

Supporting Information for

“Exploring bis-(amino)cyclopropenylidene as a non-covalent Brønsted base catalyst in conjugate addition reactions”

Gurdeep Singh, Prithwish Goswami and Ramasamy Vijaya Anand*

Indian Institute of Science Education and Research (IISER) Mohali, Sector 81, S. A. S.

Nagar, Manauli (PO). Punjab – 140306, India

E-mail: rvijayan@iisermohali.ac.in

Table of Contents

1. General methods	S2
2. General procedure for the 1,6-conjugate addition of active methylenes to <i>p</i> -QMs	S2–S3
3. Characterisation of product 3a	S3
4. Characterisation of products (3b to 3o)	S3–S10
5. Characterisation of products (13a to 13d)	S10–S12
6. General procedure for the 1,6-conjugate addition of 2-naphthols to <i>p</i> -QMs	S12
7. Characterisation of products (15a to 15e)	S12–S14
8. General procedure for the 1,4-conjugate addition of malonates to chalcones	S15
9. Characterisation of products (17a to 17n)	S15–S21
10. Synthetic elaboration of 13a	S22
11. References	S23
12. NMR spectra of products (3a to 3o)	S24–S39
13. NMR spectra of products (13a to 13d)	S39–S43
14. NMR spectra of products (15a to 15e)	S43–S48
15. NMR spectra of products (17a to 17n)	S48–S63
16. NMR spectra of product 18	S63–S64

Experimental Section

1. General methods

All reactions were carried out under an argon atmosphere in an oven dried round bottom flask. All the solvents were distilled before use and stored under argon atmosphere. Most of the reagents, starting materials and NHC precursors (**5** to **9**) were purchased from commercial sources and used as such. All *p*-quinone methides were prepared by following a literature procedure.¹ NHC precursor **4** was prepared according to the literature procedure.² BAC precursors **10**, **11** and **12** were prepared according to known procedures.³ All chalcones were prepared according to the known literature procedure.⁴ Melting points were recorded on SMP20 melting point apparatus and are uncorrected. ¹H, ¹³C and ¹⁹F spectra were recorded in CDCl₃ (400, 100 and 376 MHz respectively) on Bruker FT-NMR spectrometer. Chemical shift (δ) values are reported in parts per million relative to TMS and the coupling constants (*J*) are reported in Hz. High resolution mass spectra were recorded on Waters Q-TOF Premier-HAB213 spectrometer. FT-IR spectra were recorded on a Perkin-Elmer FTIR spectrometer. Thin layer chromatography was performed on Merck silica gel 60 F₂₅₄ TLC pellets and visualised by UV irradiation and KMnO₄ stain. Column chromatography was carried out through silica gel (100–200 mesh) using EtOAc/hexane as an eluent.

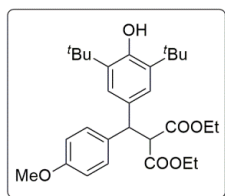
2. General General procedure for the 1,6-conjugate addition of active methylene compounds to *p*-quinone methides:

Anhydrous THF (1.0 mL) was added to the mixture of *p*-quinone methide (0.062 mmol), diethyl malonate (0.074 mmol), catalyst **11** (0.0062 mmol) and Cs₂CO₃ (0.0062 mmol) under argon atmosphere and the resulting suspension was stirred at room temperature. After the reaction was complete (based on TLC analysis), the reaction mixture was concentrated under

reduced pressure. The residue was then purified through a silica gel column, using EtOAc/Hexane mixture as an eluent, to get the pure product.

3. Characterisation of product 3a

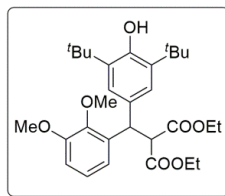
Diethyl 2-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)malonate (3a)



The reaction was performed at 0.062 mmol scale of **1a**; $R_f = 0.4$ (10% EtOAc in hexane); pale yellow gummy solid (28.1 mg, 94% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.23 (d, $J = 8.6$ Hz, 2H), 7.05 (s, 2H), 6.80 (d, $J = 8.6$ Hz, 2H), 5.03 (s, 1H), 4.59 (d, $J = 12.2$ Hz, 1H), 4.22 (d, $J = 12.2$ Hz, 1H), 4.03 – 3.92 (m, 4H), 3.75 (s, 3H), 1.38 (s, 18H), 1.04 (t, $J = 7.1$ Hz, 3H), 0.95 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.07, 168.06, 158.3, 152.6, 135.7, 134.3, 132.1, 128.9, 124.4, 114.0, 61.5, 61.4, 58.5, 55.3, 50.8, 34.4, 30.4, 14.0, 13.9; FT-IR (thin film, neat): 3442, 2958, 1758, 1732, 1612, 1513, 1436, 1303, 1250, 1179, 1036, 838, 637 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{29}\text{H}_{39}\text{O}_6$ $[\text{M}-\text{H}]^+$: 483.2747; found: 483.2727.

4. Characterisation of products (3b to 3o)

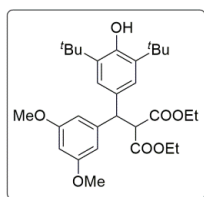
Diethyl 2-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2,3-dimethoxyphenyl)methyl)malonate (3b)



The reaction was performed at 0.0565 mmol scale of **1b**; $R_f = 0.3$ (10% EtOAc in hexane); brown solid (26.7 mg, 92% yield); m. p. = 100–104 $^\circ\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.10 (s, 2H), 7.01 – 6.94 (m, 2H), 6.75 (d, $J = 7.8$ Hz, 1H), 5.07 (d, $J = 12.5$ Hz, 1H), 4.99 (s, 1H), 4.35 (d, $J = 12.5$ Hz, 1H), 4.00 (q, $J = 7.1$ Hz, 2H), 3.96 (q, $J = 7.1$ Hz, 2H), 3.80 (s, 3H), 3.74 (s, 3H), 1.37 (s, 18H), 1.03 (t, $J = 7.1$ Hz, 3H), 0.94 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.3, 168.0, 153.1, 152.4, 147.0, 136.2, 135.4, 131.6, 124.9, 123.8, 119.0, 110.9, 61.4, 61.3, 60.4, 57.4, 55.7,

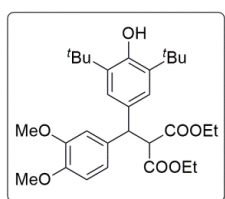
44.6, 34.4, 30.4, 13.93, 13.89; FT-IR (thin film, neat): 3417, 2959, 1758, 1732, 1586, 1479, 1435, 1368, 1274, 1155, 1094, 1037, 862, 746 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{42}\text{NaO}_7$ $[\text{M}+\text{Na}]^+$: 537.2828; found: 537.2804.

Diethyl 2-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-dimethoxyphenyl)methyl)malonate (3c)



The reaction was performed at 0.0564 mmol scale of **1c**; $R_f = 0.3$ (10% EtOAc in hexane); pale yellow solid (26.4 mg, 91% yield); m. p. = 110–114 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.08 (s, 2H), 6.48 (s, 2H), 6.27 (s, 1H), 5.05 (s, 1H), 4.56 (d, $J = 12.2$ Hz, 1H), 4.23 (d, $J = 12.2$ Hz, 1H), 4.04 (q, $J = 7.1$ Hz, 2H), 3.95 (q, $J = 7.0$ Hz, 2H), 3.75 (s, 6H), 1.39 (s, 18H), 1.07 (t, $J = 7.1$ Hz, 3H), 0.94 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.0, 167.9, 160.8, 152.8, 144.4, 135.7, 131.4, 124.5, 106.1, 98.7, 61.6, 61.4, 58.2, 55.4, 51.7, 34.5, 30.4, 14.00, 13.9; FT-IR (thin film, neat): 3616, 3443, 2959, 1758, 1732, 1597, 1463, 1435, 1368, 1204, 1156, 1065, 1036, 847, 698 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{42}\text{NaO}_7$ $[\text{M}+\text{Na}]^+$: 537.2828; found: 537.2806.

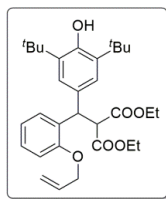
Diethyl 2-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,4-dimethoxyphenyl)methyl)malonate (3d)



The reaction was performed at 0.0564 mmol scale of **1d**; $R_f = 0.3$ (10% EtOAc in hexane); orange gummy solid (26.1 mg, 90% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.08 (s, 2H), 6.88 – 6.85 (m, 2H), 6.77 (d, $J = 8.1$ Hz, 1H), 5.04 (s, 1H), 4.58 (d, $J = 12.1$ Hz, 1H), 4.21 (d, $J = 12.1$ Hz, 1H), 4.04 – 3.93 (m, 4H), 3.85 (s, 3H), 3.82 (s, 3H), 1.39 (s, 18H), 1.05 (t, $J = 7.1$ Hz, 3H), 0.95 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.03, 168.00, 152.7, 148.8, 147.8, 135.8, 134.7, 131.9, 124.5, 119.8, 111.4, 111.3, 61.6, 61.4, 58.7, 56.0, 55.9, 51.2, 34.5, 30.4, 14.0, 13.9; FT-IR (thin film, neat): 3458, 2959, 1758, 1732, 1592, 1515, 1464, 1436, 1367, 1262, 1143, 1030,

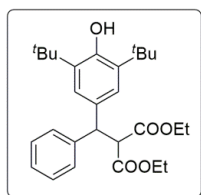
858, 663 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{30}\text{H}_{42}\text{NaO}_7$ $[\text{M}+\text{Na}]^+$: 537.2828; found : 537.2804.

Diethyl 2-((3-(allyloxy)phenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)malonate (3e)



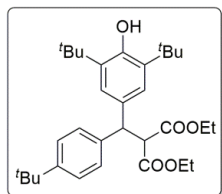
The reaction was performed at 0.0571 mmol scale of **1e**; R_f = 0.3 (10% EtOAc in hexane); pale yellow gummy solid (26.8 mg, 92% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.32 (d, J = 7.4 Hz, 1H), 7.13 – 7.09 (m, 3H), 6.89 (t, J = 7.4 Hz, 1H), 6.77 (d, J = 8.2 Hz, 1H), 6.08 – 5.99 (m, 1H), 5.37 (d, J = 17.3 Hz, 1H), 5.25 (d, J = 10.5 Hz, 1H), 5.06 (d, J = 12.4 Hz, 1H), 4.99 (s, 1H), 4.58 – 4.48 (m, 3H), 4.02 – 3.93 (m, 4H), 1.37 (s, 18H), 1.00 (t, J = 7.1 Hz, 3H), 0.94 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.5, 168.1, 156.0, 152.4, 135.3, 133.6, 131.5, 130.9, 127.7, 127.6, 125.1, 120.7, 117.3, 112.3, 69.0, 61.31, 61.27, 56.9, 45.4, 34.4, 30.4, 13.9 (2C); FT-IR (thin film, neat): 3638, 3446, 2959, 1758, 1732, 1599, 1492, 1436, 1368, 1242, 1120, 1035, 929, 868, 752, 645 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{31}\text{H}_{42}\text{NaO}_6$ $[\text{M}+\text{Na}]^+$: 533.2879; found : 533.2856.

Diethyl 2-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(phenyl)methyl)malonate (3f)



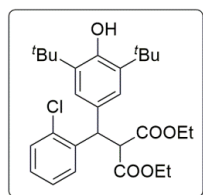
The reaction was performed at 0.0679 mmol scale of **1f**; R_f = 0.2 (5% EtOAc in hexane); white solid (29.02 mg, 94% yield); m. p. = 110–113 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.33 – 7.31 (m, 2H), 7.26 (s, 2H), 7.18 – 7.14 (m, 1H), 7.07 (s, 2H), 5.04 (s, 1H), 4.64 (d, J = 12.2 Hz, 1H), 4.27 (d, J = 12.2 Hz, 1H), 4.01 – 3.94 (m, 4H), 1.38 (s, 18H), 1.00 (t, J = 7.1 Hz, 3H), 0.95 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.1, 168.0, 152.7, 142.1, 135.8, 131.7, 128.6, 127.9, 126.8, 124.5, 61.5, 61.4, 58.3, 51.6, 34.5, 30.4, 13.92, 13.90; FT-IR (thin film, neat): 3638, 3440, 2959, 1759, 1732, 1601, 1436, 1368, 1316, 1259, 1177, 1156, 1036, 865, 700, 645 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{38}\text{NaO}_5$ $[\text{M}+\text{Na}]^+$: 477.2617; found : 477.2636.

Diethyl 2-((4-(*tert*-butyl)phenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)malonate (3g)



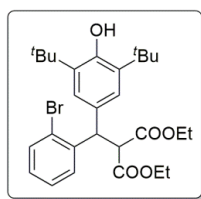
The reaction was performed at 0.0571 mmol scale of **1g**; $R_f = 0.3$ (5% EtOAc in hexane); pale yellow gummy solid (27.1 mg, 93% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.28 – 7.22 (m, 4H), 7.09 (s, 2H), 5.03 (s, 1H), 4.59 (d, $J = 12.2$ Hz, 1H), 4.25 (d, $J = 12.2$ Hz, 1H), 4.01 – 3.93 (m, 4H), 1.39 (s, 18H), 1.26 (s, 9H), 0.97 – 0.92 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 168.11, 168.07, 152.6, 149.5, 138.9, 135.7, 131.9, 127.5, 125.5, 124.6, 61.42, 61.35, 58.5, 51.4, 34.48, 34.45, 31.5, 30.4, 13.88, 13.84; FT-IR (thin film, neat): 3443, 2961, 1760, 1732, 1596, 1436, 1367, 1314, 1257, 1176, 1156, 1037, 842, 630 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{32}\text{H}_{46}\text{NaO}_5$ $[\text{M}+\text{Na}]^+$: 533.3243; found : 533.3218.

Diethyl 2-((2-chlorophenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)malonate (3h)



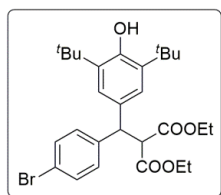
The reaction was performed at 0.061mmol scale of **1h**; $R_f = 0.2$ (5% EtOAc in hexane); pale yellow gummy solid (28.0 mg, 94% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.41 (d, $J = 7.8$ Hz, 1H), 7.32 (d, $J = 7.9$ Hz, 1H), 7.22 (t, $J = 7.3$ Hz, 1H), 7.13 (s, 2H), 7.12 – 7.08 (m, 1H), 5.24 (d, $J = 12.4$ Hz, 1H), 5.06 (s, 1H), 4.34 (d, $J = 12.4$ Hz, 1H), 4.06 – 3.94 (m, 4H), 1.38 (s, 18H), 1.02 (t, $J = 7.1$ Hz, 3H), 0.94 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.8, 167.6, 152.8, 139.8, 135.7, 134.4, 130.2, 130.1, 127.8, 127.4, 127.0, 125.0, 61.7, 61.5, 57.9, 46.7, 34.4, 30.4, 13.90, 13.87; FT-IR (thin film, neat): 3638, 3451, 2960, 2927, 1758, 1732, 1592, 1436, 1368, 1257, 1157, 1037, 867, 753, 730, 643, 600 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{37}\text{ClNaO}_5$ $[\text{M}+\text{Na}]^+$: 511.2227; found : 511.2207.

Diethyl 2-((2-bromophenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)malonate (3i)



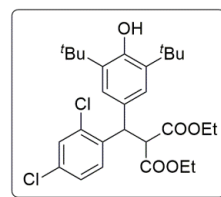
The reaction was performed at 0.0537 mmol scale of **1i**; $R_f = 0.2$ (5% EtOAc in hexane); white solid (26.6 mg, 93% yield); m. p. = 143–146 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.52 (d, $J = 7.9$ Hz, 1H), 7.40 (d, $J = 7.7$ Hz, 1H), 7.28 – 7.24 (m, 1H), 7.16 (s, 2H), 7.03 – 7.00 (m, 1H), 5.23 (d, $J = 12.4$ Hz, 1H), 5.06 (s, 1H), 4.33 (d, $J = 12.3$ Hz, 1H), 4.03 – 3.94 (m, 4H), 1.38 (s, 18H), 1.02 (t, $J = 7.1$ Hz, 3H), 0.94 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.8, 167.6, 152.8, 141.4, 135.7, 133.6, 130.1, 128.1, 127.7, 127.5, 125.4, 125.0, 61.7, 61.5, 58.1, 49.1, 34.4, 30.4, 13.9 (2C); FT-IR (thin film, neat): 3635, 2959, 1758, 1732, 1590, 1468, 1436, 1368, 1255, 1156, 1035, 808, 753, 725, 642 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{37}\text{BrNaO}_5$ $[\text{M}+\text{Na}]^+$: 555.1722; found : 555.1700.

Diethyl 2-((4-bromophenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)malonate(3j)



The reaction was performed at 0.0537 mmol scale of **1j**; $R_f = 0.2$ (5% EtOAc in hexane); pale yellow gummy solid (26.3 mg, 92% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.39 (d, $J = 8.4$ Hz, 2H), 7.19 (d, $J = 8.4$ Hz, 2H), 7.02 (s, 2H), 5.07 (s, 1H), 4.61 (d, $J = 12.2$ Hz, 1H), 4.22 (d, $J = 12.1$ Hz, 1H), 4.04 – 3.94 (m, 4H), 1.38 (s, 18H), 1.06 (t, $J = 7.1$ Hz, 3H), 0.95 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.80, 167.78, 152.8, 141.3, 136.0, 131.7, 131.1, 129.6, 124.4, 120.6, 61.7, 61.5, 58.0, 50.9, 34.5, 30.4, 14.0, 13.9; FT-IR (thin film, neat): 3407, 2959, 1758, 1732, 1592, 1489, 1436, 1468, 1239, 1155, 1036, 1011, 811 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{37}\text{BrNaO}_5$ $[\text{M}+\text{Na}]^+$: 555.1722; found : 555.1700.

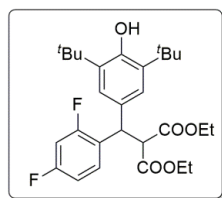
Diethyl 2-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2,4-dichlorophenyl)methyl)malonate (3k)



The reaction was performed at 0.055 mmol scale of **1k**; $R_f = 0.2$ (5% EtOAc in hexane); pale yellow gummy solid (27.4 mg, 95% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.35 (d, $J = 2.0$ Hz, 1H), 7.33 (d, $J = 8.5$, 1H),

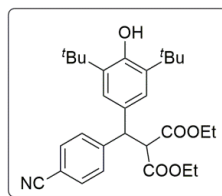
7.21 (dd, $J = 8.4, 1.9$ Hz, 1H), 7.09 (s, 2H), 5.18 (d, $J = 12.4$ Hz, 1H), 5.09 (s, 1H), 4.30 (d, $J = 12.4$ Hz, 1H), 4.08 – 4.01 (m, 2H), 3.97 (q, $J = 7.1$ Hz, 2H), 1.38 (s, 18H), 1.07 (t, $J = 7.1$ Hz, 3H), 0.95 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.6, 167.4, 152.9, 138.6, 135.8, 135.1, 132.8, 130.0, 129.6, 128.2, 127.3, 124.8, 61.8, 61.6, 57.6, 46.2, 34.4, 30.4, 13.94, 13.90; FT-IR (thin film, neat): 3385, 2960, 2922, 1756, 1732, 1588, 1471, 1436, 1368, 1239, 1155, 1106, 1036, 867, 771 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{36}\text{Cl}_2\text{NaO}_5$ $[\text{M}+\text{Na}]^+$: 545.1837; found : 545.1815.

Diethyl 2-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(2,4-difluorophenyl)methyl)malonate (3l)



The reaction was performed at 0.0606 mmol scale of **1l**; $R_f = 0.3$ (5% EtOAc in hexane); white solid (27.0 mg, 91% yield); m. p. = 110–114 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.35 (t, $J = 7.5$ Hz, 1H), 7.13 (s, 2H), 7.06 (t, $J = 7.4$ Hz, 1H), 6.98 (t, $J = 9.6$ Hz, 1H), 5.07 (s, 1H), 4.93 (d, $J = 12.4$ Hz, 1H), 4.41 (d, $J = 12.4$ Hz, 1H), 4.05 – 3.95 (m, 4H), 1.39 (s, 18H), 1.02 (t, $J = 7.1$ Hz, 3H), 0.96 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 167.9, 167.8, 160.6 (d, $J_{\text{C-F}} = 244.7$ Hz), 152.8, 135.7, 130.6, 129.4 (d, $J_{\text{C-F}} = 14.0$ Hz), 128.7 (d, $J_{\text{C-F}} = 4.2$ Hz), 128.3 (d, $J_{\text{C-F}} = 8.3$ Hz), 124.8 (d, $J_{\text{C-F}} = 1$ Hz), 124.3 (d, $J_{\text{C-F}} = 3.4$ Hz), 116.0 (d, $J_{\text{C-F}} = 22.7$ Hz), 61.6, 61.5, 56.95 (d, $J_{\text{C-F}} = 1.9$ Hz), 45.1 (d, $J_{\text{C-F}} = 0.6$ Hz), 34.4, 30.4, 13.90, 13.87; ^{19}F NMR (376 MHz, CDCl_3) δ –116.05; FT-IR (thin film, neat): 3387, 2960, 1760, 1732, 1595, 1436, 1371, 1236, 1121, 871, 757 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{37}\text{F}_2\text{O}_5$ $[\text{M}+\text{H}]^+$: 491.2609; found : 491.2625.

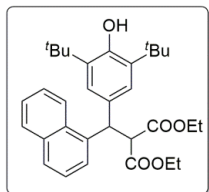
diethyl 2-((4-cyanophenyl)(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl)malonate (3m)



The reaction was performed at 0.094 mmol scale of **1m**; $R_f = 0.2$ (5% EtOAc in hexane); yellow solid (39 mg, 88% yield); m. p. = 200–203 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.57 (d, $J = 8.2$ Hz, 2H), 7.42 (d, $J = 8.2$ Hz, 2H), 7.01 (s, 2H), 5.12 (s, 1H), 4.70 (d, $J = 12.1$ Hz, 1H), 4.25 (d, $J = 12.1$ Hz, 1H), 4.05 – 3.94 (m, 4H), 1.38 (s, 18H), 1.05 (t, $J = 7.1$ Hz, 3H), 0.96 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR

(100 MHz, CDCl₃) δ 167.6, 167.5, 153.1, 147.7, 136.2, 132.5, 130.2, 128.7, 124.5, 118.9, 110.6, 61.8, 61.7, 57.6, 51.3, 34.5, 30.3, 14.0, 13.9; FT-IR (thin film, neat): 3406, 2959, 2925, 2229, 1755, 1732, 1607, 1436, 1368, 1312, 1259, 1177, 1156, 1122, 1035 cm⁻¹; HRMS (ESI): m/z calcd for C₂₉H₃₆NO₅ [M-H]⁺ : 478.2593; found : 478.2581.

Diethyl 2-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(naphthalen-2-yl)methyl)malonate (**3n**)



The reaction was performed at 0.0581mmol scale of **1n**; R_f = 0.2 (5%

EtOAc in hexane); pale yellow gummy solid (23.2 mg, 79% yield); ¹H

NMR (400 MHz, CDCl₃) δ 8.38 (d, J = 8.8 Hz, 1H), 7.80 (d, J = 8.0 Hz,

1H), 7.71 (d, J = 8.1 Hz, 1H), 7.55 – 7.50 (m, 2H), 7.46 – 7.42 (m, 2H), 7.17 (s, 2H), 5.54 (d,

J = 12.1 Hz, 1H), 5.02 (s, 1H), 4.45 (d, J = 12.1 Hz, 1H), 4.02 – 3.94 (m, 2H), 3.93 – 3.84 (m,

2H), 1.36 (s, 18H), 0.97 (t, J = 7.1 Hz, 3H), 0.83 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz,

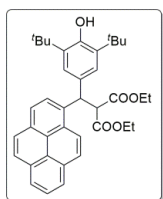
CDCl₃) δ 168.5, 167.8, 152.7, 138.1, 135.6, 134.3, 131.9, 131.0, 128.8, 127.5, 126.2, 125.6,

125.2, 124.9, 124.0, 123.1, 61.5, 58.9, 46.0, 34.4, 30.4, 29.8, 13.9, 13.8; FT-IR (thin film,

neat): 3441, 2959, 1758, 1732, 1599, 1435, 1368, 1254, 1155, 1036, 872, 777, 733 cm⁻¹;

HRMS (ESI): m/z calcd for C₃₂H₄₀NaO₅ [M+Na]⁺ : 527.2773; found : 527.2751.

Diethyl 2-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(4,6-dihydropyren-1-yl)methyl)malonate (**3o**)



The reaction was performed at 0.0478 mmol scale of **1o**; R_f = 0.2 (10% EtOAc

in hexane); orange gummy solid (25.2 mg, 91% yield); ¹H NMR (400 MHz,

CDCl₃) δ 8.70 (d, J = 9.5 Hz, 1H), 8.17 – 8.14 (m, 3H), 8.07 (d, J = 8.1 Hz,

1H), 8.01 – 7.96 (m, 3H), 7.26 (s, 2H), 7.24 (s, 1H), 5.88 (d, J = 12.0 Hz, 1H), 5.00 (s, 1H),

4.66 (d, J = 12.1 Hz, 1H), 4.06 (q, J = 7.1 Hz, 2H), 3.77 (q, J = 7.1 Hz, 2H), 1.35 (s, 18H),

1.04 (t, J = 7.1 Hz, 3H), 0.72 (t, J = 7.0 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 168.4,

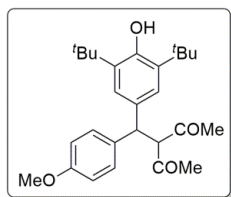
167.8, 152.6, 136.0, 135.8, 131.7, 131.5, 130.9, 130.1, 128.9, 127.7, 127.5, 127.2, 126.0,

125.4, 125.2, 125.04, 124.96, 124.7 (2C), 123.9, 123.4, 61.6, 61.5, 58.9, 46.1, 34.4, 30.4,

14.0, 13.7; FT-IR (thin film, neat): 3388, 2961, 2924, 1760, 1731, 1598, 1436, 1120, 848, 799, 723 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{38}\text{H}_{42}\text{NaO}_5$ $[\text{M}+\text{Na}]^+$: 601.2930; found : 601.2903.

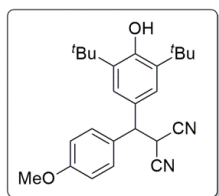
5. Characterisation of products (13a to 13d)

3-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)pentane-2,4-dione (13a)



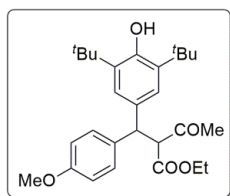
The reaction was performed at 0.062 mmol scale of **1a**; $R_f = 0.4$ (10% EtOAc in hexane); brown solid (24.6 mg, 95% yield); m. p. = 114–117 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.18 (d, $J = 8.5$ Hz, 2H), 7.00 (s, 2H), 6.80 (d, $J = 8.5$ Hz, 2H), 5.07 (s, 1H), 4.64 (s, 2H), 3.75 (s, 3H), 1.99 (s, 3H), 1.94 (s, 3H), 1.38 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 203.8, 203.7, 158.4, 152.6, 136.2, 134.2, 132.1, 128.8, 124.2, 114.3, 75.4, 55.3, 51.0, 34.5, 30.4, 30.1, 29.9; FT-IR (thin film, neat): 3636, 2958, 1698, 1611, 1513, 1436, 1357, 1252, 1180, 1154, 1120, 1035, 889, 835, 770, 738, 642, 539 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{35}\text{O}_4$ $[\text{M}-\text{H}]^+$: 423.2535; found : 423.2517.

2-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)malononitrile (13b)



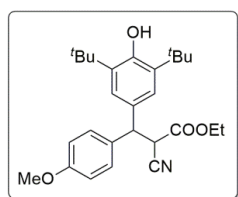
The reaction was performed at 0.062 mmol scale of **1a**; $R_f = 0.4$ (10% EtOAc in hexane); yellow solid (23.6mg, 98% yield); m. p. = 132–134°C; ^1H NMR (400 MHz, CDCl_3) δ 7.29 (d, $J = 8.6$ Hz, 2H), 7.11 (s, 2H), 6.92 (d, $J = 8.6$ Hz, 2H), 5.27 (s, 1H), 4.50 (d, $J = 7.5$ Hz, 1H), 4.30 (d, $J = 7.5$ Hz, 1H), 3.81 (s, 3H), 1.42 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 159.6, 153.9, 136.5, 129.8, 129.2, 128.1, 124.7, 114.6, 112.5, 55.4, 51.2, 34.6, 30.3, 30.1; FT-IR (thin film, neat): 3626, 2961, 2255, 2203, 1710, 1612, 1515, 1437, 1363, 1307, 1254, 1182, 1157, 1121, 1034, 836, 773, 738, 635 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{25}\text{H}_{29}\text{N}_2\text{O}_2$ $[\text{M}-\text{H}]^+$: 389.2229; found : 389.2212.

Ethyl 2-((3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl)-3-oxobutanoate (13c)



The reaction was performed at 0.062 mmol scale of **1a**; $R_f = 0.4$ (10% EtOAc in hexane); orange gummy solid (26.6 mg, 95% yield); The product was obtained as 1:1.3 diastomeric ratio. ^1H NMR (400 MHz, CDCl_3) δ 7.21 (t, $J = 8.6$ Hz, 2H), 7.03 (d, $J = 9.0$ Hz, 2H), 6.80 (d, $J = 8.6$ Hz, 2H), 5.06 (s, 0.45H), 5.04 (s, 0.57H), 4.62 (s, 0.43H), 4.59 (s, 0.58H), 4.43 (d, $J = 7.8$ Hz, 0.58H), 4.40 (d, $J = 7.8$ Hz, 0.43H), 4.00 – 3.90 (m, 2H), 3.75 (s, 3H), 2.08 (s, 1.7H), 2.03 (s, 1.3H), 1.38 (d, $J = 1.0$ Hz, 18H), 1.03 (t, $J = 7.1$ Hz, 1.3 H), 0.94 (t, $J = 7.1$ Hz, 1.7H); ^{13}C NMR (100 MHz, CDCl_3) δ 202.7, 202.5, 168.09, 168.06, 158.4, 158.3, 152.63, 152.55, 136.1, 135.8, 134.5, 134.1, 132.3, 132.0, 128.9, 128.8, 124.4, 124.3, 114.3, 114.0, 66.4, 66.1, 61.5, 61.4, 55.32, 55.30, 50.7, 34.5, 34.4, 30.4, 30.2, 30.0, 14.0, 13.9; FT-IR (thin film, neat): 3626, 2959, 1747, 1715, 1612, 1513, 1436, 1303, 1250, 1180, 1036, 889, 837, 737, 640 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{28}\text{H}_{38}\text{NaO}_5$ $[\text{M}+\text{Na}]^+$: 477.2617; found : 477.2600.

Ethyl 2-cyano-3-(3,5-di-*tert*-butyl-4-hydroxyphenyl)-3-(4-methoxyphenyl)propanoate (13d)



The reaction was performed at 0.062 mmol scale of **1a**; $R_f = 0.4$ (10% EtOAc in hexane); orange gummy solid (24.5 mg, 91% yield); The product was obtained as 1:1 diastomeric ratio. ^1H NMR (400 MHz, CDCl_3) δ 7.31 (d, $J = 8.4$ Hz, 1H), 7.23 (d, $J = 8.4$ Hz, 1H), 7.14 (s, 1H), 7.08 (s, 1H), 6.87 (t, $J = 8.3$ Hz, 2H), 5.18 (s, 0.5H), 5.17 (s, 0.5H), 4.60 (d, $J = 3.1$ Hz, 0.5H), 4.58 (d, $J = 3.0$ Hz, 0.51H), 4.14 – 4.05 (m, 3H), 3.79 (s, 1.5H), 3.78 (s, 1.5H), 1.41 (s, 9H), 1.40 (s, 9H), 1.09 – 1.05 (m, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 165.5, 165.4, 159.0, 158.9, 153.3, 153.2, 136.1, 136.0, 132.1, 131.6, 130.2, 129.43, 129.40, 129.1, 125.0, 124.5, 116.33, 116.30, 114.22, 114.17, 62.8, 55.4, 55.3, 50.8, 50.7, 44.8, 44.7, 34.5, 30.4, 30.3, 13.89, 13.88; FT-IR (thin

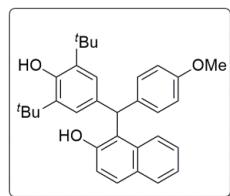
film, neat): 3627, 3458, 2960, 2249, 1745, 1612, 1514, 1437, 1368, 1305, 1251, 1181, 1034, 836, 738, 771, 636 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{34}\text{NO}_4$ $[\text{M}-\text{H}]^+$: 436.2488; found : 436.2469.

6. General procedure for the 1,6-conjugate addition of 2-naphthols to *p*-QMs

Anhydrous THF(1.0 mL) was added to the mixture of *p*-quinone methide (0.062 mmol), 2-naphthol (0.074 mmol), catalyst **11** (0.0062 mmol) and Cs_2CO_3 (0.0062 mmol) under argon atmosphere and the resulting suspension was stirred at room temperature. After the reaction was complete (based on TLC analysis), the reaction mixture was concentrated under reduced pressure. The residue was then purified through a silica gel column using EtOAc/Hexane mixture as an eluent to get the pure product.

7. Characterisation of products (15a to 15e)

1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl]naphthalen-2-ol (**15a**)⁵

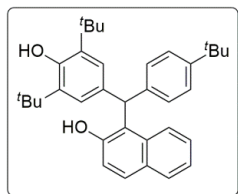


The reaction was performed at 0.062 mmol scale of **1a**; pale yellow solid; yield 78% (22.53 mg); R_f = 0.5 (20% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3), δ 8.02 (d, J = 8.6 Hz, 1H), 7.78 (dd, J = 7.9, 1.0 Hz, 1H), 7.71 (d, J = 8.8 Hz, 1H), 7.43 (ddd, J = 8.4, 6.8, 1.4 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.16 (d, J = 8.6 Hz, 2H), 7.06 (d, J = 8.8 Hz, 1H), 7.02 (s, 2H), 6.84 (d, J = 8.8 Hz, 2H), 6.23 (s, 1H), 5.44 (s, 1H), 5.20 (s, 1H), 3.78 (s, 3H), 1.33 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.5,

153.14, 153.12, 136.8, 134.1, 133.5, 132.1, 130.1, 129.6, 129.5, 128.8, 126.8, 125.7, 123.1, 123.0, 120.6, 120.1, 114.4, 55.4, 47.9, 34.6, 30.3.

1-{{4-(*tert*-butyl)phenyl}(3,5-di-*tert*-butyl-4-hydroxyphenyl)methyl}naphthalen-2-ol

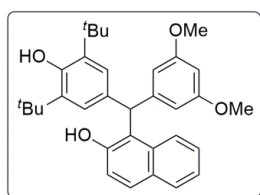
(15b)⁵



The reaction was performed at 0.057 mmol scale of **1g**; pale yellow solid; yield 74% (20.9 mg); $R_f = 0.7$ (20% EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3), δ 8.08 (d, $J = 8.6$ Hz, 1H), 7.80 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.73 (d, $J = 8.8$ Hz, 1H), 7.46 (ddd, $J = 8.3, 6.8, 1.4$ Hz, 1H), 7.36–7.32 (m, 3H), 7.18 (d, $J = 8.3$ Hz, 2H), 7.09 (d, $J = 8.8$ Hz, 1H), 7.03 (s, 2H), 6.28 (s, 1H), 5.42 (s, 1H), 5.20 (s, 1H), 1.35 (s, 18H), 1.31 (s, 9H); ^{13}C NMR (100 MHz, CDCl_3) δ 153.1, 153.0, 150.0, 139.1, 136.6, 133.6, 131.9, 129.7, 129.4, 128.8, 128.6, 126.8, 126.0, 125.8, 123.1, 123.0, 120.7, 120.1, 48.1, 34.6, 34.5, 31.5, 30.3.

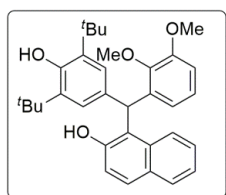
1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(3,5-dimethoxyphenyl)methyl]naphthalen-2-ol

(15c)⁵



The reaction was performed at 0.056 mmol scale of **1c**; pale yellow solid; yield 73% (20.5 mg); $R_f = 0.5$ (20%EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3), δ 8.04 (d, $J = 8.6$ Hz, 1H), 7.79 (dd, $J = 8.0, 1.0$ Hz, 1H), 7.72 (d, $J = 8.9$ Hz, 1H), 7.45 (ddd, $J = 8.5, 6.9, 1.5$ Hz, 1H), 7.35–7.31 (m, 1H), 7.08–7.06 (m, 3H), 6.41 (d, $J = 2.2$ Hz, 2H), 6.36 (t, $J = 2.2$ Hz, 1H), 6.21 (s, 1H), 5.50 (s, 1H), 5.20 (s, 1H), 3.70 (s, 6H), 1.35 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 161.3, 153.3, 153.1, 145.2, 136.7, 133.6, 131.2, 129.63, 129.56, 128.8, 126.8, 125.7, 123.1, 123.0, 120.3, 120.1, 107.3, 98.9, 55.4, 48.9, 34.5, 30.4.

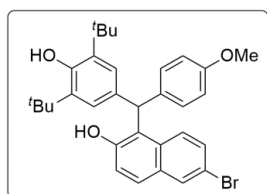
1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(2,3-dimethoxyphenyl)methyl]naphthalen-2-ol
(15d)⁵



The reaction was performed at 0.28mmol scale of **1b**; yellow solid; yield 71% (20 mg); $R_f = 0.6$ (20%EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3) δ 8.08 (d, $J = 8.6$ Hz, 1H), 7.75 (dd, $J = 8.1, 1.0$ Hz, 1H), 7.70 (d, $J = 8.9$ Hz, 1H), 7.42 (ddd, $J = 8.3, 6.8, 1.3$ Hz, 1H), 7.32–7.28 (m, 1H), 7.06 (d, $J = 8.9$ Hz, 1H), 7.03 (s, 2H), 6.99–6.95 (m, 1H), 6.84 (dd, $J = 8.2, 1.4$ Hz, 1H), 6.76 (dd, $J = 7.8, 1.4$ Hz, 1H), 6.67 (s, 1H), 5.78 (s, 1H), 5.20 (s, 1H), 3.88 (s, 3H), 3.49 (s, 3H), 1.33 (s, 18H); ^{13}C

NMR (100 MHz, CDCl_3) δ 153.5, 153.1, 152.9, 146.8, 136.8, 136.6, 133.7, 131.8, 129.6, 129.3, 128.6, 126.8, 125.5, 124.5, 123.3, 123.1, 121.7, 120.4, 120.0, 111.4, 60.6, 55.9, 42.7, 34.6, 30.4 .

6-bromo-1-[(3,5-di-*tert*-butyl-4-hydroxyphenyl)(4-methoxyphenyl)methyl]naphthalen-2-ol
(15e)⁵



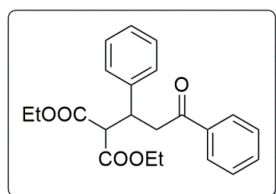
The reaction was performed at 0.062 mmol scale of **1a**; pale yellow solid; yield 75% (25.3 mg); $R_f = 0.4$ (20%EtOAc in hexane); ^1H NMR (400 MHz, CDCl_3), δ 7.92 (s, 1H), 7.87 (d, $J = 9.2$ Hz, 1H), 7.63 (d, $J = 8.9$ Hz, 1H), 7.47 (d, $J = 8.8$ Hz, 1H), 7.13 (d, $J = 8.7$ Hz, 2H), 7.08 (d, $J = 8.9$ Hz, 1H), 7.00 (s, 2H), 6.85 (d, $J = 8.7$ Hz, 2H), 6.16 (s, 1H), 5.47 (s, 1H), 5.21 (s, 1H), 3.78 (s, 3H), 1.33 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 158.7, 153.4, 153.2, 136.9, 133.8, 132.1, 131.8, 130.9, 130.6, 130.1, 129.9, 128.6, 125.6, 124.9, 121.3, 120.9, 116.9, 114.5, 55.4, 48.0, 34.6, 30.3.

8. General procedure for the 1,4-conjugate addition of malonates to chalcones

Anhydrous THF (1.0 mL) was added to the mixture of chalcone (0.096 mmol), diethyl malonate (0.115 mmol), catalyst **11** (0.0096 mmol) and Cs₂CO₃ (0.0096 mmol) under argon atmosphere, and the resulting suspension was stirred at room temperature. After the reaction was complete (based on TLC analysis), the reaction mixture was concentrated under reduced pressure. The residue was then purified through a silica gel column using EtOAc/Hexane mixture as an eluent to get the pure product.

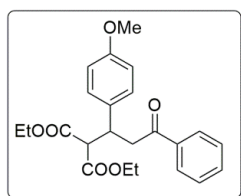
9. Characterisation of products (17a to 17n)

Diethyl 2-(3-oxo-1,3-diphenylpropyl)malonate(17a)⁶



The reaction was performed at 0.096 mmol scale of **16a**; $R_f = 0.4$ (20% EtOAc in hexane); pale yellow solid (31.5 mg, 89% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.91 – 7.88 (m, 2H), 7.53 (tt, $J = 6.6, 1.2$ Hz, 1H), 7.44 – 7.40 (m, 2H), 7.28 – 7.21 (m, 4H), 7.18 – 7.14 (m, 1H), 4.24 – 4.15 (m, 3H), 3.95 (q, $J = 7.1$ Hz, 2H), 3.82 (d, $J = 9.7$ Hz, 1H), 3.54 (dd, $J = 16.7, 4.6$ Hz, 1H), 3.45 (dd, $J = 16.7, 9.2$, 1H), 1.24 (t, $J = 7.1$ Hz, 3H), 1.00 (t, $J = 7.1$ Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 197.7, 168.5, 167.9, 140.6, 136.9, 133.2, 128.7, 128.5, 128.4, 128.2, 127.3, 61.8, 61.5, 57.7, 42.8, 40.9, 14.2, 13.9; FT-IR (thin film, neat): 2981, 1752, 1732, 1688, 1598, 1496, 1449, 1369, 1258, 1154, 1033, 861, 751, 700, 559 cm⁻¹.

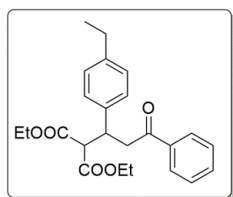
Diethyl 2-(1-(4-methoxyphenyl)-3-oxo-3-phenylpropyl)malonate (17b)



The reaction was performed at 0.084 mmol scale of **16b**; $R_f = 0.3$ (20% EtOAc in hexane); yellow gummy solid (27.01 mg, 81% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.90 – 7.88 (m, 2H), 7.52 (t, $J = 7.4$ Hz, 1H), 7.42 (t, $J = 7.8$ Hz, 2H), 7.17 (d, $J = 8.7$ Hz, 2H), 6.77 (d, $J = 8.7$ Hz, 2H), 4.24 – 4.10 (m, 3H), 3.96 (q, $J = 7.2$ Hz, 2H), 3.77 (d, $J = 9.8$ Hz, 1H), 3.73 (s, 3H), 3.51 (dd, $J = 16.5, 4.4$ Hz, 1H), 3.40 (dd, $J = 16.5, 9.4$ Hz, 1H), 1.24 (t, $J = 7.1$ Hz, 3H), 1.03 (t, $J = 7.1$ Hz, 3H); ¹³C

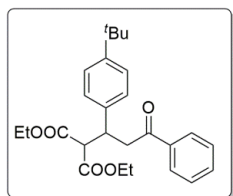
NMR (100 MHz, CDCl₃) δ 197.8, 168.5, 167.9, 158.6, 136.9, 133.1, 132.4, 129.4, 128.7, 128.2, 113.8, 61.8, 61.5, 57.9, 55.3, 42.9, 40.3, 14.2, 13.9; FT-IR (thin film, neat): 2961, 2929, 2839, 1751, 1732, 1688, 1612, 1598, 1583, 1515, 1449, 1369, 1251, 1180, 1154, 1114, 1035, 832, 737, 692, 560 cm⁻¹; HRMS (ESI): m/z calcd for C₂₃H₂₆NaO₆ [M+Na]⁺ : 421.1627; found : 421.1608.

Diethyl 2-(1-(4-ethylphenyl)-3-oxo-3-phenylpropyl)malonate (17c)



The reaction was performed at 0.085 mmol scale of **16c**; R_f = 0.4 (20% EtOAc in hexane); orange gummy solid (30.5 mg, 91% yield); ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 7.4 Hz, 2H), 7.52 (t, J = 7.3 Hz, 1H), 7.41 (t, J = 7.8 Hz, 2H), 7.16 (d, J = 8.0 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 4.22 – 4.12 (m, 3H), 3.95 (q, J = 7.1 Hz, 2H), 3.80 (d, J = 9.7 Hz, 1H), 3.53 (dd, J = 16.7, 4.6 Hz, 1H), 3.44 (dd, J = 16.6, 9.1 Hz, 1H), 2.56 (q, J = 7.6 Hz, 2H), 1.23 (t, J = 7.1 Hz, 3H), 1.16 (t, J = 7.6 Hz, 3H), 0.99 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 197.8, 168.6, 168.0, 143.1, 137.7, 137.0, 133.1, 128.6, 128.23, 128.22, 128.0, 61.7, 61.4, 57.8, 42.8, 40.6, 28.5, 15.5, 14.1, 13.9; FT-IR (thin film, neat): 2965, 2929, 1748, 1732, 1688, 1598, 1515, 1449, 1368, 1258, 1154, 1097, 1034, 831, 756, 691, 572 cm⁻¹; HRMS (ESI): m/z calcd for C₂₄H₂₈NaO₅ [M+Na]⁺ : 419.1834; found : 419.1817.

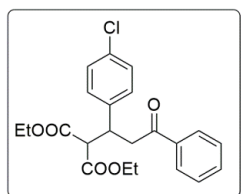
Diethyl 2-(1-(4-(tert-butyl)phenyl)-3-oxo-3-phenylpropyl)malonate (17d)



The reaction was performed at 0.076 mmol scale of **16d**; R_f = 0.5 (20% EtOAc in hexane); yellow solid (26.3 mg, 82% yield); m. p. = 102–105 °C ; ¹H NMR (400 MHz, CDCl₃) δ 7.90 (d, J = 7.8 Hz, 2H), 7.52 (t, J = 7.4 Hz, 1H), 7.41 (t, J = 7.5 Hz, 2H), 7.26 – 7.23 (m, 2H), 7.18 (d, J = 7.9 Hz, 2H), 4.21 – 4.13 (m, 3H), 3.94 (q, J = 7.0 Hz, 2H), 3.80 (d, J = 9.6 Hz, 1H), 3.55 – 3.42 (m, 2H), 1.24 (s, 9H), 1.23 (t, J = 7.2 Hz, 3H), 0.95 (t, J = 7.1 Hz, 3H); ¹³C NMR (100 MHz, CDCl₃) δ 197.8, 168.6, 168.0, 149.9, 137.5, 137.0, 133.1, 128.6, 128.2, 127.9, 125.4, 61.7, 61.4, 57.7, 42.8,

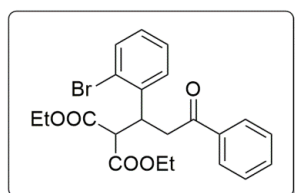
40.4, 34.5, 31.4, 14.1, 13.8; FT-IR (thin film, neat): 2964, 2929, 2871, 1748, 1732, 1689, 1598, 1582, 1513, 1464, 1449, 1368, 1257, 1154, 1097, 837, 755, 691, 586 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{26}\text{H}_{32}\text{NaO}_5$ $[\text{M}+\text{Na}]^+$: 447.2147; found : 447.2129.

Diethyl 2-(1-(4-chlorophenyl)-3-oxo-3-phenylpropyl)malonate (17e)



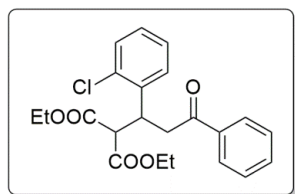
The reaction was performed at 0.082 mmol scale of **16e**; R_f = 0.3 (20% EtOAc in hexane); orange solid (31.2 mg, 94% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, J = 7.8 Hz, 2H), 7.54 (t, J = 7.3 Hz, 1H), 7.43 (t, J = 7.6 Hz, 2H), 7.26 (s, 1H), 7.21 (s, 3H), 4.24 – 4.13 (m, 3H), 3.98 (q, J = 7.1 Hz, 2H), 3.78 (d, J = 9.6 Hz, 1H), 3.53 (dd, J = 16.8, 4.3, 1H), 3.43 (dd, J = 16.9, 9.4, 1H), 1.25 (t, J = 7.1 Hz, 3H), 1.05 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.4, 168.2, 167.7, 139.1, 136.7, 133.3, 133.0, 129.8, 128.72, 128.65, 128.2, 61.9, 61.6, 57.4, 42.5, 40.2, 14.1, 13.9; FT-IR (thin film, neat): 2982, 2937, 1750, 1732, 1688, 1598, 1581, 1492, 1449, 1369, 1256, 1155, 1094, 1032, 1015, 861, 829, 754, 691, 552 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{23}\text{ClNaO}_5$ $[\text{M}+\text{Na}]^+$: 425.1132; found : 425.1115.

Diethyl 2-(1-(2-bromophenyl)-3-oxo-3-phenylpropyl)malonate (17f)



The reaction was performed at 0.070 mmol scale of **16f**; R_f = 0.3 (20% EtOAc in hexane); orange solid (28.7 mg, 92% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, J = 7.6 Hz, 2H), 7.54 (dd, J = 7.1, 4.4 Hz, 2H), 7.43 (t, J = 7.7 Hz, 2H), 7.30 (d, J = 7.7 Hz, 1H), 7.20 (t, J = 7.5 Hz, 1H), 7.04 (t, J = 7.9 Hz, 1H), 4.68 – 4.63 (m, 1H), 4.22 – 4.10 (m, 2H), 4.06 (q, J = 8.0 Hz, 3H), 3.72 – 3.60 (m, 2H), 1.19 (t, J = 7.1 Hz, 3H), 1.10 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.6, 168.4, 167.9, 139.6, 136.8, 133.5, 133.2, 128.68, 128.66, 128.3, 127.6, 127.5, 125.1, 61.7, 55.4, 40.6, 39.64, 39.62, 14.1, 14.0; FT-IR (thin film, neat): 2981, 1751, 1732, 1688, 1598, 1473, 1448, 1369, 1229, 1154, 1096, 1025, 861, 752, 691 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{23}\text{BrNaO}_5$ $[\text{M}+\text{Na}]^+$: 469.0627; found : 469.0608.

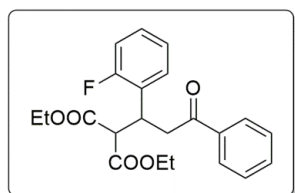
Diethyl 2-(1-(2-chlorophenyl)-3-oxo-3-phenylpropyl)malonate (17g)



The reaction was performed at 0.082 mmol scale of **16g**; $R_f = 0.3$ (20% EtOAc in hexane); orange gummy solid (32.5 mg, 98% yield);

^1H NMR (400 MHz, CDCl_3) δ 7.92 (d, $J = 7.9$ Hz, 2H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.42 (t, $J = 7.4$ Hz, 2H), 7.32 (t, $J = 7.4$ Hz, 2H), 7.13 (quint, $J = 7.3$ Hz, 2H), 4.68 – 4.62 (m, 1H), 4.22 – 4.11 (m, 2H), 4.09 – 4.00 (m, 3H), 3.69 (dd, $J = 17.2, 8.8$ Hz, 1H), 3.61 (dd, $J = 17.0, 4.6$ Hz, 1H), 1.20 (t, $J = 7.0$ Hz, 3H), 1.08 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.6, 168.4, 167.9, 137.9, 136.8, 134.2, 133.2, 130.2, 129.5, 128.7, 128.4, 128.2, 126.9, 61.7, 61.6, 55.3, 40.6, 37.5, 14.1, 13.9; FT-IR (thin film, neat): 2982, 2930, 1750, 1732, 1689, 1598, 1582, 1477, 1448, 1369, 1229, 1155, 1036, 861, 692, 566 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{23}\text{ClNaO}_5$ $[\text{M}+\text{Na}]^+$: 425.1132; found : 425.1114.

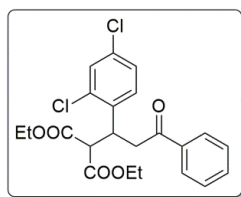
Diethyl 2-(1-(2-fluorophenyl)-3-oxo-3-phenylpropyl)malonate (17h)



The reaction was performed at 0.088 mmol scale of **16h**; $R_f = 0.3$ (20% EtOAc in hexane); orange gummy solid (29.7 mg, 87% yield);

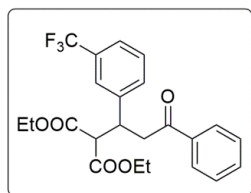
^1H NMR (400 MHz, CDCl_3) δ 7.91 – 7.89 (m, 2H), 7.53 (t, $J = 7.4$ Hz, 1H), 7.42 (t, $J = 7.8$ Hz, 2H), 7.30 – 7.26 (m, 1H), 7.19 – 7.14 (m, 1H), 7.02 – 6.95 (m, 2H), 4.34 (td, $J = 9.8, 4.3$ Hz, 1H), 4.26 – 4.14 (m, 2H), 4.01 – 3.93 (m, 3H), 3.59 (dd, $J = 17.0, 9.4$ Hz, 1H), 3.51 (dd, $J = 17.0, 4.4$ Hz, 1H), 1.24 (t, $J = 7.1$ Hz, 3H), 1.00 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.5, 168.3, 167.8, 161.3 (d, $J_{\text{C-F}} = 244.8$ Hz), 136.8, 133.2, 131.3 (d, $J_{\text{C-F}} = 4.9$ Hz), 129.0 (d, $J_{\text{C-F}} = 8.5$ Hz), 128.7, 128.2, 127.2 (d, $J_{\text{C-F}} = 13$ Hz), 124.1 (d, $J_{\text{C-F}} = 3.3$ Hz), 115.8 (d, $J_{\text{C-F}} = 22.2$ Hz), 61.9, 61.5, 55.8 (d, $J_{\text{C-F}} = 2.2$ Hz), 41.2 (d, $J_{\text{C-F}} = 1.9$ Hz), 36.7, 14.1, 13.9; ^{19}F NMR (376 MHz, CDCl_3) δ -115.6; FT-IR (thin film, neat): 2925, 1751, 1732, 1688, 1598, 1493, 1449, 1369, 1255, 1155, 1105, 1033, 758, 691 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{23}\text{FNaO}_5$ $[\text{M}+\text{Na}]^+$: 409.1427; found : 409.1411.

Diethyl 2-(1-(2,4-dichlorophenyl)-3-oxo-3-phenylpropyl)malonate (17i)



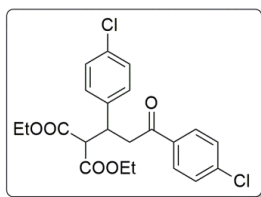
The reaction was performed at 0.072 mmol scale of **16i**; $R_f = 0.4$ (20% EtOAc in hexane); orange gummy solid (29.0 mg, 92% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.93 (d, $J = 7.8$ Hz, 2H), 7.55 (t, $J = 7.3$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.36 (s, 1H), 7.27 (d, $J = 8.4$ Hz, 1H), 7.14 (d, $J = 8.4$ Hz, 1H), 4.62 – 4.57 (m, 1H), 4.25 – 4.13 (m, 2H), 4.11 – 4.03 (m, 3H), 3.68 (dd, $J = 17.3, 9.0$ Hz, 1H), 3.61 (dd, $J = 17.2, 4.5$ Hz, 1H), 1.22 (t, $J = 7.1$ Hz, 3H), 1.13 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.3, 168.2, 167.7, 136.7, 136.6, 135.0, 133.44, 133.38, 130.4, 129.9, 128.7, 128.2, 127.2, 61.84, 61.80, 55.1, 40.4, 37.0, 14.1, 14.0; FT-IR (thin film, neat): 3066, 2982, 2929, 1751, 1732, 1689, 1560, 1475, 1449, 1369, 1302, 1230, 1155, 1106, 1033, 864, 823, 734, 691, 579 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{22}\text{Cl}_2\text{NaO}_5$ $[\text{M}+\text{Na}]^+$: 459.0742; found : 459.0733.

Diethyl 2-(3-oxo-3-phenyl-1-(3-(trifluoromethyl)phenyl)propyl)malonate (17j)



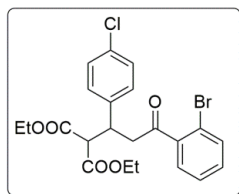
The reaction was performed at 0.072 mmol scale of **16j**; $R_f = 0.4$ (20% EtOAc in hexane); pale yellow gummy solid (25.9 mg, 82% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.89 (d, $J = 7.7$ Hz, 2H), 7.56 – 7.52 (m, 3H), 7.45 – 7.36 (m, 4H), 4.28 – 4.14 (m, 3H), 3.96 (q, $J = 7.1$ Hz, 2H), 3.83 (d, $J = 9.4$ Hz, 1H), 3.59 (dd, $J = 17.1, 4.2$ Hz, 1H), 3.48 (dd, $J = 17.1, 9.2$ Hz, 1H), 1.24 (t, $J = 7.0$ Hz, 3H), 1.01 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.2, 168.2, 167.6, 141.8, 136.7, 133.4, 132.2, 130.7 (q, $J_{\text{C-F}} = 32$ Hz), 129.0, 128.8, 128.2, 125.1 (q, $J_{\text{C-F}} = 3.7$ Hz), 124.2 (q, $J_{\text{C-F}} = 3.7$ Hz), 124.1 (q, $J_{\text{C-F}} = 270.9$ Hz), 62.0, 61.7, 57.3, 42.4, 40.5, 14.1, 13.8; ^{19}F NMR (376 MHz, CDCl_3) δ -62.6; FT-IR (thin film, neat): 2924, 1751, 1732, 1598, 1449, 1329, 1260, 1123, 1031, 868, 803, 745, 691 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{23}\text{F}_3\text{NaO}_5$ $[\text{M}+\text{Na}]^+$: 459.1395; found : 459.1377.

Diethyl 2-(1,3-bis(4-chlorophenyl)-3-oxopropyl)malonate (17k)



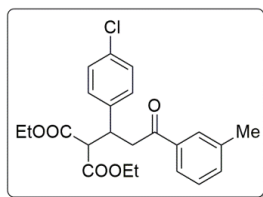
The reaction was performed at 0.070 mmol scale of **16k**; $R_f = 0.4$ (20% EtOAc in hexane); pale yellow gummy solid (23.9 mg, 77% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 8.4$ Hz, 2H), 7.40 (d, $J = 8.4$ Hz, 2H), 7.23 – 7.18 (m, 4H), 4.26 – 4.16 (m, 2H), 4.15 – 4.09 (m, 1H), 3.97 (q, $J = 7.1$ Hz, 2H), 3.76 (d, $J = 9.6$ Hz, 1H), 3.51 (dd, $J = 16.8, 4.2$ Hz, 1H), 3.37 (dd, $J = 16.8, 9.6$ Hz, 1H), 1.24 (t, $J = 7.1$ Hz, 3H), 1.04 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 196.2, 168.2, 167.6, 139.8, 138.9, 135.0, 133.1, 129.7, 129.6, 129.1, 128.7, 61.9, 61.7, 57.4, 42.5, 40.3, 14.1, 13.9; FT-IR (thin film, neat): 2983, 2937, 1751, 1732, 1689, 1590, 1491, 1446, 1401, 1369, 1256, 1155, 1093, 1032, 1014, 832, 724, 650, 530 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{22}\text{Cl}_2\text{NaO}_5$ $[\text{M}+\text{Na}]^+$: 459.0742; found : 459.0724.

Diethyl 2-(3-(2-bromophenyl)-1-(4-chlorophenyl)-3-oxopropyl)malonate (17l)



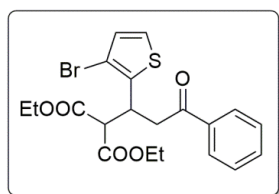
The reaction was performed at 0.062 mmol scale of **16l**; $R_f = 0.4$ (20% EtOAc in hexane); white solid (23.7 mg, 79% yield); m. p. = 77–81 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3) δ 7.53 (d, $J = 7.8$ Hz, 1H), 7.31 – 7.18 (m, 6H), 7.13 (dd, $J = 7.1, 1.3$ Hz, 1H), 4.25 – 4.17 (m, 2H), 4.06 (td, $J = 9.7, 4.3$ Hz, 1H), 3.97 (q, $J = 7.1$ Hz, 2H), 3.73 (d, $J = 9.7$ Hz, 1H), 3.50 (dd, $J = 17.2, 4.3$ Hz, 1H), 3.39 (dd, $J = 17.2, 9.8$ Hz, 1H), 1.26 (t, $J = 7.1$ Hz, 3H), 1.05 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 201.3, 168.1, 167.6, 141.2, 138.6, 133.8, 133.2, 131.8, 130.0, 128.7, 128.6, 127.5, 118.7, 62.0, 61.7, 57.3, 46.4, 40.2, 14.2, 13.9; FT-IR (thin film, neat): 2982, 2927, 1751, 1732, 1588, 1492, 1466, 1429, 1369, 1254, 1156, 1094, 1030, 860, 829, 759, 573 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{22}\text{H}_{22}\text{BrClNaO}_5$ $[\text{M}+\text{Na}]^+$: 503.0237; found : 503.0215.

Diethyl 2-(1-(4-chlorophenyl)-3-oxo-3-(m-tolyl)propyl)malonate (17m)



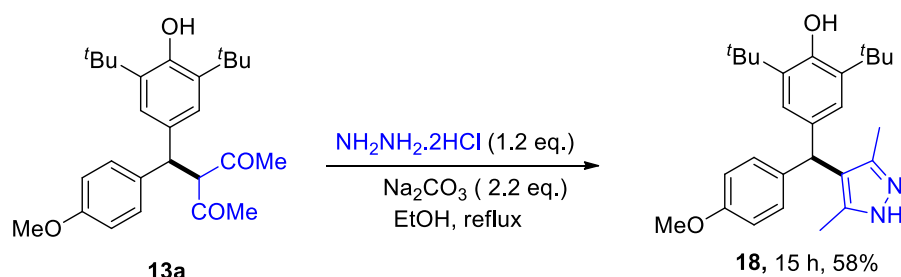
The reaction was performed at 0.078 mmol scale of **16m**; $R_f = 0.4$ (20% EtOAc in hexane); white solid (24.1 mg, 74% yield); m. p. = 80–83 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.69 (d, $J = 7.9$ Hz, 2H), 7.35 – 7.26 (m, 3H), 7.21 (s, 3H), 4.26 – 4.13 (m, 3H), 3.98 (q, $J = 7.1$ Hz, 2H), 3.78 (d, $J = 9.6$ Hz, 1H), 3.50 (dd, $J = 16.9, 4.6$ Hz, 1H), 3.43 (dd, $J = 17.0, 9.2$ Hz, 1H), 2.37 (s, 3H), 1.24 (t, $J = 7.1$ Hz, 3H), 1.05 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.5, 168.3, 167.7, 139.2, 138.5, 136.7, 134.1, 132.9, 129.8, 128.7, 128.63, 128.60, 125.4, 61.9, 61.6, 57.4, 42.5, 40.2, 21.5, 14.2, 13.9; FT-IR (thin film, neat): 2983, 2928, 1751, 1732, 1683, 1604, 1587, 1492, 1369, 1260, 1155, 1094, 1036, 1015, 859, 827, 783, 558 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{23}\text{H}_{25}\text{ClNaO}_5$ $[\text{M}+\text{Na}]^+$: 439.1288; found : 439.1271.

Diethyl 2-(1-(3-bromothiophen-2-yl)-3-oxo-3-phenylpropyl)malonate (17n)



The reaction was performed at 0.068 mmol scale of **16n**; $R_f = 0.4$ (10% EtOAc in hexane); pale yellow gummy solid (29.1 mg, 94% yield); ^1H NMR (400 MHz, CDCl_3) δ 7.94 (d, $J = 7.8$ Hz, 2H), 7.54 (t, $J = 7.2$ Hz, 1H), 7.44 (t, $J = 7.5$ Hz, 2H), 7.13 (d, $J = 5.3$ Hz, 1H), 6.86 (d, $J = 5.3$ Hz, 1H), 4.64 (td, $J = 8.5, 4.8$ Hz, 1H), 4.25 – 4.15 (m, 2H), 4.14 – 4.07 (m, 2H), 4.04 (d, $J = 8.4$ Hz, 1H), 3.66 (dd, $J = 17.3, 8.8$ Hz, 1H), 3.58 (dd, $J = 17.3, 4.4$ Hz, 1H), 1.23 (t, $J = 7.1$ Hz, 3H), 1.15 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 197.0, 168.0, 167.5, 138.1, 136.7, 133.4, 130.1, 128.7, 128.3, 124.8, 110.3, 61.9, 61.8, 56.0, 42.0, 35.5, 14.1, 14.0; FT-IR (thin film, neat): 3111, 2982, 2937, 1751, 1732, 1689, 1516, 1449, 1369, 1256, 1156, 1096, 1031, 861, 757, 691, 539 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{20}\text{H}_{21}\text{BrNaO}_5\text{S}$ $[\text{M}+\text{Na}]^+$: 475.0191; found : 475.0173.

10. Synthetic elaboration of 13a

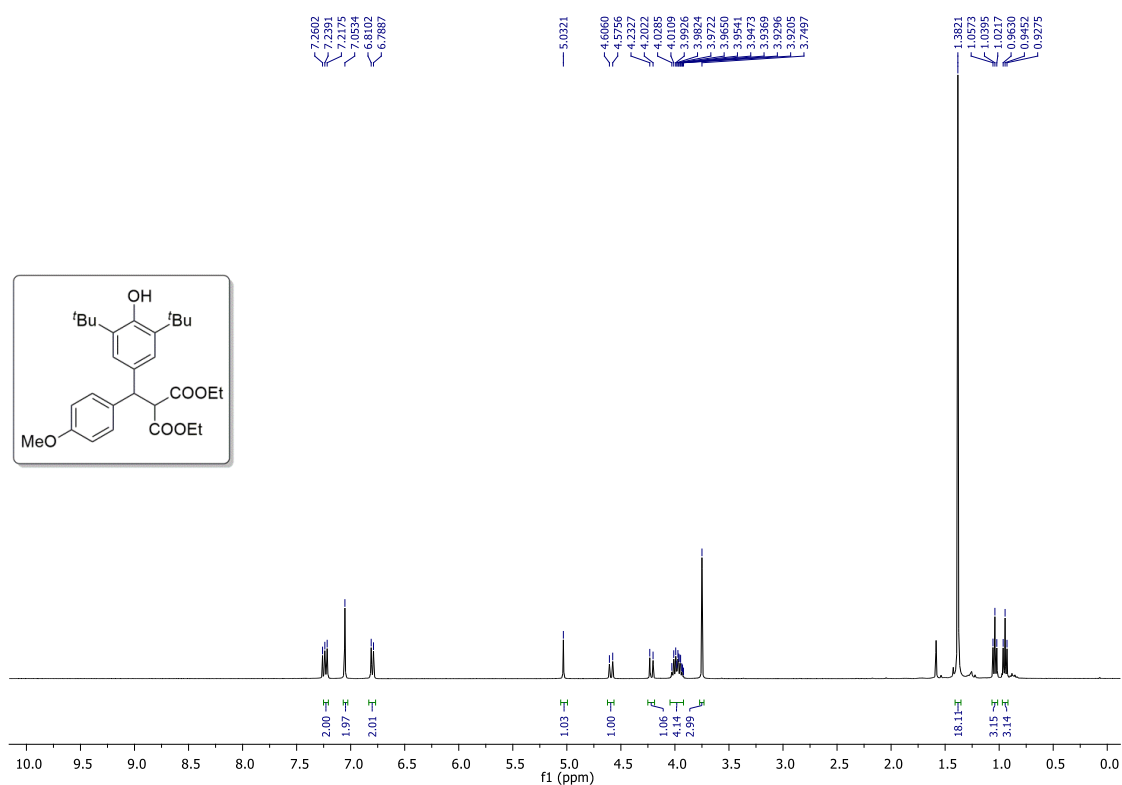


$\text{NH}_2\text{NH}_2 \cdot \text{HCl}$ (12 mg, 0.11 mmol) was added to a solution of **13a** (35 mg, 0.089 mmol) and Na_2CO_3 (21 mg, 0.196 mmol) in ethanol (3.0 mL) and the mixture was refluxed for 15 h . The reaction mixture was then concentrated under reduced pressure. The residue was purified through a neutral alumina column using EtOAc/Hexane mixture as an eluent to get the pure product **18** (20.1 mg, 58%) as pale yellow liquid; $R_f = 0.3$ (80% EtOAc in hexane); ^1H NMR (400 MHz, DMSO-d_6) δ 6.93 (d, $J = 8.6$ Hz, 2H), 6.84 – 6.82 (m, 4H), 6.78 (s, 1H), 5.76 (s, 1H), 5.22 (s, 1H), 3.71 (s, 3H), 1.78 (s, 6H), 1.29 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 157.8, 152.1, 136.2, 135.6, 133.7, 130.0, 125.7, 118.6, 113.5, 113.4, 55.4, 45.7, 34.4, 30.5, 11.8; FT-IR (thin film, neat): 3642, 3197, 3136, 2956, 2925, 2871, 1609, 1584, 1510, 1435, 1301, 1247, 1176, 1155, 1120, 1038 cm^{-1} ; HRMS (ESI): m/z calcd for $\text{C}_{27}\text{H}_{37}\text{N}_2\text{O}_2$ $[\text{M}+\text{H}]^+$: 421.2855; found : 421.2841

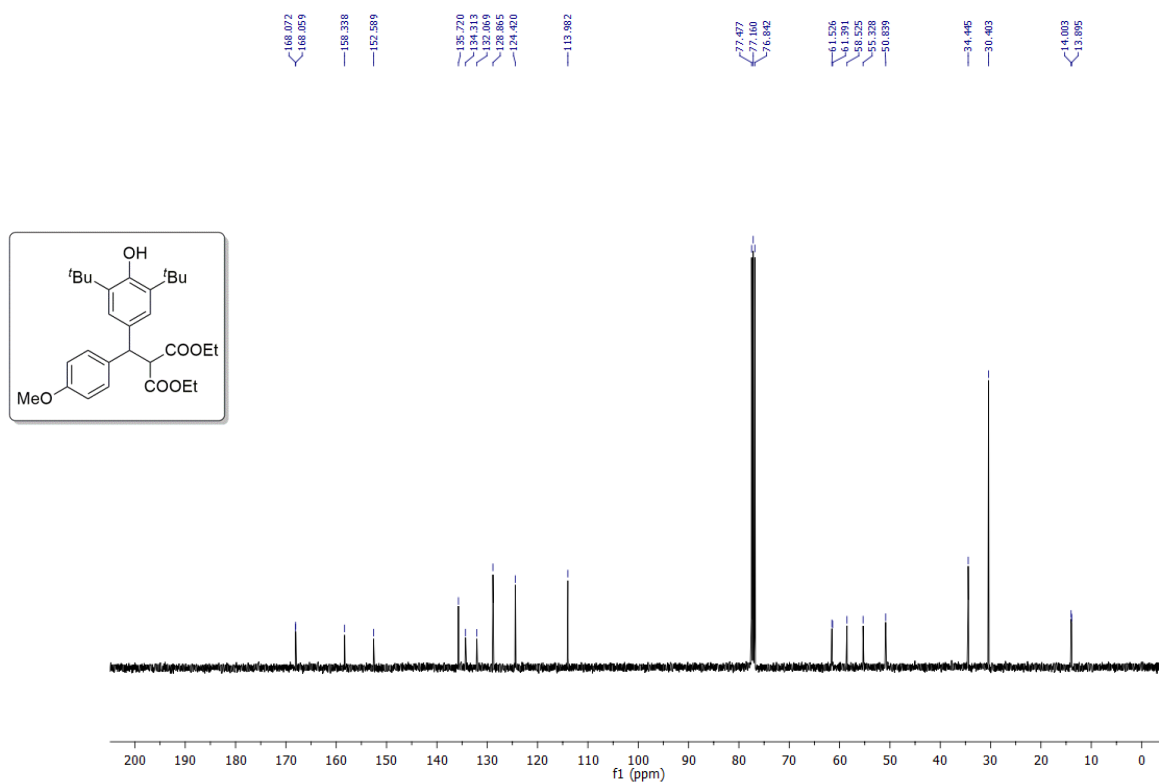
11. References:

- (1) (a) V. Reddy and R. V. Anand, *Org. Lett.*, 2015, **17**, 3390; (b) W. –D. Chu, L. –F. Zhang, X. Bao, X. –H. Zhao, C. Zeng, J. –Y. Du, G. –B. Zhang, F. –X. Wang, X. –Y. Ma and C. –A. Fan, *Angew. Chem., Int. Ed.*, 2013, **52**, 9229
- (2) (a) D. Enders, K. Breuer, U. Kallfass and T. Balensiefer, *Synthesis*, 2003, **8**, 1292.
- (3) (a) V. Lavallo, Y. Canac, B. Donnadieu, W. W. Schoeller and G. Bertrand, *Science*, 2006, **312**, 722; (b) M. M. D. Wilde and M. Gravel, *Angew. Chem. Int. Ed.*, 2013, **52**, 12651.
- (4) X. Zhang, J. Kang, P. Niu, J. Wu, W. Yu and J. Chang, *J. Org. Chem.*, 2014, **79**, 10170.
- (5) P. Arde and R. V. Anand, *RSC Adv.*, 2016, **6**, 77111.
- (6) D. Cao, G. Fang, J. Zhang, H. Wang, C. Zheng and G. Zhao, *J. Org. Chem.*, 2016, **81**, 9973.

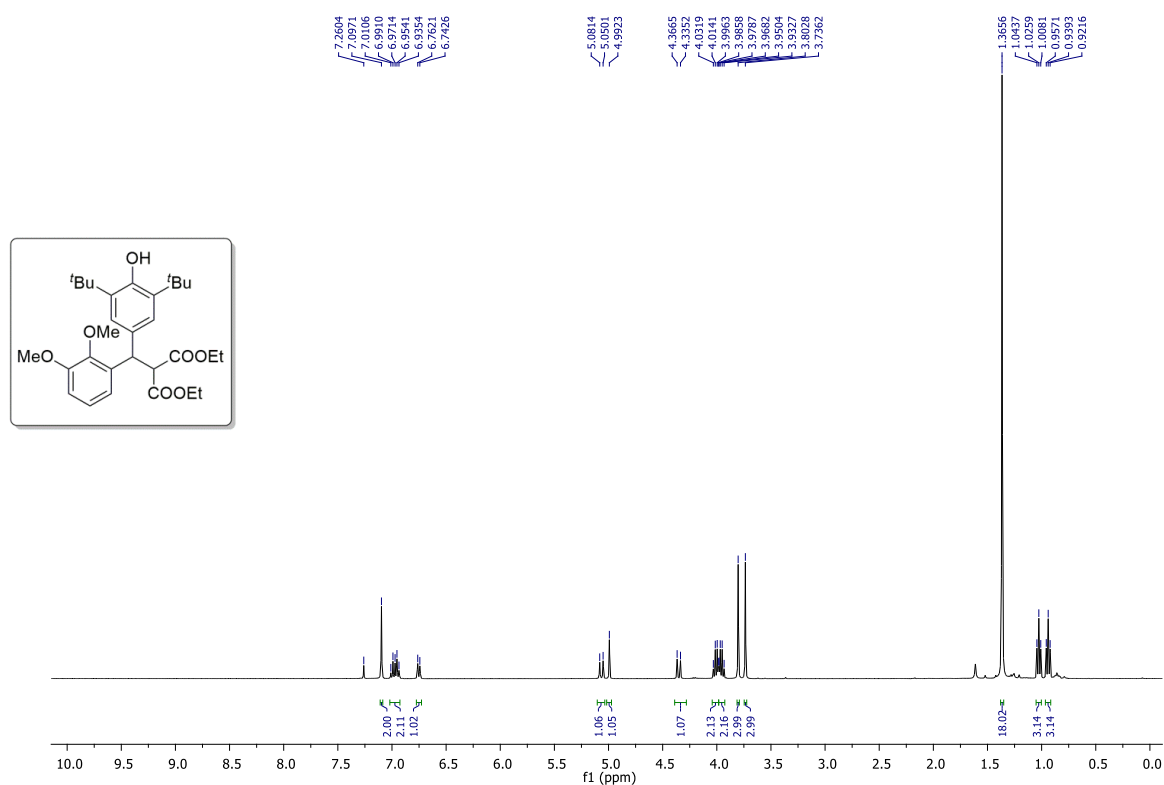
¹H NMR spectrum of **3a**



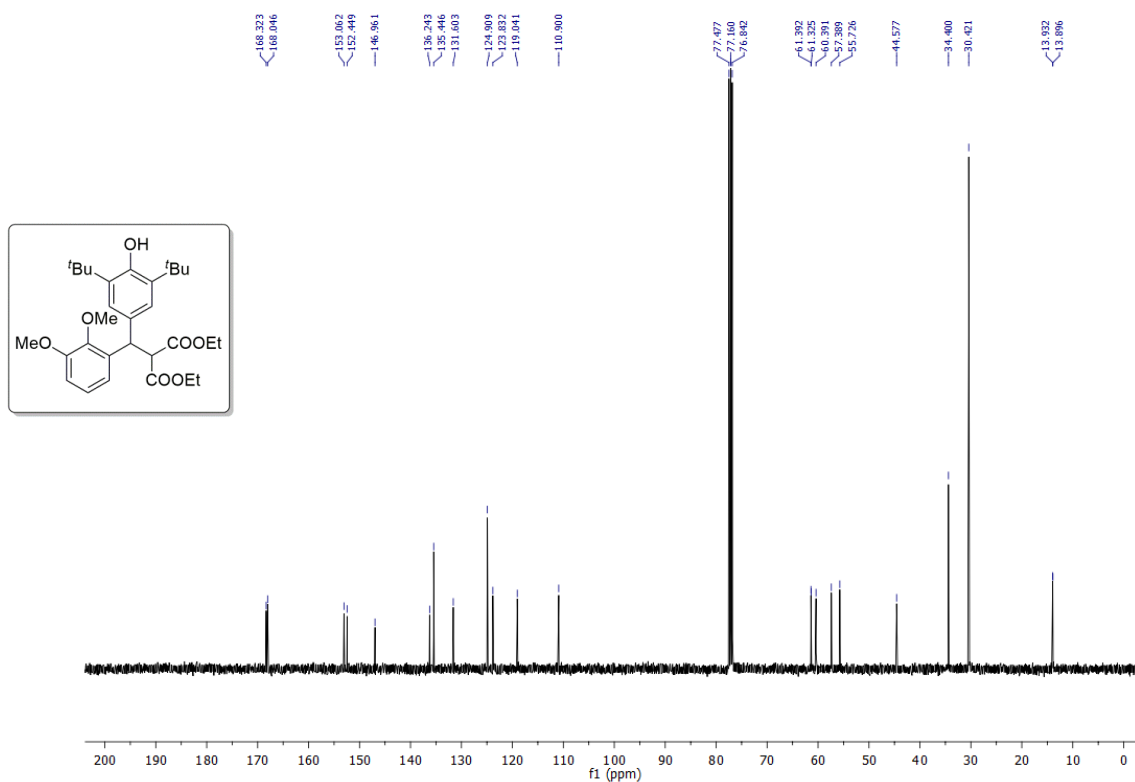
¹³C NMR spectrum of **3a**



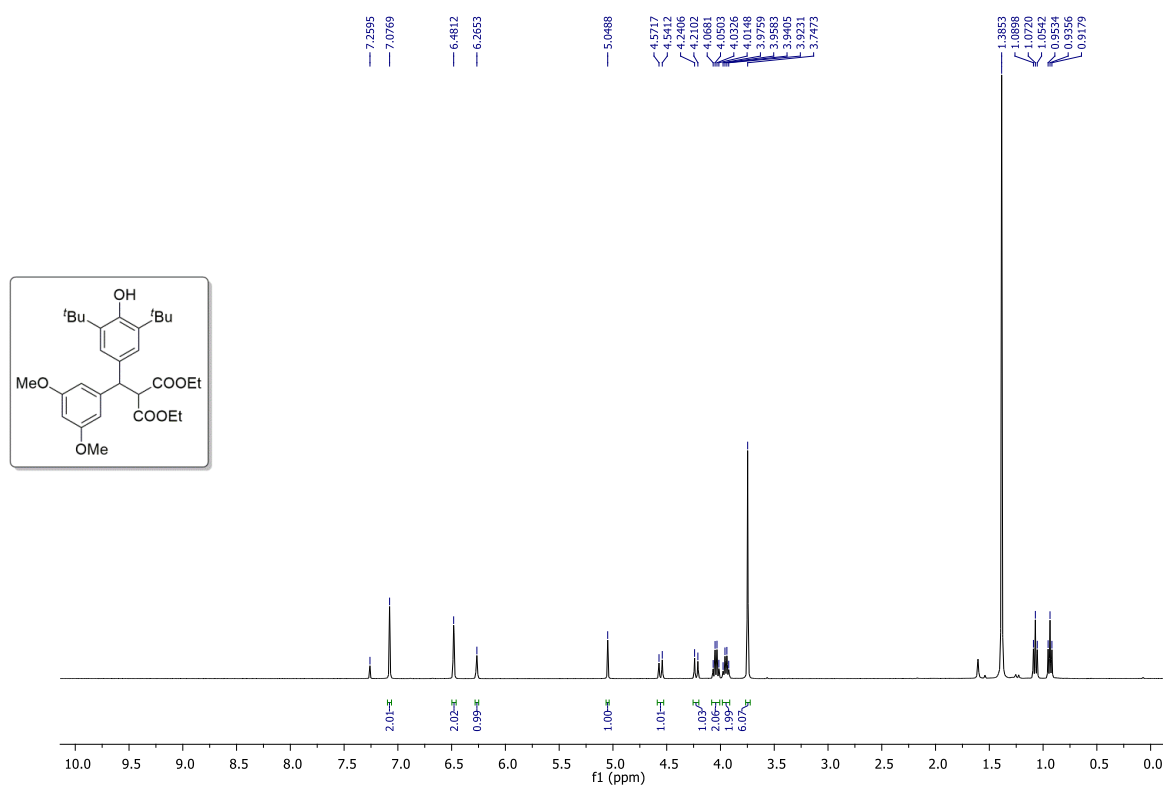
¹H NMR spectrum of **3b**



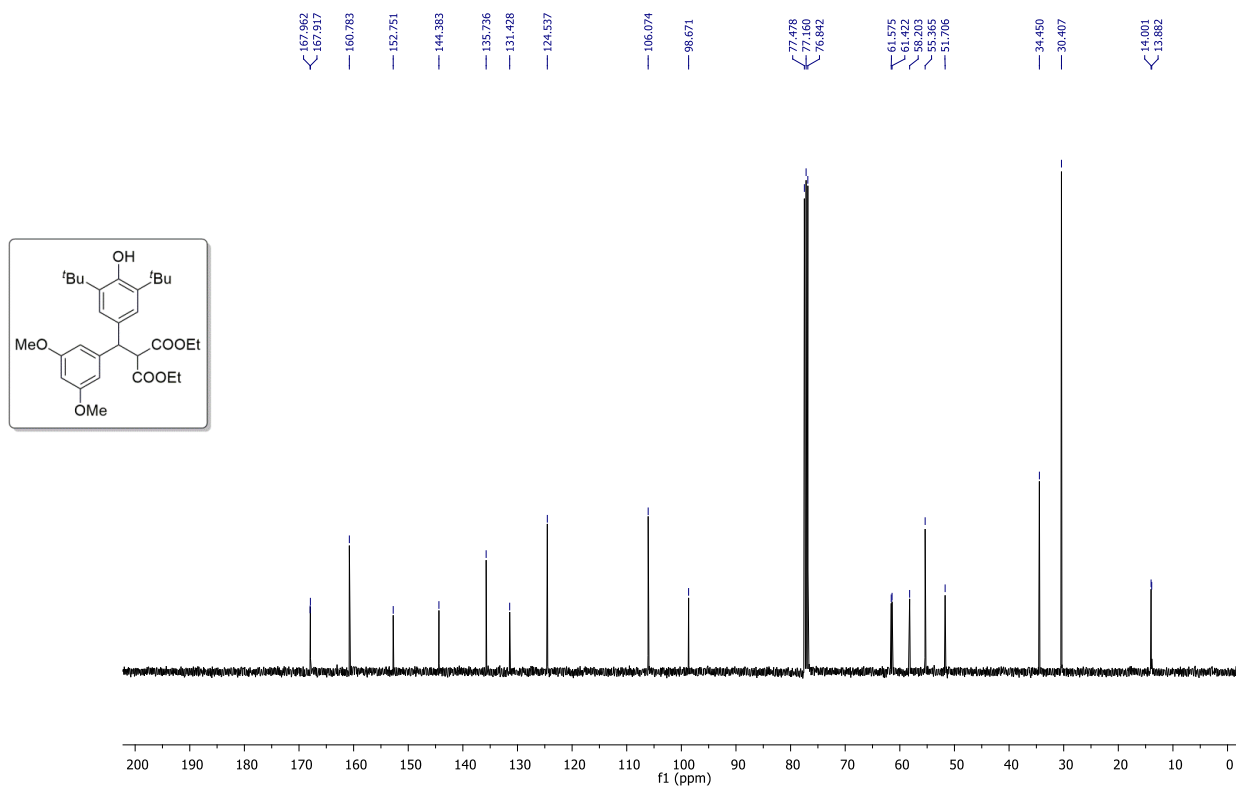
¹³C NMR spectrum of **3b**



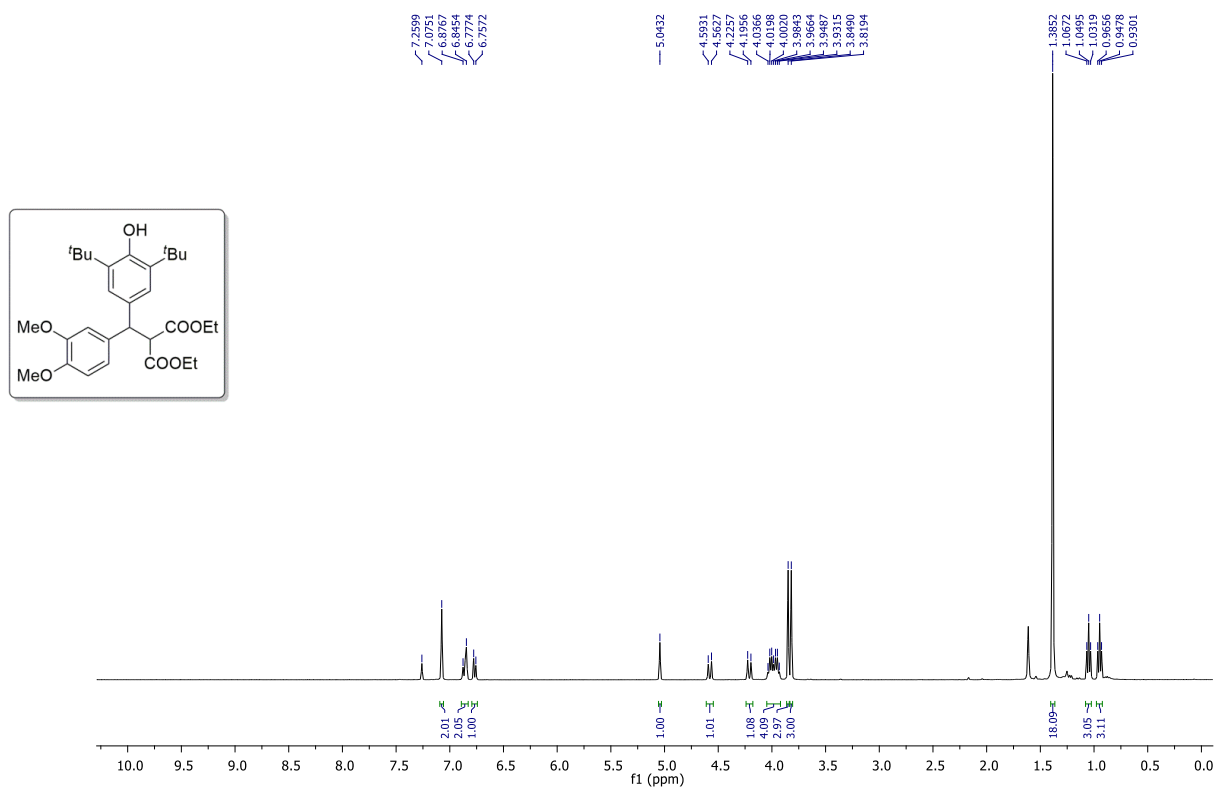
¹H NMR spectrum of **3c**



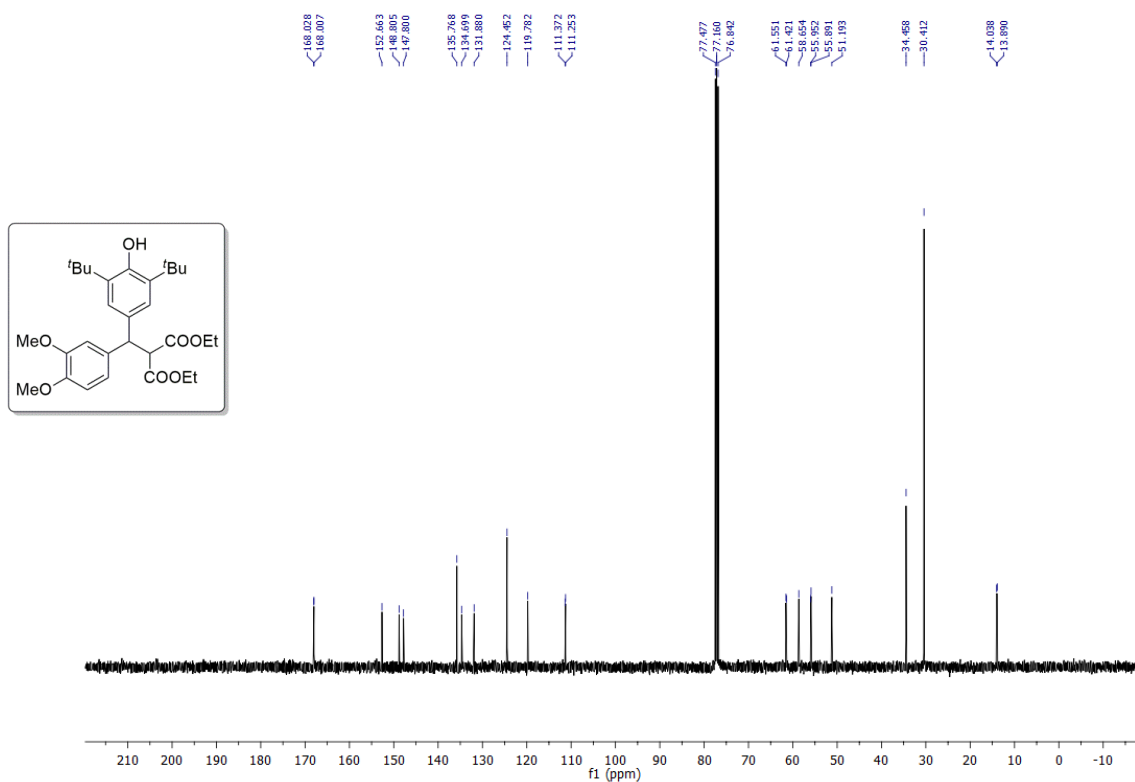
¹³C NMR spectrum of **3c**



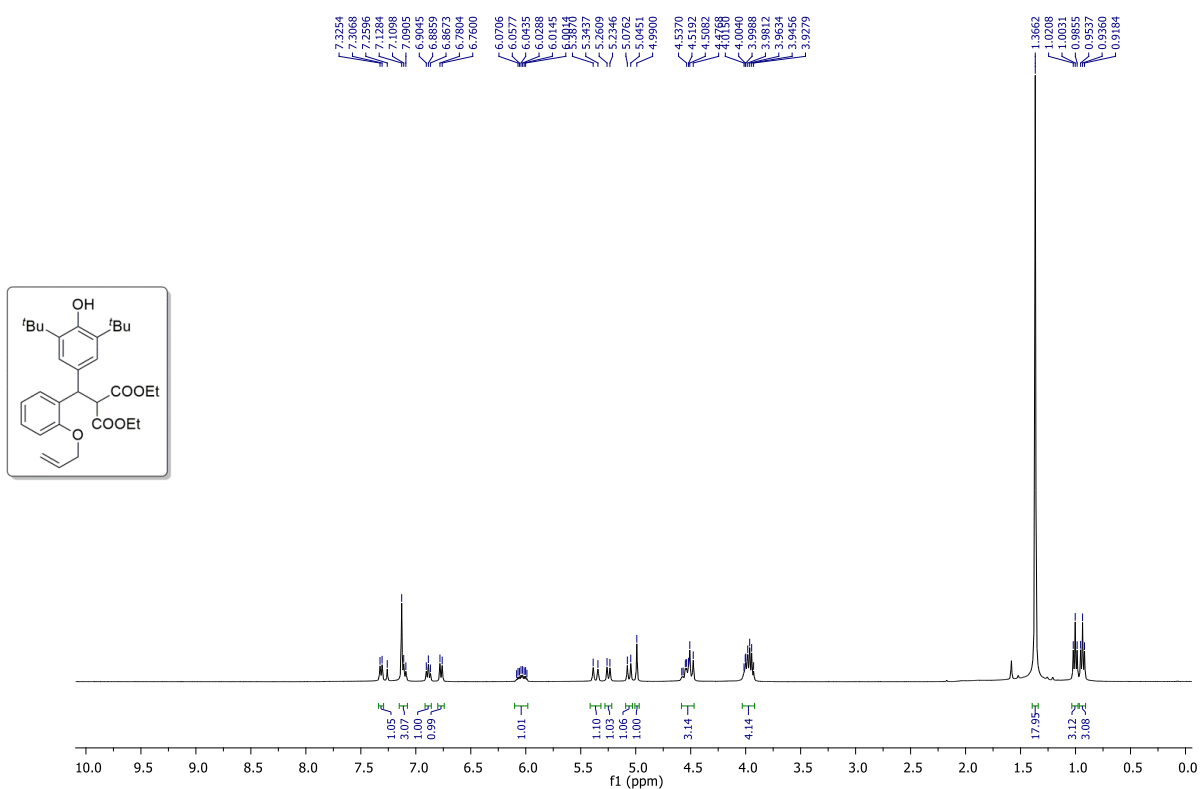
¹H NMR spectrum of 3d



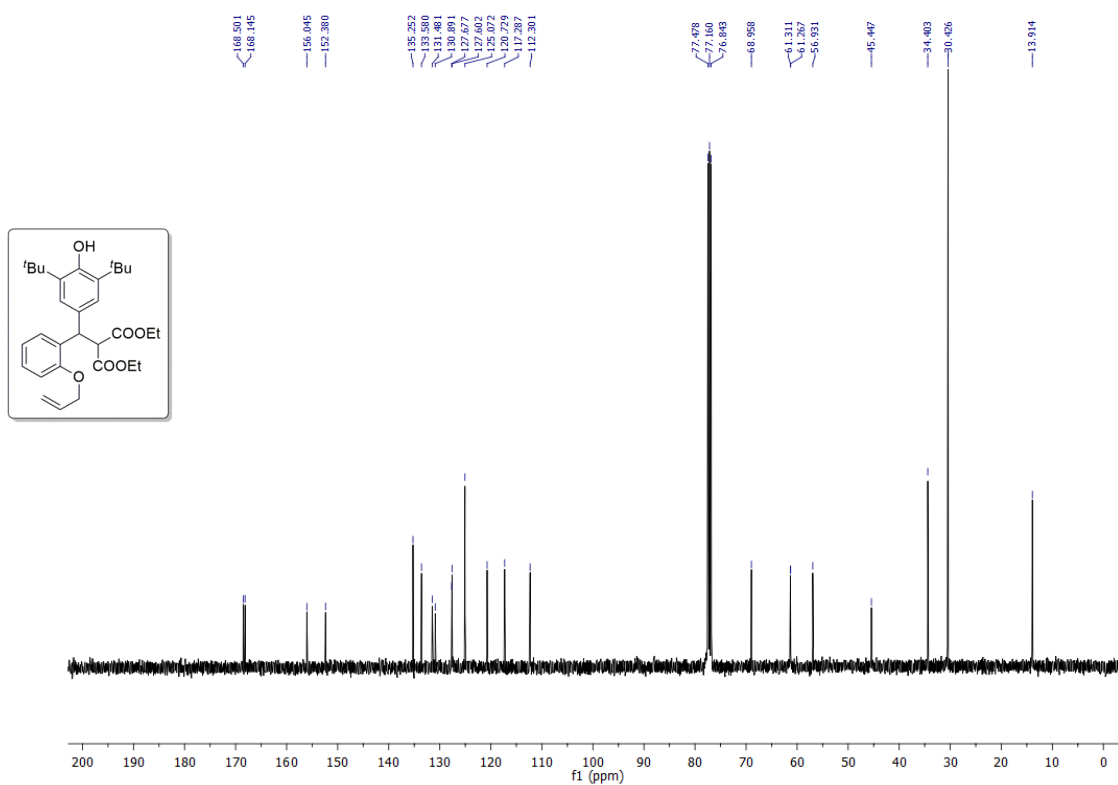
¹³C NMR spectrum of 3d



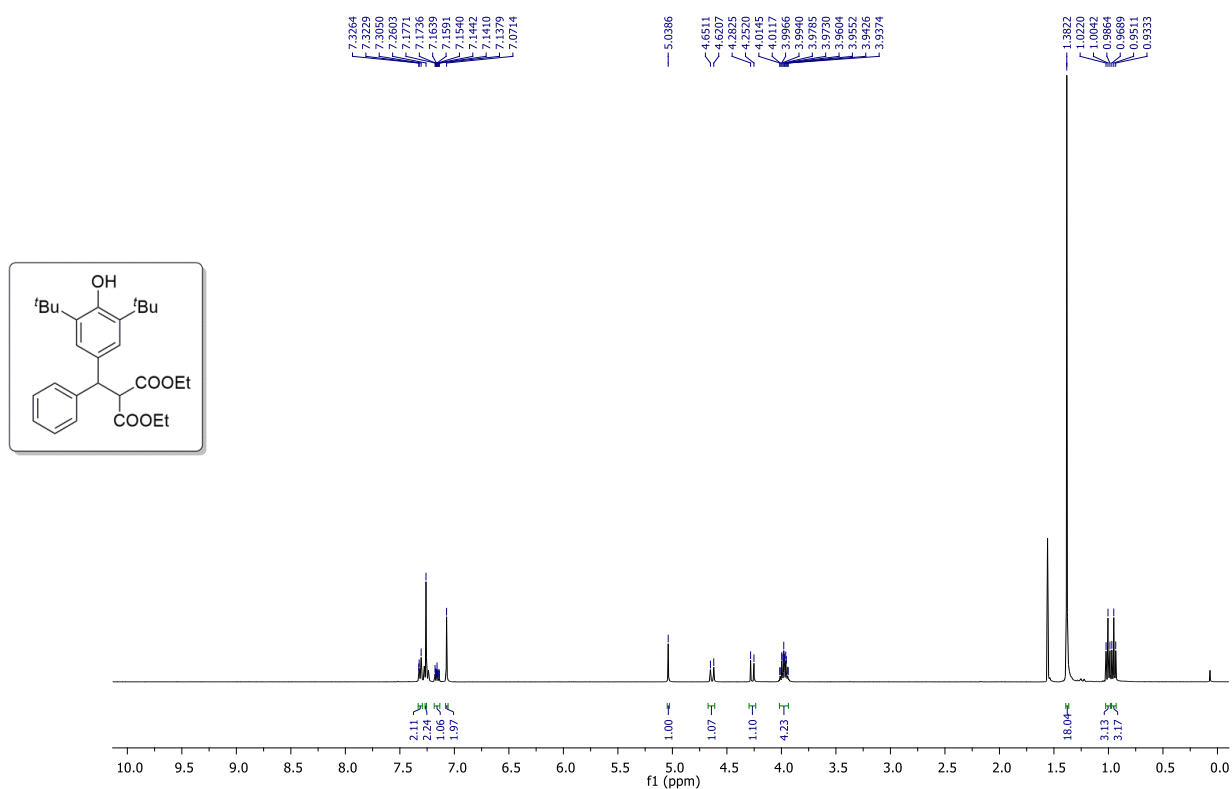
¹H NMR spectrum of **3e**



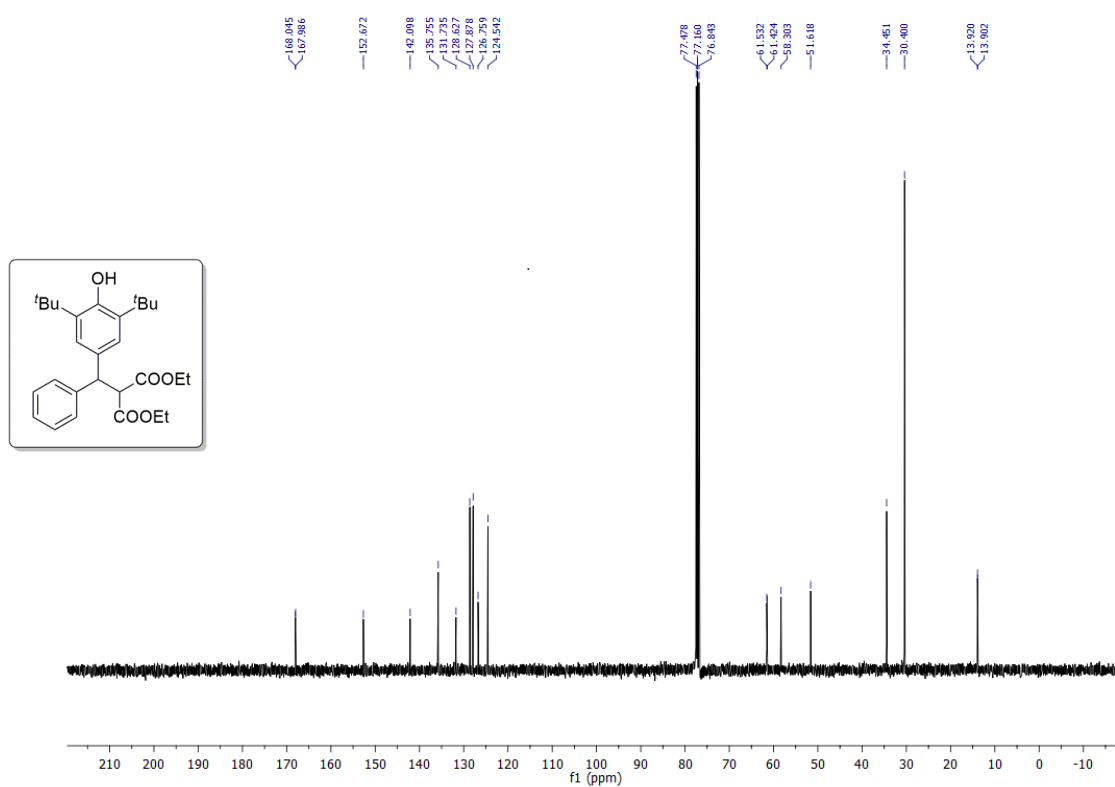
¹³C NMR spectrum of **3e**



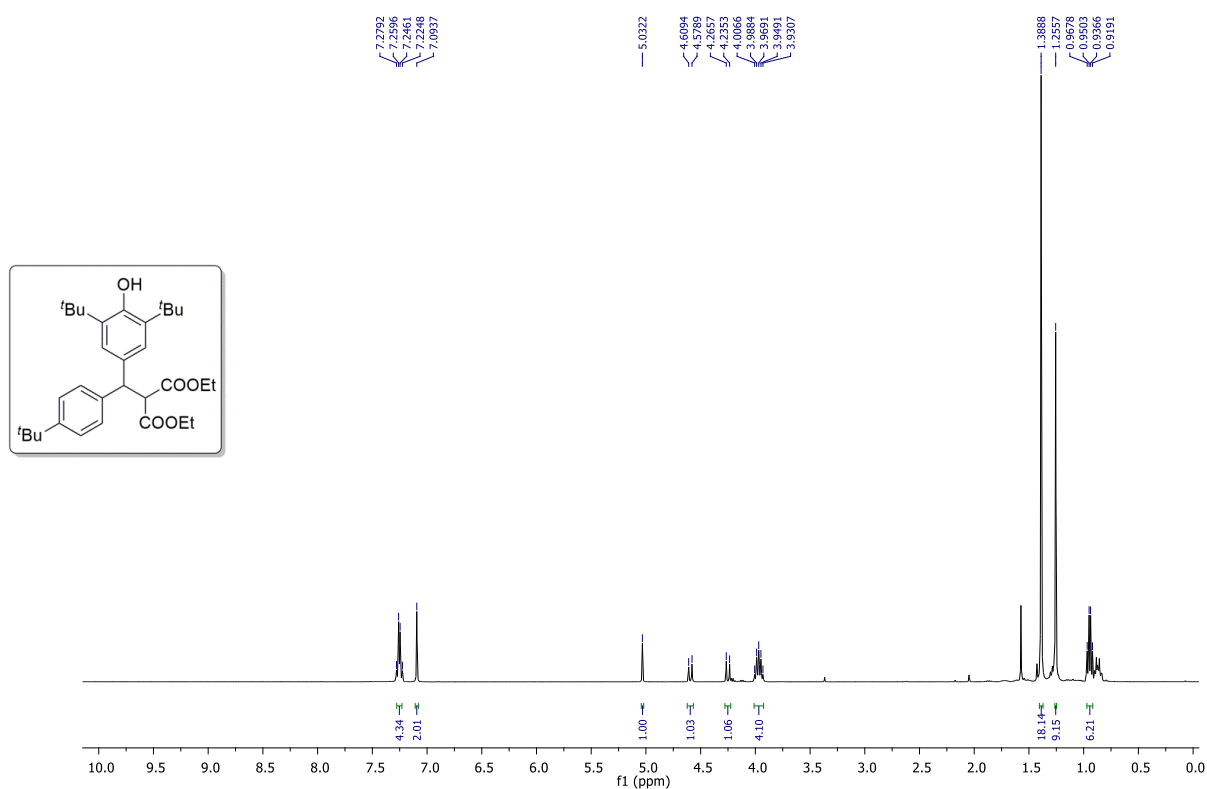
¹H NMR spectrum of **3f**



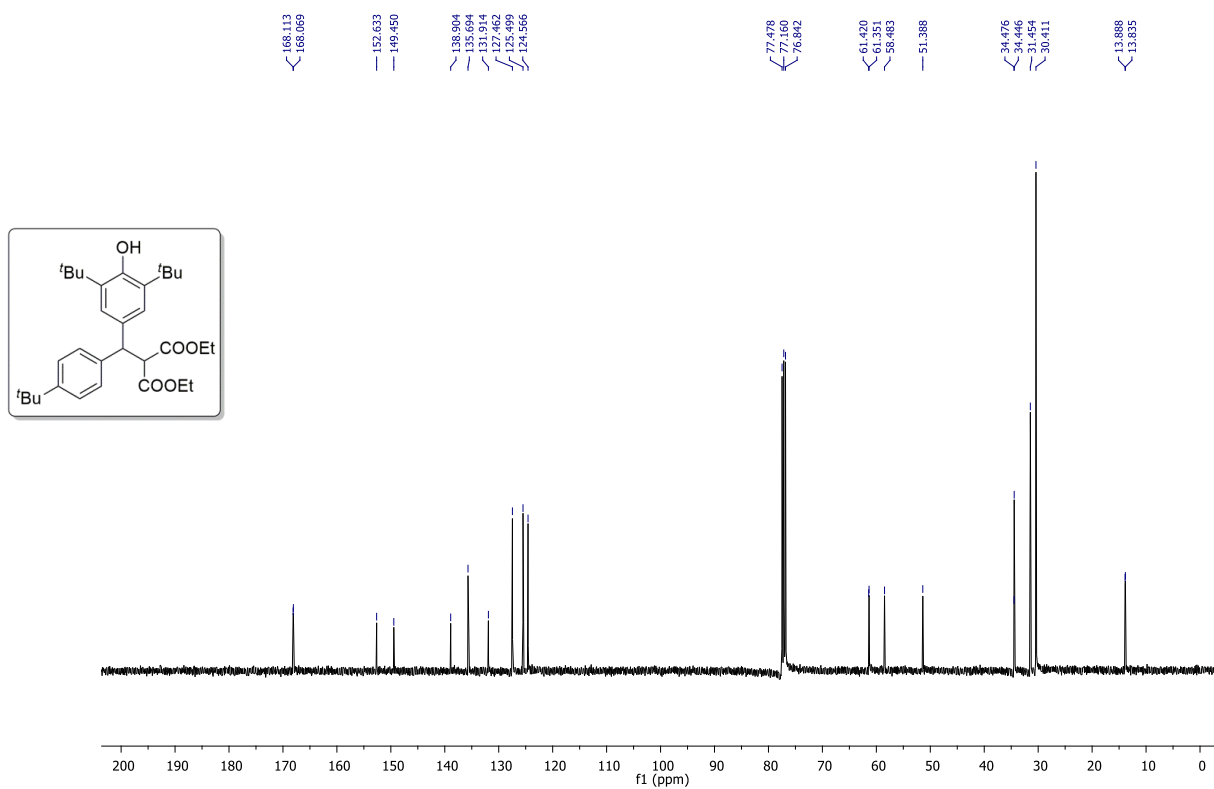
¹³C NMR spectrum of **3f**



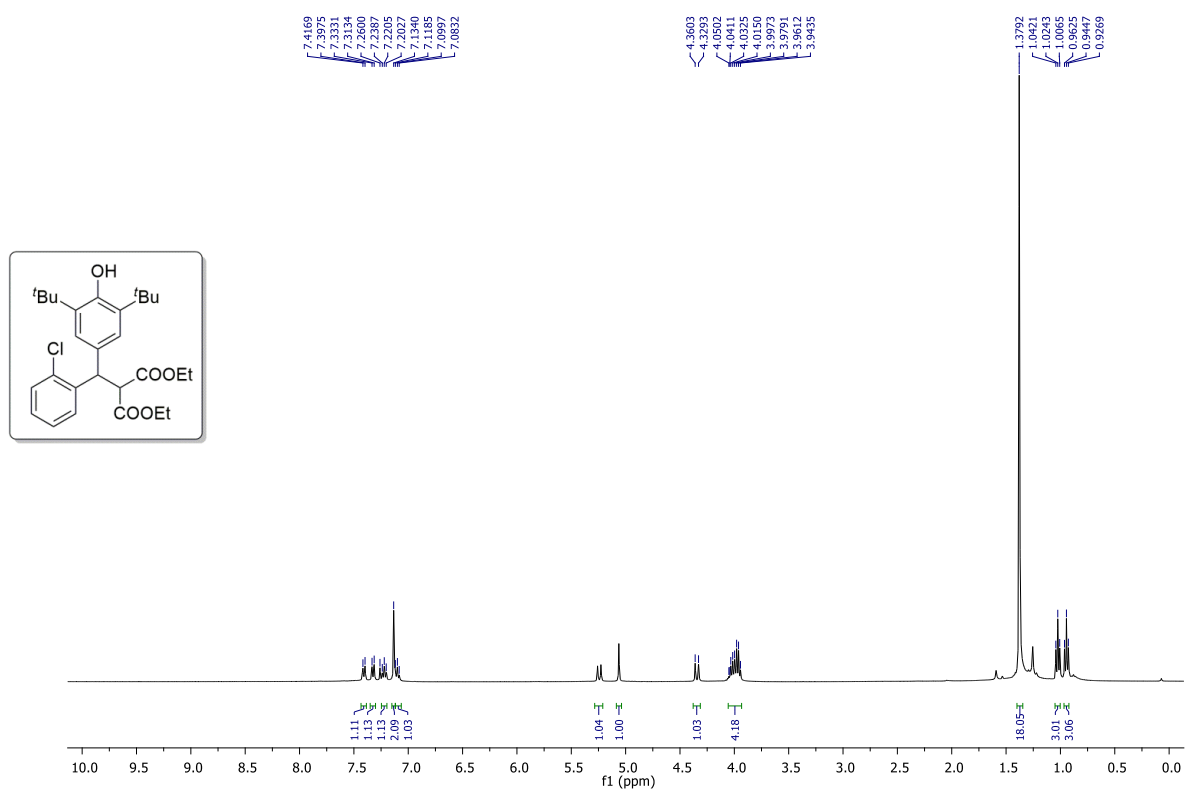
¹H NMR spectrum of **3g**



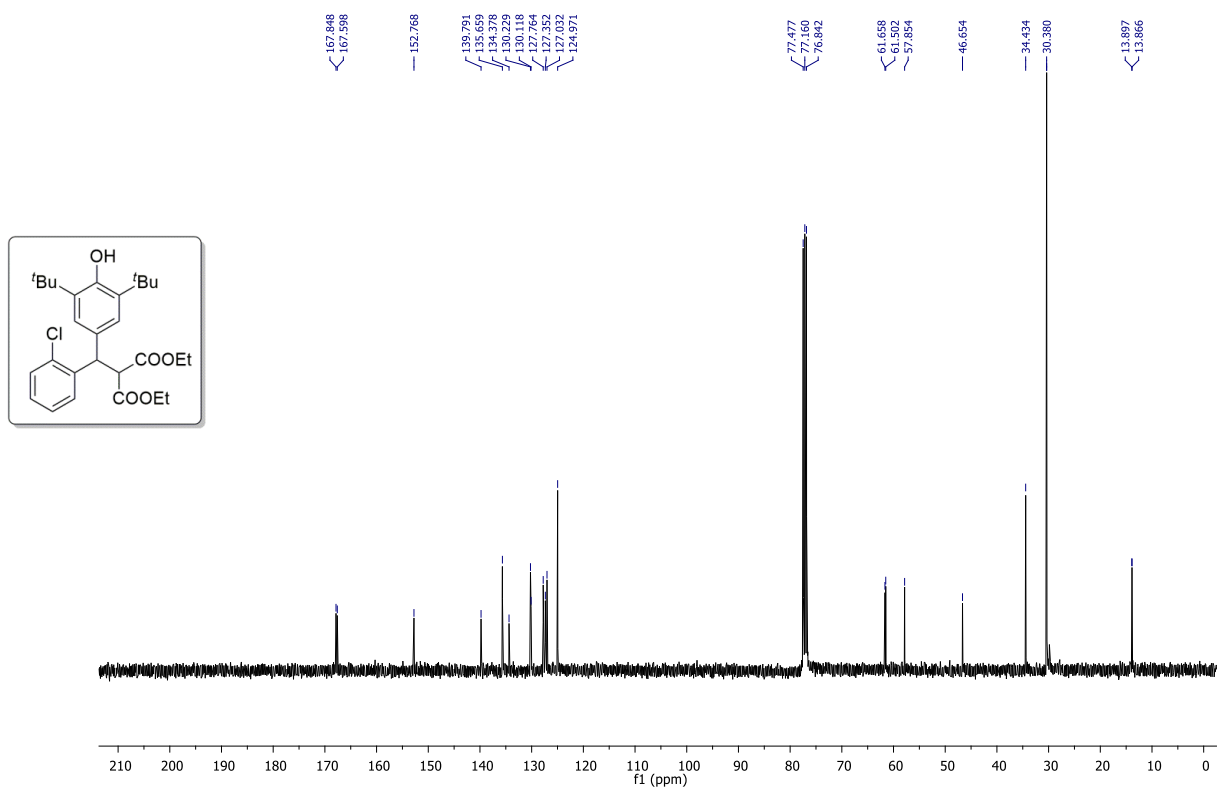
¹³C NMR spectrum of **3g**



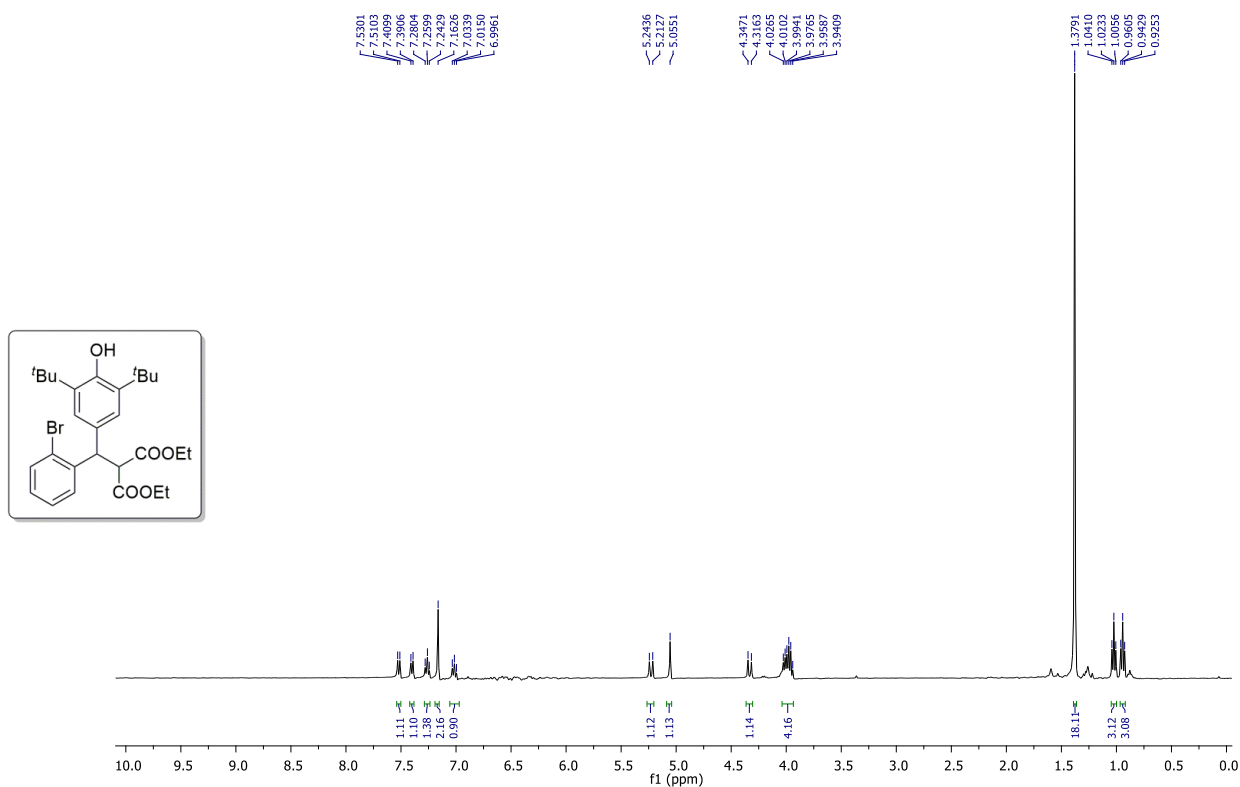
¹H NMR spectrum of **3h**



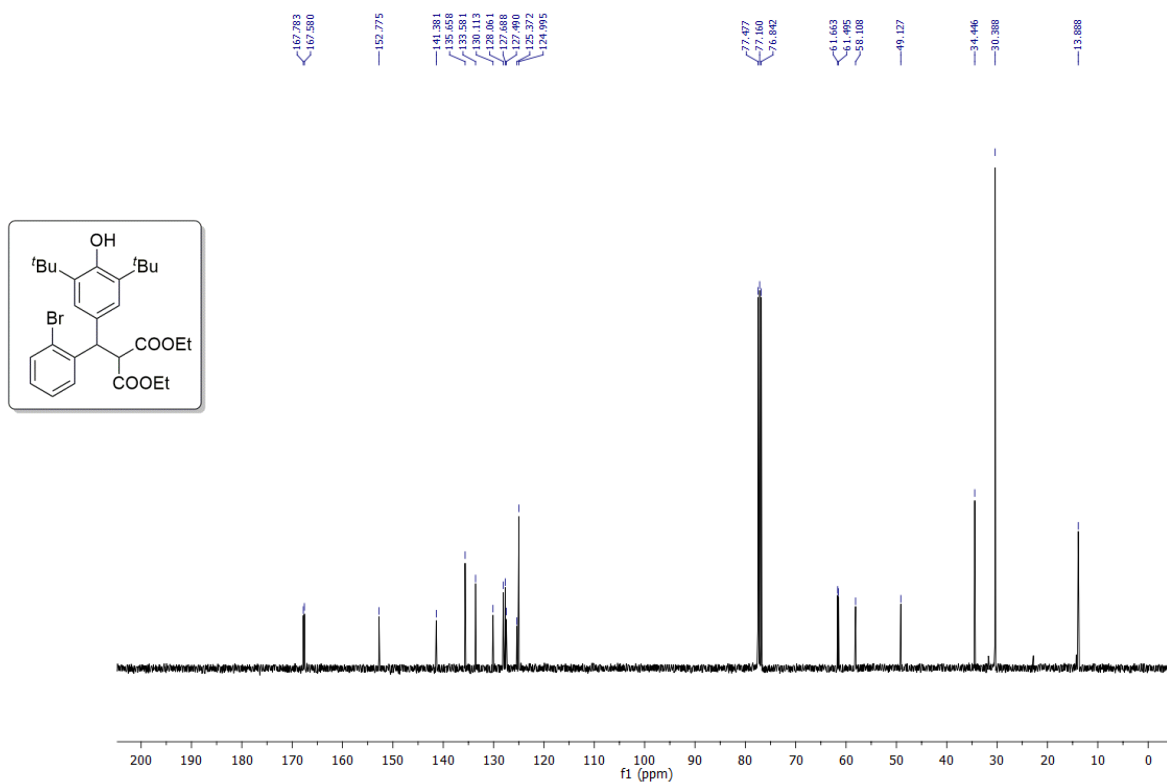
¹³C NMR spectrum of **3h**



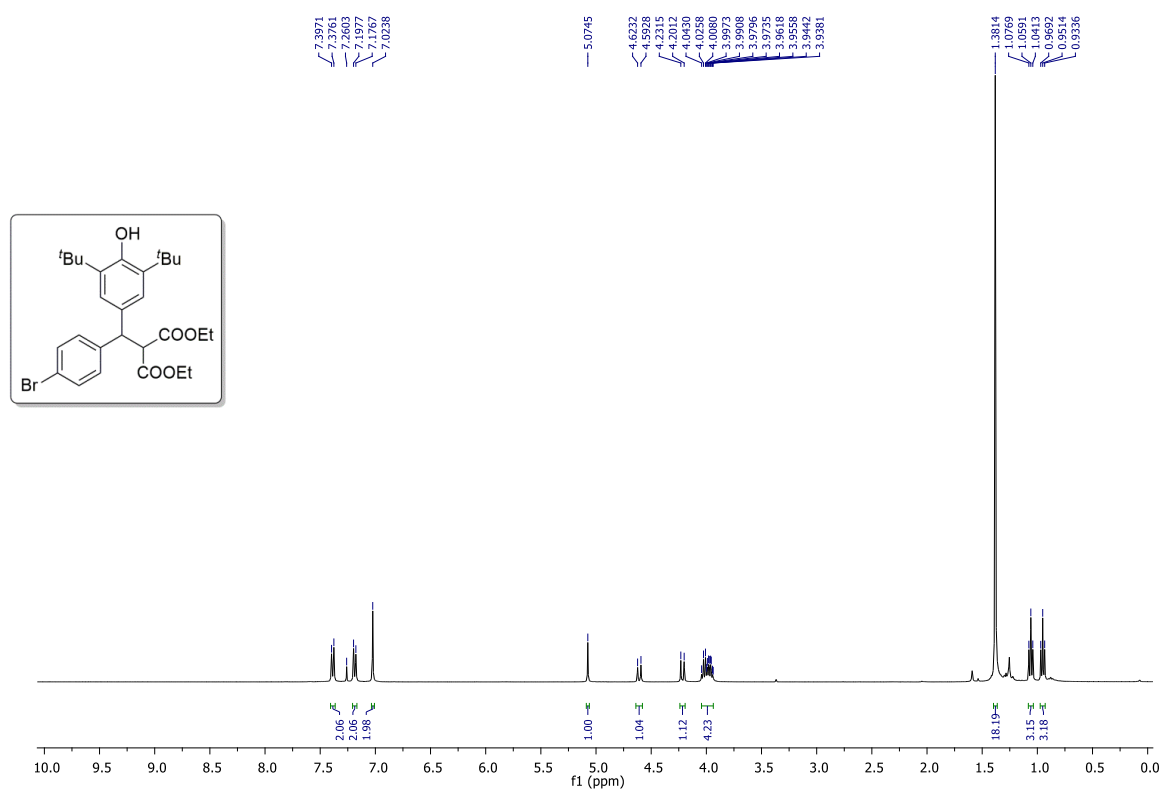
¹H NMR spectrum of **3i**



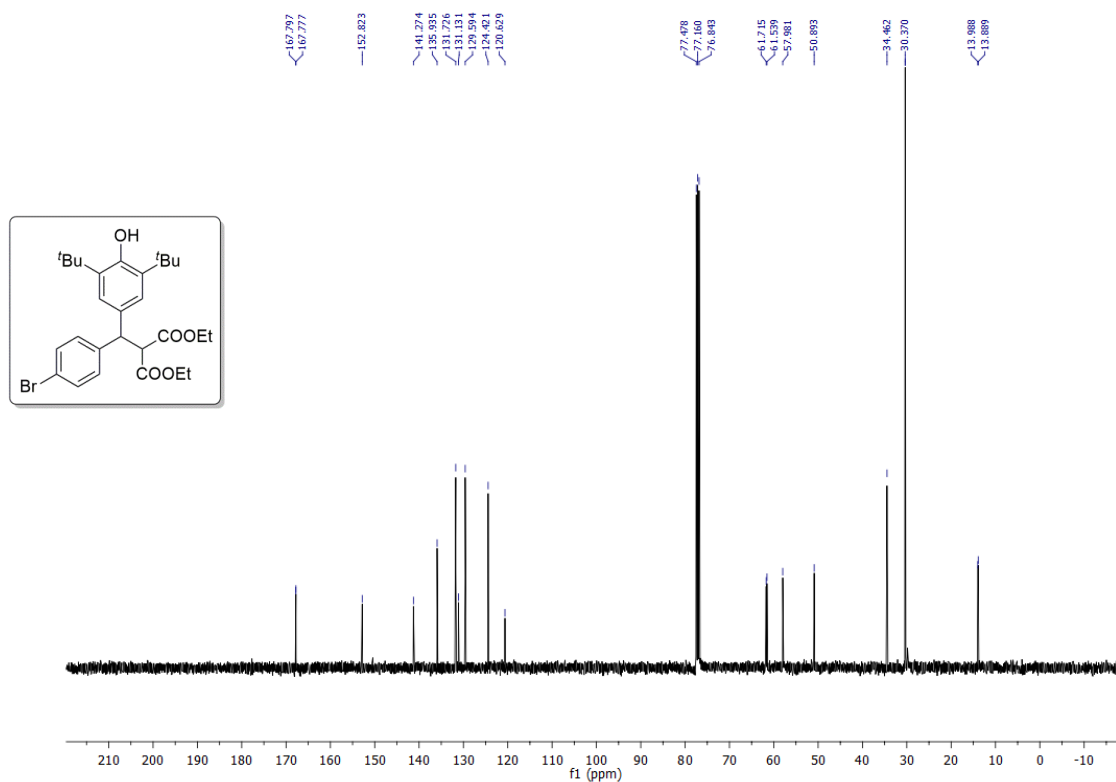
¹³C NMR spectrum of **3i**



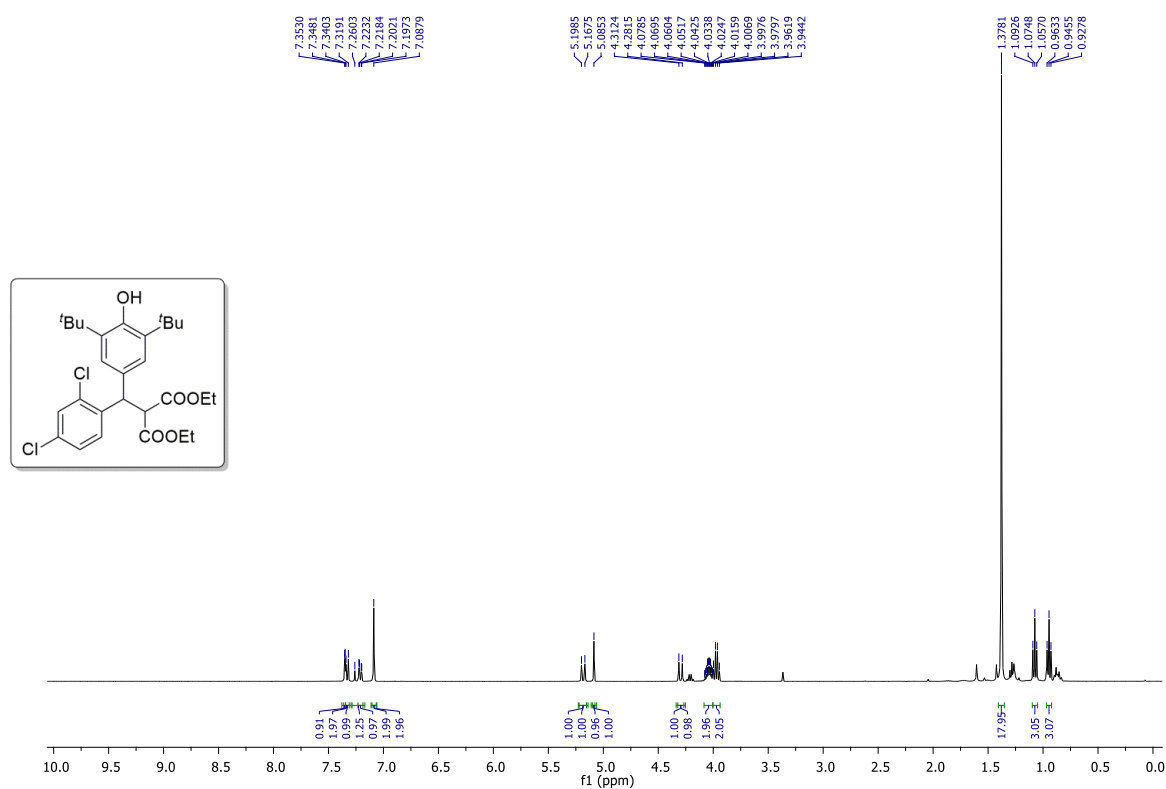
¹H NMR spectrum of **3j**



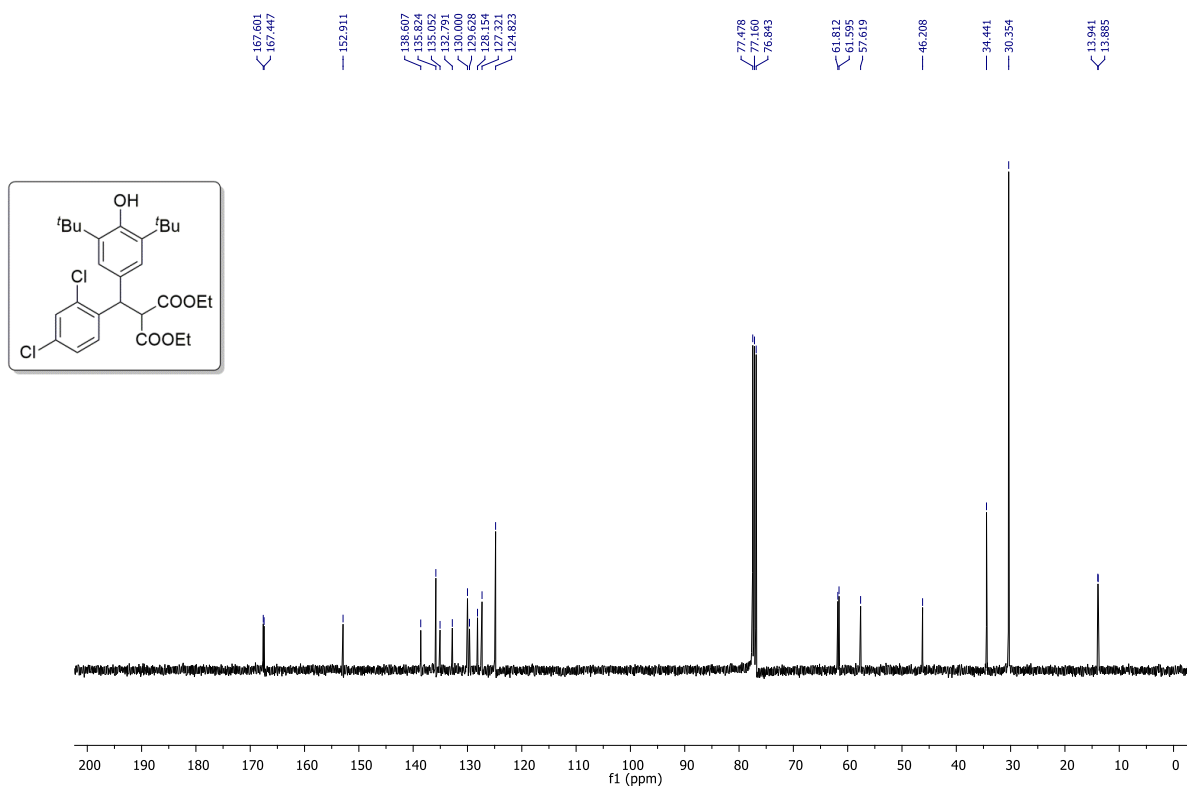
¹³C NMR spectrum of **3j**



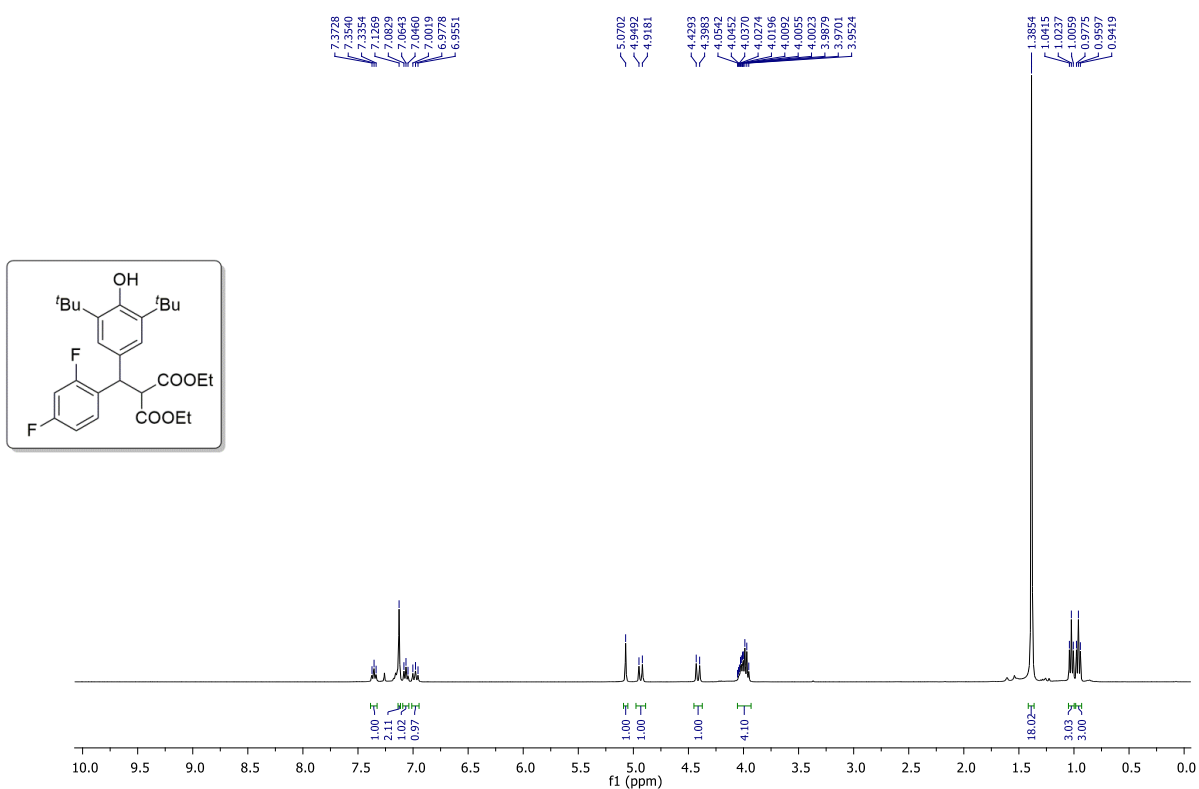
¹H NMR spectrum of **3k**



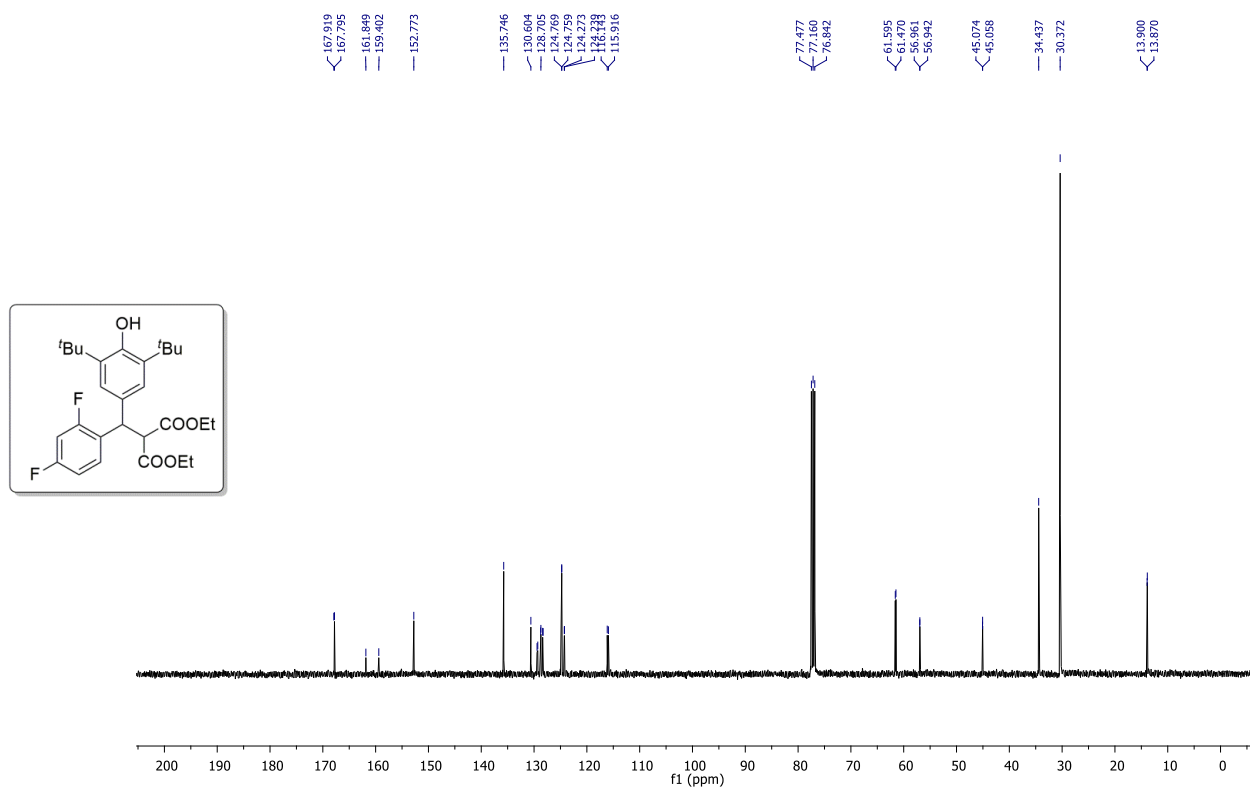
¹³C NMR spectrum of **3k**



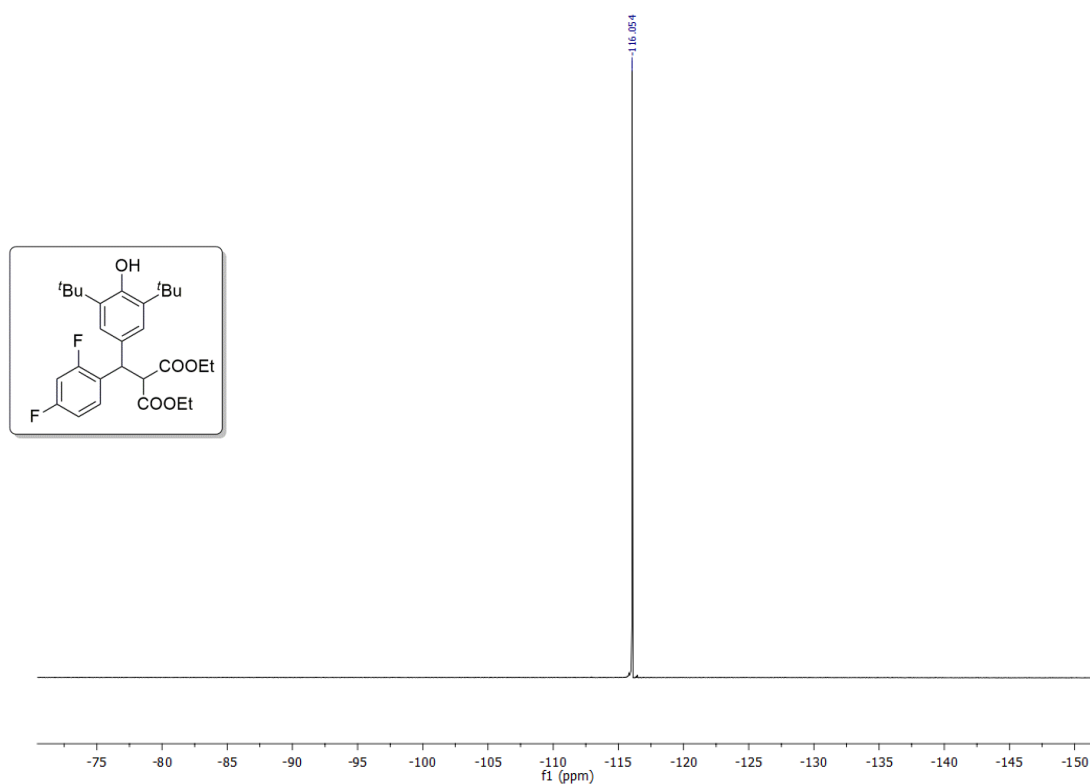
¹H NMR spectrum of **3I**



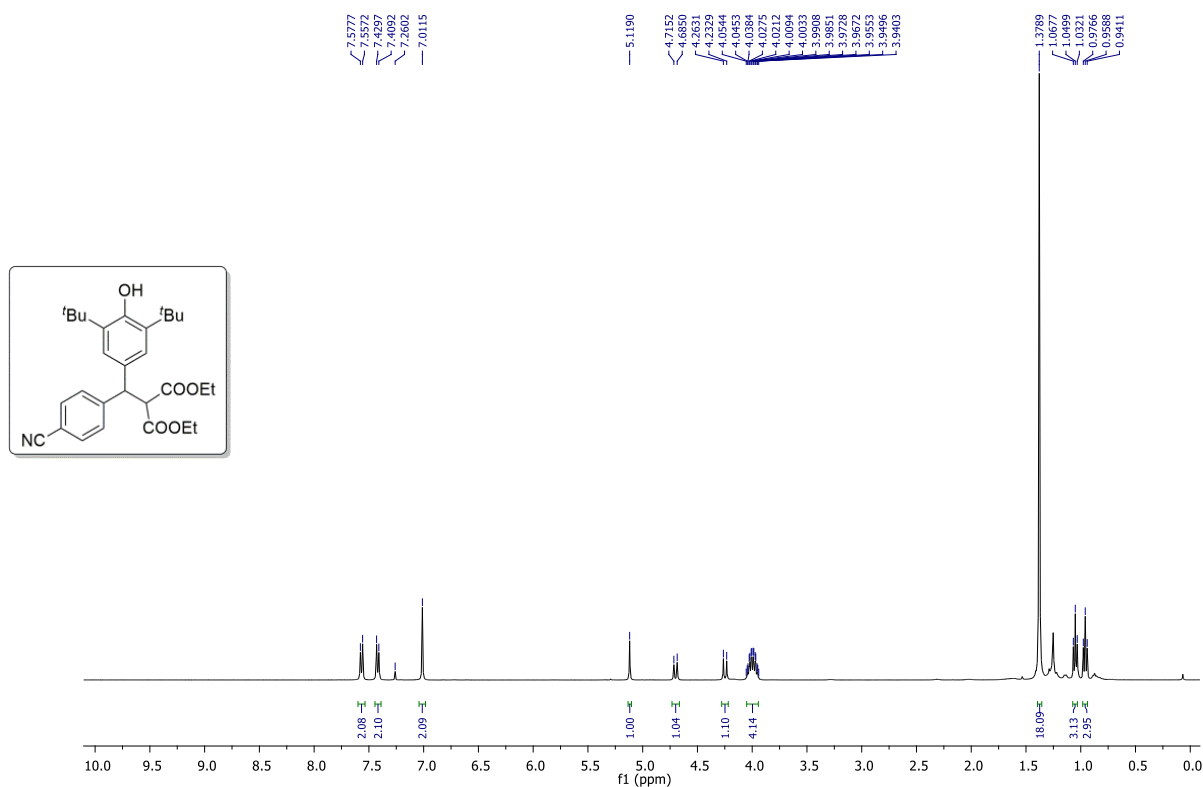
¹³C NMR spectrum of **3I**



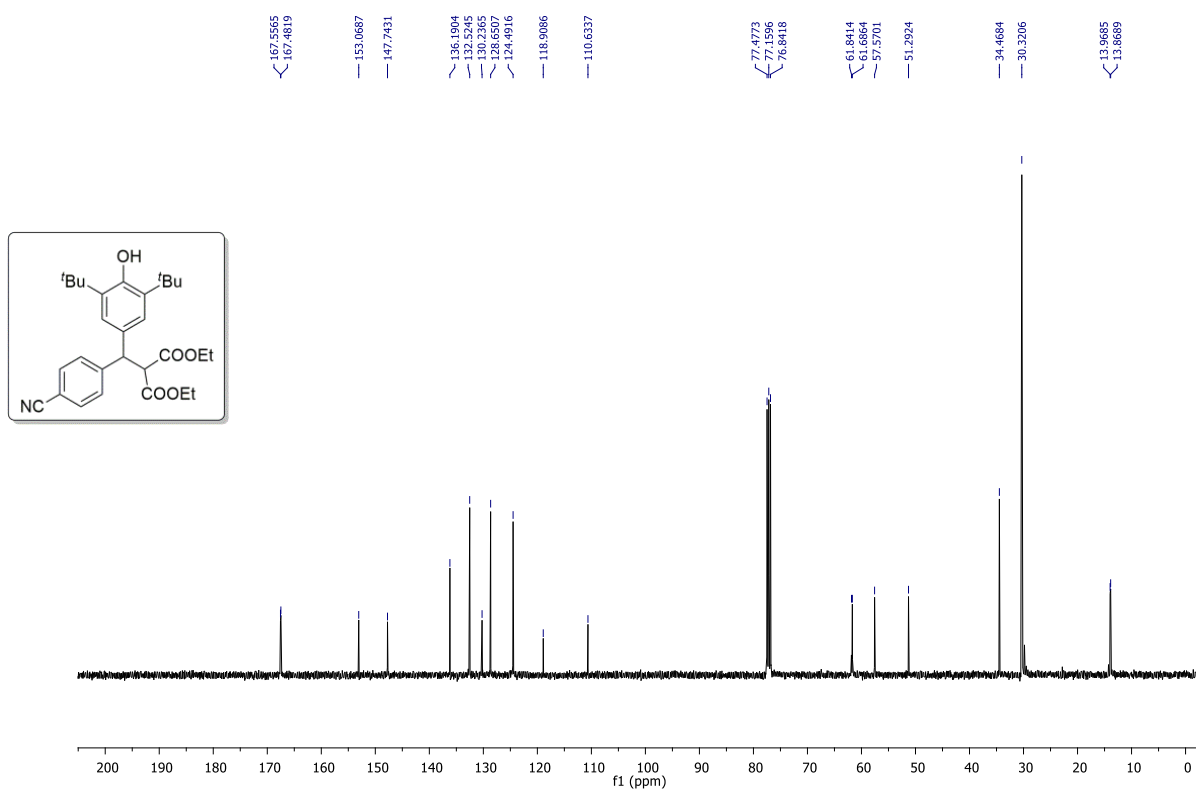
^{19}F NMR spectrum of **3l**



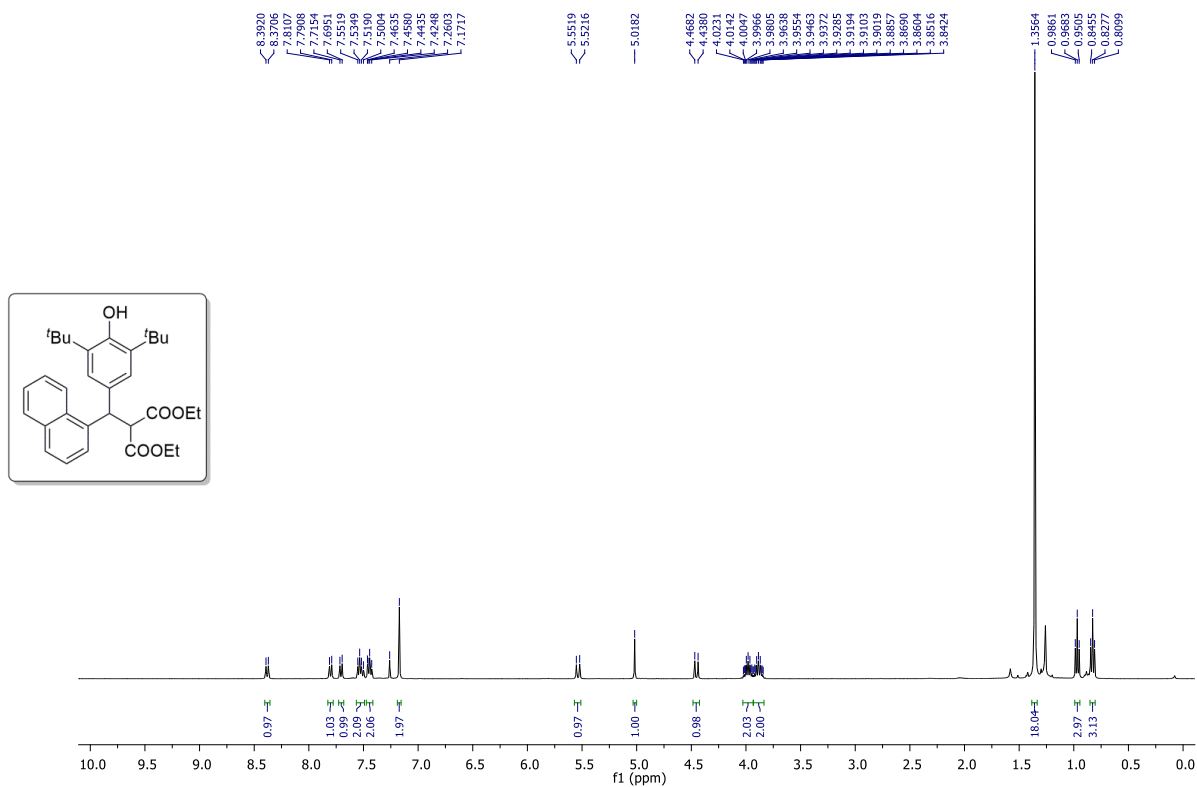
^1H NMR spectrum of **3m**



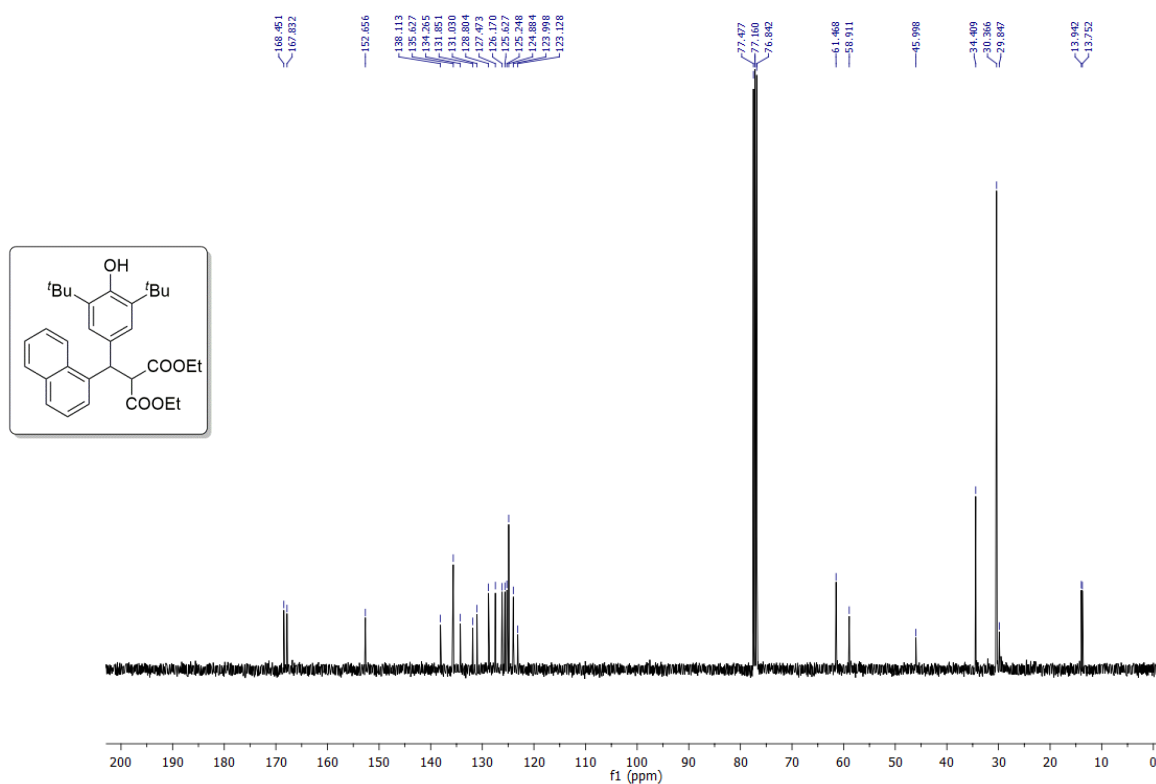
¹³C NMR spectrum of 3m



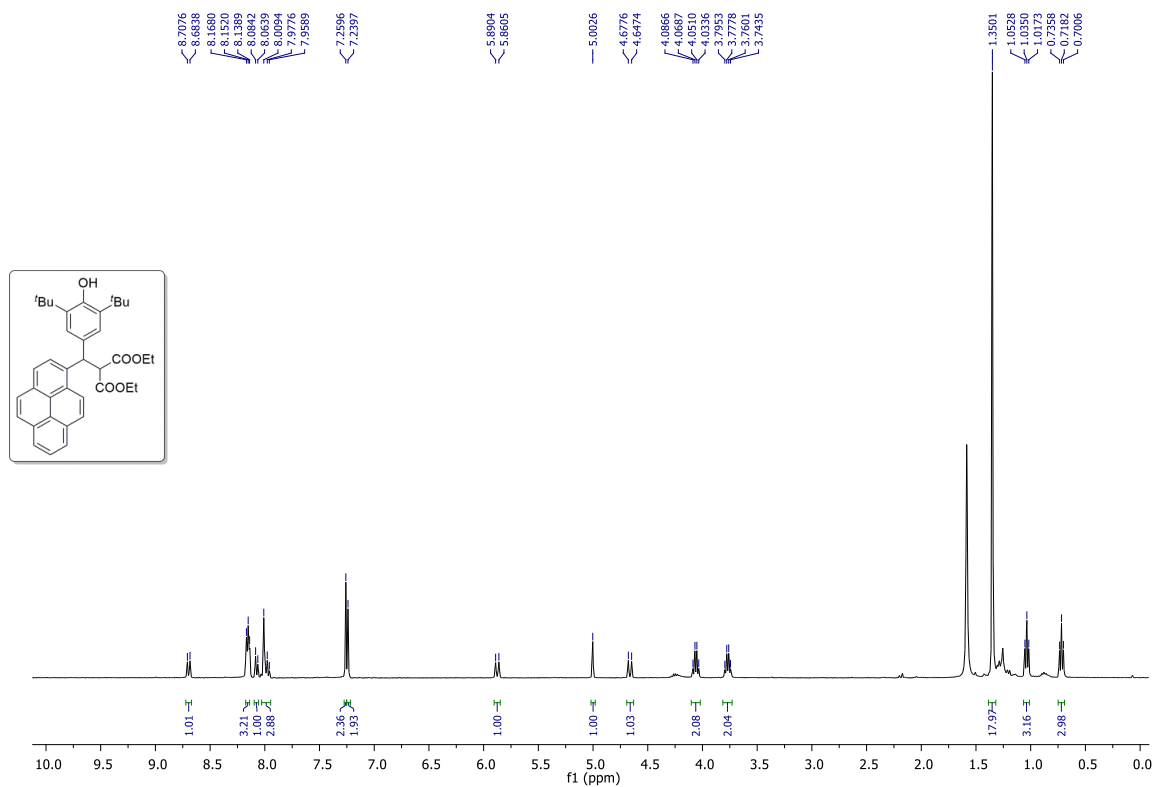
¹H NMR spectrum of 3n

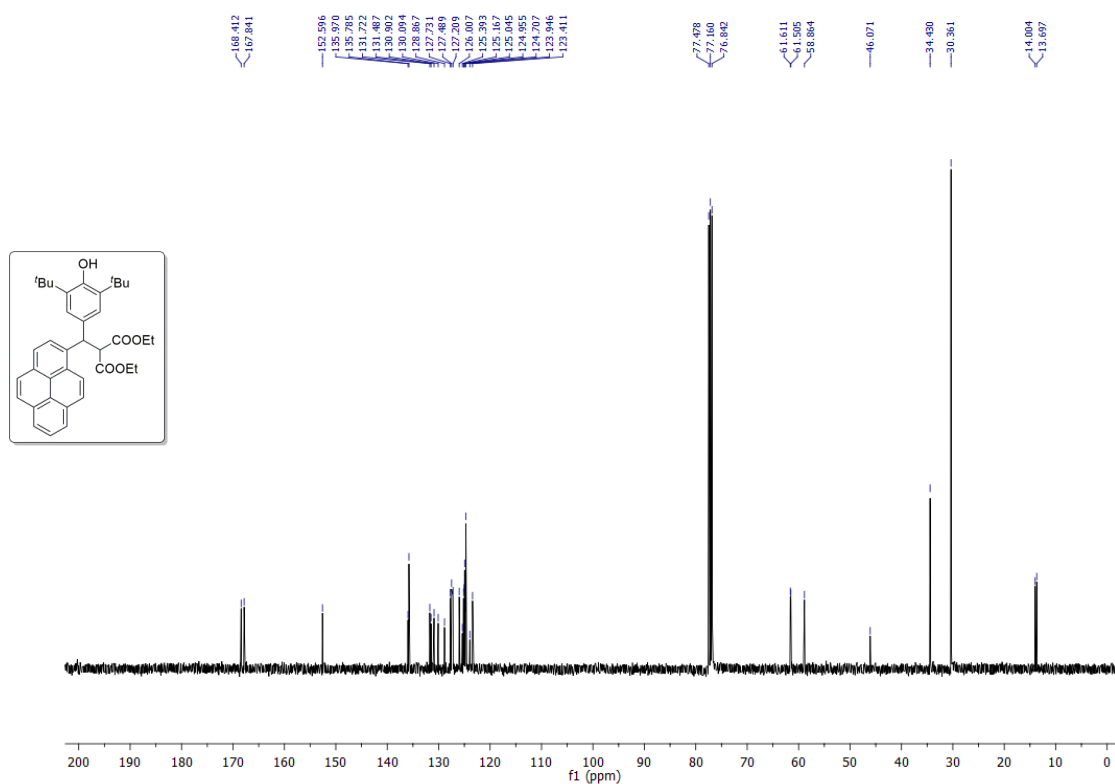
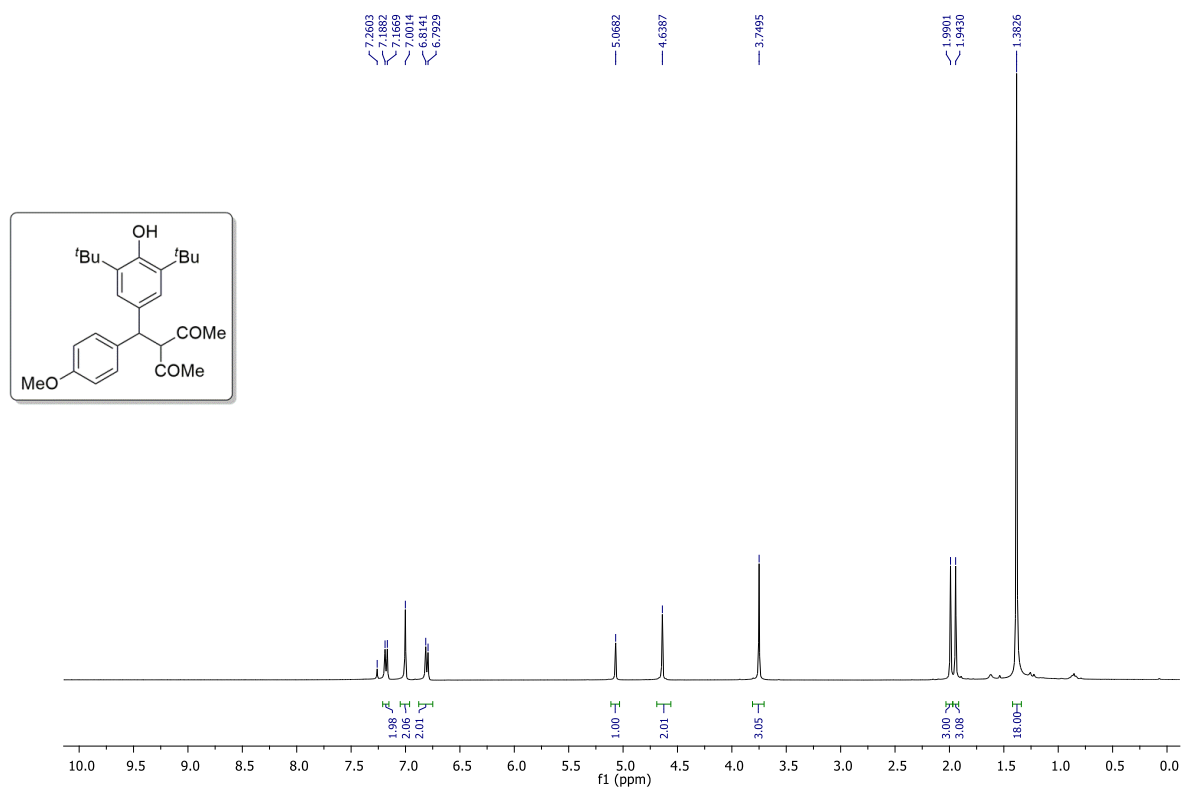


¹³C NMR spectrum of **3n**

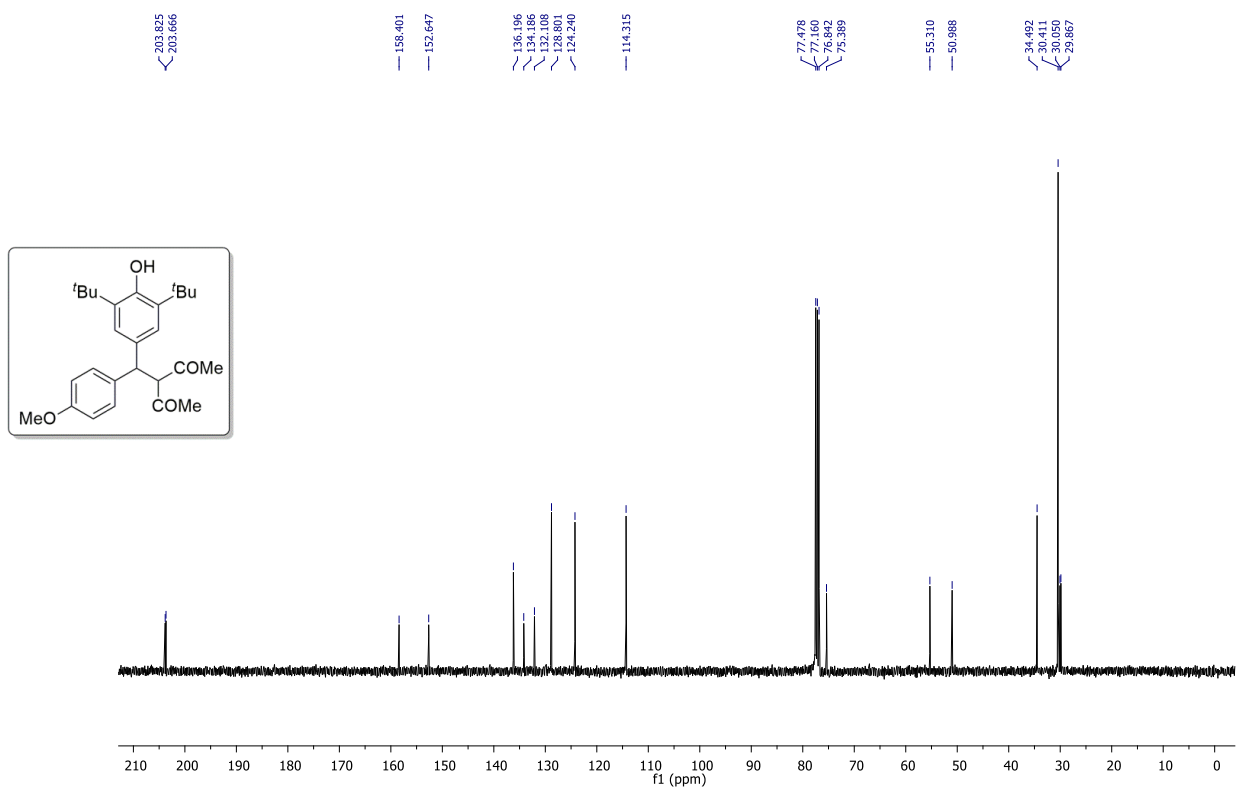


¹H NMR spectrum of **3o**

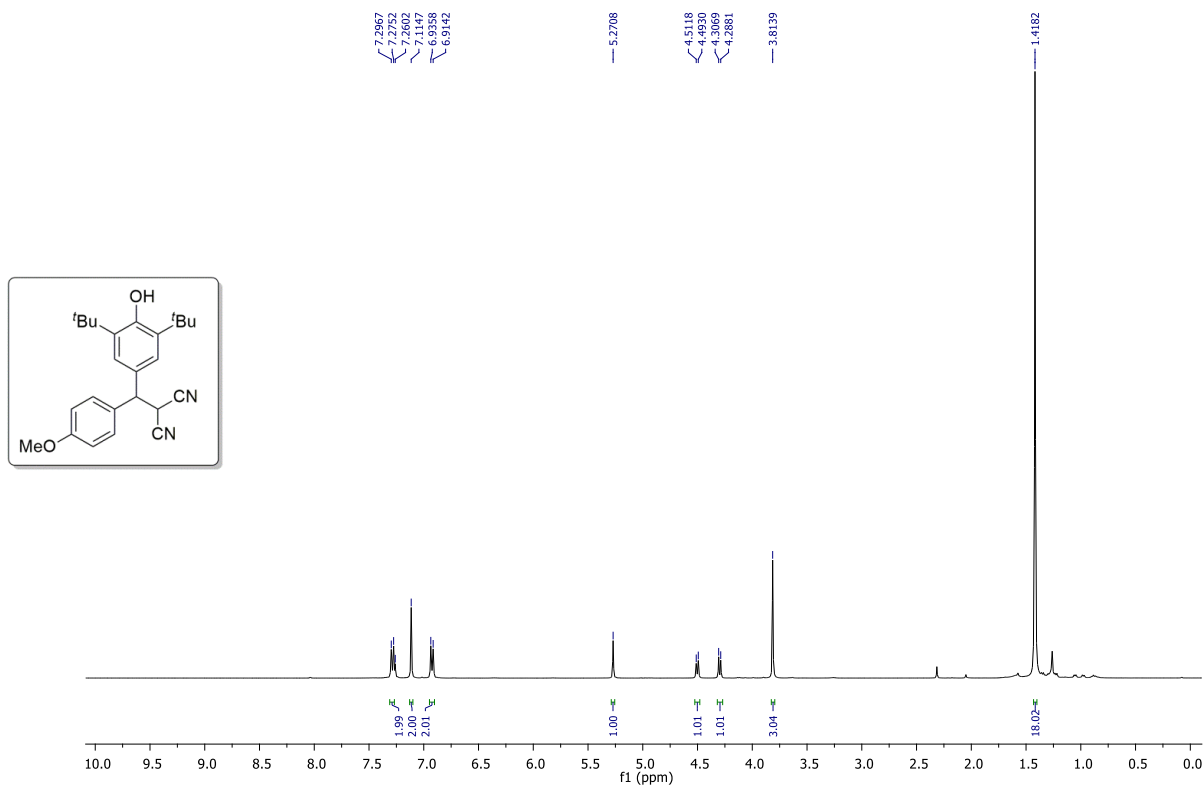


^{13}C NMR spectrum of **3o**¹H NMR spectrum of **13a**

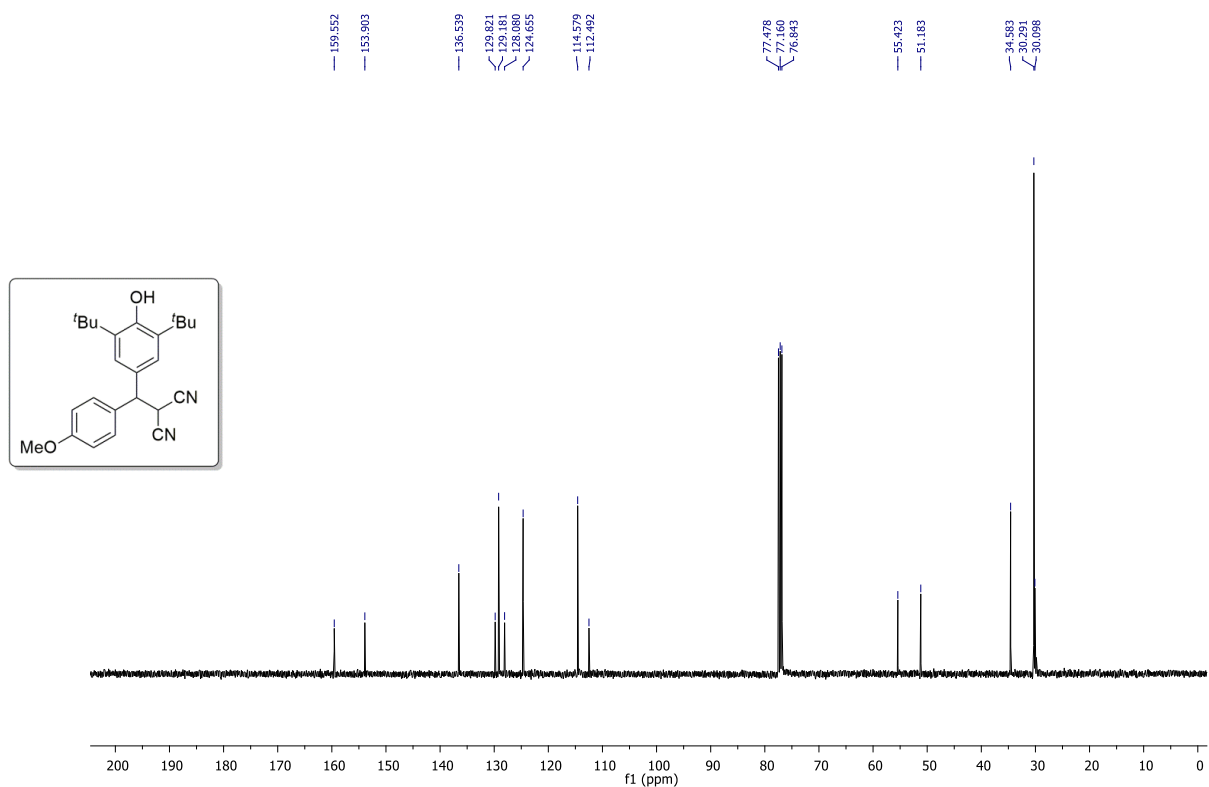
^{13}C NMR spectrum of **13a**



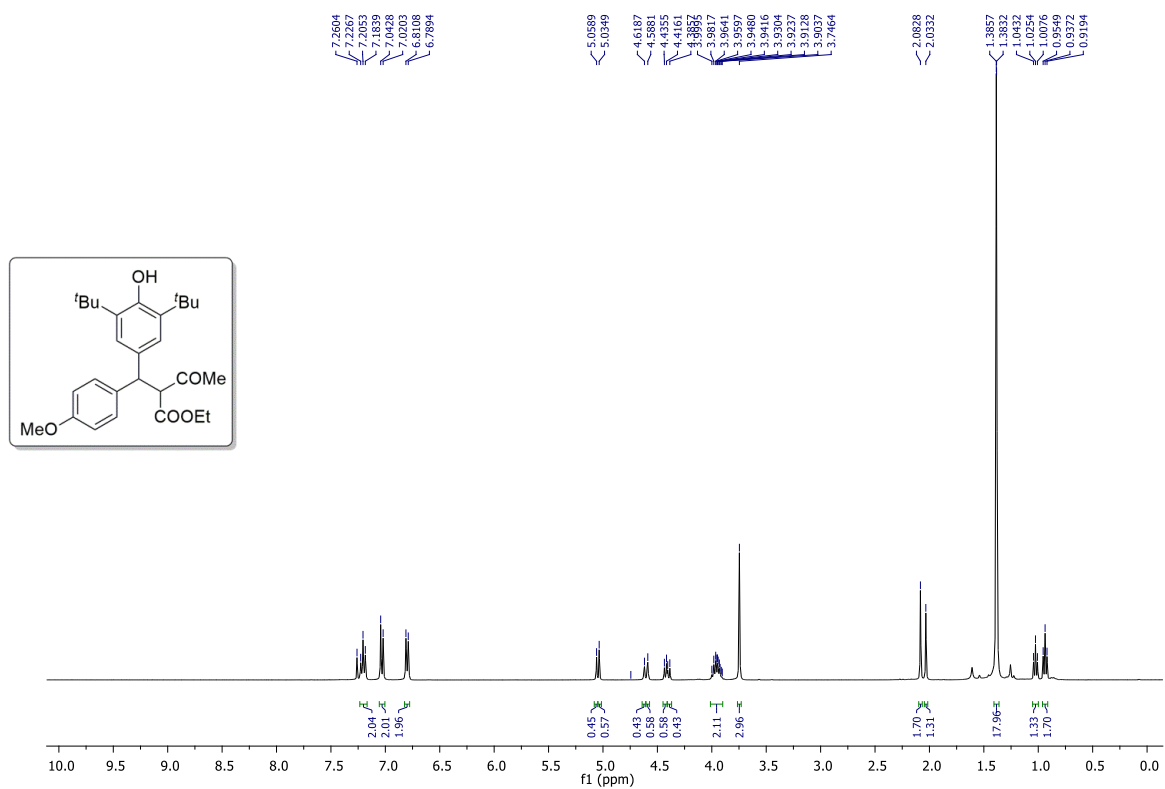
^1H NMR spectrum of **13b**



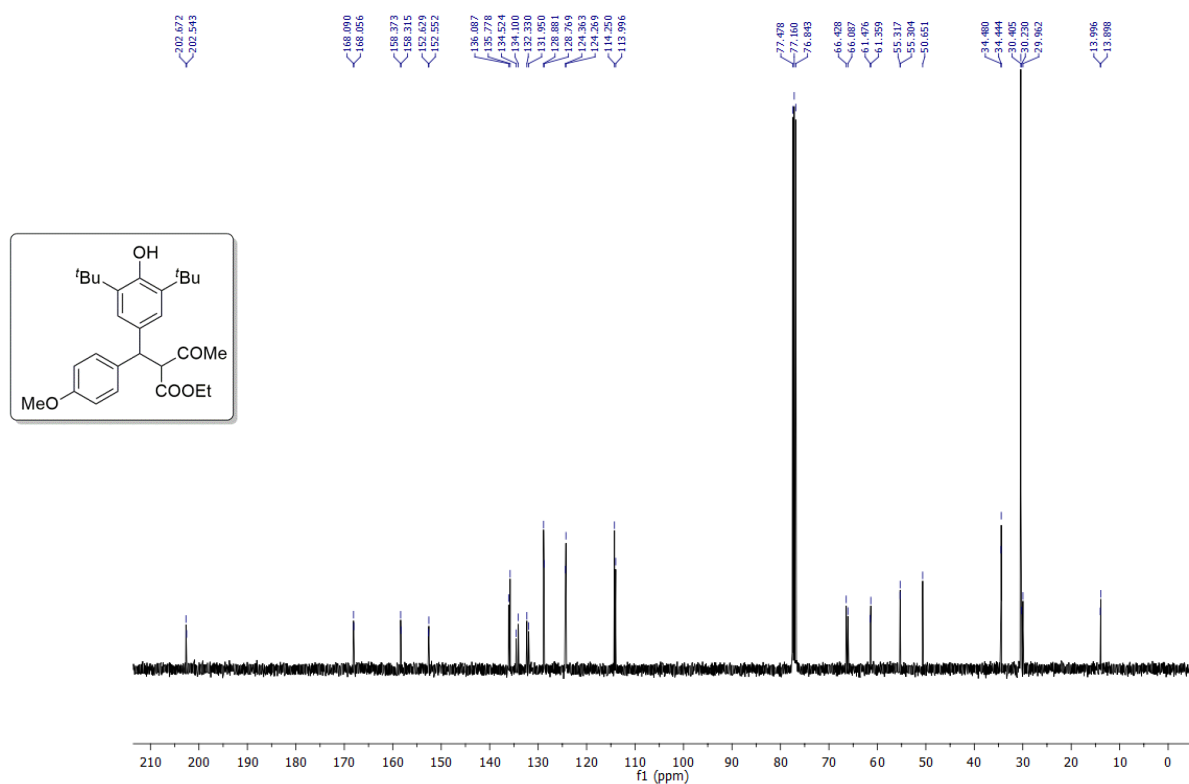
¹³C NMR spectrum of **13b**



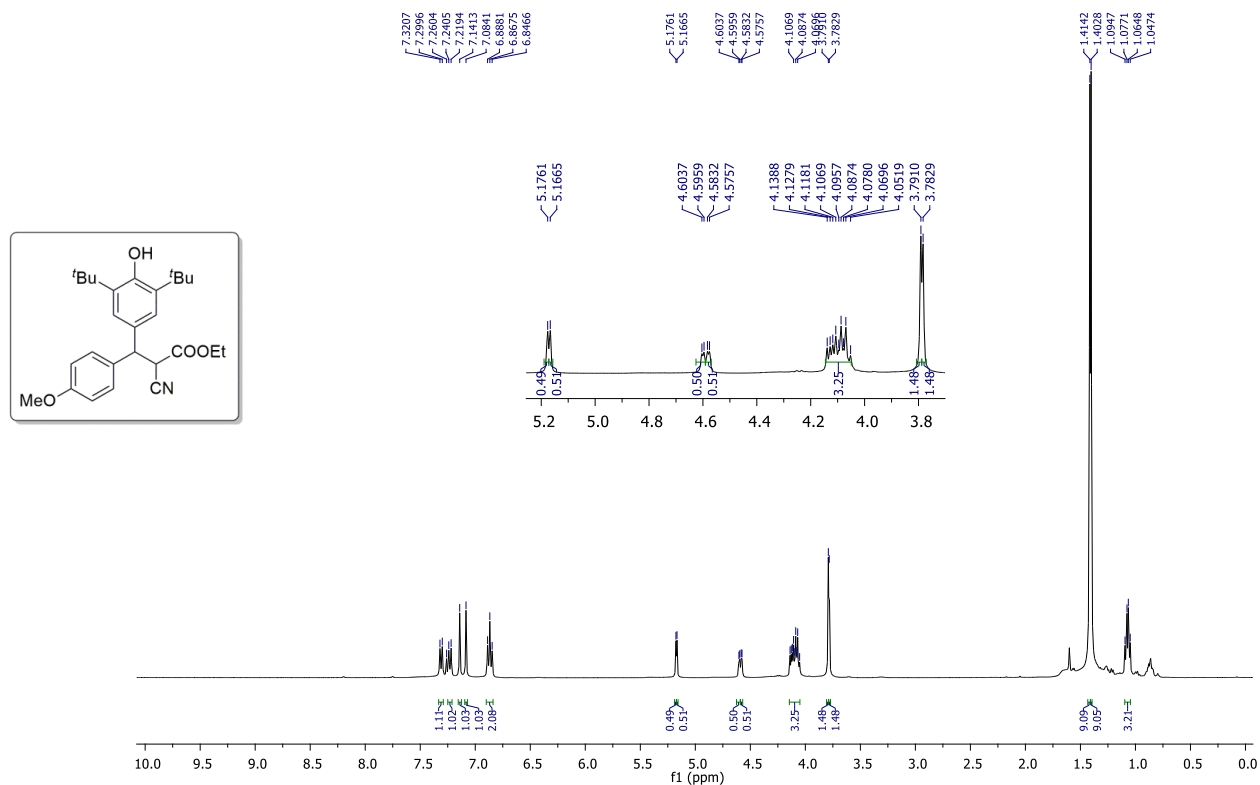
¹H NMR spectrum of **13c**



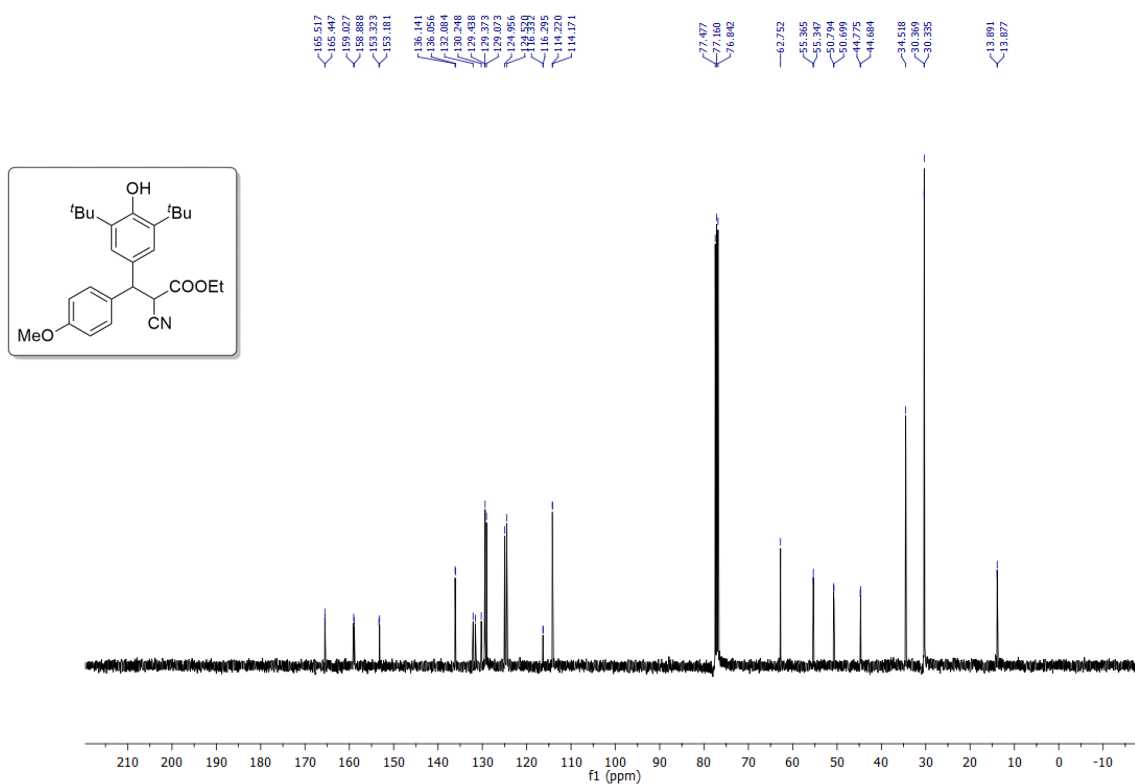
¹³C NMR spectrum of **13c**



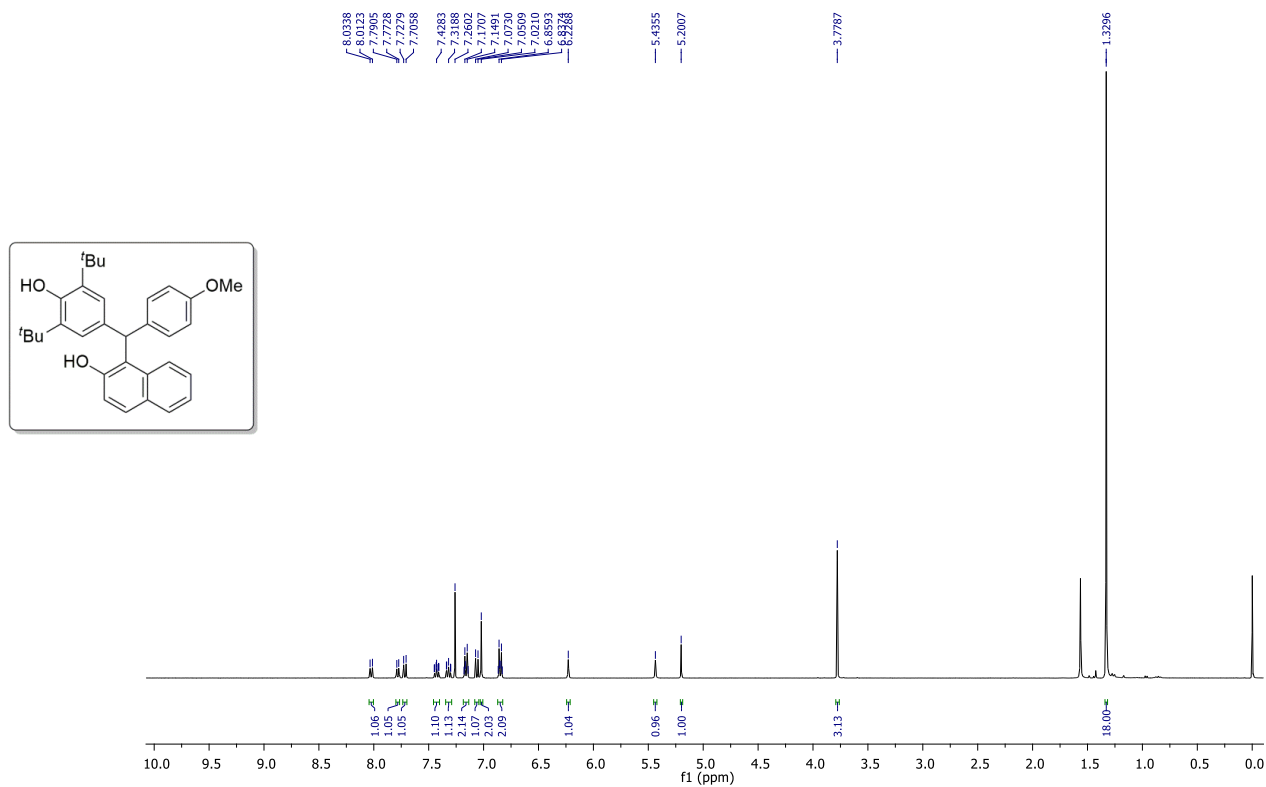
¹H NMR spectrum of **13d**



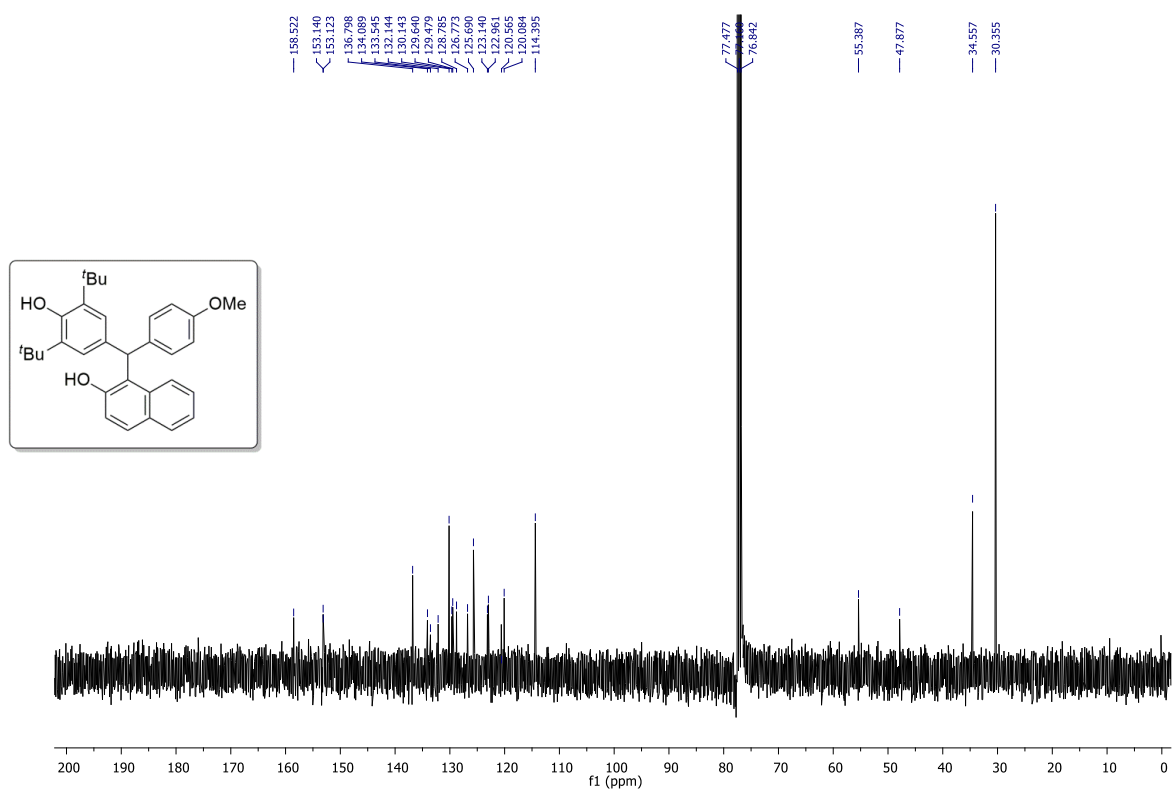
^{13}C NMR spectrum of **13d**



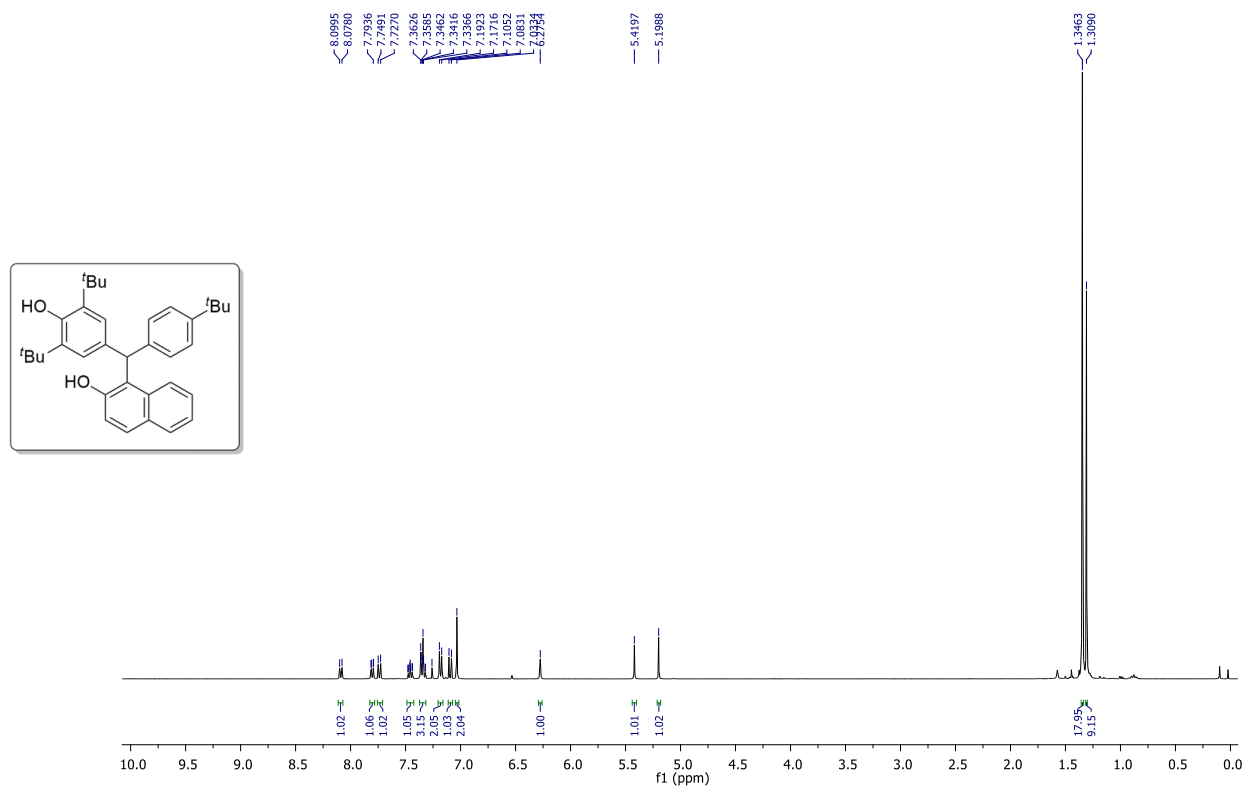
^1H NMR spectrum of **15a**

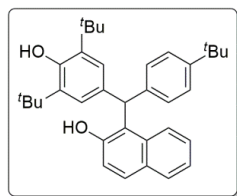
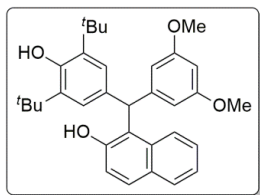


¹³C NMR spectrum of **15a**

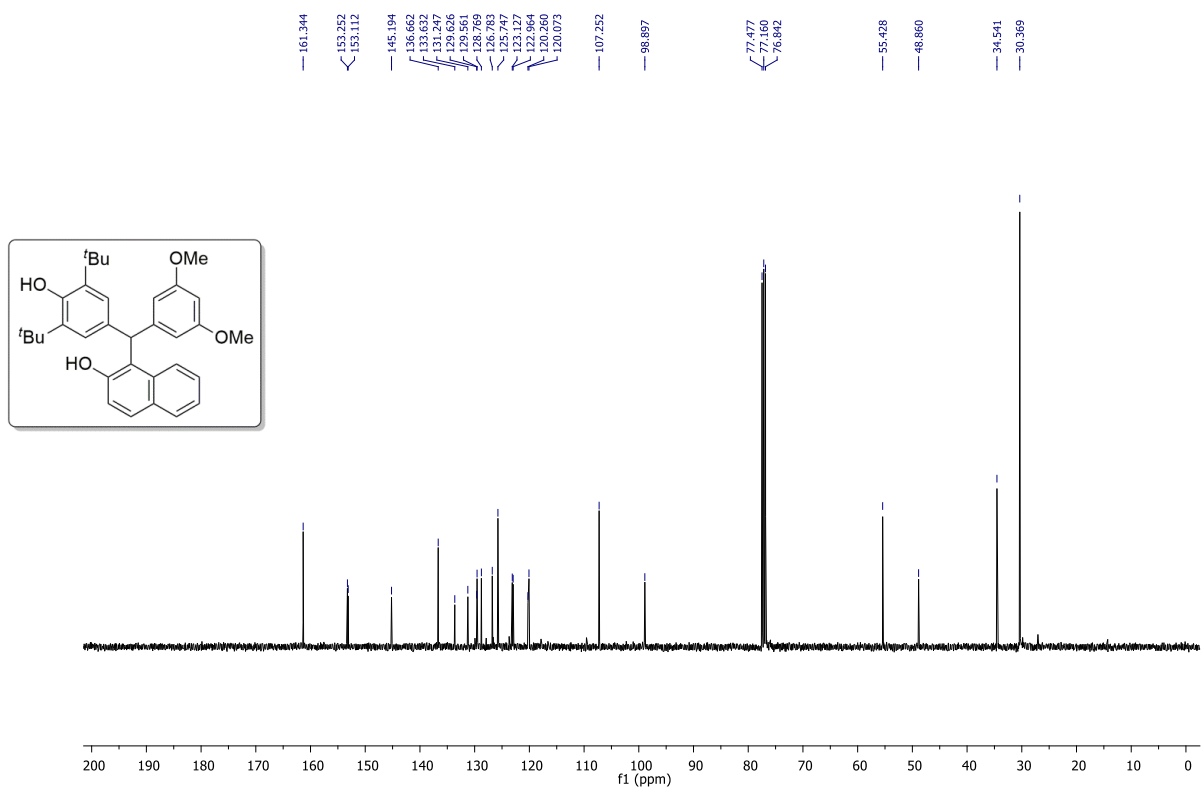


¹H NMR spectrum of **15b**

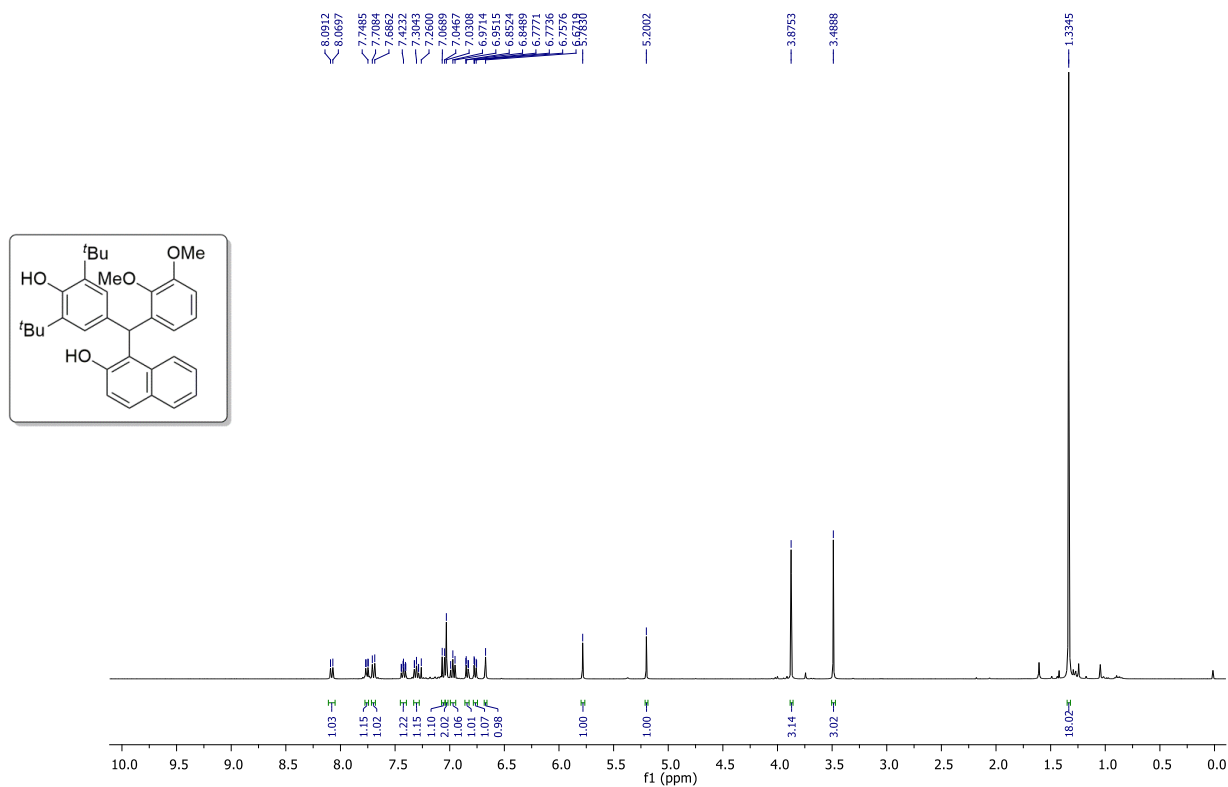


^{13}C NMR spectrum of **15b**¹H NMR spectrum of **15c**

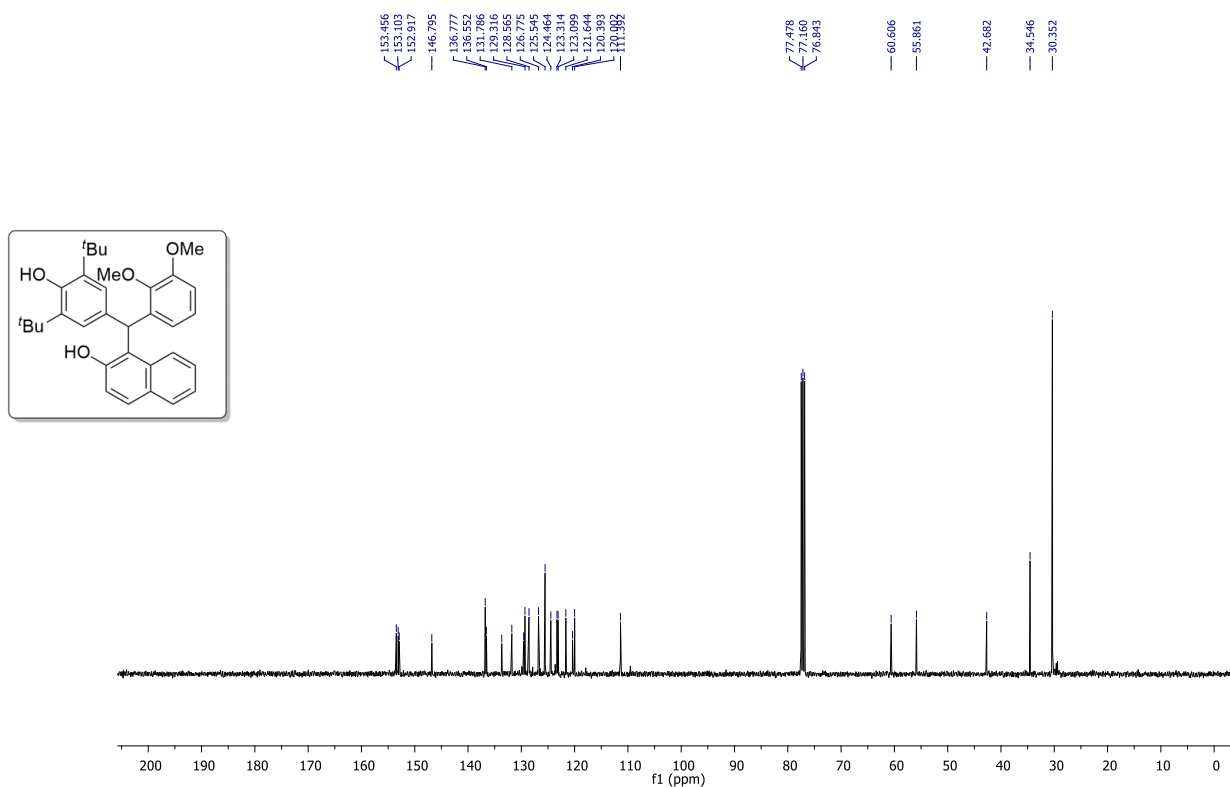
^{13}C NMR spectrum of **15c**



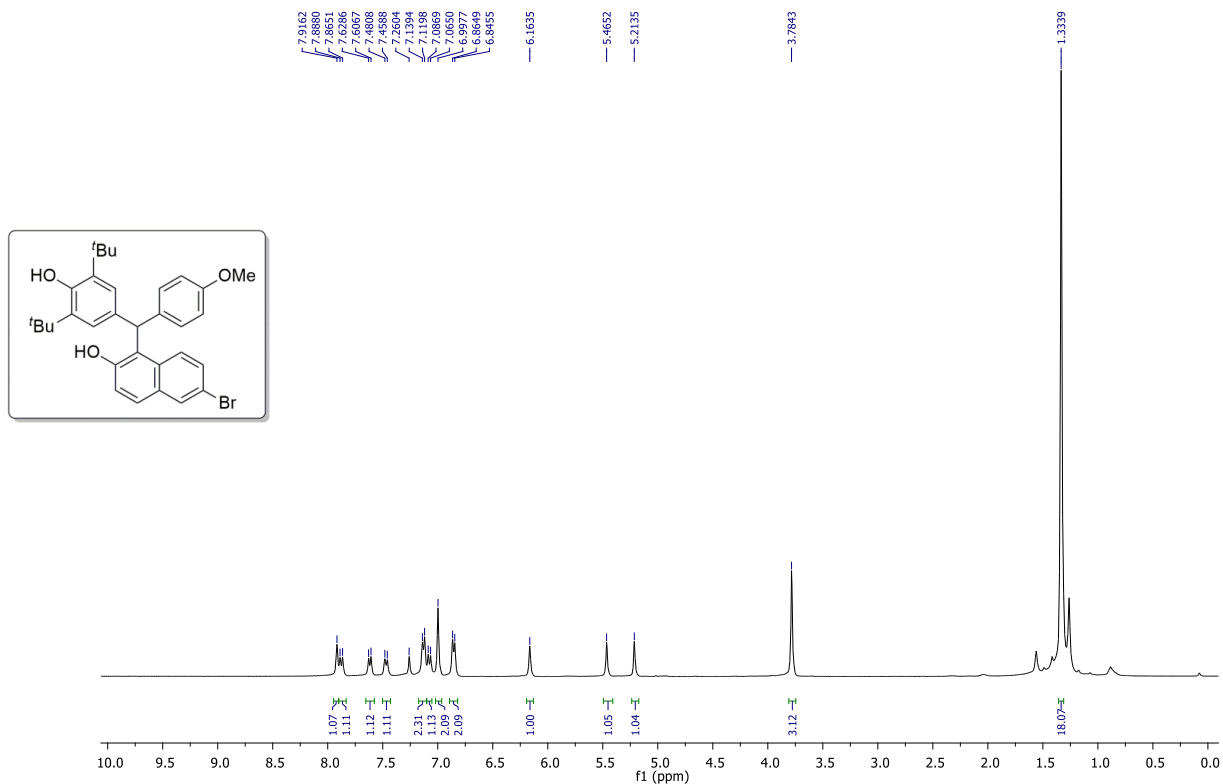
^1H NMR spectrum of **15d**



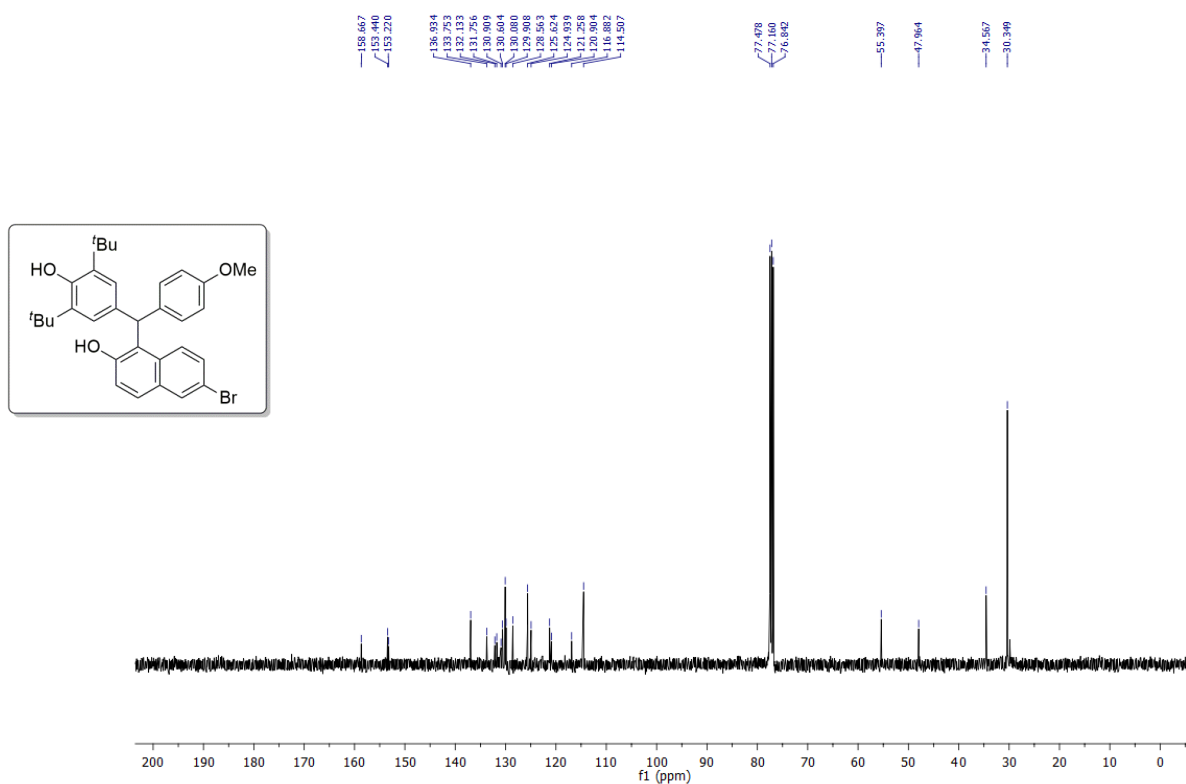
¹³C NMR spectrum of **15d**



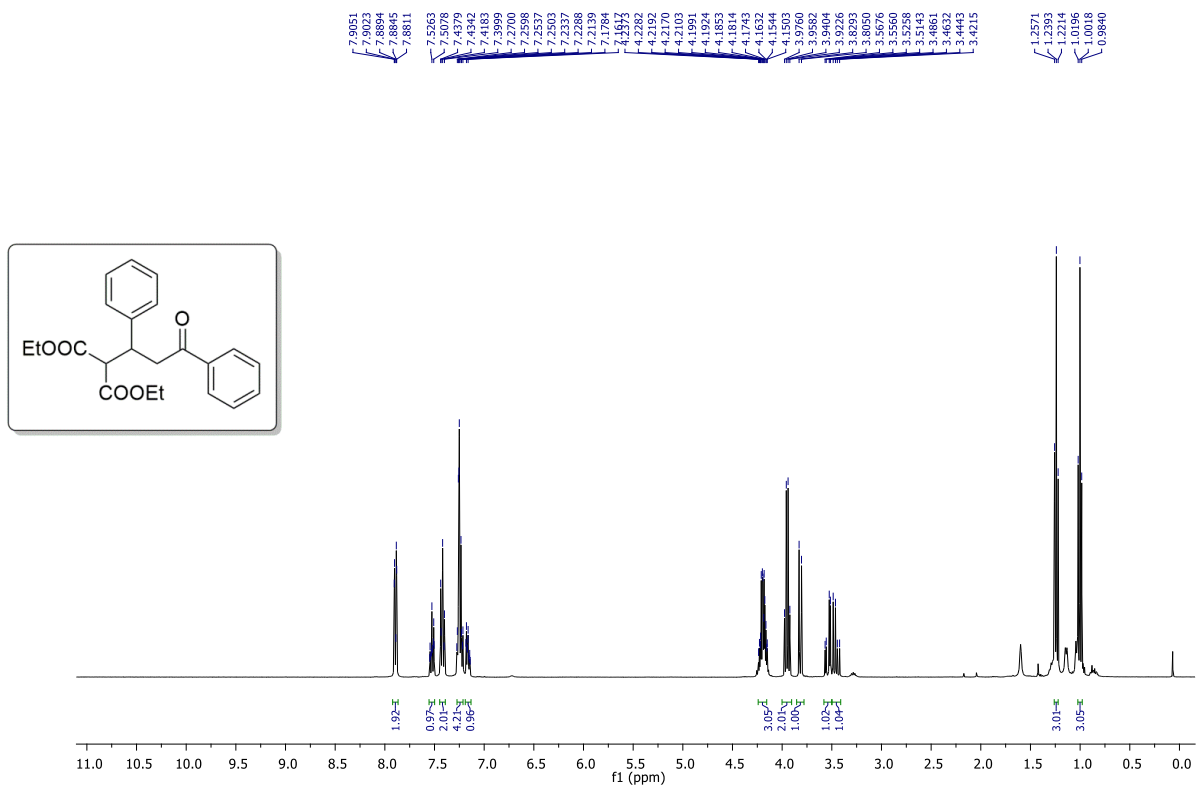
¹H NMR spectrum of **15e**



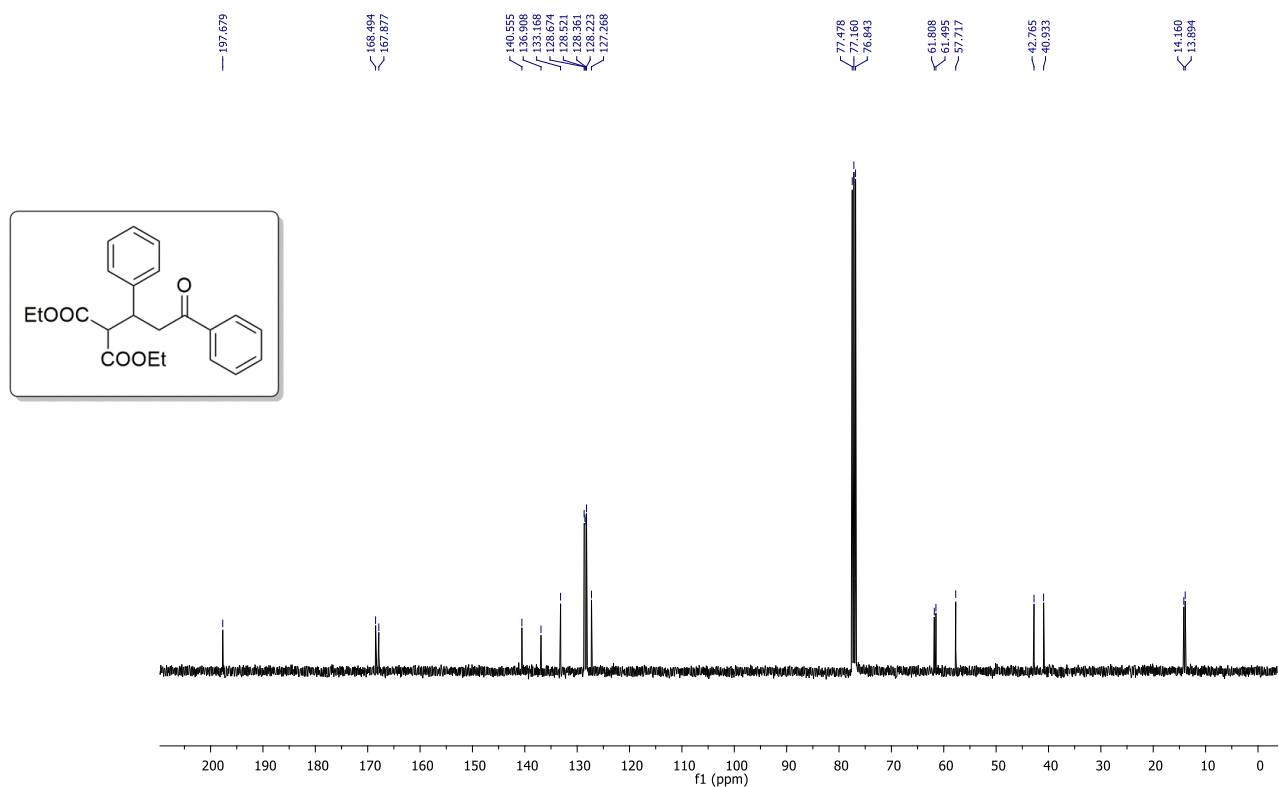
¹³C NMR spectrum of **15e**



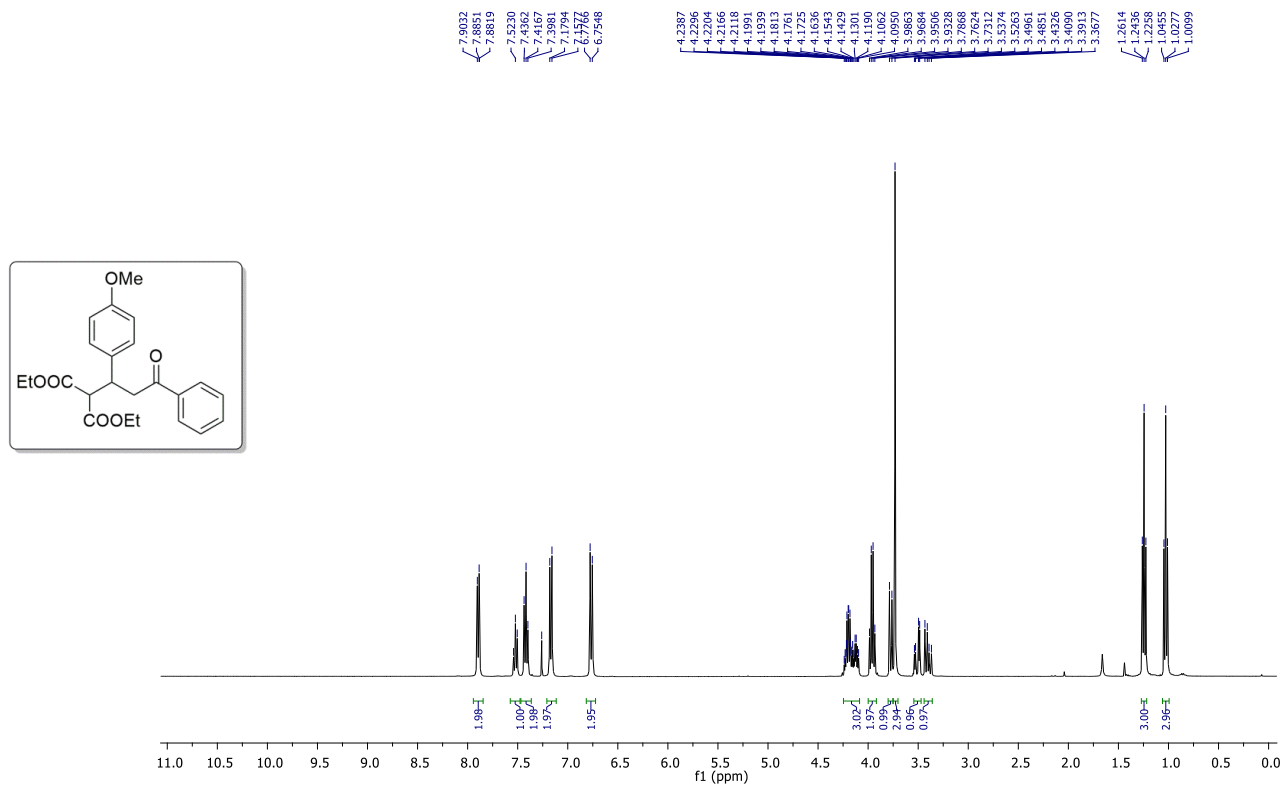
¹H NMR spectrum of **17a**



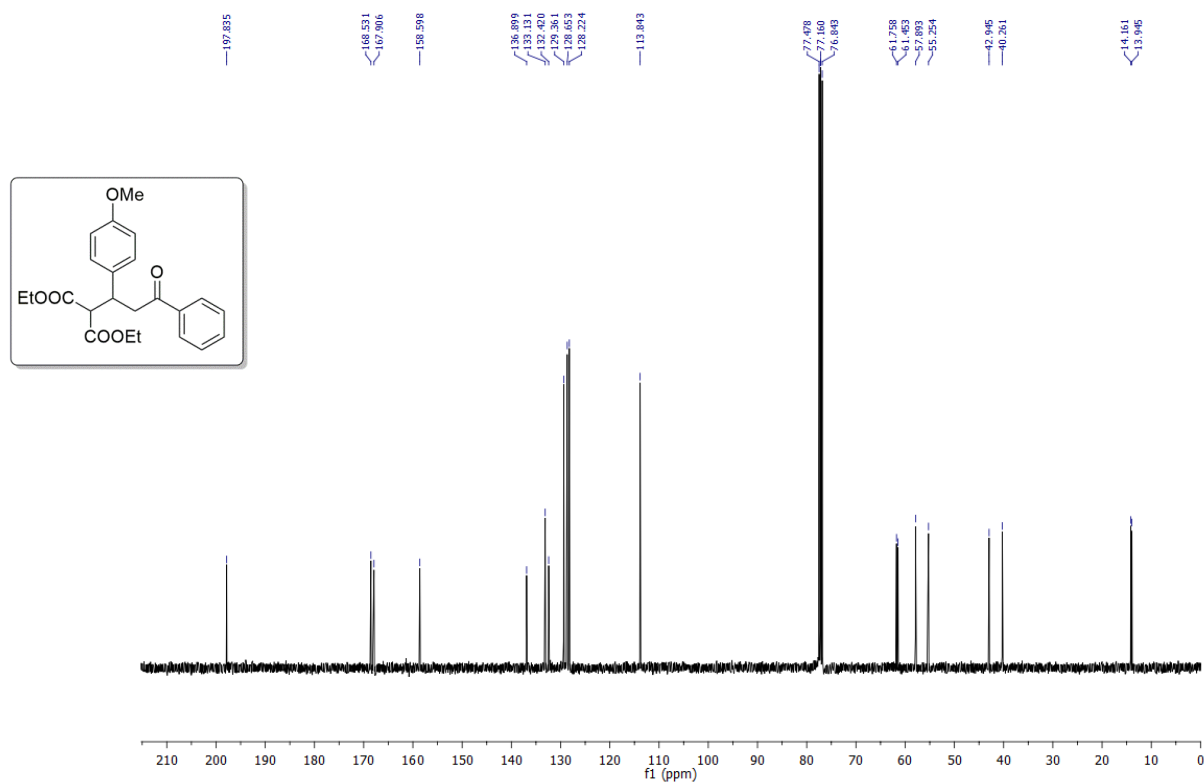
^{13}C NMR spectrum of **17a**



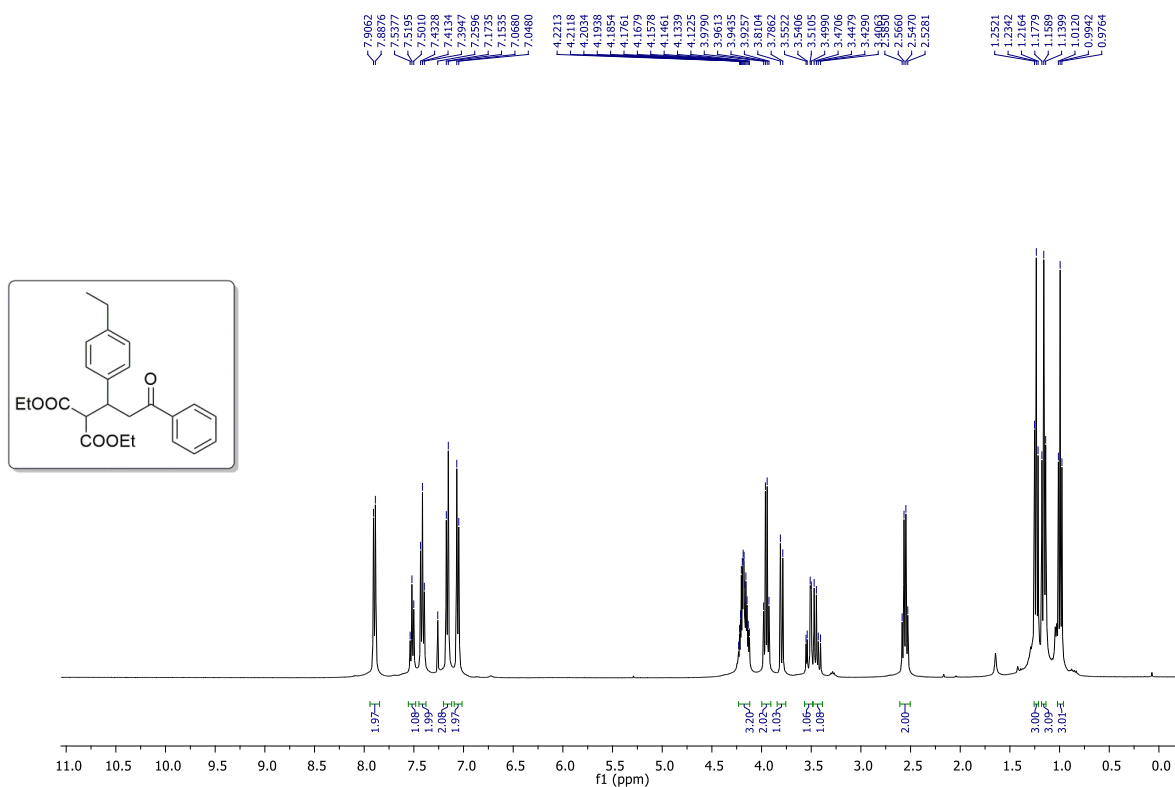
^1H NMR spectrum of **17b**



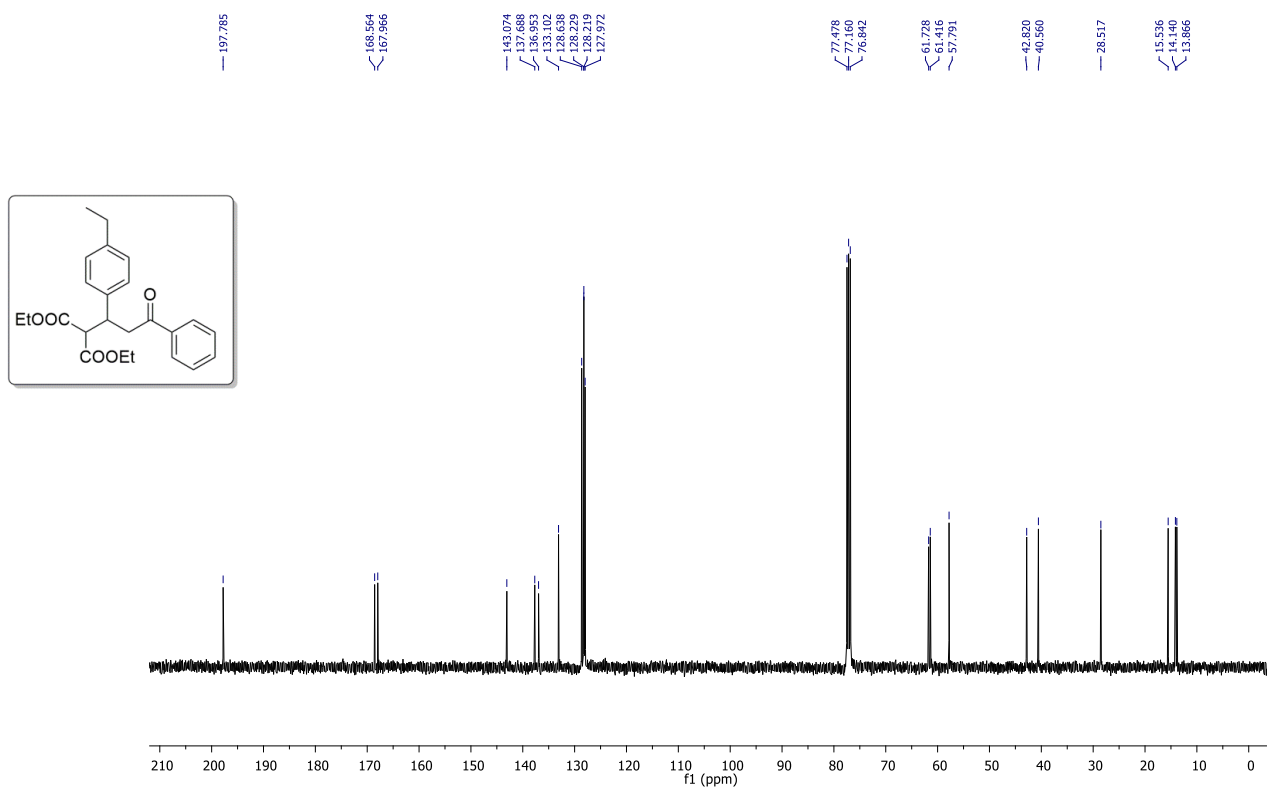
^{13}C NMR spectrum of **17b**



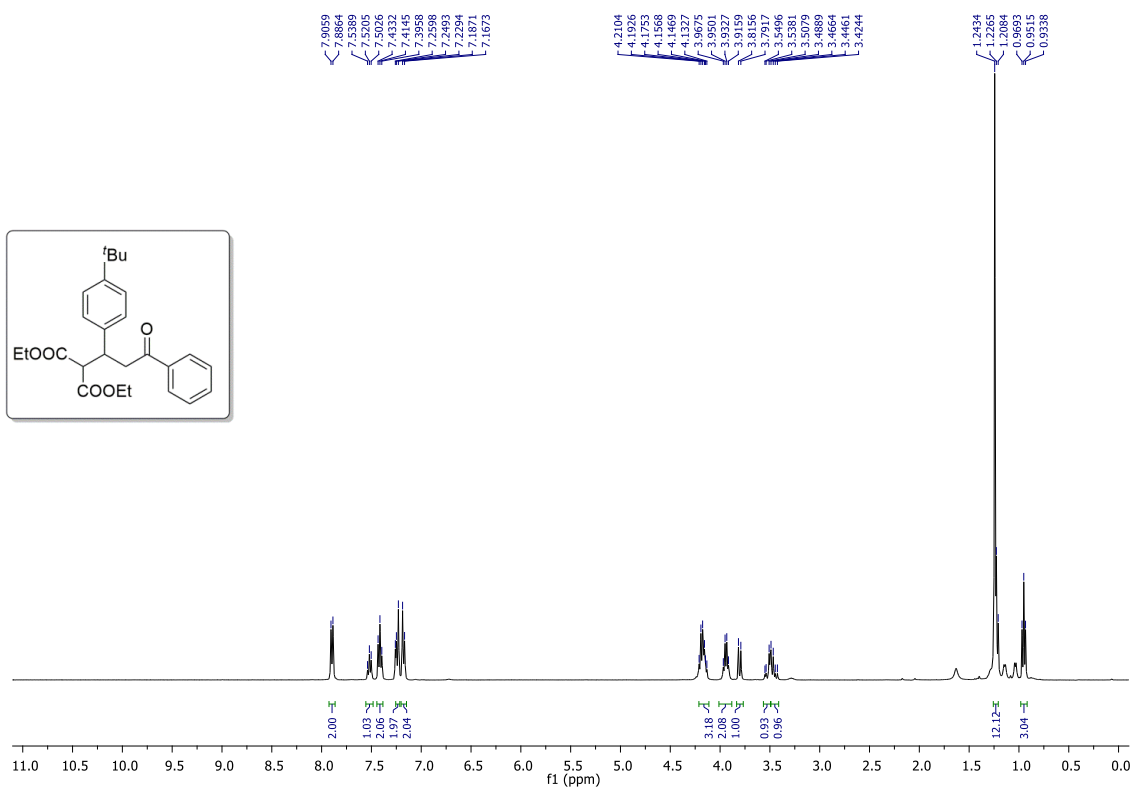
^1H NMR spectrum of **17c**



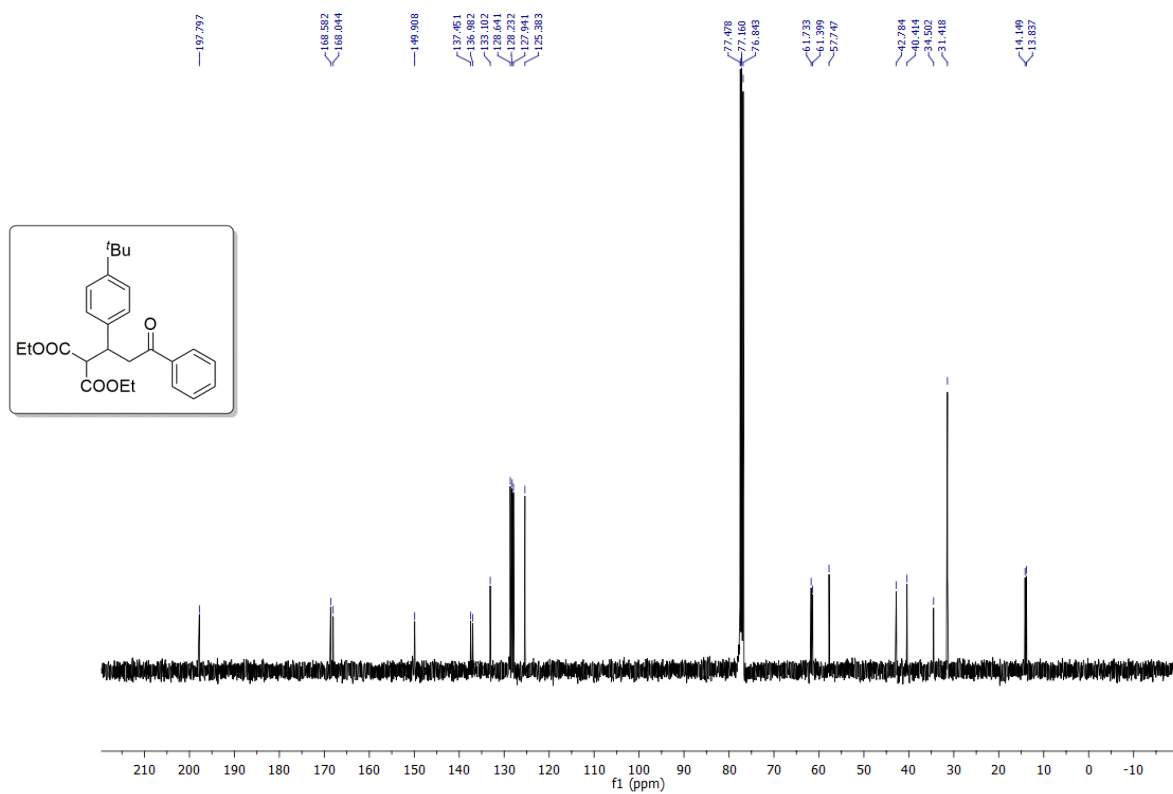
¹³C NMR spectrum of 17c



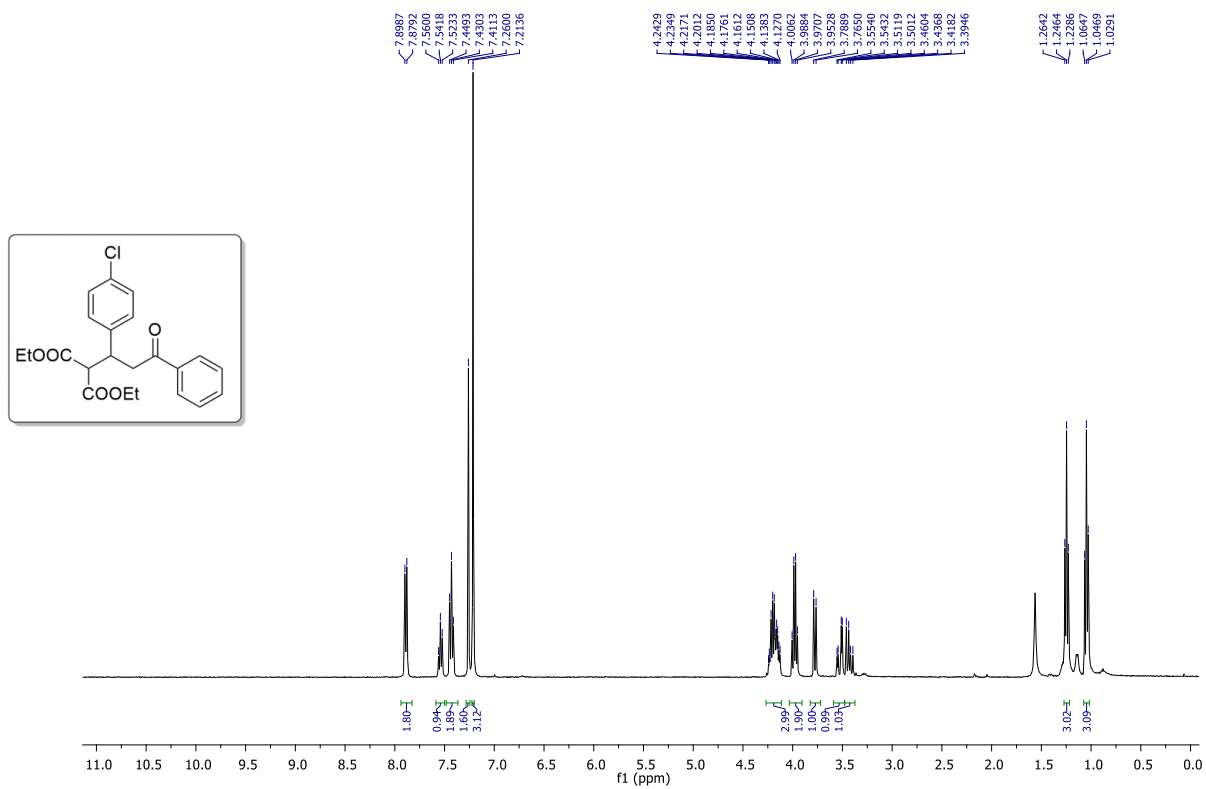
¹H NMR spectrum of 17d

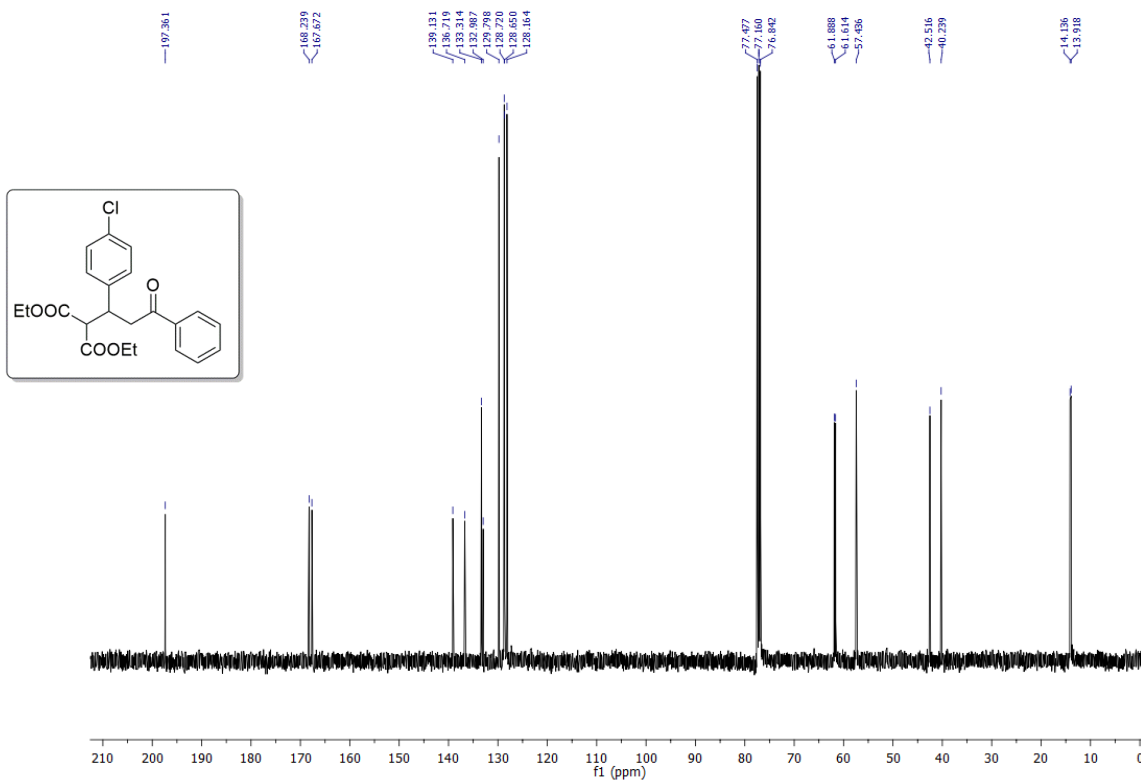
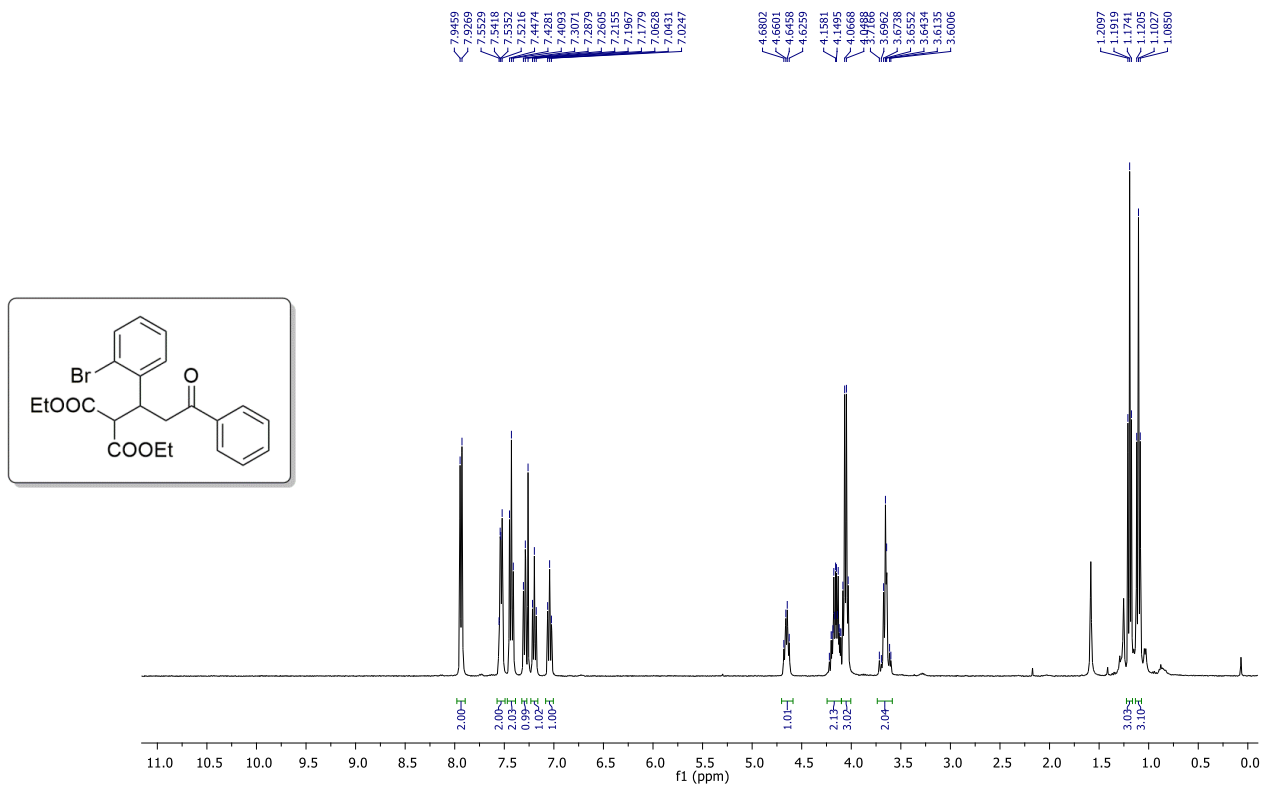


¹³C NMR spectrum of **17d**

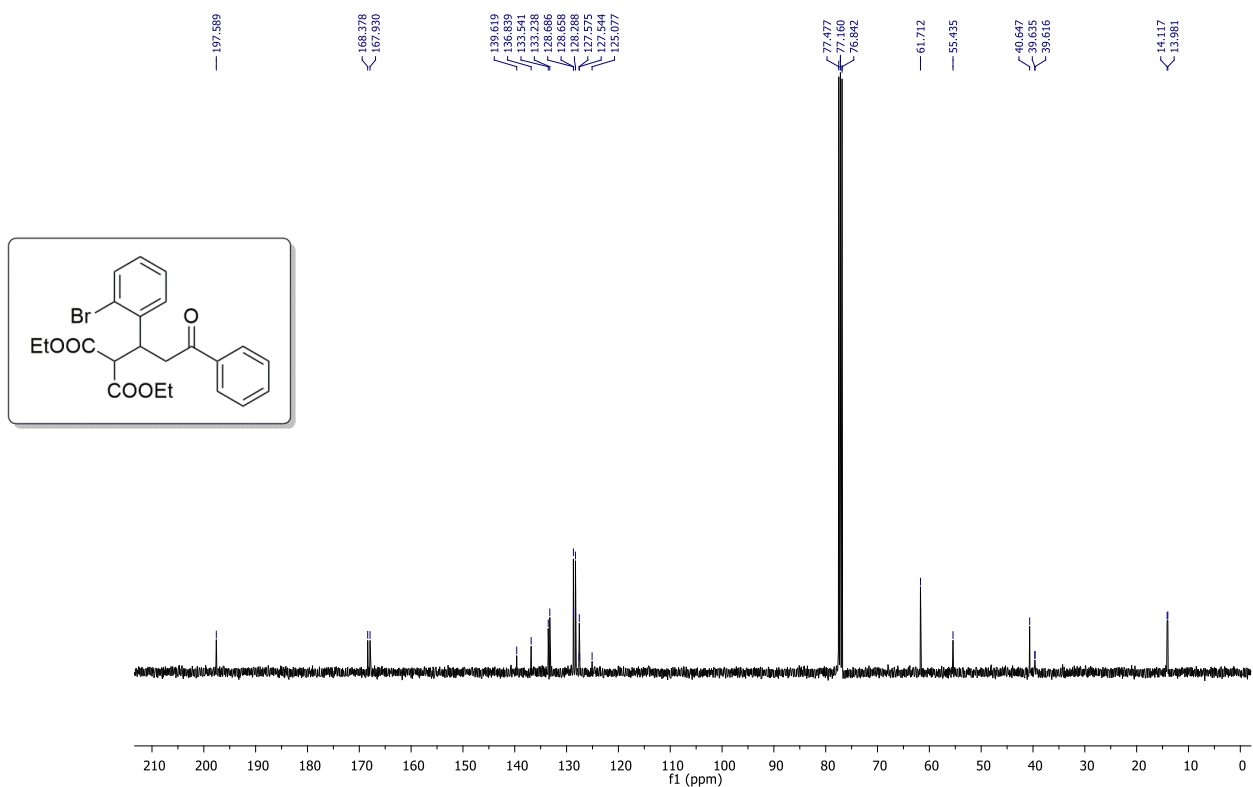


¹H NMR spectrum of **17e**

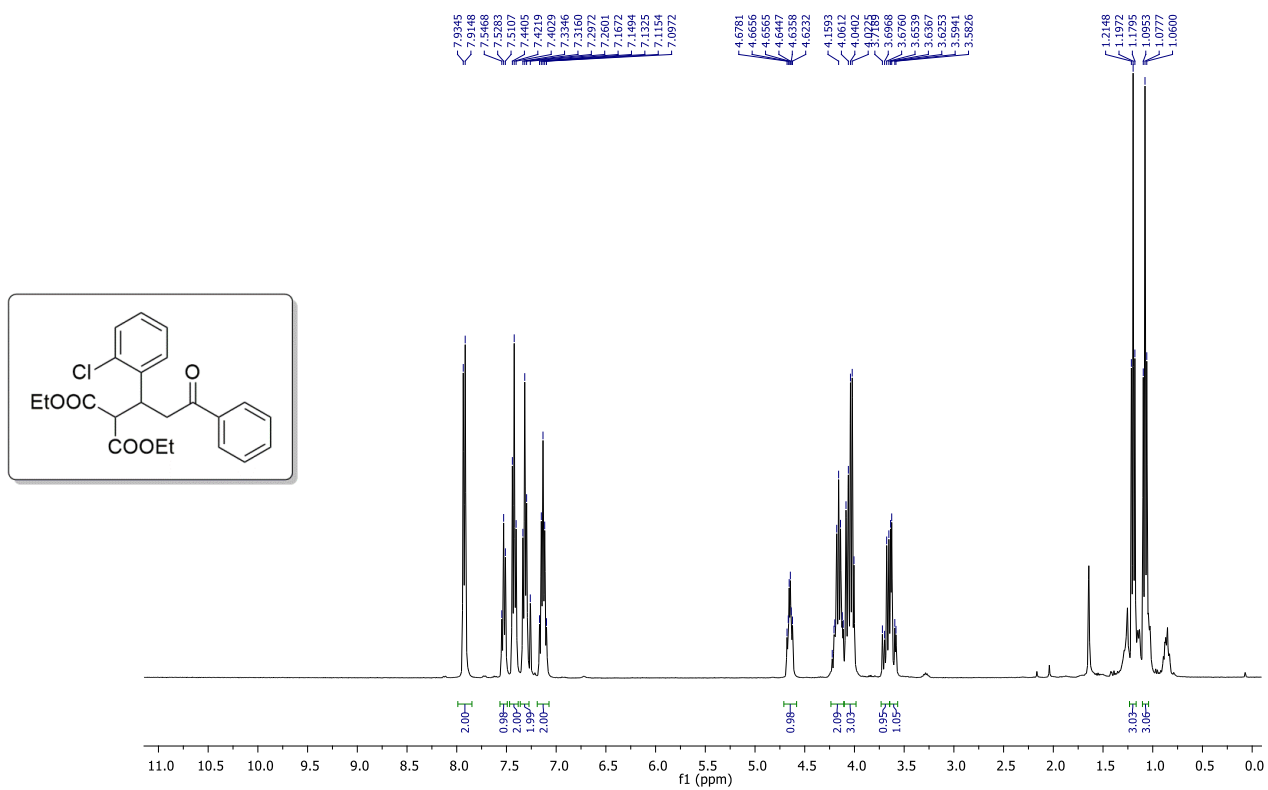


^{13}C NMR spectrum of **17e**¹H NMR spectrum of **17f**

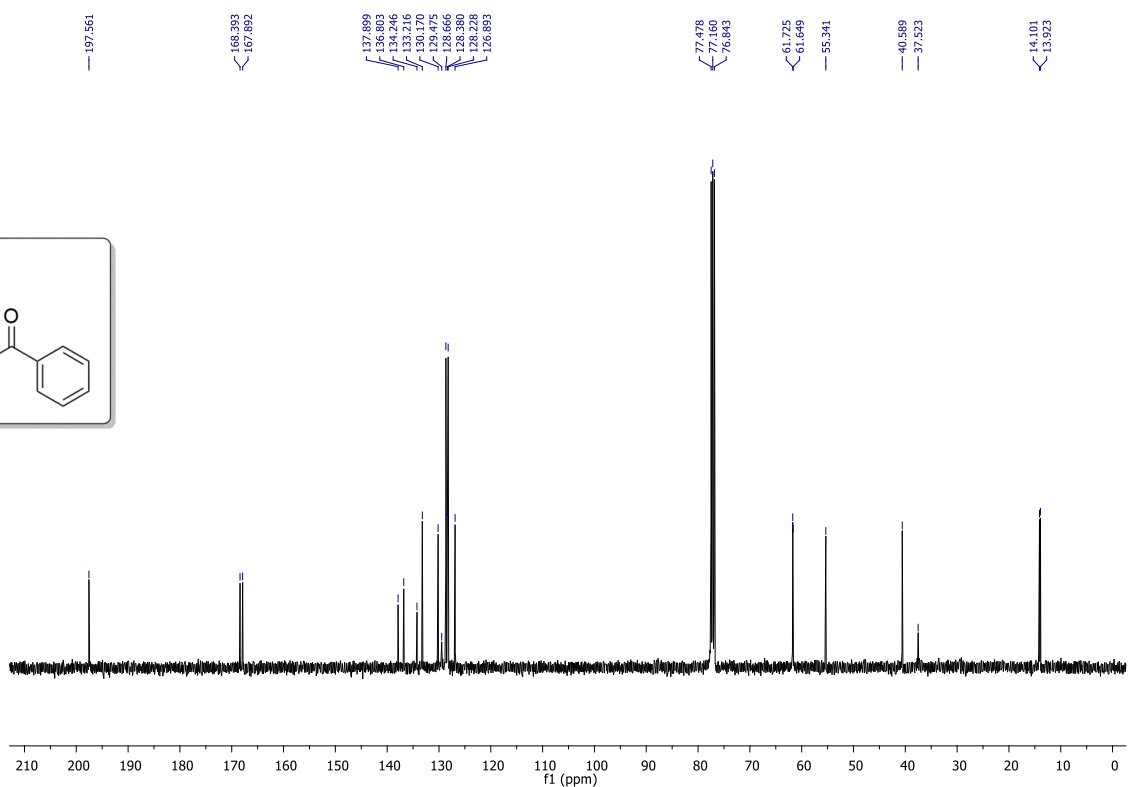
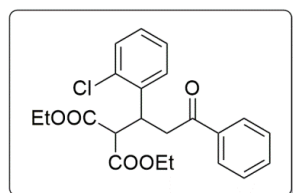
¹³C NMR spectrum of **17f**



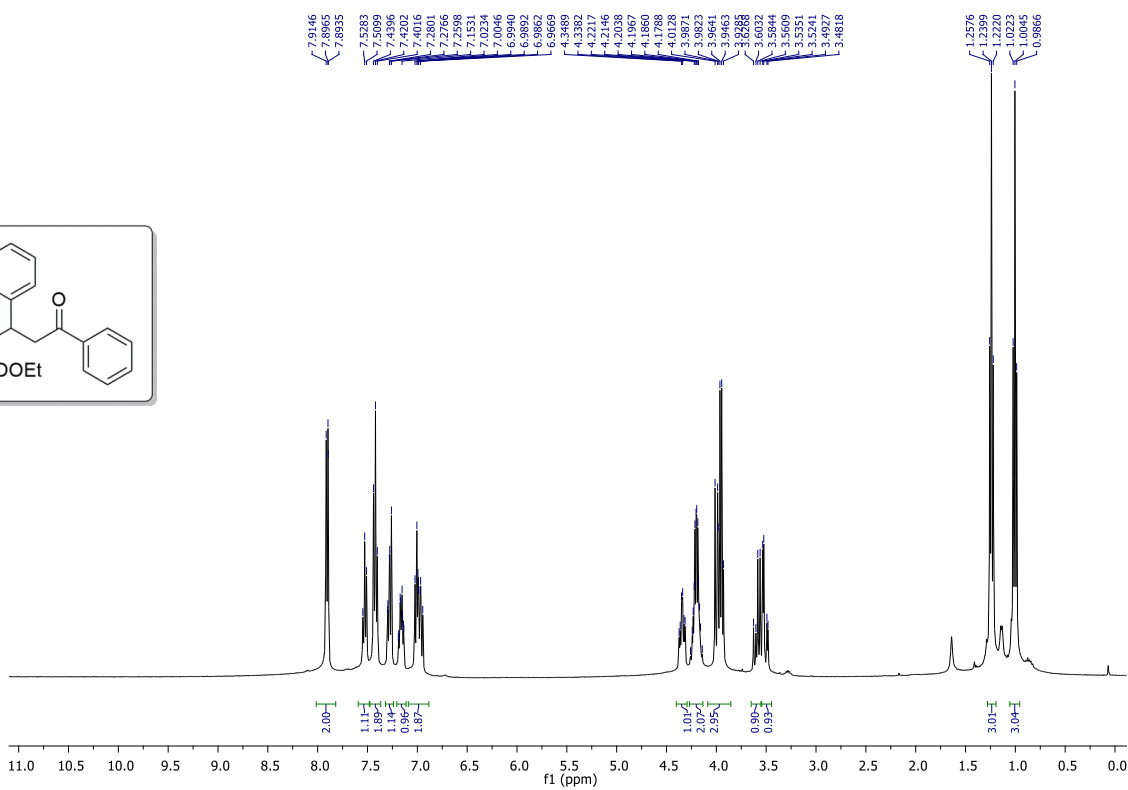
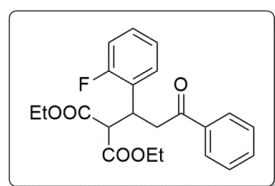
¹H NMR spectrum of **17g**



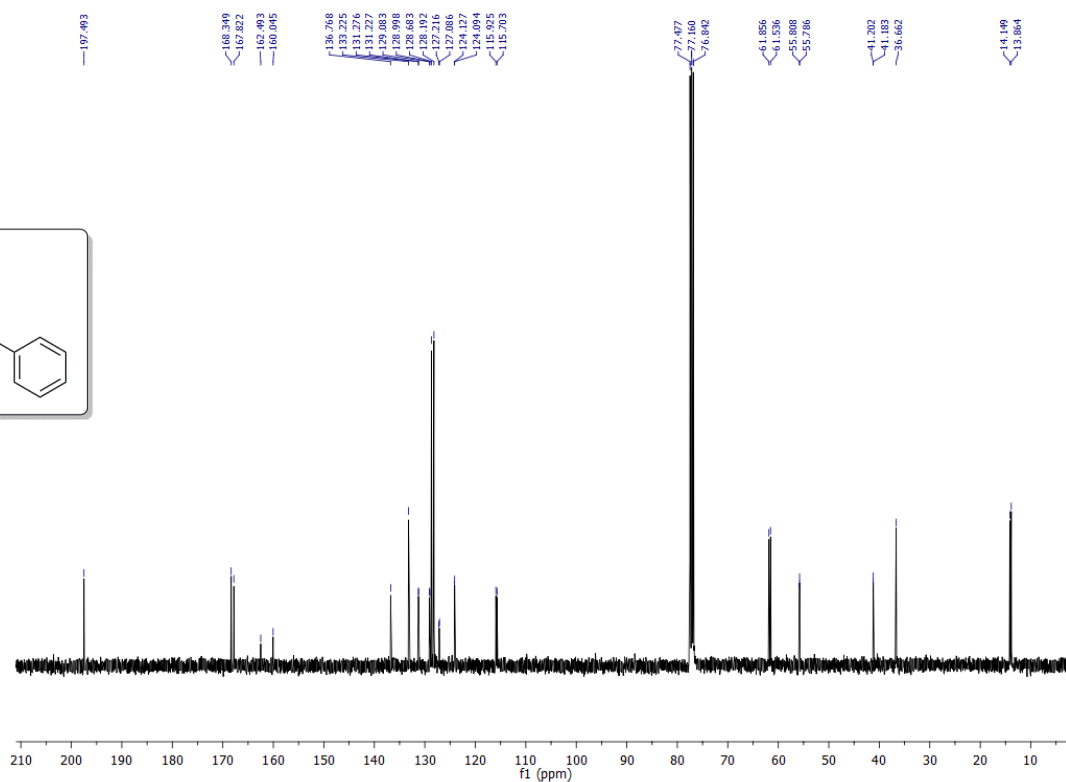
¹³C NMR spectrum of 17g



¹H NMR spectrum of 17h



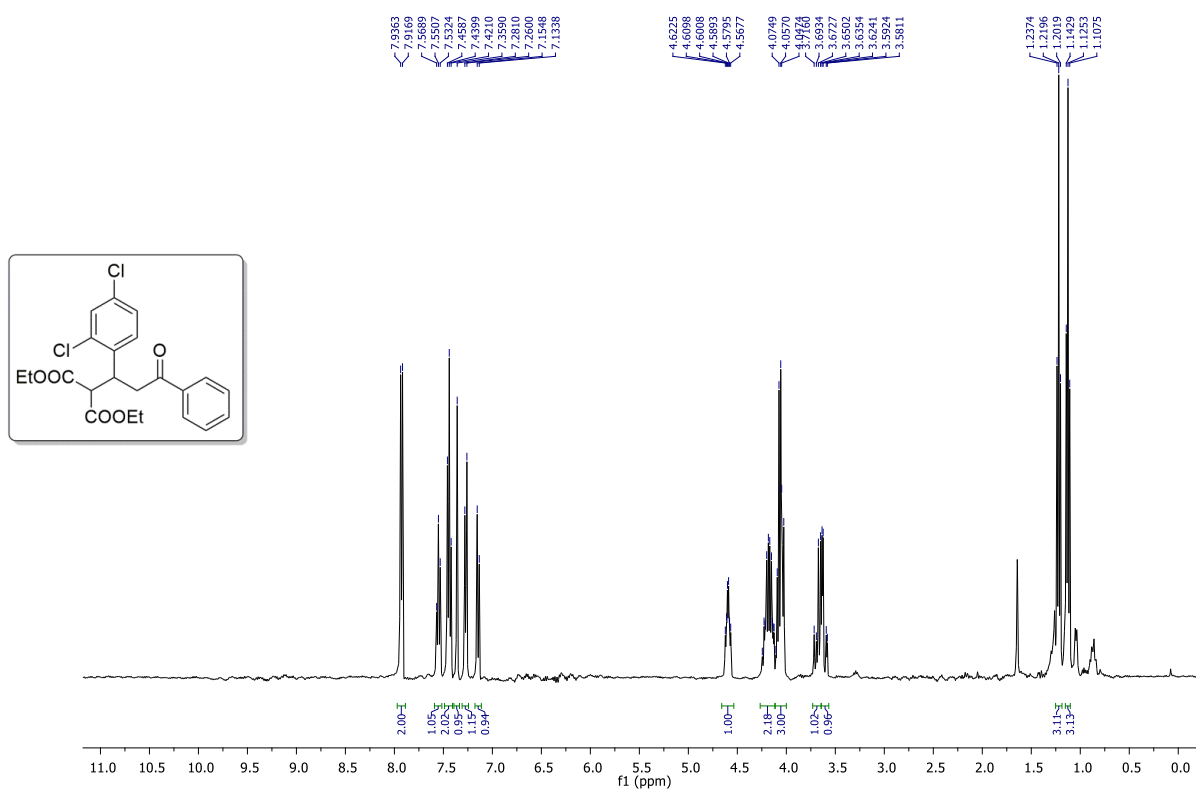
¹³C NMR spectrum of **17h**



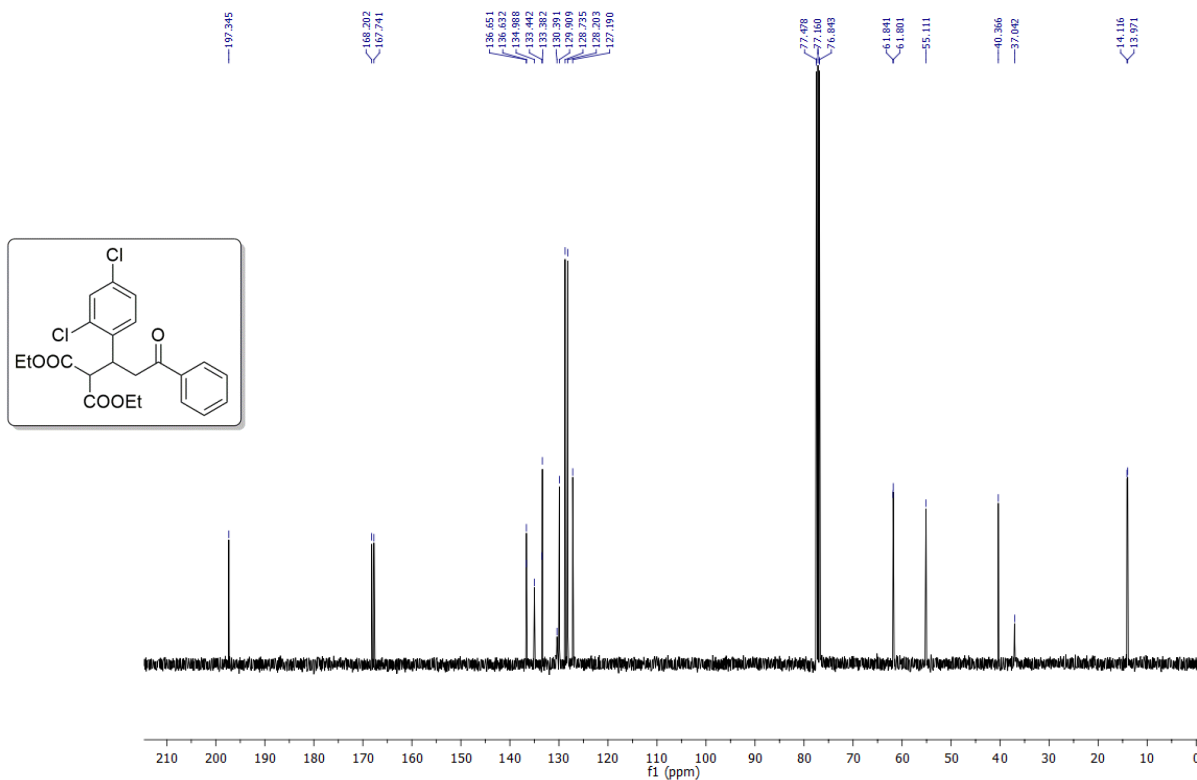
¹⁹F NMR spectrum of **17h**



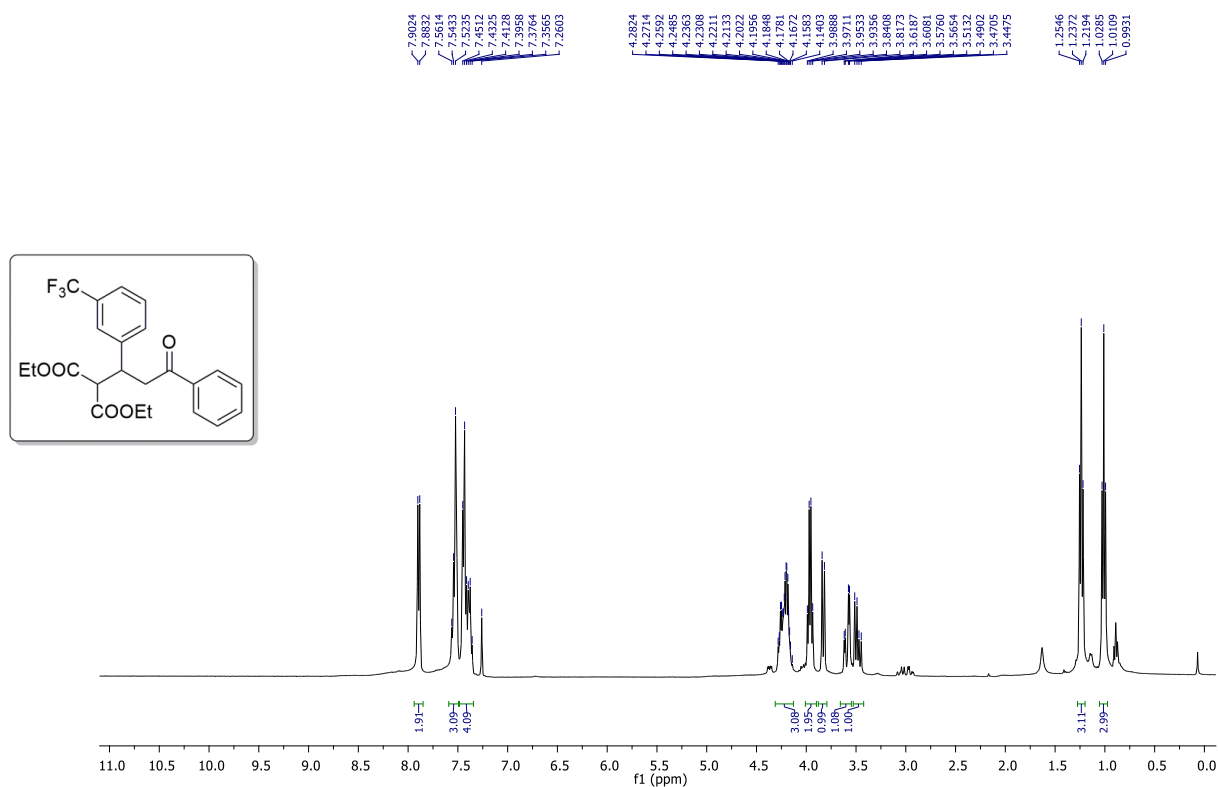
¹H NMR spectrum of **17i**



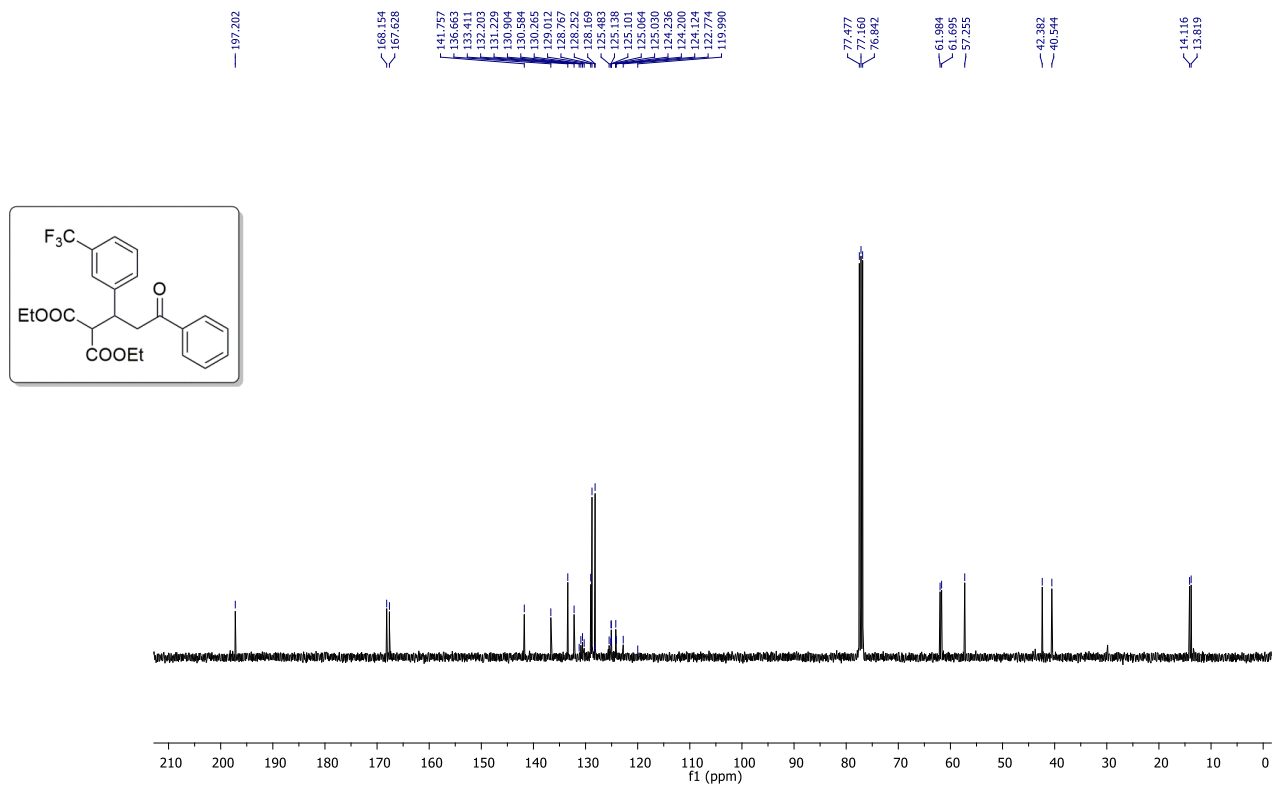
¹³C NMR spectrum of **17i**



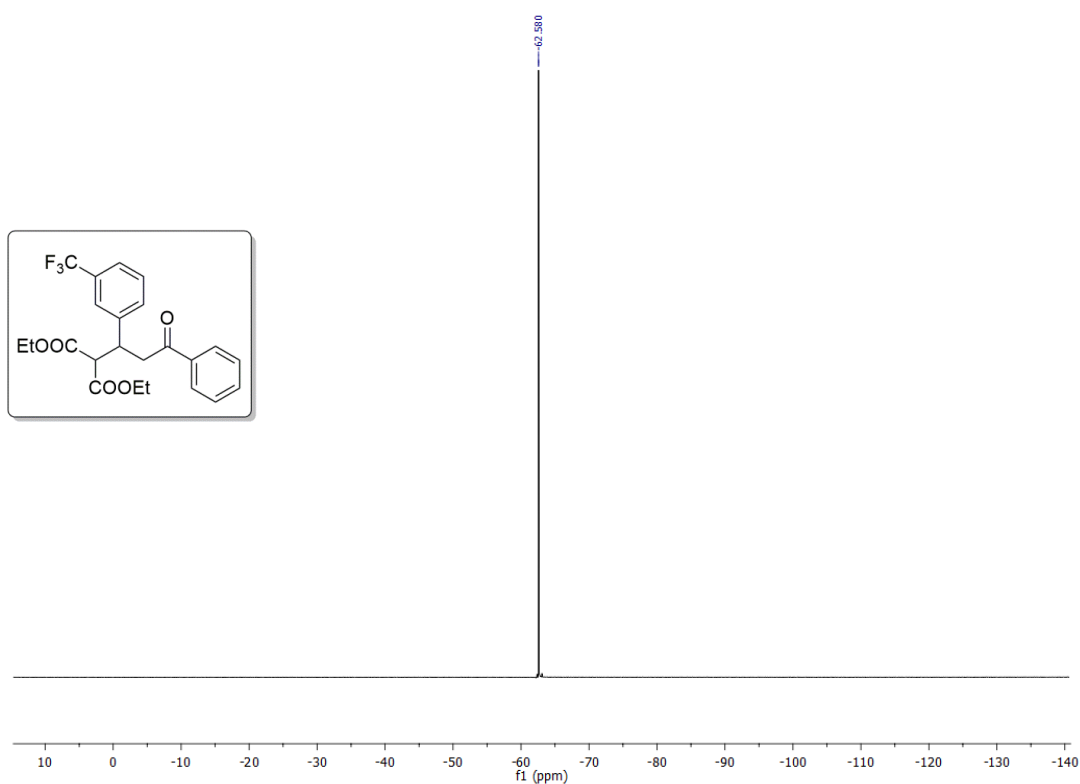
¹H NMR spectrum of **17j**



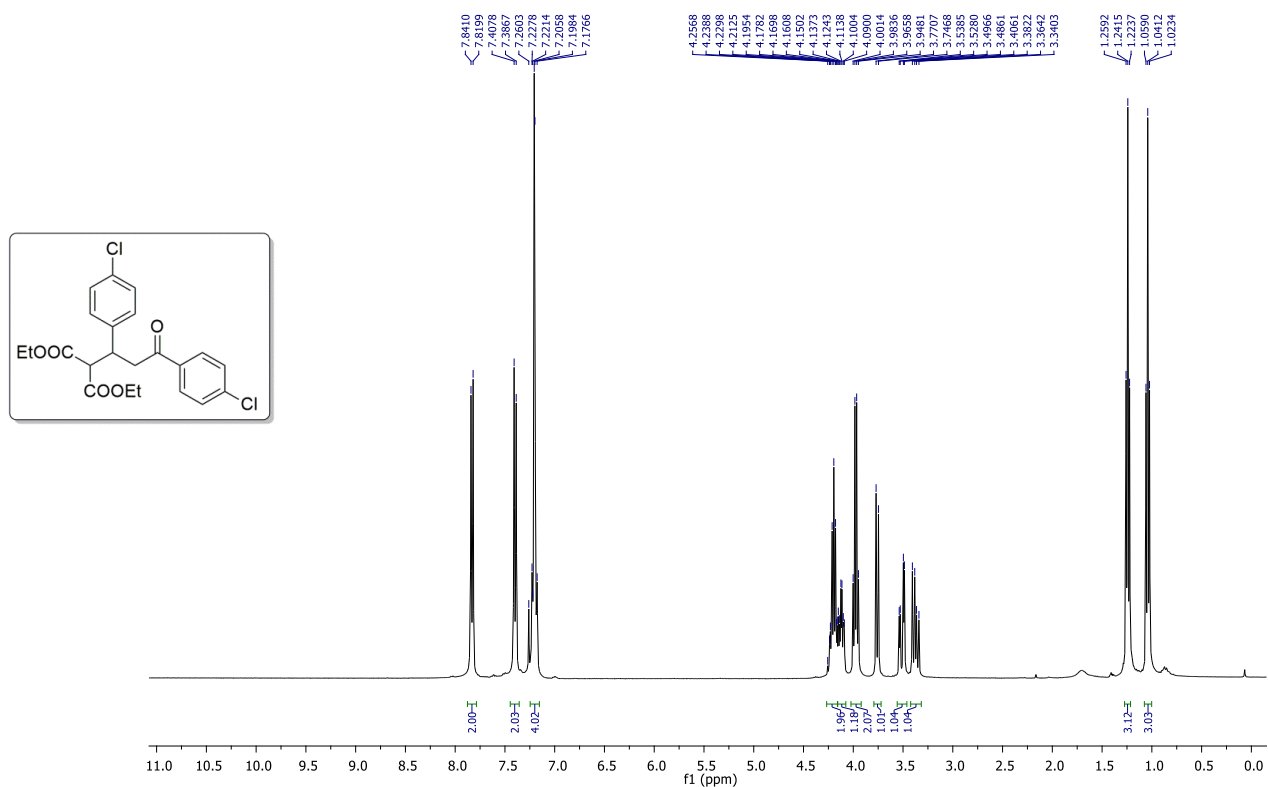
¹³C NMR spectrum of **17j**



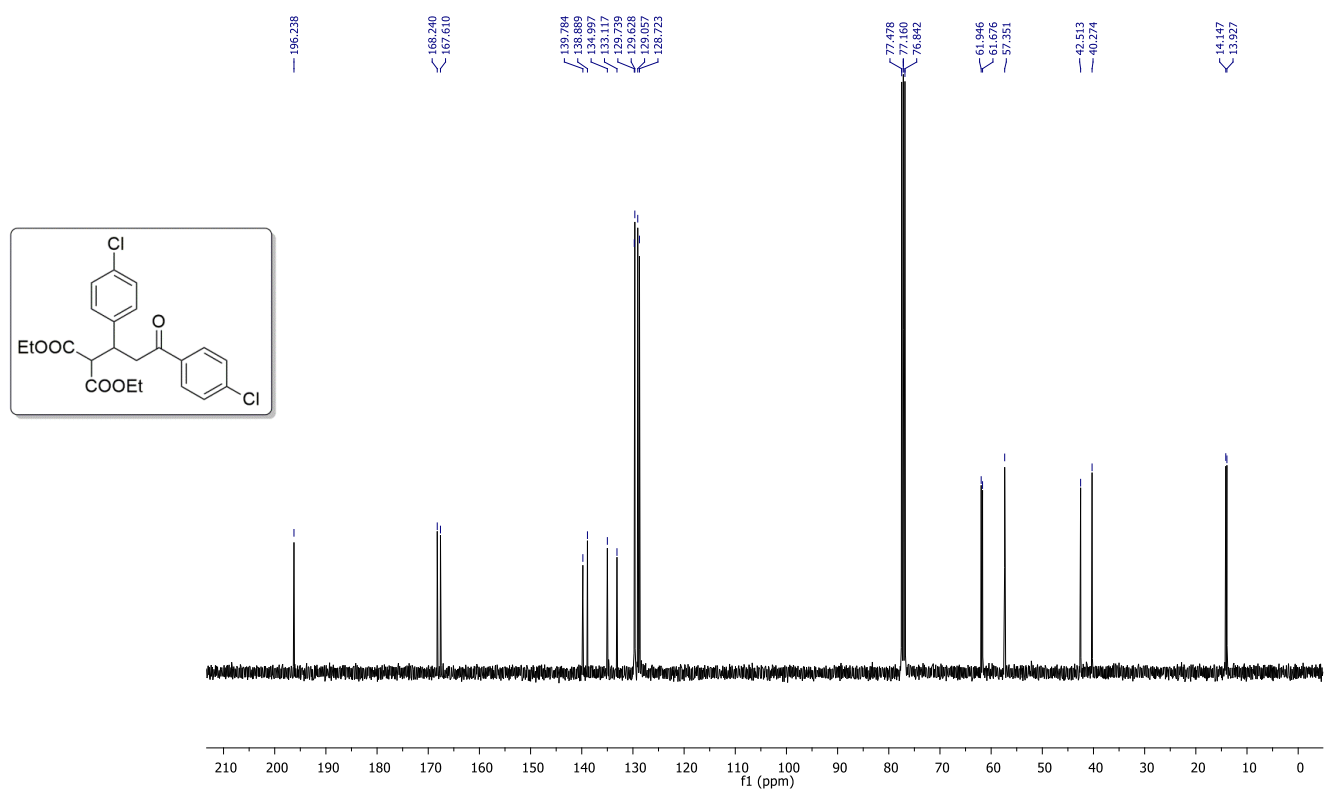
^{19}F NMR spectrum of **17j**



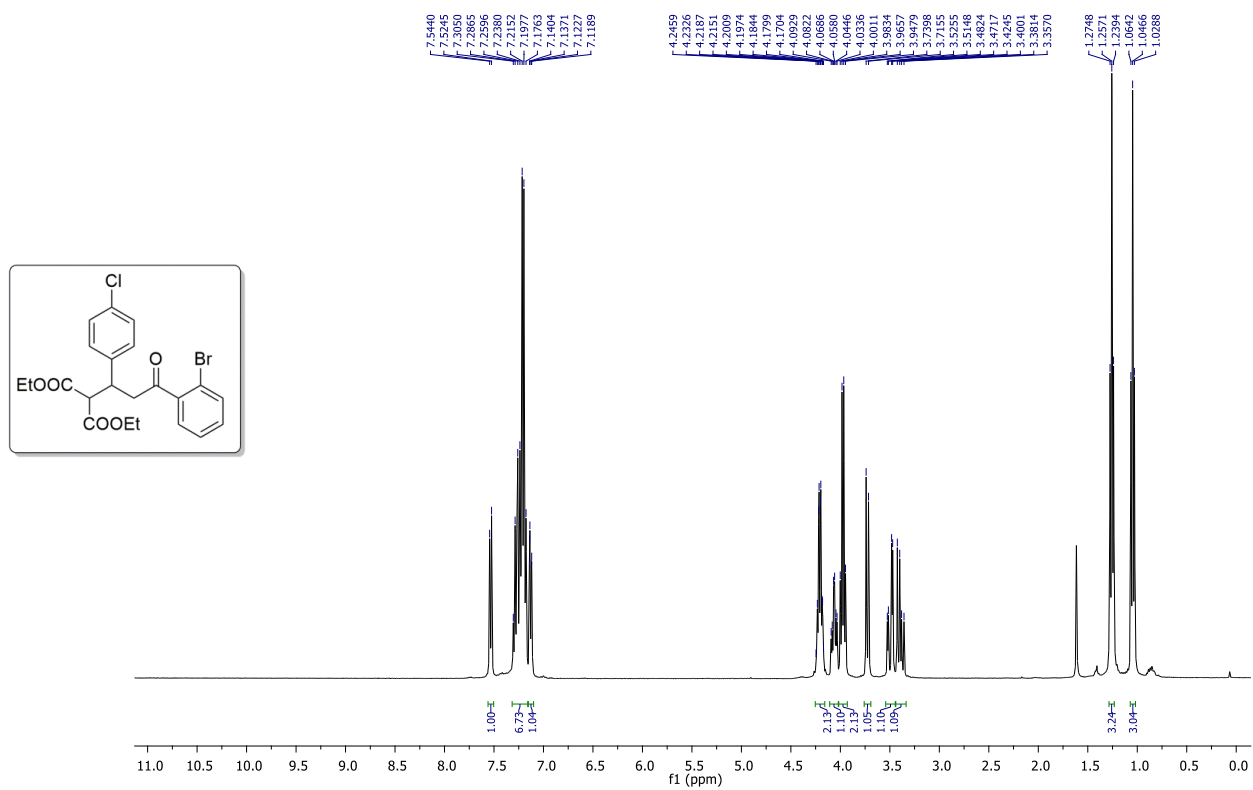
^1H NMR spectrum of **17k**



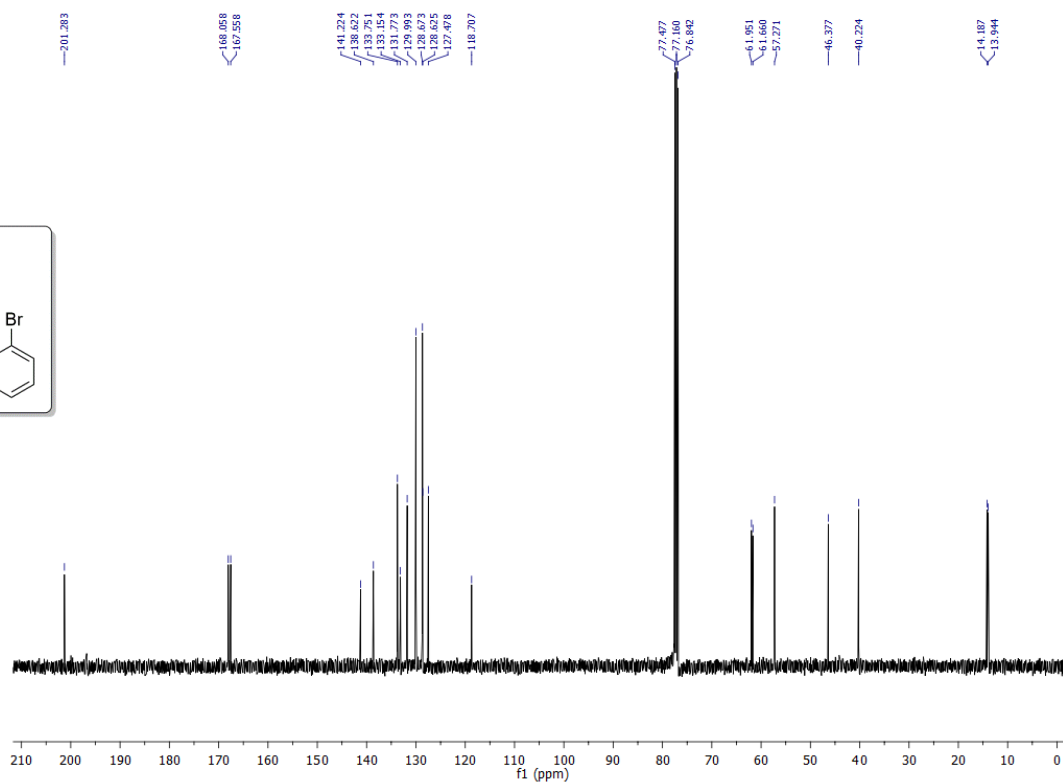
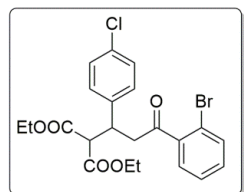
¹³C NMR spectrum of **17k**



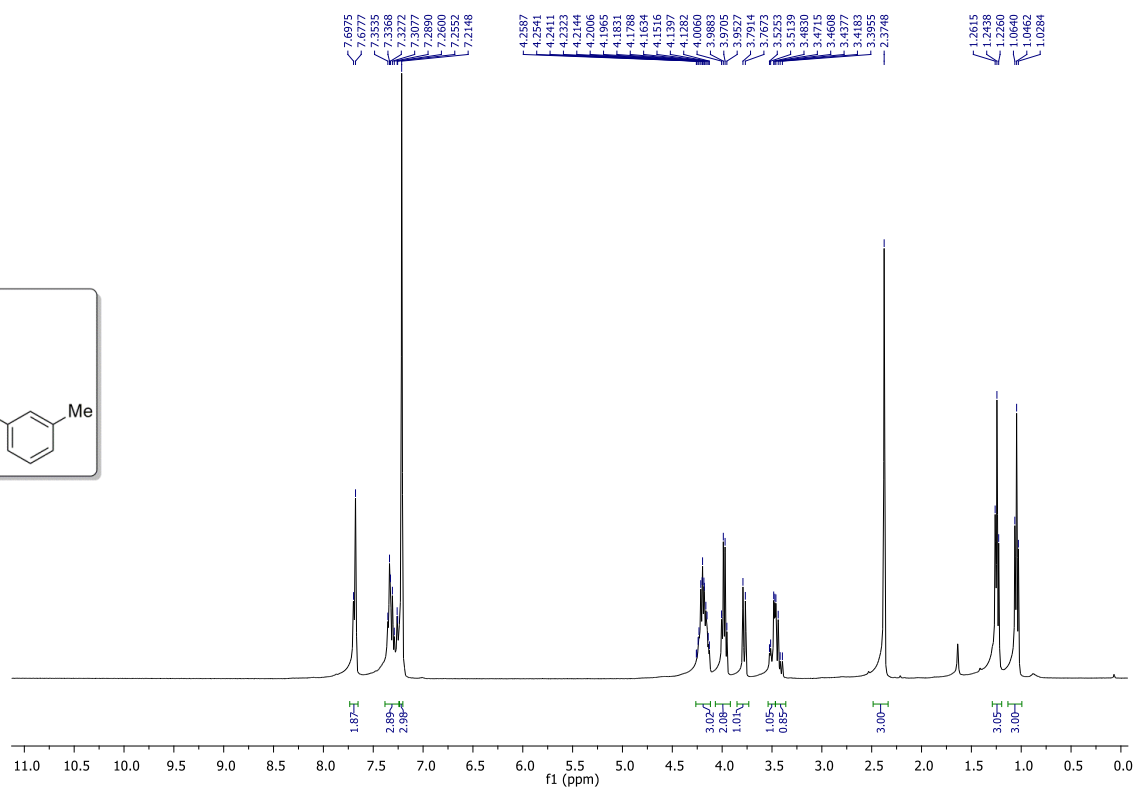
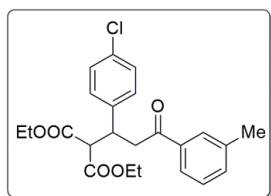
¹H NMR spectrum of **17l**

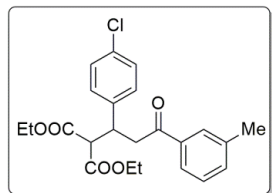
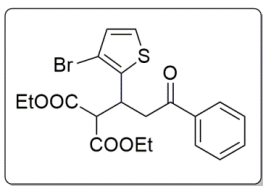


¹³C NMR spectrum of **17l**

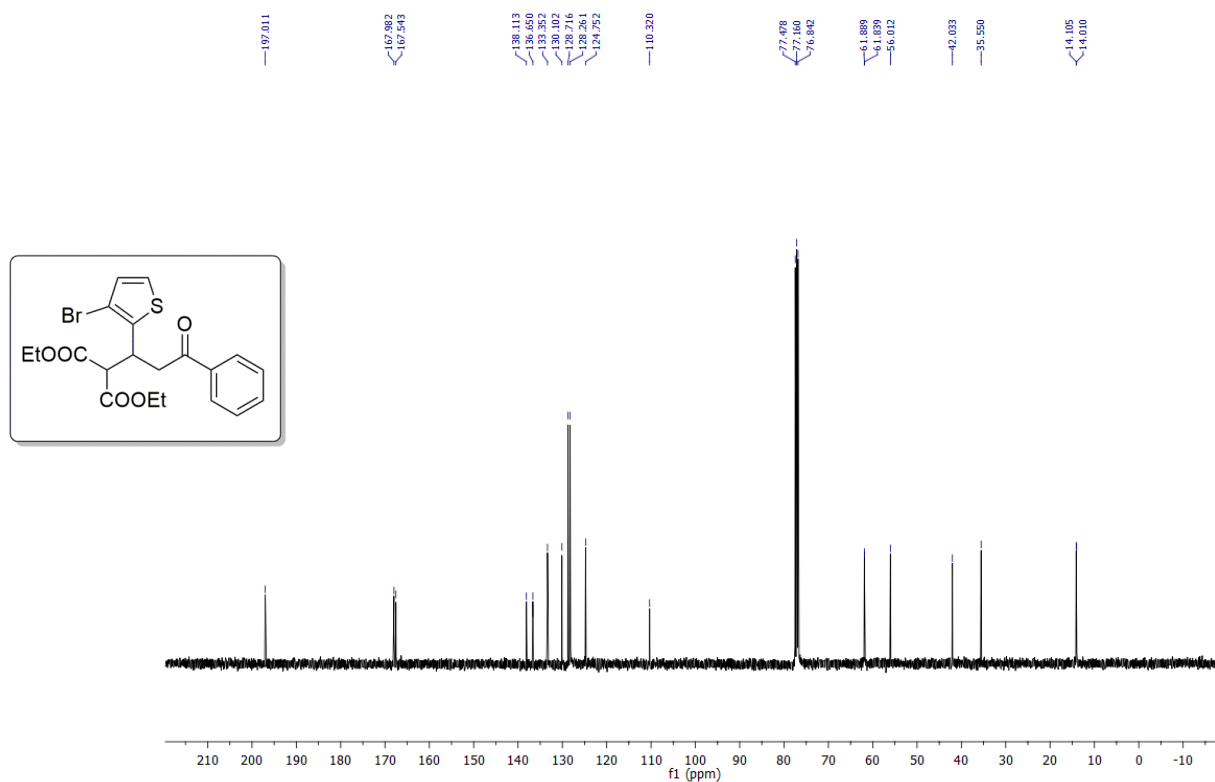


¹H NMR spectrum of **17m**

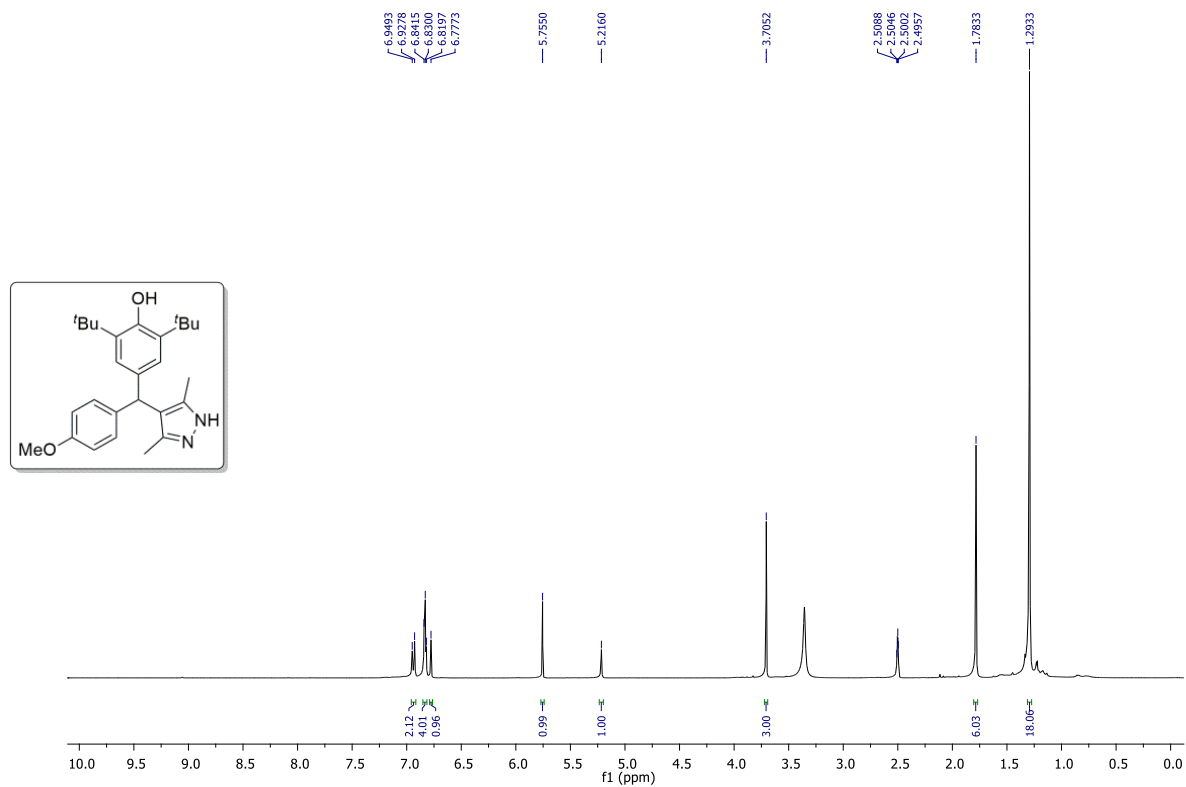


^{13}C NMR spectrum of **17m**¹H NMR spectrum of **17n**

¹³C NMR spectrum of **17n**



¹H NMR spectrum of **18**



¹³C NMR spectrum of **18**

