Supporting Information

N-Heterocyclic Carbene Ruthenium Complexes Synthesized by Hydrogen-Bonding-Assisted Strategy for Dehydrogenative Rearrangement of Esters

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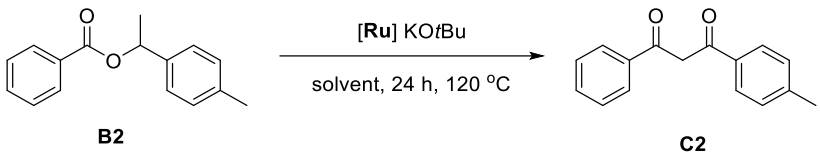
Catalogue

1. General Information

All esters used in the reactions are synthesized except for **B20**. All reactions and manipulations with air sensitive compounds being present were performed under dry nitrogen (N_2 5.0). All solvents were dried over $MgSO_4$. Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers and used without further purification. ^{1}H Nuclear Magnetic Resonance (^{1}H NMR) and ^{13}C Nuclear Magnetic Resonance (^{13}C NMR) spectra were recorded on a Bruker Avance 400 MHz spectrometer. High resolution mass spectrometry (HRMS) were recorded on a Waters UPLC G2-XS Qtof spectrometer using Electron Spray Ionization (ESI). In situ IR spectra were recorded on a METTLER TOLEDO ReactIR 702L.

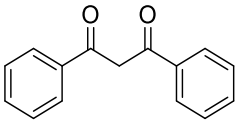
2. General steps for dehydrogenation rearrangement of esters

2.1 Experimental operation



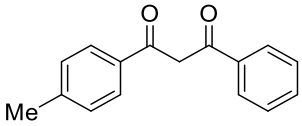
In a nitrogen-filled and oven-dried pressure tube (38 mL volume) equipped with a magnetic stirrer were added 1-(p-tolyl)ethyl benzoate (**B2** 1 mmol), **Cat 1** (0.01 mmol), KO*t*Bu (1.2 mmol), 2-MeTHF(2 mL). Then the seal tube was closed tightly with a teflon cap and stir the resulting mixture at 120 °C. After design time the reaction was cooled, quenched with HCl (500 μL) and ethyl acetate (10 mL). The reaction mixture was dried over $MgSO_4$ and concentrated. Purification of the remainder by column chromatography on silica gel gave the corresponding product **C2** in the reported yield.

2.2 Characterization data of 1,3-diketone



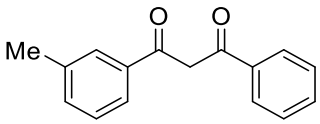
C1

(**C1**) 1,3-diphenylpropane-1,3-dione[1] (PE/EA = 50:1 DCM 2%): a white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 16.89 (s, 1H), 8.00 (m, 4H), 7.58-7.48 (m, 6H), 6.87 (s, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 185.8, 135.6, 132.6, 128.8, 127.3, 93.2.



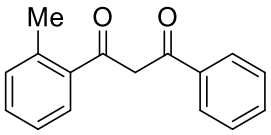
C2

(**C2**) 1-phenyl-3-(p-tolyl)propane-1,3-dione[1] (PE/EA = 50:1 DCM 2%): a white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 16.84 (s, 1H), 7.99-7.97 (m, 4H), 7.90 (d, J = 8.2 Hz, 2H), 7.57-7.46 (m, 3H), 7.23 (d, J = 8.0, 2H), 2.37 (s, 1H) ; **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 186.1, 185.2, 143.3, 135.7, 132.9, 132.3, 129.4, 128.7, 127.3, 127.1, 92.9, 21.7.



C3

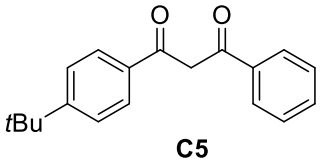
(**C3**) 1-phenyl-3-(m-tolyl)propane-1,3-dione[1] (PE/EA = 50:1 DCM 2%): a white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 16.83 (s, 1H), 7.90-7.67 (m, 4H), 7.44-7.25 (m, 5H), 6.74 (s, 1H), 2.33 (s, 3H) ; **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 186.1, 185.7, 138.5, 135.6, 135.5, 133.3, 132.5, 128.7, 128.6, 127.8, 127.2, 124.4, 93.2, 21.5.



C4

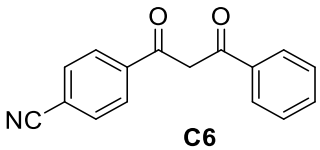
(**C4**) 1-phenyl-3-(o-tolyl)propane-1,3-dione[1] (PE/EA = 50:1 DCM 2%): a white solid; **^{1}H**

NMR (400 MHz, $CDCl_3$): δ 16.59 (s, 1H), 7.90-7.67 (m, 4H), 7.44-7.25 (m, 5H), 6.74 (s, 1H), 2.33 (s, 3H) ; **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 186.1, 185.7, 138.5, 135.6, 135.5, 133.3, 132.5, 128.7, 128.6, 127.8, 127.2, 124.4, 93.2, 21.5.



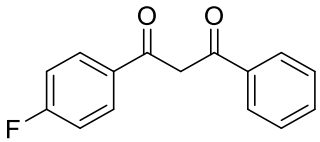
C5

(**C5**) 1-(4-(*tert*-butyl)phenyl)-3-phenylpropane-1,3-dione[1] (PE/EA = 50:1 DCM 2%): a white solid (196 mg, 70%); **^1H NMR (400 MHz, $CDCl_3$):** δ 16.85 (s, 1H), 7.91-7.84 (m, 4H), 7.47-7.39 (m, 5H), 6.77 (s, 1H), 1.28 (s, 9H) ; **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 186.0, 185.4, 156.3, 135.7, 132.8, 132.4, 128.7, 127.2, 127.1, 125.7, 93.0, 35.2, 31.2.



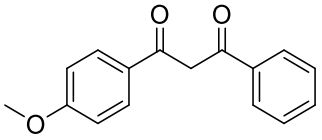
C6

(**C6**) 4-(3-oxo-3-phenylpropanoyl)benzonitrile (PE/EA = 50:1 DCM 2%)[1]: a white solid; **^1H NMR (400 MHz, $CDCl_3$):** δ 16.69 (s, 1H), 8.08-7.99 (m, 4H), 7.79-7.77 (m, 2H), 7.62-7.49, (m, 3H), 6.86 (s, 1H); **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 187.6, 182.2, 139.3, 135.2, 133.1, 132.5, 128.9, 127.6, 127.4, 118.1, 115.5, 93.9.



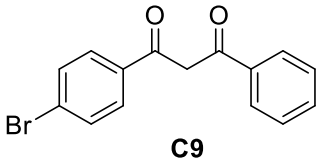
C7

(**C7**) 1-(4-fluorophenyl)-3-phenylpropane-1,3-dione[1] (PE/EA = 50:1 DCM 2%): a white solid; **^1H NMR (400 MHz, $CDCl_3$):** δ 16.86 (s, 1H), 8.03-7.97 (m, 4H), 7.57-7.48 (m, 3H), 7.19-7.15, (m, 2H), 6.81 (s, 1H); **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 185.2, 166.7, 164.2, 135.3, 132.5, 131.9, 129.7, 129.6, 128.7, 127.1, 116.0, 115.8, 92.9.



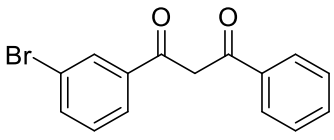
C8

(**C8**) 1-(4-methoxyphenyl)-3-phenylpropane-1,3-dione[1] (PE/EA = 50:1 DCM 2%): a white solid; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 16.99 (s, 1H), 7.99-7.96 (m, 4H), 7.54-7.48 (m, 3H), 7.00-6.97, (m, 2H), 6.80 (s, 1H), 3.89(s, 3H); **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 186.2, 184.1, 163.3, 135.6, 132.2, 129.3, 128.7, 128.3, 127.0,114.0, 92.4, 55.5.



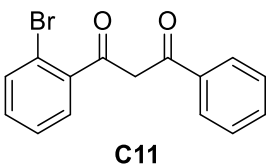
C9

(**C9**) 1-(4-bromophenyl)-3-phenylpropane-1,3-dione[1] (PE/EA = 50:1 DCM 2%): a white solid; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 16.81 (s, 1H), 8.01-7.84 (m, 4H), 7.64-7.50 (m, 5H), 6.82 (s, 1H); **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 186.0, 184.6, 135.3, 134.5, 132.7, 132.0, 128.8, 128.7,127.3, 127.2, 93.0.



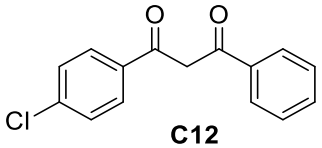
C10

(**C10**) 1-(3-bromophenyl)-3-phenylpropane-1,3-dione[1] (PE/EA = 50:1 DCM 2%): a white solid; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 16.74(s, 1H),8.12 (d, 1H), 8.01- 7.99 (m, 2H), 7.92 - 7.90 (m, 1H), 7.69-7.66 (m, 1H), 7.60-7.48 (m, 3H), 7.39- 7.35 (m, 1H), 6.81 (s, 1H) **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 186.1 184.1 137.6 135.2 132.5 130.3 130.2 128.7 127.2 125.7 122.9 93.3.



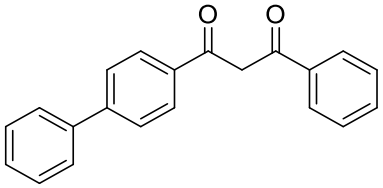
C11

(**C11**) 1-(2-bromophenyl)-3-phenylpropane-1,3-dione [1] (PE/EA = 50:1 DCM 2%): a white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 16.90 (s, 1H), 8.01-7.99 (m, 4H), 7.56-7.48 (m, 5H), 6.87 (s, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 194.3, 185.8, 135.6, 133.8, 132.5, 129.7, 128.9, 128.8,128.6, 128.5, 128.4, 127.2, 93.2.



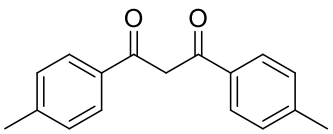
C12

(**C12**) 1-(4-chlorophenyl)-3-phenylpropane-1,3-dione[1] (PE/EA = 50:1 DCM 2%): a white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 16.83 (s, 1H), 7.99-7.92 (m, 4H), 7.59-7.44 (m, 5H), 6.82 (s, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 185.9, 184.6, 138.8, 135.3, 134.0, 132.7, 129.1, 128.8,128.6, 127.2, 93.1.



C14

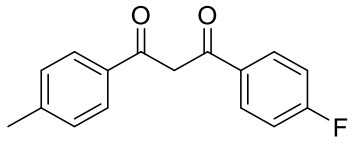
(**C14**) 1-([1,1'-biphenyl]-4-yl)-3-phenylpropane-1,3-dione[1] (PE/EA = 50:1 DCM 2%): a white solid; **^{1}H NMR (400 MHz, DMSO-d_6):** δ 17.23 (s, 1H), 8.28-8.19 (m, 4H), 7.89-7.87 (m, 2H), 7.81-7.80(m, 2H), 7.68-7.64(m, 1H), 7.60-7.56(m, 2H), 7.52-7.50(m, 2H), 7.46-7.43(m, 2H), 4.92 (s, 1H); **^{13}C{^{1}H} NMR (100 MHz, DMSO-d_6)** δ 185.8, 185.3, 145.0, 139.3, 136.1, 135.1, 133.9, 129.6, 129.4, 128.9, 128.6, 127.9, 127.5, 93.8.



C15

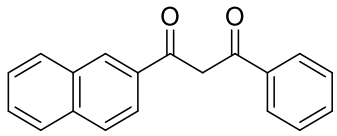
(**C15**) 1,3-di-*p*-tolylpropane-1,3-dione[1] (PE/EA = 50:1 DCM 2%): a white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 16.97 (s, 1H), 7.90-7.88 (m, 4H), 7.30-7.28 (m, 4H), 6.81 (s, 1H), 2.43(s,

6H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 185.5, 143.2, 132.9, 129.5, 127.2, 92.5, 21.7.



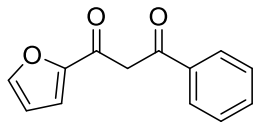
C16

(**C16**) $1\lambda^{1},16\lambda^{1}$-hexadeca-2,4,6,8,10,12,14-heptayne [1] (PE/EA = 50:1 DCM 2%): a white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 16.92 (s, 1H), 8.02-7.99 (m, 2H), 7.90-7.88 (m, 2H), 7.30-7.14(m, 4H), 6.78 (s, 1H), 2.43(s, 3H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 185.5, 184.6, 166.6, 164.1, 143.4, 132.6, 129.6, 129.5, 127.2, 115.9, 92.5, 21.7.



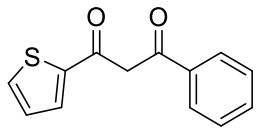
C17

(**C17**) 1-(naphthalen-2-yl)-3-phenylpropane-1,3-dione[1] (PE/EA = 50:1 DCM 2%): a white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 16.97 (s, 1H), 8.55(s, 1H), 8.06-7.95 (m, 6H), 7.62-7.50 (m, 5H), 7.02 (s, 1H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 185.8, 185.6, 135.7, 135.4, 132.8, 132.5, 129.4, 128.7, 128.5, 128.4, 128.2, 127.8, 127.2, 126.8, 123.3, 93.5.



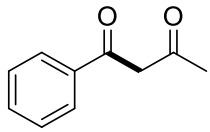
C18

(**C18**) 1-(furan-2-yl)-3-phenylpropane-1,3-dione[1] (PE/EA = 50:1 DCM 2%): a white solid; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 16.20 (s, 1H), 7.99-7.97 (m, 2H), 7.64-7.48 (m, 4H), 7.27 (s, 1H), 6.61-6.60(m, 1H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 182.5, 177.7, 151.1, 146.1, 134.7, 132.4, 128.7, 127.0, 115.8, 112.7, 92.7.



C19

(**C19**) 1-phenyl-3-(thiophen-2-yl)propane-1,3-dione[1] (PE/EA = 50:1 DCM 2%): a white solid; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 16.32 (s, 1H), 7.95-7.94 (m, 2H), 7.82-7.81 (m, 1H), 7.65-7.63 (m, 1H), 7.56-7.46 (m, 3H), 7.18-7.16 (m, 1H), 6.69 (s, 1H); **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 183.0, 180.8, 142.3, 134.5, 132.7, 132.3, 130.4, 128.7, 128.4, 126.9, 93.2.



C20

(**C20**) 1-phenylbutane-1,3-dione[2] (PE/EA = 50:1 DCM 2%): a yellow oil; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 16.16 (s, 1H), 7.89-7.87 (m, 2H), 7.54-7.43 (m, 3H), 6.18 (s, 1H), 2.21(s, 3H); **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 193.8, 183.4, 134.9, 132.3, 128.6, 127.0, 96.7, 25.9.

2.3 NMR spectrum of 1,3-diketone

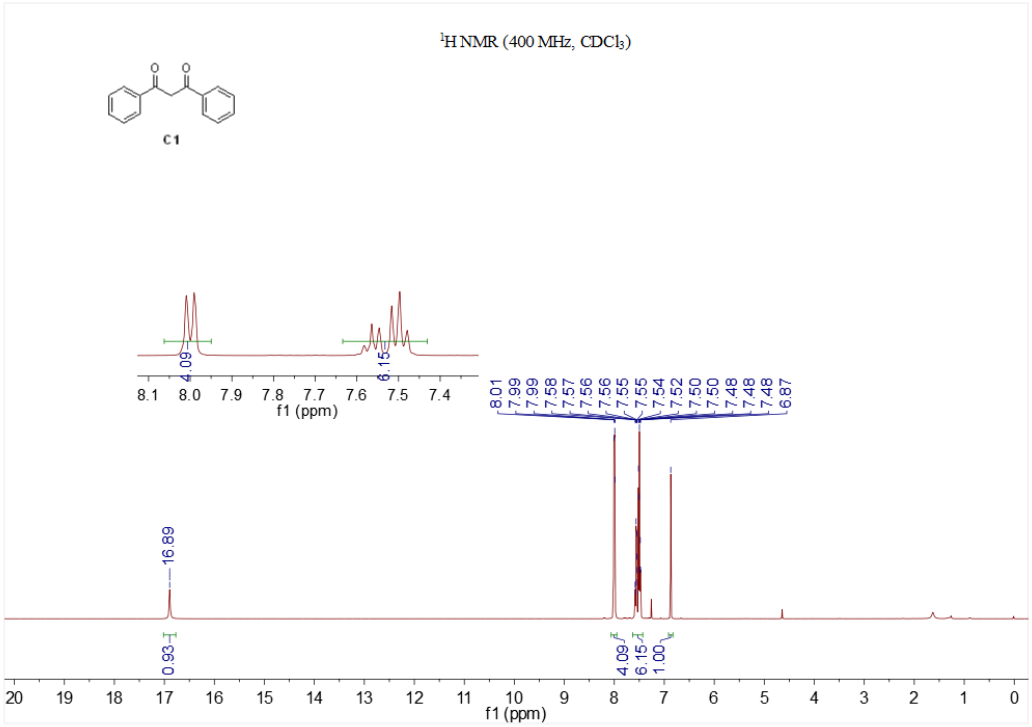


Figure S1. ^{1}H NMR spectra of **C1**

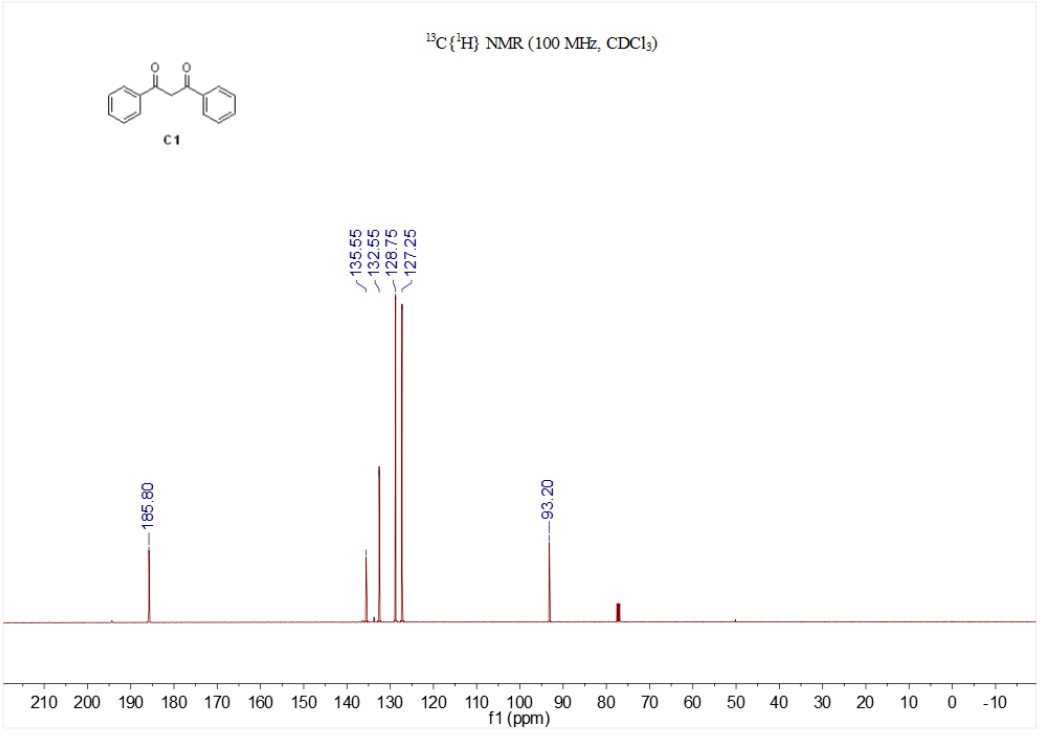


Figure S2. ^{13}C{^{1}H} NMR spectra of **C1**

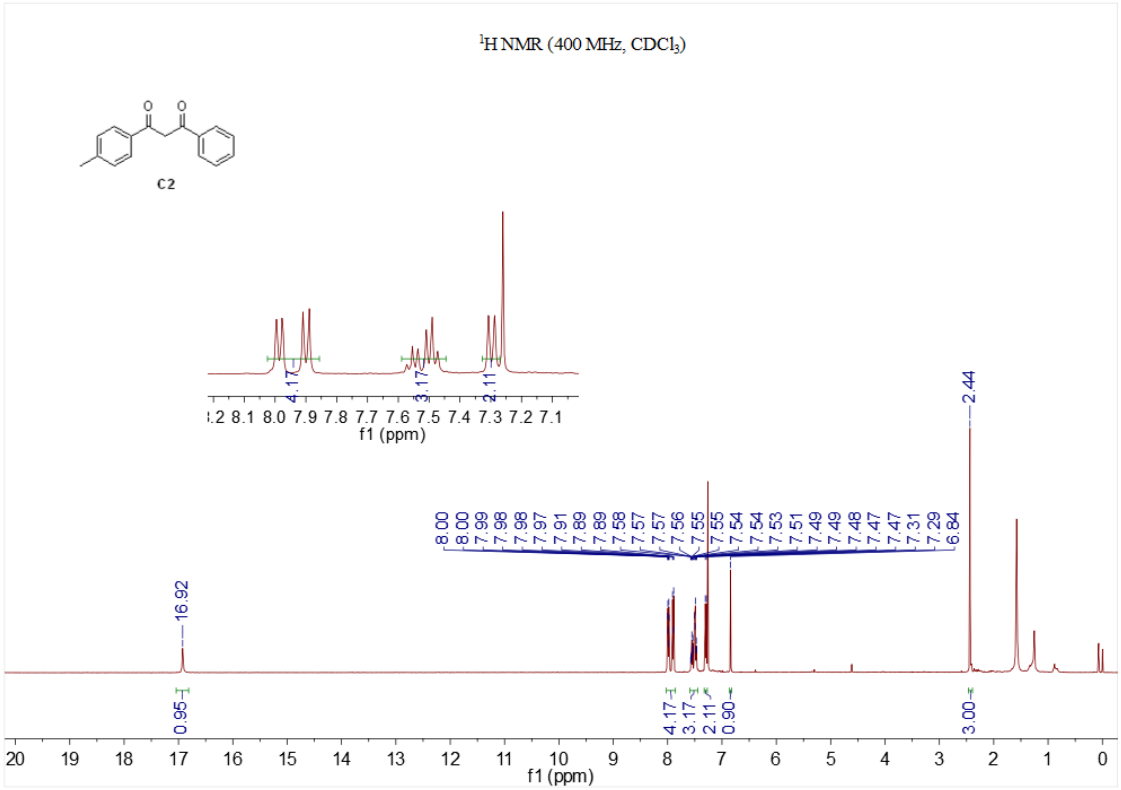


Figure S3. ^{1}H NMR spectra of **C2**

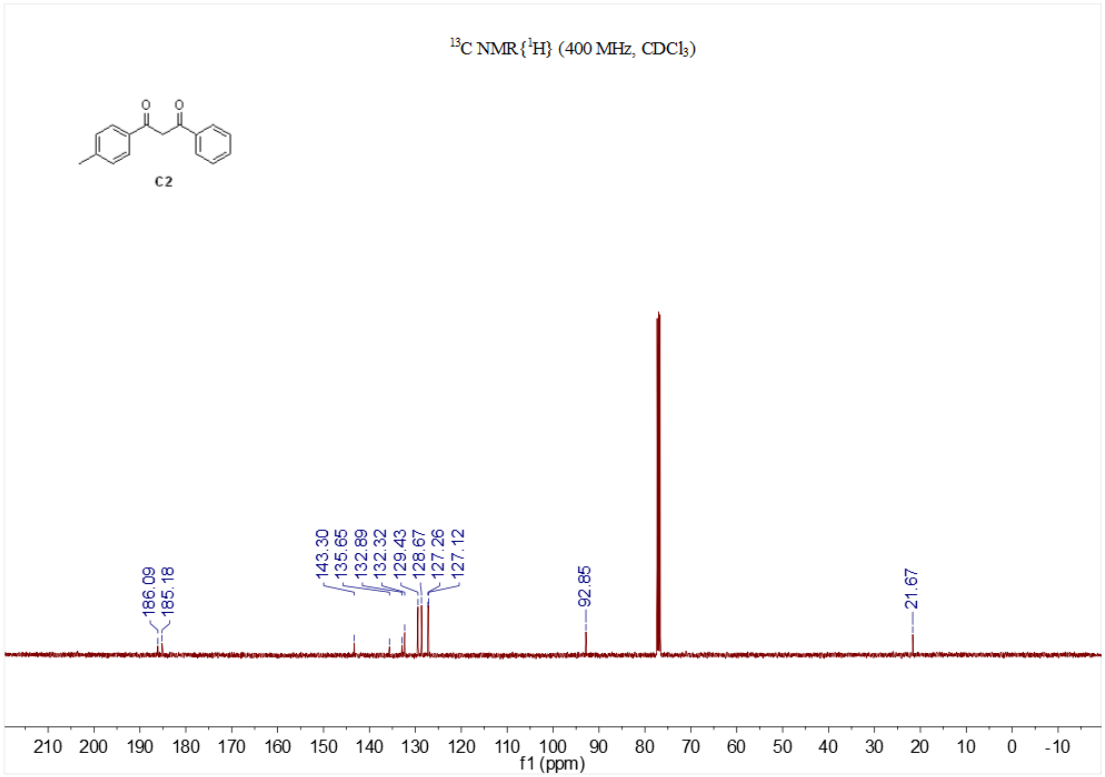


Figure S4. ^{13}C{^{1}H} NMR spectra of **C2**

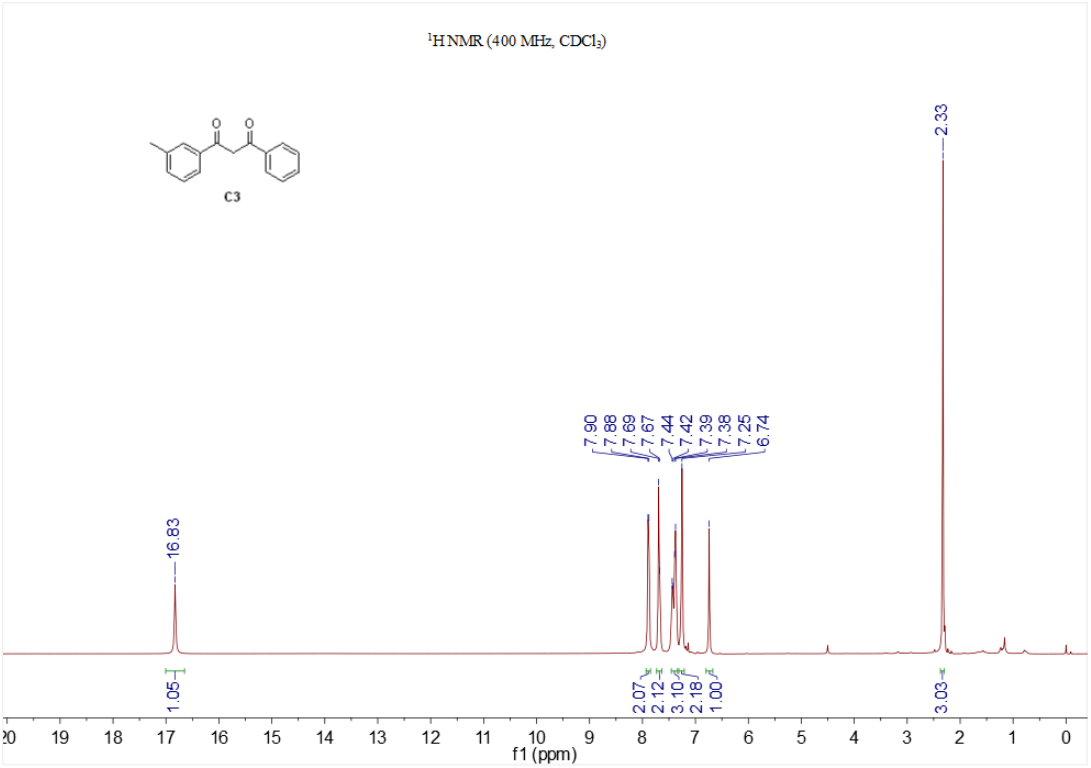


Figure S5. ^{1}H NMR spectra of **C3**

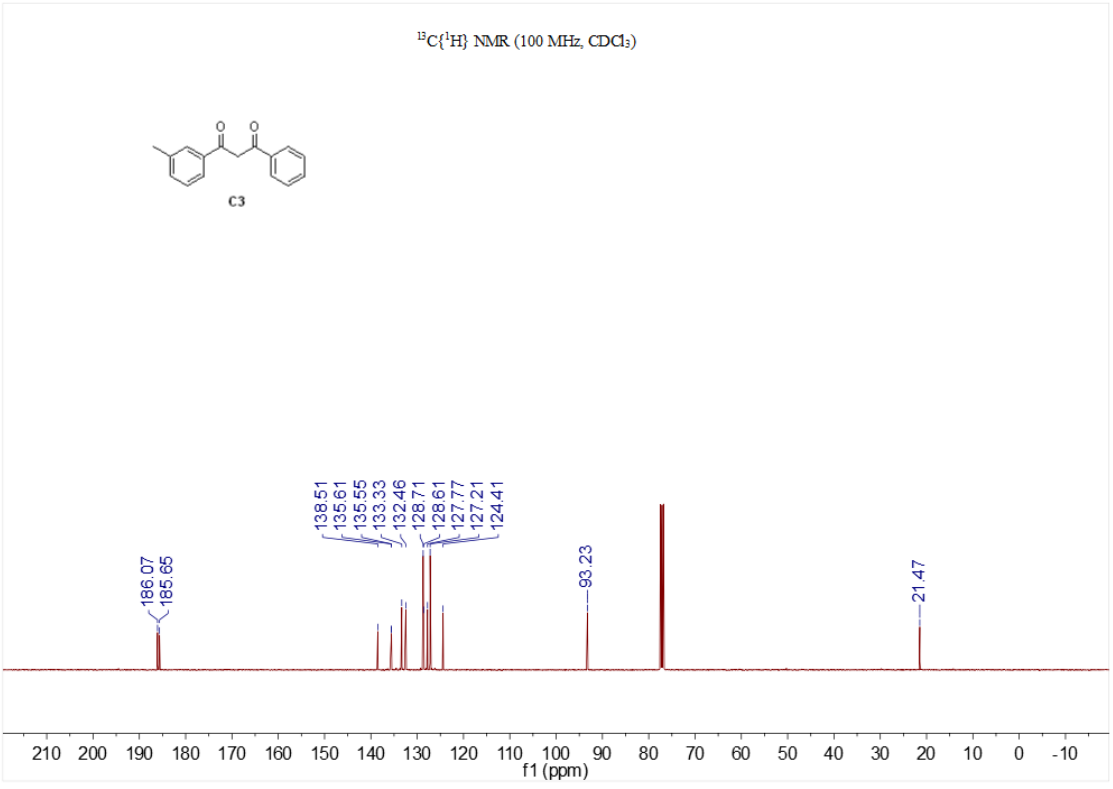


Figure S6. ^{13}C{^{1}H} NMR spectra of **C3**

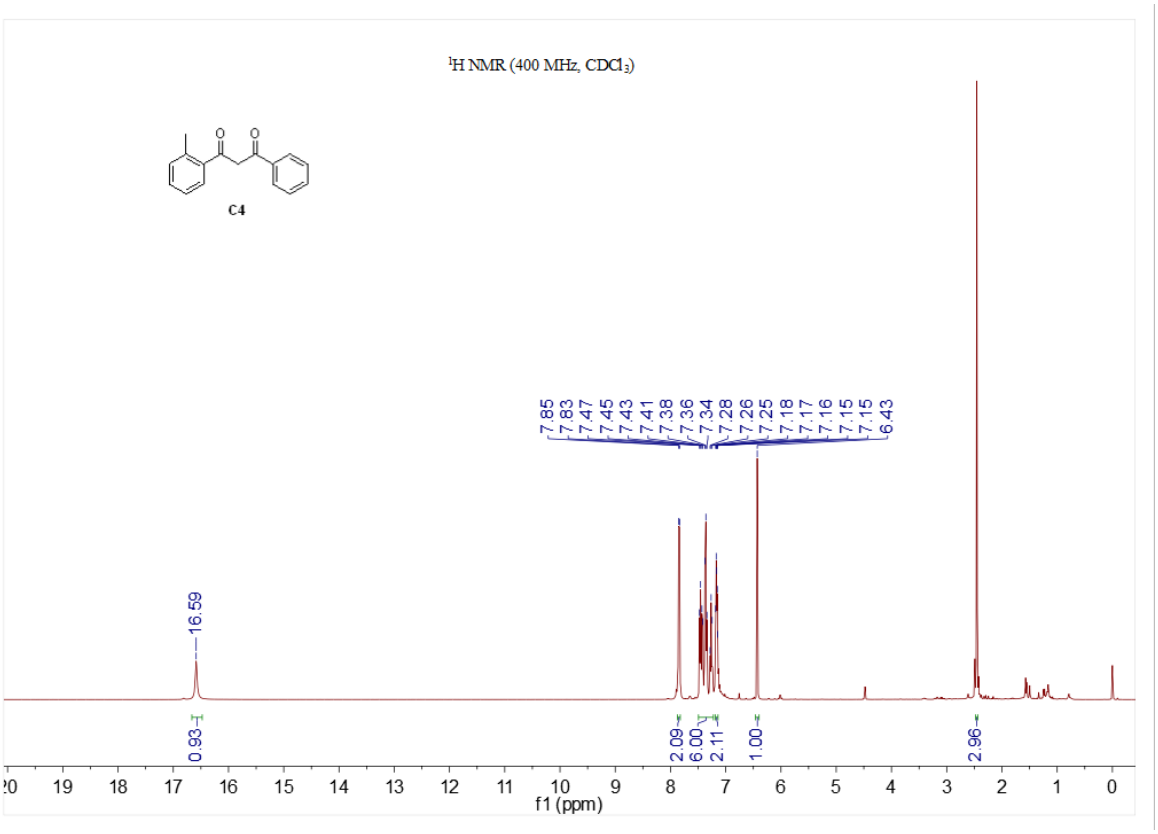


Figure S7. ^{1}H NMR spectra of **C4**

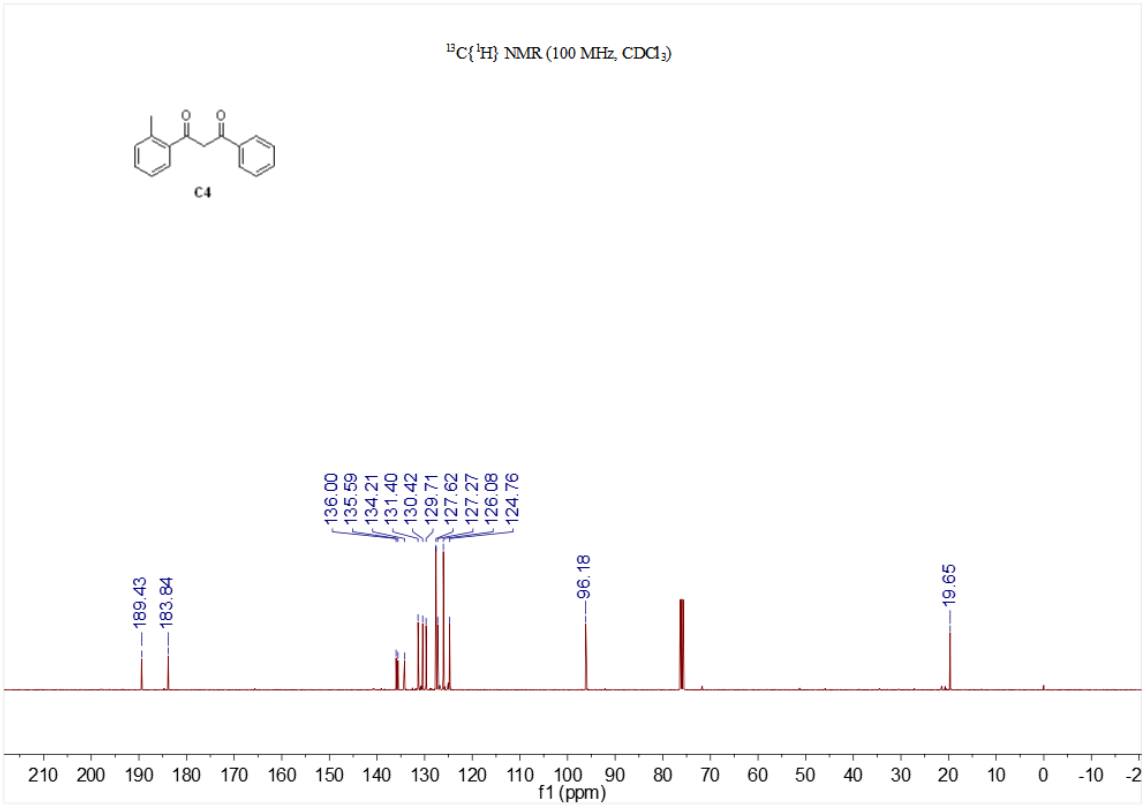


Figure S8. ^{13}C{^{1}H} NMR spectra of **C4**

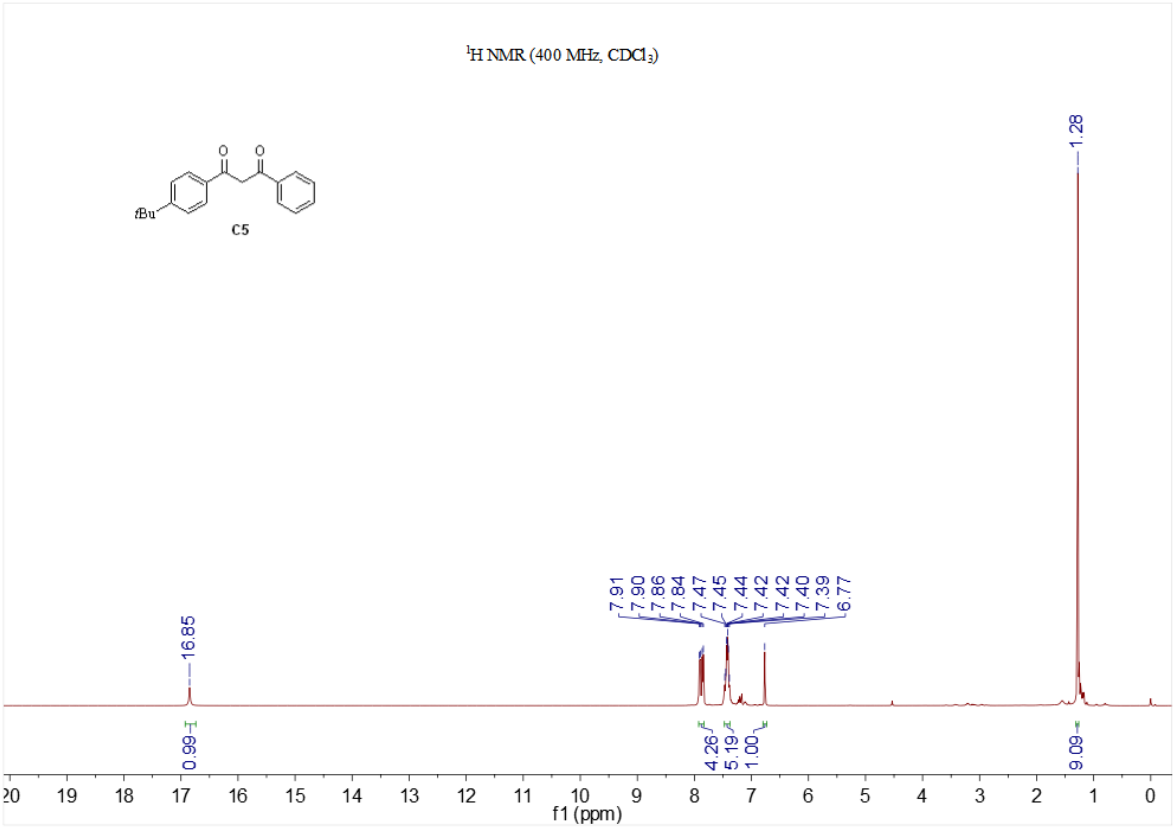


Figure S9. ^{1}H NMR spectra of **C5**

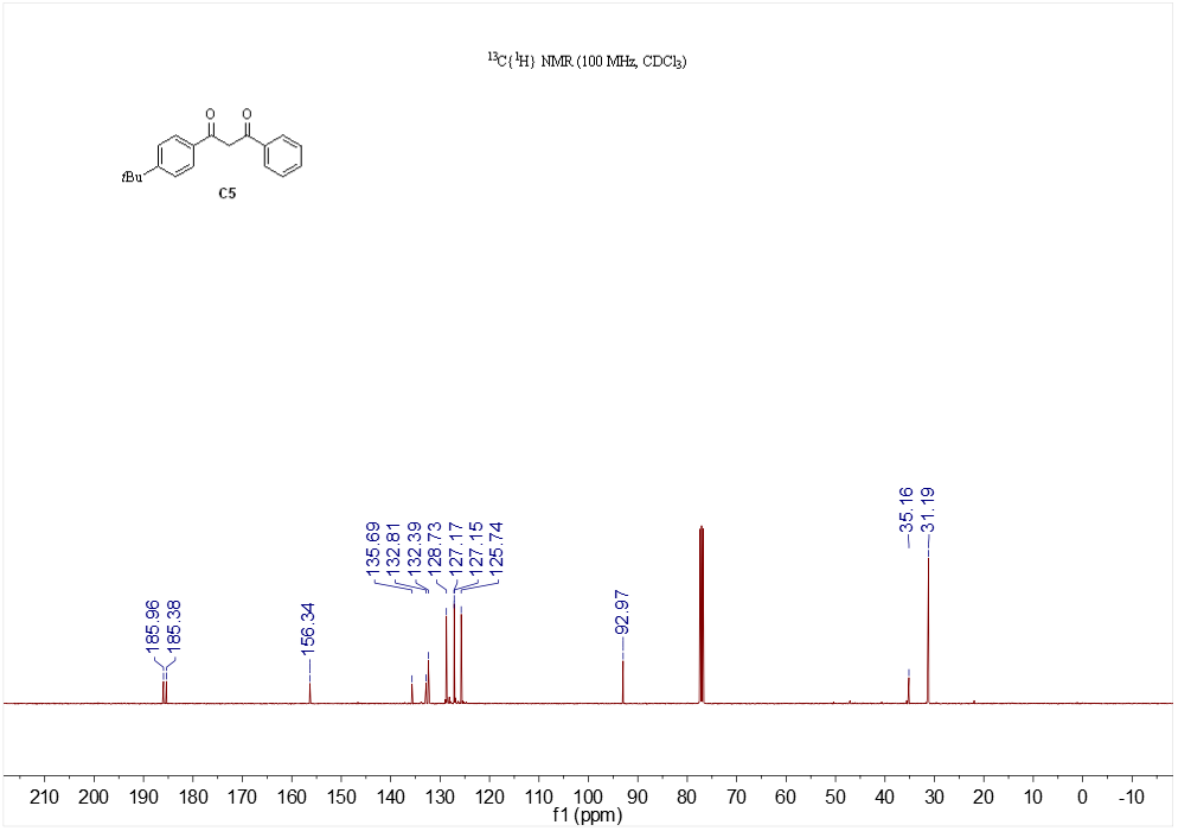


Figure S10. ^{13}C{^{1}H} NMR spectra of **C5**

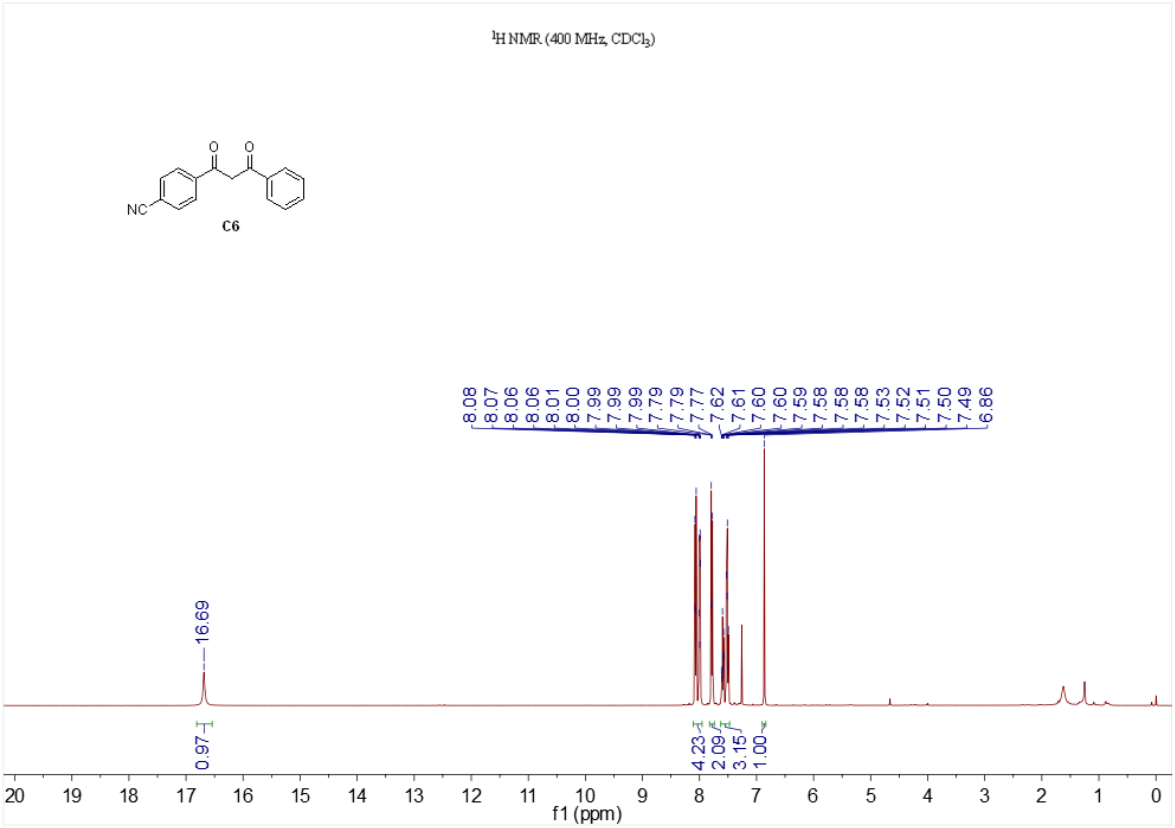


Figure S11. ^{1}H NMR spectra of **C6**

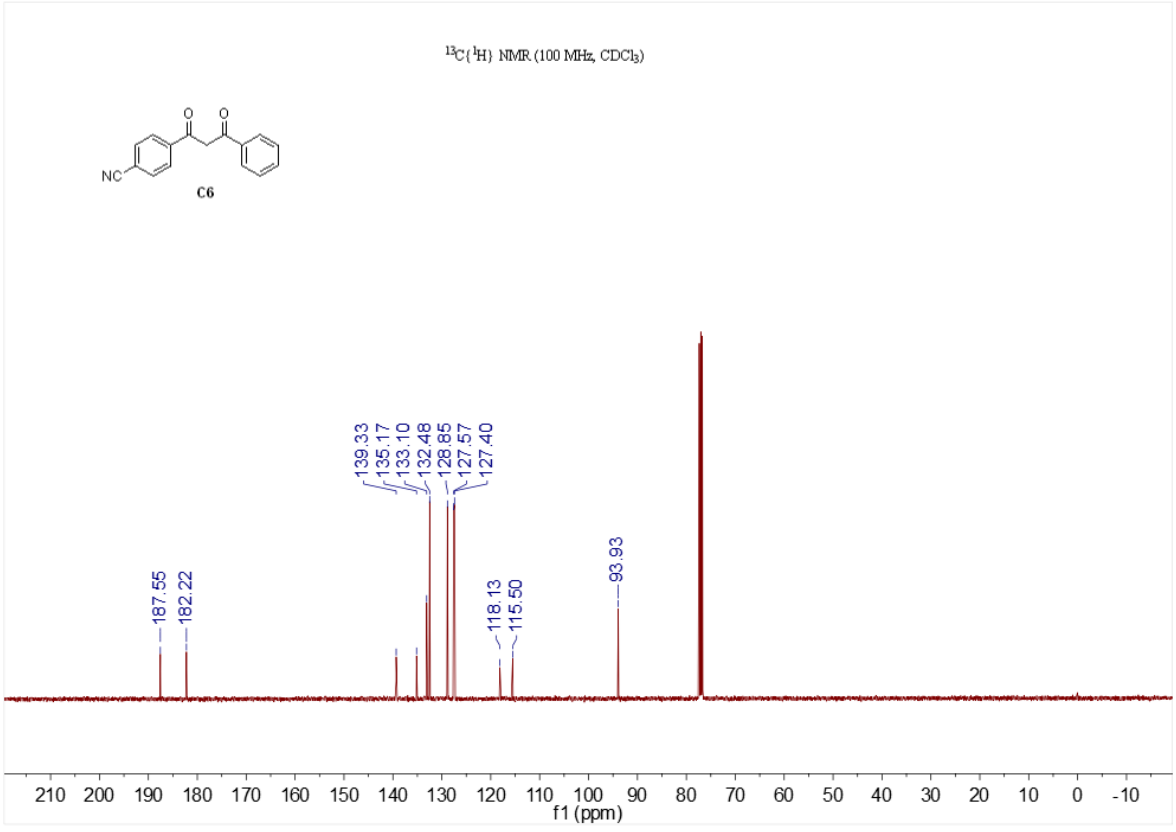


Figure S12. ^{13}C{^{1}H} NMR spectra of **C6**

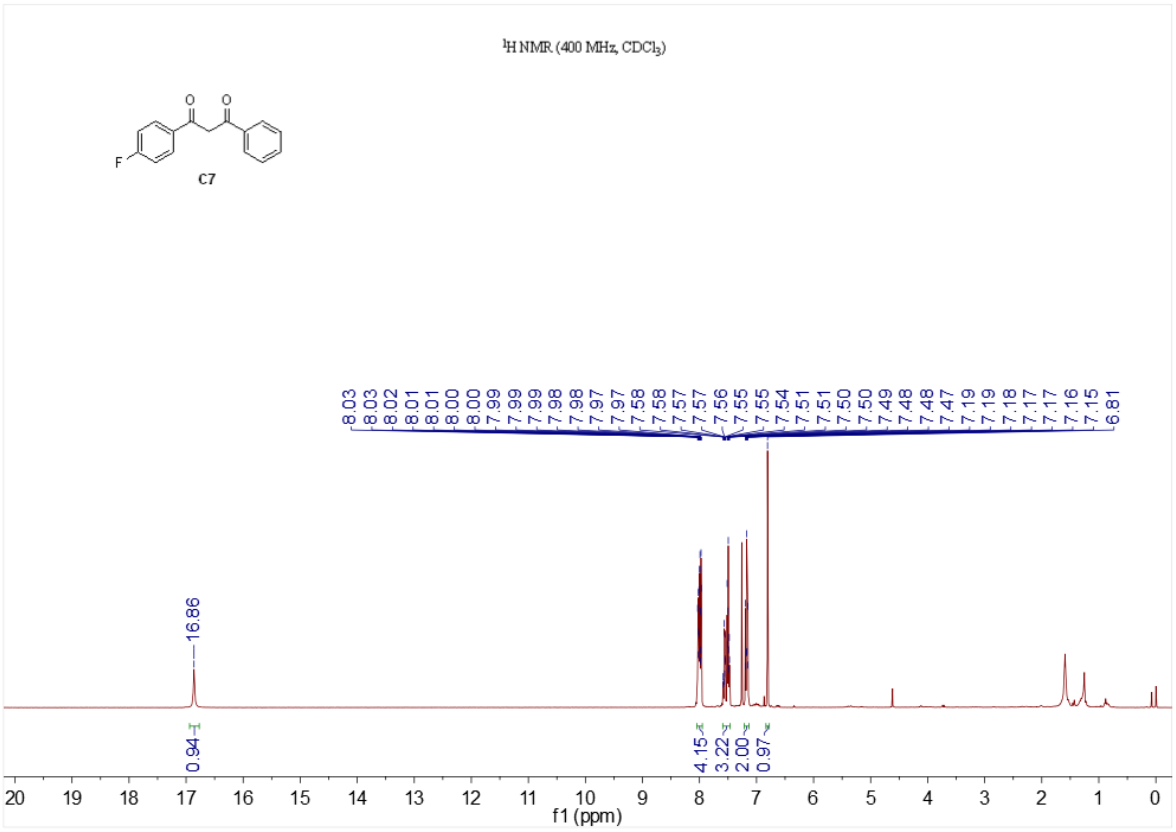


Figure S13. ^{1}H NMR spectra of **C7**

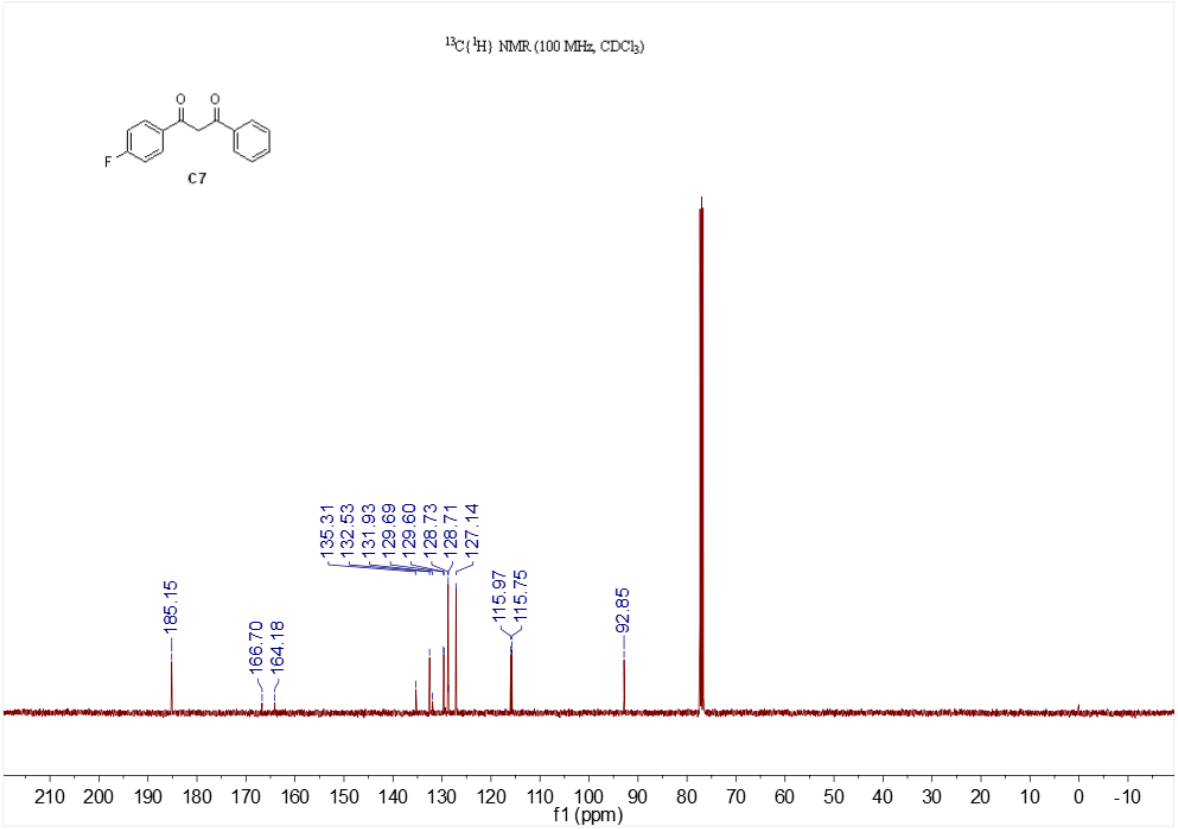


Figure S14. ^{13}C{^{1}H} NMR spectra of **C7**

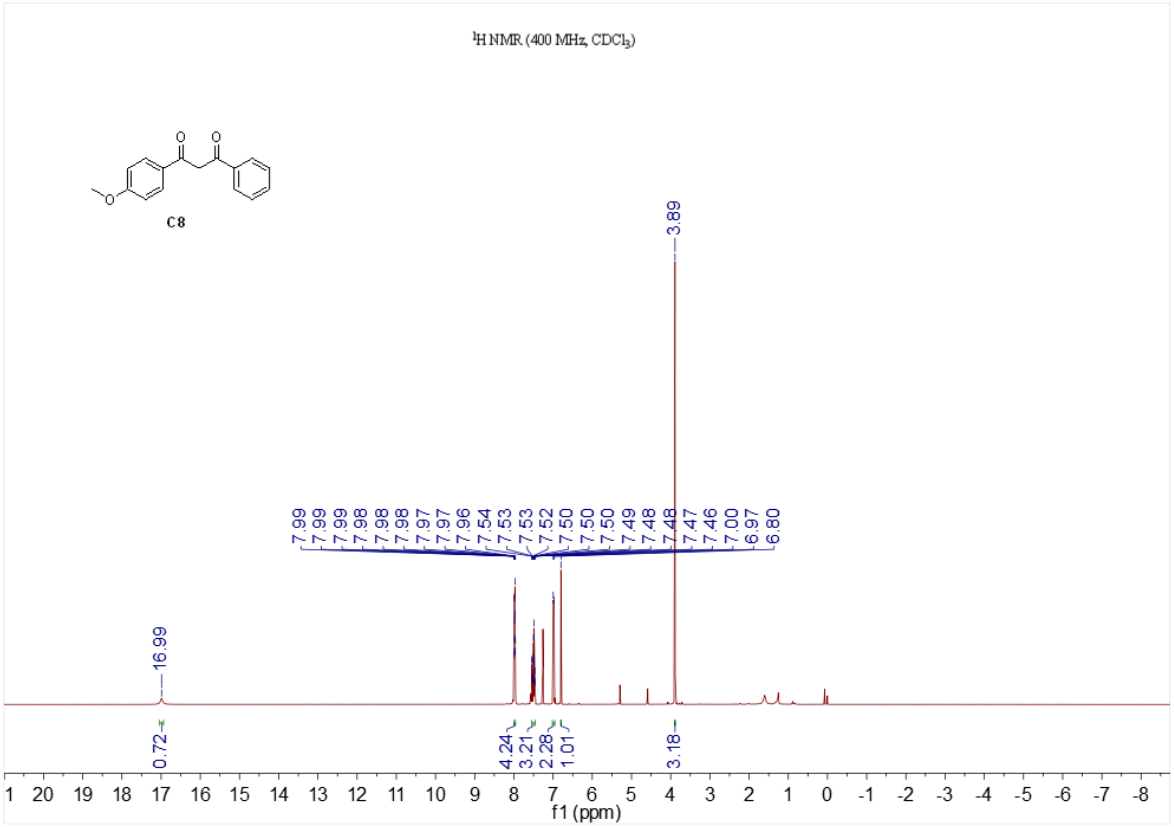


Figure S15. ^{1}H NMR spectra of **C8**

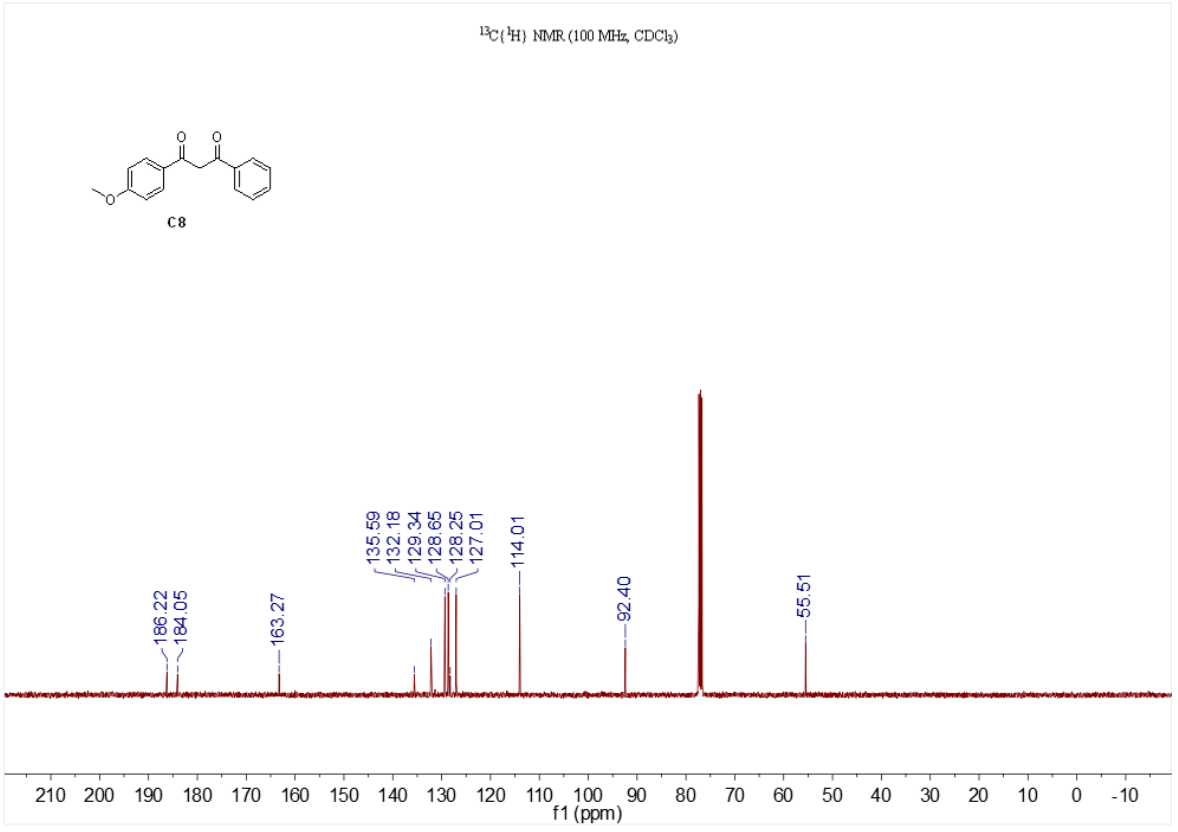


Figure S16. ^{13}C{^{1}H} NMR spectra of **C8**

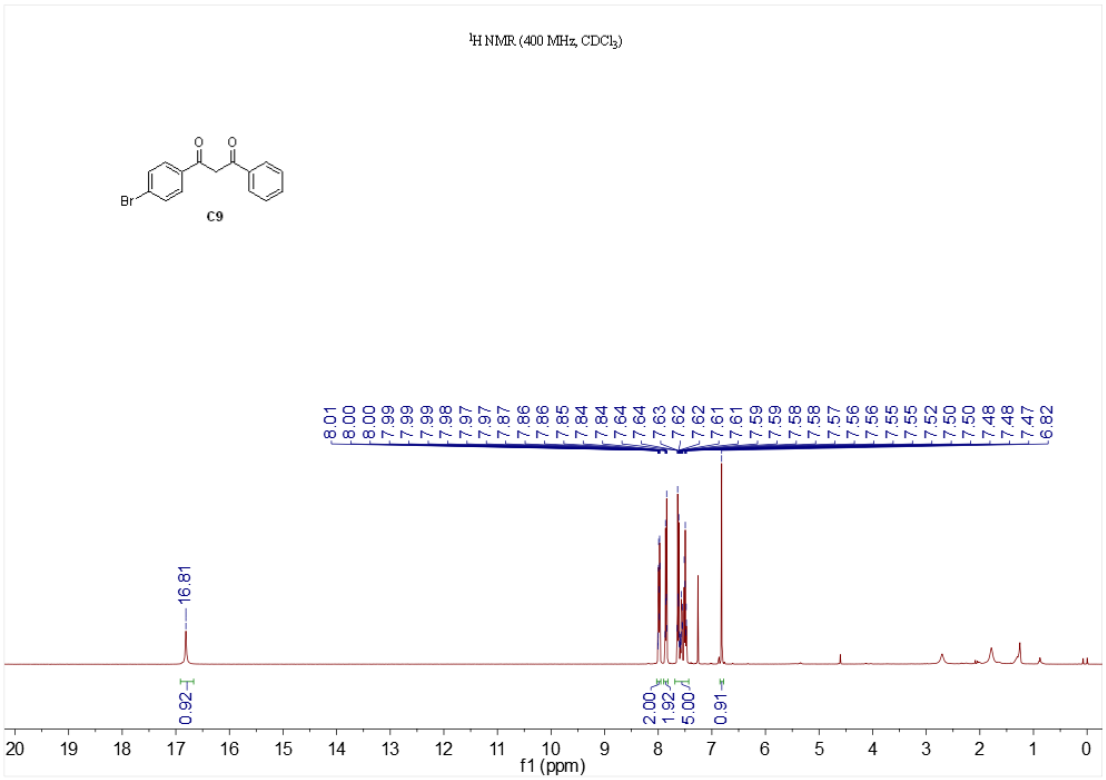


Figure S17. ^{1}H NMR spectra of **C9**

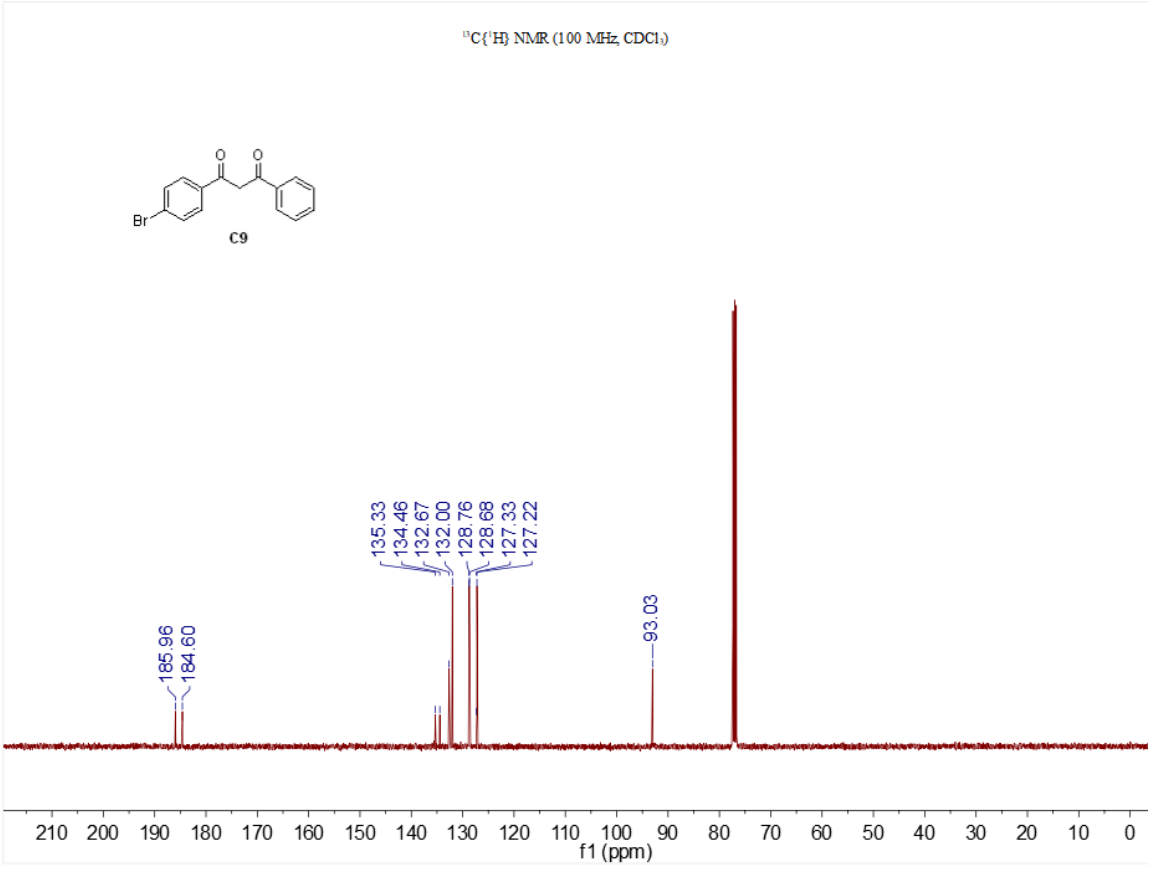


Figure S18. ^{13}C{^{1}H} NMR spectra of **C9**

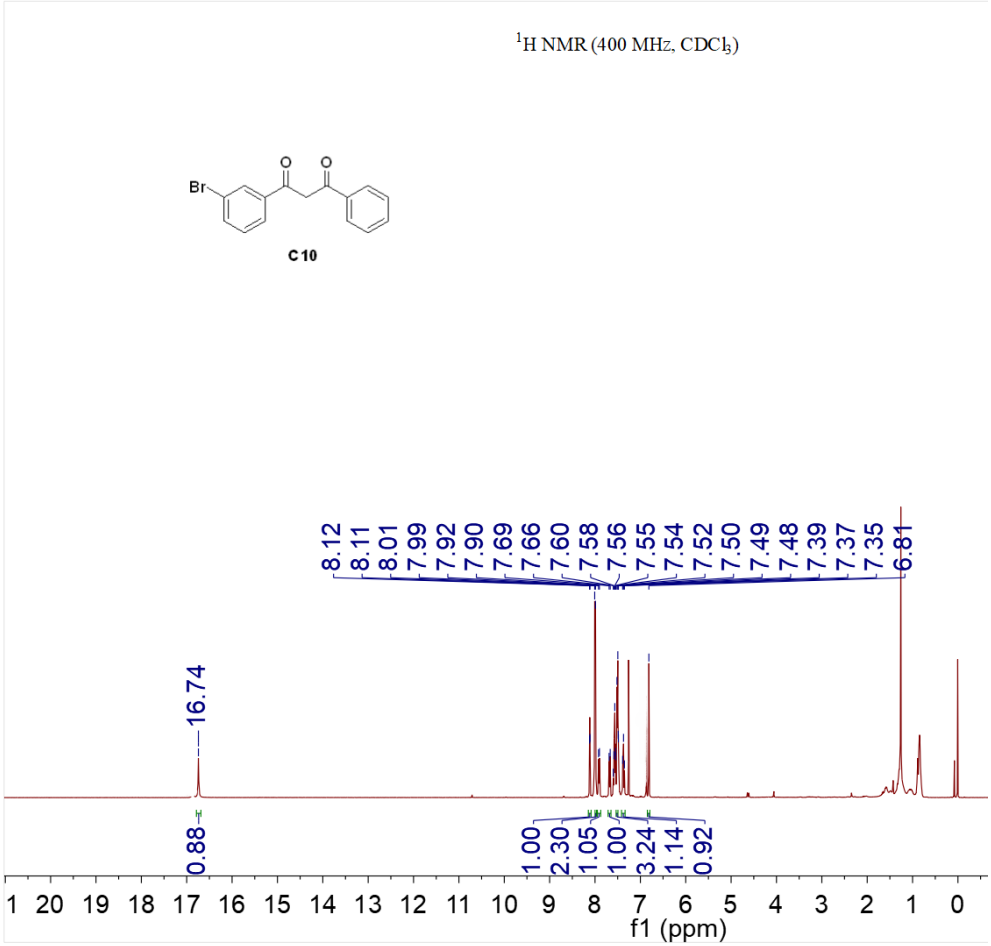


Figure S19. ^{1}H NMR spectra of **C10**

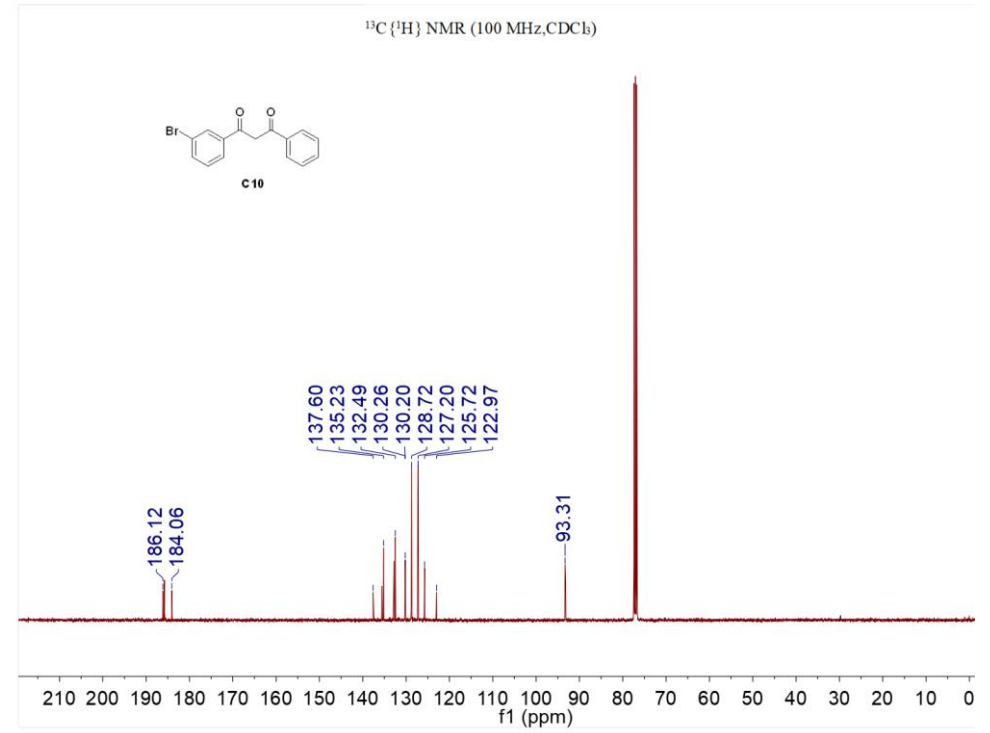


Figure S20. ^{13}C{^{1}H} NMR spectra of **C10**

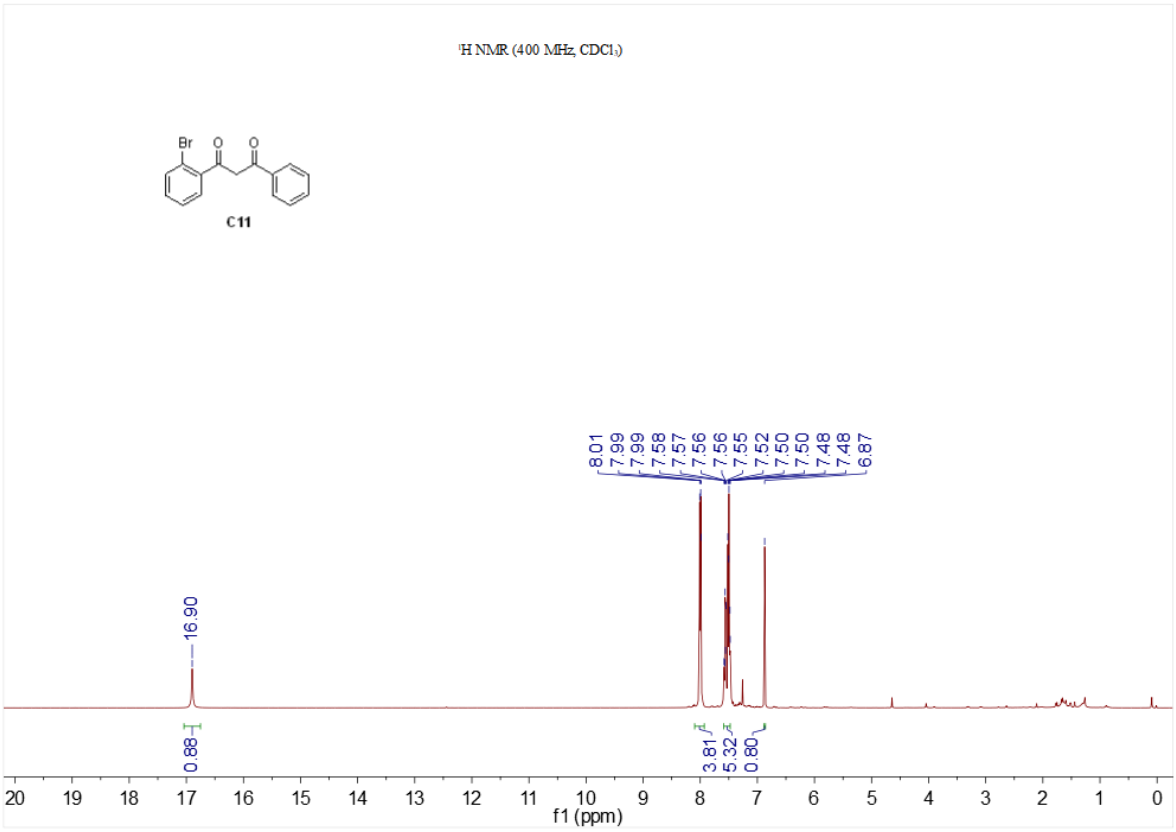


Figure S21. ^{1}H NMR spectra of **C11**

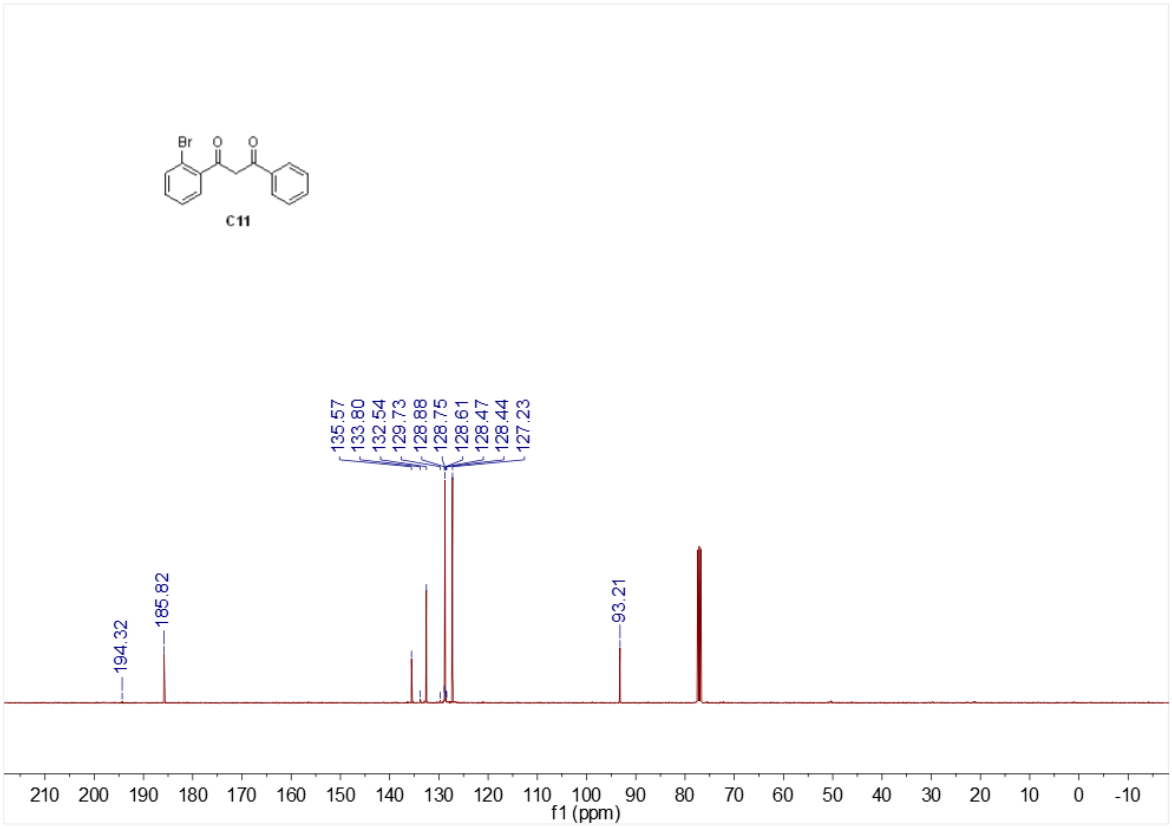


Figure S22. ^{13}C{^{1}H} NMR spectra of **C11**

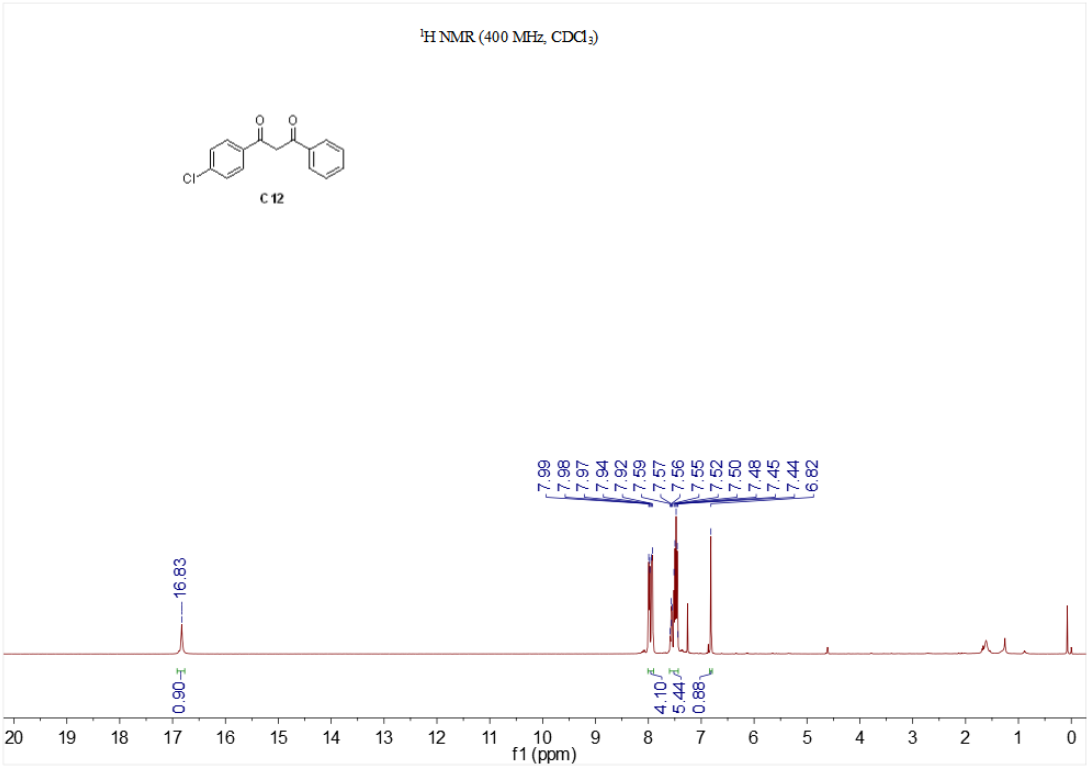


Figure S23. ^{1}H NMR spectra of **C12**

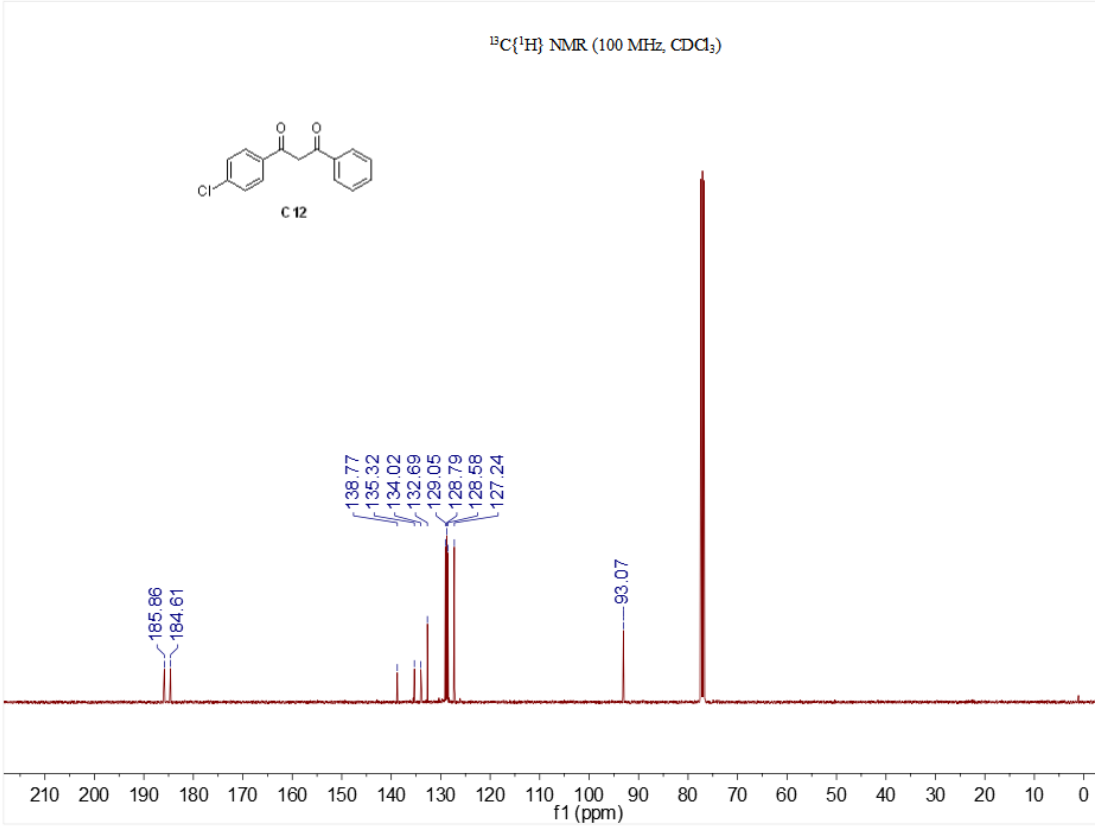


Figure S24. ^{13}C{^{1}H} NMR spectra of **C12**

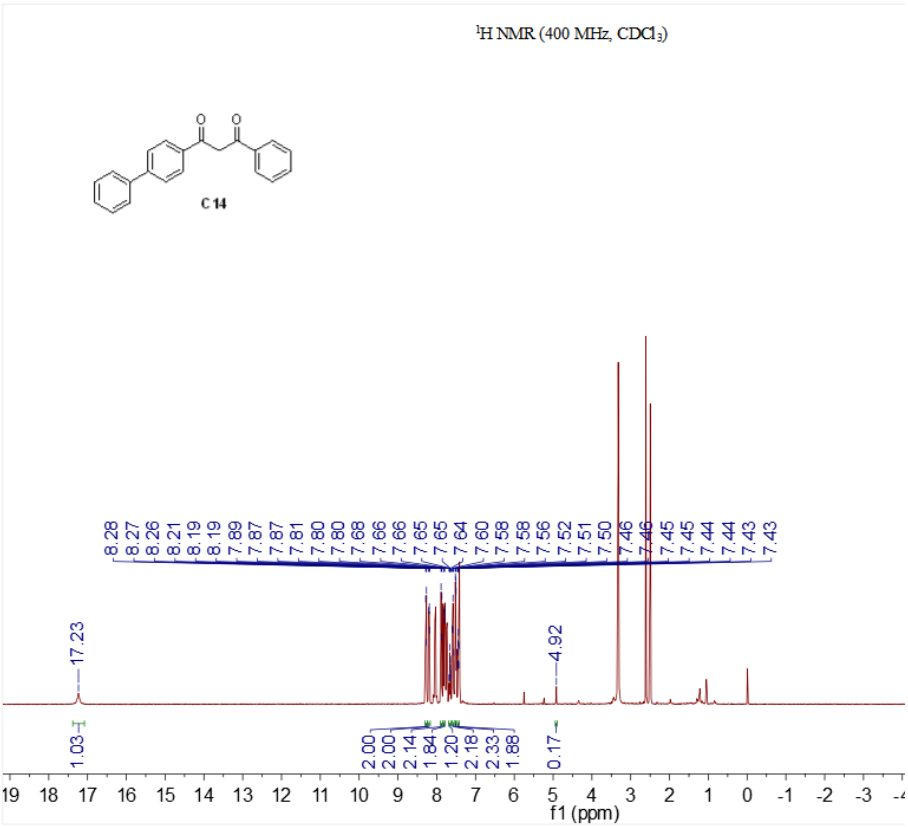


Figure S25. ^{1}H NMR spectra of **C14**

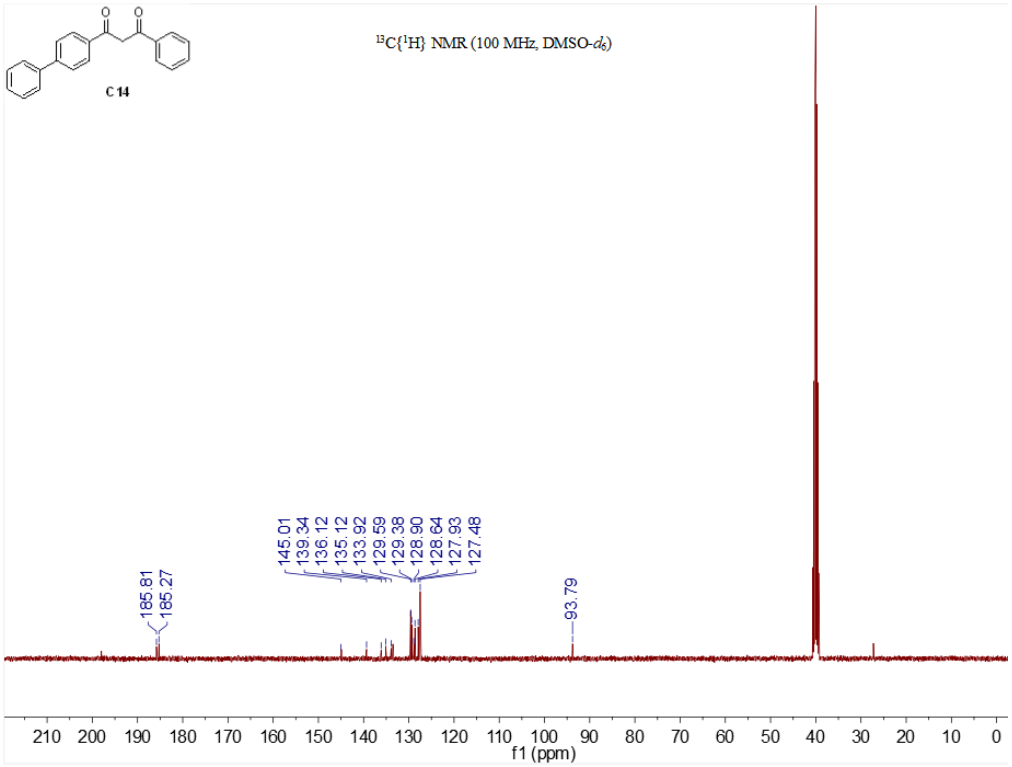


Figure S26. ^{13}C{^{1}H} NMR spectra of **C14**

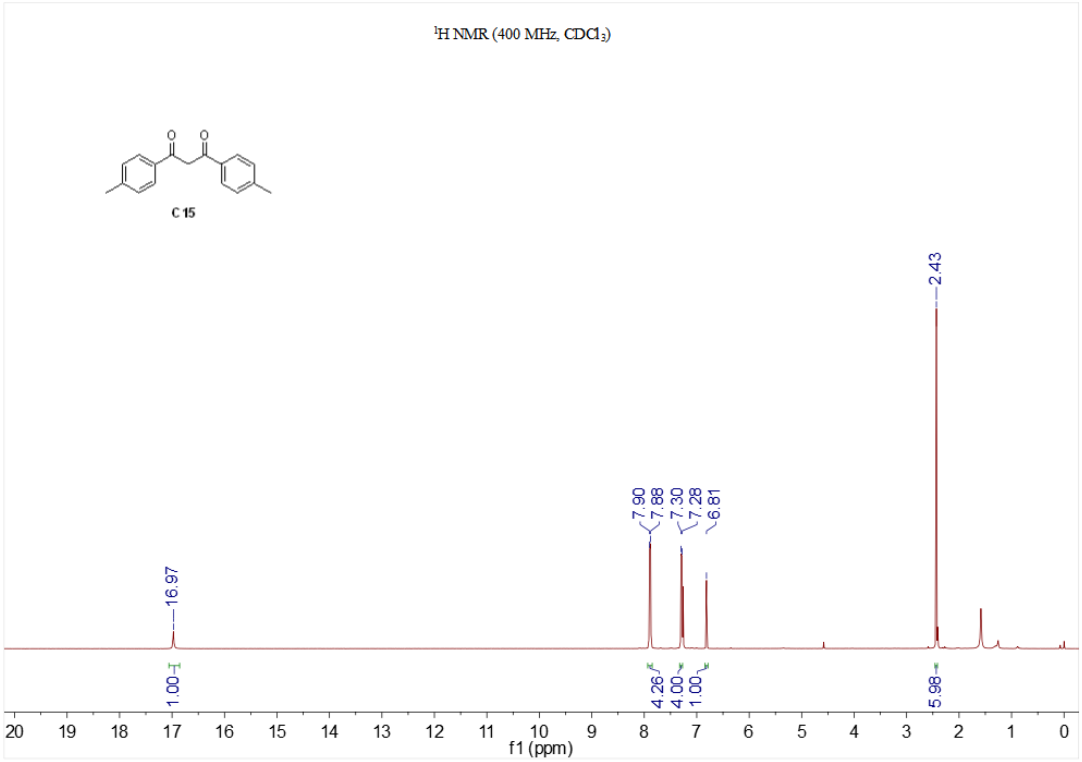


Figure S27. ^{1}H NMR spectra of **C15**

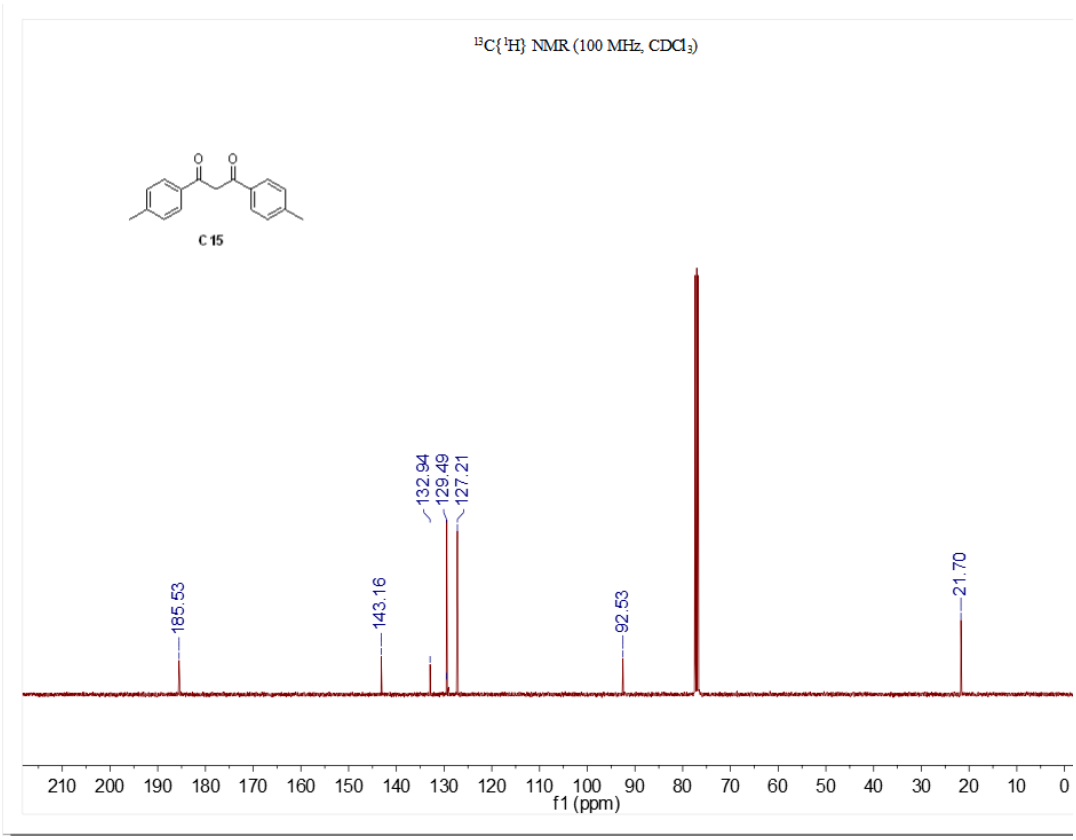


Figure S28. ^{13}C{^{1}H} NMR spectra of **C15**

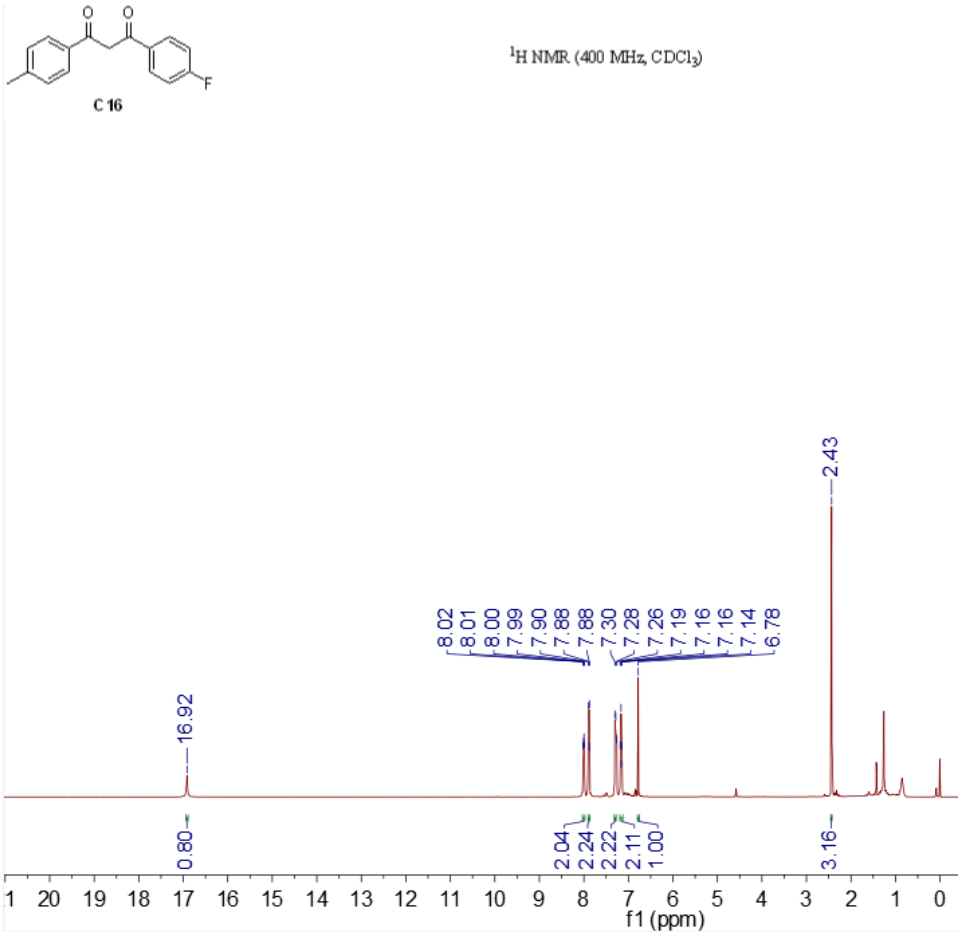


Figure S29. ^{1}H NMR spectra of **C16**

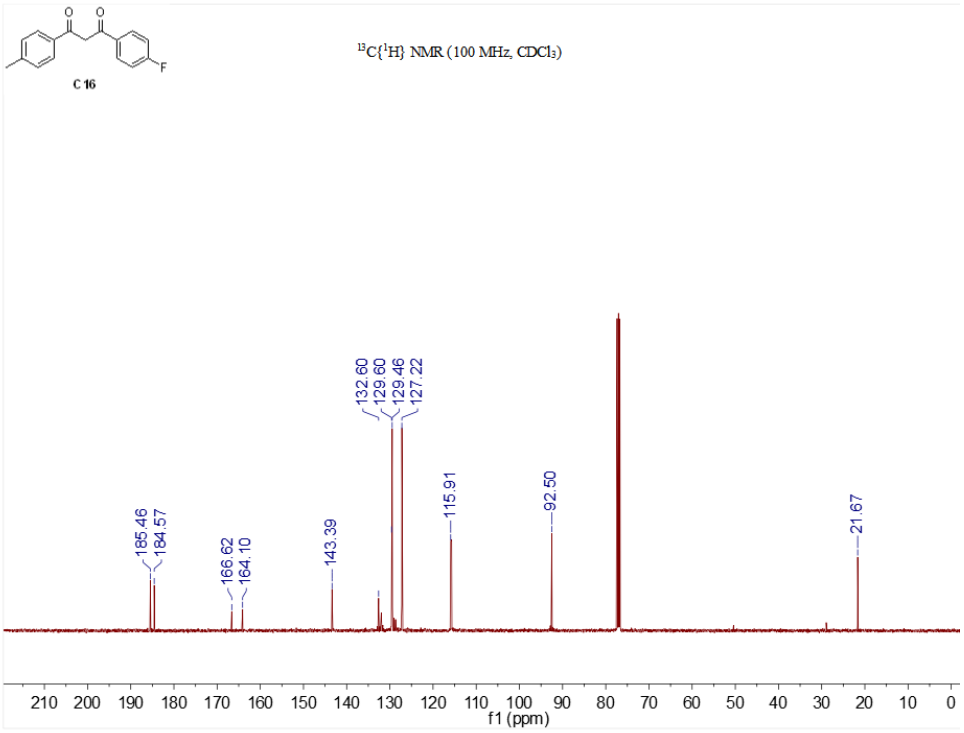


Figure S30. ^{13}C{^{1}H} NMR spectra of **C16**

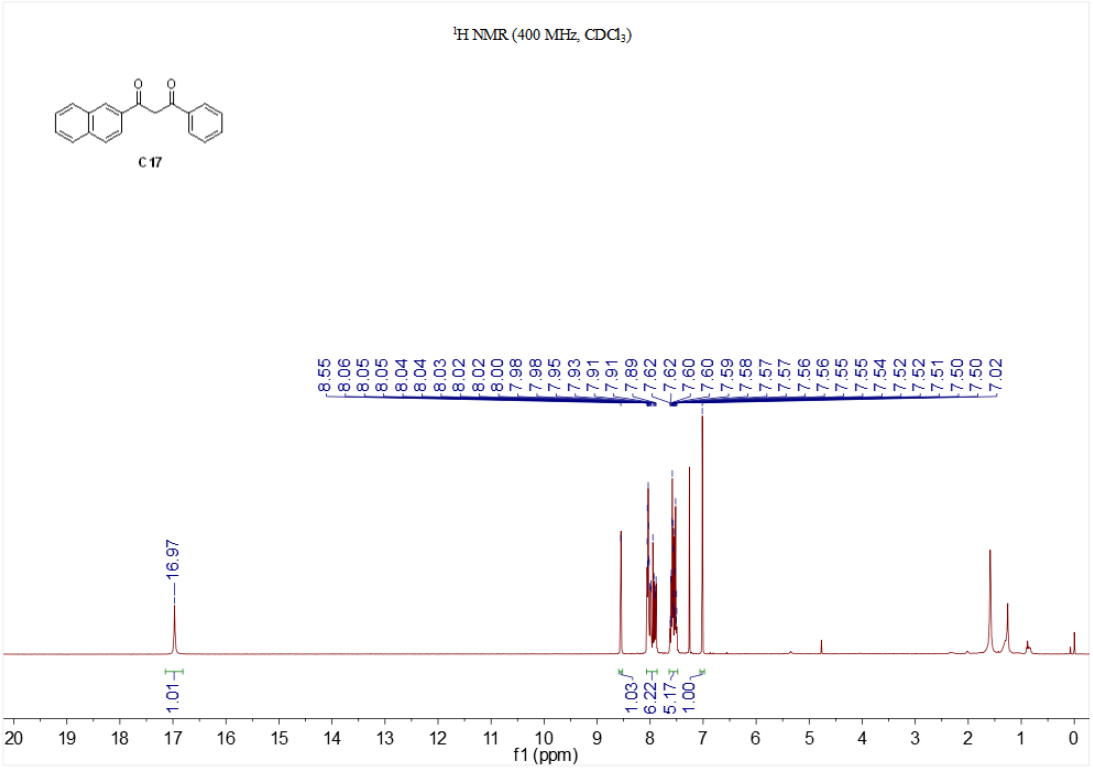


Figure S31. ^{1}H NMR spectra of **C17**

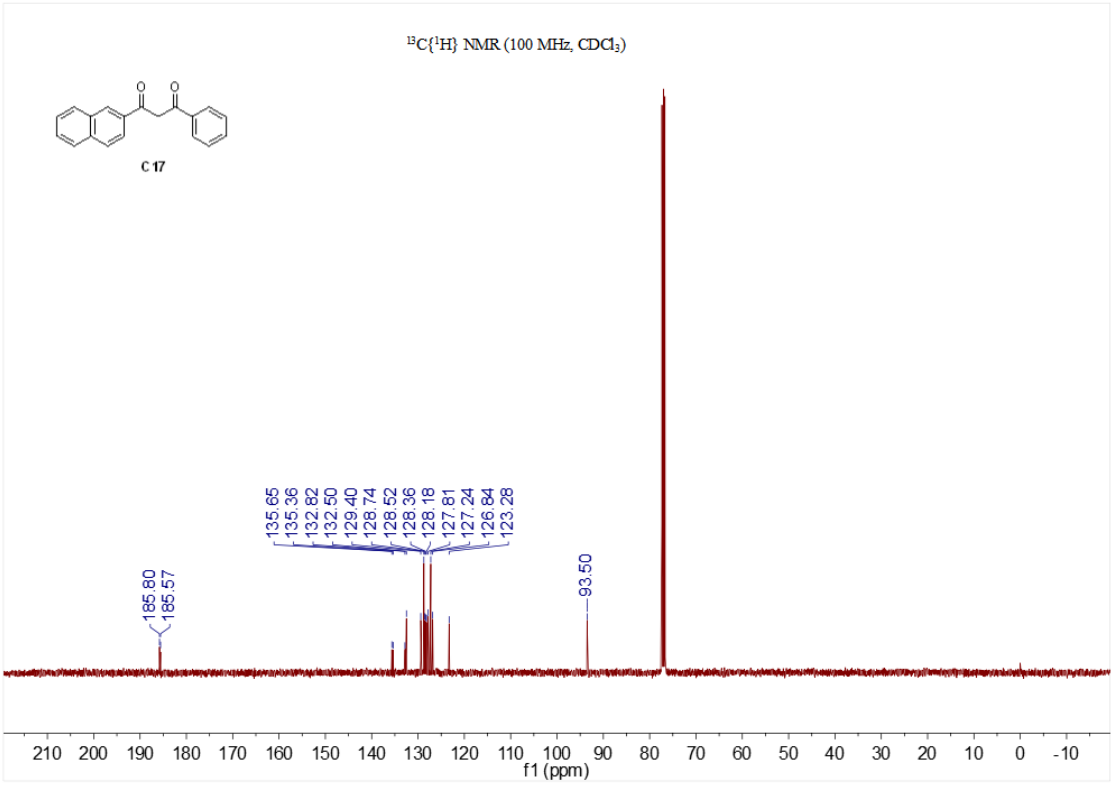


Figure S32. ^{13}C{^{1}H} NMR spectra of **C17**

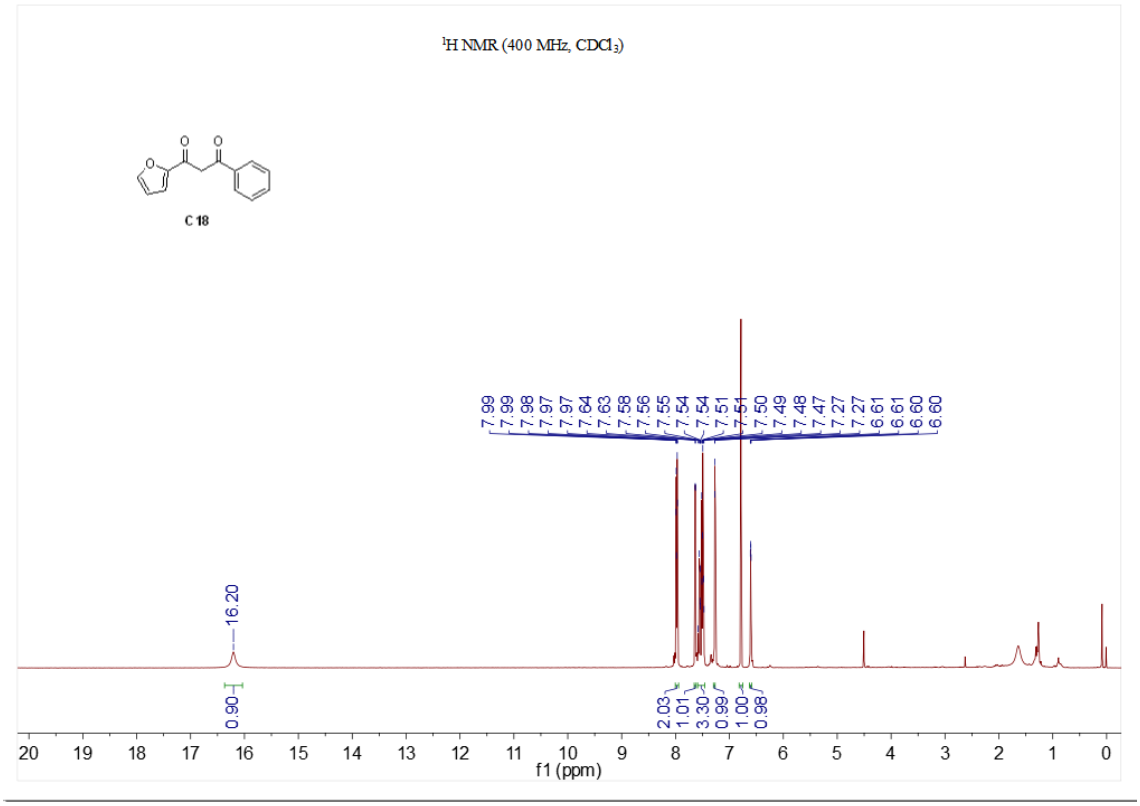


Figure S33. ^{1}H NMR spectra of **C18**

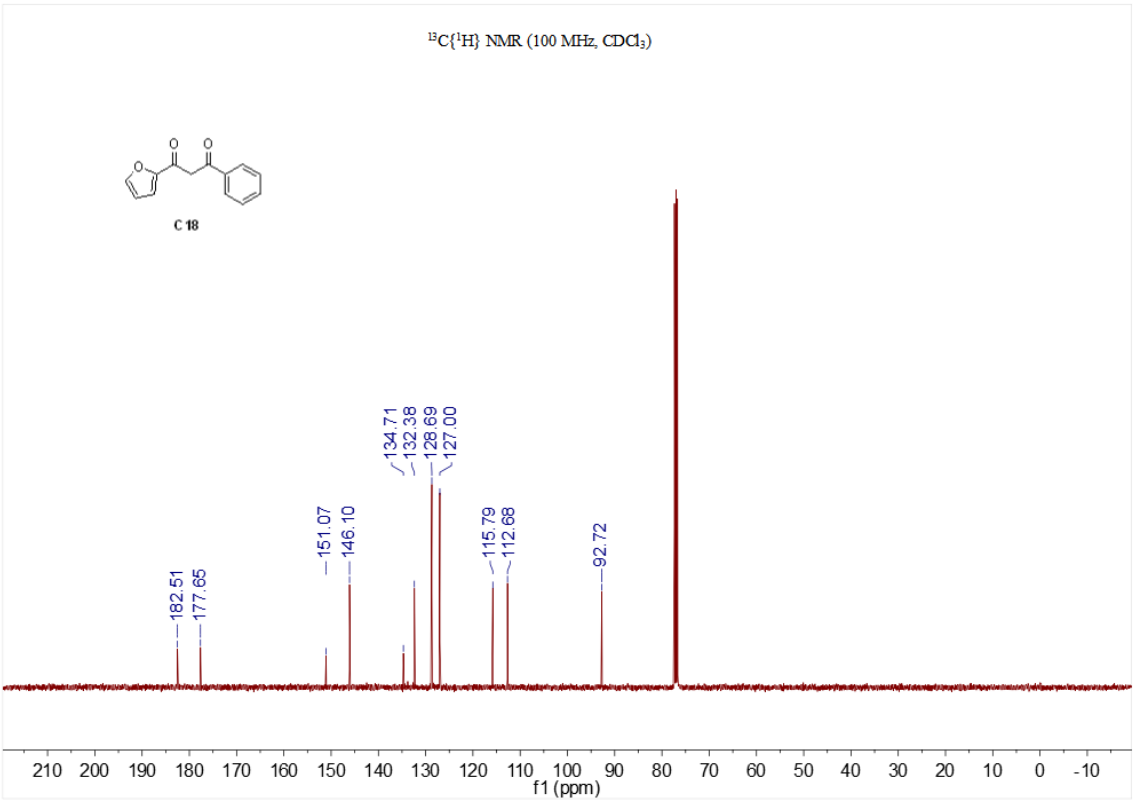


Figure S34. ^{13}C{^{1}H} NMR spectra of **C18**

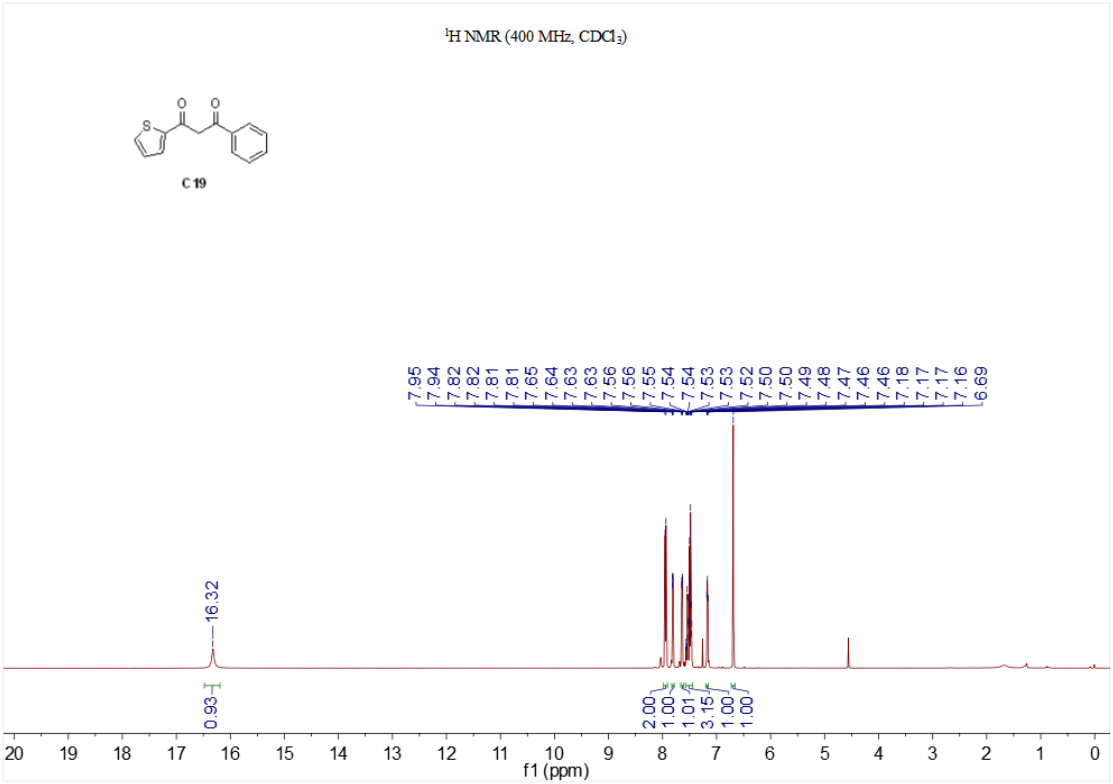


Figure S35. ^{1}H NMR spectra of **C19**

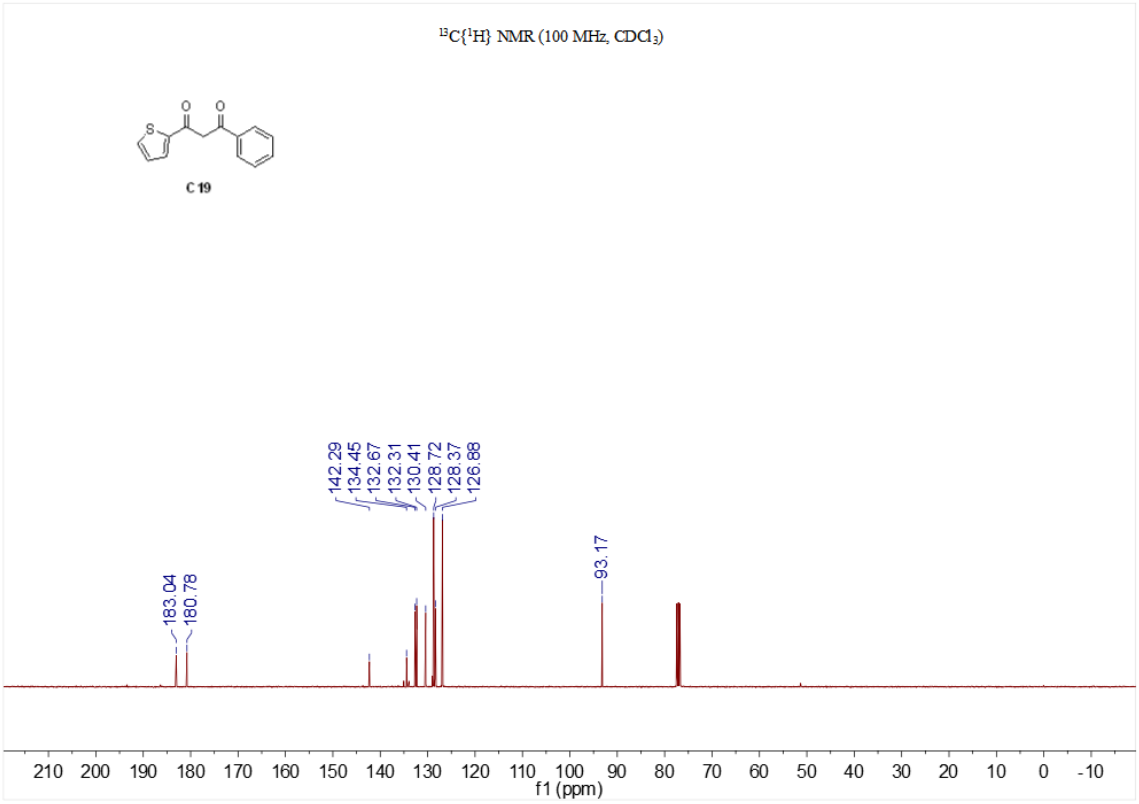


Figure S36. ^{13}C{^{1}H} NMR spectra of **C19**

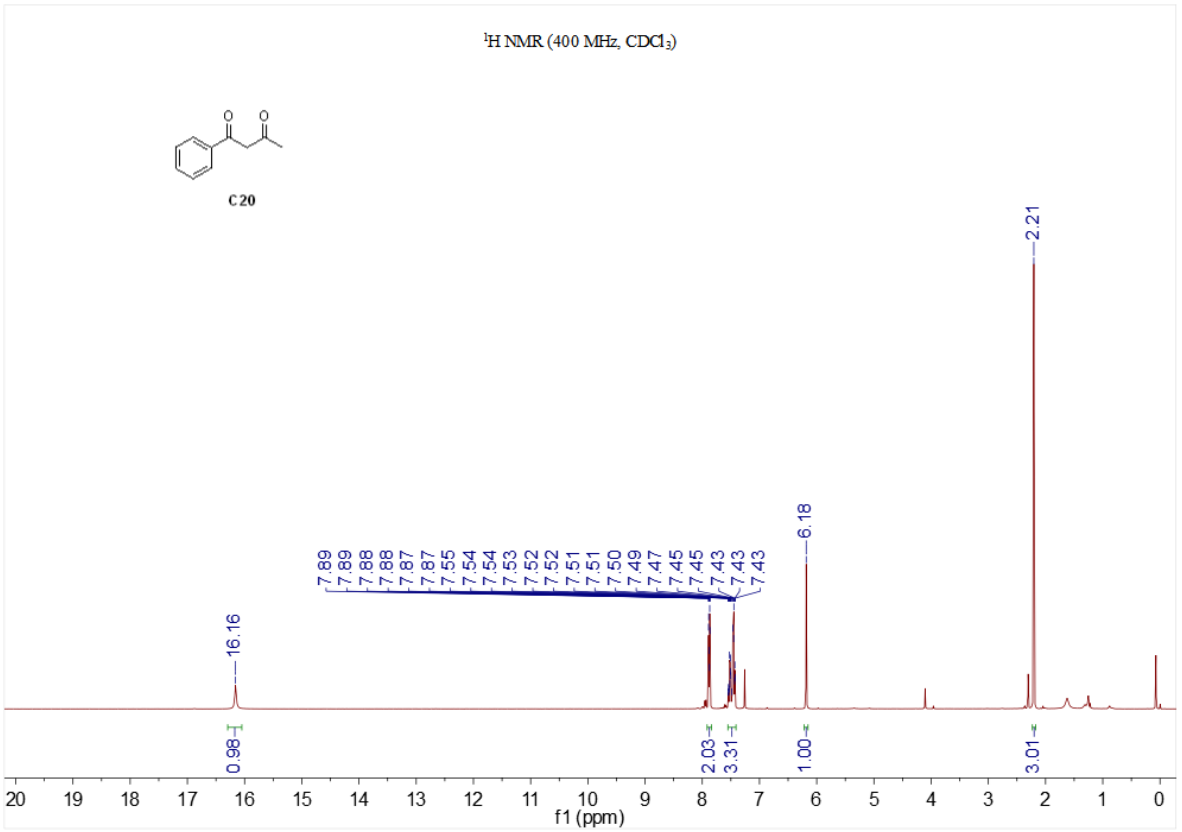


Figure S37. ^{1}H NMR spectra of **C20**

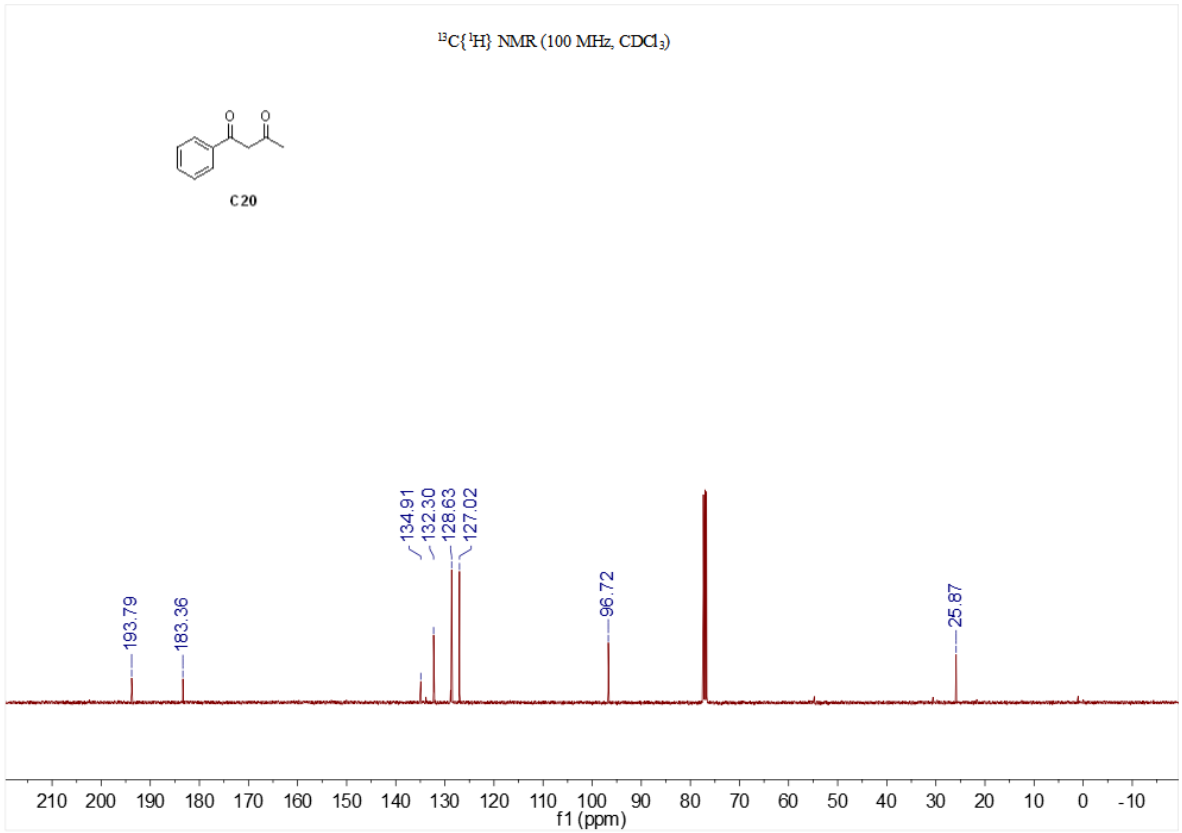
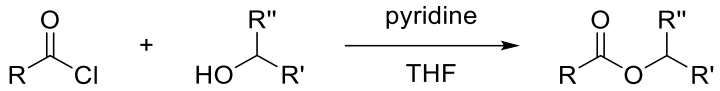


Figure S38. ^{13}C{^{1}H} NMR spectra of **C20**

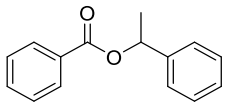
3. General synthesis methods of esters

3.1 Experimental operation



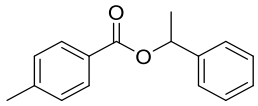
Under N_2, an oven-dried Schlenk was charged with a magnetic stirring bar, alcohol (10 mol), pyridine (10 mol) and THF (2 mL). To this, a solution of acid chloride (1.2 equiv.) was added, dropwise, over 30-40 min, at 0 °C. The solution was stirred for 2 h at 0 °C and overnight at room temperature. Then, the reaction was quenched by brine (100 mL). The mixture was extracted with dichloromethane (100 mL) and organic layer was washed by 1N $HCl_{(aq)}$ (100 mL), and brine (100 mL). The collected organic layer was dried ($MgSO_4$) for overnight. Purification of the remainder by column chromatography on silica gel gave the corresponding product esters in the reported yield.

3.2 Characterization data of esters



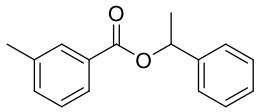
A1

(**A1**) 1-phenylethyl benzoate[1] (PE/EA=15:1): Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.12 (dt, J = 7.8 Hz, 2H), 7.57 (t, 9.4 Hz, 1H), 7.50-7.44 (m, 4H), 7.42-7.36 (t, J = 7.9 Hz, 2H), 7.36-7.29 (t, J = 7.0 Hz, 1H), 6.22-6.13 (q, J = 6.5 Hz, 1H), 1.74-1.67 (d, J = 6.6 Hz, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.8, 141.9, 133.0, 130.6, 129.7, 128.6, 128.4, 127.9, 126.1, 73.0, 22.5.



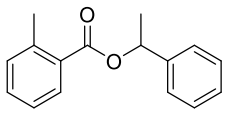
A2

(**A2**) 1-phenylethyl 4-methylbenzoate[1] (PE/EA = 15:1): Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.98 (dd, J = 8.1, 1.9 Hz, 2H), 7.45-7.42 (m, 2H), 7.34 (t, 2H), 7.29-7.25 (m, 1H), 7.21 (d, J = 7.8 Hz, 2H), 6.15-6.09 (m, 1H), 2.37 (s, 1H), 1.65 (dd, J = 6.4, 1.3 Hz, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.9, 143.6, 142.0, 129.8, 129.1, 128.6, 127.9, 126.1, 72.7, 22.5, 21.7.



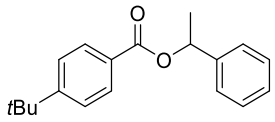
A3

(**A3**) 1-phenylethyl 3-methylbenzoate[1] (PE/EA = 15:1): Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.94 (s, 2H), 7.50 (d, J = 7.4, 2H), 7.42-7.31 (m, 5H), 6.21-6.17 (m,1H), 2.43 (s, 3H), 1.72 (d, J = 6.6 Hz, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 166.0, 141.9, 138.2, 133.7, 130.5, 130.2, 128.6, 128.3, 127.9, 126.9, 126.1, 72.9, 22.5, 21.3.



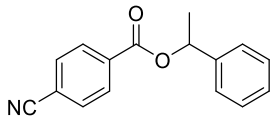
A4

(**A4**) 1-phenylethyl 2-methylbenzoate[1] (PE/EA = 15:1): Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.87 (d, J = 7.8 Hz, 1H), 7.35 (d, J = 7.8 Hz, 2H), 7.30-7.25 (m, 3H), 7.21-7.12 (m, 3H), 6.03 (q, J = 13.1, 6.6Hz, 1H), 2.50 (s, 3H), 1.57 (dd, J = 6.6, 1.2 Hz, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.7, 140.8, 139.1, 130.9, 130.6, 129.5, 128.9, 127.5, 126.8, 125.1, 124.7, 71.7, 21.4, 20.8.



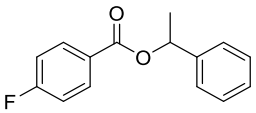
A5

(**A5**) 1-phenylethyl 4-(tert-butyl)benzoate[1] (PE/EA = 15:1): Colorless oil, **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.07(d, J = 8.4 Hz, 2H), 7.50-7.47(m, 4H), 7.41-7.37(m, 2H), 7.34-7.30(m, 1H), 6.17(q, J = 13.2, 6.6Hz, 1H), 1.70(d, J = 6.6 Hz, 3H), 1.37(s, 9H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.8, 156.6, 142.1, 129.7, 128.6, 127.9, 126.1, 125.4, 72.7, 35.1, 31.2, 22.6.



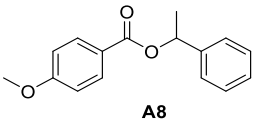
A6

(**A6**) 1-phenylethyl 4-cyanobenzoate (PE/EA = 15:1): Colorless oil, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.07(d, J = 8.4 Hz, 2H), 8.00(d, J = 7.3 Hz, 2H), 7.78(d, J = 8.4 Hz, 2H), 7.60(t, J = 7.4 Hz, 1H), 7.51(t, J = 7.7 Hz, 2H), 6.86(s, 1H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 187.6, 182.2, 139.3, 135.2, 135.1, 132.5, 128.9, 127.6, 127.4, 118.1, 115.5, 93.9. HRMS (ESI) m/z calcd for $C_{16}H_{13}NO_2$ $[M+Na]^+$ 274.0838, found 274.0848.



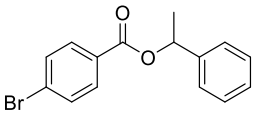
A7

(**A7**) 1-phenylethyl 4-fluorobenzoate[1] (PE/EA = 15:1): Colorless oil, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.15-8.12(m, 2H), 7.50-7.33(m, 5H), 7.16-7.10(m, 2H), 6.20-6.15(m, 1H), 1.71(d, *J* = 8.0 Hz, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 167.1, 164.9, 164.6, 141.7, 132.3, 132.2, 128.7, 128.1, 126.9, 126.1, 115.6, 115.4, 73.9, 22.4. . HRMS (ESI) m/z calcd for $C_{15}H_{13}FO_2$ $[M+Na]^+$ 267.0792, found 267.0801.



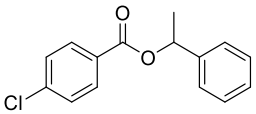
A8

(**A8**) 1-phenylethyl 4-methoxybenzoate[1] (PE/EA = 15:1): Colorless oil, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.10-8.08(m, 2H), 7.50-7.39(m, 5H), 6.97-6.94(m, 2H), 6.19-6.13(m, 1H), 3.88(s, 3H), 1.70(d, *J* = 8.0 Hz, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.6, 163.4, 142.1, 131.7, 128.6, 127.8, 126.1, 123.0, 113.6, 72.6, 55.4, 22.5.



A9

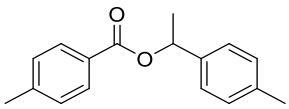
(**A9**) 1-phenylethyl 4-bromobenzoate[1] (PE/EA = 15:1): Colorless oil, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.79-7.75(m, 2H), 7.38-7.35(m, 2H), 7.29-7.27(m, 2H), 7.22-7.18(m, 2H), 7.15-7.10(m, 1H), 6.01-5.96(m, 1H), 1.51(d, *J* = 8.0 Hz, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.1, 141.6, 131.8, 131.3, 129.6, 128.7, 128.1, 126.2, 73.4, 22.4.



A12

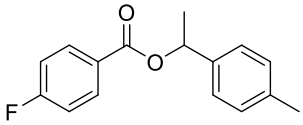
(**A12**) 1-phenylethyl 4-chlorobenzoate[1] (PE/EA = 15:1): Colorless oil, **^{1}H NMR (400 MHz, $CDCl_3$)** δ 8.04-8.02(m, 2H), 7.47-7.31(m, 7H), 6.17-6.12(m, 1H), 1.69(d, *J* = 8.0 Hz, 3H);

$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$) δ 165.1, 141.6, 131.8, 131.3, 129.6, 128.7, 128.1, 126.2, 73.4, 22.4.



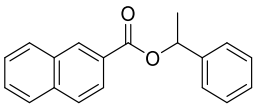
A15

(**A15**) 1-(p-tolyl)ethyl 4-methylbenzoate[1] (PE/EA = 15:1): Colorless oil, **^1H NMR (400 MHz, $CDCl_3$)** δ 7.99-7.97(m, 2H), 7.35-7.18(m, 6H), 6.14-6.09(m, 1H), 2.42(s, 3H), 2.36(s, 3H), 1.67(d, J = 8.0 Hz, 3H); **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 166.0, 143.5, 139.0, 137.6, 129.7, 129.2, 129.1, 127.9, 126.1, 72.6, 22.4, 21.7, 21.2.



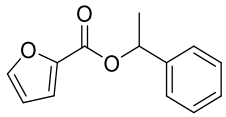
A16

(**A16**) 1-(p-tolyl)ethyl 4-fluorobenzoate (PE/EA = 15:1): Colorless oil, **^1H NMR (400 MHz, $CDCl_3$)** δ 8.12-8.07(m, 2H), 7.36-7.34(m, 2H), 7.20-7.09(m, 4H), 6.13-6.08(m, 1H), 2.36(s, 3H), 1.67(d, J = 8.0 Hz, 3H); **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 167.0, 164.9, 164.5, 138.7, 137.8, 132.3, 132.2, 129.3, 126.9, 126.1, 115.6, 115.4, 73.1, 22.3, 21.2. HRMS (ESI) m/z calcd for $C_{16}H_{15}FO_2$ $[M+Na]^+$ 281.0948, found 281.0949.



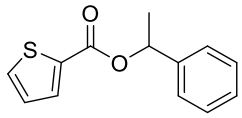
A17

(**A17**) 1-phenylethyl 2-naphthoate[1] (PE/EA = 15:1): Colorless oil, **^1H NMR (400 MHz, $CDCl_3$)** δ 8.62(s, 1H), 8.10-8.07(m, 1H), 7.87-7.75(m, 3H), 7.49-7.23(m, 7H), 6.23-6.18(m, 1H), 2.36(s, 3H), 1.69(d, J = 4.0 Hz, 3H); **$^{13}C\{^1H\}$ NMR (100 MHz, $CDCl_3$)** δ 166.1, 142.0, 135.7, 132.6, 131.2, 129.5, 128.8, 128.3, 128.1, 127.9, 126.8, 126.3, 125.5, 73.2, 22.6.



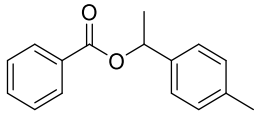
A18

(**A18**) 1-phenylethyl furan-2-carboxylate[1] (PE/EA = 15:1): Colorless oil, **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.54-7.53(m, 1H), 7.46-7.26(m, 5H), 7.21-7.20(m, 1H), 6.46-6.44(m, 1H), 6.17-6.12(m, 1H), 1.66(d, *J* = 4.0 Hz, 3H); **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 158.0, 146.4, 144.9, 141.4, 128.6, 128.1, 126.2, 118.0, 111.9, 72.9, 22.3.



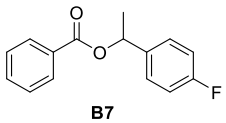
A19

(**A19**) 1-phenylethyl thiophene-2-carboxylate[1] (PE/EA = 15:1): Colorless oil, **^{1}H NMR (400 MHz, CDCl$_3$)** δ 7.87-7.85(m, 1H), 7.56-7.30(m, 6H), 7.12-7.09(m, 1H), 6.16-6.11(m, 1H), 1.69(d, *J* = 8.0 Hz, 3H); **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 161.5, 141.7, 134.2, 133.5, 132.5, 128.7, 128.0, 127.8, 126.1, 73.2, 22.5.



B2

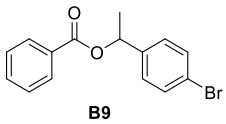
(**B2**) 1-(p-tolyl)ethyl benzoate[1] (PE/EA=15:1): Colorless oil; **^{1}H NMR (400 MHz, CDCl$_3$):** δ 8.07 (d, *J* = 8.2 Hz, 2H), 7.46(t, J = 7.4, 1H), 7.37-7.31(m, 4H), 7.13(d, *J* = 7.8 Hz, 2H), 6.13-6.09(m, 1H), 2.29(s, 3H), 1.65-1.63(m, 3H); **^{13}C{^{1}H} NMR (100 MHz, CDCl$_3$)** δ 165.9 138.9 137.7 132.9 130.7 129.7 129.3 128.4 126.1 72.9 22.4 21.2.



B7

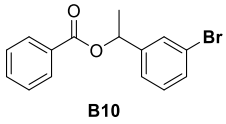
(**B7**) 1-(p-tolyl)ethyl benzoate[1] (PE/EA=15:1): Colorless oil; **^{1}H NMR (400 MHz, CDCl$_3$):**

δ 8.13-8.10 (m, 2H), 7.59-7.44(m, 5H), 7.09-7.05(m, 2H), 6.18-6.13(m, 1H), 2.29(s, 3H), 1.69(d, J = 8 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 167.1, 164.9, 164.6, 141.7, 132.3 132.2, 128.7, 128.1, 126.9,126.1,115.6, 115.4, 73.2, 22.4. HRMS (ESI) m/z calcd for $C_{15}H_{13}FO_2$ $[M+Na]^+$ 267.0792, found 267.0801.



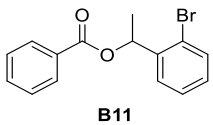
B9

(**B9**) 1-(4-bromophenyl)ethyl benzoate[3] (PE/EA=15:1): Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.09-8.06 (m, 2H), 7.59-7.55(m, 1H), 7.47-7.33(m, 6H), 6.13-6.08(m, 1H), 1.66(d, J = 8 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 165.7, 140.4, 133.7, 133.1, 130.3 129.7, 128.8, 128.4, 127.5, 72.2, 22.3.



B10

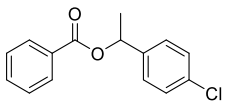
(**B10**) 1-(3-bromophenyl)ethyl benzoate (PE/EA=15:1): Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.00-7.98 (m, 2H), 7.59-7.45(m, 2H), 7.37-7.26(m, 4H), 7.15-7.11(m, 1H), 6.01-5.98(m, 1H), 1.56(d, J = 8 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 165.7, 144.2, 133.1, 131.0, 130.2 129.7, 129.2, 128.5, 124.8, 122.7, 72.1, 22.4. HRMS (ESI) m/z calcd for $C_{15}H_{13}BrO_2$ $[M+Na]^+$ 326.9991, found 327.0002.



B11

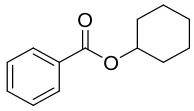
(**B11**) 1-(2-bromophenyl)ethyl benzoate (PE/EA=15:1): Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.12-7.10 (m, 2H), 7.60-7.54(m, 3H), 7.48-7.44(m, 2H), 7.35-7.31(m, 1H), 7.17-7.13(m, 1H), 6.43-6.38(m, 1H), 1.67(d, *J* = 4 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 165.5, 141.4, 133.1, 133.0, 130.3 129.7, 129.2, 128.4, 127.9, 126.8, 121.9, 72.2, 21.4. HRMS

(ESI) m/z calcd for $C_{15}H_{13}BrO_2$ $[M+Na]^+$ 326.9991, found 327.0002.



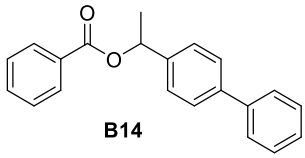
B12

(**B12**) 1-(4-chlorophenyl)ethyl benzoate[1] (PE/EA=15:1): Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.95-7.92 (m, 2H), 7.38-7.34(m, 1H), 7.38-7.14(m, 6H), 5.97-5.92(m, 1H), 1.49(d, J = 4 Hz, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.7, 140.4, 133.7, 133.1, 130.4, 129.7, 128.8, 128.5, 127.6, 72.3, 22.4.



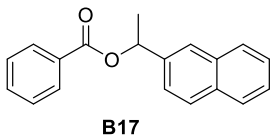
B13

(**B13**) cyclohexyl benzoate[4] (PE/EA=15:1): Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.06-8.04 (m, 2H), 7.55-7.50(m, 1H), 7.44-7.40(m, 2H), 5.06-5.00(m, 1H), 1.97-1.76(m, 4H), 1.63-1.29(m, 6H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 166.0, 132.7, 131.0, 129.5, 128.3, 73.0, 31.7, 25.5, 23.7.



B14

(**B14**) 1-([1,1'-biphenyl]-4-yl)ethyl benzoate[1] (PE/EA=15:1): Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.17-8.15 (m, 2H), 7.65-7.56(m, 7H), 7.50-7.36(m, 5H), 6.27-6.22(m, 1H), 1.76(d, J = 8 Hz, 3H); **^{13}C{^{1}H} NMR (100 MHz, $CDCl_3$)** δ 165.9, 141.0, 140.9, 140.8, 133.0, 130.6, 129.7, 128.9, 128.4, 127.4, 127.2, 126.6, 72.8, 22.4.



B17

(**B17**) 1-(naphthalen-2-yl)ethyl benzoate[1] (PE/EA=15:1): Colorless oil; **^{1}H NMR (400 MHz, $CDCl_3$):** δ 8.14-8.12 (m, 2H), 7.91-7.82(m, 4H), 7.61-7.44(m, 6H), 6.35-6.30(m, 1H), 1.78(d,

J = 8 Hz, 3H); **$^{13}C\{^{1}H\}$ NMR (100 MHz, $CDCl_3$)** δ 165.9, 139.1, 133.2, 133.1, 133.0, 130.6, 129.7, 128.5, 128.4, 128.1, 127.7, 126.3, 126.1, 125.0, 124.1, 73.1, 22.4.

3.3 NMR spectrum of esters

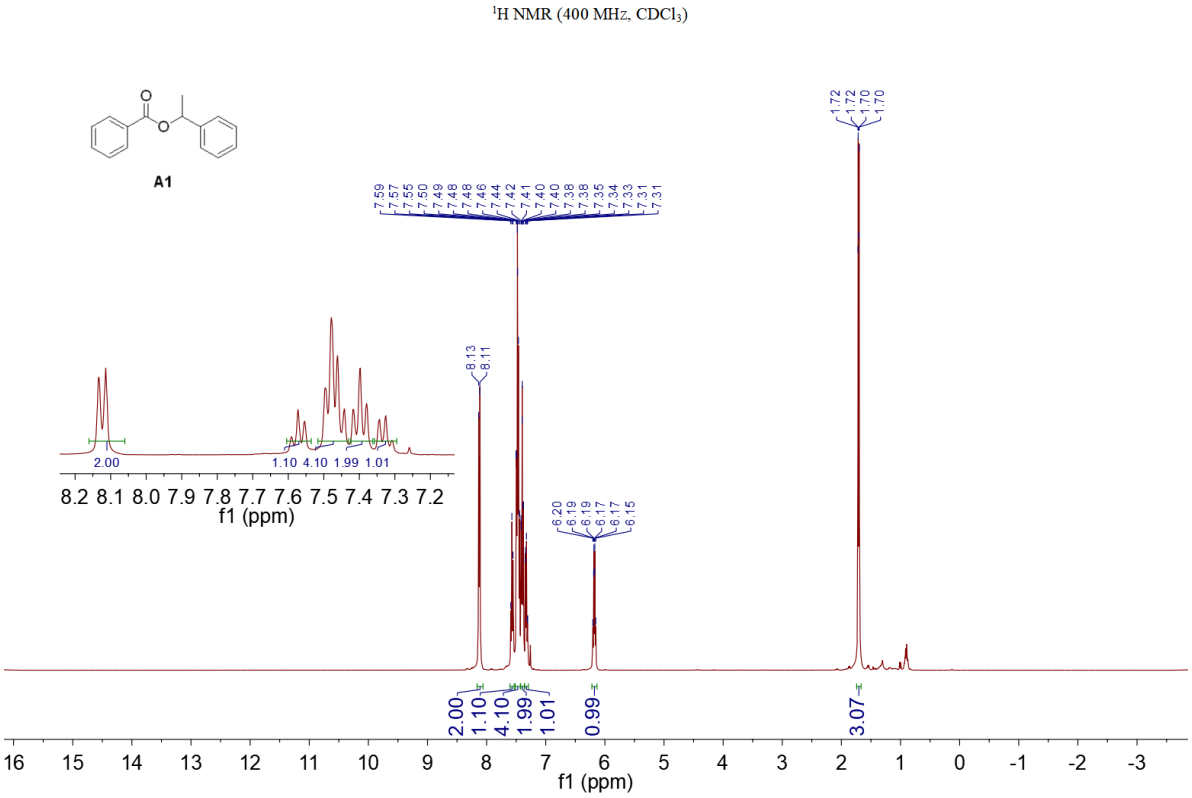


Figure S39. ^{1}H NMR spectra of **A1**

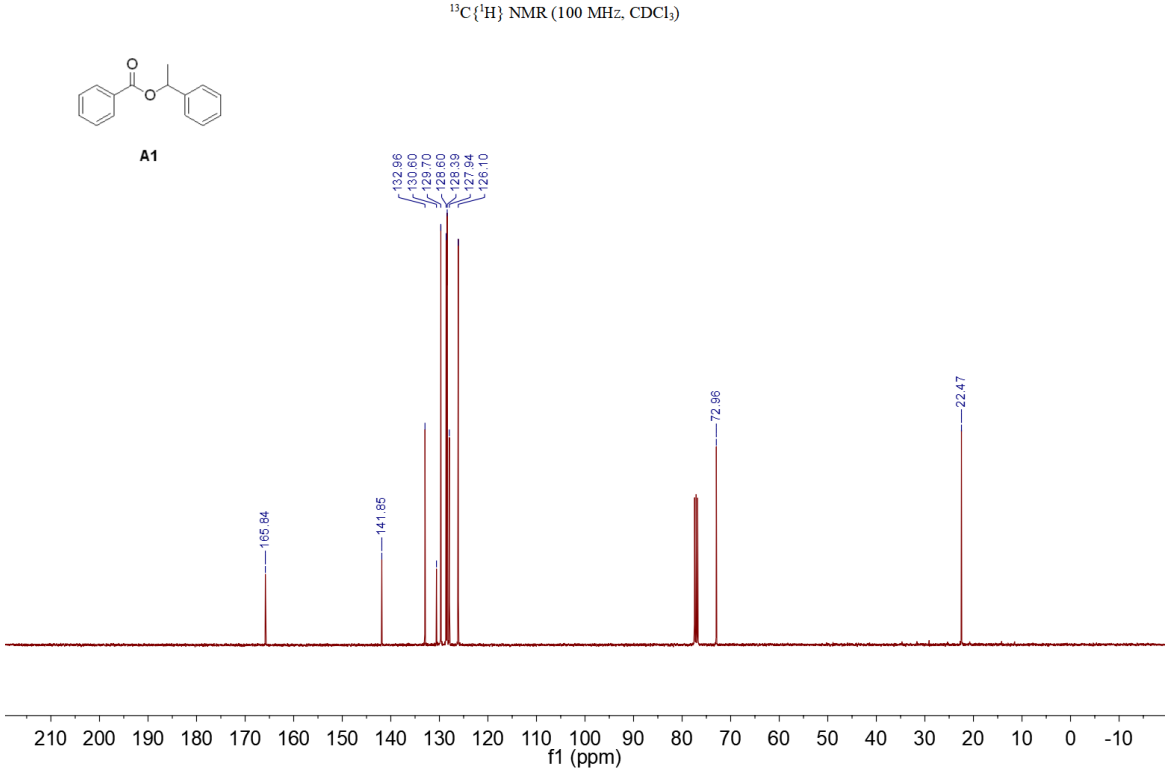


Figure S40. ^{13}C{^{1}H} NMR spectra of **A1**

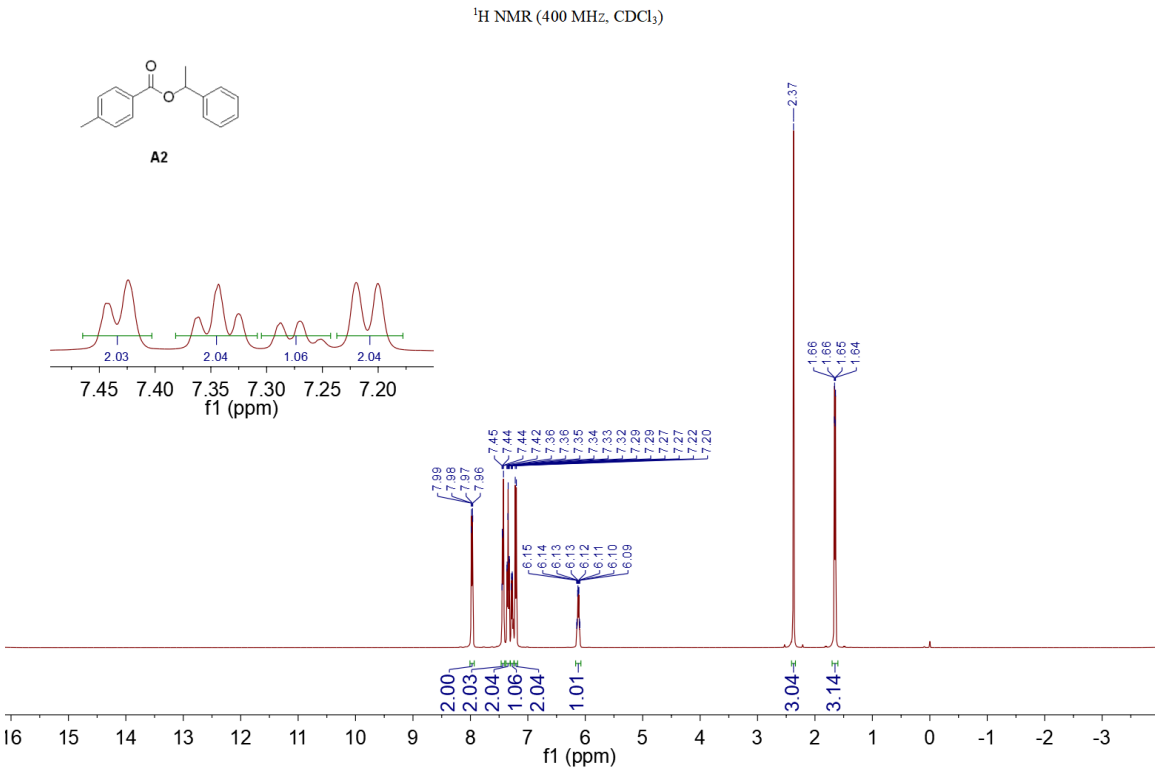


Figure S41. ^{1}H NMR spectra of **A2**

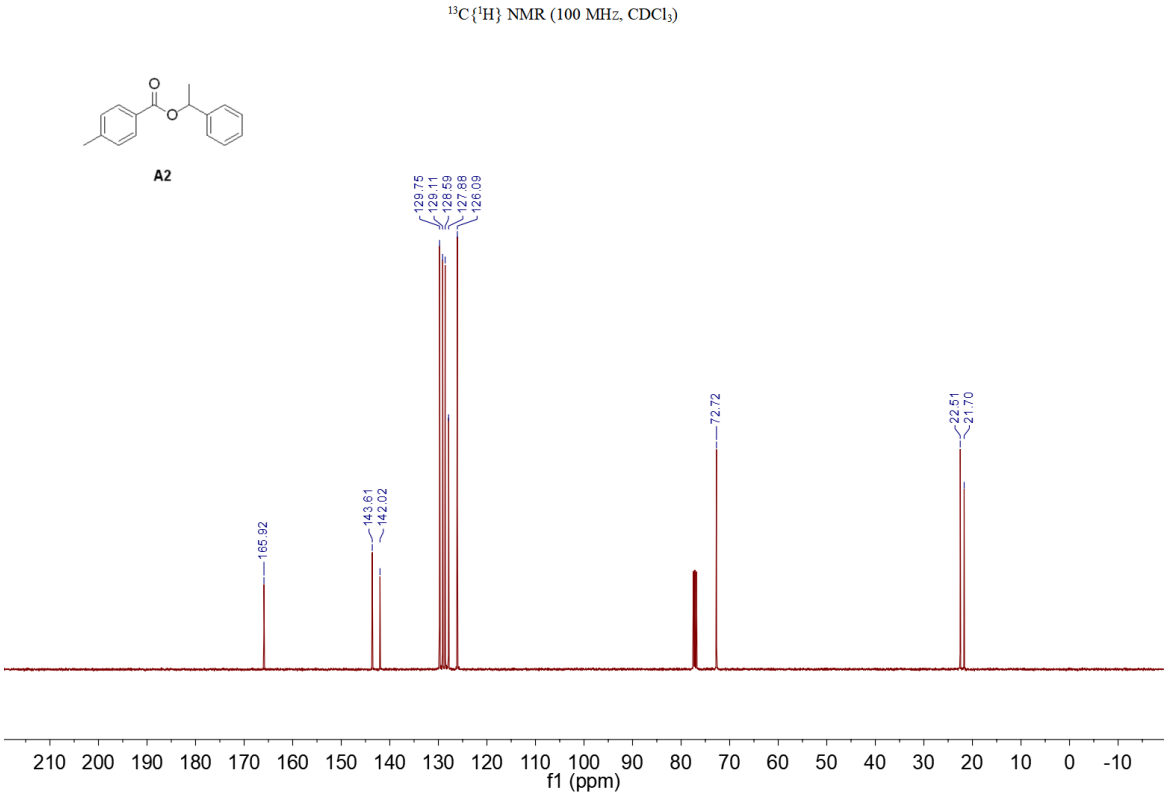


Figure S42. ^{13}C{^{1}H} NMR spectra of **A2**

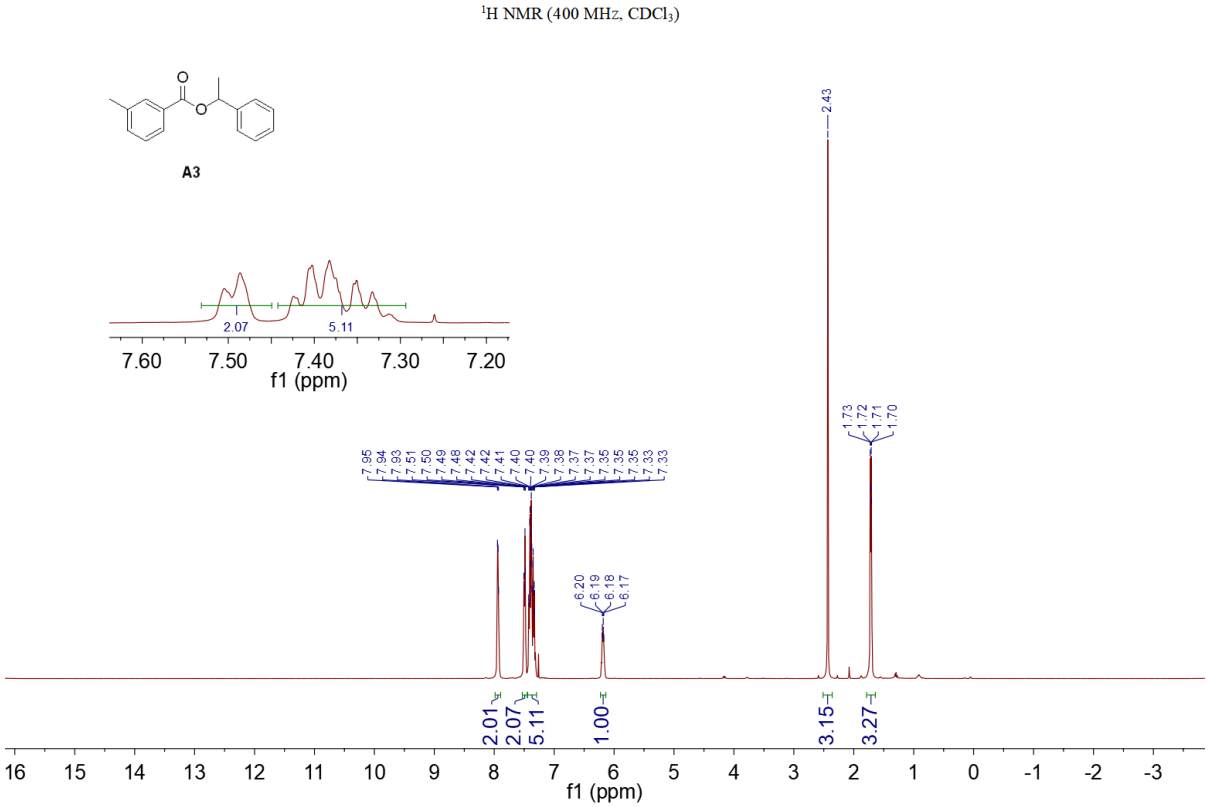


Figure S43. ^{1}H NMR spectra of **A3**

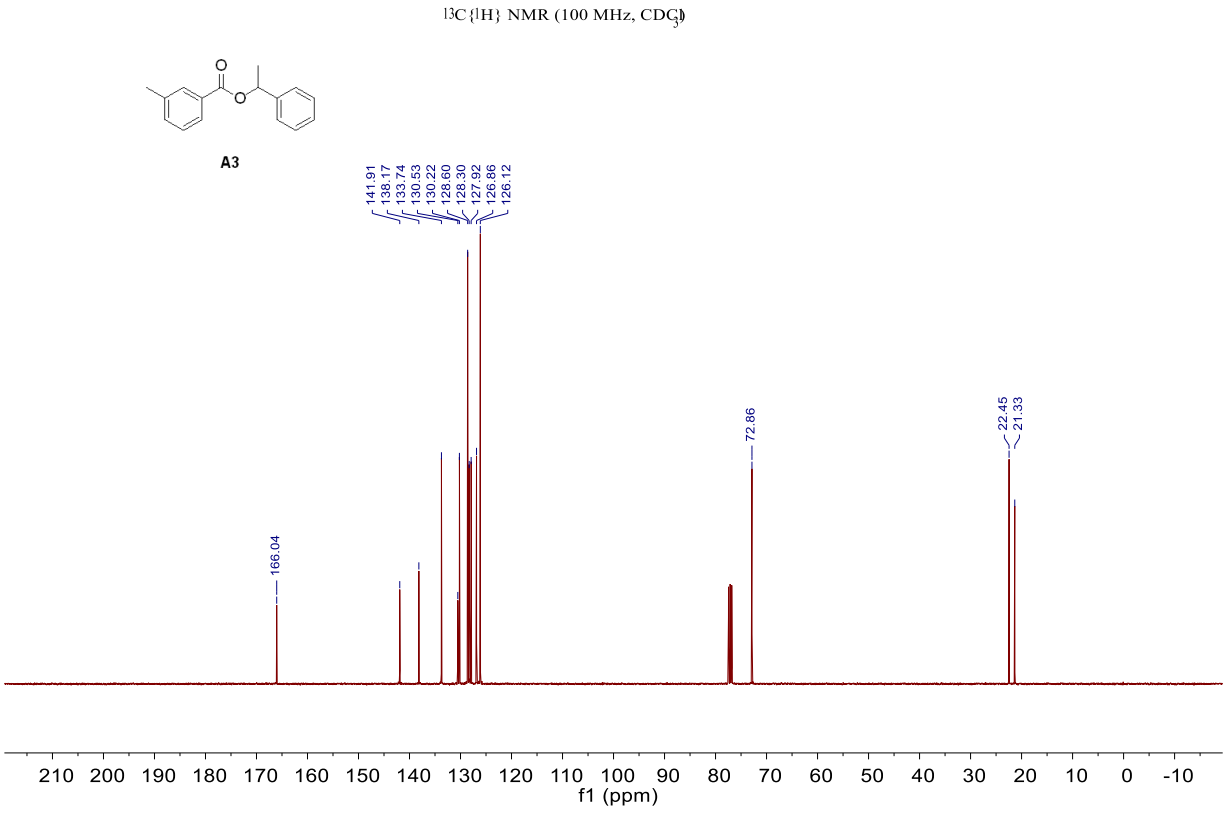


Figure S44. ^{13}C{^{1}H} NMR spectra of **A3**

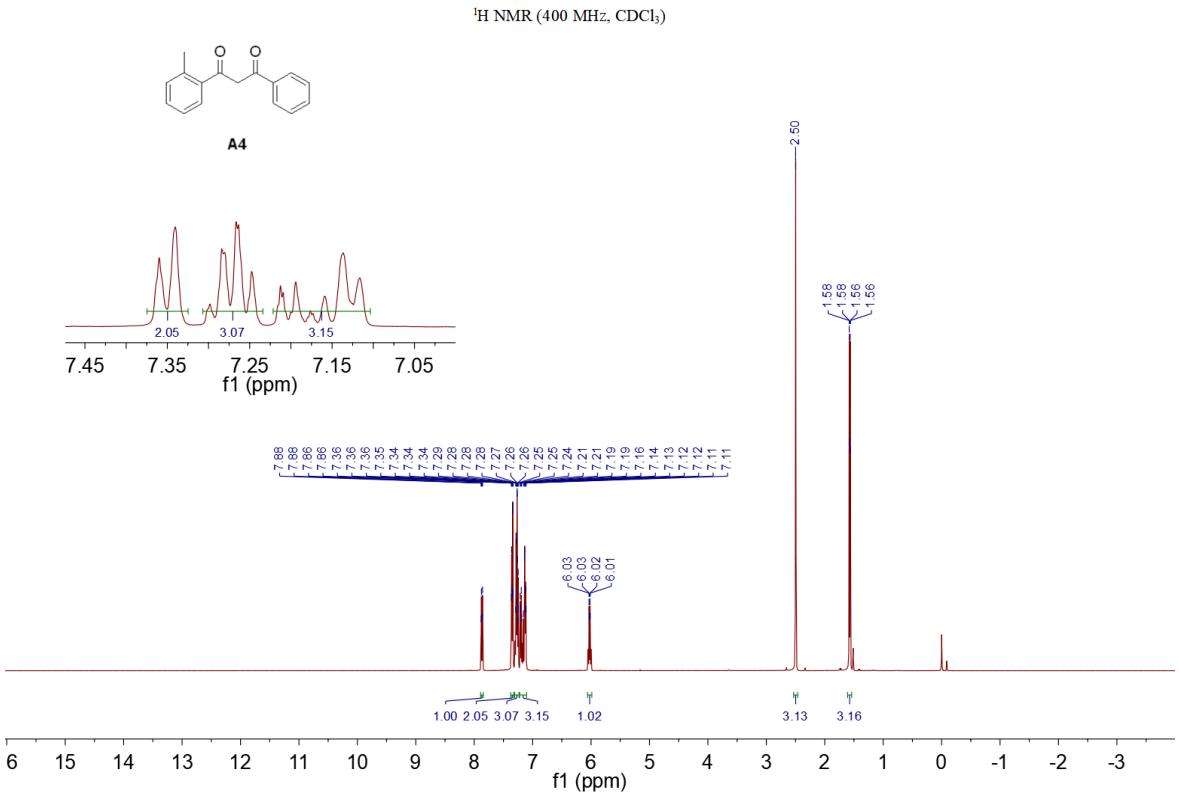


Figure S45. ^{1}H NMR spectra of **A4**

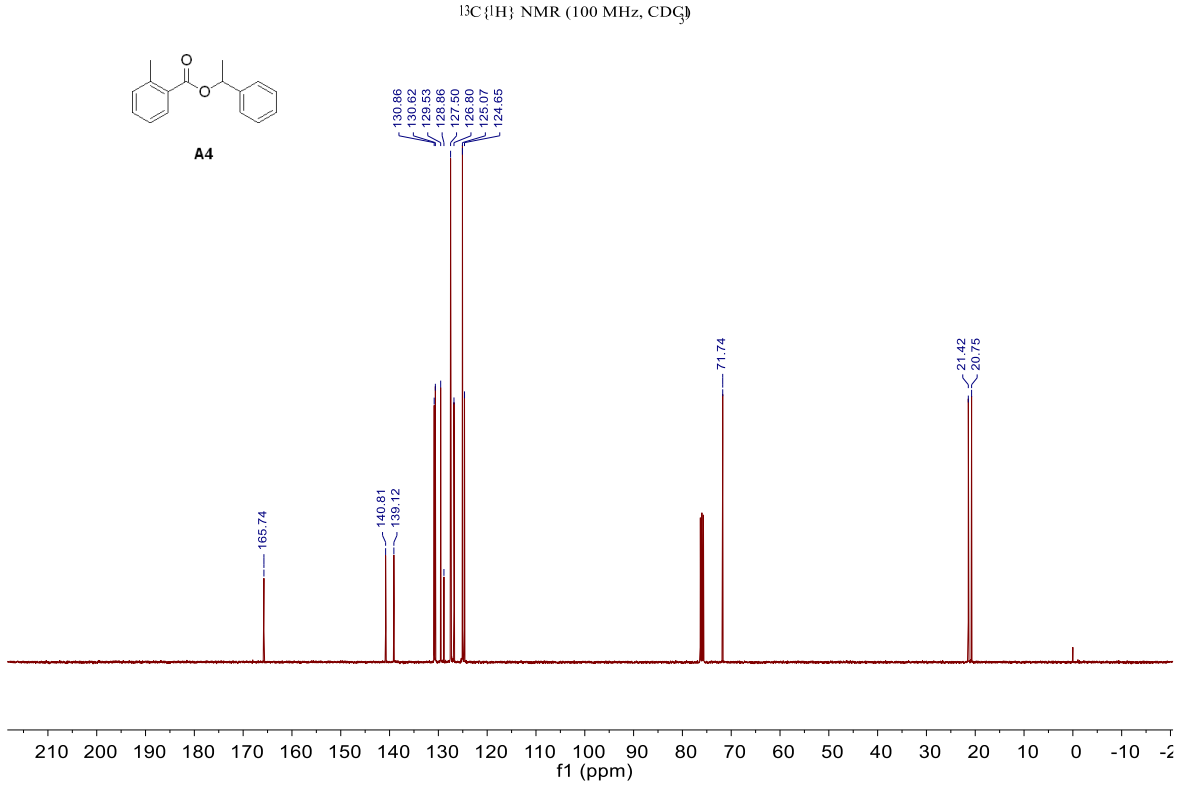


Figure S46. ^{13}C{^{1}H} NMR spectra of **A4**

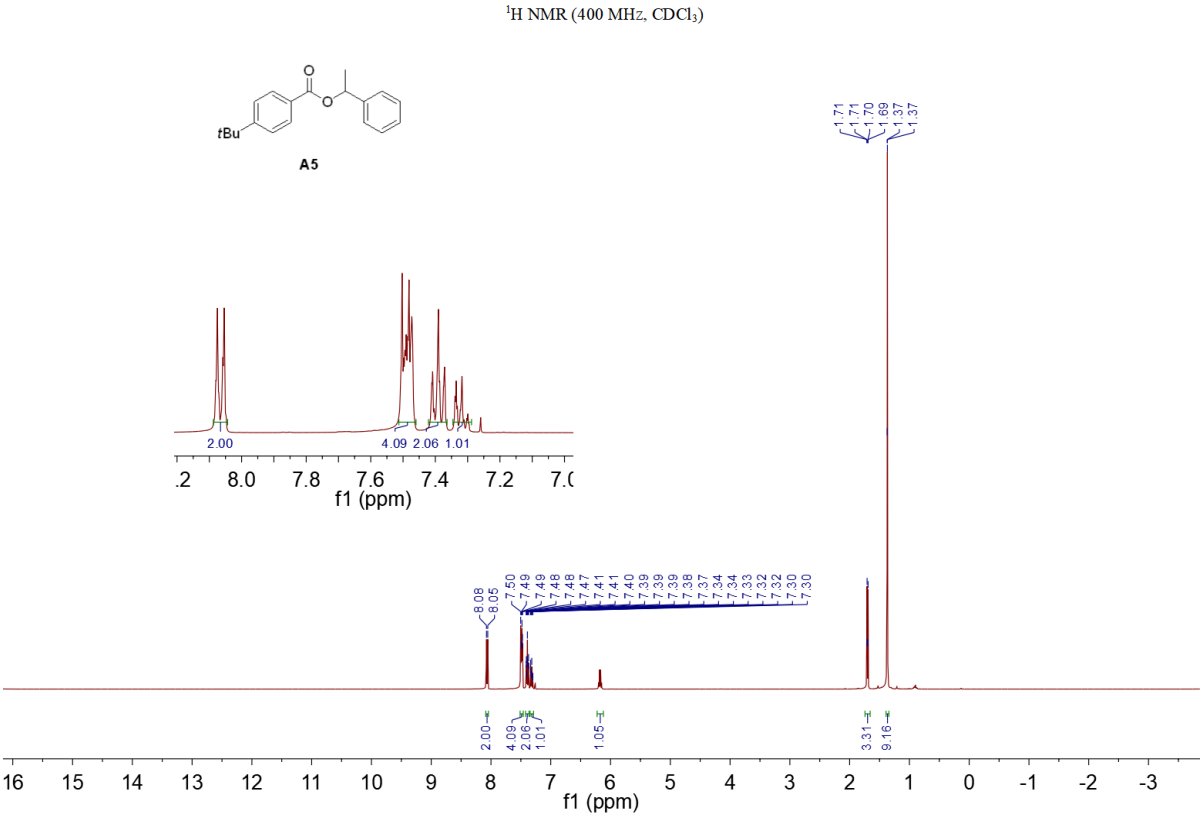


Figure S47. ^{1}H NMR spectra of **A5**

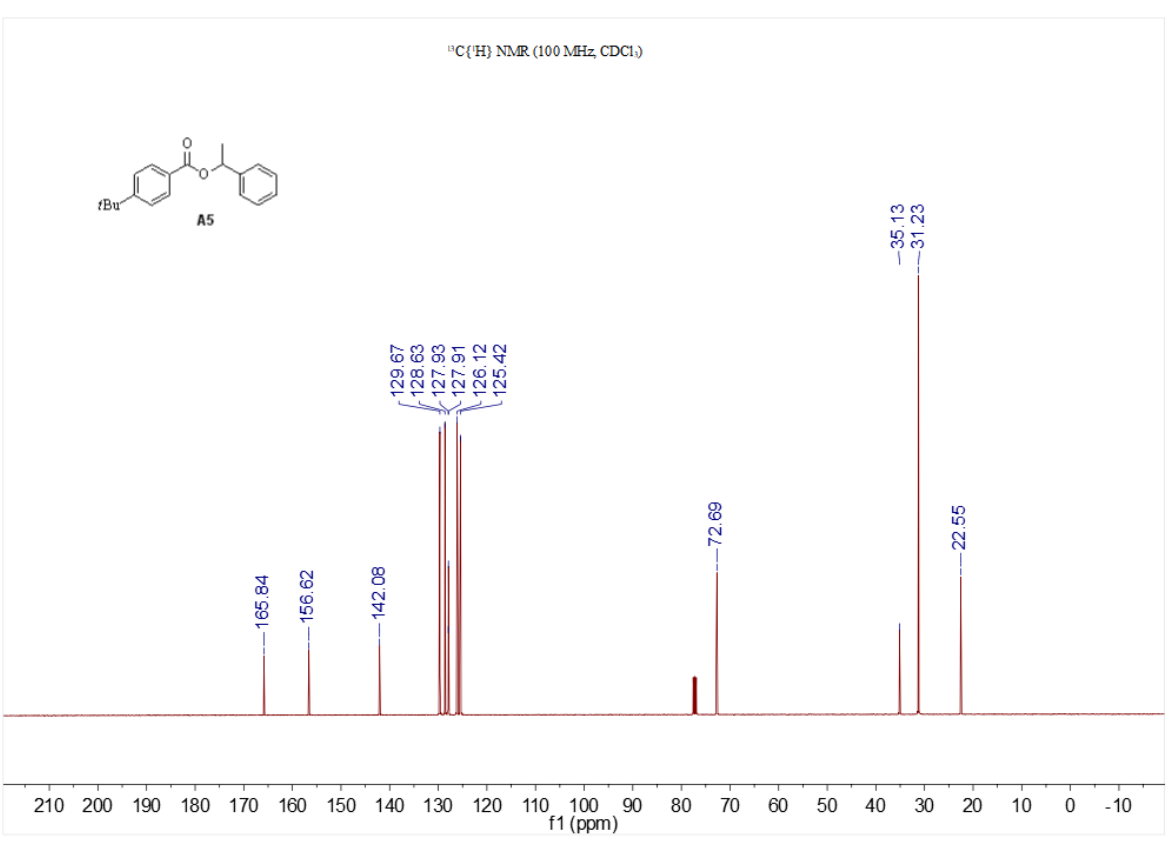


Figure S48. ^{13}C{^{1}H} NMR spectra of **A5**

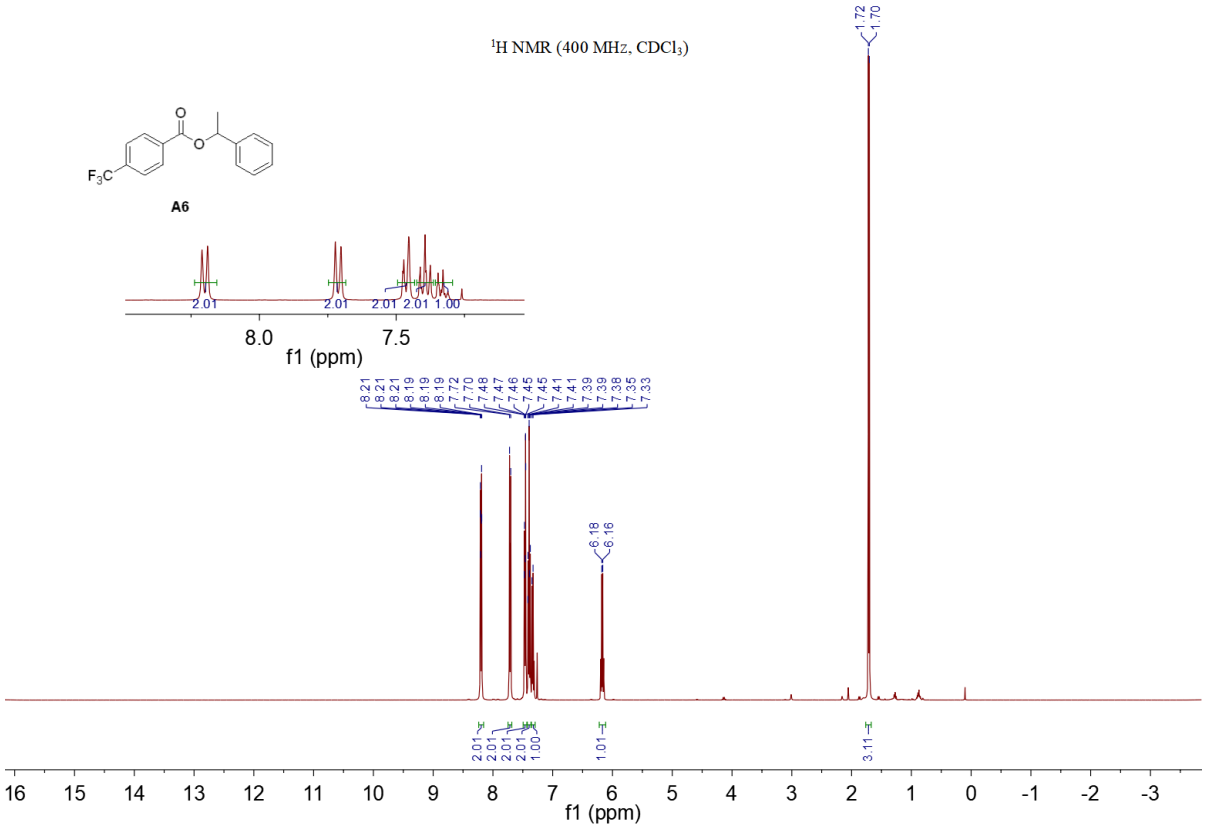


Figure S49. ^{1}H NMR spectra of **A6**

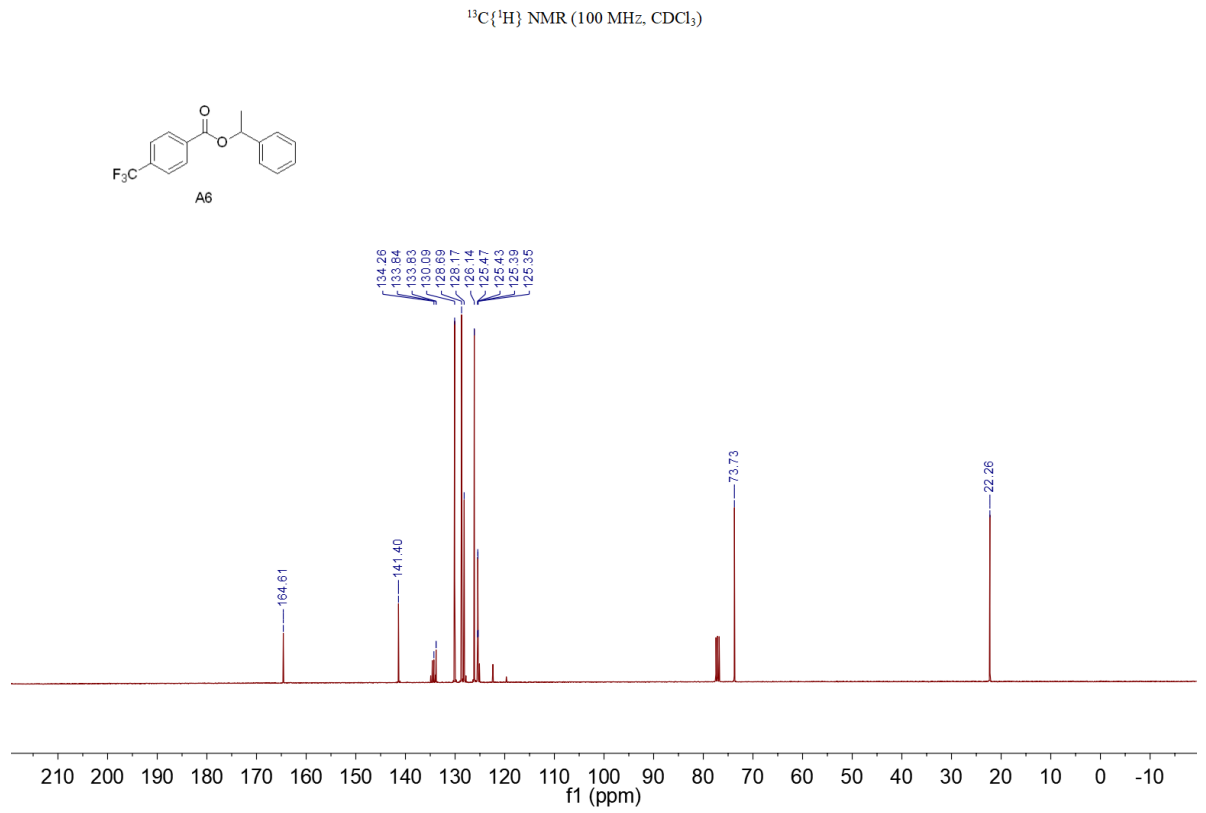


Figure S50. ^{13}C{^{1}H} NMR spectra of **A6**

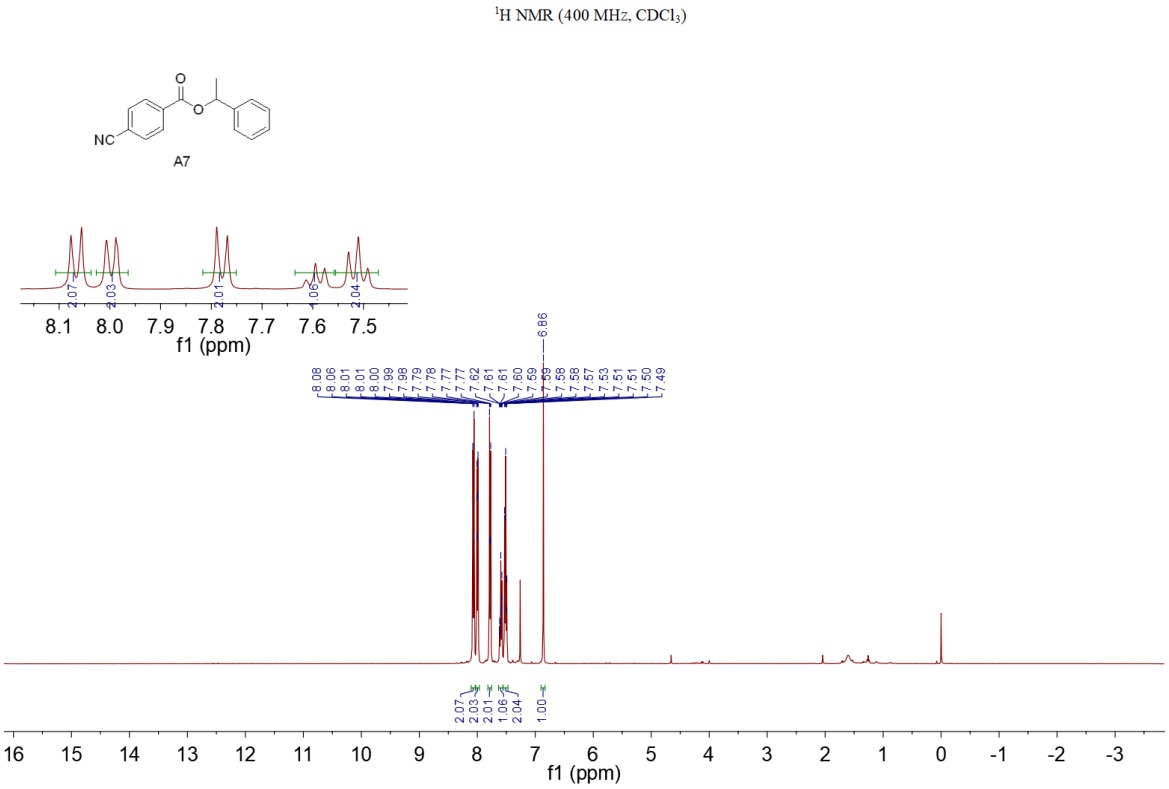


Figure S51. ^{1}H NMR spectra of **A7**

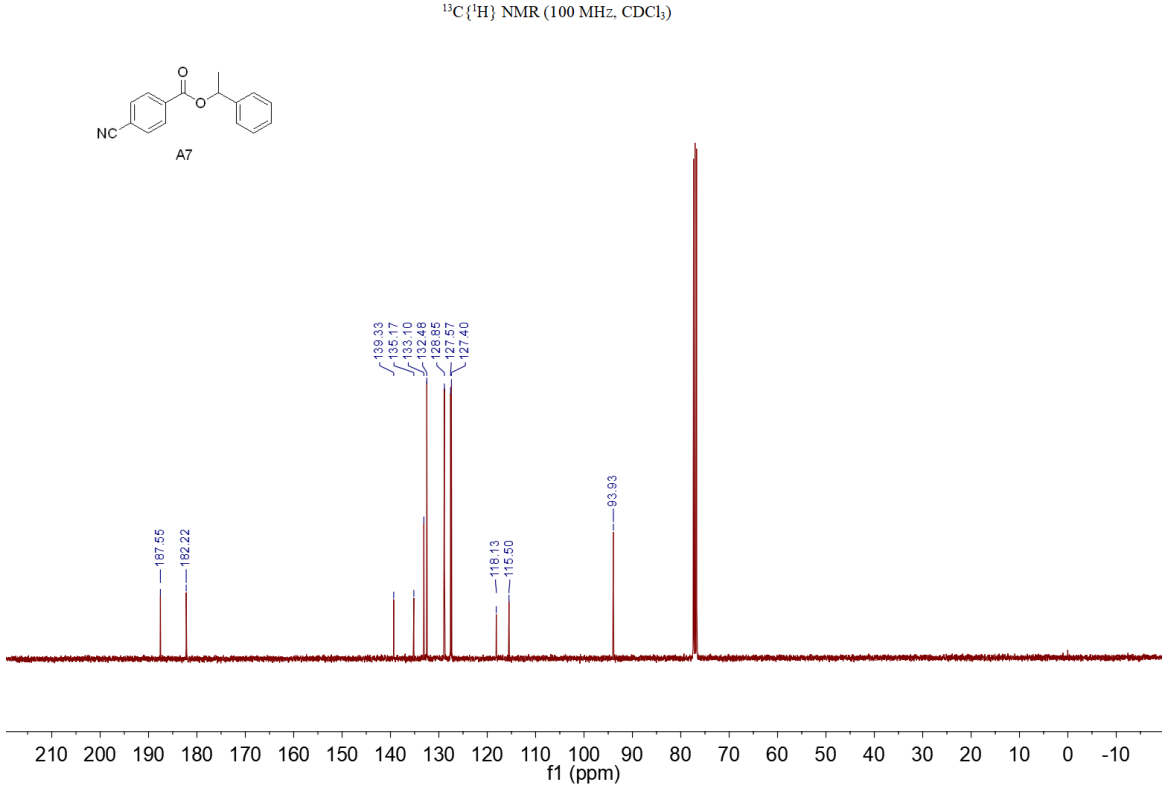


Figure S52. ^{13}C{^{1}H} NMR spectra of **A7**

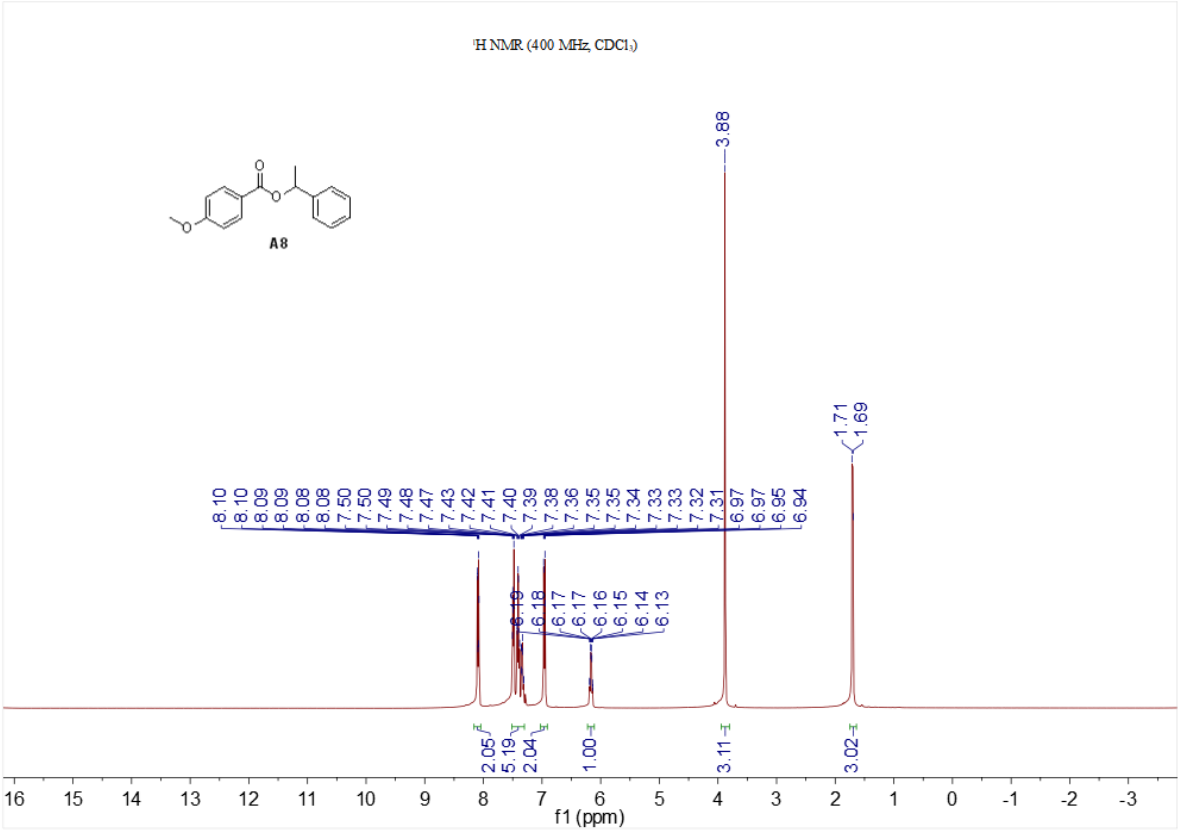


Figure S53. ^{1}H NMR spectra of **A8**

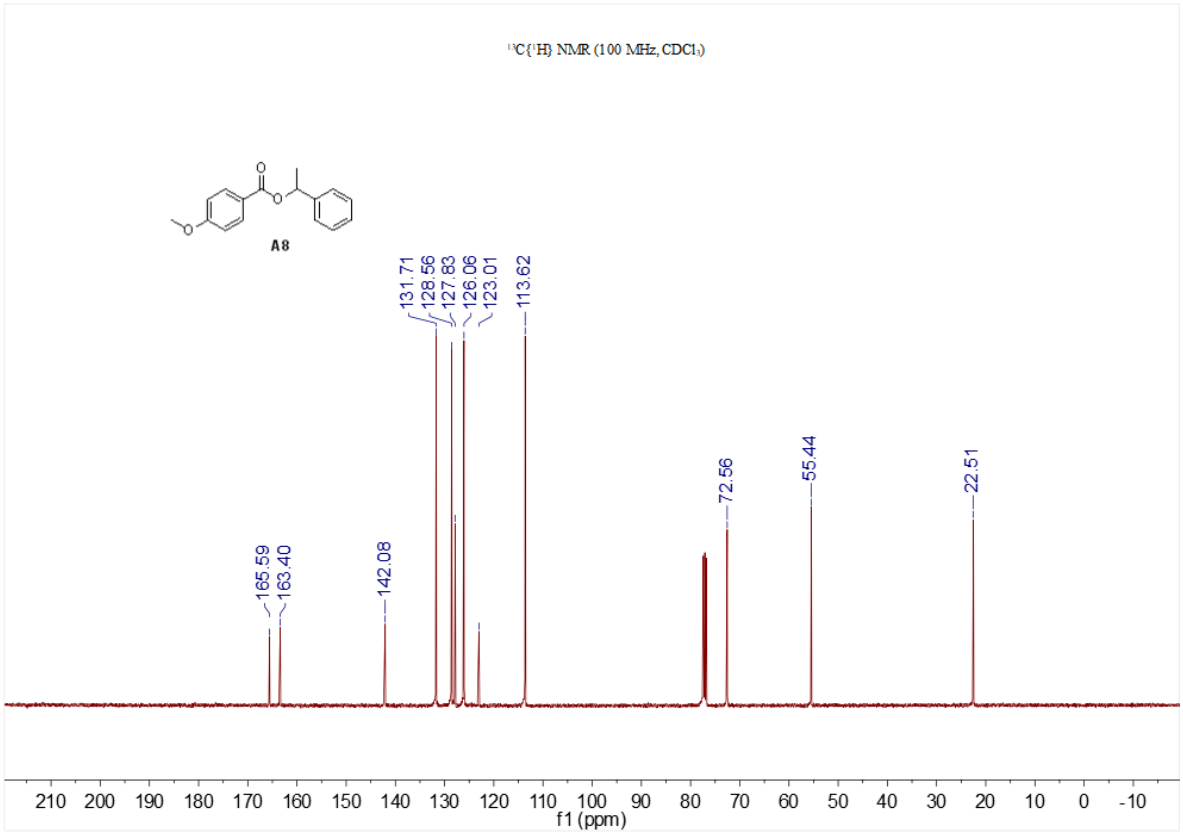


Figure S54. ^{13}C{^{1}H} NMR spectra of **A8**

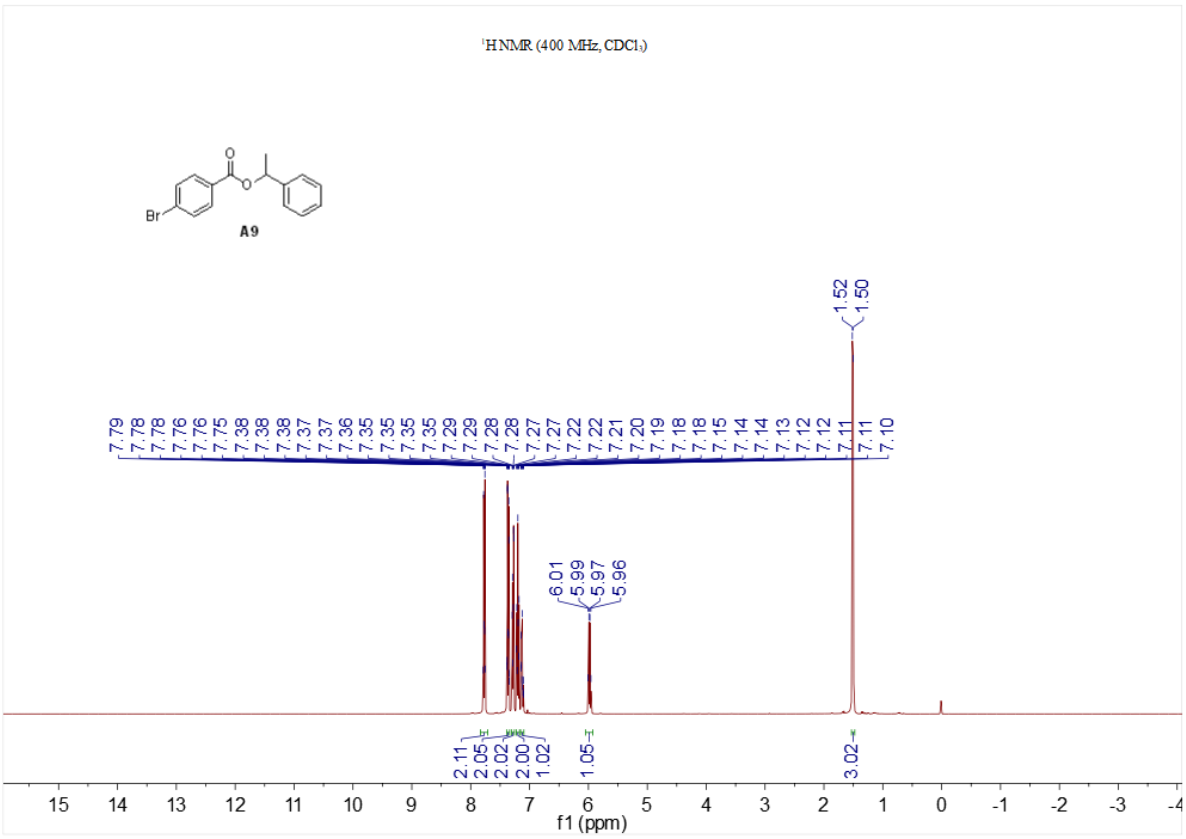


Figure S55. ^{1}H NMR spectra of **A9**

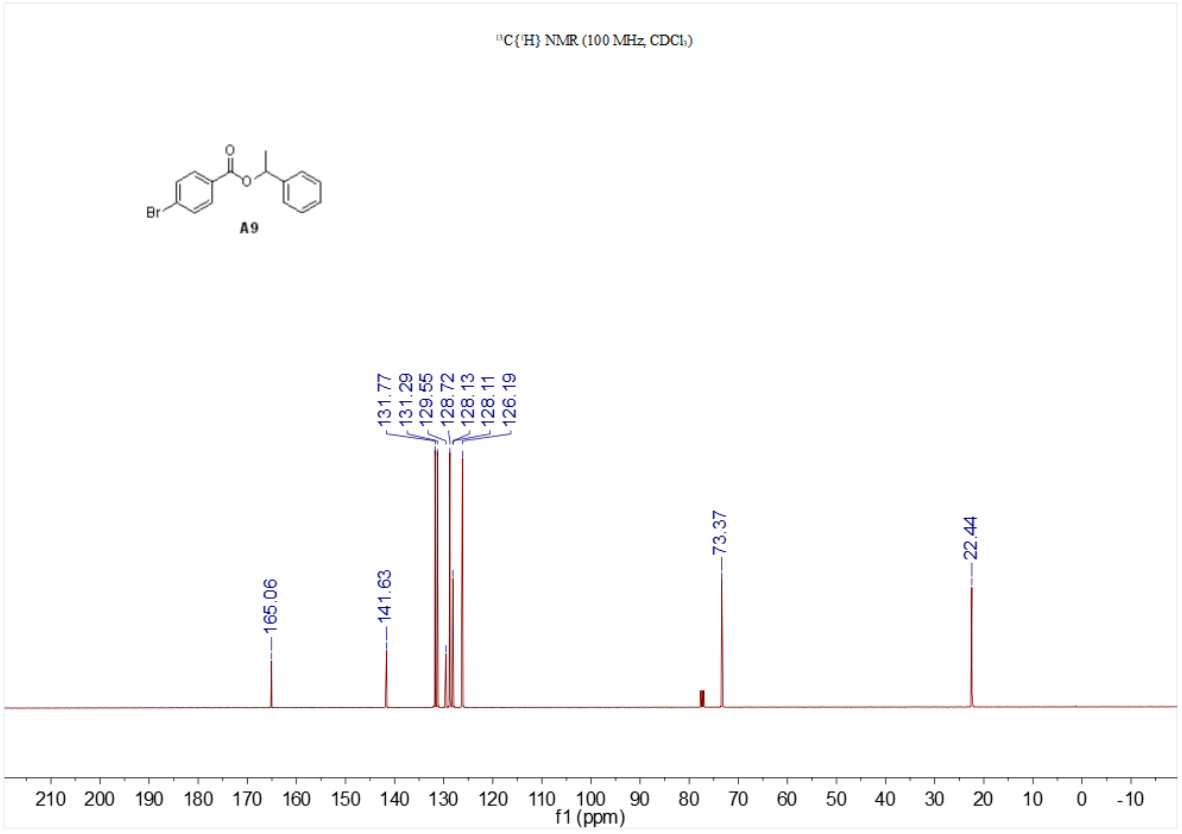


Figure S56. ^{13}C{^{1}H} NMR spectra of **A9**

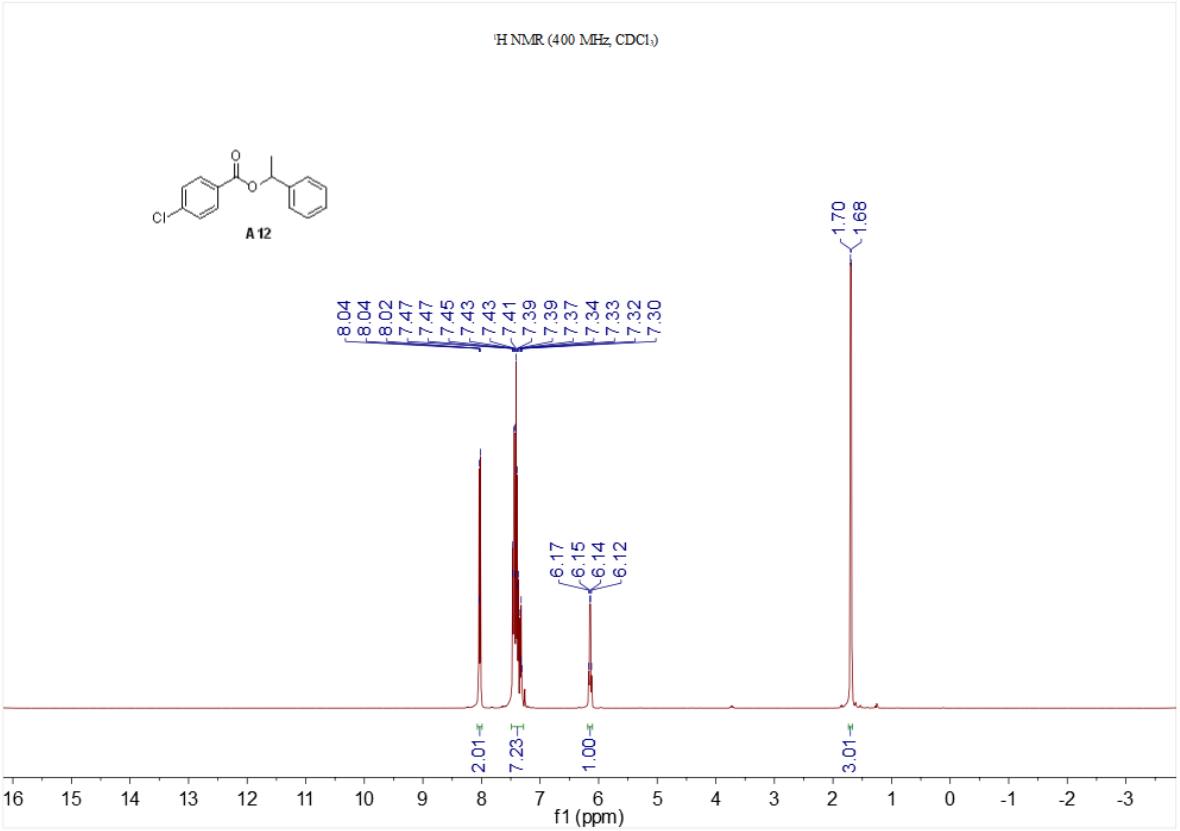


Figure S57. ^{1}H NMR spectra of **A12**

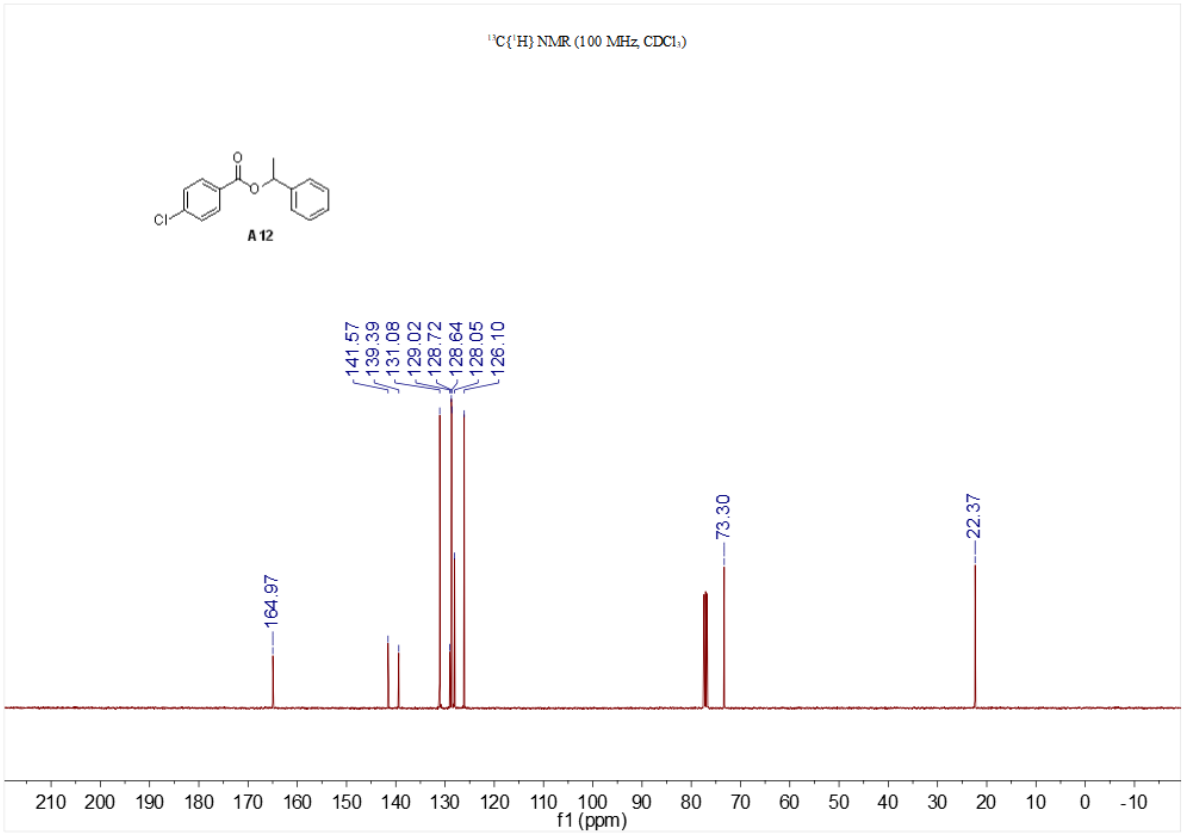


Figure S58. ^{13}C{^{1}H} NMR spectra of **A12**

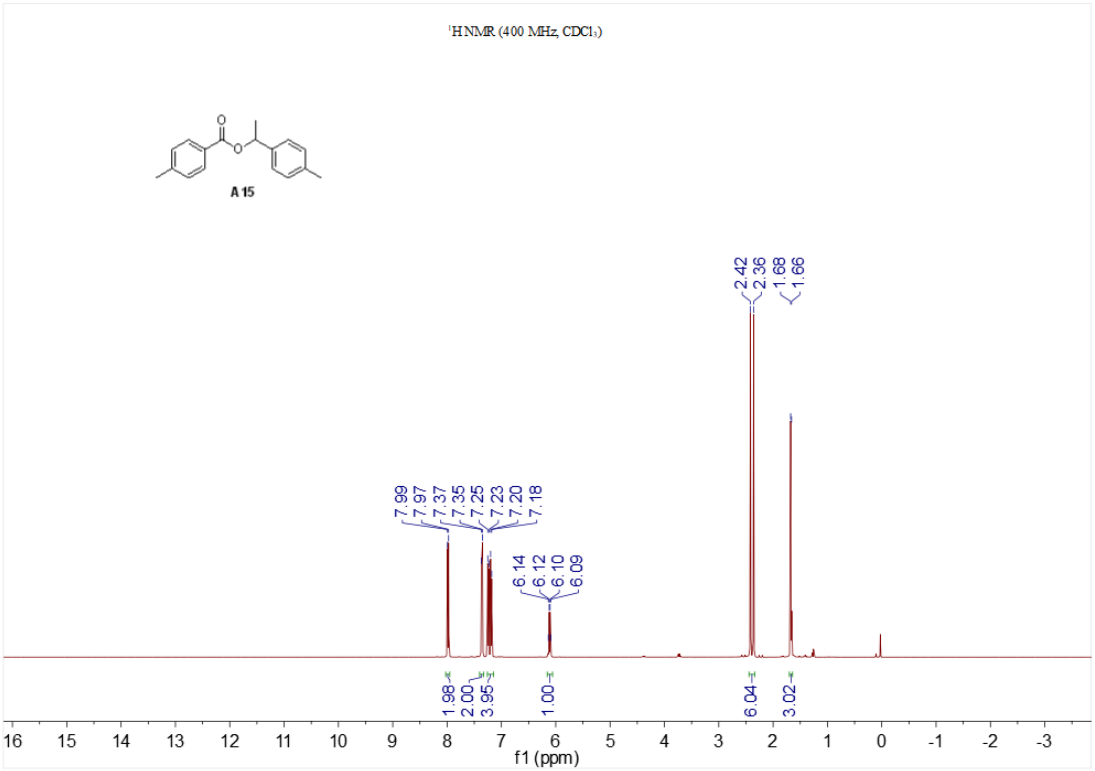


Figure S59. ^{1}H NMR spectra of **A15**

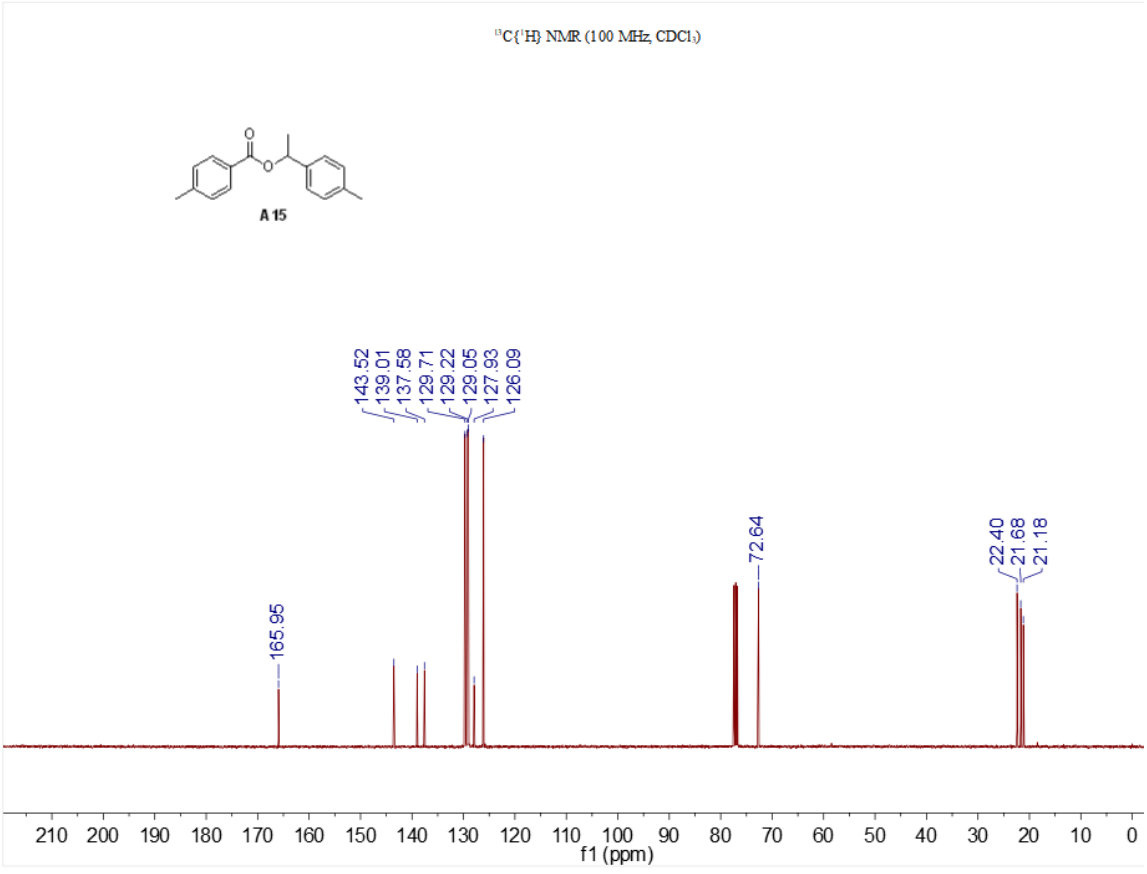


Figure S60. ^{13}C{^{1}H} NMR spectra of **A15**

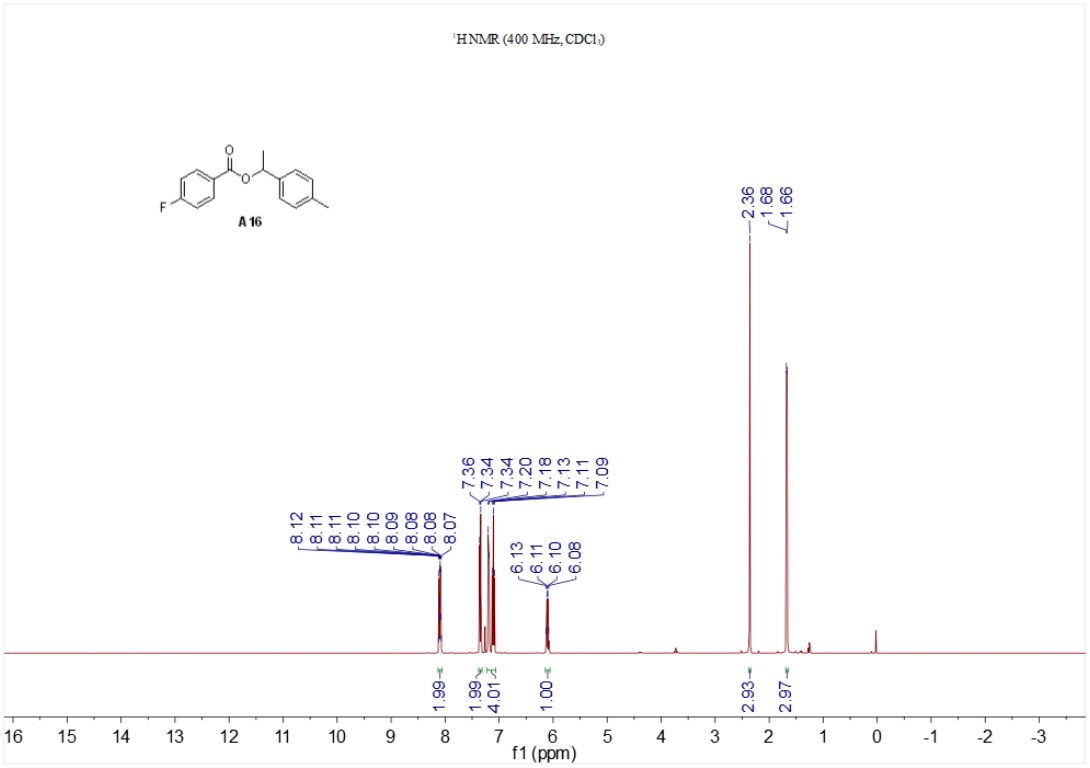


Figure S61. ^{1}H NMR spectra of **A16**

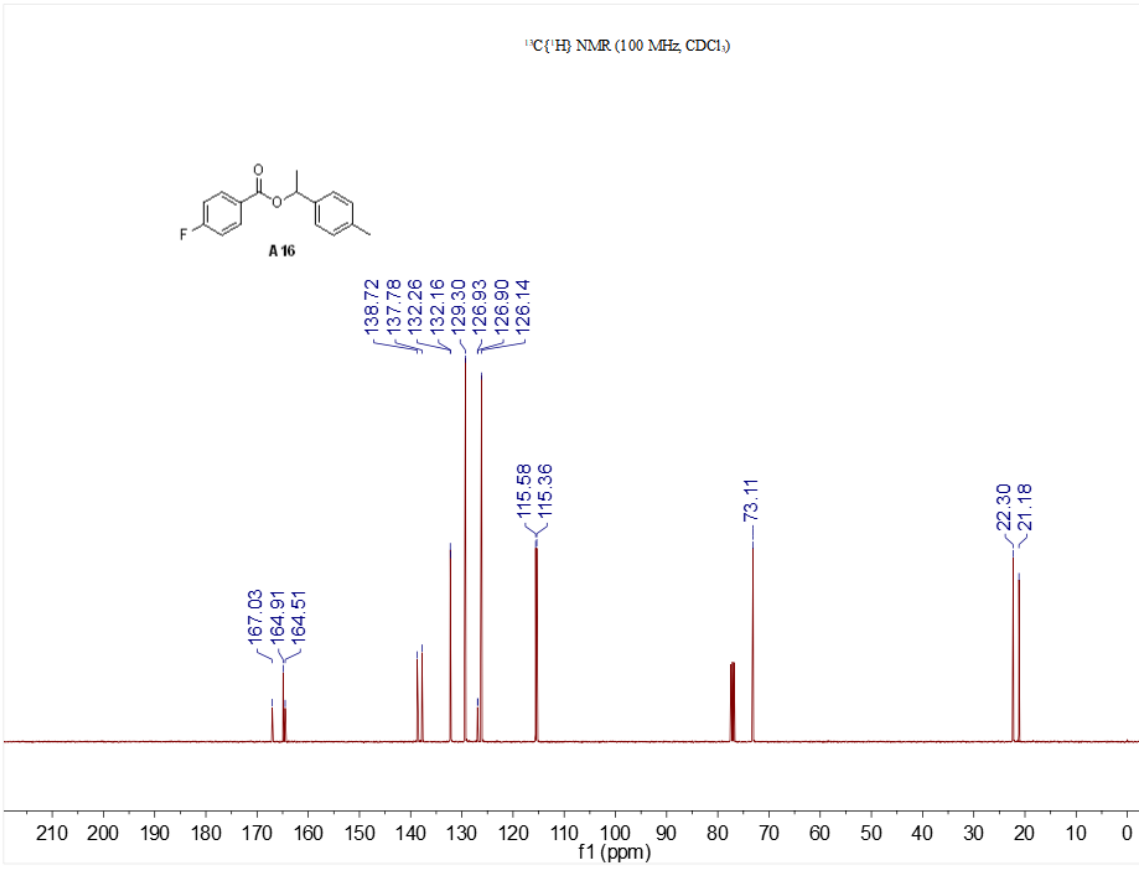


Figure S62. ^{13}C{^{1}H} NMR spectra of **A16**

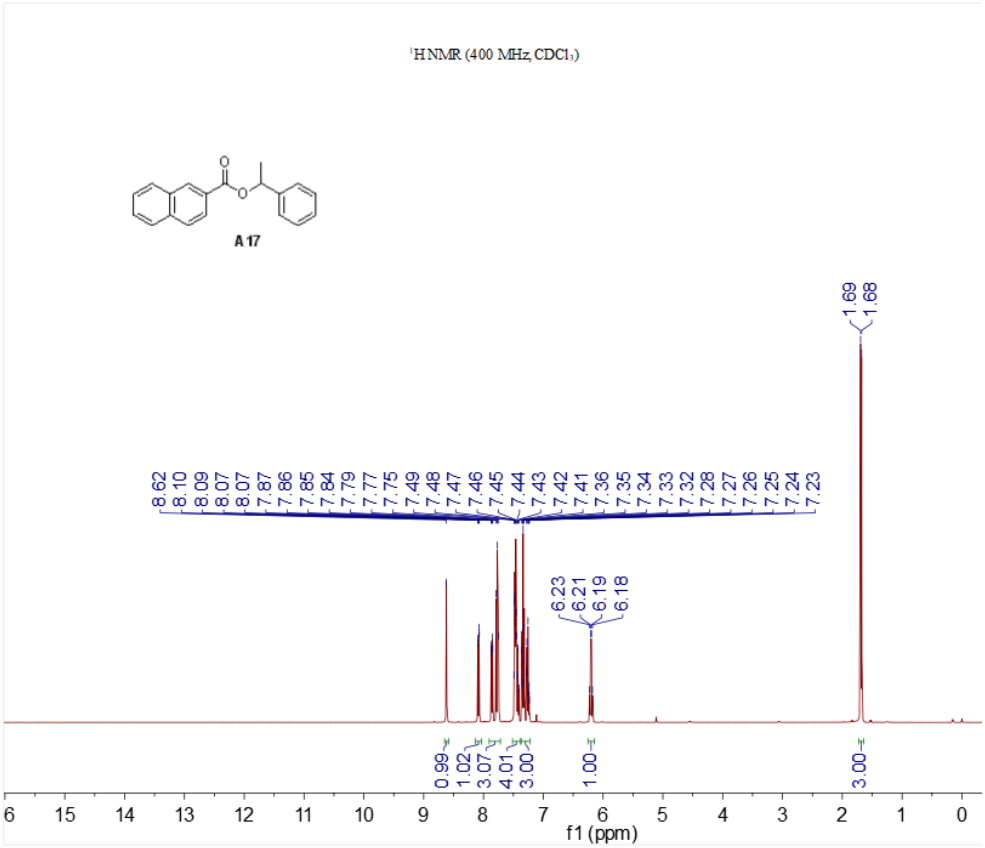


Figure S63. ^{1}H NMR spectra of **A17**

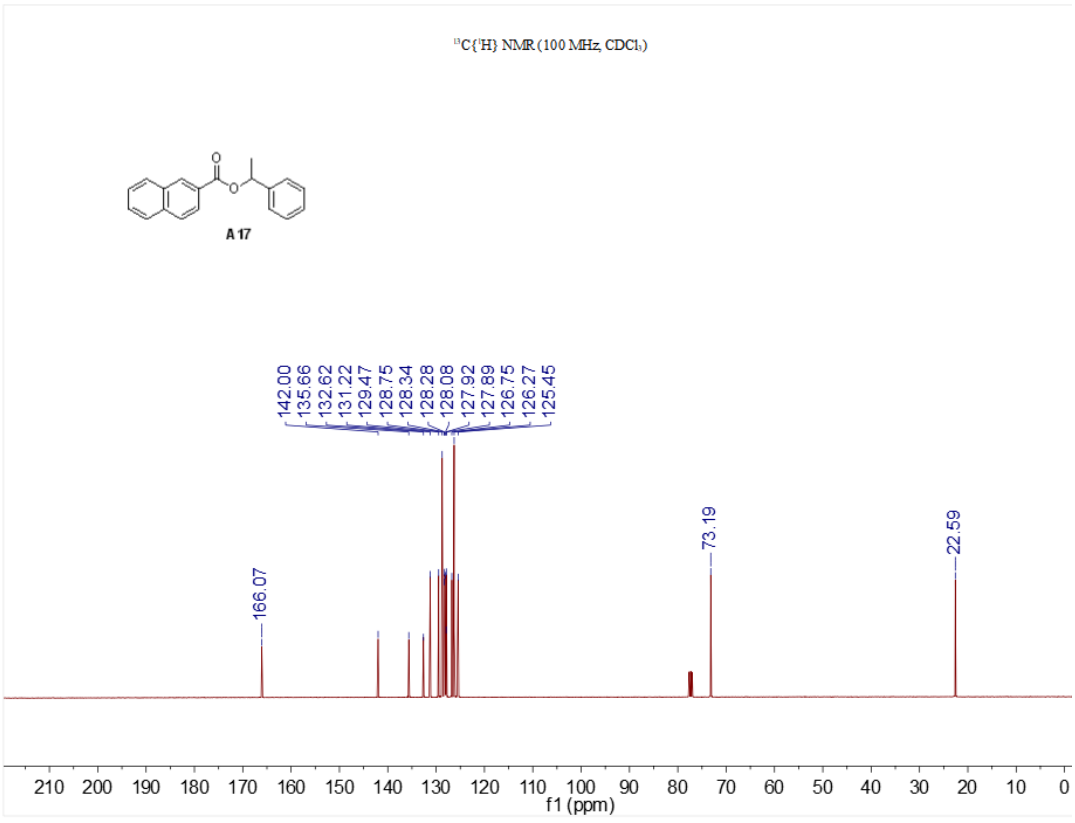


Figure S64. ^{13}C{^{1}H} NMR spectra of **A17**

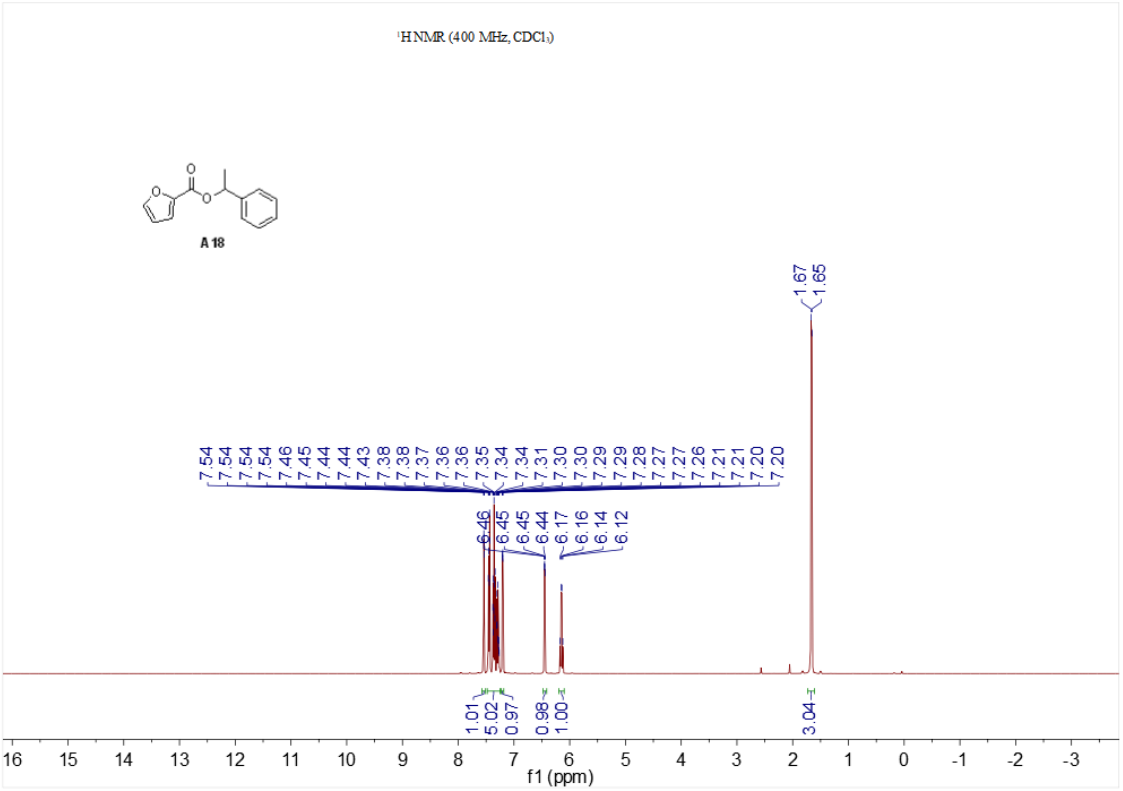


Figure S65. ^{1}H NMR spectra of **A18**

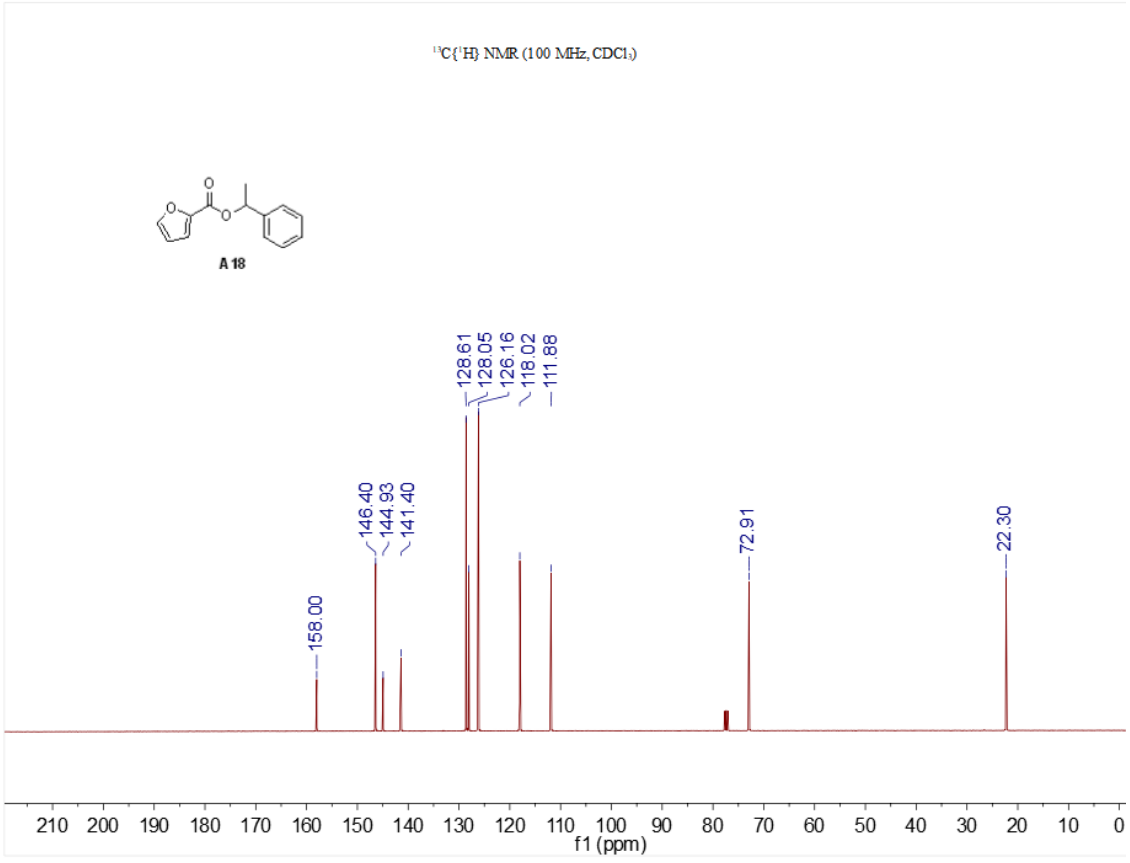


Figure S66. ^{13}C{^{1}H} NMR spectra of **A18**

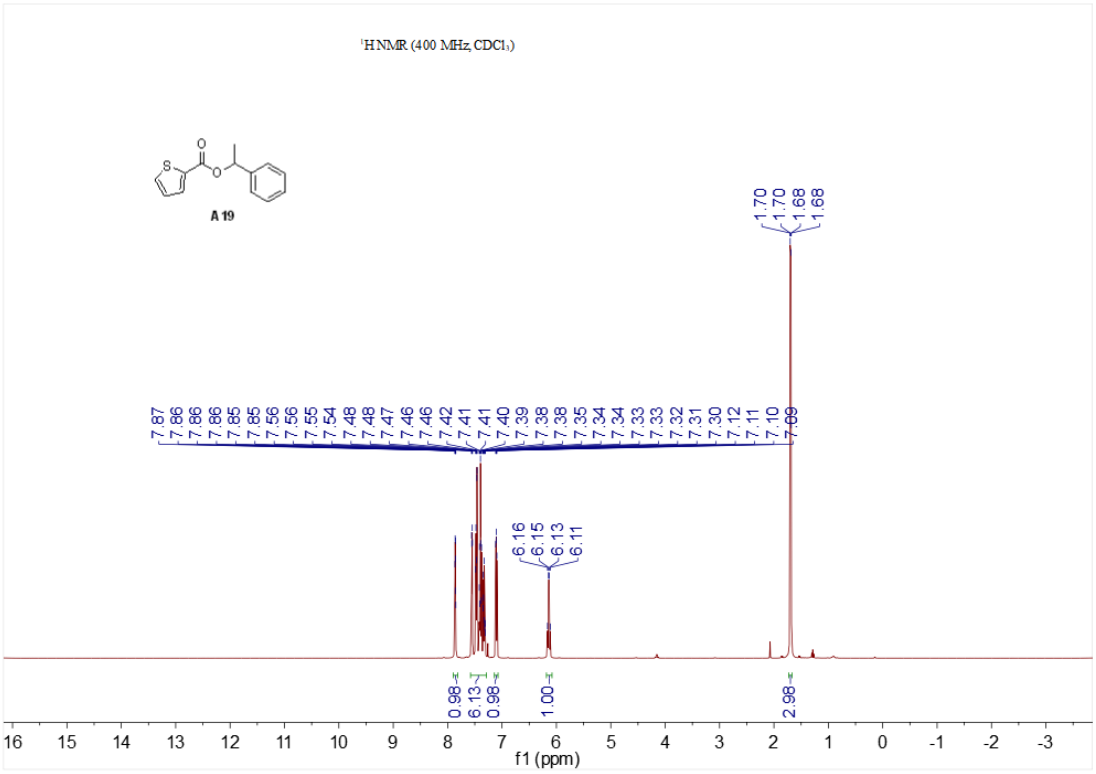


Figure S67. ^{1}H NMR spectra of **A19**

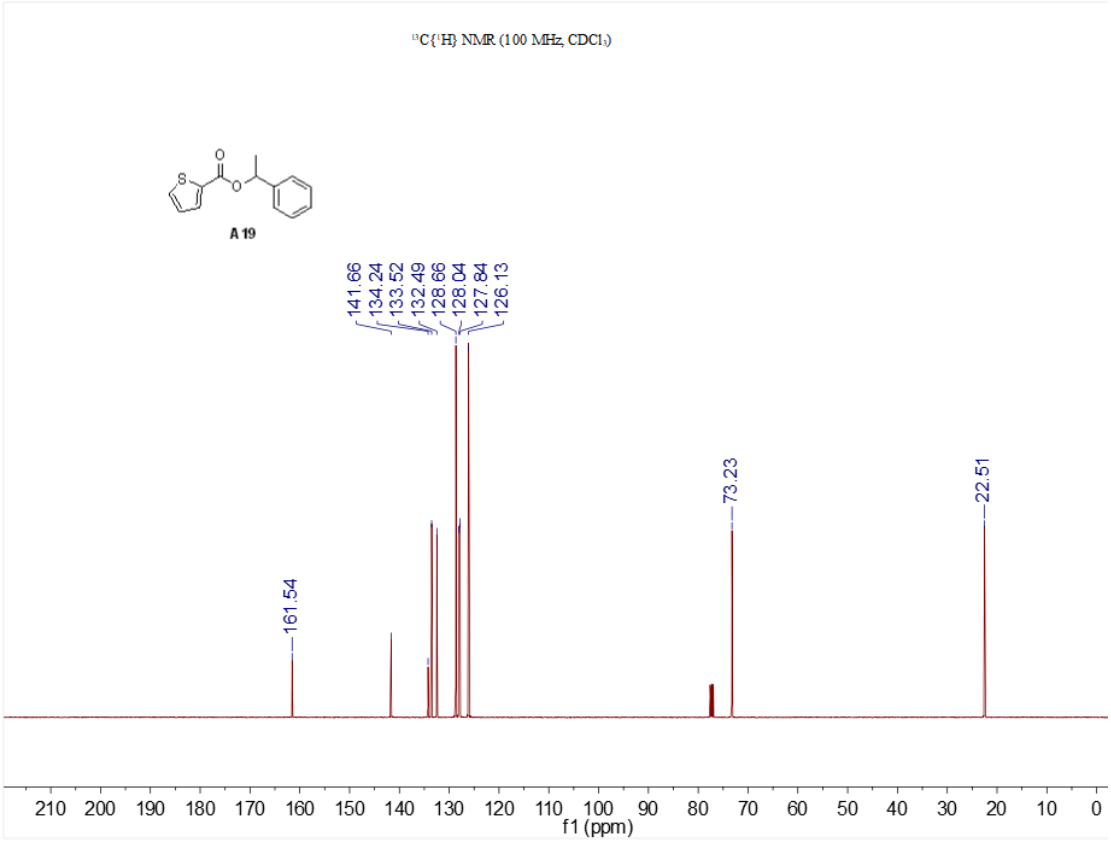


Figure S68. ^{13}C{^{1}H} NMR spectra of **A19**

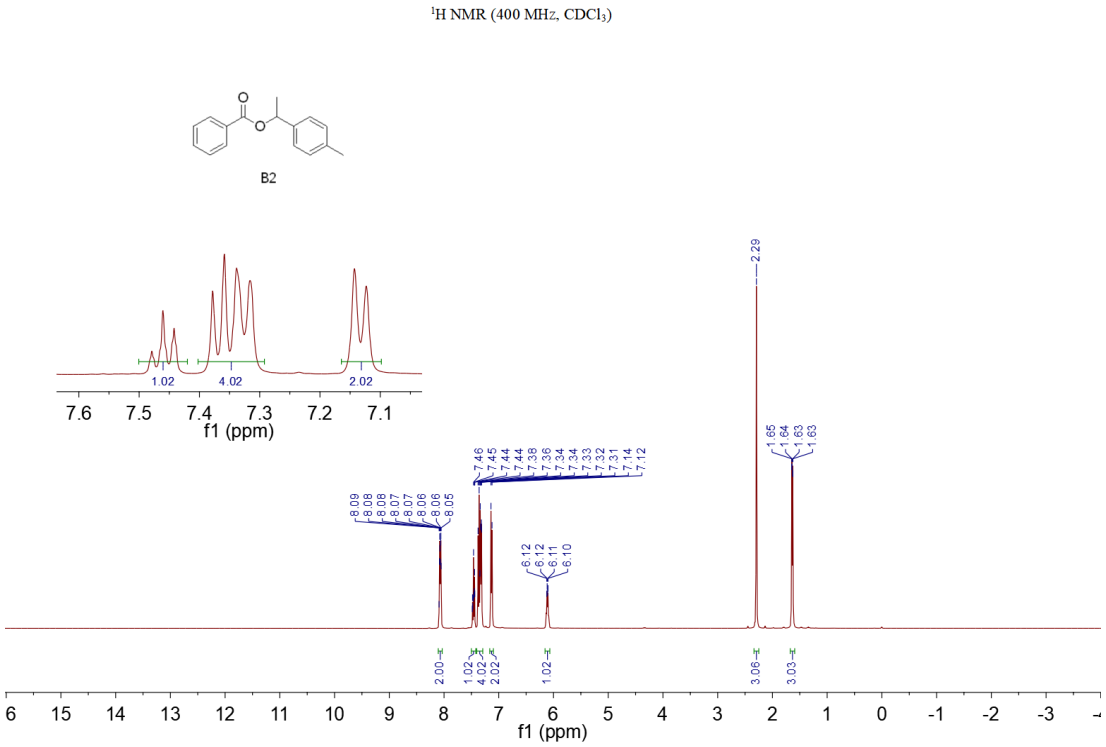


Figure S69. ^{1}H NMR spectra of **B2**

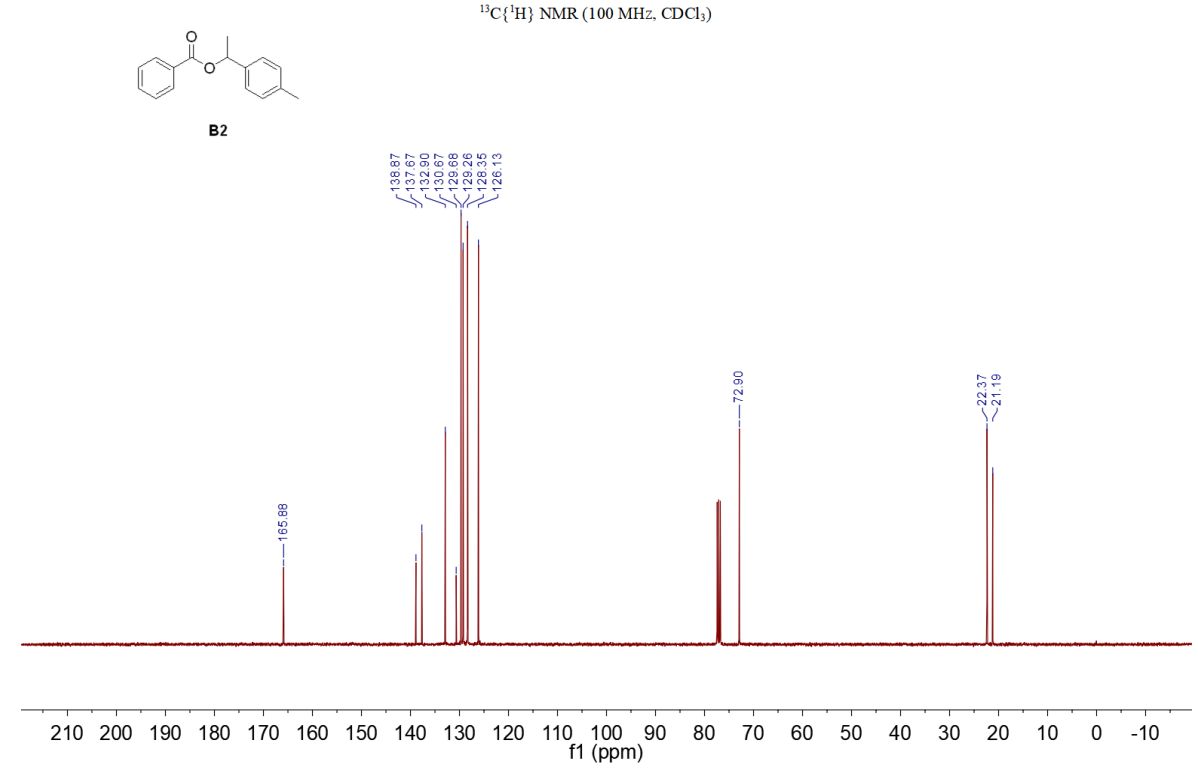


Figure S70. ^{13}C{^{1}H} NMR spectra of **B2**

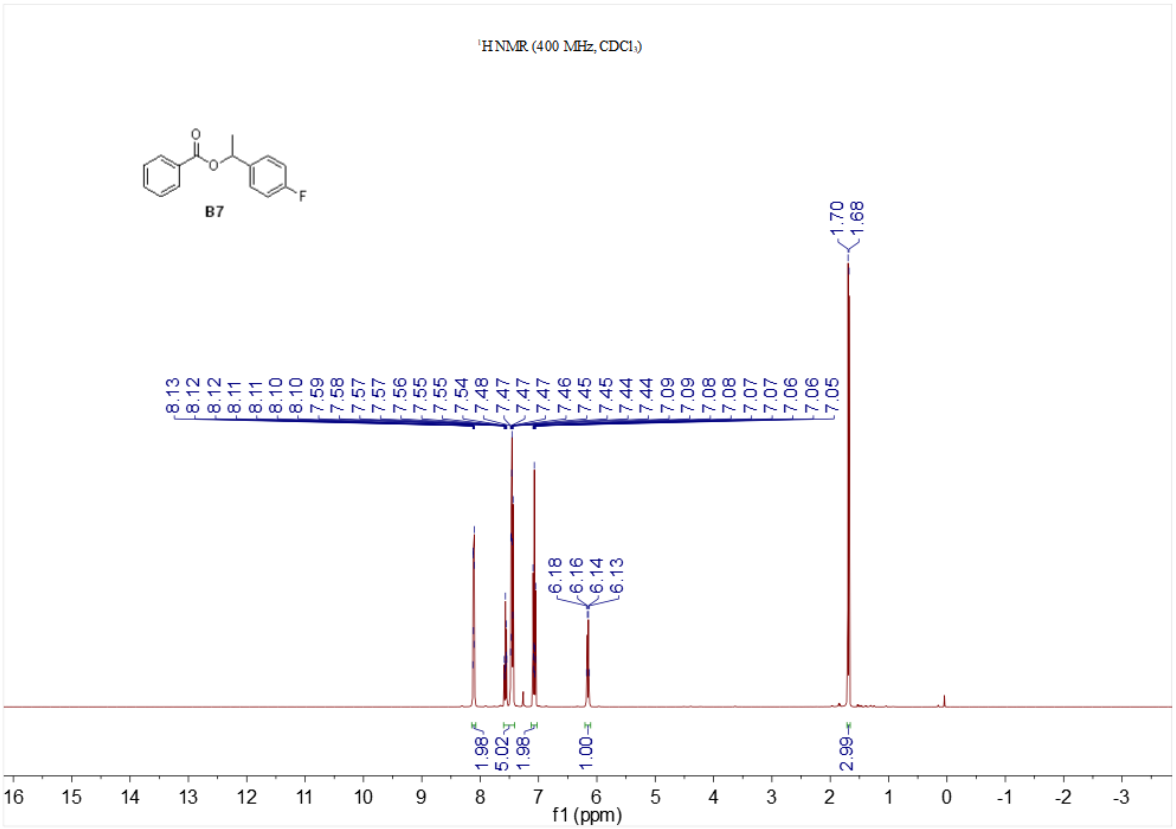


Figure S71. ^{1}H NMR spectra of **B7**

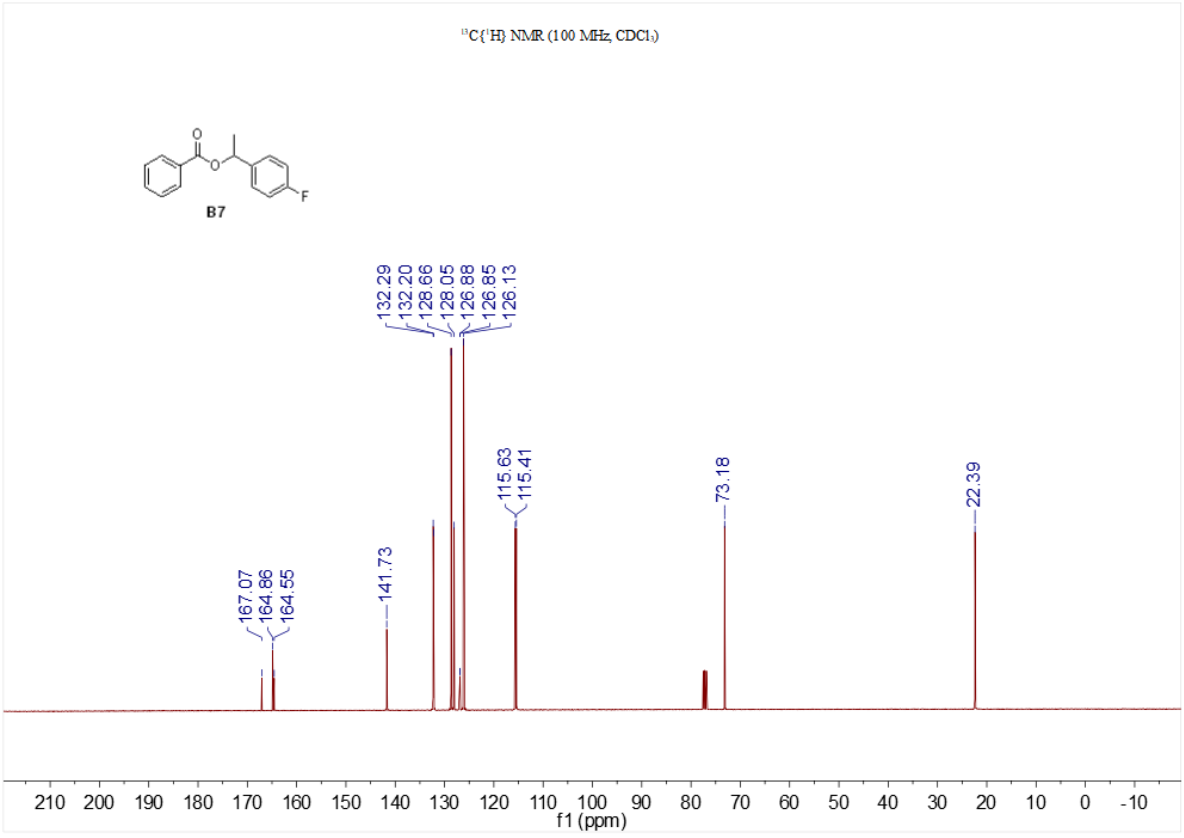


Figure S72. ^{13}C{^{1}H} NMR spectra of **B7**

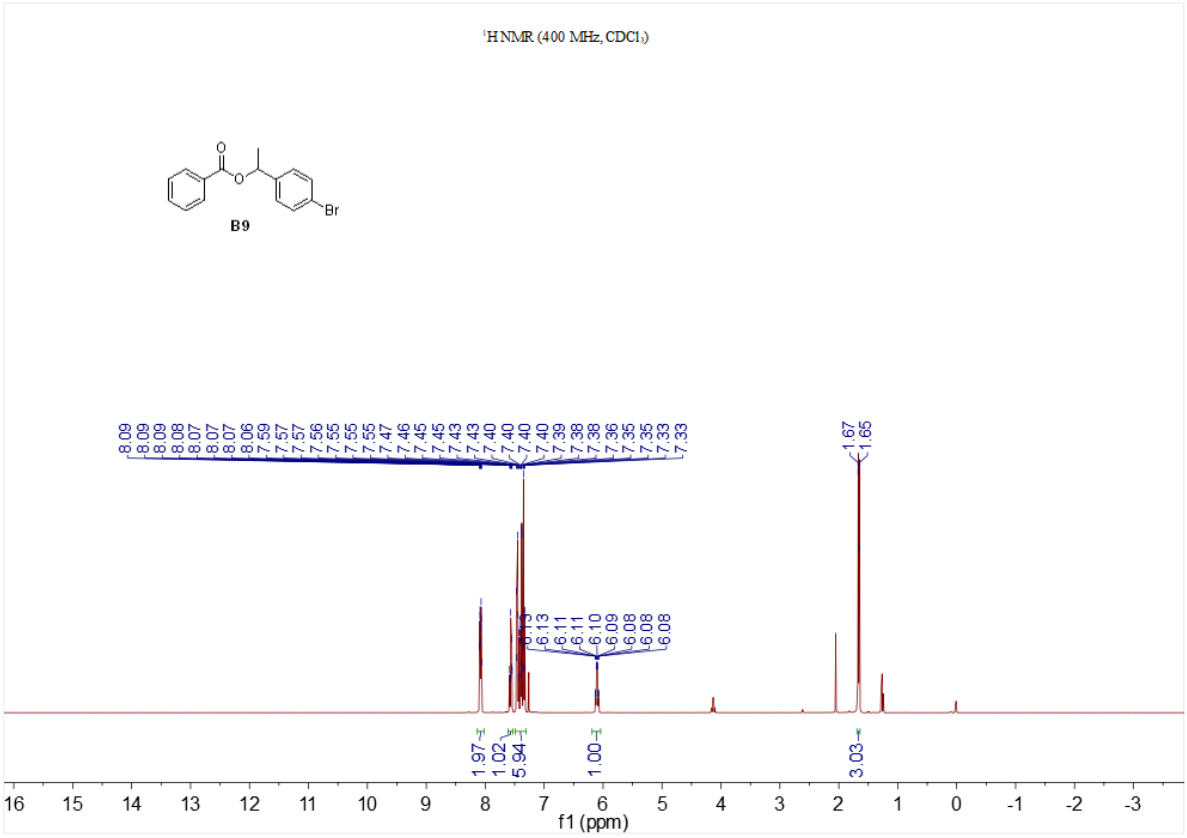


Figure S73. ^{1}H NMR spectra of **B9**

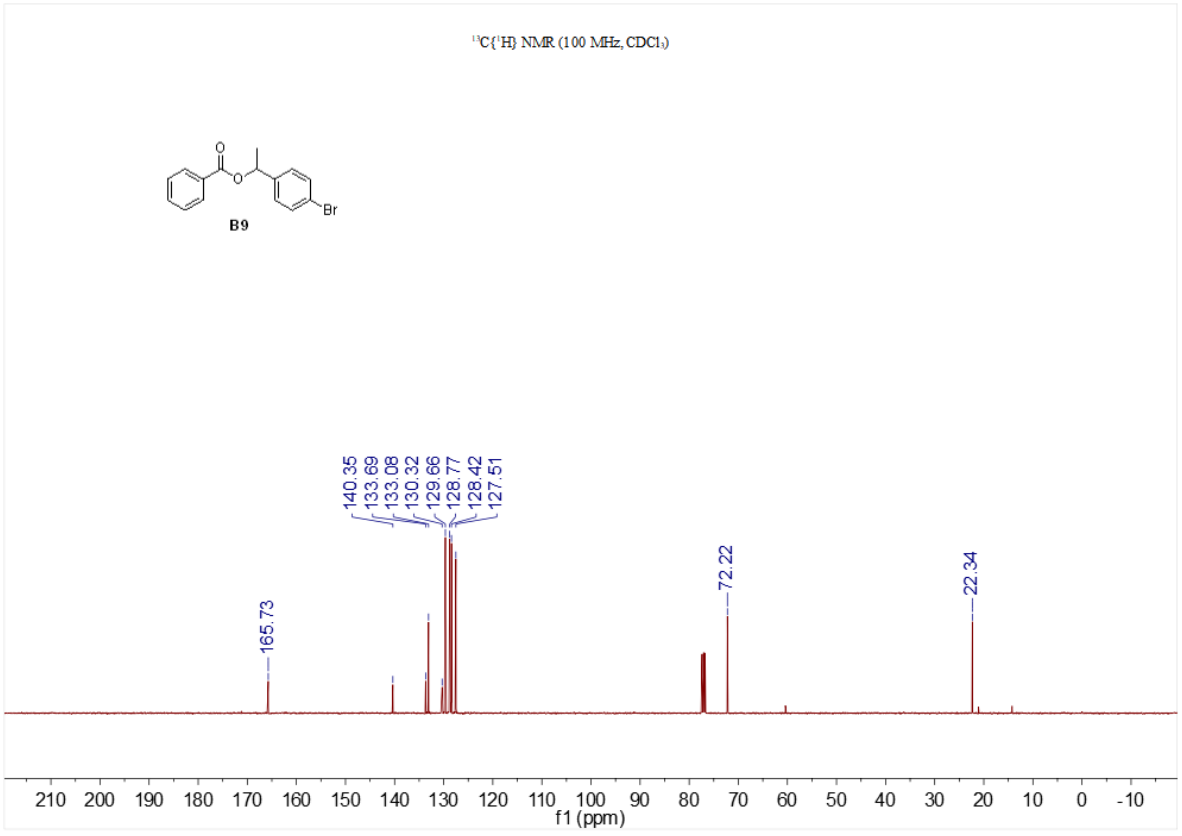


Figure S74. ^{13}C{^{1}H} NMR spectra of **B9**

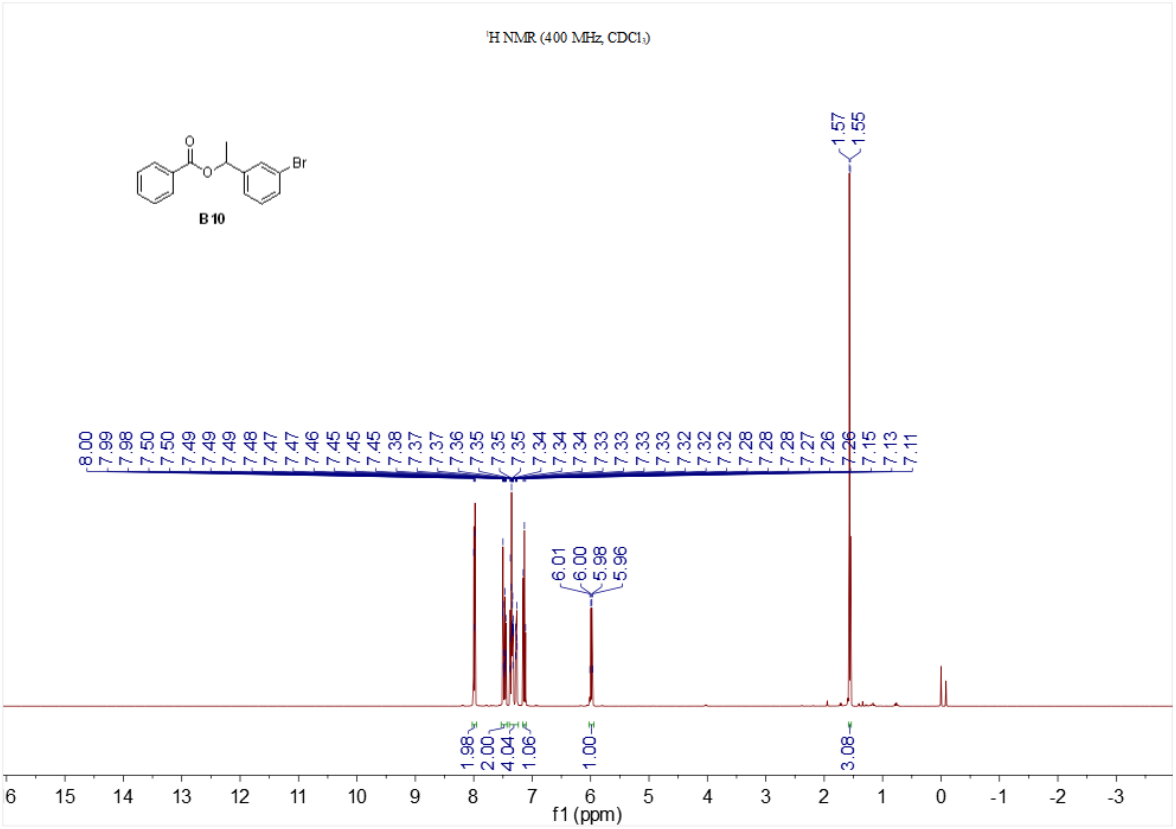


Figure S75. ^{1}H NMR spectra of **B10**

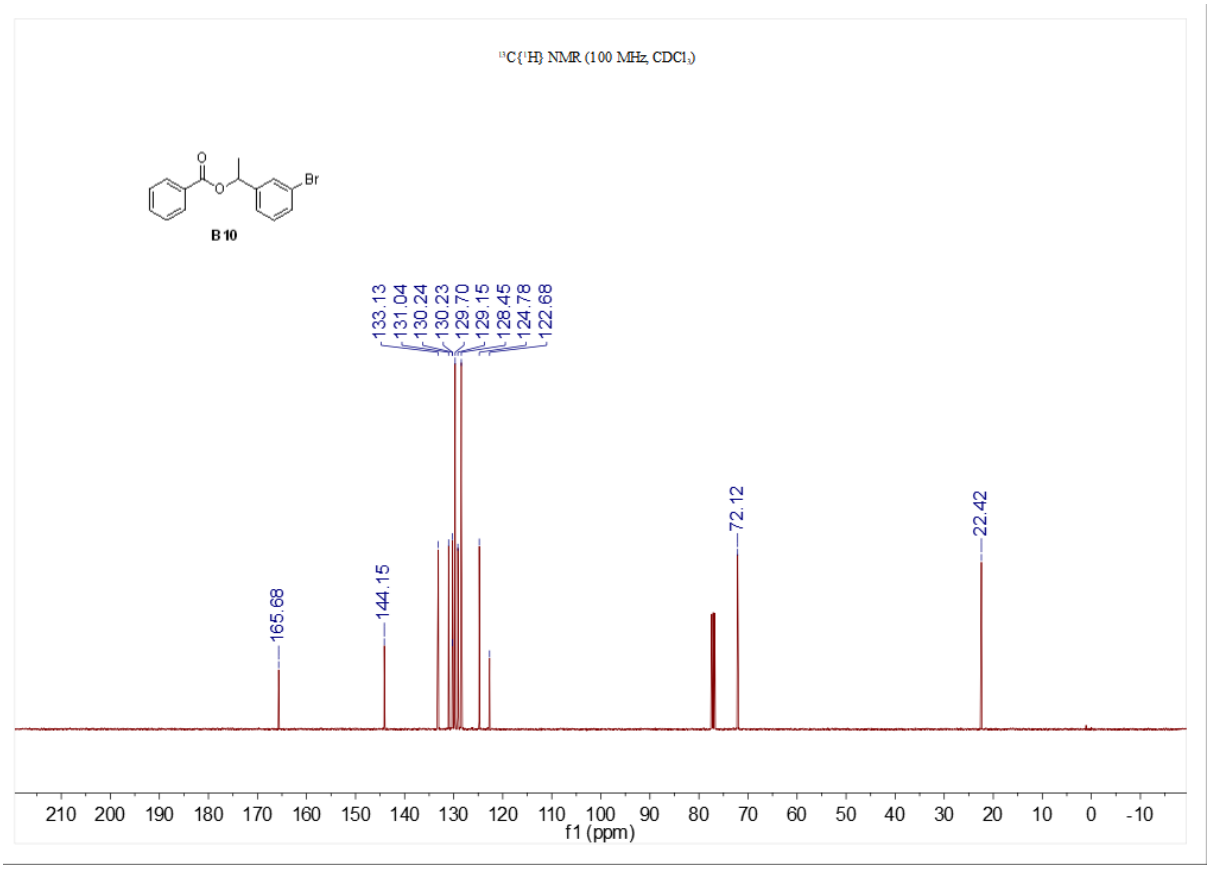


Figure S76. ^{13}C{^{1}H} NMR spectra of **B10**

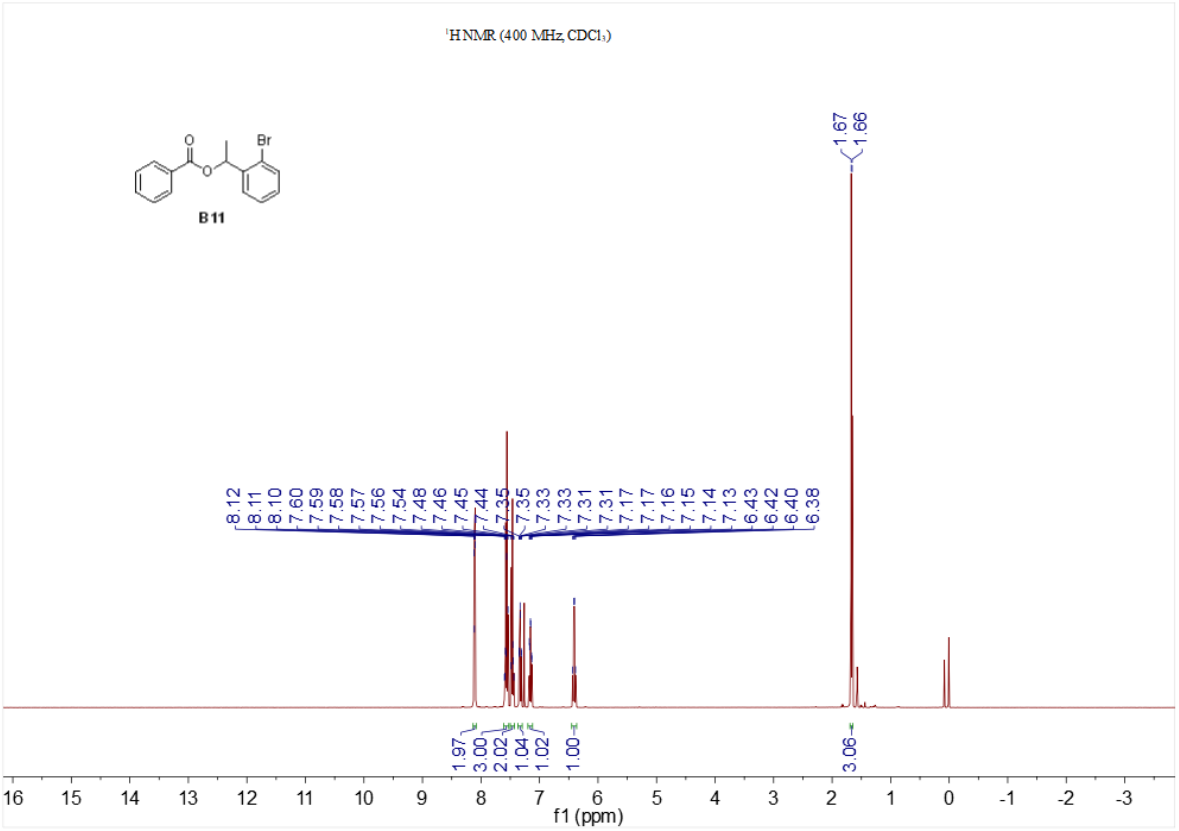


Figure S77. ^{1}H NMR spectra of **B11**

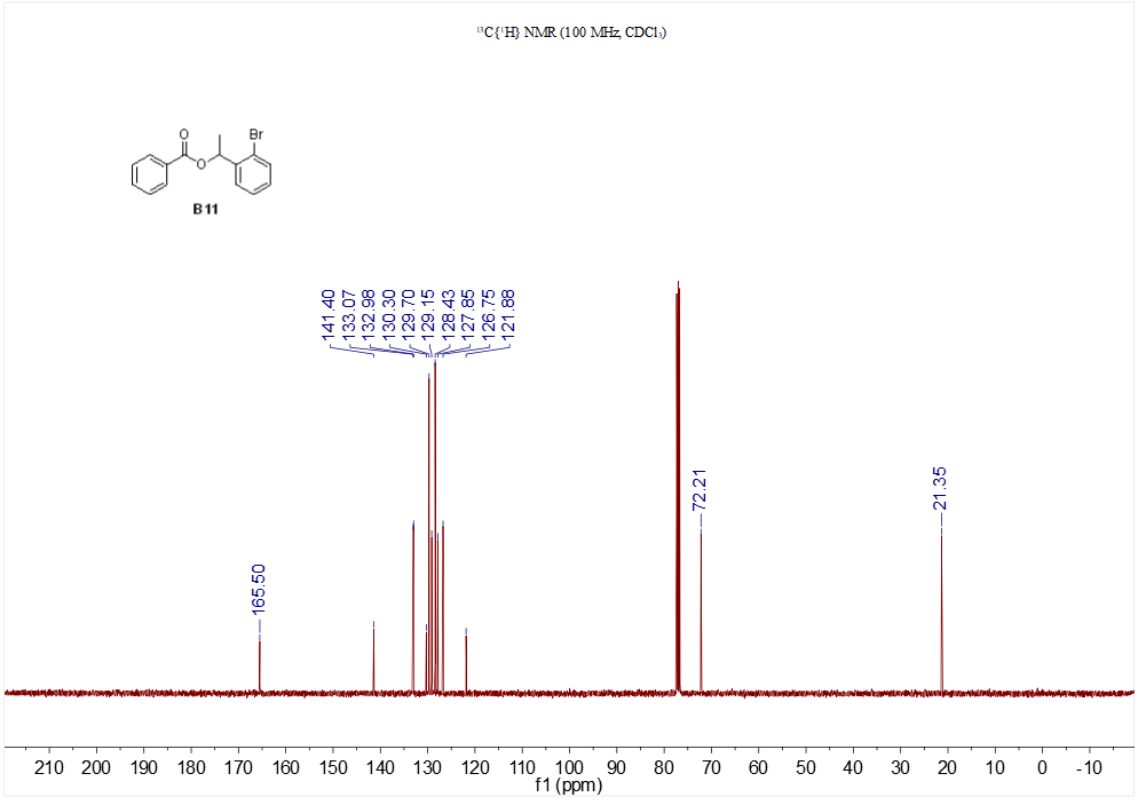


Figure S78. ^{13}C{^{1}H} NMR spectra of **B11**

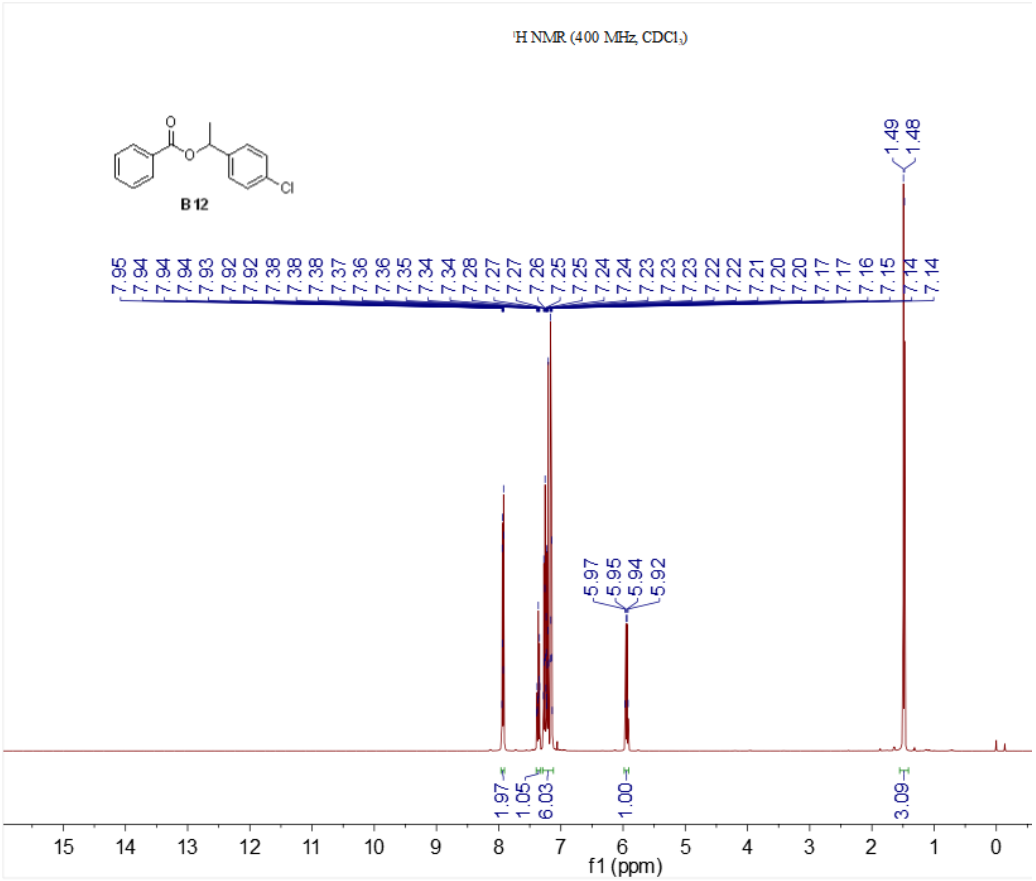


Figure S79. ^{1}H NMR spectra of **B12**

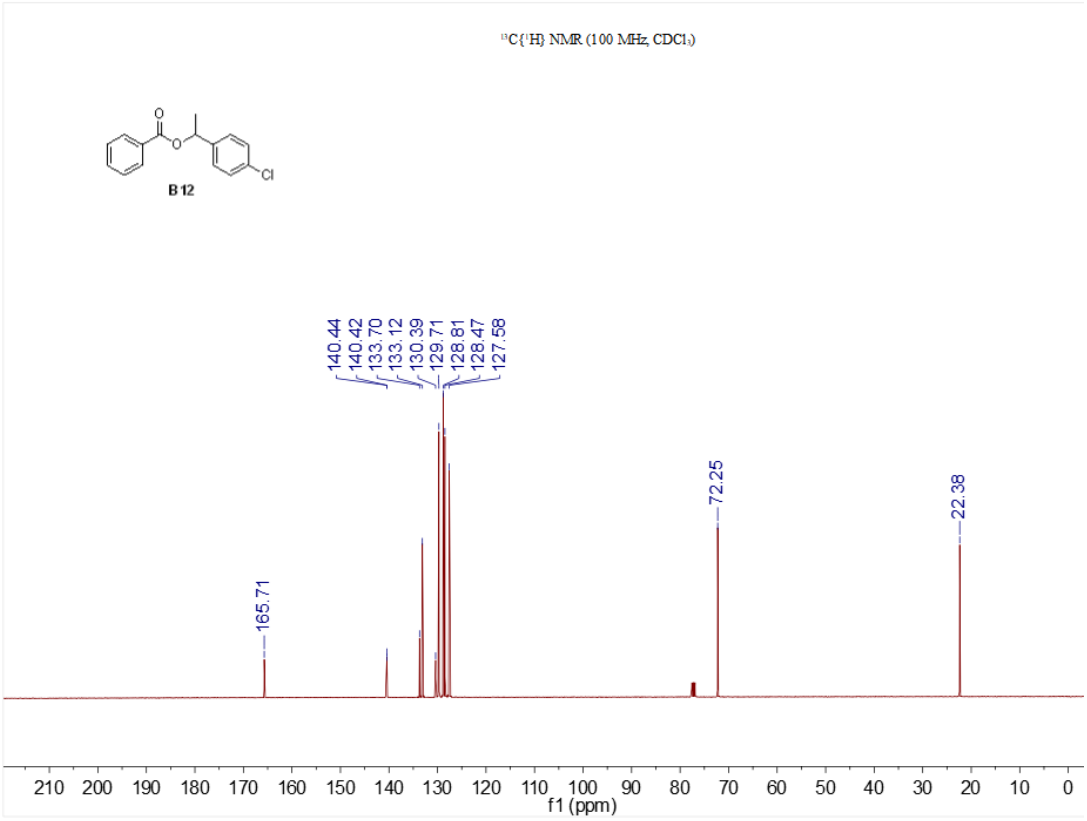


Figure S80. ^{13}C{^{1}H} NMR spectra of **B12**

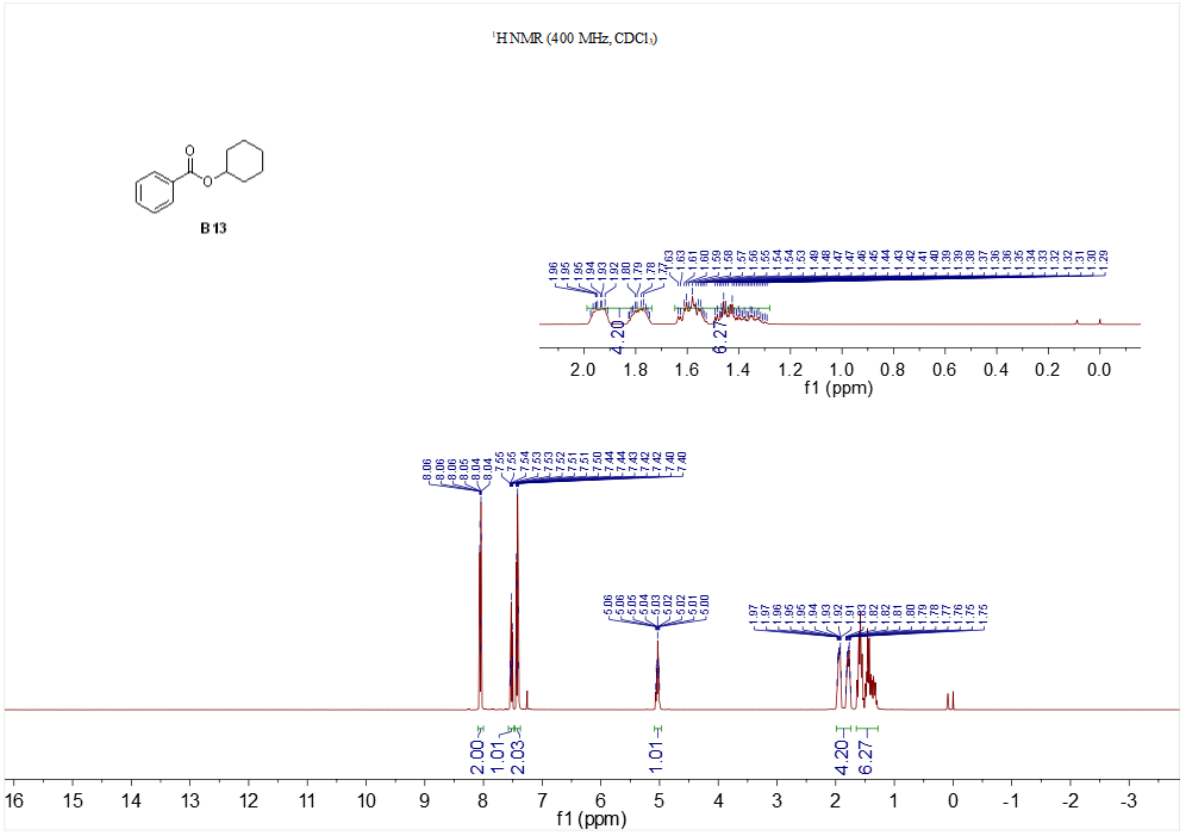


Figure S81. ^{1}H NMR spectra of **B13**

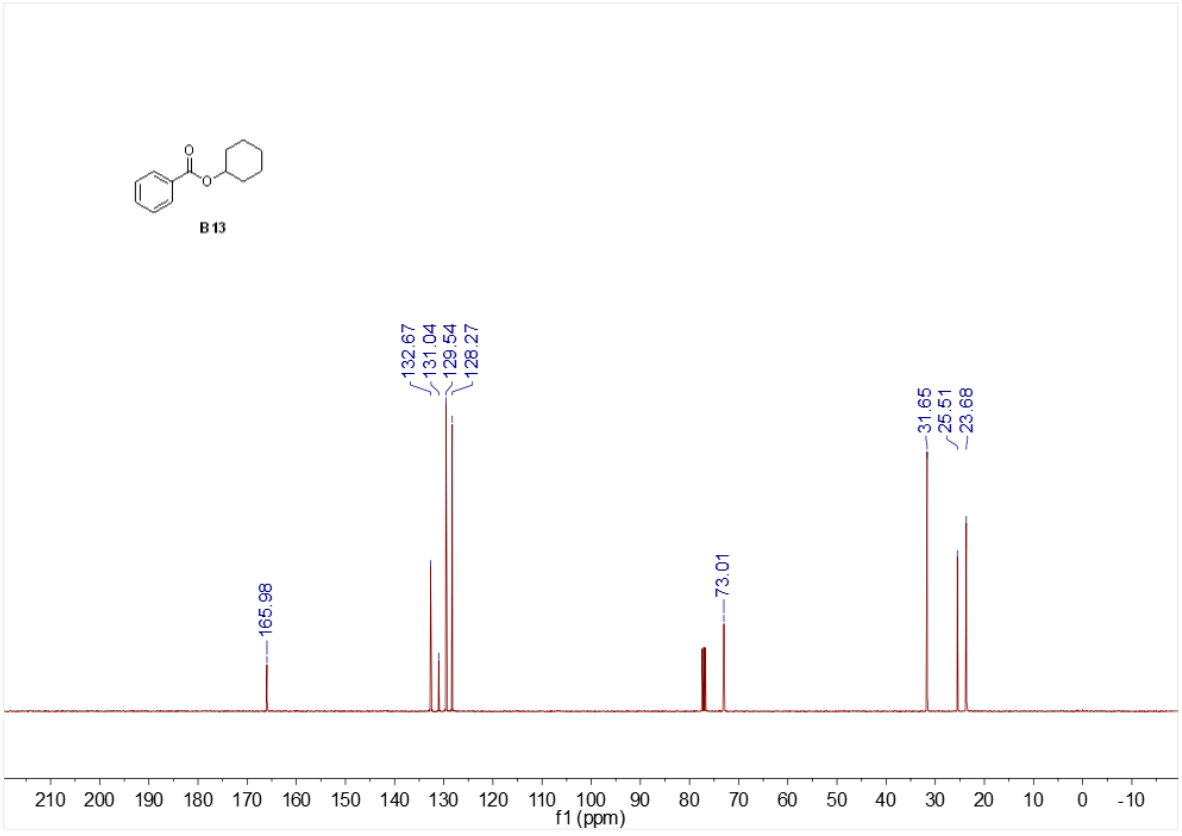


Figure S82. ^{13}C{^{1}H} NMR spectra of **B13**

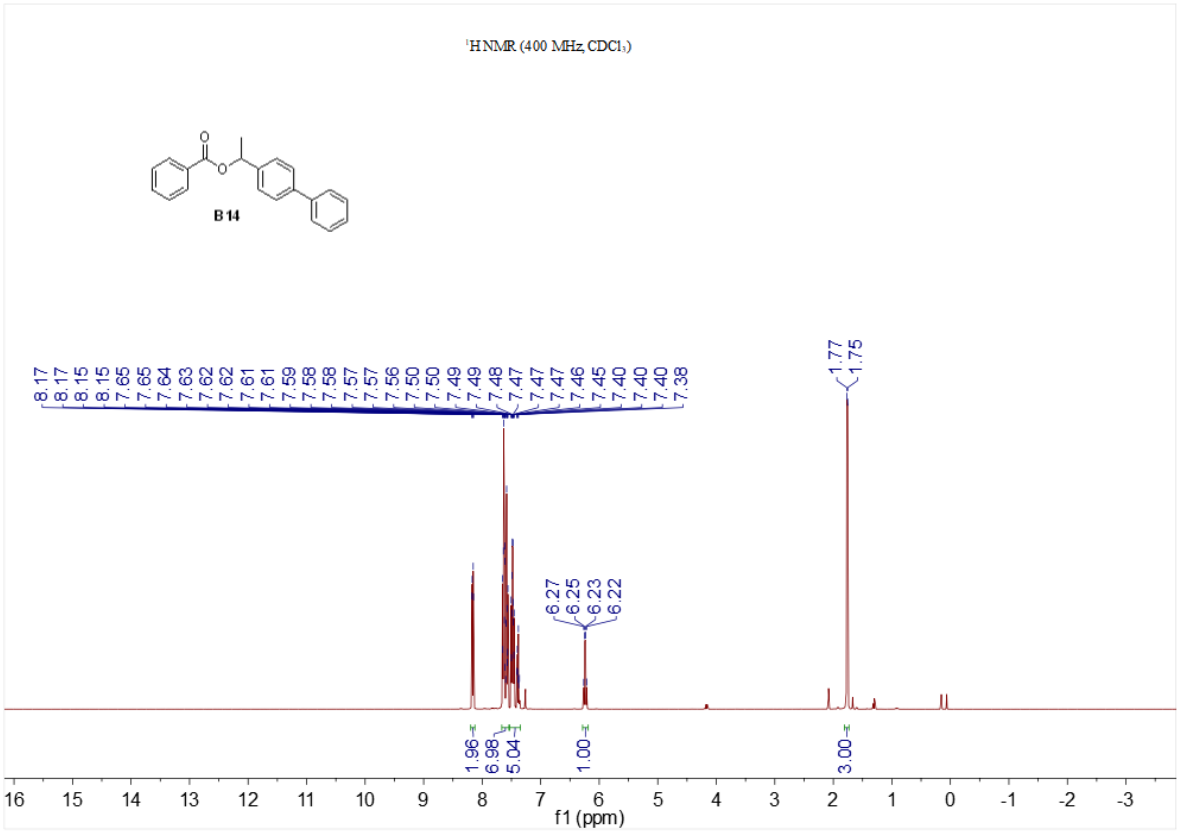


Figure S83. ^{1}H NMR spectra of **B14**

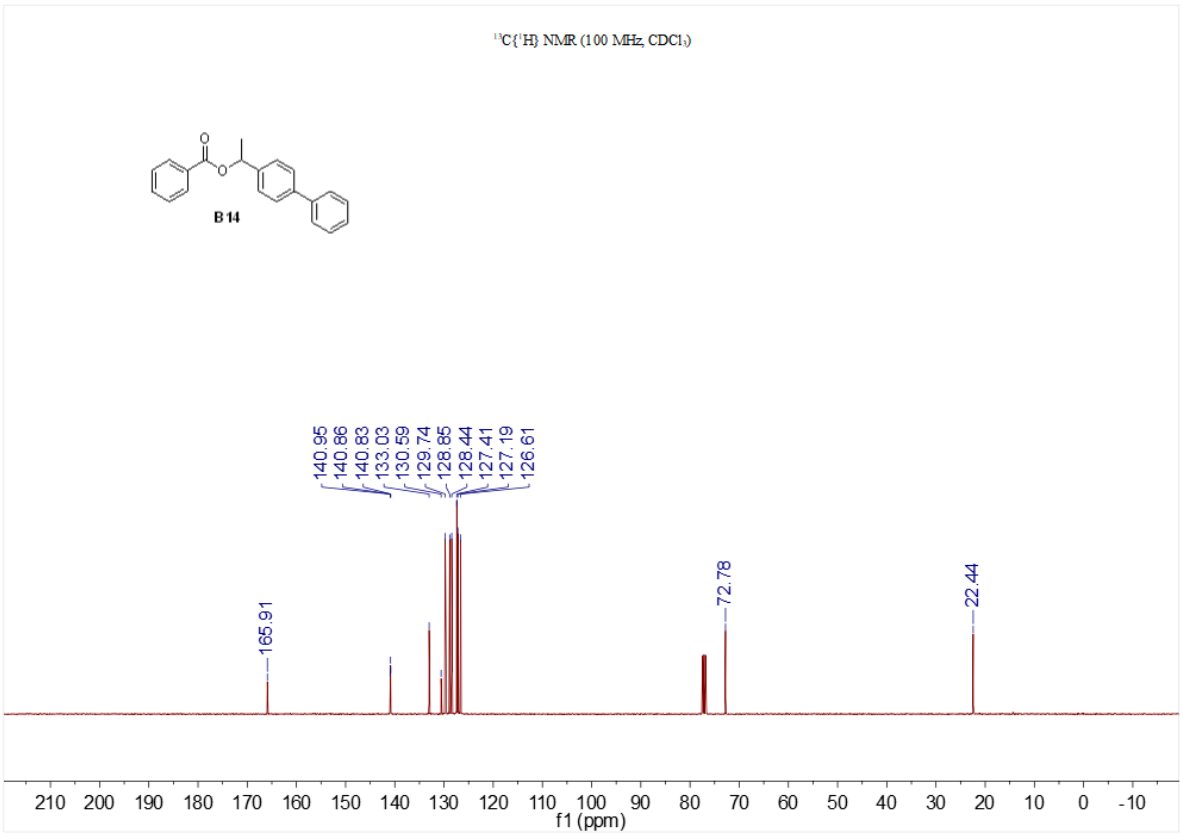


Figure S84. ^{13}C{^{1}H} NMR spectra of **B14**

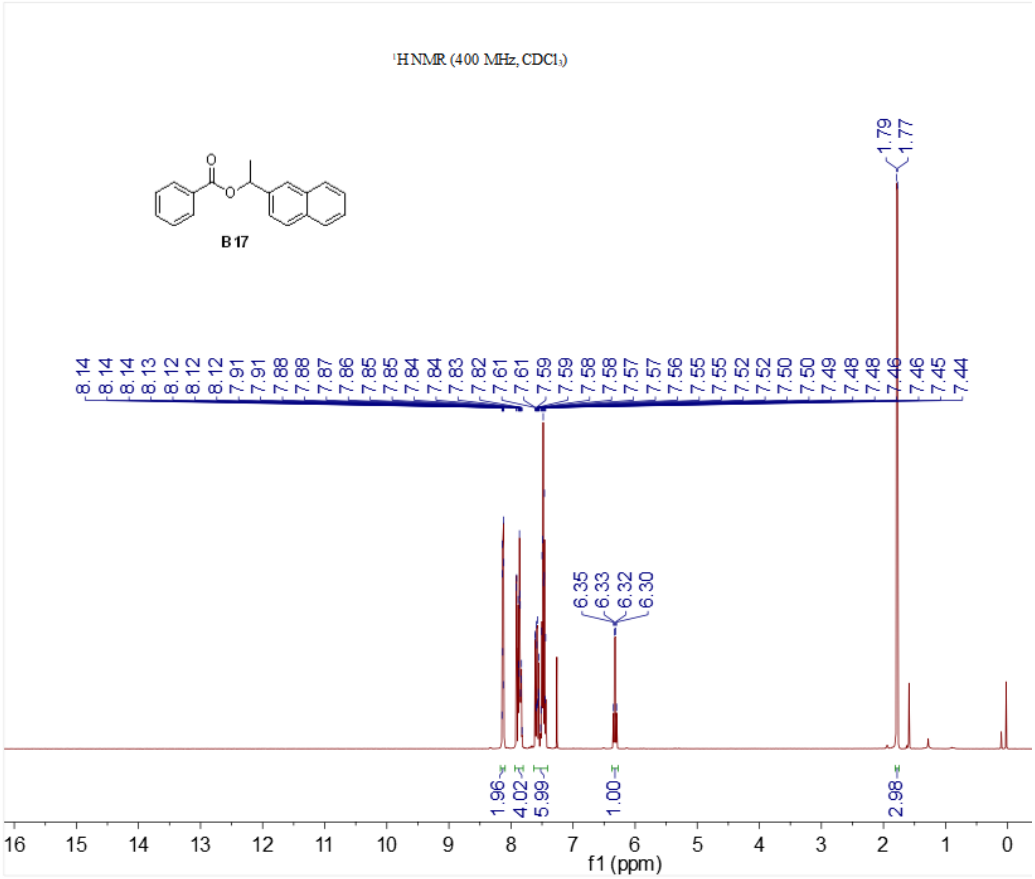


Figure S85. ^{1}H NMR spectra of **B17**

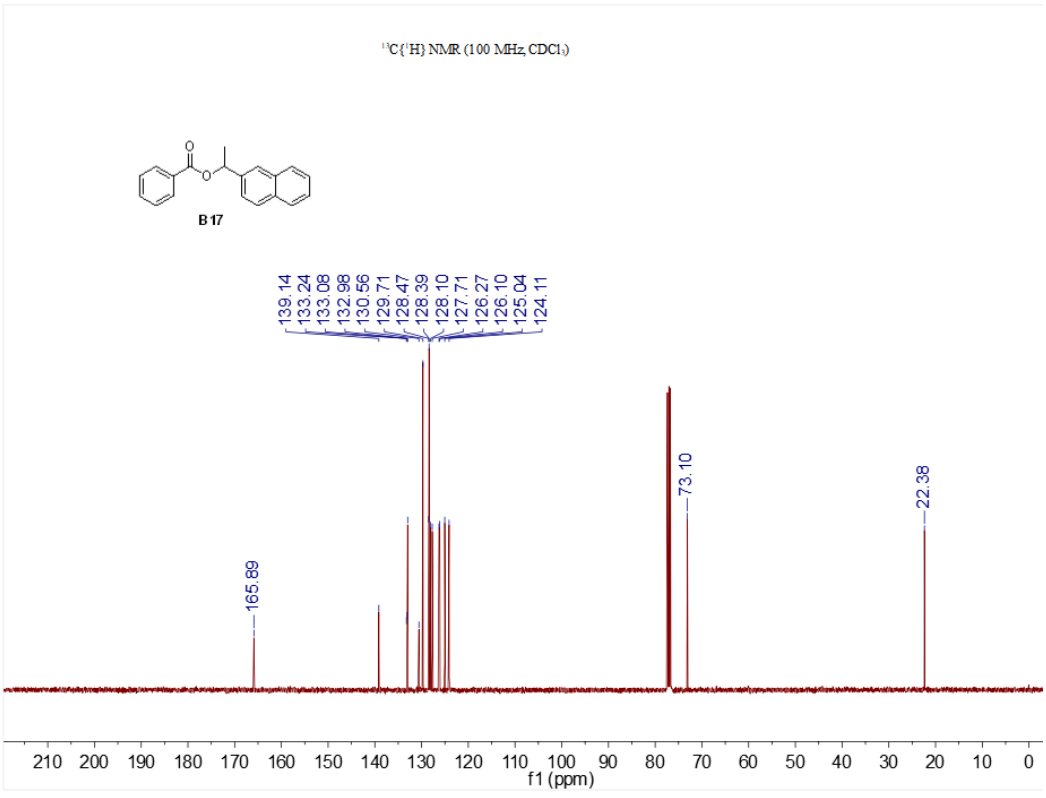
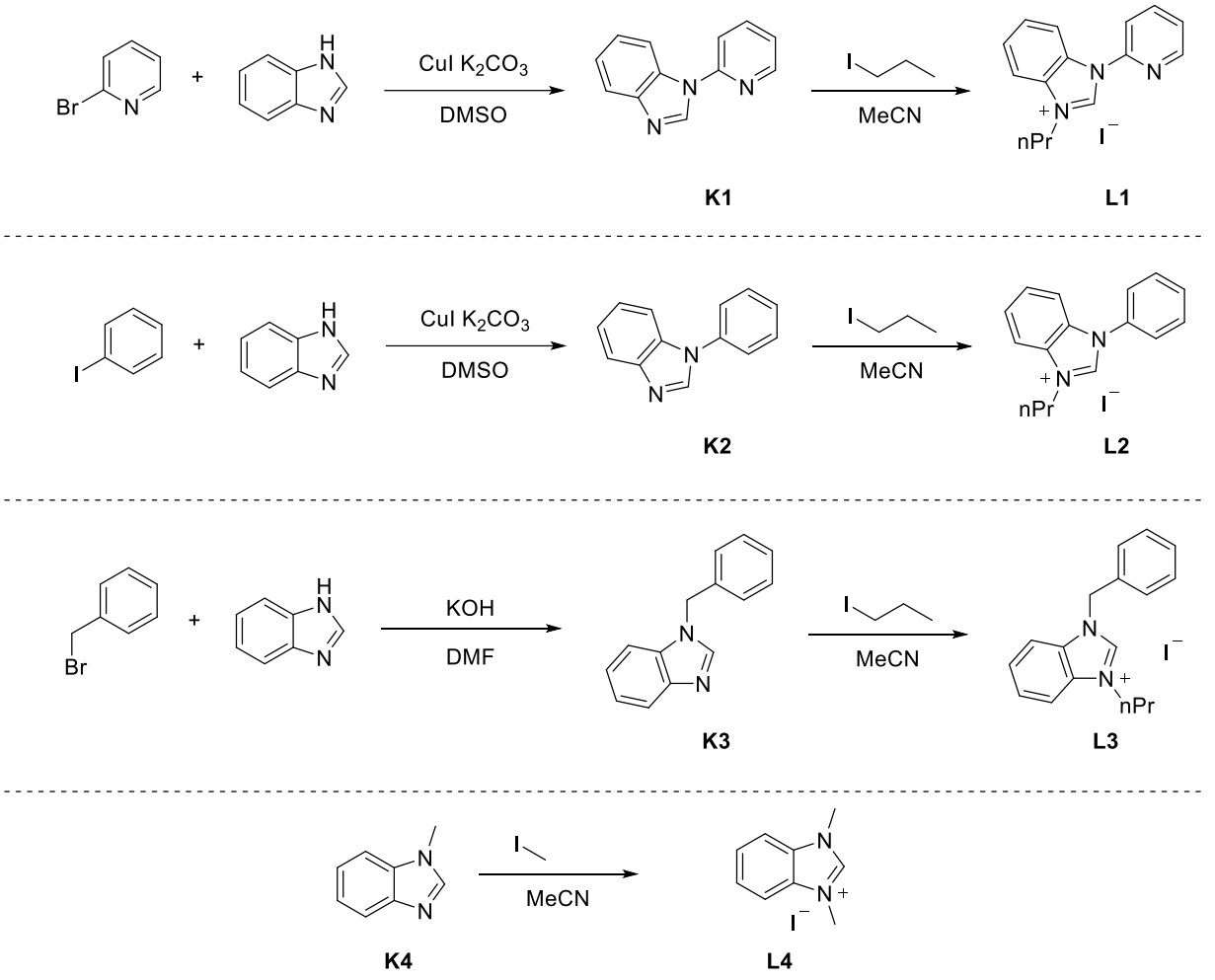


Figure S86. ^{13}C{^{1}H} NMR spectra of **B17**

4. General synthesis methods of ligands and complexes

4.1 General synthesis methods of ligands



Add a magnetic stirring rod, 10mmol 2-bromopyridine (iodobenzene), 10mmol benzimidazole, 2 mmol CuI, 12.5 mmol K_2CO_3, and 10 mL dimethyl sulfoxide to a 50 mL salenk tube. Stir and heat at 120 ° C for 24 hours. The obtained reaction mixture was extracted with saturated saline and dichloromethane. The product is in a lower organic phase, and the organic phase is collected and concentrated. K1

and K2 were separated by column chromatography. Add a magnetic stirring rod to a 50 mL Salenk tube and add 10 mmol of bromomethylbenzene, 12 mmol of benzimidazole, 22 mmol of potassium hydroxide, and 10 mL of N, N-dimethylformamide at 0 ° C. Stir at room temperature for 3 hours. The reaction mixture was extracted with saturated saline and ethyl acetate, and the product was in the upper organic phase. Collect and concentrate the organic phase, and separate K3 through column chromatography. Add a magnetic stirring rod, 10 mmol K1 (K2, K3, K4), 15 mmol 1-iodopropane (iodomethane), and 25 mL acetonitrile to a 50 mL salenk tube, stir and heat at 80 ° C for 24 hours. After the reaction is completed, vacuum distillation is carried out to remove acetonitrile and excess 1-iodopropane. Wash the imidazole salt product L1-L4 with ethyl acetate.

4.2 Characterization data of ligands

(**L1**) 3-propyl-1-(pyridin-2-yl)-1H-benzo[d]imidazol-3-ium iodide[5] (PE/EA = 2:1): a white soild (3.104 g, 85%); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.50 (s, 1H), 8.80−8.78 (m, 1H), 8.51−8.48 (m, 1H), 8.31 (t, J = 8.0 Hz, 1H), 8.26−8.24 (m, 1H), 8.10 (d, J = 8.0 Hz, 1H), 7.81−7.71 (m, 3H), 4.59 (t, J = 6.8 Hz, 2H), 2.08−2.00 (m, 2H), 1.01 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 149.3, 147.4, 142.2, 140.5, 131.6, 129.5, 127.7, 127.1, 125.0, 117.1, 116.0, 114.1, 48.7, 22.0, 10.8; HRMS (ESI) m/z calcd for $C_{15}H_{16}IN_3$ [M - I]$^+$ 238.1339, found 238.1335.

(**L2**) 1-phenyl-3-propyl-1H-benzo[d]imidazol-3-ium iodide (PE/EA = 2:1): a white soild (3.094 g, 85%); ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.20(s, 1H), 8.26-8.23(m, 3H), 7.81-7.70(m, 5H), 4.57-4.53(m, 2H), 2.08-1.99(m, 2H), 1.04-1.00(m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 143.0, 135.9, 127.9, 127.4, 125.7, 114.6, 114.0, 49.0, 22.5, 11.3. HRMS (ESI) m/z calcd for $C_{16}H_{17}I_2N_2$ [M - I]$^+$ 237.1386, found 237.1399.

(**L3**) 1-benzyl-3-propyl-1H-benzo[d]imidazol-3-ium iodide (PE/EA = 2:1): a white soild (3.213 g, 85%); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.66(s, 1H), 8.14-7.96(m, 2H), 7.71-7.64(m, 2H), 7.53-7.36(m, 5H), 5.78(s, 2H), 4.52-4.48(m, 2H), 2.51-1.93(m, 2H), 0.96-0.93(m, 3H). ^{13}C NMR (100 MHz, DMSO-d_6):142.9, 134.5, 131.8, 131.3, 129.5, 128.7, 127.2, 114.4, 50.4, 48.8, 22.5, 11.2. HRMS (ESI) m/z calcd for $C_{17}H_{19}IN_2$ [M - I]$^+$ 251.1543, found 251.1553.

(**L4**) 1,3-dimethyl-1H-benzo[d]imidazol-3-ium iodide (PE/EA = 2:1): a white soild (2.329 g, 85%); ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.67(s, 1H), 8.04-8.01(m, 2H), 7.74-7.69(m, 2H), 4.09(s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): 148.1, 132.5, 132.3, 131.6, 131.3, 125.4. HRMS (ESI) m/z calcd for $C_{17}H_{19}IN_2$ [M - I]$^+$ 147.0917, found 147.0928.

4.3 NMR spectrum of ligands

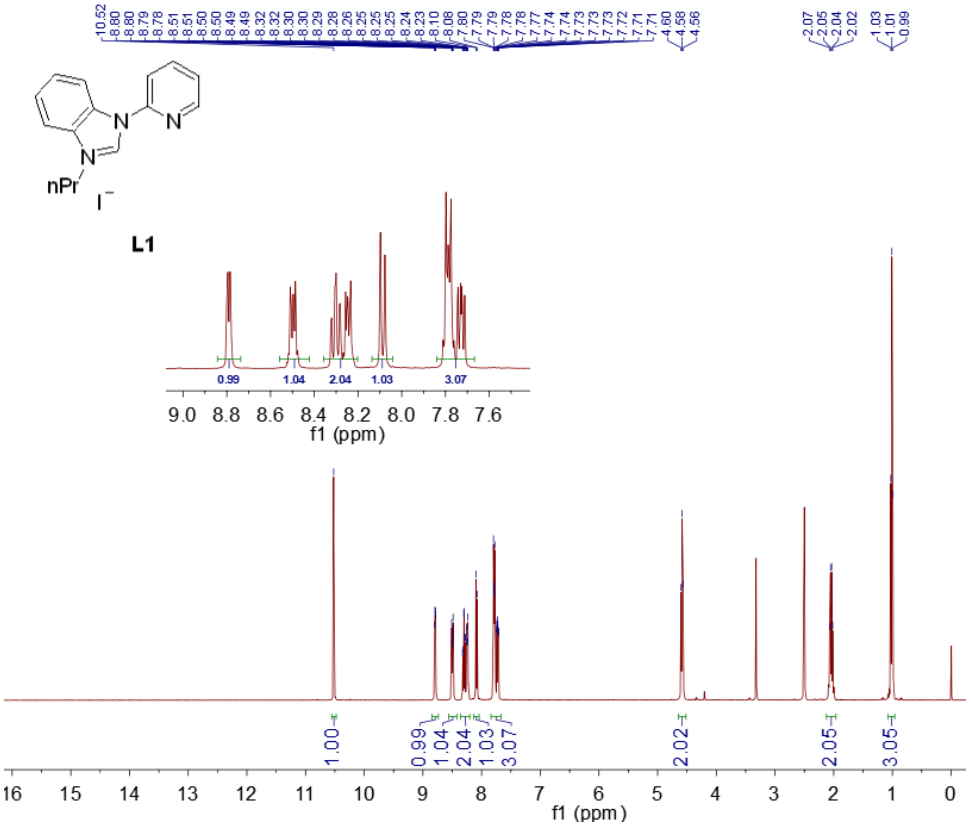


Figure S87. ^{1}H NMR spectra of **L1**

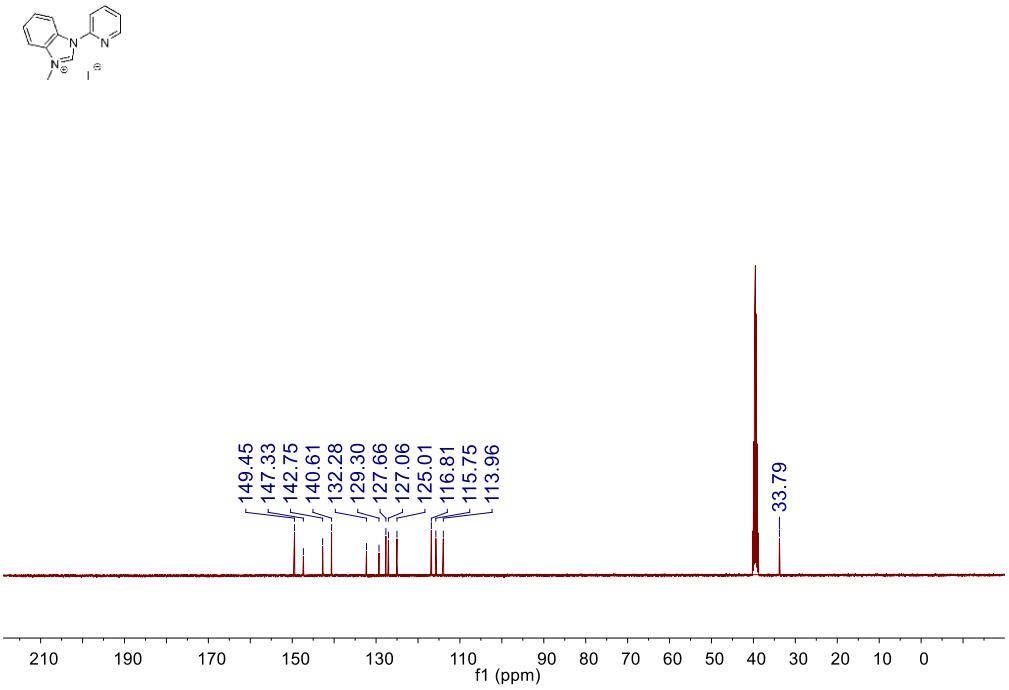


Figure S88. ^{13}C{^{1}H} NMR spectra of **L1.**

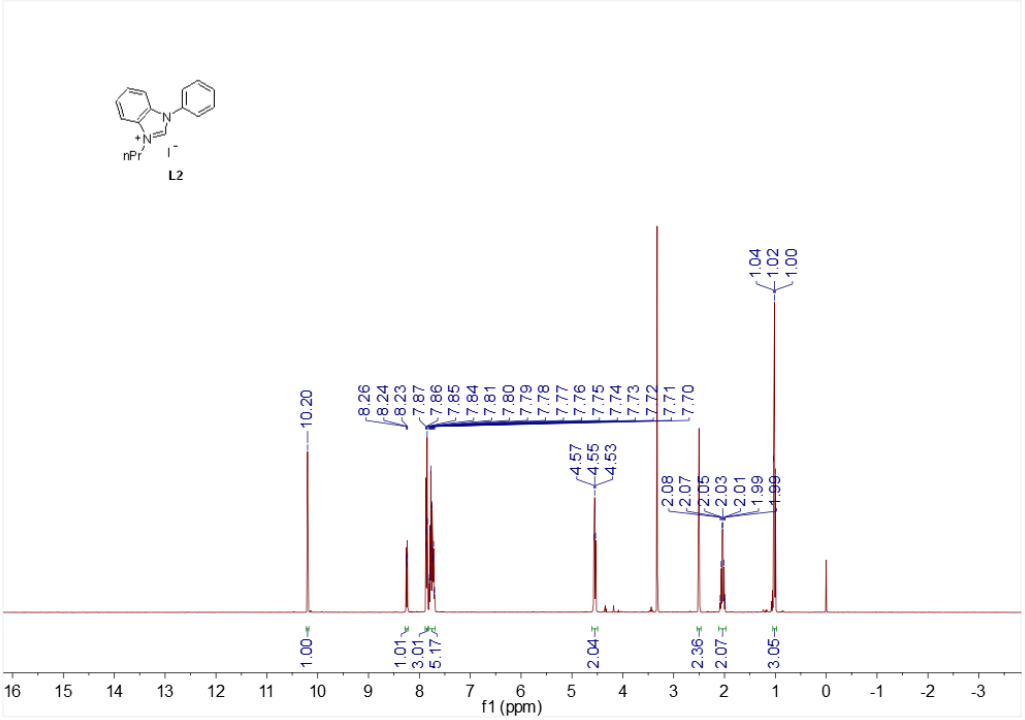


Figure S89. ^{1}H NMR spectra of **L2**

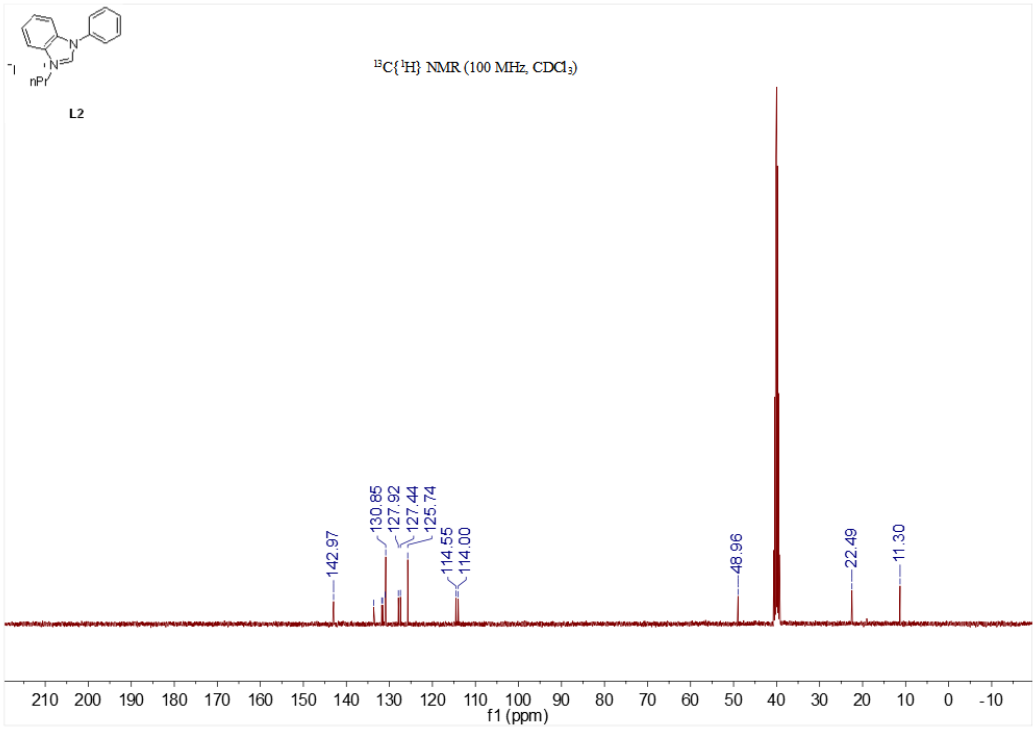


Figure S90. ^{13}C{^{1}H} NMR spectra of **L2.**

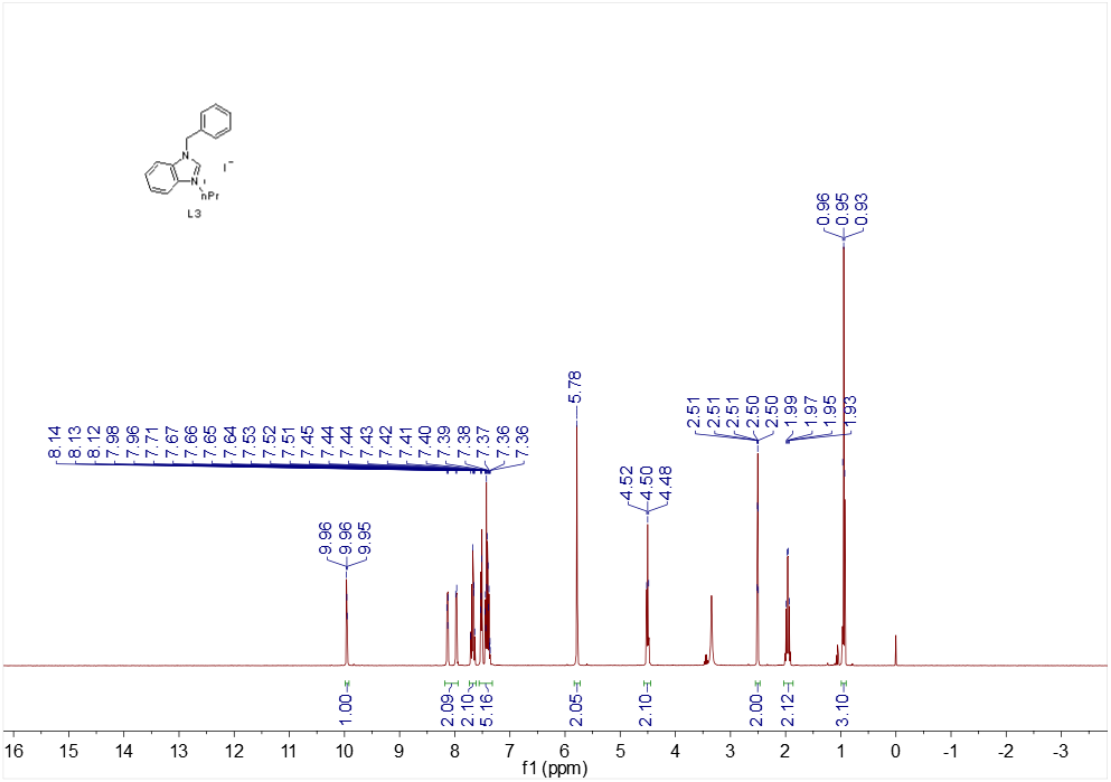


Figure S91. ^{1}H NMR spectra of **L3.**

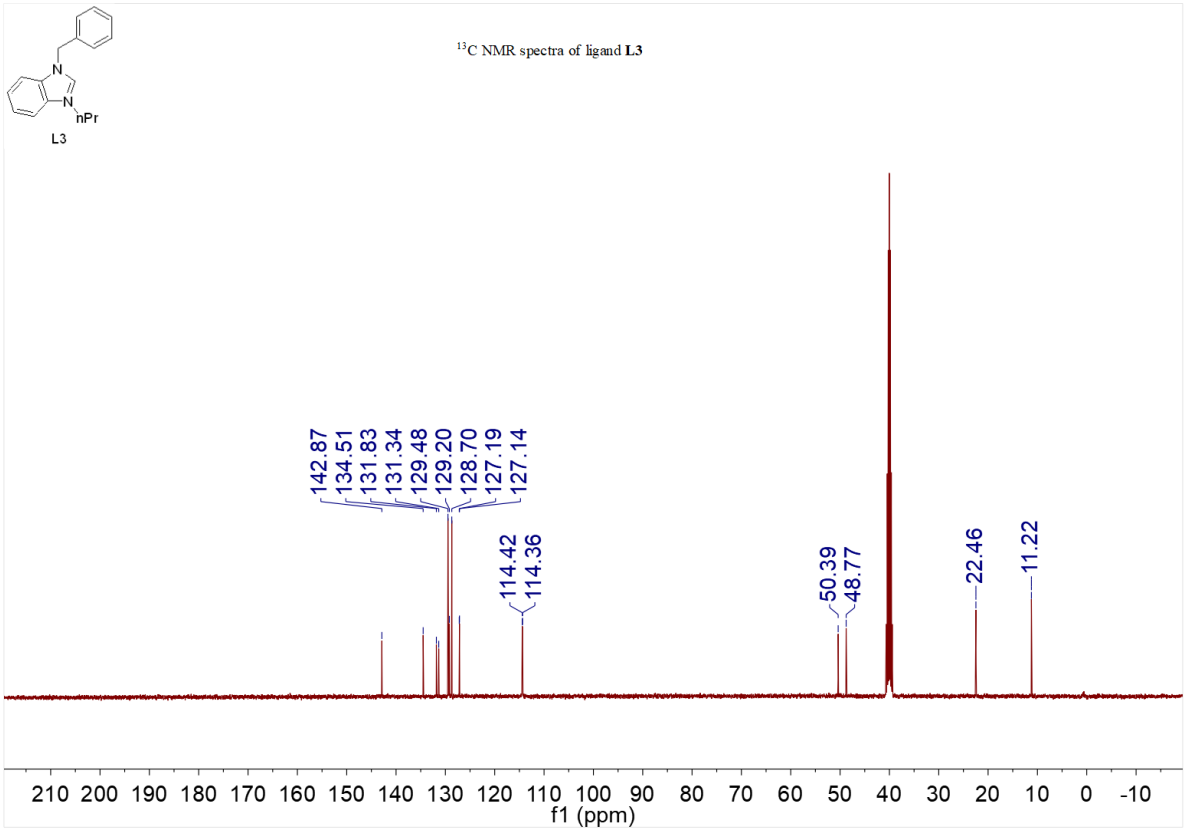


Figure S92. ^{13}C{^{1}H} NMR spectra of **L3.**

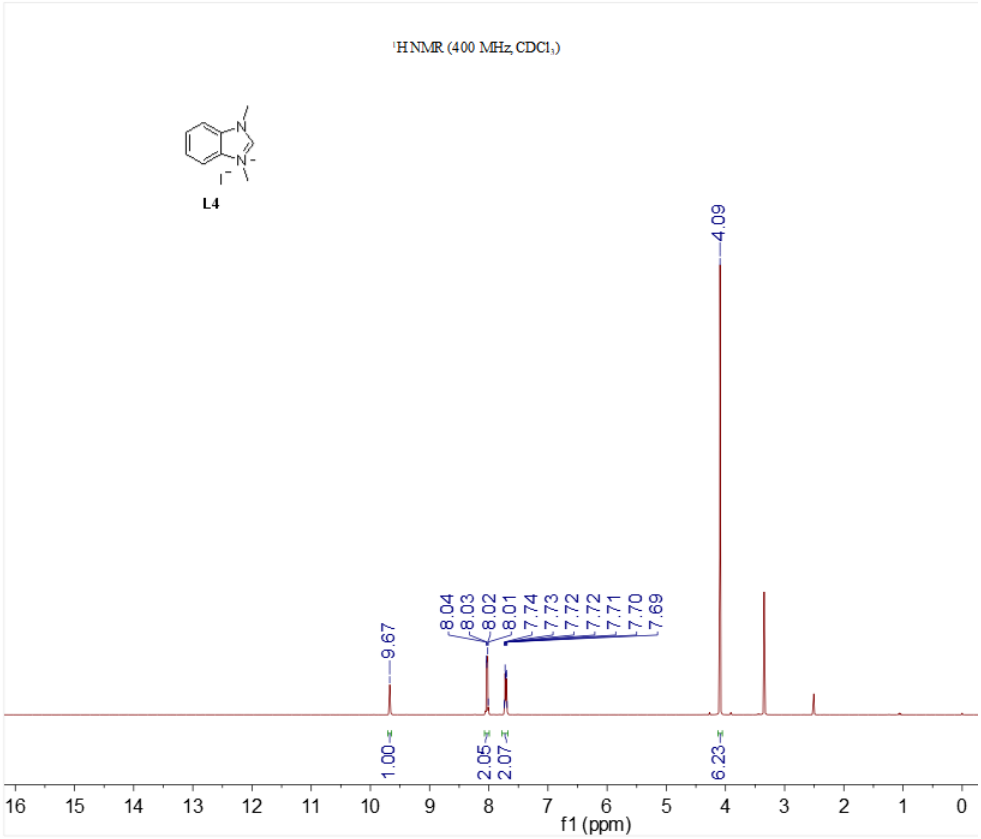


Figure S93. ^{1}H NMR spectra of **L4.**

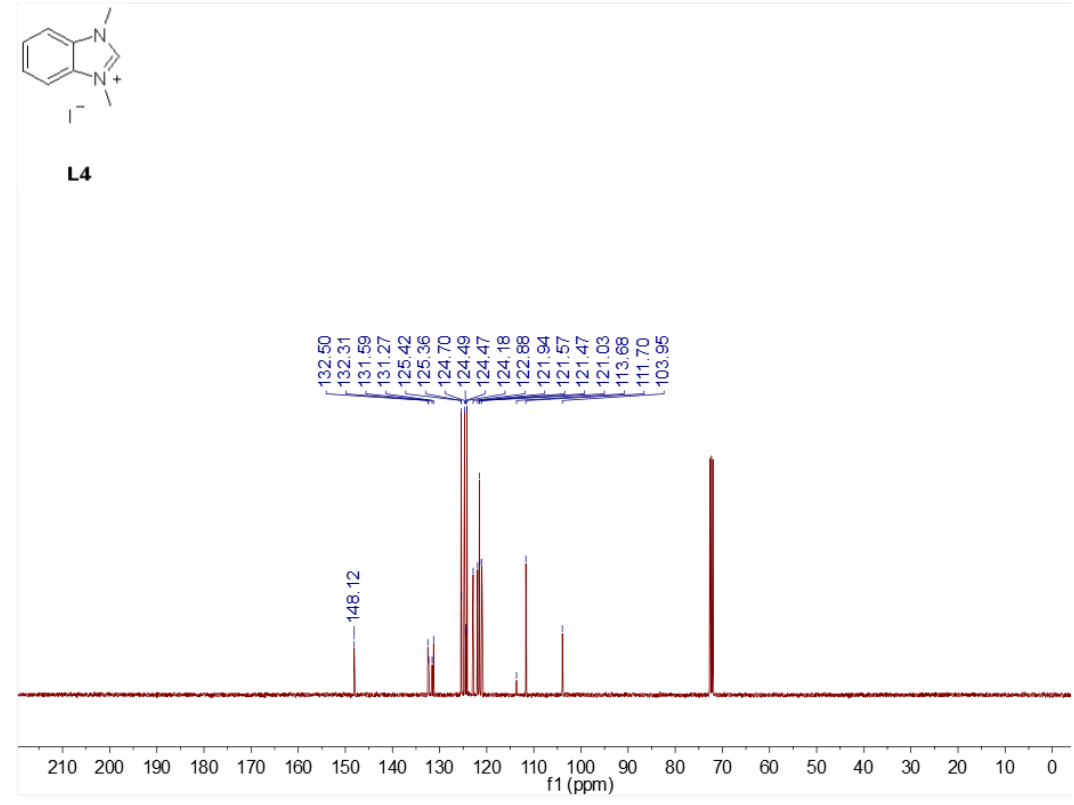
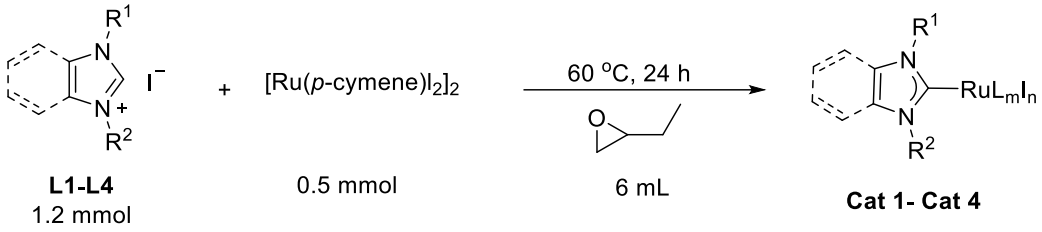


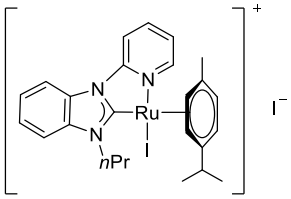
Figure S94. ^{13}C{^{1}H} NMR spectra of **L4.**

4.4 General synthesis methods of complexes



Add the synthesized ligand (1.2 mmol) and [Ru (*p*-cymene) I_2] $_2$ (0.5 mmol) into a 25 mL Schlenk tube, then add 6 mL of epoxybutane and react on a magnetic stirrer at 60 ° C for 24 hours.After the reaction is completed, let it cool down and dilute the reaction solution with DCM. Remove all solvents under reduced pressure, filter with 50 mL of EA to obtain solid crude product, and then purify the crude product by chromatography. The eluent is (DCM: MeOH=30:1), and the solvent is removed under reduced pressure to obtain a clean product. Characterize it using X-ray single crystal diffraction and high-resolution mass spectrometry.

4.5 Characterization data of complexes

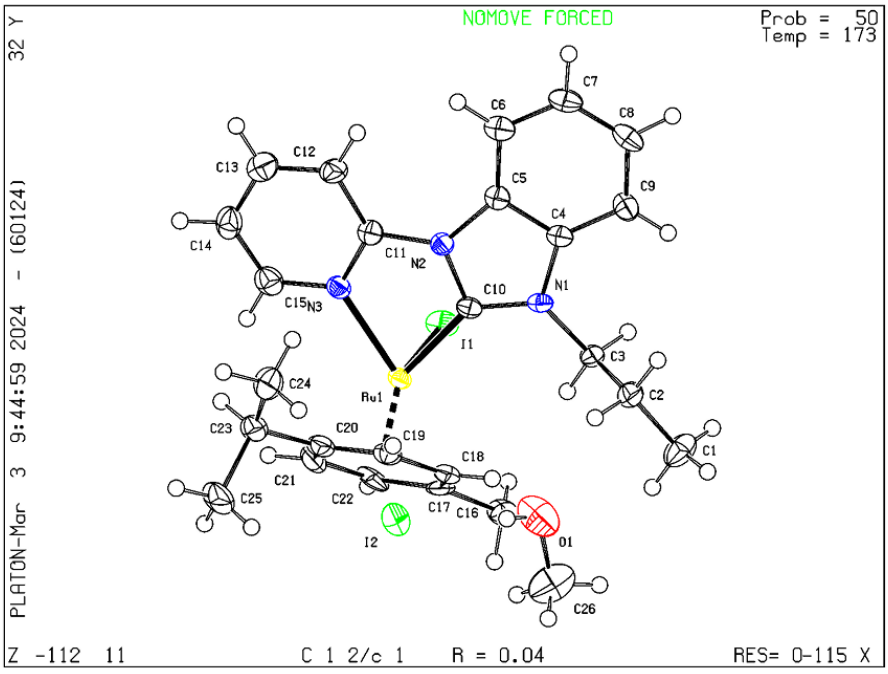


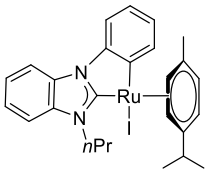
HRMS (ESI) m/z calcd for $C_{25}H_{30}I_2N_3Ru$ $[M - I]^+$ 600.0450, found 600.0588.

CCDC 2232758 (**Cat 1**). Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/

Empirical formula	$C_{26}H_{33}I_2N_3ORu$
Formula weight	758.42
Temperature/K	173.0
Crystal system	monoclinic
Space group	C2/c
a/Å	27.7159(9)
b/Å	9.3500(3)
c/Å	21.0421(6)
α/°	90
β/°	98.551(3)
γ/°	90
Volume/Å^3	5392.3(3)
Z	8
ρ_{calc}g/cm^3	1.868
μ/mm^{-1}	22.860

F(000)	2944.0
Crystal size/mm^3	0.19 × 0.17 × 0.16
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	6.45 to 144.552
Index ranges	$-34 \leq h \leq 34$, $-11 \leq k \leq 11$, $-25 \leq l \leq 25$
Reflections collected	31003
Independent reflections	5318 [R_{int} = 0.0833, R_{sigma} = 0.0521]
Data/restraints/parameters	5318/0/304
Goodness-of-fit on F^2	1.053
Final R indexes [I>=2σ (I)]	R_1 = 0.0431, wR_2 = 0.1108
Final R indexes [all data]	R_1 = 0.0501, wR_2 = 0.1172
Largest diff. peak/hole / e Å^{-3}	1.92/-1.16



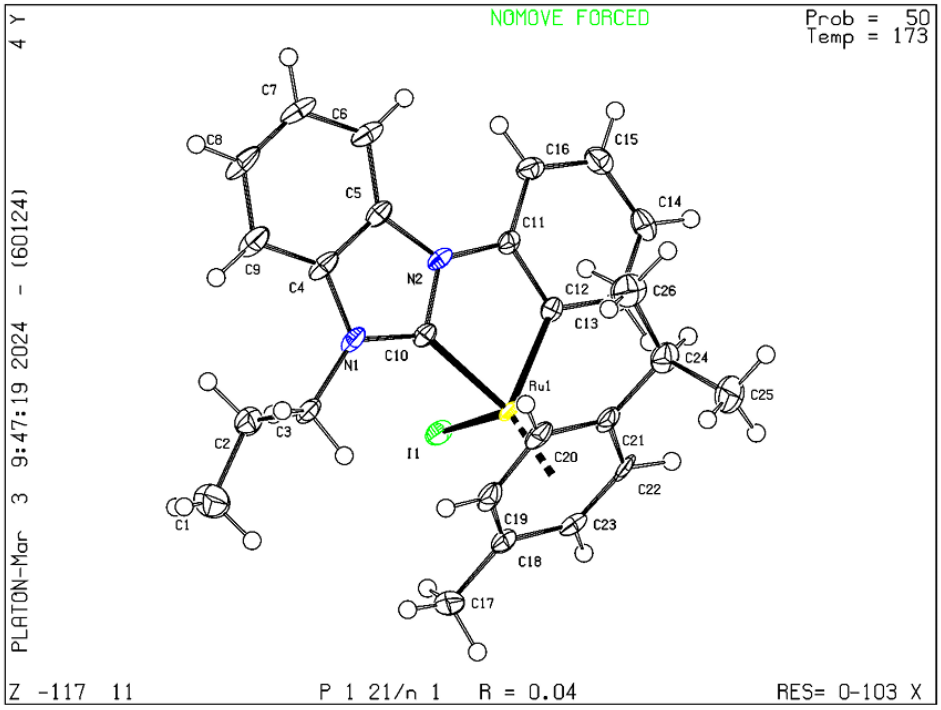


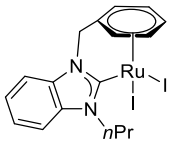
HRMS (ESI) m/z calcd for $C_{26}H_{29}I_2N_2Ru$ $[M - I]^+$ 598.0413, found 598.0421.

CCDC 2322084 (**Cat 2**). Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/

Empirical formula	$C_{26}H_{29}IN_2Ru$
Formula weight	597.48
Temperature/K	173.0
Crystal system	monoclinic
Space group	$P2_1/n$
a/Å	12.2763(4)
b/Å	11.1841(4)
c/Å	17.7735(6)
α/°	90
β/°	104.0150(10)
γ/°	90
Volume/Å^3	2367.65(14)
Z	4
ρ_{calc}g/cm^3	1.676
μ/mm^{-1}	15.695
F(000)	1184.0

Crystal size/mm^3	0.14 × 0.13 × 0.11
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.934 to 143.91
Index ranges	-14 ≤ h ≤ 15, -13 ≤ k ≤ 13, -21 ≤ l ≤ 21
Reflections collected	17284
Independent reflections	4643 [R_{int} = 0.0594, R_{sigma} = 0.0485]
Data/restraints/parameters	4643/0/275
Goodness-of-fit on F^2	1.071
Final R indexes [I>=2σ (I)]	R_1 = 0.0395, wR_2 = 0.1053
Final R indexes [all data]	R_1 = 0.0426, wR_2 = 0.1080
Largest diff. peak/hole / e Å^{-3}	1.70/-1.43



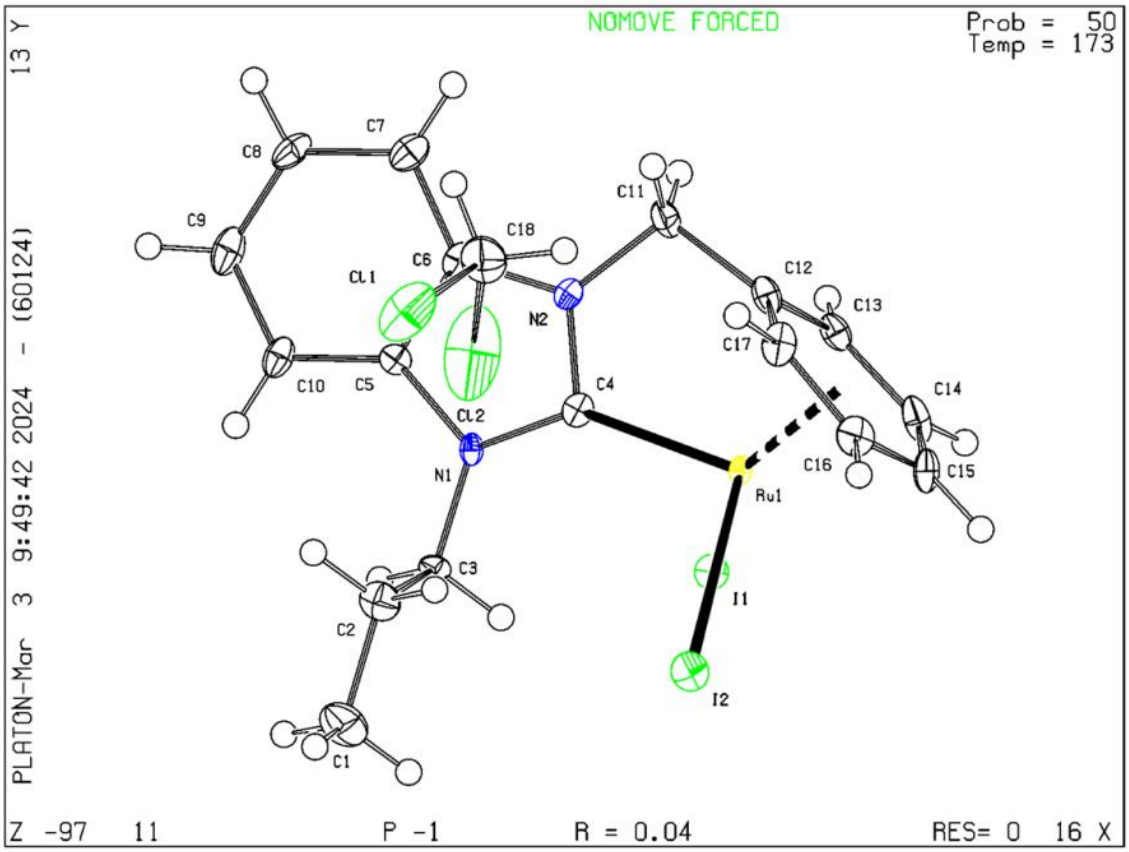


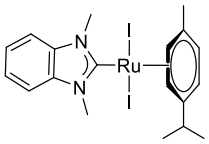
HRMS (ESI) m/z calcd for $C_{17}H_{18}I_2N_2Ru$ $[M - I]^+$= 628.0883, found 628.0886.

CCDC 2323297 (**Cat 3**). Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/

Empirical formula	$C_{18}H_{20}Cl_2I_2N_2Ru$
Formula weight	690.13
Temperature/K	173.0
Crystal system	triclinic
Space group	P-1
a/Å	8.3565(2)
b/Å	11.5771(3)
c/Å	11.7765(3)
α/°	74.7750(10)
β/°	71.8530(10)
γ/°	83.6420(10)
Volume/Å^3	1044.12(5)
Z	2
ρ_{calc}g/cm^3	2.195
μ/mm^{-1}	31.674
F(000)	652.0

Crystal size/mm^3	0.18 × 0.12 × 0.11
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	7.918 to 144.52
Index ranges	$-10 \leq h \leq 9$, $-13 \leq k \leq 14$, $-14 \leq l \leq 14$
Reflections collected	11482
Independent reflections	4024 [R_{int} = 0.0495, R_{sigma} = 0.0505]
Data/restraints/parameters	4024/13/227
Goodness-of-fit on F^2	1.076
Final R indexes [I>=2σ (I)]	R_1 = 0.0433, wR_2 = 0.1203
Final R indexes [all data]	R_1 = 0.0456, wR_2 = 0.1227
Largest diff. peak/hole / e Å^{-3}	1.99/-1.90



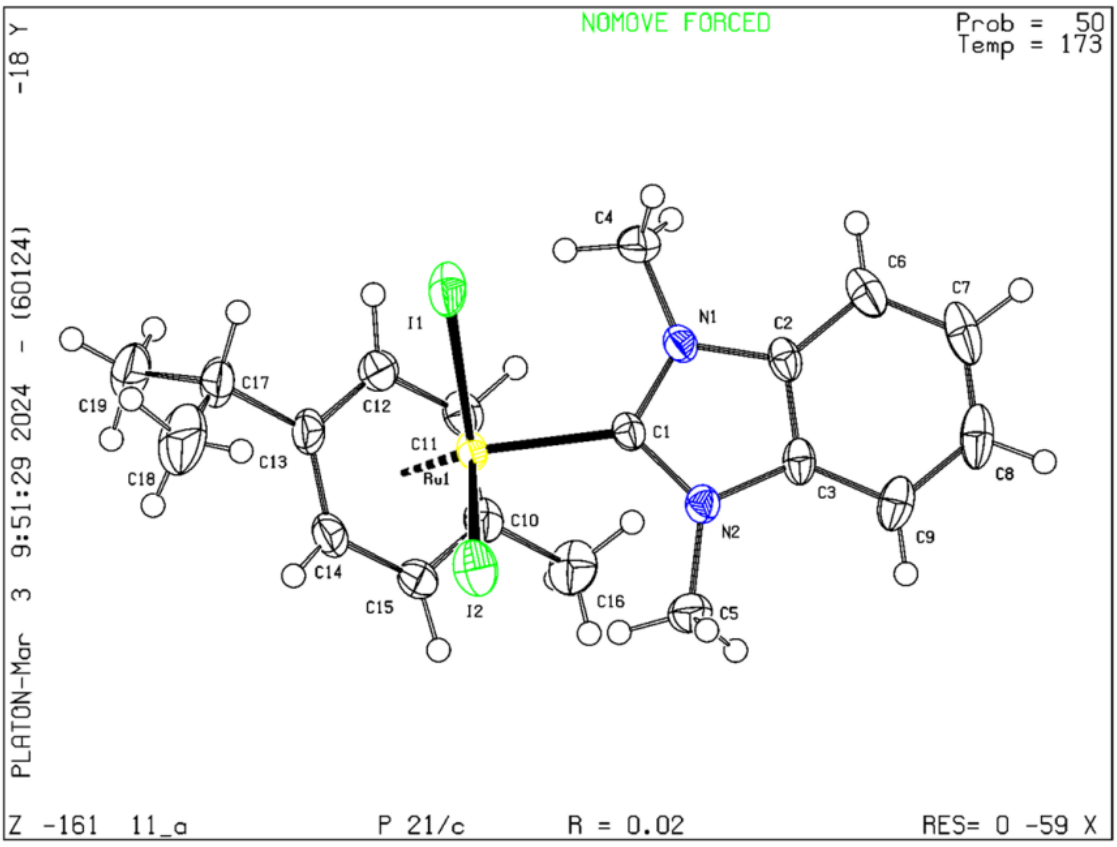


HRMS (ESI) m/z calcd for $C_{19}H_{24}I_2N_2$ $[M - I]^+$ 509.0022, found 509.0056.

CCDC 2322085 (**Cat 4**). Cambridge Crystallographic Data Centre via https://www.ccdc.cam.ac.uk/

Empirical formula	$C_{19}H_{24}I_2N_2Ru$
Formula weight	635.27
Temperature/K	173(2)
Crystal system	monoclinic
Space group	$P2_1/c$
a/Å	15.5995(4)
b/Å	7.9181(2)
c/Å	16.7838(5)
α/°	90
β/°	98.0110(10)
γ/°	90
Volume/Å^3	2052.88(10)
Z	4
ρ_{calc}g/cm^3	2.055
μ/mm^{-1}	3.775
F(000)	1208.0
Crystal size/mm^3	0.25 × 0.24 × 0.22

Radiation	MoKα (λ = 0.71073)
2Θ range for data collection/°	4.902 to 59.156
Index ranges	$-21 \leq h \leq 21$, $-10 \leq k \leq 11$, $-23 \leq l \leq 22$
Reflections collected	34781
Independent reflections	5716 [R_{int} = 0.0321, R_{sigma} = 0.0183]
Data/restraints/parameters	5716/0/222
Goodness-of-fit on F^2	1.050
Final R indexes [I>=2σ (I)]	R_1 = 0.0231, wR_2 = 0.0510
Final R indexes [all data]	R_1 = 0.0257, wR_2 = 0.0519
Largest diff. peak/hole / e Å^{-3}	1.85/-1.95



5. Hydrogen capture experiment

After the dehydrogenation rearrangement reaction is completed, wait for it to cool down, use an air bag to collect the gas in the pressure tube, and qualitatively detect the collected gas using gas chromatography GC 2014C.

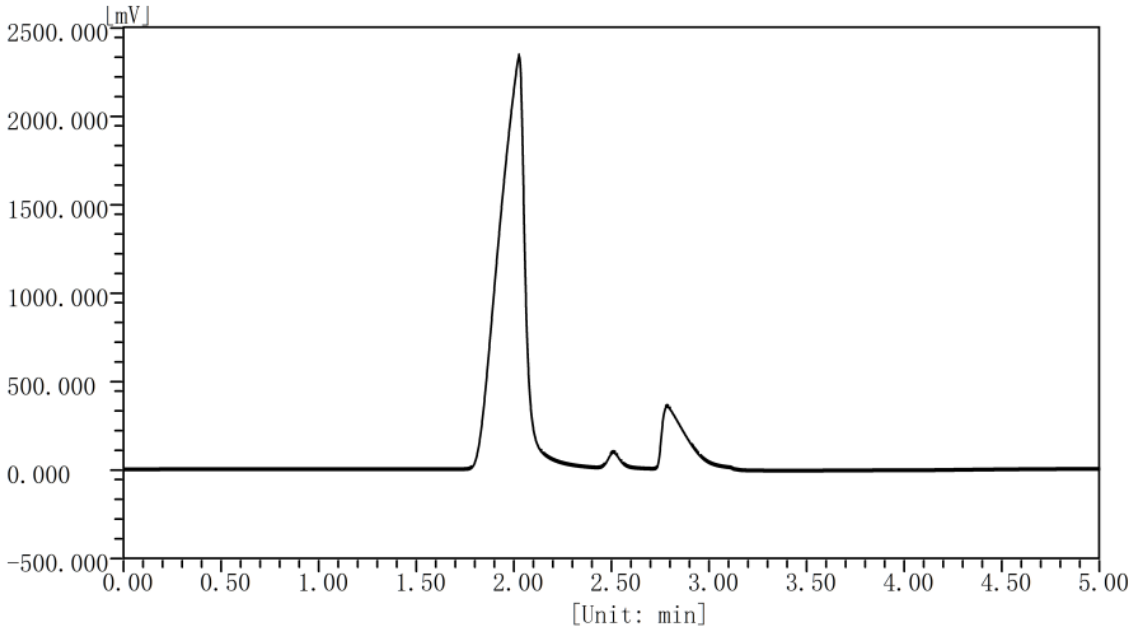


Figure S95 Qualitative detection of hydrogen gas by gas chromatography GC 2014C

References

[1] G. Zhang, T. Irrgang, M. Schlagbauer, and R. Kempe, Synthesis of 1,3-diketones from esters via liberation of hydrogen. *Chem Catal.*, **2021**, *1* (3), 681-690. DOI: 10.1016/j.checat.2021.05.007.

[2] S. Silva, C. D. Maycock, Synthesis of *β*-oxo carbonyl and thiocarbonyl compounds via basic sulfur abstraction. *Tetrahedron*, **2019**, *75* (40), 130552. DOI: 10.1016/j.tet.2019.130552.

[3] M. T. J. Williams, L. Adarve Cardona, C. Bolm, Mechanochemical Mitsunobu Reactions. *Adv. Synth. Catal.*, **2024**, *366* (10), 2220-2225. DOI: 10.1002/adsc.202400296.

[4] I. A. P. Samuel Rajan, S. Rajendran, DABCO-catalyzed esterification of N-pivaloyl-activated amides. *Org. Biomol. Chem.*, **2024**, *22* (25), 5170-5180. DOI: 10.1039/d4ob00752b.

[5] L. Wang, N. Liu, B. Dai, H. Hu. Selective C-N Bond-Forming Reaction of 2,6-Dibromopyridine with Amines. *Eur. J. Org. Chem.*, **2014**, *2014* (29), 6493-6500. DOI: 10.1002/ejoc.201402619.