

Supporting Information

Palladium-Catalyzed Esterification of Carboxylic Acids with Aryl Iodides

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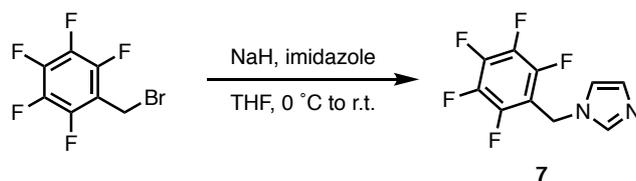
1. General

Unless otherwise noted, all reactants or reagents including dry solvents were obtained from commercial suppliers and used as received. [Pd(cinnamyl)Cl]₂ was obtained from Aldrich. Pivalic acid was purchased from TCI. Ag₂CO₃ was purchased from WAKO. MS4A was purchased from Nakalai Chemicals. AgOPiv¹, 1-iodo-4-methoxy-2-methylbenzene (**2l**)², 1-iodo-2-methoxy-4-methylbenzene (**2n**)² and IBn·HBr³ were synthesized according to procedures reported in the literature. Unless otherwise noted, all reactions were performed with dry solvents under air. All work-up and purification procedures were carried out with reagent-grade solvents in air.

Analytical thin-layer chromatography (TLC) was performed using E. Merck silica gel 60 F₂₅₄ precoated plates (0.25 mm). The developed chromatogram was analyzed by UV lamp (254 nm). Medium Pressure liquid chromatography (MPLC) was performed using Yamazen W-prep 2XY. Preparative thin-layer chromatography (PTLC) was performed using Wakogel B5-F silica coated plates (0.75 mm) prepared in our laboratory. Preparative gel permeation chromatography (GPC) was performed with a JAI LC-9204 instrument equipped with JAIGEL-1H/JAIGEL-2H columns using chloroform as an eluent. Gas chromatography (GC) analysis was conducted on a Shimadzu GC-2010 instrument equipped with a HP-5 column (30 m × 0.25 mm, Hewlett-Packard) with dodecane as an internal standard. The high-resolution mass spectra (HRMS) were conducted on Thermo Fisher Scientific Exactive. Nuclear magnetic resonance (NMR) spectra were recorded on a JEOL JNM-ECA-600 (¹H 600 MHz, ¹³C 150 MHz) spectrometer and a JEOL JNM-ECA-400 (¹H 400 MHz, ¹³C 100 MHz) spectrometer. Chemical shifts for ¹H NMR are expressed in parts per million (ppm) relative to tetramethylsilane (δ 0.00 ppm) or residual peak of acetone-*d*₆ (δ 2.05 ppm). Chemical shifts for ¹³C NMR are expressed in ppm relative to CDCl₃ (δ 77.0 ppm) or acetone-*d*₆ (δ 29.84 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, dd = doublet of doublets, ddd = doublet of doublets of doublets, t = triplet, dt = doublet of triplets, td = triplet of doublets, q = quartet, p = quintet, m = multiplet, br d = broad doublet), coupling constant (Hz), and integration.

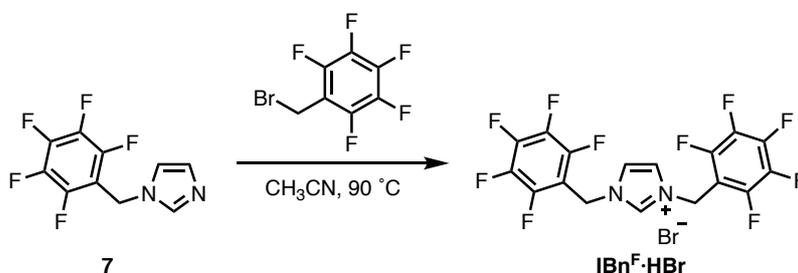
2. Synthesis of 1,3-Bis((pentafluorophenyl)methyl)-1*H*-imidazol-3-ium bromide (IBn^F·HBr)

2-1. Synthesis of 1-((pentafluorophenyl)methyl)-1*H*-imidazole (7)



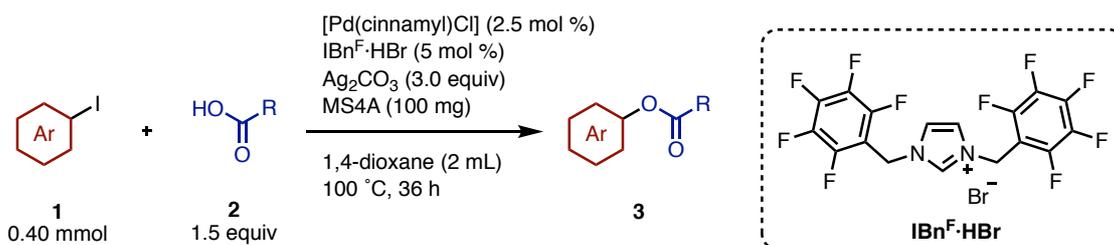
Imidazole (2.87 g, 42.2 mmol, 1.1 equiv) was placed in a 200-mL round-bottomed flask under a stream of N₂, and THF (40.0 mL) was added to the flask. After cooled to 0 °C, NaH (60% dispersion in paraffin liquid: 1.61 g, 40.2 mmol, 1.05 equiv) was added, and then the mixture was warmed to room temperature and stirred for 1 h. To this mixture, pentafluorobenzyl bromide (10.0 g, 38.3 mmol, 1.0 equiv) was added dropwise, and then the mixture was stirred for additional 4 h. The reaction was quenched by the addition of water. The organic layer was extracted with EtOAc, washed with water and brine, dried over Na₂SO₄, and then filtered. The filtrate was concentrated *in vacuo*. The crude residue was purified by MPLC (chloroform/EtOAc = 1:0 to 1:1) to afford **7** as a colorless liquid (7.2 g, 76% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.59 (s, 1 H), 7.04 (s, 1H), 6.98 (s, 1H), 5.23 (s, 2H). ¹³C NMR (150 MHz, CDCl₃) δ 145.0 (d, *J* = 253 Hz), 141.7 (d, *J* = 252 Hz), 137.5 (d, *J* = 255 Hz), 137.0, 130.0, 118.7, 109.9 (t, *J* = 18 Hz), 37.2. HRMS (ESI⁺) *m/z* calcd for C₁₀H₆F₅N₂ [M+H]⁺: 249.0446, found: 249.0441.

2-2. Synthesis of 1,3-Bis((pentafluorophenyl)methyl)-1*H*-imidazol-3-ium bromide (IBn^F·HBr)



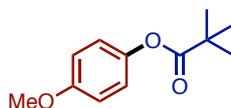
To a 200-mL glass vessel equipped with a J. Young[®] O-ring tap containing a magnetic stirring bar were added 1-((pentafluorophenyl)methyl)-1*H*-imidazole **7** (6.0 g, 24.2 mmol, 1.0 equiv) and acetonitrile (24.0 mL). To this mixture, pentafluorobenzyl bromide (8.2 g, 31.4 mmol, 1.3 equiv) was added. Then the mixture was heated at 90 °C and stirred for 20 h. After cooled to room temperature, the mixture was concentrated and the residue was purified by recrystallization from acetonitrile to afford IBn^F·HBr as a white solid (8.7 g, 71% yield). ¹H NMR (600 MHz, acetone-*d*₆) δ 10.74 (s, 1H), 8.02 (s, 2H), 5.99 (s, 4H). ¹³C NMR (150 MHz, acetone-*d*₆) δ 146.8 (d, *J* = 248 Hz), 143.1 (d, *J* = 249 Hz), 139.5, 138.8 (d, *J* = 237 Hz), 123.8, 108.8, 41.6. HRMS (ESI⁺) *m/z* calcd for C₁₇H₇F₁₀N₂ [M]⁺: 429.0444, found: 429.0443.

3. Pd-Catalyzed Esterification of Carboxylic acids with Aryl iodides



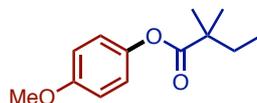
General Procedure: To a screw-capped glass tube containing a magnetic stirrer bar were added iodoarene **1a–1r** (0.40 mmol, 1.0 equiv), carboxylic acid **2a–2n** (0.60 mmol, 1.5 equiv), Ag₂CO₃ (1.2 mmol, 3.0 equiv), MS4A (100 mg), [Pd(cinnamyl)Cl]₂ (0.010 mmol, 2.5 mol%), 1,3-bis((pentafluorophenyl)methyl)-1*H*-imidazol-3-ium bromide (IBn^F·HBr) (0.02 mmol, 5.0 mol%) and 1,4-dioxane (2.0 mL) under air. After stirring at 100 °C for 36 h, the reaction mixture was cooled to room temperature, and then passed through a short pad of Celite[®] (eluent: EtOAc or CHCl₃). After the organic solvent was removed under reduced pressure, the residue was purified by PTLC or MPLC to yield aryl ester **3aa–3ra**.

4-Methoxyphenyl pivalate (**3aa**)



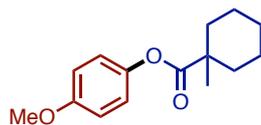
Purification by MPLC (hexane/EtOAc = 99:1 to 4:1) afforded **3aa** as a pale yellow oil (62 mg, 75% yield). ¹H NMR (600 MHz, CDCl₃) δ 6.96 (d, *J* = 9.0 Hz, 2H), 6.88 (d, *J* = 9.0 Hz, 2H), 3.79 (s, 3H), 1.34 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ 177.4, 157.1, 144.6, 122.2, 114.4, 55.8, 39.0, 27.1. HRMS (ESI⁺) *m/z* calcd for C₁₂H₁₇O₃ [M+H]⁺: 209.1172, found: 209.1172.

4-Methoxyphenyl 2,2-dimethylbutanoate (**3ab**)



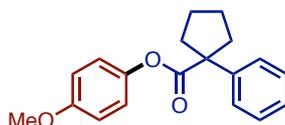
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) afforded **3ab** as a colorless oil (69 mg, 78% yield). ¹H NMR (600 MHz, CDCl₃) δ 6.96 (d, *J* = 9.6 Hz, 2H), 6.88 (d, *J* = 9.6 Hz, 2H), 3.79 (s, 3H), 1.71 (q, *J* = 7.8 Hz, 2H), 1.29 (s, 6H), 0.96 (t, *J* = 7.8 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 176.8, 157.0, 144.5, 122.2, 114.3, 55.5, 42.9, 33.4, 24.6, 9.3. HRMS (ESI⁺) *m/z* calcd for C₁₃H₁₉O₃ [M+H]⁺: 223.1329, found: 223.1329.

4-Methoxyphenyl 1-methylcyclohexane-1-carboxylate (**3ac**)



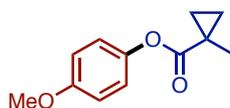
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) afforded **3ac** as a colorless oil (68 mg, 69% yield). ^1H NMR (600 MHz, CDCl_3) δ 6.96 (d, $J = 9.0$ Hz, 2H), 6.88 (d, $J = 9.0$ Hz, 2H), 3.79 (s, 3H), 2.17 (br d, $J = 7.2$ Hz, 2H), 1.67–1.55 (m, 3H), 1.52–1.43 (m, 2H), 1.36–1.29 (m, 6H). ^{13}C NMR (150 MHz, CDCl_3) δ 176.7, 157.0, 144.5, 122.3, 114.4, 55.6, 43.4, 35.6, 26.4, 25.7, 23.2. HRMS (ESI $^+$) m/z calcd for $\text{C}_{15}\text{H}_{21}\text{O}_3$ $[\text{M}+\text{H}]^+$: 249.1485, found: 249.1484.

4-Methoxyphenyl 1-phenylcyclopentane-1-carboxylate (**3ad**)



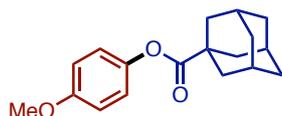
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) afforded **3ad** as a colorless oil (70 mg, 59% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.49–7.45 (m, 2H), 7.38–7.33 (m, 2H), 7.29–7.25 (m, 1H), 6.81 (s, 4H), 3.75 (s, 3H), 2.82–2.76 (m, 2H), 2.06–1.99 (m, 2H), 1.86–1.80 (m, 4H). ^{13}C NMR (150 MHz, CDCl_3) δ 174.9, 157.1, 144.6, 142.8, 128.4, 126.9, 126.8, 122.0, 114.3, 59.3, 55.5, 36.1, 23.6. HRMS (ESI $^+$) m/z calcd for $\text{C}_{19}\text{H}_{21}\text{O}_3$ $[\text{M}+\text{H}]^+$: 297.1485, found: 297.1484.

4-Methoxyphenyl 1-methylcyclopropane-1-carboxylate (**3ae**)



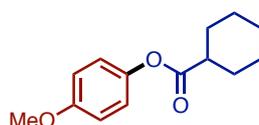
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) afforded **3ae** as a colorless oil (40 mg, 49% yield). ^1H NMR (600 MHz, CDCl_3) δ 6.97 (d, $J = 9.0$ Hz, 2H), 6.86 (d, $J = 9.0$ Hz, 2H), 3.78 (s, 3H), 1.43–1.38 (m, 5H), 0.83–0.79 (m, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 174.9, 157.0, 144.4, 122.2, 114.3, 55.5, 19.4, 18.7, 17.3. HRMS (ESI $^+$) m/z calcd for $\text{C}_{12}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 207.1016, found: 207.1017.

4-Methoxyphenyl (3*r*,5*r*,7*r*)-adamantane-1-carboxylate (**3af**)



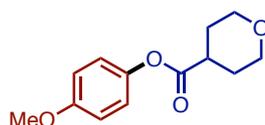
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) and PTLC (hexane/chloroform = 1:1) afforded **3af** as a colorless oil (11 mg, 10% yield). ¹H NMR (600 MHz, CDCl₃) δ 6.95 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 3.79 (s, 3H), 2.15–2.02 (m, 9H), 1.85–1.73 (m, 6H). ¹³C NMR (150 MHz, CDCl₃) δ 176.5, 157.0, 144.5, 122.3, 114.3, 55.6, 40.9, 38.8, 36.5, 27.9. HRMS (ESI⁺) *m/z* calcd for C₁₈H₂₃O₃ [M+H]⁺: 287.1642, found: 287.1641.

4-Methoxyphenyl cyclohexanecarboxylate (**3ag**)



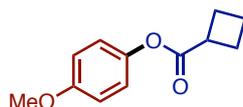
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) and PTLC (hexane/chloroform = 1:1) afforded **3ag** as a colorless oil (23 mg, 24% yield). ¹H NMR (600 MHz, CDCl₃) δ 6.97 (d, *J* = 9.0 Hz, 2H), 6.87 (d, *J* = 9.0 Hz, 2H), 3.79 (s, 3H), 2.55–2.50 (m, 1H), 2.08–2.02 (m, 2H), 1.84–1.78 (m, 2H), 1.71–1.65 (m, 1H), 1.62–1.53 (m, 2H), 1.39–1.23 (m, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 174.9, 157.1, 144.3, 122.2, 114.3, 55.5, 43.1, 28.9, 25.7, 25.3. HRMS (ESI⁺) *m/z* calcd for C₁₄H₁₉O₃ [M+H]⁺: 235.1329, found: 235.1329.

4-Methoxyphenyl tetrahydro-2*H*-pyran-4-carboxylate (**3ah**)



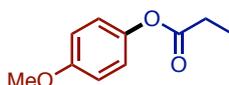
Purification by MPLC (hexane/EtOAc = 49:1 to 2:1) afforded **3ah** as a yellow oil (39 mg, 41% yield). ¹H NMR (600 MHz, CDCl₃) δ 6.98 (d, *J* = 9.0 Hz, 2H), 6.89 (d, *J* = 9.0 Hz, 2H), 4.02 (dt, *J* = 12.0, 3.6 Hz, 2H), 3.80 (s, 3H), 3.50 (td, *J* = 11.4, 2.4 Hz, 2H), 2.82–2.75 (m, 1H), 2.02–1.87 (m, 4H). ¹³C NMR (150 MHz, CDCl₃) δ 173.3, 157.2, 144.1, 122.1, 114.4, 67.0, 55.6, 40.1, 28.6. HRMS (ESI⁺) *m/z* calcd for C₁₃H₁₆O₄Na [M+Na]⁺: 259.0941, found: 259.0940.

4-Methoxyphenyl cyclobutanecarboxylate (**3ai**)



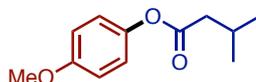
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) afforded **3ai** as a colorless oil (36 mg, 44% yield). ^1H NMR (600 MHz, CDCl_3) δ 6.99 (d, $J = 9.0$ Hz, 2H), 6.88 (d, $J = 9.0$ Hz, 2H), 3.79 (s, 3H), 3.36 (quint, $J = 9.0$ Hz, 1H), 2.46–2.38 (m, 2H), 2.34–2.27 (m, 2H), 2.09–1.93 (m, 2H). ^{13}C NMR (150 MHz, CDCl_3) δ 174.3, 157.1, 144.3, 122.2, 114.3, 55.5, 38.0, 25.3, 18.4. HRMS (ESI $^+$) m/z calcd for $\text{C}_{12}\text{H}_{15}\text{O}_3$ $[\text{M}+\text{H}]^+$: 207.1016, found: 207.1016.

4-Methoxyphenyl propionate (**3aj**)



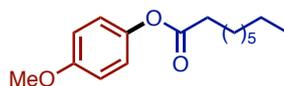
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) afforded **3aj** as a colorless oil (19 mg, 26% yield). ^1H NMR (600 MHz, CDCl_3) δ 6.99 (d, $J = 9.0$ Hz, 2H), 6.88 (d, $J = 9.0$ Hz, 2H), 3.79 (s, 3H), 2.57 (q, $J = 7.8$ Hz, 2H), 1.26 (t, $J = 7.8$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 173.4, 157.1, 144.2, 122.3, 114.4, 55.6, 27.7, 9.1. HRMS (ESI $^+$) m/z calcd for $\text{C}_{10}\text{H}_{12}\text{O}_3\text{Na}$ $[\text{M}+\text{Na}]^+$: 203.0679, found: 203.0679.

4-Methoxyphenyl 3-methylbutanoate (**3ak**)



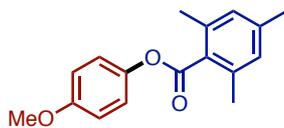
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) and PTLC (hexane/chloroform = 1:1) afforded **3ak** as a colorless oil (7 mg, 8% yield). ^1H NMR (600 MHz, CDCl_3) δ 6.99 (d, $J = 9.0$ Hz, 2H), 6.88 (d, $J = 9.0$ Hz, 2H), 3.80 (s, 3H), 2.41 (d, $J = 7.2$ Hz, 2H), 2.28–2.22 (m, 1H), 1.05 (d, $J = 6.6$ Hz, 6H). ^{13}C NMR (150 MHz, CDCl_3) δ 172.0, 157.2, 144.2, 122.3, 114.4, 55.6, 43.3, 25.9, 22.4. HRMS (ESI $^+$) m/z calcd for $\text{C}_{12}\text{H}_{17}\text{O}_3$ $[\text{M}+\text{H}]^+$: 209.1172, found: 209.1173.

4-Methoxyphenyl nonanoate (**3al**)



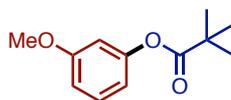
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) and PTLC (hexane/chloroform = 1:1) afforded **3al** as a colorless oil (11 mg, 10% yield). ^1H NMR (600 MHz, CDCl_3) δ 6.99 (d, $J = 9.0$ Hz, 2H), 6.88 (d, $J = 9.0$ Hz, 2H), 3.80 (s, 3H), 2.53 (t, $J = 7.8$ Hz, 2H), 1.77–1.71 (m, 2H), 1.43–1.23 (m, 10H), 0.89 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 172.7, 157.1, 144.2, 122.3, 114.4, 55.6, 34.3, 31.8, 29.2, 29.1 (2C), 25.0, 22.6, 14.1. HRMS (ESI $^+$) m/z calcd for $\text{C}_{16}\text{H}_{25}\text{O}_3$ $[\text{M}+\text{H}]^+$: 265.1798, found: 265.1799.

4-Methoxyphenyl 2,4,6-trimethylbenzoate (**3an**)



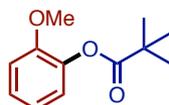
Purification by MPLC (hexane/EtOAc = 49:1 to 2:1) afforded **3an** as a white solid (45 mg, 42% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.14 (d, $J = 9.0$ Hz, 2H), 6.94 (d, $J = 9.0$ Hz, 2H), 6.91 (s, 2H), 3.81 (s, 3H), 2.44 (s, 6H), 2.31 (s, 3H). ^{13}C NMR (150 MHz, CDCl_3) δ 168.8, 157.4, 144.2, 139.8, 135.5, 130.1, 128.6, 122.3, 114.6, 55.6, 21.1, 19.9. HRMS (ESI $^+$) m/z calcd for $\text{C}_{17}\text{H}_{19}\text{O}_3$ $[\text{M}+\text{H}]^+$: 271.1329, found: 271.1329.

3-Methoxyphenyl pivalate (**3ba**)



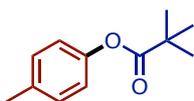
Purification by PTLC (hexane/EtOAc = 49:1 to 4:1) and GPC afforded **3ba** as a colorless oil (5 mg, 6% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.25 (t, $J = 8.4$ Hz, 1H), 6.76 (ddd, $J = 8.4, 2.4, 0.6$ Hz, 1H), 6.64 (ddd, $J = 8.4, 2.4, 0.6$ Hz, 1H), 6.59 (t, $J = 2.4$ Hz, 1H), 3.79 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (100 MHz, CDCl_3) δ 177.0, 160.5, 152.1, 129.7, 113.7, 111.5, 107.4, 55.4, 39.1, 27.1. HRMS (ESI $^+$) m/z calcd for $\text{C}_{12}\text{H}_{17}\text{O}_3$ $[\text{M}+\text{H}]^+$: 209.1172, found: 209.1173.

2-Methoxyphenyl pivalate (**3ca**)



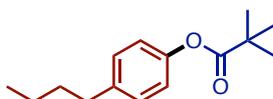
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) afforded **3ca** as a colorless oil (53 mg, 64% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.18 (ddd, $J = 8.4, 7.8, 1.8$ Hz, 1H), 7.00 (dd, $J = 7.8, 1.8$ Hz), 6.97–6.91 (m, 2H), 3.80 (s, 3H), 1.37 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 176.7, 151.2, 140.2, 126.5, 122.7, 120.7, 112.4, 55.9, 39.0, 27.2. HRMS (ESI $^+$) m/z calcd for $\text{C}_{12}\text{H}_{17}\text{O}_3$ $[\text{M}+\text{H}]^+$: 209.1172, found: 209.1173.

p-Tolyl pivalate (**3da**)



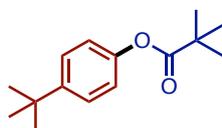
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) afforded **3da** as a pale yellow oil (31 mg, 40% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.16 (d, *J* = 8.8 Hz, 2H), 6.93 (d, *J* = 8.8 Hz, 2H), 2.34 (s, 3H), 1.35 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ 177.3, 148.8, 135.1, 129.8, 121.1, 39.0, 27.1, 20.8. HRMS (ESI⁺) *m/z* calcd for C₁₂H₁₆O₂Na [M+Na]⁺: 215.1043, found: 215.1042.

4-Butylphenyl pivalate (**3ea**)



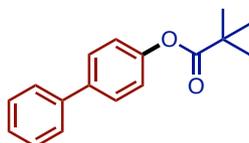
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) afforded **3ea** as a pale yellow oil (50 mg, 53% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.16 (d, *J* = 8.4 Hz, 2H), 6.95 (d, *J* = 8.4 Hz, 2H), 2.59 (t, *J* = 8.0 Hz, 2H), 1.63–1.53 (m, 2H), 1.40–1.29 (m, 11H), 0.92 (t, *J* = 8.0 Hz, 3H). ¹³C NMR (150 MHz, CDCl₃) δ 177.2, 148.9, 140.1, 129.2, 121.0, 39.0, 35.0, 33.6, 27.1, 22.3, 13.9. HRMS (ESI⁺) *m/z* calcd for C₁₅H₂₃O₂ [M+H]⁺: 235.1693, found: 235.1693.

4-(*tert*-Butyl)phenyl pivalate (**3fa**)



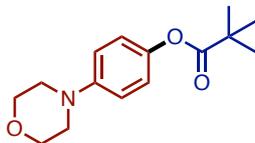
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) afforded **3fa** as a pale yellow solid (39 mg, 41% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.37 (d, *J* = 8.8 Hz, 2H), 6.97 (d, *J* = 8.8 Hz, 2H), 1.35 (s, 9H), 1.31 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ 177.2, 148.7, 148.3, 126.2, 120.7, 39.0, 34.4, 31.4, 27.1. HRMS (ESI⁺) *m/z* calcd for C₁₅H₂₃O₂⁺ [M+H]⁺: 235.1693, found: 235.1693.

(1,1'-Biphenyl)-4-yl pivalate (**3ga**)

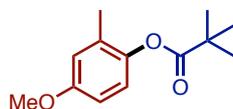


Purification by MPLC (hexane/EtOAc = 9:1 to 6:1) afforded **3ga** as a white solid (53 mg, 52% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.62–7.54 (m, 4H), 7.43 (t, *J* = 7.8 Hz, 2H), 7.36–7.32 (m, 1H), 7.13 (d, *J* = 7.8 Hz, 2H), 1.38 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ 177.1, 150.5, 140.4, 138.7, 128.7, 128.1, 127.3, 127.1, 121.7, 39.1, 27.1. HRMS (ESI⁺) *m/z* calcd for C₁₇H₁₉O₂ [M+H]⁺: 255.1380, found: 255.1380.

4-Morpholinophenyl pivalate (**3ha**)



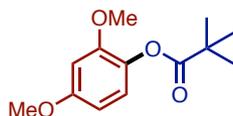
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) afforded **3ha** as a yellow solid (28 mg, 27% yield). ¹H NMR (600 MHz, CDCl₃) δ 6.96 (d, *J* = 9.6 Hz, 2H), 6.90 (d, *J* = 9.6 Hz, 2H), 3.86 (t, *J* = 4.8 Hz, 4H), 3.12 (t, *J* = 4.8 Hz, 4H), 1.34 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ 177.4, 149.1, 144.4, 121.9, 116.6, 66.9, 49.8, 39.0, 27.1. HRMS (ESI⁺) *m/z* calcd for C₁₅H₂₂NO₃ [M+H]⁺: 264.1594, found: 264.1592.



4-Methoxy-2-methylphenyl pivalate (**3la**)

Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) afforded **3la** as a colorless oil (77 mg, 86% yield). ¹H NMR (600 MHz, CDCl₃) δ 6.87 (d, *J* = 9.0 Hz, 1H), 6.74 (d, *J* = 3.0 Hz, 1H), 6.71 (dd, *J* = 9.0, 3.0 Hz, 1H), 3.77 (s, 3H), 2.13 (s, 3H), 1.37 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ 177.0, 157.1, 143.1, 131.0, 122.3, 116.2, 111.8, 55.5, 39.1, 27.2, 16.4. HRMS (ESI⁺) *m/z* calcd for C₁₃H₁₉O₃ [M+H]⁺: 223.1329, found: 223.1329.

2,4-Dimethoxyphenyl pivalate (**3ma**)



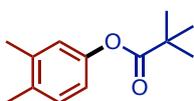
Reaction time: 42 h. Purification by MPLC (chloroform) afforded **3ma** as pale yellow solid (67 mg, 71% yield). ¹H NMR (600 MHz, CDCl₃) δ 6.89 (d, *J* = 8.4 Hz, 1H), 6.52 (d, *J* = 2.4 Hz, 1H), 6.43 (dd, *J* = 8.7, 2.7 Hz, 1H), 3.79 (s, 3H), 3.77 (s, 3H), 1.35 (s, 9H). ¹³C NMR (150 MHz, CDCl₃) δ 177.1, 158.2, 151.8, 134.0, 122.6, 103.8, 100.2, 55.8, 55.6, 39.0, 27.2. HRMS (ESI⁺) *m/z* calcd for C₁₃H₁₉O₄ [M+H]⁺: 239.1278, found: 239.1277.

2-Methoxy-4-methylphenyl pivalate (**3na**)



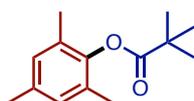
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) afforded **3na** as a colorless crystal (67 mg, 75% yield). ^1H NMR (600 MHz, CDCl_3) δ 6.86 (d, $J = 8.4$ Hz, 1H), 6.75 (s, 1H), 6.72 (d, $J = 8.4$ Hz, 1H), 3.77 (s, 3H), 2.33 (s, 3H), 1.36 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 176.8, 150.8, 137.9, 136.4, 122.2, 121.1, 113.3, 55.8, 39.0, 27.2, 21.4. HRMS (ESI $^+$) m/z calcd for $\text{C}_{13}\text{H}_{19}\text{O}_3$ $[\text{M}+\text{H}]^+$: 223.1329, found: 223.1329.

3,4-Dimethylphenyl pivalate (**3oa**)



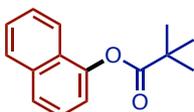
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) afforded **3oa** as a colorless crystal (50 mg, 60% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.10 (d, $J = 8.4$ Hz, 1H), 6.82 (d, $J = 2.4$ Hz, 1H), 6.77 (dd, $J = 8.4, 2.4$ Hz, 1H), 2.24 (s, 3H), 2.23 (s, 3H), 1.34 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 177.3, 149.0, 137.8, 133.8, 130.2, 122.4, 118.5, 39.0, 27.1, 19.8, 19.1. HRMS (ESI $^+$) m/z calcd for $\text{C}_{13}\text{H}_{19}\text{O}_2^+$ $[\text{M}+\text{H}]^+$: 207.1380, found: 207.1381.

Mesityl pivalate (**3pa**)



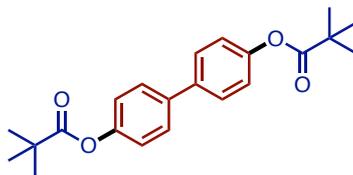
Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) afforded **3pa** as a colorless oil (68 mg, 77% yield). ^1H NMR (600 MHz, CDCl_3) δ 6.85 (s, 2H), 2.25 (s, 3H), 2.08 (s, 6H), 1.39 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 176.1, 145.9, 134.9, 129.6, 129.2, 39.2, 27.3, 20.7, 16.2. HRMS (ESI $^+$) m/z calcd for $\text{C}_{14}\text{H}_{21}\text{O}_2$ $[\text{M}+\text{H}]^+$: 221.1536, found: 221.1536.

Naphthalen-1-yl pivalate (**3qa**)



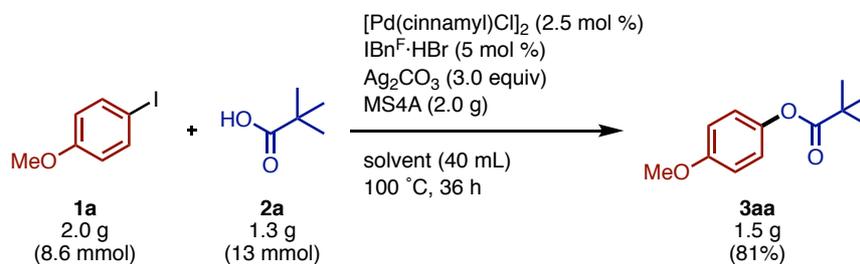
Purification by MPLC (hexane/EtOAc = 9:1 to 6:1) afforded **3qa** as a pale yellow oil (56 mg, 62% yield). ^1H NMR (600 MHz, CDCl_3) δ 7.87–7.84 (m, 2H), 7.72 (d, $J = 8.4$ Hz, 1H), 7.53–7.43 (m, 3H), 7.20 (dd, $J = 7.2, 1.2$ Hz, 1H), 1.49 (s, 9H). ^{13}C NMR (150 MHz, CDCl_3) δ 177.0, 146.9, 134.6, 128.0, 127.0, 126.35, 126.31, 125.7, 125.4, 121.0, 117.9, 39.5, 27.4. HRMS (ESI $^+$) m/z calcd for $\text{C}_{15}\text{H}_{17}\text{O}_2$ $[\text{M}+\text{H}]^+$: 229.1223, found: 229.1223.

(1,1'-Biphenyl)-4,4'-diyl bis(2,2-dimethylpropanoate) (**3ra**)



Purification by MPLC (hexane/EtOAc = 49:1 to 4:1) and PTLC (hexane/EtOAc = 3:1) afforded **3ra** as a white solid (18 mg, 25% yield). ¹H NMR (600 MHz, CDCl₃) δ 7.55 (d, *J* = 8.4 Hz, 4H), 7.12 (d, *J* = 8.4 Hz, 4H), 1.38 (s, 18H). ¹³C NMR (150 MHz, CDCl₃) δ 177.1, 150.5, 137.9, 128.0, 121.8, 39.1, 27.1. HRMS (ESI⁺) *m/z* calcd for C₂₂H₂₇O₄ [M+H]⁺: 355.1904, found: 355.1904.

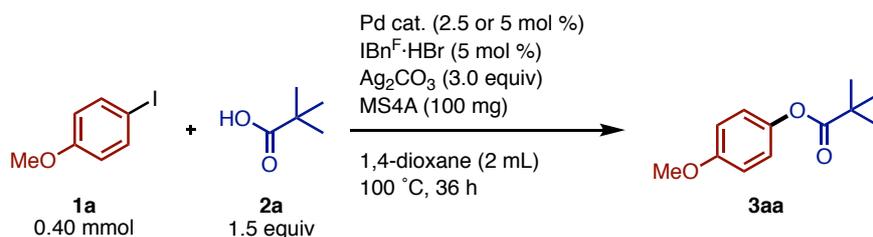
4. Gram scale synthesis of 4-methoxyphenyl pivalate



To a 300-mL round bottom flask containing a magnetic stirrer bar was added MS4A (2.00g) and dried with a heat gun and filled with N₂ after cooling to room temperature. Then to this vessel were added 4-iodoanisole (**1a**) (2.00 g, 8.55 mmol, 1.0 equiv), pivalic acid (**2a**) (1.31 g, 12.8 mmol, 1.5 equiv), Ag₂CO₃ (7.07 g, 25.6 mmol, 3.0 equiv), [Pd(cinnamyl)Cl]₂ (111 mg, 0.21 mmol, 2.5 mol%), 1,3-bis((pentafluorophenyl)methyl)-1*H*-imidazol-3-ium bromide (IBn^F·HBr) (218 mg, 0.43 mmol, 5.0 mol%) and 1,4-dioxane (40.0 mL). After stirring at 100 °C for 36 h, the reaction mixture was cooled to room temperature, and then passed through a short pad of Celite[®] (eluent: EtOAc). After the organic solvent was removed under reduced pressure, the residue was purified by MPLC (hexane/EtOAc = 1:0 to 4:1) to afford 4-methoxyphenyl pivalate (**3aa**) as a pale yellow oil (1.45 g, 81%).

5. Effect of parameters

Effect of Pd source



entry	Pd cat.	GC yield ^a (isolated yield)
1	PdCl ₂ (5.0 mol %)	5%
2	PdI ₂ (5.0 mol %)	66%
3	Pd(OAc) ₂ (5.0 mol %)	78% (75%)
4	Pd(PPh ₃) ₄ (5.0 mol %)	49%
5	Pd ₂ (dba) ₃ (2.5 mol %)	7%
6	[Pd(allyl)Cl] ₂ (2.5 mol %)	67%
7 ^c	[Pd(cinnamyl)Cl] ₂ (2.5 mol %)	77% ^b (77%)

^aDetermined by GC using dodecane as an internal standard.

^bDetermined by ¹H NMR using CH₂Br₂ as an internal standard.

^cReaction time: 42 h.

Effect of solvents



entry	solvent	GC yield ^a (isolated yield)
1	1,4-dioxane	78% (75%)
2	toluene	34%
3	ClCH ₂ CH ₂ Cl	57%
4	CH ₃ CN	0%
5	DMF	6%
6	HFIP	0%

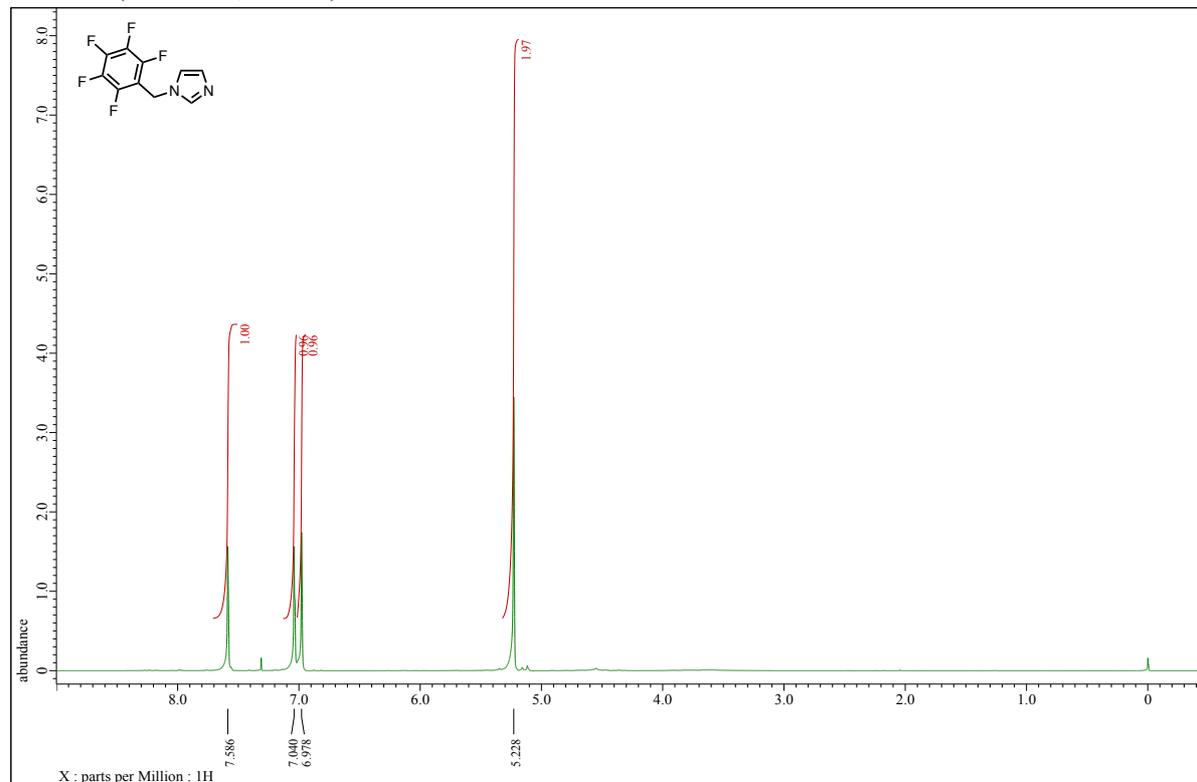
^aDetermined by GC using dodecane as an internal standard.

6. References

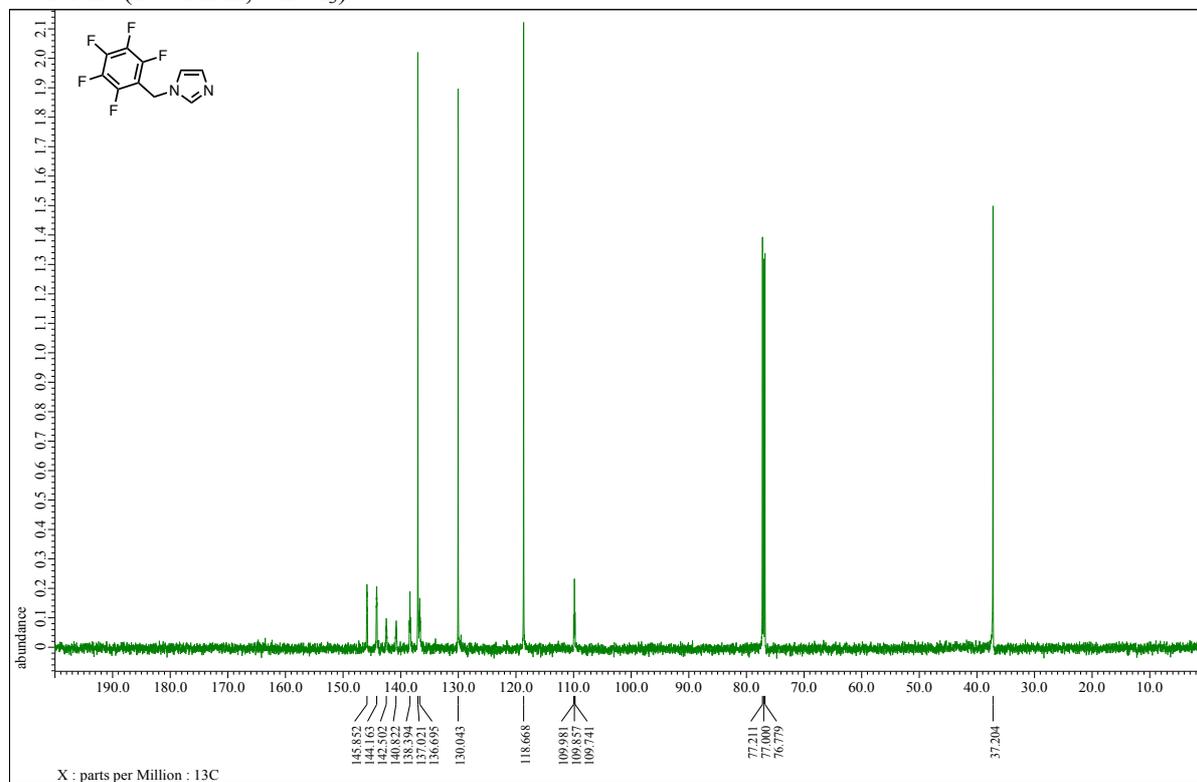
- (1) Zhu, R.-Y.; He, J.; Wang, X.-C.; Yu, J.-Q. *J. Am. Chem. Soc.* **2014**, *136*, 13194.
- (2) Perry, G. J. P.; Quibell, J. M.; Panigrahi, A.; Larrosa, I. *J. Am. Chem. Soc.* **2017**, *139*, 12430.
- (3) Chapman, M. R.; Shafi, Y. M.; Kapur, N.; Nguyen, B. N.; Willans, C. E. *Chem. Commun.* **2015**, *51*, 1282.

7. ^1H and ^{13}C NMR spectra 1-((Pentafluorophenyl)methyl)-1*H*-imidazole (7)

^1H NMR (600 MHz, CDCl_3)

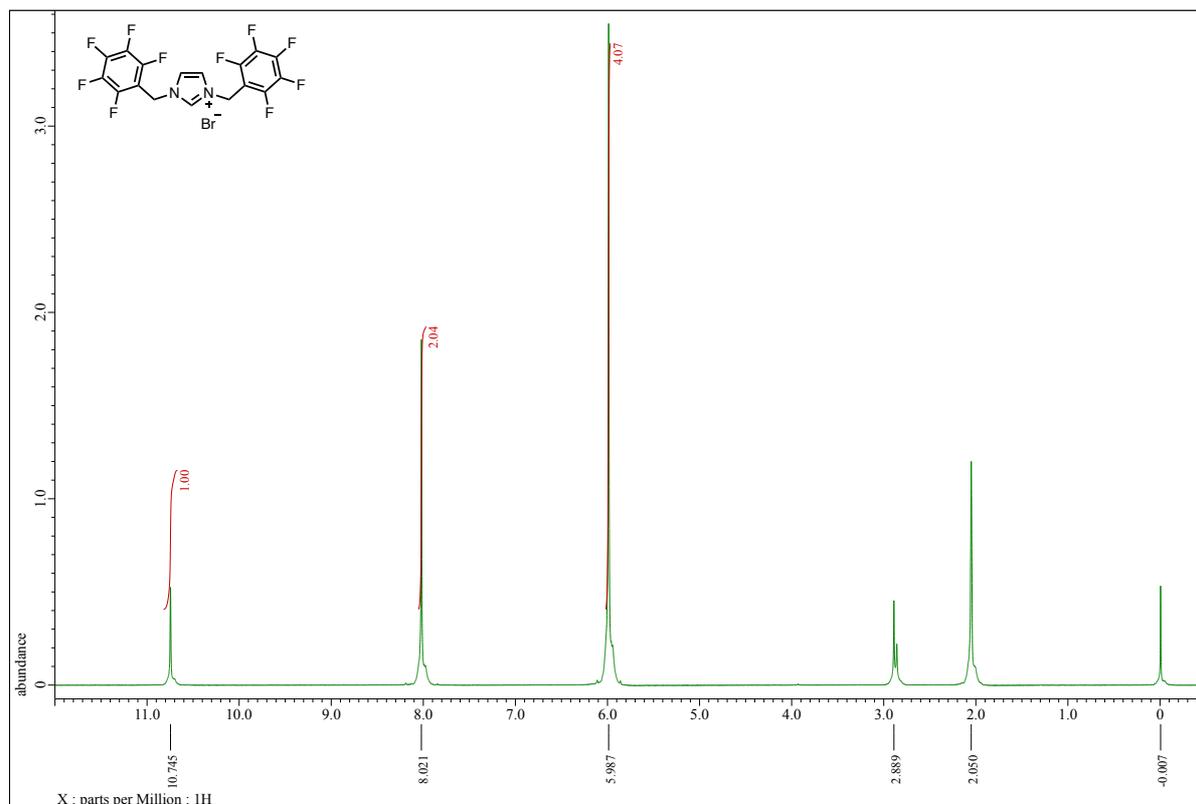


^{13}C NMR (150 MHz, CDCl_3)

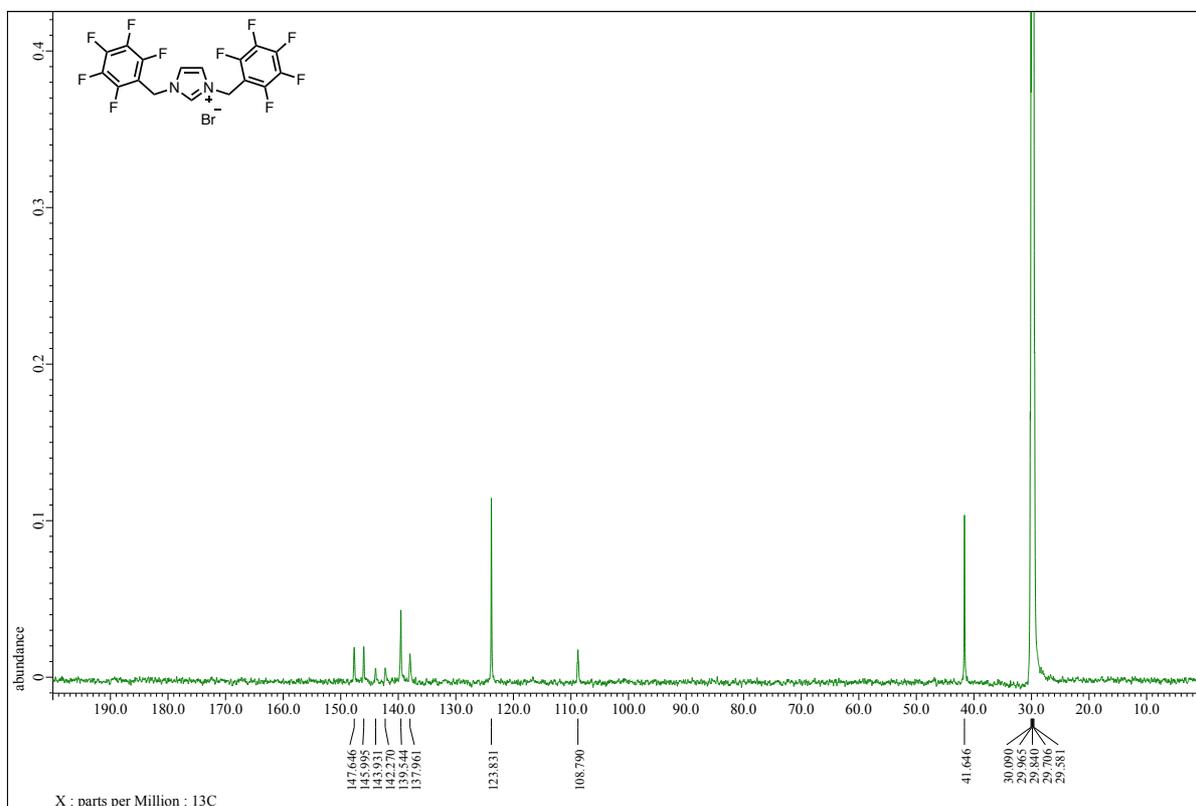


1,3-Bis((pentafluorophenyl)methyl)-1*H*-imidazol-3-ium bromide (IBn^F·HBr)

¹H NMR (600 MHz, acetone-*d*₆)

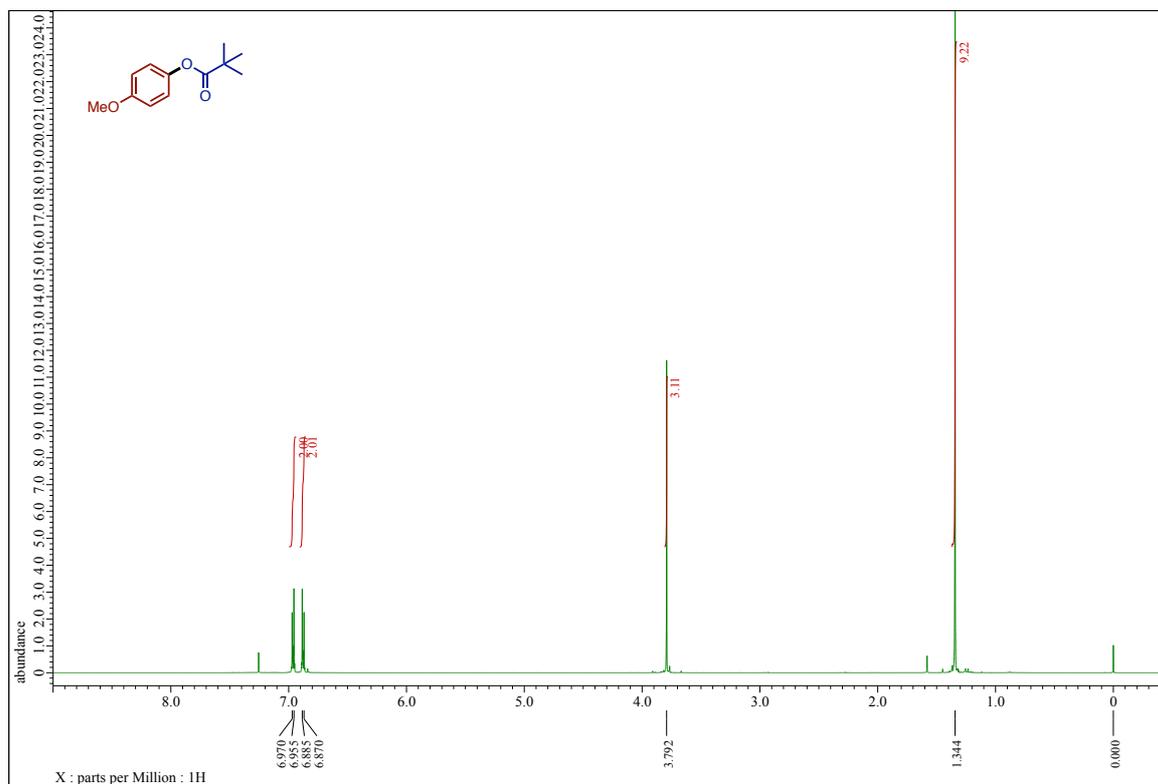


¹³C NMR (150 MHz, acetone-*d*₆)

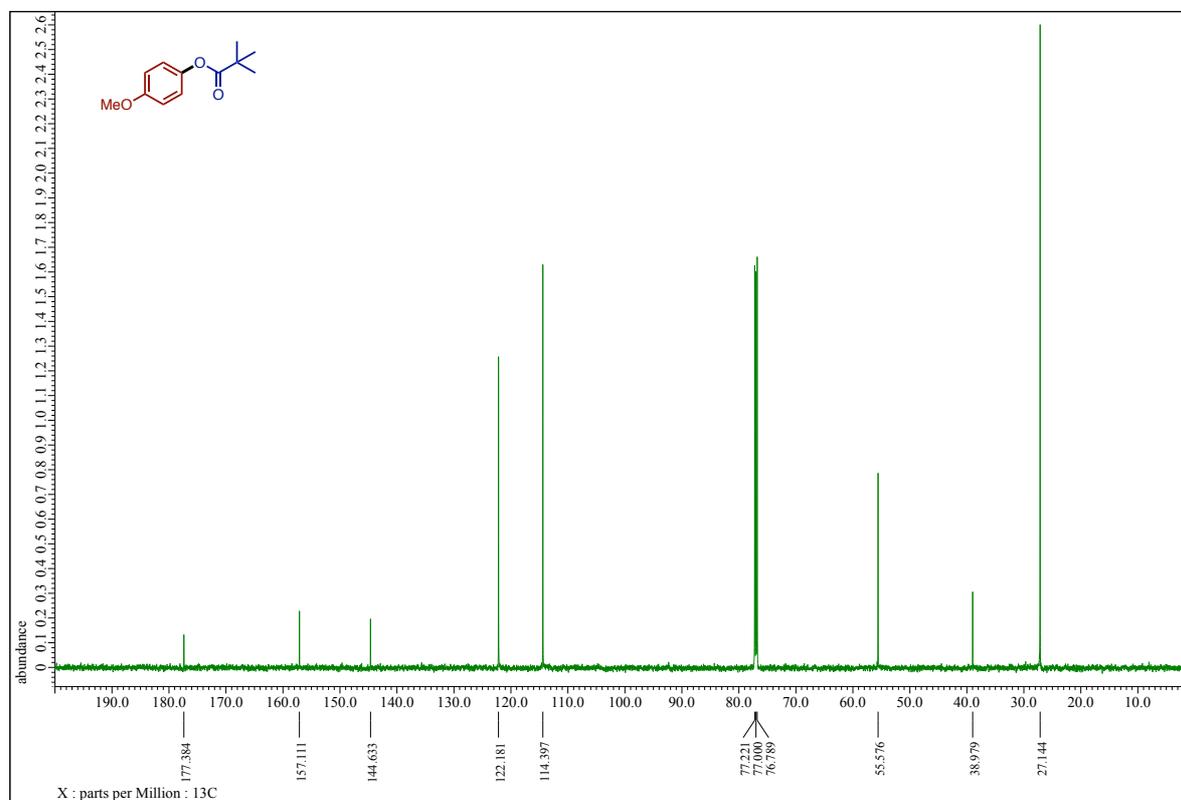


4-Methoxyphenyl pivalate (3aa)

^1H NMR (600 MHz, CDCl_3)

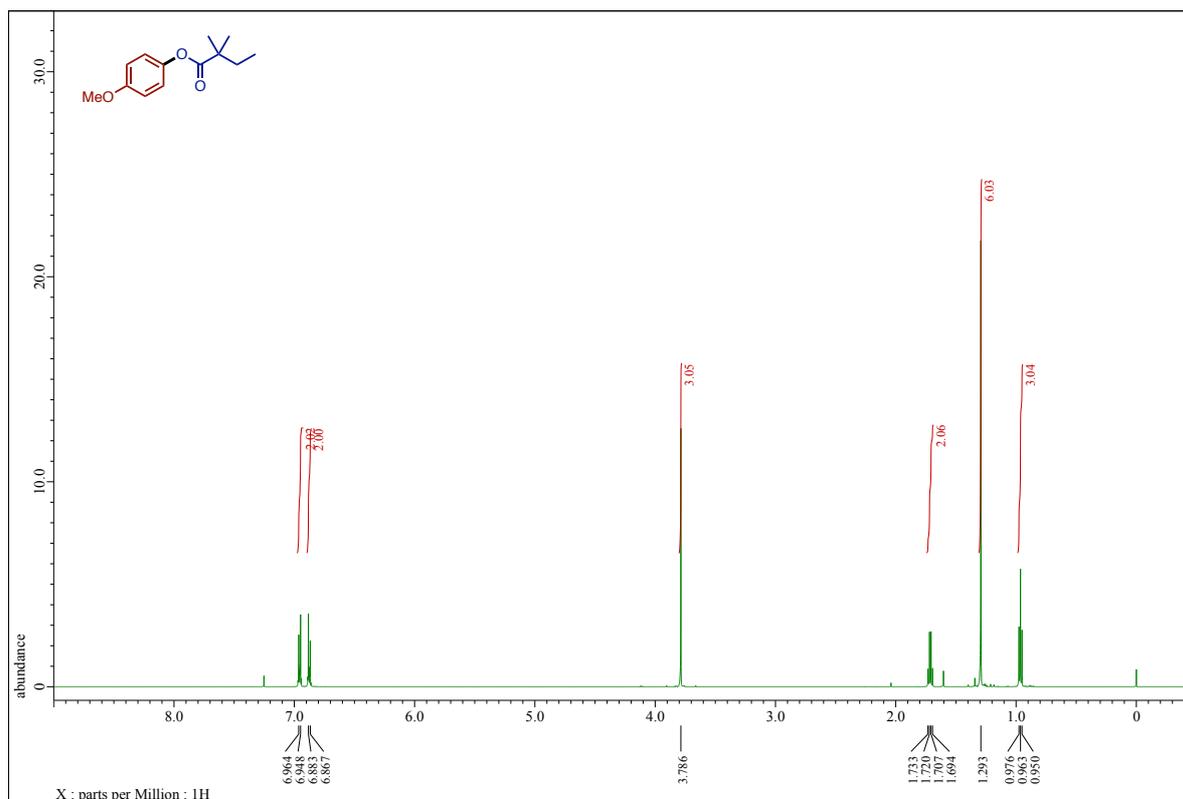


^{13}C NMR (150 MHz, CDCl_3)

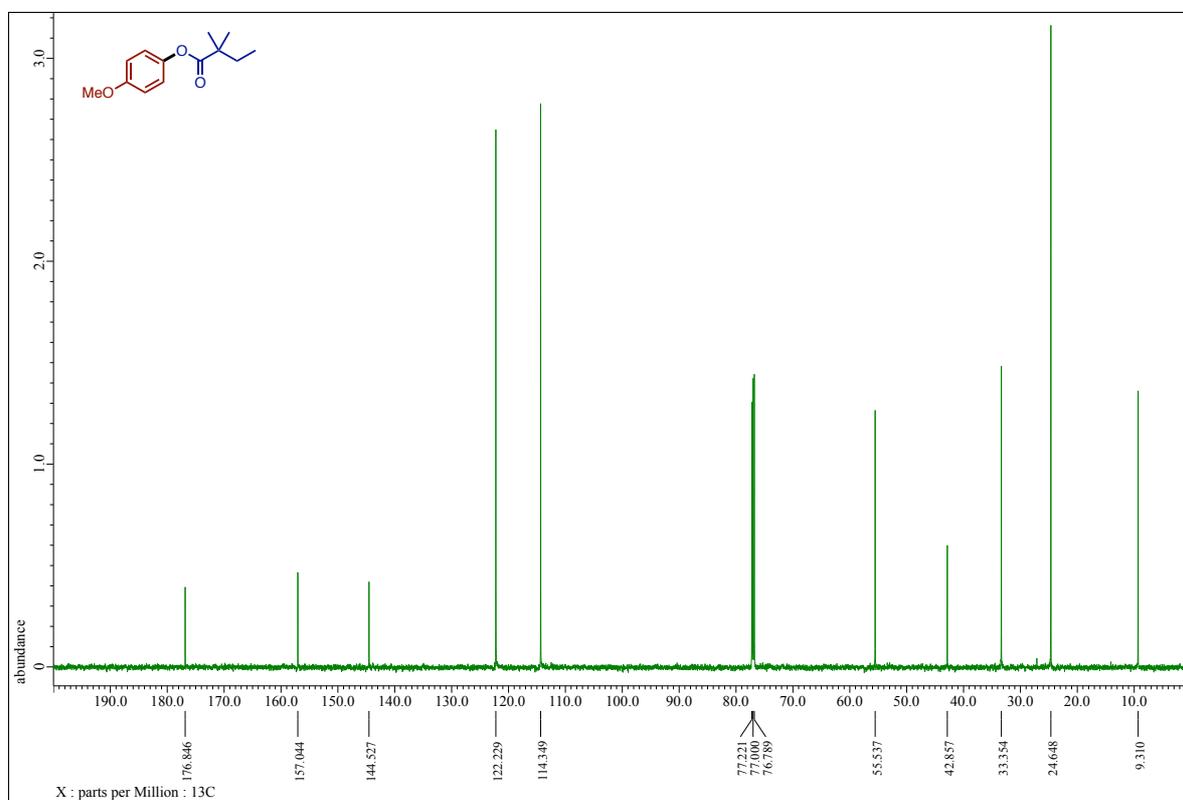


4-Methoxyphenyl 2,2-dimethylbutanoate (3ab)

^1H NMR (600 MHz, CDCl_3)

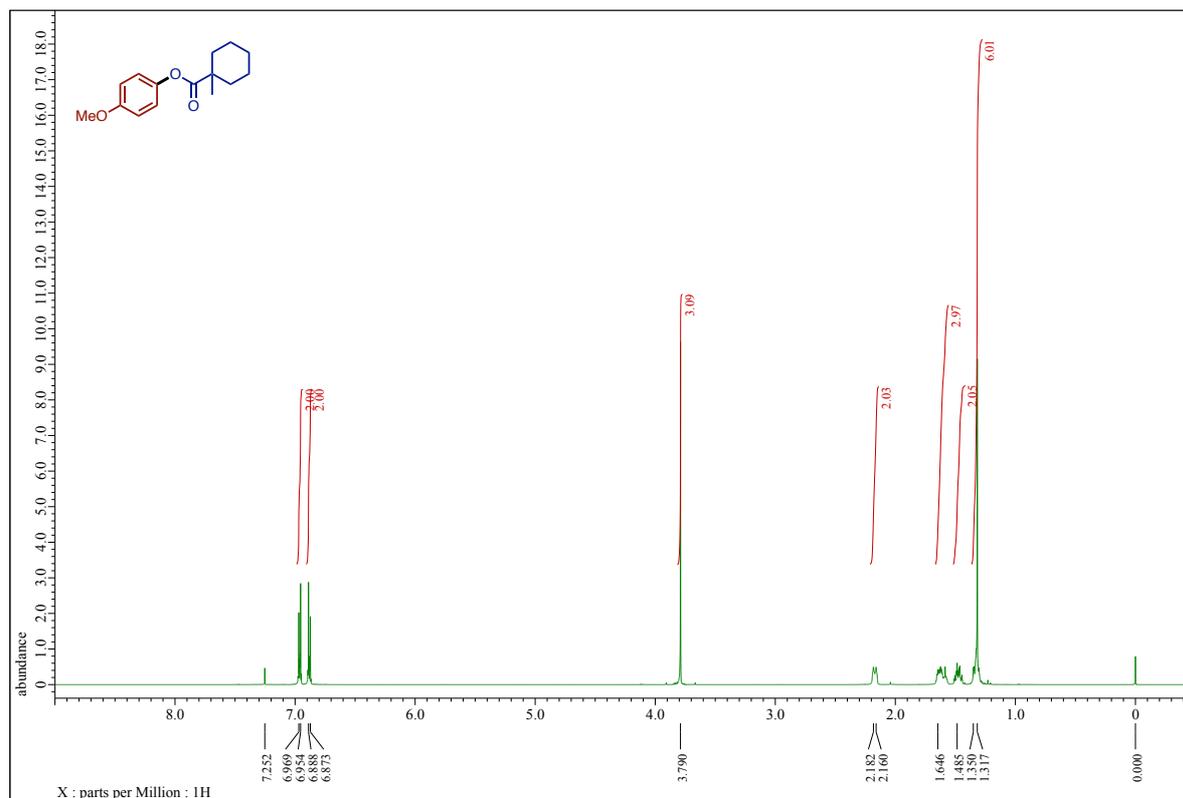


^{13}C NMR (150 MHz, CDCl_3)

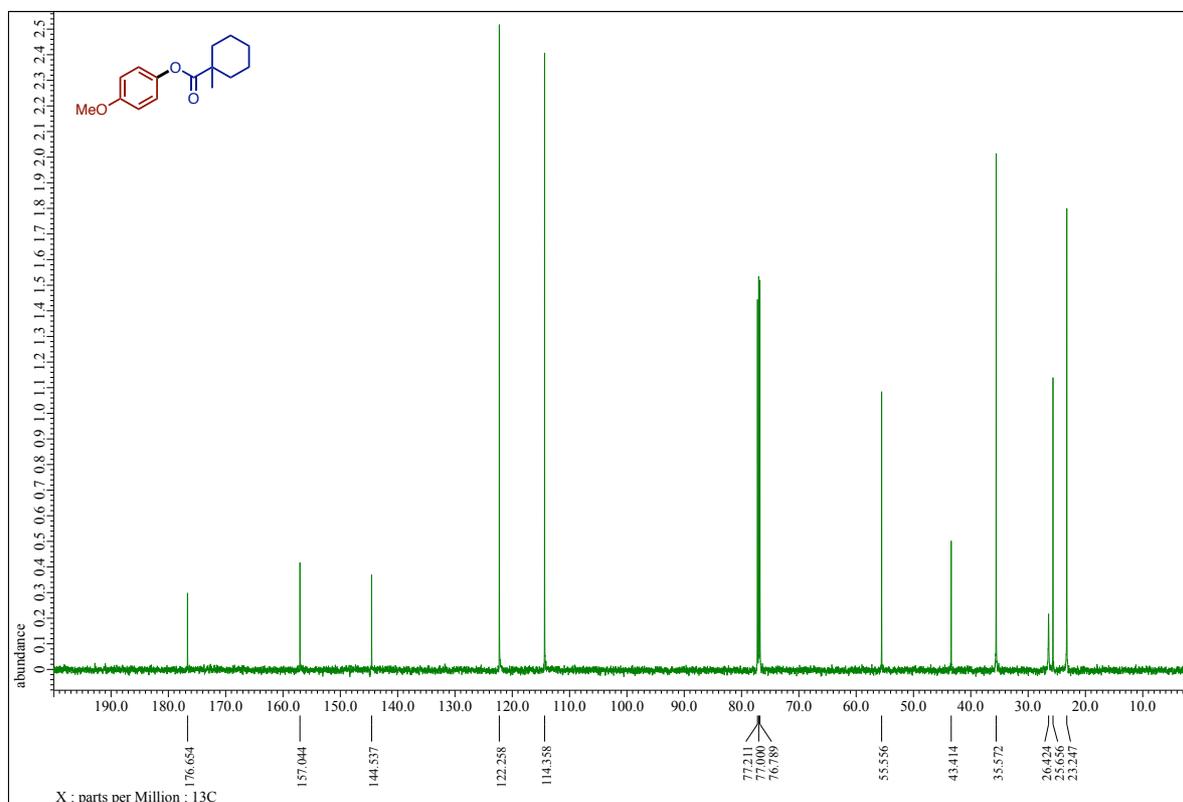


4-Methoxyphenyl 1-methylcyclohexane-1-carboxylate (3ac)

^1H NMR (600 MHz, CDCl_3)

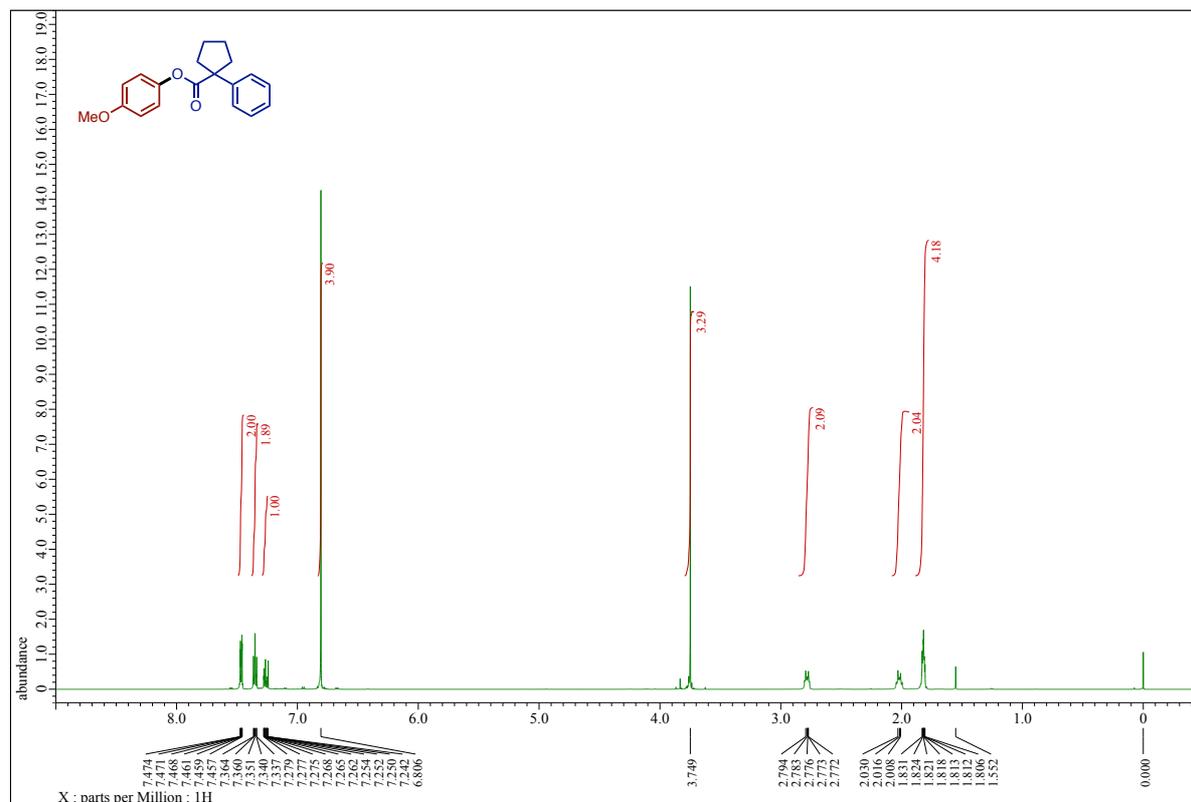


^{13}C NMR (150 MHz, CDCl_3)

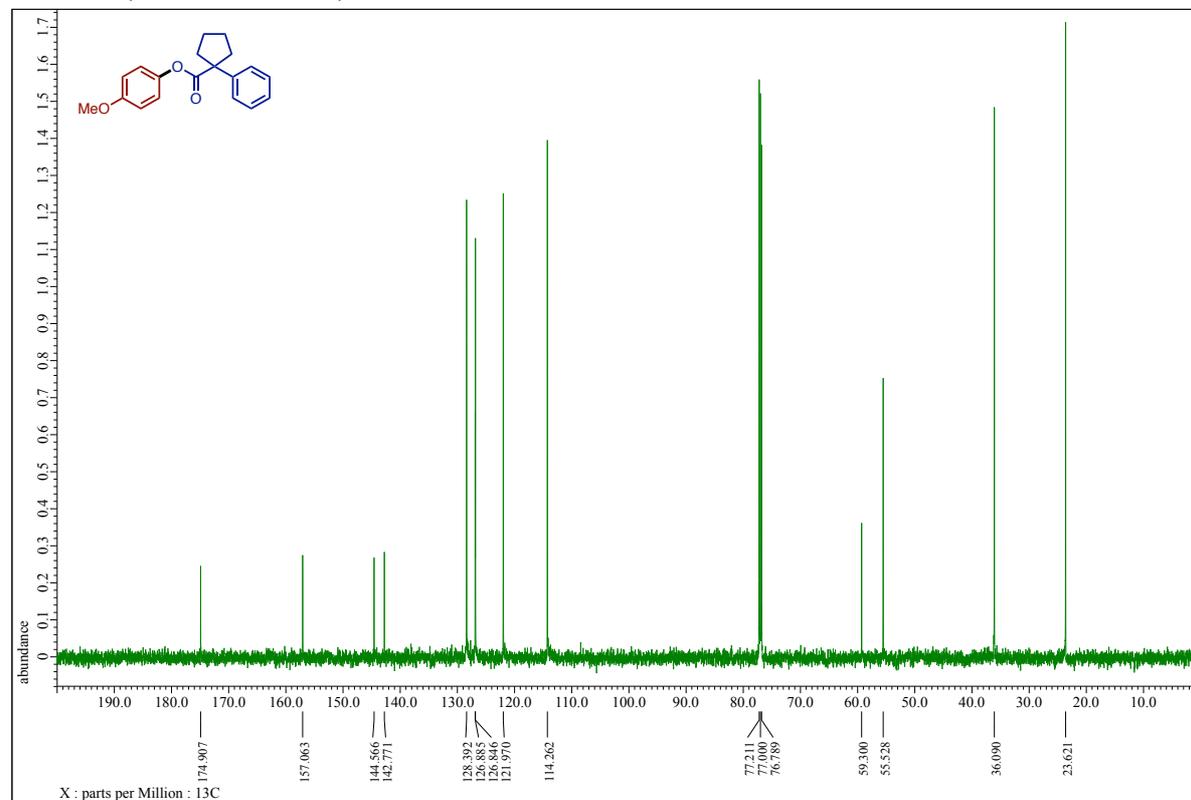


4-Methoxyphenyl 1-phenylcyclopentane-1-carboxylate (3ad)

^1H NMR (600 MHz, CDCl_3)

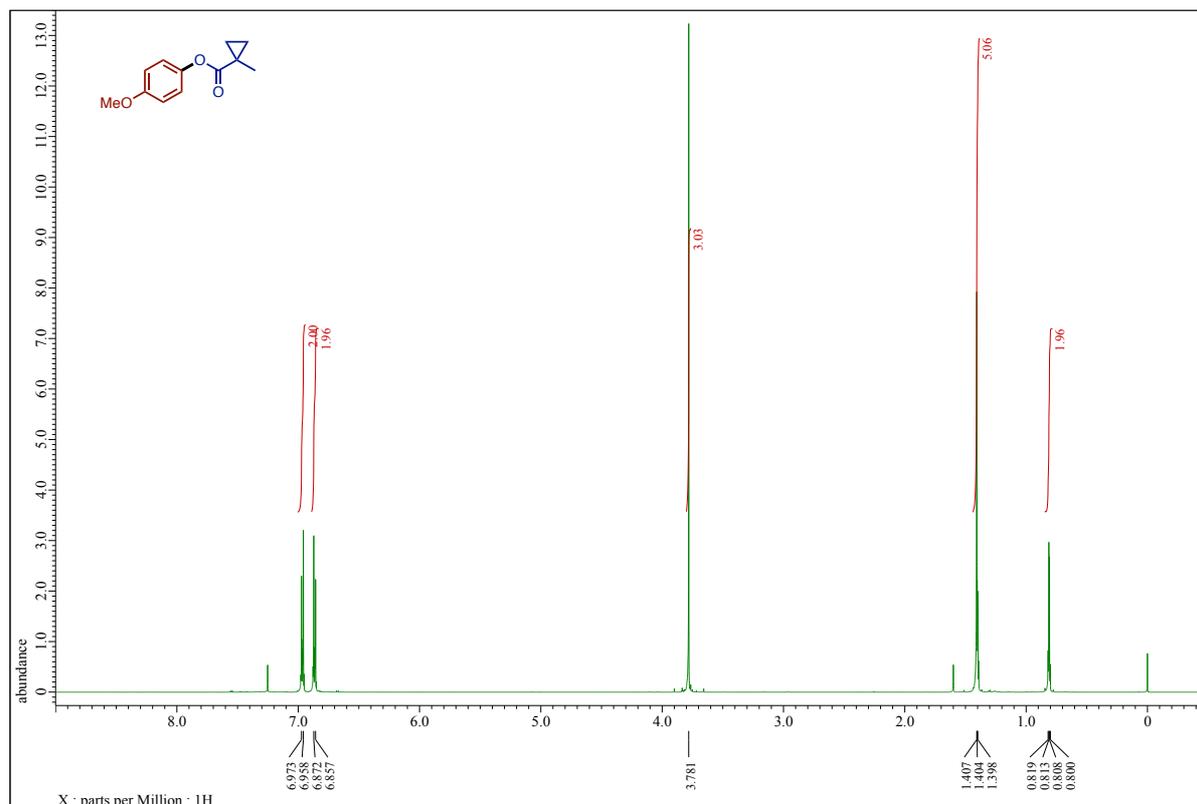


^{13}C NMR (150 MHz, CDCl_3)

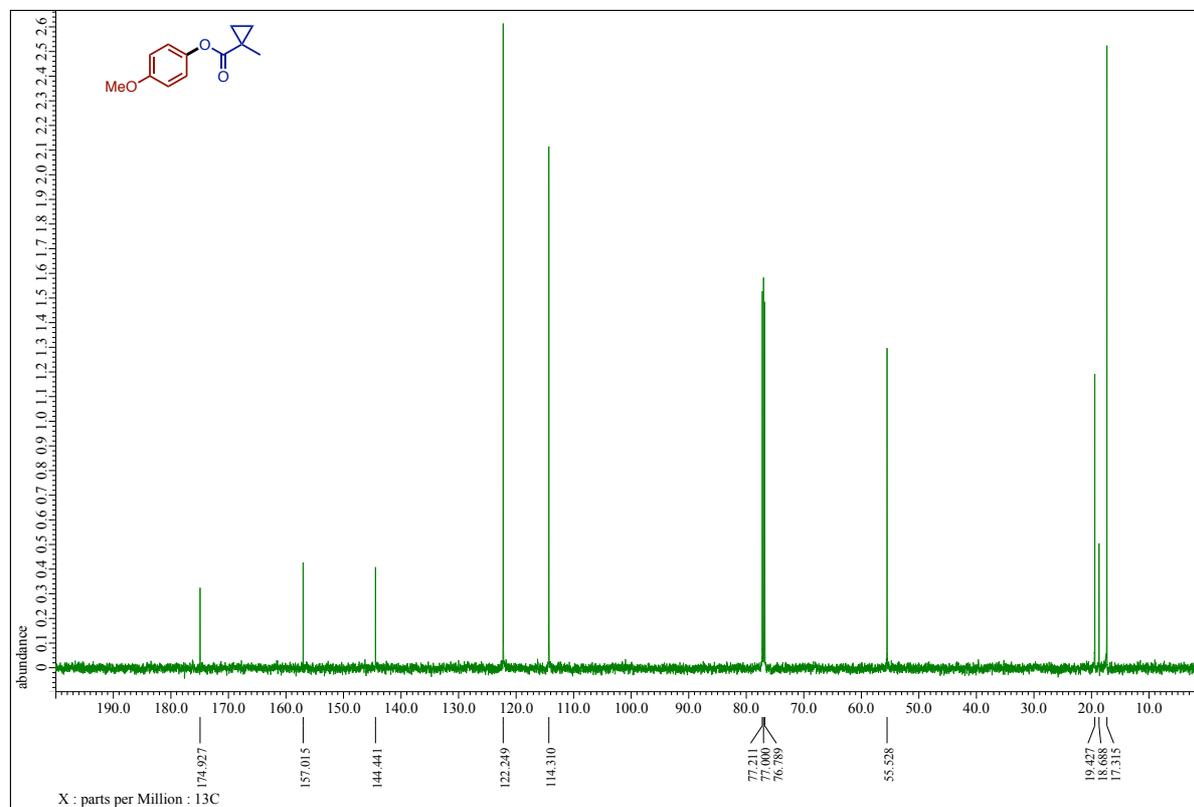


4-Methoxyphenyl 1-methylcyclopropane-1-carboxylate (3ae)

^1H NMR (600 MHz, CDCl_3)

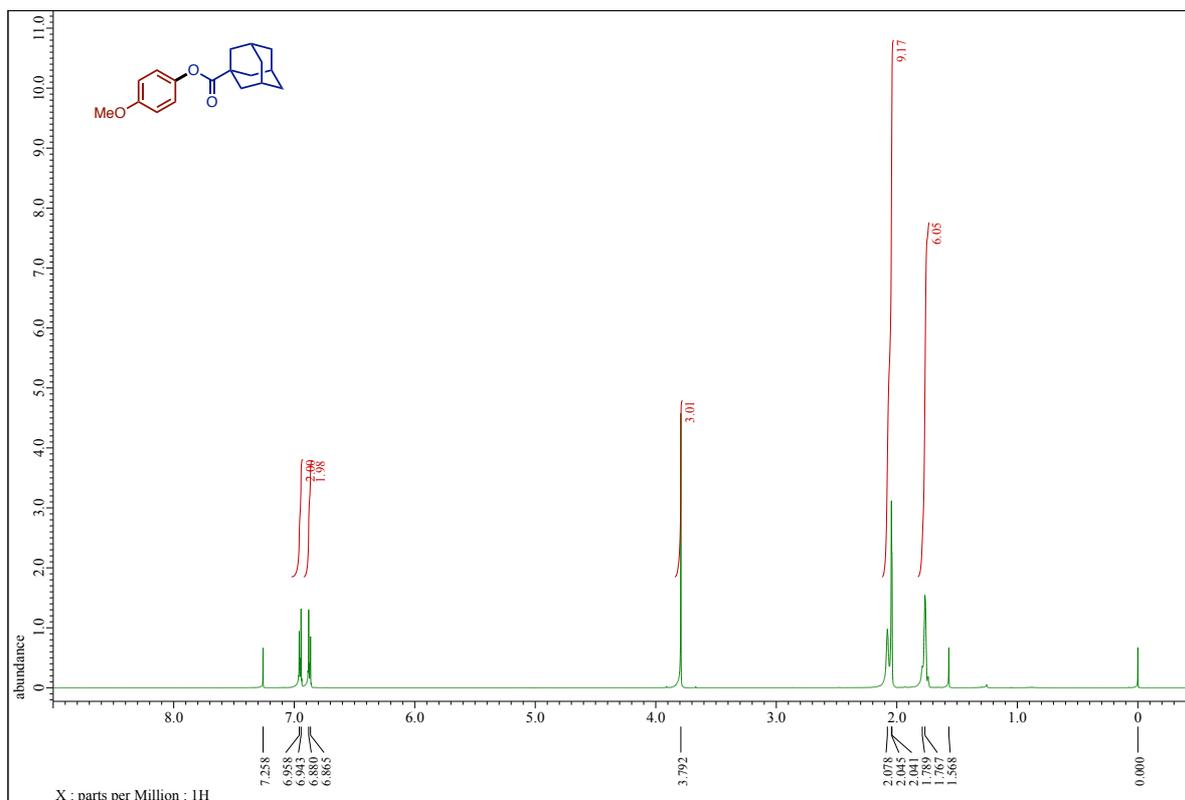


^{13}C NMR (150 MHz, CDCl_3)

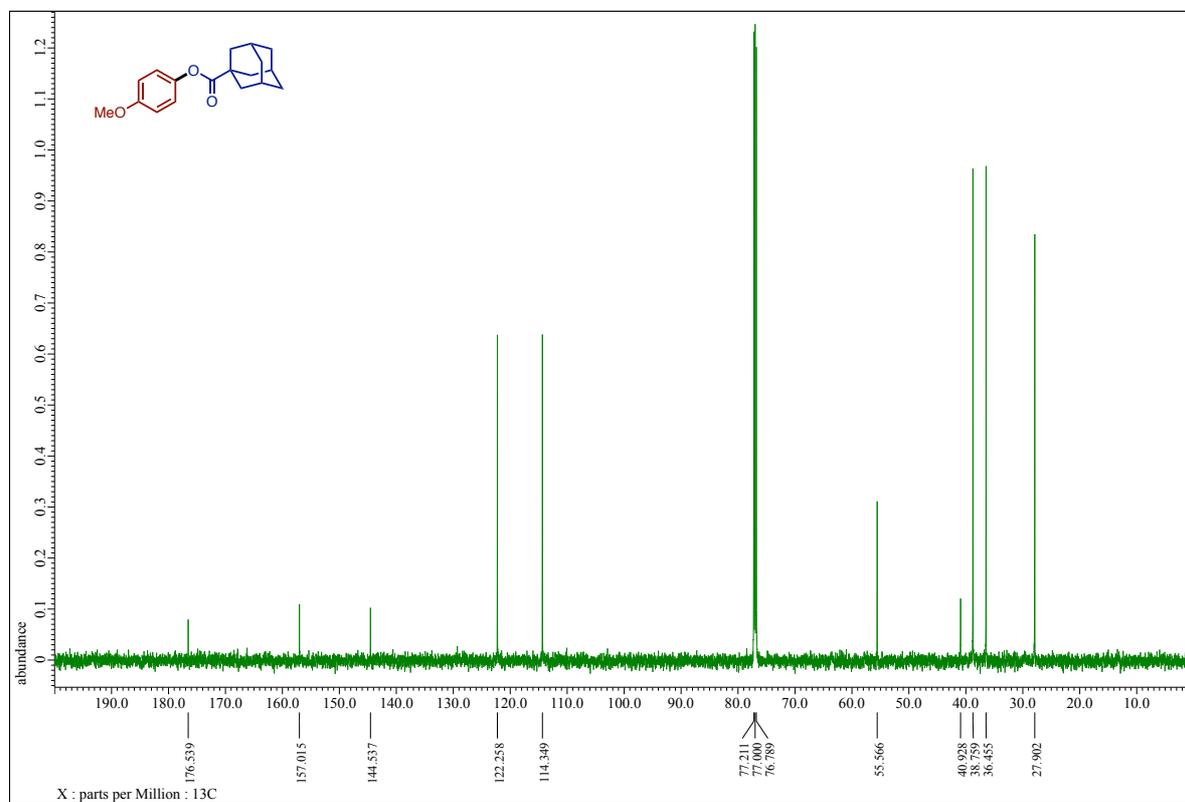


4-Methoxyphenyl (3*r*,5*r*,7*r*)-adamantane-1-carboxylate (3af)

¹H NMR (600 MHz, CDCl₃)

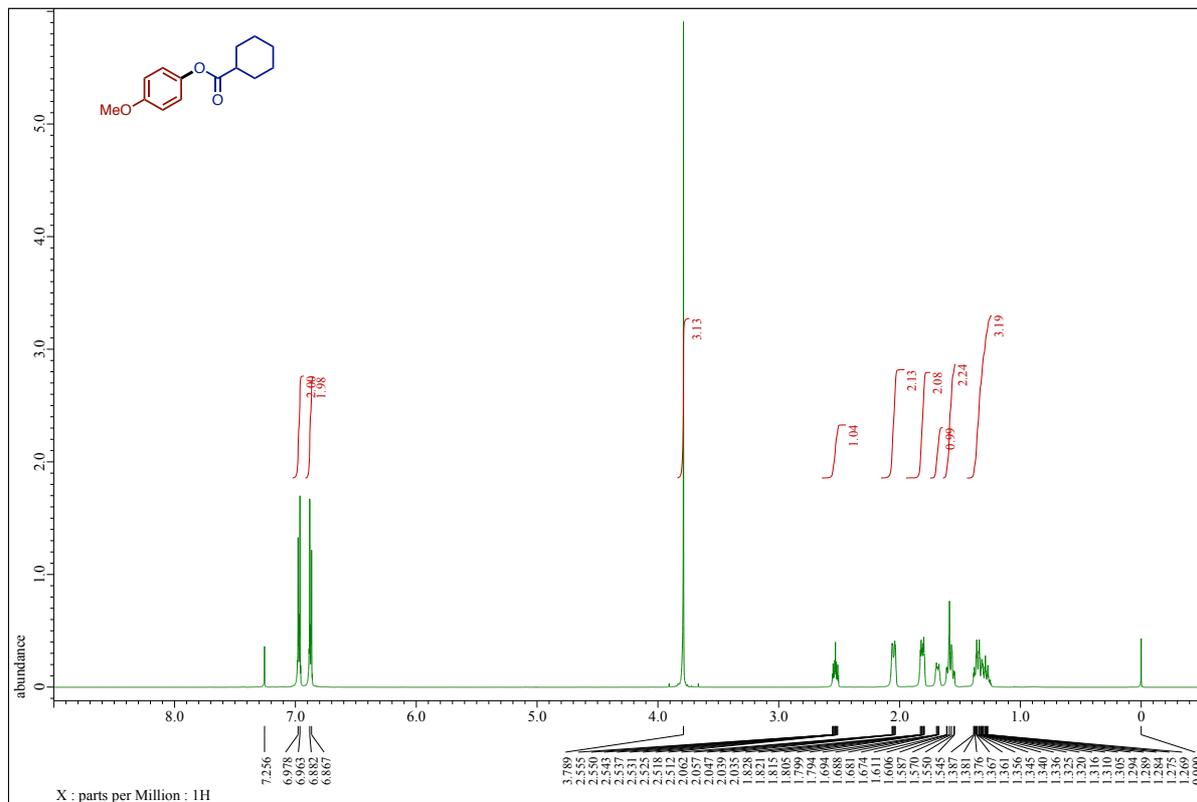


¹³C NMR (150 MHz, CDCl₃)

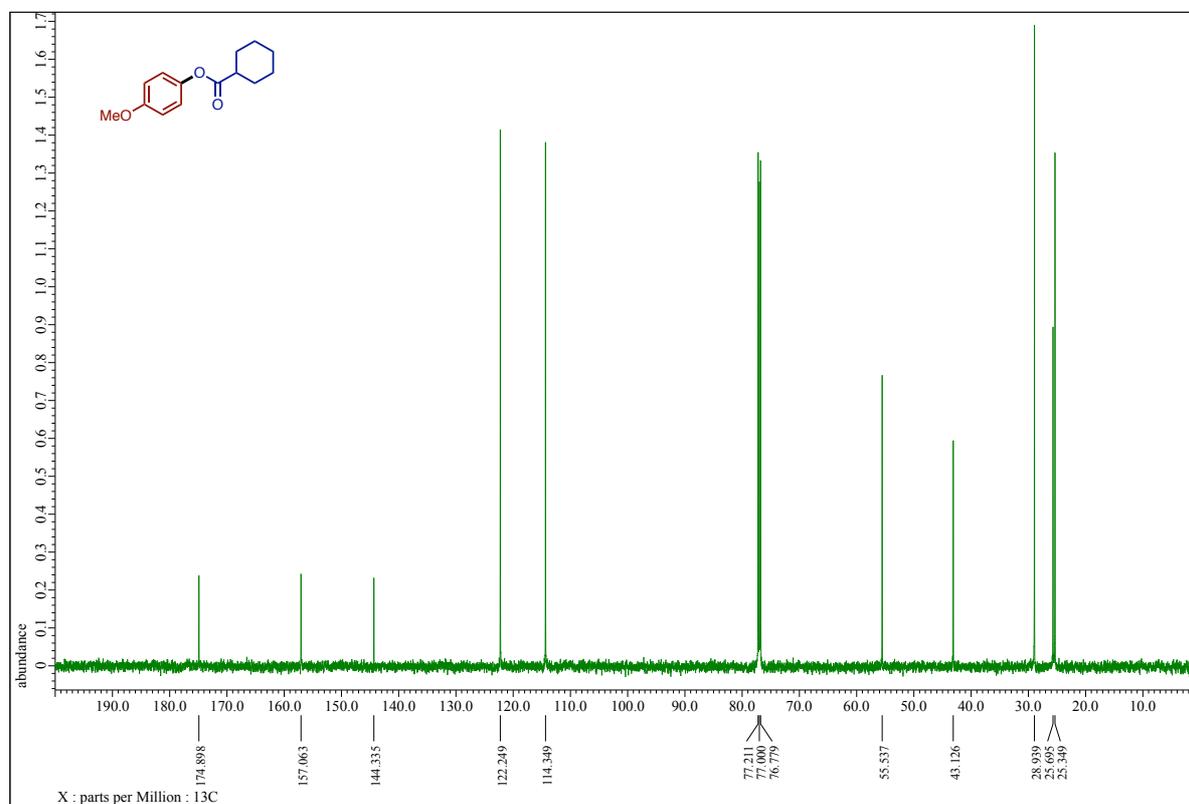


4-Methoxyphenyl cyclohexanecarboxylate (3ag)

^1H NMR (600 MHz, CDCl_3)

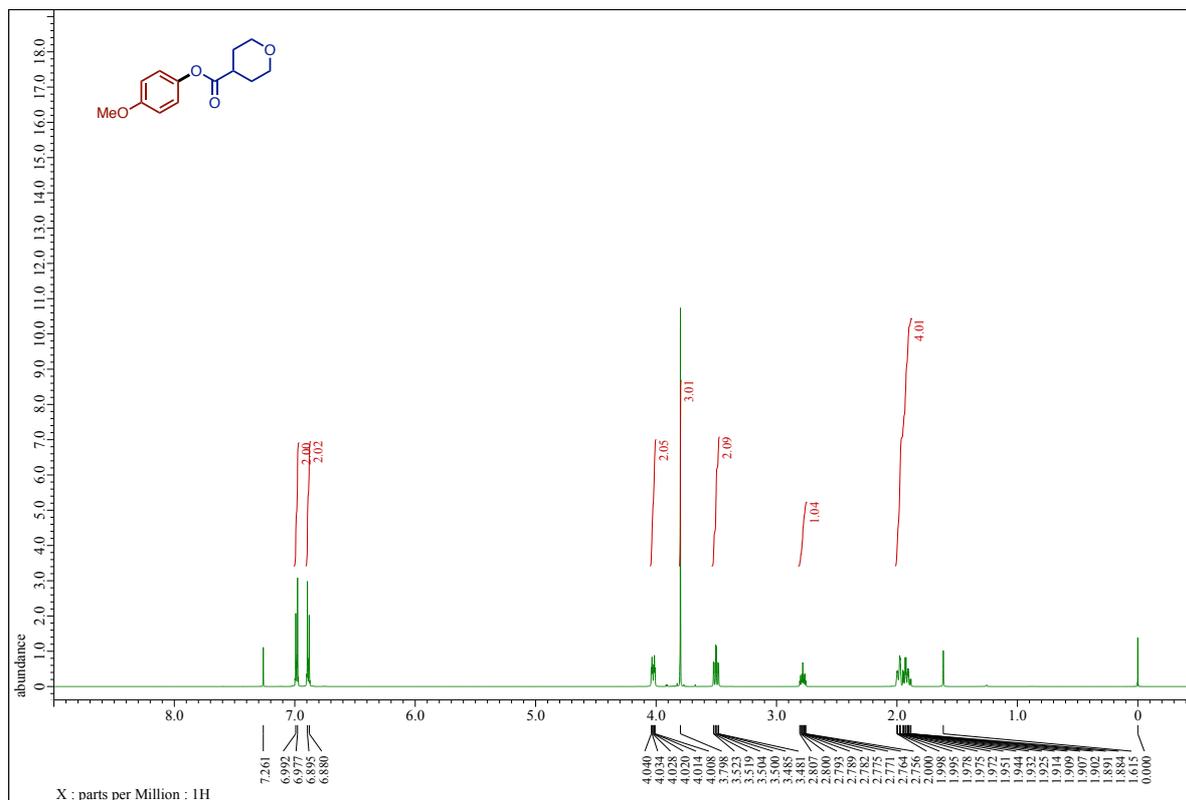


^{13}C NMR (150 MHz, CDCl_3)

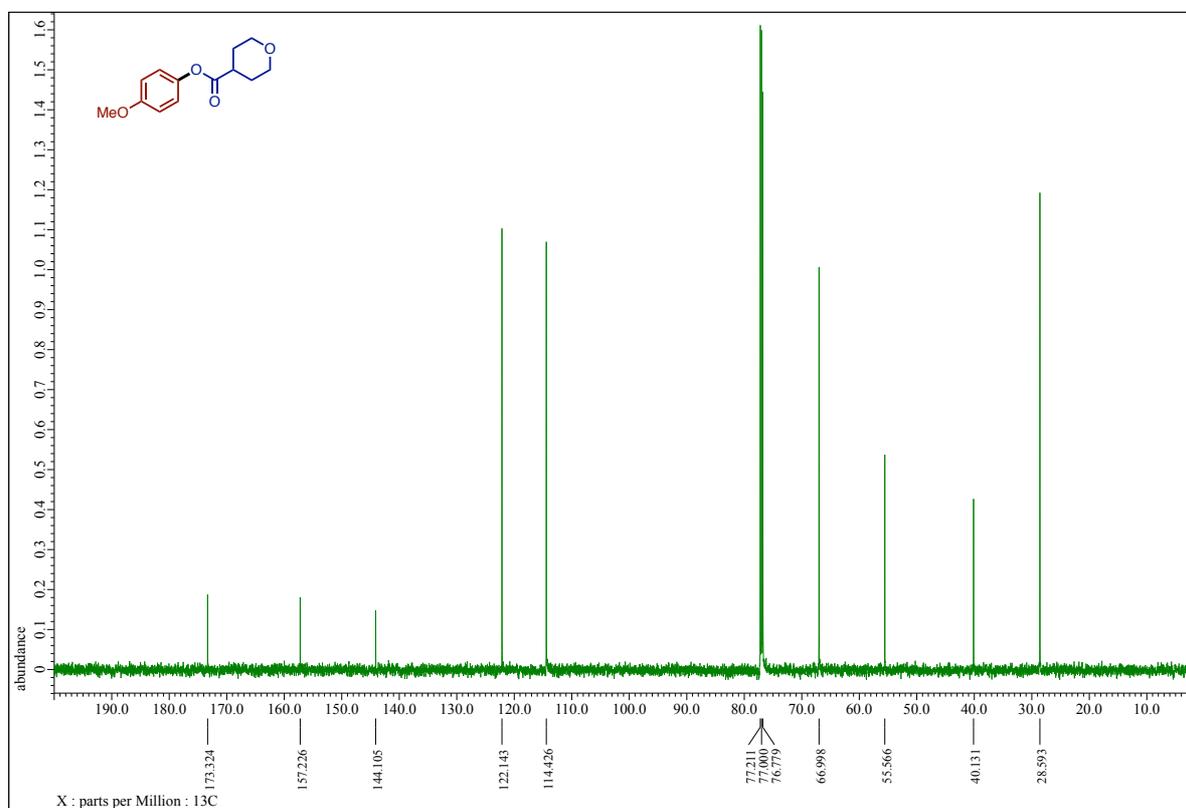


4-Methoxyphenyl tetrahydro-2H-pyran-4-carboxylate (3ah)

^1H NMR (600 MHz, CDCl_3)

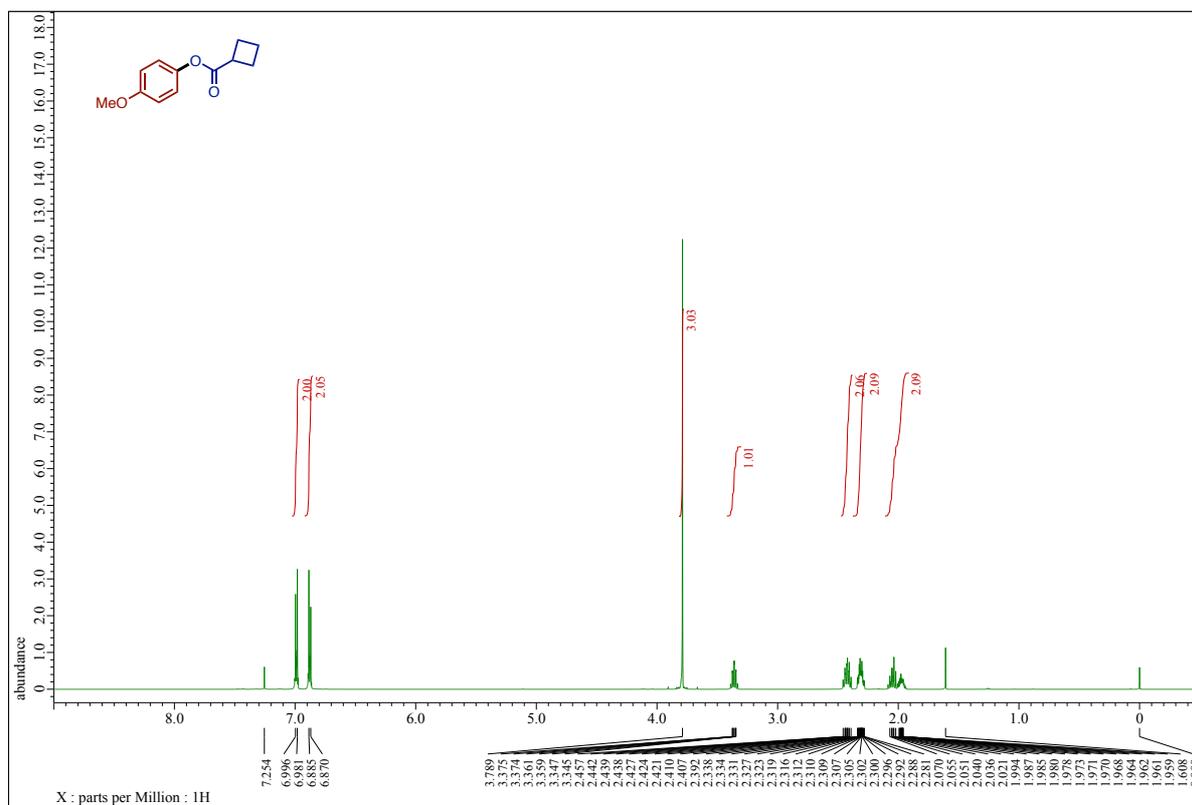


^{13}C NMR (150 MHz, CDCl_3)

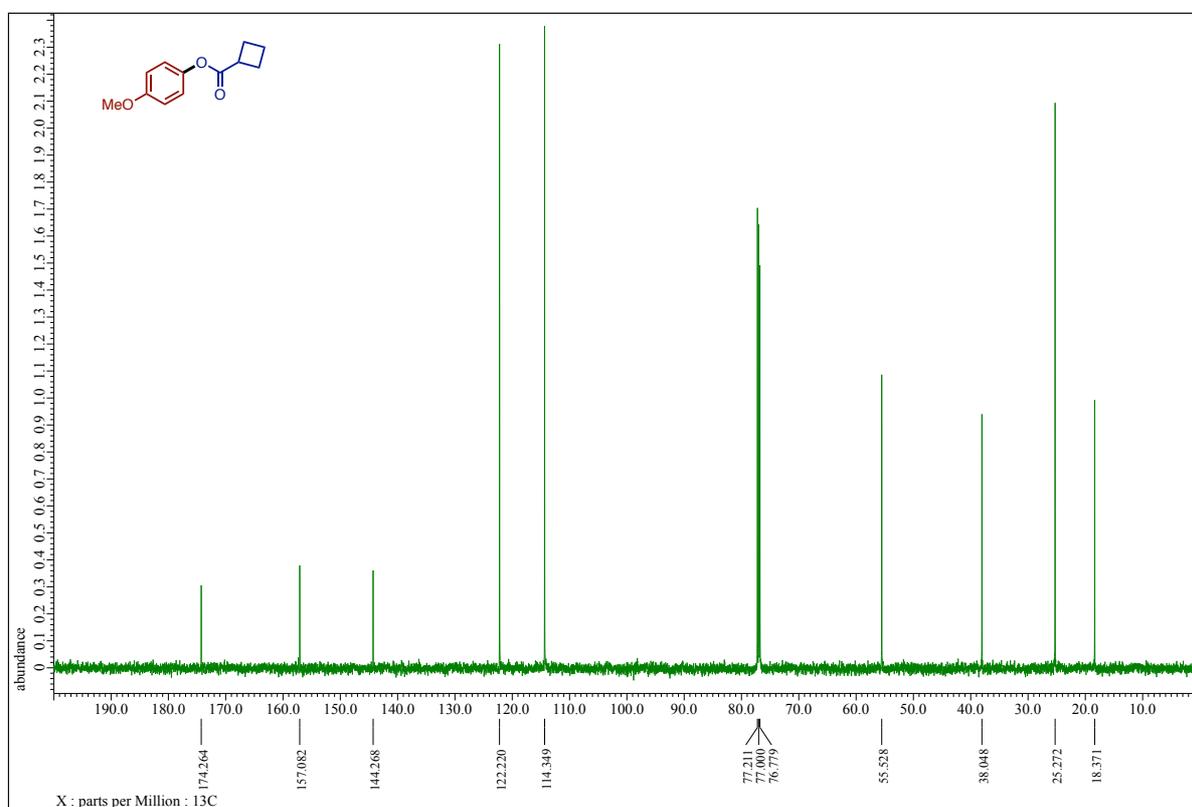


4-Methoxyphenyl cyclobutanecarboxylate (3ai)

¹H NMR (600 MHz, CDCl₃)

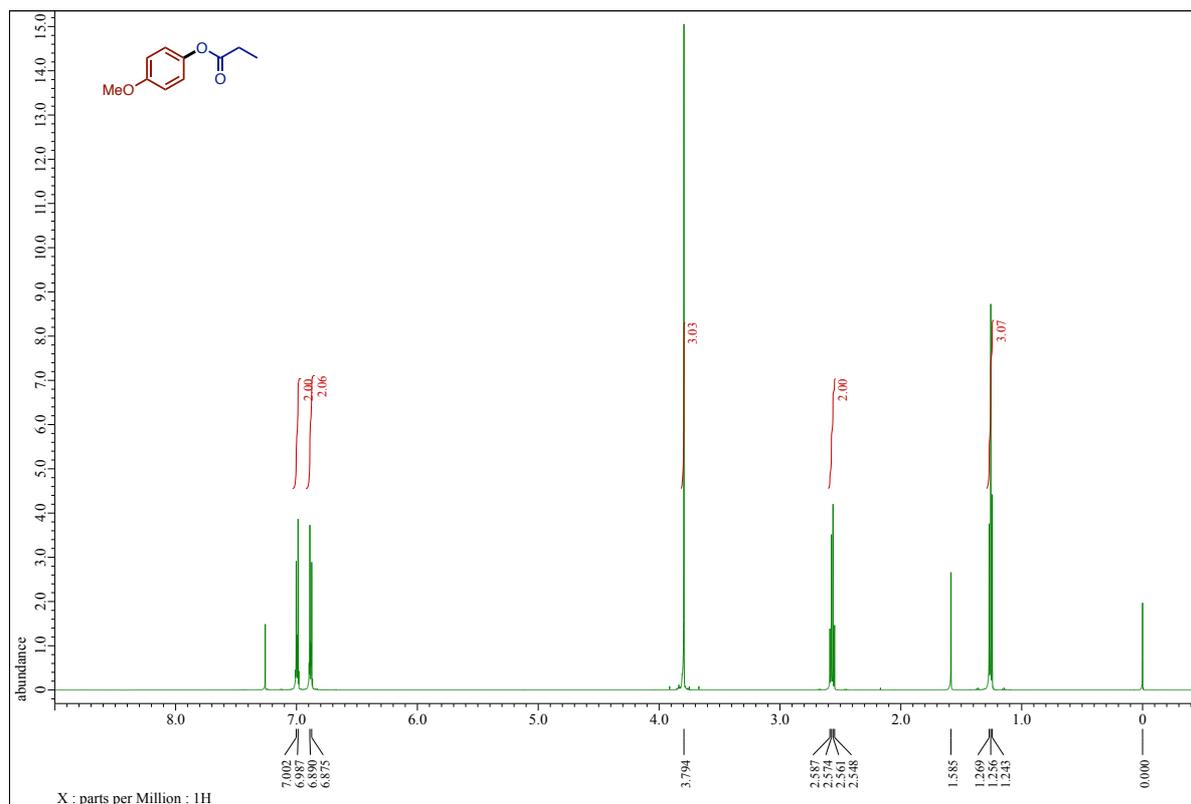


¹³C NMR (150 MHz, CDCl₃)

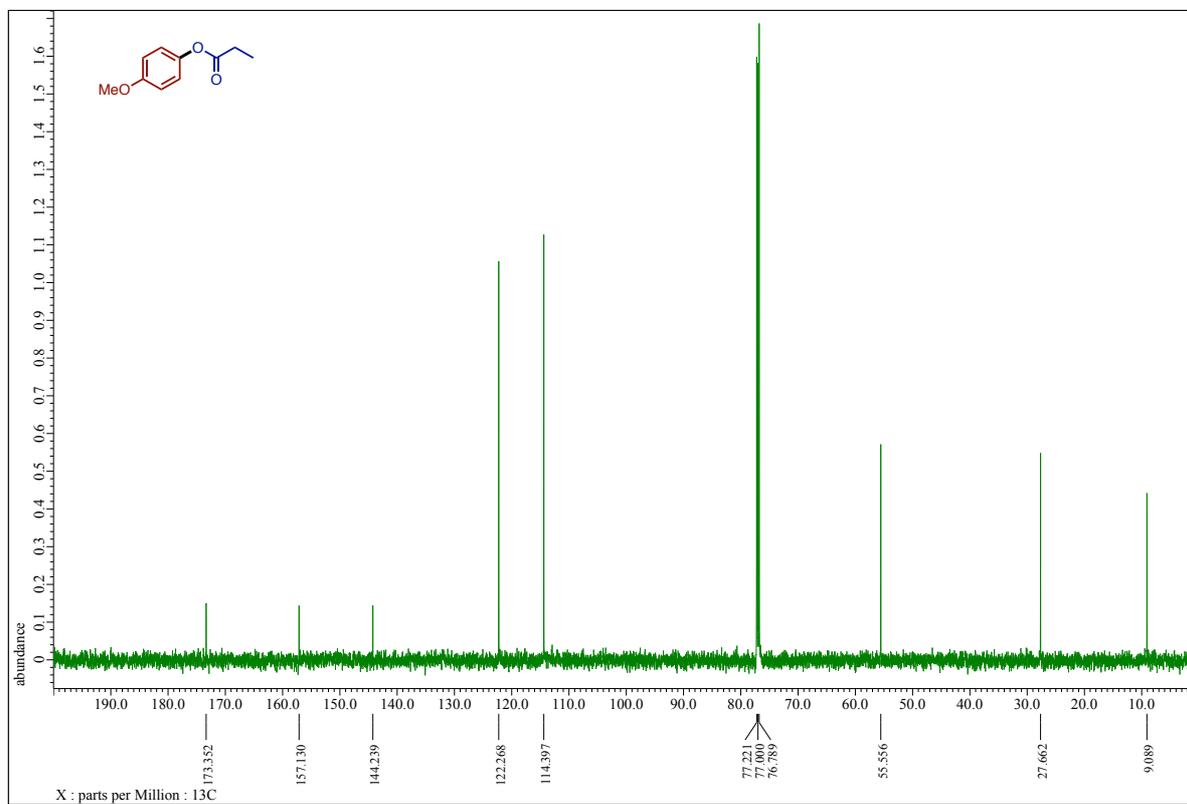


4-Methoxyphenyl propionate (3aj)

^1H NMR (600 MHz, CDCl_3)

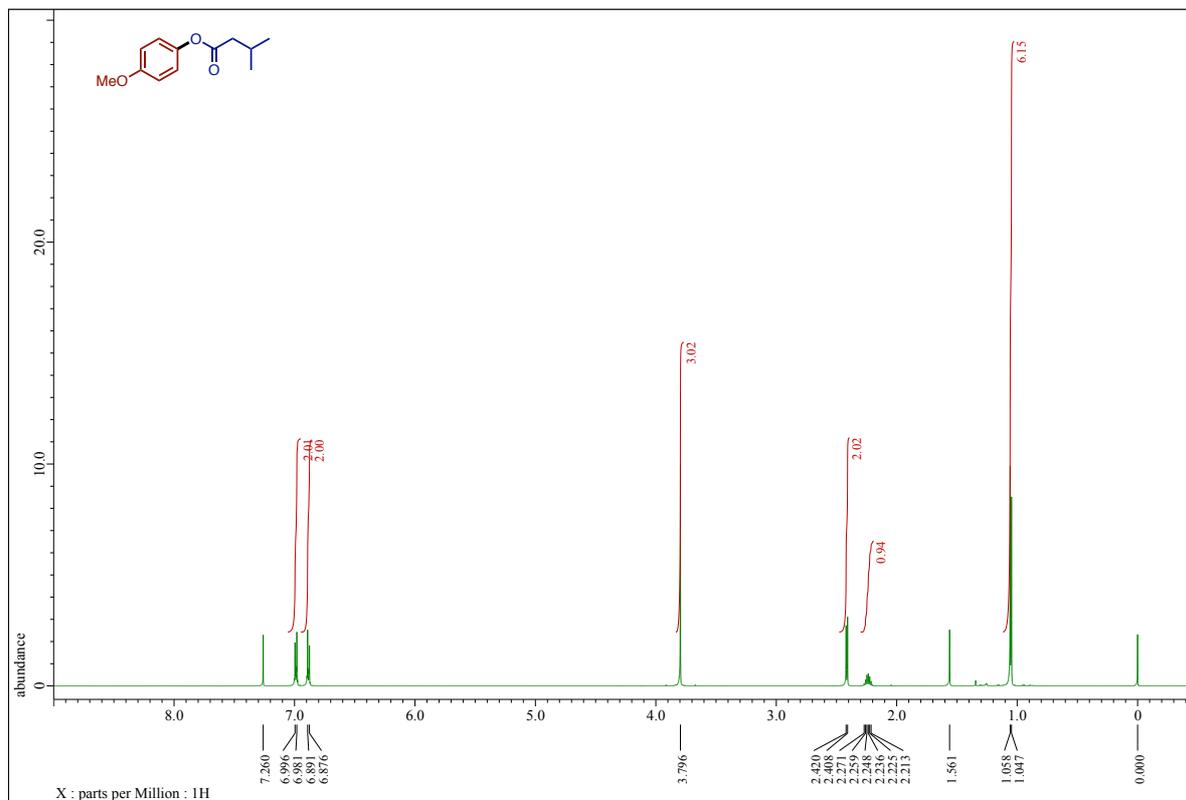


^{13}C NMR (150 MHz, CDCl_3)

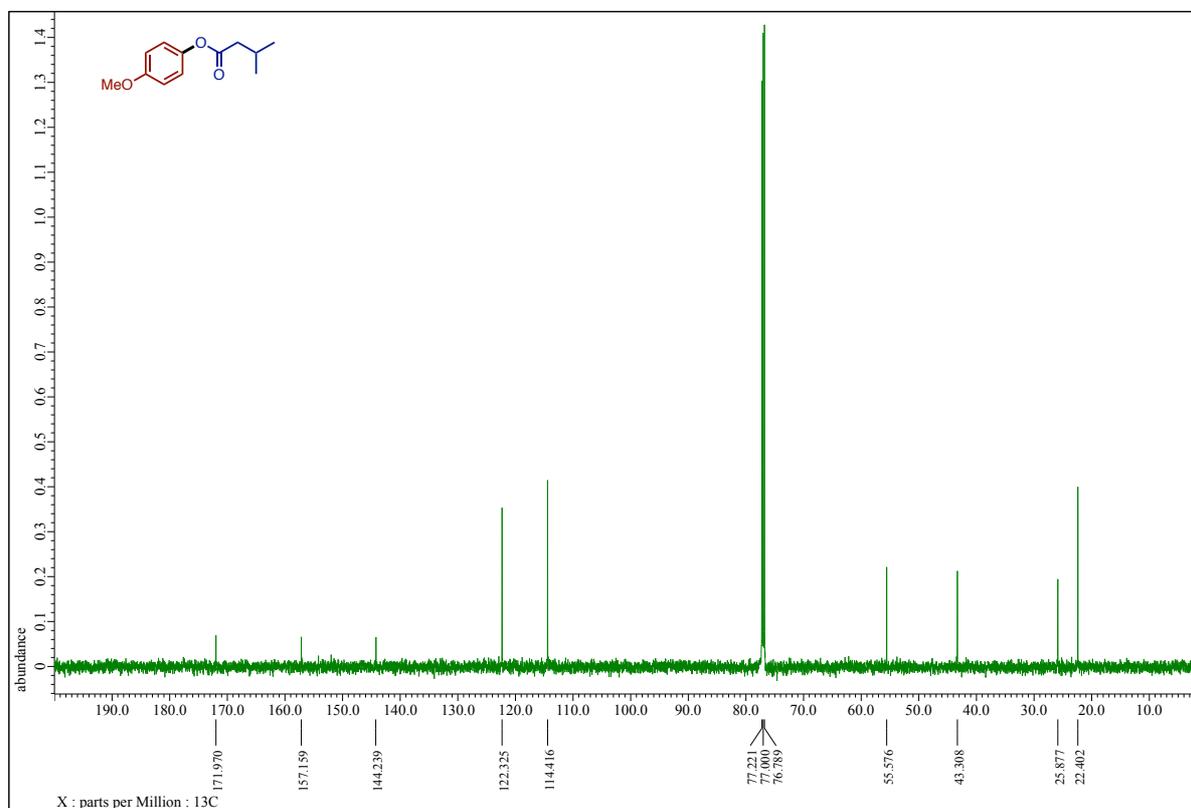


4-Methoxyphenyl 3-methylbutanoate (3ak)

^1H NMR (600 MHz, CDCl_3)

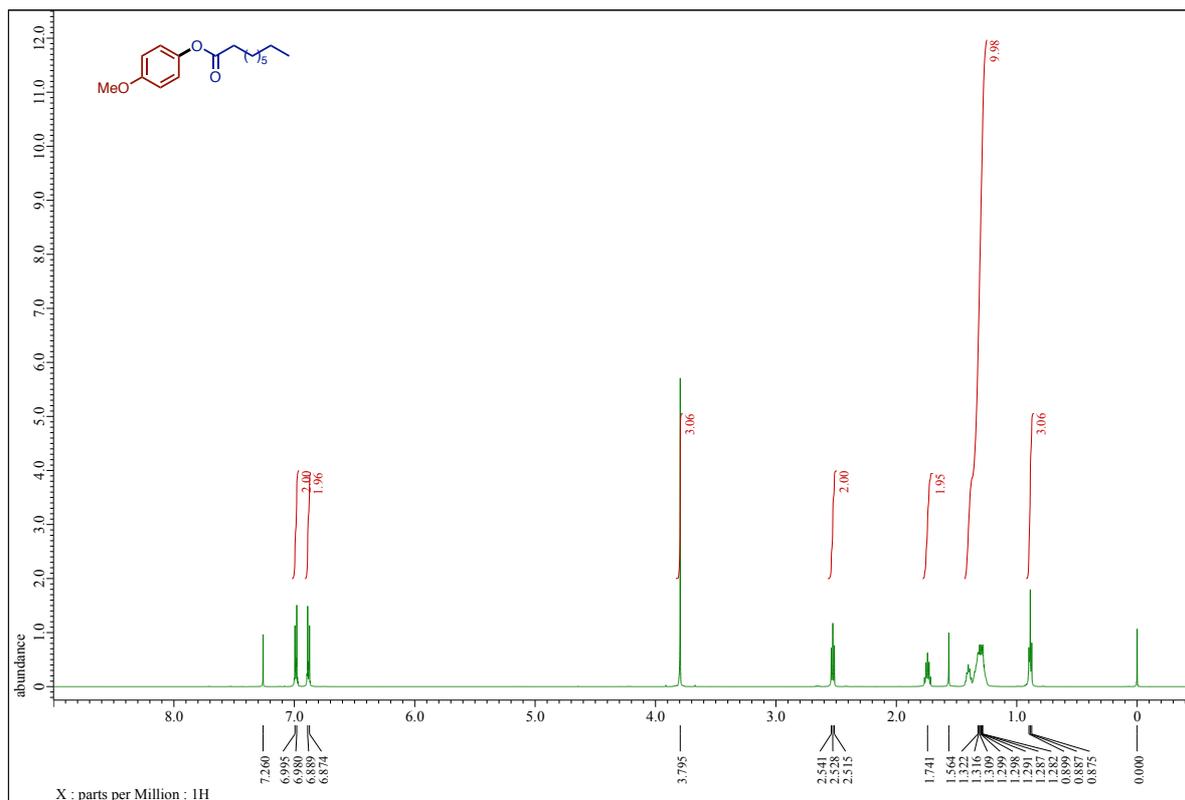


^{13}C NMR (150 MHz, CDCl_3)

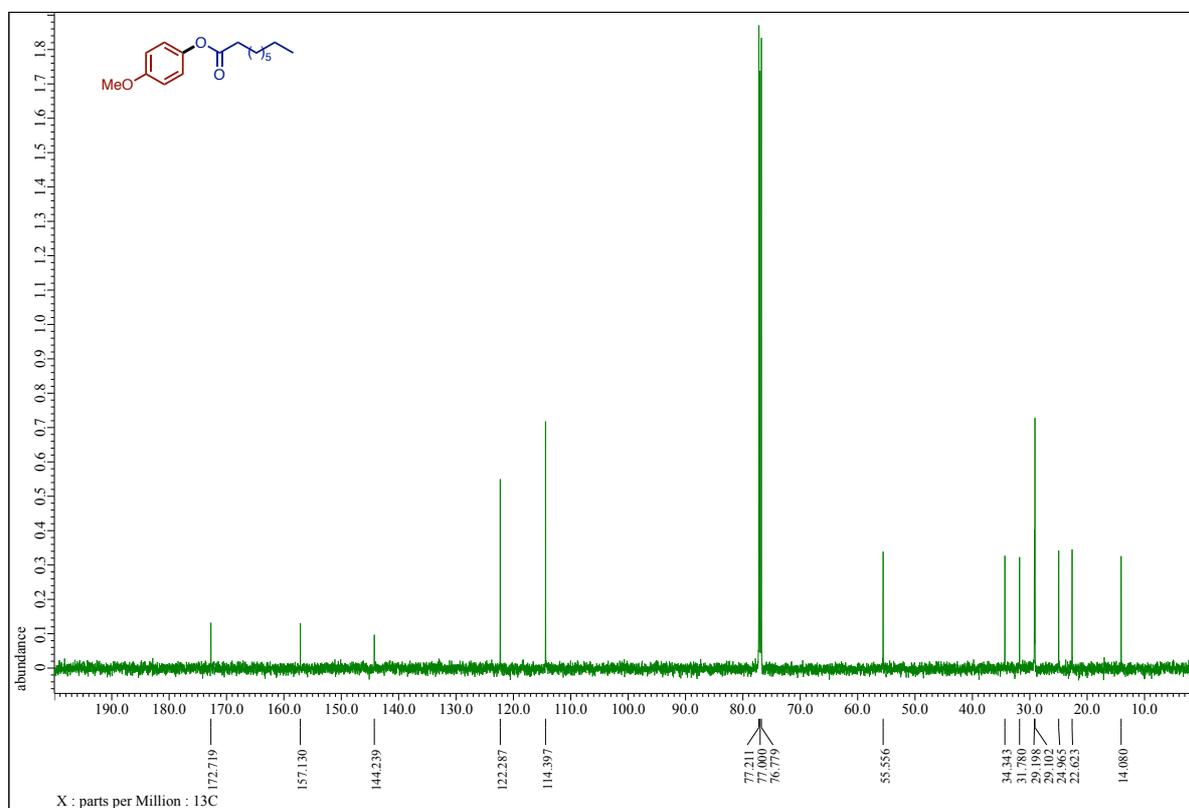


4-Methoxyphenyl nonanoate (3a)

^1H NMR (600 MHz, CDCl_3)

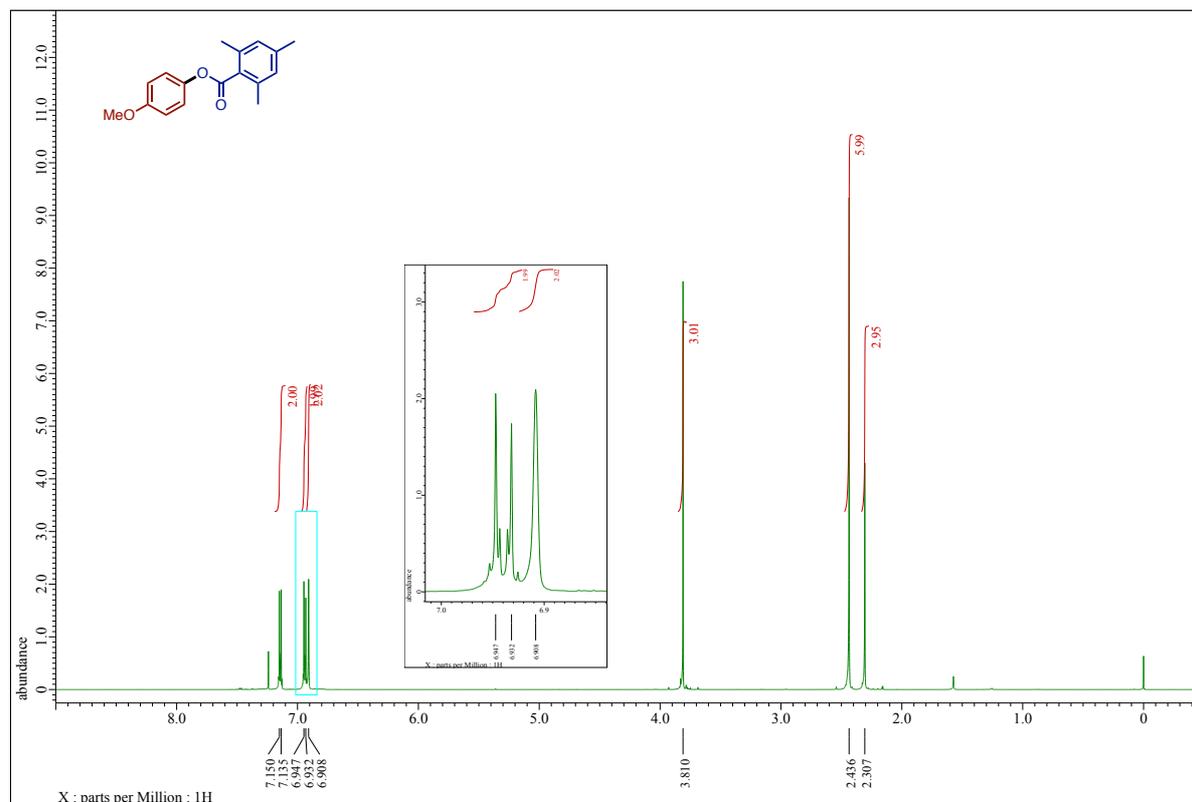


^{13}C NMR (150 MHz, CDCl_3)

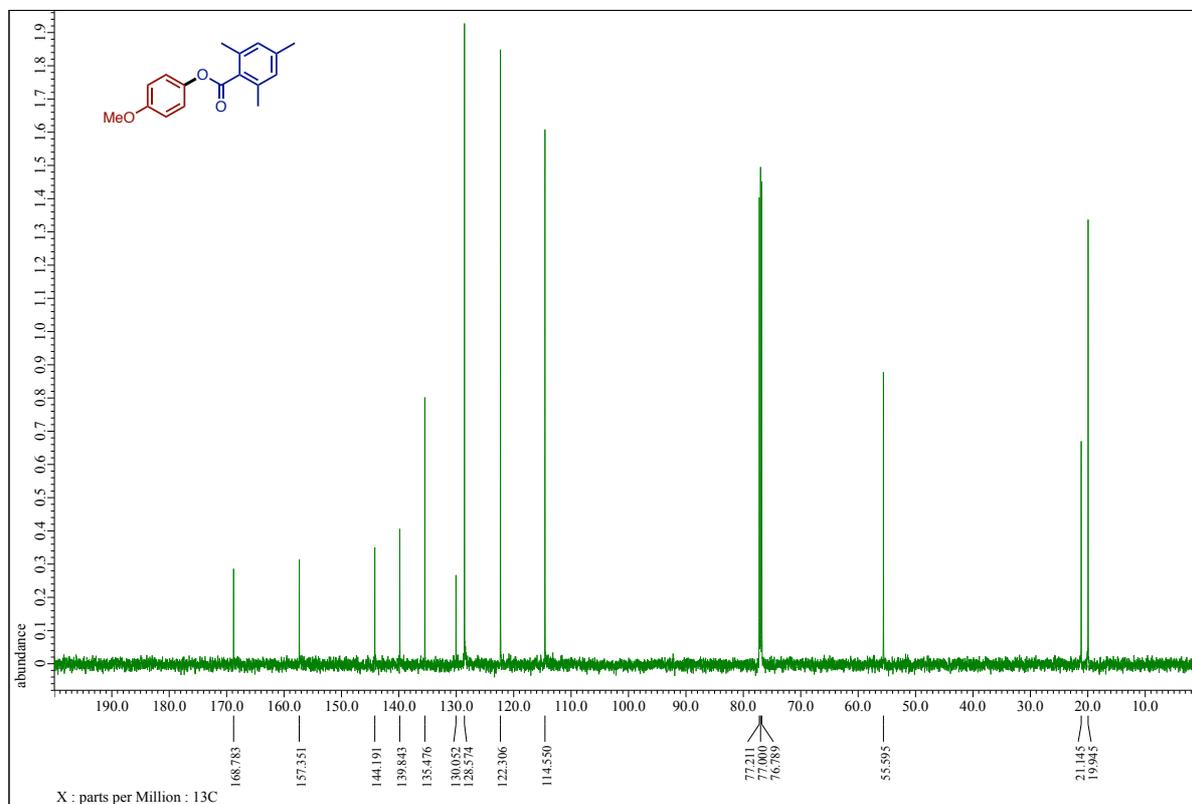


4-Methoxyphenyl 2,4,6-trimethylbenzoate (3an)

^1H NMR (600 MHz, CDCl_3)

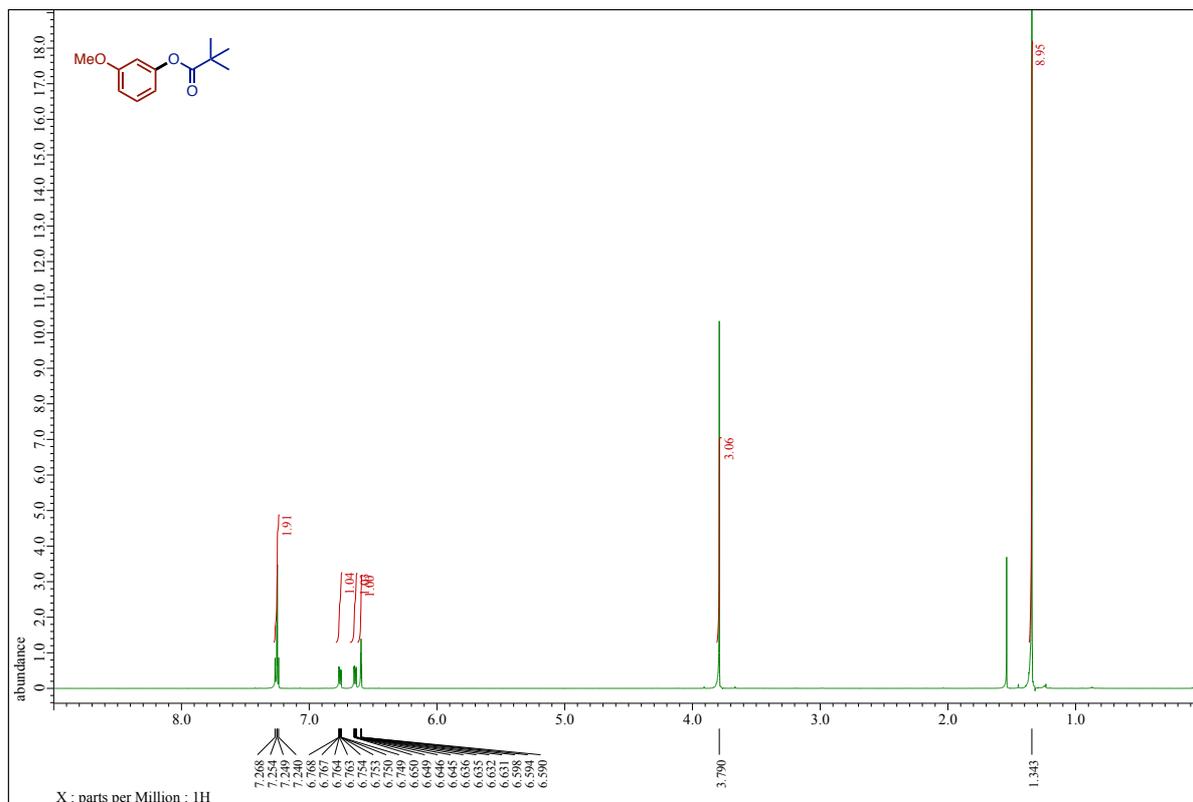


^{13}C NMR (150 MHz, CDCl_3)

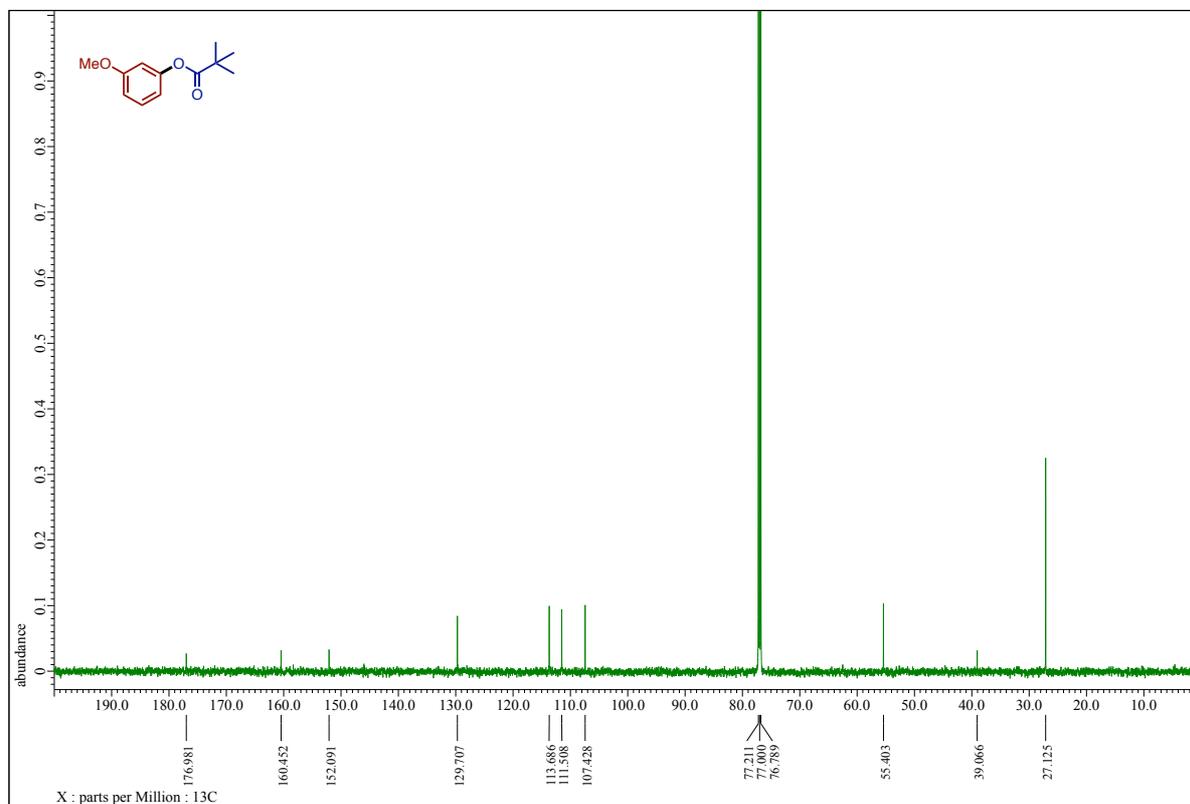


3-Methoxyphenyl pivalate (3ba)

$^1\text{H NMR}$ (600 MHz, CDCl_3)

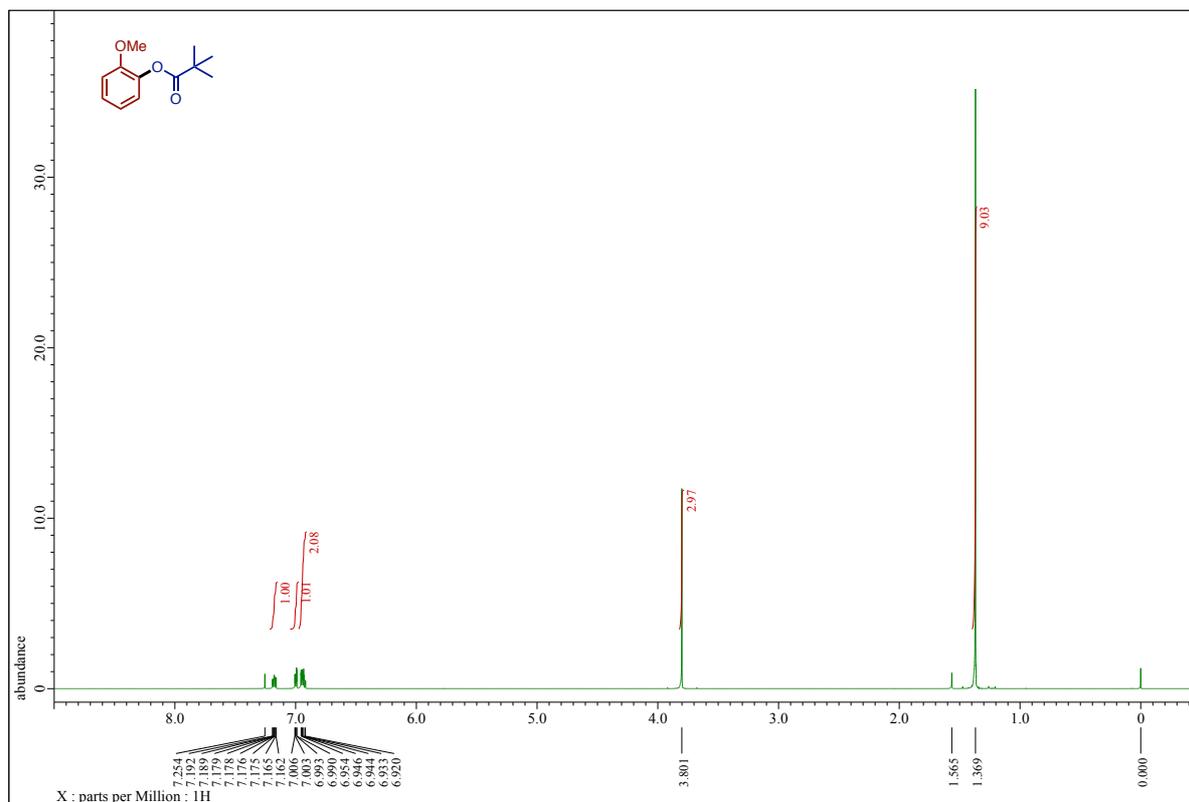


$^{13}\text{C NMR}$ (150 MHz, CDCl_3)

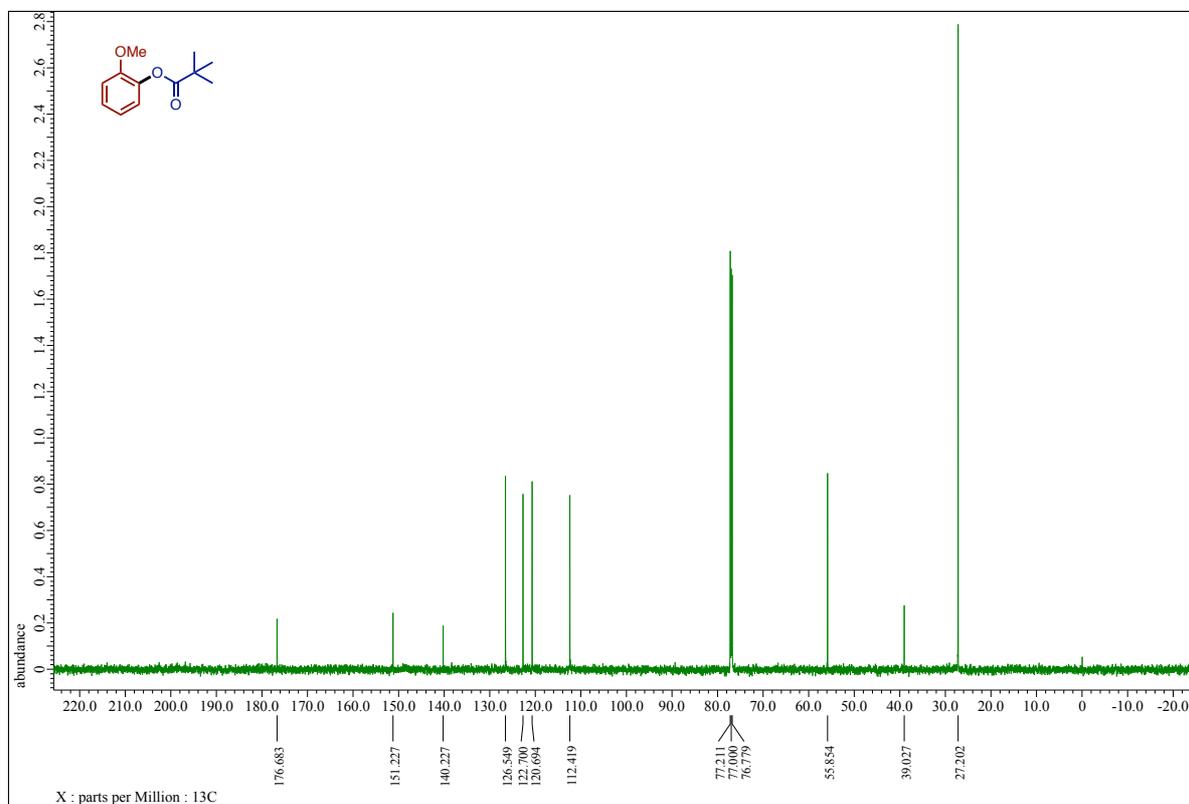


2-Methoxyphenyl pivalate (3ca)

^1H NMR (600 MHz, CDCl_3)

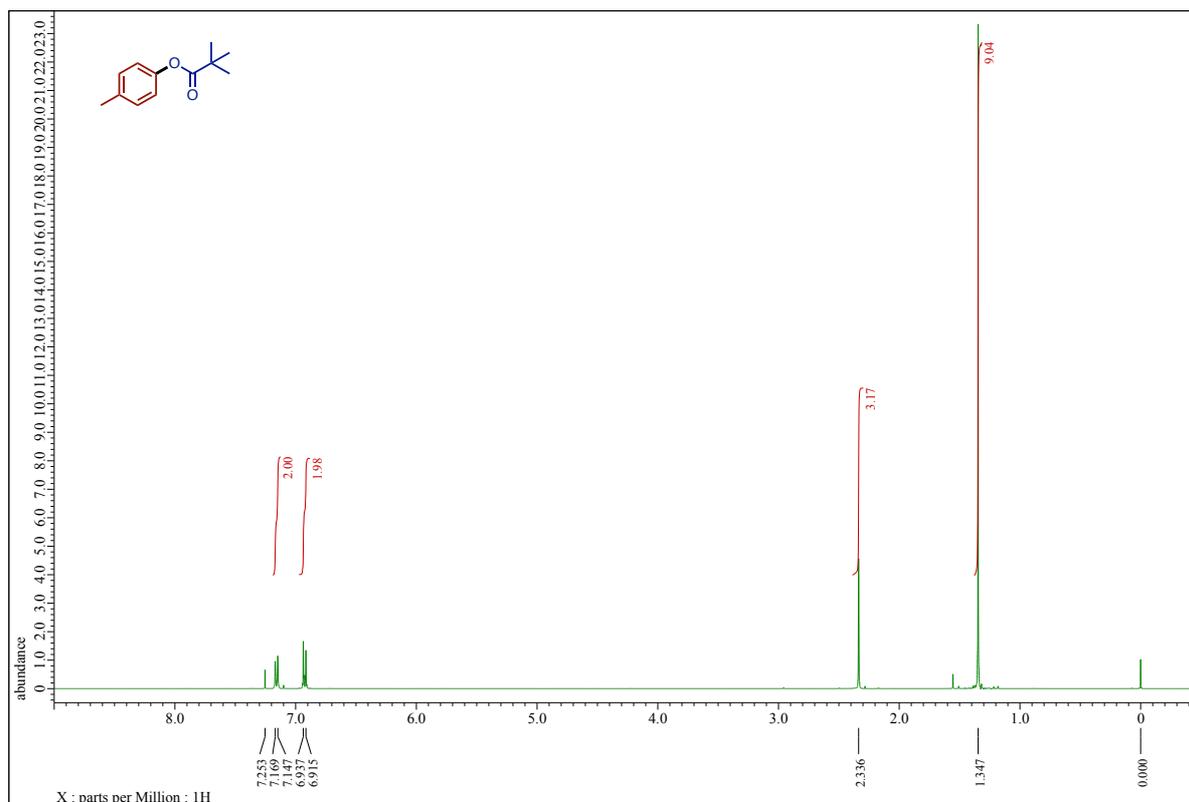


^{13}C NMR (150 MHz, CDCl_3)

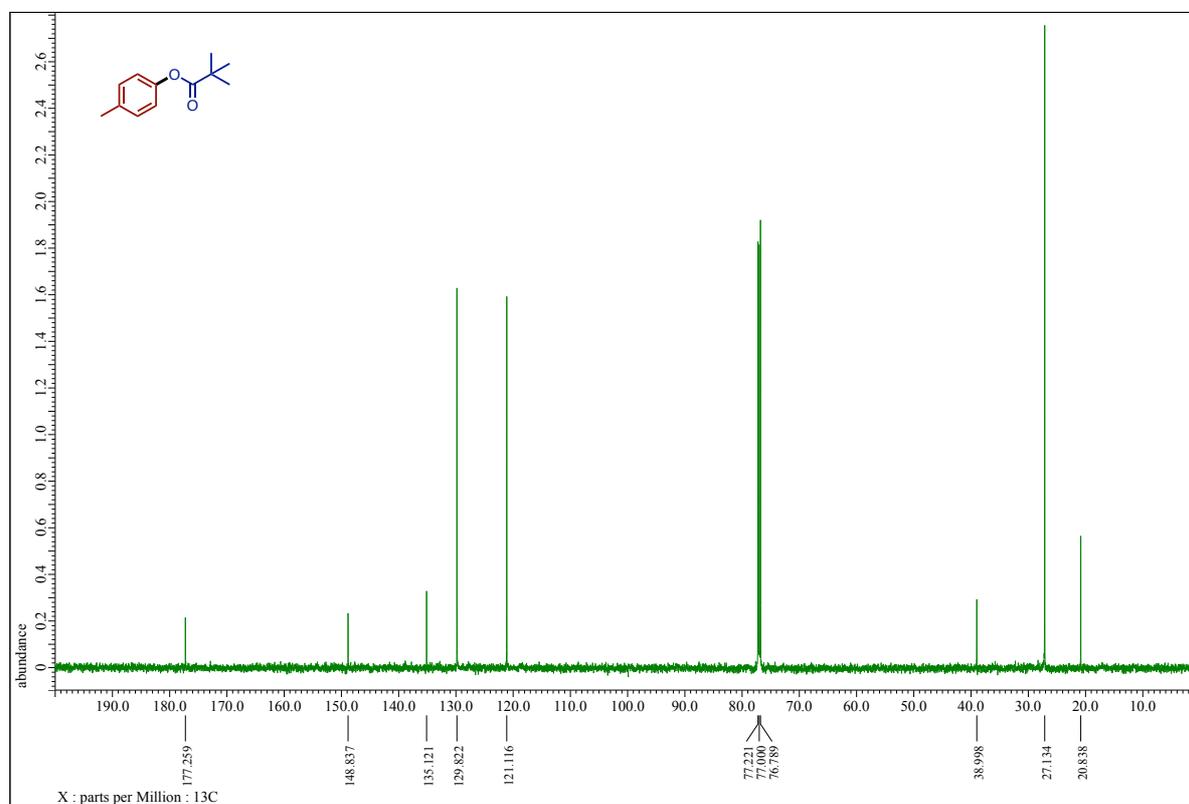


p-Tolyl pivalate (3da)

¹H NMR (400 MHz, CDCl₃)

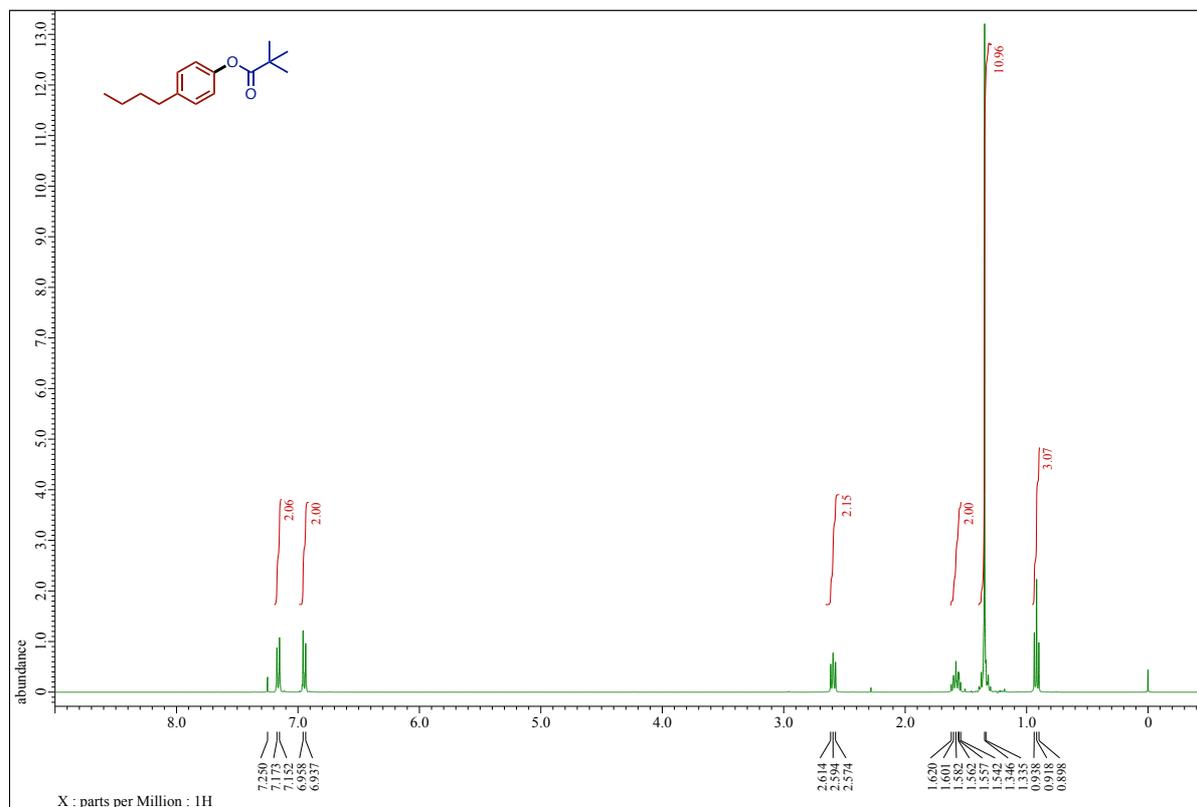


¹³C NMR (150 MHz, CDCl₃)

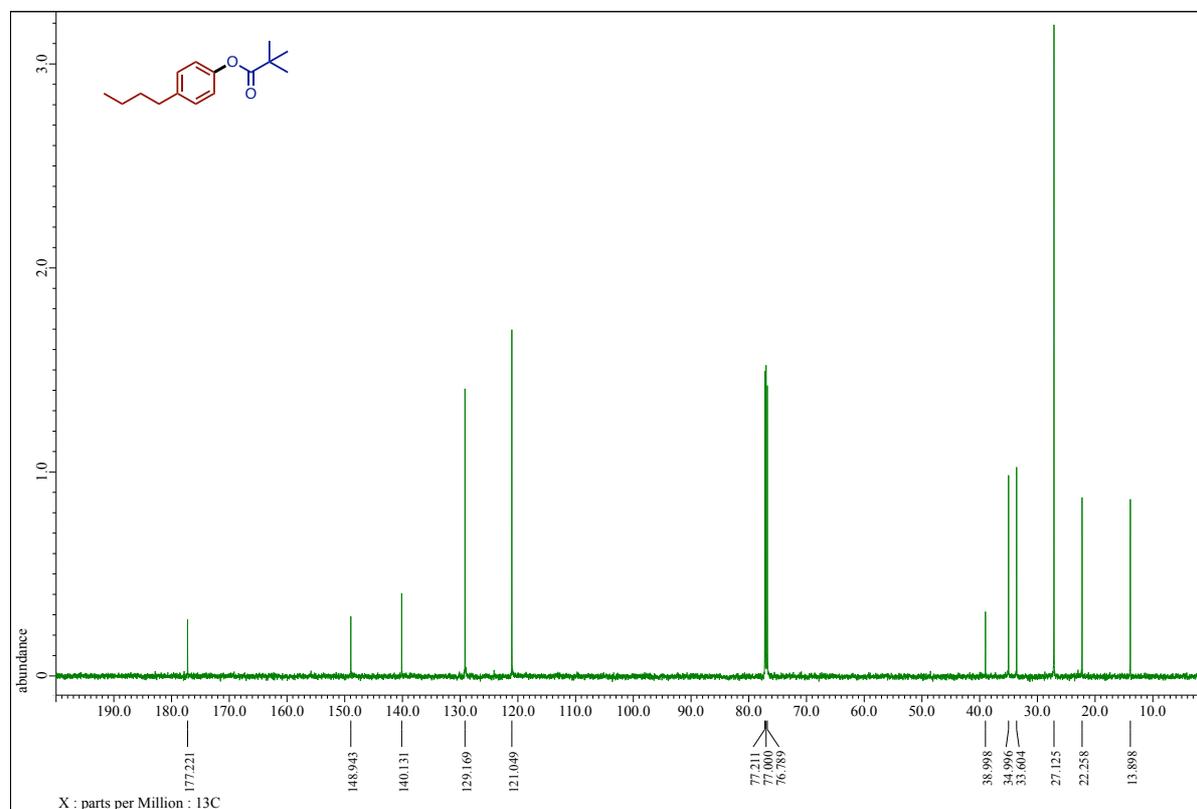


4-Butylphenyl pivalate (3ea)

^1H NMR (400 MHz, CDCl_3)

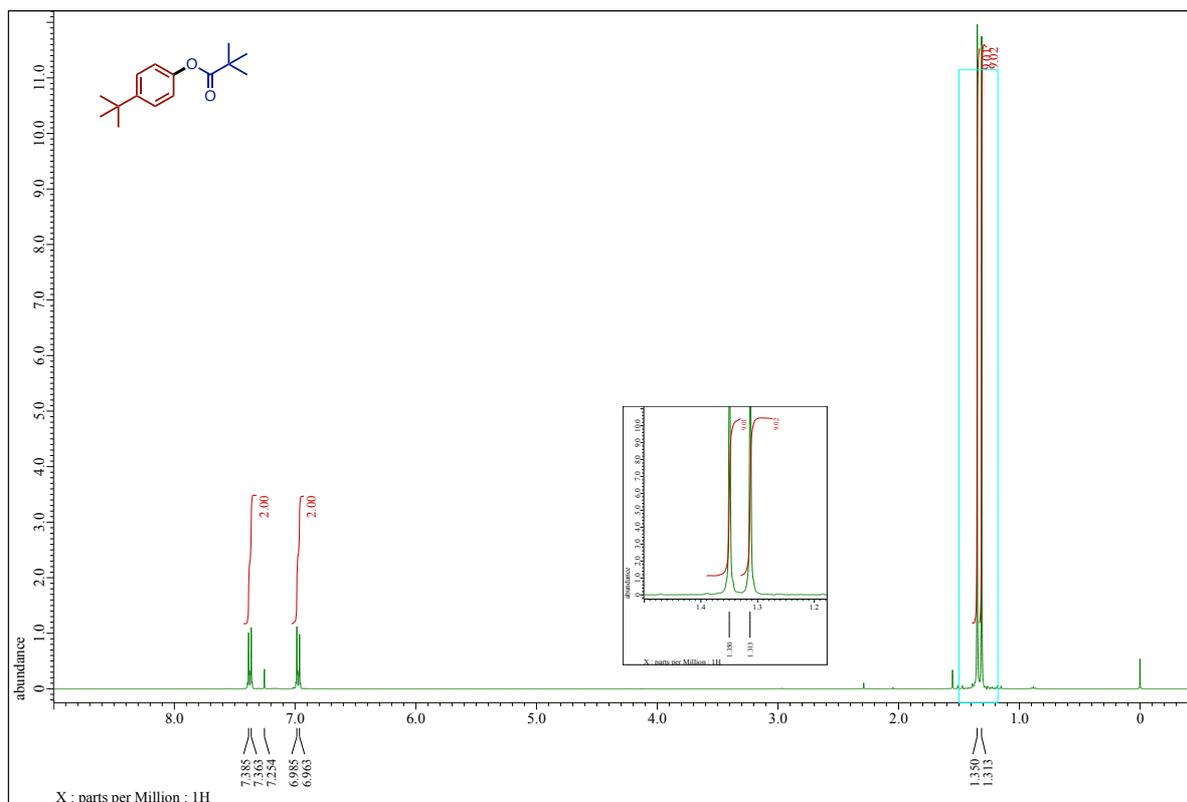


^{13}C NMR (150 MHz, CDCl_3)

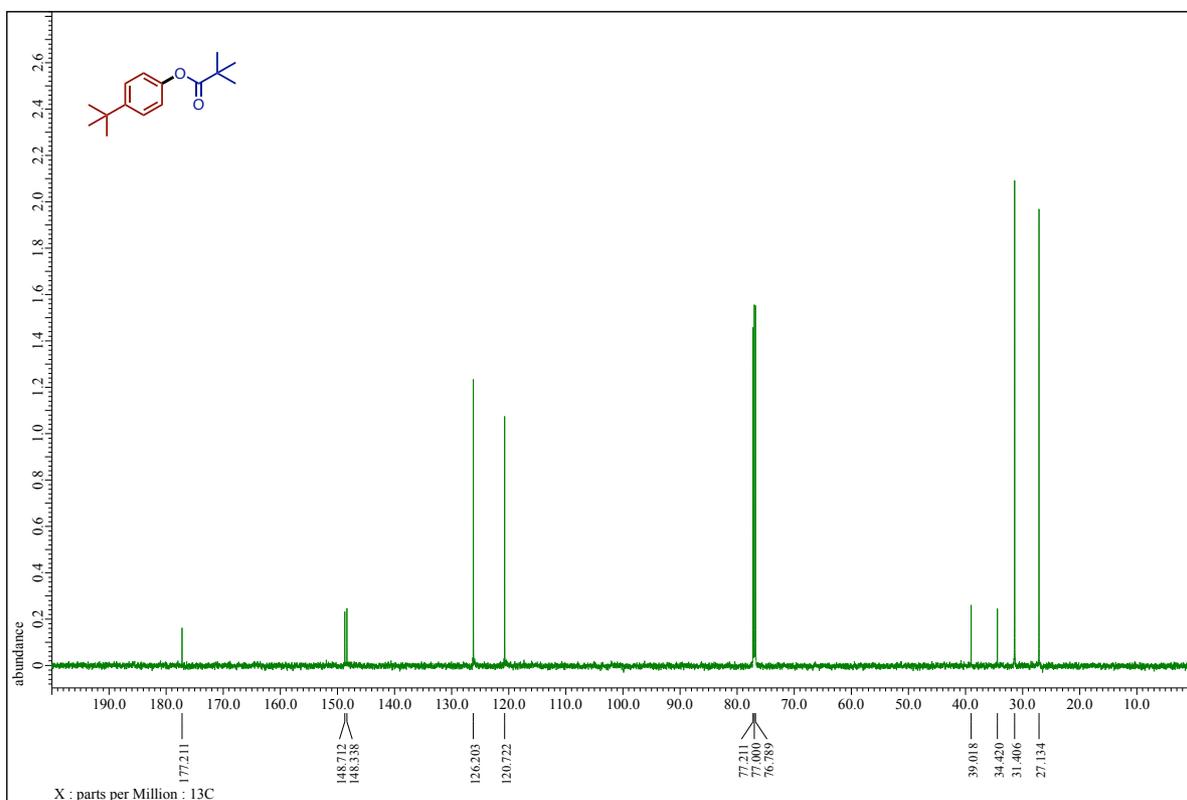


4-(*tert*-Butyl)phenyl pivalate (3fa)

^1H NMR (400 MHz, CDCl_3)

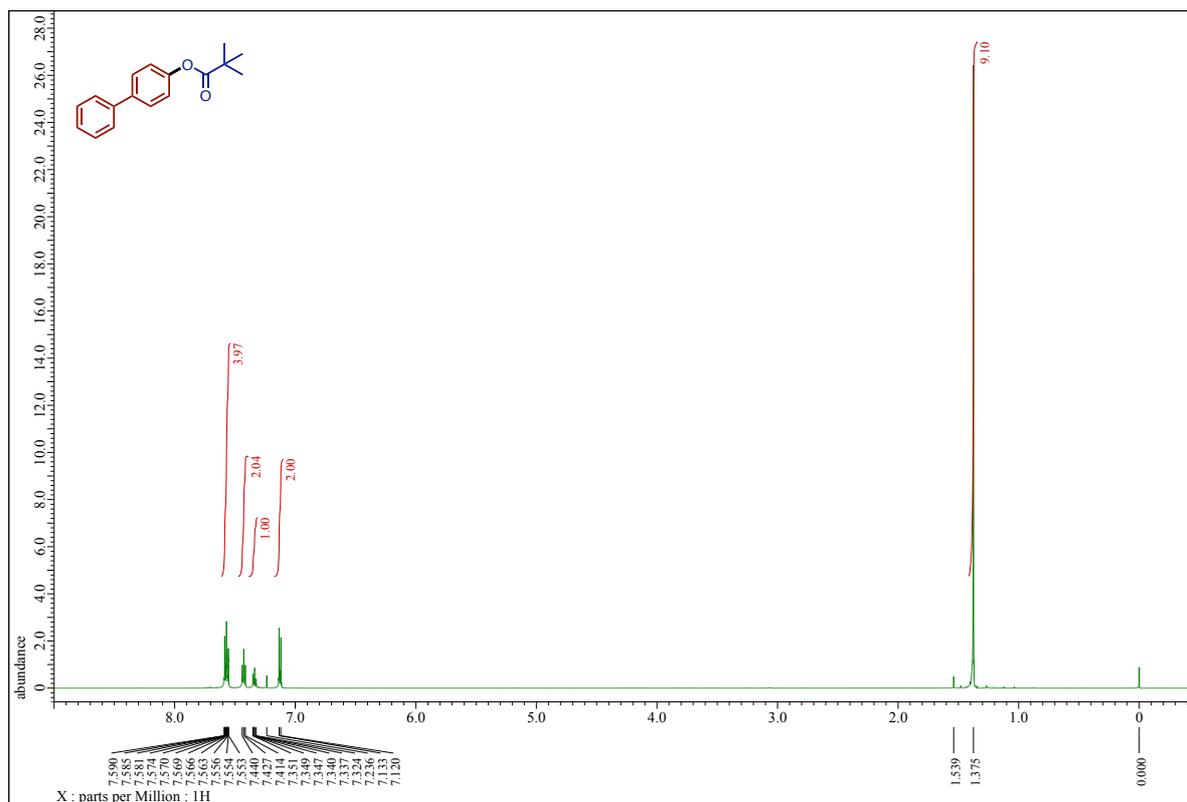


^{13}C NMR (150 MHz, CDCl_3)

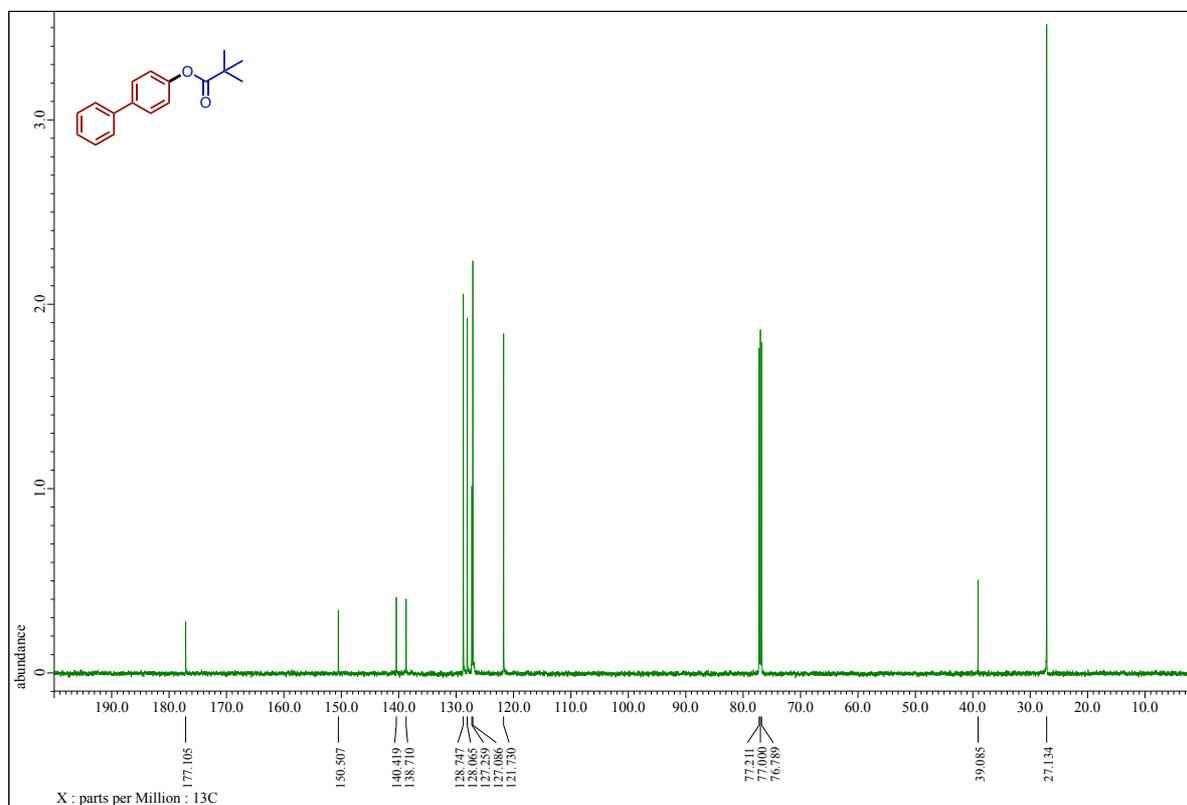


(1,1'-Biphenyl)-4-yl pivalate (3ga)

^1H NMR (600 MHz, CDCl_3)

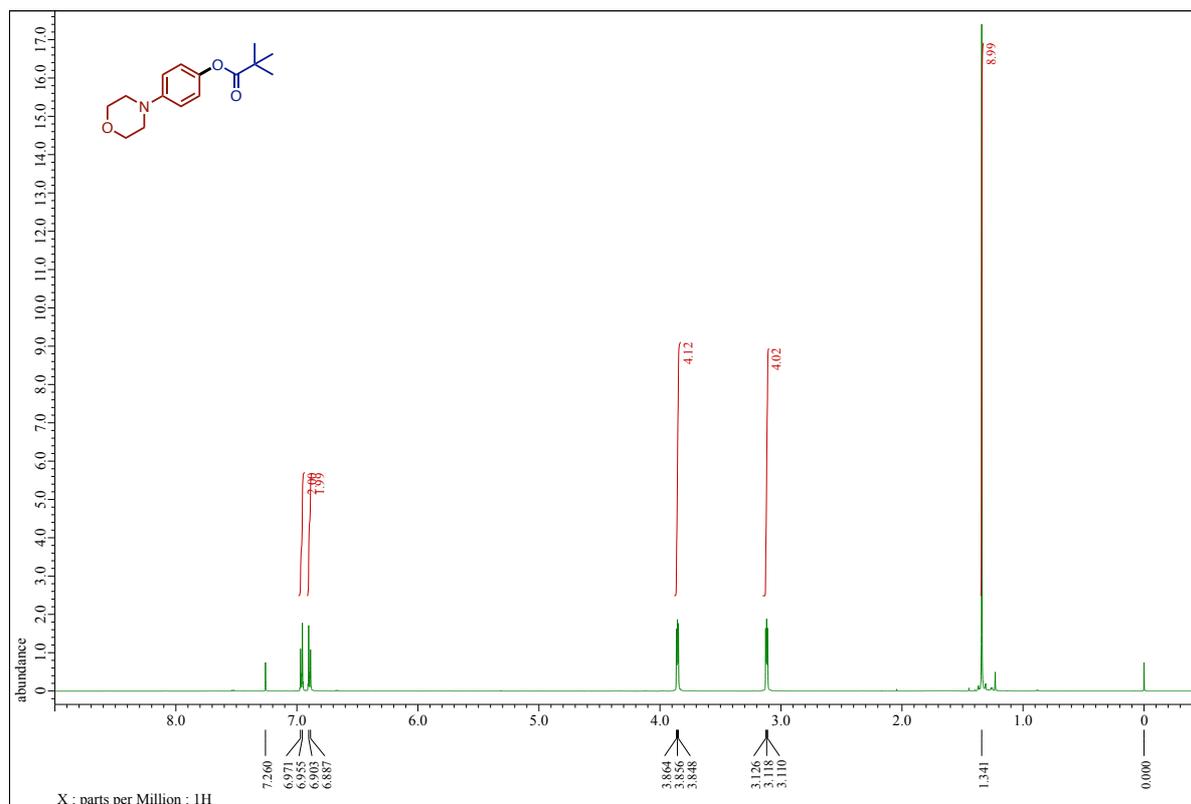


^{13}C NMR (150 MHz, CDCl_3)

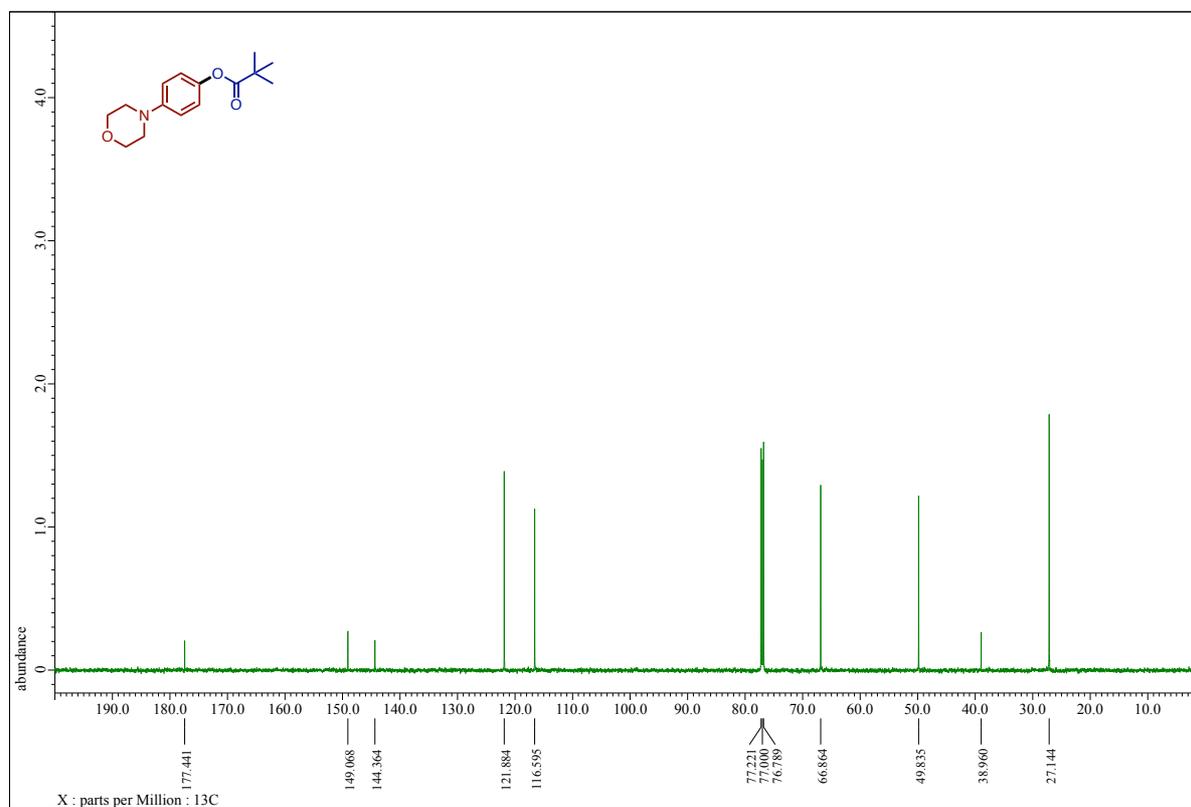


4-Morpholinophenyl pivalate (3ha)

^1H NMR (600 MHz, CDCl_3)

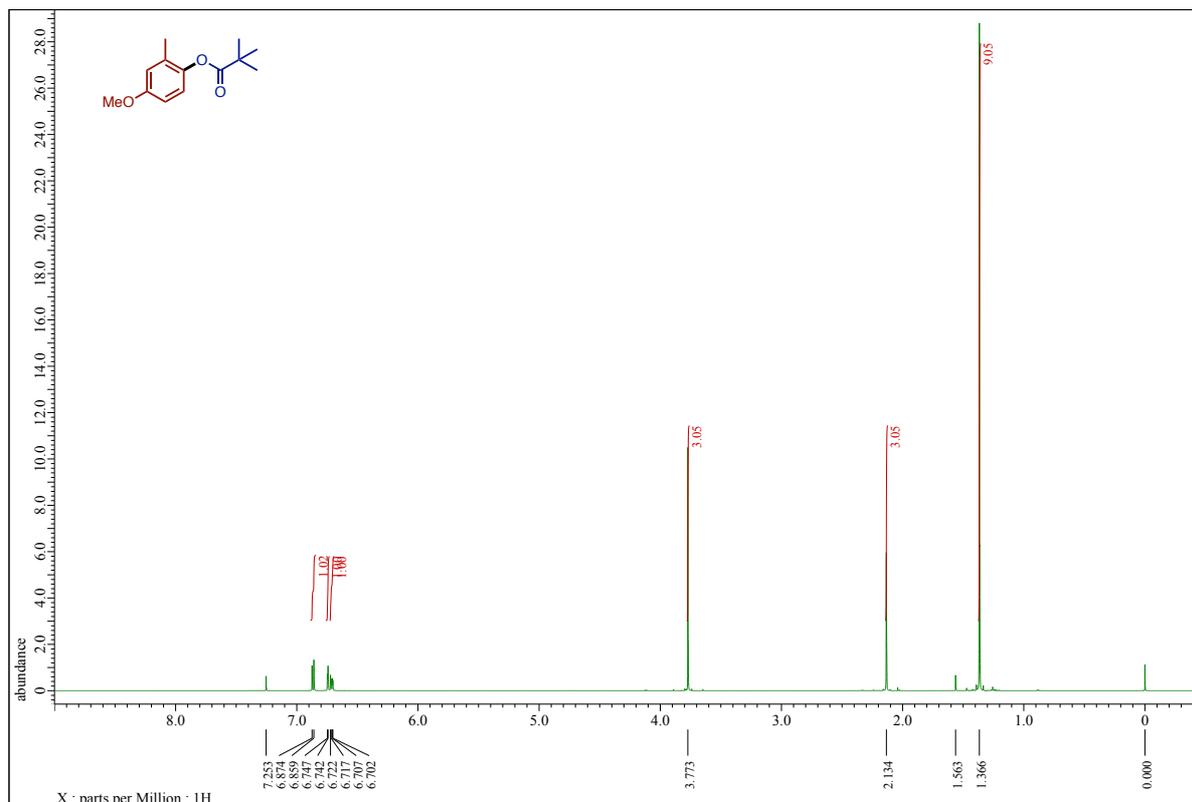


^{13}C NMR (150 MHz, CDCl_3)

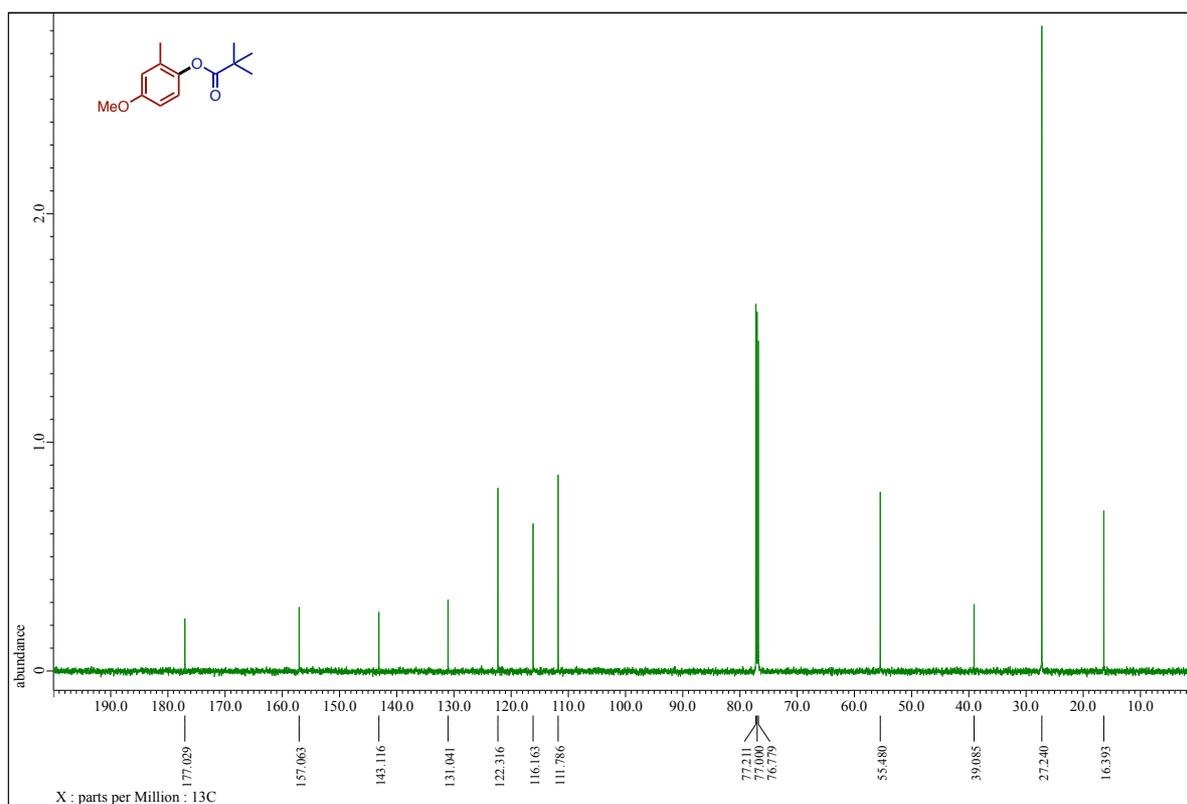


4-Methoxy-2-methylphenyl pivalate (3la)

^1H NMR (600 MHz, CDCl_3)

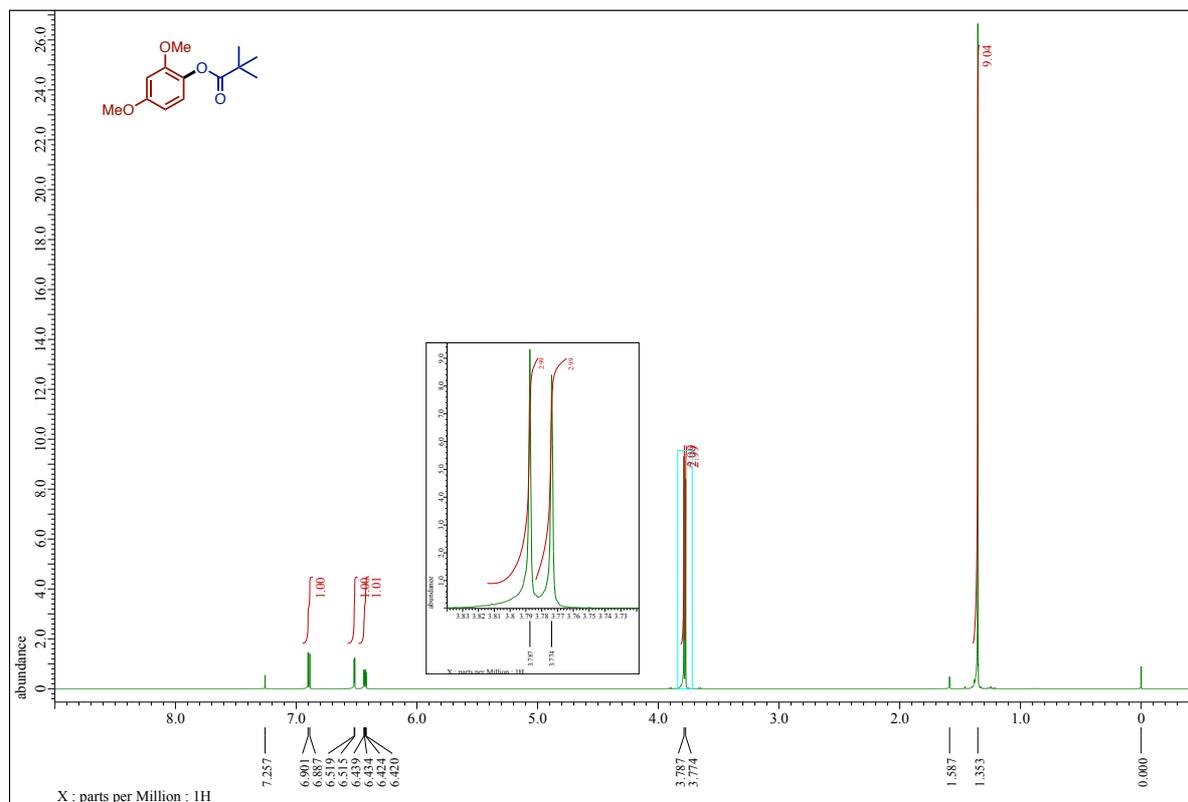


^{13}C NMR (150 MHz, CDCl_3)

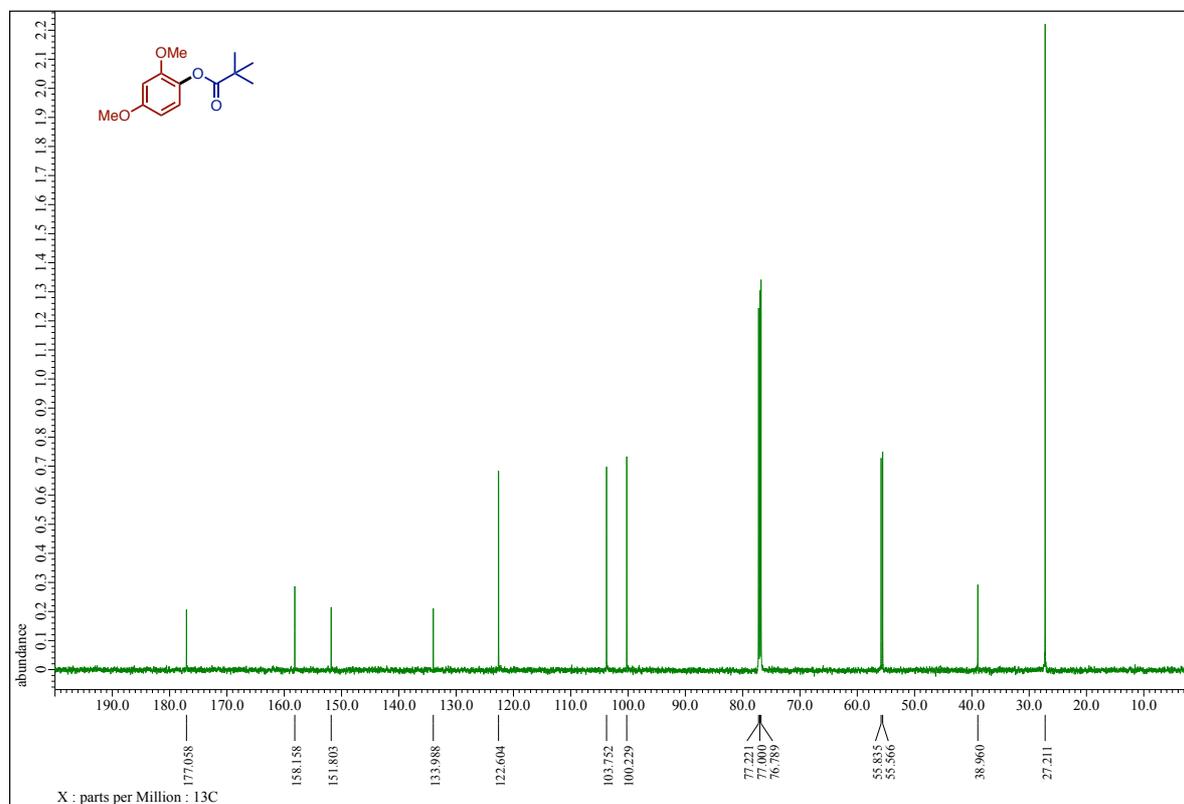


2,4-Dimethoxyphenyl pivalate (3ma)

^1H NMR (600 MHz, CDCl_3)

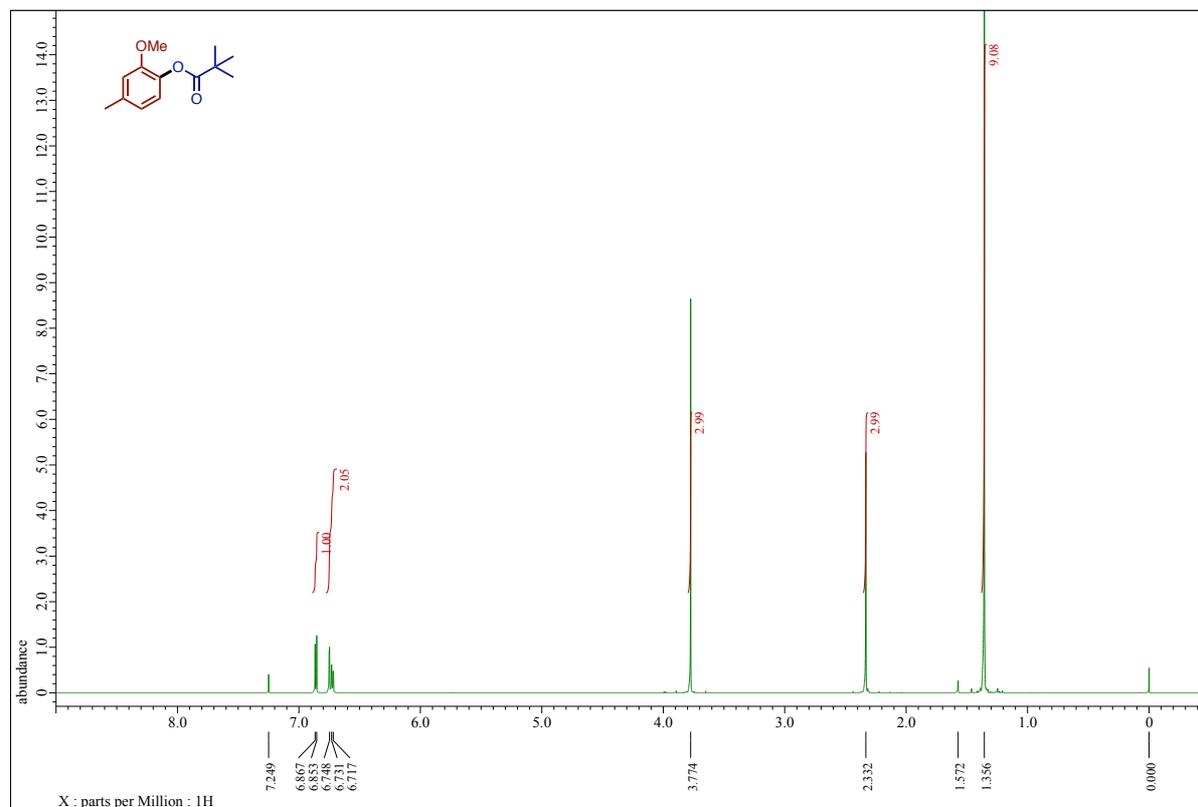


^{13}C NMR (150 MHz, CDCl_3)

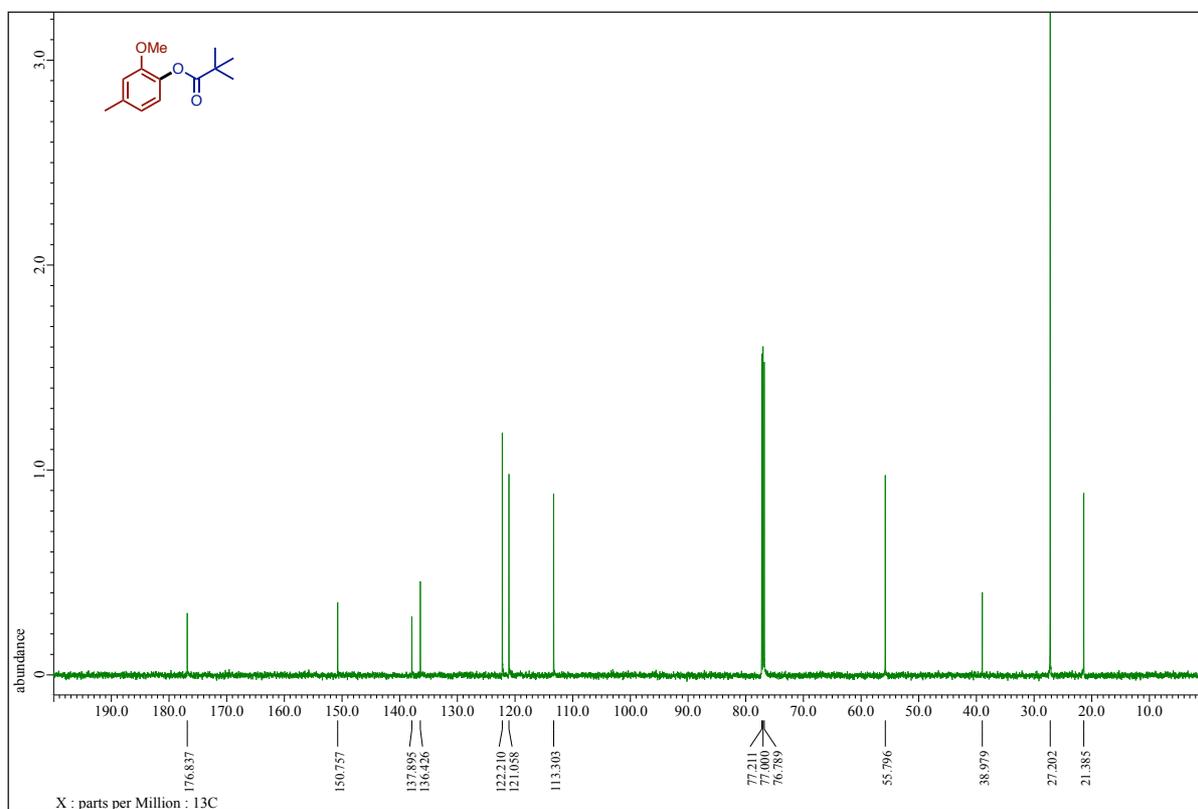


2-Methoxy-4-methylphenyl pivalate (3na)

^1H NMR (600 MHz, CDCl_3)

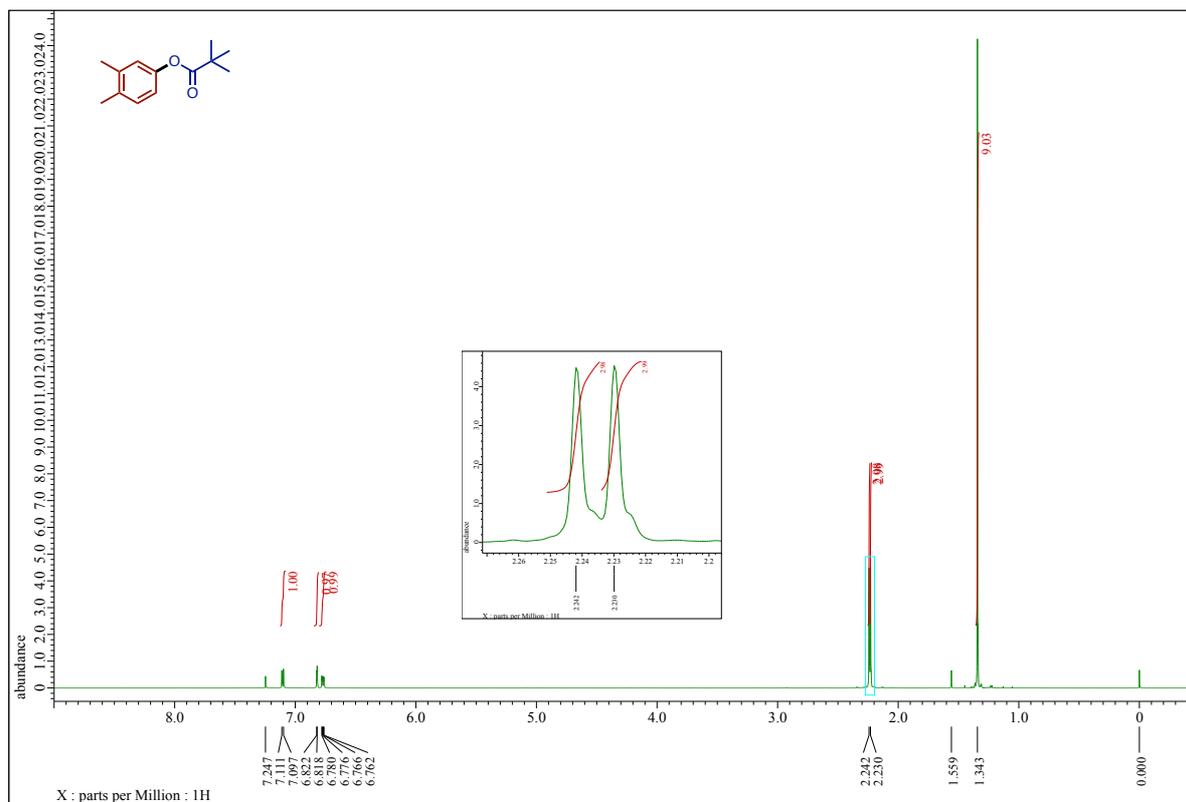


^{13}C NMR (150 MHz, CDCl_3)

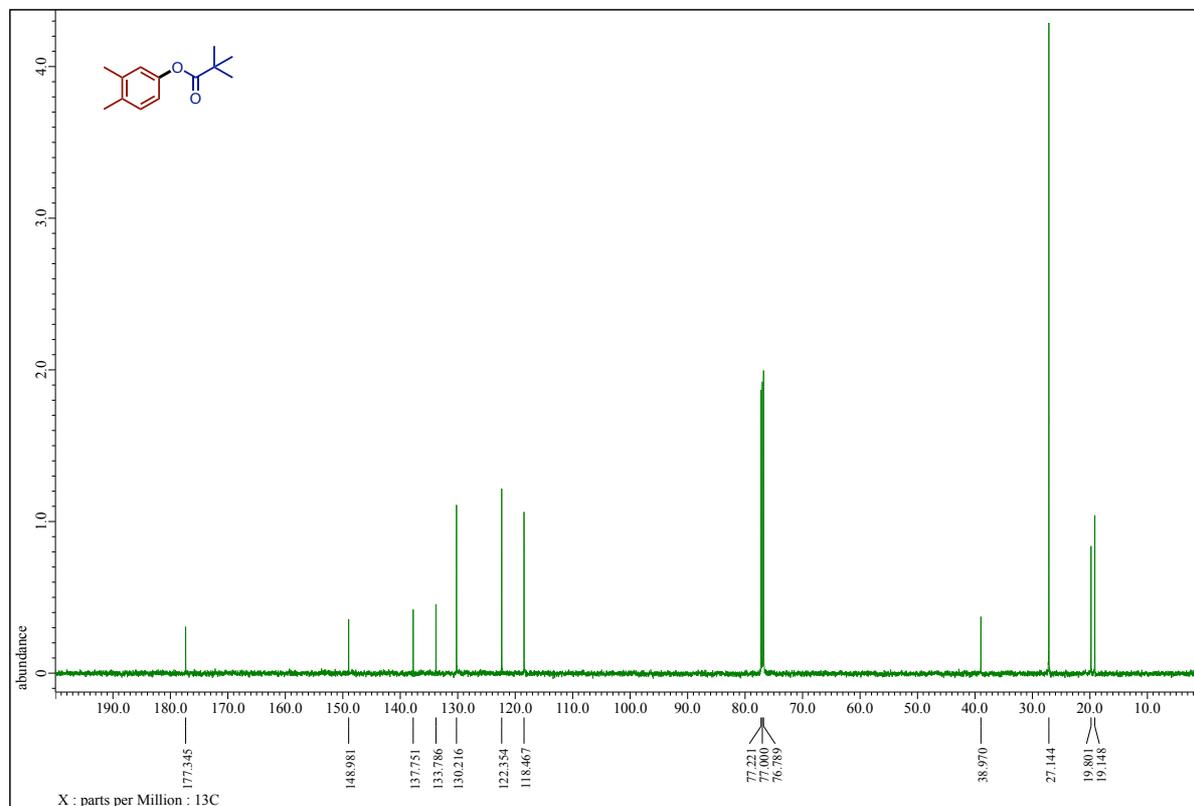


3,4-Dimethylphenyl pivalate (30a)

^1H NMR (600 MHz, CDCl_3)

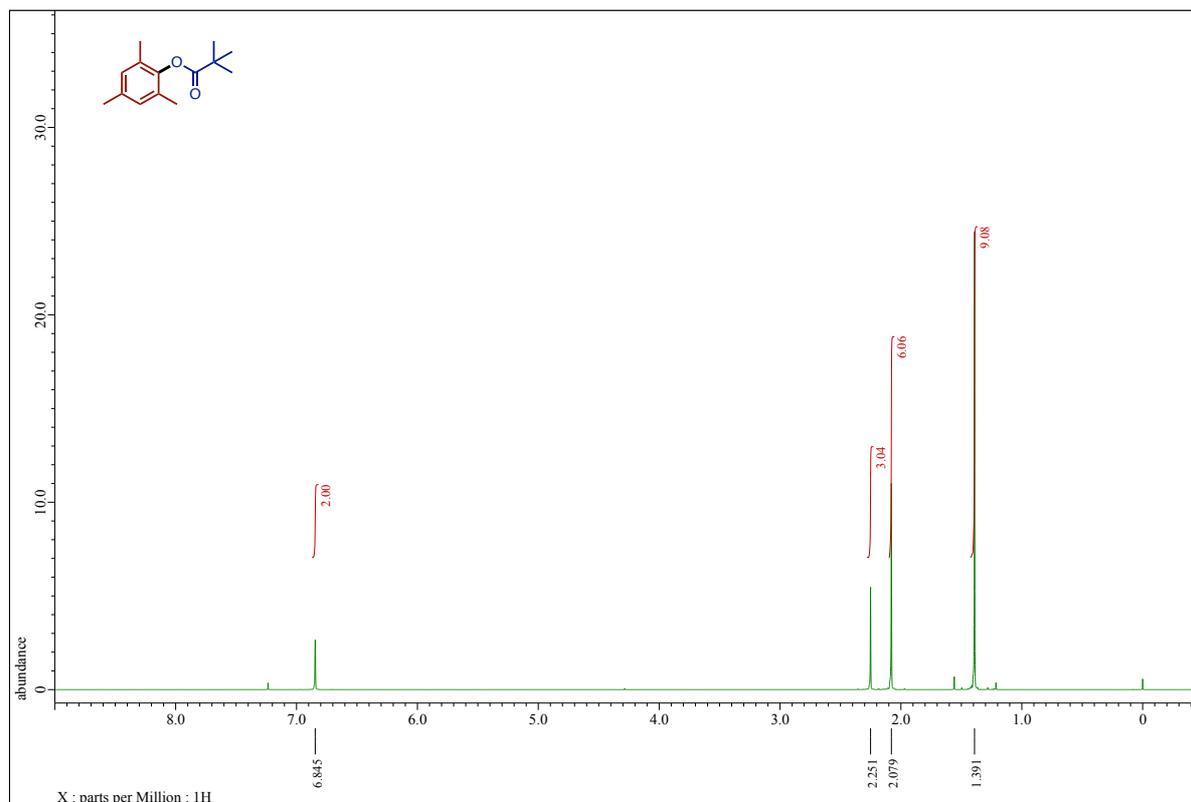


^{13}C NMR (150 MHz, CDCl_3)

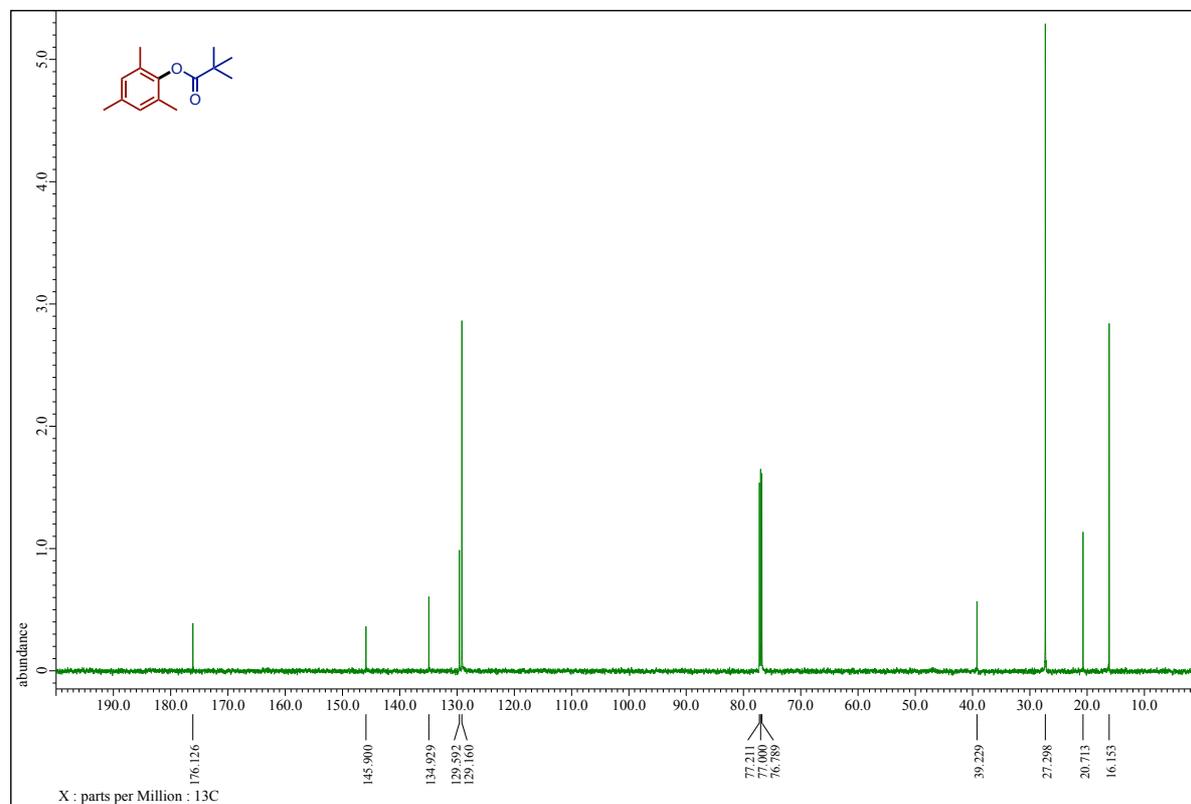


Mesityl pivalate (3pa)

^1H NMR (600 MHz, CDCl_3)

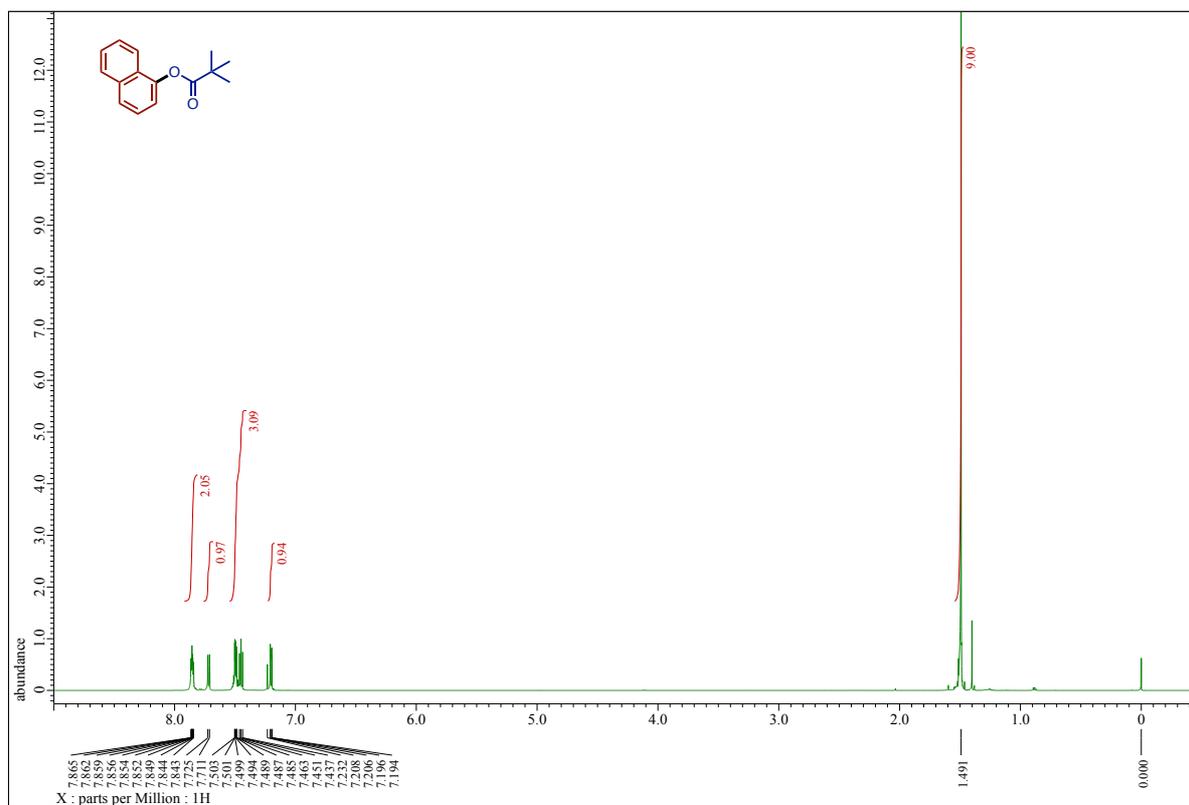


^{13}C NMR (150 MHz, CDCl_3)

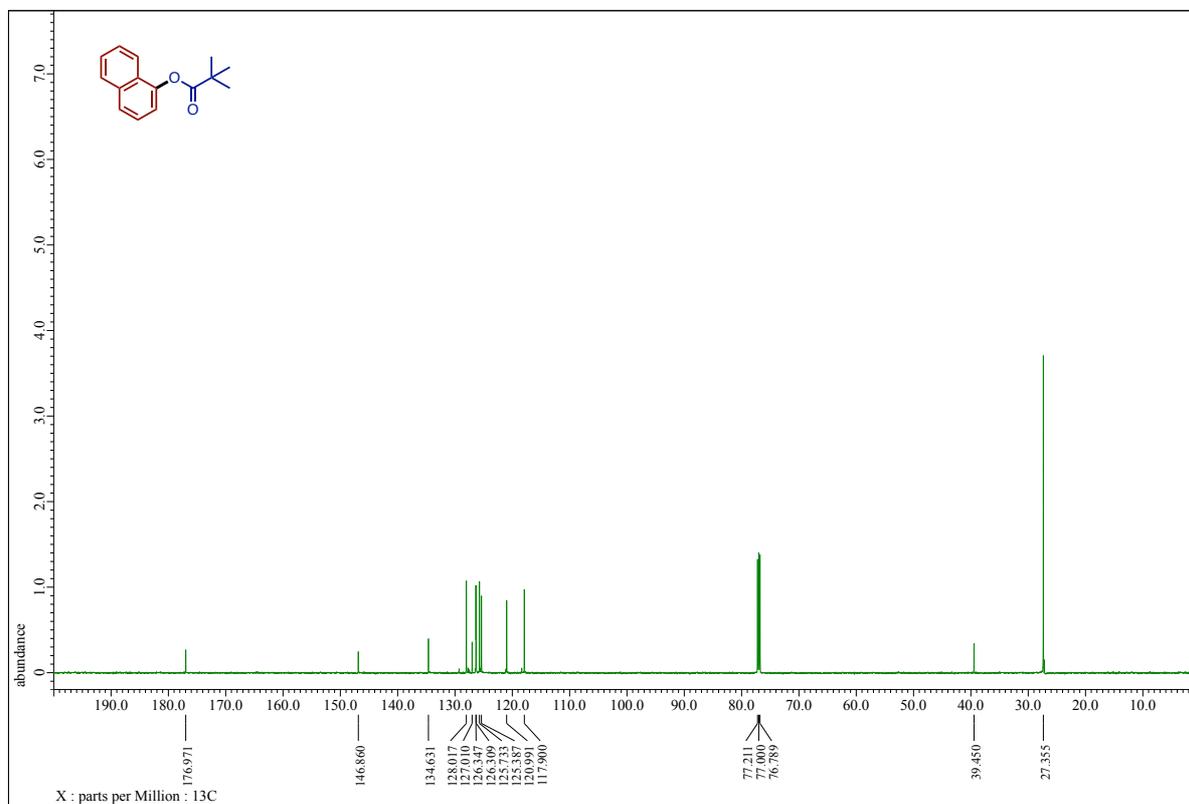


Naphthalen-1-yl pivalate (3qa)

^1H NMR (600 MHz, CDCl_3)

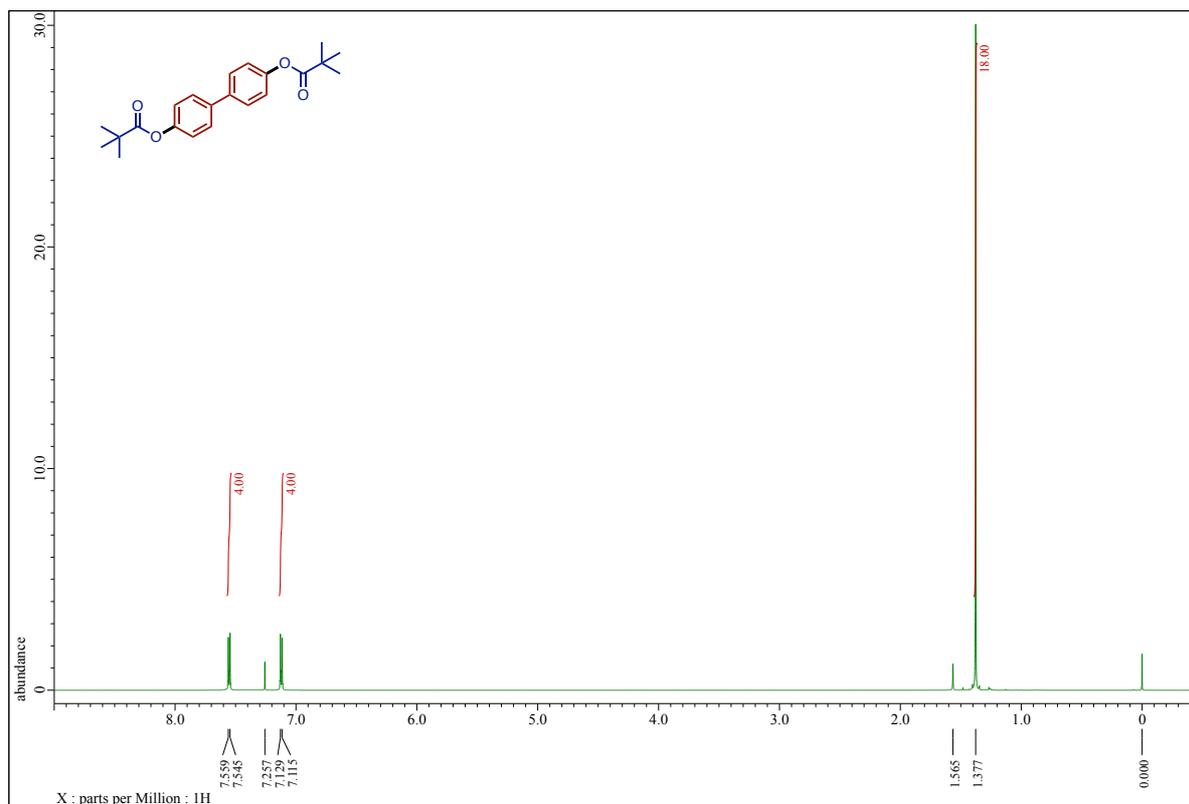


^{13}C NMR (150 MHz, CDCl_3)



(1,1'-Biphenyl)-4,4'-diyl bis(2,2-dimethylpropanoate) (3ra)

¹H NMR (600 MHz, CDCl₃)



¹³C NMR (150 MHz, CDCl₃)

