Electronic Supplementary Material (ESI) for CrystEngComm.

Supporting Information

for

Metal-free 1,3-dipolar cycloaddition polymerization *via* prearrangement of azide and alkyne in the solid state

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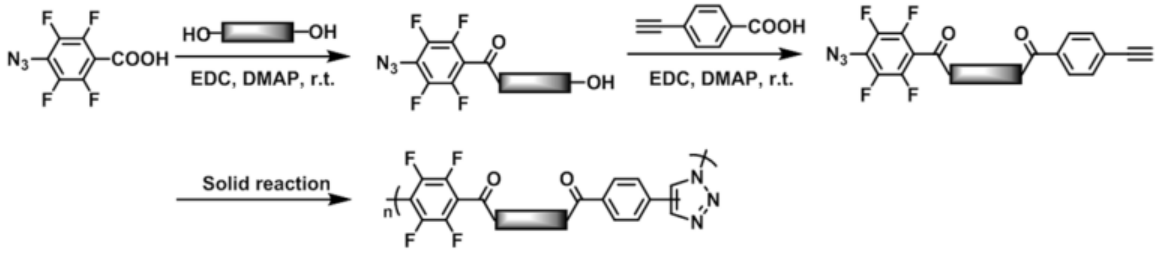
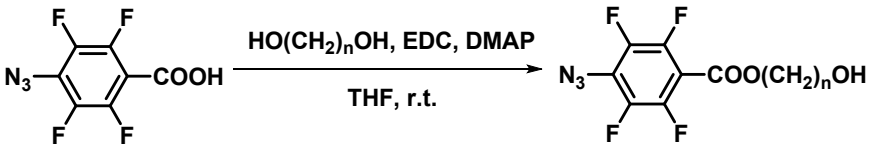
1. Experimental Section

General Methods: Chemicals were purchased commercially and used without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium under N_2 prior to use. ^{19}F NMR spectra were recorded on a Varian Mercury-300 (300 MHz) spectrometer using $CDCl_3$ as solvent. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-400 (400 MHz) spectrometer using $CDCl_3$ or DMSO-d_6 as solvent. Chemical shifts are reported in parts per million (ppm) and coupling constants are reported in hertz (Hz). ^{1}H NMR chemical shifts were referenced versus TMS (0 ppm), ^{13}C NMR chemical shifts were referenced versus $CDCl_3$ (77.0 ppm) and ^{19}F NMR chemical shifts were referenced versus a CF_3CO_2H external standard (0 ppm). Mass spectra were recorded on a VG ZAB-HS mass spectrometer. Infrared spectra was recorded in solid phase on a Bio-Rad FTS-65A FT-IR spectrometer. Single crystal X-ray diffraction data were collected with a NONIUS KappaCCD diffractometer for **C2**, **C3**, **C4**, and **C6**, with graphite monochromator and Mo Kα radiation [λ (MoKα) = 0.71073 Å]. Structures were solved by direct methods with SHELXS-97 and refined against F^2 with SHELXS-97. DSC experiments were measured on DSC Q100 (Thermal Analysis) under N_2 atmosphere with scanning rate of 10 $^{o}C \cdot min^{-1}$ from 0 to 200 ^{o}C for monomer samples. The polymer molecule weights (M_w, M_n) and polydispersity index (PDI) were measured on Waters1515 gel permeation chromatography (GPC) system. Monodisperse polystyrene was used as calibration standards and THF as the eluent at the flow rate of 1 $mL \cdot min^{-1}$. Powder X-ray diffraction data was collected on a PHILIPS X'Pert Pro diffractometer with an X'celerator detector in the reflection mode, using monochromatized Cu Kα radiation.



Scheme ***S1***. Schematic representation of syntheses of monomers and solid state reactions.



1 **C2OH-C6OH: n=2, 3, 4, 5, 6**

General procedure for the synthesis of **C2OH-C6OH**: **C2OH-C6OH** were synthesized from the corresponding diol and 4-azido-2,3,5,6-tetrafluorobenzoic acid (**1**).

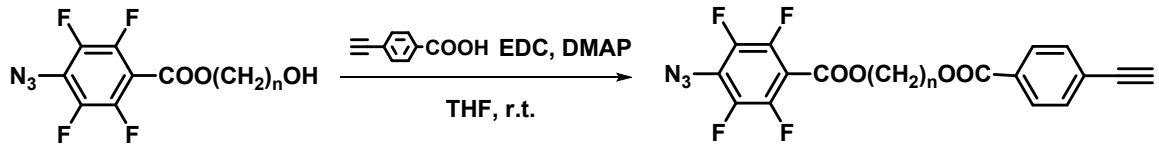
A solution of 4-azido-2,3,5,6-tetrafluorobenzoic acid **(1)** (2.0 g, 7.9 mmol), 1-ethyl-3-(3-dimethyl-aminopropyl) carbodiimide hydrochloride (EDC) (2.272 g, 11.9 mmol), 4-dimethylaminopyridine (DMAP) (0.483 g, 3.9 mmol) in anhydrous THF (20 mL) was added drop-wise of corresponding diol (15.8 mmol) and was stirred at room temperature for 24 hours. The reaction mixture was then poured into 20 mL water and the aqueous layer was extracted with 20 mL dichloromethane (DCM) twice. The organic layer was then washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure, and the residual was purified by flash column chromatography with DCM as eluent to give **C2OH-C6OH** as a transparent liquid.

3-hydroxypropyl-4-azido-2,3,5,6-tetrafluorobenzoate (C3OH): (40.7%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.71 (s, 1H), 2.02 (m, 2H), 3.80 (t, 2H, J= 6.0 Hz), 4.53 (t, 2H, J= 6.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 31.4, 58.9, 63.6, 107.7, 123.4, 139.2, 141.7 ($J_{C\text{-}F}$ = 250 Hz), 144.0, 146.6 ($J_{C\text{-}F}$ = 250 Hz), 159.5; ^{19}F NMR (282 MHz, $CDCl_3$): δ -78.2, -61.1; HR-MS (ESI, $C_{10}H_7F_4N_3O_3$, solvent: $CDCl_3$) *m/z*: Anal. Calcd. for [(M+H)$^+$]: 294.0496, Found 294.0498 [(M+H)$^+$], Error: -0.2 mDa.

5-hydroxypentyl 4-azido-2,3,5,6-tetrafluorobenzoate (C5OH): (70.0%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51, 1.61, 1.78 (m, 7H), 3.67 (t, 2H),4.38 (t, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.1, 28.2, 32.1, 62.5, 66.5, 107.9, 123.2, 139.2, 141.6 ($J_{C\text{-}F}$ = 250 Hz), 144.0, 145.5 ($J_{C\text{-}F}$ = 250 Hz), 159.4; ^{19}F NMR (282 MHz, $CDCl_3$): δ -78.21, -61.13.

6-hydroxyhexyl-4-azido-2,3,5,6-tetrafluorobenzoate(C6OH): (47.6%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.43 (m, 4H), 1.47 (s, 1H), 1.56 (m, 2H), 1.76 (m, 2H), 3.66 (t, J= 6.4 Hz), 4.37 (t, J= 6.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.3, 25.6, 28.4, 32.5, 62.8, 66.6, 108.3, 122.9, 139.1, 141.6 ($J_{C\text{-}F}$ = 250 Hz), 144.0, 146.5 ($J_{C\text{-}F}$ = 250 Hz), 159.4; ^{19}F NMR

(282 MHz, $CDCl_3$): δ -78.3, -61.2; HR-MS (ESI, $C_{13}H_{13}F_4N_3O_3$, solvent: $CDCl_3$) *m/z*: Anal. Calcd. for [$(M+H)^+$]: 336.0966, Found 336.0962 [$(M+H)^+$], Error: 0.4 mDa.



C2OH-C6OH: n=2, 3, 4, 5, 6 **C2-C6: n=2, 3, 4, 5, 6**

General procedure for the synthesis of **C2-C6**: **C2-C6** were synthesized from the corresponding **C2OH-C6OH** and 4-ethynylbenzoic acid (**2**).

A solution of 4-ethynylbenzoic acid (**2**) (0.27 g, 1.8 mmol), EDC (0.52 g, 3.6 mmol), DMAP (0.12 g, 0.9 mmol) in anhydrous THF (10 mL) was added drop-wise of **C2OH-C6OH** (1.8 mmol) and was stirred at room temperature for 24 hours. The reaction mixture was then poured into 10 mL water and the aqueous layer was extracted with 10 mL DCM twice. The organic layer was then washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure, and the residual was purified by flash column chromatography with petroleum ether (PE)/ DCM (1:1, v/v) as eluent to give **C2-C4, C6** as white solids and **C5** as colorless liquid.

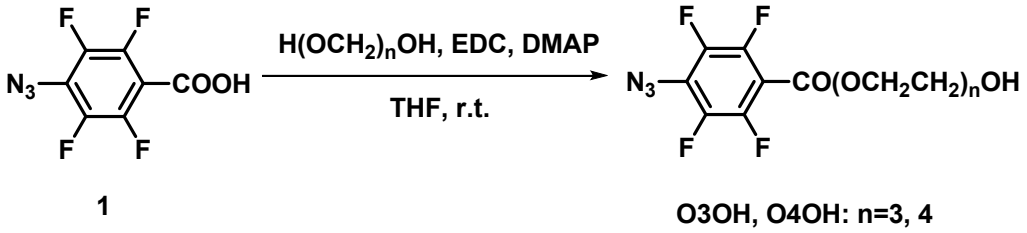
2-((4-ethynylbenzoyl)oxy)ethyl-4-azido-2,3,5,6-tetrafluorobenzoate (C2): **(**44.9%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.25 (s, 1H), 4.64 (m, 2H), 4.70 (m, 2H), 7.55 (d, 2H, *J*= 8.4 Hz), 8.00 (d, 2H, *J*= 8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 62.4, 64.0, 80.3, 82.7, 99.8, 107.3, 123.7, 127.1, 129.5, 129.6, 132.2, 139.3, 141.6 ($J_{C\text{-}F}$ = 250 Hz), 144.0, 145.6 ($J_{C\text{-}F}$ = 250 Hz), 159.2, 165.6; ^{19}F NMR (282 MHz, $CDCl_3$): δ -73.0, -60.6; HR-MS (ESI, $C_{18}H_9F_4N_3O_4$, solvent: $CDCl_3$) *m/z*: Anal. Calcd. for [$(M+H)^+$]: 430.0421, Found 430.0430 [$(M+H)^+$], Error: -0.9 mDa.

3-((4-ethynylbenzoyl)oxy)propyl-4-azido-2,3,5,6-tetrafluorobenzoate (C3): (47.8%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.24 (m, 2H), 3.25 (s, 1H), 4.48(t, 2H, *J*= 6.4 Hz), 4.53 (t, 2H, *J*= 6.4 Hz), 7.54 (d, 2H, *J*= 8.4Hz), 7.98 (d, 2H, *J*= 8.4Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 27.9, 61.6, 63.3, 80.2, 82.7, 126.9, 129.4, 129.9, 132.1, 159.2, 165.7; ^{19}F NMR (282 MHz, $CDCl_3$): δ -73.1, -60.7; HR-MS (ESI, $C_{19}H_{11}F_4N_3O_4$, solvent: $CDCl_3$) *m/z*: Anal. Calcd. for [$(M+Na)^+$]: 444.0578, Found 444.0590 [$(M+Na)^+$], Error: 1.2 mDa.

4-((4-ethynylbenzoyl)oxy)butyl-4-azido-2,3,5,6-tetrafluorobenzoate (C4): (45.6%) ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.93 (m, 4H), 3.24 (s, 1H), 4.39 (m, 2H), 4.43 (m, 2H), 7.55 (d, 2H, J= 8.4 Hz), 7.99 (d, 2H, J=8.4 Hz); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.3, 25.3, 64.5, 66.04, 80.1, 82.8, 107.4, 123.2 126.9, 129.4, 130.2, 132.1, 139.3, 141.8 ($J_{C\text{-}F}$ = 250 Hz), 144.0, 146.5 ($J_{C\text{-}F}$ = 250 Hz), 159.4, 165.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ -73.1, -60.9; HR-MS (ESI, $C_{20}H_{13}F_4N_3O_4$, solvent: $CDCl_3$) *m/z*: Anal. Calcd. for [$(M+H)^+$]: 436.0915, Found 436.0924 [$(M+H)^+$], Error: -0.9 mDa.

5-((4-ethynylbenzoyl)oxy)pentyl-4-azido-2,3,5,6-tetrafluorobenzoate (C5): ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.61 (m, 2H), 1.84 (dt, 4H), 3.24 (s, 1H), 4.38 (m, 4H), 7.54 (d, 2H), 7.98 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 22.4, 28.1, 28.2, 64.8, 66.3, 80.0, 82.8, 107.9, 122.4, 126.7, 129.4, 130.3, 132.0, 139.1, 141.7 ($J_{C\text{-}F}$ = 250 Hz), 144.0, 146.5 ($J_{C\text{-}F}$ = 250 Hz), 159.3, 165.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ -73.2, -61.1; HR-MS (ESI, $C_{21}H_{15}F_4N_3O_4$, solvent: $CDCl_3$) *m/z*: Anal. Calcd. for [$(M+H)^+$]: 450.1072, Found 450.1078 [$(M+H)^+$], Error: -0.6 mDa.

6-((4-ethynylbenzoyl)oxy)hexyl-4-azido-2,3,5,6-tetrafluorobenzoate (C6): ^{1}H NMR (400 MHz, $CDCl_3$): δ 1.51 (s, 4H), 1.79 (d, 4H), 3.23 (s, 1H), 4.36 (dt, 4H), 7.54 (d, 2H), 7.99 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 25.5, 25.6, 28.5, 28.3, 65.1, 66.5, 80.0, 82.8, 108.0, 126.7, 129.4, 130.4, 132.0, 139.1, 141.6 ($J_{C\text{-}F}$ = 250 Hz), 144.0, 146.5 ($J_{C\text{-}F}$ = 250 Hz), 159.4, 165.9; ^{19}F NMR (282 MHz, $CDCl_3$): δ (ppm)= -73.2, -61.1; HR-MS (ESI, $C_{22}H_{17}F_4N_3O_4$, solvent: $CDCl_3$) *m/z*: Anal. Calcd. for [$(M+H)^+$]: 464.1228, Found 464.1229 [$(M+H)^+$], Error: -0.1 mDa.



1 **O3OH, O4OH: n=3, 4**

General procedure for the synthesis of **O3OH, O4OH**: **O3OH, O4OH** were synthesized from the corresponding diol and 4-azido-2,3,5,6-tetrafluorobenzoic acid (**1**).

A solution of 4-azido-2,3,5,6-tetrafluorobenzoic acid **(1)** (2.0 g, 7.9 mmol), EDC (2.272 g, 11.9 mmol), DMAP (0.4827 g, 3.9 mmol) in anhydrous THF (20 mL) was added drop-wise of 2,2'-(ethane-1,2-diylbis(oxy))diethanol or 2,2'-(2,2'-oxybis(ethane-2,1-diyl)bis(oxy))diethanol (15.8 mmol) and was stirred at room temperature for 24 hours. The reaction mixture was then poured into 20 mL water and the aqueous layer was extracted with 20 mL DCM twice. The organic layer was then washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure, and the residual was purified by flash column chromatography with DCM as eluent to give **O3OH, O4OH** as colorless liquid in 82.0% yield and 85.0%.

2-(2-(2-hydroxyethoxy)ethoxy)ethyl-4-azido-2,3,5,6-tetrafluorobenzoate (O3OH): ^{1}H NMR (400 MHz, $CDCl_3$): δ 2.48 (s, 1H), 3.61 (m, 2H), 3.69 (m, 6H), 3.83 (m, 2H),4.52 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 61.8, 65.4, 68.7, 70.4, 70.7, 72.5, 107.5, 123.3, 139.3, 141.8 ($J_{C\text{-}F}$ = 250 Hz), 144.1, 146.6 ($J_{C\text{-}F}$ = 250 Hz), 159.3; ^{19}F NMR (282 MHz, $CDCl_3$): δ -72.2, -64.2; HR-MS (ESI, $C_{13}H_{13}F_4N_3O_5$, solvent: $CDCl_3$) *m/z*: Anal. Calcd. for [(M+Na)$^+$]: 390.0684, Found [(M+Na)$^+$]: 390.0695, Error: -1.1 mDa.

O3OH, O4OH: n=3, 4 **O3, O4: n=3, 4**

General procedure for the synthesis of **O3, O4**: **O3, O4** were synthesized from the corresponding **O3OH, O4OH** and 4-ethynylbenzoic acid (**2**).

A solution of 4-ethynylbenzoic acid (**2**) (0.27 g, 1.8 mmol), EDC (0.52 g, 3.6 mmol), DMAP (0.12 g, 0.9 mmol) in anhydrous THF (10 mL) was added drop-wise of **O3OH, O4OH** (1.8 mmol) and was stirred at room temperature for 24 hours. The reaction mixture was then poured into 10 mL water and the aqueous layer was extracted with 10 mL DCM twice. The organic layer was then washed with brine, dried over anhydrous Na_2SO_4 and evaporated under reduced pressure, and the residual was purified by flash column chromatography with DCM as eluent to give **O3, O4** as colorless liquid in 40.7% and 37.1% yield.

2-(2-(2-(4-ethynylbenzoyloxy)ethoxy)ethoxy)ethyl-4-azido-2,3,5,6-tetrafluorobenzoate (O3): ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23 (m, 1H), 3.72 (m, 4H), 3.82 (m, 4H), 4.49 (m, 4H), 7.53 (m, 2H), 7.99 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 64.3, 65.5, 68.8, 69.2, 70.7, 70.7, 80.1, 82.7, 107.6, 123.3, 126.8, 129.5, 130.1, 132.0, 139.2, 141.7 ($J_{C\text{-}F}$ = 250 Hz), 144.0, 145.5 ($J_{C\text{-}F}$ = 250 Hz), 159.2, 165.8; ^{19}F NMR (282 MHz, $CDCl_3$): δ -73.1, -60.6; HR-MS (ESI, $C_{22}H_{17}F_4N_3O_6$, solvent: $CDCl_3$) *m/z*: Anal. Calcd. for [(M+H)$^+$]: 496.1126, Found 496.1135 [(M+H)$^+$], Error: -0.9 mDa.

1-(4-ethynylphenyl)-1-oxo-2,5,8,11-tetraoxatridecan-13-yl-4-azido-2,3,5,6-tetrafluorobenzoate (O4): ^{1}H NMR (400 MHz, $CDCl_3$): δ 3.23 (s, 1H), 3.67 (m, 12H), 3.80 (m, 4H), 4.48 (m, 4H), 7.53 (d, 2H), 8.00 (d, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 64.3, 65.5, 68.7, 69.1, 70.7, 70.7, 80.1, 82.7, 107.6, 123.3, 126.8, 129.5, 130.1, 132.0, 139.1, 141.6 ($J_{C\text{-}F}$ = 250 Hz), 144.1, 146.6 ($J_{C\text{-}F}$ = 250 Hz), 159.2, 165.1; ^{19}F NMR (282 MHz, $CDCl_3$): δ -60.6; -73.1; HR-MS (ESI, $C_{24}H_{21}F_4N_3O_7$, solvent: $CDCl_3$) *m/z*: Anal. Calcd. for [(M+Na)$^+$]: 562.1208, Found 562.1220 [(M+Na)$^+$], Error: -1.2 mDa.

2. ^{1}H NMR, ^{13}C NMR and ^{19}F NMR Spectra

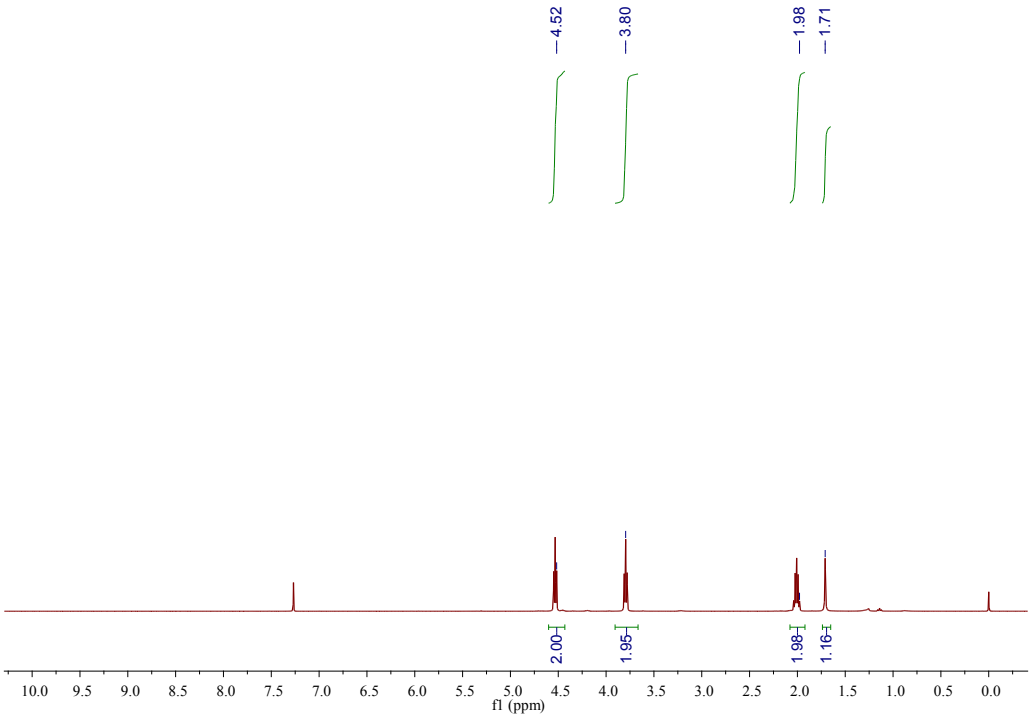


Figure S2-1. ^{1}H NMR spectrum of **C3OH** in $CDCl_3$.

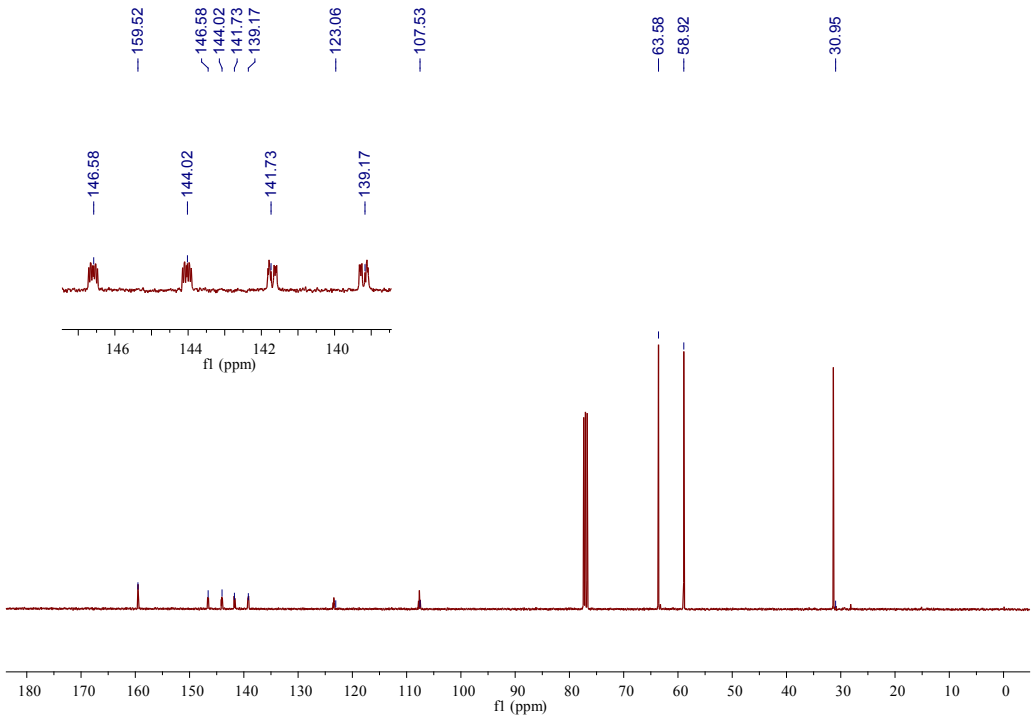


Figure S2-2. ^{13}C NMR spectrum of **C3OH** in $CDCl_3$.

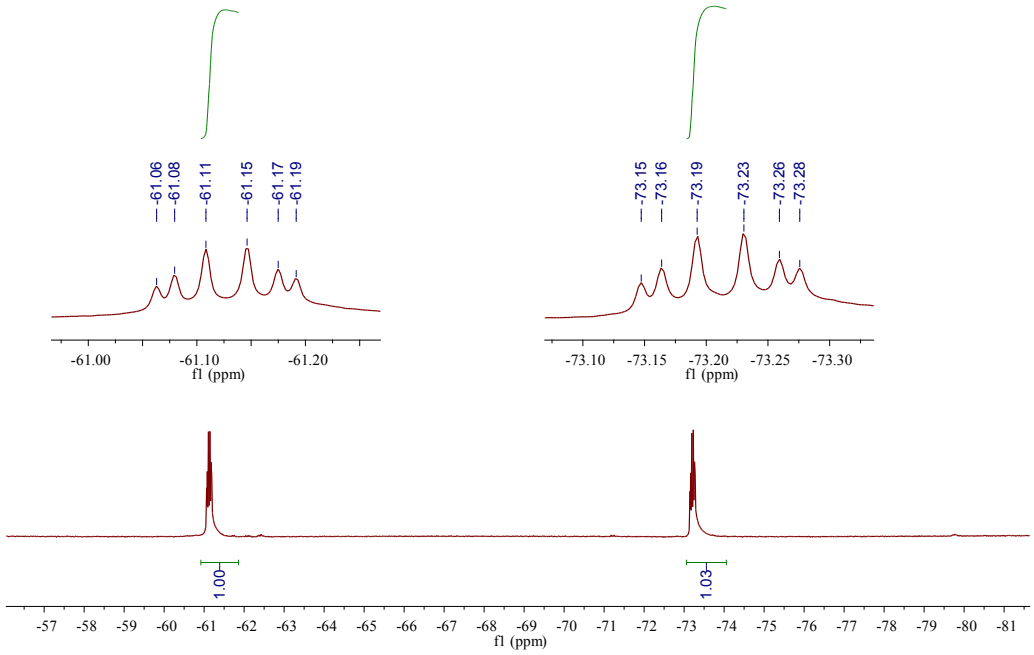


Figure S2-3. ^{19}F NMR spectrum of **C3OH** in $CDCl_3$.

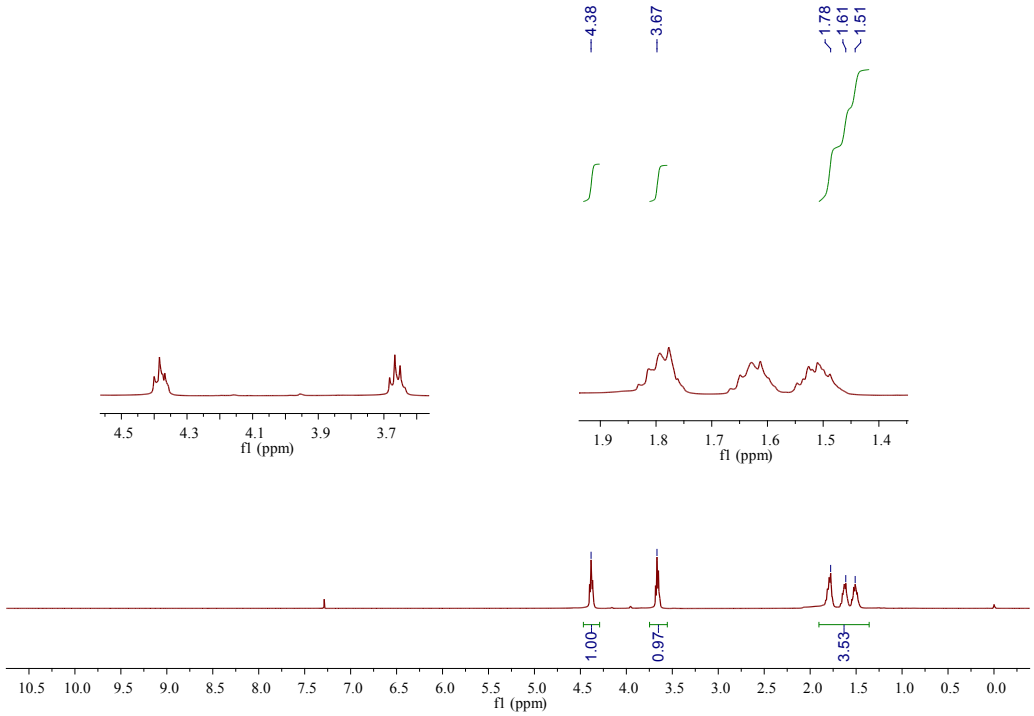


Figure S2-4. ^{1}H NMR spectrum of **C5OH** in $CDCl_3$.

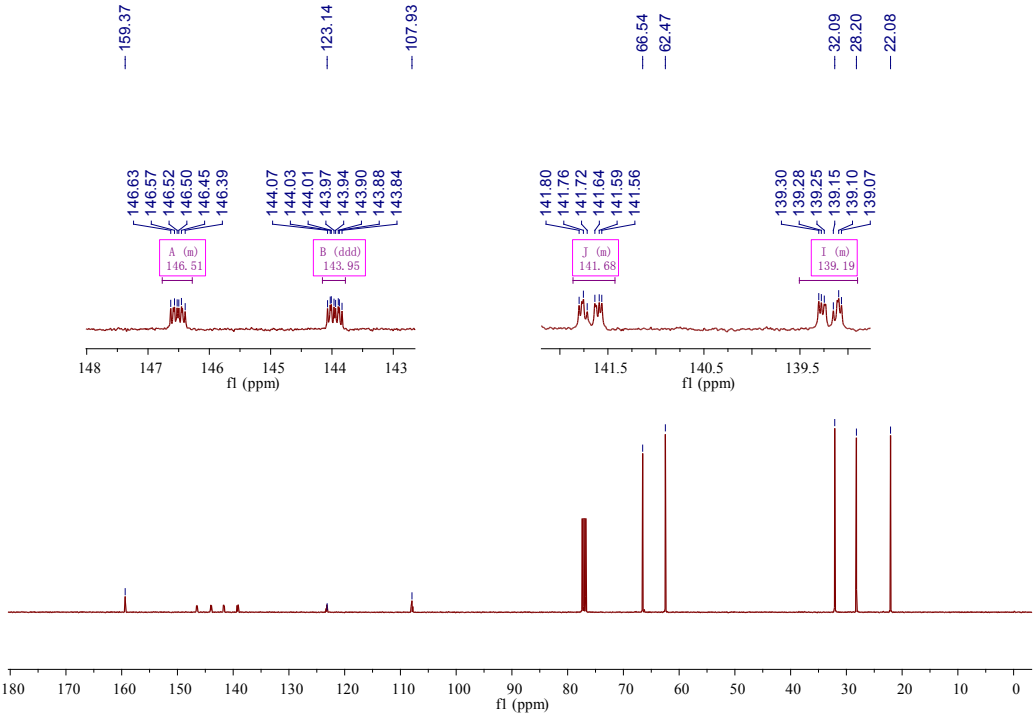


Figure S2-5. ^{13}C NMR spectrum of **C5OH** in $CDCl_3$.

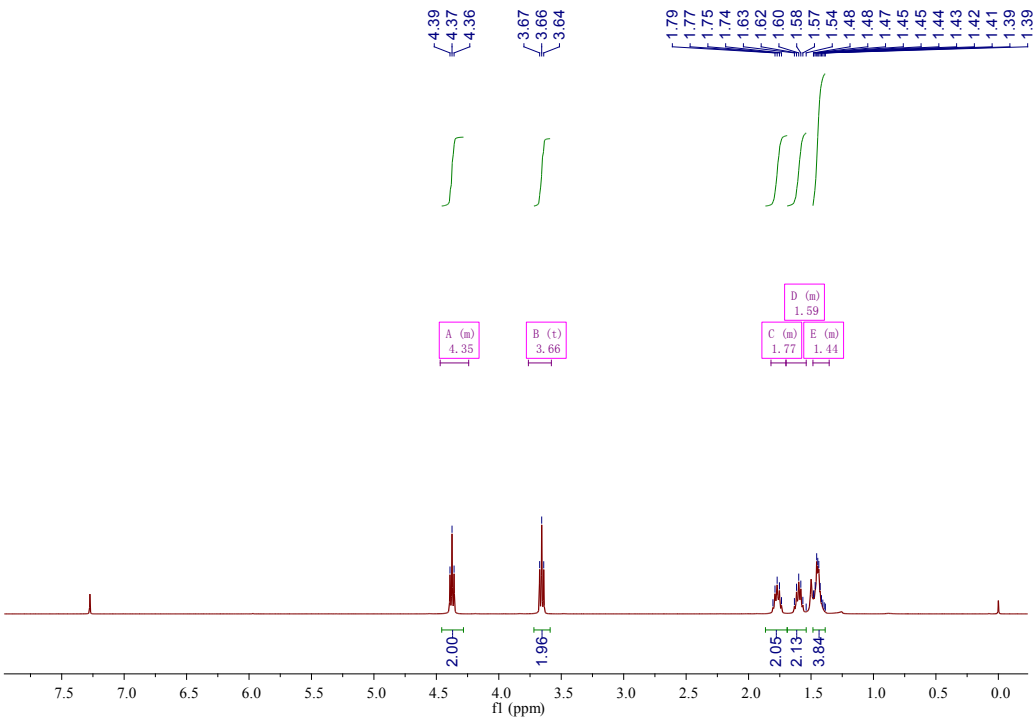


Figure S2-6. ^{1}H NMR spectrum of **C6OH** in $CDCl_3$.

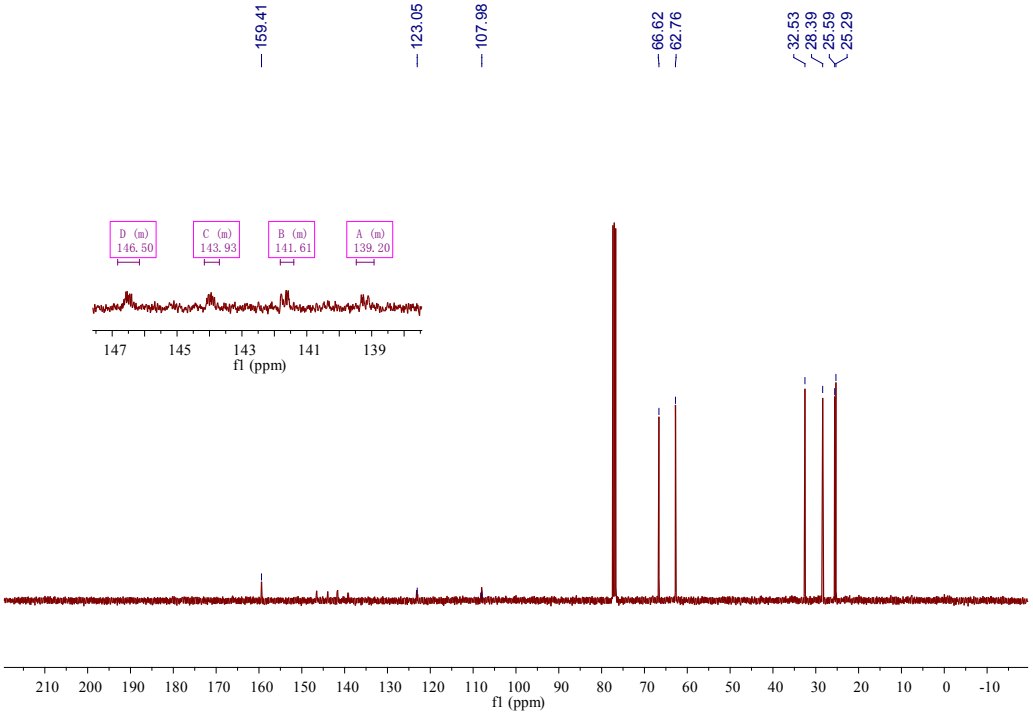


Figure S2-7. ^{13}C NMR spectrum of **C6OH** in $CDCl_3$.

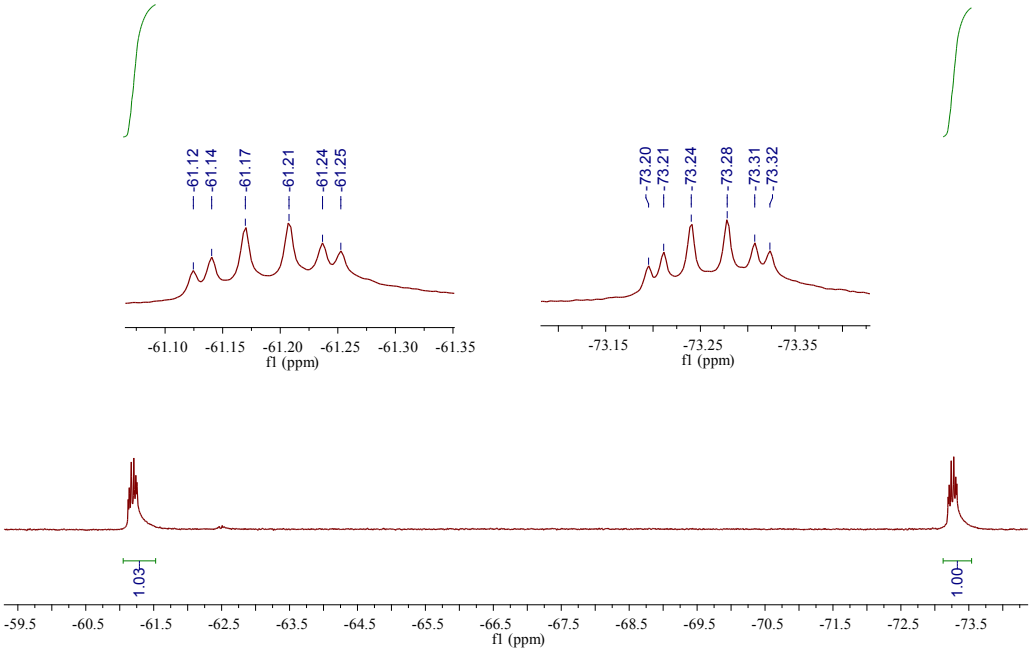


Figure S2-8. ^{19}F NMR spectrum of **C6OH** in $CDCl_3$.

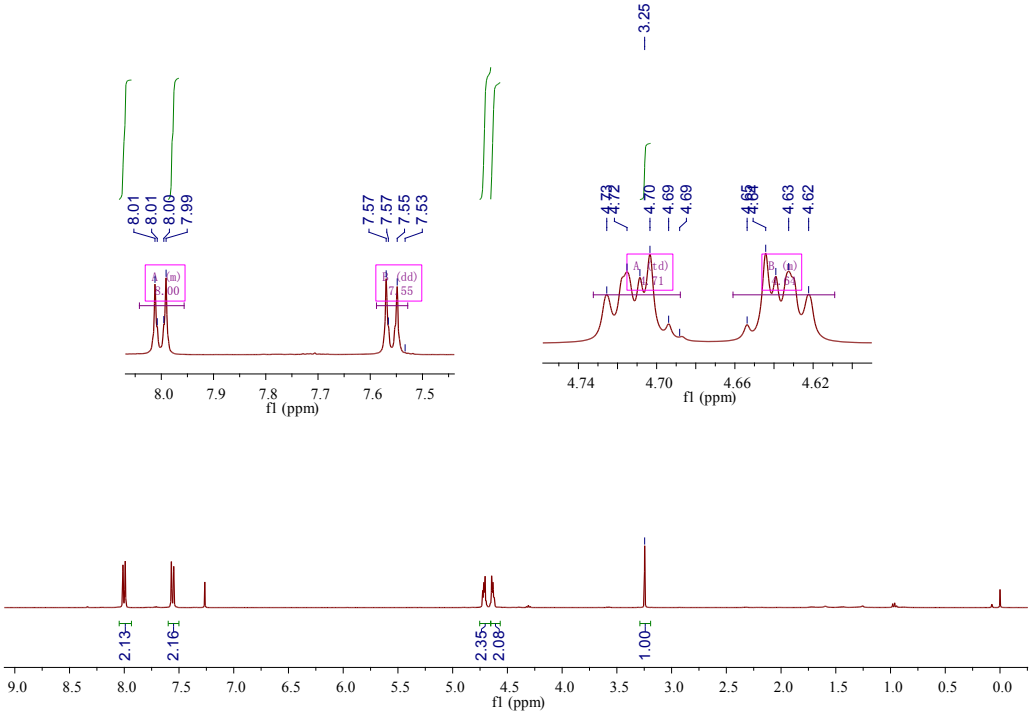


Figure S2-9. ^{1}H NMR spectrum of **C2** in $CDCl_3$.

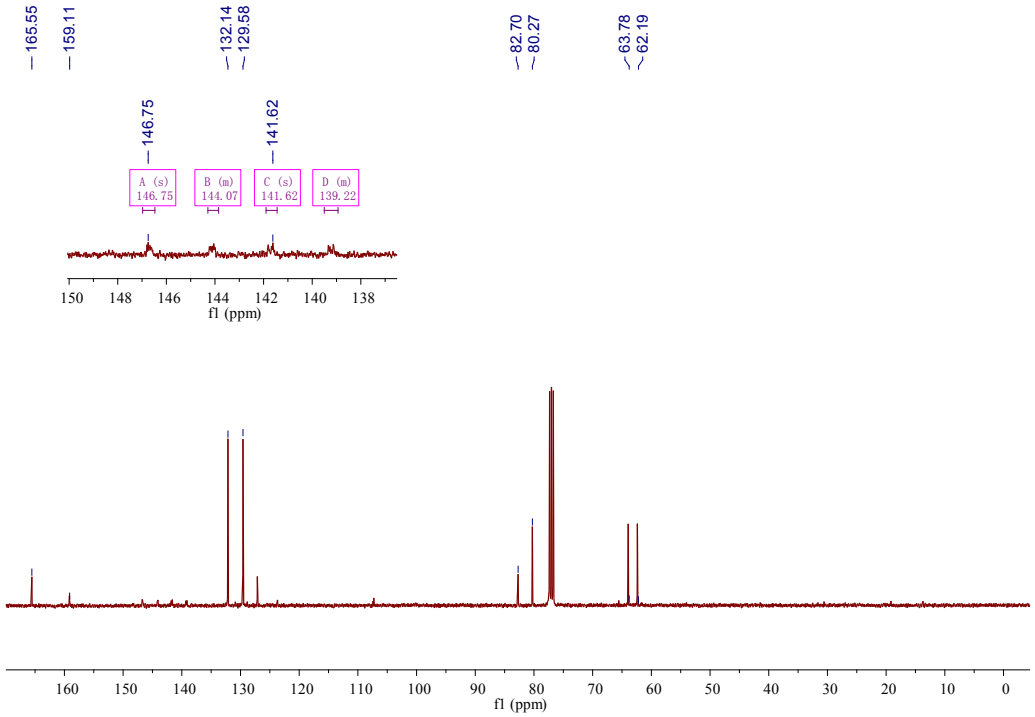


Figure S2-10. ^{13}C NMR spectrum of **C2** in $CDCl_3$.

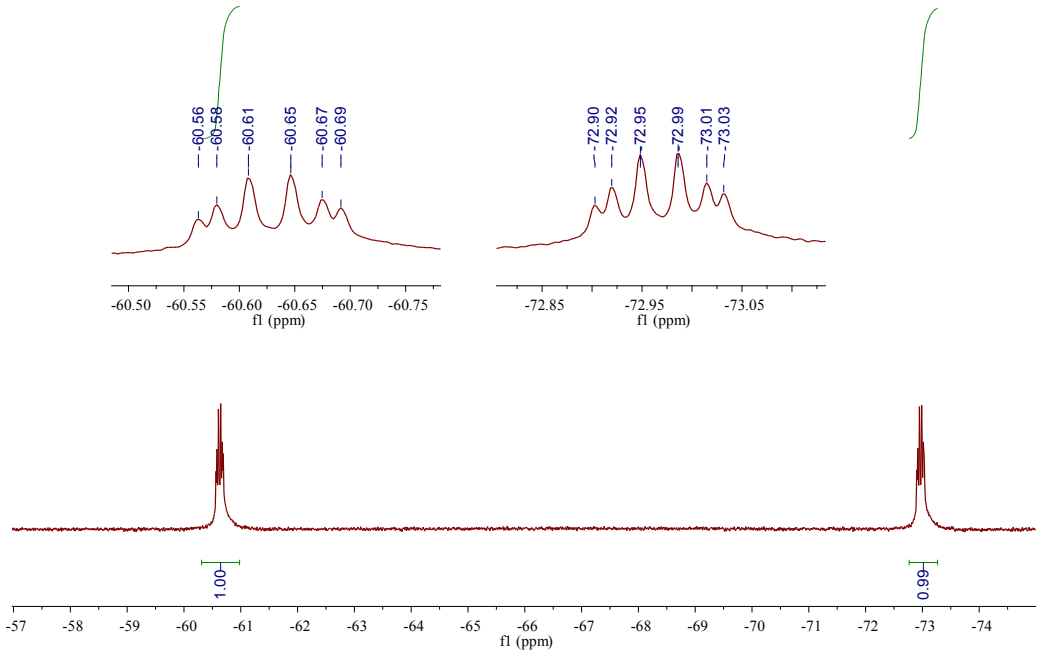


Figure S2-11. ^{19}F NMR spectrum of **C2** in $CDCl_3$.

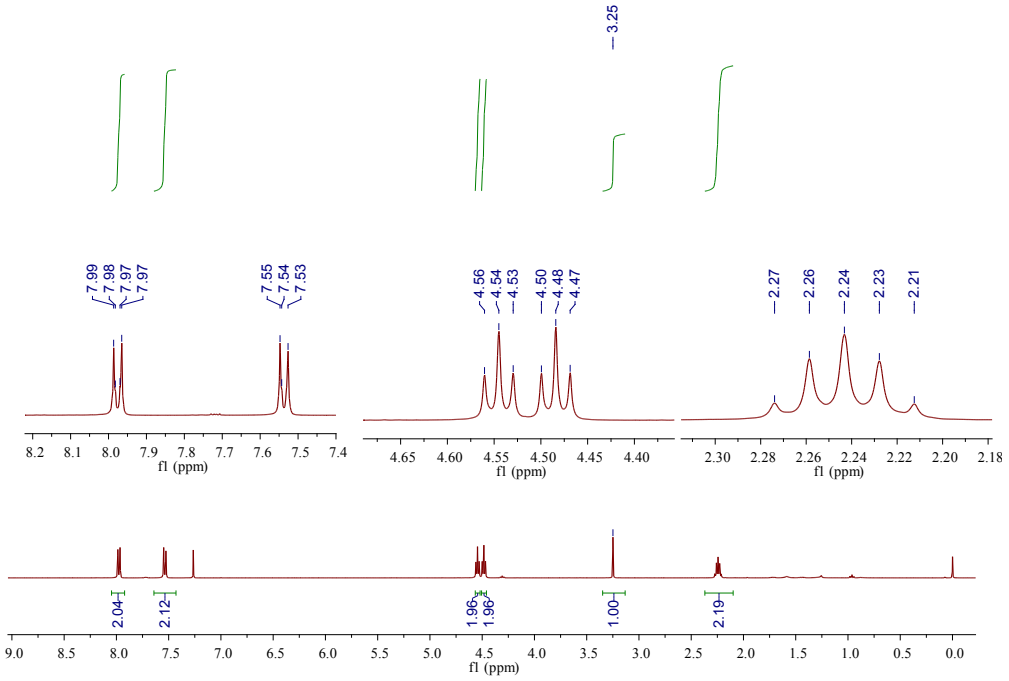


Figure S2-12. ^{1}H NMR spectrum of **C3** in $CDCl_3$.

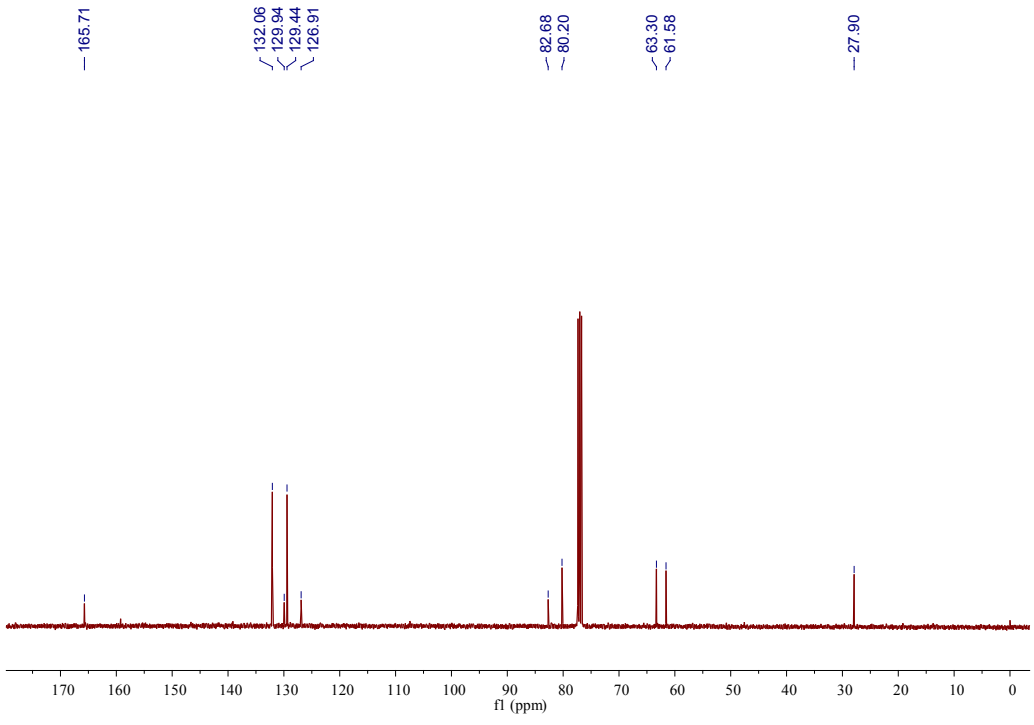


Figure S2-13. ^{13}C NMR spectrum of **C3** in $CDCl_3$.

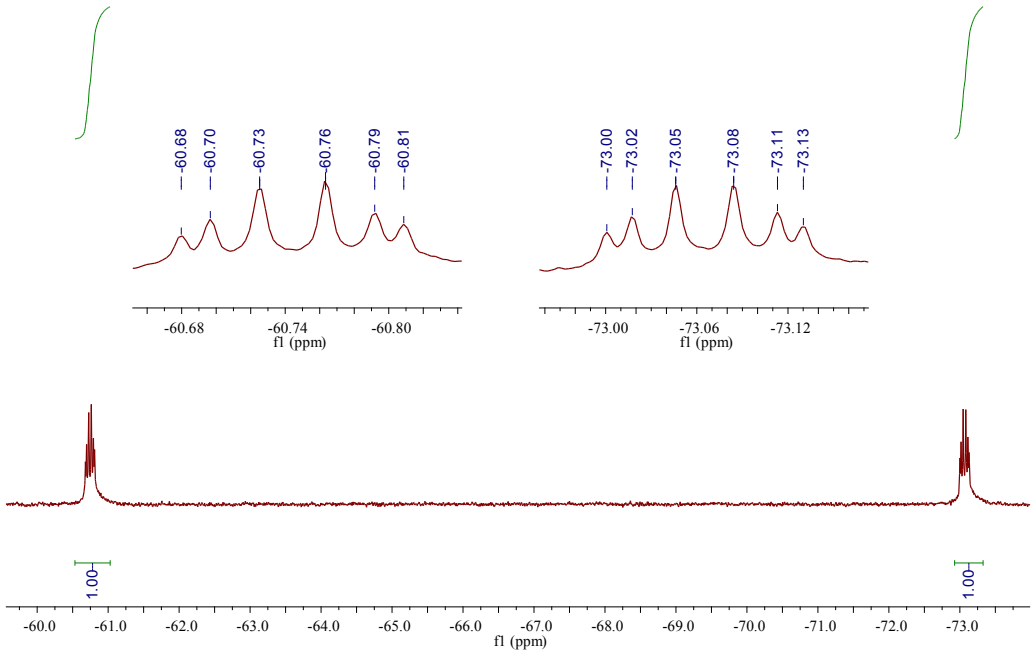


Figure S2-14. ^{19}F NMR spectrum of **C3** in $CDCl_3$.

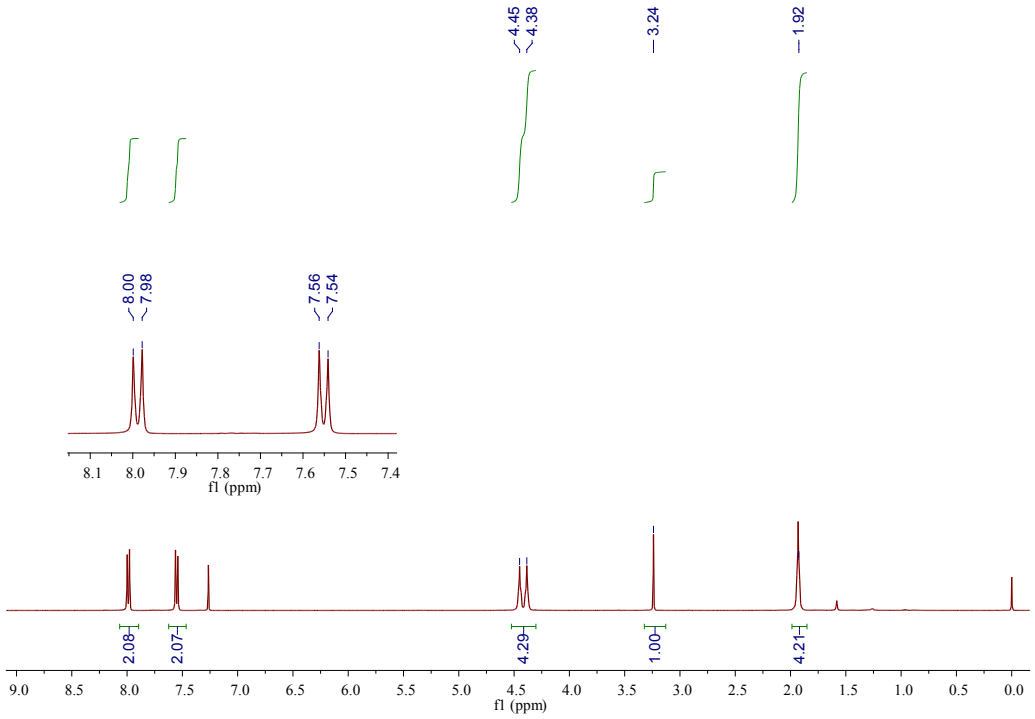


Figure S2-15. ^{1}H NMR spectrum of **C4** in $CDCl_3$.

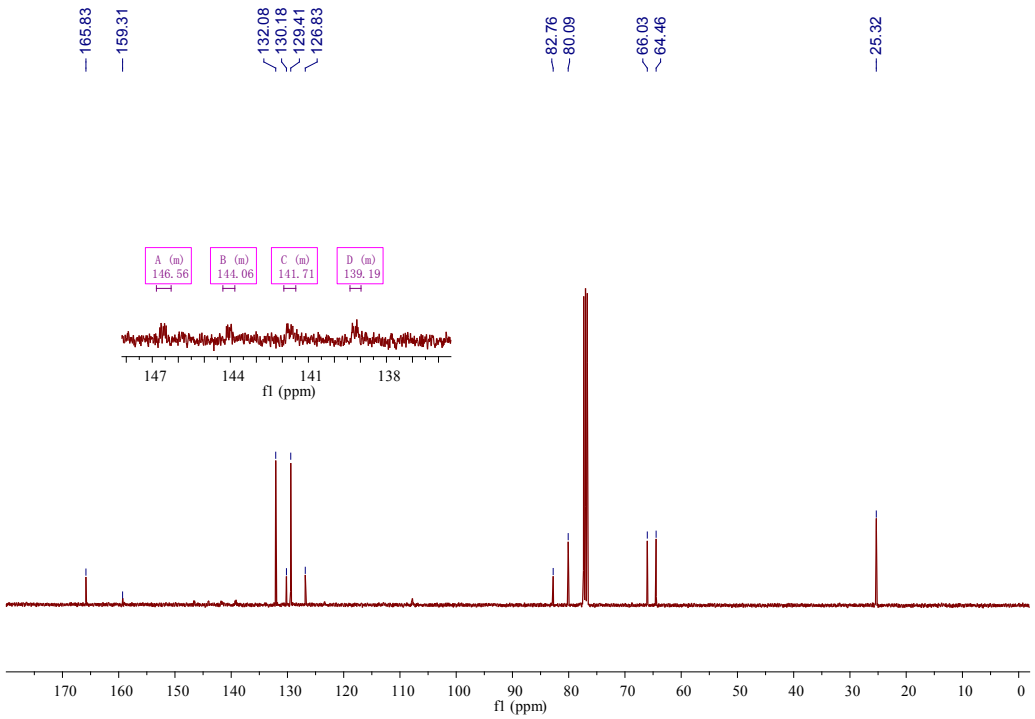


Figure S2-16. ^{13}C NMR spectrum of **C4** in $CDCl_3$.

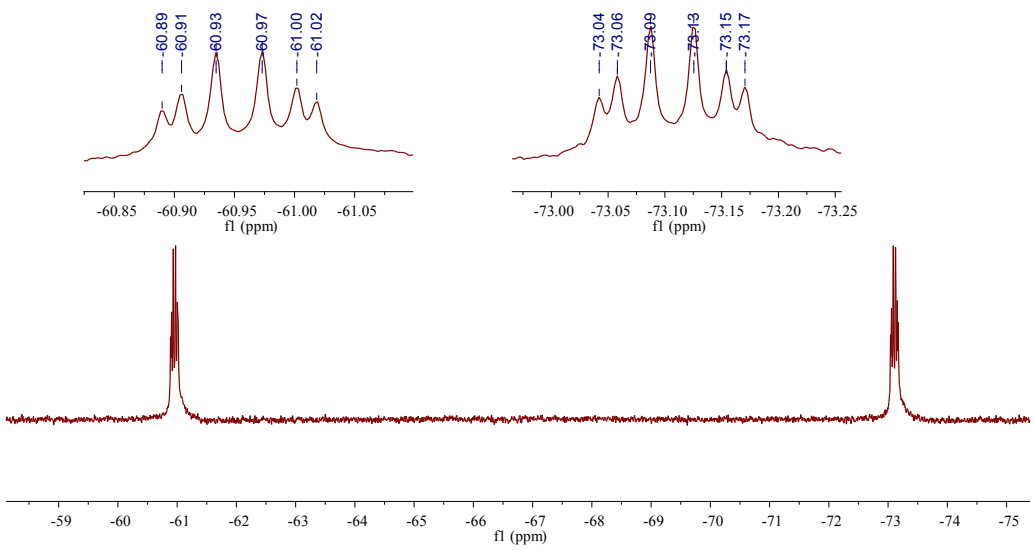


Figure S2-17. ^{19}F NMR spectrum of **C4** in $CDCl_3$.

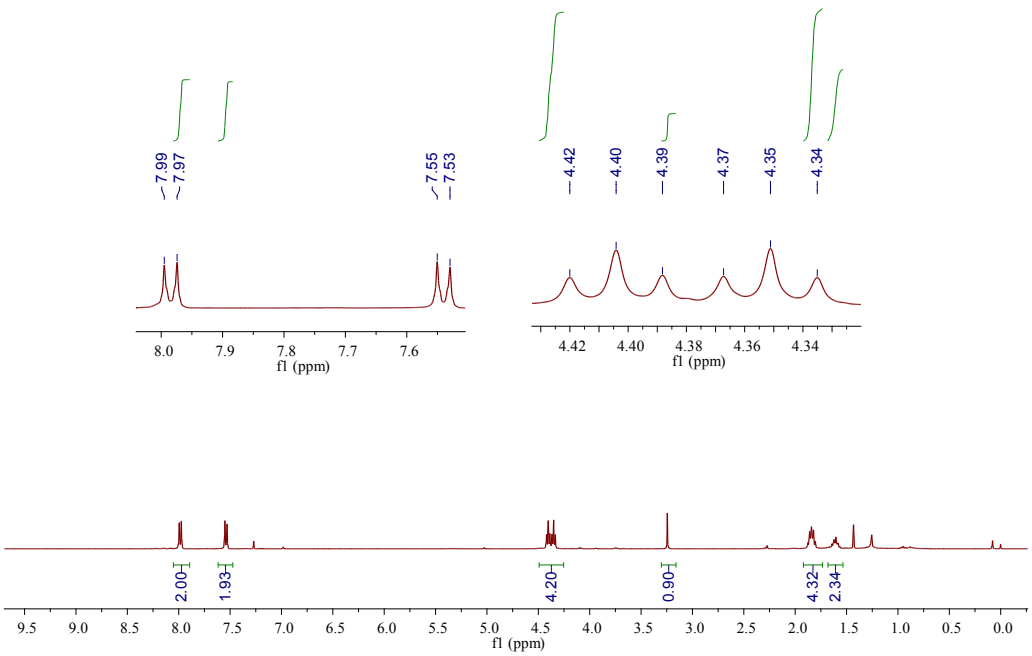


Figure S2-18. ^{1}H NMR spectrum of **C5** in $CDCl_3$.

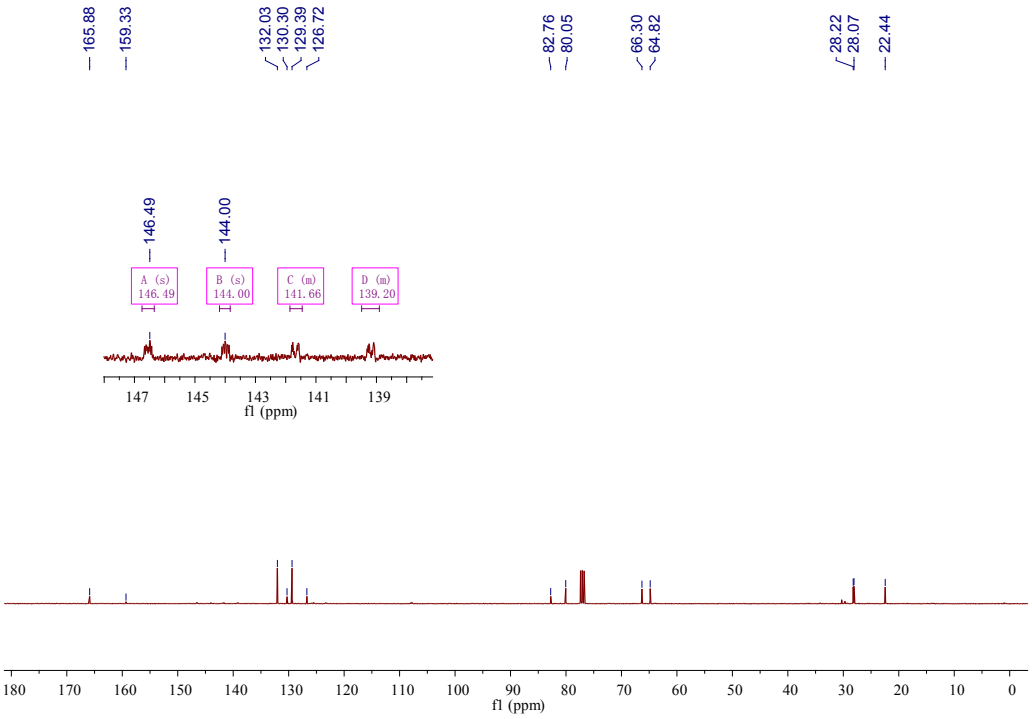


Figure S2-19. ^{13}C NMR spectrum of **C5** in $CDCl_3$.

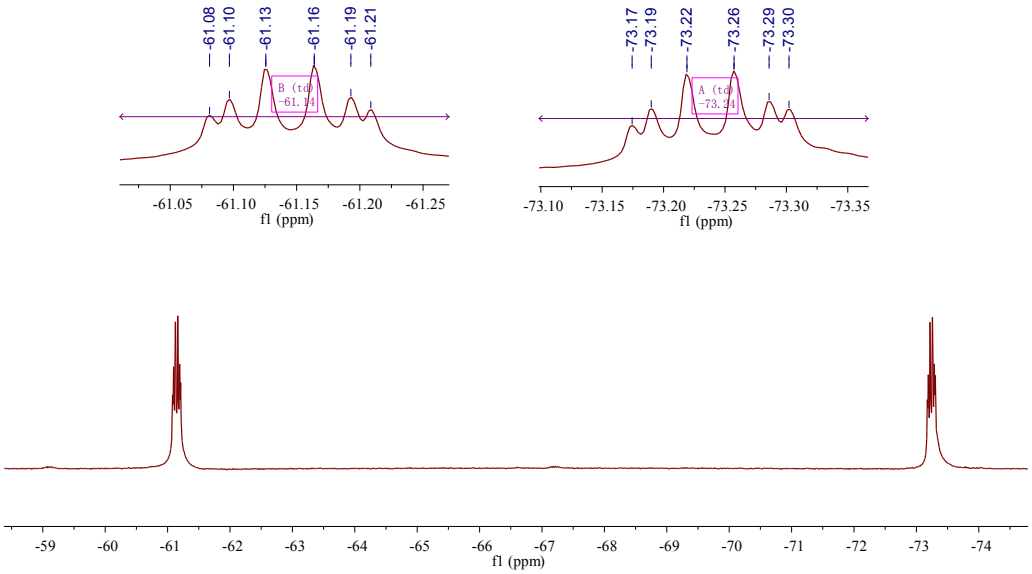


Figure S2-20. ^{19}F NMR spectrum of **C5** in $CDCl_3$.

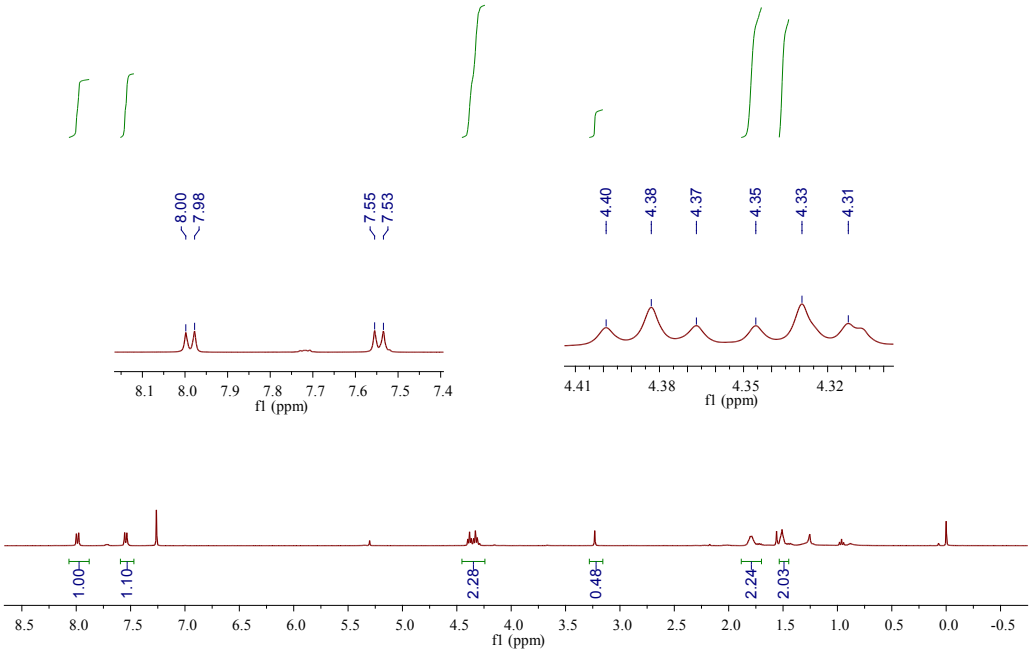


Figure S2-21. ^{1}H NMR spectrum of **C6** in $CDCl_3$.

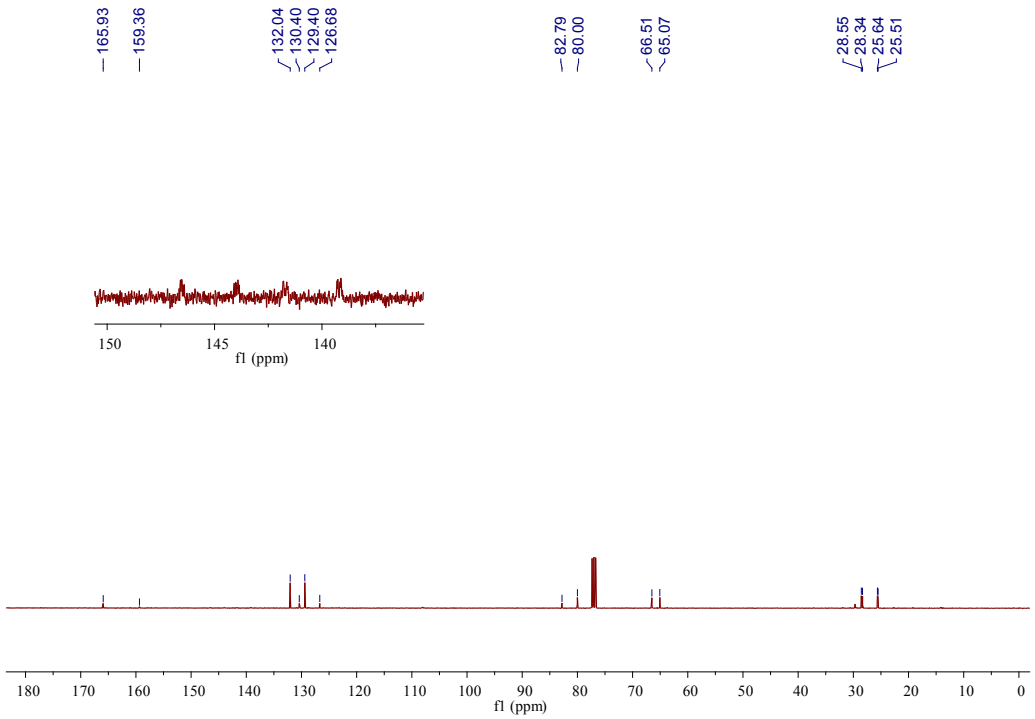


Figure S2-22. ^{13}C NMR spectrum of **C6** in $CDCl_3$.

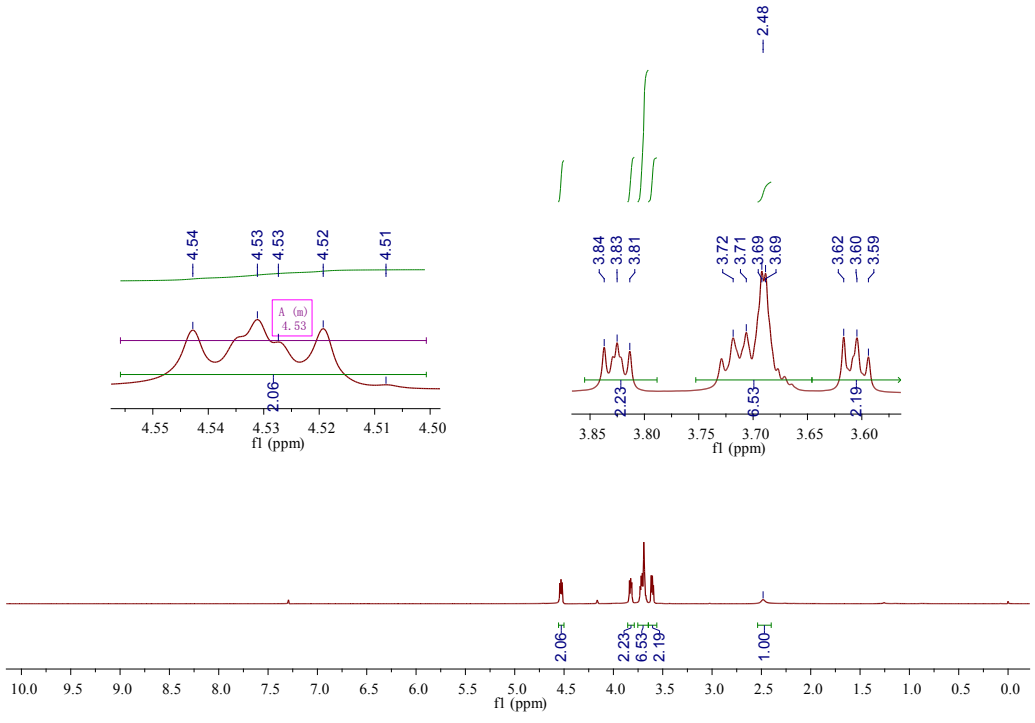


Figure S2-23. ^{1}H NMR spectrum of **O3OH** in $CDCl_3$.

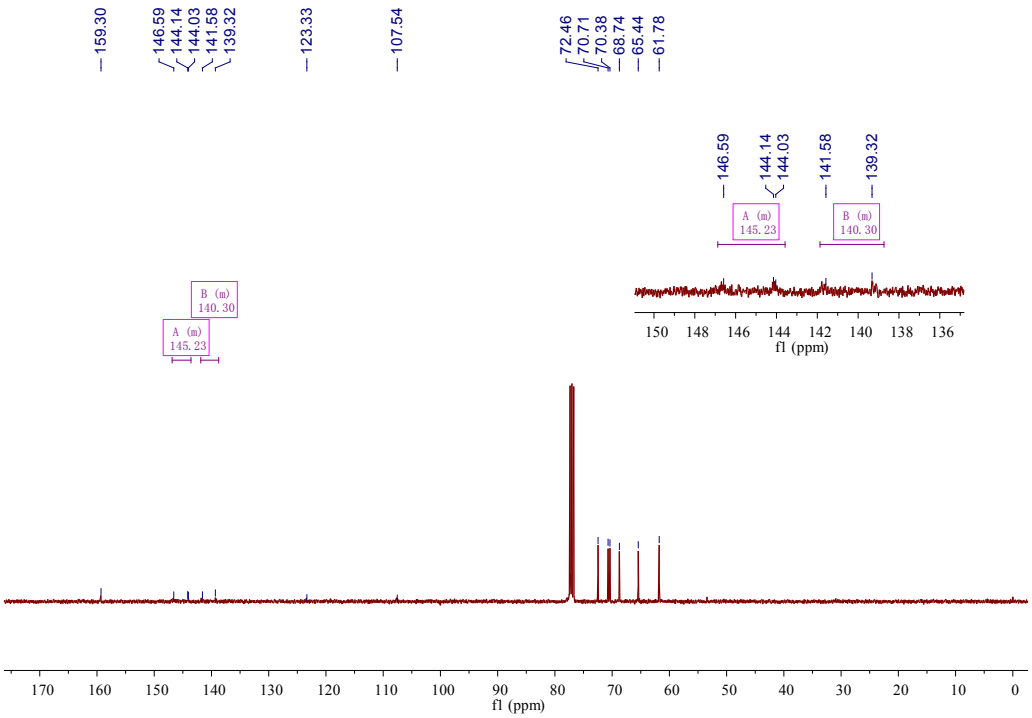


Figure S2-24. ^{13}C NMR spectrum of **O3OH** in $CDCl_3$.

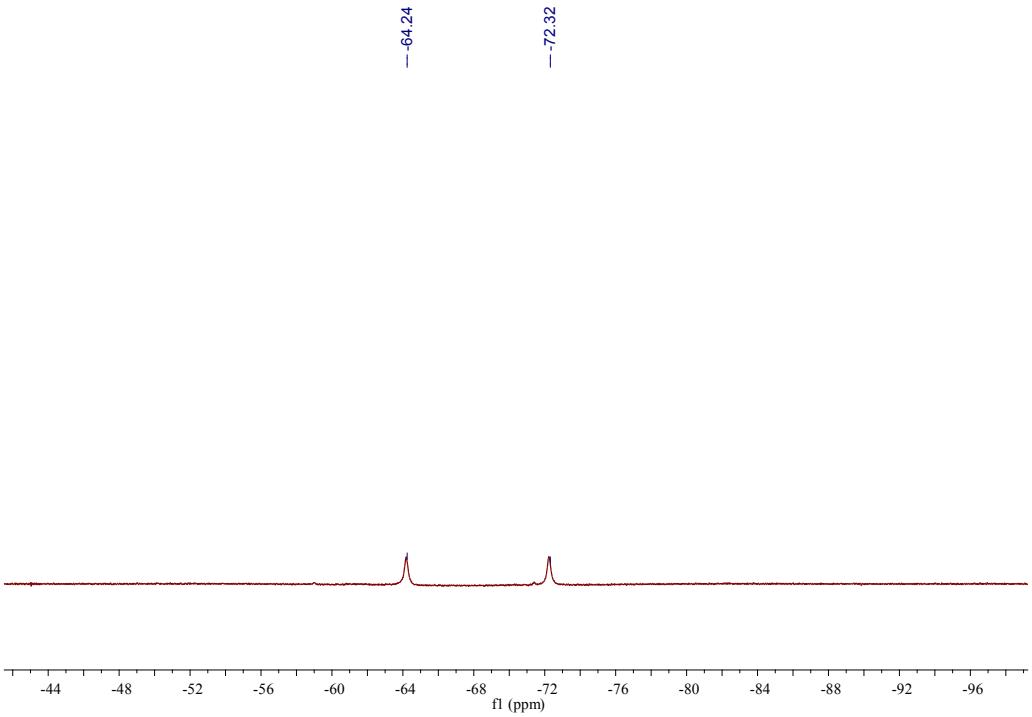


Figure S2-25. ^{19}F NMR spectrum of **O3OH** in $CDCl_3$.

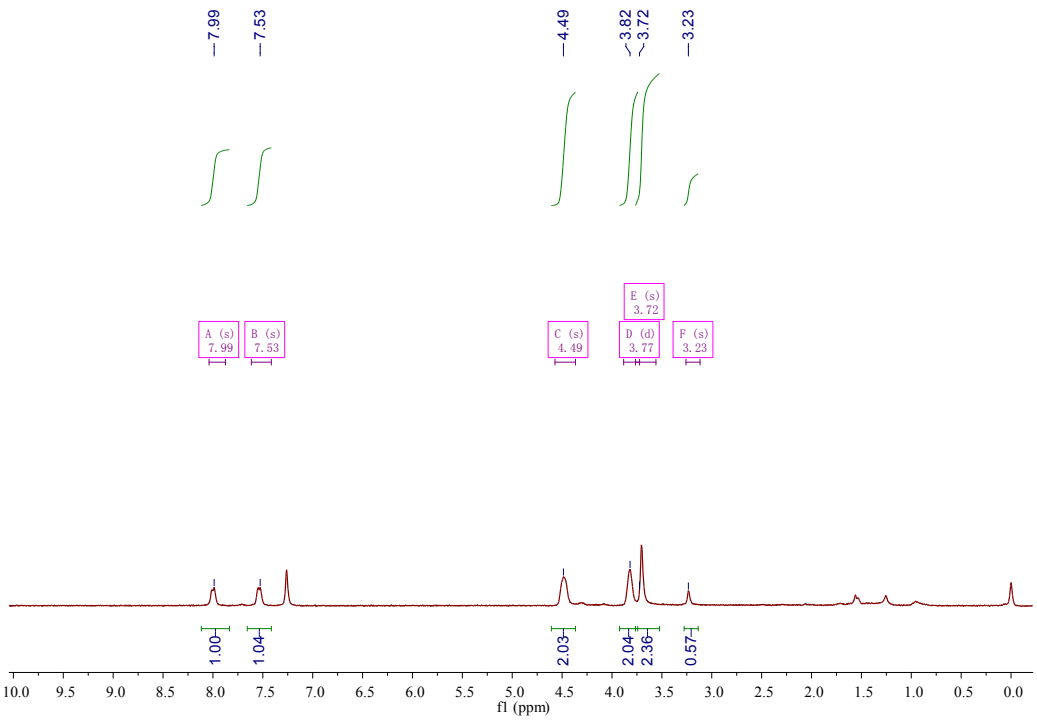


Figure S2-26. ^{1}H NMR spectrum of **O3** in $CDCl_3$.

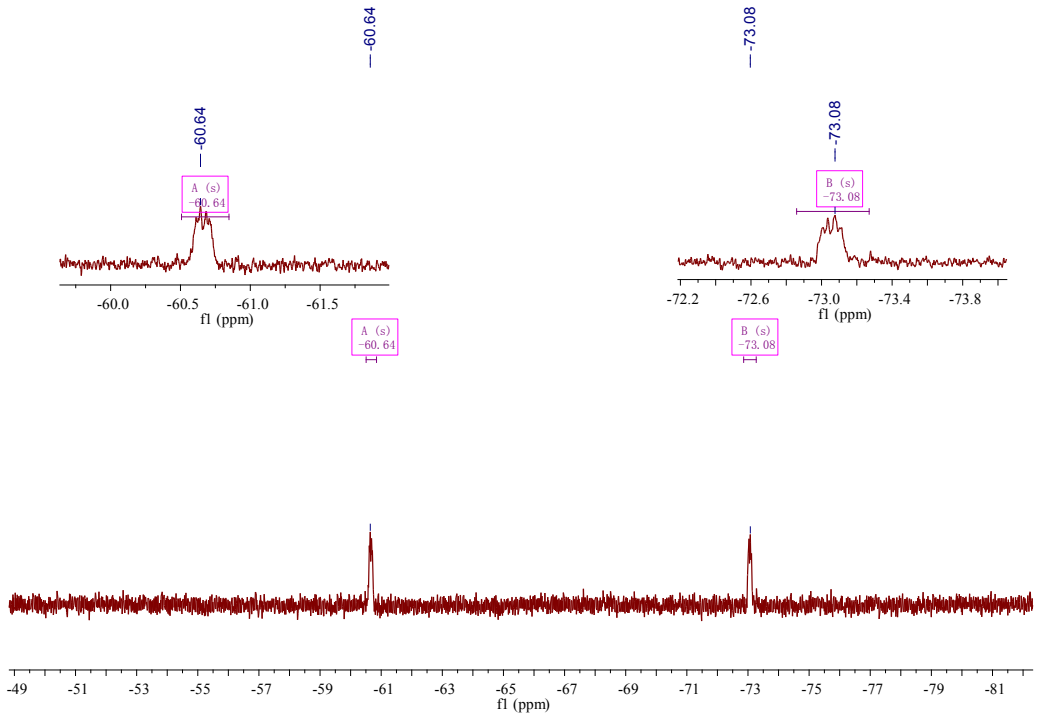


Figure S2-27. ^{19}F NMR spectrum of **O3** in $CDCl_3$.

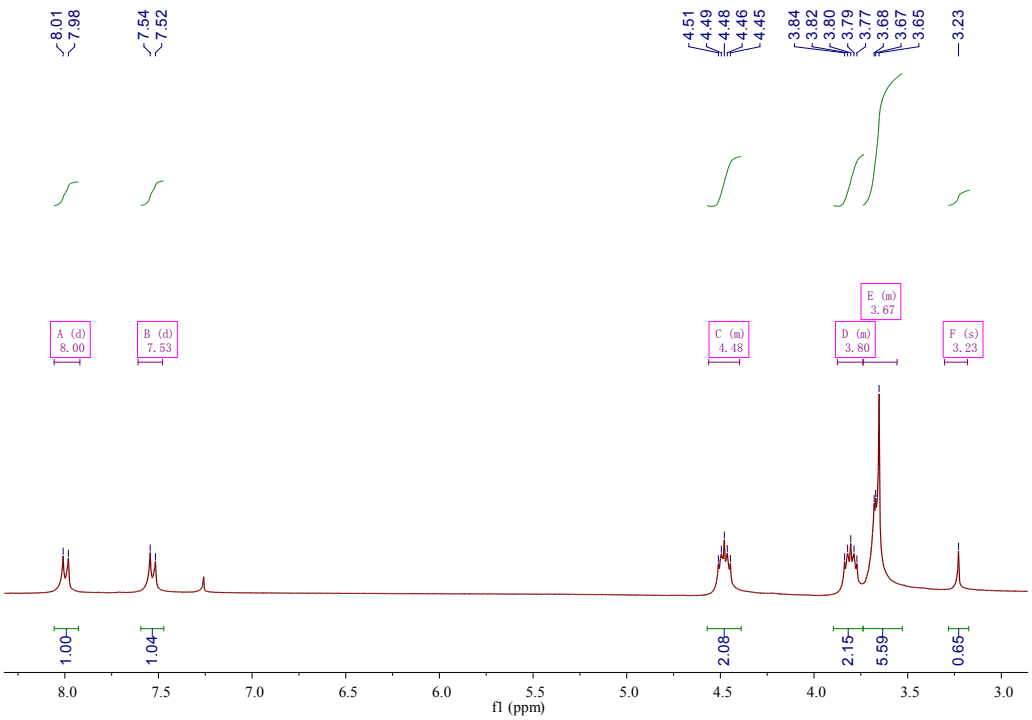


Figure S2-28. ^{1}H NMR spectrum of **O4** in $CDCl_3$.

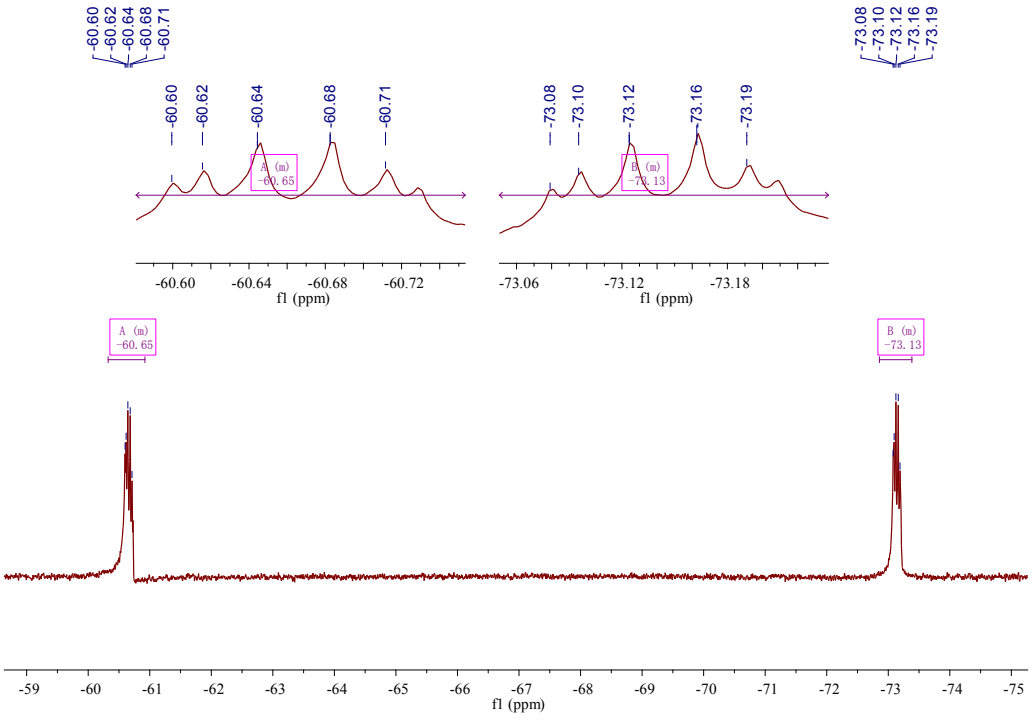


Figure S2-29. ^{19}F NMR spectrum of **O4** in $CDCl_3$.

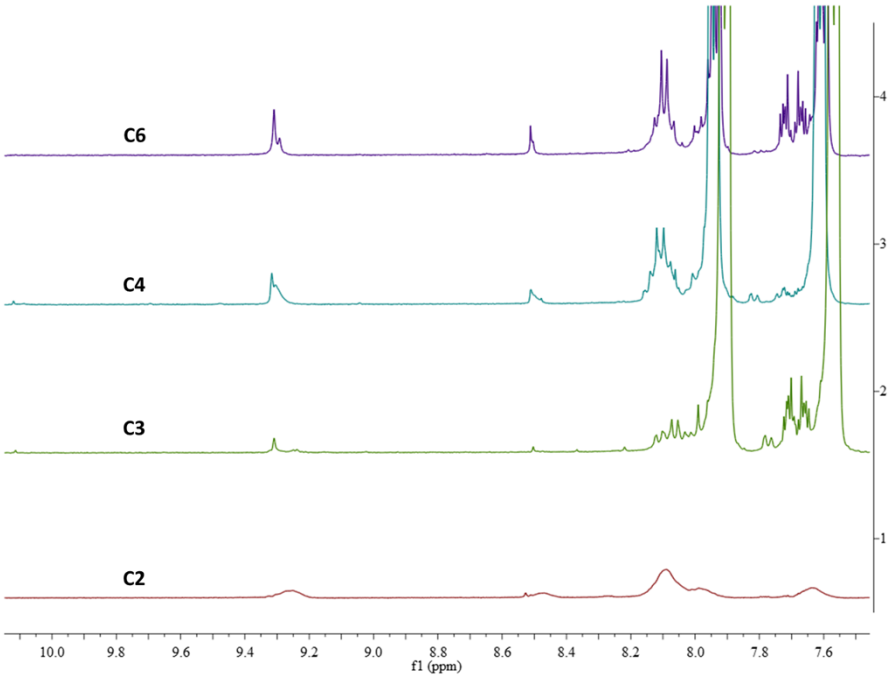


Figure S2-30. ^{1}H NMR spectra of **PC2-PC6** in DMSO-d_6.

The solubility of the products was limited. The regioselectivity was deduced from the oligomer which was soluble in the system reacted by heating.

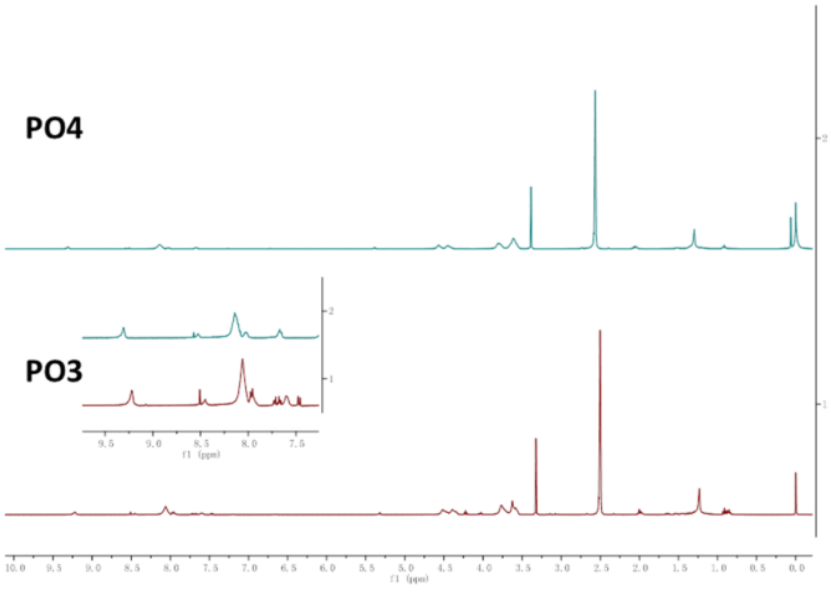


Figure S2-31. ^{1}H NMR spectra of **PO3-PO4** in DMSO-d_6.

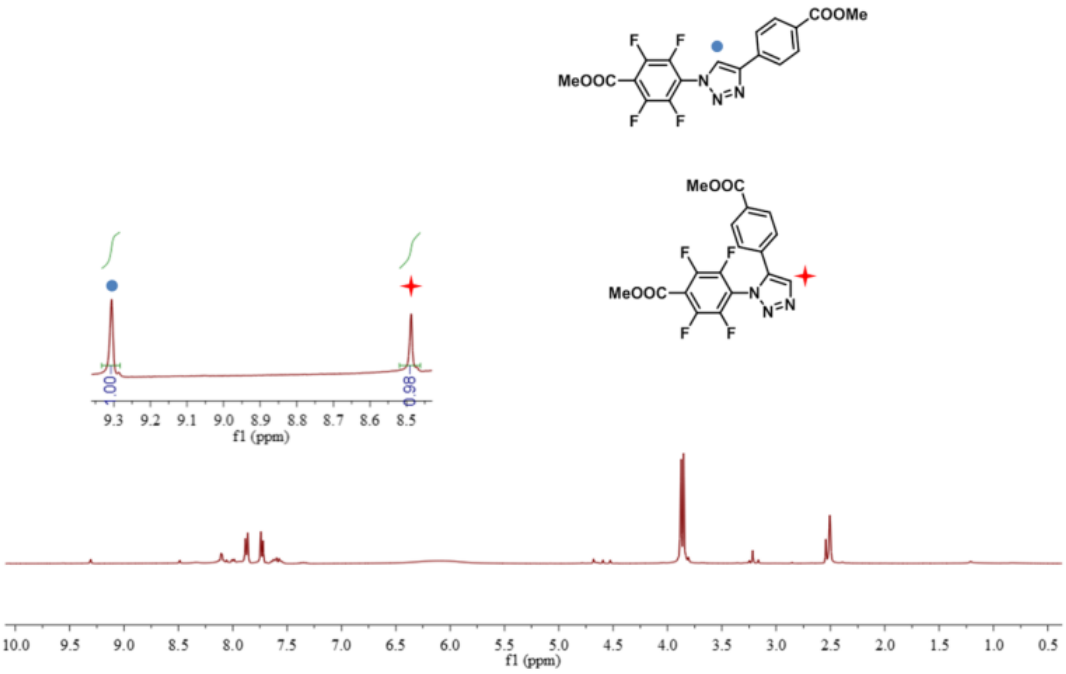


Figure *S2-32.* ^{1}H NMR spectrum of control experiment in DMSO-d_6 *in situ*.

To conveniently characterize the products, in control experiment, the 1,3-dipolar cycloaddition reaction of two control molecules (corresponding esters) containing azide and alkyne groups respectively, but not linked together, was conducted in DMSO-d_6 at 100 ^{o}C for 10 h. The fraction of 1,4-regioisomers was 52% from ^{1}H NMR *in situ*.

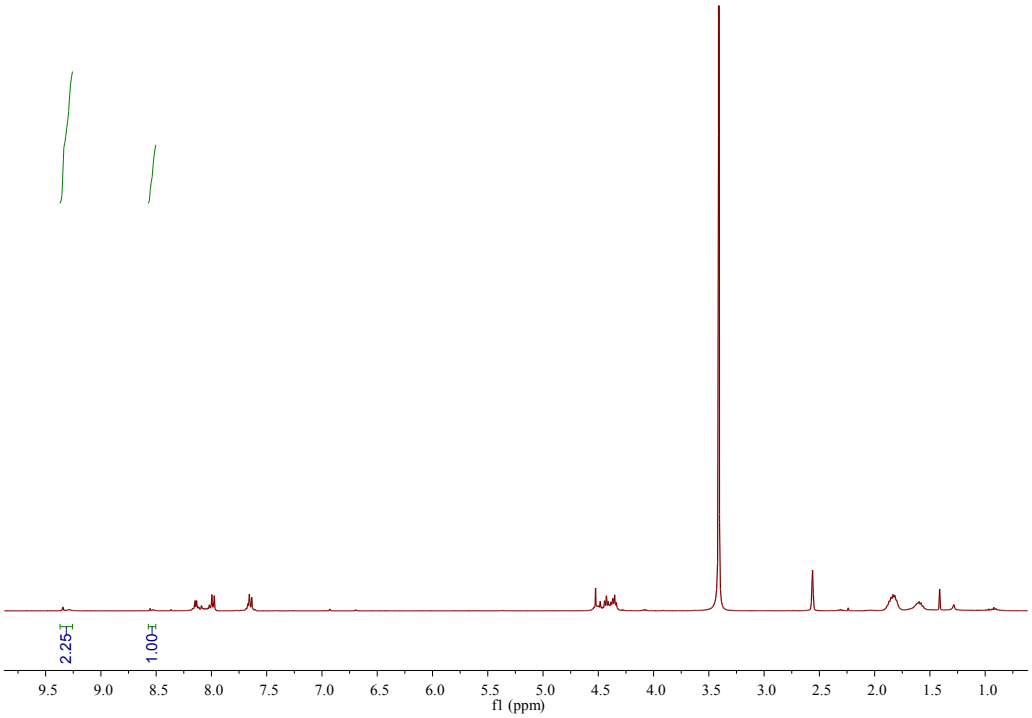


Figure *S2-33.* ^{1}H NMR spectrum in DMSO-d_6 of **PC5** obtained by polymerizing **C5** at 100 ^{o}C for 2 hours without solvents and catalysts.

3. FT-IR Spectra, DSC Thermograms, and GPC Traces

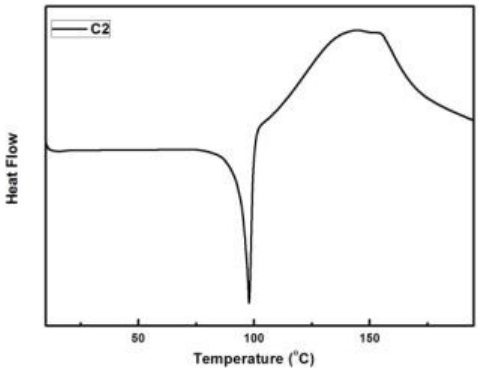


Figure *S3-1*. DSC thermogram of **C2** under N_2 atmosphere with a heating rate of 10 °C · min $^{-1}$.

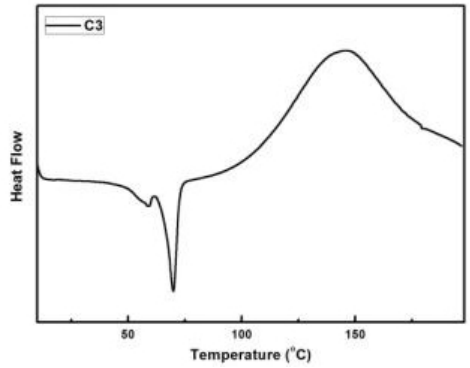


Figure *S3-2*. DSC thermogram of **C3** under N_2 atmosphere with a heating rate of 10 °C · min $^{-1}$.

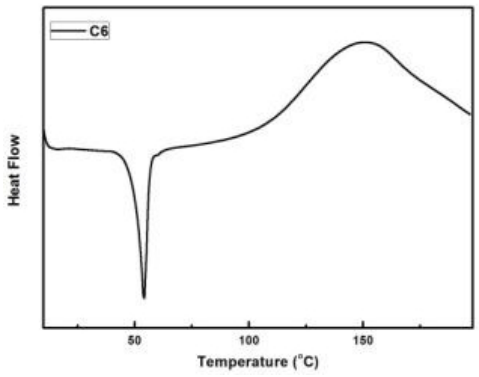


Figure *S3-3*. DSC thermogram of **C6** under N_2 atmosphere with a heating rate of 10 °C · min $^{-1}$.

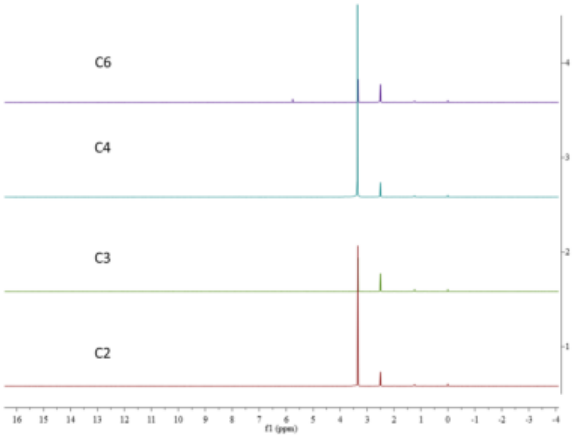


Figure *S3-4*. ^{1}H NMR spectra in DMSO-d_6 of the products after the DSC measurement which demonstrate that 1,3-dipolar cycloaddition polymerization was completed.

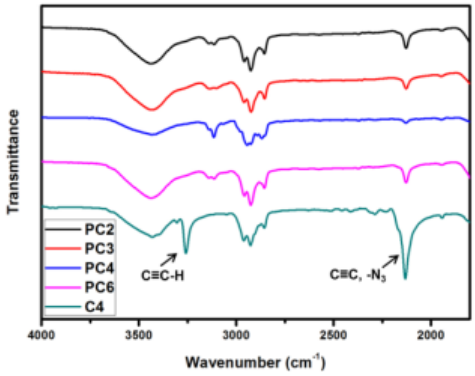


Figure *S3-5*. FT-IR spectra of monomer **C4** and polymers **PC2-PC6**.

All the monomers exhibited strong stretching vibration bands at 3280 cm^{-1} and 2120 cm^{-1} assigned to C≡C-H, and C≡C, -N_3, respectively. After the thermal treatments, FT-IR spectra confirmed the cycloaddition reaction of the azide and alkyne resulting in the bands significantly reduced after thermal treatments. The residue was attributed to the unreacted terminal azide and alkyne groups.

Table *S3-1*. Properties of **PO3** and **PO4** synthesized in solid state by heating.

	M_w[a](kDa)	PDI[a]	Yield (%)	$F_{1,4}$[b](%)	Solubility
PO3	12.6	1.4	98%	78%	√
PO4	22.1	1.9	98%	89%	√

[a] Estimated by GPC in THF using PS as standards. [b] Fraction of 1,4-regioisomers determined by ^{1}H NMR.

4. ORTEP Drawings of the Crystal Structures

Single crystal **C2**, **C3**, **C4**, and **C6** were prepared by solvent evaporation method. The monomers (2 mg) were dissolved in a mixture of DCM and PE (1 mL). The solutions were kept in a fridge at 5 °C until transparent crystals suitable for single-crystal diffraction were obtained. Cambridge Crystallographic Data Centre (CCDC) Deposition Number: **C2**: CCDC-998247; **C3**: CCDC-998248; **C4**: CCDC-998369; **C6**: CCDC-998250.

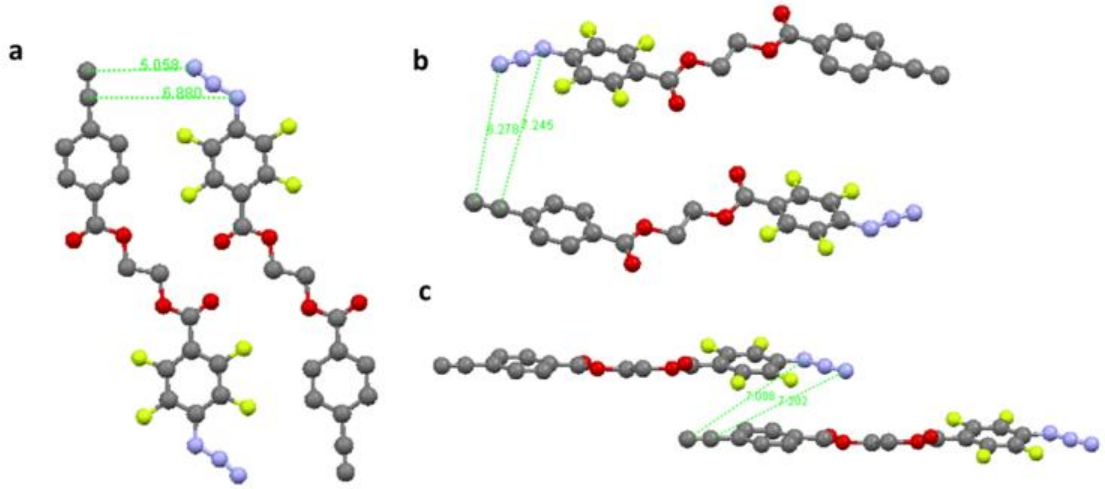


Figure *S4-1.* ORTEP drawings of the crystal structure of **C2**.

For **C2**, the shortest distances between azide and alkyne groups were 5.058 Å and 6.880 Å (a) to give 1,5-regioisomers, but the orientation was not proper due to the steric hindrance of phenyl and tetrafluorophenyl groups.

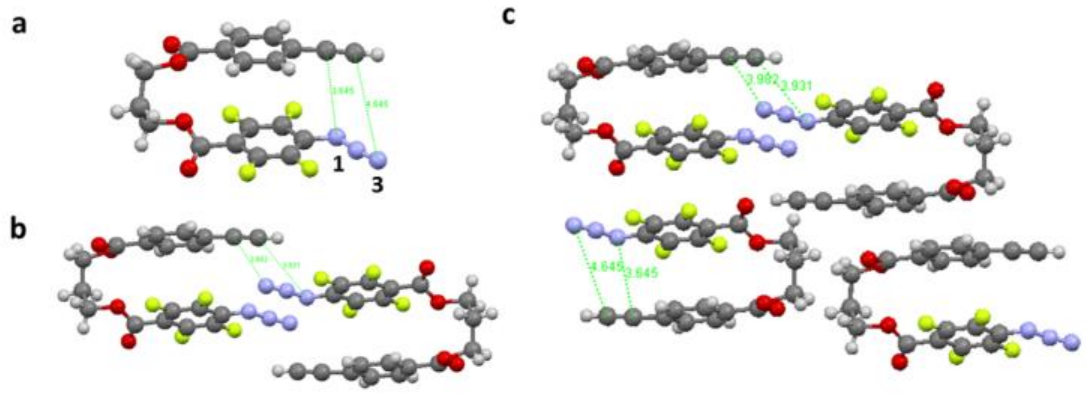


Figure *S4-2.* ORTEP drawings of the crystal structure of **C3**.

For **C3**, the shortest distances between the alkyne carbon atoms and 1- and 3-nitrogen atoms of azide group within the same column were 3.646 Å and 4.645 Å, which was expected to give intramolecularly reacted 1,5-triazole product. Although the two reacting groups were close to each other within the same molecule, the ring tension disfavored the formation of intramolecularly reacted 1,5-triazole product. For comparison, the shortest distances of corresponding atoms between neighboring columns were 3.982 Å and 3.931 Å, which would give intermolecularly reacted 1,4–triazole product and the orientation was proper for the 1,3-dipolar cycloaddition reaction.

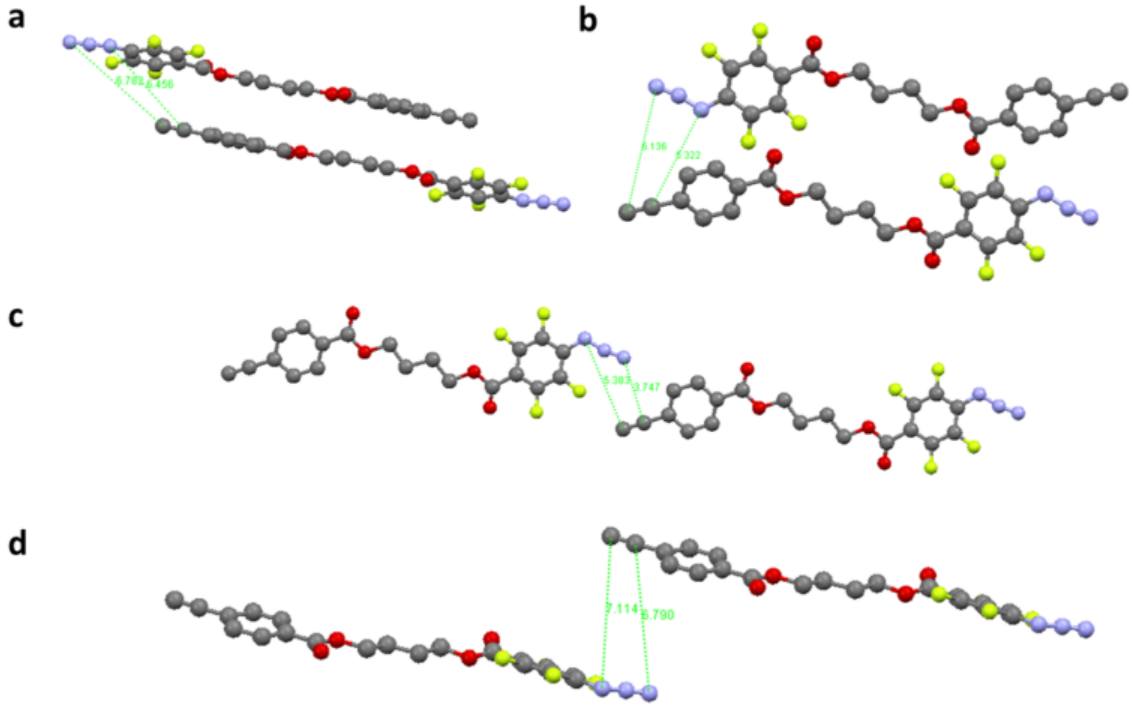


Figure *S4-3.* ORTEP drawings of the crystal structure of **C4**.

For **C4**, the shortest distances between the alkyne carbon atom and 1- and 3-nitrogen atoms of azide group to give 1,5-regioisomers were 6.136 Å and 5.322 Å, while the shortest distances of corresponding atoms to give 1,4-regioisomers were 3.747 Å and 5.383 Å.

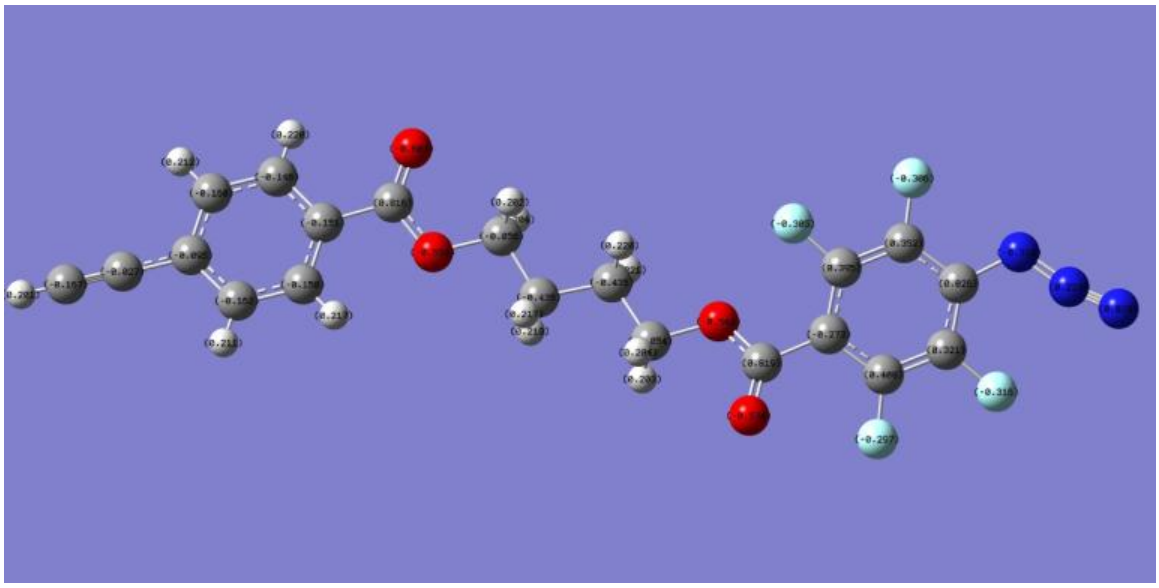


Figure *S4-4.* Natural Bond Orbital (NBO) charge analysis from the B3LYP/6-31G* method to demonstrate the dipole-dipole interaction in **C4**.

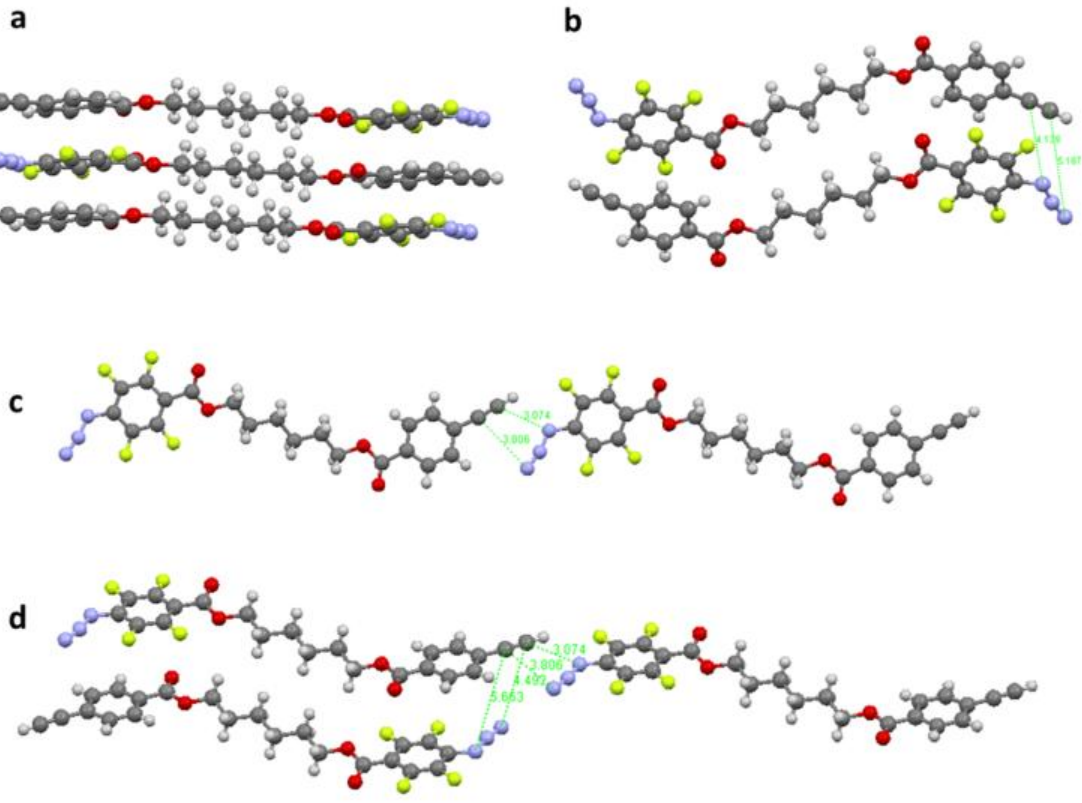


Figure *S4-5.* ORTEP drawings of the crystal structure of **C6.**

For **C6**, the shortest distances between the alkyne carbon atom and 1- and 3-nitrogen atoms of azide group within the same column were 4.139 Å and 5.187 Å to give 1,5-triazoles, while the shortest distances of corresponding atoms between neighboring columns were 3.074 Å and 3.806 Å to give 1,4-triazoles.

Table *S4-1.* The distances (Å) of azide and alkyne groups possible for 1,3-dipolar cycloaddition reaction.

	1,4		1,5	
	N1-C2	**N3-C1**	**N1-C1**	**N3-C2**
C2	8.056[a]	7.313	6.278	7.245
C3	3.645 3.477	4.645 5.179	3.931	3.982
C4	3.747 6.790	5.383 7.114	6.782	6.456
C6	4.139 5.653	5.187 4.492	3.074	3.806

5. Crystal Data and Structure Refinement

Table *S5-1-1.* Crystal data and structure refinement for **C2**

Identification code	**C2**
Empirical formula	C18 H9 F4 N3 O4
Formula weight	407.28
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.1325(14) Å alpha = 61.83(3) deg. b = 11.657(2) Å beta = 86.14(3) deg. c = 11.979(2) Å gamma = 76.85(3) deg.
Volume	854.1(3) $Å^3$
Z, Calculated density	2, 1.584 Mg/m^3
Absorption coefficient	0.142 mm^{-1}
F(000)	412
Crystal size	0.36 x 0.23 x 0.04 mm
Theta range for data collection	3.18 to 25.00 deg.
Limiting indices	-8<=h<=8, -13<=k<=13, -13<=l<=14
Reflections collected / unique	6665 / 2983 [R(int) = 0.0653]
Completeness to theta = 25.00	99.2 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.4090
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2983 / 0 / 262
Goodness-of-fit on F^2	1.155
Final R indices [I>2sigma(I)]	R1 = 0.1067, wR2 = 0.2711
R indices (all data)	R1 = 0.1244, wR2 = 0.2900
Largest diff. peak and hole	0.570 and -0.416 e. $Å^{-3}$

Table *S5-1-2.* Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **C2**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
F(4)	11851(3)	-849(2)	5887(2)	47(1)
F(2)	8129(3)	931(2)	9060(2)	45(1)
F(3)	10863(4)	1747(2)	5094(2)	46(1)
O(3)	7174(5)	6237(3)	7846(3)	54(1)
F(1)	9215(4)	-1664(2)	9852(2)	48(1)
C(5)	10377(6)	947(4)	6276(4)	37(1)
C(11)	5873(6)	8052(4)	8228(4)	39(1)
C(12)	5037(6)	8546(4)	9033(4)	42(1)
C(3)	9079(6)	544(4)	8254(4)	38(1)
O(2)	8709(5)	3297(3)	7443(3)	48(1)
N(3)	11046(6)	-2738(4)	8434(4)	49(1)
C(6)	10933(6)	-417(4)	6686(4)	36(1)
C(14)	4631(6)	10810(4)	7322(4)	39(1)
C(10)	6606(7)	6585(4)	8743(4)	46(1)
C(4)	9454(6)	1471(4)	7038(4)	37(1)
C(13)	4392(6)	9919(4)	8586(4)	39(1)
O(4)	6670(6)	5799(3)	9865(3)	63(1)
C(1)	10563(6)	-1335(4)	7903(4)	37(1)
C(15)	5461(6)	10298(4)	6509(4)	41(1)
C(16)	6076(6)	8933(4)	6951(4)	42(1)
O(1)	8511(5)	3724(3)	5430(3)	57(1)
C(17)	4056(7)	12216(4)	6874(4)	46(1)
C(2)	9635(6)	-813(4)	8668(4)	38(1)
C(7)	8838(6)	2955(4)	6526(4)	43(1)
N(2)	11840(6)	-3246(4)	7769(4)	54(1)
C(8)	8072(8)	4715(4)	7052(5)	55(1)
C(9)	7855(8)	4825(5)	8252(5)	57(1)
C(18)	3560(8)	13380(5)	6502(5)	63(1)

N(1)	12557(8)	-3895(5)	7334(5)	77(2)

Table *S5-1-3.* Bond lengths [Å] and angles [deg] for **C2**.

F(4)-C(6)	1.350(4)
F(2)-C(3)	1.334(4)
F(3)-C(5)	1.352(4)
O(3)-C(10)	1.326(5)
O(3)-C(9)	1.448(5)
F(1)-C(2)	1.355(5)
C(5)-C(4)	1.379(6)
C(5)-C(6)	1.389(6)
C(11)-C(12)	1.382(6)
C(11)-C(16)	1.404(6)
C(11)-C(10)	1.489(6)
C(12)-C(13)	1.396(6)
C(12)-H(12)	0.9500
C(3)-C(2)	1.381(6)
C(3)-C(4)	1.397(6)
O(2)-C(7)	1.325(5)
O(2)-C(8)	1.454(5)
N(3)-N(2)	1.240(5)
N(3)-C(1)	1.410(5)
C(6)-C(1)	1.394(6)
C(14)-C(13)	1.401(6)
C(14)-C(15)	1.402(6)
C(14)-C(17)	1.427(6)
C(10)-O(4)	1.215(6)
C(4)-C(7)	1.501(6)
C(13)-H(13)	0.9500
C(1)-C(2)	1.382(6)
C(15)-C(16)	1.387(6)

C(15)-H(15)	0.9500
C(16)-H(16)	0.9500
O(1)-C(7)	1.191(5)
C(17)-C(18)	1.182(7)
N(2)-N(1)	1.125(6)
C(8)-C(9)	1.497(7)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(18)-H(18)	0.9500

C(10)-O(3)-C(9)	116.8(4)
F(3)-C(5)-C(4)	121.2(4)
F(3)-C(5)-C(6)	116.2(4)
C(4)-C(5)-C(6)	122.5(4)
C(12)-C(11)-C(16)	119.9(4)
C(12)-C(11)-C(10)	119.2(4)
C(16)-C(11)-C(10)	120.8(4)
C(11)-C(12)-C(13)	120.4(4)
C(11)-C(12)-H(12)	119.8
C(13)-C(12)-H(12)	119.8
F(2)-C(3)-C(2)	116.8(4)
F(2)-C(3)-C(4)	121.5(4)
C(2)-C(3)-C(4)	121.7(4)
C(7)-O(2)-C(8)	116.1(3)
N(2)-N(3)-C(1)	118.8(4)
F(4)-C(6)-C(5)	118.9(3)
F(4)-C(6)-C(1)	120.0(4)
C(5)-C(6)-C(1)	121.2(4)
C(13)-C(14)-C(15)	118.9(4)
C(13)-C(14)-C(17)	120.5(4)
C(15)-C(14)-C(17)	120.6(4)

O(4)-C(10)-O(3)	124.1(4)
O(4)-C(10)-C(11)	123.2(4)
O(3)-C(10)-C(11)	112.7(4)
C(5)-C(4)-C(3)	116.0(4)
C(5)-C(4)-C(7)	120.0(4)
C(3)-C(4)-C(7)	123.9(4)
C(12)-C(13)-C(14)	120.2(4)
C(12)-C(13)-H(13)	119.9
C(14)-C(13)-H(13)	119.9
C(2)-C(1)-C(6)	116.4(4)
C(2)-C(1)-N(3)	116.8(4)
C(6)-C(1)-N(3)	126.8(4)
C(16)-C(15)-C(14)	120.8(4)
C(16)-C(15)-H(15)	119.6
C(14)-C(15)-H(15)	119.6
C(15)-C(16)-C(11)	119.7(4)
C(15)-C(16)-H(16)	120.1
C(11)-C(16)-H(16)	120.1
C(18)-C(17)-C(14)	179.3(5)
F(1)-C(2)-C(3)	119.1(4)
F(1)-C(2)-C(1)	118.7(4)
C(3)-C(2)-C(1)	122.2(4)
O(1)-C(7)-O(2)	124.6(4)
O(1)-C(7)-C(4)	123.8(4)
O(2)-C(7)-C(4)	111.7(4)
N(1)-N(2)-N(3)	168.9(5)
O(2)-C(8)-C(9)	105.8(4)
O(2)-C(8)-H(8A)	110.6
C(9)-C(8)-H(8A)	110.6
O(2)-C(8)-H(8B)	110.6
C(9)-C(8)-H(8B)	110.6
H(8A)-C(8)-H(8B)	108.7
O(3)-C(9)-C(8)	105.0(4)

O(3)-C(9)-H(9A)	110.7
C(8)-C(9)-H(9A)	110.7
O(3)-C(9)-H(9B)	110.7
C(8)-C(9)-H(9B)	110.7
H(9A)-C(9)-H(9B)	108.8
C(17)-C(18)-H(18)	180.0

Table *S5-1-4.* Anisotropic displacement parameters ($Å^2$ x 10^3) for **C2**. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U11	U22	U33	U23	U13	U12
F(4)	45(2)	50(2)	53(2)	-30(1)	15(1)	-18(1)
F(2)	45(2)	48(1)	48(1)	-25(1)	17(1)	-18(1)
F(3)	53(2)	45(1)	43(1)	-18(1)	17(1)	-21(1)
O(3)	74(2)	35(2)	57(2)	-25(2)	10(2)	-16(2)
F(1)	55(2)	46(2)	41(1)	-13(1)	9(1)	-24(1)
C(5)	37(2)	44(2)	34(2)	-17(2)	8(2)	-20(2)
C(11)	35(2)	36(2)	50(2)	-21(2)	4(2)	-15(2)
C(12)	42(2)	41(2)	46(2)	-20(2)	10(2)	-19(2)
C(3)	33(2)	41(2)	41(2)	-21(2)	8(2)	-11(2)
O(2)	63(2)	37(2)	49(2)	-23(1)	10(2)	-15(1)
N(3)	52(2)	37(2)	59(2)	-23(2)	7(2)	-14(2)
C(6)	35(2)	39(2)	43(2)	-24(2)	9(2)	-16(2)
C(14)	24(2)	47(2)	52(2)	-26(2)	6(2)	-14(2)
C(10)	51(3)	42(2)	50(3)	-24(2)	11(2)	-15(2)
C(4)	37(2)	36(2)	42(2)	-18(2)	5(2)	-16(2)
C(13)	32(2)	43(2)	44(2)	-22(2)	9(2)	-13(2)
O(4)	86(3)	48(2)	53(2)	-23(2)	15(2)	-17(2)
C(1)	33(2)	36(2)	44(2)	-19(2)	-1(2)	-14(2)
C(15)	38(2)	41(2)	40(2)	-14(2)	3(2)	-14(2)
C(16)	41(2)	46(2)	46(2)	-26(2)	10(2)	-15(2)
O(1)	73(2)	41(2)	49(2)	-17(2)	5(2)	-10(2)

C(17)	46(3)	38(2)	55(3)	-19(2)	5(2)	-13(2)
C(2)	32(2)	37(2)	40(2)	-12(2)	4(2)	-14(2)
C(7)	43(2)	36(2)	48(3)	-18(2)	10(2)	-12(2)
N(2)	65(3)	42(2)	60(2)	-26(2)	3(2)	-14(2)
C(8)	64(3)	40(3)	60(3)	-26(2)	11(2)	-10(2)
C(9)	67(3)	43(3)	66(3)	-29(2)	16(2)	-19(2)
C(18)	60(3)	49(3)	70(3)	-21(3)	10(3)	-15(2)
N(1)	110(4)	50(3)	68(3)	-31(2)	10(3)	-5(3)

Table *S5-1-5.* Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **C2**.

	x	y	z	U(eq)
H(12)	4900	7948	9897	50
H(13)	3790	10249	9141	46
H(15)	5605	10892	5645	49
H(16)	6633	8595	6392	51
H(8A)	6828	5086	6558	66
H(8B)	9037	5205	6524	66
H(9A)	6912	4319	8791	68
H(9B)	9105	4477	8737	68
H(18)	3162	14315	6203	75

Table *S5-1-6.* Torsion angles [deg] for **C2**

C(16)-C(11)-C(12)-C(13)	0.0(6)
C(10)-C(11)-C(12)-C(13)	178.0(4)
F(3)-C(5)-C(6)-F(4)	-1.9(5)
C(4)-C(5)-C(6)-F(4)	-179.2(3)
F(3)-C(5)-C(6)-C(1)	177.9(3)
C(4)-C(5)-C(6)-C(1)	0.6(6)

C(9)-O(3)-C(10)-O(4)	1.8(7)
C(9)-O(3)-C(10)-C(11)	-178.1(4)
C(12)-C(11)-C(10)-O(4)	-6.9(7)
C(16)-C(11)-C(10)-O(4)	171.0(4)
C(12)-C(11)-C(10)-O(3)	173.0(4)
C(16)-C(11)-C(10)-O(3)	-9.0(6)
F(3)-C(5)-C(4)-C(3)	-178.1(3)
C(6)-C(5)-C(4)-C(3)	-0.9(6)
F(3)-C(5)-C(4)-C(7)	4.6(6)
C(6)-C(5)-C(4)-C(7)	-178.2(4)
F(2)-C(3)-C(4)-C(5)	-177.4(3)
C(2)-C(3)-C(4)-C(5)	1.1(6)
F(2)-C(3)-C(4)-C(7)	-0.2(6)
C(2)-C(3)-C(4)-C(7)	178.3(4)
C(11)-C(12)-C(13)-C(14)	-1.6(6)
C(15)-C(14)-C(13)-C(12)	2.3(6)
C(17)-C(14)-C(13)-C(12)	-177.1(4)
F(4)-C(6)-C(1)-C(2)	179.3(3)
C(5)-C(6)-C(1)-C(2)	-0.5(6)
F(4)-C(6)-C(1)-N(3)	-0.3(6)
C(5)-C(6)-C(1)-N(3)	179.9(4)
N(2)-N(3)-C(1)-C(2)	178.4(4)
N(2)-N(3)-C(1)-C(6)	-2.0(7)
C(13)-C(14)-C(15)-C(16)	-1.4(6)
C(17)-C(14)-C(15)-C(16)	178.0(4)
C(14)-C(15)-C(16)-C(11)	-0.2(6)
C(12)-C(11)-C(16)-C(15)	1.0(6)
C(10)-C(11)-C(16)-C(15)	-177.0(4)
C(13)-C(14)-C(17)-C(18)	-79(42)
C(15)-C(14)-C(17)-C(18)	102(42)
F(2)-C(3)-C(2)-F(1)	-0.7(6)
C(4)-C(3)-C(2)-F(1)	-179.3(3)
F(2)-C(3)-C(2)-C(1)	177.5(3)

C(4)-C(3)-C(2)-C(1)	-1.1(6)
C(6)-C(1)-C(2)-F(1)	179.0(3)
N(3)-C(1)-C(2)-F(1)	-1.4(5)
C(6)-C(1)-C(2)-C(3)	0.7(6)
N(3)-C(1)-C(2)-C(3)	-179.6(4)
C(8)-O(2)-C(7)-O(1)	1.7(7)
C(8)-O(2)-C(7)-C(4)	-178.5(4)
C(5)-C(4)-C(7)-O(1)	25.1(7)
C(3)-C(4)-C(7)-O(1)	-152.0(5)
C(5)-C(4)-C(7)-O(2)	-154.8(4)
C(3)-C(4)-C(7)-O(2)	28.2(6)
C(1)-N(3)-N(2)-N(1)	180(3)
C(7)-O(2)-C(8)-C(9)	174.4(4)
C(10)-O(3)-C(9)-C(8)	170.8(4)
O(2)-C(8)-C(9)-O(3)	-178.6(4)

Table *S5-2-1.* Crystal data and structure refinement for **C3**

Identification code	**C3**
Empirical formula	C19 H11 F4 N3 O4
Formula weight	421.31
Temperature	100(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 5.8306(12) Å alpha = 71.39(3) deg. b = 9.969(2) Å beta = 87.46(3) deg. c = 15.544(3) Å gamma = 86.71(3) deg.
Volume	854.5(3) $Å^3$
Z, Calculated density	2, 1.637 Mg/m^3
Absorption coefficient	0.145 mm^{-1}
F(000)	428
Crystal size	0.33 x0.13 x0.12 mm
Theta range for data collection	2.16 to 27.50 deg.
Limiting indices	-7<=h<=7, -12<=k<=12, -20<=l<=20
Reflections collected / unique	11287 / 3914 [R(int) = 0.0405]
Completeness to theta = 27.50	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.7703
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3914 / 0 / 271
Goodness-of-fit on F^2	1.093
Final R indices [I>2sigma(I)]	R1 = 0.0453, wR2 = 0.1157
R indices (all data)	R1 = 0.0475, wR2 = 0.1176
Largest diff. peak and hole	0.411 and -0.265 e. $Å^{-3}$

Table *S5-2-2.* Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$ x 10^3) for **C3**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
F(1)	8029(1)	5106(1)	5532(1)	21(1)
F(2)	6319(1)	7687(1)	4776(1)	22(1)
F(3)	-423(1)	6595(1)	6606(1)	20(1)
F(4)	1247(1)	3990(1)	7376(1)	23(1)
O(1)	7203(2)	2428(1)	6511(1)	26(1)
O(2)	3714(2)	2397(1)	9844(1)	32(1)
O(3)	5085(2)	2372(1)	7769(1)	24(1)
O(4)	7240(2)	3006(1)	9229(1)	23(1)
N(1)	1723(2)	8541(1)	5277(1)	21(1)
N(2)	2720(2)	9441(1)	4636(1)	20(1)
N(3)	3320(2)	10377(1)	4069(1)	27(1)
C(1)	2863(2)	7214(1)	5655(1)	16(1)
C(2)	5045(2)	6783(1)	5415(1)	17(1)
C(3)	5934(2)	5422(1)	5820(1)	17(1)
C(4)	4746(2)	4421(1)	6502(1)	17(1)
C(5)	2573(2)	4872(1)	6748(1)	17(1)
C(6)	1676(2)	6227(1)	6341(1)	17(1)
C(7)	5819(2)	2966(2)	6915(1)	20(1)
C(8)	6073(3)	952(2)	8238(1)	27(1)
C(9)	8304(3)	1021(2)	8678(1)	26(1)
C(10)	8091(3)	1536(2)	9499(1)	27(1)
C(11)	5011(2)	3275(2)	9390(1)	23(1)
C(12)	4337(2)	4794(2)	8931(1)	21(1)
C(13)	2112(2)	5282(2)	9074(1)	24(1)
C(14)	1406(2)	6675(2)	8632(1)	25(1)
C(15)	2900(2)	7585(2)	8022(1)	22(1)
C(16)	5147(2)	7090(2)	7888(1)	22(1)
C(17)	5854(2)	5704(2)	8340(1)	21(1)

C(18)	2110(2)	8993(2)	7502(1)	25(1)
C(19)	1433(3)	10135(2)	7048(1)	31(1)

Table *S5-2-3.* Bond lengths [Å] and angles [deg] for **C3**

F(1)-C(3)	1.3374(15)
F(2)-C(2)	1.3386(16)
F(3)-C(6)	1.3427(15)
F(4)-C(5)	1.3369(16)
O(1)-C(7)	1.2060(18)
O(2)-C(11)	1.2135(19)
O(3)-C(7)	1.3317(18)
O(3)-C(8)	1.4673(17)
O(4)-C(11)	1.3405(17)
O(4)-C(10)	1.4534(18)
N(1)-N(2)	1.2551(18)
N(1)-C(1)	1.4047(17)
N(2)-N(3)	1.1205(18)
C(1)-C(6)	1.389(2)
C(1)-C(2)	1.3928(18)
C(2)-C(3)	1.3818(19)
C(3)-C(4)	1.392(2)
C(4)-C(5)	1.3977(18)
C(4)-C(7)	1.4983(19)
C(5)-C(6)	1.3788(19)
C(8)-C(9)	1.512(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.518(2)
C(9)-H(9A)	0.9900

C(9)-H(9B)	0.9900
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(12)	1.491(2)
C(12)-C(17)	1.392(2)
C(12)-C(13)	1.393(2)
C(13)-C(14)	1.386(2)
C(13)-H(13)	0.9500
C(14)-C(15)	1.396(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.4037(19)
C(15)-C(18)	1.439(2)
C(16)-C(17)	1.384(2)
C(16)-H(16)	0.9500
C(17)-H(17)	0.9500
C(18)-C(19)	1.187(2)
C(19)-H(19)	0.9500

C(7)-O(3)-C(8)	116.00(12)
C(11)-O(4)-C(10)	118.06(12)
N(2)-N(1)-C(1)	117.73(11)
N(3)-N(2)-N(1)	169.27(14)
C(6)-C(1)-C(2)	116.63(12)
C(6)-C(1)-N(1)	116.20(12)
C(2)-C(1)-N(1)	127.17(13)
F(2)-C(2)-C(3)	118.59(11)
F(2)-C(2)-C(1)	120.13(12)
C(3)-C(2)-C(1)	121.27(13)
F(1)-C(3)-C(2)	116.64(12)

F(1)-C(3)-C(4)	120.93(12)
C(2)-C(3)-C(4)	122.42(12)
C(3)-C(4)-C(5)	115.84(12)
C(3)-C(4)-C(7)	119.60(12)
C(5)-C(4)-C(7)	124.56(13)
F(4)-C(5)-C(6)	116.95(12)
F(4)-C(5)-C(4)	121.16(12)
C(6)-C(5)-C(4)	121.87(13)
F(3)-C(6)-C(5)	119.04(12)
F(3)-C(6)-C(1)	119.02(12)
C(5)-C(6)-C(1)	121.93(12)
O(1)-C(7)-O(3)	125.18(13)
O(1)-C(7)-C(4)	122.85(13)
O(3)-C(7)-C(4)	111.97(12)
O(3)-C(8)-C(9)	111.52(12)
O(3)-C(8)-H(8A)	109.3
C(9)-C(8)-H(8A)	109.3
O(3)-C(8)-H(8B)	109.3
C(9)-C(8)-H(8B)	109.3
H(8A)-C(8)-H(8B)	108.0
C(8)-C(9)-C(10)	115.68(13)
C(8)-C(9)-H(9A)	108.4
C(10)-C(9)-H(9A)	108.4
C(8)-C(9)-H(9B)	108.4
C(10)-C(9)-H(9B)	108.4
H(9A)-C(9)-H(9B)	107.4
O(4)-C(10)-C(9)	110.06(12)
O(4)-C(10)-H(10A)	109.6
C(9)-C(10)-H(10A)	109.6

O(4)-C(10)-H(10B)	109.6
C(9)-C(10)-H(10B)	109.6
H(10A)-C(10)-H(10B)	108.2
O(2)-C(11)-O(4)	124.43(14)
O(2)-C(11)-C(12)	124.56(13)
O(4)-C(11)-C(12)	111.01(13)
C(17)-C(12)-C(13)	120.03(14)
C(17)-C(12)-C(11)	121.18(13)
C(13)-C(12)-C(11)	118.73(13)
C(14)-C(13)-C(12)	120.14(14)
C(14)-C(13)-H(13)	119.9
C(12)-C(13)-H(13)	119.9
C(13)-C(14)-C(15)	120.18(13)
C(13)-C(14)-H(14)	119.9
C(15)-C(14)-H(14)	119.9
C(14)-C(15)-C(16)	119.35(14)
C(14)-C(15)-C(18)	120.35(13)
C(16)-C(15)-C(18)	120.23(14)
C(17)-C(16)-C(15)	120.26(14)
C(17)-C(16)-H(16)	119.9
C(15)-C(16)-H(16)	119.9
C(16)-C(17)-C(12)	120.00(13)
C(16)-C(17)-H(17)	120.0
C(12)-C(17)-H(17)	120.0
C(19)-C(18)-C(15)	177.49(16)
C(18)-C(19)-H(19)	180.0

Table *S5-2-4.* Anisotropic displacement parameters ($Å^2$ x 10^3) for **C3**. The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U11	U22	U33	U23	U13	U12
F(1)	12(1)	26(1)	26(1)	-11(1)	1(1)	3(1)
F(2)	18(1)	21(1)	24(1)	-5(1)	5(1)	-2(1)
F(3)	13(1)	25(1)	23(1)	-9(1)	3(1)	2(1)
F(4)	21(1)	22(1)	22(1)	-2(1)	4(1)	-3(1)
O(1)	28(1)	24(1)	24(1)	-9(1)	-3(1)	9(1)
O(2)	26(1)	34(1)	29(1)	-1(1)	5(1)	-5(1)
O(3)	27(1)	22(1)	19(1)	-3(1)	-3(1)	4(1)
O(4)	20(1)	24(1)	22(1)	-5(1)	-2(1)	0(1)
N(1)	17(1)	19(1)	23(1)	-5(1)	3(1)	2(1)
N(2)	19(1)	18(1)	24(1)	-8(1)	-1(1)	4(1)
N(3)	28(1)	20(1)	29(1)	-3(1)	3(1)	2(1)
C(1)	15(1)	18(1)	18(1)	-8(1)	-2(1)	0(1)
C(2)	14(1)	20(1)	17(1)	-7(1)	2(1)	-2(1)
C(3)	11(1)	24(1)	19(1)	-12(1)	-1(1)	2(1)
C(4)	16(1)	20(1)	18(1)	-9(1)	-4(1)	2(1)
C(5)	17(1)	20(1)	15(1)	-6(1)	-1(1)	-2(1)
C(6)	12(1)	22(1)	19(1)	-10(1)	0(1)	1(1)
C(7)	20(1)	20(1)	21(1)	-7(1)	-6(1)	3(1)
C(8)	31(1)	20(1)	26(1)	-1(1)	-4(1)	2(1)
C(9)	25(1)	22(1)	26(1)	-1(1)	-2(1)	4(1)
C(10)	28(1)	24(1)	22(1)	0(1)	-6(1)	2(1)
C(11)	21(1)	31(1)	17(1)	-8(1)	-1(1)	-2(1)
C(12)	19(1)	27(1)	17(1)	-9(1)	-1(1)	-1(1)
C(13)	19(1)	31(1)	24(1)	-12(1)	5(1)	-4(1)
C(14)	17(1)	34(1)	28(1)	-16(1)	1(1)	0(1)
C(15)	19(1)	28(1)	22(1)	-14(1)	-3(1)	2(1)

C(16)	18(1)	27(1)	22(1)	-8(1)	1(1)	-1(1)
C(17)	16(1)	28(1)	20(1)	-8(1)	-1(1)	0(1)
C(18)	18(1)	32(1)	30(1)	-17(1)	-2(1)	3(1)
C(19)	24(1)	33(1)	36(1)	-14(1)	-1(1)	6(1)

Table *S5-2-5.* Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **C3**.

	x	y	z	U(eq)
H(8A)	6353	427	7797	32
H(8B)	4962	428	8708	32
H(9A)	9320	1655	8217	31
H(9B)	9068	63	8865	31
H(10A)	7023	943	9957	32
H(10B)	9611	1449	9776	32
H(13)	1076	4658	9475	29
H(14)	-98	7011	8744	30
H(16)	6186	7710	7486	27
H(17)	7375	5372	8246	25
H(19)	891	11048	6684	37

Table *S5-2-6.* Torsion angles [deg] for **C3**

C(1)-N(1)-N(2)-N(3)	-179(100)
N(2)-N(1)-C(1)-C(6)	-177.84(12)
N(2)-N(1)-C(1)-C(2)	2.0(2)
C(6)-C(1)-C(2)-F(2)	-178.22(11)
N(1)-C(1)-C(2)-F(2)	1.9(2)
C(6)-C(1)-C(2)-C(3)	2.34(19)
N(1)-C(1)-C(2)-C(3)	-177.52(12)
F(2)-C(2)-C(3)-F(1)	-0.46(18)
C(1)-C(2)-C(3)-F(1)	178.98(11)
F(2)-C(2)-C(3)-C(4)	178.77(11)

C(1)-C(2)-C(3)-C(4)	-1.8(2)
F(1)-C(3)-C(4)-C(5)	179.91(11)
C(2)-C(3)-C(4)-C(5)	0.72(19)
F(1)-C(3)-C(4)-C(7)	-0.44(18)
C(2)-C(3)-C(4)-C(7)	-179.64(12)
C(3)-C(4)-C(5)-F(4)	178.02(11)
C(7)-C(4)-C(5)-F(4)	-1.6(2)
C(3)-C(4)-C(5)-C(6)	-0.36(19)
C(7)-C(4)-C(5)-C(6)	-179.98(12)
F(4)-C(5)-C(6)-F(3)	1.41(18)
C(4)-C(5)-C(6)-F(3)	179.84(11)
F(4)-C(5)-C(6)-C(1)	-177.37(11)
C(4)-C(5)-C(6)-C(1)	1.1(2)
C(2)-C(1)-C(6)-F(3)	179.22(11)
N(1)-C(1)-C(6)-F(3)	-0.90(18)
C(2)-C(1)-C(6)-C(5)	-2.00(19)
N(1)-C(1)-C(6)-C(5)	177.88(12)
C(8)-O(3)-C(7)-O(1)	0.1(2)
C(8)-O(3)-C(7)-C(4)	-178.97(11)
C(3)-C(4)-C(7)-O(1)	-27.4(2)
C(5)-C(4)-C(7)-O(1)	152.19(14)
C(3)-C(4)-C(7)-O(3)	151.70(12)
C(5)-C(4)-C(7)-O(3)	-28.69(18)
C(7)-O(3)-C(8)-C(9)	86.75(15)
O(3)-C(8)-C(9)-C(10)	70.43(17)
C(11)-O(4)-C(10)-C(9)	101.11(15)
C(8)-C(9)-C(10)-O(4)	-65.20(16)
C(10)-O(4)-C(11)-O(2)	9.5(2)
C(10)-O(4)-C(11)-C(12)	-170.02(11)
O(2)-C(11)-C(12)-C(17)	-172.78(14)
O(4)-C(11)-C(12)-C(17)	6.79(19)
O(2)-C(11)-C(12)-C(13)	4.6(2)
O(4)-C(11)-C(12)-C(13)	-175.85(12)

C(17)-C(12)-C(13)-C(14)	-0.3(2)
C(11)-C(12)-C(13)-C(14)	-177.70(13)
C(12)-C(13)-C(14)-C(15)	1.8(2)
C(13)-C(14)-C(15)-C(16)	-2.4(2)
C(13)-C(14)-C(15)-C(18)	174.45(13)
C(14)-C(15)-C(16)-C(17)	1.6(2)
C(18)-C(15)-C(16)-C(17)	-175.26(13)
C(15)-C(16)-C(17)-C(12)	-0.1(2)
C(13)-C(12)-C(17)-C(16)	-0.5(2)
C(11)-C(12)-C(17)-C(16)	176.83(13)
C(14)-C(15)-C(18)-C(19)	-88(4)
C(16)-C(15)-C(18)-C(19)	88(4)

Table *S5-8-1.* Crystal data and structure refinement for **C4**

Identification code	**C4**
Empirical formula	C20 H13 F4 N3 O4
Formula weight	435.33
Temperature	100(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 7.5088(15) A alpha = 112.78(3) deg.
	b = 10.929(2) A beta = 93.81(3) deg.
	c = 12.823(3) A gamma = 105.56(3) deg.
Volume	917.3(3) A^3
Z, Calculated density	2, 1.576 Mg/m^3
Absorption coefficient	0.138 mm^-1
F(000)	444
Crystal size	0.24 x 0.14 x 0.09 mm
Theta range for data collection	1.75 to 27.48 deg.
Limiting indices	-9<=h<=9, -14<=k<=14, -16<=l<=16
Reflections collected / unique	8119 / 4156 [R(int) = 0.0399]
Completeness to theta = 27.48	98.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.6406
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4156 / 0 / 280
Goodness-of-fit on F^2	1.085
Final R indices [I>2sigma(I)]	R1 = 0.0523, wR2 = 0.1245
R indices (all data)	R1 = 0.0575, wR2 = 0.1291
Largest diff. peak and hole	0.370 and -0.281 e. $Å^{-3}$

Table *S5-3-2.* Atomic coordinates ($x10^4$) and equivalent isotropic displacement parameters ($Å^2x10^3$) for **C4**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
F(1)	1882(1)	8613(1)	8325(1)	24(1)
F(2)	2011(1)	6265(1)	8384(1)	24(1)
F(3)	-2756(2)	3719(1)	5002(1)	27(1)
F(4)	-2841(2)	6099(1)	4962(1)	27(1)
O(1)	4498(2)	2569(1)	12539(1)	26(1)
O(2)	2964(2)	1066(1)	10737(1)	20(1)
O(3)	235(2)	3636(1)	7740(1)	20(1)
O(4)	-797(2)	2406(1)	5825(1)	26(1)
N(1)	-379(2)	8768(2)	6711(1)	23(1)
N(2)	-1241(2)	8829(2)	5865(1)	22(1)
N(3)	-1903(2)	9110(2)	5215(1)	30(1)
C(1)	-447(2)	7435(2)	6629(1)	18(1)
C(2)	745(2)	7401(2)	7489(1)	18(1)
C(3)	781(2)	6155(2)	7514(1)	18(1)
C(4)	-368(2)	4861(2)	6687(1)	18(1)
C(5)	-1569(2)	4900(2)	5828(1)	19(1)
C(6)	-1617(2)	6147(2)	5804(1)	20(1)
C(7)	-350(2)	3487(2)	6679(1)	19(1)
C(8)	483(2)	2406(2)	7840(1)	19(1)
C(9)	1402(2)	2906(2)	9084(1)	20(1)
C(10)	1657(2)	1689(2)	9330(1)	19(1)
C(11)	2752(2)	2250(2)	10540(1)	20(1)
C(12)	3897(2)	1392(2)	11789(1)	18(1)
C(13)	4081(2)	127(2)	11923(1)	19(1)
C(14)	3488(2)	-1201(2)	11009(1)	19(1)
C(15)	3675(2)	-2344(2)	11184(1)	19(1)
C(16)	4464(2)	-2168(2)	12275(1)	19(1)
C(17)	5064(2)	-826(2)	13188(2)	22(1)
C(18)	4884(2)	315(2)	13011(2)	21(1)
C(19)	4669(2)	-3347(2)	12462(1)	21(1)

C(20)	4871(2)	-4313(2)	12619(2)	24(1)

Table *S5-3-3.* Bond lengths [Å] and angles [deg] for **C4**

F(1)-C(2)	1.3431(19)
F(2)-C(3)	1.3456(17)
F(3)-C(5)	1.334(2)
F(4)-C(6)	1.3463(17)
O(1)-C(12)	1.207(2)
O(2)-C(12)	1.3439(19)
O(2)-C(11)	1.4562(17)
O(3)-C(7)	1.3347(19)
O(3)-C(8)	1.4571(18)
O(4)-C(7)	1.202(2)
N(1)-N(2)	1.2591(19)
N(1)-C(1)	1.406(2)
N(2)-N(3)	1.123(2)
C(1)-C(6)	1.390(2)
C(1)-C(2)	1.392(2)
C(2)-C(3)	1.382(2)
C(3)-C(4)	1.390(2)
C(4)-C(5)	1.397(2)
C(4)-C(7)	1.501(2)
C(5)-C(6)	1.385(2)
C(8)-C(9)	1.516(2)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.536(2)
C(9)-H(9B)	0.9900
C(9)-H(9A)	0.9900
C(10)-C(11)	1.511(2)
C(10)-H(10B)	0.9900

C(10)-H(10A)	0.9900
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.497(2)
C(13)-C(14)	1.394(2)
C(13)-C(18)	1.397(2)
C(14)-C(15)	1.392(2)
C(14)-H(14)	0.9500
C(15)-C(16)	1.403(2)
C(15)-H(15)	0.9500
C(16)-C(17)	1.403(2)
C(16)-C(19)	1.443(2)
C(17)-C(18)	1.390(2)
C(17)-H(17)	0.9500
C(18)-H(18)	0.9500
C(19)-C(20)	1.194(2)
C(20)-H(20)	0.9500

C(12)-O(2)-C(11)	115.22(13)
C(7)-O(3)-C(8)	116.51(13)
N(2)-N(1)-C(1)	117.54(14)
N(3)-N(2)-N(1)	168.82(17)
C(6)-C(1)-C(2)	116.29(14)
C(6)-C(1)-N(1)	127.20(14)
C(2)-C(1)-N(1)	116.47(15)
F(1)-C(2)-C(3)	118.97(13)
F(1)-C(2)-C(1)	119.14(14)
C(3)-C(2)-C(1)	121.89(15)
F(2)-C(3)-C(2)	116.04(14)
F(2)-C(3)-C(4)	121.71(14)
C(2)-C(3)-C(4)	122.24(14)
C(3)-C(4)-C(5)	115.71(14)
C(3)-C(4)-C(7)	123.70(14)

C(5)-C(4)-C(7)	120.58(14)
F(3)-C(5)-C(6)	117.11(14)
F(3)-C(5)-C(4)	120.71(14)
C(6)-C(5)-C(4)	122.17(15)
F(4)-C(6)-C(5)	118.66(15)
F(4)-C(6)-C(1)	119.66(14)
C(5)-C(6)-C(1)	121.68(14)
O(4)-C(7)-O(3)	125.05(15)
O(4)-C(7)-C(4)	124.03(14)
O(3)-C(7)-C(4)	110.92(14)
O(3)-C(8)-C(9)	105.69(13)
O(3)-C(8)-H(8A)	110.6
C(9)-C(8)-H(8A)	110.6
O(3)-C(8)-H(8B)	110.6
C(9)-C(8)-H(8B)	110.6
H(8A)-C(8)-H(8B)	108.7
C(8)-C(9)-C(10)	111.32(14)
C(8)-C(9)-H(9B)	109.4
C(10)-C(9)-H(9B)	109.4
C(8)-C(9)-H(9A)	109.4
C(10)-C(9)-H(9A)	109.4
H(9B)-C(9)-H(9A)	108.0
C(11)-C(10)-C(9)	109.68(13)
C(11)-C(10)-H(10B)	109.7
C(9)-C(10)-H(10B)	109.7
C(11)-C(10)-H(10A)	109.7
C(9)-C(10)-H(10A)	109.7
H(10B)-C(10)-H(10A)	108.2
O(2)-C(11)-C(10)	107.89(13)
O(2)-C(11)-H(11A)	110.1
C(10)-C(11)-H(11A)	110.1
O(2)-C(11)-H(11B)	110.1
C(10)-C(11)-H(11B)	110.1

H(11A)-C(11)-H(11B)	108.4
O(1)-C(12)-O(2)	123.58(14)
O(1)-C(12)-C(13)	124.21(14)
O(2)-C(12)-C(13)	112.21(14)
C(14)-C(13)-C(18)	120.10(14)
C(14)-C(13)-C(12)	122.35(14)
C(18)-C(13)-C(12)	117.55(15)
C(15)-C(14)-C(13)	120.00(14)
C(15)-C(14)-H(14)	120.0
C(13)-C(14)-H(14)	120.0
C(14)-C(15)-C(16)	120.31(15)
C(14)-C(15)-H(15)	119.8
C(16)-C(15)-H(15)	119.8
C(15)-C(16)-C(17)	119.24(14)
C(15)-C(16)-C(19)	120.65(15)
C(17)-C(16)-C(19)	120.11(14)
C(18)-C(17)-C(16)	120.39(15)
C(18)-C(17)-H(17)	119.8
C(16)-C(17)-H(17)	119.8
C(17)-C(18)-C(13)	119.95(15)
C(17)-C(18)-H(18)	120.0
C(13)-C(18)-H(18)	120.0
C(20)-C(19)-C(16)	178.93(18)
C(19)-C(20)-H(20)	180.0

Table *S5-3-4.* Anisotropic displacement parameters ($Å^2$ x 10^3) for **C4.** The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U11	U22	U33	U23	U13	U12
F(1)	30(1)	16(1)	20(1)	6(1)	-5(1)	5(1)
F(2)	29(1)	22(1)	21(1)	11(1)	-7(1)	8(1)
F(3)	34(1)	17(1)	21(1)	6(1)	-9(1)	4(1)

F(4)	34(1)	25(1)	22(1)	12(1)	-10(1)	9(1)
O(1)	34(1)	18(1)	22(1)	8(1)	-4(1)	8(1)
O(2)	27(1)	17(1)	19(1)	11(1)	-1(1)	8(1)
O(3)	28(1)	18(1)	17(1)	10(1)	1(1)	9(1)
O(4)	41(1)	19(1)	19(1)	8(1)	2(1)	12(1)
N(1)	32(1)	19(1)	19(1)	10(1)	-3(1)	10(1)
N(2)	29(1)	19(1)	19(1)	8(1)	1(1)	11(1)
N(3)	43(1)	27(1)	26(1)	14(1)	1(1)	18(1)
C(1)	23(1)	18(1)	17(1)	10(1)	4(1)	9(1)
C(2)	21(1)	16(1)	16(1)	6(1)	-1(1)	4(1)
C(3)	21(1)	22(1)	14(1)	10(1)	1(1)	9(1)
C(4)	22(1)	17(1)	17(1)	9(1)	3(1)	7(1)
C(5)	24(1)	17(1)	15(1)	6(1)	0(1)	6(1)
C(6)	23(1)	23(1)	16(1)	10(1)	-1(1)	9(1)
C(7)	22(1)	19(1)	18(1)	10(1)	3(1)	8(1)
C(8)	23(1)	17(1)	22(1)	12(1)	2(1)	8(1)
C(9)	24(1)	19(1)	19(1)	10(1)	0(1)	8(1)
C(10)	21(1)	18(1)	20(1)	11(1)	0(1)	7(1)
C(11)	25(1)	17(1)	22(1)	13(1)	3(1)	10(1)
C(12)	20(1)	20(1)	18(1)	10(1)	2(1)	7(1)
C(13)	19(1)	20(1)	21(1)	12(1)	3(1)	7(1)
C(14)	19(1)	23(1)	17(1)	10(1)	2(1)	8(1)
C(15)	21(1)	19(1)	18(1)	8(1)	3(1)	7(1)
C(16)	18(1)	21(1)	23(1)	13(1)	3(1)	8(1)
C(17)	25(1)	23(1)	19(1)	11(1)	-1(1)	9(1)
C(18)	25(1)	20(1)	20(1)	10(1)	-1(1)	7(1)
C(19)	21(1)	22(1)	20(1)	11(1)	2(1)	7(1)
C(20)	27(1)	22(1)	24(1)	12(1)	1(1)	9(1)

Table *S5-3-5.* Hydrogen coordinates (x 10^4) and isotropic displacement parameters (Å^2 x 10^3) for **C4**.

	x	y	z	U(eq)
H(8A)	1297	2020	7313	23
H(8B)	-749	1669	7648	23
H(9B)	612	3351	9598	24
H(9A)	2646	3620	9252	24
H(10B)	409	1022	9245	23
H(10A)	2342	1184	8770	23
H(11A)	4004	2915	10630	23
H(11B)	2068	2749	11106	23
H(14)	2957	-1325	10267	22
H(15)	3266	-3248	10560	23
H(17)	5597	-697	13930	26
H(18)	5306	1223	13630	26
H(20)	5031	-5083	12744	28

Table *S5-3-6.* Torsion angles [deg] for **C4**.

C(1)-N(1)-N(2)-N(3)	-179.2(9)
N(2)-N(1)-C(1)-C(6)	-11.9(3)
N(2)-N(1)-C(1)-C(2)	170.36(15)
C(6)-C(1)-C(2)-F(1)	-178.62(15)
N(1)-C(1)-C(2)-F(1)	-0.6(2)
C(6)-C(1)-C(2)-C(3)	0.8(2)
N(1)-C(1)-C(2)-C(3)	178.76(16)
F(1)-C(2)-C(3)-F(2)	-1.4(2)
C(1)-C(2)-C(3)-F(2)	179.25(14)
F(1)-C(2)-C(3)-C(4)	179.33(15)
C(1)-C(2)-C(3)-C(4)	-0.1(3)

F(2)-C(3)-C(4)-C(5)	-179.51(14)
C(2)-C(3)-C(4)-C(5)	-0.2(2)
F(2)-C(3)-C(4)-C(7)	-0.1(3)
C(2)-C(3)-C(4)-C(7)	179.21(15)
C(3)-C(4)-C(5)-F(3)	-178.77(15)
C(7)-C(4)-C(5)-F(3)	1.8(2)
C(3)-C(4)-C(5)-C(6)	-0.2(2)
C(7)-C(4)-C(5)-C(6)	-179.67(16)
F(3)-C(5)-C(6)-F(4)	0.0(2)
C(4)-C(5)-C(6)-F(4)	-178.62(15)
F(3)-C(5)-C(6)-C(1)	179.58(15)
C(4)-C(5)-C(6)-C(1)	1.0(3)
C(2)-C(1)-C(6)-F(4)	178.37(14)
N(1)-C(1)-C(6)-F(4)	0.6(3)
C(2)-C(1)-C(6)-C(5)	-1.2(3)
N(1)-C(1)-C(6)-C(5)	-178.94(16)
C(8)-O(3)-C(7)-O(4)	5.1(2)
C(8)-O(3)-C(7)-C(4)	-174.59(12)
C(3)-C(4)-C(7)-O(4)	-153.64(18)
C(5)-C(4)-C(7)-O(4)	25.8(3)
C(3)-C(4)-C(7)-O(3)	26.1(2)
C(5)-C(4)-C(7)-O(3)	-154.52(15)
C(7)-O(3)-C(8)-C(9)	172.21(14)
O(3)-C(8)-C(9)-C(10)	177.07(13)
C(8)-C(9)-C(10)-C(11)	174.28(14)
C(12)-O(2)-C(11)-C(10)	-179.27(13)
C(9)-C(10)-C(11)-O(2)	-179.89(13)
C(11)-O(2)-C(12)-O(1)	1.3(2)
C(11)-O(2)-C(12)-C(13)	-179.30(13)
O(1)-C(12)-C(13)-C(14)	-175.19(17)
O(2)-C(12)-C(13)-C(14)	5.5(2)
O(1)-C(12)-C(13)-C(18)	4.7(3)
O(2)-C(12)-C(13)-C(18)	-174.69(14)

C(18)-C(13)-C(14)-C(15)	0.8(2)
C(12)-C(13)-C(14)-C(15)	-179.37(15)
C(13)-C(14)-C(15)-C(16)	-0.2(2)
C(14)-C(15)-C(16)-C(17)	-0.1(2)
C(14)-C(15)-C(16)-C(19)	-179.74(15)
C(15)-C(16)-C(17)-C(18)	-0.2(3)
C(19)-C(16)-C(17)-C(18)	179.49(16)
C(16)-C(17)-C(18)-C(13)	0.7(3)
C(14)-C(13)-C(18)-C(17)	-1.0(3)
C(12)-C(13)-C(18)-C(17)	179.11(15)
C(15)-C(16)-C(19)-C(20)	110(10)
C(17)-C(16)-C(19)-C(20)	-70(10)

Table *S5-4-1.* Crystal data and structure refinement for **C6**

Identification code	**C6**
Empirical formula	C22 H17 F4 N3 O4
Formula weight	463.39
Temperature	173(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 5.653(4) Å alpha = 93.602(15) deg. b = 9.661(8) Å beta = 91.807(14) deg. c = 18.613(14) Å gamma = 96.604(14) deg.
Volume	1006.9(13) $Å^3$
Z, Calculated density	2, 1.528 Mg/m^3
Absorption coefficient	0.131 mm^{-1}
F(000)	476
Crystal size	0.52 x 0.28 x 0.07 mm
Theta range for data collection	2.95 to 27.53 deg.
Limiting indices	-7<=h<=7, -12<=k<=12, -24<=l<=24
Reflections collected / unique	13144 / 4589 [R (int) = 0.0466]
Completeness to theta = 27.53	98.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	1.0000 and 0.5864
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4589 / 0 / 298
Goodness-of-fit on F^2	1.142
Final R indices [I>2sigma(I)]	R1 = 0.0697, wR2 = 0.1598
R indices (all data)	R1 = 0.0825, wR2 = 0.1685
Largest diff. peak and hole	0.320 and -0.232 e. $Å^{-3}$

Table *S5-4-2.* Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (Å^2 x 10^3) for **C6**. U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
F(1)	-9242(2)	337(2)	1722(1)	53(1)
F(2)	-6760(2)	-402(1)	2813(1)	50(1)
F(3)	-550(2)	3141(1)	2375(1)	44(1)
F(4)	-3051(2)	3813(1)	1261(1)	46(1)
O(1)	-2680(4)	-233(2)	3543(1)	70(1)
O(2)	-344(3)	1776(2)	3529(1)	43(1)
O(3)	10988(3)	3500(2)	6782(1)	44(1)
O(4)	14088(3)	5145(2)	6714(1)	53(1)
N(1)	-7782(4)	2351(2)	897(1)	57(1)
N(2)	-7266(4)	3323(2)	498(1)	50(1)
N(3)	-7215(5)	4112(3)	82(1)	67(1)
C(1)	-6229(4)	2089(2)	1456(1)	41(1)
C(2)	-7070(4)	1024(2)	1875(1)	40(1)
C(3)	-5758(4)	643(2)	2456(1)	39(1)
C(4)	-3519(4)	1337(2)	2659(1)	36(1)
C(5)	-2696(4)	2410(2)	2236(1)	35(1)
C(6)	-3973(4)	2781(2)	1650(1)	36(1)
C(7)	-2168(4)	867(2)	3290(1)	41(1)
C(8)	1014(4)	1353(2)	4140(1)	41(1)
C(9)	2931(4)	2520(2)	4367(1)	41(1)
C(10)	4495(4)	2114(2)	4985(1)	41(1)
C(11)	6430(4)	3267(2)	5255(1)	40(1)
C(12)	7906(4)	2856(2)	5890(1)	40(1)
C(13)	9785(4)	4001(2)	6165(1)	44(1)
C(14)	13115(4)	4167(2)	6999(1)	39(1)
C(15)	14117(4)	3541(2)	7640(1)	37(1)
C(16)	12836(4)	2462(2)	7966(1)	38(1)
C(17)	13788(4)	1930(2)	8564(1)	42(1)

C(18)	16071(4)	2447(2)	8840(1)	41(1)
C(19)	17358(4)	3524(2)	8505(1)	43(1)
C(20)	16383(4)	4067(2)	7912(1)	42(1)
C(21)	17043(4)	1848(3)	9456(1)	48(1)
C(22)	17724(5)	1288(3)	9960(2)	60(1)

Table *S5-4-3.* Bond lengths [Å] and angles [deg] for **C6**.

F(1)-C(2)	1.340(3)
F(2)-C(3)	1.326(3)
F(3)-C(5)	1.341(2)
F(4)-C(6)	1.336(2)
O(1)-C(7)	1.198(3)
O(2)-C(7)	1.322(3)
O(2)-C(8)	1.458(3)
O(3)-C(14)	1.335(3)
O(3)-C(13)	1.453(3)
O(4)-C(14)	1.199(3)
N(1)-N(2)	1.248(3)
N(1)-C(1)	1.395(3)
N(2)-N(3)	1.119(3)
C(1)-C(2)	1.380(3)
C(1)-C(6)	1.395(3)
C(2)-C(3)	1.384(3)
C(3)-C(4)	1.392(3)
C(4)-C(5)	1.387(3)
C(4)-C(7)	1.503(3)
C(5)-C(6)	1.378(3)
C(8)-C(9)	1.501(3)
C(8)-H(8A)	0.9900
C(8)-H(8B)	0.9900
C(9)-C(10)	1.528(3)

C(9)-H(9A)	0.9900
C(9)-H(9B)	0.9900
C(10)-C(11)	1.517(3)
C(10)-H(10A)	0.9900
C(10)-H(10B)	0.9900
C(11)-C(12)	1.525(3)
C(11)-H(11A)	0.9900
C(11)-H(11B)	0.9900
C(12)-C(13)	1.496(3)
C(12)-H(12A)	0.9900
C(12)-H(12B)	0.9900
C(13)-H(13A)	0.9900
C(13)-H(13B)	0.9900
C(14)-C(15)	1.494(3)
C(15)-C(16)	1.384(3)
C(15)-C(20)	1.390(3)
C(16)-C(17)	1.375(3)
C(16)-H(16)	0.9500
C(17)-C(18)	1.399(3)
C(17)-H(17)	0.9500
C(18)-C(19)	1.391(3)
C(18)-C(21)	1.437(3)
C(19)-C(20)	1.378(3)
C(19)-H(19)	0.9500
C(20)-H(20)	0.9500
C(21)-C(22)	1.187(4)
C(22)-H(22)	0.9500
C(7)-O(2)-C(8)	114.86(17)
C(14)-O(3)-C(13)	117.66(17)
N(2)-N(1)-C(1)	121.2(2)
N(3)-N(2)-N(1)	166.9(3)
C(2)-C(1)-N(1)	115.1(2)
C(2)-C(1)-C(6)	116.6(2)

N(1)-C(1)-C(6)	128.3(2)
F(1)-C(2)-C(1)	119.2(2)
F(1)-C(2)-C(3)	118.5(2)
C(1)-C(2)-C(3)	122.3(2)
F(2)-C(3)-C(2)	116.51(19)
F(2)-C(3)-C(4)	121.9(2)
C(2)-C(3)-C(4)	121.6(2)
C(5)-C(4)-C(3)	115.6(2)
C(5)-C(4)-C(7)	125.24(19)
C(3)-C(4)-C(7)	119.17(19)
F(3)-C(5)-C(6)	115.80(18)
F(3)-C(5)-C(4)	120.93(19)
C(6)-C(5)-C(4)	123.26(19)
F(4)-C(6)-C(5)	119.92(18)
F(4)-C(6)-C(1)	119.40(19)
C(5)-C(6)-C(1)	120.7(2)
O(1)-C(7)-O(2)	123.5(2)
O(1)-C(7)-C(4)	123.1(2)
O(2)-C(7)-C(4)	113.32(18)
O(2)-C(8)-C(9)	108.22(17)
O(2)-C(8)-H(8A)	110.1
C(9)-C(8)-H(8A)	110.1
O(2)-C(8)-H(8B)	110.1
C(9)-C(8)-H(8B)	110.1
H(8A)-C(8)-H(8B)	108.4
C(8)-C(9)-C(10)	110.78(18)
C(8)-C(9)-H(9A)	109.5
C(10)-C(9)-H(9A)	109.5
C(8)-C(9)-H(9B)	109.5
C(10)-C(9)-H(9B)	109.5
H(9A)-C(9)-H(9B)	108.1
C(11)-C(10)-C(9)	113.43(18)
C(11)-C(10)-H(10A)	108.9

C(9)-C(10)-H(10A) 108.9
C(11)-C(10)-H(10B) 108.9
C(9)-C(10)-H(10B) 108.9
H(10A)-C(10)-H(10B) 107.7
C(10)-C(11)-C(12) 112.43(18)
C(10)-C(11)-H(11A) 109.1
C(12)-C(11)-H(11A) 109.1
C(10)-C(11)-H(11B) 109.1
C(12)-C(11)-H(11B) 109.1
H(11A)-C(11)-H(11B) 107.8
C(13)-C(12)-C(11) 112.49(18)
C(13)-C(12)-H(12A) 109.1
C(11)-C(12)-H(12A) 109.1
C(13)-C(12)-H(12B) 109.1
C(11)-C(12)-H(12B) 109.1
H(12A)-C(12)-H(12B) 107.8
O(3)-C(13)-C(12) 106.95(18)
O(3)-C(13)-H(13A) 110.3
C(12)-C(13)-H(13A) 110.3
O(3)-C(13)-H(13B) 110.3
C(12)-C(13)-H(13B) 110.3
H(13A)-C(13)-H(13B) 108.6
O(4)-C(14)-O(3) 124.0(2)
O(4)-C(14)-C(15) 124.6(2)
O(3)-C(14)-C(15) 111.45(18)
C(16)-C(15)-C(20) 119.6(2)
C(16)-C(15)-C(14) 121.5(2)
C(20)-C(15)-C(14) 118.9(2)
C(17)-C(16)-C(15) 120.1(2)
C(17)-C(16)-H(16) 120.0
C(15)-C(16)-H(16) 120.0
C(16)-C(17)-C(18) 120.7(2)
C(16)-C(17)-H(17) 119.6

C(18)-C(17)-H(17)	119.6
C(19)-C(18)-C(17)	118.9(2)
C(19)-C(18)-C(21)	121.6(2)
C(17)-C(18)-C(21)	119.5(2)
C(20)-C(19)-C(18)	120.1(2)
C(20)-C(19)-H(19)	119.9
C(18)-C(19)-H(19)	119.9
C(19)-C(20)-C(15)	120.5(2)
C(19)-C(20)-H(20)	119.7
C(15)-C(20)-H(20)	119.7
C(22)-C(21)-C(18)	175.8(3)
C(21)-C(22)-H(22)	180.0

Table *S5-4-4.* Anisotropic displacement parameters ($Å^2$ x 10^3) for **C6.** The anisotropic displacement factor exponent takes the form: $-2\ pi^2\ [h^2\ a^{*2}U^{11} + ... + 2\ h\ k\ a^*\ b^*\ U^{12}]$

	U11	U22	U33	U23	U13	U12
F(1)	33(1)	54(1)	68(1)	4(1)	-3(1)	-10(1)
F(2)	47(1)	44(1)	57(1)	10(1)	9(1)	-9(1)
F(3)	37(1)	44(1)	47(1)	9(1)	-3(1)	-11(1)
F(4)	47(1)	41(1)	49(1)	13(1)	-1(1)	-4(1)
O(1)	82(1)	57(1)	64(1)	27(1)	-20(1)	-27(1)
O(2)	47(1)	36(1)	45(1)	10(1)	-8(1)	-4(1)
O(3)	41(1)	43(1)	48(1)	15(1)	-5(1)	-1(1)
O(4)	51(1)	45(1)	61(1)	17(1)	4(1)	-6(1)
N(1)	47(1)	59(1)	63(1)	14(1)	-13(1)	-5(1)
N(2)	48(1)	51(1)	49(1)	0(1)	-8(1)	4(1)
N(3)	74(2)	67(2)	60(1)	16(1)	-12(1)	3(1)
C(1)	38(1)	40(1)	45(1)	0(1)	0(1)	3(1)
C(2)	30(1)	39(1)	50(1)	-1(1)	4(1)	-4(1)
C(3)	36(1)	35(1)	45(1)	-2(1)	9(1)	-3(1)

C(4)	37(1)	31(1)	38(1)	-2(1)	5(1)	-1(1)
C(5)	32(1)	32(1)	39(1)	-2(1)	2(1)	-1(1)
C(6)	36(1)	32(1)	39(1)	4(1)	3(1)	-1(1)
C(7)	43(1)	40(1)	37(1)	5(1)	3(1)	-2(1)
C(8)	49(1)	33(1)	40(1)	9(1)	-2(1)	2(1)
C(9)	49(1)	32(1)	41(1)	10(1)	-3(1)	1(1)
C(10)	46(1)	35(1)	43(1)	12(1)	-1(1)	4(1)
C(11)	46(1)	33(1)	42(1)	9(1)	-2(1)	2(1)
C(12)	47(1)	34(1)	41(1)	10(1)	0(1)	7(1)
C(13)	47(1)	40(1)	45(1)	13(1)	-4(1)	4(1)
C(14)	38(1)	34(1)	43(1)	2(1)	6(1)	5(1)
C(15)	36(1)	34(1)	40(1)	-1(1)	4(1)	3(1)
C(16)	33(1)	36(1)	45(1)	1(1)	-2(1)	-1(1)
C(17)	39(1)	40(1)	45(1)	4(1)	-2(1)	-3(1)
C(18)	39(1)	45(1)	40(1)	-3(1)	2(1)	7(1)
C(19)	32(1)	48(1)	48(1)	-5(1)	0(1)	2(1)
C(20)	35(1)	40(1)	49(1)	0(1)	6(1)	-1(1)
C(21)	40(1)	54(1)	47(1)	-2(1)	-5(1)	1(1)
C(22)	52(2)	69(2)	56(2)	8(1)	-16(1)	1(1)

Table *S5-4-5.* Hydrogen coordinates ($x10^4$) and isotropic displacement parameters ($Å^2 \times 10^3$) for **C6**.

	x	y	z	U(eq)
H(8A)	1734	494	4001	49
H(8B)	-48	1159	4543	49
H(9A)	2192	3366	4521	49
H(9B)	3928	2744	3952	49
H(10A)	3474	1857	5390	49
H(10B)	5250	1280	4822	49
H(11A)	5685	4113	5402	48
H(11B)	7495	3499	4857	48

H(12A)	6836	2606	6284	48
H(12B)	8676	2020	5739	48
H(13A)	10932	4227	5786	53
H(13B)	9052	4854	6310	53
H(16)	11298	2089	7777	46
H(17)	12885	1204	8793	50
H(19)	18911	3886	8686	52
H(20)	17266	4806	7688	50
H(22)	18268	840	10363	72

Table *S5-4-6.* Torsion angles [deg] for **C6**.

C(1)-N(1)-N(2)-N(3)	-178.6(11)
N(2)-N(1)-C(1)-C(2)	177.2(2)
N(2)-N(1)-C(1)-C(6)	-1.6(4)
N(1)-C(1)-C(2)-F(1)	0.1(3)
C(6)-C(1)-C(2)-F(1)	178.98(19)
N(1)-C(1)-C(2)-C(3)	-179.4(2)
C(6)-C(1)-C(2)-C(3)	-0.5(3)
F(1)-C(2)-C(3)-F(2)	0.9(3)
C(1)-C(2)-C(3)-F(2)	-179.7(2)
F(1)-C(2)-C(3)-C(4)	-178.13(19)
C(1)-C(2)-C(3)-C(4)	1.3(4)
F(2)-C(3)-C(4)-C(5)	-179.91(19)
C(2)-C(3)-C(4)-C(5)	-1.0(3)
F(2)-C(3)-C(4)-C(7)	1.7(3)
C(2)-C(3)-C(4)-C(7)	-179.40(19)
C(3)-C(4)-C(5)-F(3)	-179.14(18)
C(7)-C(4)-C(5)-F(3)	-0.8(3)
C(3)-C(4)-C(5)-C(6)	-0.2(3)
C(7)-C(4)-C(5)-C(6)	178.2(2)
F(3)-C(5)-C(6)-F(4)	0.0(3)

C(4)-C(5)-C(6)-F(4)	-179.02(19)
F(3)-C(5)-C(6)-C(1)	-179.99(19)
C(4)-C(5)-C(6)-C(1)	1.0(3)
C(2)-C(1)-C(6)-F(4)	179.36(19)
N(1)-C(1)-C(6)-F(4)	-1.9(4)
C(2)-C(1)-C(6)-C(5)	-0.6(3)
N(1)-C(1)-C(6)-C(5)	178.1(2)
C(8)-O(2)-C(7)-O(1)	-0.7(3)
C(8)-O(2)-C(7)-C(4)	-179.87(17)
C(5)-C(4)-C(7)-O(1)	-163.3(2)
C(3)-C(4)-C(7)-O(1)	15.0(4)
C(5)-C(4)-C(7)-O(2)	15.8(3)
C(3)-C(4)-C(7)-O(2)	-165.88(19)
C(7)-O(2)-C(8)-C(9)	-177.27(19)
O(2)-C(8)-C(9)-C(10)	-177.38(18)
C(8)-C(9)-C(10)-C(11)	-178.4(2)
C(9)-C(10)-C(11)-C(12)	177.86(19)
C(10)-C(11)-C(12)-C(13)	-178.9(2)
C(14)-O(3)-C(13)-C(12)	162.32(19)
C(11)-C(12)-C(13)-O(3)	177.75(18)
C(13)-O(3)-C(14)-O(4)	-0.3(3)
C(13)-O(3)-C(14)-C(15)	179.55(17)
O(4)-C(14)-C(15)-C(16)	176.2(2)
O(3)-C(14)-C(15)-C(16)	-3.6(3)
O(4)-C(14)-C(15)-C(20)	-3.5(3)
O(3)-C(14)-C(15)-C(20)	176.71(19)
C(20)-C(15)-C(16)-C(17)	1.1(3)
C(14)-C(15)-C(16)-C(17)	-178.6(2)
C(15)-C(16)-C(17)-C(18)	-1.4(3)
C(16)-C(17)-C(18)-C(19)	0.9(3)
C(16)-C(17)-C(18)-C(21)	-178.5(2)
C(17)-C(18)-C(19)-C(20)	0.0(3)
C(21)-C(18)-C(19)-C(20)	179.4(2)

C(18)-C(19)-C(20)-C(15)	-0.4(3)
C(16)-C(15)-C(20)-C(19)	-0.2(3)
C(14)-C(15)-C(20)-C(19)	179.51(19)
C(19)-C(18)-C(21)-C(22)	-170(4)
C(17)-C(18)-C(21)-C(22)	9(4)

6. X-ray Diffraction Pattern

Powder X-ray diffraction pattern (PXRD) was taken *in situ* during the heating process for the 1,3-dipolar cycloaddition reaction. **C4** was taken as the example. PXRD was measured at 35 °C. Then, the sample was heated to 85 °C for 10 hours and PXRD was measured every two hours. From the PXRD, it was found that the diffraction peak position of X-ray diffraction pattern was similar with limited changes which might result from the polymerization of monomers.

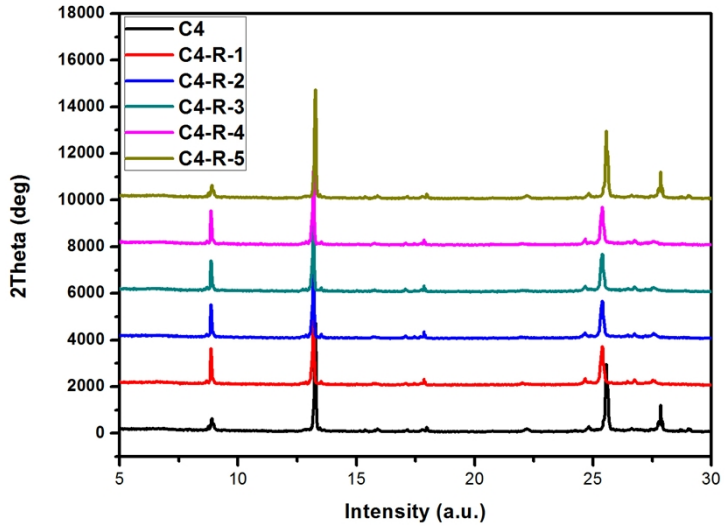


Figure *S6-1*. X-ray diffraction pattern measured *in situ* of **C4** and the products at 85 °C in every two hours.

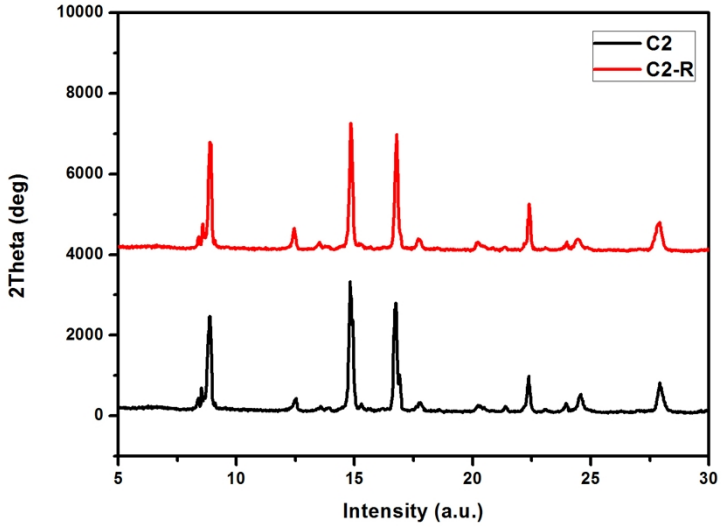


Figure *S6-2*. X-ray diffraction pattern measured *in situ* of **C2** and the products at 85 °C in every two hours.

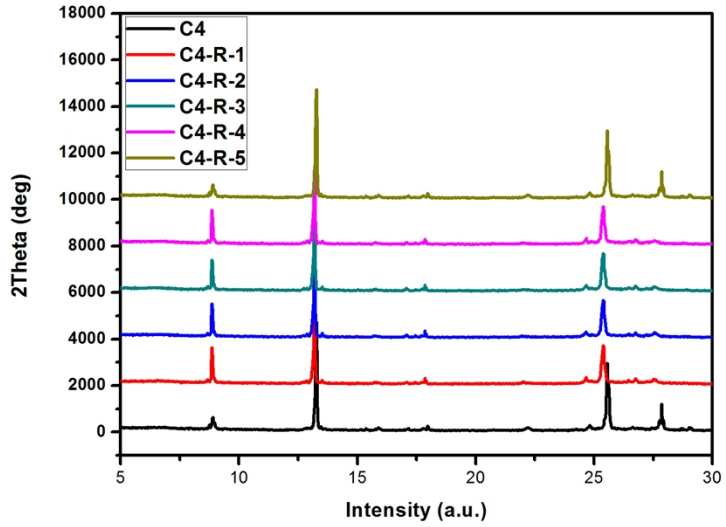


Figure *S6-3*. X-ray diffraction pattern measured *in situ* of **C3** and the products at 45 °C in every two hours.

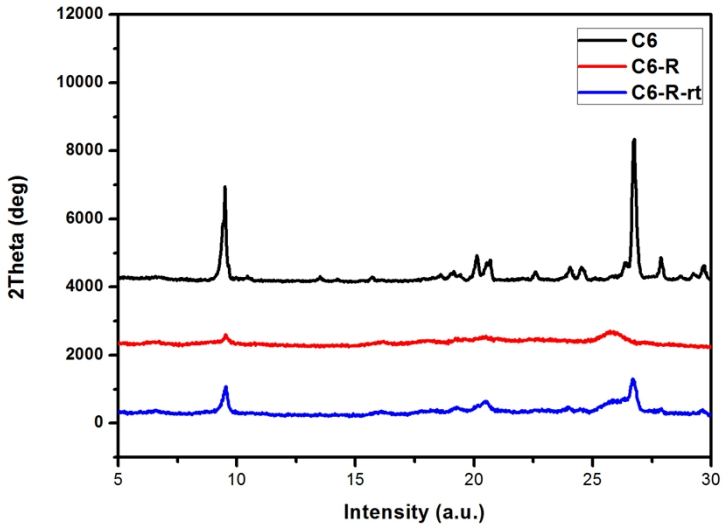


Figure *S6-4*. X-ray diffraction pattern measured *in situ* of **C6** and the products at 45 °C in every two hours. The pattern of the products was also measured in room temperature which was similar to the pattern at 45 °C in two hours. The change of peaks may result from the 1,3-dipolar cycloaddition reaction.