

Supporting Information for:

**Copper-catalyzed reaction of oximes with diisopropyl
azodicarboxylate: An alternative method for the synthesis of oxime
carbonates**

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CONTENTS

1. General information	S2
2. Synthesis of oximes	S2
3. Typical procedure for for synthesis of oxime carbonates	S2-S3
4. Characterization data of oxime carbonates	S3-S11
5. Copies of ¹H and ¹³C NMR spectra	S12-S73

1. General information

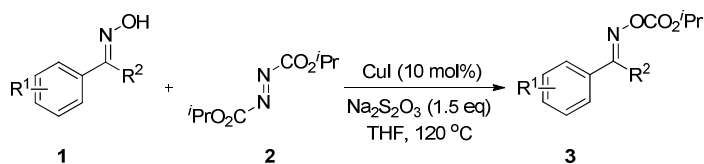
^1H , ^{13}C and ^{19}F NMR spectra were recorded at 400, 100 and 376 MHz respectively in CDCl_3 . Multiplicities were given as: s = singlet, d = doublet, dd = doublets of doublet, t = triplet, q = quartet and m = multiplet. Coupling constants, J were reported in Hertz unit (Hz). All products were further characterized by HRMS (ESI-TOF-Q). Flash column chromatography was performed with SiO_2 (Silicycle Silica Gel 60 (200-300 mesh)). Analytical thin layer chromatography (TLC) plates (silica gel GF254) were analyzed under UV light. All reactions were carried out under argon atmosphere in dried glassware with magnetic stirring. Solvents were distilled by standard methods. Reagents were purchased from commercial suppliers and used without further purification unless otherwise noted.

2. Synthesis of oximes

The ketoximes are very useful molecules, which can easily prepare from the corresponding ketones according to literature procedures¹⁻³ and can be used in the reaction without further purification.

- (1) H. Zhao, C. P. Vandenbossche, S. G. Koenig, S. P. Singh and R. P. Bakale, *Org Lett.*, 2008, **10**, 505.
- (2) G. Zhang, X. Wen, Y. Wang, W. Mo and C. Ding, *J. Org. Chem.*, 2011, **76**, 4665.
- (3) P. C. Too, Y.-F. Wang and S. Chiba, *Org Lett.*, 2010, **12**, 5688.

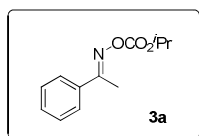
3. Typical procedure for synthesis of oxime carbonates



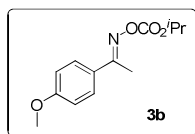
In a 10 mL round bottom flask, the mixture of ketoxime **1** (0.2 mmol), diisopropyl azodicarboxylate **2** (0.8 mmol), $\text{Na}_2\text{S}_2\text{O}_3$ (0.3 mmol, 74.4 mg) and CuI (10 mol%, 3.8 mg) was stirred in THF (2 mL) at 120 °C under Ar. When the reaction was completed (detected by TLC), the reaction mixture was cooled to room temperature. The reaction

was quenched with H₂O (10 mL) and extracted with EtOAc (3 × 10 mL). The combined organic layers were dried over anhydrous Na₂SO₄ and then evaporated under vacuum. The residue was purified by column chromatography on silica gel to afford the corresponding oxime carbonates **3** with hexane/ethyl acetate as the eluent.

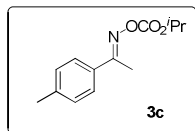
4. Characterization data of oxime carbonates.



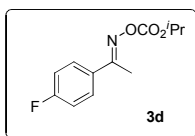
3a: Yield: 98% (43.3 mg), transparent oil; ¹H NMR (CDCl₃, 400 MHz) δ 7.74 (d, *J* = 6.8 Hz, 2 H), 7.44-7.38 (m, 3 H), 5.08-5.02 (m, 1 H), 2.40 (s, 3 H), 1.38 (d, *J* = 6.4 Hz, 6 H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.2, 153.4, 134.6, 130.5, 128.5, 126.9, 72.8, 21.7, 14.3; HRMS Calcd (ESI) *m/z* for C₁₂H₁₅NNaO₃ [M+Na]⁺ 244.0944, found 244.0938.



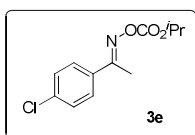
3b: Yield: 95% (47.7 mg), white solid, mp 53-55 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.71 (d, *J* = 7.6 Hz, 2 H), 6.91 (d, *J* = 7.6 Hz, 2 H), 5.06-5.03 (m, 1 H), 3.83 (s, 3 H), 2.36 (s, 3 H), 1.38 (d, *J* = 4.8 Hz, 6 H); ¹³C NMR (CDCl₃, 100 MHz) δ 161.6, 161.4, 153.4, 128.4, 126.8, 113.8, 72.7, 55.3, 21.7, 14.0; HRMS Calcd (ESI) *m/z* for C₁₃H₁₇NNaO₄ [M+Na]⁺ 274.1050, found 274.1040.



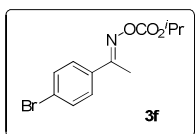
3c: Yield: 84% (39.5 mg), white solid, mp 49-51 °C; ¹H NMR (CDCl₃, 400 MHz) δ 7.64 (d, *J* = 8.4 Hz, 2 H), 7.20 (d, *J* = 8.4 Hz, 2 H), 5.06-5.03 (m, 1 H), 2.37 (s, 6 H), 1.38 (d, *J* = 6.0 Hz, 6 H); ¹³C NMR (CDCl₃, 100 MHz) δ 162.1, 153.5, 140.8, 131.8, 129.3, 126.9, 72.8, 21.8, 21.4, 14.2; HRMS Calcd (ESI) *m/z* for C₁₃H₁₇NNaO₃ [M+Na]⁺ 258.1101, found 258.1094.



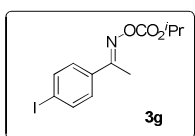
3d: Yield: 62% (29.7 mg), transparent oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.77-7.73 (m, 2 H), 7.11-7.07 (m, 2 H), 5.08-5.02 (m, 1 H), 2.38 (s, 3 H), 1.38 (d, $J = 6.4$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 164.2 (d, $J_{\text{CF}} = 249.4$ Hz), 161.2, 153.4, 130.8 (d, $J_{\text{CF}} = 3.3$ Hz), 129.0 (d, $J_{\text{CF}} = 8.5$ Hz), 115.7 (d, $J_{\text{CF}} = 21.7$ Hz), 73.0, 21.8, 14.3; ^{19}F NMR (CDCl_3 , 376 MHz) δ -109.8 (s, 1 F); HRMS Calcd (ESI) m/z for $\text{C}_{12}\text{H}_{14}\text{FNNaO}_3$ $[\text{M}+\text{Na}]^+$ 262.0850, found. 262.0845.



3e: Yield: 83% (42.5 mg), transparent oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.70 (d, $J = 8.4$ Hz, 2 H), 7.38 (d, $J = 8.4$ Hz, 2 H), 5.10-5.02 (m, 1 H), 2.38 (s, 3 H), 1.38 (d, $J = 6.4$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.1, 153.3, 136.7, 133.1, 128.8, 128.3, 73.1, 21.8, 14.2; HRMS Calcd (ESI) m/z for $\text{C}_{12}\text{H}_{14}\text{ClNNaO}_3$ $[\text{M}+\text{Na}]^+$ 278.0554, found 278.0541.

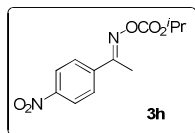


3f: Yield: 80% (48.1 mg), transparent oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.66 (d, $J = 8.8$ Hz, 2 H), 7.53 (d, $J = 8.8$ Hz, 2 H), 5.08-5.02 (m, 1 H), 2.37 (s, 3 H), 1.38 (d, $J = 6.4$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.2, 153.3, 133.6, 131.8, 128.5, 125.1, 73.1, 21.8, 14.1; HRMS Calcd (ESI) m/z for $\text{C}_{12}\text{H}_{14}\text{BrNNaO}_3$ $[\text{M}+\text{Na}]^+$ 322.0049, found 322.0038.

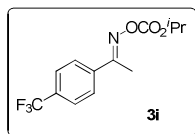


3g: Yield: 58% (40.1 mg), white solid, mp 63 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.74 (d, $J = 8.4$ Hz, 2 H), 7.48 (d, $J = 8.4$ Hz, 2 H), 5.08-5.01 (m, 1 H), 2.36 (s, 3 H), 1.38

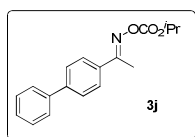
(d, $J = 6.0$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.3, 153.3, 137.7, 134.2, 128.6, 97.2, 73.1, 21.8, 14.1; HRMS Calcd (ESI) m/z for $\text{C}_{12}\text{H}_{14}\text{INNaO}_3$ $[\text{M}+\text{Na}]^+$ 369.9911, found 369.9898.



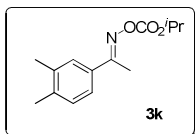
3h: Yield: 88% (46.9 mg), almost white solid, mp 101-103 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.26 (d, $J = 9.2$ Hz, 2 H), 7.94 (d, $J = 8.8$ Hz, 2 H), 5.10-5.04 (m, 1 H), 2.45 (s, 3 H), 1.40 (d, $J = 6.0$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 160.2, 153.0, 149.0, 140.7, 128.0, 123.7, 73.5, 21.7, 14.3; HRMS Calcd (ESI) m/z for $\text{C}_{12}\text{H}_{14}\text{N}_2\text{NaO}_5$ $[\text{M}+\text{Na}]^+$ 289.0795, found 289.0786.



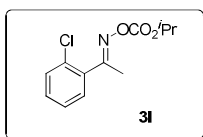
3i: Yield: 75% (43.5 mg), white solid, mp 57-59 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.87 (d, $J = 8.0$ Hz, 2 H), 7.67 (d, $J = 8.4$ Hz, 2 H), 5.09-5.05 (m, 1 H), 2.42 (s, 3 H), 1.39 (d, $J = 6.0$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 160.9, 153.2, 138.2, 132.3 (d, $J_{\text{CF}} = 32.5$ Hz), 127.4, 125.5 (q, $J_{\text{CF}} = 3.6$ Hz), 123.8 (d, $J_{\text{CF}} = 270.7$ Hz), 73.2, 21.7, 14.3; ^{19}F NMR (CDCl_3 , 376 MHz): δ -62.9 (s, 3 F); HRMS Calcd (ESI) m/z for $\text{C}_{13}\text{H}_{14}\text{F}_3\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 312.0818, found 312.0806.



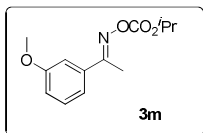
3j: Yield: 90% (53.5 mg), white solid, mp 144-146 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 7.83 (d, $J = 8.4$ Hz, 2 H), 7.62 (t, $J = 8.4$ Hz, 4 H), 7.45 (t, $J = 7.2$ Hz, 2 H), 7.36 (t, $J = 7.2$ Hz, 1 H), 5.10-5.03 (m, 1 H), 2.42 (s, 3 H), 1.39 (d, $J = 6.4$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 161.7, 153.4, 143.2, 140.0, 133.4, 128.8, 127.8, 127.4, 127.1, 127.0, 72.8, 21.7, 14.1; HRMS Calcd (ESI) m/z for $\text{C}_{18}\text{H}_{19}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 320.1257, found 320.1237.



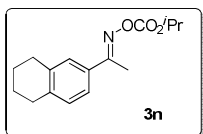
3k: Yield: 91% (45.4 mg), transparent oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.55 (s, 1 H), 7.44 (dd, $J = 7.6, 1.6$ Hz, 1 H), 7.15 (d, $J = 8.0$ Hz, 1 H), 5.07-5.01 (m, 1 H), 2.36 (s, 3 H), 2.28 (s, 6 H), 1.37 (d, $J = 6.0$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.3, 153.5, 139.5, 136.8, 132.2, 129.8, 128.0, 124.5, 72.7, 21.8, 19.7, 19.7, 14.2; HRMS Calcd (ESI) m/z for $\text{C}_{14}\text{H}_{19}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 272.1257, found 272.1250.



3l: Yield: 53% (26.9 mg), transparent oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.42-7.29 (m, 4 H), 5.09-5.04 (m, 1 H), 2.39 (s, 3 H), 1.38 (d, $J = 6.4$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 163.8, 153.2, 135.1, 132.5, 130.8, 130.4, 130.0, 126.9, 73.1, 21.8, 17.9; HRMS Calcd (ESI) m/z for $\text{C}_{12}\text{H}_{14}\text{ClNNaO}_3$ $[\text{M}+\text{Na}]^+$ 278.0554, found 278.0540.

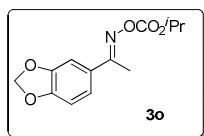


3m: Yield: 89% (44.9 mg), transparent oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.31-7.27 (m, 3 H), 7.00-6.97 (m, 1 H), 5.07-5.03 (m, 1 H), 3.83 (s, 3 H), 2.37 (s, 3 H), 1.38 (d, $J = 6.0$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.2, 159.7, 153.4, 136.1, 129.5, 119.5, 116.5, 112.1, 72.9, 55.4, 21.8, 14.4; HRMS Calcd (ESI) m/z for $\text{C}_{13}\text{H}_{17}\text{NNaO}_4$ $[\text{M}+\text{Na}]^+$ 274.1050, found .274.1043.

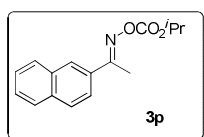


3o: Yield: 88% (48.6 mg), transparent oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.47 (s, 1 H), 7.44 (d, $J = 8.0$ Hz, 1 H), 7.09 (d, $J = 8.0$ Hz, 1 H), 5.09-5.00 (m, 1 H), 2.78 (s, 4 H), 2.36 (s, 3 H), 1.80-1.78 (m, 4 H), 1.38 (d, $J = 6.4$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 162.3, 153.4, 140.0, 137.3, 131.6, 129.2, 127.5, 123.9, 72.7, 29.3, 29.2, 22.9,

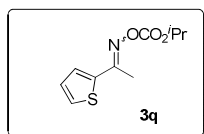
22.9, 21.7, 14.2; HRMS Calcd (ESI) m/z for $C_{16}H_{21}NNaO_3$ $[M+Na]^+$ 298.1414, found 298.1402.



3p: Yield: 68% (36.1 mg), white solid, mp 100-102 °C; 1H NMR ($CDCl_3$, 400 MHz) δ 7.31 (d, J = 1.6 Hz, 1 H), 7.22 (dd, J = 8.0, 1.6 Hz, 1 H), 6.82 (d, J = 8.0 Hz, 1 H), 6.00 (s, 2 H), 5.07-4.99 (m, 1 H), 2.34 (s, 3 H), 1.38 (d, J = 6.4 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.5, 153.4, 149.7, 148.0, 128.7, 121.7, 108.1, 107.1, 101.6, 72.9, 21.8, 14.2; HRMS Calcd (ESI) m/z for $C_{13}H_{15}NNaO_5$ $[M+Na]^+$ 288.0842, found 288.0828.



3n: Yield: 89% (48.4 mg), white solid, mp 85-86 °C; 1H NMR ($CDCl_3$, 400 MHz) δ 8.14 (s, 1 H), 7.96 (dd, J = 8.8, 2.0 Hz, 1 H), 7.89-7.83 (m, 3 H), 7.52-7.50 (m, 2 H), 5.10-5.04 (m, 1 H), 2.50 (s, 3 H), 1.39 (d, J = 6.4 Hz, 6 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 161.9, 153.4, 134.2, 132.8, 132.0, 128.7, 128.2, 127.6, 127.3, 127.2, 126.5, 123.7, 72.9, 21.8, 14.1; HRMS Calcd (ESI) m/z for $C_{16}H_{17}NNaO_3$ $[M+Na]^+$ 294.1101, found 294.1088.



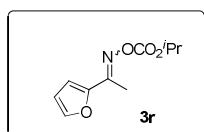
3q: Yield: 98% (44.6 mg), transparent oil; 1H NMR ($CDCl_3$, 400 MHz) δ 7.65 (dd, J = 5.2, 1.2 Hz, 1 H), 7.60 (dd, J = 4.0, 1.2 Hz, 1 H), 7.42 (t, J = 3.6 Hz, 2 H), 7.15-7.13 (m, 1 H), 7.07-7.05 (m, 1 H), 5.11-5.00 (m, 2 H), 2.49 (s, 4 H), 2.41 (s, 2 H), 1.40-1.36 (m, 12 H); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 157.6, 153.1, 153.1, 137.7, 132.8, 132.4, 131.7, 129.2, 129.0, 127.2, 126.3, 73.1, 73.0, 21.8, 21.8, 20.0, 14.4; HRMS Calcd (ESI) m/z for $C_{10}H_{13}NNaO_3S$ $[M+Na]^+$ 250.0508, found 250.0502.

The isomers can be separated by careful chromatography on silica gel eluting with

12:1 hexane:ethyl acetate.

3q': ^1H NMR (CDCl_3 , 400 MHz) δ 7.44-7.41 (m, 2 H), 7.08-7.05 (m, 1 H), 5.07-5.00 (m, 1 H), 2.41 (s, 3 H), 1.37 (d, $J = 6.0$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 157.6, 153.1, 137.7, 129.2, 129.0, 127.2, 73.1, 21.8, 14.4; HRMS Calcd (ESI) m/z for $\text{C}_{10}\text{H}_{13}\text{NNaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 250.0508, found .250.0502.

3q'': ^1H NMR (CDCl_3 , 400 MHz) δ 7.66 (d, $J = 5.2$ Hz, 1 H), 7.61-7.60 (m, 1 H), 7.15-7.13 (m, 1 H), 5.12-5.04 (m, 1 H), 2.49 (s, 3 H), 1.39 (d, $J = 6.0$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.1, 153.1, 132.8, 132.4, 131.7, 126.3, 73.2, 21.8, 20.1; HRMS Calcd (ESI) m/z for $\text{C}_{10}\text{H}_{13}\text{NNaO}_3\text{S}$ $[\text{M}+\text{Na}]^+$ 250.0508, found .250.0502.



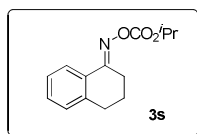
3r: Yield: 96% (40.5 mg), transparent oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.54 (s, 2 H), 7.46 (d, $J = 3.6$ Hz, 1 H), 6.90 (d, $J = 3.2$ Hz, 1 H), 6.59-6.58 (m, 1 H), 6.49-6.48 (m, 1 H), 5.08-5.02 (m, 2 H), 2.40 (s, 3 H), 2.32 (s, 3 H), 1.37 (d, $J = 6.4$ Hz, 12 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.7, 153.3, 153.1, 150.3, 148.1, 145.0, 144.7, 144.1, 120.4, 113.1, 112.6, 111.7, 73.1, 72.9, 21.8, 21.8, 17.4, 13.0; HRMS Calcd (ESI) m/z for $\text{C}_{10}\text{H}_{13}\text{NNaO}_4$ $[\text{M}+\text{Na}]^+$ 234.0737, found .234.0739.

The isomers can be separated by careful chromatography on silica gel eluting with 12:1 hexane:ethyl acetate and can be differentiated by their different ^1H NMR signal patterns of the furan ring.

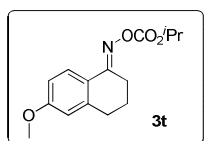
3r': ^1H NMR (CDCl_3 , 400 MHz) δ 7.54 (d, $J = 1.6$ Hz, 1 H), 7.46 (d, $J = 3.6$ Hz, 1 H), 6.59-6.58 (m, 1 H), 5.10-5.01 (m, 1 H), 2.40 (s, 3 H), 1.37 (d, $J = 6.4$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 153.4, 150.3, 144.7, 144.1, 120.4, 112.6, 72.9, 21.8, 17.5; HRMS Calcd (ESI) m/z for $\text{C}_{10}\text{H}_{13}\text{NNaO}_4$ $[\text{M}+\text{Na}]^+$ 234.0737, found .234.0733.

3r'': ^1H NMR (CDCl_3 , 400 MHz) δ 7.53 (s, 1 H), 6.90 (d, $J = 3.6$ Hz, 1 H), 6.49-6.48 (m, 1 H), 5.09-5.00 (m, 1 H), 2.32 (s, 3 H), 1.37 (d, $J = 6.0$ Hz, 6 H); ^{13}C NMR

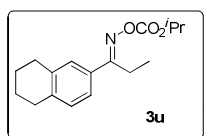
(CDCl₃, 100 MHz) δ 153.7, 153.1, 148.1, 145.0, 113.2, 111.7, 73.1, 21.8, 13.0; HRMS Calcd (ESI) m/z for C₁₀H₁₃NNaO₄ [M+Na]⁺ 234.0737, found .234.0739.



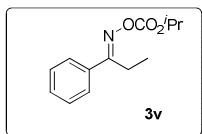
3s: Yield: 88% (43.6 mg), transparent oil; ¹H NMR (CDCl₃, 400 MHz) δ 8.16 (d, *J* = 8.0 Hz, 1 H), 7.33 (td, *J* = 7.6, 1.6 Hz, 1 H), 7.23 (t, *J* = 8.0 Hz, 1 H), 7.17 (d, *J* = 7.6 Hz, 1 H), 5.09-5.00 (m, 1 H), 2.89 (t, *J* = 6.4 Hz, 2 H), 2.78 (t, *J* = 6.0 Hz, 2 H), 1.91-1.85 (m, 2 H), 1.38 (d, *J* = 6.0 Hz, 6 H); ¹³C NMR (CDCl₃, 100 MHz) δ 161.0, 153.4, 140.7, 130.6, 128.7, 128.6, 126.5, 125.5, 72.7, 29.4, 25.4, 21.7, 21.1; HRMS Calcd (ESI) m/z for C₁₄H₁₇NNaO₃ [M+Na]⁺ 270.1101, found 270.1088.



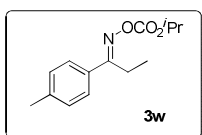
3t: Yield: 77% (42.6 mg), white solid, mp 85-87 °C; ¹H NMR (CDCl₃, 400 MHz) δ 8.10 (d, *J* = 8.8 Hz, 1 H), 6.78 (dd, *J* = 8.8, 2.4 Hz, 1 H), 6.66 (d, *J* = 2.4 Hz, 1 H), 5.05-5.02 (m, 1 H), 3.82 (s, 3 H), 2.86 (t, *J* = 6.8 Hz, 2 H), 2.74 (t, *J* = 6.0 Hz, 2 H), 1.89-1.83 (m, 1 H), 1.37 (d, *J* = 6.0 Hz, 6 H); ¹³C NMR (CDCl₃, 100 MHz) δ 161.4, 160.9, 153.6, 142.8, 127.4, 121.4, 113.0, 112.9, 72.7, 55.3, 29.8, 25.4, 21.8, 21.3; HRMS Calcd (ESI) m/z for C₁₅H₁₉NNaO₄ [M+Na]⁺ 300.1206, found 300.1192.



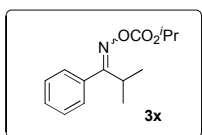
3u: Yield: 82% (47.2 mg), transparent oil; ¹H NMR (CDCl₃, 100 MHz) δ 7.45 (s, 1 H), 7.42 (d, *J* = 8.0 Hz, 1 H), 7.09 (d, *J* = 8.0 Hz, 1 H), 5.07-5.01 (m, 1 H), 2.87-2.81 (m, 2 H), 2.78 (d, *J* = 2.8 Hz, 4 H), 1.81-1.78 (m, 4 H), 1.38 (d, *J* = 6.4 Hz, 6 H), 1.18 (t, *J* = 7.6 Hz, 3 H); ¹³C NMR (CDCl₃, 100 MHz) δ 167.2, 153.6, 140.0, 137.4, 130.5, 129.3, 127.8, 124.1, 72.7, 29.3, 29.3, 23.0, 22.9, 21.8, 21.4, 11.4; HRMS Calcd (ESI) m/z for C₁₇H₂₃NNaO₃ [M+Na]⁺ 312.1570, found 312.1550.



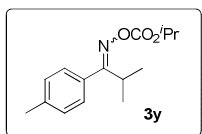
3v: Yield: 77% (36.1 mg), transparent oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.72 (d, J = 6.4 Hz, 2 H), 7.44-7.38 (m, 3 H), 5.08-5.02 (m, 1 H), 2.90-2.84 (m, 2 H), 1.38 (d, J = 6.4 Hz, 6 H), 1.19 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.2, 153.6, 133.7, 130.5, 128.6, 127.3, 72.9, 21.8, 21.6, 11.4; HRMS Calcd (ESI) m/z for $\text{C}_{13}\text{H}_{17}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 258.1101, found 258.1090.



3w: Yield: 79% (39.6 mg), transparent oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.62 (d, J = 8.0 Hz, 2 H), 7.21 (d, J = 8.0 Hz, 2 H), 5.07-5.01 (m, 1 H), 2.87-2.82 (m, 2 H), 2.37 (s, 3 H), 1.38 (d, J = 6.0 Hz, 6 H), 1.18 (t, J = 7.6 Hz, 3 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 167.0, 153.7, 140.7, 130.7, 129.3, 127.1, 72.8, 21.8, 21.4, 21.4, 11.4; HRMS Calcd (ESI) m/z for $\text{C}_{14}\text{H}_{19}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 272.1257, found 272.1242.

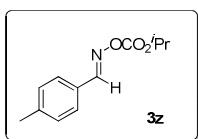


3x: Yield: 85% (42.3 mg), transparent oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.44-7.35 (m, 8 H), 7.20-7.19 (m, 1 H), 7.18-7.17 (m, 1 H), 5.07-5.01 (m, 1 H), 4.94-4.88 (m, 1 H), 3.63-3.56 (m, 1 H), 3.03-2.96 (m, 1 H), 1.37 (d, J = 6.4 Hz, 7 H), 1.25 (d, J = 6.0 Hz, 6 H), 1.21 (d, J = 6.8 Hz, 7 H), 1.17 (d, J = 6.8 Hz, 4 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.9, 170.8, 153.8, 153.6, 133.6, 132.5, 129.4, 128.9, 128.2, 128.2, 127.0, 72.8, 72.6, 35.0, 29.5, 21.8, 21.7, 19.9, 19.6; HRMS Calcd (ESI) m/z for $\text{C}_{14}\text{H}_{19}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 272.1257, found 272.1245.



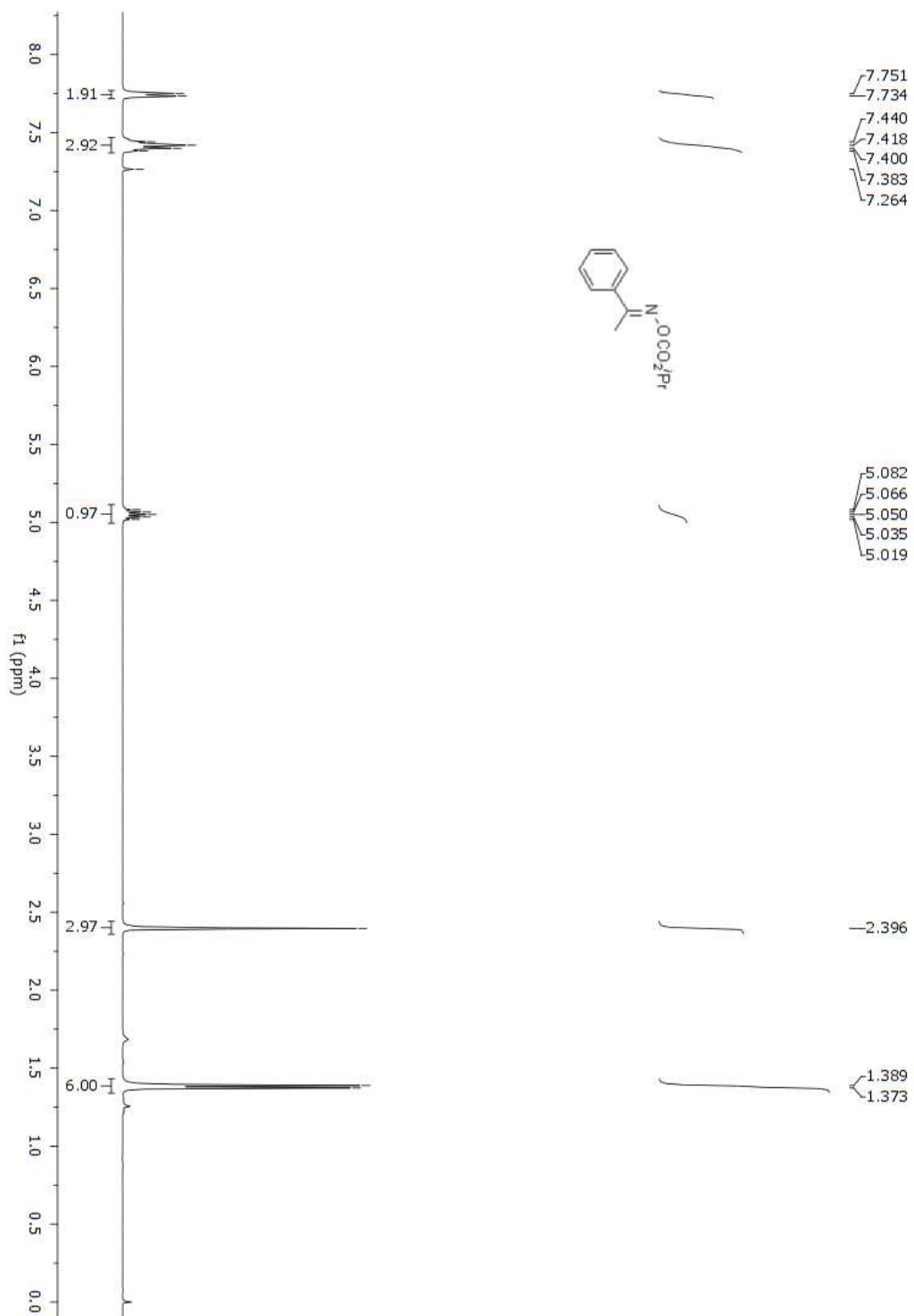
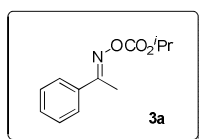
3y: Yield: 87% (46.0 mg), transparent oil; ^1H NMR (CDCl_3 , 400 MHz) δ 7.34 (d, J =

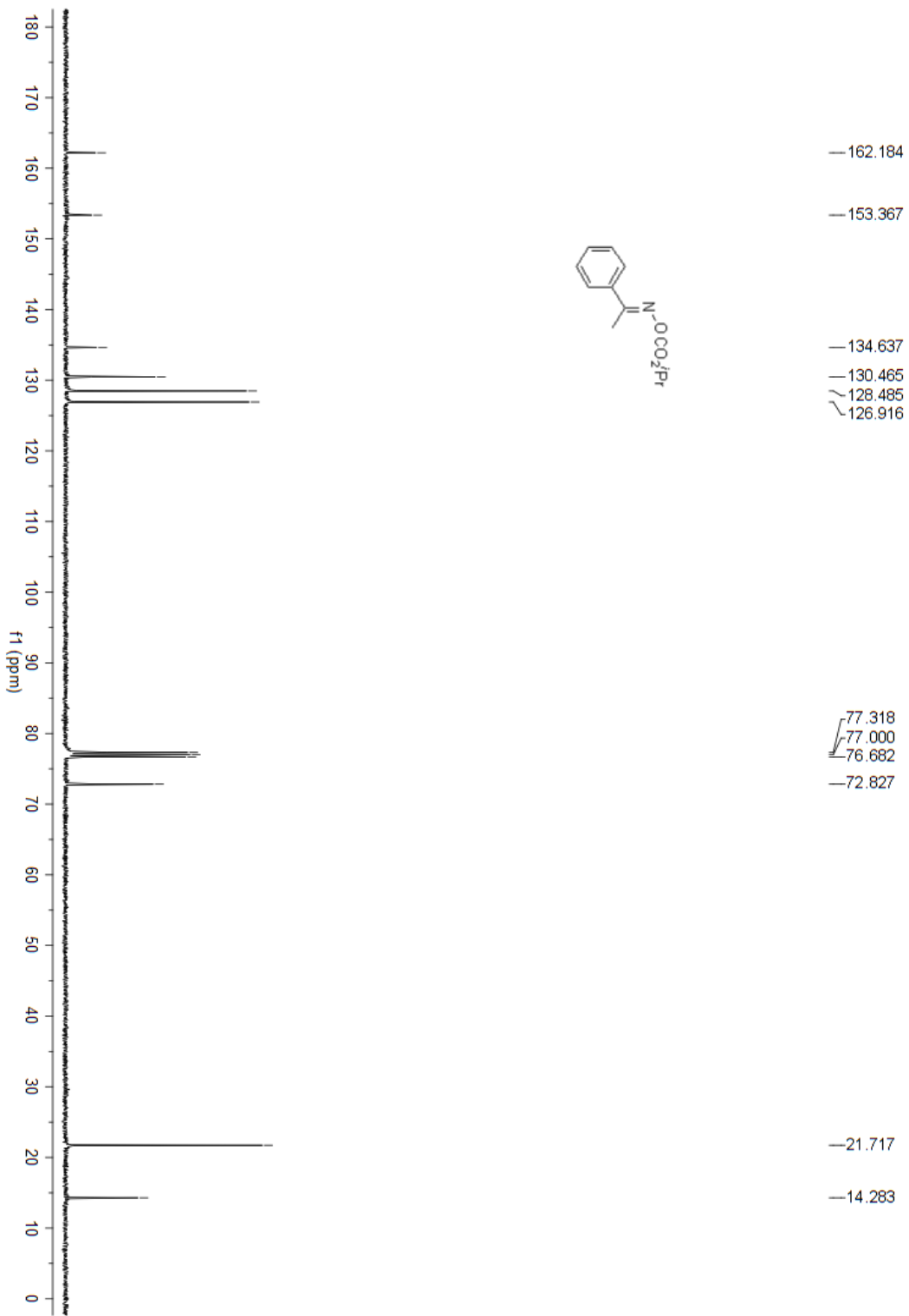
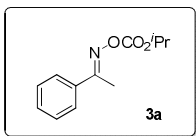
8.0 Hz, 2 H), 7.23-7.17 (m, 4 H), δ 7.09 (d, $J = 8.0$ Hz, 2 H), 5.06-5.00 (m, 1 H), 4.94-4.88 (m, 1 H), 3.60-3.53 (m, 1 H), 3.01-2.95 (m, 1 H), 2.37 (d, $J = 5.6$ Hz, 6 H), 1.36 (d, $J = 6.4$ Hz, 4 H), 1.26 (d, $J = 6.4$ Hz, 8 H), 1.21 (d, $J = 7.2$ Hz, 5 H), 1.17 (d, $J = 6.8$ Hz, 7 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 171.8, 170.8, 153.8, 153.6, 139.5, 138.9, 130.8, 129.6, 128.9, 128.9, 128.1, 127.0, 72.7, 72.5, 35.0, 29.6, 21.8, 21.7, 21.4, 21.3, 19.9, 19.6; HRMS Calcd (ESI) m/z for $\text{C}_{15}\text{H}_{21}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 286.1414, found 286.1400.

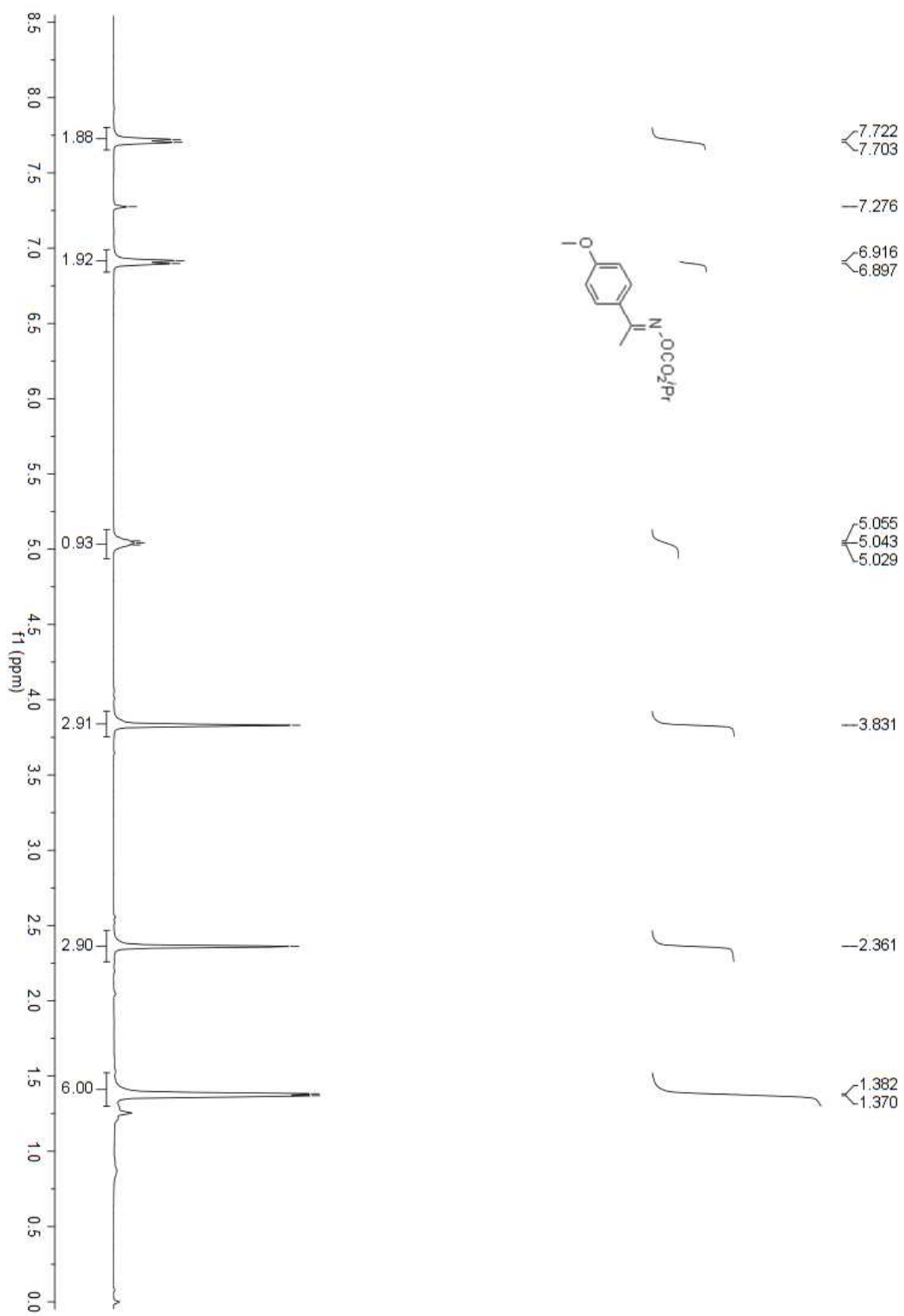
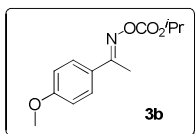


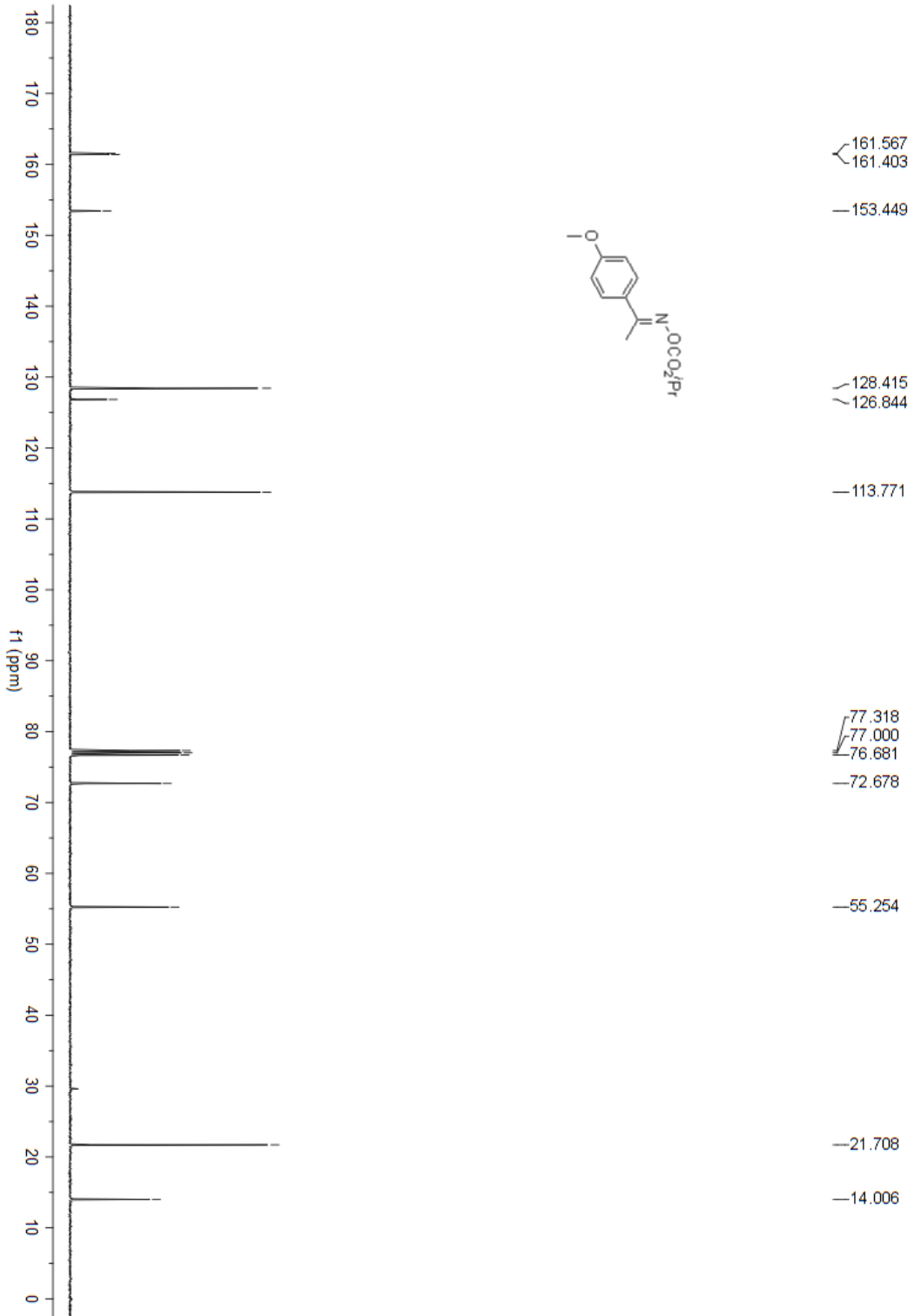
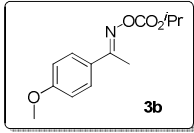
3z: Yield: 19% (43.1 mg), white solid, mp 74-76 °C; ^1H NMR (CDCl_3 , 400 MHz) δ 8.30 (s, 1 H), 7.62 (d, $J = 8.0$ Hz, 2 H), 7.23 (d, $J = 8.0$ Hz, 2 H), 5.07-5.01 (m, 1 H), 2.39 (s, 3 H), 1.38 (d, $J = 6.4$ Hz, 6 H); ^{13}C NMR (CDCl_3 , 100 MHz) δ 155.6, 153.3, 142.3, 129.6, 128.3, 127.1, 73.1, 21.8, 21.6; HRMS Calcd (ESI) m/z for $\text{C}_{12}\text{H}_{15}\text{NNaO}_3$ $[\text{M}+\text{Na}]^+$ 244.0944, found 244.0952.

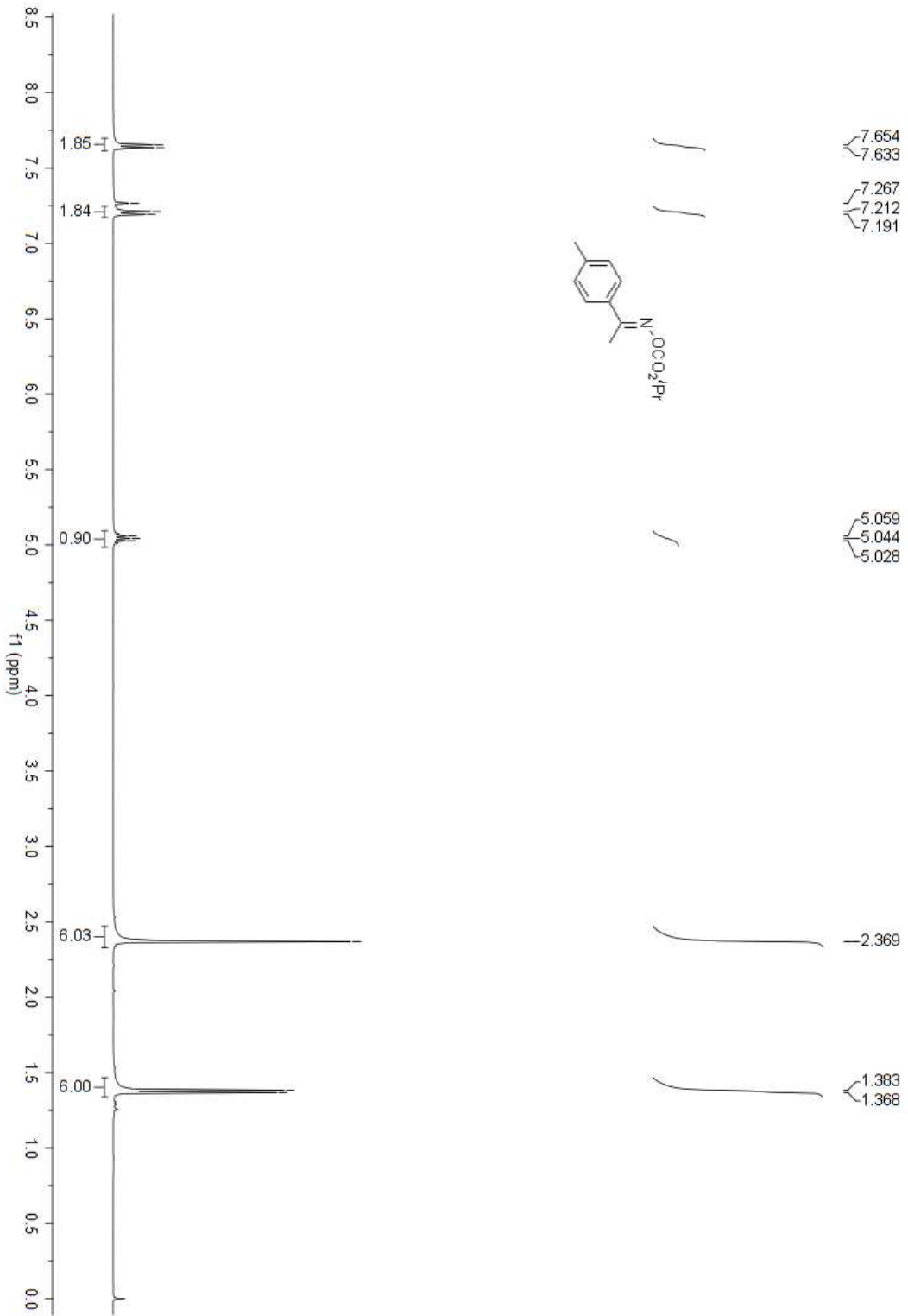
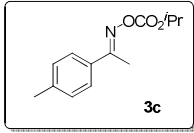
5. Copies of ^1H and ^{13}C NMR spectra

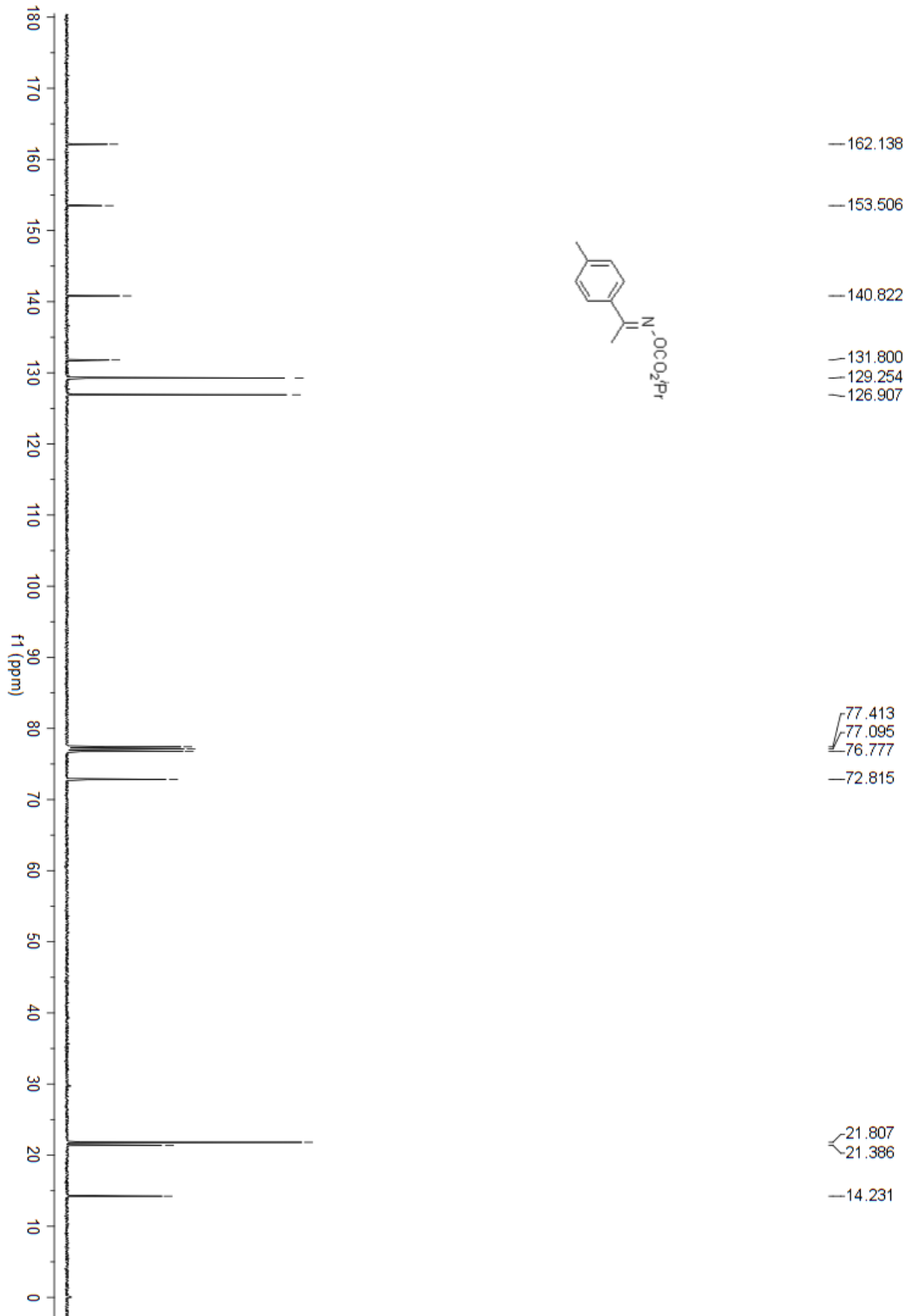
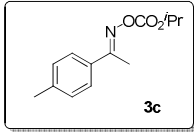


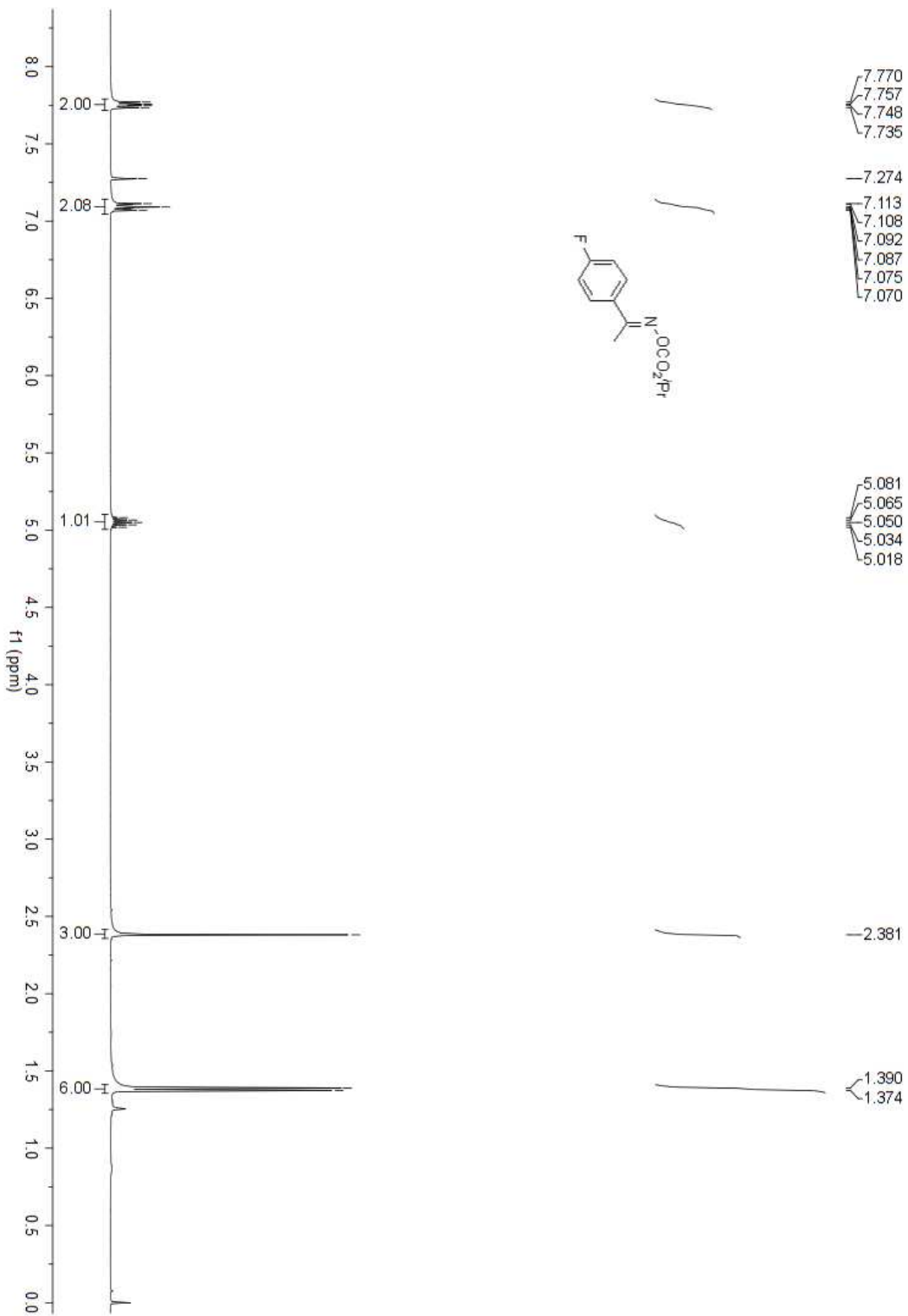
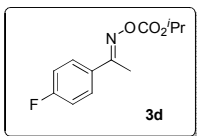


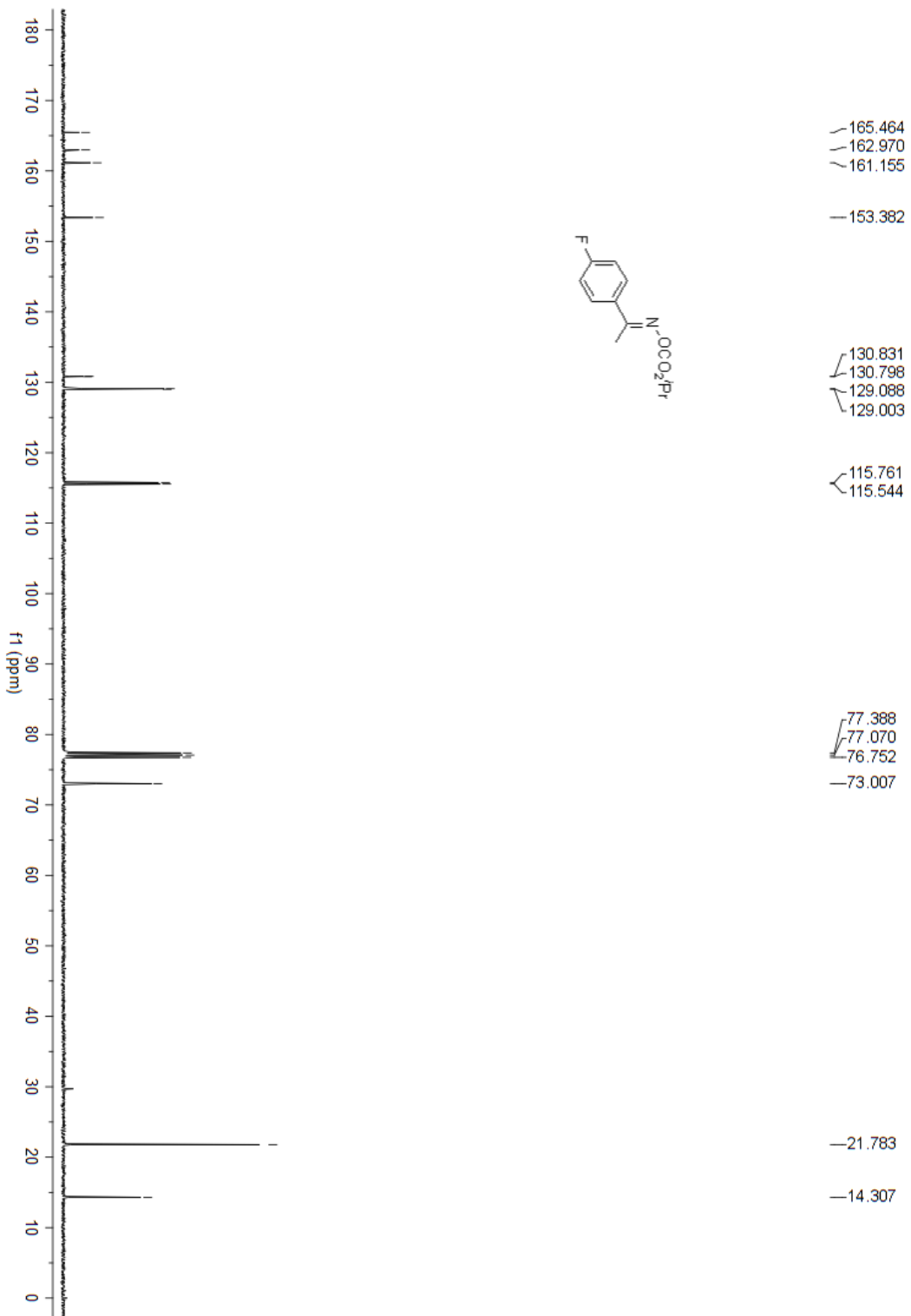
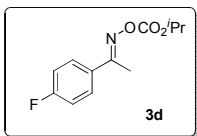


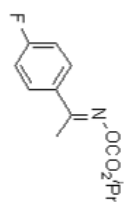
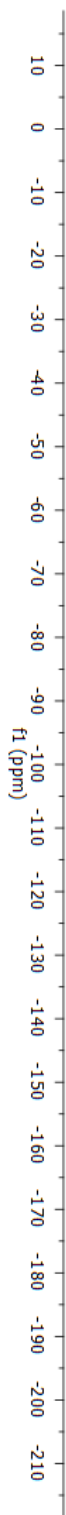
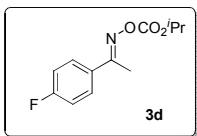












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