Solvent-Promoted Catalyst-Free Aminolytic Upcycling of Waste Polyethylene Terephthalate under Low-Temperature Conditions

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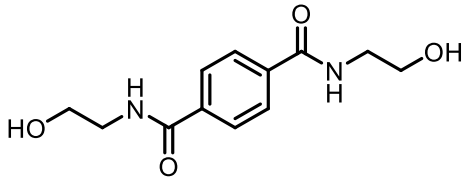
Experimental Section

Materials

The commercial PET, PTT and PBT pellets were purchased from Adamas. All other chemicals were purchased from Adamas-beta, Energy Chemical and Shanghai Chemical Reagents Co., Ltd. and used without further purification unless mentioned. All real-world waste PET plastic were washed, and then dried for further depolymerization.

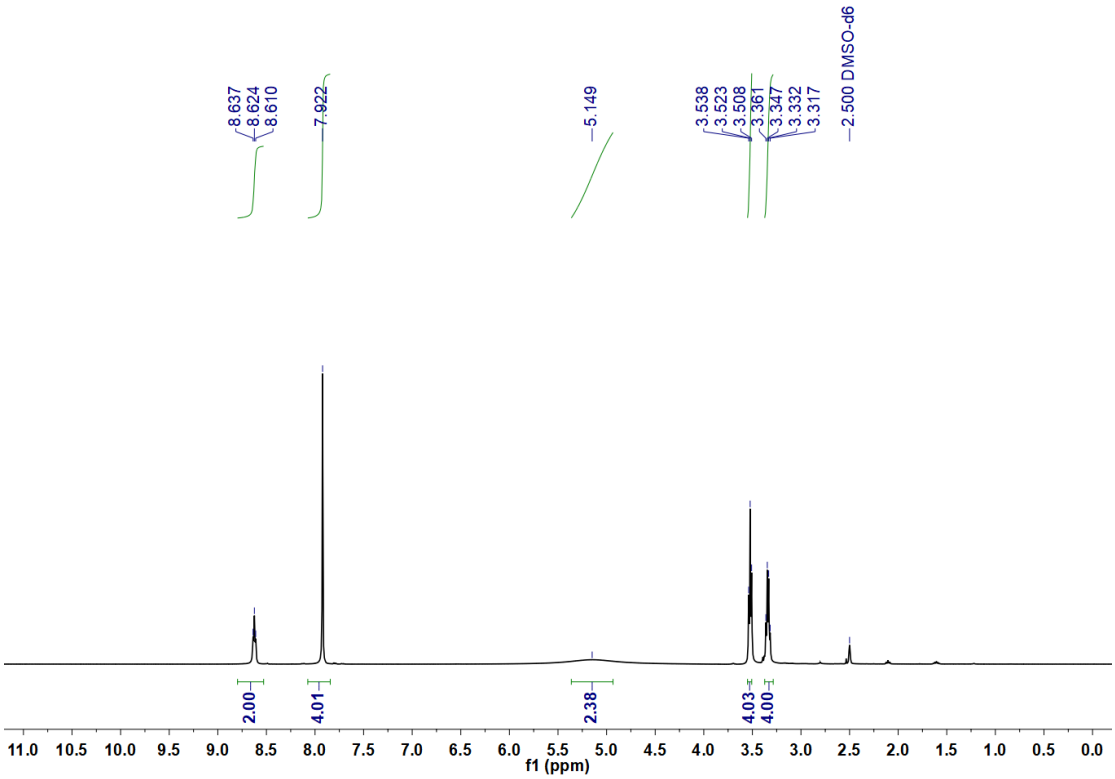
General procedures for the depolymerization of PET

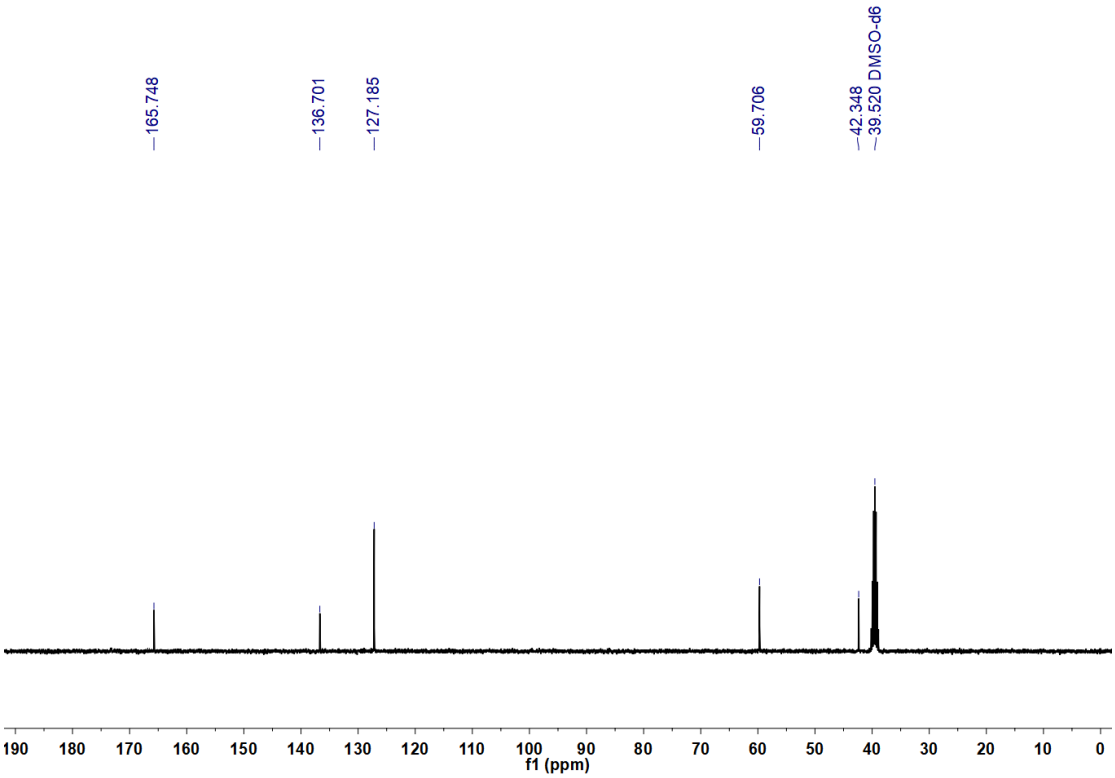
A 25 mL Schlenk tube was equipped with a stir bar and charged with PET (192 mg, 1 mmol, based on repeating unit), ethanolamine (20 mmol) and THF (0.5 M) was added. Then, the reaction was performed at 60 ºC for 5 h. After 5 h, the reaction mixture was cooled to room temperature (around 5~10 ºC). The filtered solid was then collected and vacuum-dried and obtain the desired product BHETA.

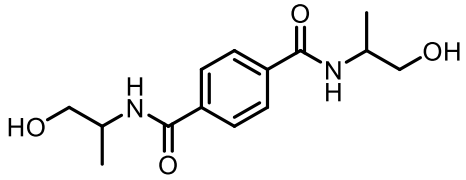


N^1,N^4-bis(2-hydroxyethyl)terephthalamide **2a**

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.53 (t, J = 5.2 Hz, 2H), 7.92 (s, 4H), 5.15 (s, 2H), 3.54 - 3.51 (m, 4H), 3.36 - 3.12 (m, 4H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 165.75, 136.70, 127.18, 59.71, 42.35.



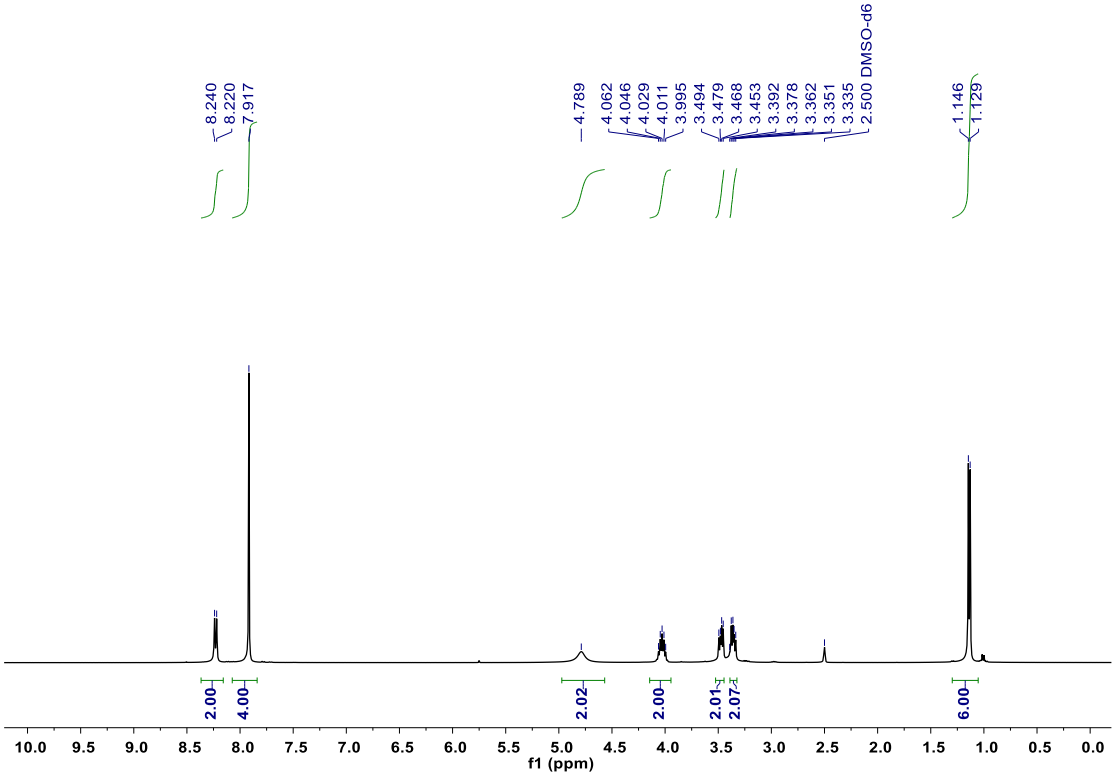


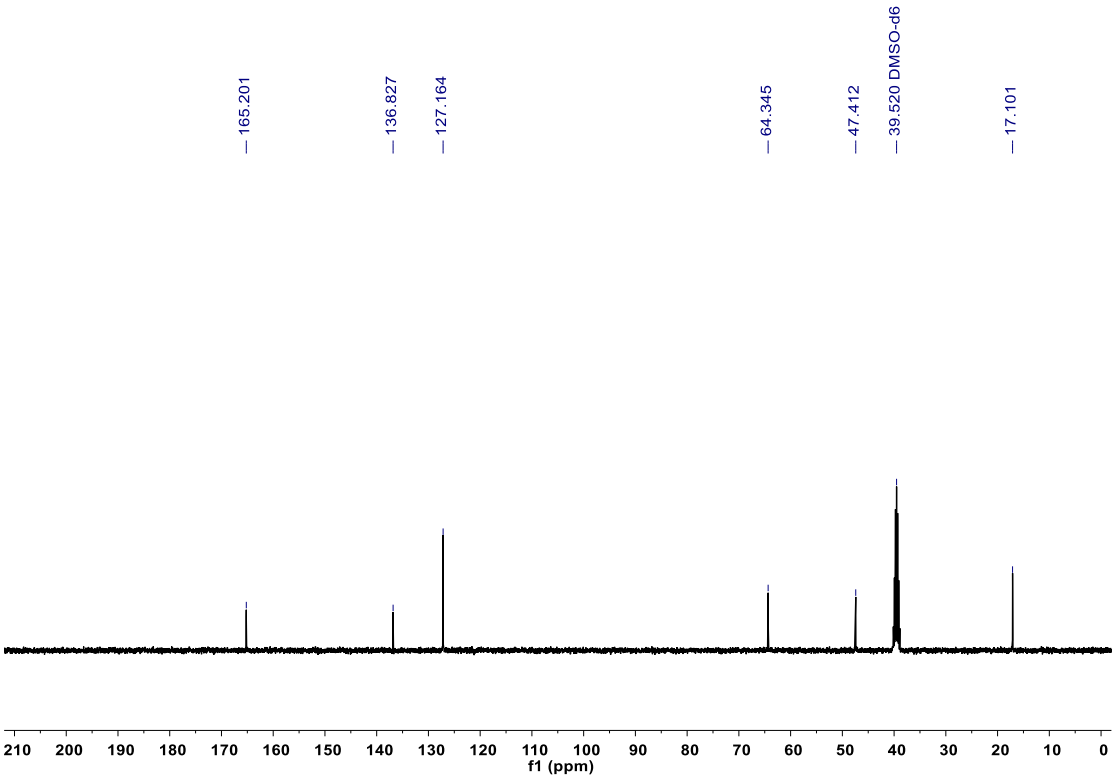


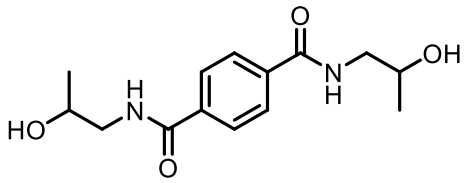
N^1,N^4-bis(1-hydroxypropan-2-yl)terephthalamide, **2b**

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.23 (d, J = 8.0 Hz, 2H), 7.92 (s, 4H), 4.79 (s, 2H), 4.08 – 3.98 (m, 2H), 3.49 – 3.45 (m, 2H), 3.39 – 3.34 (m, 2H), 1.14 (d, J = 6.7 Hz, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 165.20, 136.83, 127.16, 64.35, 47.41, 17.10.



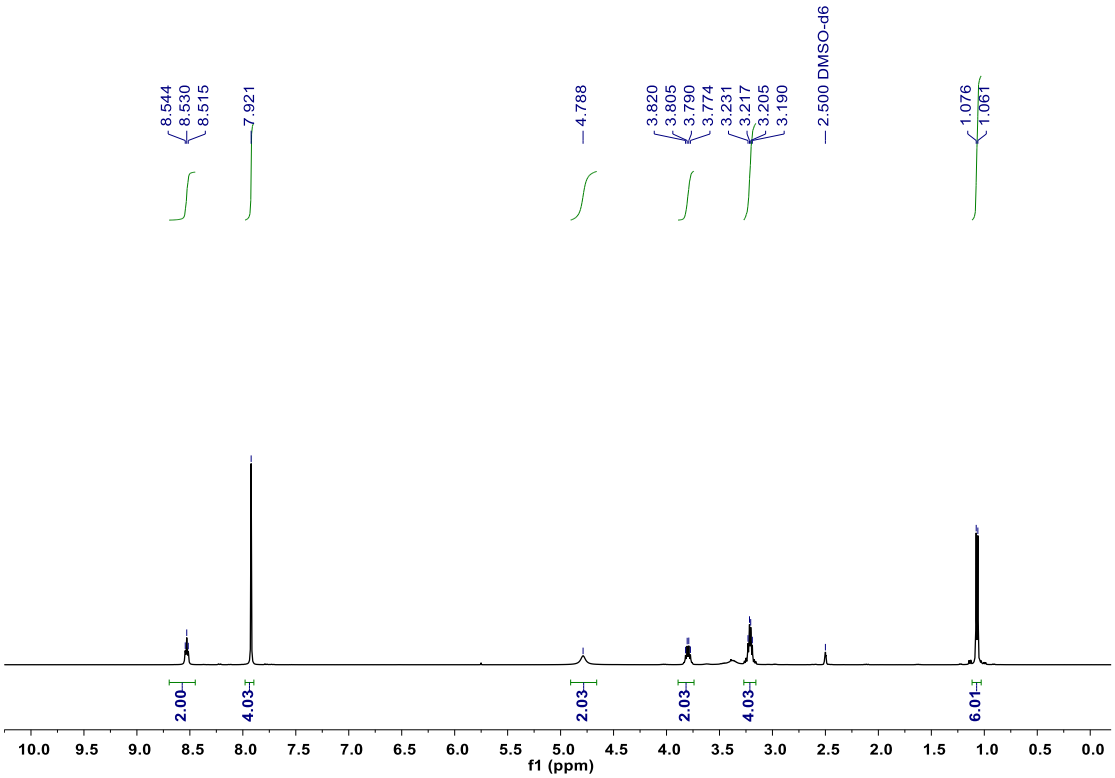


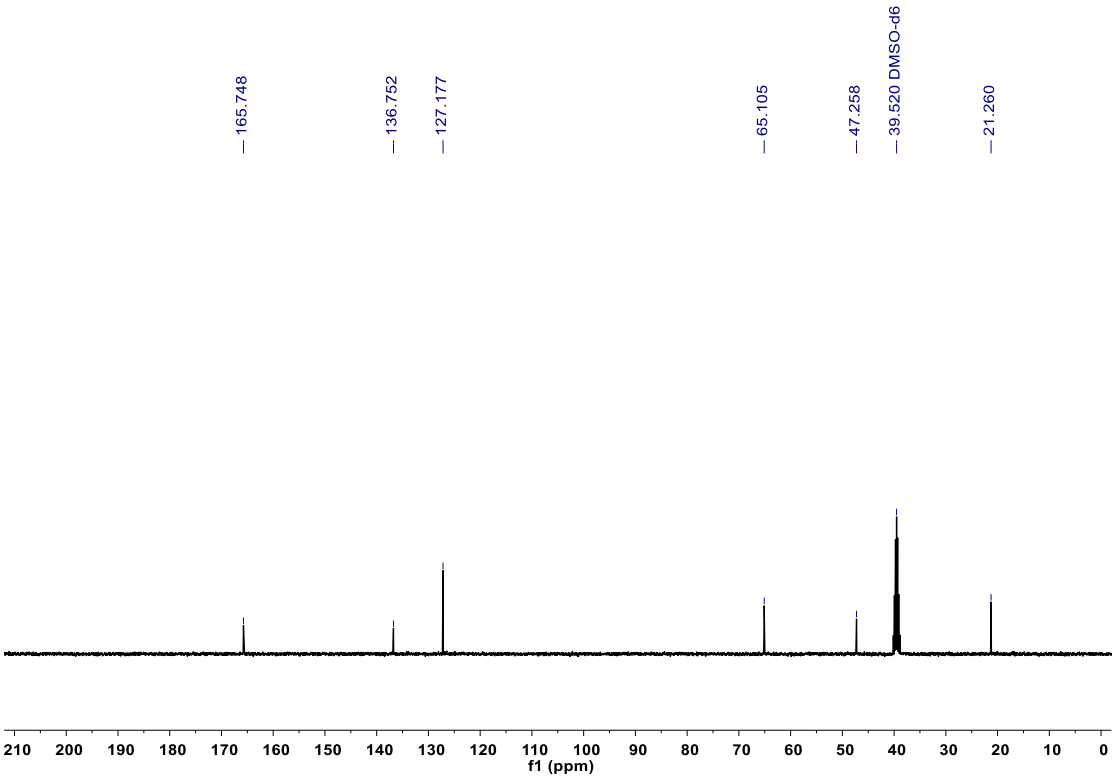


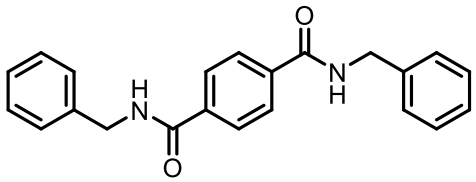
N^1,N^4-bis(2-hydroxypropyl)terephthalamide, **2c**

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.53 (t, J = 5.7 Hz, 2H), 7.92 (s, 4H), 4.79 (s, 2H), 3.84 - 3.76 (m, 2H), 3.29 - 3.13 (m, 4H), 1.07 (d, J = 6.2 Hz, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 165.75, 136.75, 127.18, 65.11, 47.26, 21.26.



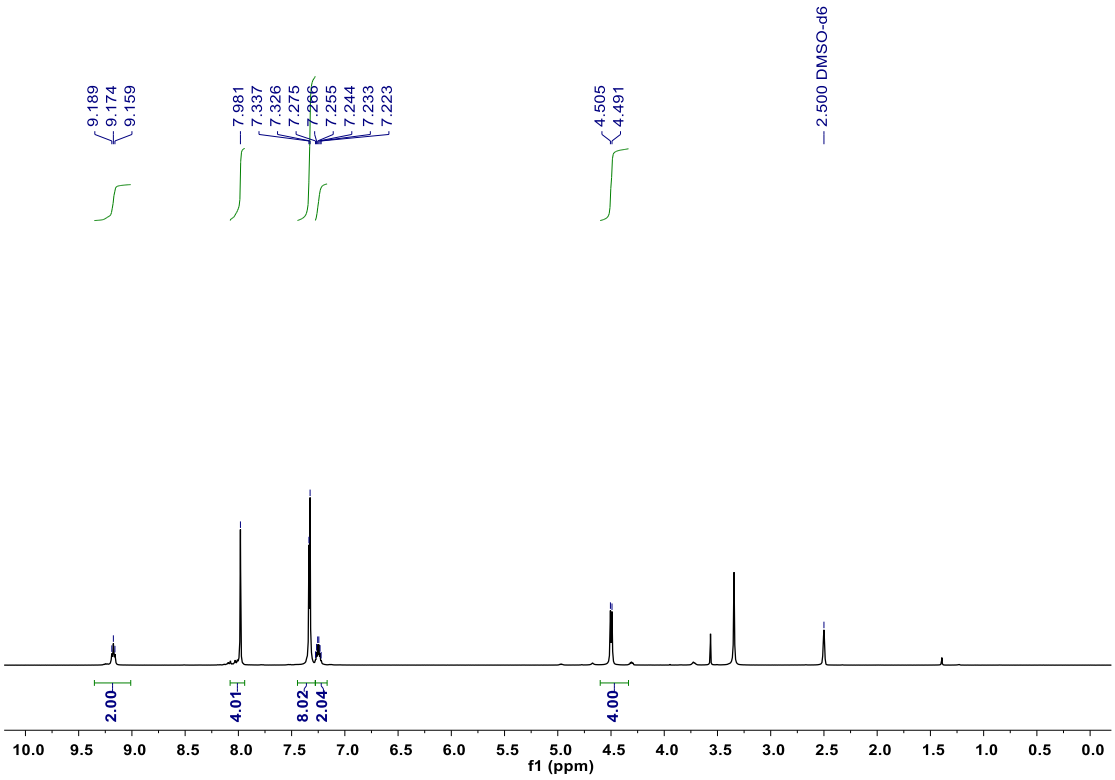


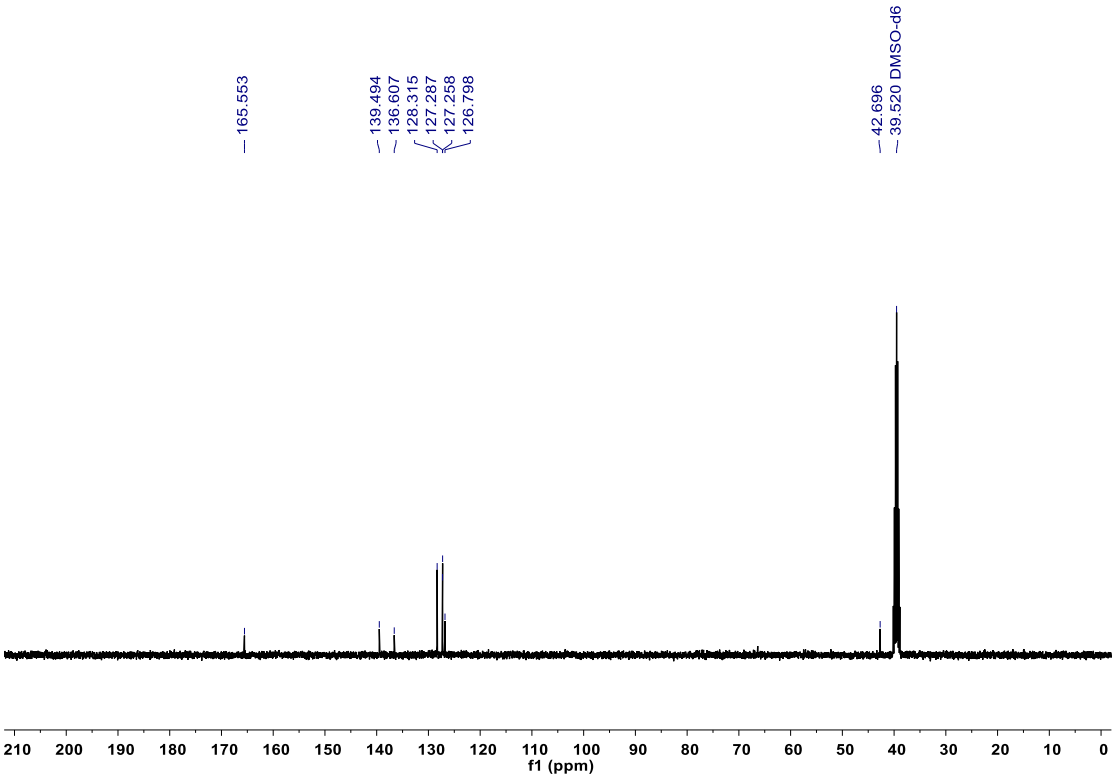


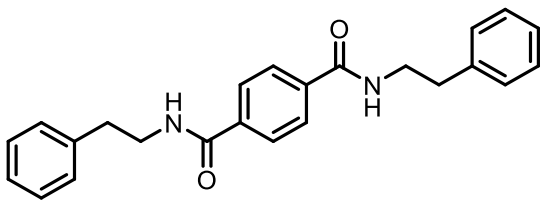
N^1,N^4-dibenzylterephthalamide, **2d**

^{13}C NMR (101 MHz, DMSO-d_6) δ 165.55, 139.49, 136.61, 128.32, 127.29, 127.26, 126.80, 42.70.

^{1}H NMR (400 MHz, DMSO-d_6) δ 9.17 (t, J = 5.8 Hz, 2H), 7.98 (s, 4H), 7.34 – 7.33 (m, 8H), 7.28 – 7.22 (m, 2H), 4.50 (d, J = 5.9 Hz, 4H).



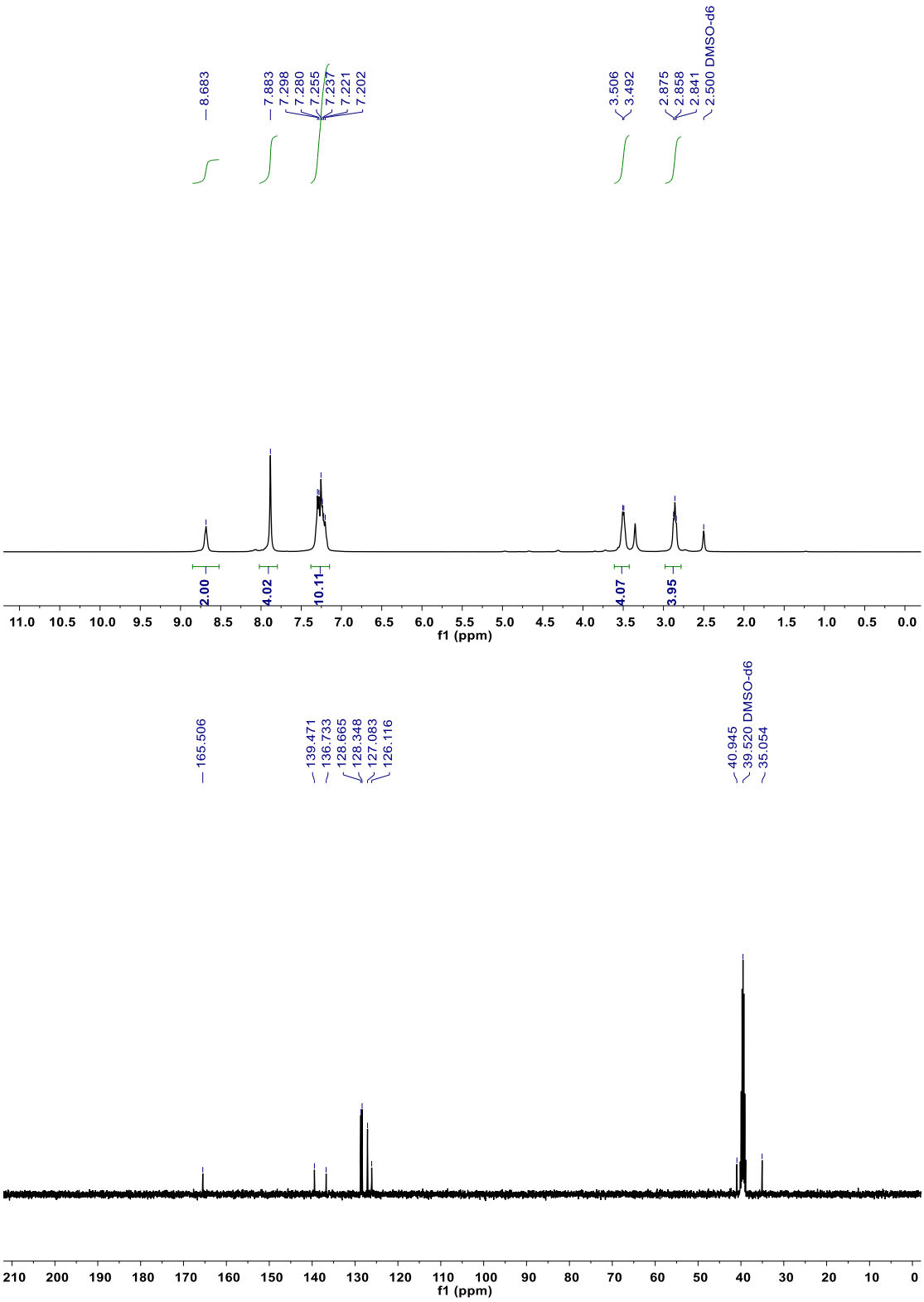


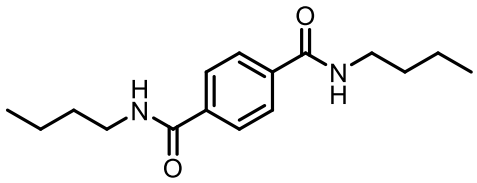


N1,N4-diphenethylterephthalamide, **2e**

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.68 (s, 2H), 7.88 (s, 4H), 7.30 – 7.20 (m, 10H), 3.61 – 3.43 (m, 4H), 2.88 – 2.84 (m, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 165.51, 139.47, 136.73, 128.67, 128.35, 127.08, 126.12, 40.94, 35.05.

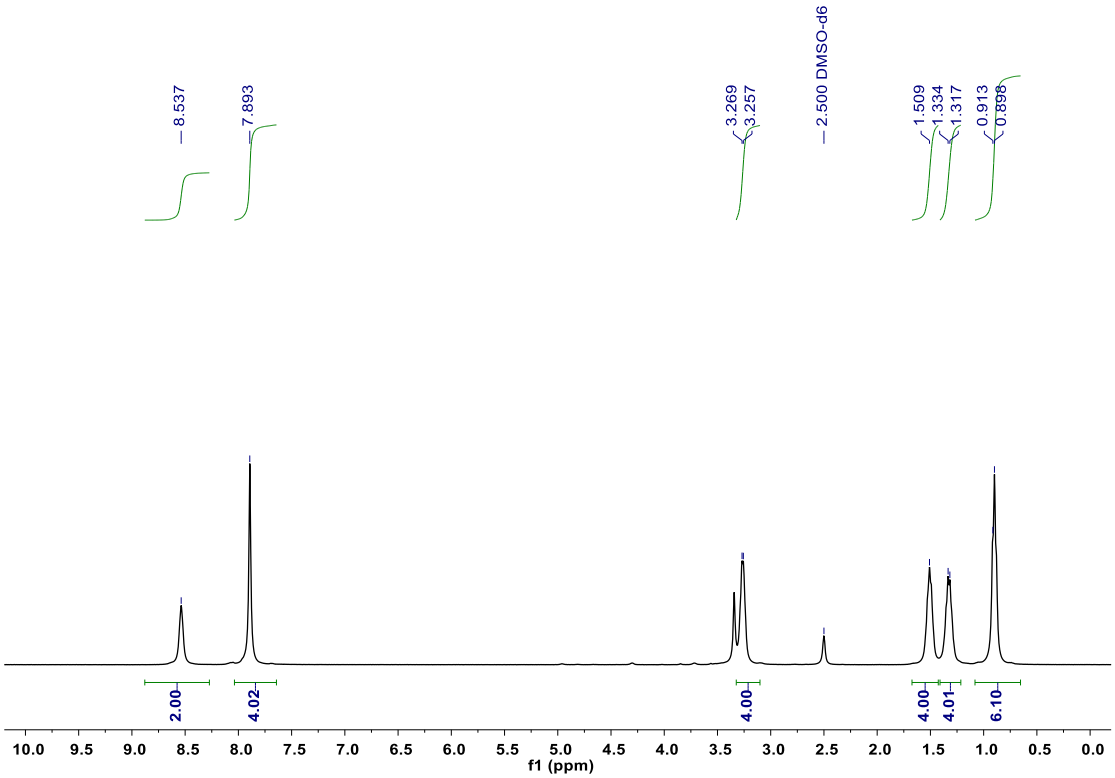


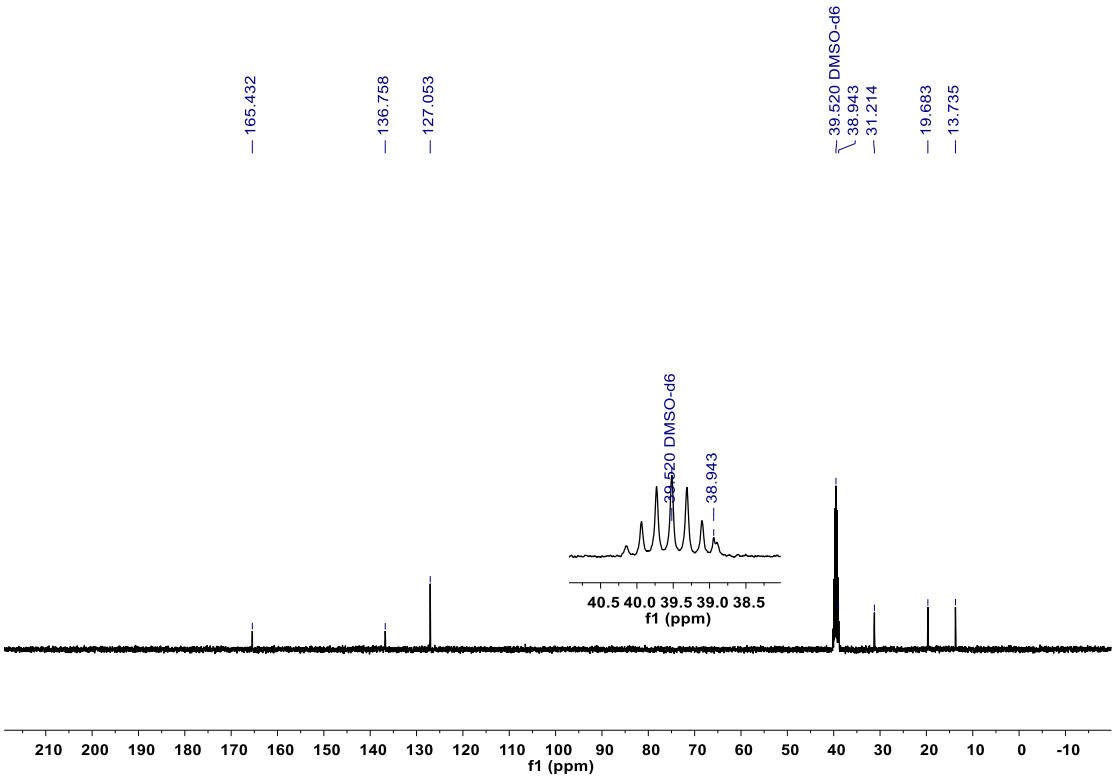


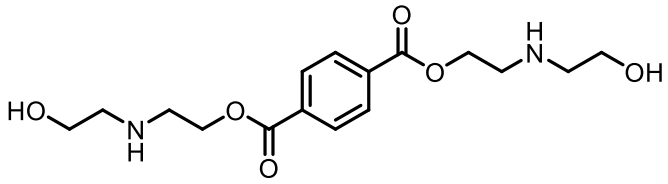
N^1,N^4-dibutylterephthalamide, **2f**

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.54 (s, 2H), 7.89 (s, 4H), 3.32 – 3.10 (m, 4H), 1.51 (s, 4H), 1.41 – 1.21 (m, 4H), 1.08 – 0.65 (m, 6H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 165.43, 136.76, 127.05, 38.94, 31.21, 19.68, 13.73.



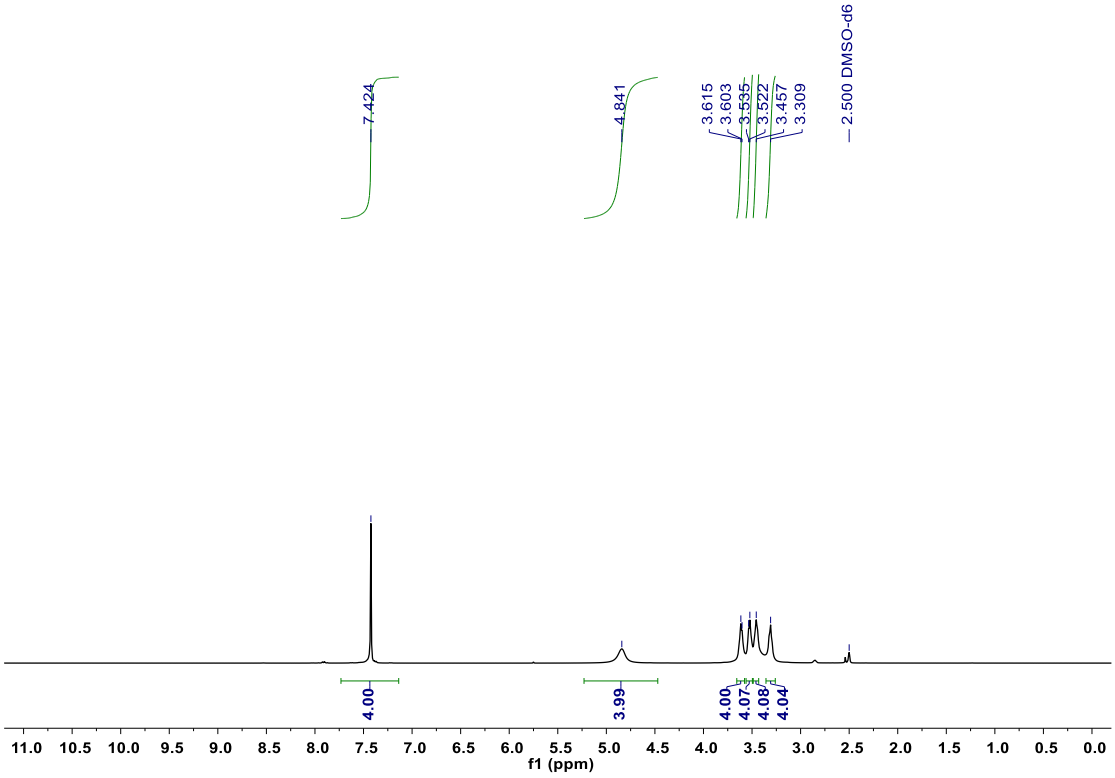


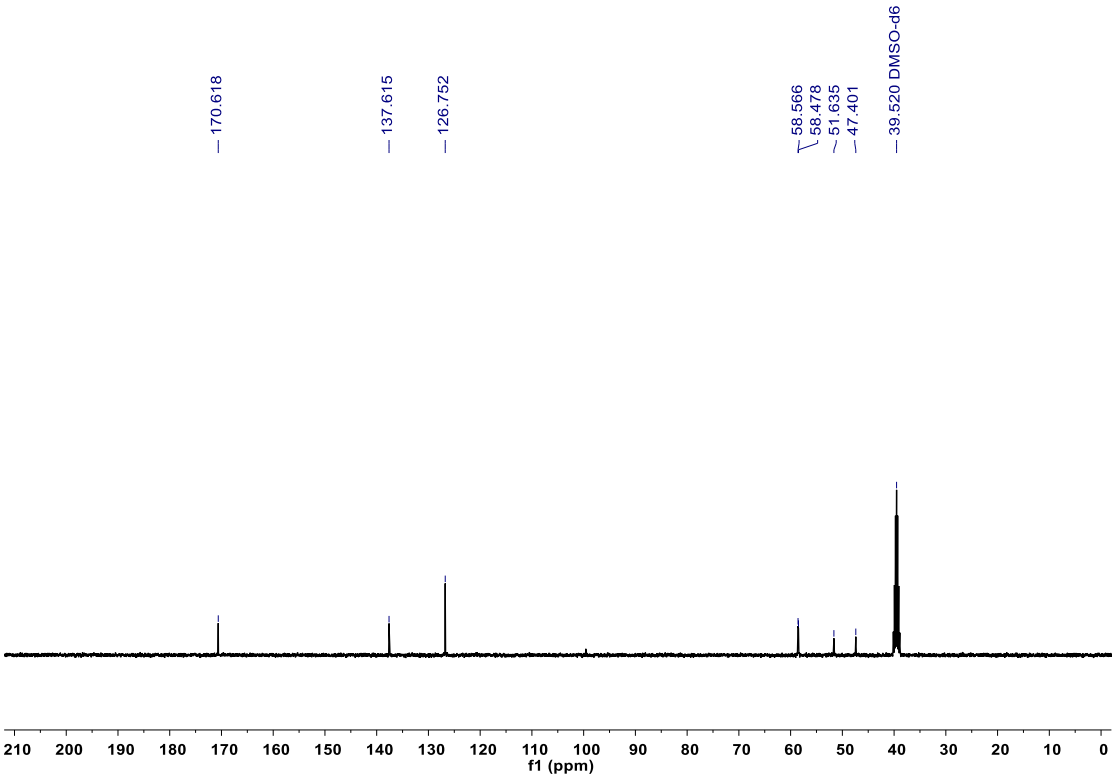


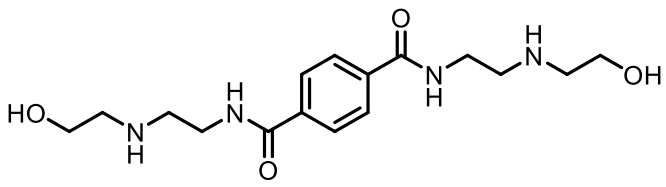
bis(2-((2-hydroxyethyl)amino)ethyl) terephthalate, **2h**

^{1}H NMR (400 MHz, DMSO-d_6) δ 7.42 (s, 4H), 4.84 (s, 4H), 3.66 – 3.58 (m, 4H), 3.56 – 3.50 (m, 4H), 3.46 (s, 4H), 3.31 (s, 4H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 170.62, 137.61, 126.75, 58.57, 58.48, 51.63, 47.40.



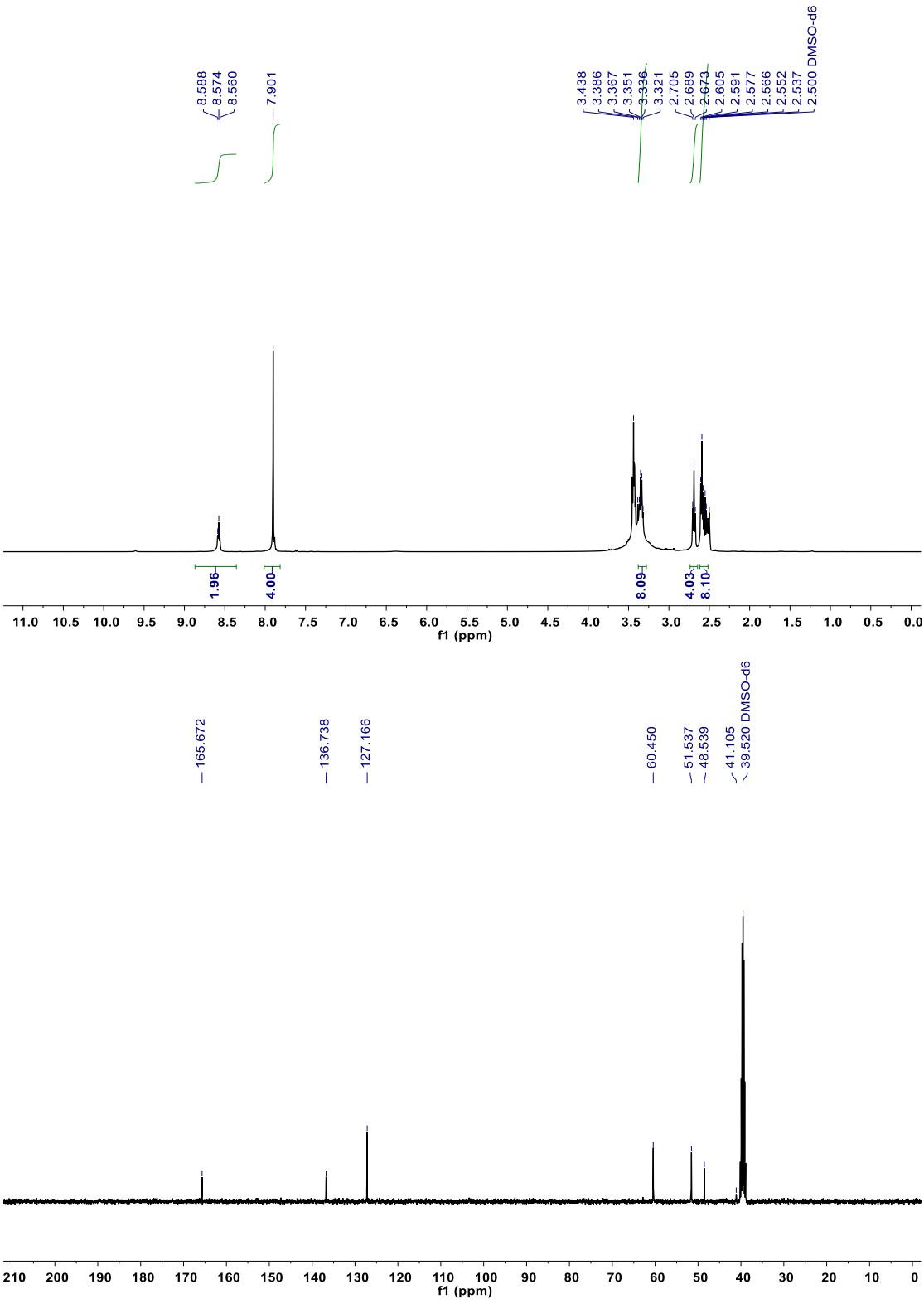


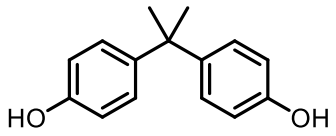


N^1,N^4-bis(2-((2-hydroxyethyl)amino)ethyl)terephthalamide, **2g**

^{1}H NMR (400 MHz, DMSO-d_6) δ 8.57 (t, J = 5.5 Hz, 2H), 7.90 (s, 4H), 3.34 (q, J = 6.2 Hz, 8H), 2.69 (t, J = 6.5 Hz, 4H), 2.57 (dt, J = 15.9, 5.8 Hz, 8H).

^{13}C NMR (101 MHz, DMSO-d_6) δ 165.67, 136.74, 127.17, 60.45, 51.54, 48.54, 41.10, 39.52.

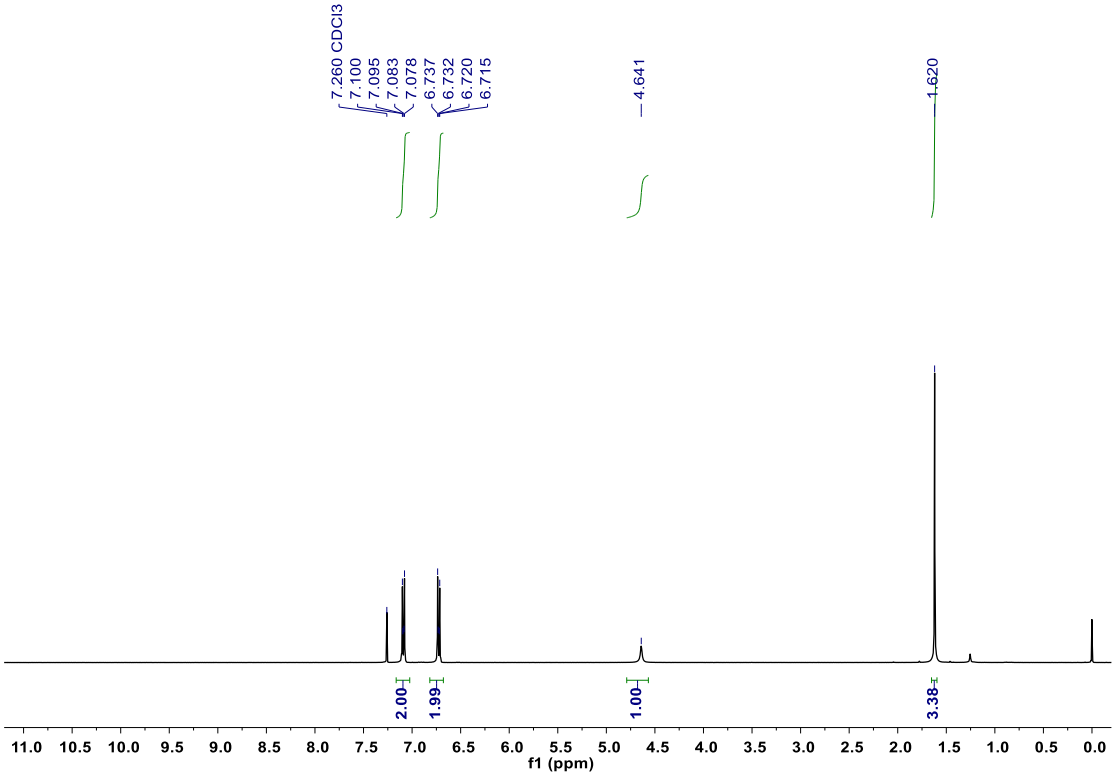




bisphenol A, **2i**

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.16 – 7.02 (m, 2H), 6.82 – 6.68 (m, 2H), 4.64 (s, 1H), 1.62 (s, 3H).

^{13}C NMR (101 MHz, $CDCl_3$) δ 153.35, 143.46, 128.07, 114.82, 41.83, 31.21.



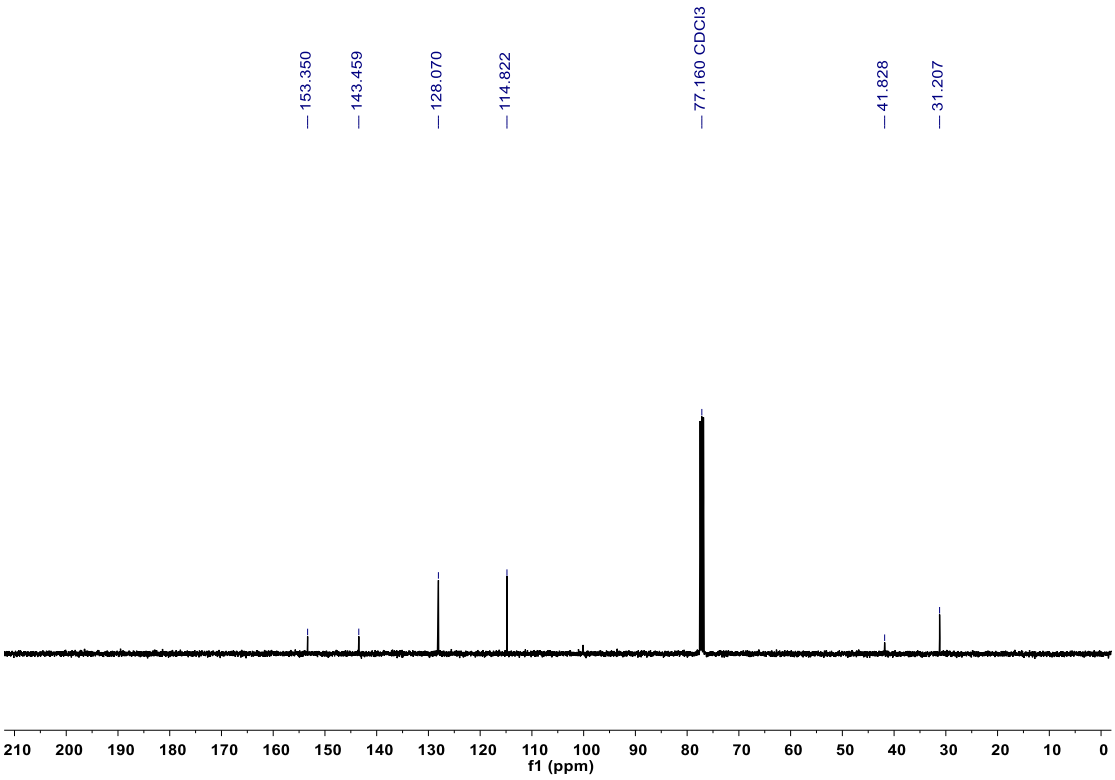


Table S1. Comparison of aminolytic (MEA) upcycling of PET (this work with other works)

entry	catalyst	temperature (°C)	time	solvent	yield	References
1	-	60	5 h	THF	>98%	This work
2	-	80	24 h	-	96%	Wang et al.[7k]
3	TBD : MSA	180	10 min	-	93%	Sardon et al.[7j]
4	TBD	120	2 h	-	93%	Sardon et al.[7i]
5	DBTO	190	1 h	-	62%	Tawfik et al.[7h]
6	-	reflux	30 min	deep eutectic solvent (Choline chloride-2$ZnCl_2$)	95%	Shukla et al. [7f]
7	PWA	160	2 h	-	96%	Vajiravelu et al.[7e]
8	-	r.t.	24 h	1. TFA; 2. -	81%	Jiang et al.[10a]

Table S2. The prices of ethanolamine and BHETA.

Chemical	Brand	Grades	Price
ethanolamine	Sigma-aldrich	500 mL	$40
BHETA	Sigma-aldrich	1 g	$270

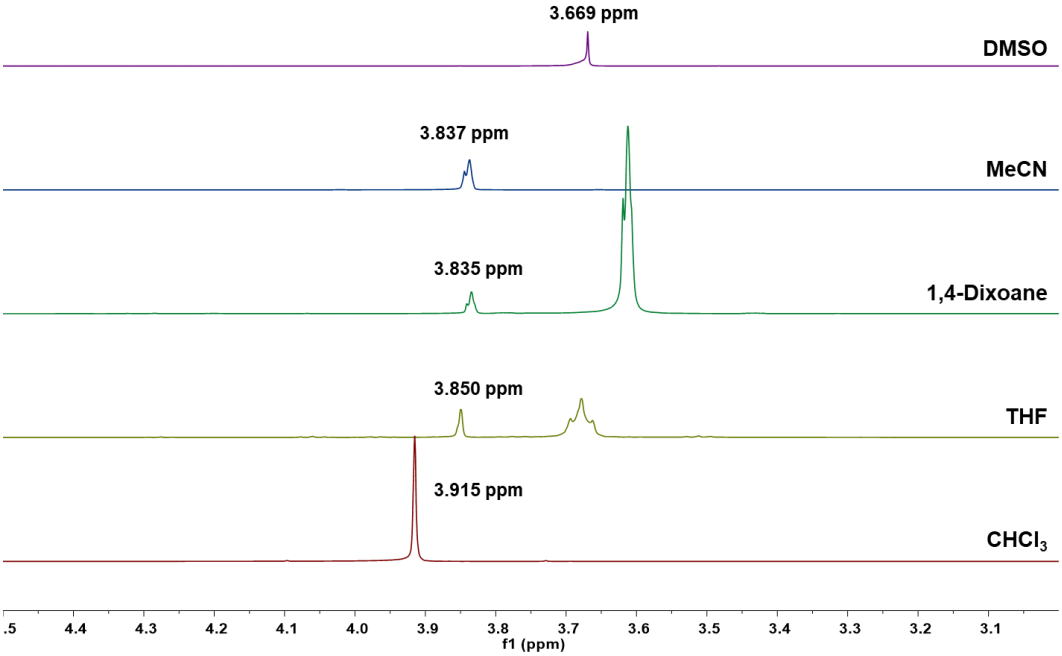


Figure S1. ^{1}H NMR of the methyl proton in methyl benzoate with different solvent

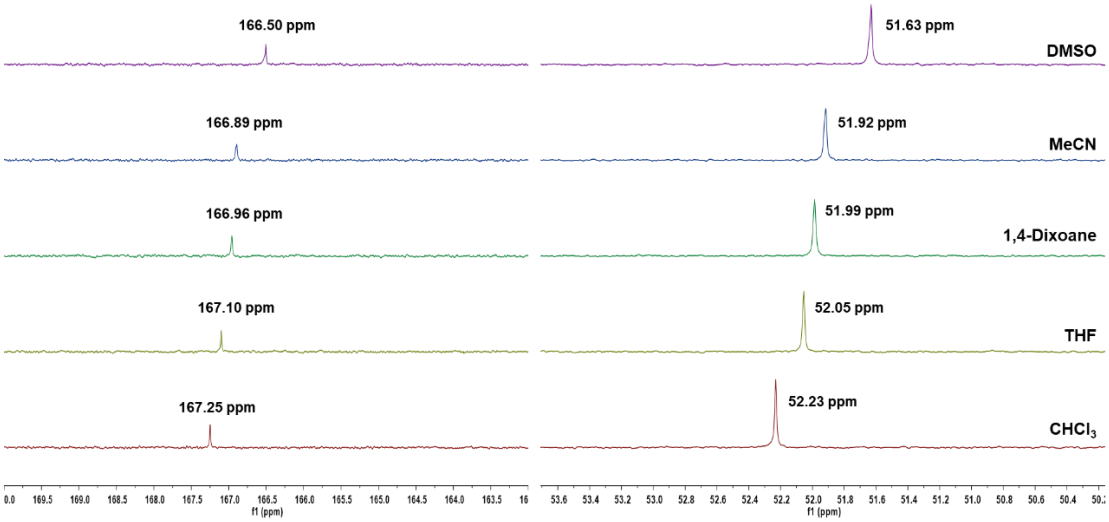


Figure S2. ^{13}C NMR of the carbonyl and methyl carbon in methyl benzoate with different solvent

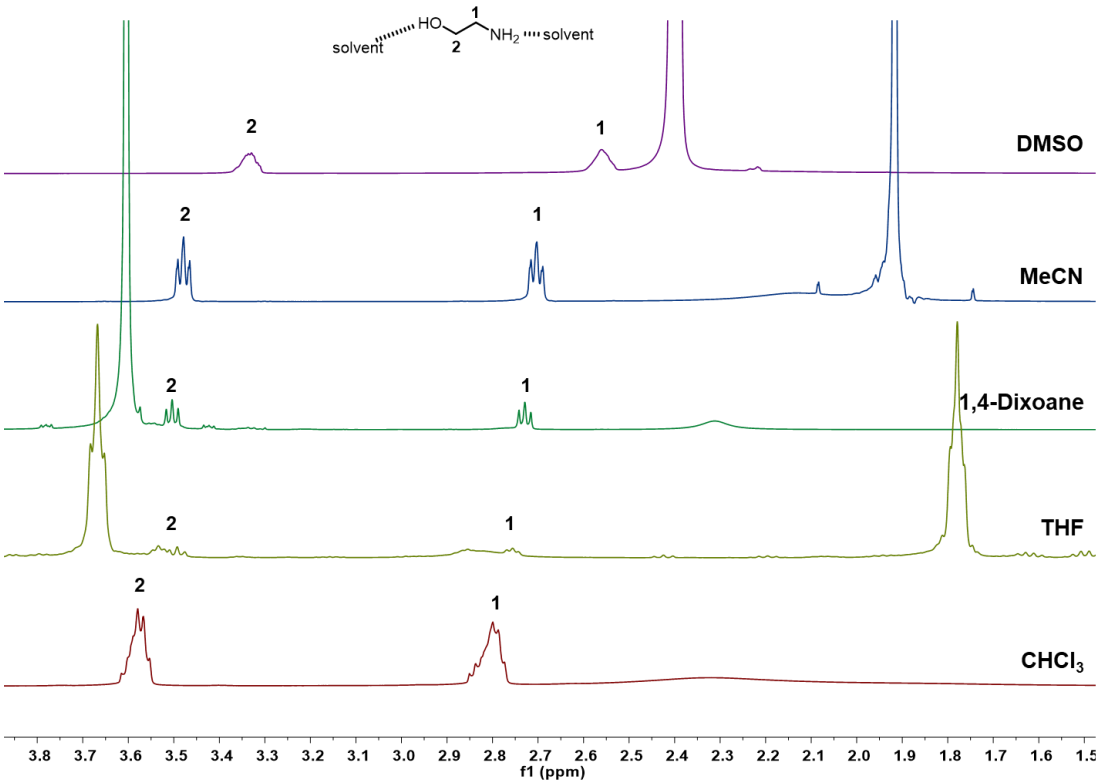


Figure S3. ^{1}H NMR of the methylene proton in ethanolamine with different solvent

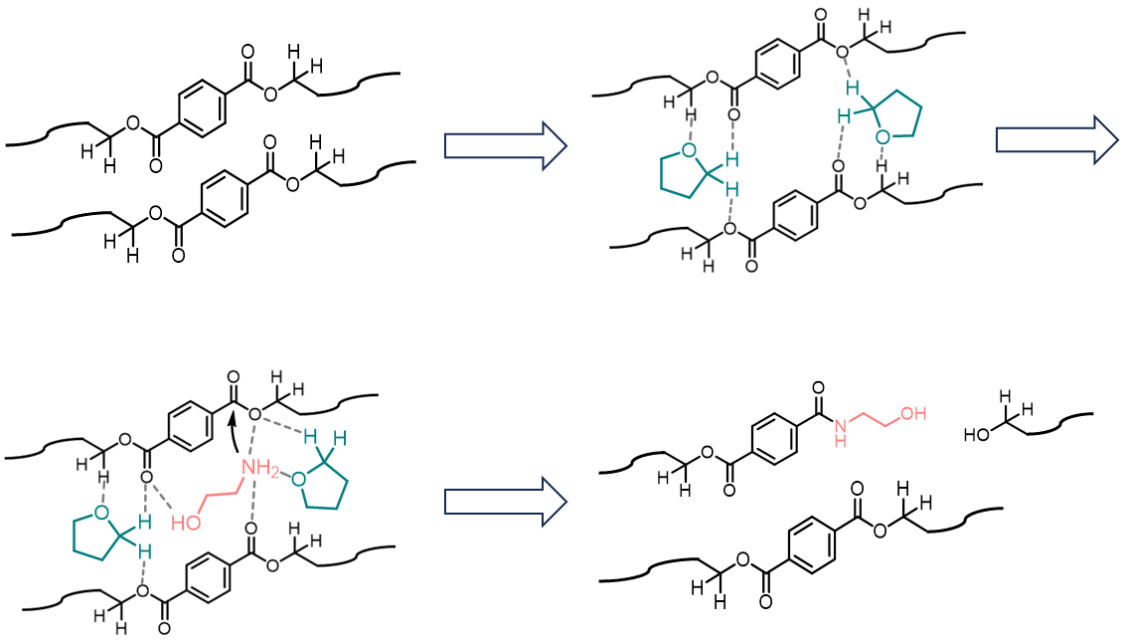


Figure S4. The proposed mechanism for THF-promoted PET aminolysis

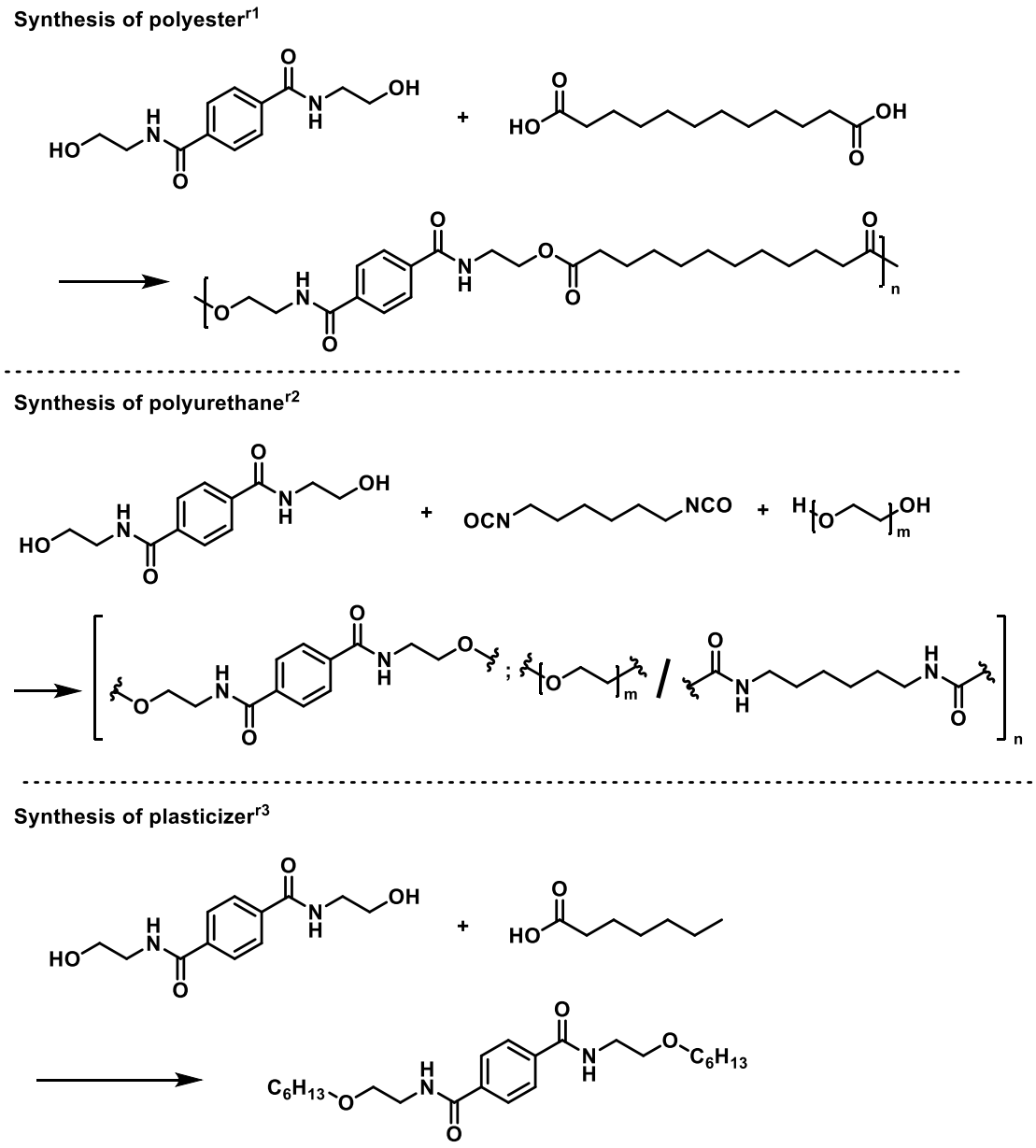


Figure S5. The application of aminolysis product (BHETA)

Reference

r1. a) J. Natarajan, G. Madras and K. Chatterjee, *ACS Appl. Mater. Interfaces*, 2017, **9**, 28281-2829; b) S. M. Elsaeed and R. K. Farag, *J. Appl. Polym. Sci*., 2009, **112**, 3327-3336.

r2. a) M. Y. Tan, L. Goh, D. Safanama, W. W. Loh, N. Ding, S. W. Chien, S. S. Goh, W. Thitsartarn, J. Y. C. Lim and D. W. H. Fam, *J. Mater. Chem. A*, 2022, **10**, 24468-24474; b) G. Pastore, R. Giacomantonio, G. Lupidi, F. Stella, R. Risoluti, E. Papa, R. Ballini, F. Sarasini, J. Tirillo, E. Macrantoni and S. Gabrielli, *Front. Chem*. 2023, **11**,1234763; c) R. Shamsi, M. Abdouss, G. M. M. Sadeghi and F. A. Taromi, *Polym. Int*., 2009, **58**, 22-30.

r3. A. P. More, R. A. Kute and S. T. Mhaske, *Iran. Polym. J.*2014, **23**, 59-67.