

Supporting Information

Divergent Functionalization of α,β -Enones: Catalyst-free Access to β -Azido Ketones and β -Amino α -Diazo Ketones

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Table of Contents

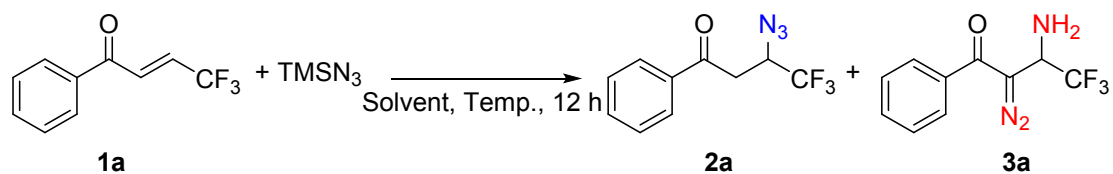
| | |
|---|-----|
| 1. General information..... | S2 |
| 2. Optimization of the reaction conditions..... | S3 |
| 3. General experimental procedure... .. | S4 |
| 4. X-ray Crystal Structure for 2s | S5 |
| 5. References | S6 |
| 6. Characterization data of products | S6 |
| 7. ¹ H, ¹³ C, and ¹⁹ F NMR Spectra | S23 |

1. General information:

Unless otherwise noted, all reactions were carried out under an air atmosphere; materials obtained from commercial suppliers were used directly without further purification. ^1H NMR spectra, ^{13}C NMR spectra and ^{19}F NMR spectra were recorded on a Bruker 400 (or 300, 500) MHz spectrometer in chloroform- d_3 . Chemical shifts (in ppm) were referenced to tetramethylsilane ($\delta = 0$ ppm) in CDCl_3 as an internal standard. ^{13}C NMR spectra were obtained by using the same NMR spectrometers and were calibrated with CDCl_3 ($\delta = 77.00$ ppm). The data is being reported as (s = singlet, d = doublet, dd = doublet of doublet, t = triplet, m = multiplet or unresolved, br = broad signal, coupling constant(s) in Hz, integration).

Reactions were monitored by thin layer chromatography (TLC) using silicycle pre-coated silica gel plates. Flash column chromatography was performed on silica gel 60 (particle size 200-400 mesh ASTM, purchased from Yantai, China) and eluted with petroleum ether/ethyl acetate. The Substrates **1** were synthesized according to the reported methods¹. All reagents and solvents were used as received from commercial sources (*Energy Chemical*, *J&K*[®], *Adamas-beta*[®]) without further purification.

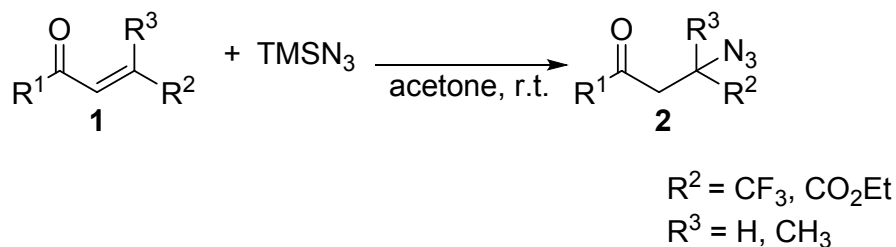
2.Optimization of the reaction conditions.^[a]



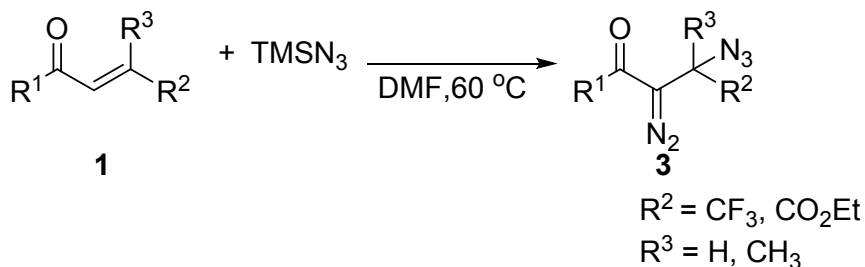
| Entry | Temp./°C | Solvent | 2a /Yield(%) ^[b] | 3a /Yield(%) ^[b] |
|-------|----------|-------------------------|------------------------------------|------------------------------------|
| 1 | r.t | DMF | 23 | 67 |
| 2 | r.t | DMSO | 15 | 77 |
| 3 | r.t | THF | 86 | N.D. |
| 4 | r.t | Et ₂ O | 87 | N.D. |
| 5 | r.t | 1,4-dioxane | trace | N.D. |
| 6 | r.t | toluene | 8 | N.D. |
| 7 | r.t | DCM | 76 | N.D. |
| 8 | r.t | MeCN | 92 | N.D. |
| 9 | r.t | acetone | 99 | N.D. |
| 10 | 0 | acetone | 92 | N.D. |
| 11 | 40 | acetone | 90 | N.D. |
| 12 | 50 | acetone | 80 | 6 |
| 13 | 60 | acetone | 76 | 7 |
| 14 | 70 | acetone | N.D. | 10 |
| 15 | 70 | toluene | N.D. | trace |
| 16 | 70 | ethylene glycol | N.D. | trace |
| 17 | 70 | 1,4-dioxane | N.D. | trace |
| 18 | 70 | cyclohexane | N.D. | trace |
| 19 | 70 | THF | N.D. | N.D. |
| 20 | 70 | n-hexane | N.D. | N.D. |
| 21 | 70 | tert-Butyl methyl ether | N.D. | N.D. |
| 22 | 70 | MeCN | 10 | 58 |
| 23 | 70 | DMF | 7 | 81 |
| 24 | 70 | DMSO | 34 | 64 |
| 25 | 80 | DMF | N.D. | 49 |
| 26 | 60 | DMF | 11 | 89(81) |

[a]: Reactions conducted on 0.1 mmol scale of **1a**, TMSN₃ (2.0 equiv) in 1 mL of solvent for overnight; [b]: ¹⁹F NMR yield with PhCF₃ as an internal standard, The isolated yield in the brackets; N.D. = not detected.

3. General experimental procedure

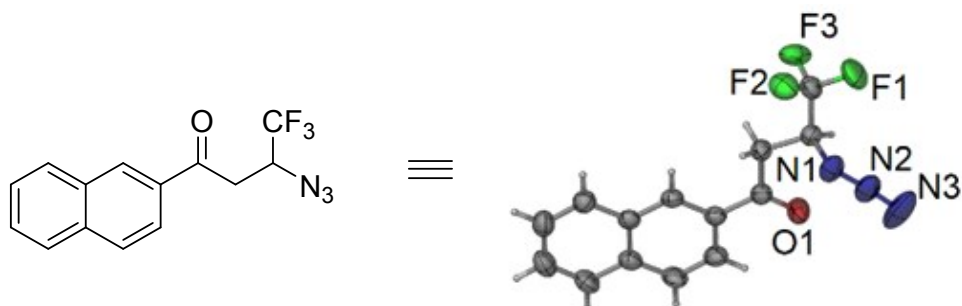


To a solution of **1** (0.2 mmol) in 1 mL acetone was added TMSN_3 (0.4 mmol, 46.1 mg), and the reaction mixture was stirred at room temperature overnight and monitored by TLC. After the completion of the reaction, the mixture was directly applied to column chromatography on silica gel (hexane/ethyl acetate as eluent) to give product **2**.



To a solution of **1** (0.2 mmol) in 1 mL DMF was added TMSN_3 (0.4 mmol, 46.1 mg), and the reaction mixture was stirred at 60 °C and monitored by TLC. After the completion of the reaction, the mixture was directly applied to column chromatography on silica gel (hexane/ethyl acetate as eluent) to give product **3**.

4. Single Crystal X-ray Crystallography of 2s.



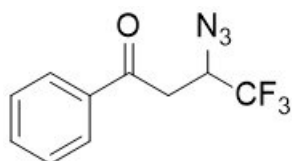
| | | |
|--|-----------------|---------------------------------|
| Bond precision: | C-C = 0.0031 Å | Wavelength=1.54184 |
| Cell: | a=7.6547(1) | b=8.3977(2) |
| | alpha=90 | beta=90 |
| | | gamma=90 |
| Temperature: 293 K | | |
| | Calculated | Reported |
| Volume | 1354.66(4) | 1354.66(4) |
| Space group | P 21 21 21 | P 21 21 21 |
| Hall group | P 2ac 2ab | P 2ac 2ab |
| Moiety formula | C14 H10 F3 N3 O | C14 H10 F3 N3 O |
| Sum formula | C14 H10 F3 N3 O | C14 H10 F3 N3 O |
| Mr | 293.25 | 293.25 |
| Dx, g cm ⁻³ | 1.438 | 1.438 |
| Z | 4 | 4 |
| Mu (mm ⁻¹) | 1.058 | 1.058 |
| F000 | 600.0 | 600.0 |
| F000' | 602.34 | |
| h, k, lmax | 9, 10, 25 | 9, 10, 25 |
| Nref | 2411 [1421] | 2394 |
| Tmin, Tmax | 0.699, 0.760 | 0.590, 1.000 |
| Tmin' | 0.585 | |
| Correction method= # Reported T Limits: Tmin=0.590 Tmax=1.000 AbsCorr = MULTI-SCAN | | |
| Data completeness= | 1.68/0.99 | Theta(max)= 67.073 |
| R(reflections)= | 0.0302(2283) | wR2(reflections)= 0.0842(2394) |
| S = | 1.082 | Npar= 191 |

Figure S1 Crystallographic data for the structures provided

5. References

[1] (a) H. Wang, L. Zhang, Y. Tu, R. Xiang, Y.-L. Guo, J. Zhang. *Angew. Chem. Int. Ed.*, 2018, **57**, 15787; (b) X. Su, W. Zhou, Y. Li, J. Zhang, *Angew. Chem. Int. Ed.* 2015, **54**, 6874; *Angew. Chem.* 2015, **127**, 6978; (c) W. Zhou, X. Su, M. Tao, C. Zhu, Q. Zhao, J. Zhang, *Angew. Chem. Int. Ed.* 2015, **54**, 14853; *Angew. Chem.* 2015, **127**, 15066; (d) W. Zhou, P. Chen, M. Tao, X. Su, Q. Zhao, J. Zhang, *Chem. Commun.* 2016, **52**, 7612; (e) P. Chen, X. Su, W. Zhou, Y. Xiao, J. Zhang, *Tetrahedron* 2016, **72**, 2700; (f) T. Yamazaki, T. Kawasaki-Takasuka, A. Furuta, S. Sakamoto, *Tetrahedron*, 2009, **65**, 5945.

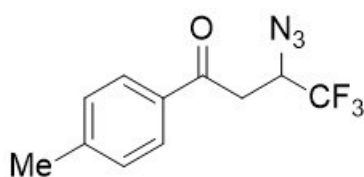
6. Characterization data of products.



(**2a**) 3-azido-4,4,4-trifluoro-1-phenylbutan-1-one

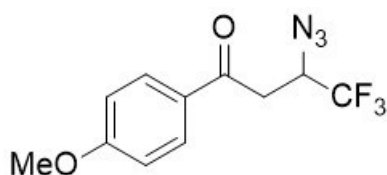
The reaction of (*E*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one (***E*-1a**, 0.2 mmol, 40.0 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature give **2a** as colorless oil (eluent: petroleum ether/ethyl acetate = 15:1); 44.3 mg, 91% yield.

The reaction of (*Z*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one (***Z*-1a**, 0.2 mmol, 40.0 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2a** as colorless oil (silica gel, petroleum ether/ethyl acetate = 15:1); 29.7 mg, yield 61%.
¹H NMR (400 MHz, CDCl₃) δ 8.00-7.93 (m, 2H), 7.63 (dd, J = 10.6, 4.2 Hz, 1H), 7.50 (t, J = 7.6 Hz, 2H), 4.74-4.54 (m, 1H), 3.31 (ddd, J = 20.2, 17.9, 6.1 Hz, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -75.38; ¹³C NMR (101 MHz, CDCl₃) δ 194.30, 135.87, 134.10, 128.93, 128.22, 124.87 (q, J = 280.8 Hz), 58.26 (q, J = 31.0 Hz), 37.29; HRMS (EI): Exact mass calcd for C₁₀H₇F₃NO [M-N₂-H]⁺ = 214.0480, Found 214.0482.



(**2b**) 3-azido-4,4,4-trifluoro-1-(p-tolyl)butan-1-one

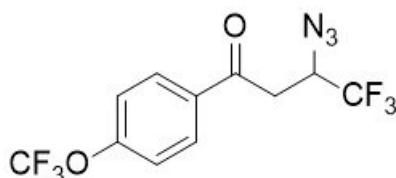
The reaction of (*E*)-4,4,4-trifluoro-1-(p-tolyl)but-2-en-1-one (**1b**, 0.2 mmol, 42.8 mg), and TMSN₃ (0.4 mmol, 46.1 mg) in acetone (1 mL) at 0 °C to give **2b** as colorless oil (silica gel, petroleum ether/ethyl acetate = 15:1); 47.5 mg, 92% yield
¹H NMR (400 MHz, CDCl₃) δ 7.86 (d, J = 8.0 Hz, 1H), 7.29 (d, J = 8.0 Hz, 1H), 4.71-4.53 (m, 1H), 3.28 (ddd, J = 19.6, 17.8, 5.9 Hz, 2H), 2.43 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -75.34; ¹³C NMR (101 MHz, CDCl₃) δ 193.80, 145.11, 133.36, 129.67, 129.53, 128.93, 128.27, 124.83 (q, J = 280.7 Hz), 58.21 (q, J = 31.0 Hz), 37.04, 21.62; HRMS (EI): Exact mass calcd for C₁₁H₉F₃NO [M-N₂-H]⁺ = 228.0636, Found 228.0638.



(2c) 3-azido-4,4,4-trifluoro-1-(4-methoxyphenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(4-methoxyphenyl)but-2-en-1-one (**1c**, 0.2 mmol, 46.1 mg), and TMSN₃ (0.4 mmol, 46.1 mg) in acetone (1 mL) at 0 °C to give **2c** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 54.0 mg, 99% yield.

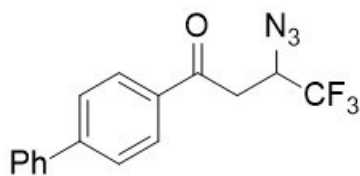
¹H NMR (400 MHz, CDCl₃) δ 7.94 (d, *J* = 8.8 Hz, 2H), 6.96 (d, *J* = 8.8 Hz, 2H), 4.77-4.49 (m, 1H), 3.88 (s, 3H), 3.26 (ddd, *J* = 19.8, 17.7, 6.1 Hz, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -75.34; ¹³C NMR (101 MHz, CDCl₃) δ 192.59, 164.27, 131.24, 130.50, 128.86, 124.85 (q, *J* = 280.7 Hz), 114.03, 77.32, 77.00, 76.68, 58.25 (q, *J* = 30.9 Hz), 55.49, 36.76; HRMS (ESI): Exact mass calcd for C₁₁H₁₀F₃N₃NaO₂ [M+Na]⁺ = 296.0617, found 296.0619.



(2d) 3-azido-4,4,4-trifluoro-1-(4-(trifluoromethoxy)phenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(4-(trifluoromethoxy)phenyl)but-2-en-1-one (**1d**, 0.2 mmol, 56.9 mg), and TMSN₃ (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2d** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 58.5 mg, 89% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.05–8.01 (m, 2H), 7.33 (d, *J* = 8.1 Hz, 2H), 4.69–4.60 (m, 1H), 3.29 (ddd, *J* = 20.4, 17.9, 6.2 Hz, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -57.71, -75.46; ¹³C NMR (126 MHz, CDCl₃) δ 192.86, 153.34 (d, *J* = 1.7 Hz), 133.86, 130.28, 124.70 (q, *J* = 280.7 Hz), 120.24 (q, *J* = 259.3 Hz), 120.57 (d, *J* = 0.6 Hz), 58.10 (q, *J* = 31.1 Hz), 37.28; HRMS (EI): Exact mass calcd for C₁₁H₆F₆N₂O₂ [M-N₂-H]⁺ = 298.0303, Found 298.0305.

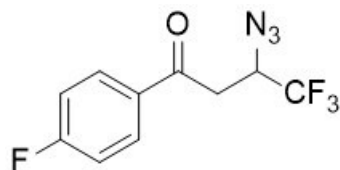


(2e) 1-([1,1'-biphenyl]-4-yl)-3-azido-4,4,4-trifluorobutan-1-one

The reaction of (*E*)-1-([1,1'-biphenyl]-4-yl)-4,4,4-trifluorobut-2-en-1-one (**1e**, 0.2 mmol, 55.3 mg), and TMSN₃ (0.4 mmol, 46.1 mg) in acetone (1 mL) at 0 °C to give **2e** (silica gel, petroleum ether/ethyl acetate = 15:1) as white powder; 57.0 mg, 97% yield.

¹H NMR (400 MHz, CDCl₃) δ 8.03 (d, *J* = 8.4 Hz, 2H), 7.75-7.66 (m, 2H), 7.64-7.61 (m, 2H), 7.44 (dt, *J* = 25.4, 7.2 Hz, 3H), 4.75-4.56 (m, 1H), 3.33 (ddd, *J* = 20.2, 17.8, 6.1 Hz, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -75.29; ¹³C NMR (101 MHz, CDCl₃) δ 193.80, 146.81, 139.51, 134.44, 129.41, 129.01, 128.77, 128.50, 127.57, 127.46,

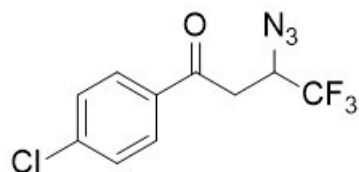
127.27, 124.82 (q, J = 280.7 Hz), 58.23 (q, J = 31.0 Hz), 37.24; HRMS (ESI): Exact mass calcd for C₁₆H₁₂F₃N₃NaO [M+Na]⁺ = 342.0825, found 342.0823.



(2f) 3-azido-4,4,4-trifluoro-1-(4-fluorophenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(4-fluorophenyl)but-2-en-1-one (**1f**, 0.2 mmol, 43.7 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2f** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 39 mg, 89% yield.

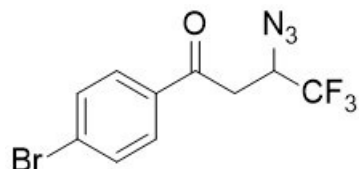
¹H NMR (400 MHz, CDCl₃) δ 8.08-7.93 (m, 2H), 7.18 (t, J = 8.5 Hz, 2H), 4.75-4.57 (m, 1H), 3.28 (ddd, J = 20.1, 17.8, 6.1 Hz, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -75.39, -103.16; ¹³C NMR (101 MHz, CDCl₃) δ 192.69, 167.61, 165.06, 132.27, 130.96, 130.86, 124.76 (q, J = 280.7 Hz), 116.21, 115.99, 58.19 (q, J = 31.0 Hz), 37.17; HRMS (EI): Exact mass calcd for C₁₀H₆F₄NO [M-N₂-H]⁺ = 232.0386, Found 232.0384.



(2g) 3-azido-1-(4-chlorophenyl)-4,4,4-trifluorobutan-1-one

The reaction of (*E*)-1-(4-chlorophenyl)-4,4,4-trifluorobut-2-en-1-one (**1g**, 0.2 mmol, 44.7 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2g** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 44.6 mg, 88.6% yield.

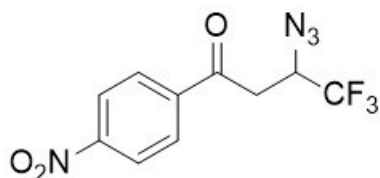
¹H NMR (400 MHz, CDCl₃) δ 7.91 (d, J = 8.5 Hz, 2H), 7.48 (d, J = 8.5 Hz, 2H), 4.65-4.62 (m, 1H), 3.27 (ddd, J = 20.2, 17.8, 6.1 Hz, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -75.38; ¹³C NMR (101 MHz, CDCl₃) δ 193.11, 140.73, 134.11, 130.14, 129.55, 129.26, 124.73 (q, J = 280.7 Hz), 58.15 (q, J = 31.1 Hz), 37.23; HRMS (EI): Exact mass calcd for C₁₀H₇ClF₃N₃O[M]⁺ = 277.0230, Found 277.0232.



(2h) 3-azido-1-(4-bromophenyl)-4,4,4-trifluorobutan-1-one

The reaction of (*E*)-1-(4-bromophenyl)-4,4,4-trifluorobut-2-en-1-one (**1h**, 0.2 mmol, 55.8 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2h** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 54.9 mg, 92.7% yield.

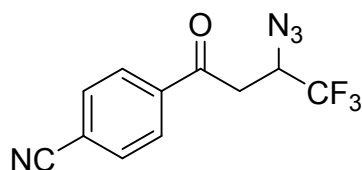
^1H NMR (400 MHz, CDCl_3) δ 7.83 (d, $J = 8.6$ Hz, 2H), 7.65 (d, $J = 8.6$ Hz, 2H), 4.64 (ddd, $J = 9.6, 7.1, 2.4$ Hz, 1H), 3.27 (ddd, $J = 20.4, 17.9, 6.2$ Hz, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ -75.36; ^{13}C NMR (101 MHz, CDCl_3) δ 193.32, 134.48, 132.26, 129.60, 129.46, 124.71 (d, $J = 280.7$ Hz), 58.12 (q, $J = 31.1$ Hz), 37.21; HRMS (EI): Exact mass calcd for $\text{C}_{10}\text{H}_6\text{BrF}_3\text{NO}$ $[\text{M}-\text{N}_2-\text{H}]^+ = 291.9585$, Found 291.9583.



(2i) 3-azido-4,4,4-trifluoro-1-(4-nitrophenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(4-nitrophenyl)but-2-en-1-one (**1i**, 0.2 mmol, 49.0 mg) and TMSN_3 (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2i** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 21.7 mg, 41% yield.

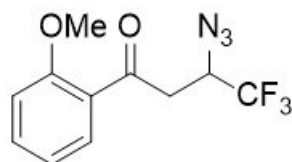
^1H NMR (400 MHz, CDCl_3) δ 8.36 (d, $J = 8.7$ Hz, 2H), 8.15 (d, $J = 8.7$ Hz, 2H), 4.66 (ddd, $J = 9.4, 7.0, 2.4$ Hz, 1H), 3.36 (qd, $J = 18.0, 6.1$ Hz, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ -75.35; ^{13}C NMR (101 MHz, CDCl_3) δ 193.03, 150.93, 139.98, 129.28, 124.12, 124.60 (q, $J = 280.7$ Hz), 77.32, 77.00, 76.68, 58.05 (q, $J = 31.3$ Hz), 37.86; HRMS (EI): Exact mass calcd for $\text{C}_{10}\text{H}_6\text{F}_3\text{N}_2\text{O}_3$ $[\text{M}-\text{N}_2-\text{H}]^+ = 259.0331$, Found 259.0333.



(2j) 4-(3-azido-4,4,4-trifluorobutanoyl)benzonitrile

The reaction of (*E*)-4-(4,4,4-trifluorobut-2-enoyl)benzonitrile (**1j**, 0.2 mmol, 45.0 mg) and TMSN_3 (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2j** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 21.5 mg, 44% yield.

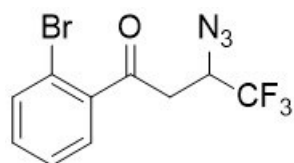
^1H NMR (400 MHz, CDCl_3) δ 8.11-8.04 (m, 2H), 7.90-7.80 (m, 2H), 4.65 (ddd, $J = 9.6, 7.0, 2.6$ Hz, 1H), 3.32 (ddd, $J = 20.7, 18.0, 6.2$ Hz, 1H); ^{19}F NMR (376 MHz, CDCl_3) δ -75.42; ^{13}C NMR (126 MHz, CDCl_3) δ 193.21, 138.45, 132.73, 128.58, 127.78, 124.56 (q, $J = 280.8$ Hz), 57.96 (q, $J = 31.3$ Hz), 37.60; HRMS (EI): Exact mass calcd for $\text{C}_{11}\text{H}_6\text{F}_3\text{N}_2\text{O}$ $[\text{M}-\text{N}_2-\text{H}]^+ = 239.0432$, Found 239.0434.



(2l) 3-azido-4,4,4-trifluoro-1-(2-methoxyphenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(2-methoxyphenyl)but-2-en-1-one (**1l**, 0.2 mmol, 46.1 mg) and TMSN_3 (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2l** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 48.9 mg, 99% yield.

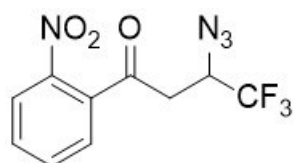
^1H NMR (400 MHz, CDCl_3) δ 7.84 (dd, $J = 7.7, 1.6$ Hz, 1H), 7.59-7.44 (m, 1H), 7.02 (dd, $J = 18.1, 8.0$ Hz, 2H), 4.60 (td, $J = 7.4, 4.9$ Hz, 1H), 3.93 (s, 3H), 3.47-3.27 (m, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ -75.35; ^{13}C NMR (101 MHz, CDCl_3) δ 195.45, 159.18, 134.80, 130.82, 126.19, 124.88 (q, $J = 280.7$ Hz), 120.87, 111.69, 58.20 (q, $J = 30.7$ Hz), 55.48, 42.31; HRMS (EI): Exact mass calcd for $\text{C}_{10}\text{H}_9\text{F}_3\text{NO}_2$ $[\text{M}-\text{N}_2-\text{H}]^+$ = 244.0662, Found 244.0660.



(2m) 3-azido-1-(2-bromophenyl)-4,4,4-trifluorobutan-1-one

The reaction of (*E*)-1-(2-bromophenyl)-4,4,4-trifluorobut-2-en-1-one (**1m**, 0.2 mmol, 55.8 mg) and TMSN_3 (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2m** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 53.1 mg, 82% yield.

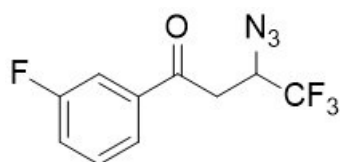
^1H NMR (400 MHz, CDCl_3) δ 7.65 (dd, $J = 7.9, 1.0$ Hz, 1H), 7.48 (dd, $J = 7.6, 1.8$ Hz, 1H), 7.38 (dtd, $J = 17.1, 7.4, 1.5$ Hz, 2H), 4.90-4.22 (m, 1H), 3.32-3.27 (m, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ -75.31; ^{13}C NMR (101 MHz, CDCl_3) δ 197.74, 139.67, 134.12, 132.61, 129.03, 127.66, 124.57 (d, $J = 281.0$ Hz), 119.01, 58.13 (q, $J = 31.2$ Hz), 40.94; HRMS (EI): Exact mass calcd for $\text{C}_{10}\text{H}_6\text{BrF}_3\text{NO}$ $[\text{M}-\text{N}_2-\text{H}]^+$ = 291.9672, Found 291.9674.



(2n) 3-azido-4,4,4-trifluoro-1-(2-nitrophenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(2-nitrophenyl)but-2-en-1-one (**1n**, 0.2 mmol, 49.0 mg) and TMSN_3 (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2n** (silica gel, petroleum ether/ethyl acetate = 10:1) as yellow oil; 50.5 mg, 96% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.17 (d, $J = 8.2$ Hz, 1H), 7.79 (t, $J = 7.4$ Hz, 1H), 7.69 (dd, $J = 11.5, 4.1$ Hz, 1H), 7.45 (d, $J = 7.5$ Hz, 1H), 4.64 (ddd, $J = 9.4, 6.9, 2.3$ Hz, 1H), 3.18 (ddd, $J = 28.0, 18.0, 6.1$ Hz, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ -75.38; ^{13}C NMR (101 MHz, CDCl_3) δ 196.93, 145.52, 136.43, 134.55, 131.29, 128.63, 127.22, 124.66, 124.44 (q, $J = 281.0$ Hz), 57.85 (q, $J = 31.3$ Hz), 41.23; HRMS (EI): Exact mass calcd for $\text{C}_{10}\text{H}_6\text{F}_3\text{N}_2\text{O}_3$ $[\text{M}-\text{N}_2-\text{H}]^+$ = 259.0331, Found 259.0333.

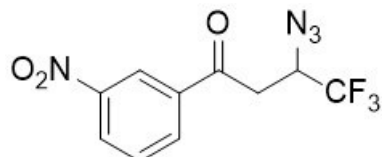


(2o) 3-azido-4,4,4-trifluoro-1-(3-fluorophenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(3-fluorophenyl)but-2-en-1-one (**1o**, 0.2 mmol, 43.7 mg) and TMSN_3 (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2o** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 34.1 mg,

72.5% yield.

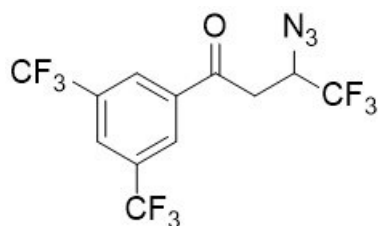
^1H NMR (400 MHz, CDCl_3) δ 7.75 (d, $J = 7.7$ Hz, 1H), 7.66 (d, $J = 9.1$ Hz, 1H), 7.50 (td, $J = 7.9, 5.7$ Hz, 1H), 7.33 (td, $J = 8.1, 2.2$ Hz, 1H), 4.65 (dd, $J = 11.8, 4.7$ Hz, 1H), 3.29 (qd, $J = 17.9, 6.1$ Hz, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ -75.40, -111.00; ^{13}C NMR (101 MHz, CDCl_3) δ 193.18, 193.16, 164.19, 161.71, 137.77 (d, $J = 6.3$ Hz), 130.64 (d, $J = 7.7$ Hz), 124.71 (q, $J = 280.7$ Hz), 123.94 (d, $J = 3.0$ Hz), 121.16 (d, $J = 21.5$ Hz), 120.54, 114.94 (d, $J = 22.6$ Hz), 58.12 (q, $J = 31.1$ Hz), 37.46; HRMS (EI): Exact mass calcd for $\text{C}_{10}\text{H}_6\text{F}_3\text{NO}$ $[\text{M}-\text{N}_2-\text{H}]^+ = 232.0386$, Found 232.0385.



(2p) 3-amino-4,4,4-trifluoro-1-(3-nitrophenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(3-nitrophenyl)but-2-en-1-one (**1p**, 0.2 mmol, 49.0 mg) and TMSN_3 (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2p** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 40.6 mg, 70% yield.

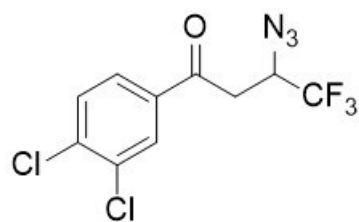
^1H NMR (400 MHz, CDCl_3) δ 8.79 (t, $J = 1.9$ Hz, 1H), 8.50 (ddd, $J = 8.2, 2.2, 1.0$ Hz, 1H), 8.33-8.31 (m, 1H), 7.76 (t, $J = 8.0$ Hz, 1H), 4.72-4.64 (m, 1H), 3.38 (ddd, $J = 20.6, 18.0, 6.2$ Hz, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ -75.33; ^{13}C NMR (126 MHz, CDCl_3) δ 192.39, 148.46, 136.76, 133.54, 130.21, 128.20, 124.48 (q, $J = 280.9$ Hz), 122.97, 57.90 (q, $J = 31.2$ Hz), 37.54; HRMS (EI): Exact mass calcd for $\text{C}_{10}\text{H}_6\text{F}_3\text{N}_2\text{O}_3$ $[\text{M}-\text{N}_2-\text{H}]^+ = 259.0331$, Found 259.0330.



(2q) 3-amino-1-(3,5-bis(trifluoromethyl)phenyl)-4,4,4-trifluorobutan-1-one

The reaction of (*E*)-1-(3,5-bis(trifluoromethyl)phenyl)-4,4,4-trifluorobut-2-en-1-one (**1q**, 0.2 mmol, 67.2 mg) and TMSN_3 (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2q** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 53.8 mg, 62.6% yield.

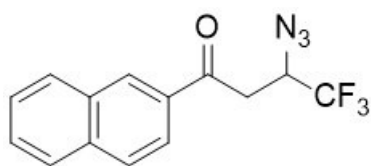
^1H NMR (400 MHz, CDCl_3) δ 8.40 (s, 2H), 8.15 (s, 1H), 4.86-4.54 (m, 1H), 3.36 (ddd, $J = 20.6, 18.0, 6.2$ Hz, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ -63.06, -75.36; ^{13}C NMR (126 MHz, CDCl_3) δ 191.98, 137.10, 132.85 (q, $J = 34.3$ Hz), 128.18 (d, $J = 3.0$ Hz), 127.26 (dd, $J = 7.2, 3.6$ Hz), 125.94, 124.54 (q, $J = 280.9$ Hz), 122.69 (q, $J = 273.4$ Hz), 121.60, 57.97 (q, $J = 31.4$ Hz), 37.65; HRMS (EI): Exact mass calcd for $\text{C}_{12}\text{H}_5\text{F}_3\text{NO}_3$ $[\text{M}-\text{N}_2-\text{H}]^+ = 350.0301$, Found 350.0229.



(2r) 3-amino-1-(3,4-dichlorophenyl)-4,4,4-trifluorobutan-1-one

The reaction of ethyl (*E*)-1-(3,4-dichlorophenyl)-4,4,4-trifluorobut-2-en-1-one (**1r**, 0.2 mmol, 53.8 mg), and TMSN₃ (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2r** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 27.7 mg, 48% yield.

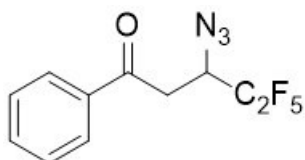
¹H NMR (400 MHz, CDCl₃) δ 8.05 (dd, *J* = 4.4, 2.1 Hz, 1H), 7.79 (ddd, *J* = 8.4, 4.4, 2.1 Hz, 1H), 7.61 (t, *J* = 8.4 Hz, 1H), 4.63 (ddd, *J* = 9.7, 7.0, 2.6 Hz, 1H), 3.26 (ddd, *J* = 20.5, 17.9, 6.2 Hz, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -75.35; ¹³C NMR (126 MHz, CDCl₃) δ 192.29, 138.89, 135.14, 133.78, 131.04, 130.14, 127.10, 124.60 (q, *J* = 280.8 Hz), 58.01 (d, *J* = 31.2 Hz), 37.33; HRMS (ESI): Exact mass calcd. for C₁₀H₆Cl₂F₃N₃NaO [M+Na]⁺ = 333.9732, found 333.9729.



(2s) 3-amino-4,4,4-trifluoro-1-(naphthalen-2-yl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(naphthalen-2-yl)but-2-en-1-one (**1s**, 0.2 mmol, 50.1 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2s** (silica gel, petroleum ether/ethyl acetate = 15:1) as white powder; 53.4 mg, 99% yield.

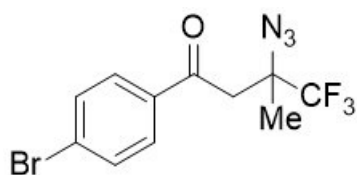
¹H NMR (400 MHz, CDCl₃) δ 8.42 (s, 1H), 8.07-7.77 (m, 2H), 7.59 (dt, *J* = 14.7, 7.0 Hz, 1H), 4.84-4.59 (m, 1H), 3.42 (ddd, *J* = 19.9, 17.8, 6.1 Hz, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -75.25; ¹³C NMR (101 MHz, CDCl₃) δ 194.13, 135.95, 133.08, 132.37, 130.17, 129.63, 129.02, 128.80, 127.83, 127.10, 124.86 (q, *J* = 280.8 Hz), 123.39, 58.28 (q, *J* = 30.9 Hz), 37.24; HRMS (ESI): Exact mass calcd. for C₁₄H₁₀F₃N₃NaO [M+Na]⁺ = 316.0668, found 316.0661.



(2t) 3-azido-4,4,5,5,5-pentafluoro-1-phenylpentan-1-one

The reaction of ethyl (*E*)-4,4,5,5,5-pentafluoro-1-phenylpent-2-en-1-one (**1t**, 0.2 mmol, 50.0 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2t** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 20.9 mg, 39% yield.

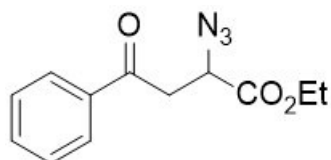
¹H NMR (400 MHz, CDCl₃) δ 8.05-7.94 (m, 2H), 7.67-7.60 (m, 1H), 7.51 (dd, *J* = 10.6, 4.8 Hz, 2H), 4.74 (dt, *J* = 16.4, 8.1 Hz, 1H), 3.38 (ddd, *J* = 20.2, 17.9, 6.1 Hz, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -81.39, -121.85 (dd, *J* = 2130.5, 274.7 Hz); ¹³C NMR (126 MHz, CDCl₃) δ 194.41, 135.69, 134.15, 129.02, 128.91, 128.84, 128.19, 119.86 (t, *J* = 35.6 Hz), 117.59 (t, *J* = 35.3 Hz), 56.93 (dd, *J* = 26.8, 22.5 Hz), 36.59; HRMS (ESI): Exact mass calcd. for C₁₁H₈F₅N₃NaO [M+Na]⁺ = 316.0480, found 316.0480.



(2v) 3-azido-1-(4-bromophenyl)-4,4,4-trifluoro-3-methylbutan-1-one

The reaction of (*E*)-1-(4-chlorophenyl)-4,4,5,5,5-pentafluoropent-2-en-1-one (**1v**, 0.2 mmol, 58.6 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2v** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 20.9 mg, 39% yield.

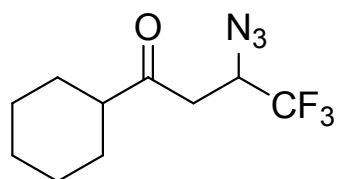
¹H NMR (400 MHz, CDCl₃) δ 7.81 (d, *J* = 8.6 Hz, 2H), 7.63 (d, *J* = 8.6 Hz, 2H), 3.42 (d, *J* = 16.3 Hz, 1H), 3.10 (d, *J* = 16.3 Hz, 1H), 1.75 (s, 3H); ¹⁹F NMR (376 MHz, CDCl₃) δ -80.79; ¹³C NMR (126 MHz, CDCl₃) δ 193.79, 135.49, 132.08, 129.70, 125.45 (q, *J* = 284.6 Hz), 63.21 (q, *J* = 27.8 Hz), 39.84, 16.12; HRMS (ESI): Exact mass calcd. for C₁₁H₉BrF₃N₃NaO [M+Na]⁺ = 357.9773, found 357.9775.



(2x) ethyl 2-amino-4-oxo-4-phenylbutanoate

The reaction of ethyl (*E*)-4-oxo-4-phenylbut-2-enoate (**1x**, 0.2 mmol, 50.1 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2x** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 34.5 mg, 80% yield.

¹H NMR (400 MHz, CDCl₃) δ 7.96 (d, *J* = 7.4 Hz, 2H), 7.60 (t, *J* = 7.4 Hz, 1H), 7.48 (t, *J* = 7.6 Hz, 2H), 4.63-4.60 (m, 1H), 4.29 (q, *J* = 6.9 Hz, 2H), 3.46 (ddd, *J* = 24.8, 17.7, 6.3 Hz, 2H), 1.33 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 195.66, 169.70, 136.08, 133.67, 128.73, 128.10, 62.16, 58.03, 39.98, 14.08; HRMS (ESI): Exact mass calcd. for C₁₂H₁₃N₃NaO₃ [M+Na]⁺ = 270.0849, found 270.0845.

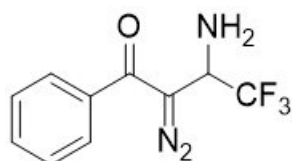


(2y) 3-azido-1-cyclohexyl-4,4,4-trifluorobutan-1-one

The reaction of ethyl (*E*)-1-cyclohexyl-4,4,4-trifluorobut-2-en-1-one (**1y**, 0.2 mmol, 41.2 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in acetone (1 mL) at room temperature to give **2x** (silica gel, petroleum ether/ethyl acetate = 15:1) as yellow oil; 40.4 mg, 81% yield.

¹H NMR (400 MHz, CDCl₃) δ 4.52–4.32 (m, 1H), 2.78 (qd, *J* = 17.9, 6.2 Hz, 2H), 2.47–2.26 (m, 1H), 2.04–1.74 (m, 4H), 1.69 (d, *J* = 10.8 Hz, 1H), 1.48–1.09 (m, 5H). ¹⁹F NMR (376 MHz, CDCl₃) δ -75.59. ¹³C NMR (101 MHz, CDCl₃) δ 208.13, 124.68 (q, *J* = 280.6 Hz), 120.50, 57.76 (q, *J* = 31.0 Hz), 57.29, 50.98, 38.67, 28.14, 28.08,

25.63, 25.41, 25.38. HRMS (ESI): Exact mass calcd. for $C_{10}H_{14}NNaO_3$ $[M-N_2-H]^+ = 22.1106$, found 22.1104.

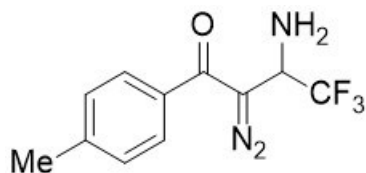


(3a) 3-amino-2-diazo-4,4,4-trifluoro-1-phenylbutan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one (*E*-**1a**, 0.2 mmol, 40.0 mg) and $TMSN_3$ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3a** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 39.4 mg, 81% yield.

The reaction of (*Z*)-4,4,4-trifluoro-1-phenylbut-2-en-1-one (*Z*-**1a**, 0.2 mmol, 40.0 mg) and $TMSN_3$ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3a** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 35.7 mg, 74% yield.

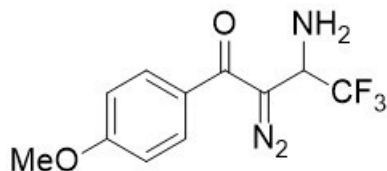
1H NMR (400 MHz, $CDCl_3$) δ 7.64-7.57 (m, 2H), 7.54 (t, $J = 7.4$ Hz, 1H), 7.46 (t, $J = 7.4$ Hz, 2H), 4.75 (q, $J = 6.8$ Hz, 1H), 1.80 (s, 1H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.02; ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.29, 136.71, 132.07, 128.75, 127.14, 126.89, (q, $J = 281.9$ Hz), 67.84, 49.77 (q, $J = 32.3$ Hz); HRMS (ESI): Exact mass calcd. for $C_{10}H_8F_3N_3NaO$ $[M+Na]^+ = 266.0512$, found 266.0512.



(3b) 3-amino-2-diazo-4,4,4-trifluoro-1-(p-tolyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(p-tolyl)but-2-en-1-one (**1b**, 0.2 mmol, 42.8 mg) and $TMSN_3$ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3b** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 39.3 mg, 76% yield.

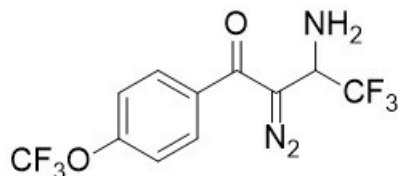
1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, $J = 8.1$ Hz, 2H), 7.33-7.20 (m, 2H), 4.75 (d, $J = 6.5$ Hz, 1H), 2.41 (s, 3H), 1.78 (s, 2H); ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.98; ^{13}C NMR (101 MHz, $CDCl_3$) δ 187.11, 142.81, 134.04, 129.38, 127.30, 125.53 (q, $J = 282.0$ Hz), 67.22, 49.84 (q, $J = 32.1$ Hz), 21.53; HRMS (ESI): Exact mass calcd. for $C_{11}H_{10}F_3N_3NaO$ $[M+Na]^+ = 280.0668$, found 280.0664.



(3c) 3-amino-2-diazo-4,4,4-trifluoro-1-(4-methoxyphenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(4-methoxyphenyl)but-2-en-1-one (**1c**, 0.2 mmol, 46.0 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3c** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 43.5 mg, 80% yield.

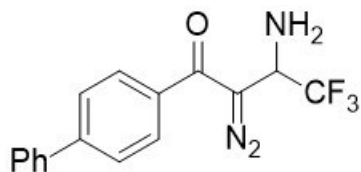
¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 8.6 Hz, 2H), 6.94 (d, *J* = 8.6 Hz, 2H), 4.75 (dd, *J* = 13.4, 6.6 Hz, 1H), 3.86 (s, 3H), 1.79 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -76.94; ¹³C NMR (101 MHz, CDCl₃) δ 186.12, 162.74, 129.41, 129.30, 126.95, 125.55 (q, *J* = 282.0 Hz), 66.69, 55.45, 49.93 (q, *J* = 32.2 Hz); HRMS (ESI): Exact mass calcd. for C₁₁H₁₀F₃N₃NaO₂ [M+Na]⁺ = 296.0617, found 296.0620.



(3d)3-amino-2-diazo-4,4,4-trifluoro-1-(4-(trifluoromethoxy)phenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(4-(trifluoromethyl)phenyl)but-2-en-1-one (**1d**, 0.2 mmol, 56.8 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3d** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 54.0 mg, 83% yield.

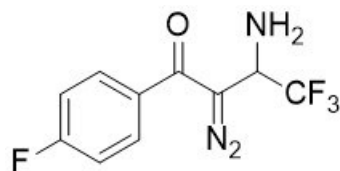
¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.7 Hz, 2H), 7.30 (d, *J* = 8.1 Hz, 2H), 4.73 (d, *J* = 6.6 Hz, 1H), 1.81 (s, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -57.79, -77.12; ¹³C NMR (101 MHz, CDCl₃) δ 185.58, 151.76, 135.01, 129.18, 126.84, 124.04, 120.83, 120.31 (q, *J* = 258.8 Hz), 67.87, 49.82 (q, *J* = 31.8 Hz); HRMS (ESI): Exact mass calcd. for C₁₁H₁₀F₃N₃NaO₂ [M+Na]⁺ = 328.0515, found 328.0511.



(3e)1-([1,1'-biphenyl]-4-yl)-3-amino-2-diazo-4,4,4-trifluorobutan-1-one

The reaction of (*E*)-1-([1,1'-biphenyl]-4-yl)-4,4,4-trifluorobut-2-en-1-one (**1e**, 0.2 mmol, 55.3 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3e** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow solid; 53.8 mg, 84% yield.

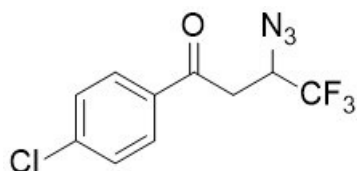
¹H NMR (400 MHz, CDCl₃) δ 7.67 (d, *J* = 8.8 Hz, 4H), 7.60 (d, *J* = 7.8 Hz, 2H), 7.46 (t, *J* = 7.4 Hz, 2H), 7.41-7.37 (m, 1H), 4.77 (d, *J* = 6.6 Hz, 1H), 1.81 (s, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -76.95; ¹³C NMR (101 MHz, CDCl₃) δ 186.78, 145.03, 139.75, 135.40, 128.95, 128.21, 127.80, 127.39, 127.20, 125.52 (q, *J* = 282.1 Hz), 67.53, 49.87 (q, *J* = 32.2 Hz); HRMS (ESI): Exact mass calcd. for C₁₆H₁₂F₃N₃NaO [M+Na]⁺ = 342.0825, found 342.0822.



(3f)3-amino-2-diazo-4,4,4-trifluoro-1-(4-fluorophenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(4-fluorophenyl)but-2-en-1-one (**1f**, 0.2 mmol, 43.7 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) 60 °C to give **3f** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 38.8 mg, 83% yield.

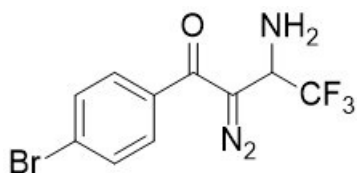
^1H NMR (400 MHz, CDCl_3) δ 7.66-7.63 (m, 2H), 7.15 (t, $J = 8.6$ Hz, 2H), 4.74 (q, $J = 6.9$ Hz, 1H), 1.79 (s, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ -77.05, -106.06; ^{13}C NMR (101 MHz, CDCl_3) δ 185.81, 166.12, 163.60, 132.92, 132.88, 129.71 (d, $J = 9.0$ Hz), 125.46 (q, $J = 281.9$ Hz), 115.99 (d, $J = 22.0$ Hz), 67.50, 49.82 (q, $J = 32.4$ Hz), 29.67; HRMS (ESI): Exact mass calcd. for $\text{C}_{10}\text{H}_8\text{F}_4\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+ = 262.0600$, found 262.0598.



(3g) 3-amino-1-(4-chlorophenyl)-2-diazo-4,4,4-trifluorobutan-1-one

The reaction of (*E*)-1-(4-chlorophenyl)-4,4,4-trifluorobut-2-en-1-one (**1g**, 0.2 mmol, 46.8 mg) and TMSN_3 (0.4 mmol, 46.1 mg) in DMF (1 mL) 60 °C to give **3g** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 41.2 mg, 74% yield.

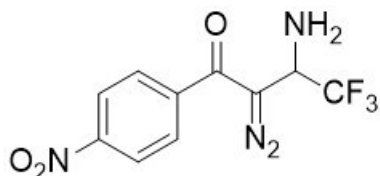
^1H NMR (400 MHz, CDCl_3) δ 7.56 (d, $J = 8.4$ Hz, 2H), 7.44 (d, $J = 8.4$ Hz, 2H), 4.73 (dd, $J = 13.6, 6.7$ Hz, 1H), 1.81 (s, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ -77.04; ^{13}C NMR (101 MHz, CDCl_3) δ 185.90, 138.40, 134.98, 129.13, 128.63, 125.42 (q, $J = 281.9$ Hz), 67.74, 49.78 (q, $J = 32.4$ Hz); HRMS (ESI): Exact mass calcd. for $\text{C}_{10}\text{H}_8\text{ClF}_3\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+ = 278.0303$, found 278.0301.



(3h) 3-amino-1-(4-bromophenyl)-2-diazo-4,4,4-trifluorobutan-1-one

The reaction of (*E*)-1-(4-bromophenyl)-4,4,4-trifluorobut-2-en-1-one (**1h**, 0.2 mmol, 55.9 mg) and TMSN_3 (0.4 mmol, 46.1 mg) in DMF (1 mL) 60 °C to give **3h** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 43.4 mg, 67% yield.

^1H NMR (400 MHz, CDCl_3) δ 7.61 (d, $J = 8.5$ Hz, 2H), 7.48 (d, $J = 8.5$ Hz, 2H), 4.72 (dd, $J = 13.5, 6.7$ Hz, 1H), 1.81 (s, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ -77.04; ^{13}C NMR (101 MHz, CDCl_3) δ 185.99, 135.46, 132.11, 128.75, 125.43 (q, $J = 281.6$ Hz), 67.76, 49.82 (q, $J = 32.3$ Hz); HRMS (ESI): Exact mass calcd. for $\text{C}_{10}\text{H}_8\text{BrF}_3\text{N}_3\text{O}$ $[\text{M}+\text{H}]^+ = 321.9797$, found 321.9790.

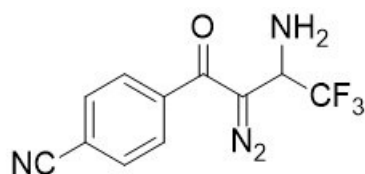


(3i) 3-amino-2-diazo-4,4,4-trifluoro-1-(4-nitrophenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(4-nitrophenyl)but-2-en-1-one (**1i**, 0.2 mmol, 49.1 mg) and TMSN_3 (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3g** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 13.1 mg, 23% yield.

^1H NMR (400 MHz, CDCl_3) δ 8.34 (d, $J = 8.7$ Hz, 2H), 7.78 (d, $J = 8.7$ Hz, 2H), 4.74 (s, 1H), 1.76 (s, 2H); ^{19}F NMR (376 MHz, CDCl_3) δ -77.10; ^{13}C NMR (101 MHz,

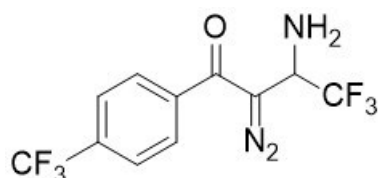
CDCl₃) δ 185.24, 149.84, 141.90, 128.30, 125.31 (q, J = 282.8 Hz). 124.15, 69.05, 49.72 (q, J = 32.2 Hz); HRMS (ESI): Exact mass calcd. for C₁₀H₈F₃N₄O₃ [M+H]⁺ = 289.0539, found 289.0537.



(3j)4-(3-amino-2-diazo-4,4,4-trifluorobutanoyl)benzonitrile

The reaction of (*E*)-4-(4,4,4-trifluorobut-2-enoyl)benzonitrile (**1j**, 0.2 mmol, 45.0 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3j** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 19.1 mg, 36% yield.

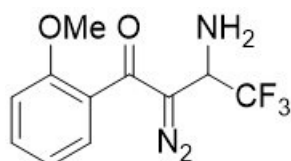
¹H NMR (400 MHz, CDCl₃) δ 7.78 (d, J = 7.9 Hz, 2H), 7.71 (d, J = 7.7 Hz, 2H), 4.73 (s, 1H), 1.79 (s, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -77.10; ¹³C NMR (101 MHz, CDCl₃) δ 185.25, 140.24, 132.70, 127.80, 125.31 (q, J = 282.0 Hz), 117.61, 115.70, 68.60, 49.70 (q, J = 32.3 Hz); HRMS (ESI): Exact mass calcd. for C₁₁H₈F₃N₄O [M+H]⁺ = 269.0626, found 269.0624.



(3k)3-amino-2-diazo-4,4,4-trifluoro-1-(4-(trifluoromethyl)phenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(4-(trifluoromethyl)phenyl)but-2-en-1-one (**1k**, 0.2 mmol, 53.7 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3k** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 30.1 mg, 48% yield.

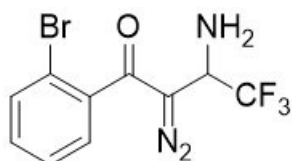
¹H NMR (400 MHz, CDCl₃) δ 7.95 -7.57 (m, 4H), 4.74 (d, J = 5.6 Hz, 1H), 1.81 (s, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.15, -77.12; ¹³C NMR (101 MHz, CDCl₃) δ 185.87, 139.75, 133.73 (q, J = 33.0 Hz), 127.59, 125.39 (q, J = 282.8 Hz), 125.93 (q, J = 3.7 Hz), 124.80, 122.09, 68.40, 49.73 (q, J = 32.4 Hz); HRMS (ESI) m/z calcd. for C₁₁H₈F₆N₃O [M+H]⁺ = 312.0566, found 312.0569.



(3l)3-amino-2-diazo-4,4,4-trifluoro-1-(2-methoxyphenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(2-methoxyphenyl)but-2-en-1-one (**1l**, 0.2 mmol, 46.1 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3l** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 48.2 mg, 88% yield.

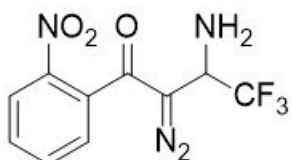
¹H NMR (400 MHz, CDCl₃) δ 7.46-7.38 (m, 2H), 7.02 (t, J = 7.5 Hz, 1H), 6.94 (d, J = 8.4 Hz, 1H), 4.74 (s, 1H), 3.87 (s, 3H), 1.80 (s, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -77.10; ¹³C NMR (101 MHz, CDCl₃) δ 186.68, 156.17, 132.53, 129.40, 125.46 (q, J = 282.8 Hz), 121.14, 111.26, 77.32, 77.00, 76.68, 70.16, 55.80, 49.55 (q, J = 20.2 Hz); HRMS (ESI): Exact mass calcd. for C₁₁H₁₀F₃N₃NaO₂ [M+Na]⁺ = 296.0617, found 296.0612.



(3m)3-amino-1-(2-bromophenyl)-2-diazo-4,4,4-trifluorobutan-1-one

The reaction of (*E*)-1-(2-bromophenyl)-4,4,4-trifluorobut-2-en-1-one (**1m**, 0.2 mmol, 55.8 mg), and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60°C to give **3m** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 42.2mg, 67 yield %.

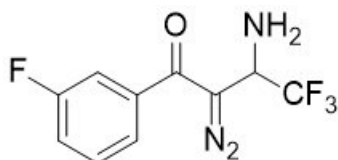
¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, *J* = 7.9 Hz, 1H), 7.47-7.23 (m, 4H), 4.75 (d, *J* = 6.2 Hz, 1H), 1.80 (s, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -76.94; ¹³C NMR (101 MHz, CDCl₃) δ 186.66, 138.49, 133.26, 131.80, 128.31, 127.89, 125.27 (q, *J* = 280.8 Hz), 118.76, 70.43, 49.12 (q, *J* = 30.9 Hz); HRMS (ESI): Exact mass calcd. for C₁₀H₈BrF₃N₃O [M+H]⁺ = 321.9797, found 321.9800.



(3n)3-amino-2-diazo-4,4,4-trifluoro-1-(2-nitrophenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(2-nitrophenyl)but-2-en-1-one (**1n**, 0.2 mmol, 49.0 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60°C to give **3n** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 24.3 mg, 42% yield.

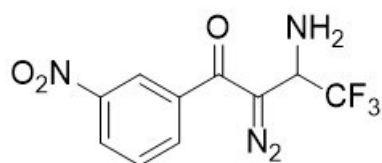
¹H NMR (400 MHz, CDCl₃) δ 8.20 (d, *J* = 8.1 Hz, 1H), 7.78 (t, *J* = 7.3 Hz, 1H), 7.67 (t, *J* = 7.6 Hz, 1H), 7.50 (d, *J* = 7.2 Hz, 1H), 4.77 (d, *J* = 6.7 Hz, 1H), 1.85 (s, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -76.96; ¹³C NMR (101 MHz, CDCl₃) δ 184.80, 145.96, 134.50, 133.24, 131.28, 128.15, 125.24 (q, *J* = 283.7 Hz), 125.05, 69.78, 49.14 (q, *J* = 33.2 Hz); HRMS (ESI): Exact mass calcd. for C₁₀H₇F₃N₄NaO₃ [M+Na]⁺ = 311.0362, found 311.0355.



(3o)3-amino-2-diazo-4,4,4-trifluoro-1-(3-fluorophenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(3-fluorophenyl)but-2-en-1-one (**1o**, 0.2 mmol, 43.7 mg), and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3o** (silica gel, petroleum ether/ethyl acetate = 5:1) as yellow oil; 27.2 mg, 52% yield.

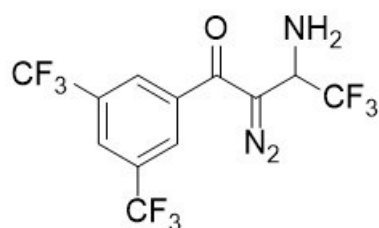
¹H NMR (400 MHz, CDCl₃) δ 7.50-7.37 (m, 2H), 7.31 (d, *J* = 8.8 Hz, 1H), 7.28-7.19 (m, 1H), 4.74 (d, *J* = 6.6 Hz, 1H), 1.80 (s, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -77.08, -110.73; ¹³C NMR (101 MHz, CDCl₃) δ 185.66, 163.93, 161.45, 138.61 (d, *J* = 6.5 Hz), 130.57 (d, *J* = 7.9 Hz), 125.41 (q, *J* = 282.0 Hz), 122.73, 122.70, 119.13 (d, *J* = 21.3 Hz), 114.48 (d, *J* = 22.9 Hz), 68.03, 49.75 (q, *J* = 32.4 Hz); HRMS (ESI): Exact mass calcd. for C₁₀H₇F₄N₃NaO [M+Na]⁺ = 284.0417, found 284.0411.



(3p)3-amino-2-diazo-4,4,4-trifluoro-1-(3-nitrophenyl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(3-nitrophenyl)but-2-en-1-one (**1p**, 0.2 mmol, 49.0 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3p** (silica gel, petroleum ether/ethyl acetate = 5:1) as yellow oil; 27.8 mg, 48% yield.

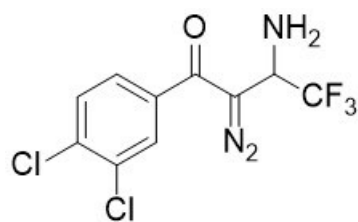
¹H NMR (400 MHz, CDCl₃) δ 8.47 (s, 1H), 8.40 (d, *J* = 8.2 Hz, 1H), 7.95 (d, *J* = 7.6 Hz, 1H), 7.70 (t, *J* = 7.9 Hz, 1H), 4.75 (d, *J* = 5.8 Hz, 1H), 1.84 (s, 1H); ¹⁹F NMR (376 MHz, CDCl₃) δ -77.07; ¹³C NMR (101 MHz, CDCl₃) δ 184.40, 148.33, 137.99, 132.80, 130.18, 126.47, 125.31 (q, *J* = 282.1 Hz), 122.29, 68.62, 49.76 (q, *J* = 32.1 Hz); HRMS (ESI): Exact mass calcd. for C₁₀H₈F₃N₄O₃ [M+H]⁺ = 289.0543, found 289.0541.



(3q)3-amino-1-(3,5-bis(trifluoromethyl)phenyl)-2-diazo-4,4,4-trifluorobutan-1-one

The reaction of (*E*)-1-(3,5-bis(trifluoromethyl)phenyl)-4,4,4-trifluorobut-2-en-1-one (**1q**, 0.2 mmol, 67.2 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3q** (silica gel, petroleum ether/ethyl acetate = 5:1) as yellow oil; 39.8 mg, 53% yield.

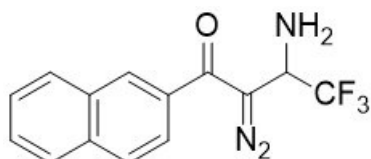
¹H NMR (400 MHz, CDCl₃) δ 8.06 (s, 3H), 4.73 (s, 1H), 1.82 (s, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -63.07, -77.10; ¹³C NMR (101 MHz, CDCl₃) δ 183.76, 138.31, 132.67 (q, *J* = 34.3 Hz), 129.47, 127.45 (d, *J* = 2.7 Hz), 126.71 (d, *J* = 8.2 Hz), 125.46 (d, *J* = 3.6 Hz), 123.95 (d, *J* = 17.0 Hz), 121.32, 68.89, 49.78 (q, *J* = 32.3 Hz); HRMS (ESI): Exact mass calcd. for C₁₂H₉F₆N₃NaO₃ [M+Na]⁺ = 380.0440, found 380.0438.



(3r)3-amino-2-diazo-1-(3,4-dichlorophenyl)-4,4,4-trifluorobutan-1-one

The reaction of ethyl (*E*)-1-(3,4-dichlorophenyl)-4,4,4-trifluorobut-2-en-1-one (**1r**, 0.2 mmol, 53.8 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **2r** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 28.8 mg, 46% yield.

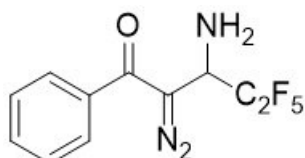
¹H NMR (400 MHz, CDCl₃) δ 7.71 (d, *J* = 1.9 Hz, 1H), 7.55 (d, *J* = 8.3 Hz, 1H), 7.44 (dd, *J* = 8.3, 1.9 Hz, 1H), 4.71 (d, *J* = 6.6 Hz, 1H), 1.79 (s, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -77.06; ¹³C NMR (101 MHz, CDCl₃) δ 184.44, 136.64, 136.20, 133.63, 130.88, 129.39, 126.14, 125.35 (q, *J* = 282.0 Hz), 68.13, 49.76 (q, *J* = 32.4 Hz); HRMS (ESI): Exact mass calcd. for C₁₀H₇Cl₂F₃N₃O [M+H]⁺ = 311.9913, found 311.9913.



(3s)3-amino-2-diazo-4,4,4-trifluoro-1-(naphthalen-2-yl)butan-1-one

The reaction of (*E*)-4,4,4-trifluoro-1-(naphthalen-2-yl)but-2-en-1-one (**1s**, 0.2 mmol, 50.0 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3s** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow powder; 38.2 mg, 65% yield.

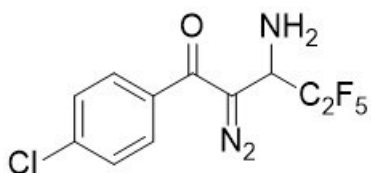
¹H NMR (400 MHz, CDCl₃) δ 8.11 (s, 1H), 7.89 (dd, *J* = 14.9, 8.2 Hz, 3H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.61-7.54 (m, 2H), 4.81 (q, *J* = 6.8 Hz, 1H), 1.82 (s, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -76.90; ¹³C NMR (101 MHz, CDCl₃) δ 187.18, 134.90, 133.99, 132.36, 130.07, 128.96, 128.85, 128.15, 127.86, 127.76, 125.54 (q, *J* = 281.9 Hz), 123.64, 67.84, 49.88 (q, *J* = 31.9 Hz); HRMS (ESI): Exact mass calcd. for C₁₄H₁₀F₃N₃NaO [M+Na]⁺ = 316.0668, found 316.0673.



(3t)3-amino-2-diazo-4,4,5,5,5-pentafluoro-1-phenylpentan-1-one

The reaction of ethyl (*E*)-4,4,5,5,5-pentafluoro-1-phenylpent-2-en-1-one (**1t**, 0.2 mmol, 50.0 mg) and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3t** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 44.4 mg, 76% yield.

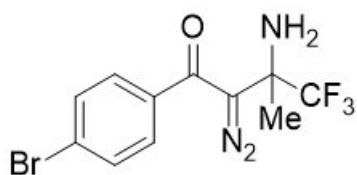
¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, *J* = 7.2 Hz, 2H), 7.54 (t, *J* = 7.4 Hz, 1H), 7.46 (t, *J* = 7.4 Hz, 2H), 4.85 (t, *J* = 13.0 Hz, 1H), 1.80 (s, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -81.67, -123.67, -123.69 (d, *J* = 11.9 Hz); ¹³C NMR (101 MHz, CDCl₃) δ 187.16, 136.63, 132.11, 128.78, 127.11, 120.32 (t, *J* = 35.7 Hz), 118.23-116.66 (m), 114.41 (t, *J* = 36.1 Hz), 112.03 (d, *J* = 36.2 Hz), 67.60, 48.19 (t, *J* = 23.9 Hz); HRMS (ESI): Exact mass calcd. for C₁₁H₈F₅N₃NaO [M+Na]⁺ = 316.0480, found 316.0487.



(3u)3-amino-1-(4-chlorophenyl)-2-diazo-4,4,5,5,5-pentafluoropentan-1-one

The reaction of (*E*)-1-(4-chlorophenyl)-4,4,5,5,5-pentafluoropent-2-en-1-one (**1u**, 0.2 mmol, 49.7 mg), and TMSN₃ (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3u** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 48.4 mg, 74% yield.

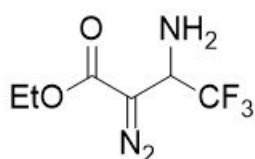
¹H NMR (400 MHz, CDCl₃) δ 7.55 (d, *J* = 8.5 Hz, 2H), 7.45 (d, *J* = 8.5 Hz, 2H), 4.83 (t, *J* = 12.9 Hz, 1H), 1.80 (s, 2H); ¹⁹F NMR (376 MHz, CDCl₃) δ -81.65, -123.68 (d, *J* = 46.9 Hz); ¹³C NMR (101 MHz, CDCl₃) δ 185.79, 138.45, 134.88, 129.15, 128.59, 120.64, 120.28 (t, *J* = 35.7 Hz), 117.52 (d, *J* = 53.3 Hz), 117.43, 116.99 (d, *J* = 18.4 Hz), 114.51 (q, *J* = 36.2 Hz), 111.95 (q, *J* = 35.9 Hz), 67.73, 48.20 (t, *J* = 23.9 Hz); HRMS (ESI): Exact mass calcd. for C₁₁H₈ClF₅N₃O [M+H]⁺ = 328.0271, found 328.0269.



(3v)3-amino-1-(4-bromophenyl)-2-diazo-4,4,4-trifluoro-3-methylbutan-1-one

The reaction of (*E*)-1-(4-chlorophenyl)-4,4,5,5,5-pentafluoropent-2-en-1-one (**1v**, 0.2 mmol, 58.6 mg) and TMSN_3 (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3v** (silica gel, petroleum ether/ethyl acetate = 4:1) as yellow oil; 32.2 mg, 48% yield.

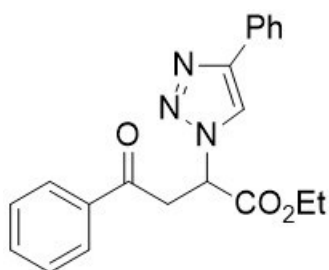
^1H NMR (400 MHz, CDCl_3) δ 7.59 (d, $J = 8.5$ Hz, 2H), 7.45 (d, $J = 8.5$ Hz, 2H), 2.56 (s, 2H), 1.60 (s, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -81.11; ^{13}C NMR (101 MHz, CDCl_3) δ 187.89, 136.19, 132.02, 128.73, 126.82 (q, $J = 286.5$ Hz), 126.56, 68.95, 56.82 (q, $J = 29.8$ Hz), 21.25; HRMS (ESI): Exact mass calcd. for $\text{C}_{11}\text{H}_9\text{BrF}_3\text{N}_3\text{NaO}$ $[\text{M}+\text{Na}]^+ = 357.9773$, found 357.9777.



(3w)ethyl 3-amino-2-diazo-4,4,4-trifluorobutanoate

The reaction of ethyl (*E*)-4,4,4-trifluorobut-2-enoate (**1w**, 0.2 mmol, 34 mg) and TMSN_3 (0.4 mmol, 46.1 mg) in DMF (1 mL) at 60 °C to give **3w** (silica gel, petroleum ether/ethyl acetate = 5:1) as yellow oil; 21.5 mg, 51% yield.

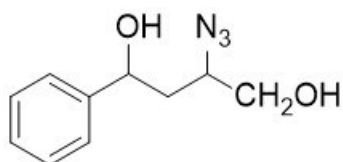
^1H NMR (400 MHz, CDCl_3) δ 4.36 (q, $J = 6.8$ Hz, 1H), 4.26 (q, $J = 7.0$ Hz, 2H), 1.73 (s, 2H), 1.30 (t, $J = 7.1$ Hz, 3H); ^{19}F NMR (376 MHz, CDCl_3) δ -77.65; ^{13}C NMR (101 MHz, CDCl_3) δ 164.92, 129.58, 125.38 (q, $J = 281.9$ Hz), 61.40, 50.10 (q, $J = 32.5$ Hz), 14.36; HRMS (ESI): Exact mass calcd. for $\text{C}_6\text{H}_9\text{F}_3\text{N}_3\text{O}_2$ $[\text{M}+\text{H}]^+ = 212.0641$, found 212.0635.



(4x)ethyl 4-oxo-4-phenyl-2-(4-phenyl-1H-1,2,3-triazol-1-yl)butanoate

2x (0.3 mmol, 1.0 equiv.), Phenylacetylene (2 equiv.), L-ascorbate (16 mg), CuSO_4 (10mg), were dissolved in a mixture of $t\text{BuOH}$ (1 mL) and water (1mL) under the atmosphere of nitrogen. The mixture was then stirred at ambient temperature for 12 hours. After completion, the reaction mixture was extracted with DCM and brine. The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated at a reduced pressure. The residue was purified by flash chromatography with eluent (petroleum ether/ethyl acetate = 4/1) to yield the desired product **4x** as yellow solid, yield 50%.

^1H NMR (400 MHz, CDCl_3) δ 8.02 (s, 1H), 7.87 (d, $J = 7.3$ Hz, 2H), 7.76 (d, $J = 7.3$ Hz, 2H), 7.50 (t, $J = 7.4$ Hz, 1H), 7.34 (dt, $J = 15.0, 7.8$ Hz, 4H), 7.23 (t, $J = 7.4$ Hz, 1H), 5.84 (t, $J = 6.0$ Hz, 1H), 4.23-4.10 (m, 2H), 4.01 (qd, $J = 18.2, 6.1$ Hz, 2H), 1.15 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 195.34, 167.75, 147.46, 135.44, 133.91, 130.15, 128.72, 128.15, 128.11, 125.67, 121.23, 62.60, 58.35, 40.64, 13.85. HRMS (ESI): Exact mass calcd. for $\text{C}_{20}\text{H}_{19}\text{N}_3\text{NaO}_3$ $[\text{M}+\text{Na}]^+ = 372.1319$, found 372.1315.

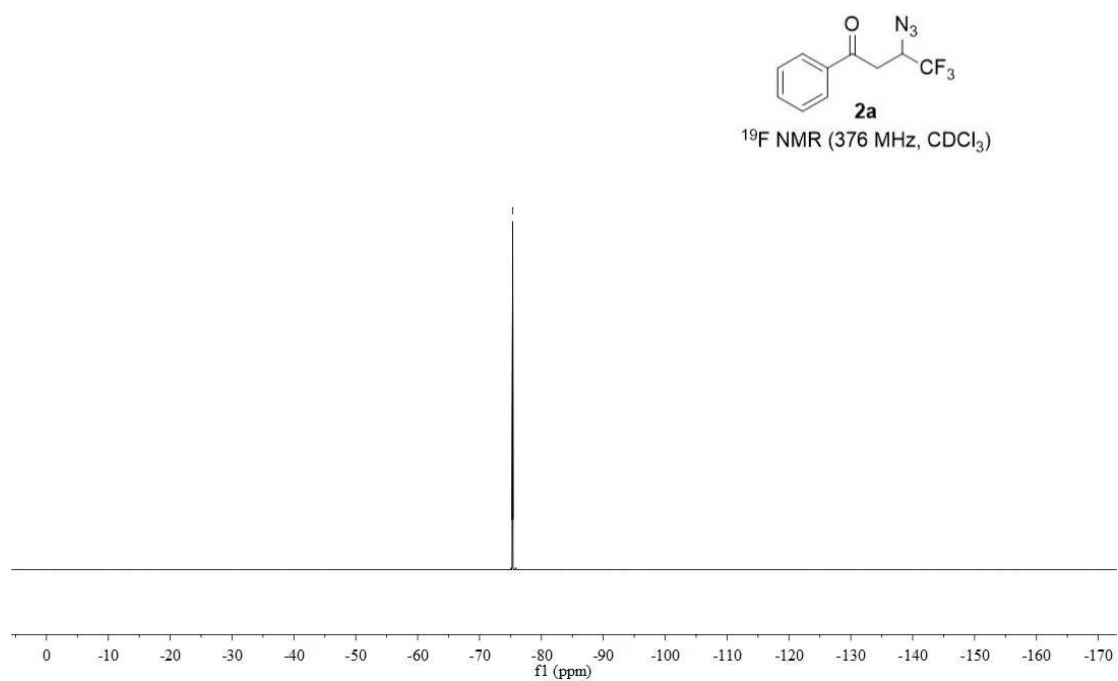
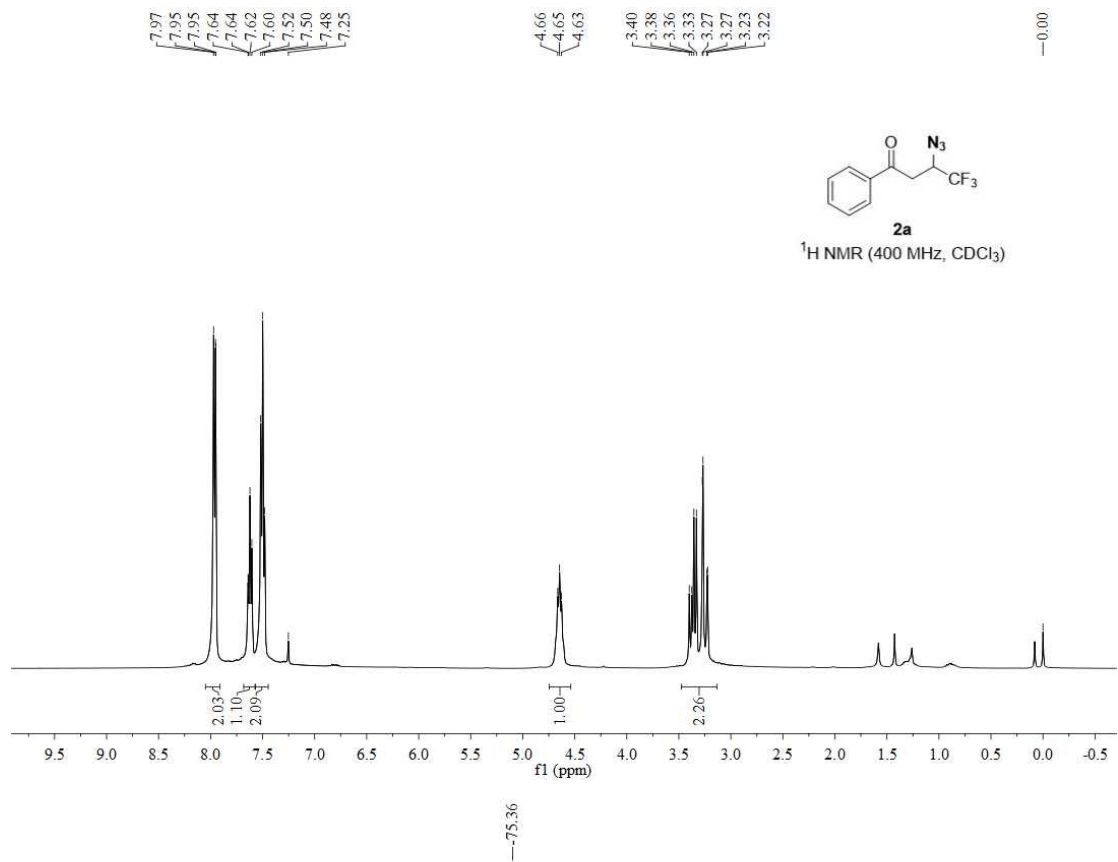


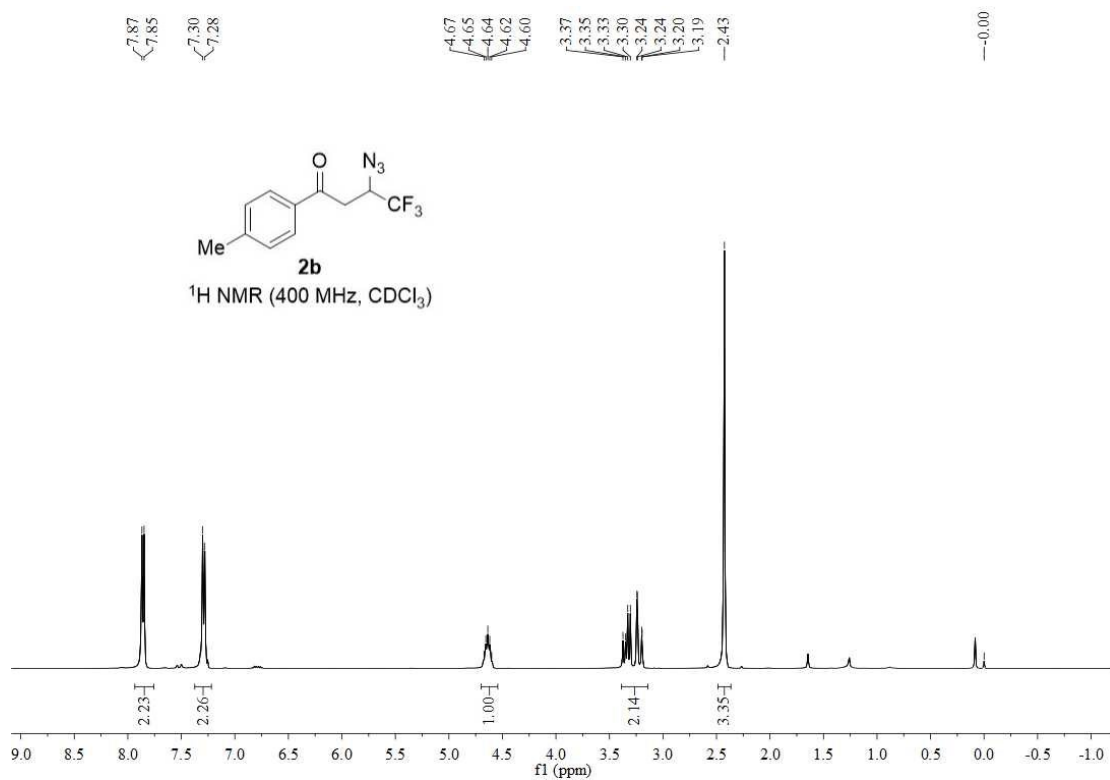
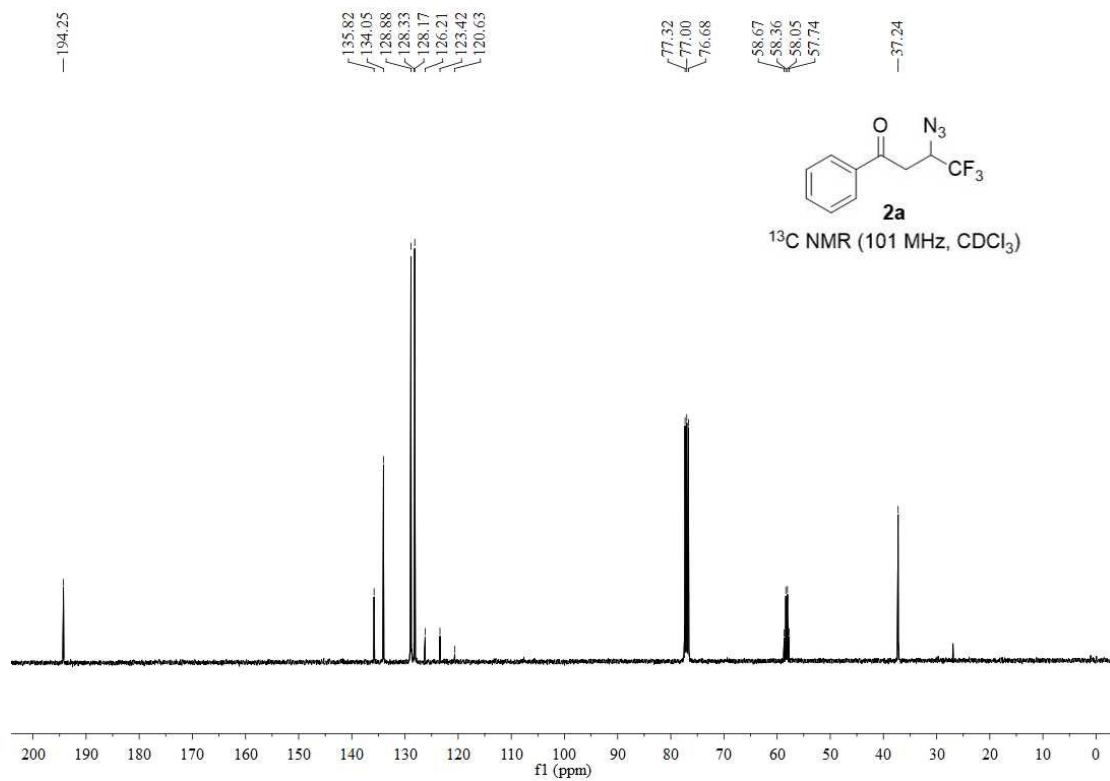
(**5x**)3-azido-1-phenylbutane-1,4-diol

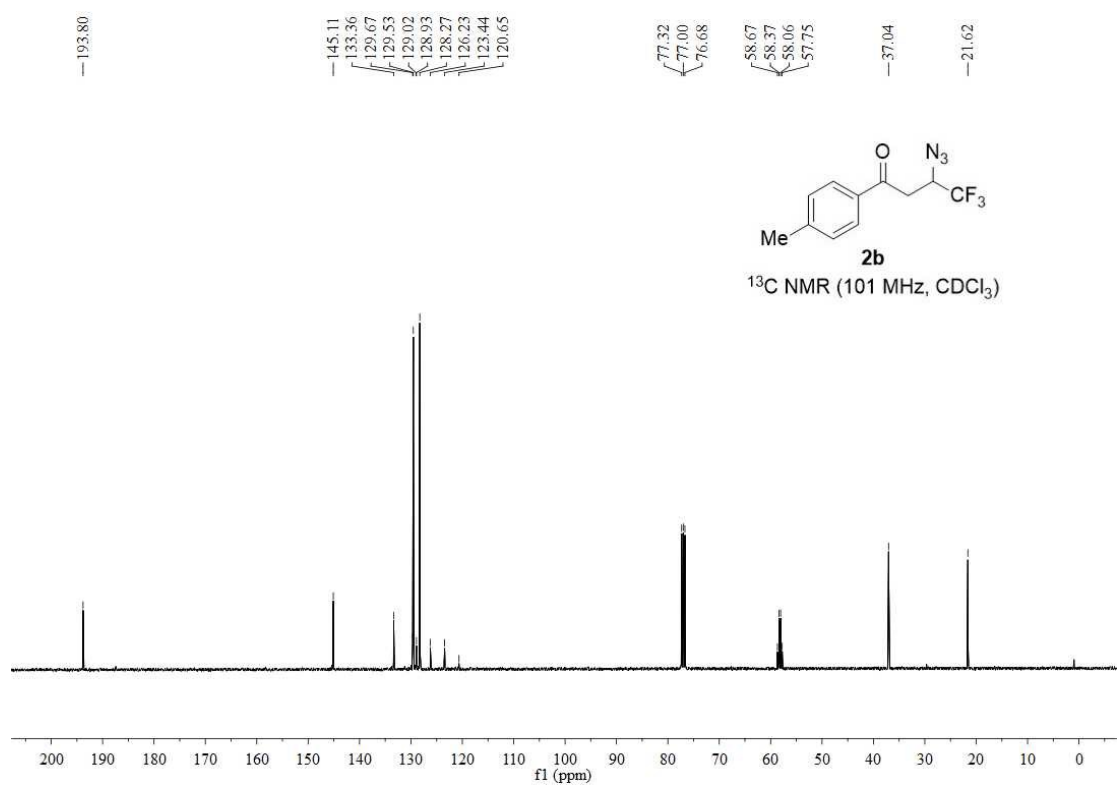
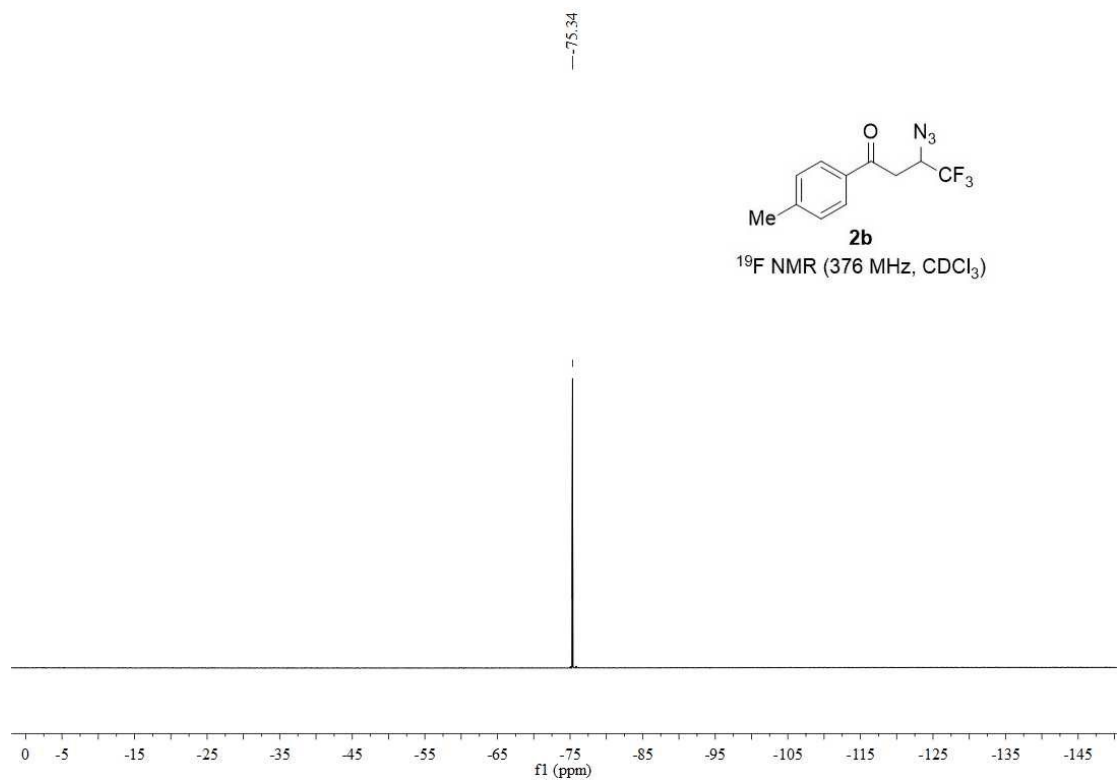
To a flame-dried Schlenk tube were added **2x** (0.2 mmol, 1.0 equiv.), NaBH_4 (2.0 equiv.) and MeOH (1 mL) at 0 °C under the atmosphere of nitrogen. The mixture was stirred at 0 °C for 10 mins. Then the mixture was stirred for 12 h at ambient temperature under the atmosphere of nitrogen. The reaction was quenched with brine and extracted with DCM. The combined organic layers were dried over anhydrous Na_2SO_4 , filtered, and concentrated at a reduced pressure. The residue was purified by flash chromatography with eluent (petroleum ether/ethyl acetate = 3/1) to obtain the product **5x** as Colorless oil yield 99%.

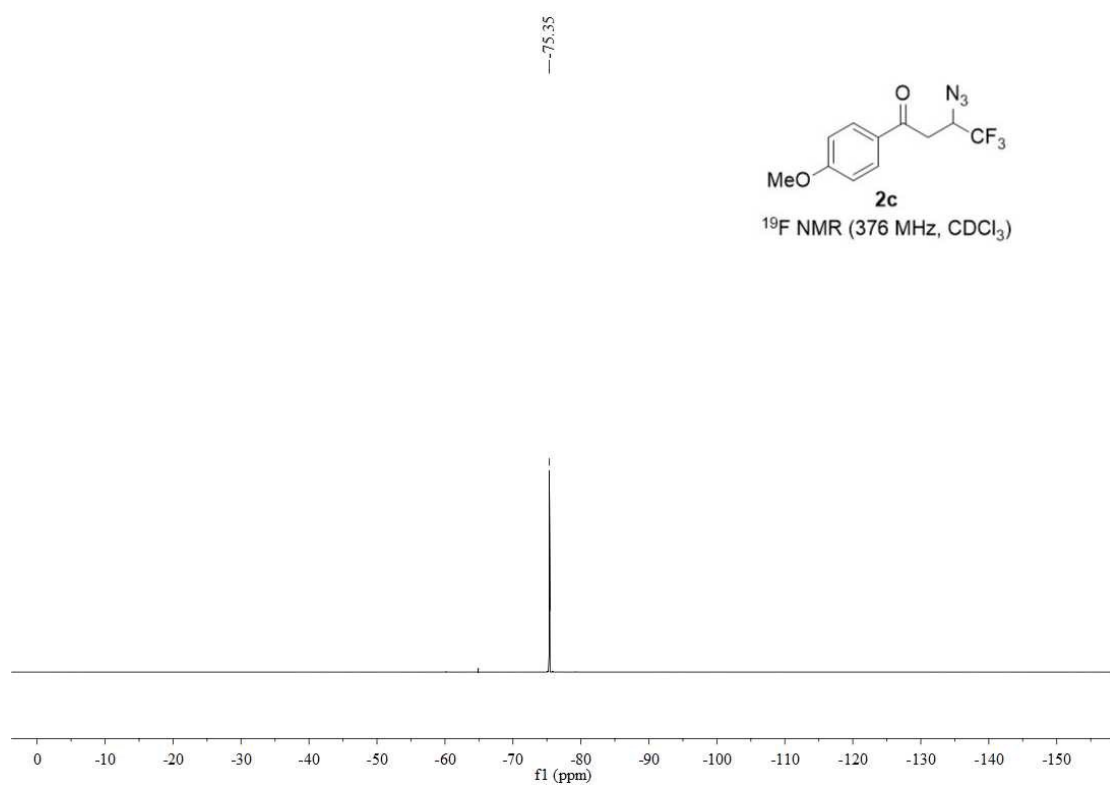
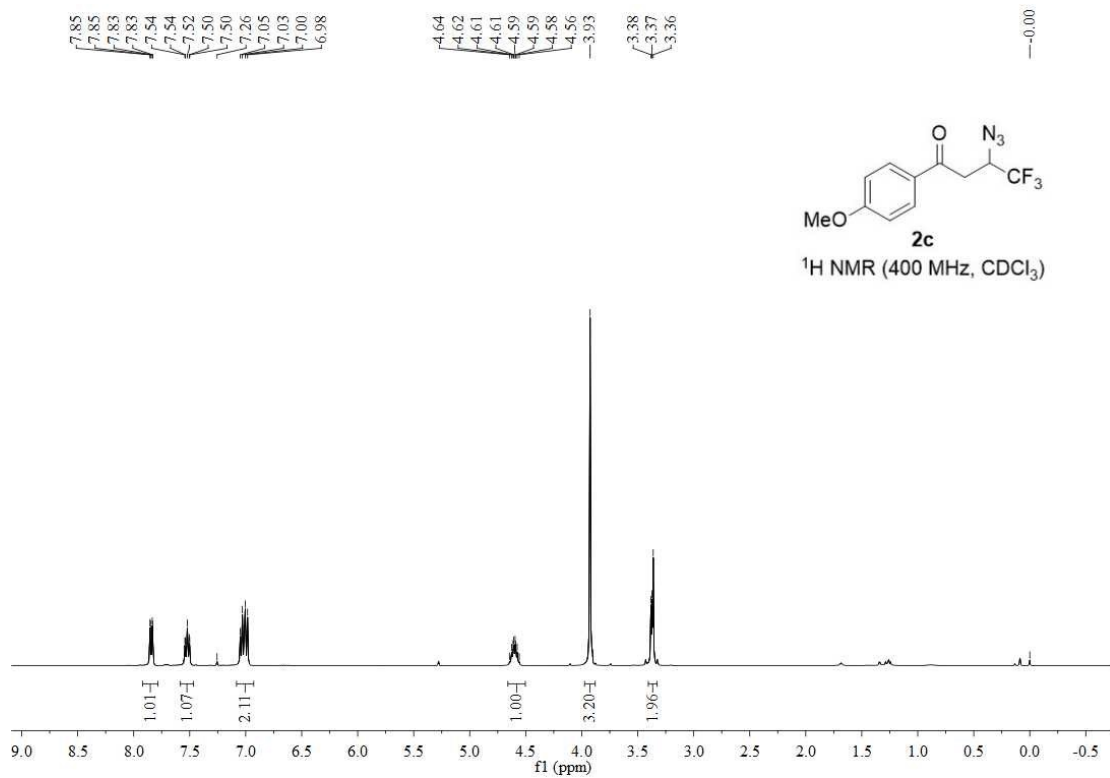
^1H NMR (400 MHz, CDCl_3) δ 7.56–7.18 (m, 5H), 4.81–4.77 (m, 1H), 3.73–3.44 (m, 3H), 2.86 (s, 2H), 2.12–1.46 (m, 2H). ^{13}C NMR (101 MHz, CDCl_3) δ 144.02, 143.38, 128.68, 128.62, 127.96, 127.82, 125.78, 125.48, 77.32, 77.00, 76.68, 71.46, 71.06, 65.46, 64.69, 61.22, 61.14, 40.07, 39.60. HRMS (ESI): Exact mass calcd. for $\text{C}_{10}\text{H}_{13}\text{N}_3\text{NaO}_2$ $[\text{M}+\text{Na}]^+ = 230.0900$, found 230.0890.

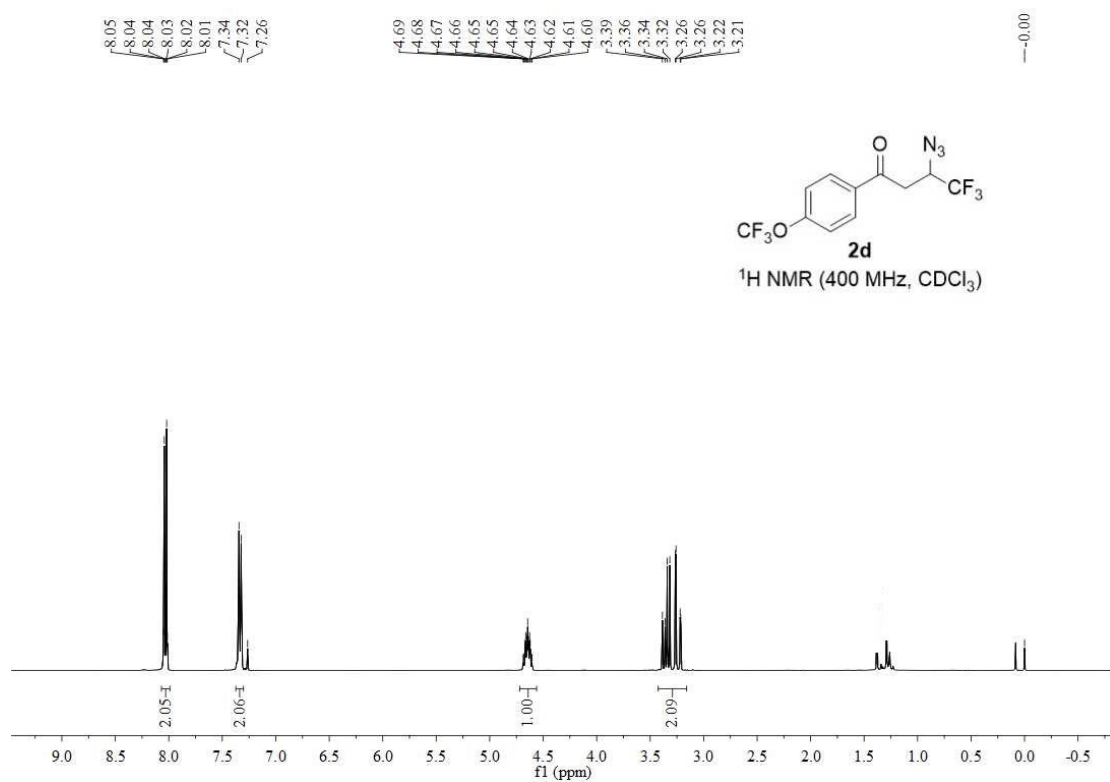
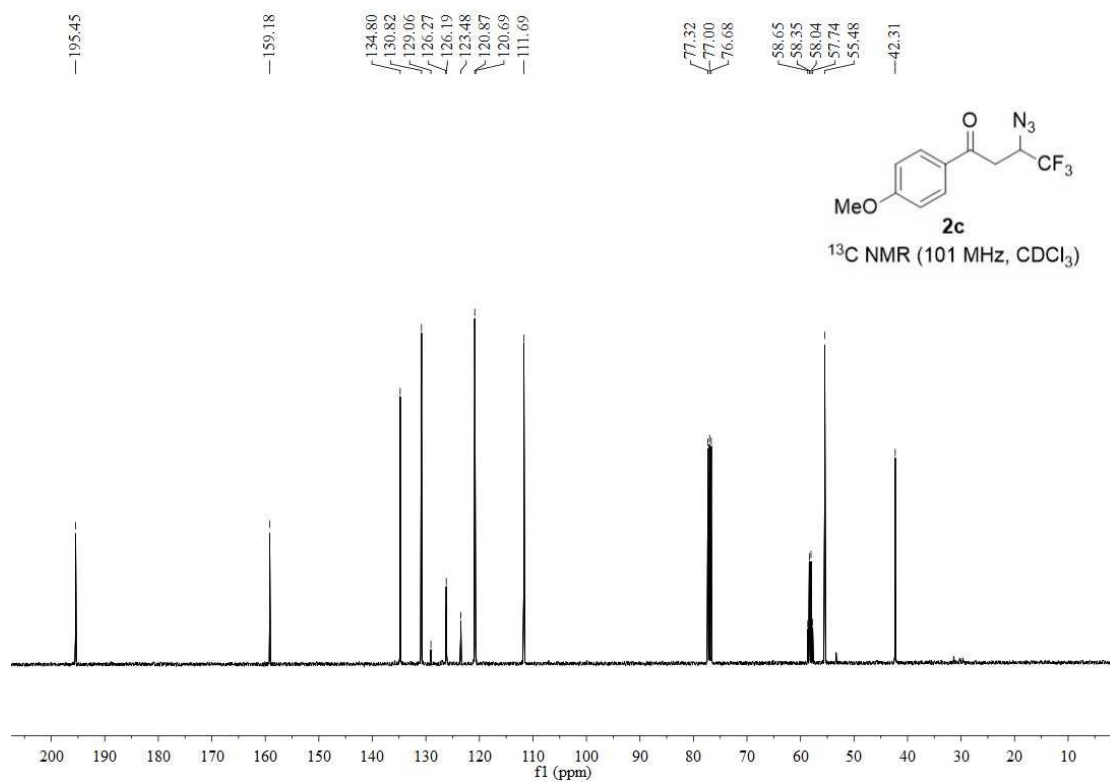
7. ^1H , ^{13}C and ^{19}F NMR Spectra

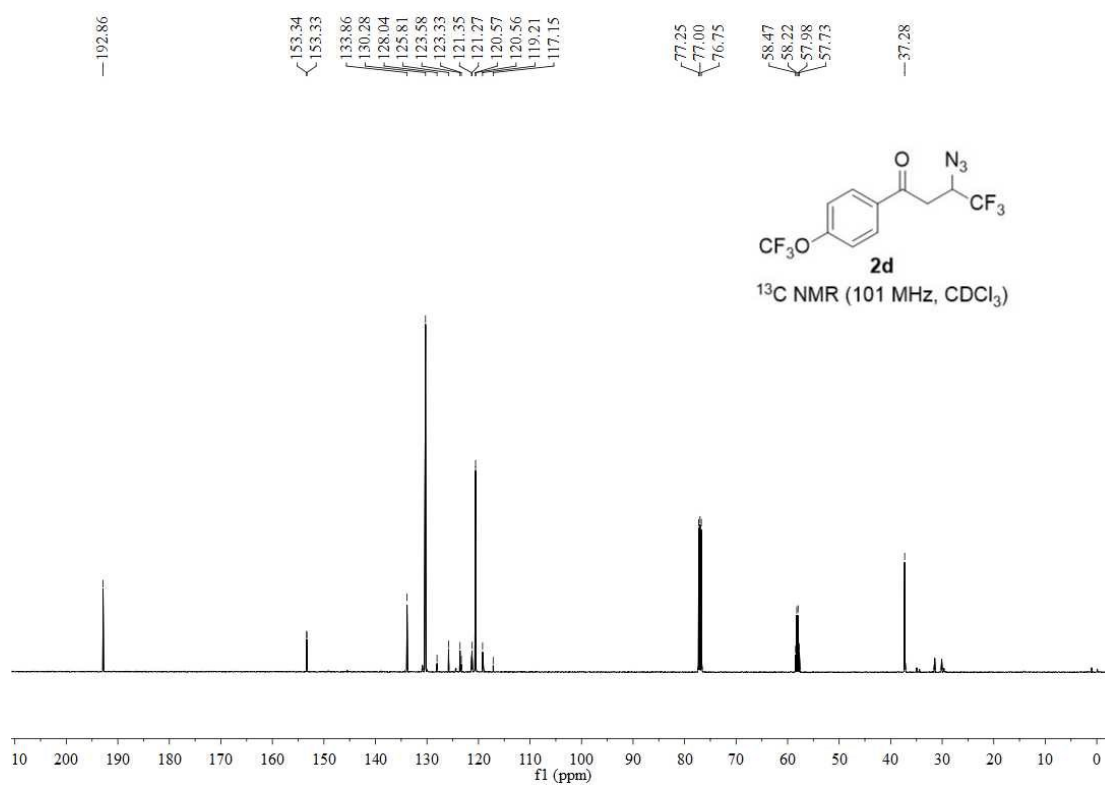
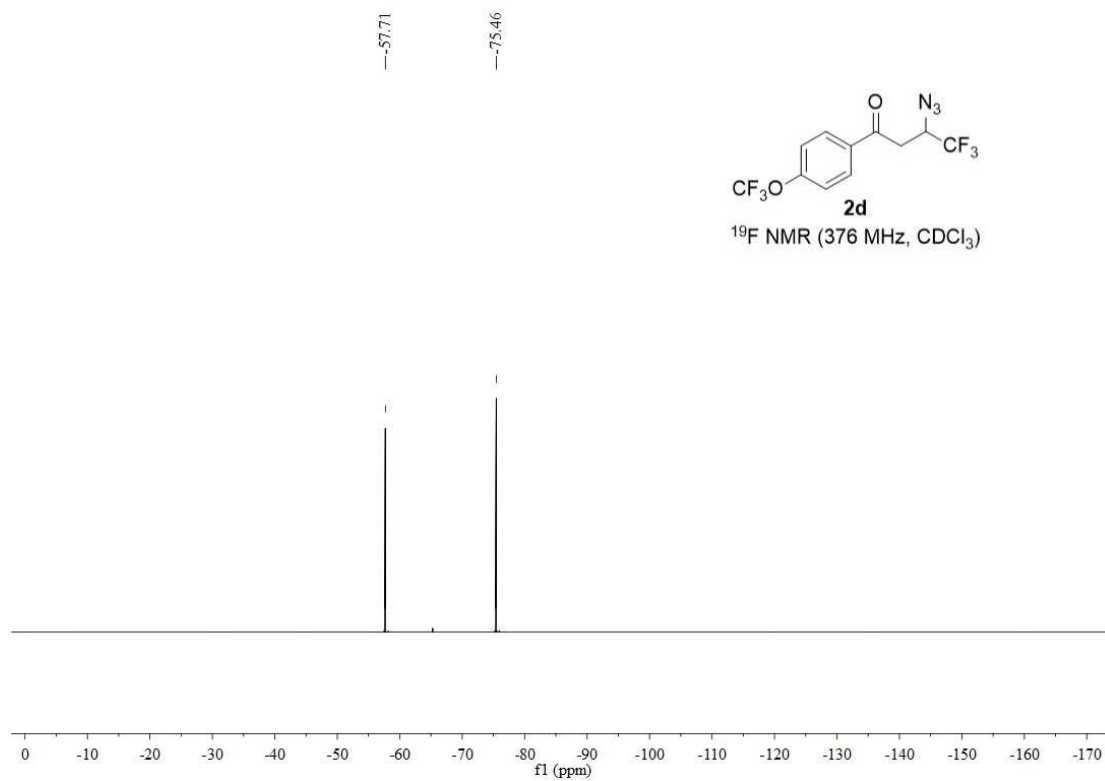


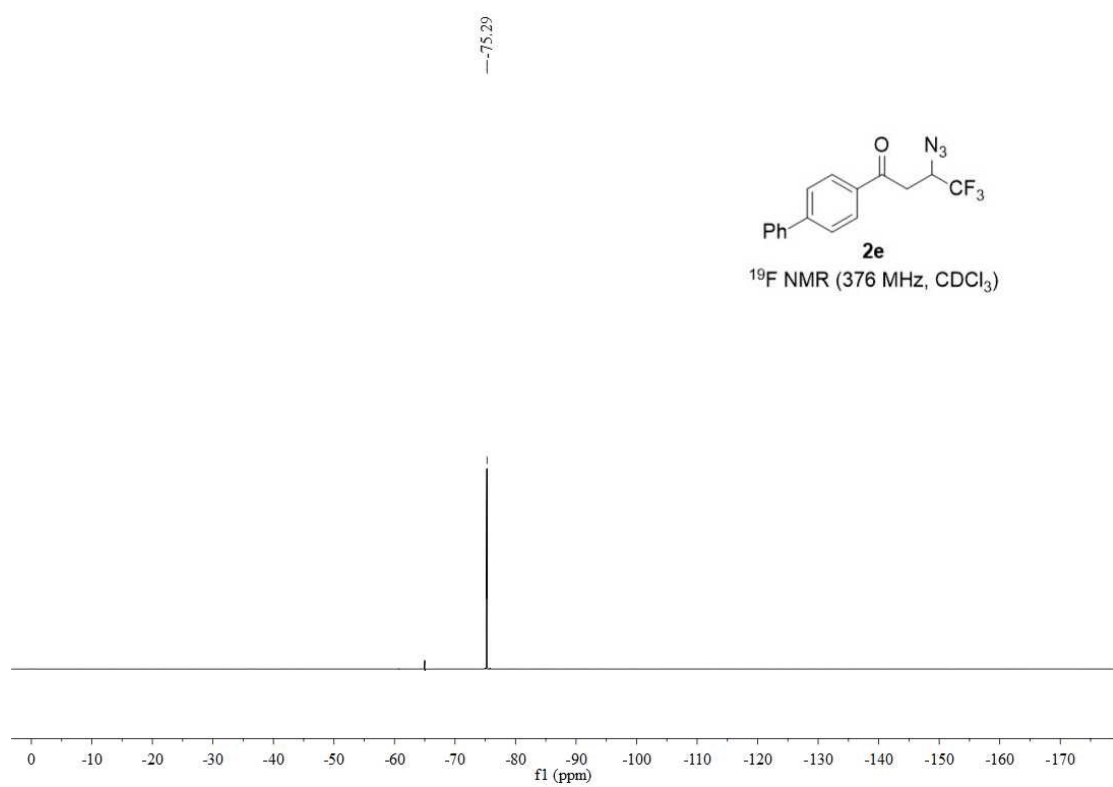
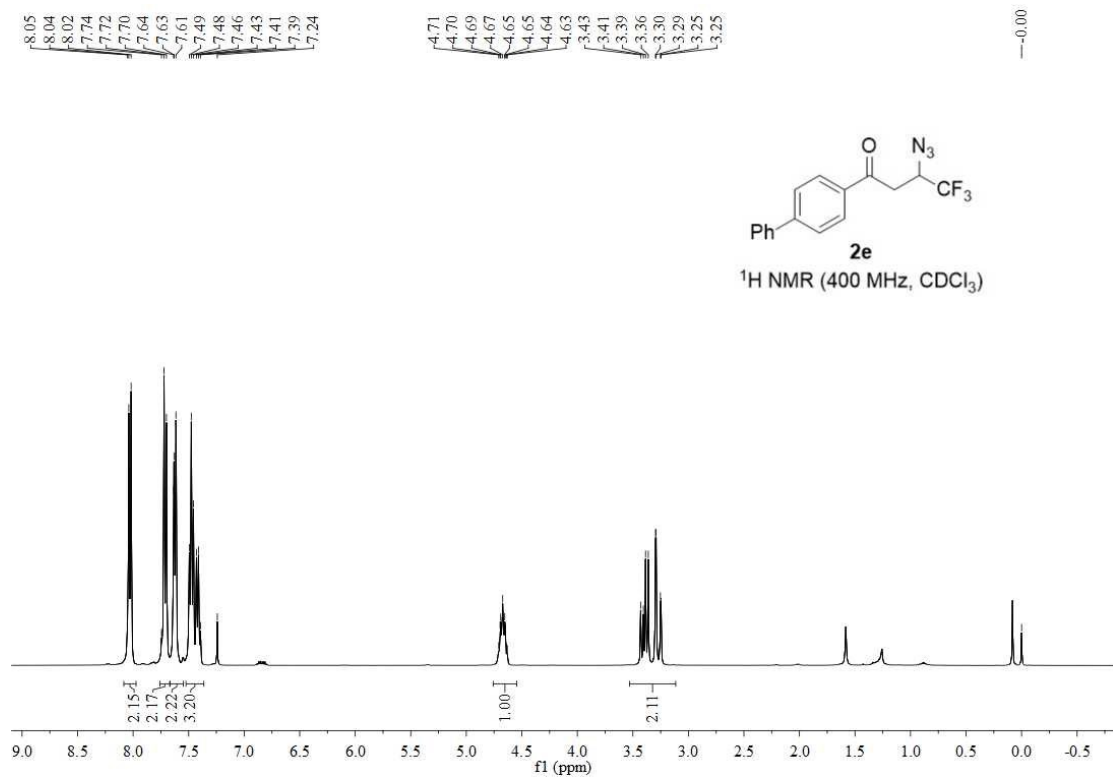


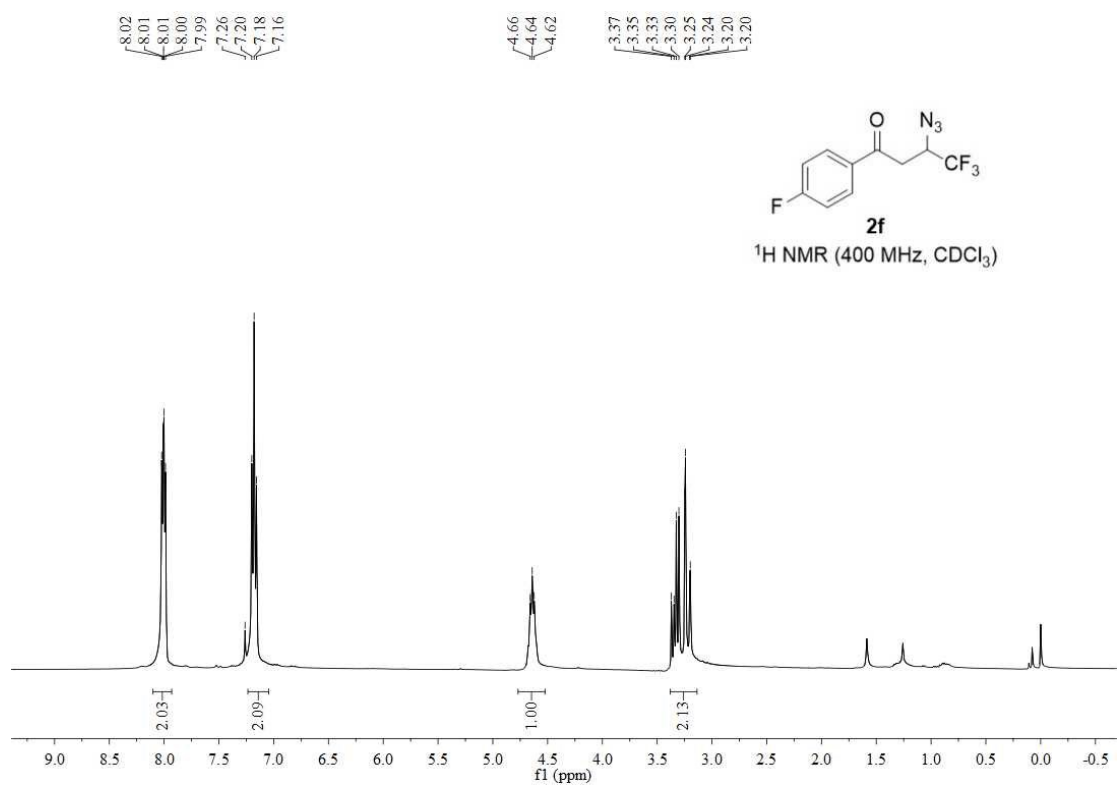
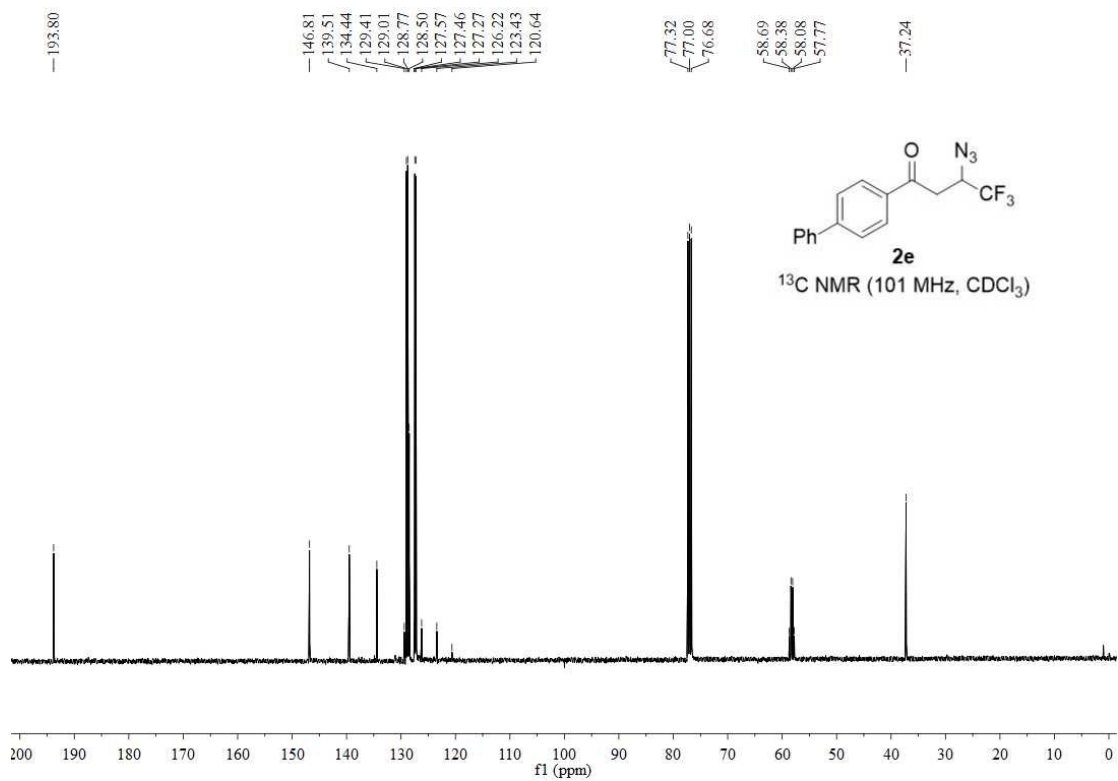


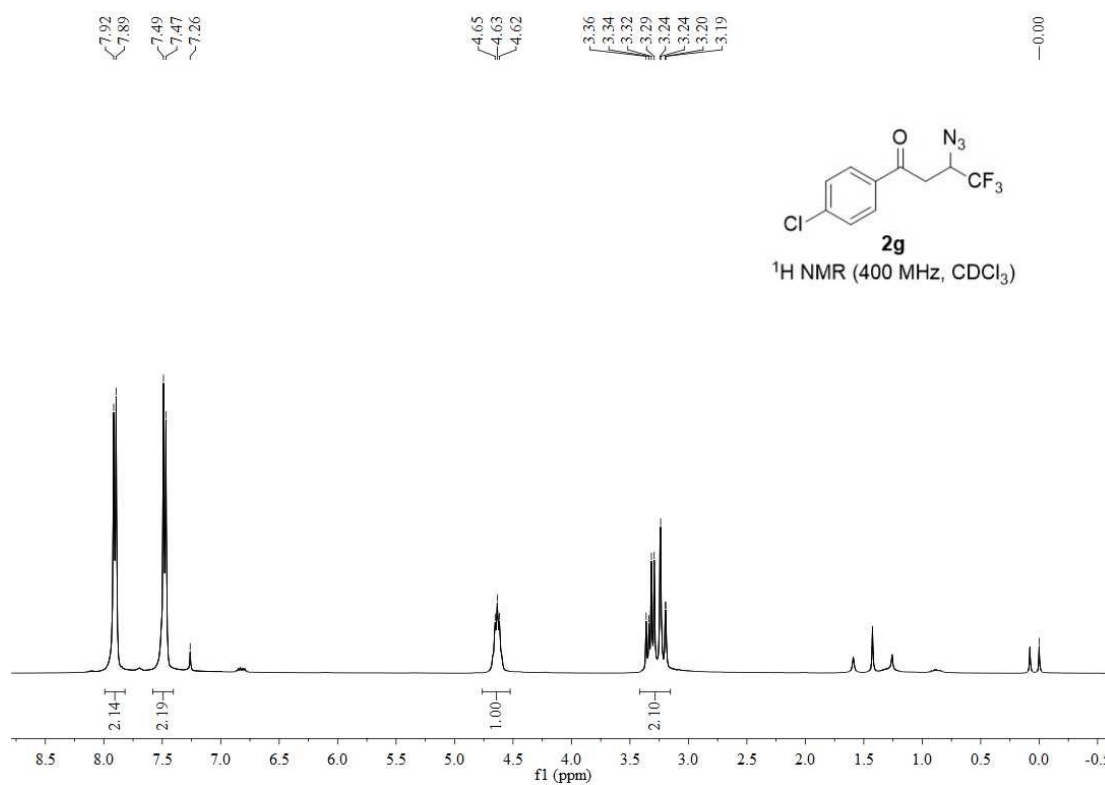
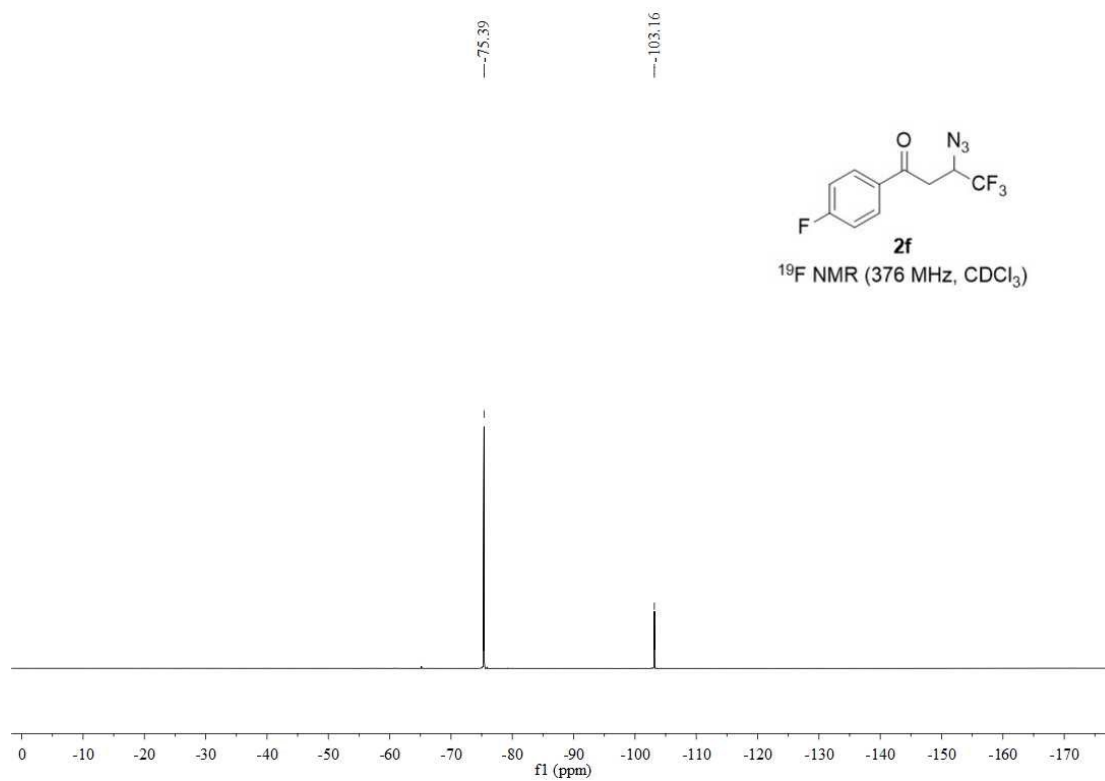


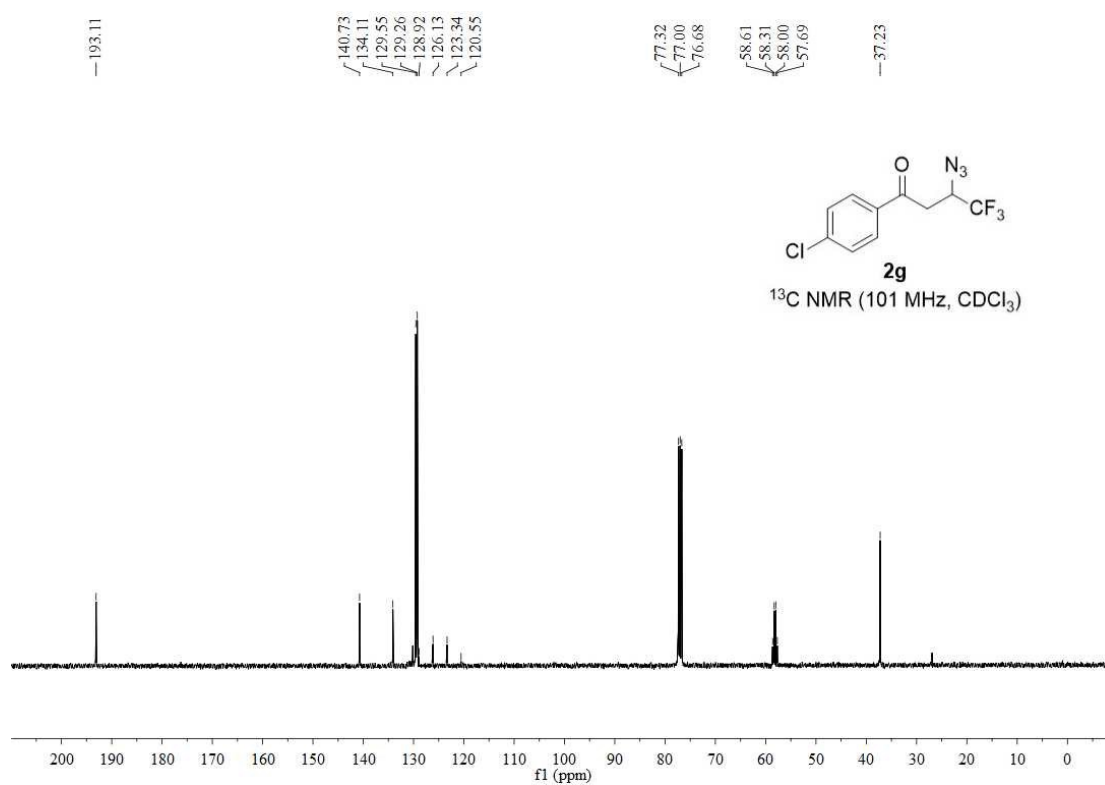
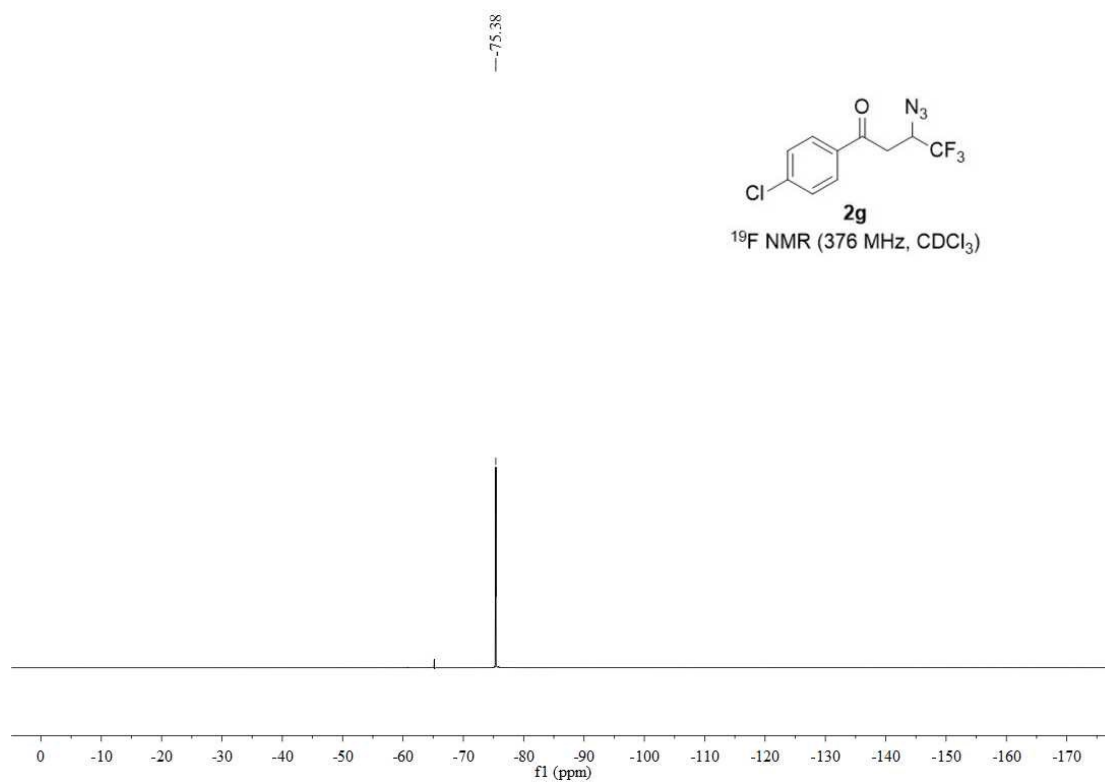










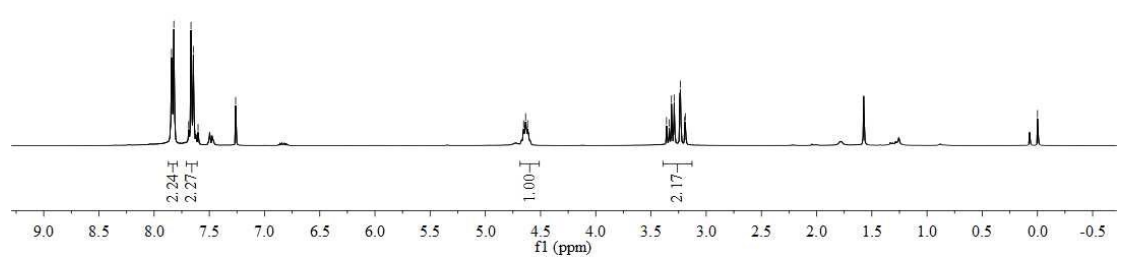


7.84
7.82
7.69
7.67
7.64
7.60
7.26

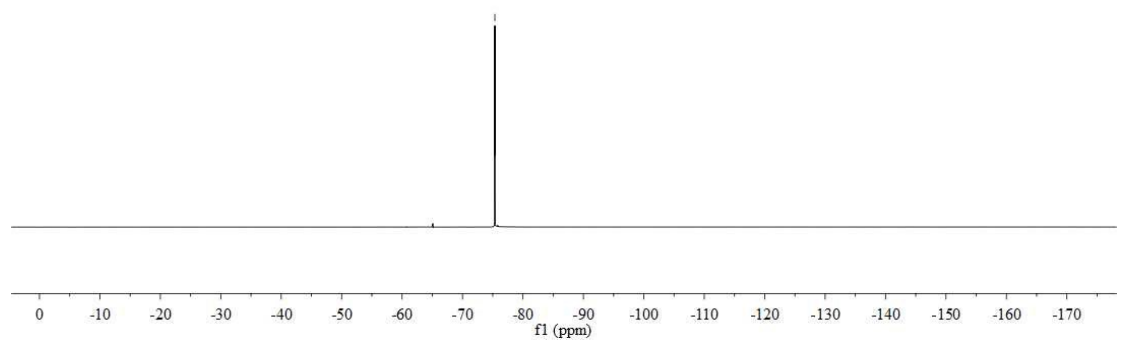
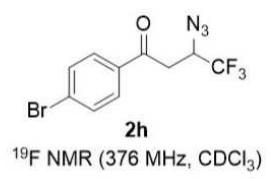
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4.64
4.62

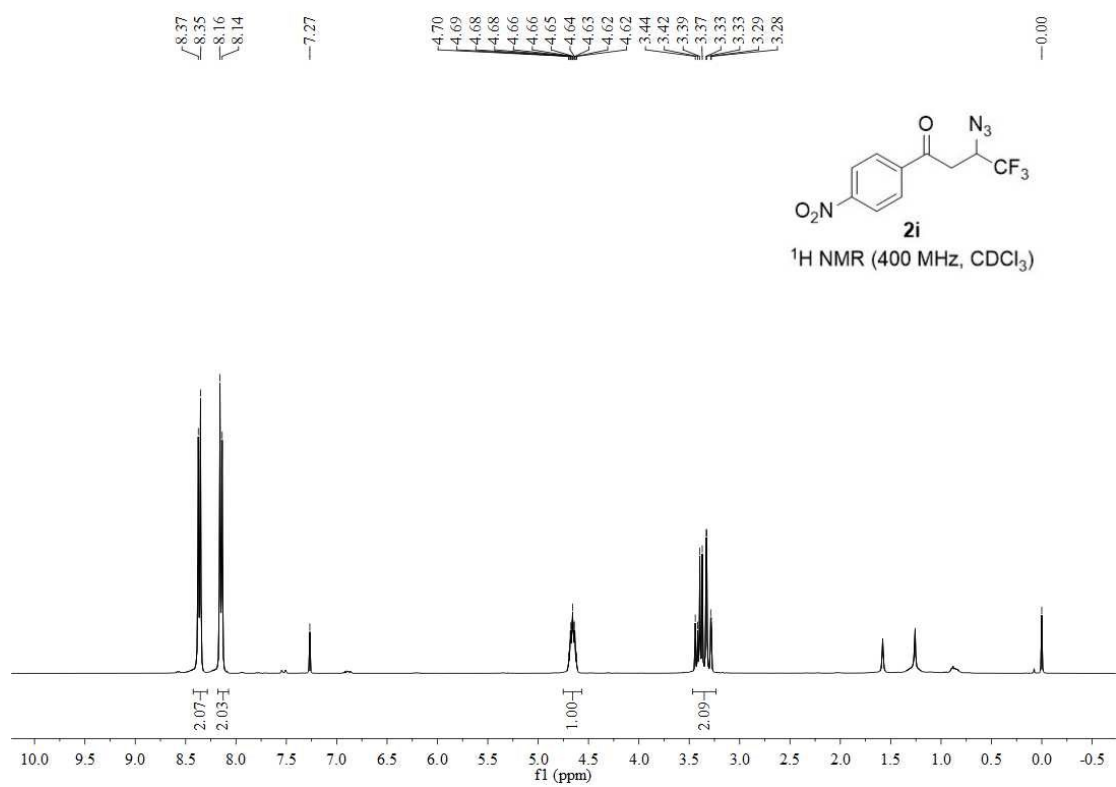
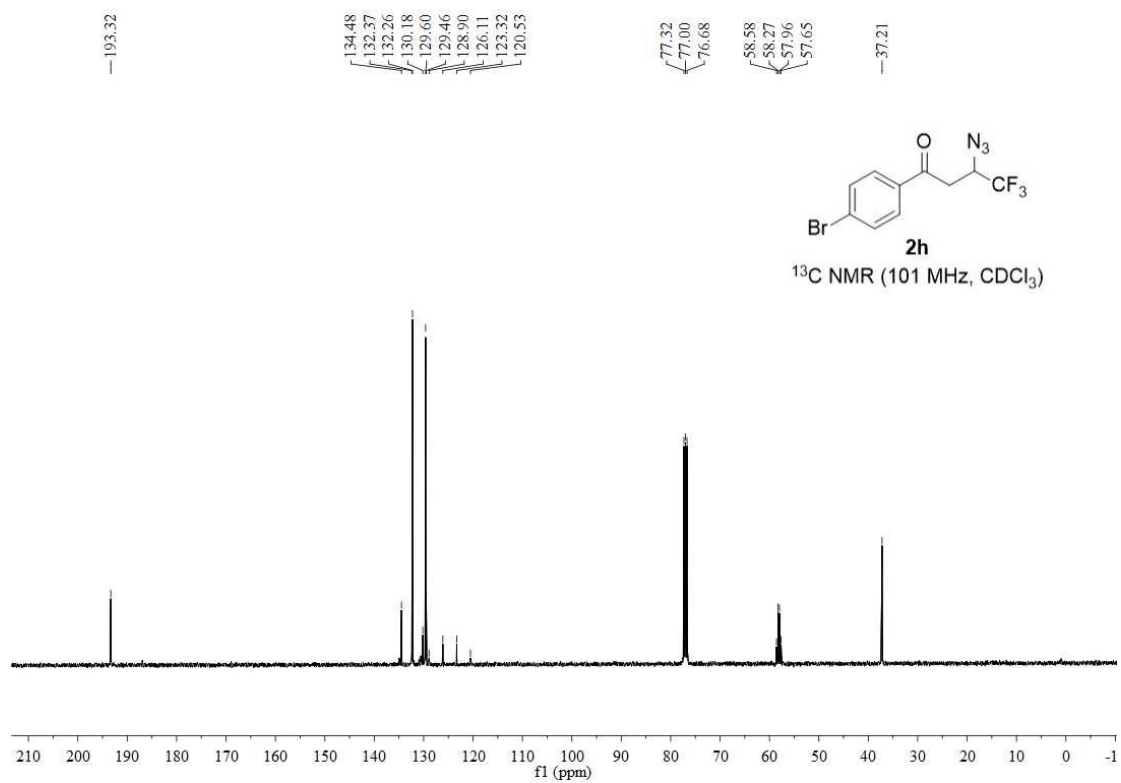
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3.33
3.31
3.29
3.24
3.23
3.19
3.19

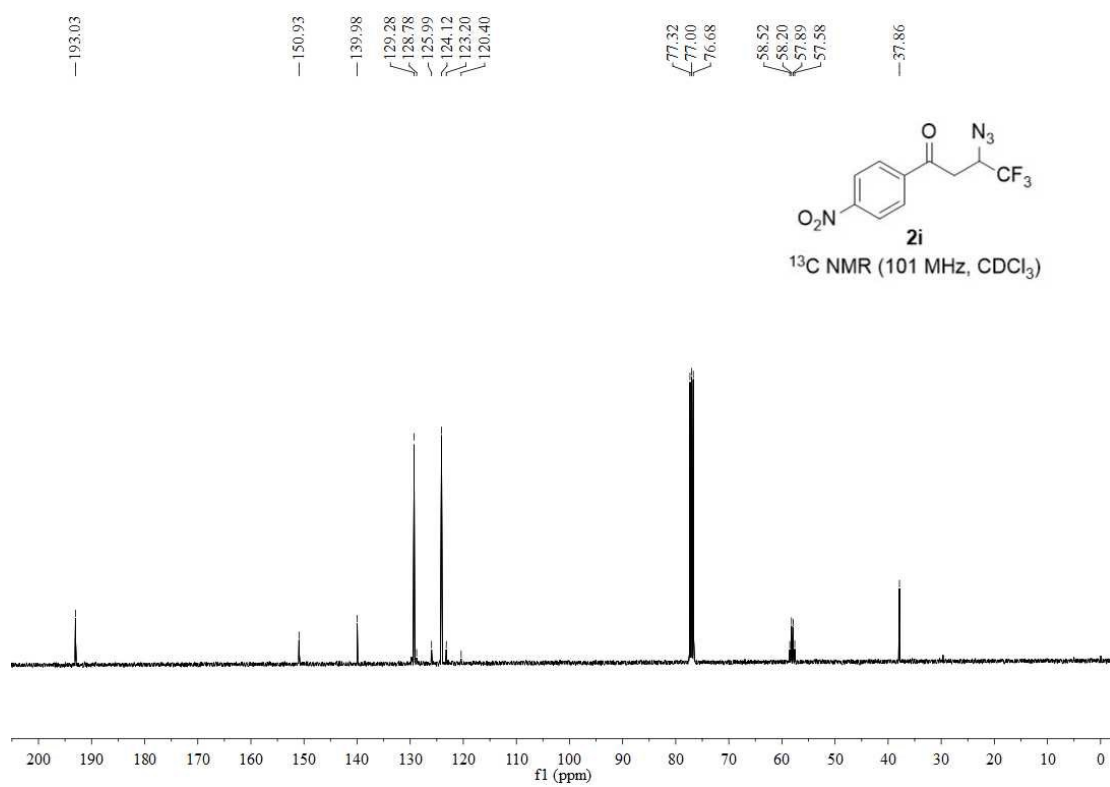
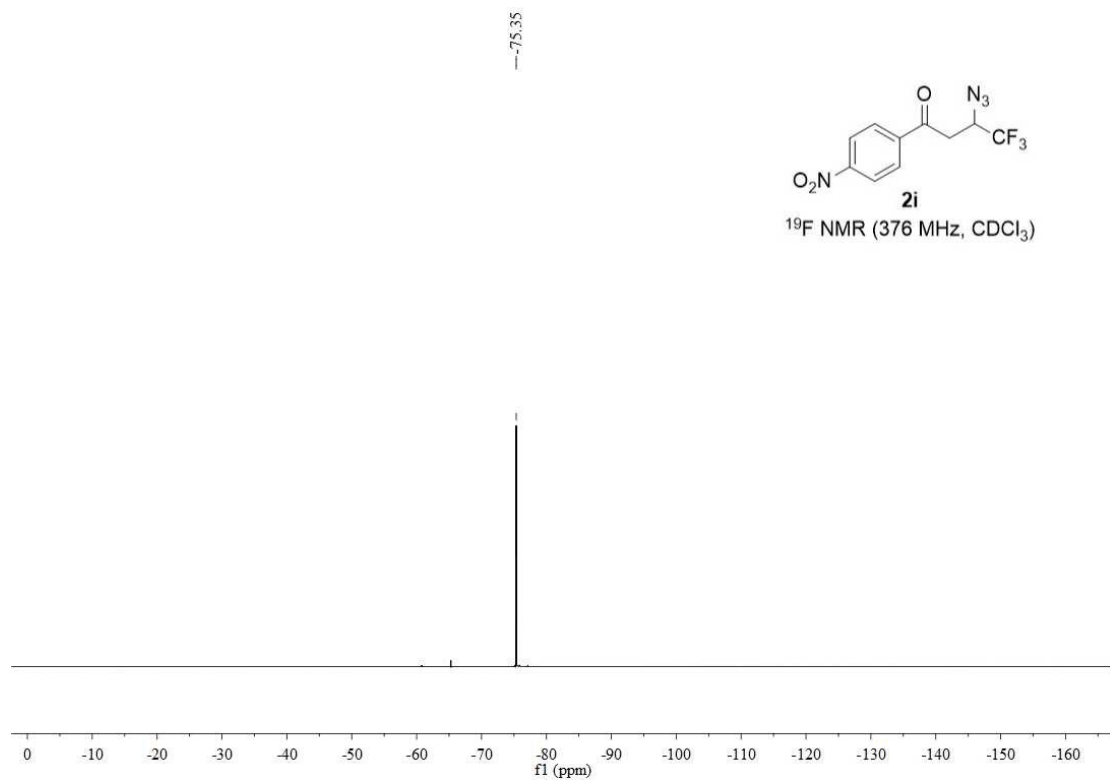
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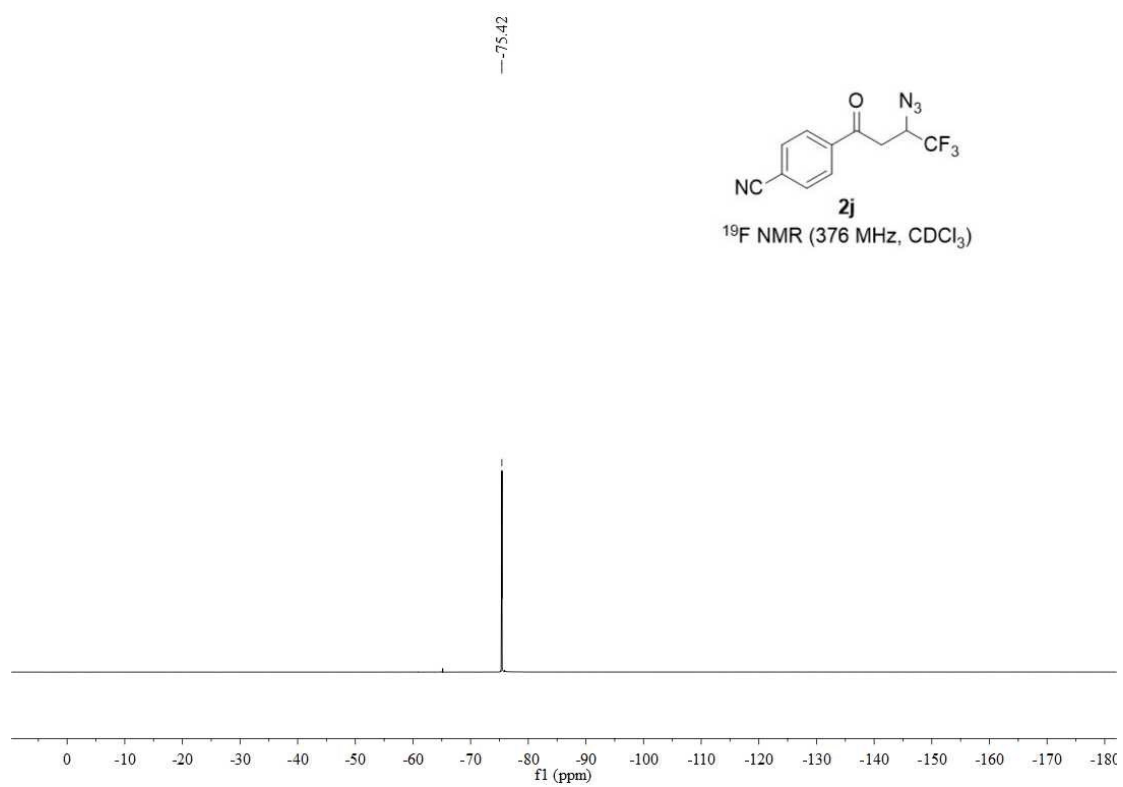
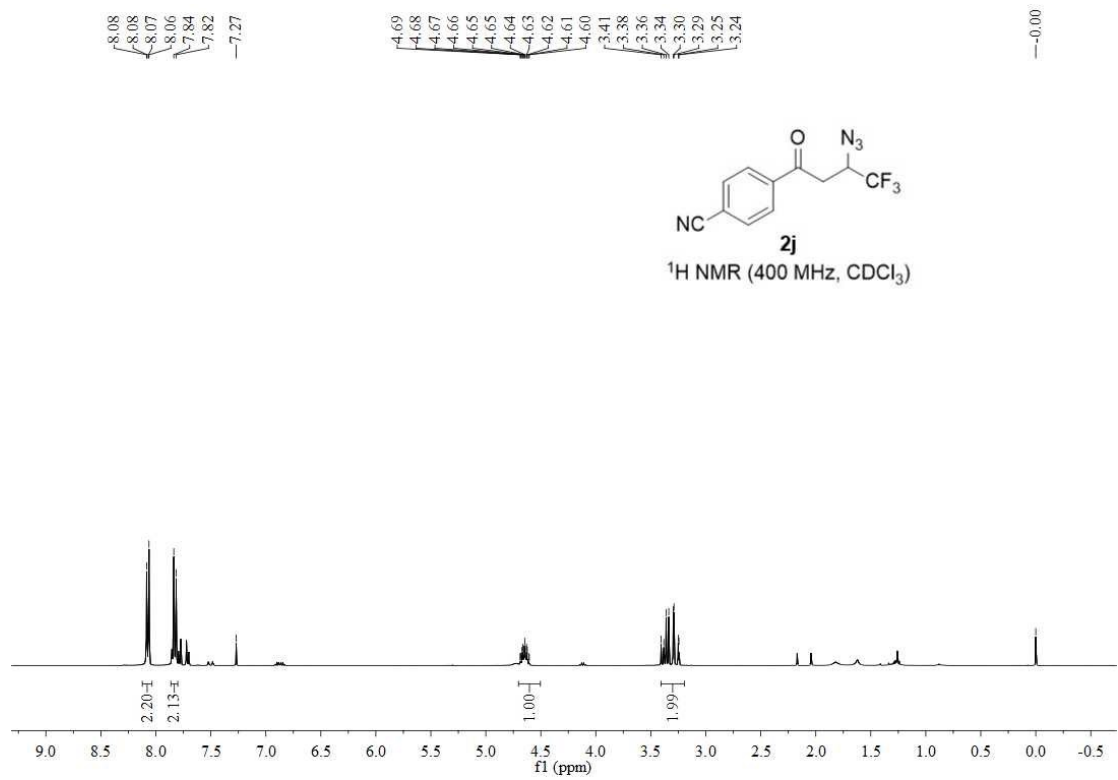


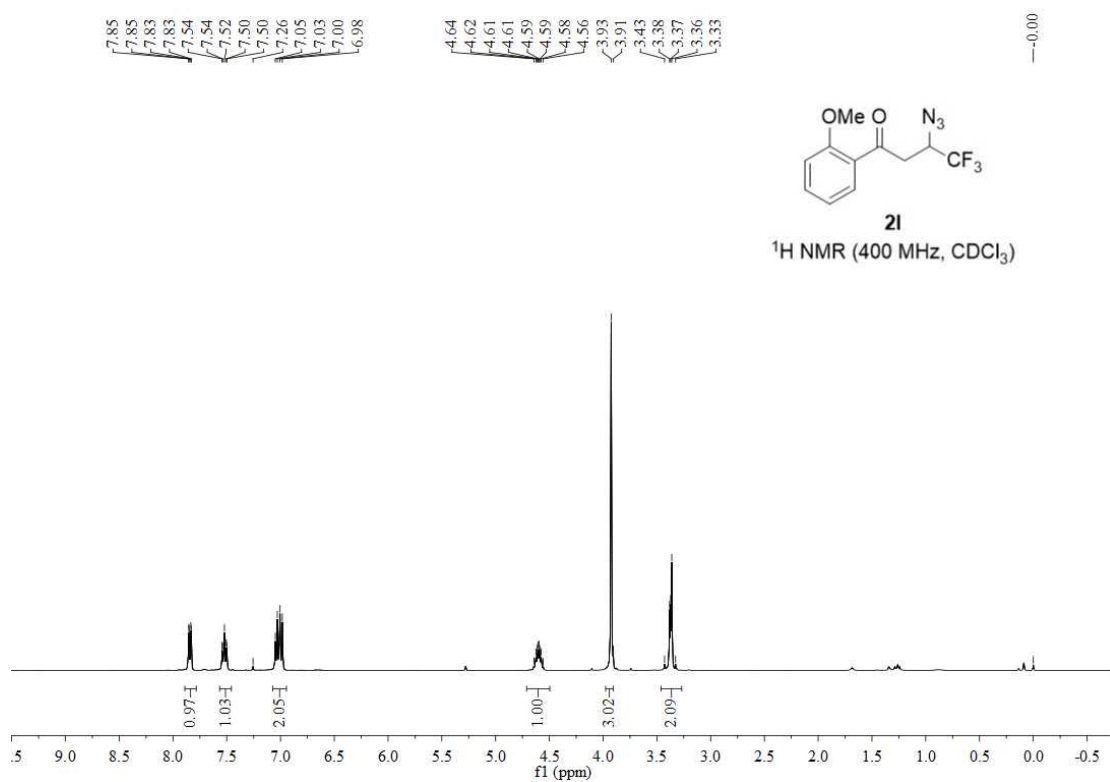
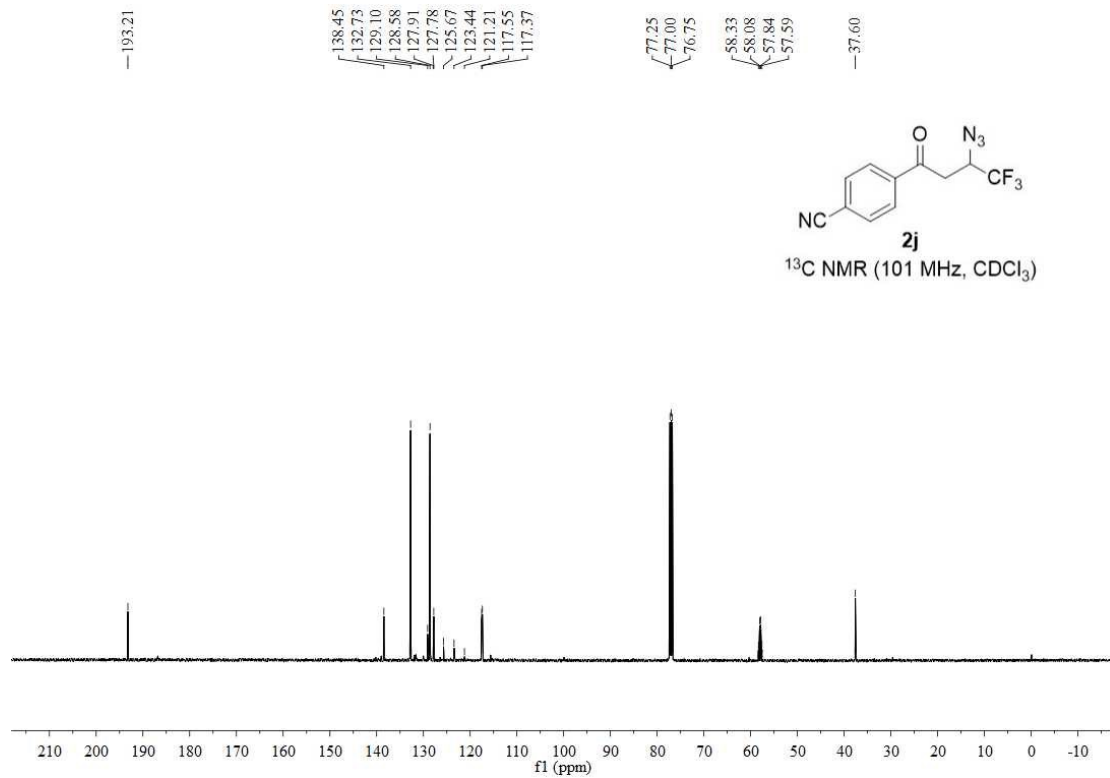
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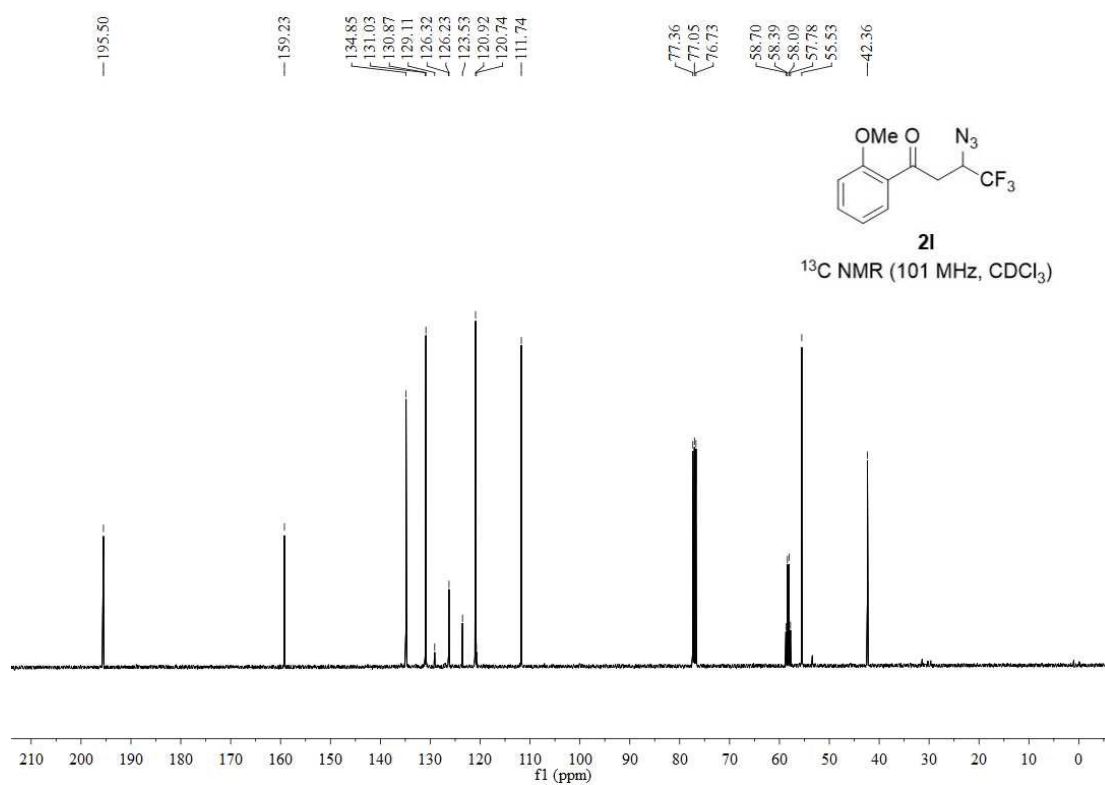
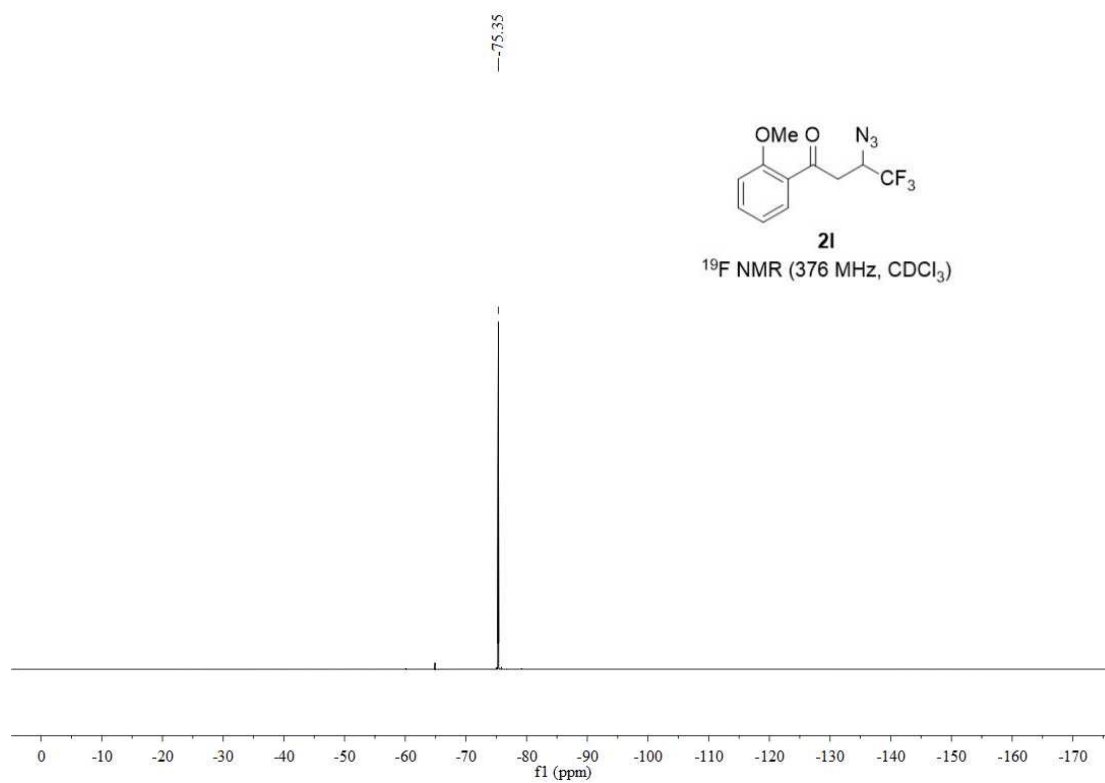


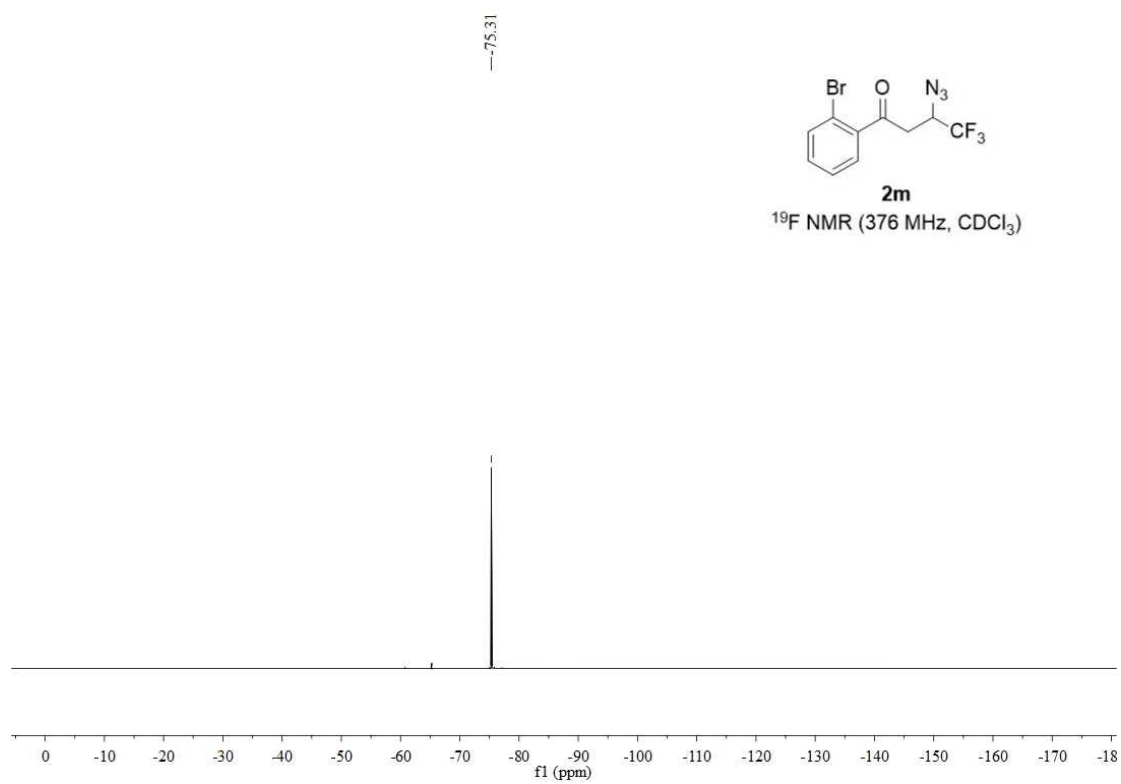
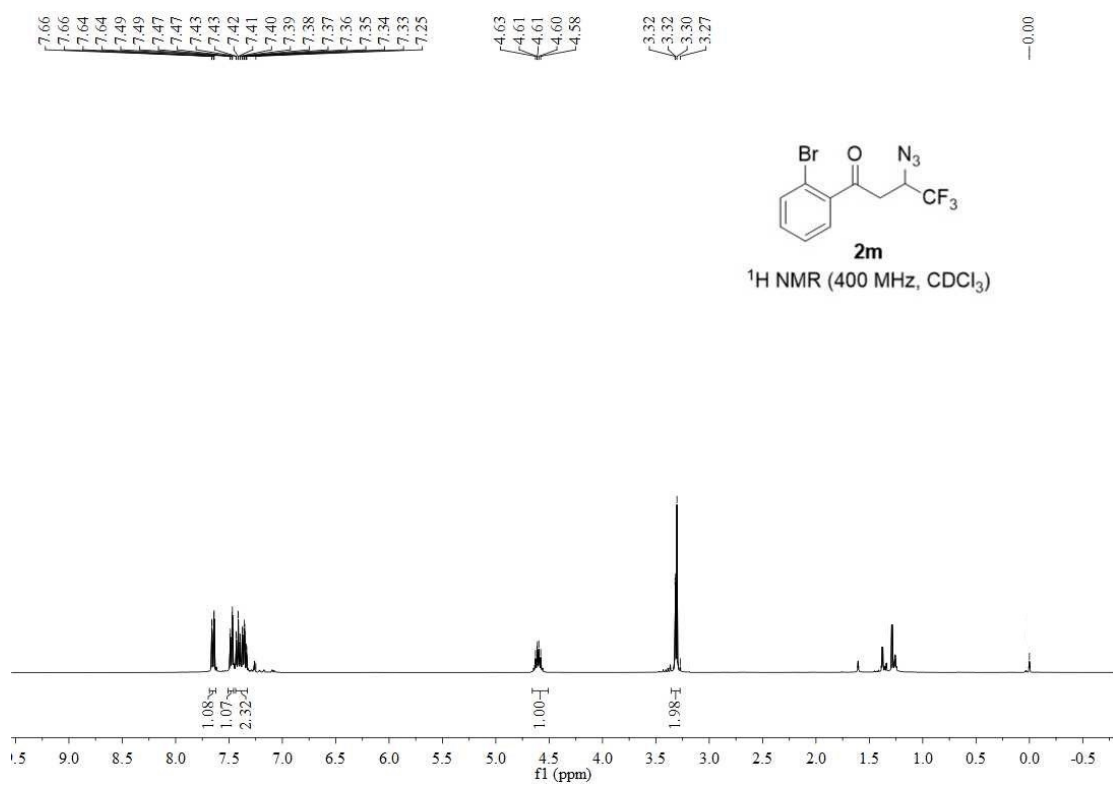












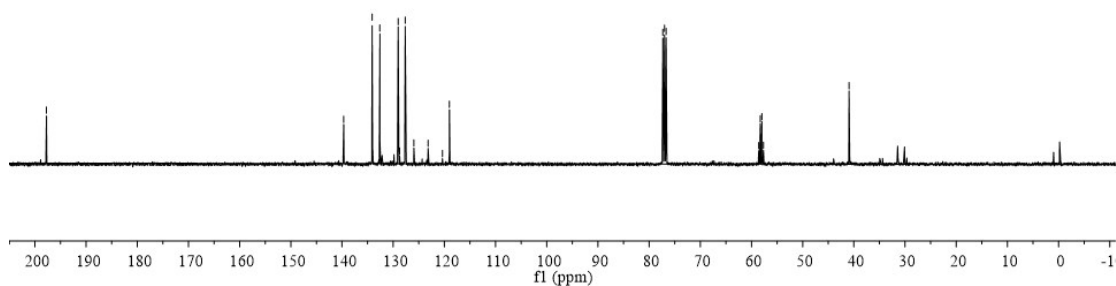
— 197.74

139.67
134.12
132.61
129.03
128.75
127.66
125.96
123.17
120.38
119.01

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77.00
76.68
58.59
58.28
57.97
57.66
— 40.94



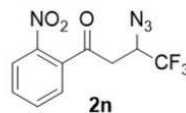
¹³C NMR (101 MHz, CDCl₃)



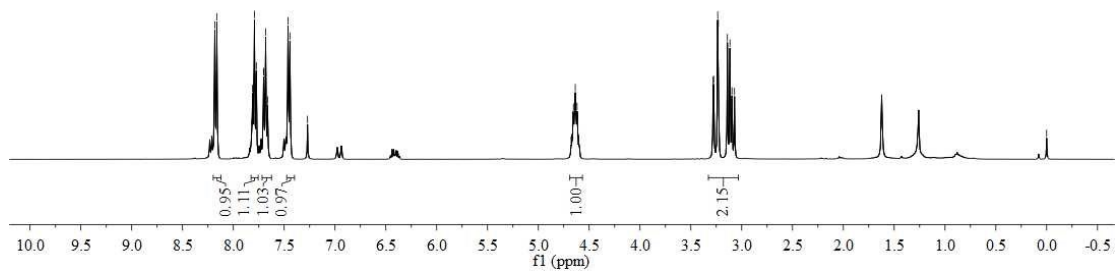
8.18
8.16
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7.70
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7.66
7.46
7.44
7.27

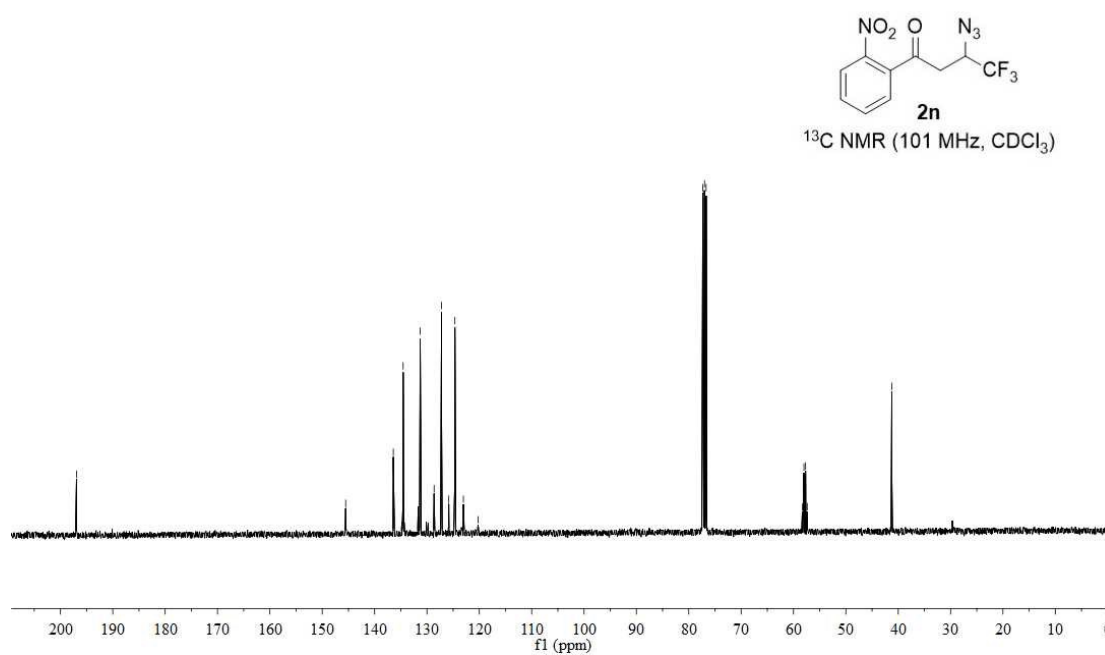
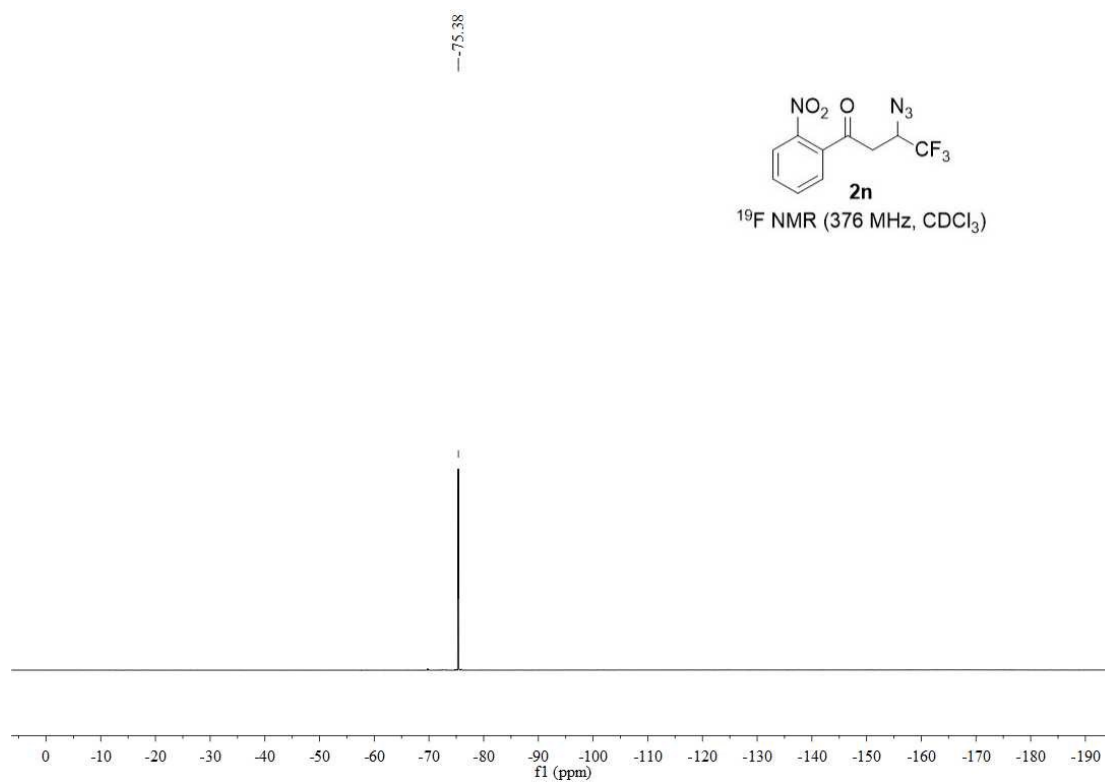
4.68
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4.64
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3.23
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3.12
3.10
3.07

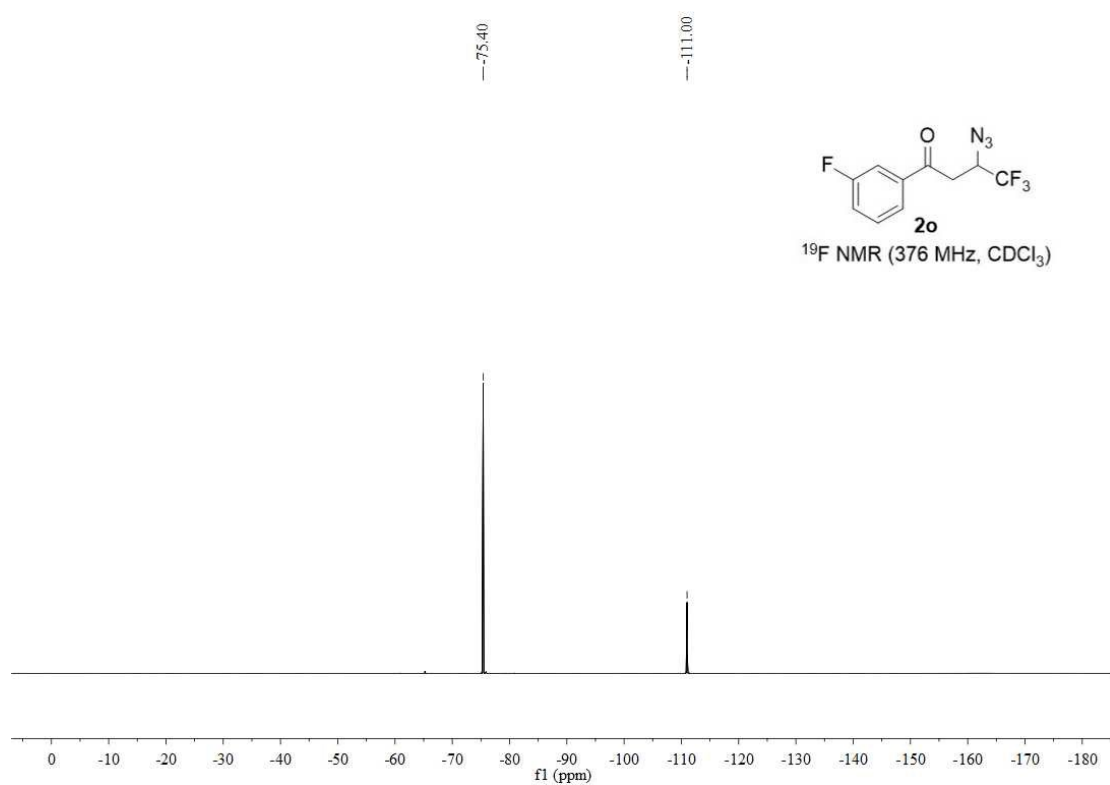
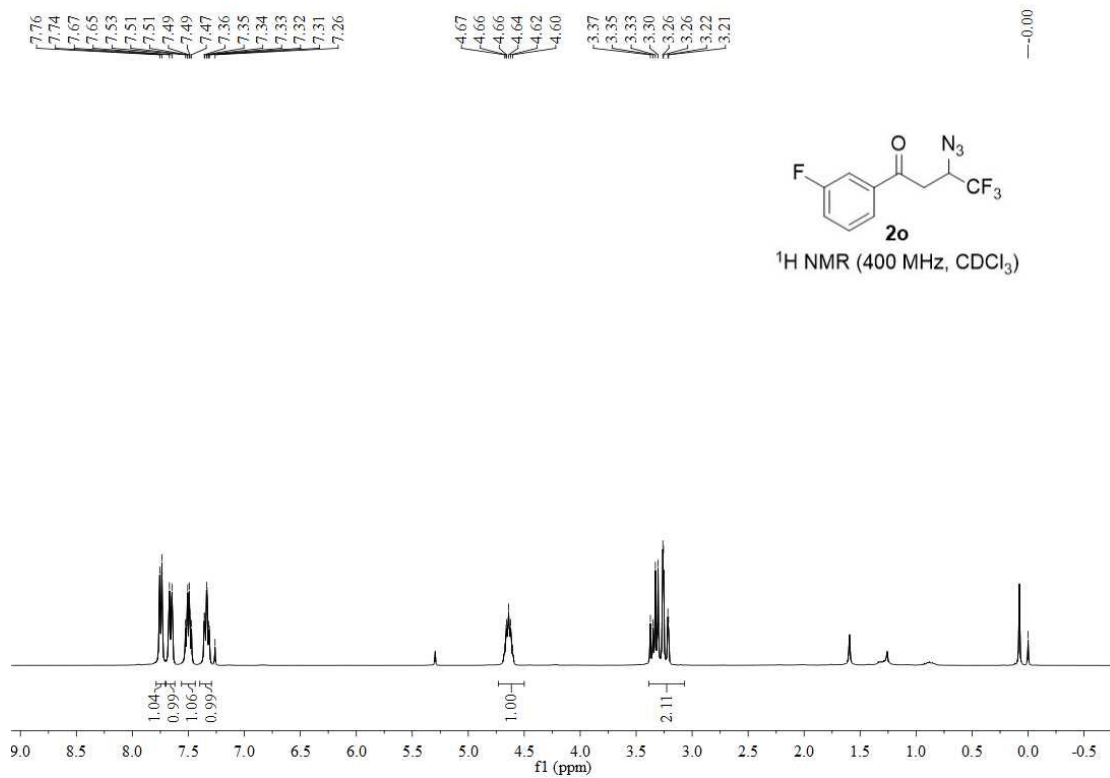
— 0.00

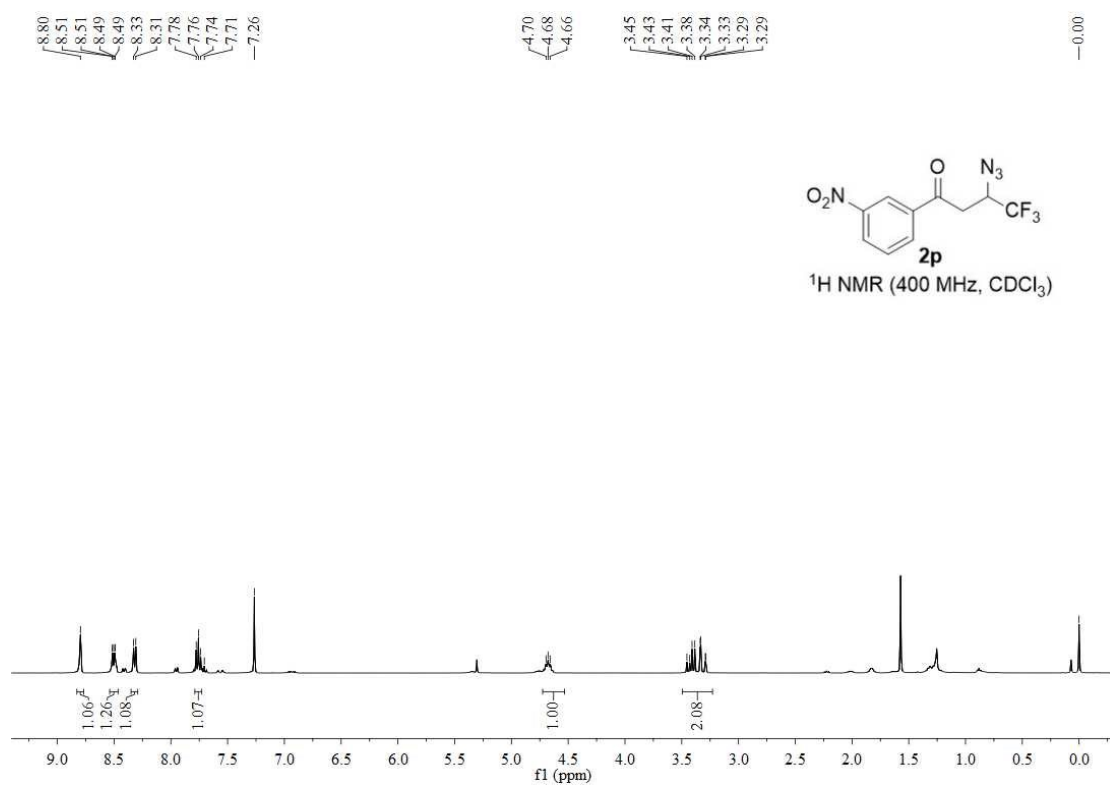
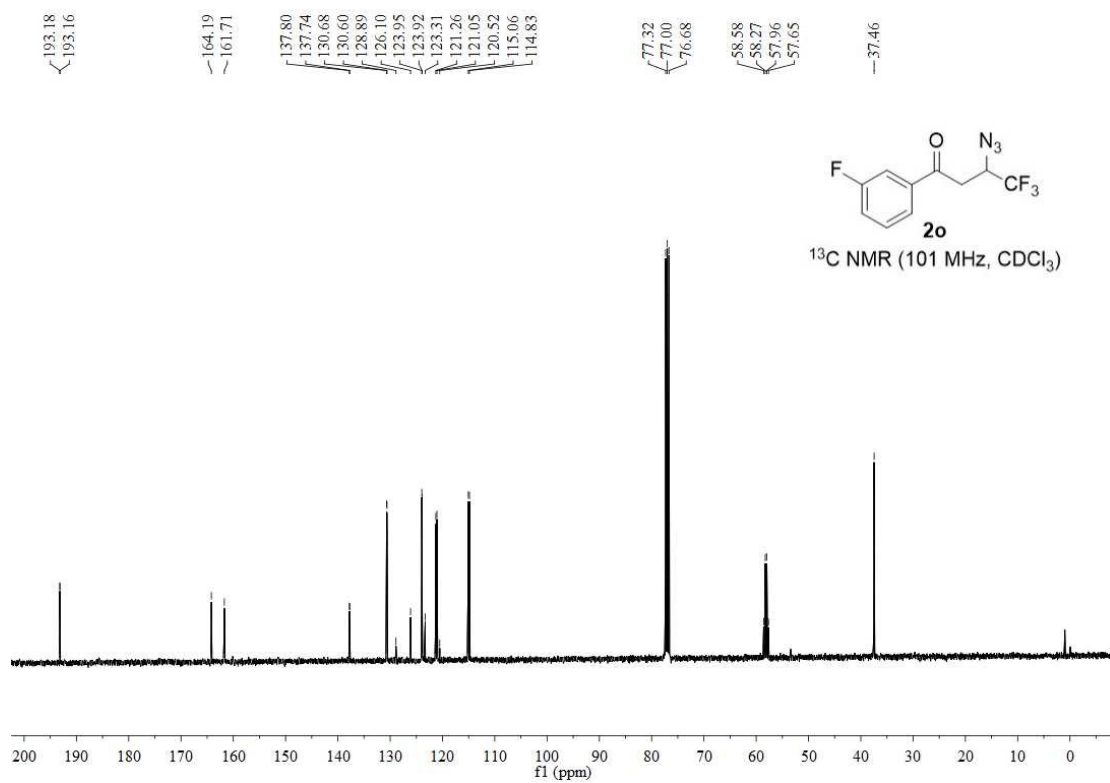


¹H NMR (400 MHz, CDCl₃)

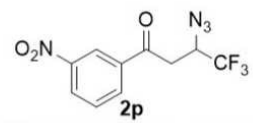




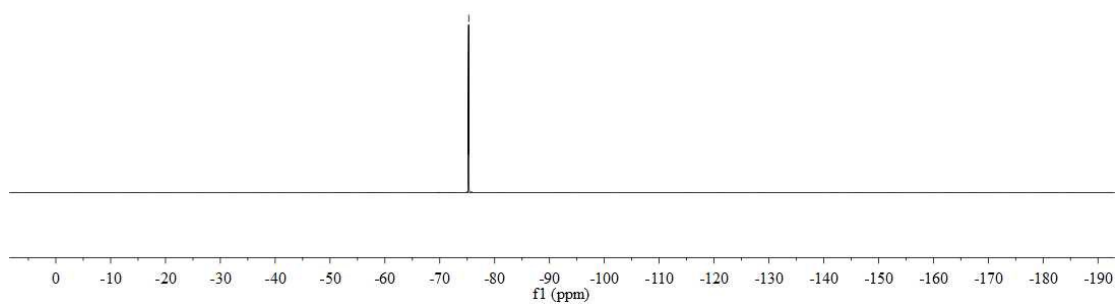




-75.29



¹⁹F NMR (376 MHz, CDCl₃)



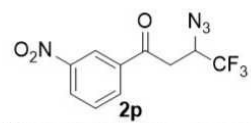
192.46

148.54
136.84
133.61
130.29
128.28
127.91
125.68
123.45
123.05
121.22

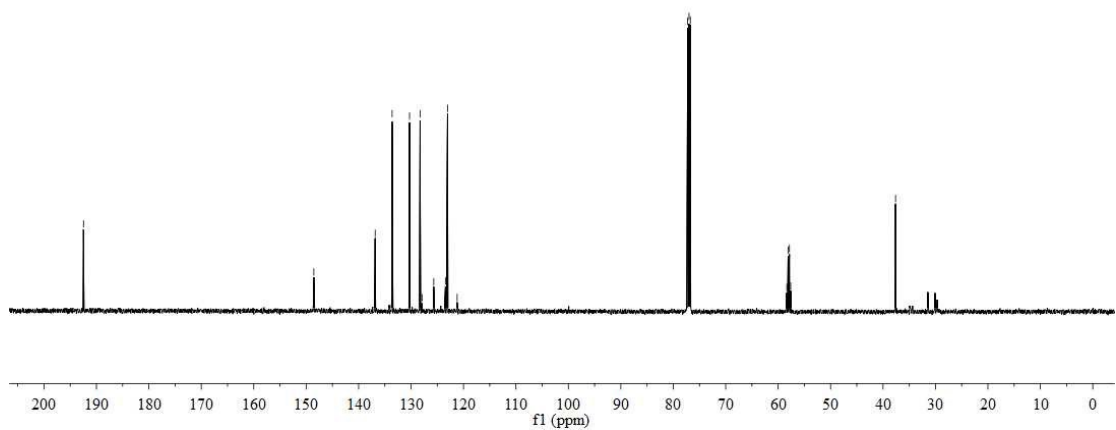
77.25
77.00
76.75

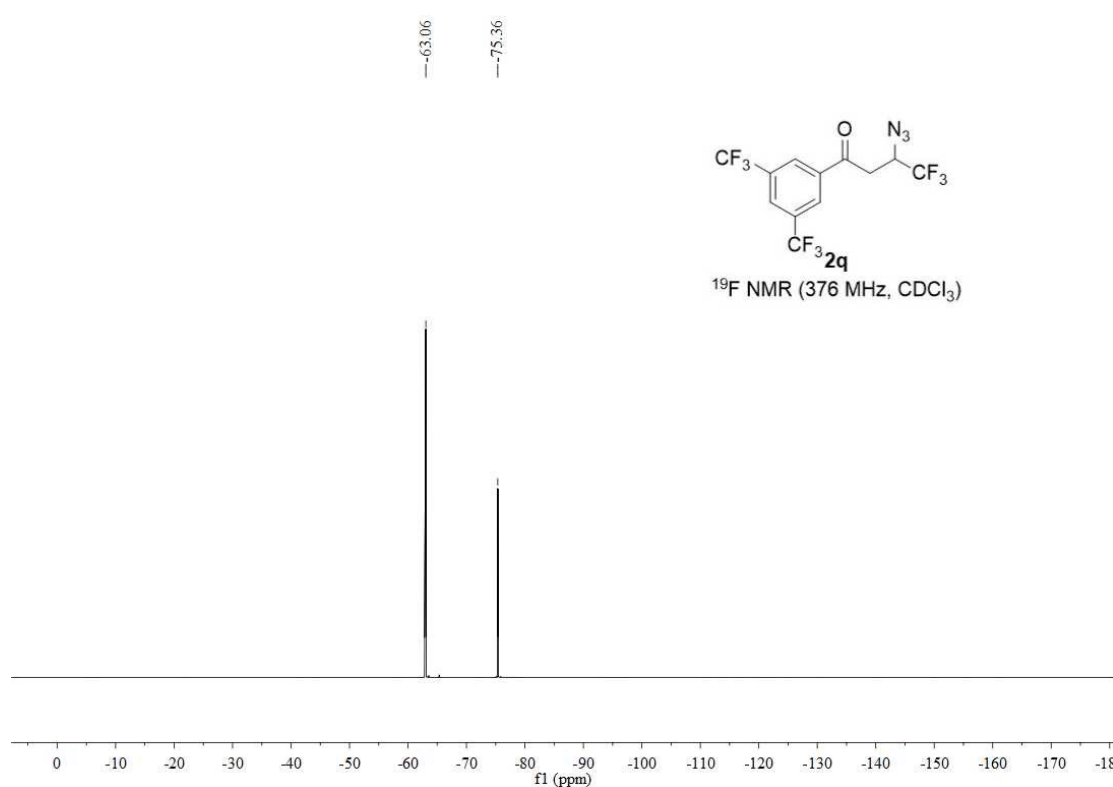
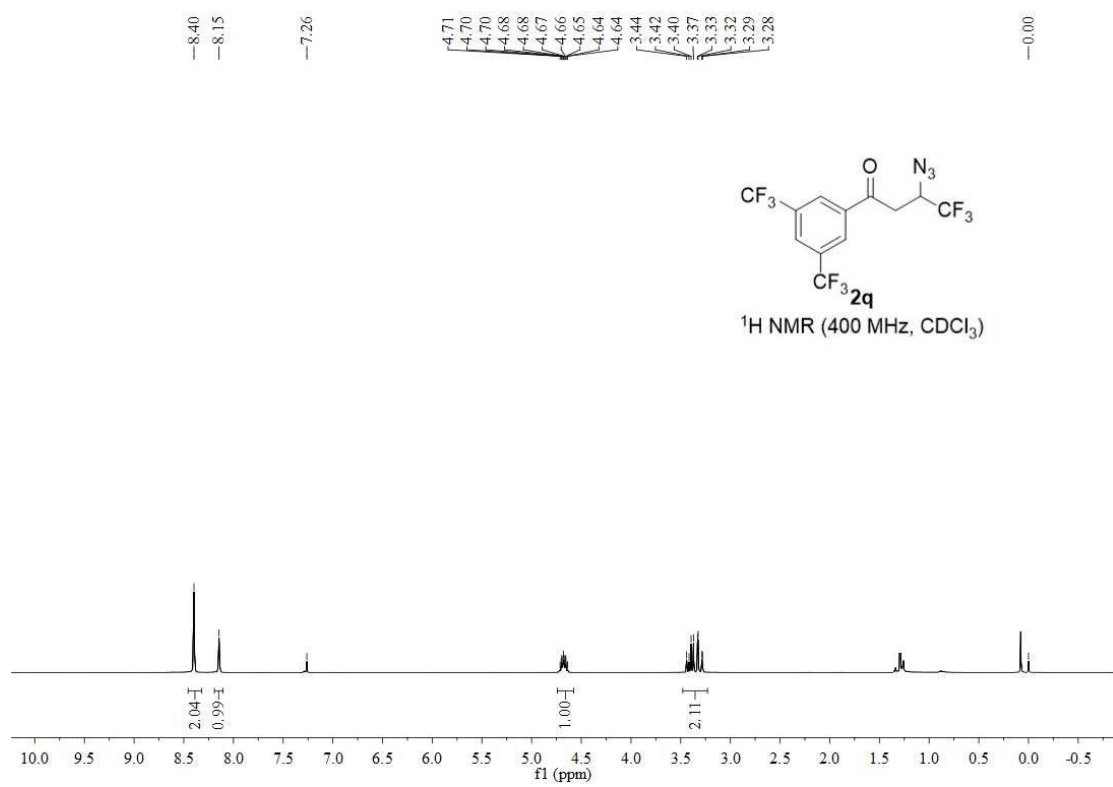
58.35
58.10
57.86
57.61

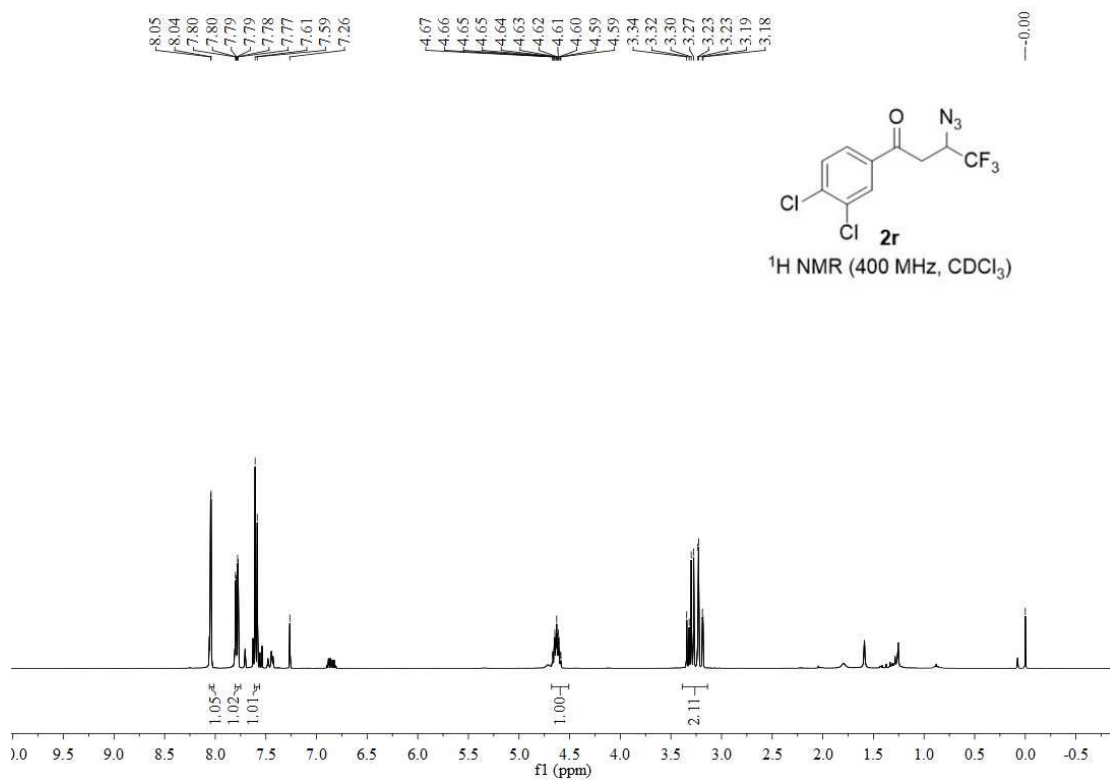
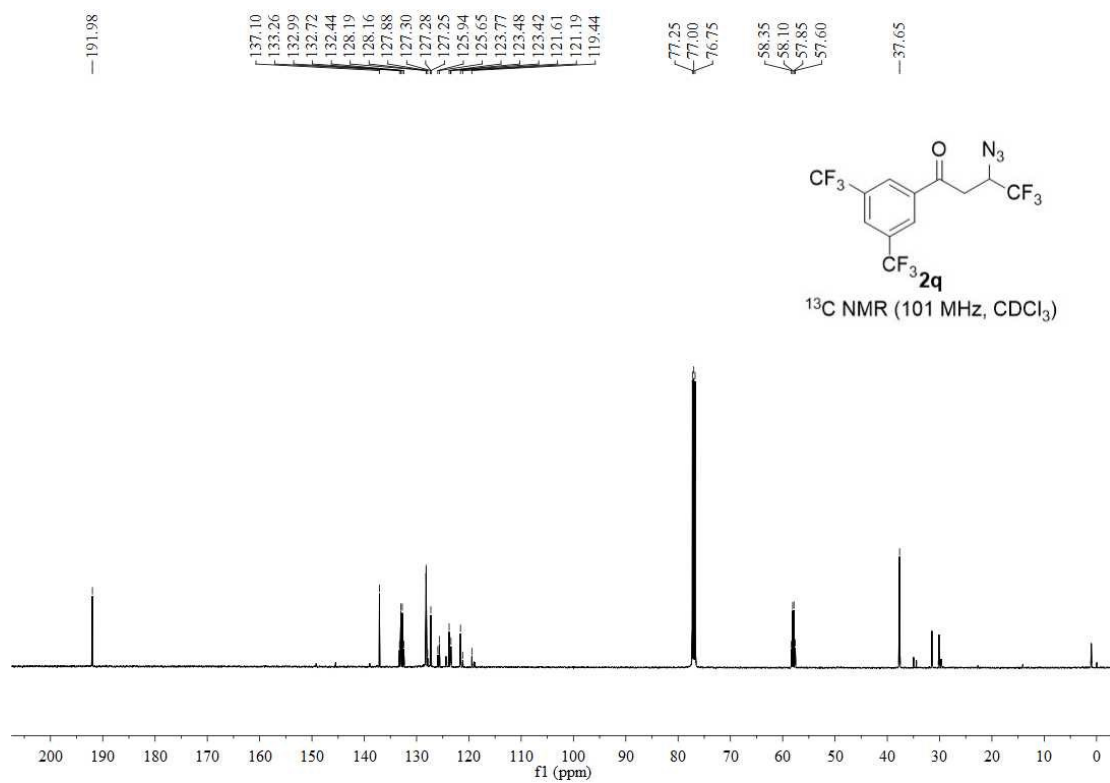
37.61

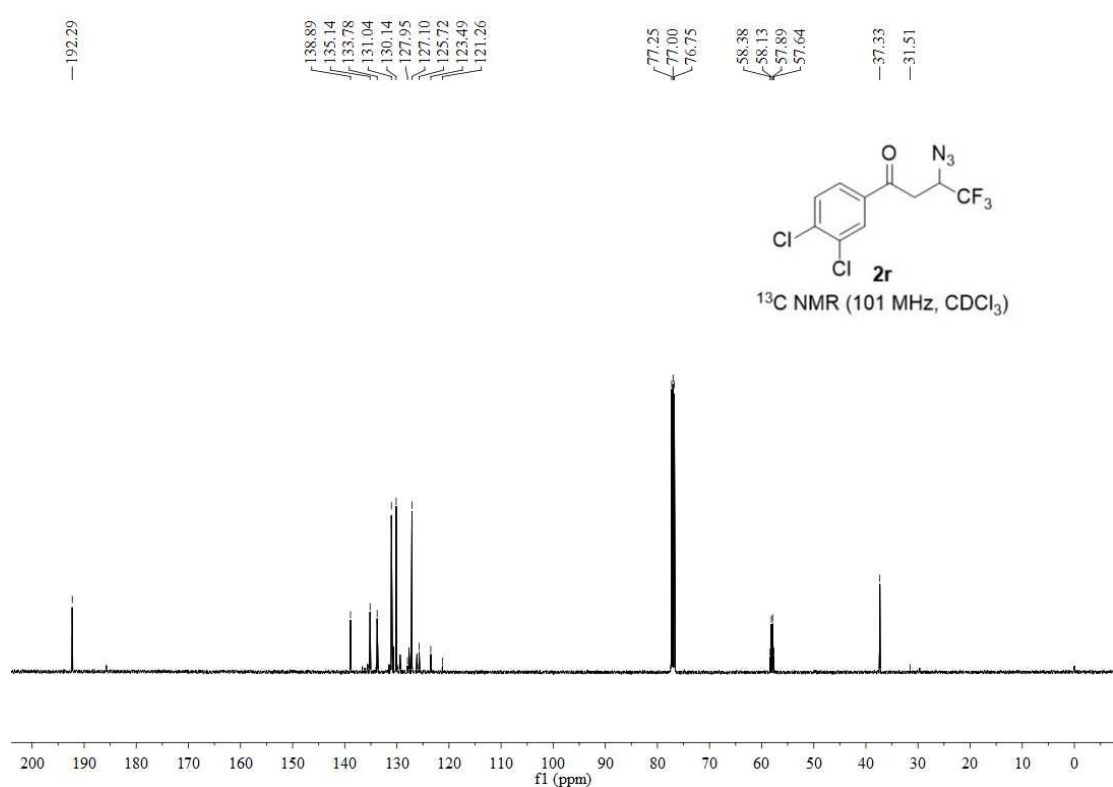
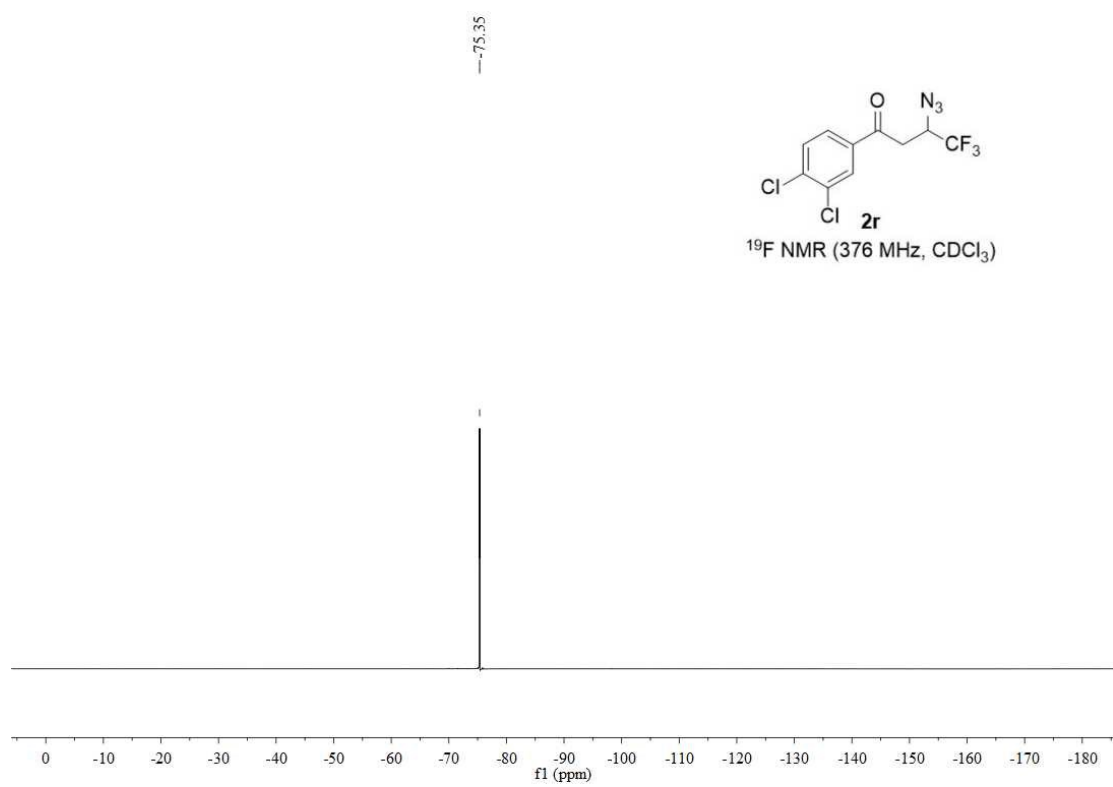


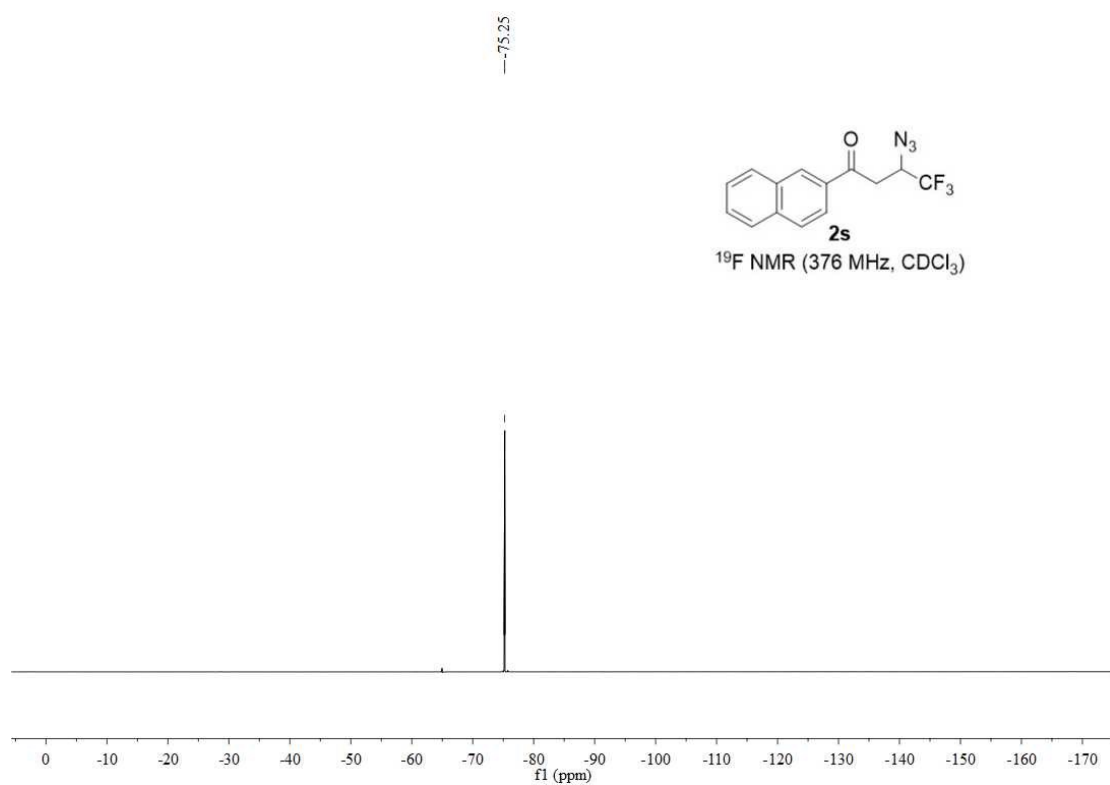
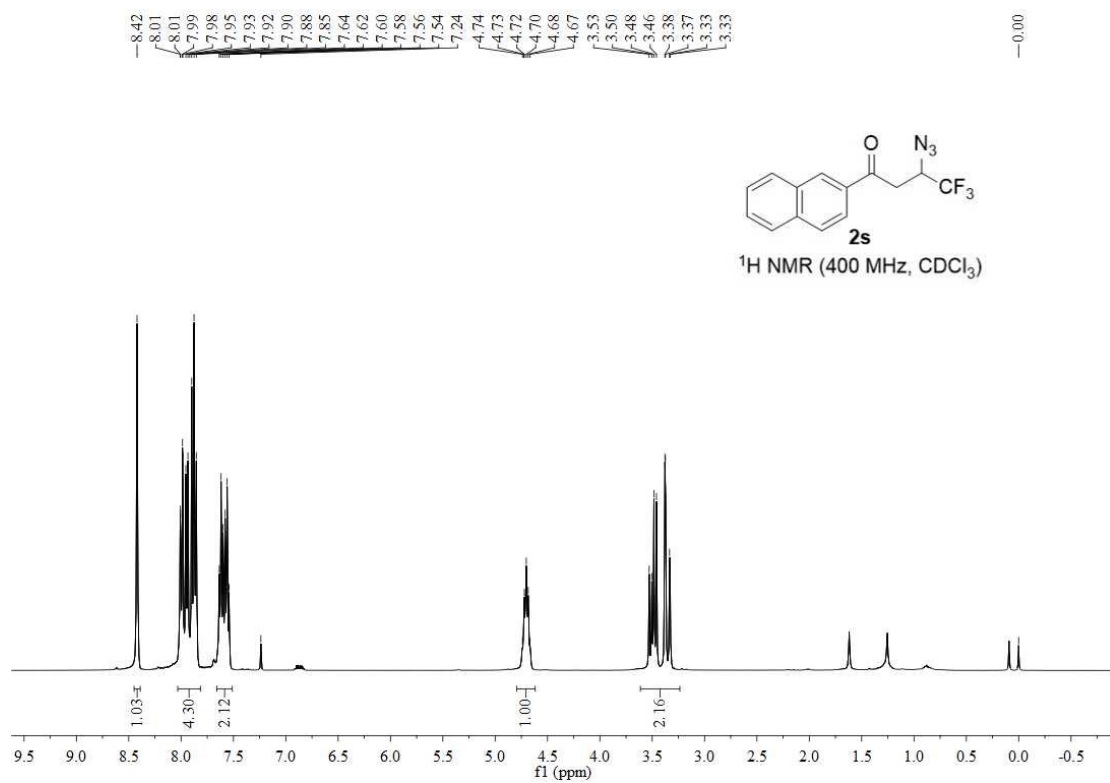
¹³C NMR (101 MHz, CDCl₃)

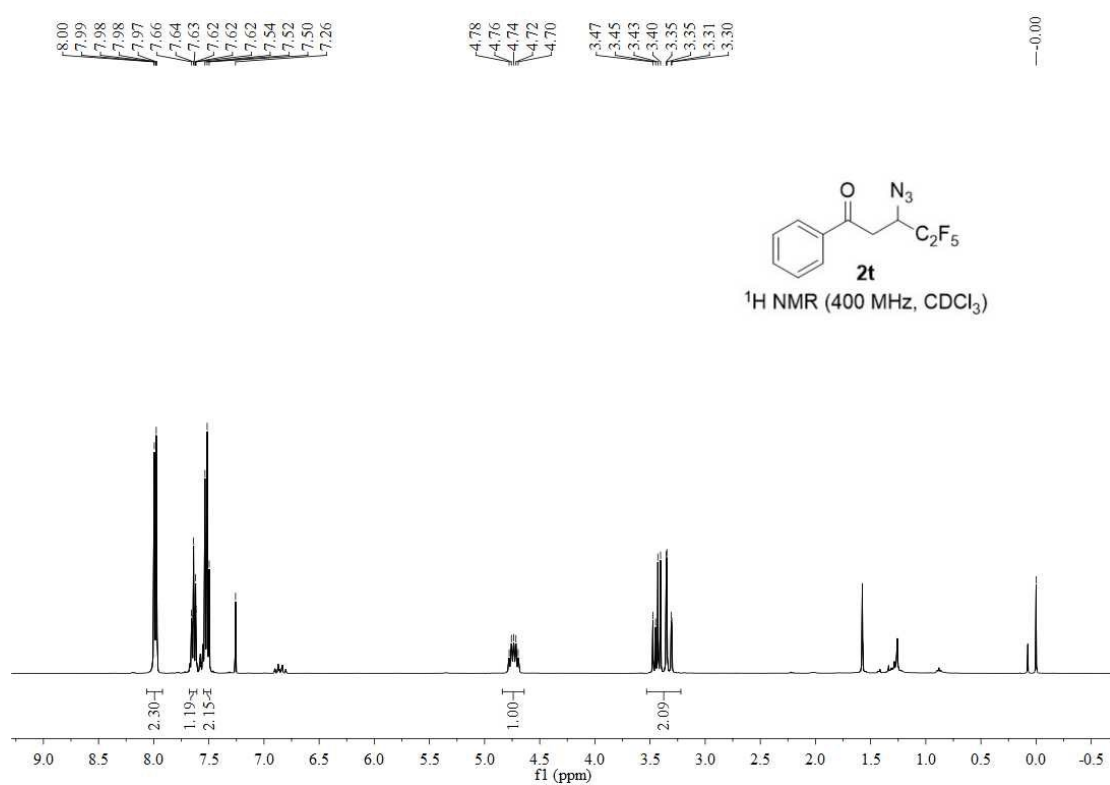
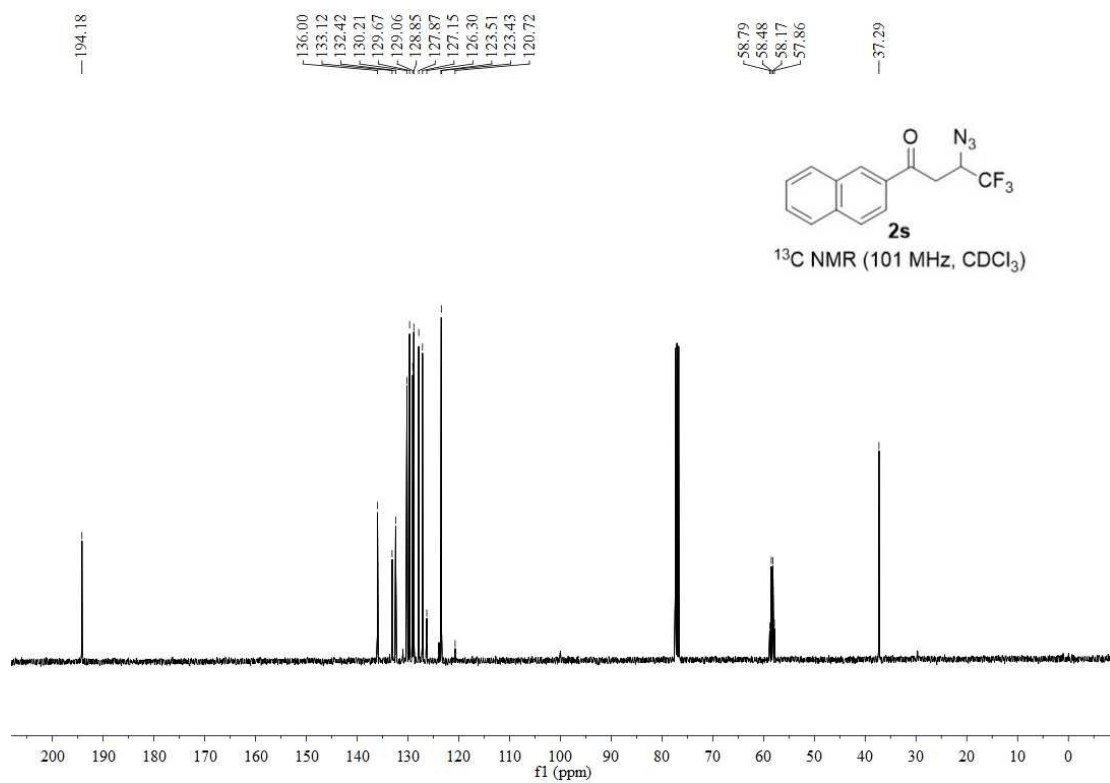


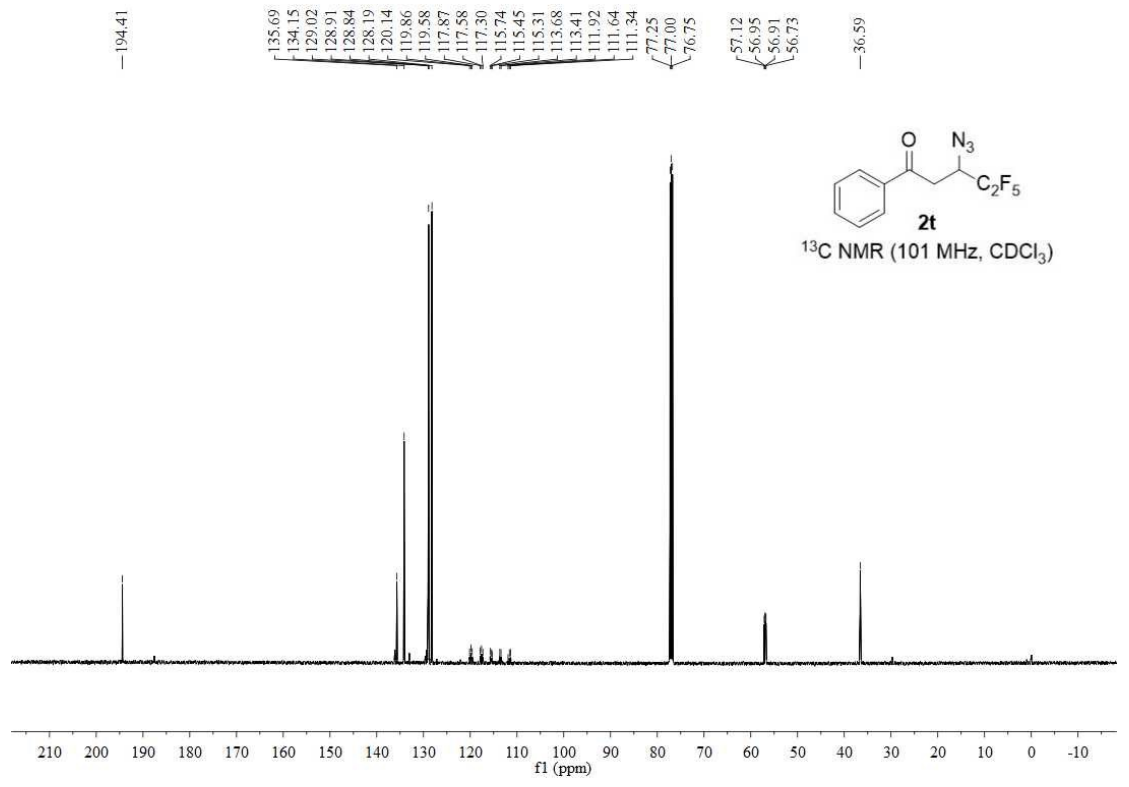
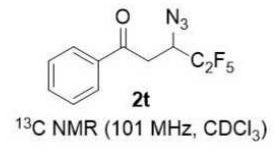
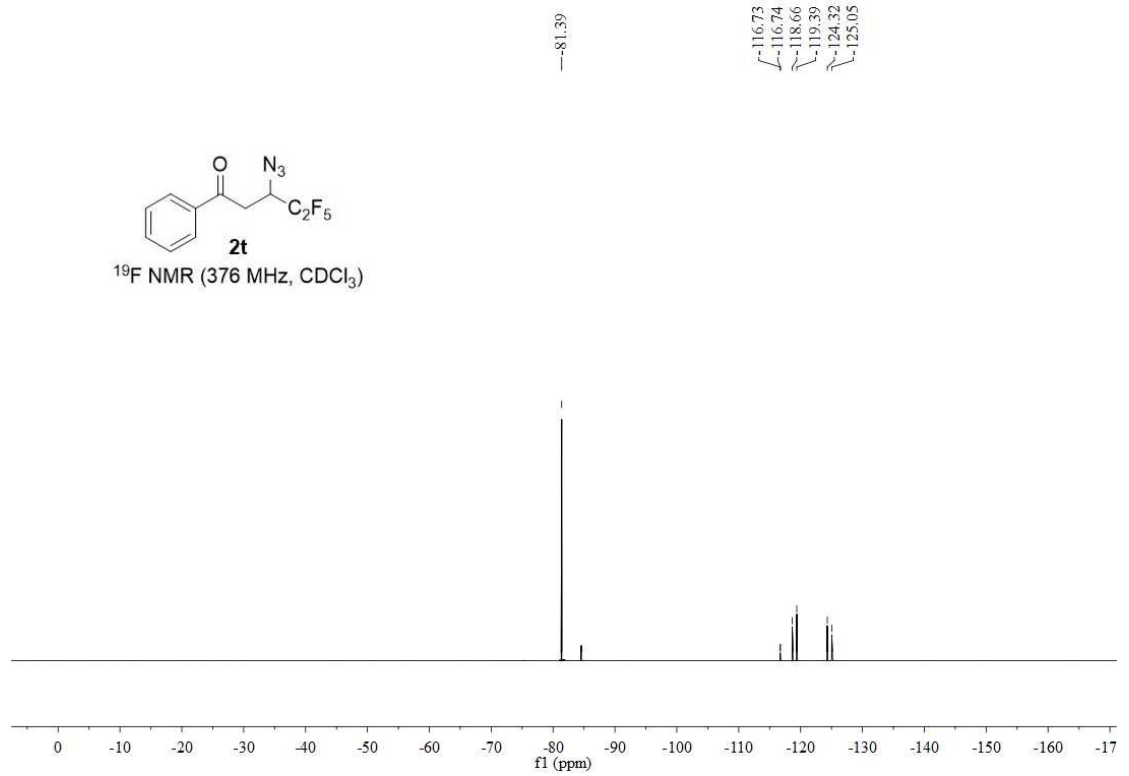
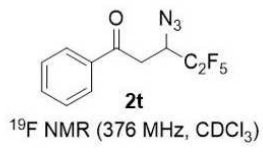


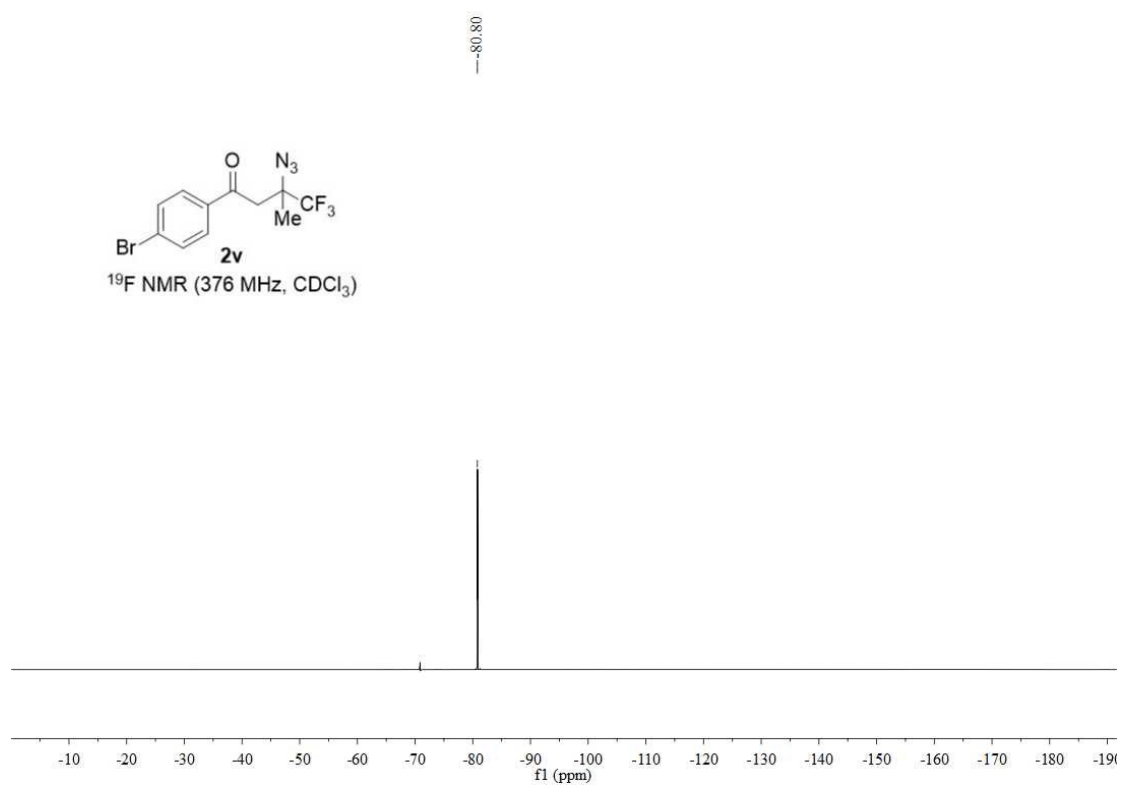
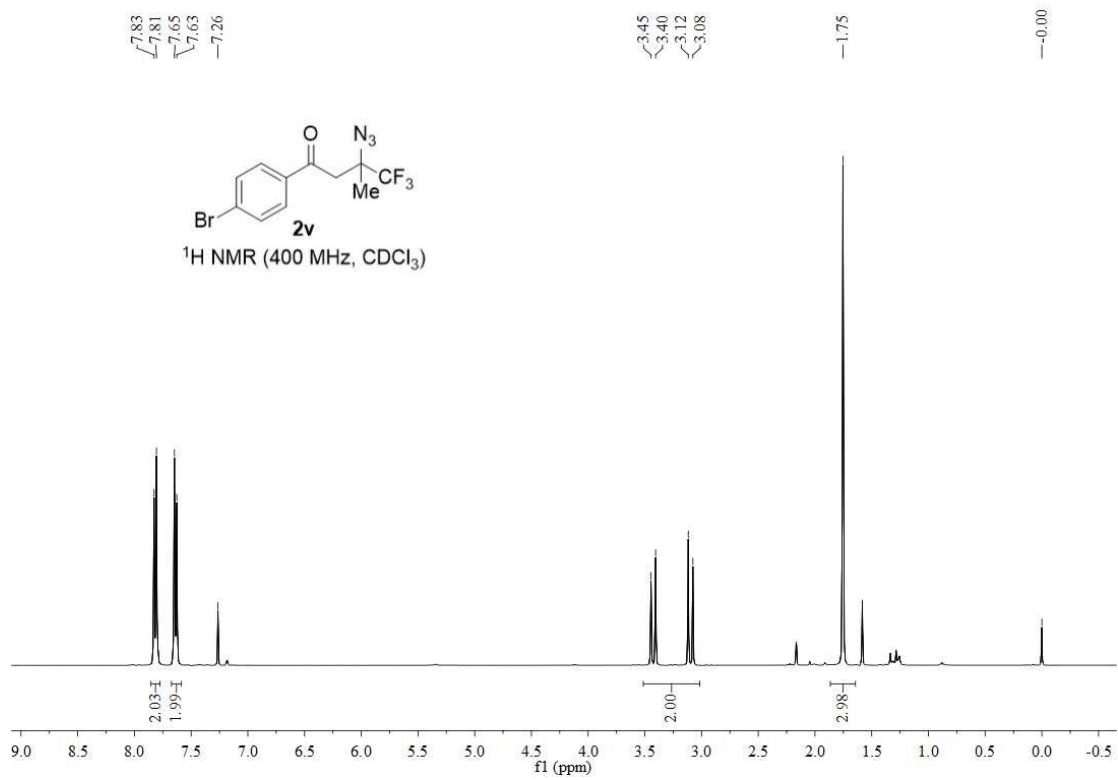


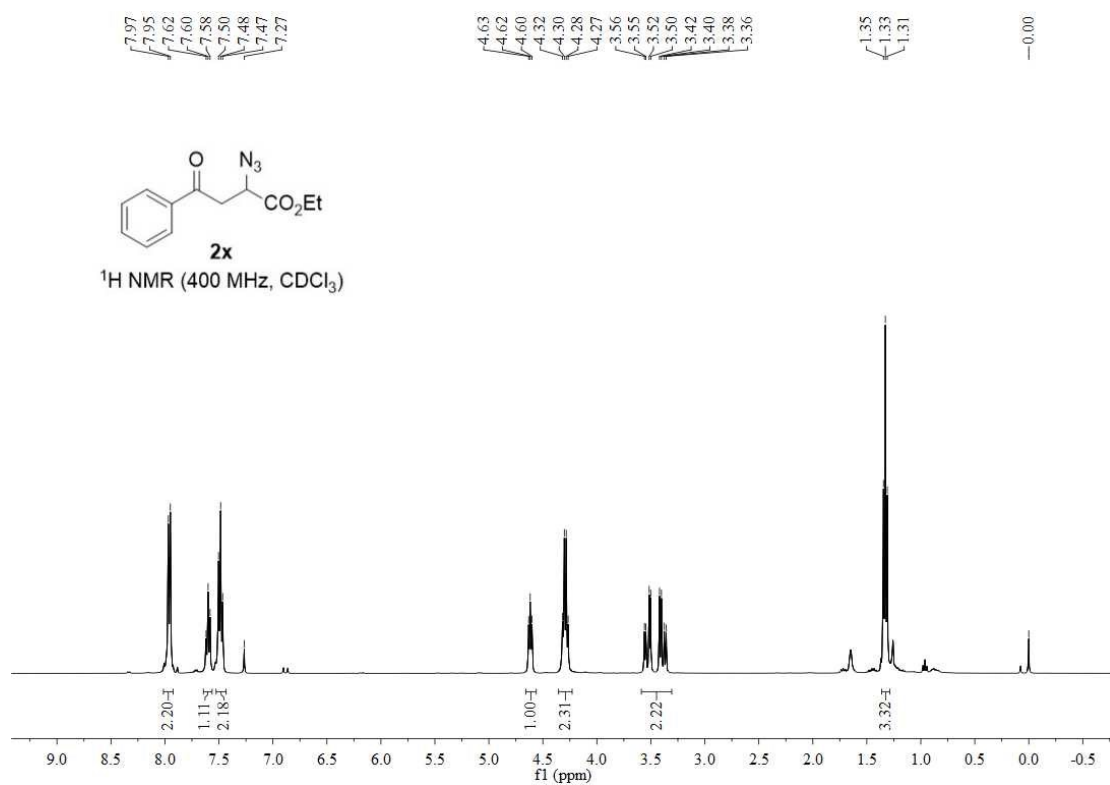
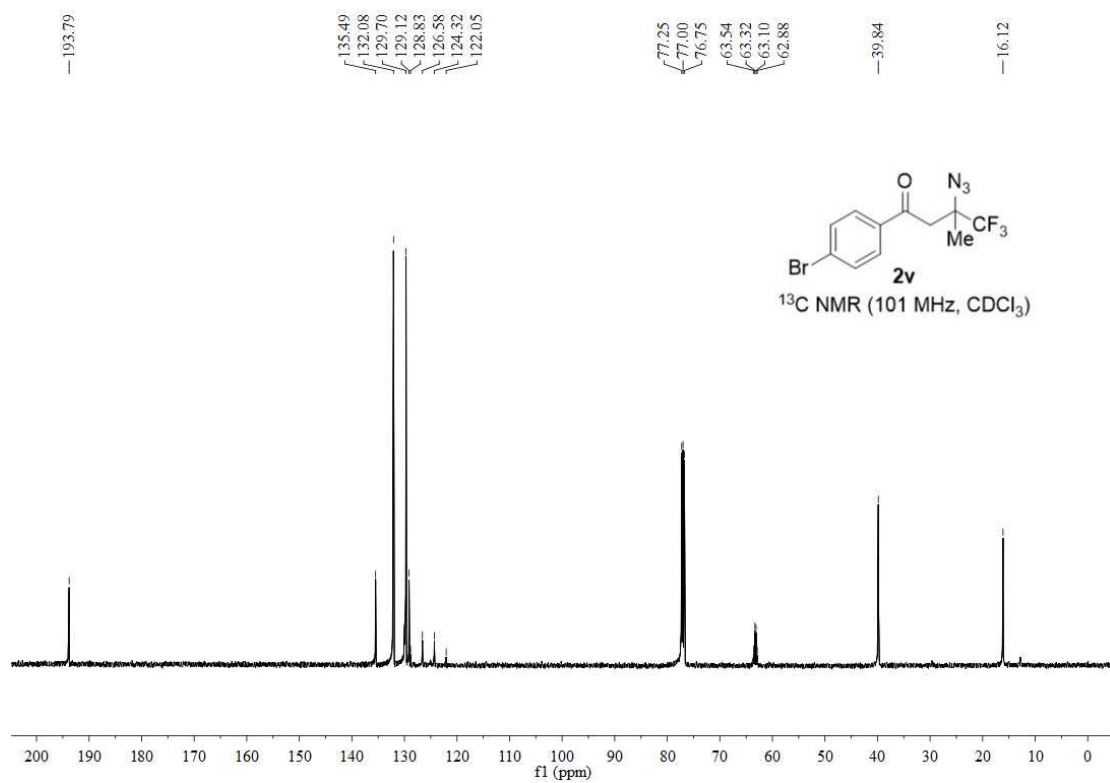


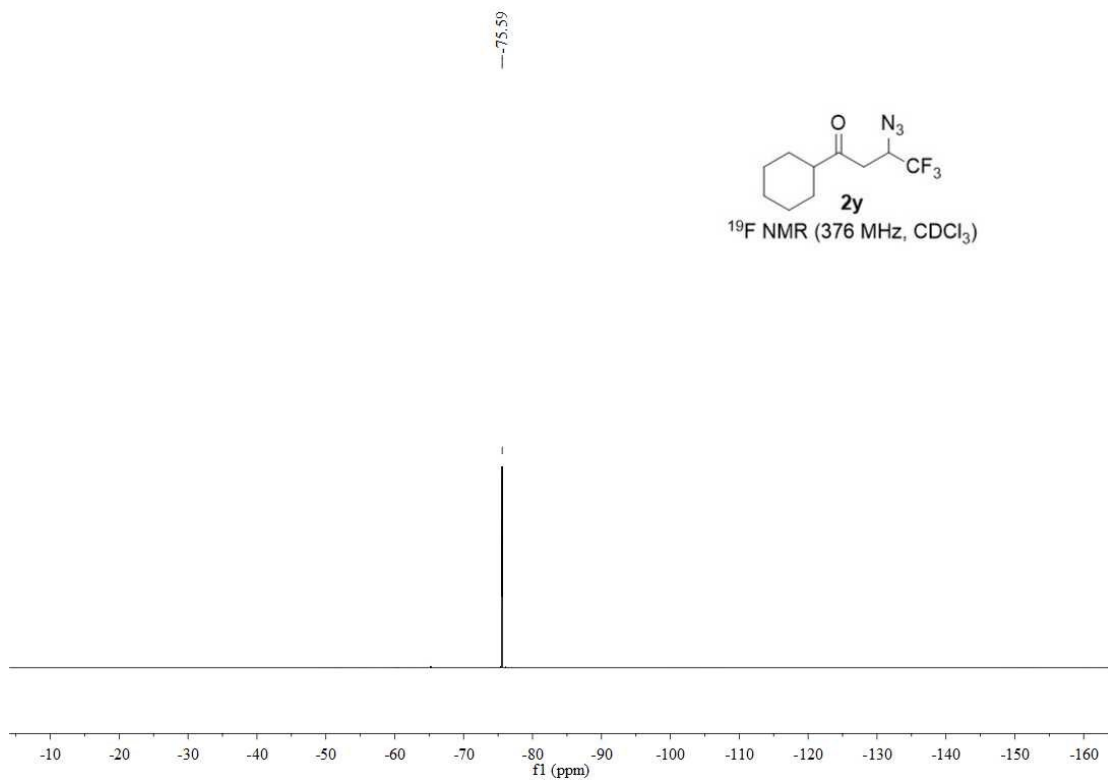
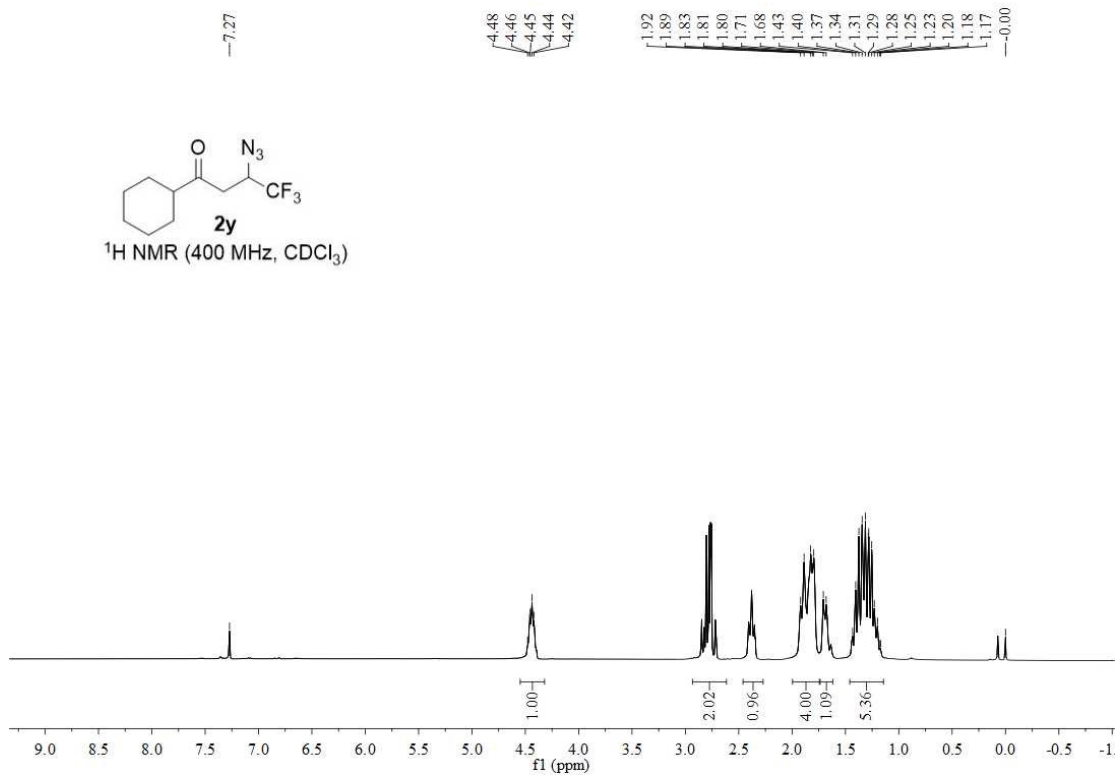












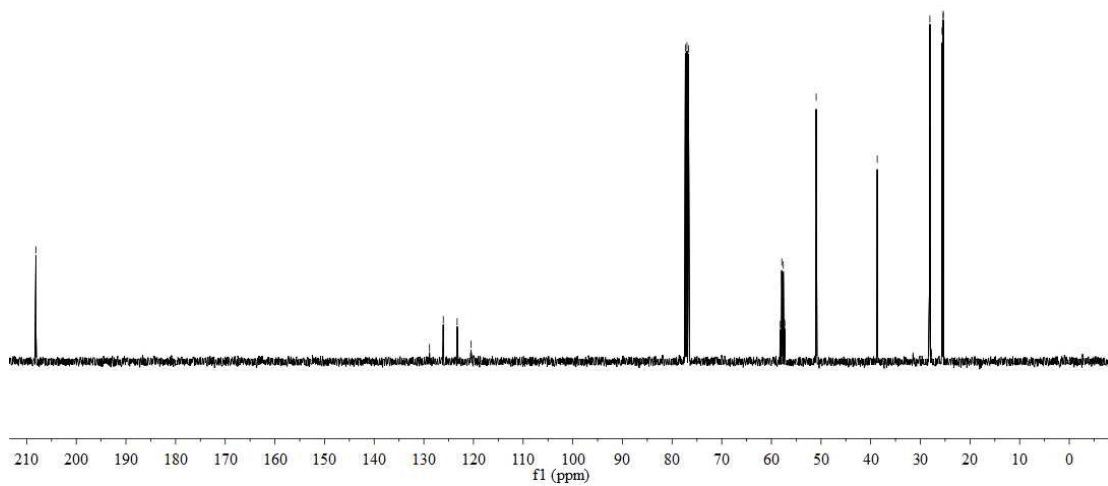
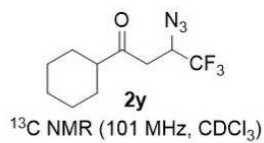
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128.86
126.08
123.29
120.50

77.32
77.00
76.68

58.22
57.91
57.60
57.29
50.98

38.67
28.14
28.08
25.63
25.41
25.38



195.66

169.70

136.08

133.67

128.73

128.10

77.32

77.00

76.68

62.16

58.03

58.22

57.91

57.60

57.29

50.98

39.98

38.67

28.14

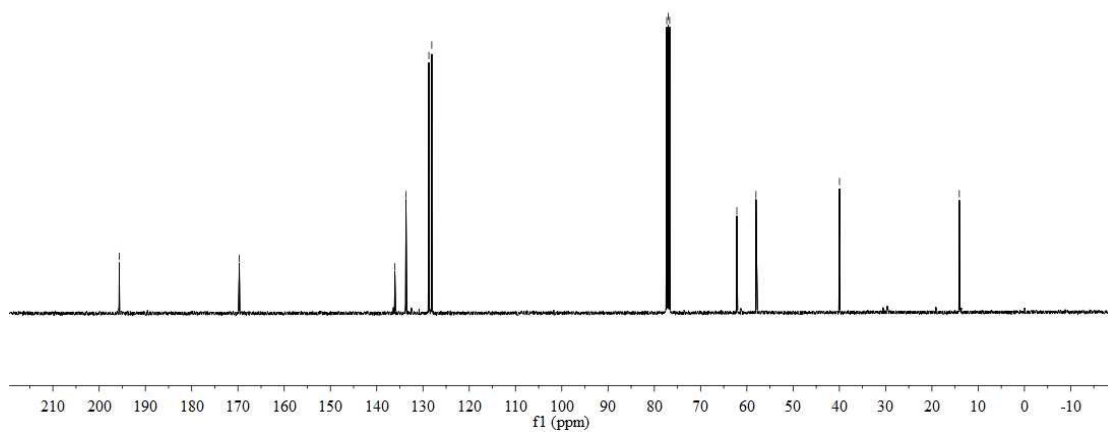
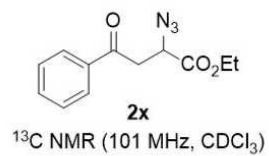
28.08

25.63

25.41

25.38

14.08



210

200

190

180

170

160

150

140

130

120

110

100

90

80

70

60

50

40

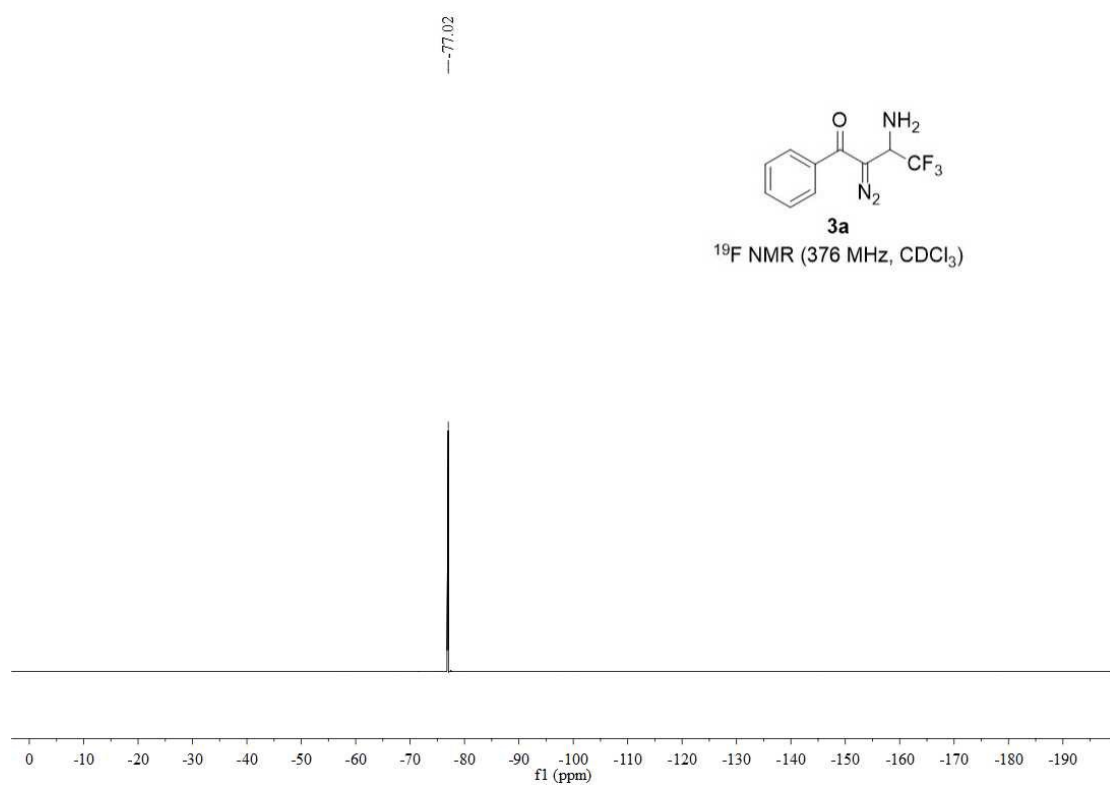
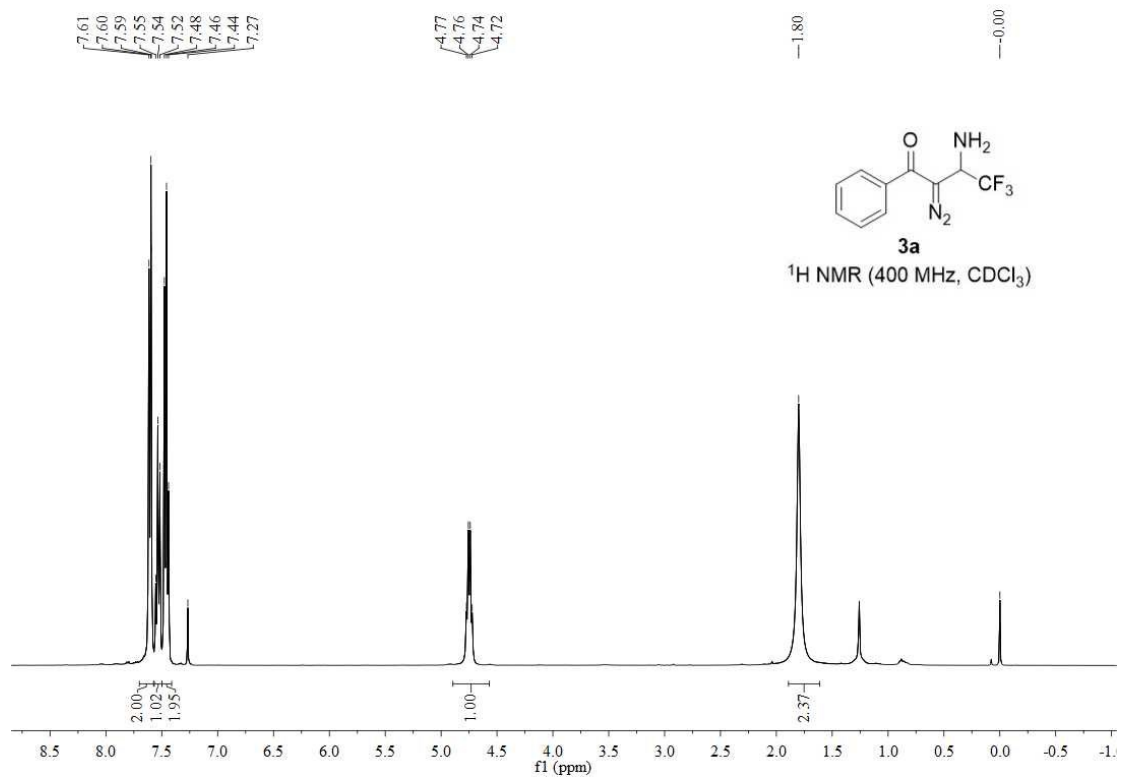
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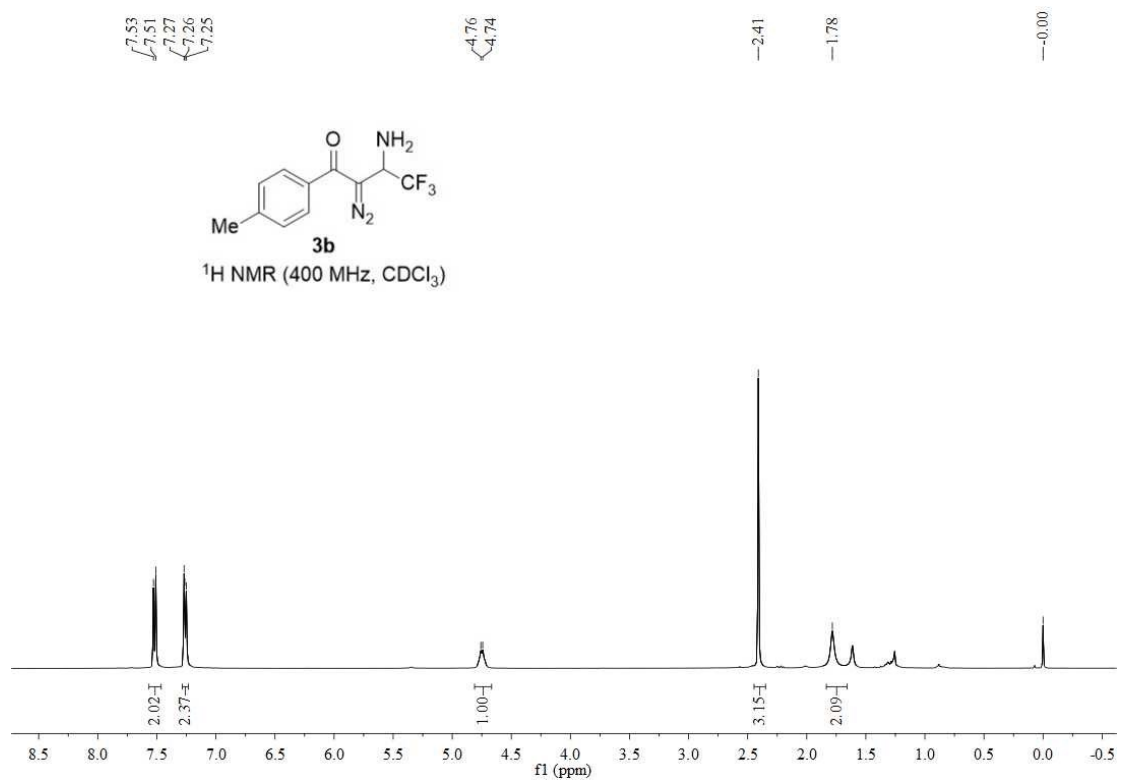
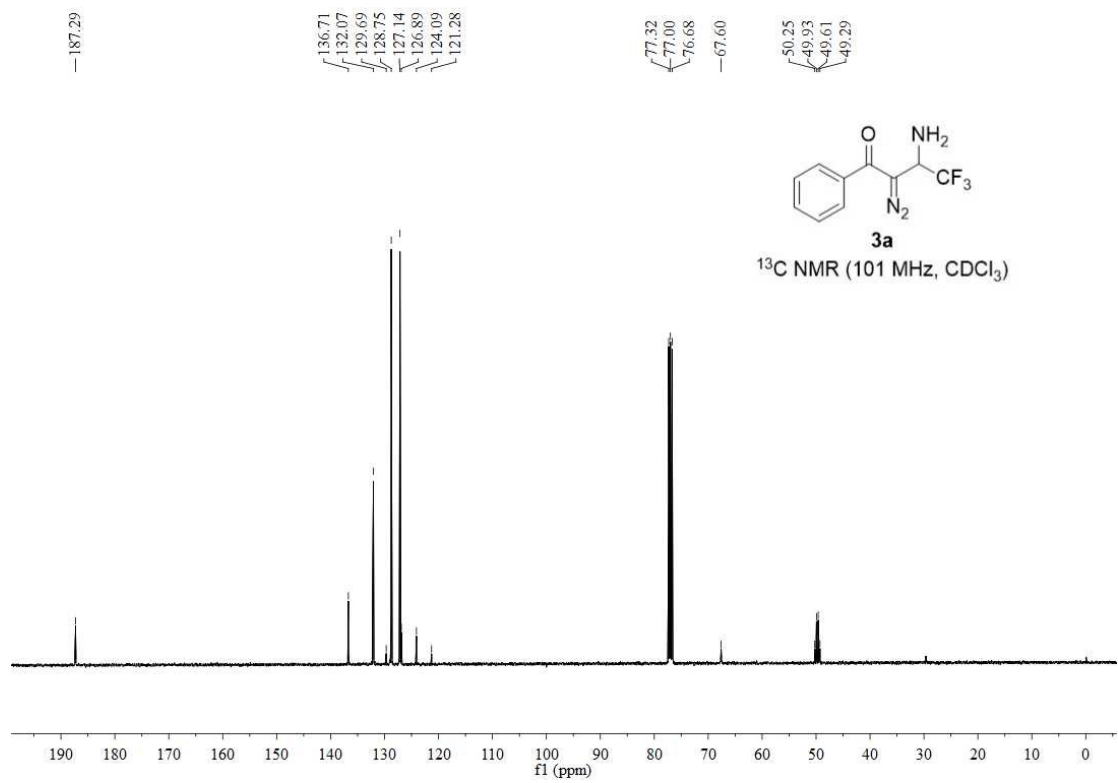
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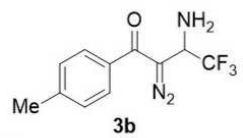
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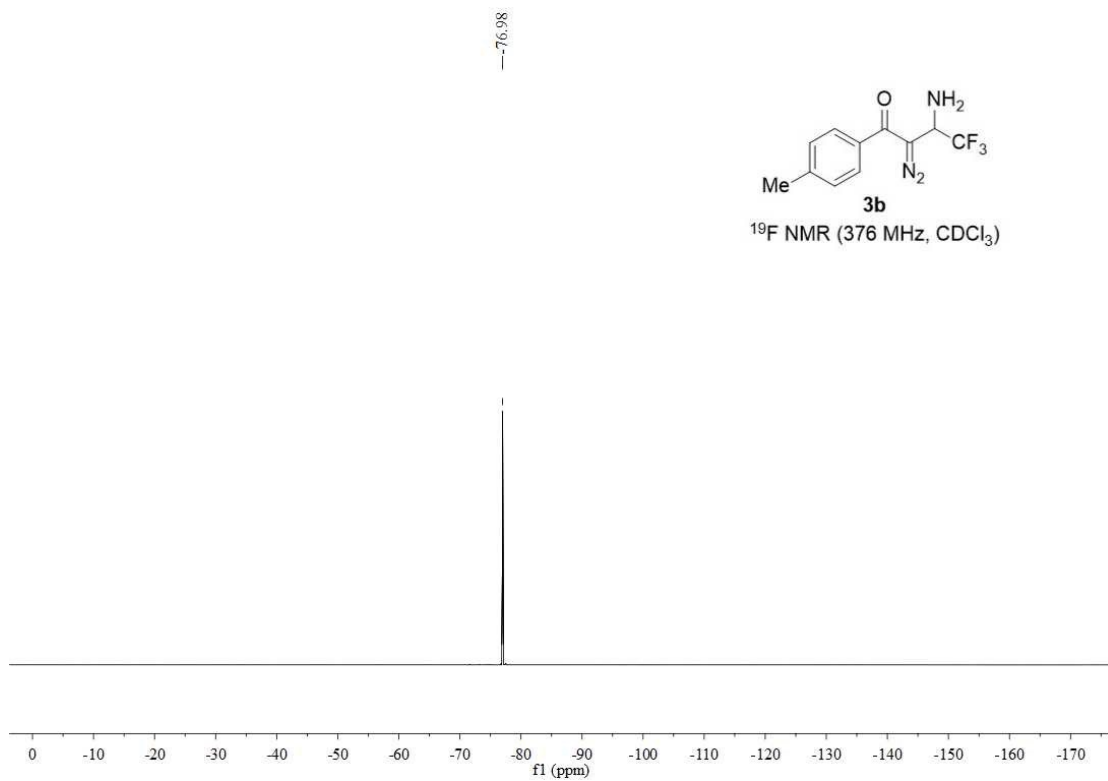
-10







¹⁹F NMR (376 MHz, CDCl₃)



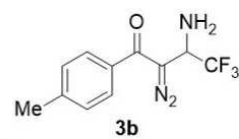
-187.09

-142.79
-134.03
-129.72
-129.37
-127.28
-126.92
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-121.32

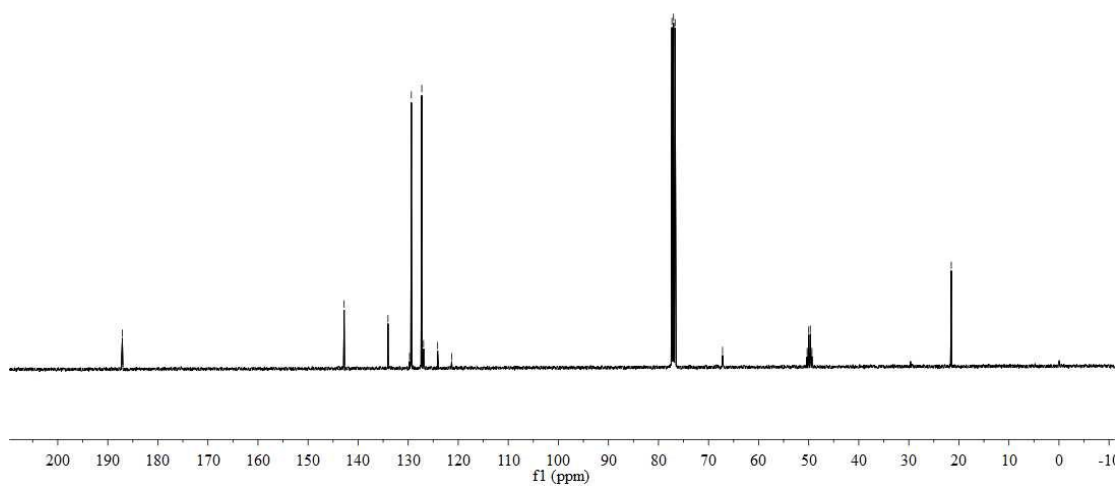
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-77.00
-76.68
-67.20

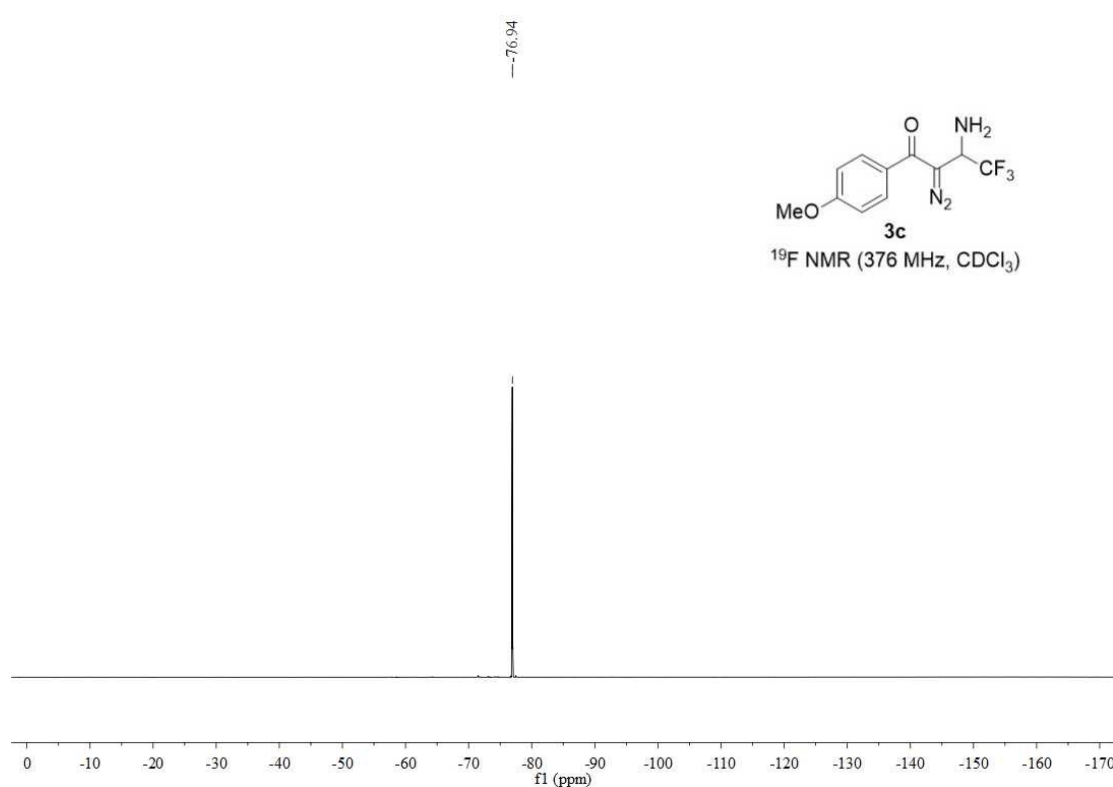
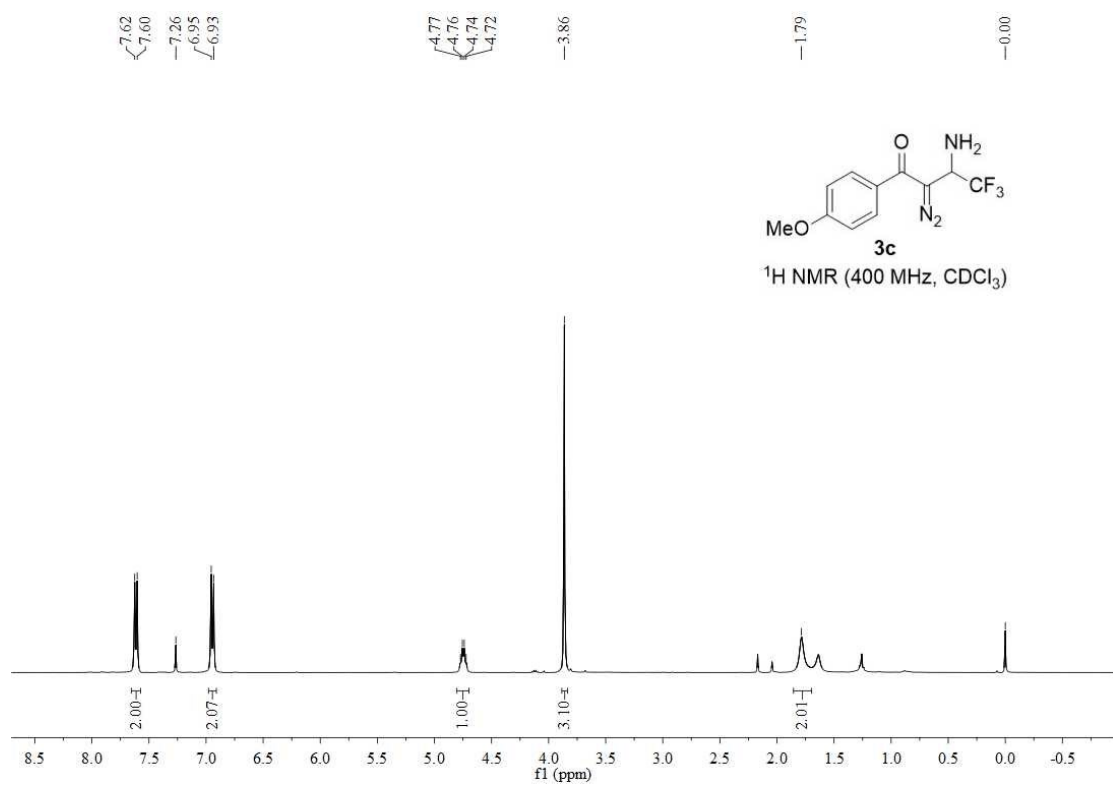
-50.31
-49.99
-49.67
-49.35

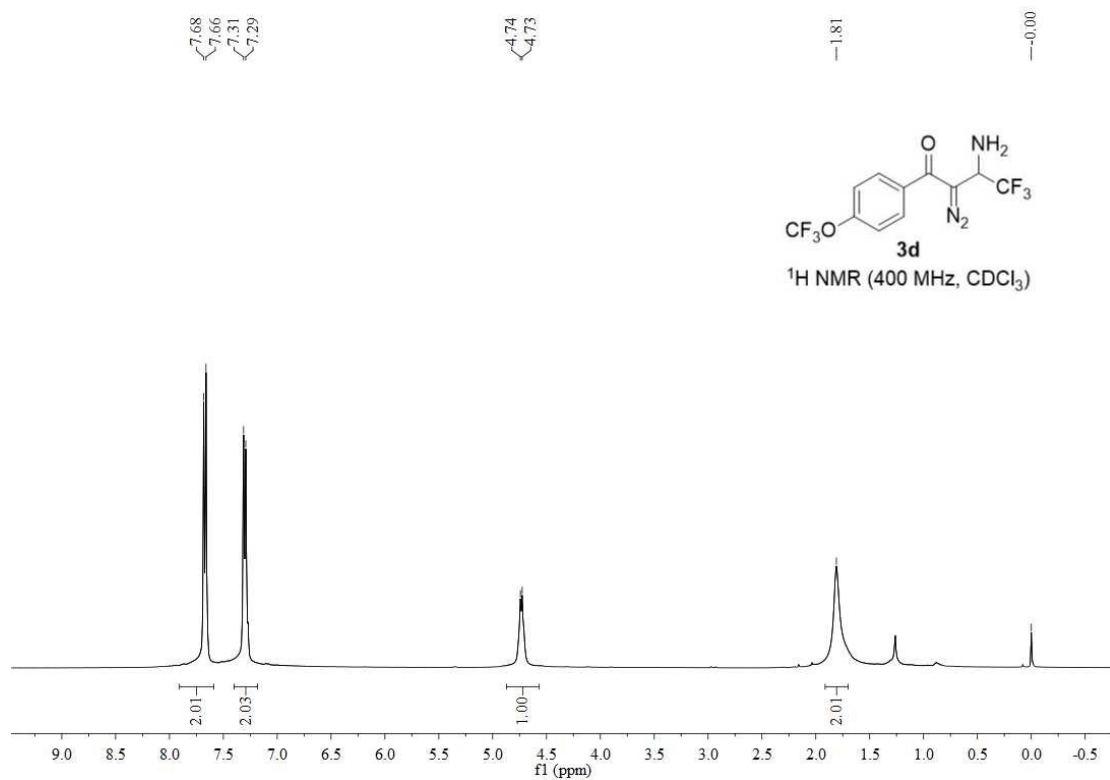
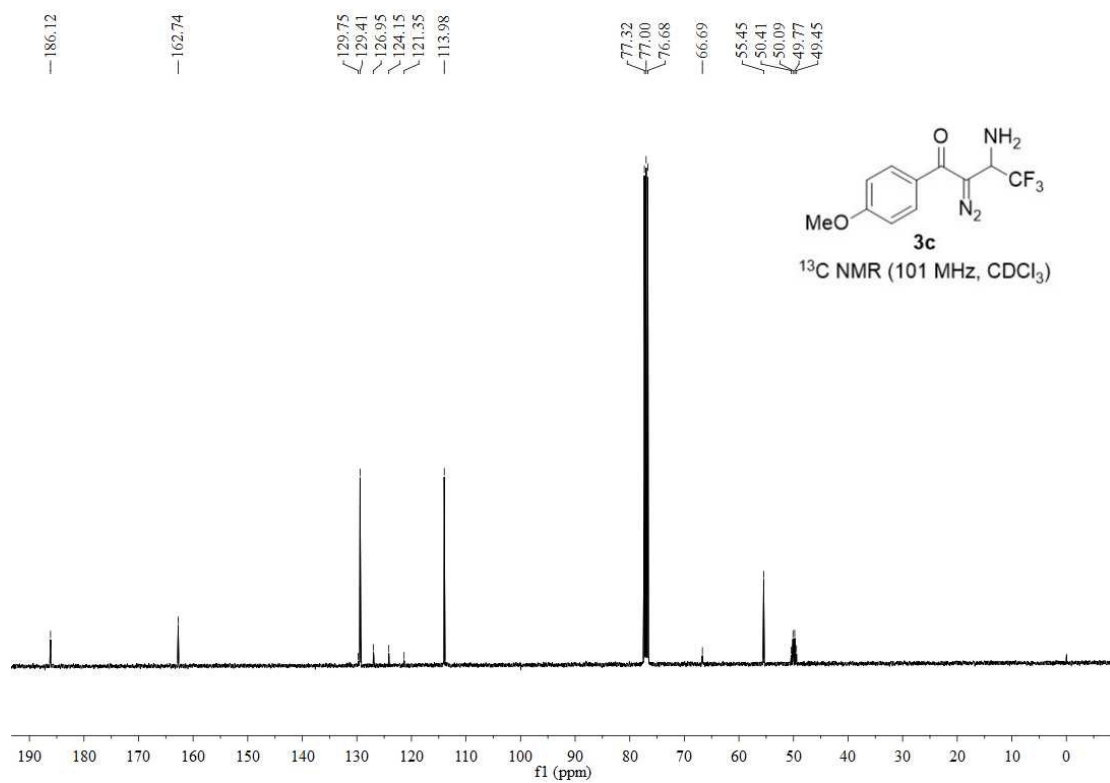
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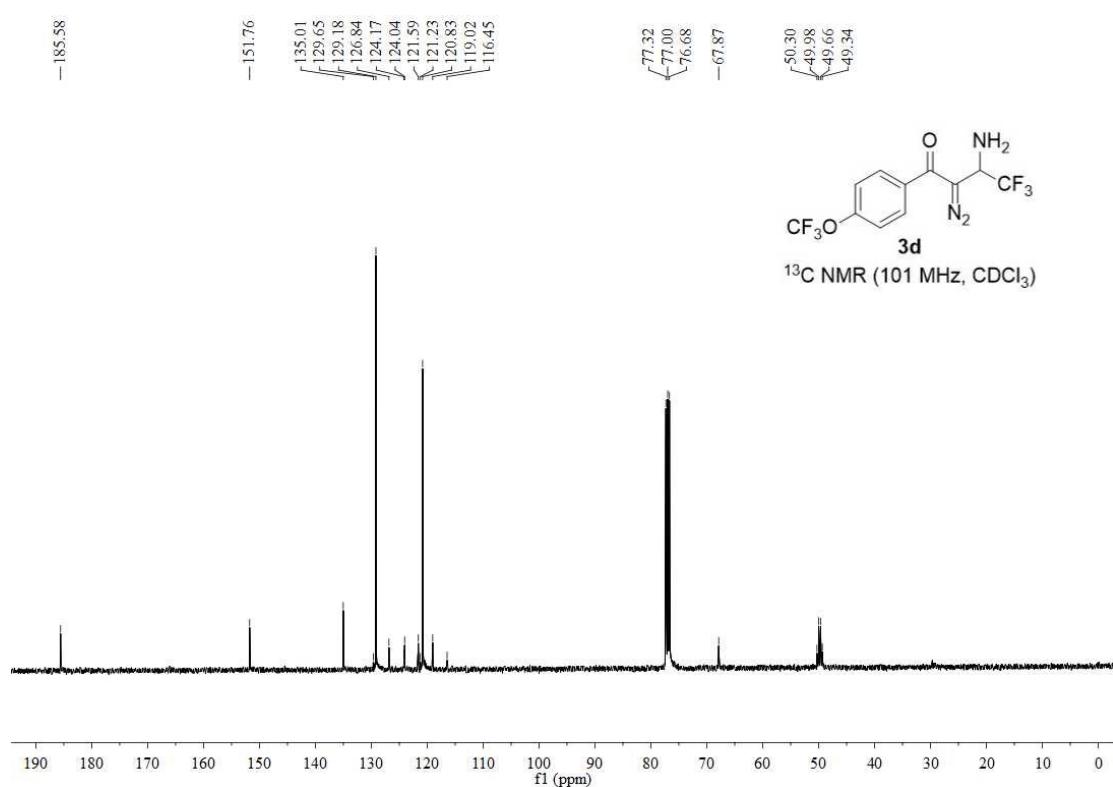
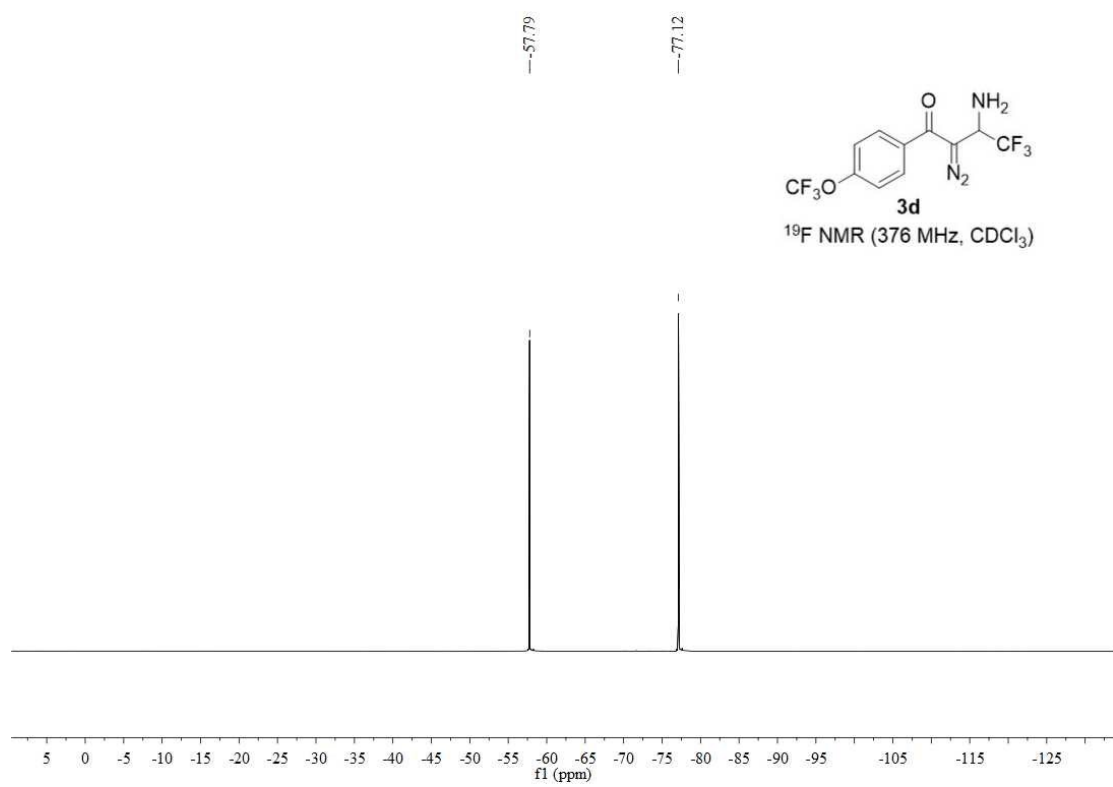


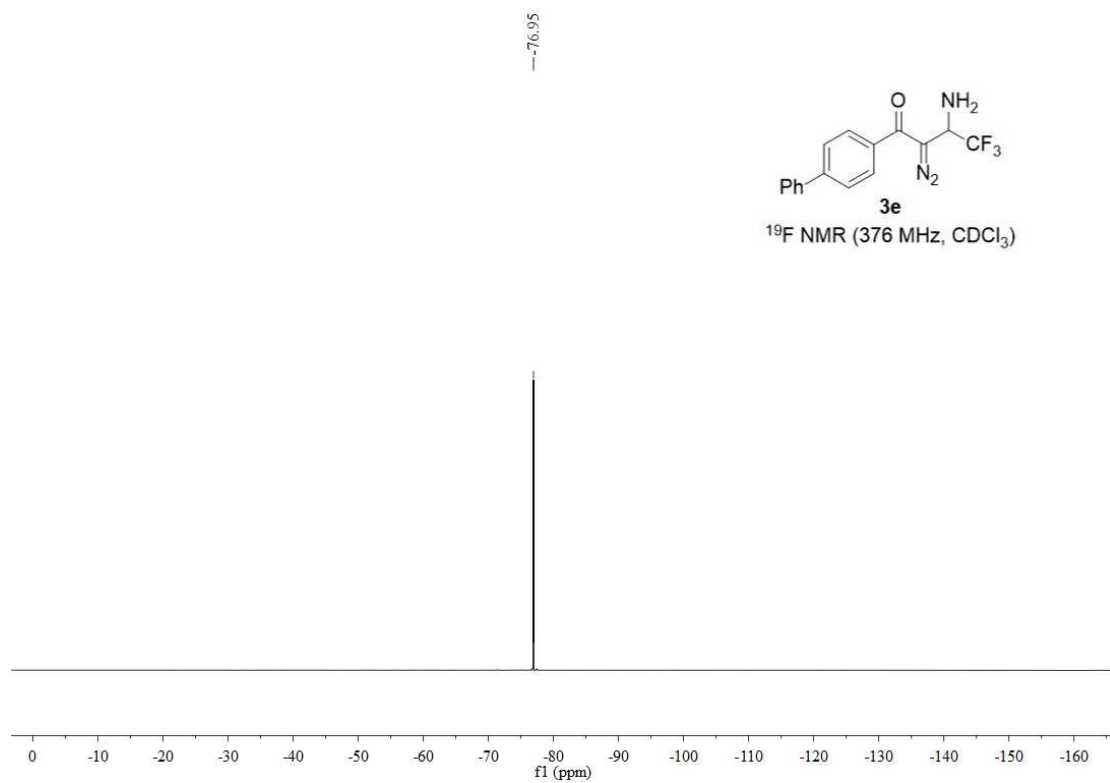
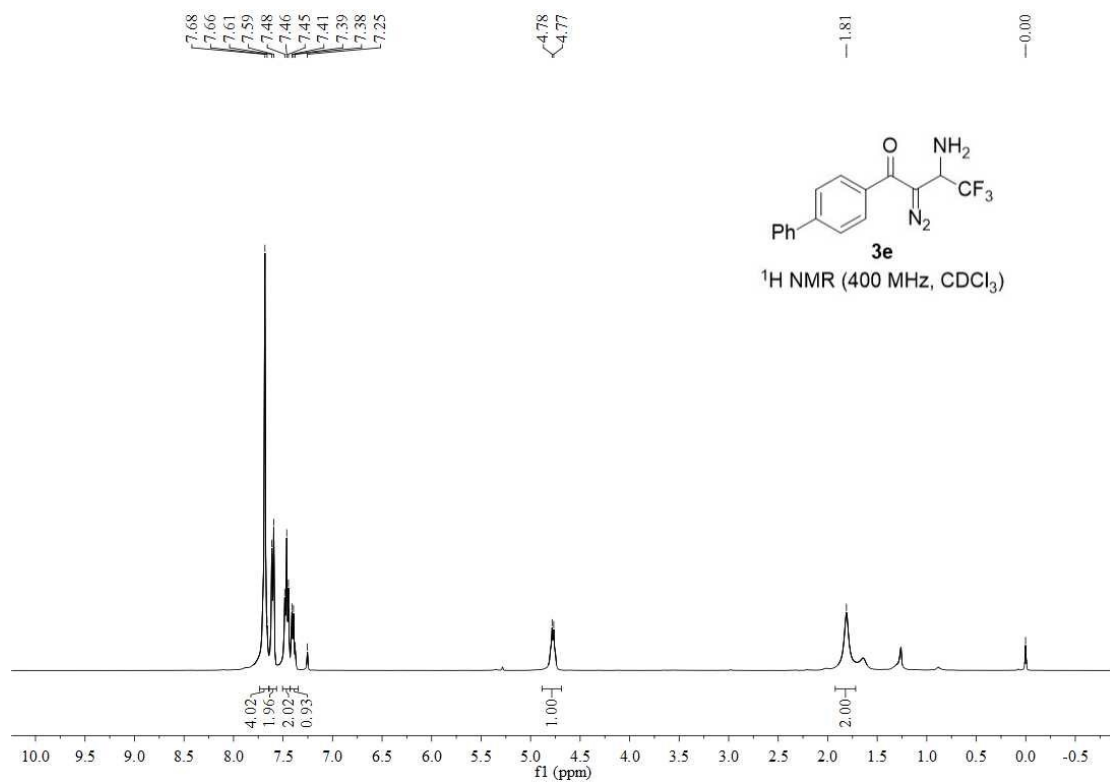
¹³C NMR (101 MHz, CDCl₃)

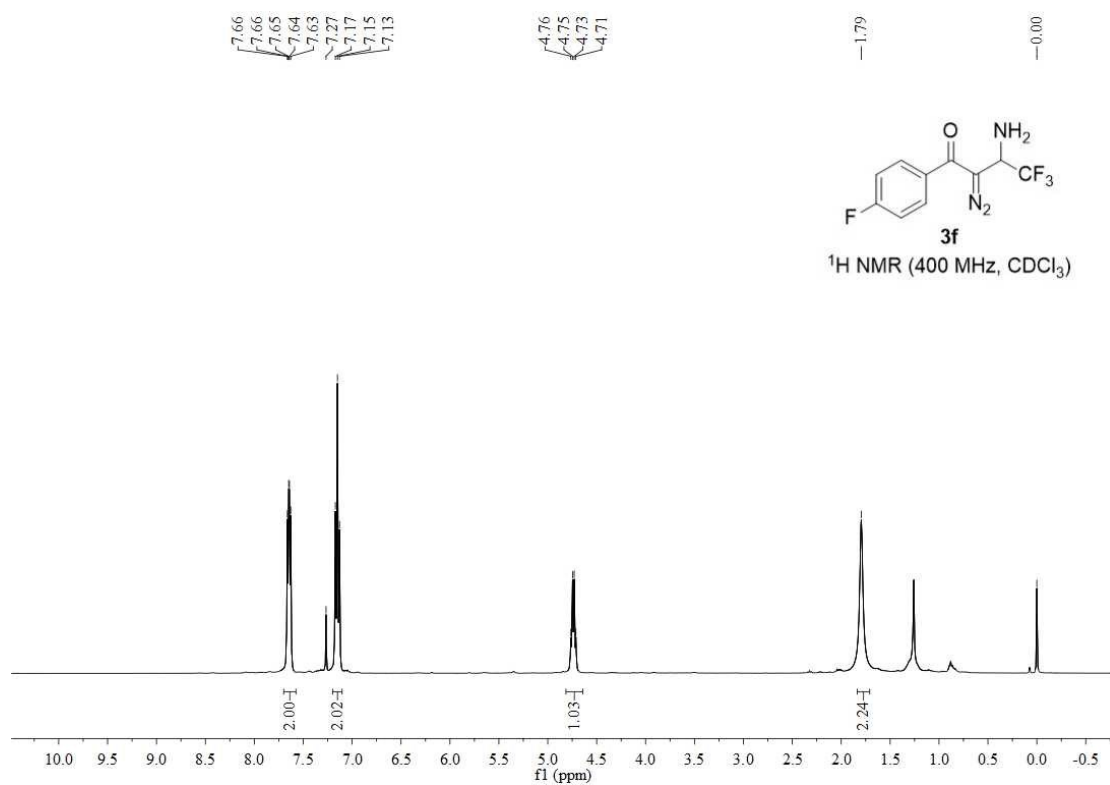
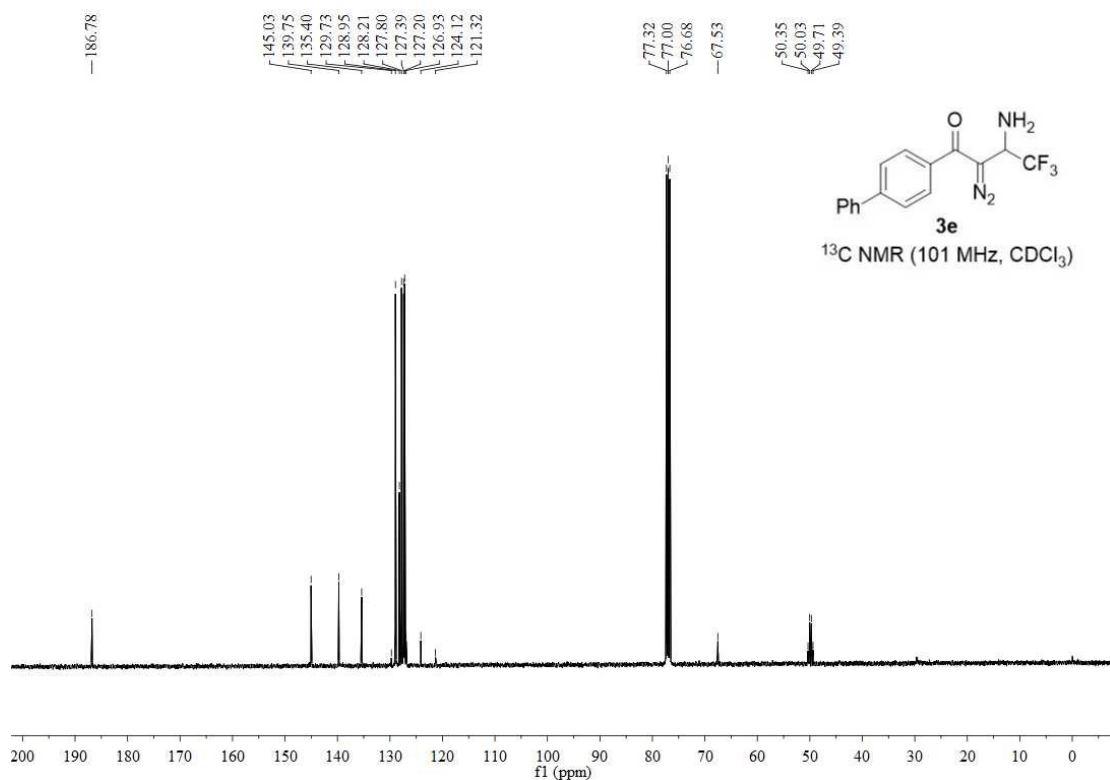


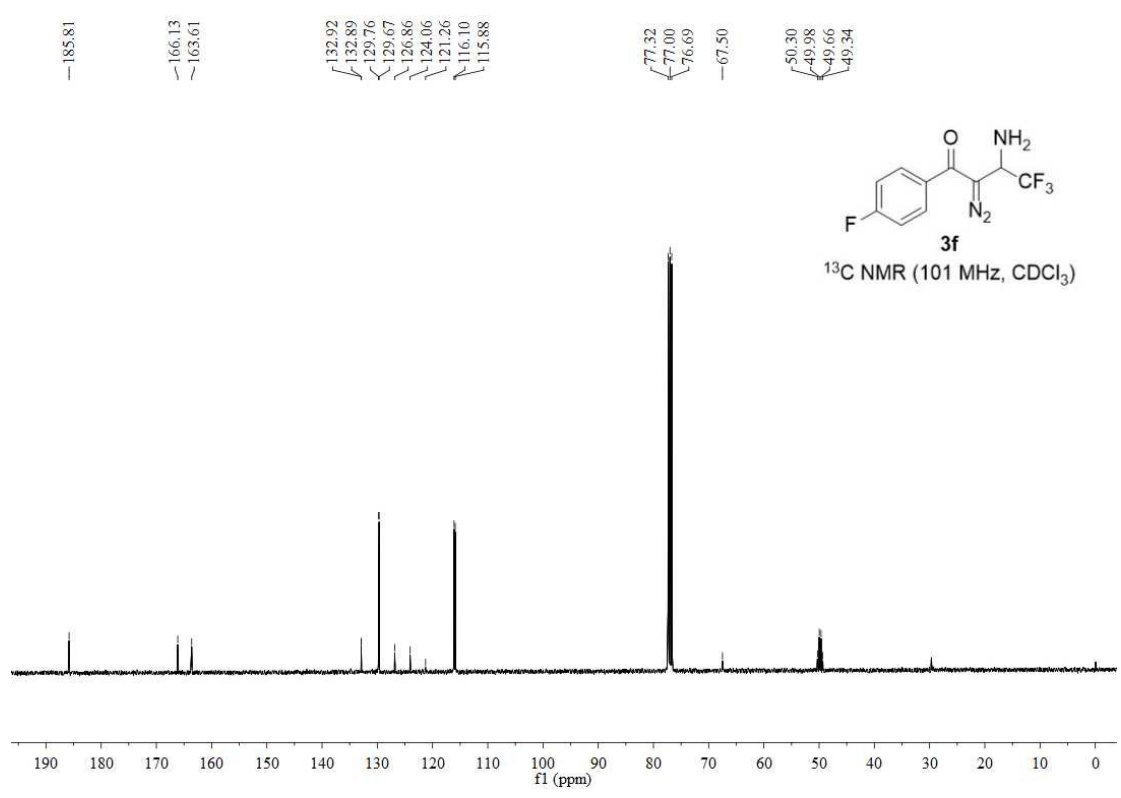
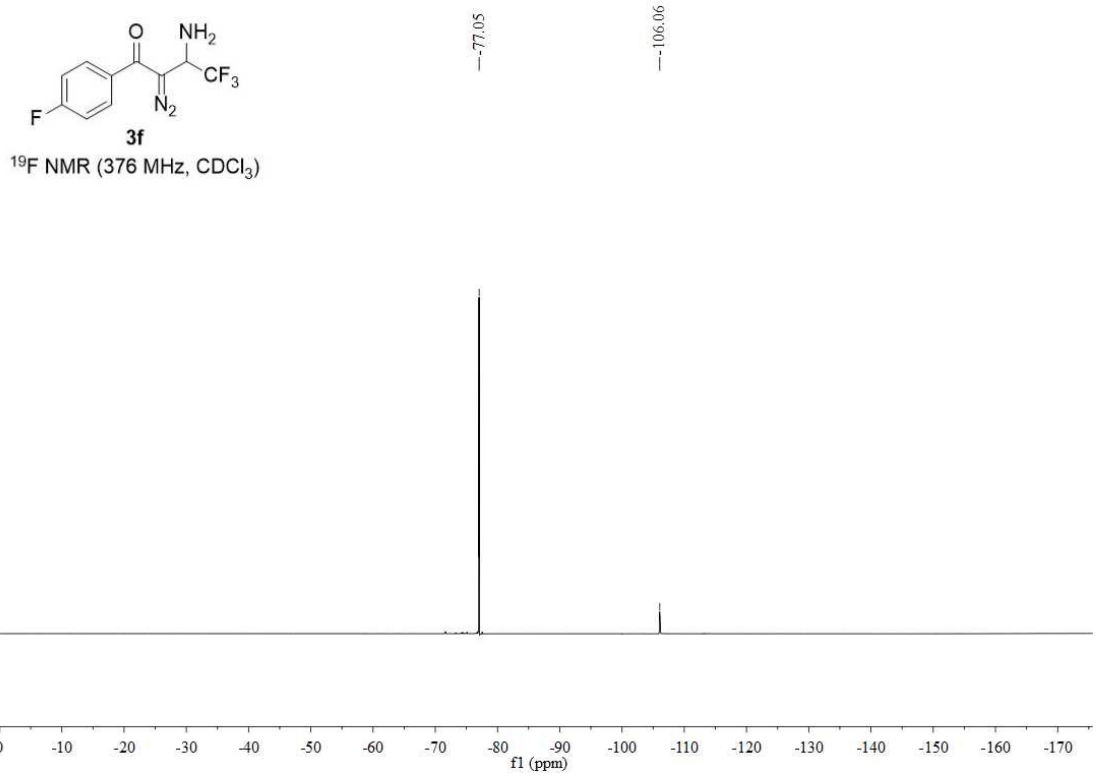


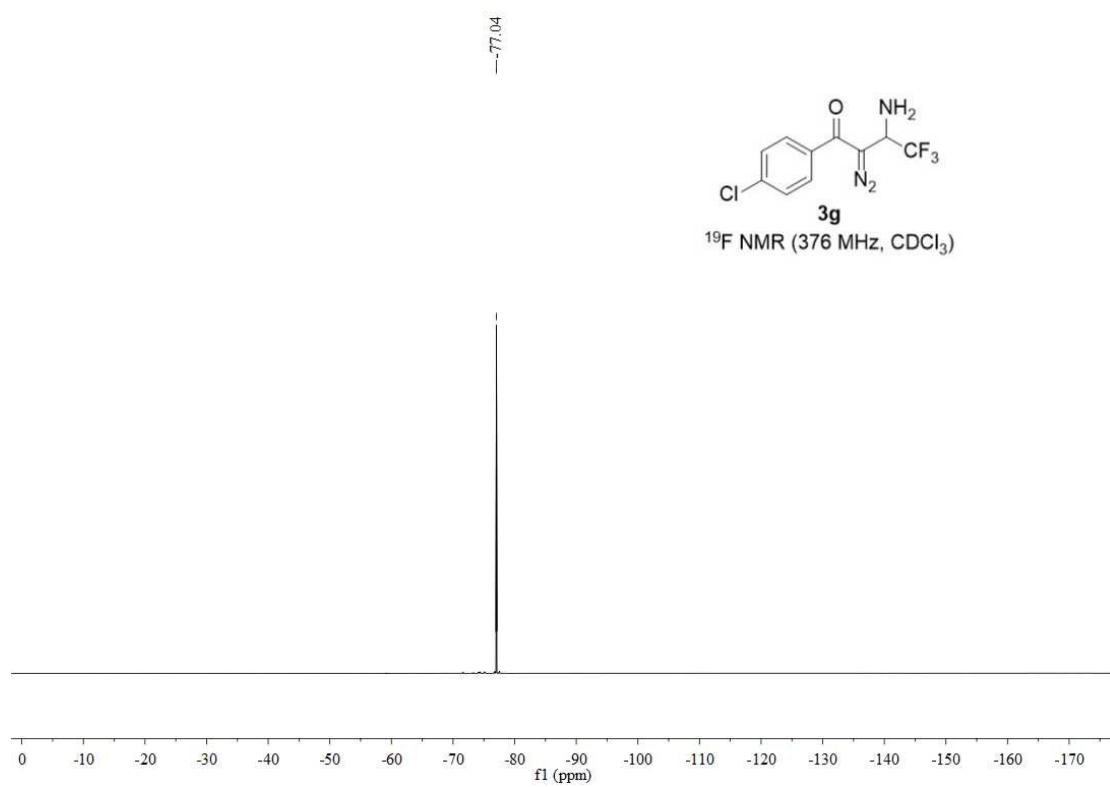
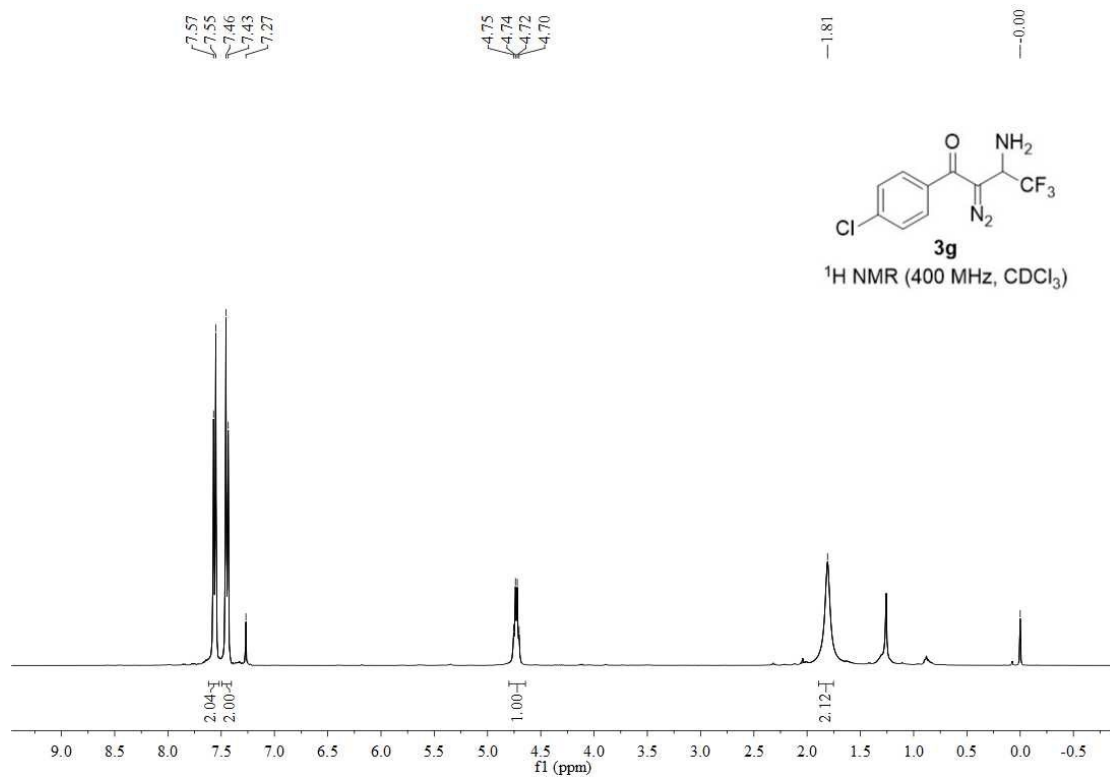


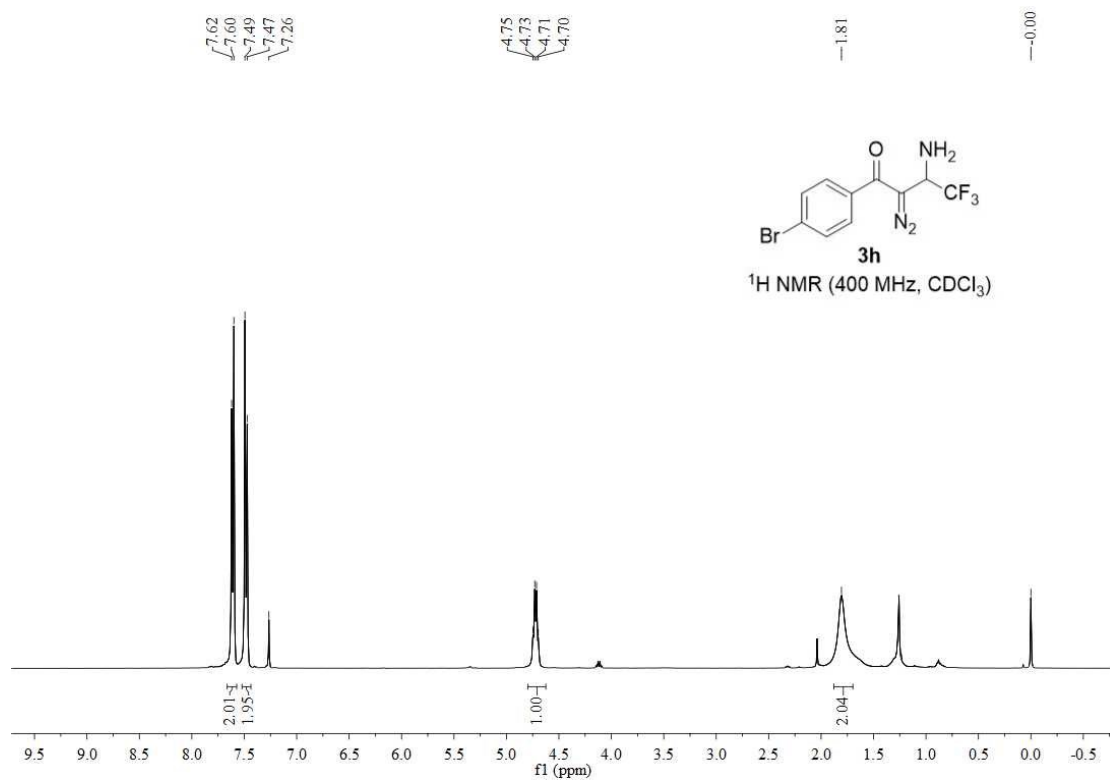
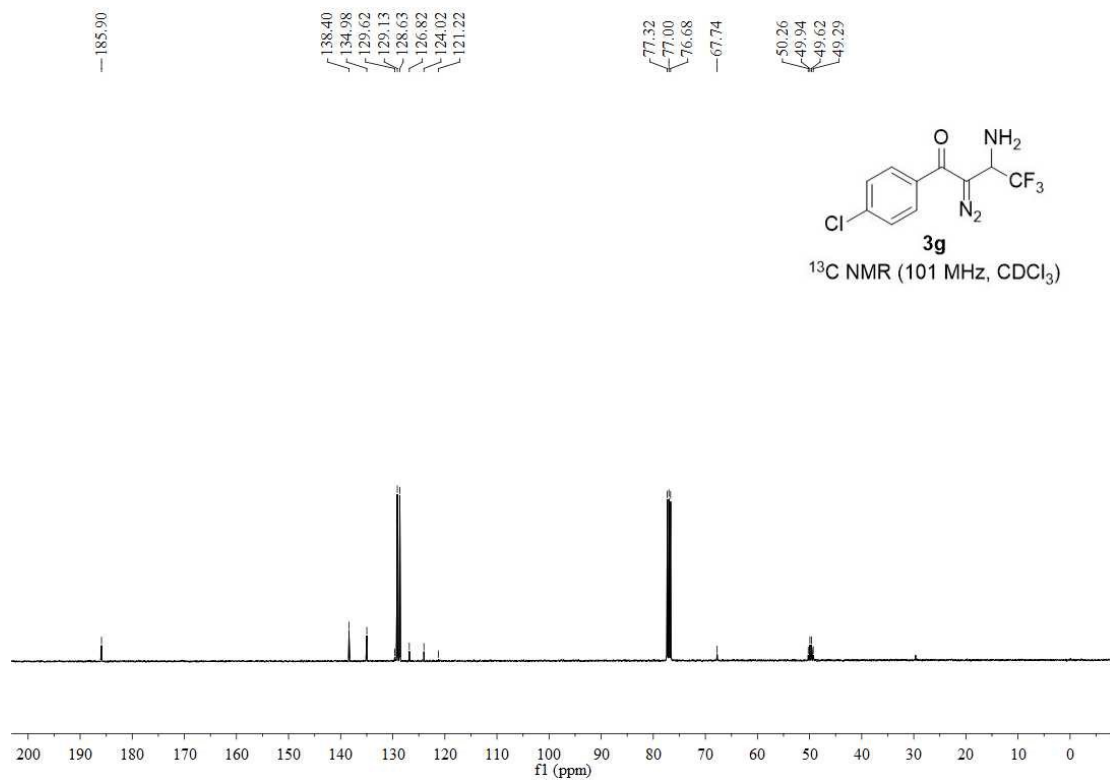


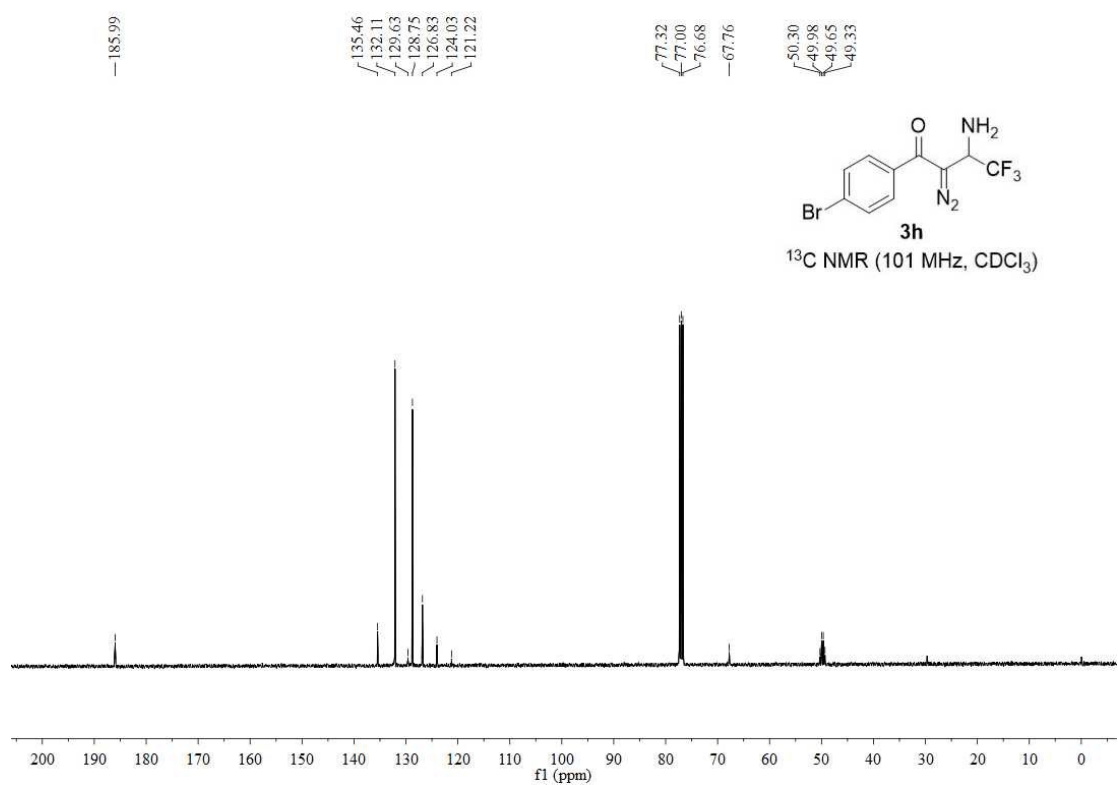
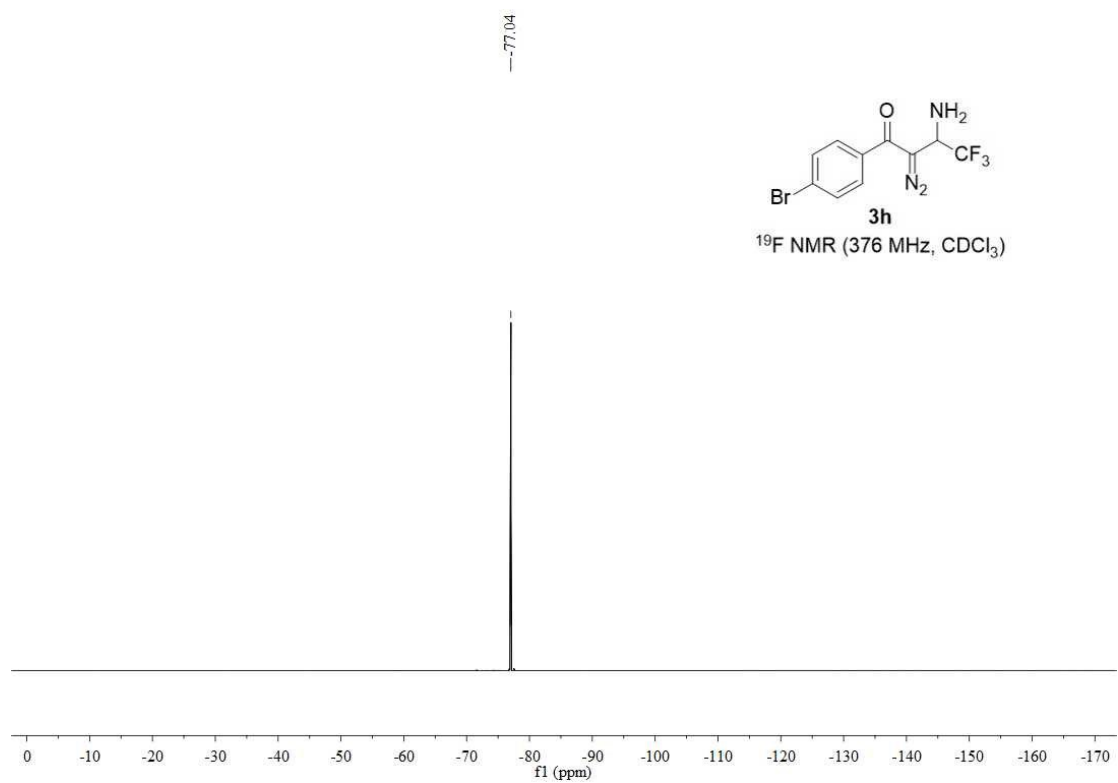


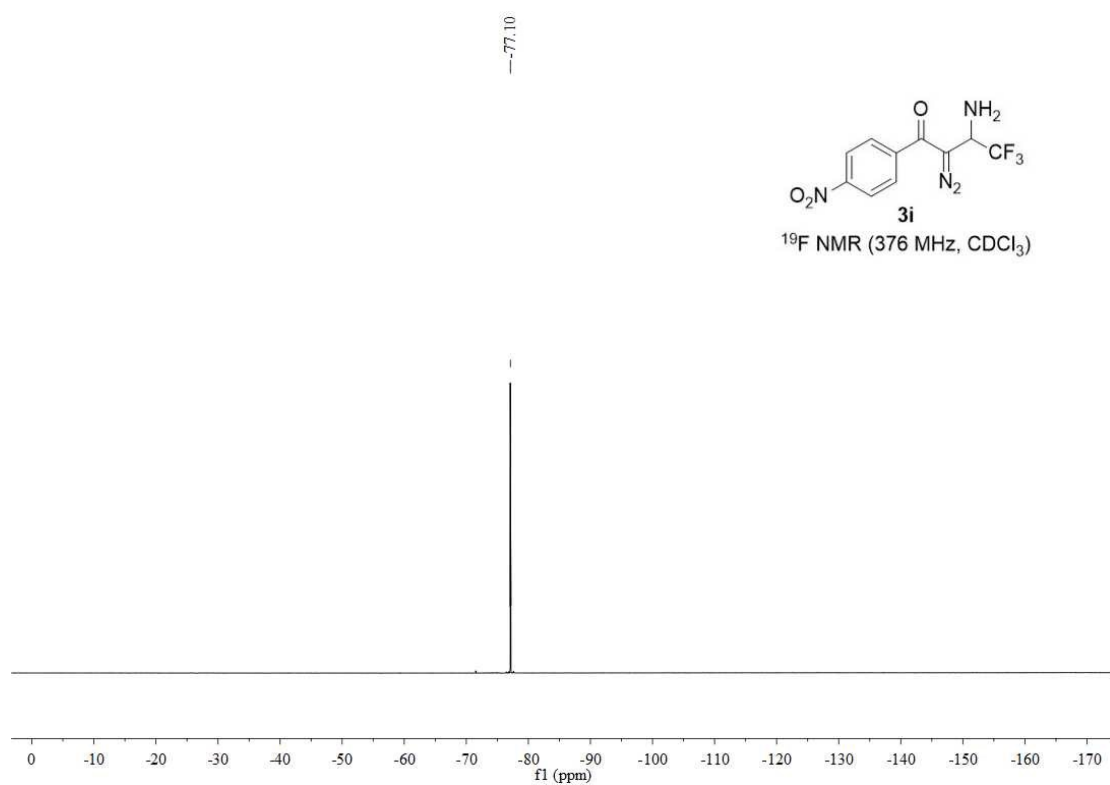
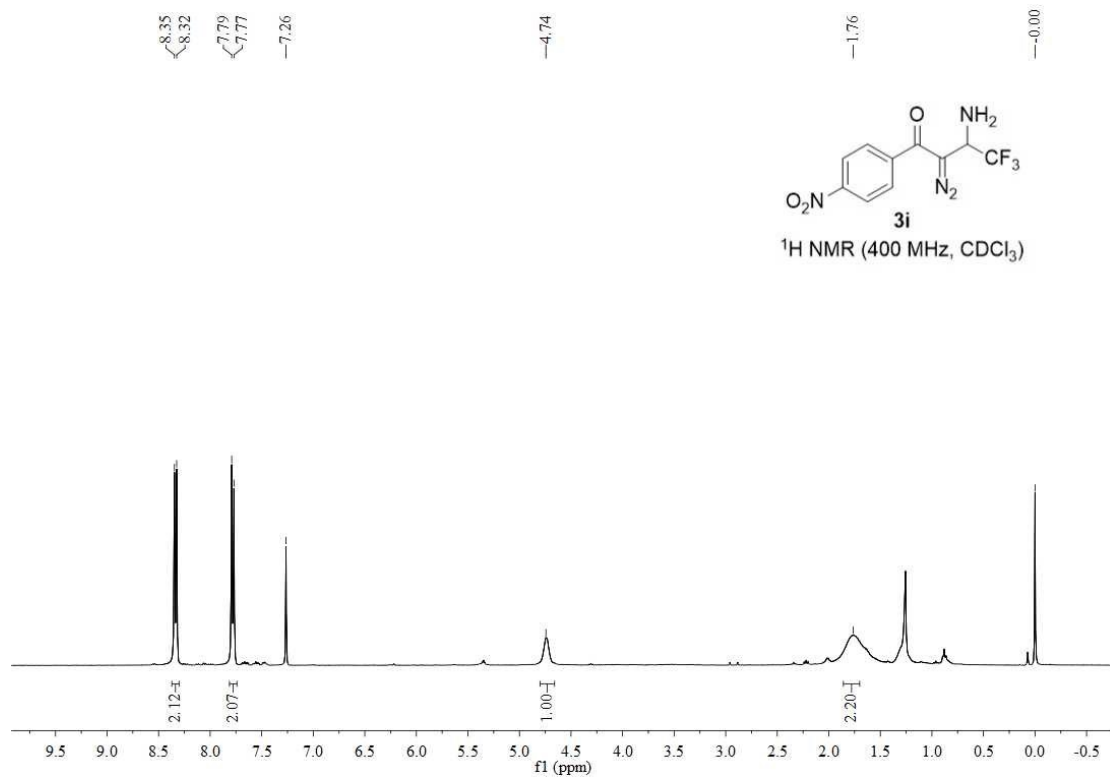


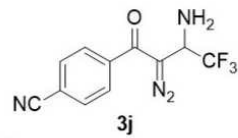
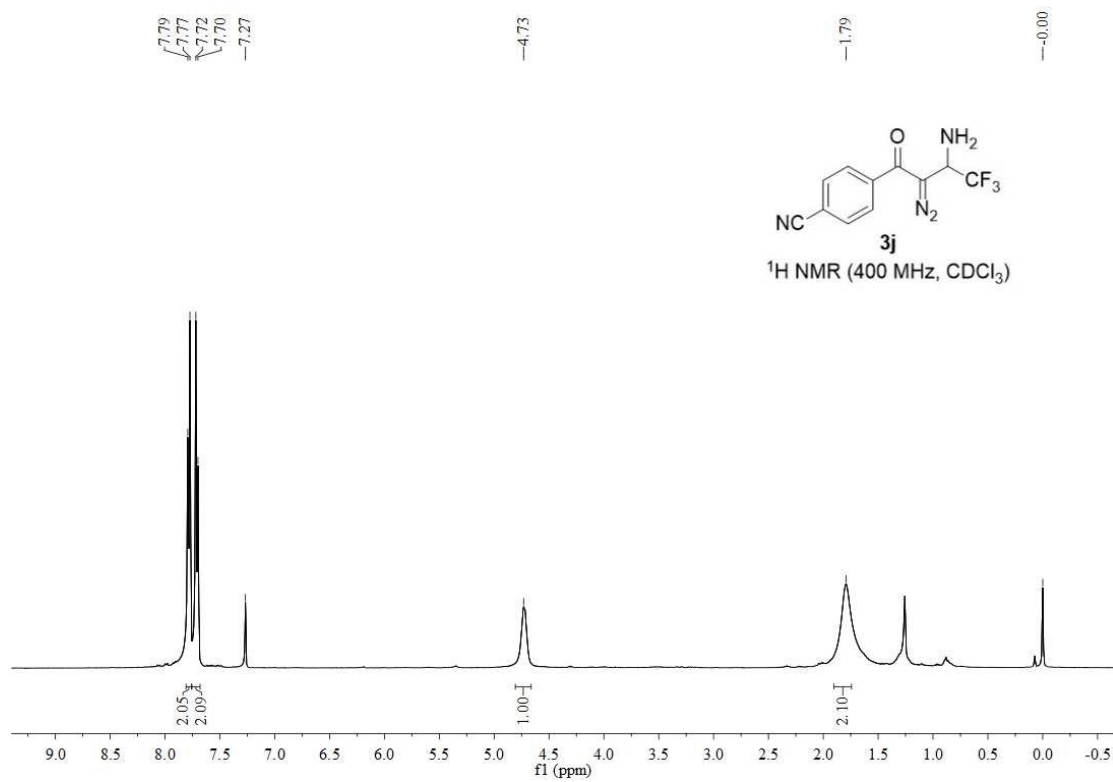
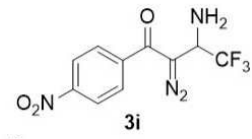
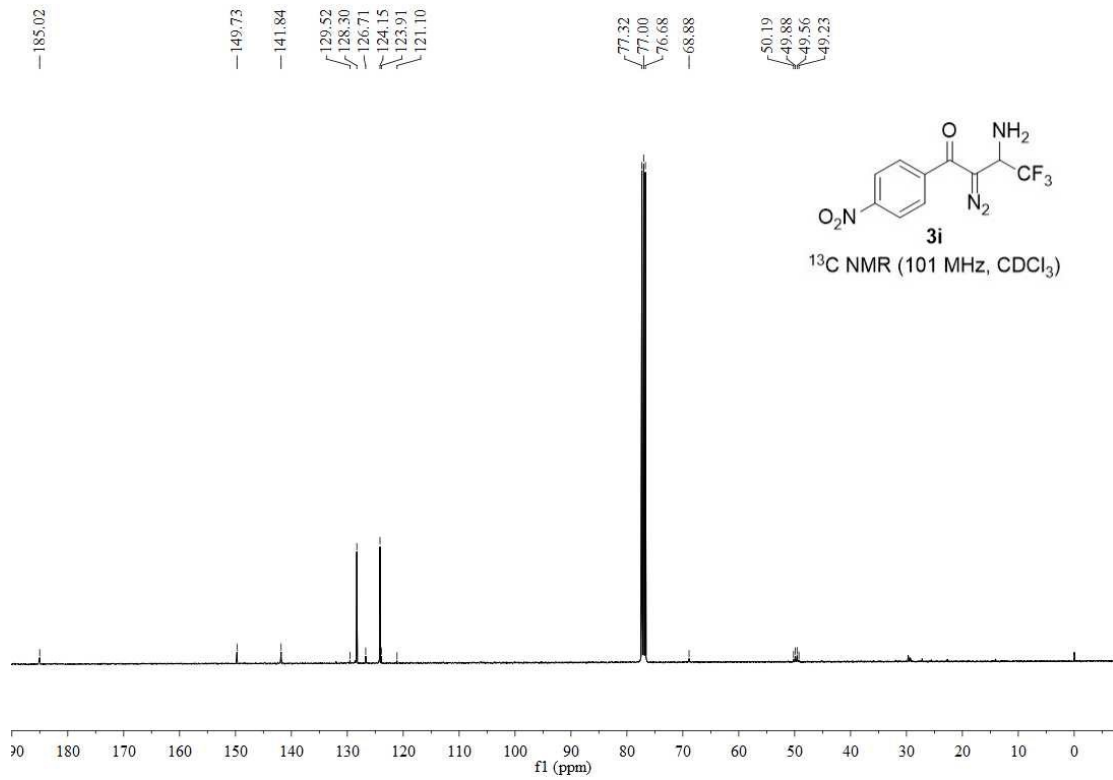


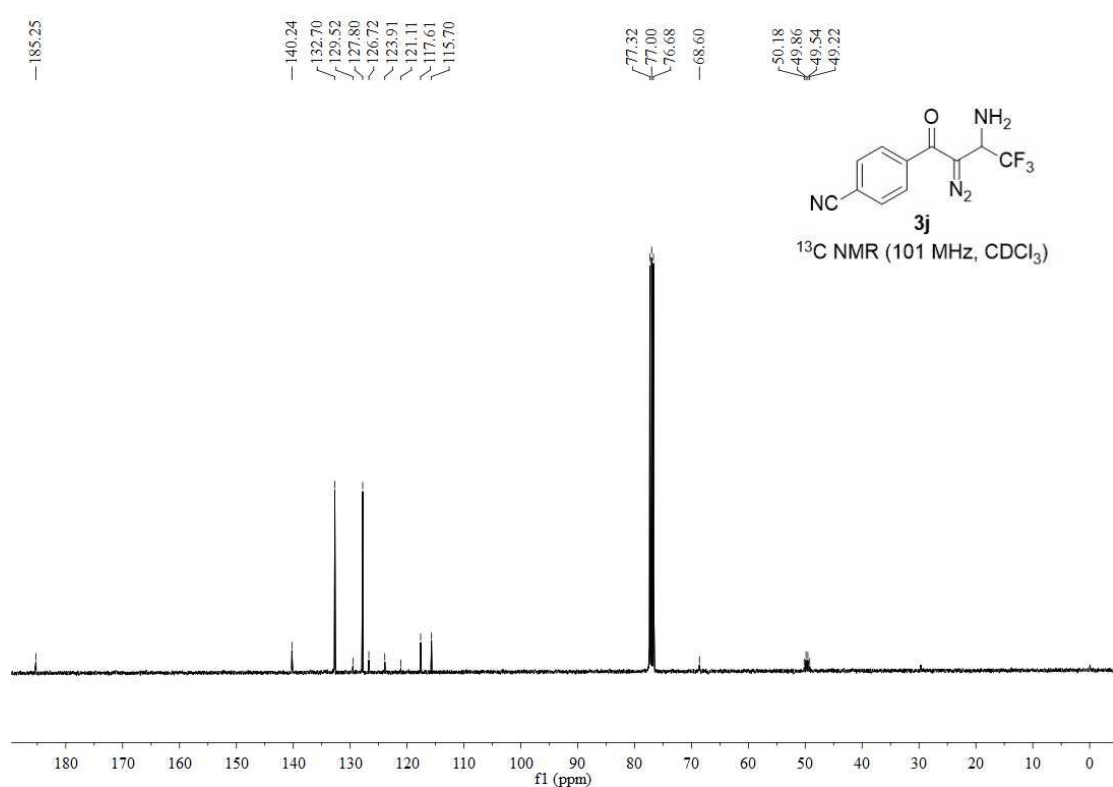
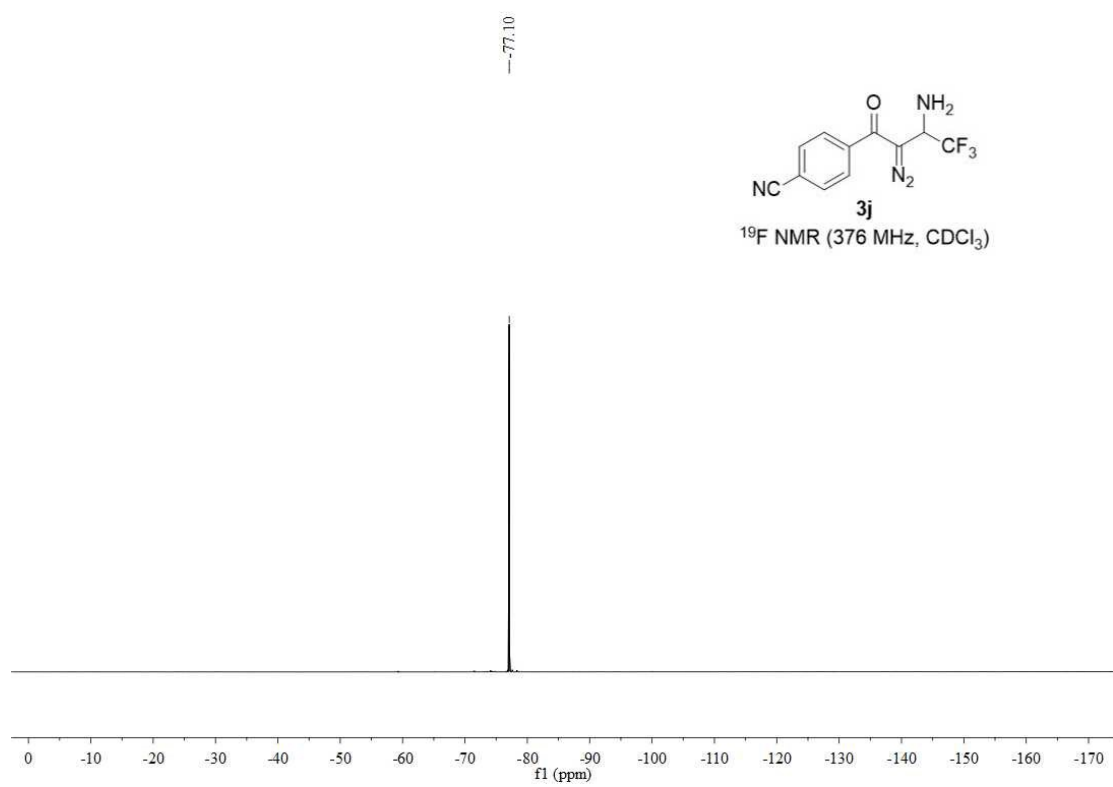


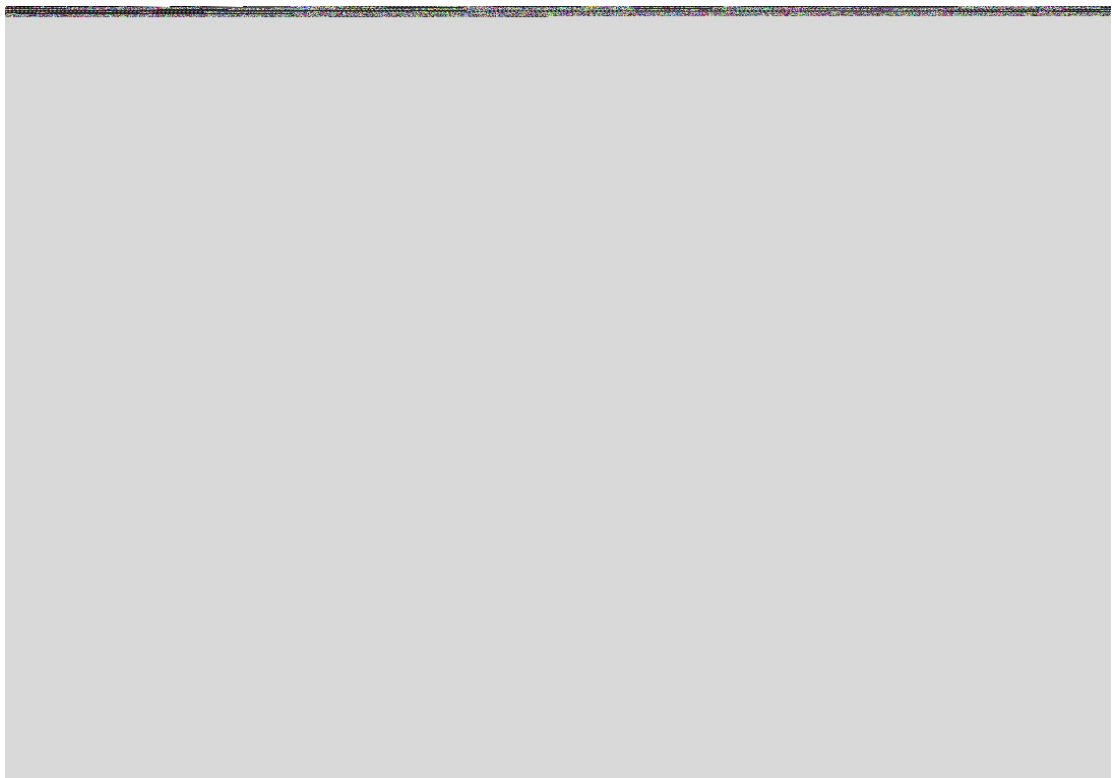
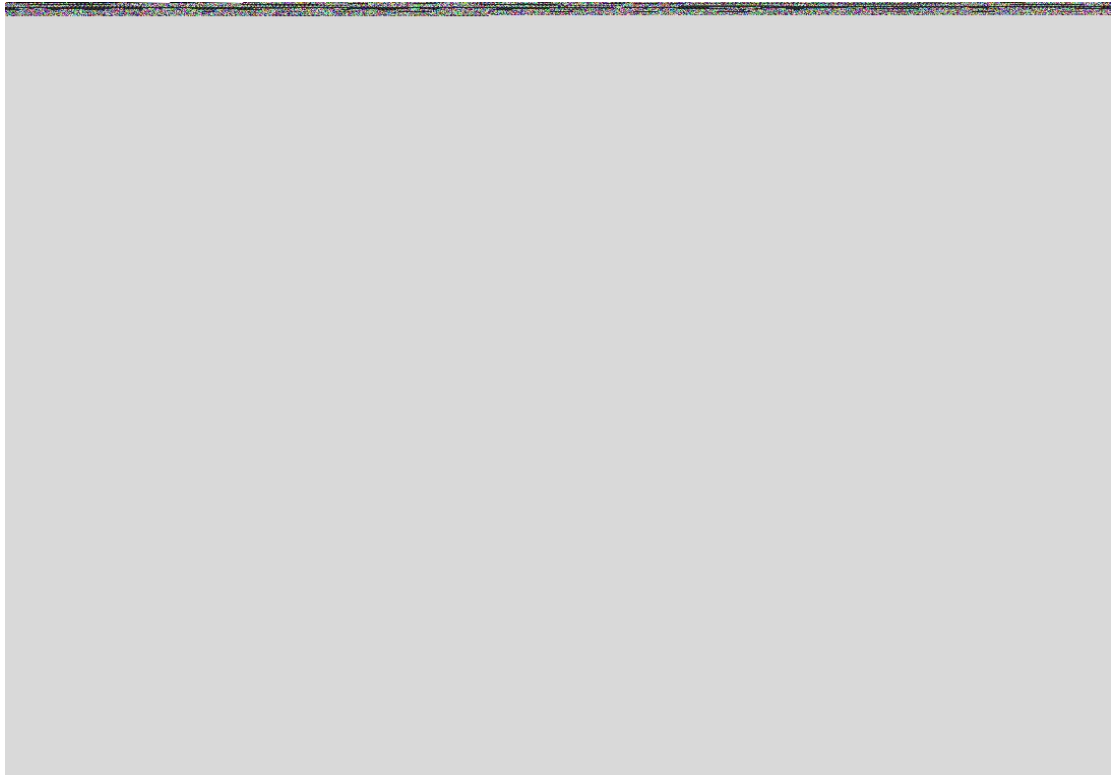


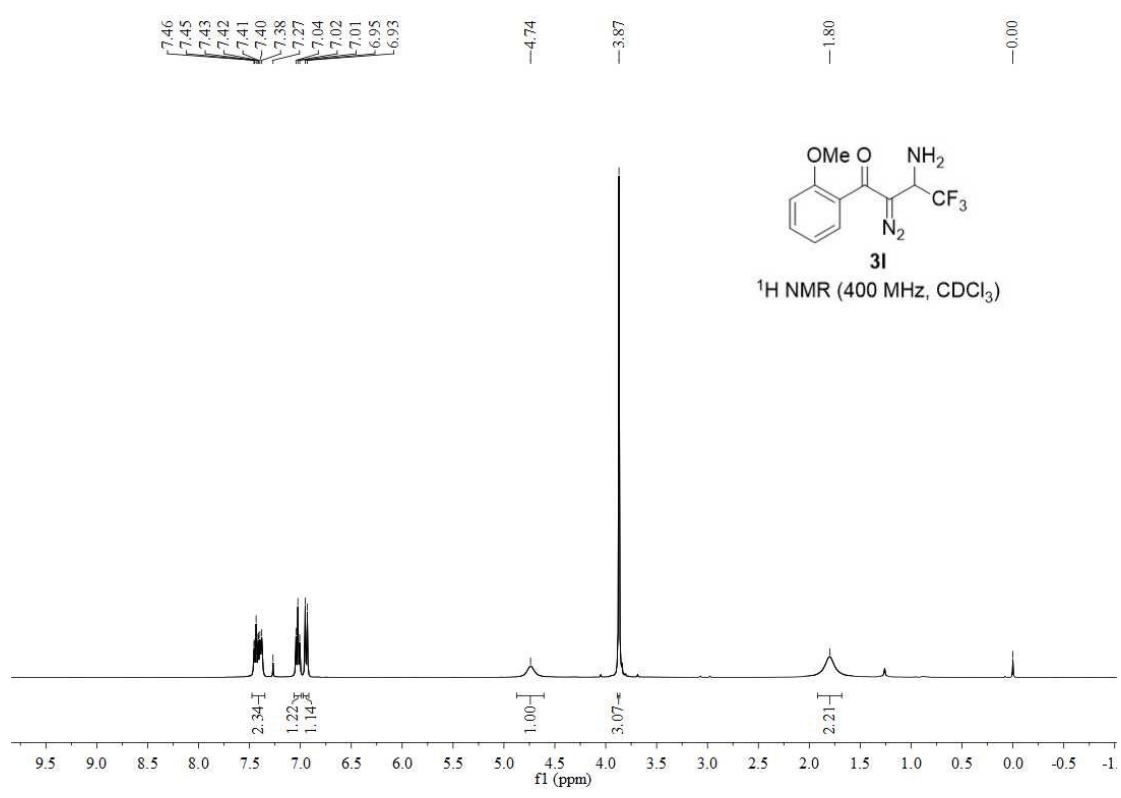


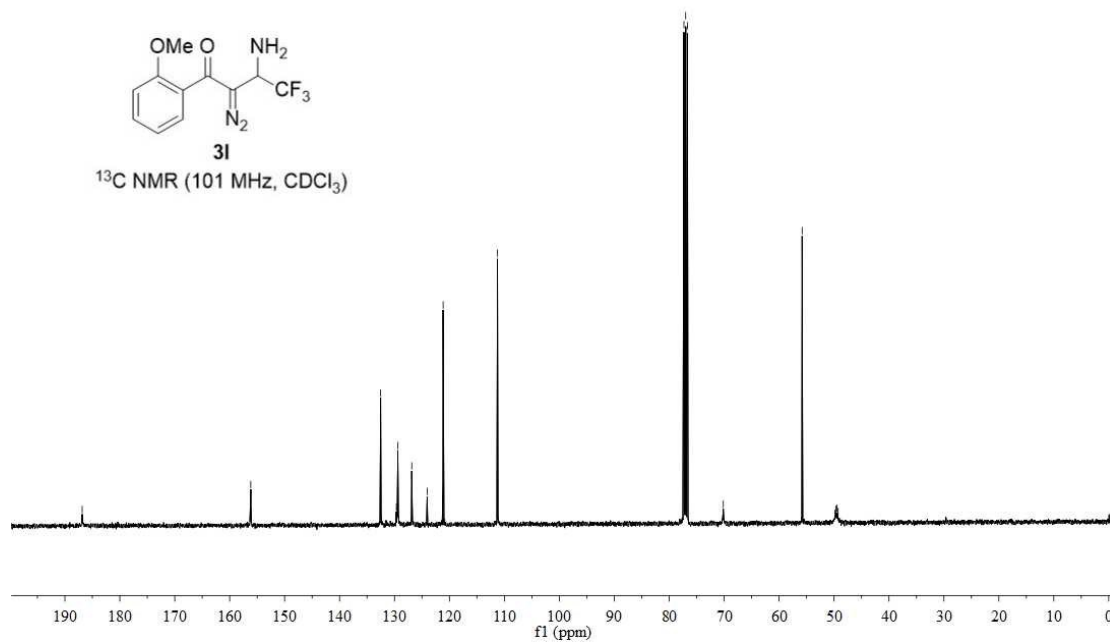
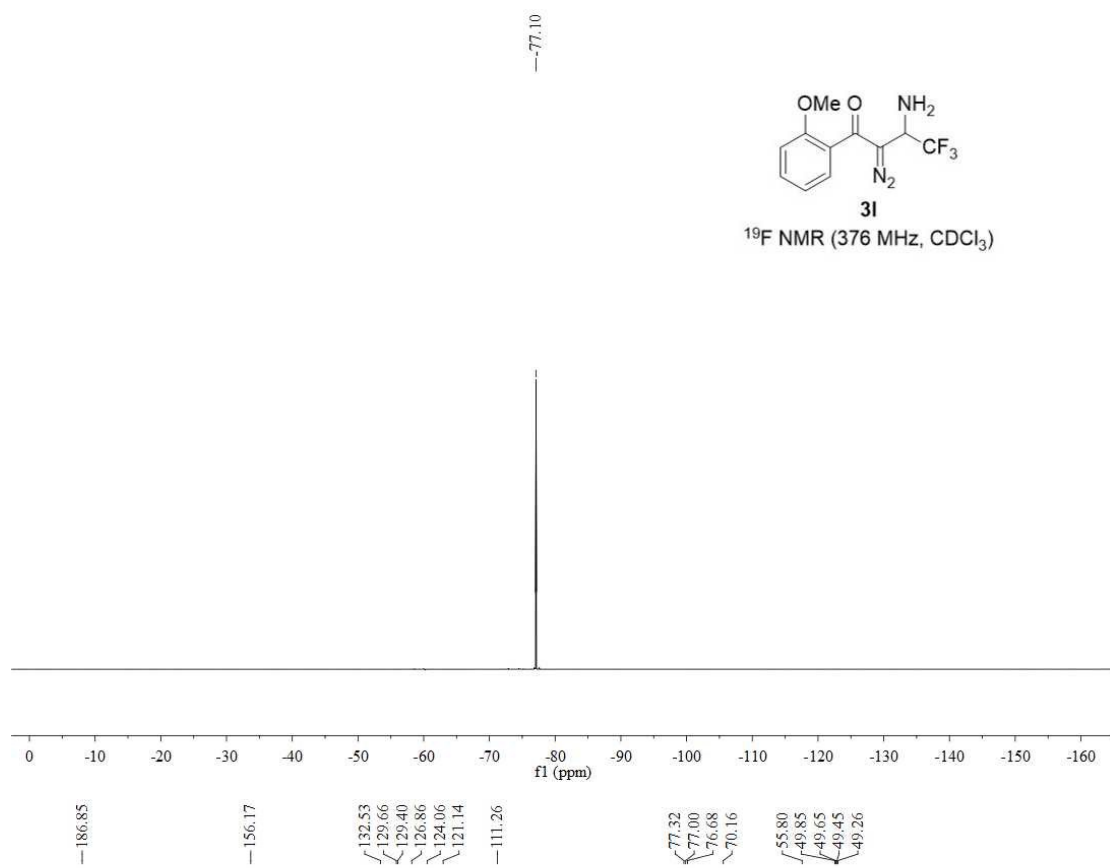


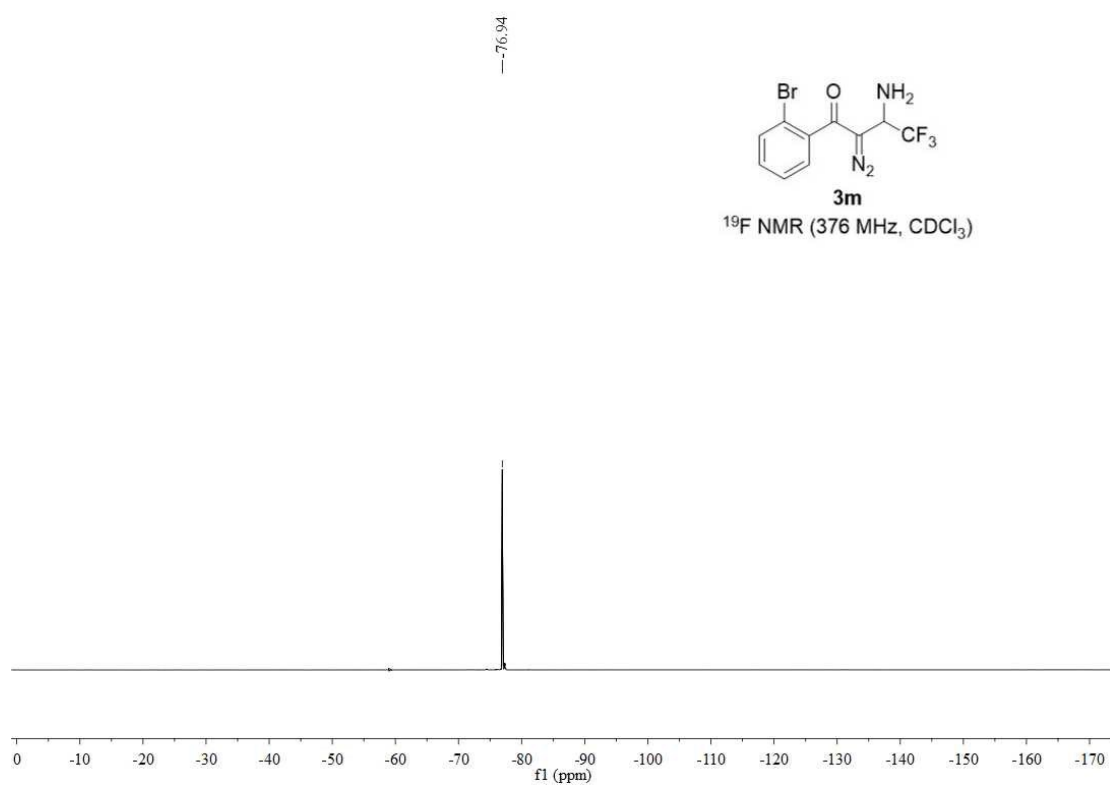
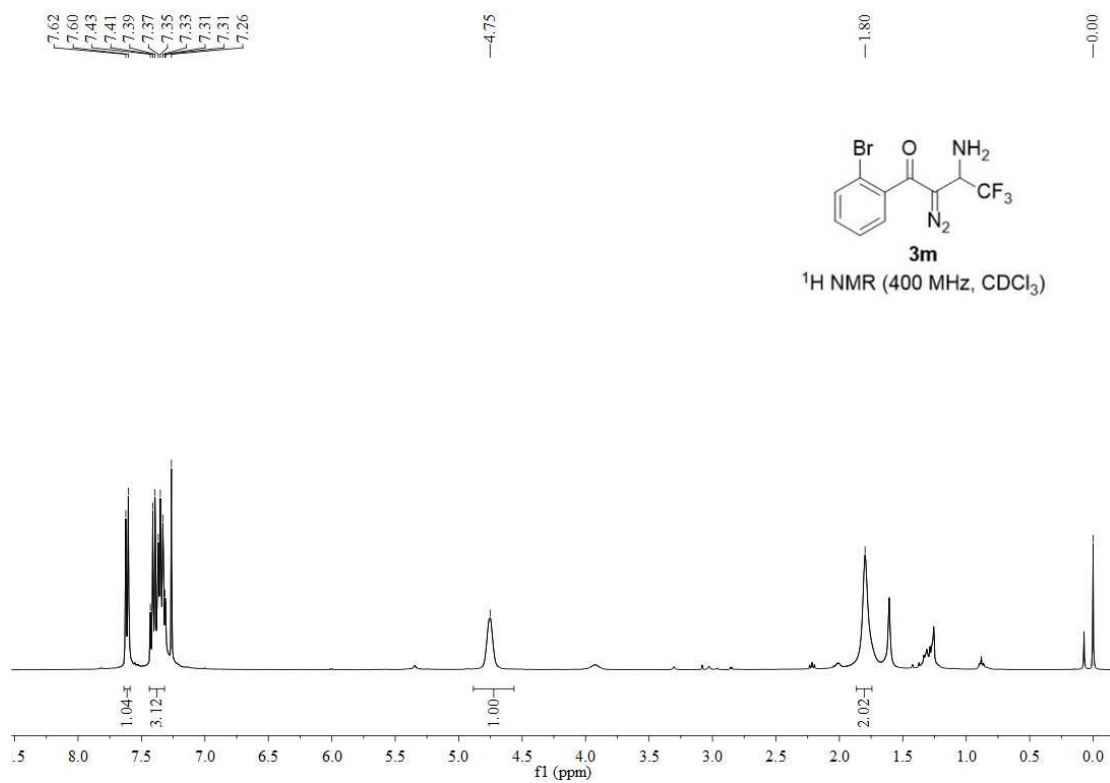


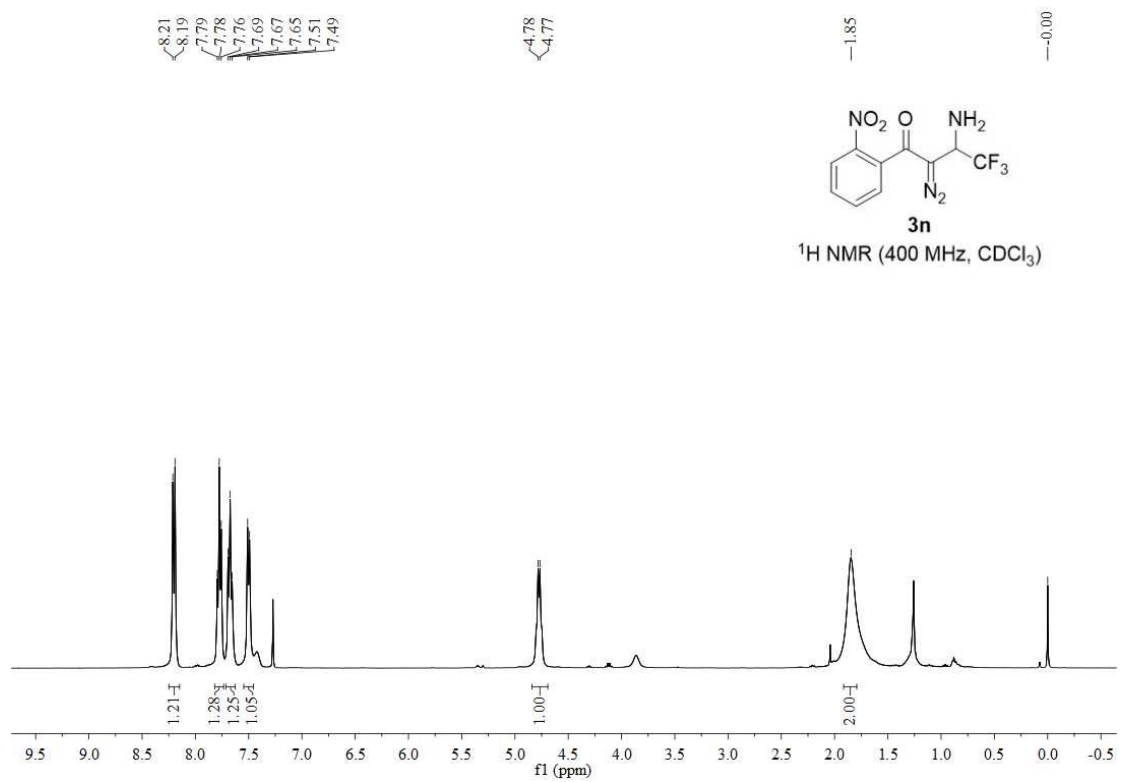
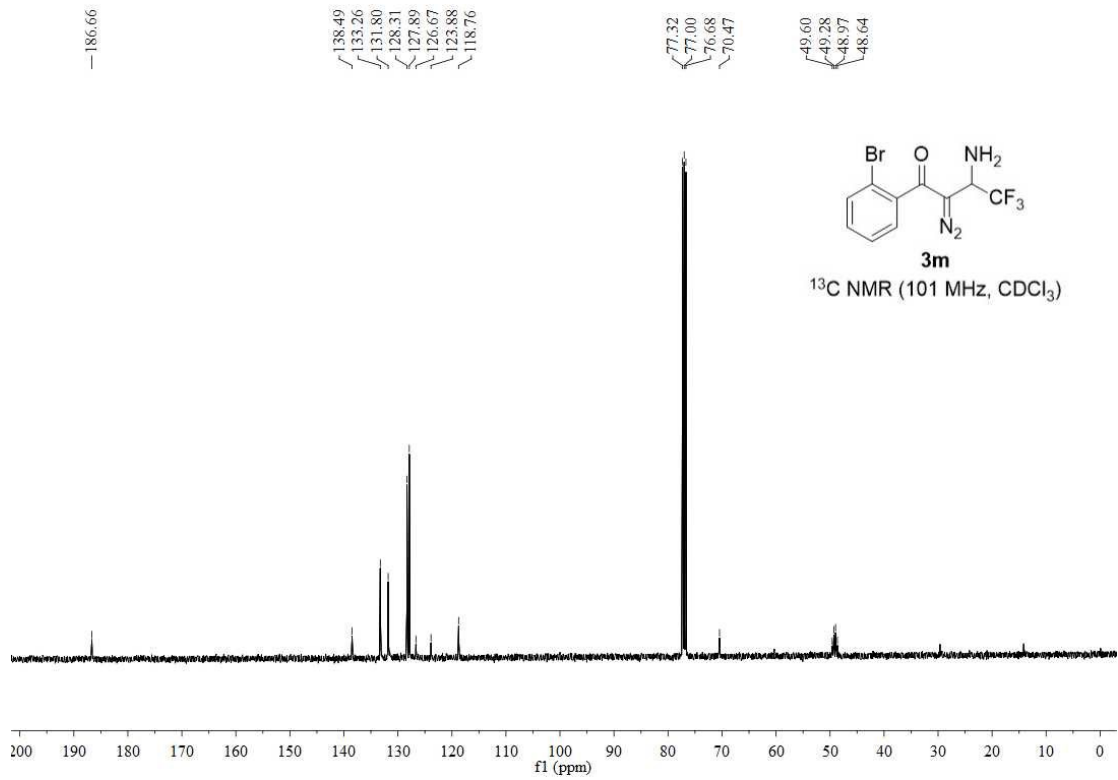


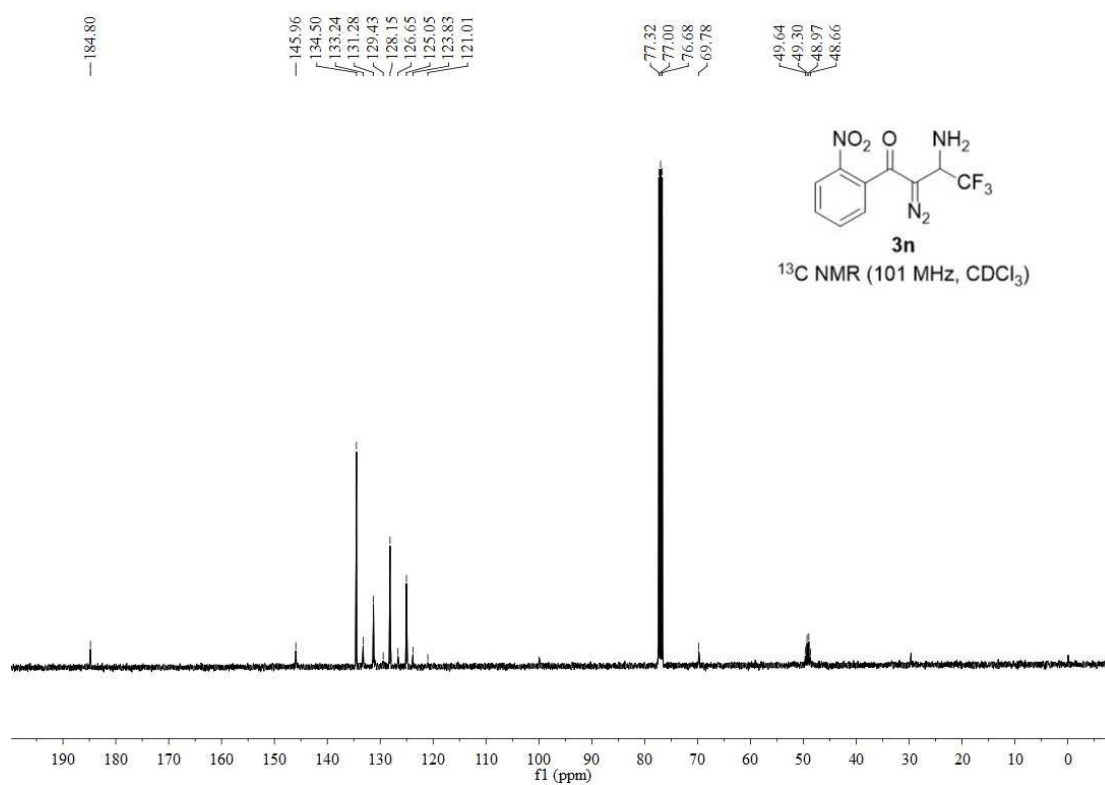
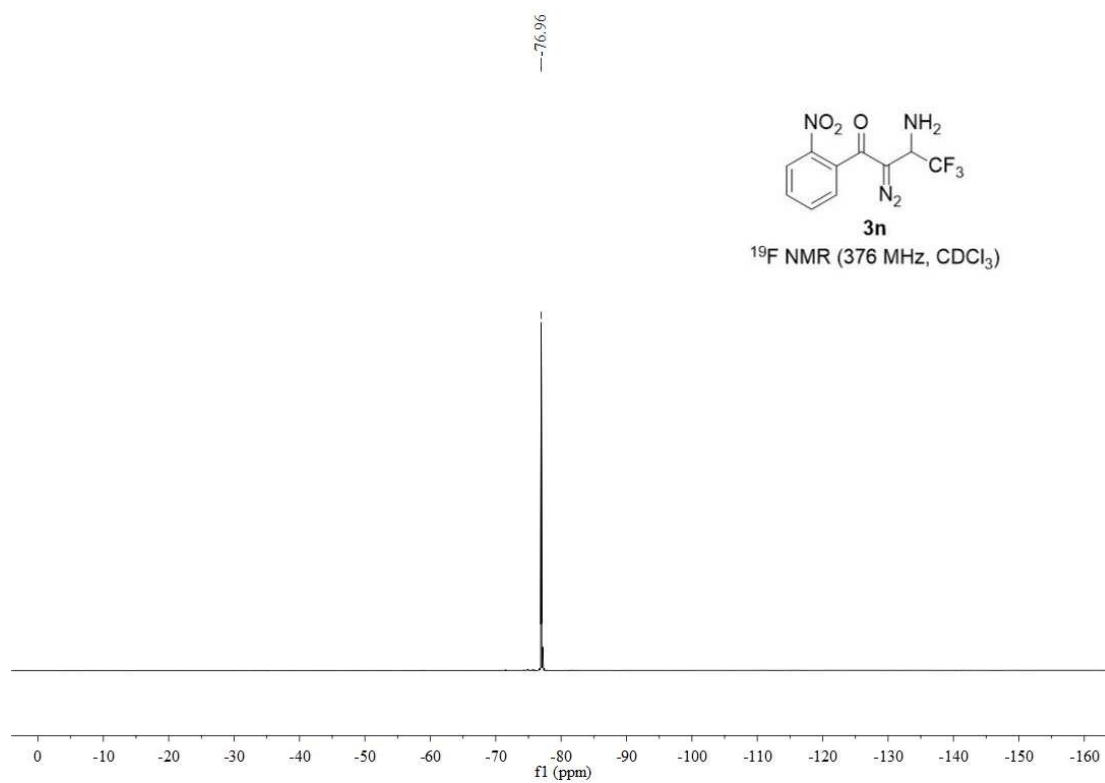


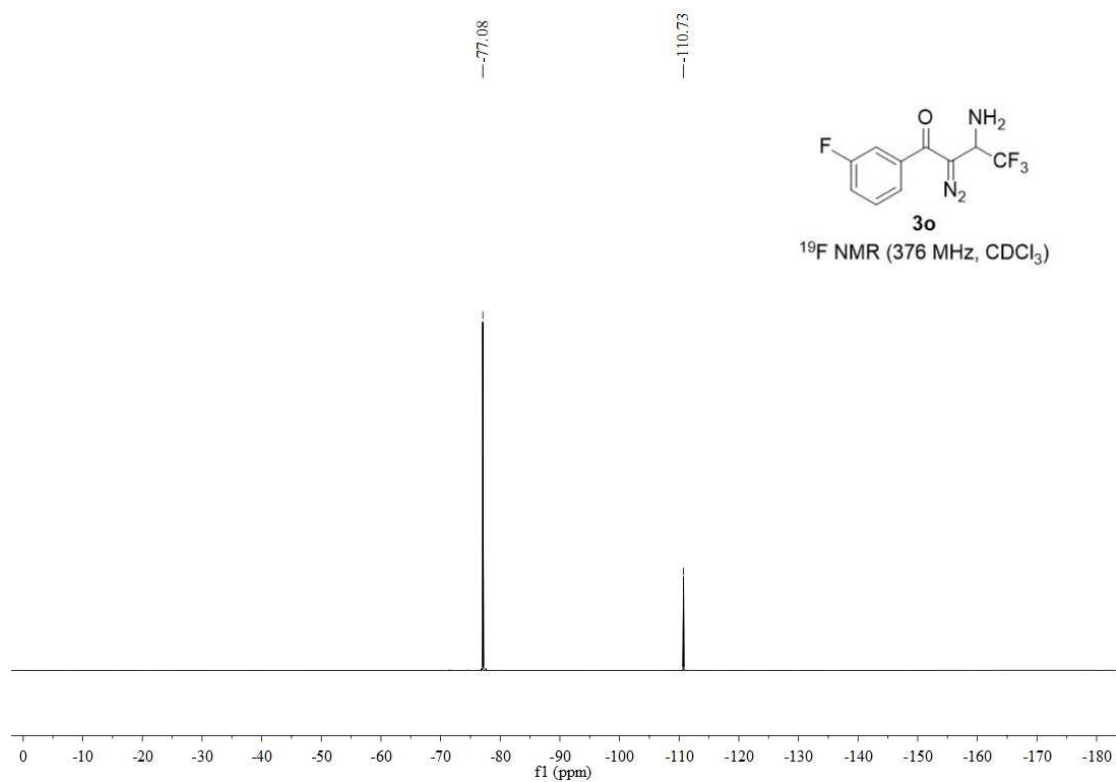
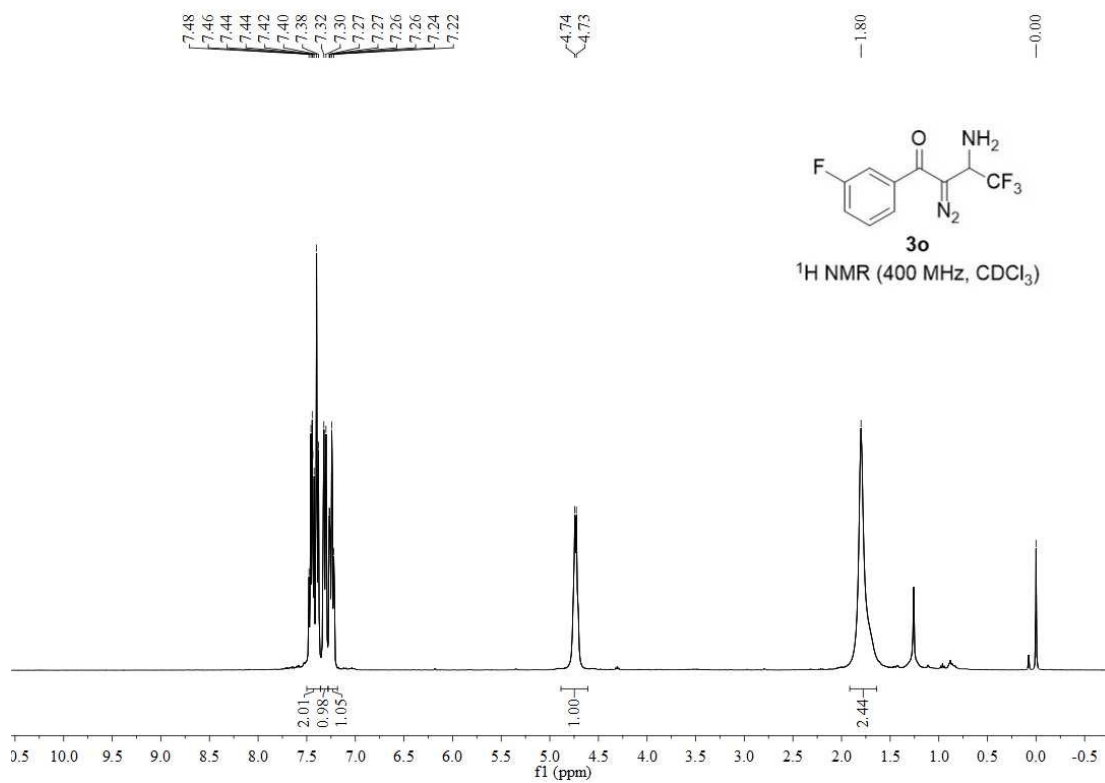


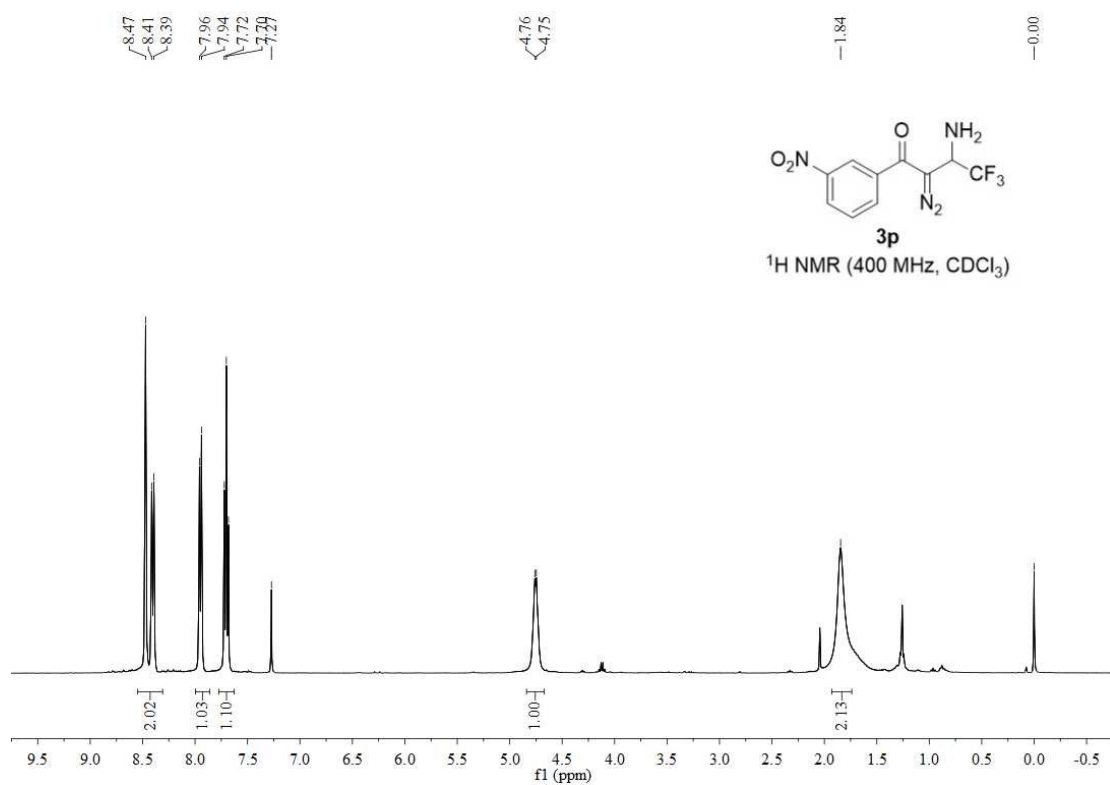
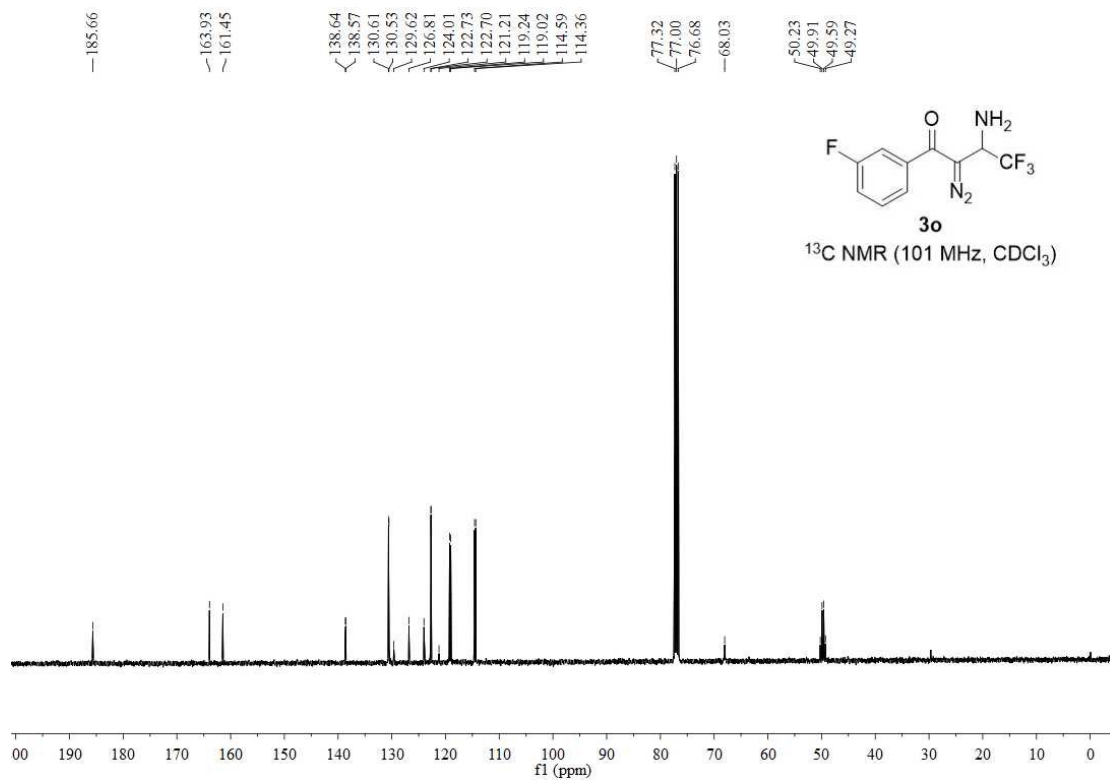


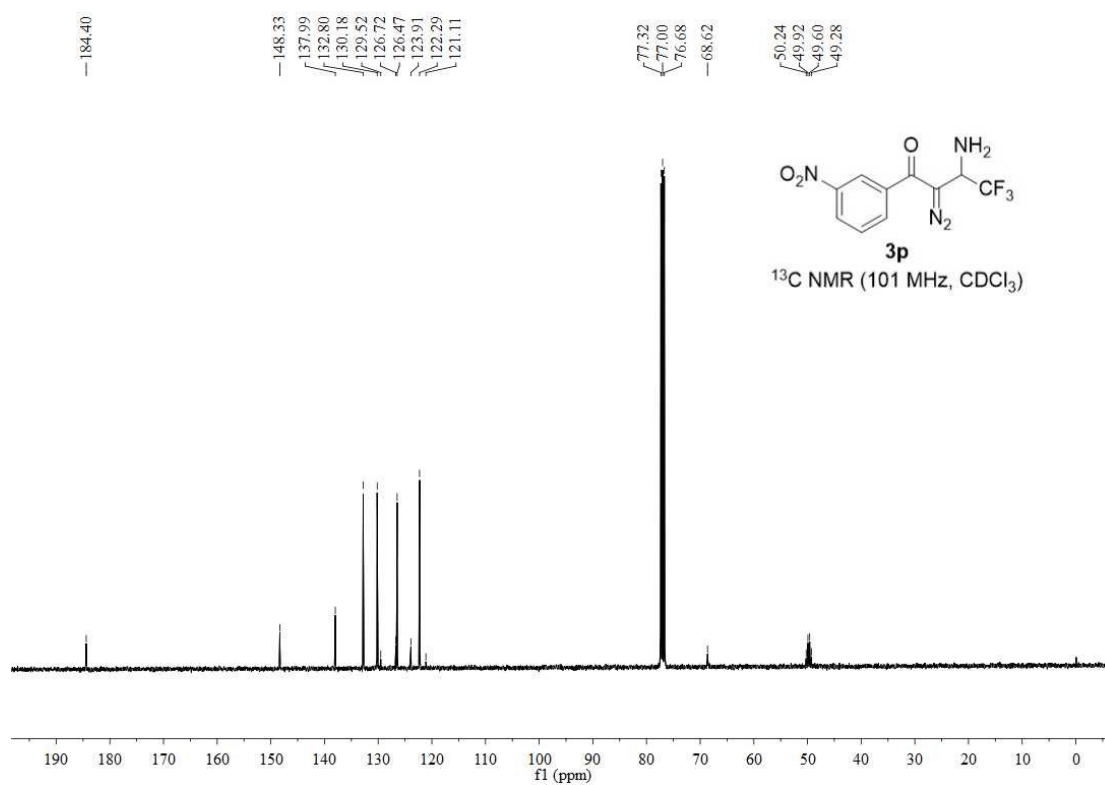
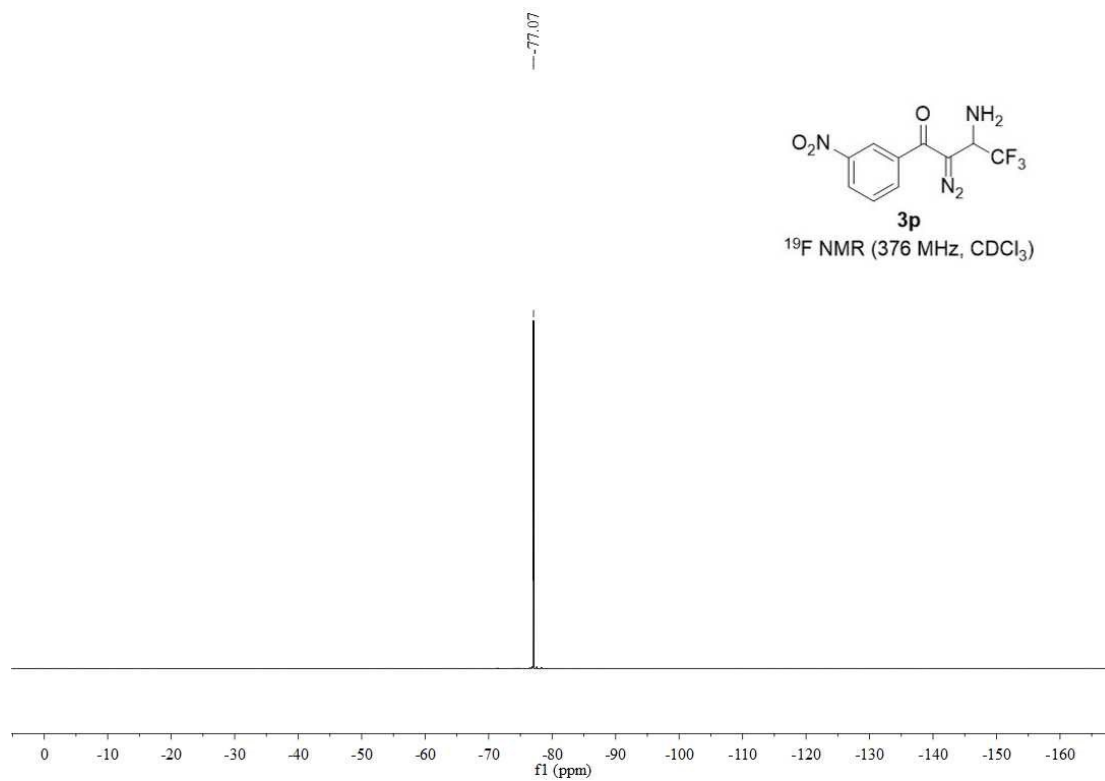


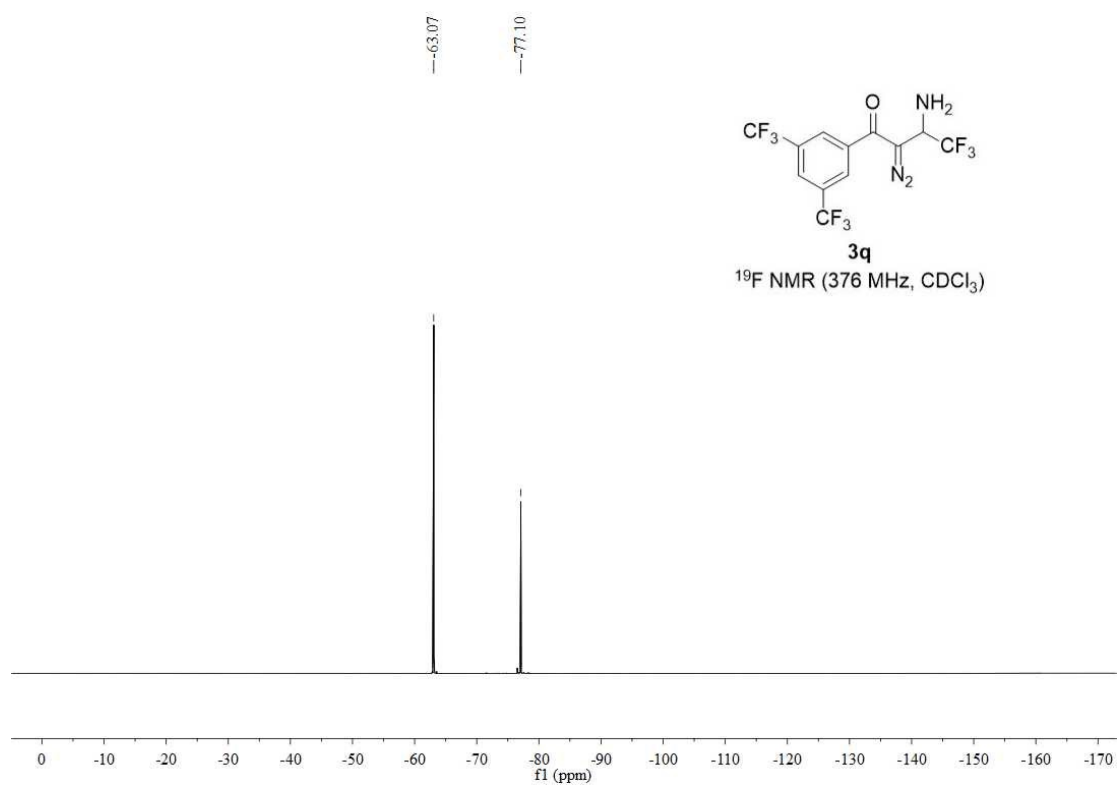
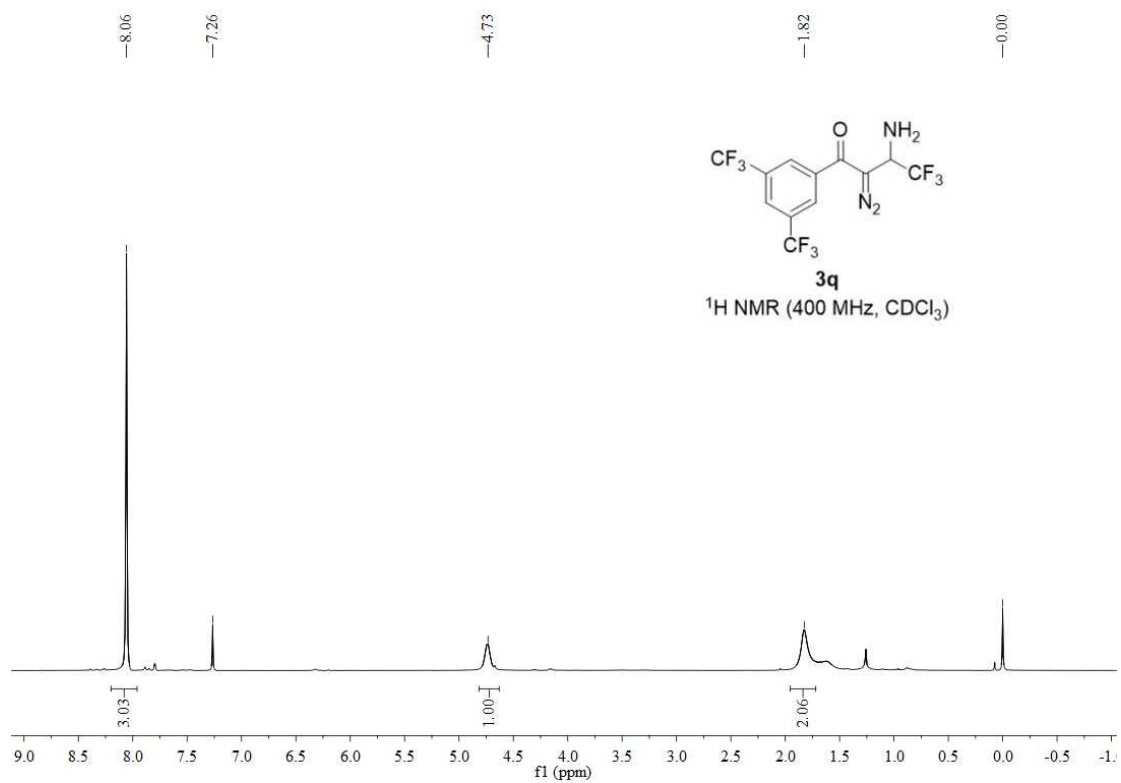


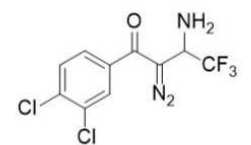
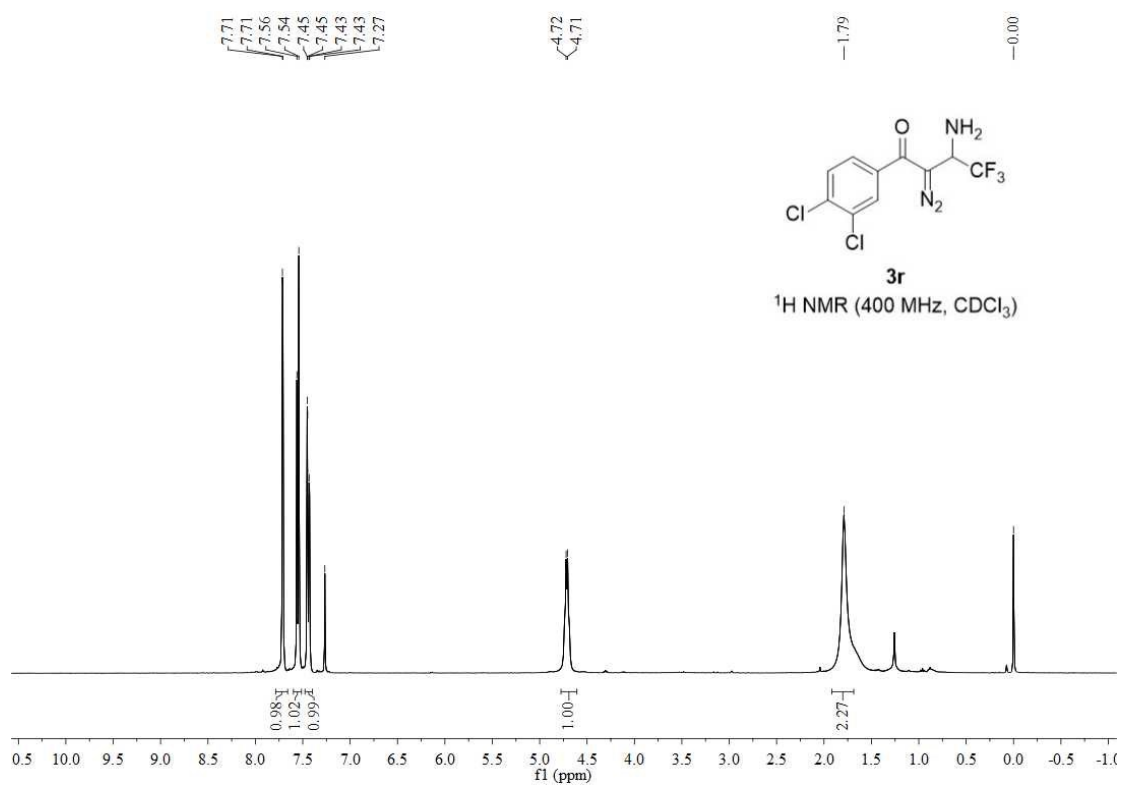
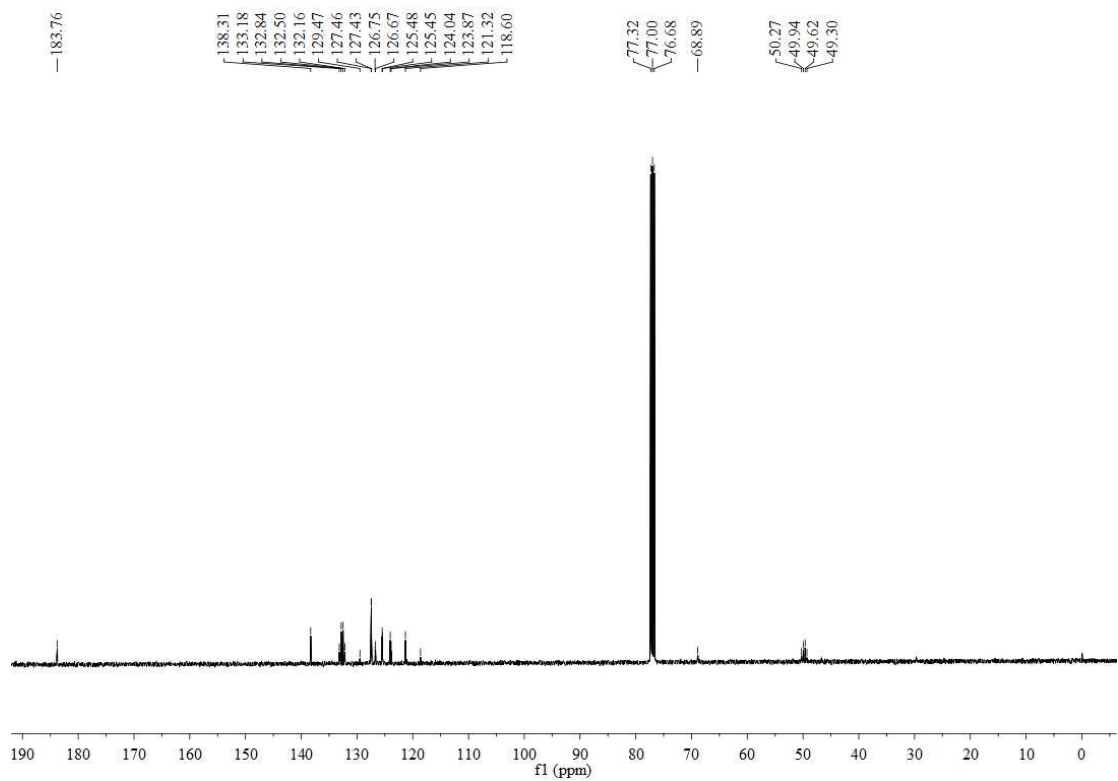












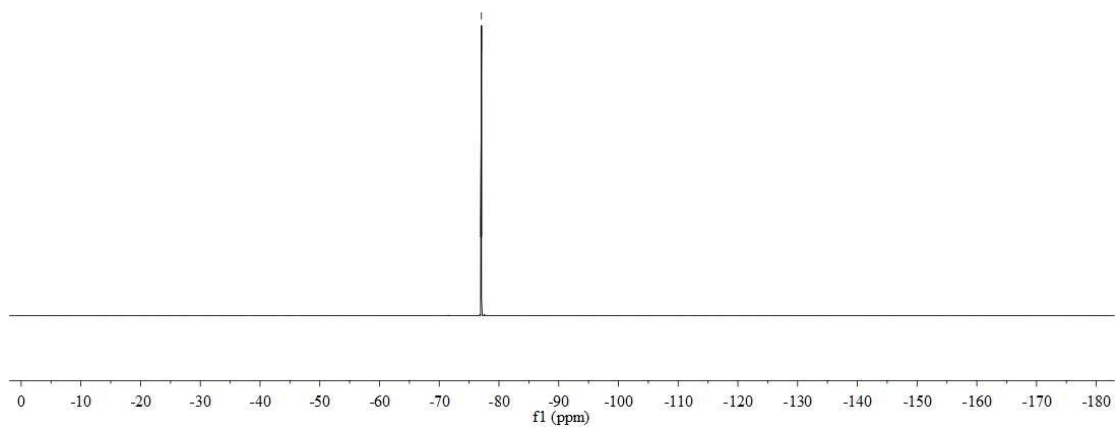
3r
¹H NMR (400 MHz, CDCl₃)

--77.06



3r

¹⁹F NMR (376 MHz, CDCl₃)

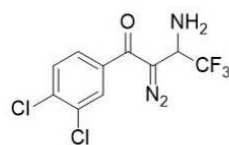


184.44

136.64
136.20
133.63
130.88
129.55
129.39
126.75
126.14
123.94
121.14

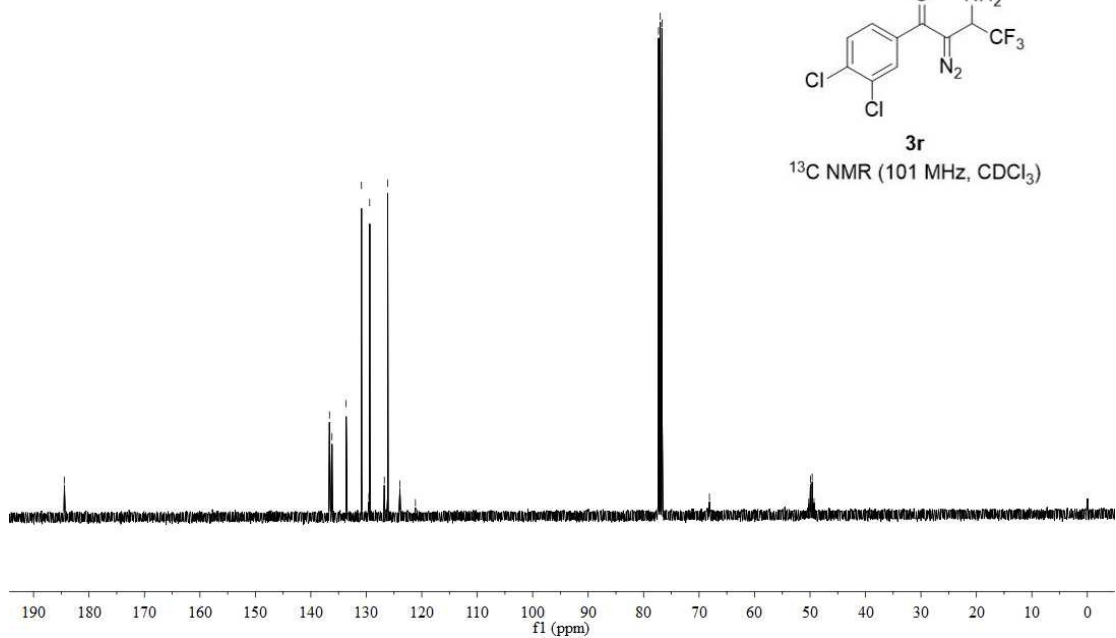
77.32
77.00
76.68
68.13

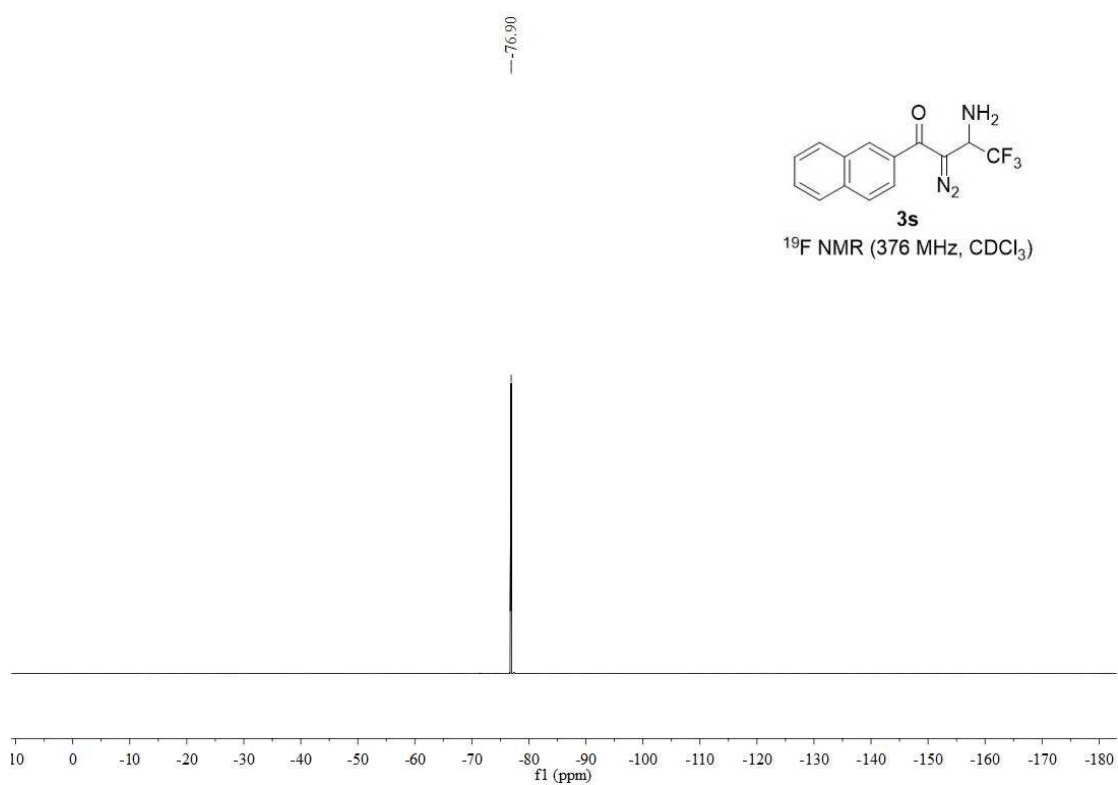
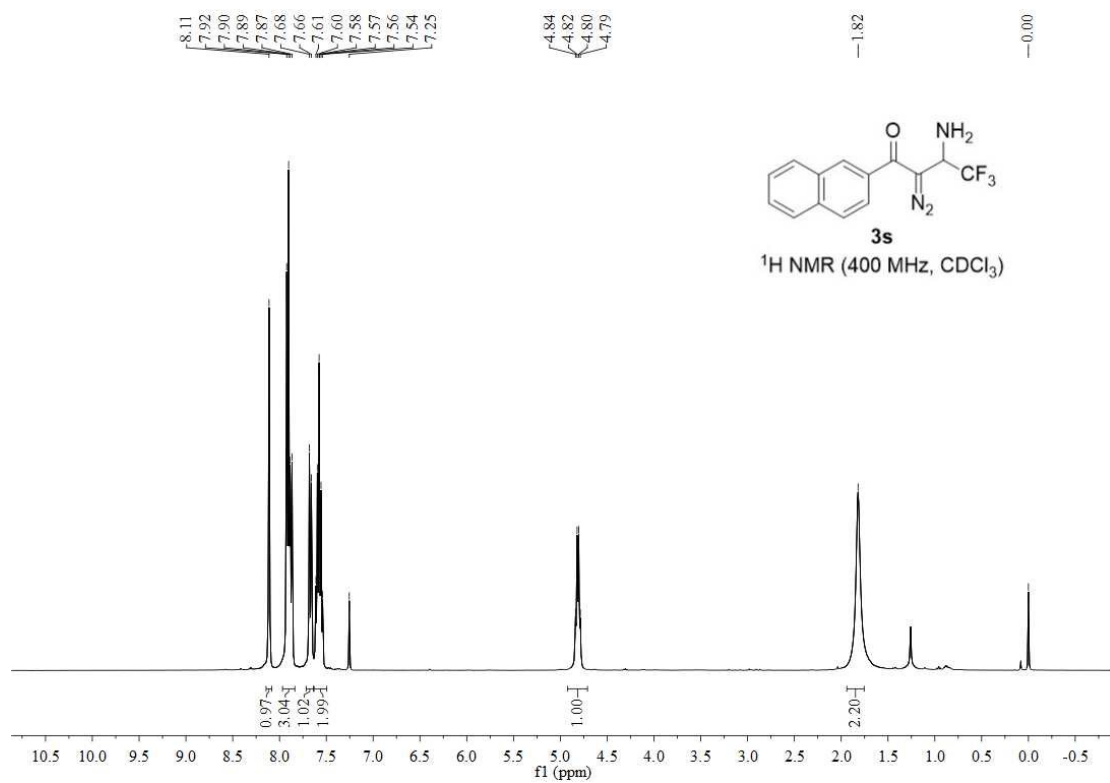
50.23
49.92
49.60
49.27

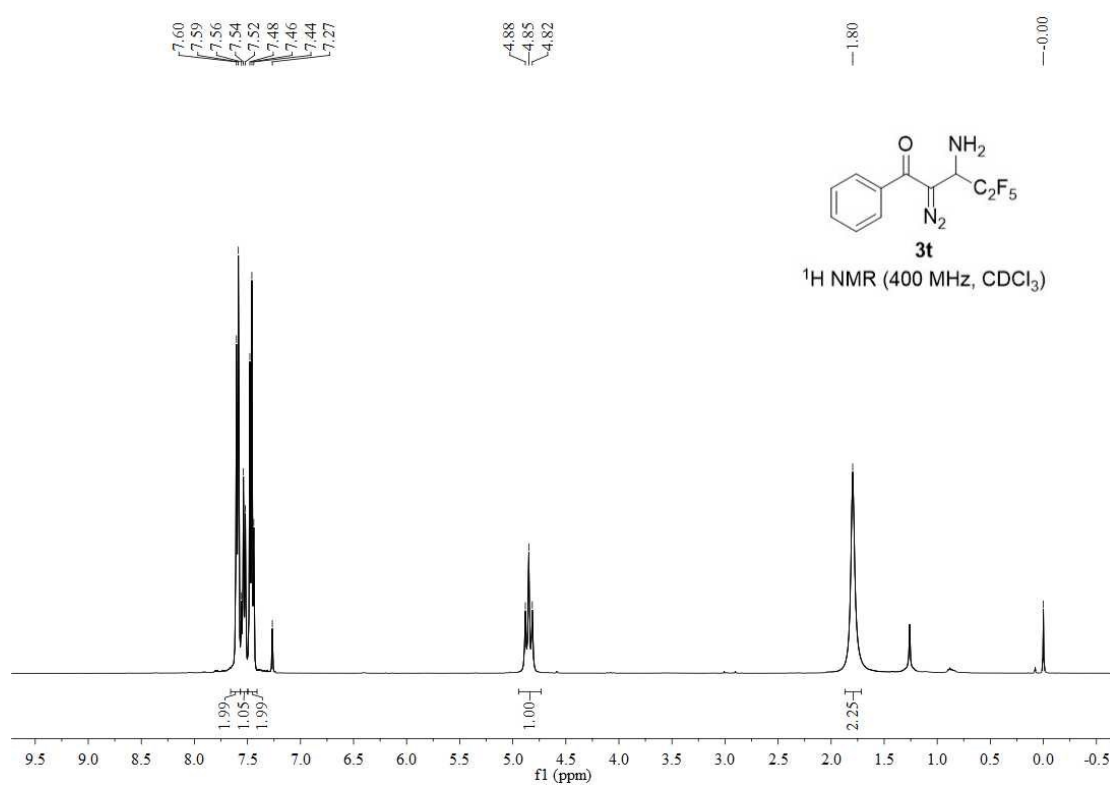
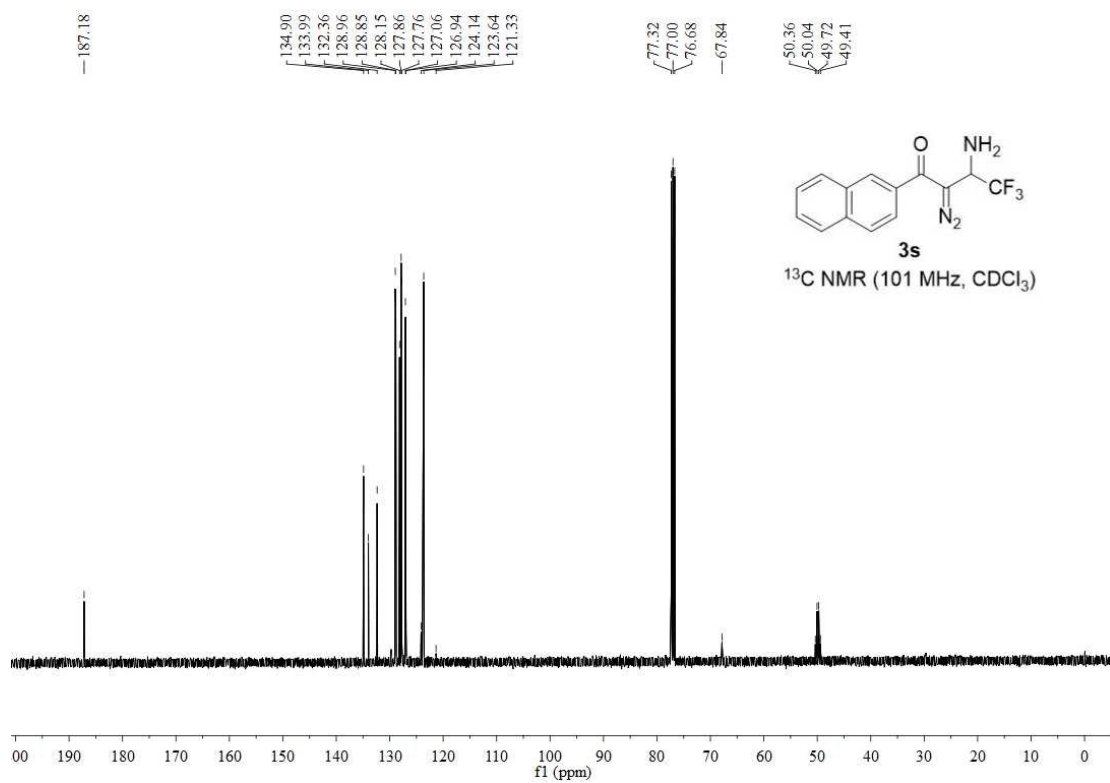


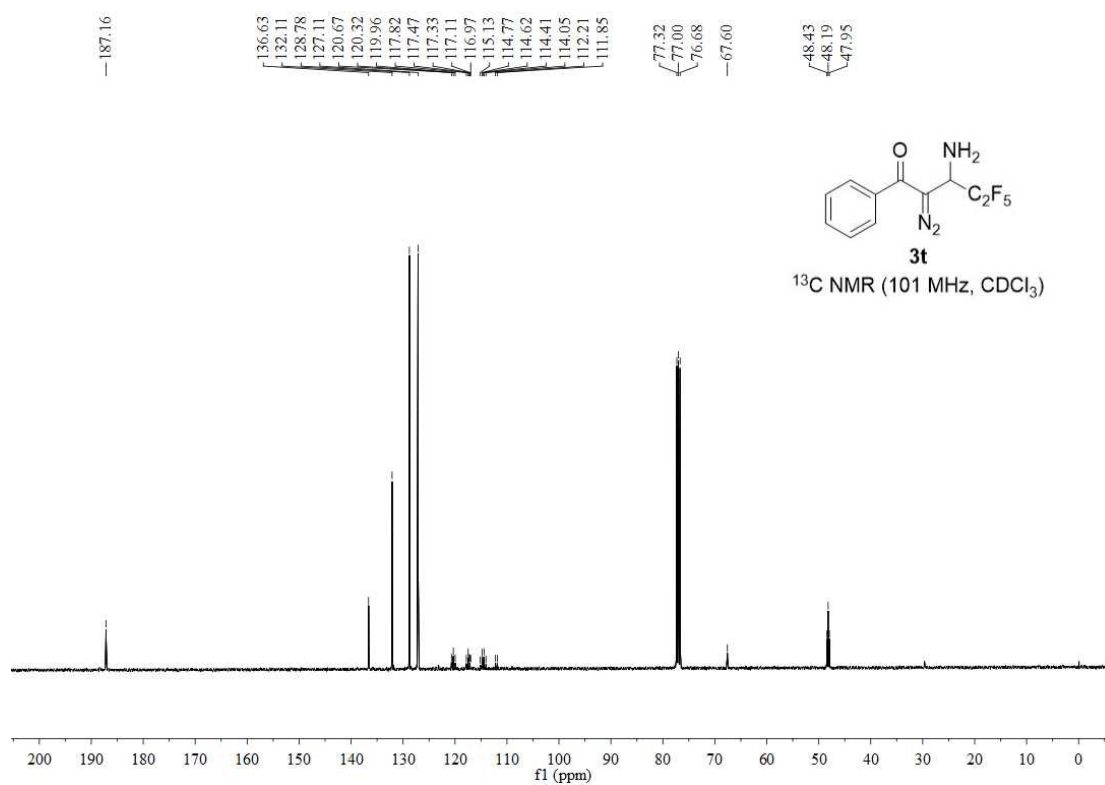
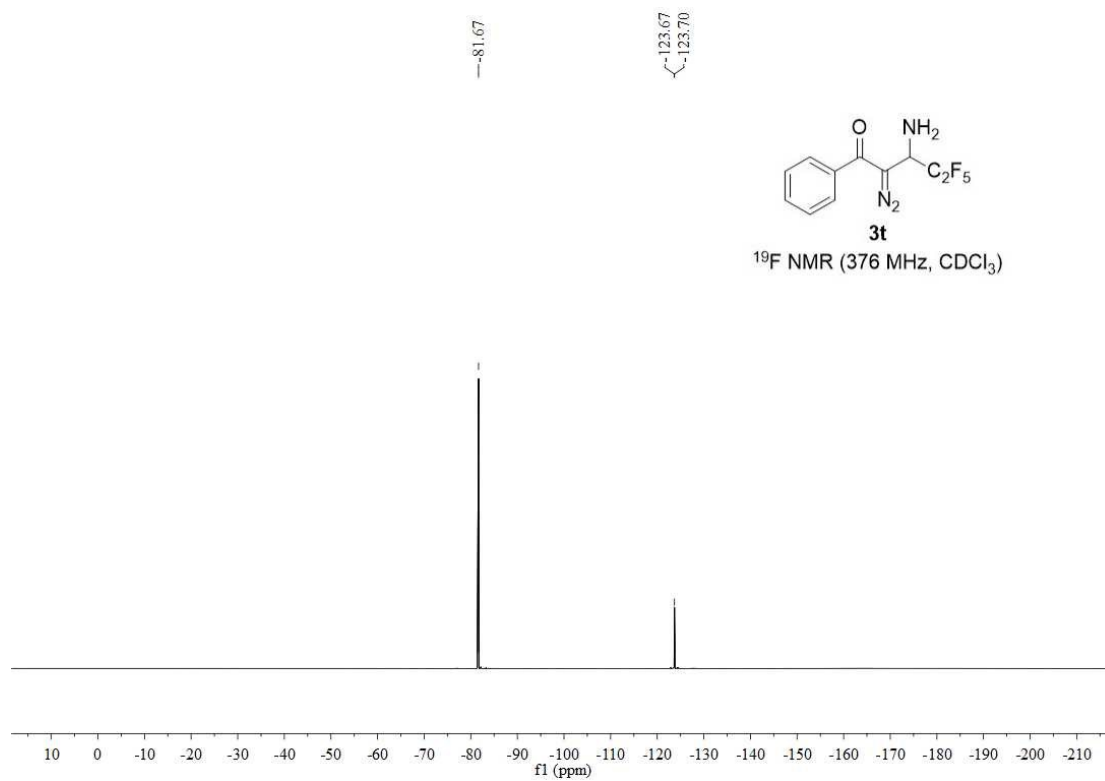
3r

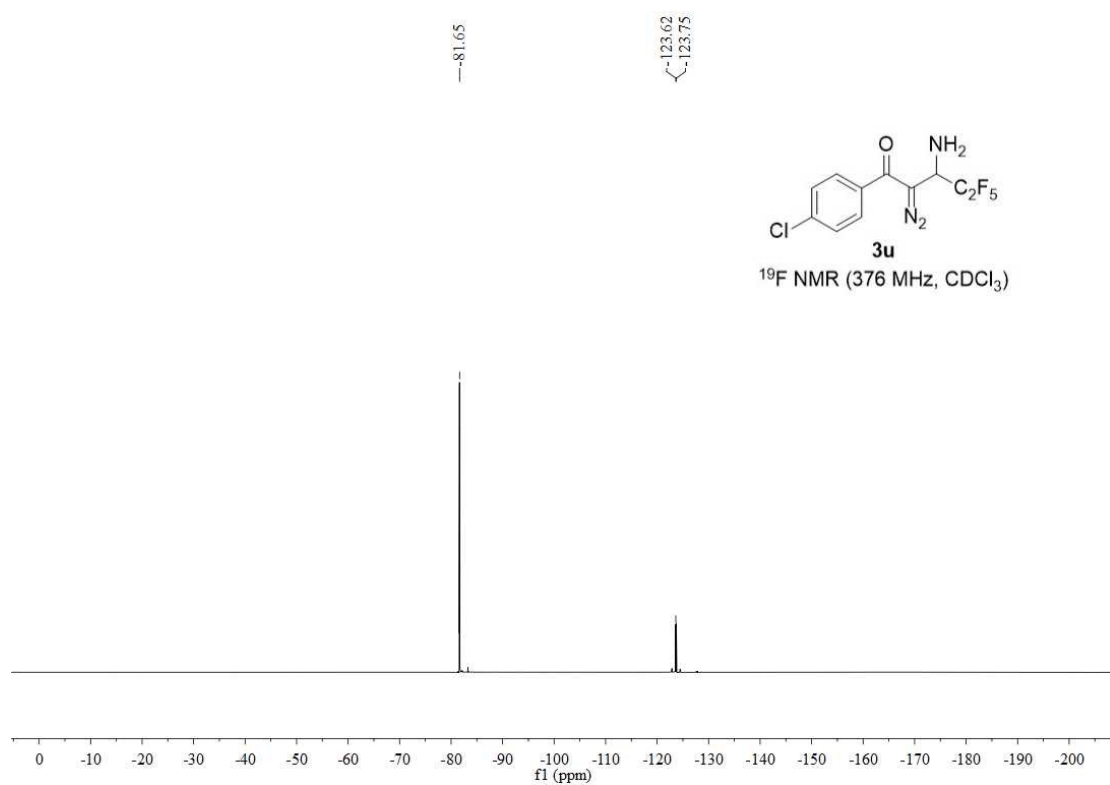
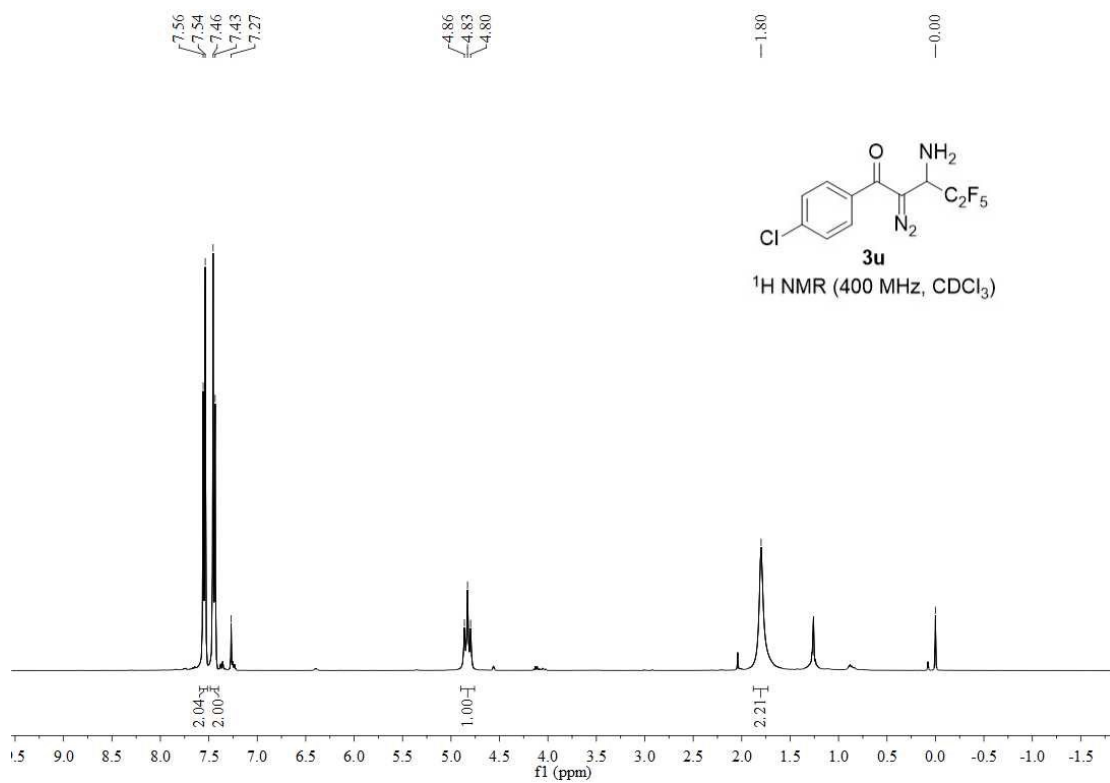
¹³C NMR (101 MHz, CDCl₃)

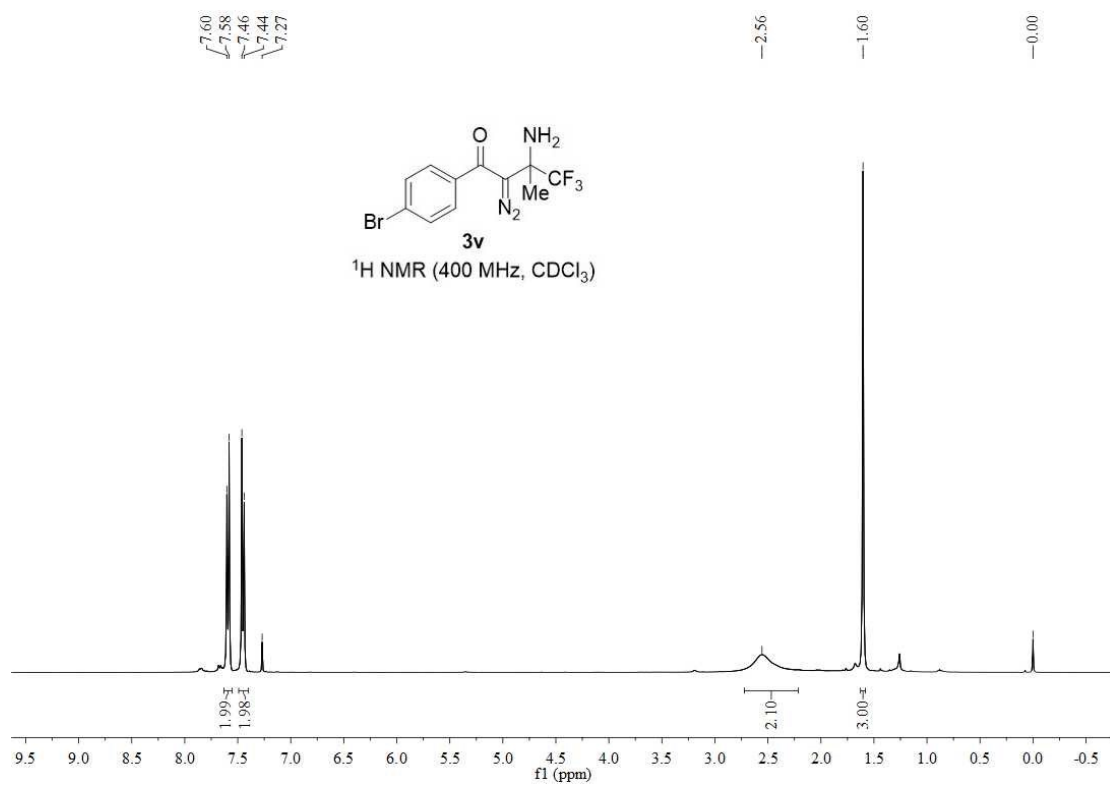
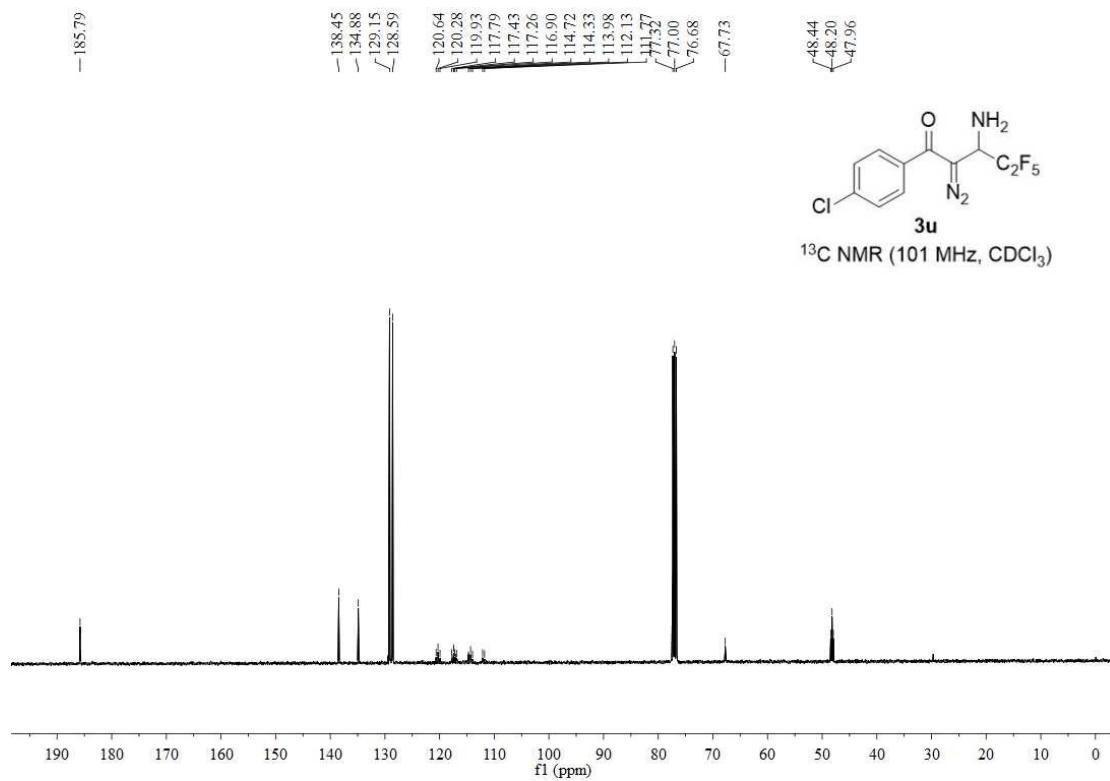


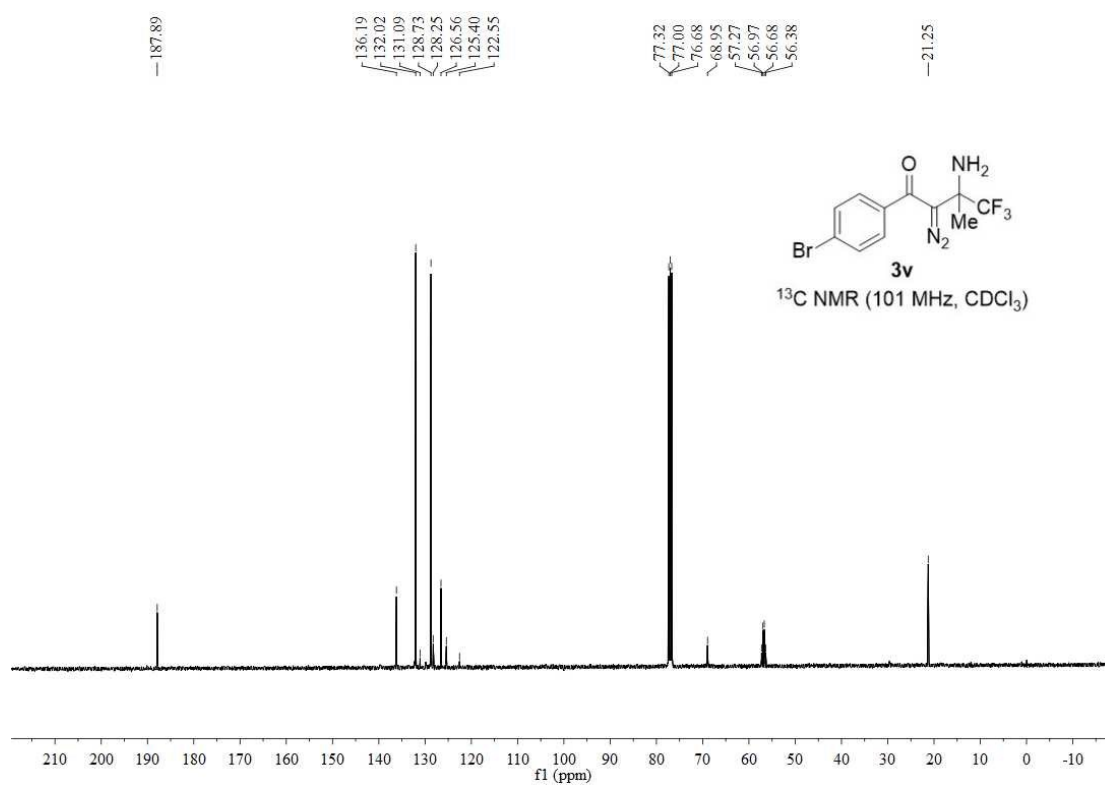
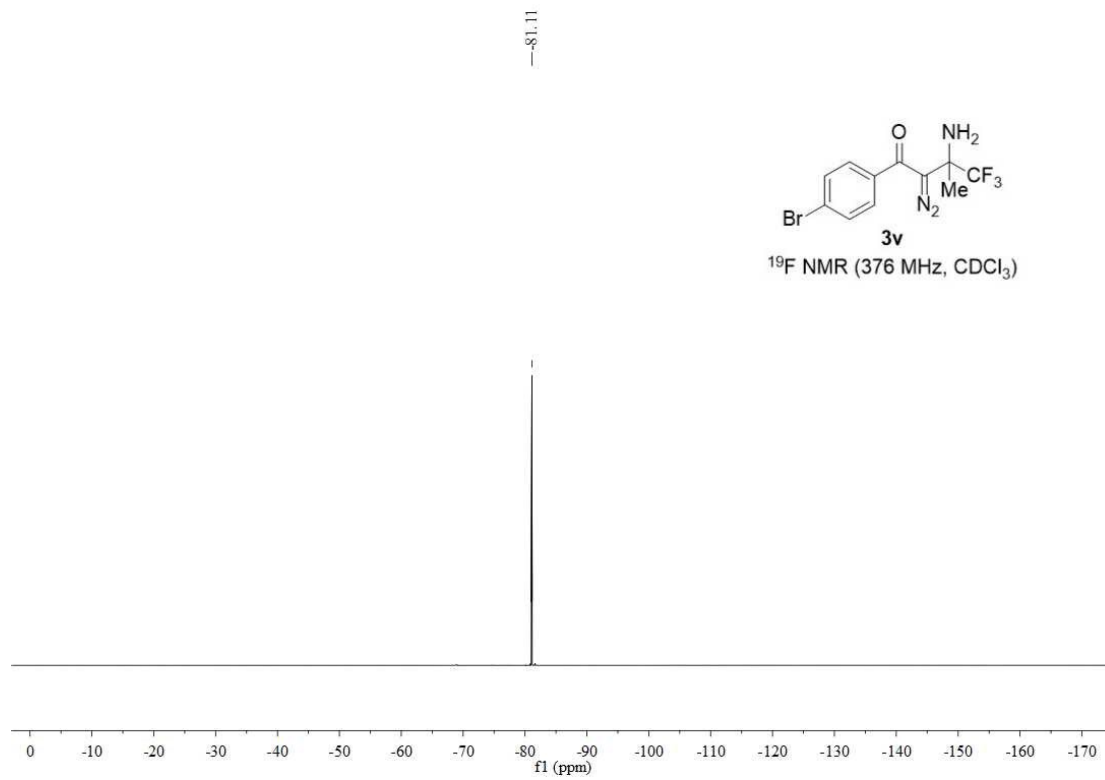










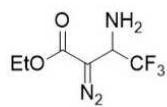


-7.27

4.38
4.37
4.35
4.33
4.29
4.27
4.25
4.24

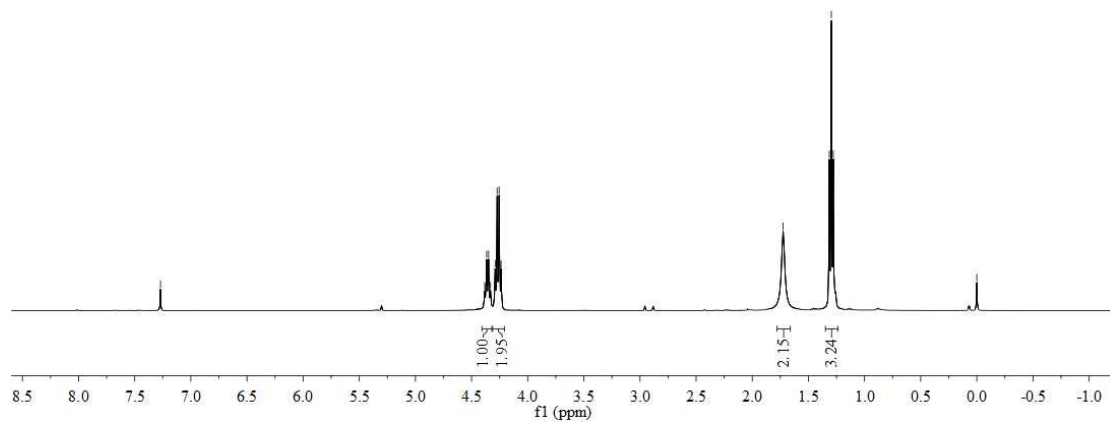
1.73
1.31
1.30
1.28

-0.00

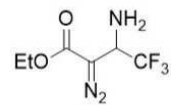


3w

¹H NMR (400 MHz, CDCl₃)



-77.65



3w

¹⁹F NMR (376 MHz, CDCl₃)

