Electronic Supplementary Material (ESI) for ChemComm.


# Highly Efficient Cu Catalyst System for the Radical Reactions of α-Bromocarbonyls

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# Supporting Information

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## 1. General procedures

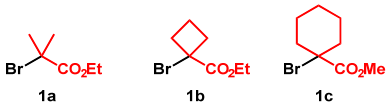
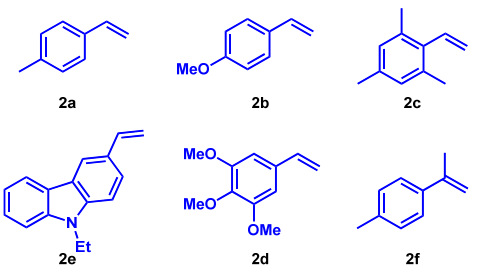
### General Information

All reactions were carried out under nitrogen (99.95%) atmosphere. For TLC analyses precoated Kieselgel 60 F254 plates (Merck, 0.25 mm thick) were used; for column chromatography Silica *Flash*® P60 (SiliCycle, 40-63 μm) was used. Visualization was accomplished by UV light (254 nm), $^{1}H$ and $^{13}C$ NMR spectra were obtained using a JEOL 400 MHz NMR spectrometer. Chemical shifts for 1H NMR were described in parts per million (chloroform as an internal standard δ = 7.26) in $CDCl_3$, unless otherwise noted. Chemical shifts for $^{13}C$ NMR were expressed in parts per million in $CDCl_3$ as an internal standard (δ = 77.16), unless otherwise noted. High resolution mass analyses were obtained using an ACQUITY UPLC/ TOF-MS for ESI. Anhydrous solvents were purchased from Kanto Chemical Co., Ltd. Other chemicals were purchased from TCI, Aldrich and Wako and directly used from the bottles.

### Typical experimental procedure for radical reactions

Cu salt (5 x $10^{-4}$ M in MeCN), ligand (0.1 mmol), **1** (1.0 mmol), and **2** (0.50 mmol) [or **4** (Scheme 2) or **6** (Scheme 3)] were sequentially added under air to a dram vial equipped with a stir bar. amine (0.6 mmol), and dried solvent (0.5 mL) were added by syringe, and the resulting mixture was vigorously stirred under nitrogen atmosphere [charged by general $N_2$ (99.95%) gas flow] for 20 h at the temperature, as shown in the tables. After this time, the contents of the flask were filtered through a plug of silica gel and then concentrated by rotary evaporation. The residue was purified by flash chromatography, eluting with hexane/EtOAc to afford the product **3**.

Table S1

| α-bromo carbonyl compounds | styrenes |
|---|---|
|  1a, 1b, 1c, 1d, 1e |  2a, 2b, 2c, 2d, 2e, 2f, 2g, 2h, 2i |

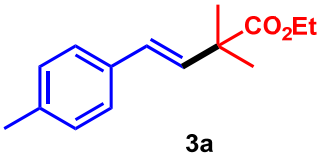
Compounds 3a-3e[1], 3j-3n[2] and 5[3] are known.

[Reference]

[1]. Nishikata, T.; Noda, Y.; Fujimoto, R.; Sakashita, T. *J. Am. Chem. Soc.* **2013**, *135*, 16372

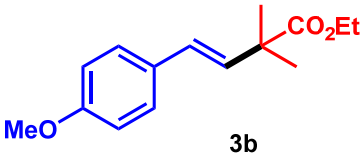
[2]. Nihiskata, T.; Nakamura, K.; Itonaga, K.; Ishikawa, S. *Org. Lett*, **2014**, *16*, 5816

[3]. Ackermann, L.; Vicente, R.; Hofmann, N. *Org Lett*, **2009**, *11*, 4274



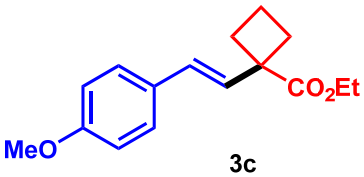

**3a**

Following the general procedure above, using 1a (1.0 mmol, 198 mg), 2a (0.50 mmol, 59 mg), CuI solution (5 x $10^{-5}$ mmol, 5 x $10^{-4}$ M in MeCN, 0.1 ml), TPMA (0.02 mmol, 2.9 mg), diisopropylmethylamine (0.75mmol, 131µl) and dried 1, 2-dimethoxyethane (0.5 mL) at 100 °C, yielded the product 3a (64 mg, 55%); $^{1}$H NMR ($CDCl_3$) δ: 1.25 (t, J = 7.2 Hz, 3H), 1.40 (s, 6H), 2.33 (s, 3H), 4.14 (q, J = 7.1 Hz, 2H), 6.35 (d, J = 16.2 Hz, 1H), 6.41 (d, J = 16.2 Hz, 1H), 7.11 (d, J = 8.0 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H). $^{13}$C NMR ($CDCl_3$) δ: 14.20, 21.18, 30.80, 44.38, 60.80, 126.35, 127.89, 129.35, 133.62, 134.52, 137.26, 176.53.




**3b**

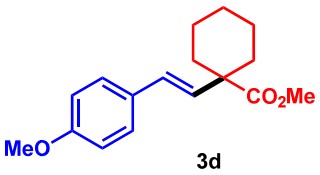
Following the general procedure above, using 1a (1.0 mmol, 198 mg), 2b (0.50 mmol, 67 mg), CuI solution (5 x $10^{-5}$ mmol, 5 x $10^{-4}$ M in MeCN, 0.1 ml), TPMA (0.02 mmol, 2.9 mg), diisopropylmethylamine (0.75mmol, 131µl) and dried 1, 2-dimethoxyethane (0.5 mL) at 60 °C, yielded the product 3b (110 mg,89%); $^{1}$H NMR ($CDCl_3$) δ:1.25 (t, J = 7.1 Hz, 3H), 1.39 (s, 6H), 3.79 (s, 3H), 4.13 (q, J = 7.1 Hz, 2H), 6.26 (d, J = 16.1 Hz, 1H), 6.38 (d, J = 16.1 Hz, 1H), 6.84 (d, J = 8.8 Hz, 2H), 7.31 (d, J = 8.8 Hz, 2H). $^{13}$C NMR ($CDCl_3$) δ:14.16, 25.11, 44.26, 55.26, 60.74, 113.90, 127.26, 127.43, 129.88, 132.33, 159.02, 176.45




**3c**

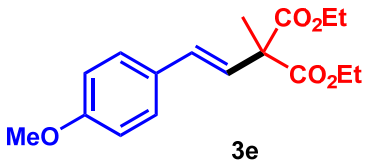
Following the general procedure above, using 1b (1.0 mmol, 207 mg), 2b (0.50 mmol, 67 mg), CuI solution (5 x $10^{-5}$ mmol, 5 x $10^{-4}$ M in MeCN, 0.1 ml), TPMA (0.02 mmol, 2.9 mg), diisopropylmethylamine (0.75mmol, 131µl) and dried 1, 2-dimethoxyethane (0.5 mL) at 60 °C, yielded the product 3c (87 mg, 70%); $^{1}$H NMR ($CDCl_3$) δ: 1.27 (t, J = 7.2 Hz, 3H), 1.90-19.4 (m, 2H),

2.22-2.27 (m, 2H), 2.56-2.62 (m, 2H), 3.81 (s, 3H), 4.17 (q, J = 7.2 Hz, 2H), 6.15 (d, J = 16.1 Hz, 1H), 6.55 (d, J = 16.1 Hz, 1H), 6.86 (d, J = 8.7 Hz, 2H), 7.33 (d, J = 8.7 Hz, 2H). $^{13}$C NMR ($CDCl_3$) δ: 14.46, 16.17, 31.16, 50.17, 55.57, 61.03, 114.29, 127.79, 128.57, 129.63, 130.15, 159.47, 176.14.



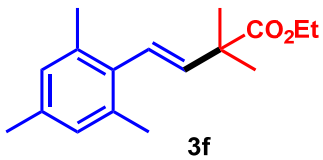

**3d**

Following the general procedure above, using 1c (1.0 mmol, 221 mg), 2b (0.50 mmol, 67 mg), CuI solution (5 x $10^{-5}$ mmol, 5 x $10^{-4}$ M in MeCN, 0.1 ml), TPMA (0.02 mmol, 2.9 mg), diisopropylmethylamine (0.75mmol, 131µl) and dried 1,2-dimethoxyethane (0.5 mL) at 60 °C, yielded the product 3d (127 mg, 88%); $^1$H NMR ($CDCl_3$) δ: 1.30-1.44 (m, 3H), 1.55-1.65 (m, 5H), 2.18 (m, 2H), 3.69 (s, 3H), 3.80 (s, 3H), 6.02 (d, J = 16.3 Hz, 1H), 6.37 (d, J = 16.3 Hz, 1H), 6.84 (d, J = 8.7 Hz, 2H), 7.30 (d, J = 8.7 Hz, 2H). $^{13}$C NMR ($CDCl_3$) δ:23.47, 25.99, 34.36, 49.24, 52.28, 55.63, 114.31, 127.80, 129.11, 130.26, 132.13, 159.54, 176.17.




**3e**

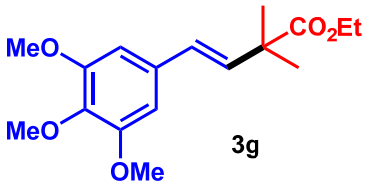
Following the general procedure above, using 1d (1.0 mmol, 187 µl), 2b (0.50 mmol, 67 mg), CuI solution (5 x $10^{-5}$ mmol, 5 x $10^{-4}$ M in MeCN, 0.1 ml), TPMA (0.02 mmol, 2.9 mg), diisopropylmethylamine (0.75mmol, 131µl) and dried 1, 2-dimethoxyethane (0.5 mL) at 60 °C, yielded the product 3e (124 mg, 81%); $^1$H NMR ($CDCl_3$) δ: 1.26 (t, J = 7.1 Hz, 6H), 1.65 (s, 3H), 3.80 (s, 3H), 4.19-4.23 (m, 4H), 6.43 (d, J = 16.2 Hz, 1H), 6.54 (d, J = 16.2 Hz, 1H), 6.58 (d, 8.7 Hz, 2H), 7.34 ( d, J = 8.7 Hz, 2H). $^{13}$C NMR ($CDCl_3$) 14.11, 20.46, 55.41, 55.71, 61.74, 114.12, 125.59, 127.98, 129.52, 130.36, 159.63, 171.51.




**3f**

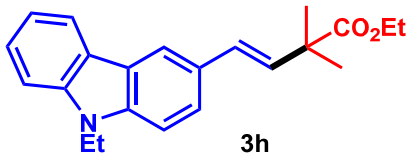
Following the general procedure above, using 1a (1.0 mmol, 198 mg), 2c (0.50 mmol, 73 mg), CuI solution (5 x $10^{-5}$ mmol, 5 x $10^{-4}$ M in MeCN, 0.1 ml), TPMA (0.02 mmol, 2.9 mg), diisopropylmethylamine (0.75mmol, 131µl) and dried 1, 2-dimethoxyethane (0.5 mL) at 100 °C, yielded the product 3f (90 mg, 69%); IR (neat) ν 1727, 1611, 973 cm$^{-1}$; $^1$H NMR ($CDCl_3$) δ: 1.25 (t, J

= 7.3 Hz, 3H), 1.42 (s, 6H), 2.24 (s, 6H), 2.27 (s, 3H), 4.15 (q, J = 7.1 Hz, 2H), 5.82 (d, J = 16.6 Hz, 1H), 6.35 (d, J = 16.6 Hz, 1H), 6.86 (s, 2H). $^{13}$C NMR ($CDCl_3$) δ: 14.33, 20.76, 21.06, 25.13, 44.76, 60.82, 125.62, 128.54, 134.21, 135.96, 136.13, 139.37, 176.62; HREIMS calcd. for $C_{17}H_{25}O_2$ ($M+H^+$): 261.1854; found 261.1853.



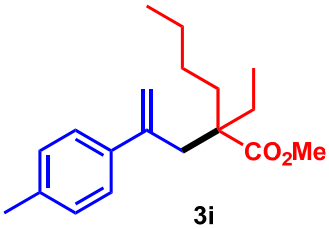

**3g**

Following the general procedure above, using 1a (1.0 mmol, 198 mg), 2e (0.50 mmol, 97 mg), CuI solution (5 x $10^{-5}$ mmol, 5 x $10^{-4}$ M in MeCN, 0.1 ml), TPMA (0.02 mmol, 2.9 mg), diisopropylmethylamine (0.75mmol, 131µl) and dried 1, 2-dimethoxyethane (0.5 mL) at 60 °C, yielded the product 3e (134 mg, 87%); IR (neat) ν 1722, 1236, 1120, 965 $cm^{-1}$; $^1$H NMR ($CDCl_3$) δ: 1.26 (t, J = 7.2 Hz, 3H), 1.40 (s, 6H), 3.83 (s, 3H), 3.88 (s, 6H), 4.15 (q, J = 7.1 Hz, 2H), 6.30 (d, J = 16.1 Hz, 1H), 6.36 (d, J = 16.1 Hz, 1H), 6.60 (s, 2H). $^{13}$C NMR ($CDCl_3$) δ:14.24, 25.20, 44.44, 56.19, 60.94, 61.03, 103.50, 128.10, 133.04, 134.13, 153.49, 176.49; HRESIMS calcd. for $C_{17}H_{25}O_5$ ($M+H^+$): 309.1702; found 309.1707.



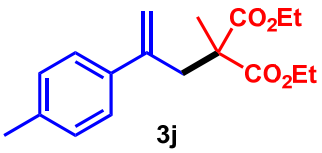

**3h**

Following the general procedure above, using 1a (1.0 mmol, 198 mg), 2d (0.50 mmol, 111 mg), CuI solution (5 x $10^{-5}$ mmol, 5 x $10^{-4}$ M in MeCN, 0.1 ml), TPMA (0.02 mmol, 2.9 mg), diisopropylmethylamine (0.75mmol, 131µl) and dried 1, 2-dimethoxyethane (0.5 mL) at 100 °C, yielded the product 3c (102 mg, 61%); IR (neat) ν 2973, 1720, 1229, 1124, 1023 $cm^{-1}$; $^1$H NMR ($CDCl_3$) δ: 1.28 (t, J = 7.0 Hz, 3H), 1.42 (t, J = 7.3 Hz, 3H), 1.46 (s, 6H), 4.17 (q, J = 7.3 Hz, 2H), 4.6 (q, J = 7.2 Hz, 2H), 6.41 (d, J = 16.2 Hz, 1H), 6.62 (d, J = 16.2 Hz, 1H), 7.23-7.26 (m, 1H), 7.34 (d, J = 8.6 Hz, 1H), 7.40 (d, J = 7.9, 1H), 7.47 (dd, J = 7.1, and 8.2 Hz, 1H), 7.54 (d, J = 7.5 Hz, 1H), 8.11-8.12 (m, 2H) $^{13}$C NMR ($CDCl_3$) δ: 13.82, 14.26, 25.32, 37.61, 44.46, 60.83, 108.56, 108.68, 118.56, 119.01, 120.58, 123.10, 123.29, 124.36, 125.85, 128.45, 128.78, 131.91, 139.68, 140.44, 176.82; HRESIMS calcd. for $C_{22}H_{26}NO_2$ ($M+H^+$): 336.1963; found 336.1964.



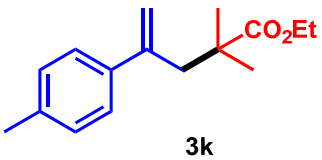

**3i**

Following the general procedure above, using 1e (1.0 mmol, 236 mg), 2f (0.50 mmol, 59 mg), CuI solution (5 x $10^{-5}$ mmol, 5 x $10^{-4}$ M in MeCN, 0.1 ml), TPMA (0.02 mmol, 2.9 mg), diisopropylmethylamine (0.75mmol, 131µl) and dried 1, 2-dimethoxyethane (0.5 mL) at 100 °C, yielded the product 3f (62 mg, 43%(exo:endo =9:1(the isomers are inseparable))); IR (neat) ν 1726, 1130, 1075 $cm^{-1}$; $^{1}H$ NMR ($CDCl_3$) δ:0.71 (t, J = 7.43 Hz, 3H), 0.81 (t, J = 7.40 Hz, 3H), 0.99-1.16 (m, 4H), 1.40-1.53 (m, 2H), 1.58-1.65 (m, 2H), 2.32 (s, 3H), 2.75 (s, 2H), 3.29 (s, 3H), 4.99 (d, J = 1.7 Hz, 1H), 5.14 (d, J = 1.8 Hz, 1H), 7.08 (d, J = 8.1 Hz, 2H), 7.19 (d, J = 8.1 Hz, 2H). $^{13}C$ NMR ($CDCl_3$) δ: 8.35, 14.04. 21.14, 23.14, 26.00, 26.51, 33.09, 40.66, 49.96, 51.11, 116.56, 126.86, 128.77, 136.95, 139.96, 146.36, 177.14; HRESIMS calcd. for $C_{20}H_{31}O_2$ ($M+H^+$): 303.2324; found 303.2324.




**3j**

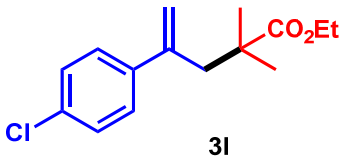
Following the general procedure above, using 1d (1.0 mmol, 187 µl), 2f (0.50 mmol, 59 mg), CuI solution (5 x $10^{-5}$ mmol, 5 x $10^{-4}$ M in MeCN, 0.1 ml), TPMA (0.02 mmol, 2.9 mg), diisopropylmethylamine (0.75mmol, 131µl) and dried 1, 2-dimethoxyethane (0.5 mL) at 100 °C, yielded the product 3a (93 mg, 61%(exo:endo=9:1(the isomers are inseparable))); $^{1}H$ NMR ($CDCl_3$) δ:1.15 (t, J =7.1 Hz, 6H), 1.27 (s, 3H), 2.32 (s, 3H), 3.14 (s, 2H), 3.86-3.92 (m, 2H), 3.95-4.02 (m, 2H), 5.06 (d, J = 0.8 Hz, 1H), 5.2 (d, J = 1.6 Hz, 1H), 7.08 (d, J = 7.9 Hz, 2H), 7.21 (d, J = 8.0 Hz, 2H). $^{13}C$ NMR ($CDCl_3$) δ:13.94, 19.94, 21.14, 40.04, 53.61, 61.19, 117.59, 126.82, 128.86, 137.32, 139.00, 144.56, 172.06.




**3k**

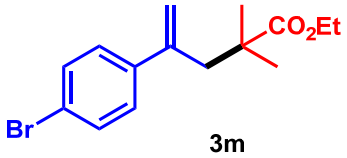
Following the general procedure above, using 1a (1.0 mmol, 198 mg), 2a (0.50 mmol, 59 mg), CuI solution (5 x $10^{-5}$ mmol, 5 x $10^{-4}$ M in MeCN, 0.1 ml), TPMA (0.02 mmol, 2.9 mg), diisopropylmethylamine (0.75mmol, 131µl) and dried 1, 2-dimethoxyethane (0.5 mL) at 100 °C, yielded the product 3a (102 mg, 83%(exo:endo =9:1(the isomers are inseparable))); $^{1}H$ NMR ($CDCl_3$)

δ: 1.10 (s, 6H), 1.11-1.14 (t, J = 7.0 Hz, 3H), 2.32 (s, 3H), 2.77 (s, 2H), 3.77 (J = 7.0 Hz, 2H), 5.01 (s, 1H), 5.21 (d, J = 1.76 Hz, 1H), 7.09 (d, J = 7.8 Hz, 2H), 7.23 (d, J = 7.8 Hz, 2H). $^{13}$C NMR ($CDCl_3$) δ: 14.02, 21.13, 25.57, 42.60, 45.80, 60.25, 116.36, 126.73, 128.87, 137.07, 146.12, 177.51.



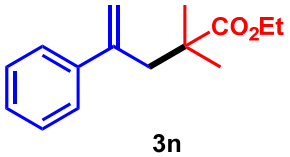

**3l**

Following the general procedure above, using 1a (1.0 mmol, 198 mg), 2a (0.50 mmol, 76 mg), CuI solution (5 x $10^{-5}$ mmol, 5 x $10^{-4}$ M in MeCN, 0.2 ml), TPMA (0.02 mmol, 2.9 mg), diisopropylmethylamine (0.75mmol, 131µl) and dried 1, 2-dimethoxyethane (0.5 mL) at 100 °C, yielded the product 3a (65 mg, 49%(exo:endo =93:7(the isomers are inseparable))); IR (neat) ν 1722, 1133, 835 $cm^{-1}$; $^1$H NMR ($CDCl_3$) δ: 1.01 (s, 6H), 1.12 (t, J = 7.1 Hz, 3H), 2.75 (s, 2H), 3.77 (q, J = 7.1 J, 2H), 5.07 (d, J = 1.3 Hz, 1H), 5.22 (d, J = 1.5 Hz, 1H), 7.20 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H). $^{13}$C NMR ($CDCl_3$) δ: 14.03, 25.57, 42.57, 45.75, 60.36, 117.73, 121.35, 128.57, 131.30, 141.41, 145.26, 177.26; HRESIMS calcd. for $C_{15}H_{20}ClO_2$ ($M+H^+$ ): 267.1151; found 267.1153.




**3m**

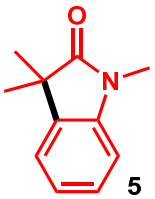
Following the general procedure above, using 1a (1.0 mmol, 198 mg), 2a (0.50 mmol, 98 mg), CuI solution (5 x $10^{-5}$ mmol, 5 x $10^{-4}$ M in MeCN, 0.2 ml), TPMA (0.02 mmol, 2.9 mg), diisopropylmethylamine (0.75mmol, 131µl) and dried 1, 2-dimethoxyethane (0.5 mL) at 100 °C, yielded the product 3a (83 mg, 54%(exo:endo =93:7(the isomers are inseparable))); IR (neat) ν 1722, 1193, 1008, $cm^{-1}$; $^1$H NMR ($CDCl_3$) δ: 1.10 (s, 6H), 1.12 (t, J = 7.1 Hz, 3H), 2.75 (s, 2H), 3.76 (q, J = 7.1 Hz, 2H), 5.06 ( J = 1.3 Hz, 1H), 5.22 (d, J = 1.5 Hz, 1H), 7.19 (d, J = 8.5 Hz, 2H), 7.41 (d, J = 8.5 Hz, 2H). $^{13}$C NMR ($CDCl_3$) δ: 14.03, 25.57, 42.56, 45.81, 60.35, 117.68, 128.22, 128.33, 133.23, 140.93, 145.22, 177.27; HRESIMS calcd. for $C_{15}H_{20}BrO_2$ ($M+H^+$): 311.0646; found 311.0645.




**3n**

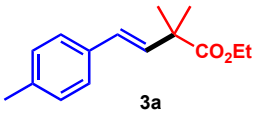
Following the general procedure above, using 1a (1.0 mmol, 198 mg), 2i (0.50 mmol, 98 mg), CuI solution (5 x $10^{-5}$ mmol, 5 x $10^{-4}$ M in MeCN, 0.2 ml), TPMA (0.02 mmol, 2.9 mg),

diisopropylmethylamine (0.75mmol, 131µl) and dried 1, 2-dimethoxyethane (0.5 mL) at 100 °C, yielded the product 3a (85 mg, 73%); $^{1}$H NMR ($CDCl_3$) δ:1.11 (t, J = 7.2 Hz, 3H), 1.11 (s, 6H), 2.80 (s, 2H), 3.72 (q, J = 7.1 Hz, 2H), 5.05 (d, J = 1.6 Hz, 1H), 5.23 (d, J = 1.7 Hz, 1H), 7.23-7.32 (m, 5H). $^{13}$C NMR ($CDCl_3$) δ: 14.02, 25.57, 42.55, 45.91, 60.25, 117.11, 126.90, 127.40, 128.20, 142.51, 146.35, 177.43.




**5**

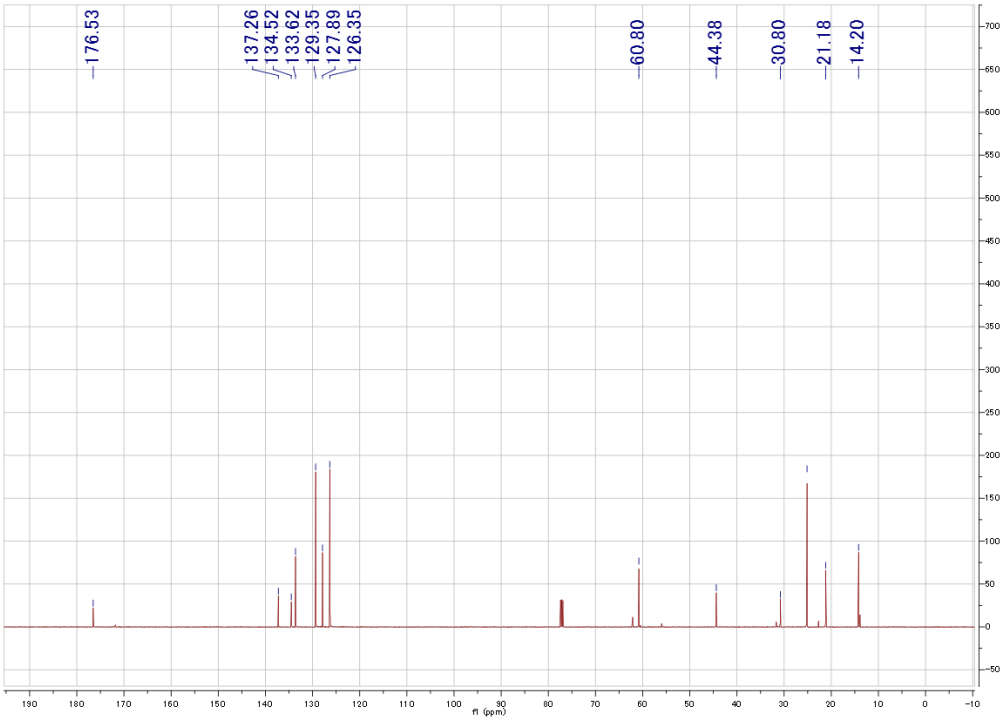
Following the general procedure above, using 4 (0.5 mmol, 127 mg), CuI solution (5 x $10^{-5}$ mmol, 5 x $10^{-4}$ M in MeCN, 0.2 ml), TPMA (0.02 mmol, 2.9 mg), diisopropylmethylamine (0.75mmol, 131µl) and dried 1, 2-dimethoxyethane (0.5 mL) at 100 °C, yielded the product 5 (88 mg, 100%); 1H NMR ($CDCl_3$) δ: 1.37(s, 6H), 3.21 (s, 3H), 6.85 (d. J = 7.7 Hz, 1H), 7.06 (t, J = 7.5 Hz, 1H), 7.20 (d, J = 7.3 Hz, 1H), 7.26 (dt, J = 1.2, 7.6 Hz, 1H). $^{13}$C NMR ($CDCl_3$) δ: 24.35, 26.16, 44.14, 108.07, 122.31, 122.54, 127.73, 135.89, 142.72, 181.46.

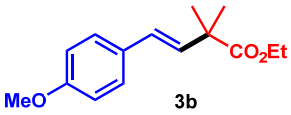



3a

1H NMR

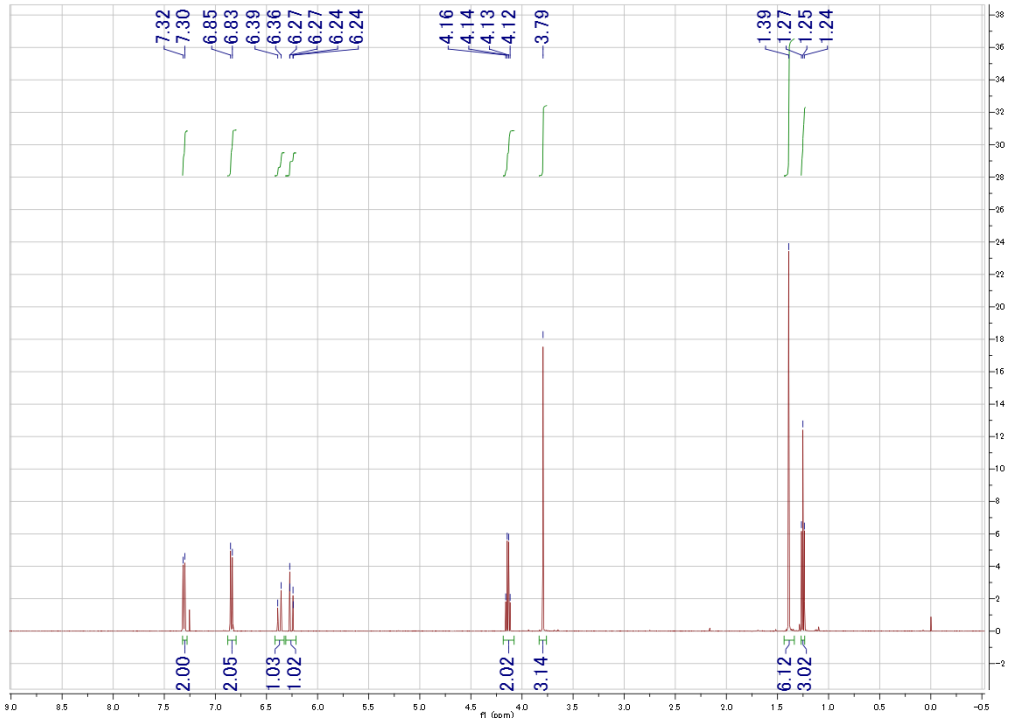

13C NMR



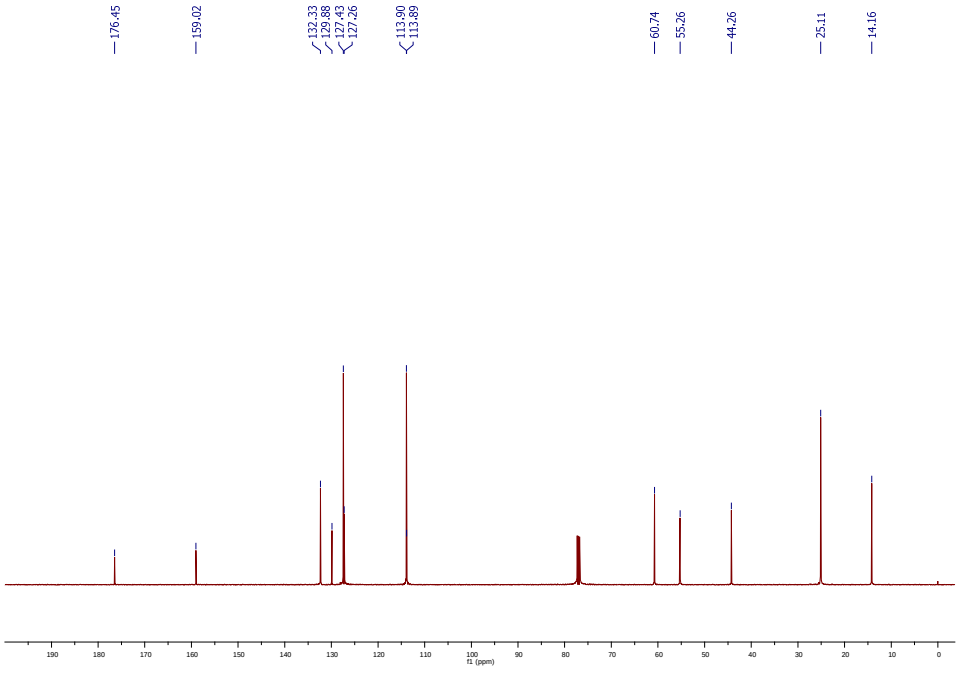


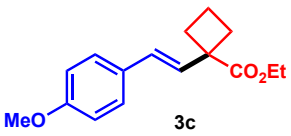

3b

1H NMR



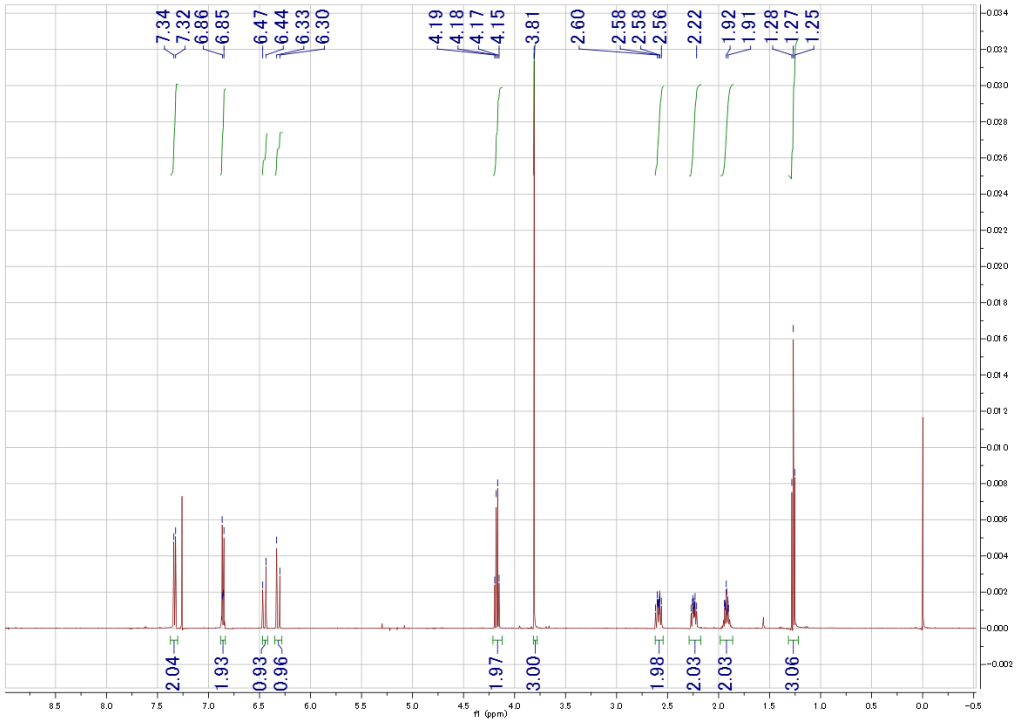

13C NMR



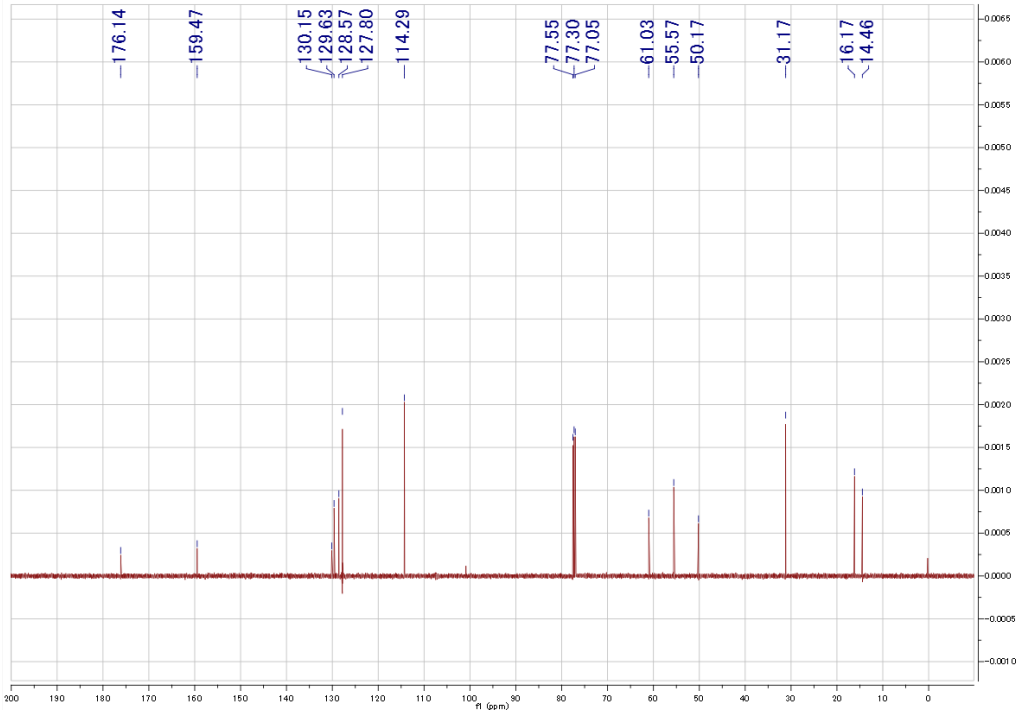


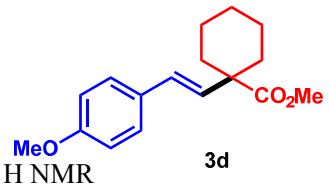

3c

1H NMR



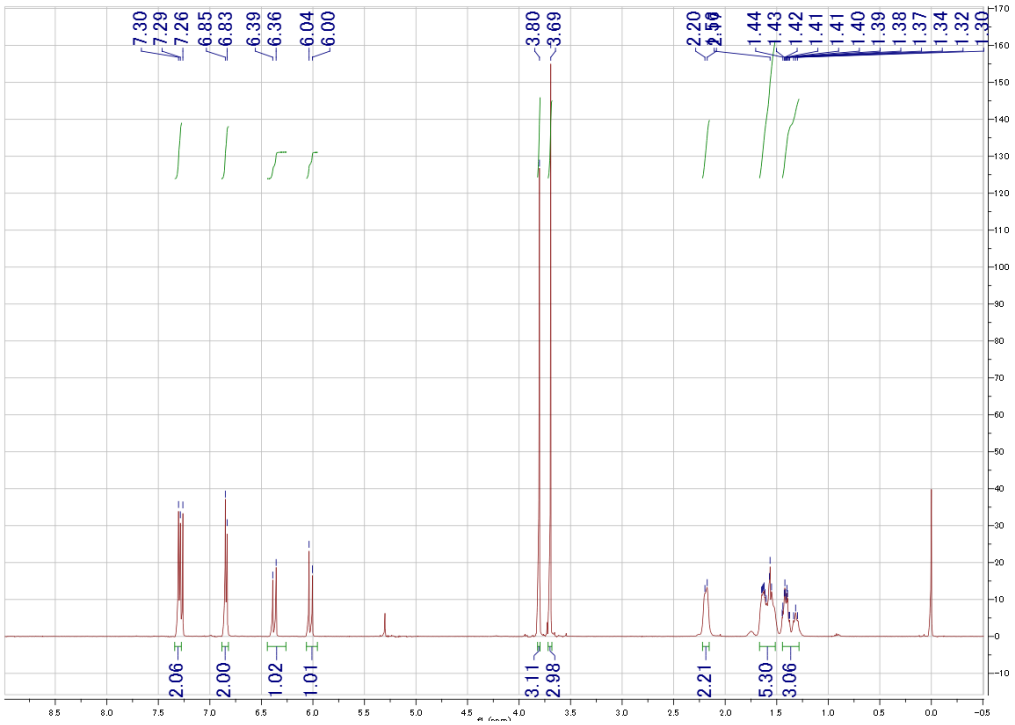

13C NMR



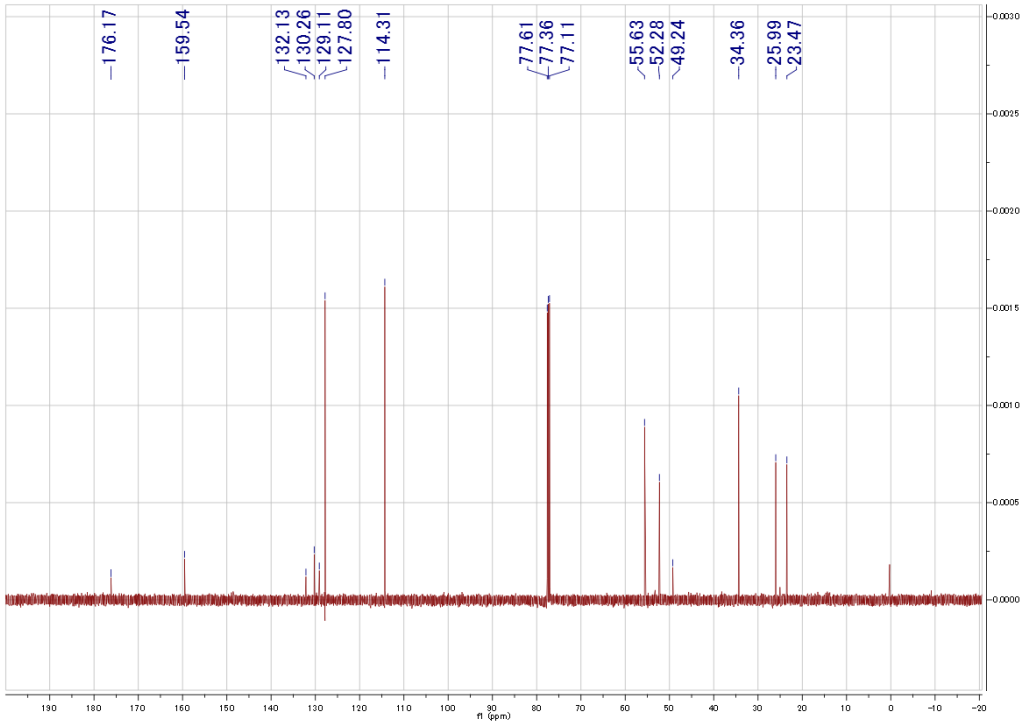


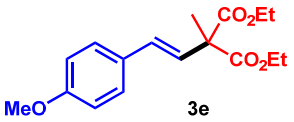

3d

1H NMR



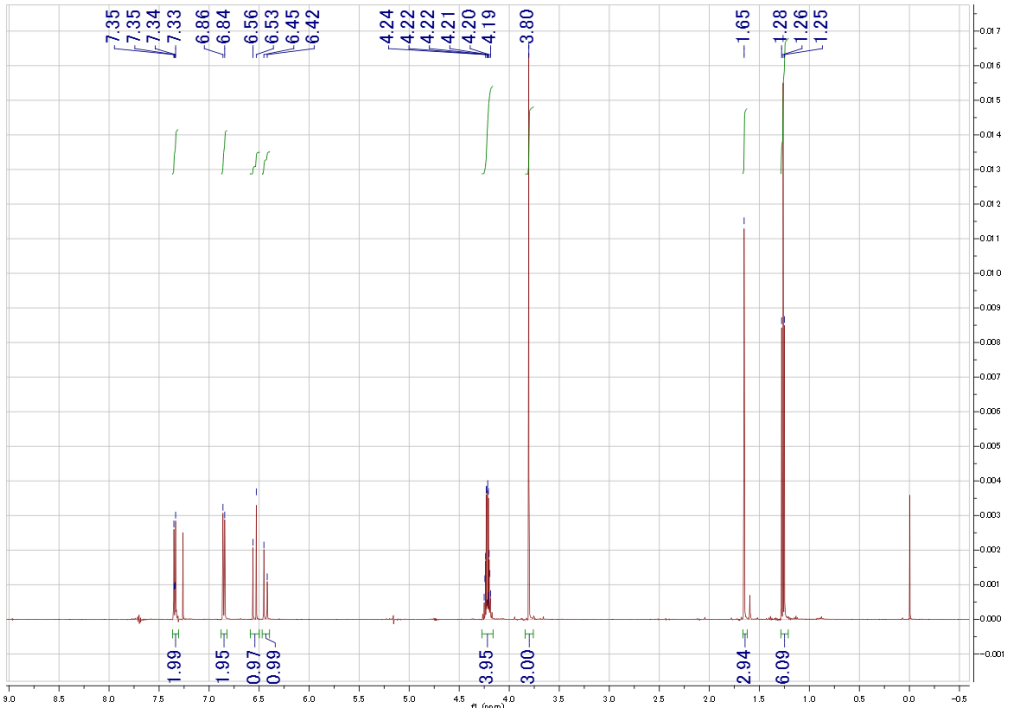

13C NMR



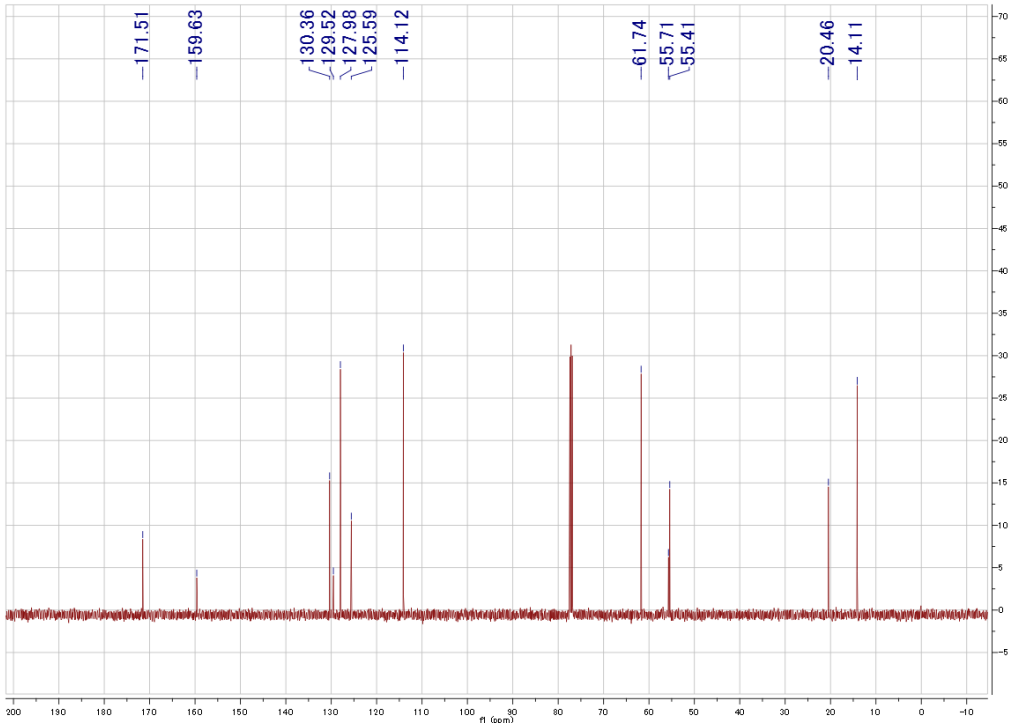


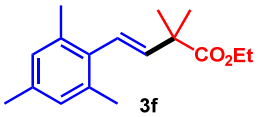

3e

1H NMR



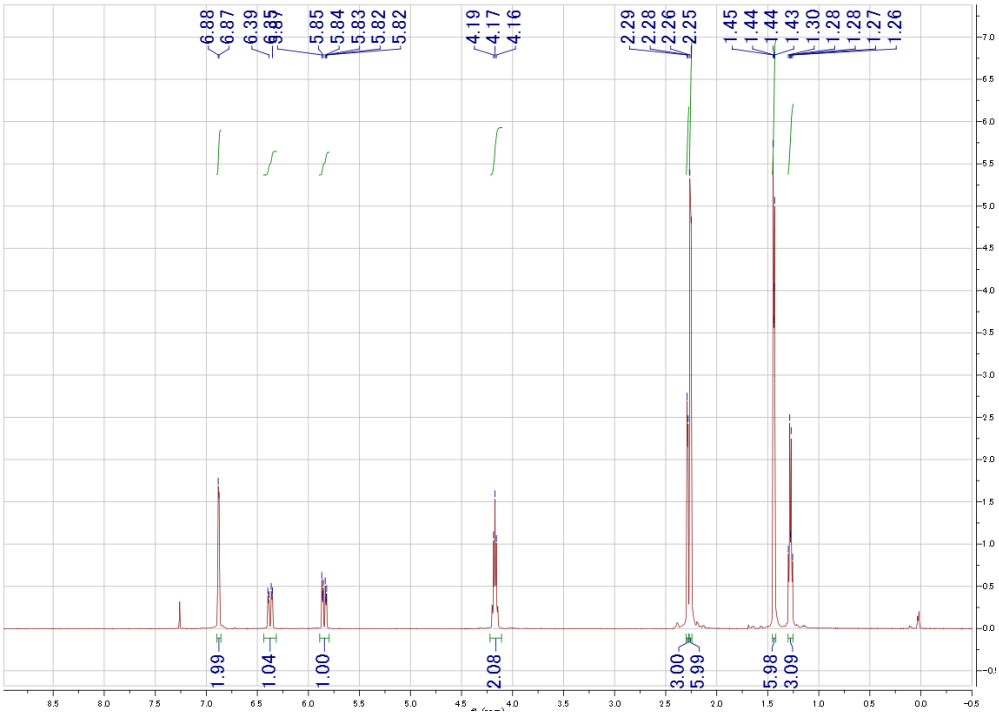

13C NMR



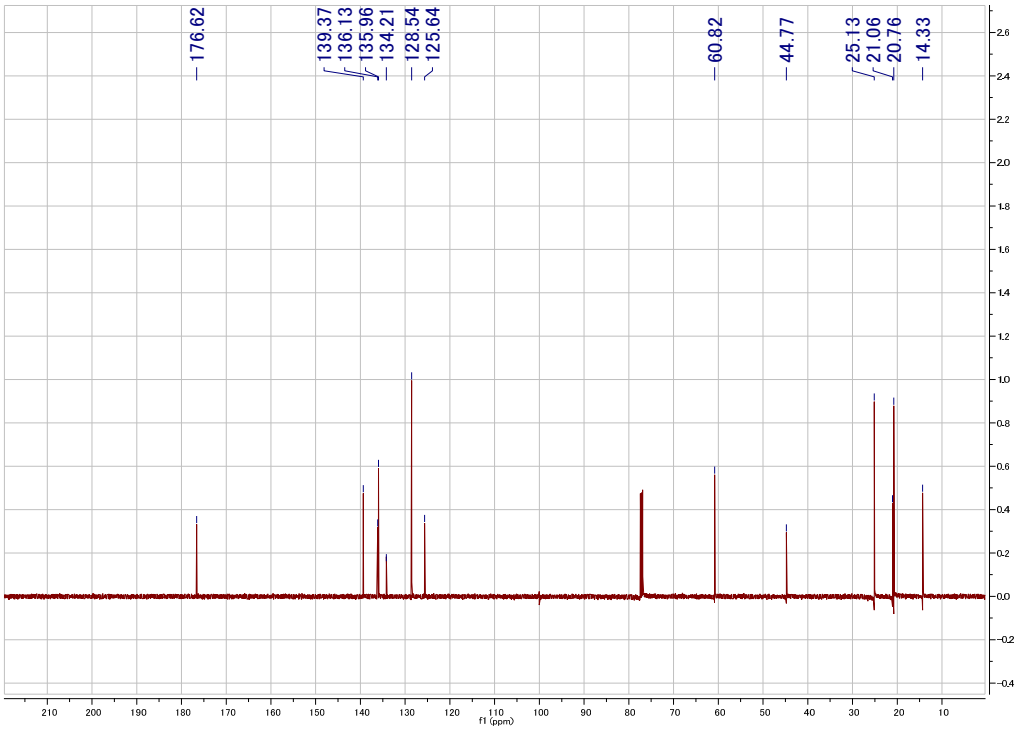


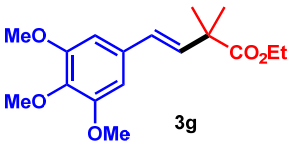

3f

1H NMR



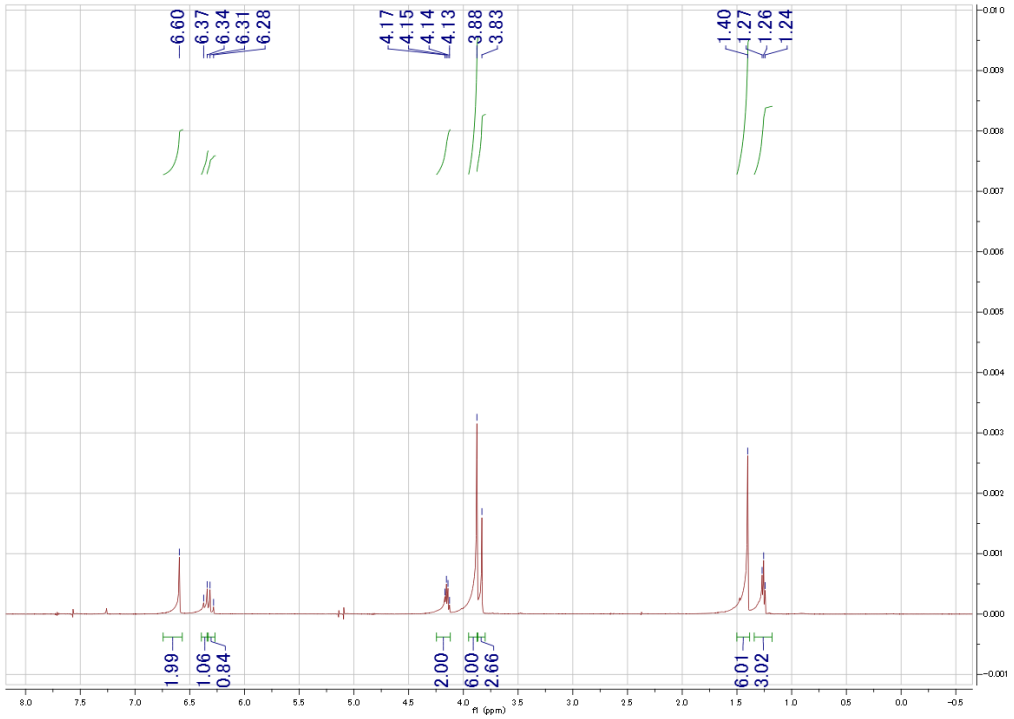

13C NMR



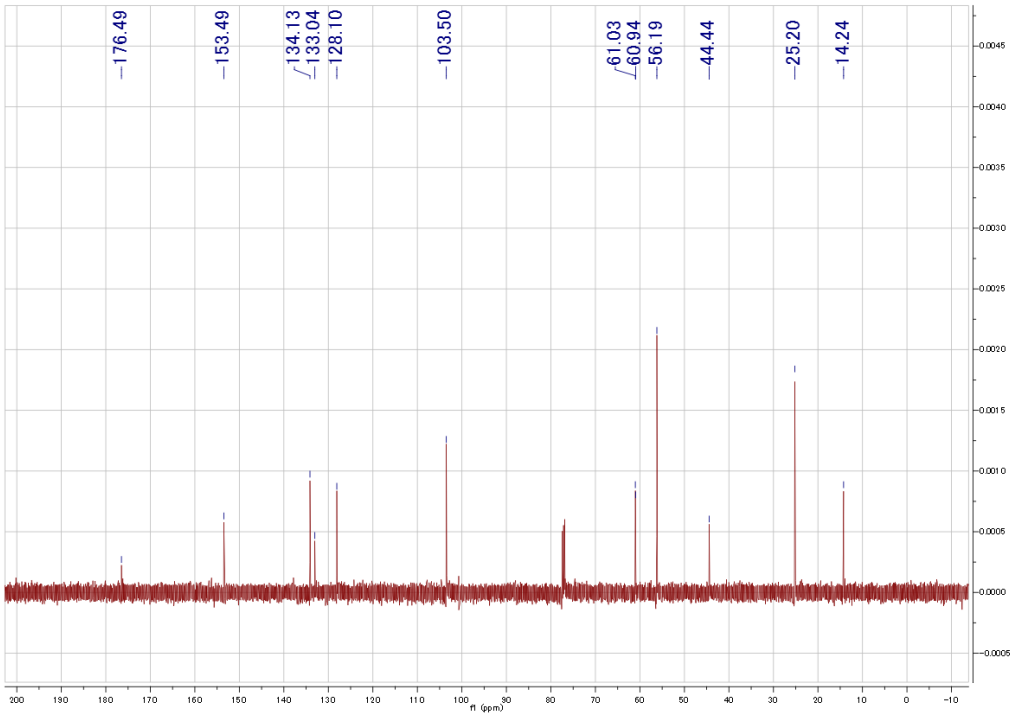


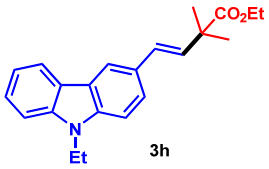

3g

1H NMR



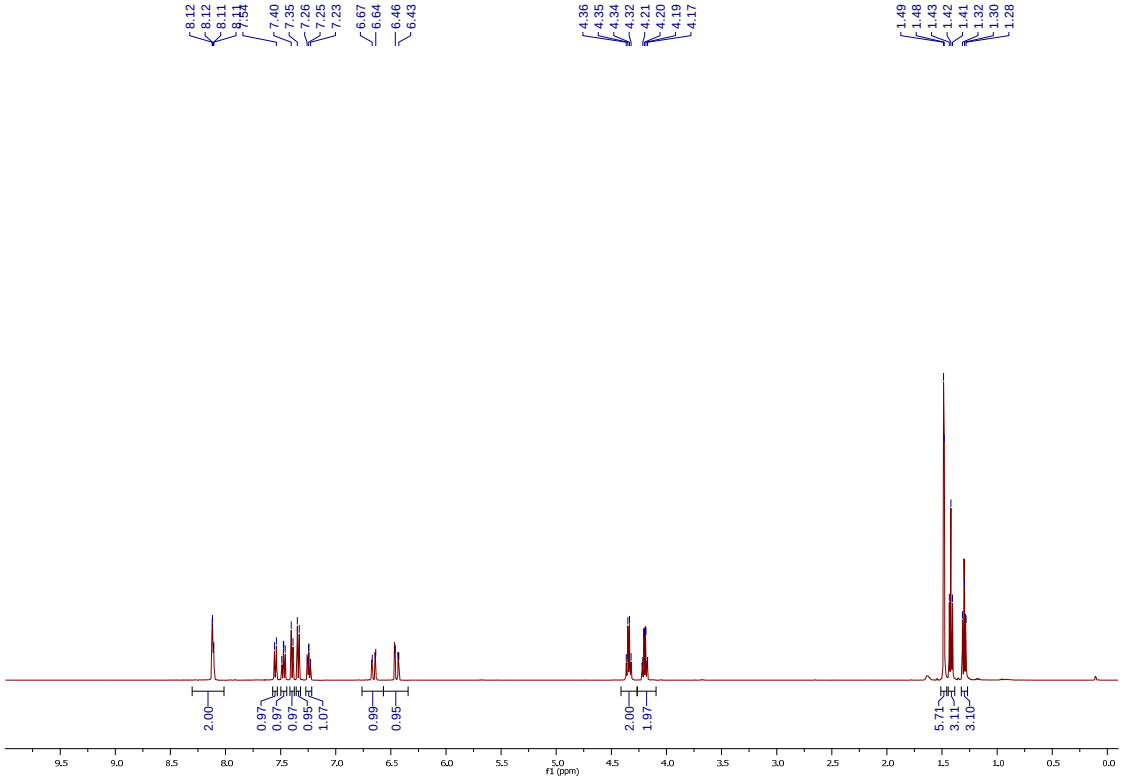

13C NMR



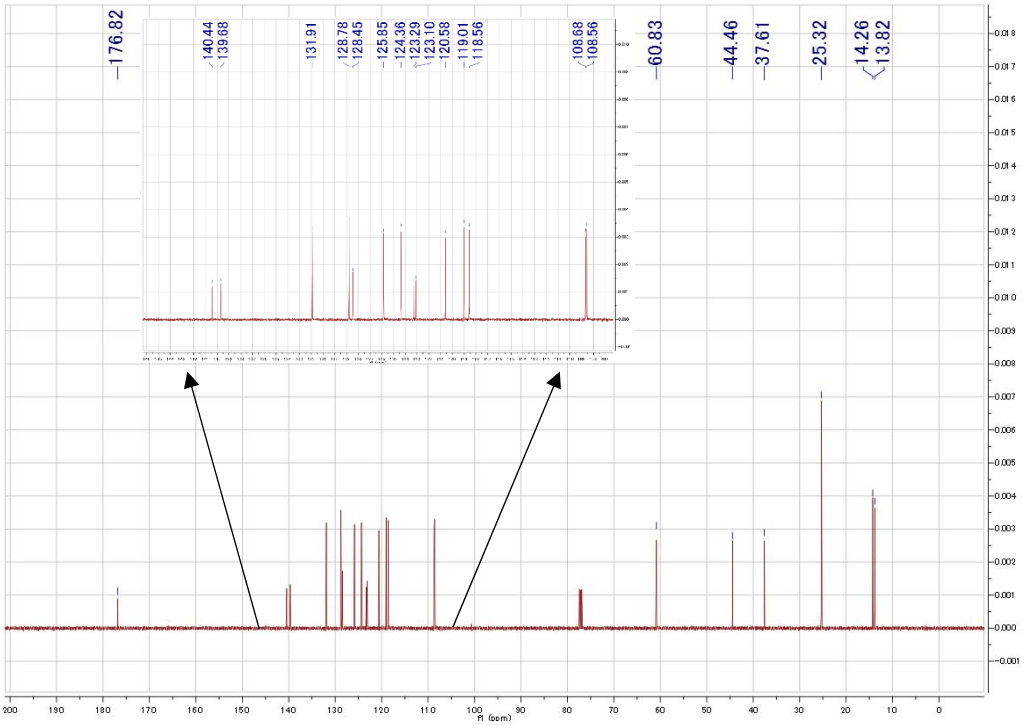


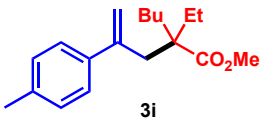

3h

1H NMR



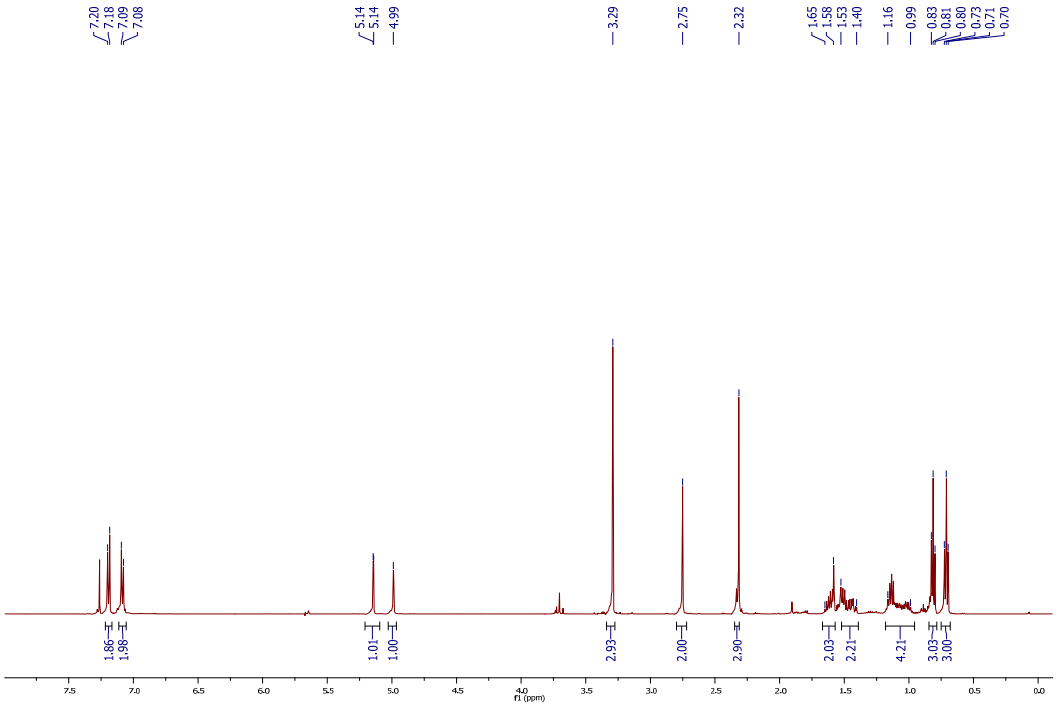

13C NMR



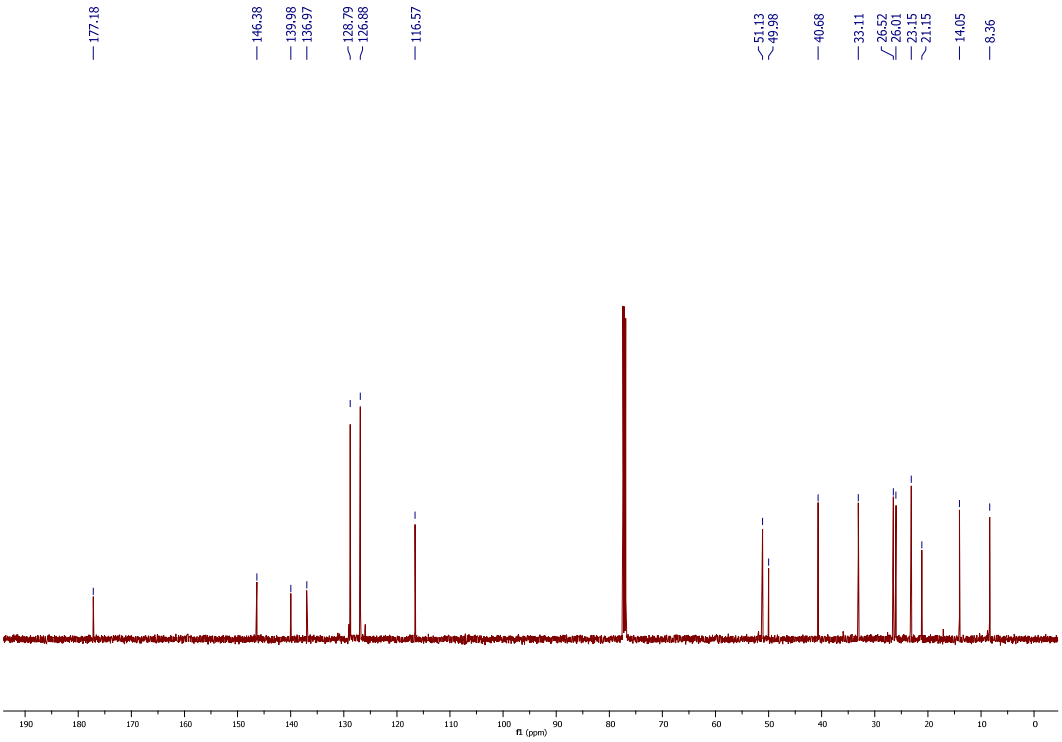


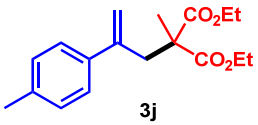

3i

1H NMR



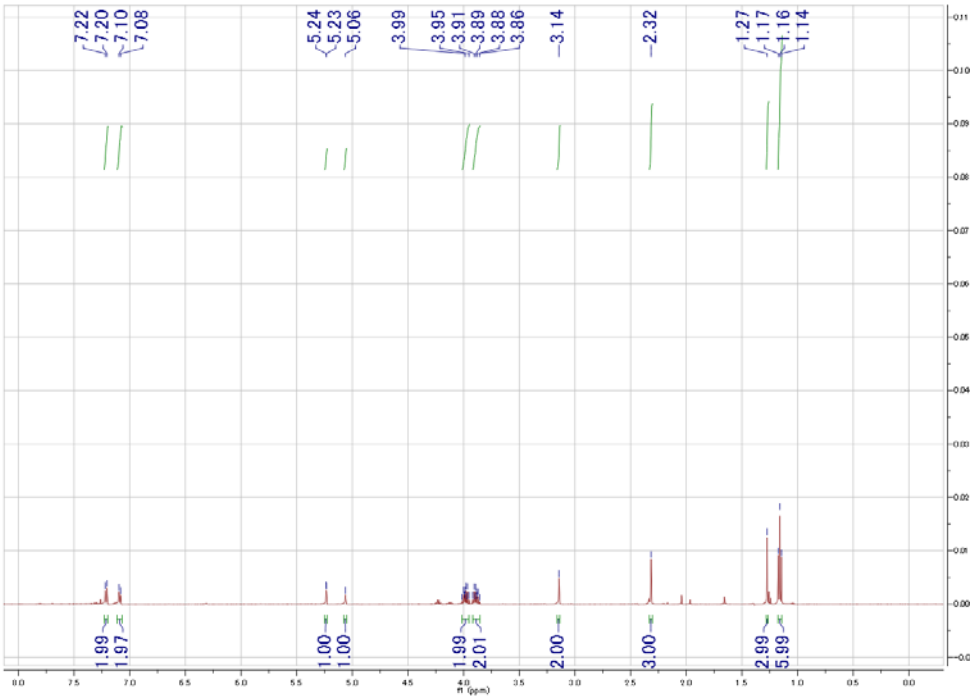

13C NMR



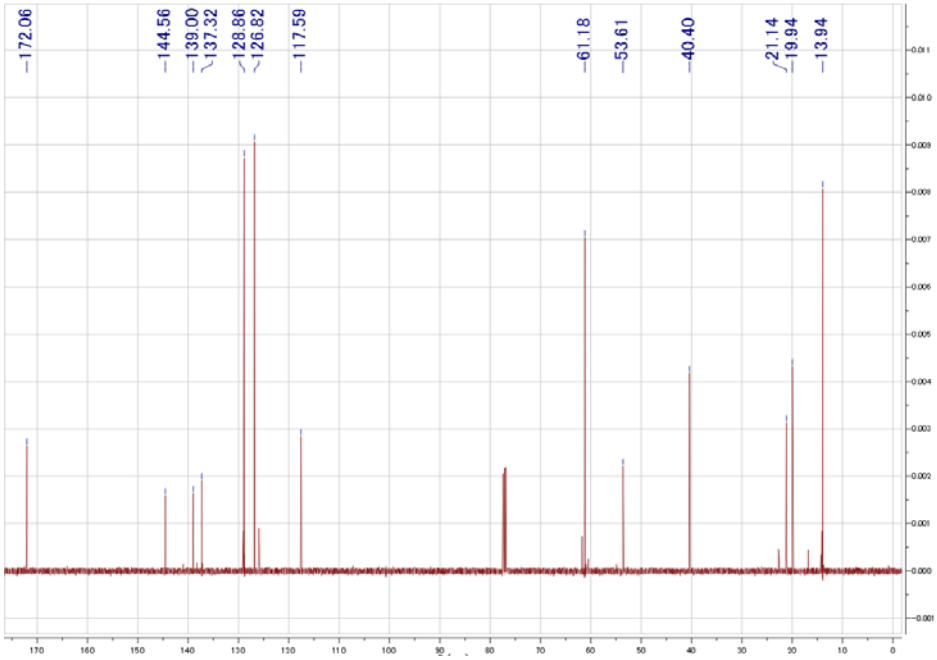


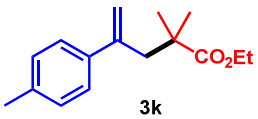

3j

1H NMR



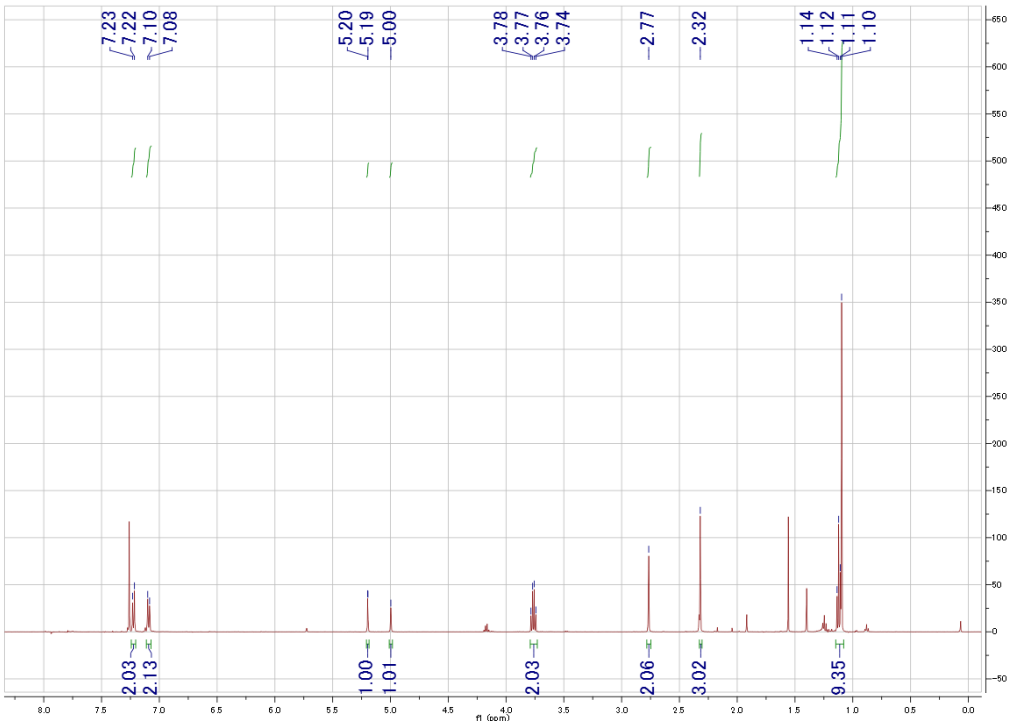

13C NMR



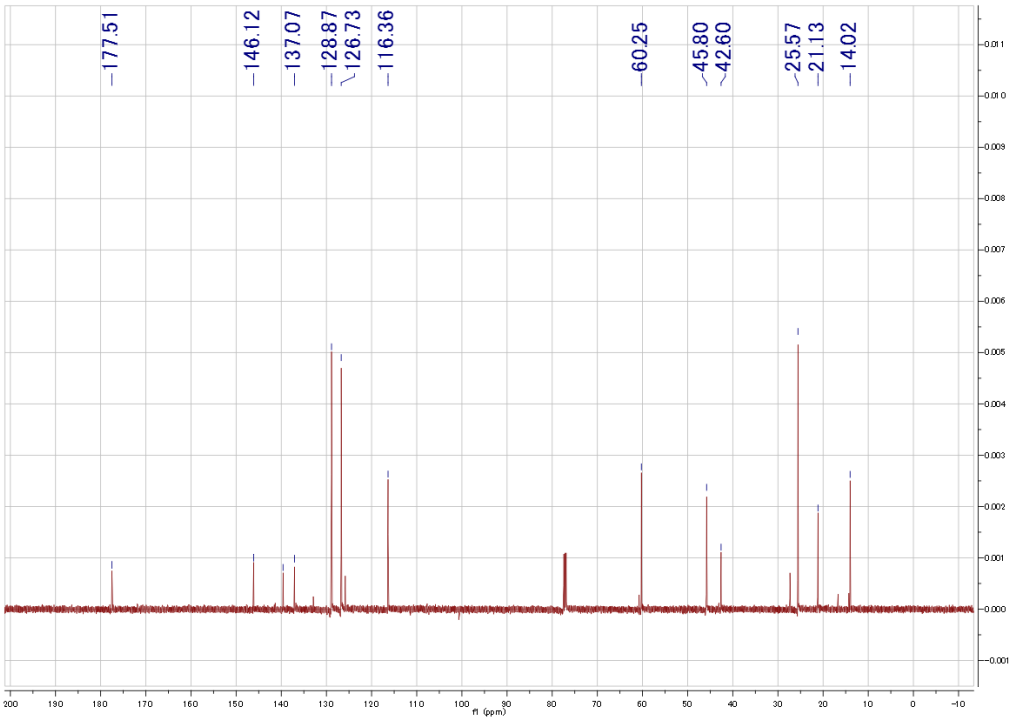


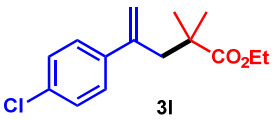

3k

1H NMR



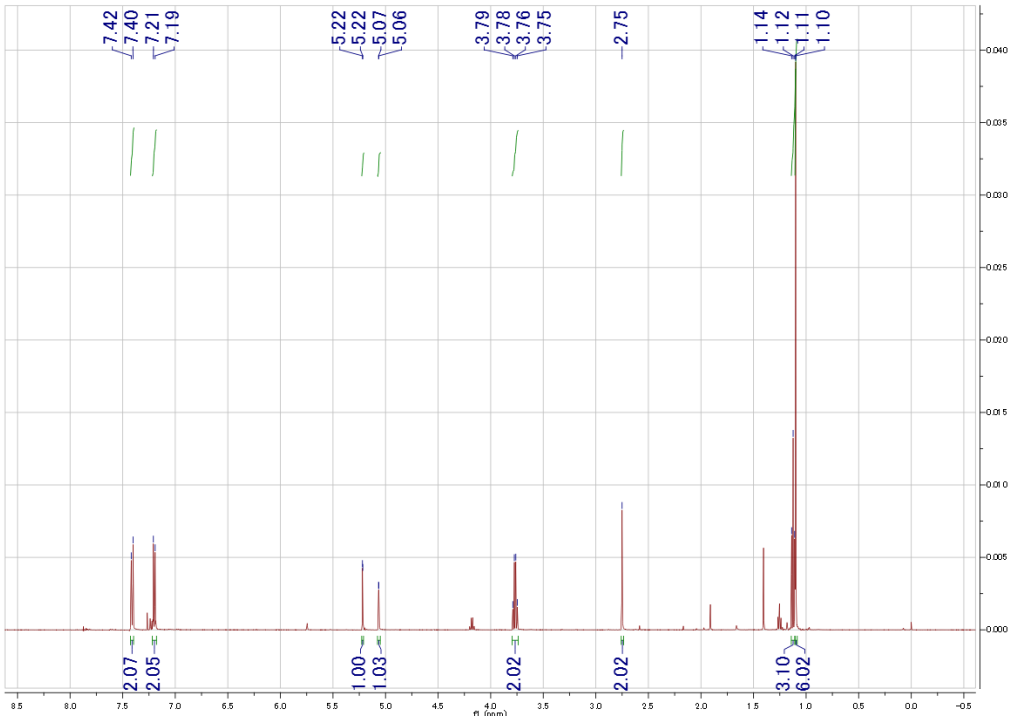

13C NMR



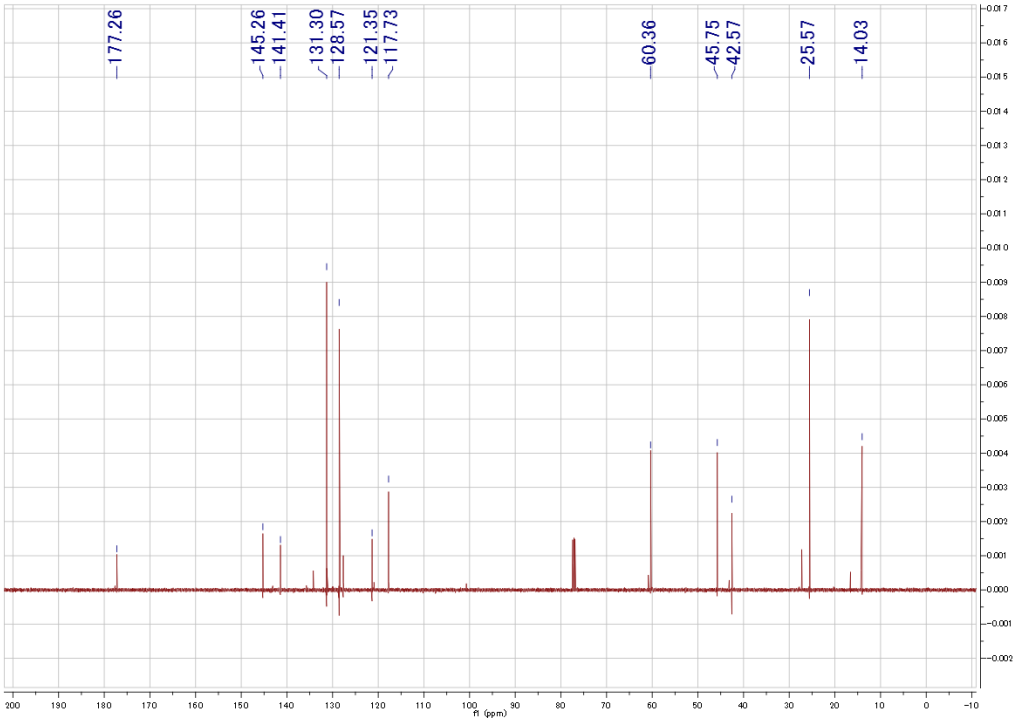


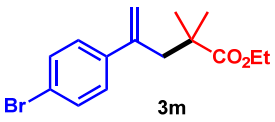

3l

1H NMR



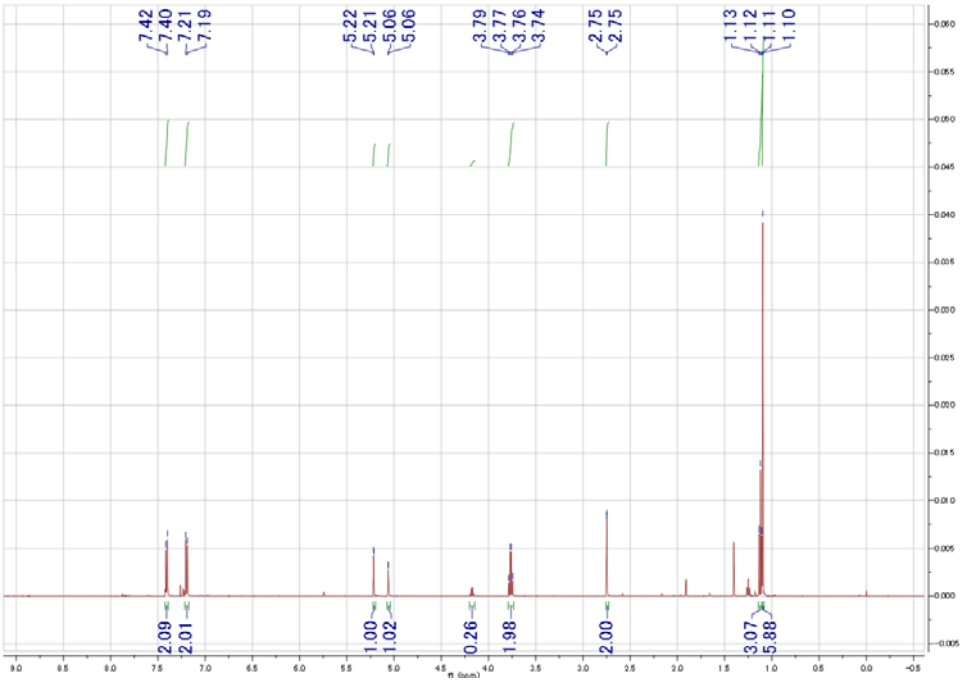

13C NMR



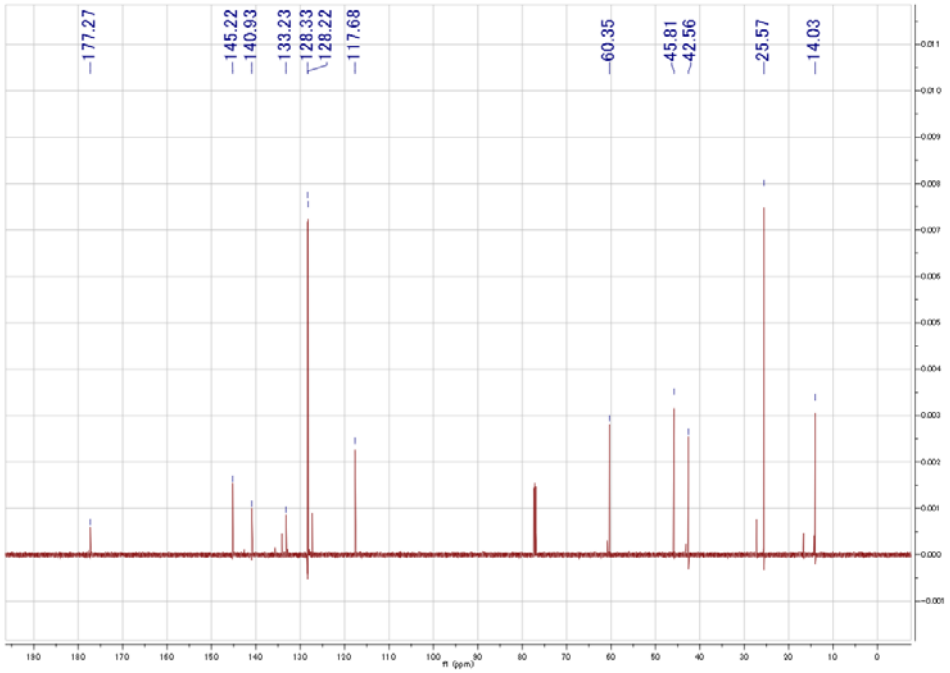


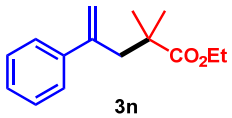

3m

1H NMR



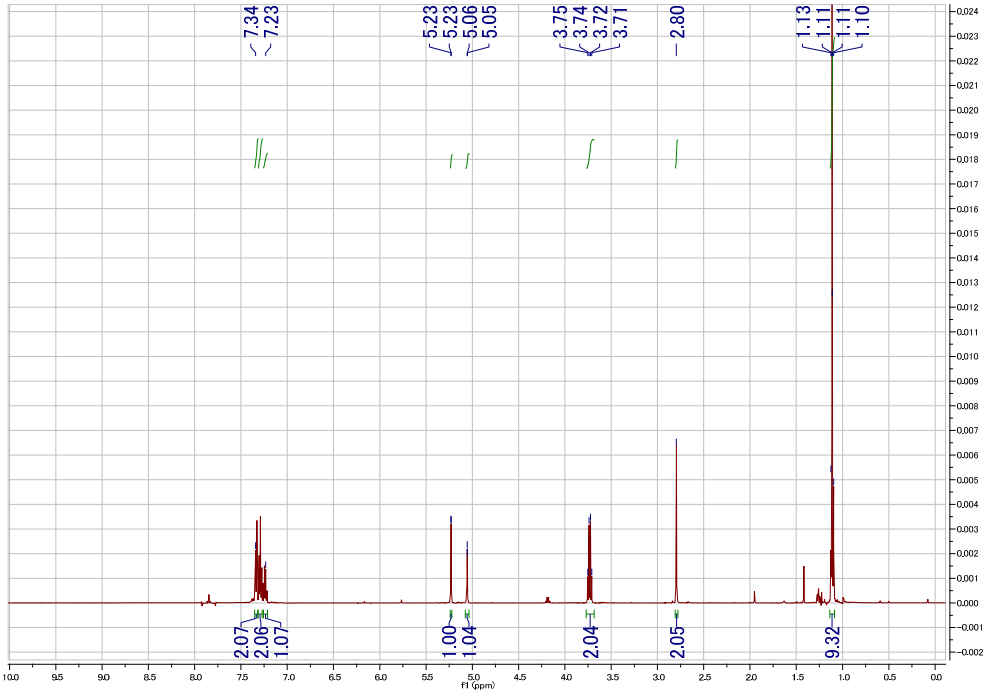

13C NMR



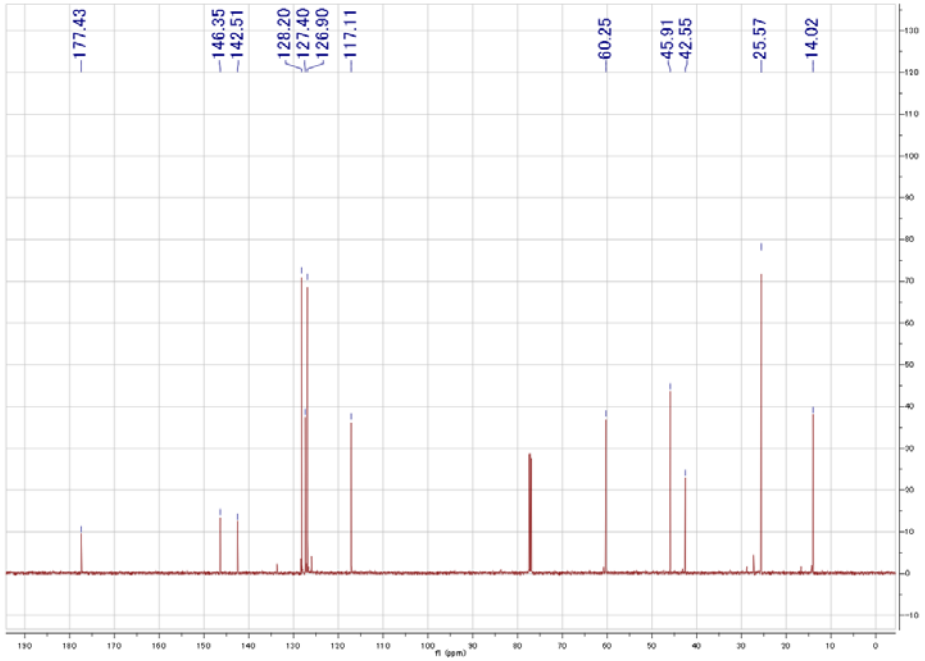


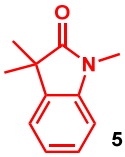

3n

1H NMR



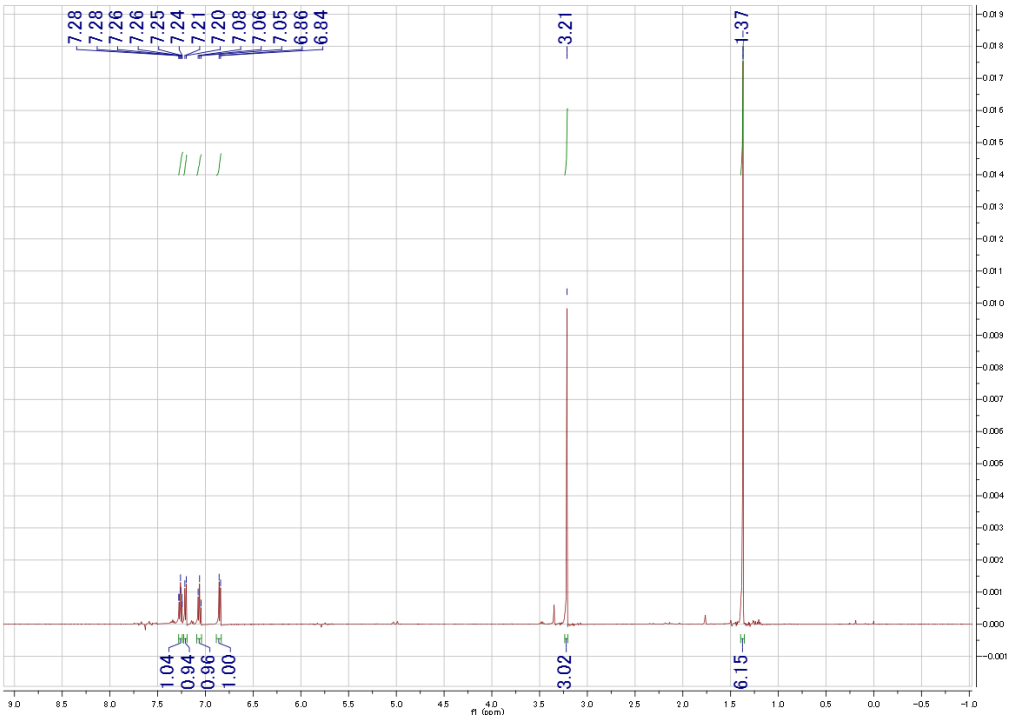

13C NMR





5

1H NMR




13C NMR