
6.9276
6.5576
6.1521
6.1283
6.1117
6.0886
4.8150
4.7920
4.0198
4.0023
3.7944
3.7765
3.6852
3.2084
3.1740
2.9854
2.9509
2.2504
1.0921
1.0743
1.0564
0.9399
0.9220
0.9042
-0.0003
EtO2C
HN
Ts
Ph
CO2Et
(trans, E)-3z
1.98
1.99
2.04
4.58
2.98
1.90
0.97
0.94
1.91
0.94
1.80
1.05
0.95
0.96
0.96
2.87
3.05
3.13
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)