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Supplementary Information

Constructing Stable Phenalenyl-Based Neutral Radicals: A Theoretical Approach

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Contents

1. Calculations of BDEs and RSEs in solvent (DMF and toluene)

Table S1 BDEs of the most stable precursors and RSEs for PLY-based radicals in DMF and toluene.

Molecule	*H*(RPLY) / a.u.	*H*(H▪) / a.u.	*H*(RPLY-H) / a.u.	BDE / kJ mol^{-1}	RSE / kJ mol^{-1}
Solvent: DMF					
PLY	-500.629	-0.498	-501.220	245.146	0.000
147-CN	-777.367	-0.498	-777.958	243.717	1.428
147-CH_3	-618.492	-0.498	-619.084	245.957	-0.811
147-NH_2	-666.644	-0.498	-667.233	239.438	5.708
147-OCH_3	-844.096	-0.498	-844.687	246.041	-0.895
147-F	-798.350	-0.498	-798.944	250.488	-5.343
147-*t*-Bu	-972.004	-0.498	-972.599	254.529	-9.384
258-CN	-777.363	-0.498	-777.960	260.326	-15.181
1349-CN	-869.594	-0.498	-870.184	240.866	4.280
13467-CN	-961.831	-0.498	-962.422	243.531	1.615
134679-CN	-1054.060	-0.498	-1054.644	227.465	17.680
Solvent: toluene					
PLY	-500.627	-0.498	-501.218	245.188	0.000
147-CN	-777.360	-0.498	-777.950	241.688	3.500
147-CH_3	-618.490	-0.498	-619.081	245.938	-0.751
147-NH_2	-666.635	-0.498	-667.224	240.464	4.723
147-OCH_3	-844.091	-0.498	-844.683	246.734	-1.546
147-F	-798.349	-0.498	-798.942	250.092	-4.904
147-*t*-Bu	-972.001	-0.498	-972.596	255.078	-9.890
258-CN	-777.354	-0.498	-777.951	259.423	-14.235
1349-CN	-869.581	-0.498	-870.169	236.001	9.187
13467-CN	-961.817	-0.498	-962.406	238.267	6.921
134679-CN	-1054.043	-0.498	-1054.626	224.877	20.311

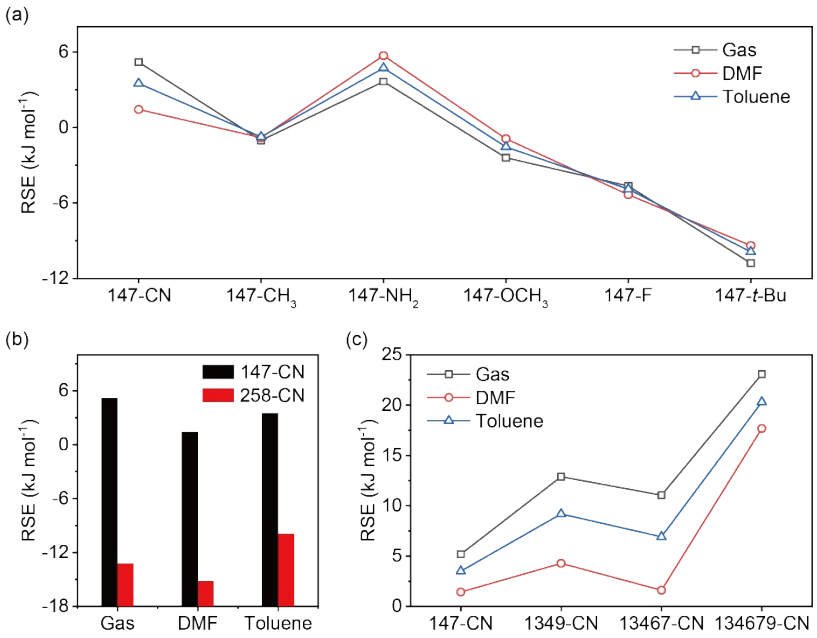


Fig. S1 RSEs of (a) 147-Rs, (b) 147-CN and 258-CN, and (c) 147-CN,1349-CN, 13467-CN and 134679-CN in gas phase and solvents of DMF and toluene.

2. Enthalpies of the precursors

2.1 Precursors of PLY

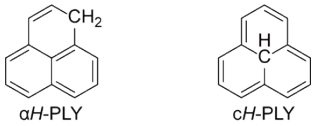


Fig. S2 The precursors of PLY.

Table S2 Enthalpies of PLY (*H*(PLY)), hydrogen radical (*H*(H▪)) and two possible precursors of PLY (*H* (PLY-H)), and the relative enthalpies (Δ*H*) and C-H BDEs of the precursors.

Position of H	*H*(PLY) / a.u.	*H*(H▪) / a.u.	*H*(PLY-H)	Δ*H* / kJ mol^{-1}	BDE / kJ mol^{-1}
α*H*-PLY	-500.624930	-0.497912	-501.216191	0	245.088
c*H*-PLY	-500.624930	-0.497912	-501.139216	202.098	42.990

Noted that Δ*H*(*xH*-PLY)=*H*(*xH*-PLY)-*H*(α*H*-PLY), where *x*=α and c, and the most stable precursor of PLY with the lowest enthalpy is highlighted in red.

2.2 Precursors of PLY-based radicals with identical substituents

2.2.1 Precursors of mono-substituted PLY-based radicals

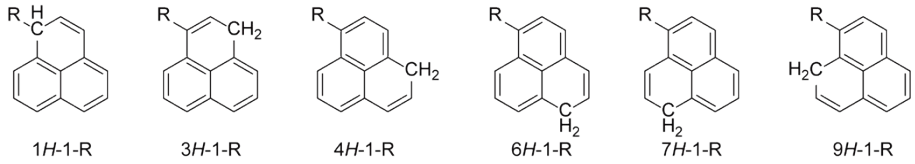


Fig. S3 The precursors of 1-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S3 Enthalpies (*H*(R-H)) and relative enthalpies (ΔH) for the precursors of 1-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	ΔH / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	ΔH / kJ mol^{-1}
1*H*-1-CH_3	-540.499991	11.634	1*H*-1-*t*-Bu	-658.345196	0
3*H*-1-CH_3	-540.503845	1.515	3*H*-1-*t*-Bu	-658.340488	12.361
4*H*-1-CH_3	-540.503410	2.657	4*H*-1-*t*-Bu	-658.341056	10.870
6*H*-1-CH_3	-540.503582	2.205	6*H*-1-*t*-Bu	-658.341067	10.841
7*H*-1-CH_3	-540.502031	6.278	7*H*-1-*t*-Bu	-658.339061	16.107
9*H*-1-CH_3	-540.504422	0	9*H*-1-*t*-Bu	-658.338136	18.536
1*H*-1-F	-600.452257	16.606	1*H*-1-CN	-593.448721	32.942
3*H*-1-F	-600.457326	3.298	3*H*-1-CN	-593.458611	6.976
4*H*-1-F	-600.456939	4.314	4*H*-1-CN	-593.460464	2.111
6*H*-1-F	-600.457070	3.970	6*H*-1-CN	-593.460834	1.139
7*H*-1-F	-600.456772	4.752	7*H*-1-CN	-593.460588	1.785
9*H*-1-F	-600.458582	0	9*H*-1-CN	-593.461268	0
1*H*-1-NH_2	-556.540052	30.747	1*H*-1-OCH_3	-615.695195	22.763
3*H*-1-NH_2	-556.548563	8.402	3*H*-1-OCH_3	-615.703865	0
4*H*-1-NH_2	-556.548818	7.732	4*H*-1-OCH_3	-615.702902	2.528
6*H*-1-NH_2	-556.549471	6.018	6*H*-1-OCH_3	-615.703527	0.887
7*H*-1-NH_2	-556.548290	9.118	7*H*-1-OCH_3	-615.700885	7.824
9*H*-1-NH_2	-556.551763	0	9*H*-1-OCH3	-615.703634	0.606

Noted that for R=CH_3, F, CN and NH_2, ΔH(*xH*-1-R)=*H*(*xH*-1-R)-*H*(9*H*-1-R); for R=*t*-Bu, ΔH(*xH*-1-R)=*H*(*xH*-1-R)-*H*(1*H*-1-R); for R=OCH_3, ΔH(*xH*-1-R)=*H*(*xH*-1-R)-*H*(3*H*-1-R), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursors with the lowest enthalpies among the six isomers are highlighted in red.

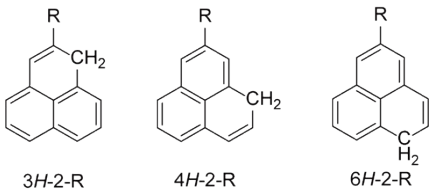


Fig. S4 The precursors of 2-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S4 Enthalpies (*H*(R-H)) and relative enthalpies (ΔH) for the precursors of 2-R (R=CH_3, *t*-Bu, F, CN, NH_2 and

OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
3*H*-2-CH_3	-540.507312	0	3*H*-2-*t*-Bu	-658.353018	0.050
4*H*-2-CH_3	-540.505122	5.750	4*H*-2-*t*-Bu	-658.352880	0.412
6*H*-2CH_3	-540.505246	5.424	6*H*-2-*t*-Bu	-658.353037	0
3*H*-2-F	-600.459088	0	3*H*-2-CN	-593.461685	0
4*H*-2-F	-600.457267	4.781	4*H*-2-CN	-593.459674	5.280
6*H*-2-F	-600.457195	4.970	6*H*-2-CN	-593.459717	5.167
3*H*-2-NH_2	-556.555160	0	3*H*-2-OCH_3	-615.708663	0
4*H*-2-NH_2	-556.551565	9.439	4*H*-2-OCH_3	-615.704443	11.080
6*H*-2-NH_2	-556.551660	9.189	6*H*-2-OCH_3	-615.704538	10.830

Noted that for R=CH_3, F, CN, NH_2 and OCH_3, Δ*H*(*xH*-2-R)=*H*(*xH*-2-R)-*H*(3*H*-2-R); for R=*t*-Bu, Δ*H*(*xH*-2-R)=*H*(*xH*-2-R)-*H*(6*H*-2-R), where *x*=3, 4 and 6, and the most stable precursors with the lowest enthalpies among the three isomers are highlighted in red.

2.2.2 Precursors of di-substituted PLY-based radicals

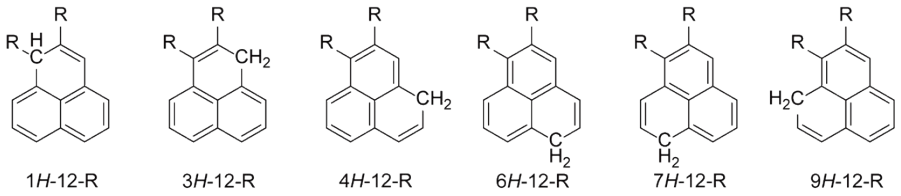


Fig. S5 The precursors of 12-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S5 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 12-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-12-CH_3	-579.789186	2.578241	1*H*-12-*t*-Bu	-815.466661	0
3*H*-12-CH_3	-579.78884	3.486664	3*H*-12-*t*-Bu	-815.43074	94.31058
4*H*-12-CH_3	-579.788423	4.581497	4*H*-12-*t*-Bu	-815.42173	117.9663
6*H*-12-CH_3	-579.788607	4.098405	6*H*-12-*t*-Bu	-815.429719	96.99121
7*H*-12-CH_3	-579.787554	6.863056	7*H*-12-*t*-Bu	-815.423948	112.143
9*H*-12-CH_3	-579.790168	0	9*H*-12-*t*-Bu	-815.422467	116.0313
1*H*-12-F	-699.691971	1.86673	1*H*-12-CN	-685.689257	24.29637
3*H*-12-F	-699.691648	2.714767	3*H*-12-CN	-685.696804	4.481728
4*H*-12-F	-699.690452	5.854864	4*H*-12-CN	-685.697151	3.57068
6*H*-12-F	-699.690449	5.862741	6*H*-12-CN	-685.69761	2.365575
7*H*-12-F	-699.691002	4.41084	7*H*-12-CN	-685.697847	1.743332
9*H*-12-F	-699.692682	0	9*H*-12-CN	-685.698511	0

1*H*-12-NH_2	-611.873508	25.68789	1*H*-12-OCH_3	-730.1836	3.334385
3*H*-12-NH_2	-611.880951	6.146295	3*H*-12-OCH_3	-730.180538	11.37366
4*H*-12-NH_2	-611.882799	1.294371	4*H*-12-OCH_3	-730.181163	9.732728
6*H*-12-NH_2	-611.883288	0.010502	6*H*-12-OCH_3	-730.181205	9.622457
7*H*-12-NH_2	-611.880093	8.398974	7*H*-12-OCH_3	-730.183775	2.874922
9*H*-12-NH_2	-611.883292	0	9*H*-12-OCH_3	-730.18487	0

Noted that for R=CH_3, F, CN, NH_2 and OCH_3, Δ*H*(*xH*-12-R)=*H*(*xH*-12-R)-*H*(9*H*-12-R); for R=*t*-Bu, Δ*H*(*xH*-12-R)=*H*(*xH*-12-R)-*H*(1*H*-12-R), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursors with the lowest enthalpies among the six isomers are highlighted in red.

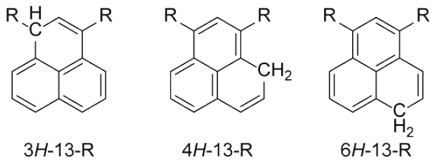


Fig. S6 The precursors of 13-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S6 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 13-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
3*H*-13-CH_3	-579.787743	10.077	3*H*-13-*t*-Bu	-815.470624	0
4*H*-13-CH_3	-579.791581	0	4*H*-13-*t*-Bu	-815.461900	2.993
6*H*-13-CH_3	-579.789430	5.647	6*H*-13-*t*-Bu	-815.463040	16.244
3*H*-13-F	-699.693555	12.686	3*H*-13-CN	-685.687539	37.595
4*H*-13-F	-699.698387	0	4*H*-13-CN	-685.701858	0
6*H*-13-F	-699.696725	4.364	6*H*-13-CN	-685.701665	0.507
3*H*-13-NH_2	-611.868049	43.644	3*H*-13-OCH_3	-730.181731	21.393
4*H*-13-NH_2	-611.884672	0	4*H*-13-OCH_3	-730.189879	0
6*H*-13-NH_2	-611.881880	7.330	6*H*-13-OCH_3	-730.187695	5.734

Noted that for R=CH_3, F, CN, NH_2 and OCH_3, Δ*H*(*xH*-13-R)=*H*(*xH*-13-R)-*H*(4*H*-13-R); for R=*t*-Bu, Δ*H*(*xH*-13-R)=*H*(*xH*-13-R)-*H*(3*H*-13-R), where *x*=3, 4 and 6, and the most stable precursors with the lowest enthalpies among the three isomers are highlighted in red.

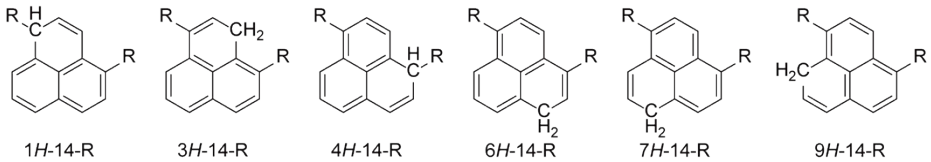


Fig. S7 The precursors of 14-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S7 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 14-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-14-CH_3	-579.785927	16.118	1*H*-14-*t*-Bu	-815.469227	3.106
3*H*-14-CH_3	-579.792066	0	3*H*-14-*t*-Bu	-815.462379	21.085
4*H*-14-CH_3	-579.787247	12.652	4*H*-14-*t*-Bu	-815.470410	0
6*H*-14-CH_3	-579.791246	2.153	6*H*-14-*t*-Bu	-815.465180	13.731
7*H*-14-CH_3	-579.789236	7.430	7*H*-14-*t*-Bu	-815.463683	17.662
9*H*-14-CH_3	-579.791797	0.706	9*H*-14-*t*-Bu	-815.462682	20.290
1*H*-14-F	-699.692919	17.276	1*H*-14-CN	-685.690635	34.011
3*H*-14-F	-699.699499	0	3*H*-14-CN	-685.701868	4.518
4*H*-14-F	-699.693136	16.706	4*H*-14-CN	-685.690438	34.528
6*H*-14-F	-699.698134	3.584	6*H*-14-CN	-685.700924	6.997
7*H*-14-F	-699.697453	5.372	7*H*-14-CN	-685.702416	3.080
9*H*-14-F	-699.699379	0.315	9*H*-14-CN	-685.703589	0
1*H*-14-NH_2	-611.868023	44.954	1*H*-14-OCH_3	-730.178289	34.323
3*H*-14-NH_2	-611.884174	2.549	3*H*-14-OCH_3	-730.191215	0.386
4*H*-14-NH_2	-611.867823	45.479	4*H*-14-OCH_3	-730.180411	28.752
6*H*-14-NH_2	-611.882015	8.218	6*H*-14-OCH_3	-730.191362	0
7*H*-14-NH_2	-611.880927	11.074	7*H*-14-OCH_3	-730.187897	9.097
9*H*-14-NH_2	-611.885145	0	9*H*-14-OCH_3	-730.191184	0.467

Noted that for R=CH_3 and F, Δ*H*(*x*H-14-R)=*H*(*x*H-14-R)-*H*(3*H*-14-R); for R=*t*-Bu, Δ*H*(*x*H-14-R)=*H*(*x*H-14-R)-*H*(4*H*-14-R); for R=CN and NH_2, Δ*H*(*x*H-14-R)=*H*(*x*H-14-R)-*H*(9*H*-14-R); for R=OCH_3, Δ*H*(*x*H-14-R)=*H*(*x*H-14-R)-*H*(6*H*-14-R), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursors with the lowest enthalpies among the six isomers are highlighted in red.

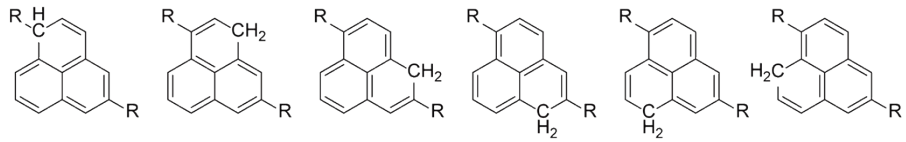


Fig. S8 The precursors of 15-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S8 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 15-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-15-CH_3	-579.789082	14.574	1*H*-15-*t*-Bu	-815.480825	0
3*H*-15-CH_3	-579.792846	4.692	3*H*-15-*t*-Bu	-815.477351	9.121

4*H*-15-CH_3	-579.794434	0.522	4*H*-15-*t*-Bu	-815.478091	7.178
6*H*-15-CH_3	-579.794633	0	6*H*-15-*t*-Bu	-815.478019	7.367
7*H*-15-CH_3	-579.790939	9.699	7*H*-15-*t*-Bu	-815.475950	12.799
9*H*-15-CH_3	-579.793316	3.458	9*H*-15-*t*-Bu	-815.474982	15.341
1*H*-15-F	-699.692581	18.662	1*H*-15-CN	-685.690297	35.704
3*H*-15-F	-699.698136	4.077	3*H*-15-CN	-685.700377	9.239
4*H*-15-F	-699.699689	0	4*H*-15-CN	-685.703896	0
6*H*-15-F	-699.699578	0.291	6*H*-15-CN	-685.703589	0.806
7*H*-15-F	-699.697419	5.960	7*H*-15-CN	-685.701615	5.989
9*H*-15-F	-699.699103	1.539	9*H*-15-CN	-685.702255	4.308
1*H*-15-NH_2	-611.870097	46.561	1*H*-15-OCH_3	-730.180949	37.757
3*H*-15-NH_2	-611.883904	10.310	3*H*-15-OCH_3	-730.191988	8.774
4*H*-15-NH_2	-611.887831	0	4*H*-15-OCH_3	-730.195330	0
6*H*-15-NH_2	-611.886850	2.576	6*H*-15-OCH_3	-730.195160	0.446
7*H*-15-NH_2	-611.882325	14.456	7*H*-15-OCH_3	-730.186457	23.296
9*H*-15-NH_2	-611.885591	5.881	9*H*-15-OCH_3	-730.188982	16.667

Noted that for R=CH_3, ΔH(*xH*-15-R)=*H*(*xH*-15-R)-*H*(6*H*-15-R); for R=*t*-Bu, ΔH(*xH*-15-R)=*H*(*xH*-15-R)-*H*(1*H*-15-R); for R=F, CN, NH_2 and OCH_3, ΔH(*xH*-15-R)=*H*(*xH*-15-R)-*H*(4*H*-15-R), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursors with the lowest enthalpies among the six isomers are highlighted in red.

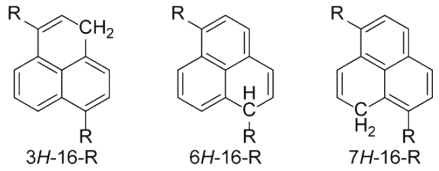


Fig. S9 The precursors of 16-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S9 Enthalpies (*H*(R-H)) and relative enthalpies (ΔH) for the precursors of 16-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	ΔH / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	ΔH / kJ mol^{-1}
3*H*-16-CH_3	-579.790914	0	3*H*-16-*t*-Bu	-815.464179	15.716
6*H*-16-CH_3	-579.787379	9.281	6*H*-16-*t*-Bu	-815.470165	0
7*H*-16-CH_3	-579.790079	2.192	7*H*-16-*t*-Bu	-815.459733	27.389
3*H*-16-F	-699.697825	3.442	3*H*-16-CN	-685.700934	6.065
6*H*-16-F	-699.693055	15.966	6*H*-16-CN	-685.691062	31.984
7*H*-16-F	-699.699136	0	7*H*-16-CN	-685.703244	0
3*H*-16-NH_2	-611.880830	8.113	3*H*-16-OCH_3	-730.190442	0
6*H*-16-NH_2	-611.868377	40.808	6*H*-16-OCH_3	-730.180609	25.817
7*H*-16-NH_2	-611.883920	0	7*H*-16-OCH_3	-730.188346	5.503

Noted that for R=CH_3 and OCH_3, ΔH(*xH*-16-R)=*H*(*xH*-16-R)-*H*(3*H*-16-R); for R=*t*-Bu, ΔH(*xH*-16-R)=*H*(*xH*-16-

R)-*H*(6*H*-16-R); for R=F, CN and NH_2, Δ*H*(*xH*-16-R)=*H*(*xH*-16-R)-*H*(7*H*-16-R), where *x*=3, 6 and 7, and the most stable precursors with the lowest enthalpies among the three isomers are highlighted in red.

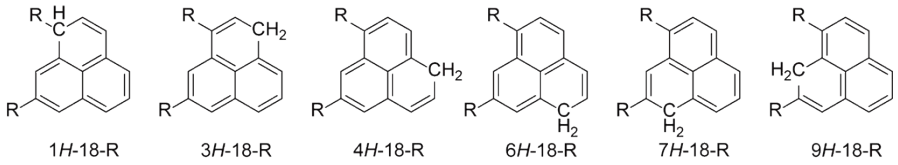


Fig. S10 The precursors of 18-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S10 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 18-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-18-CH_3	-579.788944	17.166	1*H*-18-*t*-Bu	-815.480773	0
3*H*-18-CH_3	-579.792931	6.698	3*H*-18-*t*-Bu	-815.477106	9.628
4*H*-18-CH_3	-579.792361	8.194	4*H*-18-*t*-Bu	-815.476384	11.523
6*H*-18-CH_3	-579.792472	7.903	6*H*-18-*t*-Bu	-815.476518	11.172
7*H*-18-CH_3	-579.793170	6.070	7*H*-18-*t*-Bu	-815.475673	13.390
9*H*-18-CH_3	-579.795482	0	9*H*-18-*t*-Bu	-815.475188	14.663
1*H*-18-F	-699.692641	22.532	1*H*-18-CN	-685.689547	37.610
3*H*-18-F	-699.697966	8.551	3*H*-18-CN	-685.699580	11.269
4*H*-18-F	-699.697662	9.349	4*H*-18-CN	-685.700892	7.824
6*H*-18-F	-699.697896	8.735	6*H*-18-CN	-685.701337	6.656
7*H*-18-F	-699.699581	4.311	7*H*-18-CN	-685.702674	3.145
9*H*-18-F	-699.701223	0	9*H*-18-CN	-685.703872	0
1*H*-18-NH_2	-611.875651	38.387	1*H*-18-OCH_3	-730.180841	39.889
3*H*-18-NH_2	-611.884195	15.955	3*H*-18-OCH_3	-730.192171	10.142
4*H*-18-NH_2	-611.883901	16.727	4*H*-18-OCH_3	-730.188774	19.061
6*H*-18-NH_2	-611.884658	14.740	6*H*-18-OCH_3	-730.189618	16.845
7*H*-18-NH_2	-611.886715	9.339	7*H*-18-OCH_3	-730.186389	25.323
9*H*-18-NH_2	-611.890272	0	9*H*-18-OCH_3	-730.196034	0

Noted that for R=CH_3, F, CN, NH_2 and OCH_3, Δ*H*(*xH*-18-R)=*H*(*xH*-18-R)-*H*(9*H*-18-R) ; for R=*t*-Bu, Δ*H*(*xH*-18-R)=*H*(*xH*-18-R)-*H*(1*H*-18-R), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursors with the lowest enthalpies among the six isomers are highlighted in red.

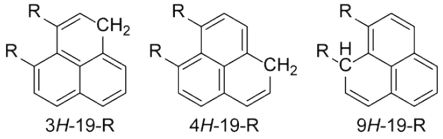


Fig. S11 The precursors of 19-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S11 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 19-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
3*H*-19-CH_3	-579.778673	16.018	3*H*-19-*t*-Bu	-815.433869	55.086
4*H*-19-CH_3	-579.779618	13.537	4*H*-19-*t*-Bu	-815.425927	75.937
9*H*-19-CH_3	-579.784774	0	9*H*-19-*t*-Bu	-815.454850	0
3*H*-19-F	-699.692701	0.131	3*H*-19-CN	-685.690151	6.921
4*H*-19-F	-699.692751	0	4*H*-19-CN	-685.692757	0
9*H*-19-F	-699.692564	0.491	9*H*-19-CN	-685.688088	15.258
3*H*-19-NH_2	-611.881715	1.242	3*H*-19-OCH_3	-730.177967	6.356
4*H*-19-NH_2	-611.882148	0.097	4*H*-19-OCH_3	-730.180388	0
9*H*-19-NH_2	-611.882185	0	9*H*-19-OCH_3	-730.179281	2.906

Noted that for R=CH_3, *t*-Bu and NH_2, Δ*H*(*xH*-19-R)=*H*(*xH*-19-R)-*H*(9*H*-19-R); for R=F, CN and OCH_3, Δ*H*(*xH*-19-R)=*H*(*xH*-19-R)-*H*(4*H*-19-R), where *x*=3, 4 and 9, and the most stable precursors with the lowest enthalpies among the three isomers are highlighted in red.

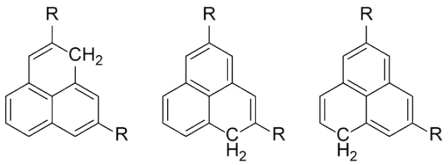


Fig. S12 The precursors of 25-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S12 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 25-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
3*H*-25-CH_3	-579.796216	0.336	3*H*-25-*t*-Bu	-815.489593	0.139
6*H*-25-CH_3	-579.796344	0	6*H*-25-*t*-Bu	-815.489646	0
7*H*-25-CH_3	-579.794134	5.802	7*H*-25-*t*-Bu	-815.488268	3.618
3*H*-25-F	-699.699835	0.449	3*H*-25-CN	-685.703007	0
6*H*-25-F	-699.700006	0	6*H*-25-CN	-685.702720	0.754
7*H*-25-F	-699.698285	4.518	7*H*-25-CN	-685.700602	6.314
3*H*-25-NH_2	-611.890114	1.665	3*H*-25-OCH_3	-730.196790	0.964
6*H*-25-NH_2	-611.890748	0	6*H*-25-OCH_3	-730.197157	0
7*H*-25-NH_2	-611.887088	9.609	7*H*-25-OCH_3	-730.190976	16.228

Noted that for R=CH_3, *t*-Bu, F, NH_2 and OCH_3, Δ*H*(*xH*-25-R)=*H*(*xH*-25-R)-*H*(6*H*-25-R); for R=CN, Δ*H*(*xH*-25-R)=*H*(*xH*-25-R)-*H*(3*H*-25-R), where *x*=3, 6 and 7, and the most stable precursors with the lowest enthalpies among

the three isomers are highlighted in red.

2.2.3 Precursors of tri-substituted PLY-based radicals

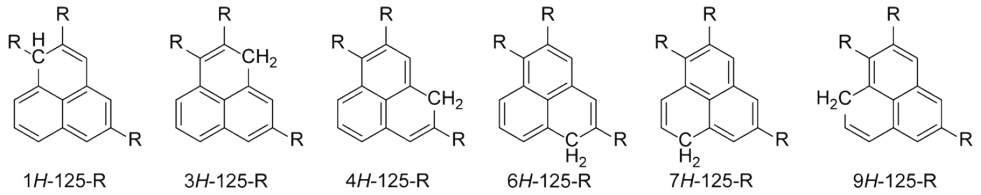


Fig. S13 The precursors of 125-R (R=*t*-Bu).

Table S13 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 125-*t*-Bu.

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-125-*t*-Bu	-972.602263	0
3*H*-125-*t*-Bu	-972.557908	116.454
4*H*-125-*t*-Bu	-972.558791	114.1357
6*H*-125-*t*-Bu	-972.558349	115.2962
7*H*-125-*t*-Bu	-972.560704	109.1131
9*H*-125-*t*-Bu	-972.556020	121.411

Noted that Δ*H*(*x*H-125-*t*-Bu)=*H*(*x*H-125-*t*-Bu)-*H*(1*H*-125-*t*-Bu), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursor with the lowest enthalpy among the six isomers is highlighted in red.

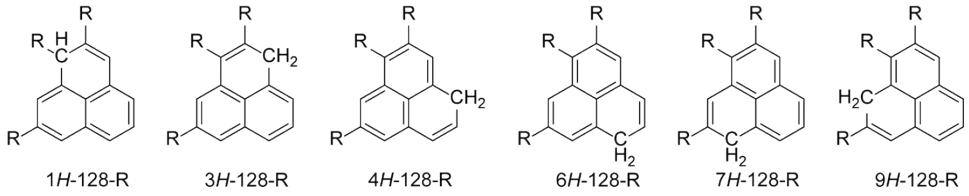


Fig. S14 The precursors of 128-R (R=*t*-Bu).

Table S14 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 128-*t*-Bu.

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-128-*t*-Bu	-972.603247	0
3*H*-128-*t*-Bu	-972.567039	95.06409
4*H*-128-*t*-Bu	-972.564875	100.7457
6*H*-128-*t*-Bu	-972.564862	100.7798
7*H*-128-*t*-Bu	-972.561109	110.6333
9*H*-128-*t*-Bu	-972.556221	123.4668

Noted that Δ*H*(*x*H-128-*t*-Bu)=*H*(*x*H-128-*t*-Bu)-*H*(1*H*-128-*t*-Bu), where *x*=1, 3, 4, 6, 7 and 9, and the most stable

precursor with the lowest enthalpy among the six isomers is highlighted in red.

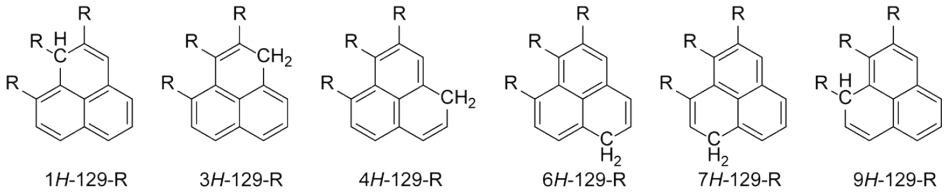


Fig. S15 The precursors of 129-R (R=CH_3, F, CN, NH_2 and OCH_3).

Table S15 Enthalpies (*H*(R-H)) and relative enthalpies (ΔH) for the precursors of 129-R (R=CH_3, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	ΔH / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	ΔH / kJ mol^{-1}
1*H*-129-CH_3	-619.074318	0			
3*H*-129-CH_3	-619.063855	27.471			
4*H*-129-CH_3	-619.062791	30.264			
6*H*-129-CH_3	-619.062806	30.225			
7*H*-129-CH_3	-619.063600	28.140			
9*H*-129-CH_3	-619.071291	7.947			
1*H*-129-F	-798.932320	0	1*H*-129-CN	-777.926751	0
3*H*-129-F	-798.926757	14.606	3*H*-129-CN	-777.925341	3.702
4*H*-129-F	-798.925895	16.869	4*H*-129-CN	-777.926615	0.357
6*H*-129-F	-798.925730	17.302	6*H*-129-CN	-777.926639	0.294
7*H*-129-F	-798.926484	15.322	7*H*-129-CN	-777.924641	5.540
9*H*-129-F	-798.925916	16.814	9*H*-129-CN	-777.923195	9.336
1*H*-129-NH_2	-667.219849	0	1*H*-129-OCH_3	-844.669936	0
3*H*-129-NH_2	-667.214617	13.737	3*H*-129-OCH_3	-844.655472	37.975
4*H*-129-NH_2	-667.215524	11.355	4*H*-129-OCH_3	-844.660179	25.617
6*H*-129-NH_2	-667.215354	11.802	6*H*-129-OCH_3	-844.659420	27.610
7*H*-129-NH_2	-667.217373	6.501	7*H*-129-OCH_3	-844.662515	19.484
9*H*-129-NH_2	-667.215135	12.377	9*H*-129-OCH_3	-844.658923	28.915

Noted that for R=CH_3, F, CN, NH_2 and OCH_3, ΔH(*x*H-129-R)=*H*(*x*H-129-R)-*H*(1*H*-129-R), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursors with the lowest enthalpies among the six isomers are highlighted in red.

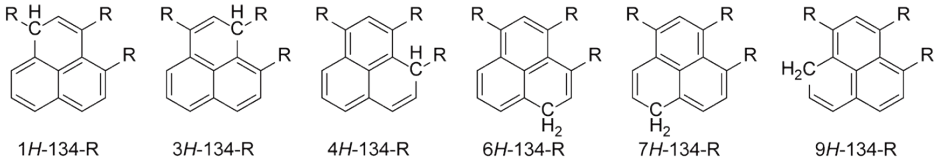


Fig. S16 The precursors of 134-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S16 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 134-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-134-CH_3	-619.063252	24.210	1*H*-134-*t*-Bu	-972.566863	41.882
3*H*-134-CH_3	-619.072473	0	3*H*-134-*t*-Bu	-972.582815	0
4*H*-134-CH_3	-619.072085	1.019	4*H*-134-*t*-Bu	-972.582180	1.667
6*H*-134-CH_3	-619.066115	16.701	6*H*-134-*t*-Bu	-972.563172	51.573
7*H*-134-CH_3	-619.065259	18.940	7*H*-134-*t*-Bu	-972.550429	85.029
9*H*-134-CH_3	-619.067726	15.463	9*H*-134-*t*-Bu	-972.549342	87.883
1*H*-134-F	-798.929270	15.736	1*H*-134-CN	-777.917164	39.115
3*H*-134-F	-798.933824	0.780	3*H*-134-CN	-777.925485	17.265
4*H*-134-F	-798.932589	4.022	4*H*-134-CN	-777.926415	14.824
6*H*-134-F	-798.932582	4.041	6*H*-134-CN	-777.929011	8.008
7*H*-134-F	-798.932319	4.731	7*H*-134-CN	-777.931348	1.872
9*H*-134-F	-798.934151	0	9*H*-134-CN	-777.932061	0
1*H*-134-NH_2	-667.200244	47.136	1*H*-134-OCH_3	-844.657338	27.670
3*H*-134-NH_2	-667.215341	7.498	3*H*-134-OCH_3	-844.667001	2.300
4*H*-134-NH_2	-667.215609	6.795	4*H*-134-OCH_3	-844.665656	5.831
6*H*-134-NH_2	-667.215506	7.065	6*H*-134-OCH_3	-844.665883	5.235
7*H*-134-NH_2	-667.214602	9.439	7*H*-134-OCH_3	-844.665043	7.441
9*H*-134-NH_2	-667.218197	0	9*H*-134-OCH_3	-844.667877	0

Noted that for R=CH_3 and *t*-Bu, Δ*H*(*xH*-134-R)=*H*(*xH*-134-R)-*H*(3*H*-134-R); for R=F, CN, NH_2 and OCH_3, Δ*H*(*xH*-134-R)=*H*(*xH*-134-R)-*H*(9*H*-134-R), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursors with the lowest enthalpies among the six isomers are highlighted in red.

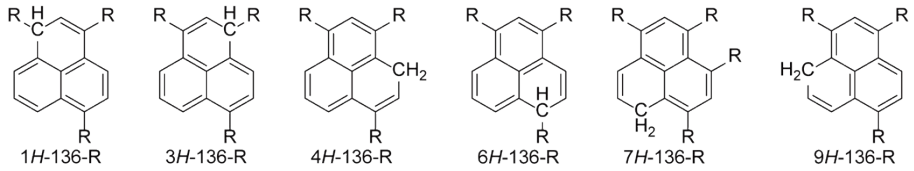


Fig. S17 The precursors of 136-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S17 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 136-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-136-CH_3	-619.075003	10.607	1*H*-136-*t*-Bu	-972.595483	0
3*H*-136-CH_3	-619.074743	11.290	3*H*-136-*t*-Bu	-972.594850	1.662
4*H*-136-CH_3	-619.079043	0	4*H*-136-*t*-Bu	-972.585259	26.843
6*H*-136-CH_3	-619.073322	15.020	6*H*-136-*t*-Bu	-972.593669	4.763

7*H*-136-CH_3	-619.077537	3.954	7*H*-136-*t*-Bu	-972.583495	31.474
9*H*-136-CH_3	-619.077373	4.385	9*H*-136-*t*-Bu	-972.583350	31.855
1*H*-136-F	-798.934291	15.579	1*H*-136-CN	-777.927825	37.928
3*H*-136-F	-798.934216	15.776	3*H*-136-CN	-777.927586	38.555
4*H*-136-F	-798.939082	0	4*H*-136-CN	-777.940709	4.101
6*H*-136-F	-798.932758	16.604	6*H*-136-CN	-777.929645	33.150
7*H*-136-F	-798.938999	0.218	7*H*-136-CN	-777.942271	0
9*H*-136-F	-798.938897	0.486	9*H*-136-CN	-777.941719	1.449
1*H*-136-NH_2	-667.206630	28.728	1*H*-136-OCH_3	-844.669713	20.040
3*H*-136-NH_2	-667.205969	30.464	3*H*-136-OCH_3	-844.662987	37.700
4*H*-136-NH_2	-667.216853	1.888	4*H*-136-OCH_3	-844.677346	0
6*H*-136-NH_2	-667.206408	29.311	6*H*-136-OCH_3	-844.665622	30.781
7*H*-136-NH_2	-667.217572	0	7*H*-136-OCH_3	-844.675424	5.046
9*H*-136-NH_2	-667.216796	2.037	9*H*-136-OCH_3	-844.674952	6.285

Noted that for R=CH_3, F and OCH_3, ΔH(*xH*-136-R)=*H*(*xH*-136-R)-*H*(4*H*-136-R); for R=*t*-Bu, ΔH(*xH*-136-R)=*H*(*xH*-136-R)-*H*(1*H*-136-R); for R=CN and NH_2, ΔH(*xH*-136-R)=*H*(*xH*-136-R)-*H*(7*H*-136-R), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursors with the lowest enthalpies among the six isomers are highlighted in red.

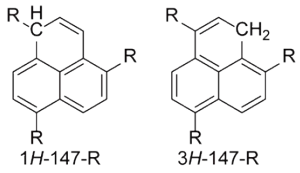


Fig. S18 The precursors of 147-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S18 Enthalpies (*H*(R-H)) and relative enthalpies (ΔH) for the precursors of 147-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	ΔH / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	ΔH / kJ mol^{-1}
1*H*-147-CH_3	-619.073199	16.349	1*H*-147-*t*-Bu	-972.594436	0
3*H*-147-CH_3	-619.079426	0	3*H*-147-*t*-Bu	-972.586834	19.959
1*H*-147-F	-798.933715	17.156	1*H*-147-CN	-777.930183	31.023
3*H*-147-F	-798.940235	0	3*H*-147-CN	-777.941999	0
1*H*-147-NH_2	-667.200167	45.516	1*H*-147-OCH_3	-844.666144	33.638
3*H*-147-NH_2	-667.217503	0	3*H*-147-OCH_3	-844.678956	0

Noted that for R=CH_3, F, CN, NH_2 and OCH_3, ΔH(*xH*-147-R)=*H*(*xH*-147-R)-*H*(3*H*-147-R); for R=*t*-Bu, ΔH(*xH*-147-R)=*H*(*xH*-147-R)-*H*(1*H*-147-R), where *x*=1 and 3, and the most stable precursors with the lowest enthalpies between the two isomers are highlighted in red.

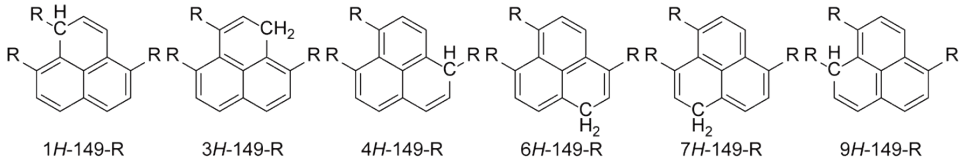


Fig. S19 The precursors of 149-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S19 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 149-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-149-CH_3	-619.070605	3.946	1*H*-149-*t*-Bu	-972.580069	4.967
3*H*-149-CH_3	-619.066097	15.782	3*H*-149-*t*-Bu	-972.558188	62.416
4*H*-149-CH_3	-619.063523	22.540	4*H*-149-*t*-Bu	-972.553994	73.427
6*H*-149-CH_3	-619.066756	14.052	6*H*-149-*t*-Bu	-972.548261	88.479
7*H*-149-CH_3	-619.065573	17.158	7*H*-149-*t*-Bu	-972.560180	57.186
9*H*-149-CH_3	-619.072108	0	9*H*-149-*t*-Bu	-972.581961	0
1*H*-149-F	-798.933249	4.371	1*H*-149-CN	-777.927786	8.974
3*H*-149-F	-798.934914	0	3*H*-149-CN	-777.931504	0
4*H*-149-F	-798.929088	15.296	4*H*-149-CN	-777.920809	27.292
6*H*-149-F	-798.933615	3.418	6*H*-149-CN	-777.931070	0.352
7*H*-149-F	-798.933078	4.820	7*H*-149-CN	-777.930201	2.633
9*H*-149-F	-798.933238	4.400	9*H*-149-CN	-777.928308	7.603
1*H*-149-NH_2	-667.203191	36.011	1*H*-149-OCH_3	-844.663906	10.681
3*H*-149-NH_2	-667.216907	0	3*H*-149-OCH_3	-844.665339	6.918
4*H*-149-NH_2	-667.201963	39.235	4*H*-149-OCH_3	-844.658633	24.525
6*H*-149-NH_2	-667.214519	6.270	6*H*-149-OCH_3	-844.667974	0
7*H*-149-NH_2	-667.207633	24.349	7*H*-149-OCH_3	-844.664766	8.423
9*H*-149-NH_2	-667.215906	2.628	9*H*-149-OCH_3	-844.666365	4.224

Noted that for R=CH_3 and *t*-Bu, Δ*H*(*xH*-149-R)=*H*(*xH*-149-R)-*H*(9*H*-149-R); for R= F, CN and NH_2, Δ*H*(*xH*-149-R)=*H*(*xH*-149-R)-*H*(3*H*-149-R); for R=OCH_3, Δ*H*(*xH*-149-R)=*H*(*xH*-149-R)-*H*(6*H*-149-R), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursors with the lowest enthalpies among the six isomers are highlighted in red.

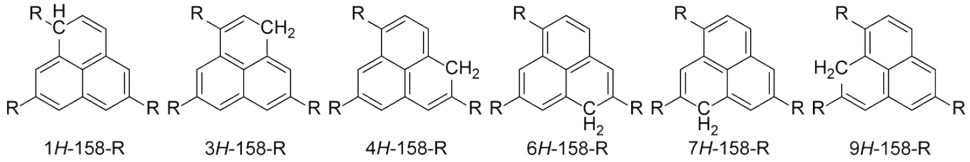


Fig. S20 The precursors of 158-R (R=-*t*-Bu).

Table S20 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 158-*t*-Bu.

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}

1*H*-158-*t*-Bu	-972.618375	0
3*H*-158-*t*-Bu	-972.614020	11.434
4*H*-158-*t*-Bu	-972.614246	10.841
6*H*-158-*t*-Bu	-972.613627	12.466
7*H*-158-*t*-Bu	-972.612501	15.422
9*H*-158-*t*-Bu	-972.608646	25.543

Noted that Δ*H*(*x*H-158-*t*-Bu)=*H*(*x*H-158-*t*-Bu)-*H*(1*H*-158-*t*-Bu), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursor with the lowest enthalpy among the six isomers is highlighted in red.

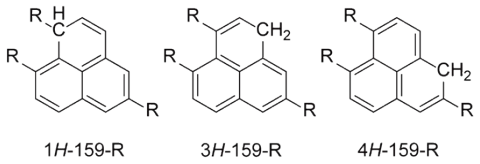


Fig. S21 The precursors of 159-R (R=CH_3, F, CN, NH_2 and OCH_3).

Table S21 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 159-R (R=CH_3, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-159-CH_3	-619.073803	0			
3*H*-159-CH_3	-619.067743	15.911			
4*H*-159-CH_3	-619.070875	7.687			
1*H*-159-F	-798.932374	7.228	1*H*-159-CN	-777.927363	17.179
3*H*-159-F	-798.933042	5.474	3*H*-159-CN	-777.929749	10.914
4*H*-159-F	-798.935127	0	4*H*-159-CN	-777.933906	0
1*H*-159-NH_2	-667.215504	11.001	1*H*-159-OCH_3	-844.663573	21.891
3*H*-159-NH_2	-667.215744	10.371	3*H*-159-OCH_3	-844.663600	21.821
4*H*-159-NH_2	-667.219694	0	4*H*-159-OCH_3	-844.671911	0

Noted that for R=CH_3, Δ*H*(*x*H-159-R)=*H*(*x*H-159-R)-*H*(1*H*-159-R); for R=F, CN, NH_2 and OCH_3, Δ*H*(*x*H-159-R)=*H*(*x*H-159-R)-*H*(4*H*-159-R), where *x*=1, 3 and 4, and the most stable precursors with the lowest enthalpies among the six isomers are highlighted in red.

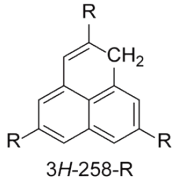


Fig. S22 The precursor of 258-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S22 Enthalpies (*H*(R-H)) for the precursors of 258-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Molecule	*H*(R-H) / a.u.
3*H*-258-CH_3	-619.085166
3*H*-258-*t*-Bu	-972.626150
3*H*-258-F	-798.940682
3*H*-258-CN	-777.941631
3*H*-258-NH_2	-667.225675
1*H*-258-OCH_3	-844.683589

2.2.4 Precursors of tetra-substituted PLY-based radicals

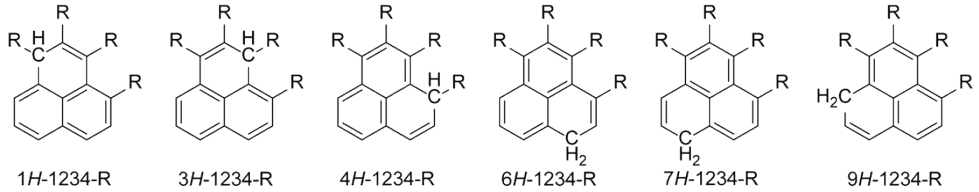


Fig. S23 The precursors of 1234-R (R=CH_3).

Table S23 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 1234-CH_3.

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-1234-CH_3	-658.347556	23.078
3*H*-1234-CH_3	-658.356346	0
4*H*-1234-CH_3	-658.350874	14.367
6*H*-1234-CH_3	-658.343483	33.772
7*H*-1234-CH_3	-658.341363	39.338
9*H*-1234-CH_3	-658.343758	33.050

Noted that Δ*H*(*x*H-1234-CH_3)=*H*(*x*H-1234-CH_3)-*H*(3*H*-1234-CH_3), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursor with the lowest enthalpy among the six isomers is highlighted in red.

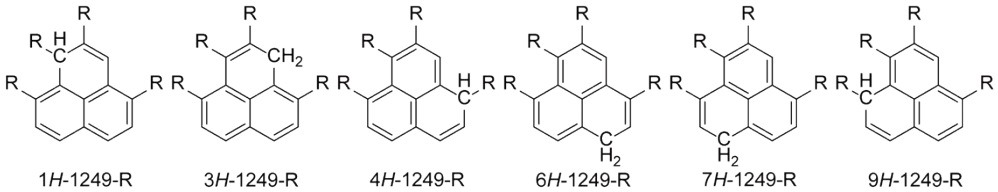


Fig. S24 The precursors of 1249-R (R=CH_3, F, CN, NH_2 and OCH_3).

Table S24 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 1249-R (R= F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-1249-F	-898.172899	0	1*H*-1249-CN	-870.163696	1.342
3*H*-1249-F	-898.168710	10.998	3*H*-1249-CN	-870.164207	0
4*H*-1249-F	-898.161577	29.726	4*H*-1249-CN	-870.152592	30.495
6*H*-1249-F	-898.166259	17.433	6*H*-1249-CN	-870.162973	3.240
7*H*-1249-F	-898.166595	16.551	7*H*-1249-CN	-870.162213	5.235
9*H*-1249-F	-898.166327	17.255	9*H*-1249-CN	-870.161020	8.367
1*H*-1249-NH_2	-722.551389	0	1*H*-1249-OCH_3	-959.155421	0
3*H*-1249-NH_2	-722.549877	3.970	3*H*-1249-OCH_3	-959.143300	31.824
4*H*-1249-NH_2	-722.541108	26.993	4*H*-1249-OCH_3	-959.138103	45.468
6*H*-1249-NH_2	-722.547473	10.281	6*H*-1249-OCH_3	-959.147390	21.085
7*H*-1249-NH_2	-722.549174	5.815	7*H*-1249-OCH_3	-959.149173	16.404
9*H*-1249-NH_2	-722.548159	8.480	9*H*-1249-OCH_3	-959.146846	22.514

Noted that for R=F, NH_2 and OCH_3, Δ*H*(*x*H-1249-R)=*H*(*x*H-1249-R)-*H*(1*H*-1249-R); for R=CN, Δ*H*(*x*H-1249-R)=*H*(*x*H-1249-R)-*H*(3*H*-1249-R), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursors with the lowest enthalpies among the six isomers are highlighted in red.

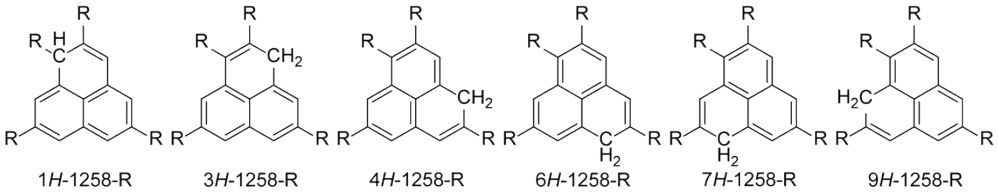


Fig. S25 The precursors of 1258-R (R=-*t*-Bu).

Table S25 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 1258-*t*-Bu.

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-1258-*t*-Bu	-1129.739741	0
3*H*-1258-*t*-Bu	-1129.703389	95.442
4*H*-1258-*t*-Bu	-1129.693719	120.831
6*H*-1258-*t*-Bu	-1129.701709	99.853
7*H*-1258-*t*-Bu	-1129.697679	110.434
9*H*-1258-*t*-Bu	-1129.693082	122.503

Noted that Δ*H*(*x*H-1258-*t*-Bu)=*H*(*x*H-1258-*t*-Bu)-*H*(1*H*-1258-*t*-Bu), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursor with the lowest enthalpy among the six isomers is highlighted in red.

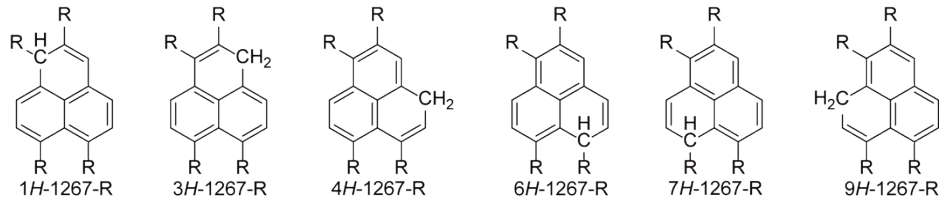


Fig. S26 The precursors of 1267-R (R=CH_3, F, CN, NH_2 and OCH_3).

Table S26 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 1267-R (R= F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-1267-F	-898.168211	0	1*H*-1267-CN	-870.157442	22.028
3*H*-1267-F	-898.167272	2.465	3*H*-1267-CN	-870.165832	0
4*H*-1267-F	-898.165836	6.236	4*H*-1267-CN	-870.163774	5.403
6*H*-1267-F	-898.165459	7.225	6*H*-1267-CN	-870.161687	10.883
7*H*-1267-F	-898.166234	5.191	7*H*-1267-CN	-870.161432	11.552
9*H*-1267-F	-898.168166	0.118	9*H*-1267-CN	-870.165130	1.843
1*H*-1267-NH_2	-722.544266	18.901	1*H*-1267-OCH_3	-959.148605	0
3*H*-1267-NH_2	-722.547409	10.649	3*H*-1267-OCH_3	-959.146159	6.422
4*H*-1267-NH_2	-722.546823	12.188	4*H*-1267-OCH_3	-959.142877	15.039
6*H*-1267-NH_2	-722.548415	8.008	6*H*-1267-OCH_3	-959.143344	13.813
7*H*-1267-NH_2	-722.549207	5.928	7*H*-1267-OCH_3	-959.145287	8.711
9*H*-1267-NH_2	-722.551465	0	9*H*-1267-OCH_3	-959.145996	6.850

Noted that for R=F and OCH_3, Δ*H*(*xH*-1267-R)=*H*(*xH*-1267-R)-*H*(1*H*-1267-R); for R=CN, Δ*H*(*xH*-1267-R)=*H*(*xH*-1267-R)-*H*(3*H*-1267-R); for R=NH_2, Δ*H*(*xH*-1267-R)=*H*(*xH*-1267-R)-*H*(9*H*-1267-R), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursors with the lowest enthalpies among the six isomers are highlighted in red.

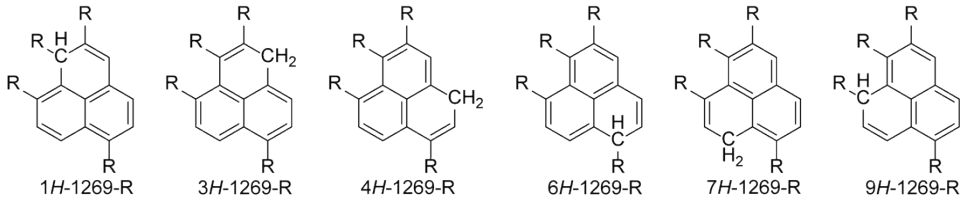


Fig. S27 The precursors of 1269-R (R=CH_3, F, CN, NH_2 and OCH_3).

Table S27 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 1269-R (R= F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-1269-F	-898.172591	0.000	1*H*-1269-CN	-870.164831	0.000
3*H*-1269-F	-898.167008	14.658	3*H*-1269-CN	-870.164022	2.124

4*H*-1269-F	-898.166494	16.008	4*H*-1269-CN	-870.163682	3.017
6*H*-1269-F	-898.161395	29.395	6*H*-1269-CN	-870.153257	30.388
7*H*-1269-F	-898.168201	11.526	7*H*-1269-CN	-870.163700	2.969
9*H*-1269-F	-898.166132	16.958	9*H*-1269-CN	-870.161005	10.045
1*H*-1269-NH_2	-722.552267	0.000	1*H*-1269-OCH_3	-959.157065	0.000
3*H*-1269-NH_2	-722.547083	13.611	3*H*-1269-OCH_3	-959.142447	38.380
4*H*-1269-NH_2	-722.547720	11.938	4*H*-1269-OCH_3	-959.147821	24.270
6*H*-1269-NH_2	-722.540297	31.427	6*H*-1269-OCH_3	-959.137135	52.326
7*H*-1269-NH_2	-722.551411	2.247	7*H*-1269-OCH_3	-959.149166	20.739
9*H*-1269-NH_2	-722.546485	15.181	9*H*-1269-OCH_3	-959.143826	34.759

Noted that for R=F, CN, NH_2 and OCH_3, ΔH(*x*H-1269-R)=*H*(*x*H-1269-R)-*H*(1*H*-1269-R), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursors with the lowest enthalpies among the six isomers are highlighted in red.

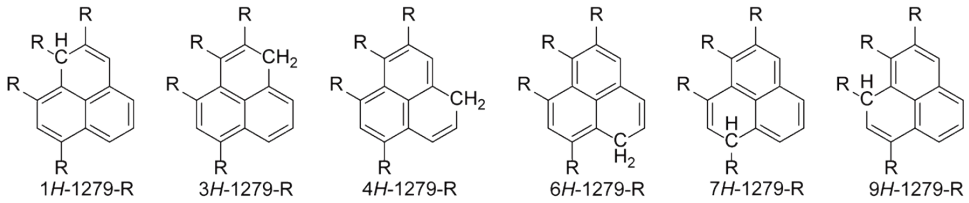


Fig. S28 The precursors of 1279-R (R=CH_3).

Table S28 Enthalpies (*H*(R-H)) and relative enthalpies (ΔH) for the precursors of 1279-CH_3.

Position of H	*H*(R-H) / a.u.	ΔH / kJ mol^{-1}
1*H*-1279-CH_3	-658.361662	0
3*H*-1279-CH_3	-658.351382	26.990
4*H*-1279-CH_3	-658.348657	34.145
6*H*-1279-CH_3	-658.351042	27.883
7*H*-1279-CH_3	-658.345804	41.635
9*H*-1279-CH_3	-658.358944	7.136

Noted that ΔH(*x*H-1279-CH_3)=*H*(*x*H-1279-CH_3)-*H*(1*H*-1279-CH_3), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursor with the lowest enthalpy among the six isomers is highlighted in red.

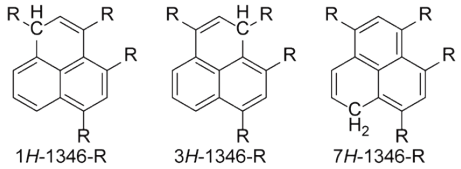


Fig. S29 The precursors of 1346-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S29 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 1346-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-1346-CH_3	-658.350647	23.343	1*H*-1346-*t*-Bu	-1159.689882	45.799
3*H*-1346-CH_3	-658.359538	0	3*H*-1346-*t*-Bu	-1159.707326	0
7*H*-1346-CH_3	-658.353397	16.153	7*H*-1346-*t*-Bu	-1159.670331	97.130
1*H*-1346-F	-898.169053	15.177	1*H*-1346-CN	-870.154231	38.109
3*H*-1346-F	-898.173627	0.168	3*H*-1346-CN	-870.162255	17.042
7*H*-1346-F	-898.173691	0	7*H*-1346-CN	-870.168746	0
1*H*-1346-NH_2	-722.540915	25.173	1*H*-1346-OCH_3	-959.145147	23.795
3*H*-1346-NH_2	-722.548668	4.810	3*H*-1346-OCH_3	-959.154210	0
7*H*-1346-NH_2	-722.550500	0	7*H*-1346-OCH_3	-959.152432	4.668

Noted that for R=CH_3, *t*-Bu and OCH_3, Δ*H*(*x*H-1346-R)=*H*(*x*H-1346-R)-*H*(3*H*-1346-R); for R= F, CN and NH_2, Δ*H*(*x*H-1346-R)=*H*(*x*H-1346-R)-*H*(7*H*-1346-R), where *x*=1, 3 and 7, and the most stable precursors with the lowest enthalpies among the three isomers are highlighted in red.

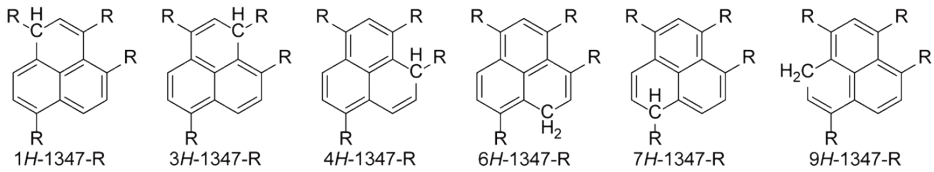


Fig. S30 The precursors of 1347-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S30 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 1347-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-1347-CH_3	-658.350147	25.158	1*H*-1347-*t*-Bu	-1159.692911	39.109
3*H*-1347-CH_3	-658.359729	0	3*H*-1347-*t*-Bu	-1159.707807	0
4*H*-1347-CH_3	-658.357881	4.852	4*H*-1347-*t*-Bu	-1159.705285	6.622
6*H*-1347-CH_3	-658.353488	16.386	6*H*-1347-*t*-Bu	-1159.687596	53.064
7*H*-1347-CH_3	-658.349376	27.182	7*H*-1347-*t*-Bu	-1159.679196	75.118
9*H*-1347-CH_3	-658.354917	15.634	9*H*-1347-*t*-Bu	-1159.673065	91.215
1*H*-1347-F	-898.169809	13.191	1*H*-1347-CN	-870.155184	35.959
3*H*-1347-F	-898.174393	1.155	3*H*-1347-CN	-870.163737	13.503
4*H*-1347-F	-898.173191	4.311	4*H*-1347-CN	-870.164158	15.476
6*H*-1347-F	-898.174682	0.396	6*H*-1347-CN	-870.168146	1.927
7*H*-1347-F	-898.168751	15.968	7*H*-1347-CN	-870.157333	30.317
9*H*-1347-F	-898.174833	0	9*H*-1347-CN	-870.168880	0
1*H*-1347-NH_2	-722.535797	39.304	1*H*-1347-OCH_3	-959.145171	26.625

3*H*-1347-NH_2	-722.549104	4.366	3*H*-1347-OCH_3	-959.155154	0.415
4*H*-1347-NH_2	-722.548091	7.026	4*H*-1347-OCH_3	-959.151403	10.263
6*H*-1347-NH_2	-722.550767	0	6*H*-1347-OCH_3	-959.152729	6.782
7*H*-1347-NH_2	-722.534370	43.050	7*H*-1347-OCH_3	-959.144023	29.639
9*H*-1347-NH_2	-722.549989	2.043	9*H*-1347-OCH_3	-959.155315	0

Noted that for R=CH_3 and *t*-Bu, Δ*H*(*xH*-1347-R)=*H*(*xH*-1347-R)-*H*(3*H*-1347-R); for R= F, CN and OCH_3, Δ*H*(*xH*-1347-R)=*H*(*xH*-1347-R)-*H*(9*H*-1347-R); for R=NH_2, Δ*H*(*xH*-1347-R)=*H*(*xH*-1347-R)-*H*(6*H*-1347-R), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursors with the lowest enthalpies among the six isomers are highlighted in red.

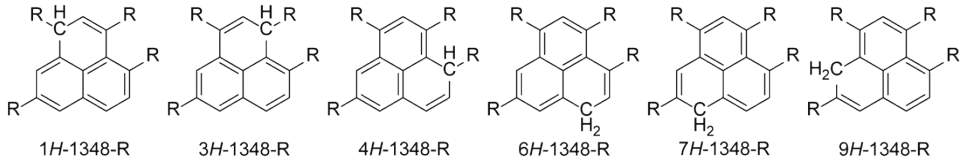


Fig. S31 The precursors of 1348-R (R=CH_3).

Table S31 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 1348-CH_3.

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-1348-CH_3	-658.352310	24.031
3*H*-1348-CH_3	-658.361463	0
4*H*-1348-CH_3	-658.361128	0.880
6*H*-1348-CH_3	-658.355140	16.601
7*H*-1348-CH_3	-658.356483	13.075
9*H*-1348-CH_3	-658.358962	6.566

Noted that Δ*H*(*xH*-1348-CH_3)=*H*(*xH*-1348-CH_3)-*H*(3*H*-1348-CH_3), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursor with the lowest enthalpy among the six isomers is highlighted in red.

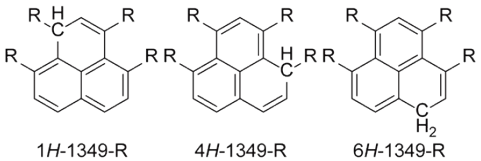


Fig. S32 The precursors of 1349-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S32 Enthalpies (H(R-H)) and relative enthalpies (ΔH) for the precursors of 1349-R (R=CH3, t-Bu, F, CN, NH2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}

1*H*-1349-CH_3	-658.348430	0	1*H*-1349-*t*-Bu	-1159.673729	0
4*H*-1349-CH_3	-658.348321	0.286	4*H*-1349-*t*-Bu	-1159.663153	27.846
6*H*-1349-CH_3	-658.341755	17.525	6*H*-1349-*t*-Bu	-1159.640559	87.088
1*H*-1349-F	-898.169553	0	1*H*-1349-CN	-870.153336	9.363
4*H*-1349-F	-898.168416	2.985	4*H*-1349-CN	-870.154884	5.298
6*H*-1349-F	-898.167741	4.757	6*H*-1349-CN	-870.156902	0
1*H*-1349-NH_2	-722.535251	37.679	1*H*-1349-OCH_3	-959.142803	3.657
4*H*-1349-NH_2	-722.549602	0	4*H*-1349-OCH_3	-959.144196	0
6*H*-1349-NH_2	-722.548231	3.600	6*H*-1349-OCH_3	-959.141803	6.283

Noted that for R=CH_3, *t*-Bu and F, ΔH(*xH*-1349-R)=*H*(*xH*-1349-R)-*H*(1*H*-1349-R); for R=CN, ΔH(*xH*-1349-R)=*H*(*xH*-1349-R)-*H*(6*H*-1349-R); for R=NH_2 and OCH_3, ΔH(*xH*-1349-R)=*H*(*xH*-1349-R)-*H*(4*H*-1349-R), where *x*=1, 4 and 6, and the most stable precursors with the lowest enthalpies among the three isomers are highlighted in red.

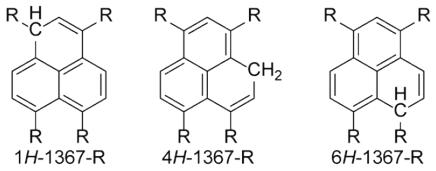


Fig. S33 The precursors of 1367-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S33 Enthalpies (*H*(R-H)) and relative enthalpies (ΔH) for the precursors of 1367-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	ΔH / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	ΔH / kJ mol^{-1}
1*H*-1367-CH_3	-658.350692	18.990	1*H*-1367-*t*-Bu	-1159.679877	64.283
4*H*-1367-CH_3	-658.352950	13.062	4*H*-1367-*t*-Bu	-1159.686343	47.306
6*H*-1367-CH_3	-658.357925	0	6*H*-1367-*t*-Bu	-1159.704361	0
1*H*-1367-F	-898.170097	11.143	1*H*-1367-CN	-870.155952	31.640
4*H*-1367-F	-898.174341	0	4*H*-1367-CN	-870.168003	0
6*H*-1367-F	-898.172984	3.563	6*H*-1367-CN	-870.164877	8.207
1*H*-1367-NH_2	-722.533568	42.026	1*H*-1367-OCH_3	-959.147579	10.636
4*H*-1367-NH_2	-722.549575	0	4*H*-1367-OCH_3	-959.151630	0
6*H*-1367-NH_2	-722.548963	1.607	6*H*-1367-OCH_3	-959.151401	0.601

Noted that for R=CH_3 and *t*-Bu, ΔH(*xH*-1367-R)=*H*(*xH*-1367-R)-*H*(6*H*-1367-R); for R=F, CN, NH_2 and OCH_3, ΔH(*xH*-1367-R)=*H*(*xH*-1367-R)-*H*(4*H*-1367-R), where *x*=1, 4 and 6, and the most stable precursors with the lowest enthalpies among the three isomers are highlighted in red.

2.2.5 Precursors of penta-substituted PLY-based radicals

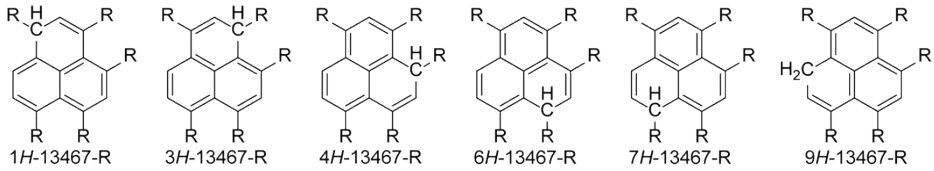


Fig. S34 The precursors of 13467-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S34 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 13467-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}	Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-13467-CH_3	-697.626386	24.921	1*H*-13467-*t*-Bu	-1586.776602	65.018
3*H*-13467-CH_3	-697.635581	0.780	3*H*-13467-*t*-Bu	-1586.791520	25.851
4*H*-13467-CH_3	-697.635508	0.971	4*H*-13467-*t*-Bu	-1586.801027	0.890
6*H*-13467-CH_3	-697.635878	0	6*H*-13467-*t*-Bu	-1586.801366	0
7*H*-13467-CH_3	-697.634229	4.329	7*H*-13467-*t*-Bu	-1586.791373	26.237
9*H*-13467-CH_3	-697.628801	18.581	9*H*-13467-*t*-Bu	-1586.769755	82.995
1*H*-13467-F	-997.404655	15.529	1*H*-13467-CN	-962.379941	34.134
3*H*-13467-F	-997.409427	0	3*H*-13467-CN	-962.388915	10.581
4*H*-13467-F	-997.409259	0.441	4*H*-13467-CN	-962.388257	15.300
6*H*-13467-F	-997.409275	0.399	6*H*-13467-CN	-962.388632	11.316
7*H*-13467-F	-997.408142	3.374	7*H*-13467-CN	-962.389645	8.656
9*H*-13467-F	-997.409028	1.048	9*H*-13467-CN	-962.392942	0
1*H*-13467-NH_2	-777.873834	24.375	1*H*-13467-OCH_3	-1073.623056	25.956
3*H*-13467-NH_2	-777.882233	2.324	3*H*-13467-OCH_3	-1073.632942	0
4*H*-13467-NH_2	-777.881527	4.177	4*H*-13467-OCH_3	-1073.630178	7.257
6*H*-13467-NH_2	-777.883019	0.260	6*H*-13467-OCH_3	-1073.630740	5.781
7*H*-13467-NH_2	-777.882553	1.483	7*H*-13467-OCH_3	-1073.629622	8.717
9*H*-13467-NH_2	-777.883118	0	9*H*-13467-OCH_3	-1073.628735	11.045

Noted that for R=CH_3 and *t*-Bu, Δ*H*(*xH*-13467-R)=*H*(*xH*-13467-R)-*H*(6*H*-13467-R); for R=F and OCH_3, Δ*H*(*xH*-13467-R)=*H*(*xH*-13467-R)-*H*(3*H*-13467-R); for R=CN and NH_2, Δ*H*(*xH*-13467-R)=*H*(*xH*-13467-R)-*H*(3*H*-13467-R), where *x*=1, 3, 4, 6, 7 and 9, and the most stable precursors with the lowest enthalpies among the SIX isomers are highlighted in red.

2.2.6 Precursors of hexa-substituted PLY-based radicals

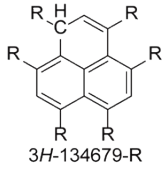


Fig. S35 The precursor of 134679-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Table S35 Enthalpies (*H*(R-H)) for the precursors of 134679-R (R=CH_3, *t*-Bu, F, CN, NH_2 and OCH_3).

Molecule	*H*(R-H) / a.u.
3*H*-134679-CH_3	-736.911861
3*H*-134679-*t*-Bu	-1443.883798
3*H*-134679-F	-1096.644070
3*H*-134679-CN	-1054.615032
3*H*-134679-NH_2	-833.201852
3*H*-134679-OCH_3	-1188.108433

2.3 Precursors of the PLY-based radicals with two kinds of substituents

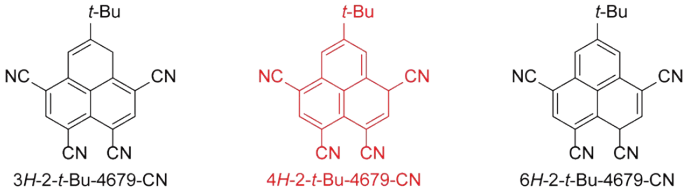


Fig. S36 The precursors of 2-*t*-Bu-4679-CN. Noted that the most stable precursor is highlighted in red.

Table S36 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 2-*t*-Bu-4679-CN.

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
3*H*-2-*t*-Bu-4679-CN	-1027.308628	0
4*H*-2-*t*-Bu-4679-CN	-1027.293298	40.249
6*H*-2-*t*-Bu-4679-CN	-1027.301415	18.946

Noted that Δ*H*(*x*H-2-*t*-Bu-4679-CN)=*H*(*x*H-2-*t*-Bu-4679-CN)-*H*(3*H*-2-*t*-Bu-4679-CN), where *x*=3, 4, and 6, and the most stable precursor with the lowest enthalpies is highlighted in red.

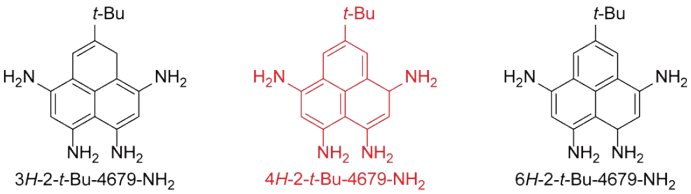


Fig. S37 The precursors of 2-*t*-Bu-4679-NH_2. Noted that the most stable precursor is highlighted in red.

Table S37 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 2-*t*-Bu-4679-NH_2.

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
3*H*-2-*t*-Bu-4679-NH_2	-879.686976	0
4*H*-2-*t*-Bu-4679-NH_2	-879.677592	24.638
6*H*-2-*t*-Bu-4679-NH_2	-879.684416	6.721

Noted that Δ*H*(*x*H-2-*t*-Bu-4679-NH_2)=*H*(*x*H-2-*t*-Bu-4679-NH_2)-*H*(3*H*-2-*t*-Bu-4679-NH_2), where *x*=3, 4, and 6, and the most stable precursor with the lowest enthalpies is highlighted in red.

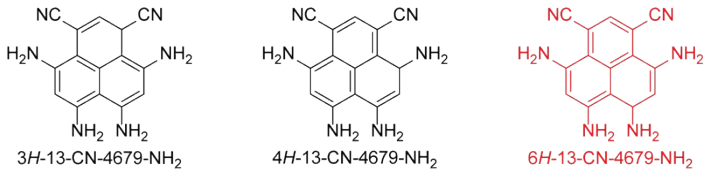


Fig. S38 The precursors of 13-CN-4679-NH_2. Noted that the most stable precursor is highlighted in red.

Table S38 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 13-CN-4679-NH_2.

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
3*H*-13-CN-4679-NH_2	-907.024588	5.414
4*H*-13-CN-4679-NH_2	-907.023141	9.213
6*H*-13-CN-4679-NH_2	-907.026650	0

Noted that Δ*H*(*x*H-13-CN-4679-NH_2)=*H*(*x*H-13-CN-4679-NH_2)-*H*(6*H*-13-CN-4679-NH_2), where *x*=3, 4, and 6, and the most stable precursor with the lowest enthalpies is highlighted in red.

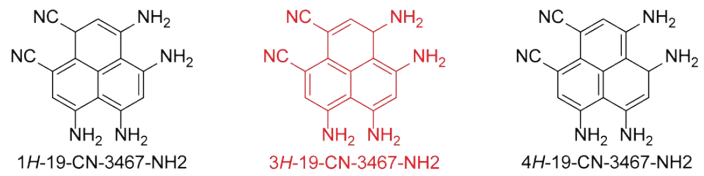


Fig. S39 The precursors of 19-CN-3467-NH_2. Noted that the most stable precursor is highlighted in red.

Table S39 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 19-CN-3467-NH_2.

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-19-CN-3467-NH_2	-907.024115	5.729
3*H*-19-CN-3467-NH_2	-907.026294	0
4*H*-19-CN-3467-NH_2	-907.026037	0.675

Noted that Δ*H*(*x*H-19-CN-3467-NH_2)=*H*(*x*H-19-CN-3467-NH_2)-*H*(3*H*-19-CN-3467-NH_2), where *x*=1, 3, and 4, and

the most stable precursor with the lowest enthalpies is highlighted in red.

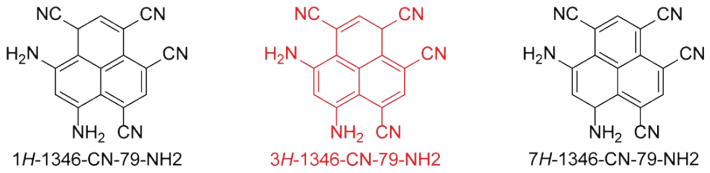


Fig. S40 The precursors of 1346-CN-79-NH_2. Noted that the most stable precursor is highlighted in red.

Table S40 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 1346-CN-79-NH_2.

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
1*H*-1346-CN-79-NH_2	-980.826830	13.157
3*H*-1346-CN-79-NH_2	-980.831830	0
7*H*-1346-CN-79-NH_2	-980.816145	41.181

Noted that Δ*H*(*xH*-1346-CN-79-NH_2)=*H*(*xH*-1346-CN-79-NH_2)-*H*(3*H*-1346-CN-79-NH_2), where *x*=1, 3, and 7, and the most stable precursor with the lowest enthalpies is highlighted in red.

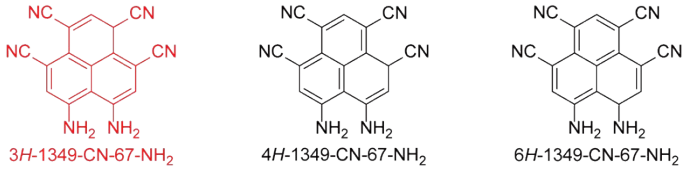


Fig. S41 The precursors of 1349-CN-67-NH_2. Noted that the most stable precursor is highlighted in red.

Table S41 Enthalpies (*H*(R-H)) and relative enthalpies (Δ*H*) for the precursors of 1349-CN-67-NH_2.

Position of H	*H*(R-H) / a.u.	Δ*H* / kJ mol^{-1}
3*H*-1349-CN-67-NH_2	-980.825023	0
4*H*-1349-CN-67-NH_2	-980.822701	6.096
6*H*-1349-CN-67-NH_2	-980.824578	1.168

Noted that Δ*H*(*xH*-1349-CN-67-NH_2)=*H*(*xH*-1349-CN-67-NH_2)-*H*(3*H*-1349-CN-67-NH_2), where *x*=3, 4, and 6, and the most stable precursor with the lowest enthalpies is highlighted in red.

3. Enthalpies of the radicals

Table S42 Enthalpies (*H*(R▪)) of PLY-based radicals with identical substituents.

R	CH_3	*t*-Bu	F	CN	NH_2	OCH_3
1-R	-539.915597	-657.750061	-599.865884	-592.870183	-555.960015	-615.115475

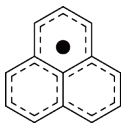
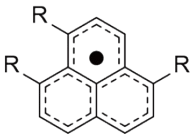
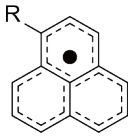
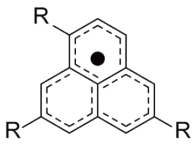
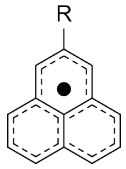
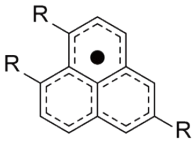
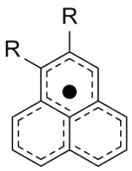
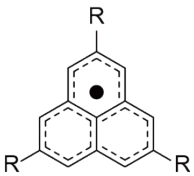
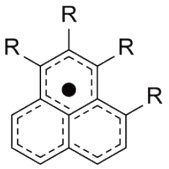
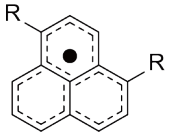
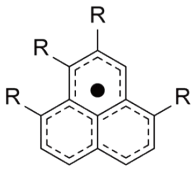
2-R	-539.913503	-657.761155	-599.865616	-592.867421	-555.959858	-615.111822
12-R	-579.197890	-814.840465	-699.099356	-685.106298	-611.290986	-729.591916
13-R	-579.200247	-814.874214	-699.105676	-685.111589	-611.294419	-729.598974
14-R	-579.200220	-814.874930	-699.106632	-685.112655	-611.294120	-729.599682
15-R	-579.201084	-814.886332	-699.106268	-685.110322	-611.294353	-729.599147
16-R	-579.200084	-814.874077	-699.106575	-685.112657	-611.293794	-729.599404
18-R	-579.201168	-814.885990	-699.106386	-685.109708	-611.294855	-729.599431
19-R	-579.189400	-814.839385	-699.101964	-685.103030	-611.293831	-729.590190
25-R	-579.201989	-814.897027	-699.105993	-685.107485	-611.294495	-729.598571
125-R	--	-971.970706	--	--	--	--
128-R	--	-971.970444	--	--	--	--
129-R	-618.473006	--	-798.335168	-777.336376	-666.628231	-844.071154
134-R	-618.476875	-971.965826	-798.341515	-777.342131	-666.627577	-844.076465
136-R	-618.487704	-971.997559	-798.346222	-777.351773	-666.627592	-844.085660
147-R	-618.487771	-971.999067	-798.347203	-777.352713	-666.627630	-844.086779
149-R	-618.476443	-971.961275	-798.342453	-777.343268	-666.626742	-844.076673
158-R	--	-972.022304	--	--	--	--
159-R	-618.478097	--	-798.342120	-777.341320	-666.627914	-844.076591
258-R	-618.490443	-972.033020	-798.346079	-777.345344	-666.629078	-844.085707
1234-R	-657.75327	--	--	--	--	--
1249-R	--	--	-897.575488	-869.574329	-721.96063	-958.558093
1258-R	--	-1129.10667	--	--	--	--
1267-R	--	--	-897.575337	-869.575979	-721.96064	-958.556302
1269-R	--	--	-897.575411	-869.574897	-721.96064	-958.557686
1279-R	-657.7606	--	--	--	--	--
1346-R	-657.764295	-1129.088096	-897.580965	-869.579240	-721.960487	-958.562237
1347-R	-657.763869	-1129.090175	-897.581893	-869.580315	-721.960100	-958.562839
1348-R	-657.76548	--	--	--	--	--
1349-R	-657.752054	-1129.056504	-897.576940	-869.570550	-721.959166	-958.552559
1367-R	-657.763612	-1129.088052	-897.581793	-869.580412	-721.959379	-958.562231
13467-R	-697.039070	-1586.179547	-996.816154	-961.805889	-777.291619	-1073.038001
134679-R	-736.313748	-1443.275157	-1096.050109	-1054.029559	-832.622186	-1187.515029

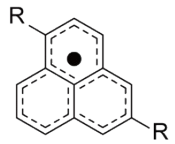
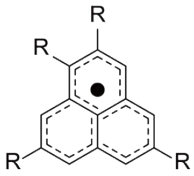
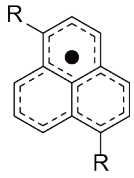
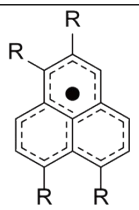
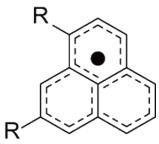
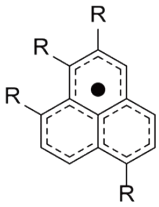
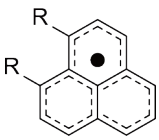
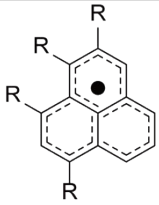
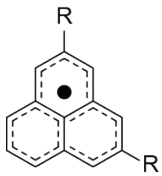
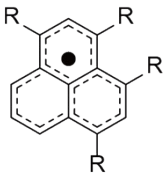
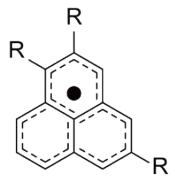
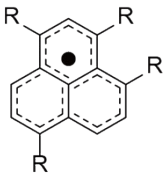
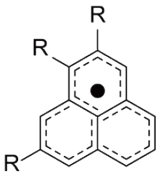
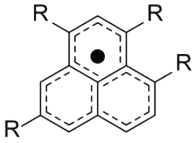
Table S43 Enthalpies (H(R▪)) of the PLY-based radicals with two kinds of substituents.

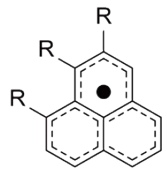
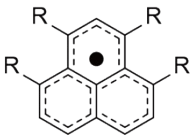
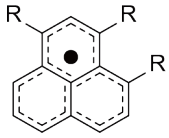
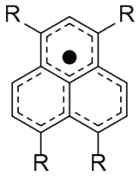
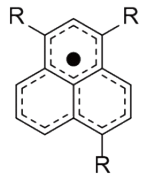
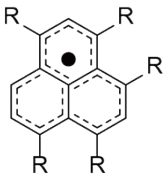
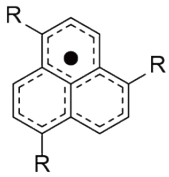
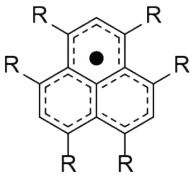
Molecule	H(R▪) / a.u.
2-*t*-Bu-4679-CN	-1026.718150
2-*t*-Bu-4679-NH_2	-879.096493
13-CN-4679-NH_2	-906.453069
19-CN-3467-NH_2	-906.444746
1346-CN-79-NH_2	-980.254780
1349-CN-67-NH_2	-980.246184

4. C-H BDEs and RSEs

Table S44 C-H BDEs of the most stable precursors and RSEs for PLY-based radicals. Noted that the radicals more stable than PLY are marked in red.

Molecule	R	BDE (kJ mol^{-1})	RSE (kJ mol^{-1})	Molecule	R	BDE (kJ mol^{-1})	RSE (kJ mol^{-1})
 PLY	--	245.088	0	 149-R (194-R)	CH_3	256.650	-11.563
					t-Bu	322.343	-77.255
					F	248.238	-3.151
					CN	236.358	8.730
					NH_2	242.210	2.878
					OCH_3	245.193	-0.105
 1-R	CH_3	246.569	-1.481	 158-R	*t*-Bu	257.716	-12.629
	t-Bu	255.259	-10.171				
	F	248.861	-3.773				
	CN	244.626	0.462				
	NH_2	246.374	-1.286				
	OCH_3	245.426	-0.339				
 2-R	CH_3	251.778	-6.690	 159-R (195-R)	CH_3	256.758	-11.670
	t-Bu	246.718	-1.630		F	249.672	-4.584
	F	250.893	-5.805		CN	248.567	-3.479
	CN	252.972	-7.884		NH_2	246.450	-1.363
	NH_2	255.697	-10.610		OCH_3	255.745	-10.657
	OCH_3	259.738	-14.650				
 12-R (21-R)	CH_3	247.758	-2.670	 258-R	CH_3	254.177	-9.089
	t-Bu	336.810	-91.722		*t*-Bu	249.995	-4.907
	F	250.509	-5.422		F	253.862	-8.774
	CN	247.587	-2.499		CN	258.284	-13.196
	NH_2	247.831	-2.744		NH_2	259.097	-14.010
	OCH_3	249.533	-4.445		OCH_3	262.471	-17.383
 13-R	CH_3	245.279	-0.192	 1234-R (1932-R)	CH_3	276.121	-31.033
	t-Bu	258.606	-13.519				
	F	248.895	-3.807				
	CN	242.483	2.604				
	NH_2	242.441	2.647				
	OCH_3	244.153	0.935				
 14-R	CH_3	246.624	-1.536	 1249-R (1942-R)	F	261.235	-16.147
	t-Bu	256.165	-11.077		CN	241.457	3.631
	F	249.304	-4.217		NH_2	243.767	1.321
	CN	244.229	0.859		OCH_3	261.017	-15.929
	NH_2	244.468	0.620				
	OCH_3	246.188	-1.100				

 15-R (26-R)	CH_3 *t*-Bu F CN NH_2 OCH_3	251.095 253.573 250.759 251.161 250.909 258.010	-6.007 -8.486 -5.671 -6.073 -5.821 -12.923	 1258-R (2581-R)	*t*-Bu	354.868	-109.780
 16-R	CH_3 *t*-Bu F CN NH_2 OCH_3	243.956 257.761 248.501 243.318 242.108 244.502	1.132 -15.673 -3.413 1.770 2.980 0.585	 1267-R (1945-R)	F CN NH_2 OCH_3	249.323 241.391 243.948 247.824	-4.235 3.697 1.139 -2.736
 18-R (24-R)	CH_3 *t*-Bu F CN NH_2 OCH_3	253.103 254.335 254.477 252.710 255.999 259.113	-8.016 -9.247 -9.389 -7.622 -10.912 -14.025	 1269-R (1948-R)	F CN NH_2 OCH_3	260.628 241.604 246.038 266.402	-15.540 3.484 -0.950 -21.314
 19-R	CH_3 *t*-Bu F CN NH_2 OCH_3	239.868 308.635 243.843 241.060 237.455 242.297	5.219 -63.548 1.244 4.028 7.632 2.791	 1279-R (1938-R)	CH_3	270.820	-25.733
 25-R	CH_3 *t*-Bu F CN NH_2 OCH_3	253.211 248.653 252.313 256.275 258.194 263.356	-8.153 -3.565 -7.225 -11.187 -13.106 -18.268	 1346-R (1937-R)	CH_3 *t*-Bu F CN NH_2 OCH_3	255.543 318.520 248.934 240.480 241.811 246.957	-10.455 -73.433 -3.846 4.608 3.277 -1.869
 125-R (251-R)	*t*-Bu	350.885	-105.797	 1347-R (1936-R, 1947-R)	CH_3 *t*-Bu F CN NH_2 OCH_3	257.162 314.325 249.496 238.009 243.528 248.270	-15.075 -69.237 -4.408 7.078 1.560 -3.182
 128-R (253-R)	*t*-Bu	354.156	-109.069	 1348-R (1935-R)	CH_3	257.496	-12.408

 129-R (192-R)	CH_3	271.477	-26.389	 1349-R (1934-R,1947-R)	CH_3	258.517	-13.429
	t-Bu	260.555	-15.467		*t*-Bu	313.256	-68.168
	F	242.762	2.326		F	248.637	-3.550
	CN	246.025	-0.937		CN	232.199	15.889
	NH_2	264.834	-19.746		NH_2	242.922	2.166
	OCH_3				OCH_3	246.075	-0.987
 134-R (193-R)	CH_3	256.475	-11.387	 1367-R (1946-R)	CH_3	253.101	-8.013
	t-Bu	315.637	-67.549		*t*-Bu	310.851	-65.764
	F	248.619	-3.531		F	248.467	-3.379
	CN	241.593	3.495		CN	235.452	9.636
	NH_2	243.405	1.683		NH_2	242.292	2.796
	OCH_3	245.484	-0.396		OCH_3	240.199	4.889
 136-R	CH_3	245.293	-0.205	 13467-R	CH_3	259.651	-14.564
	t-Bu	262.581	-17.494		*t*-Bu	324.428	-79.340
	F	249.286	-4.198		F	250.370	-5.283
	CN	243.085	2.003		CN	234.040	11.048
	NH_2	241.725	3.363		NH_2	245.713	-0.625
	OCH_3	246.204	-1.116		OCH_3	254.750	-9.662
 147-R	CH_3	246.152	-1.034	 134679-R	CH_3	263.078	-17.990
	t-Bu	255.873	-10.786		*t*-Bu	290.719	-45.631
	F	249.738	-4.650		F	252.177	-7.089
	CN	239.902	5.185		CN	222.015	23.073
	NH_2	241.444	3.644		NH_2	214.645	30.443
	OCH_3	247.493	-2.405		OCH_3	258.591	-13.503

5. Spin density distributions

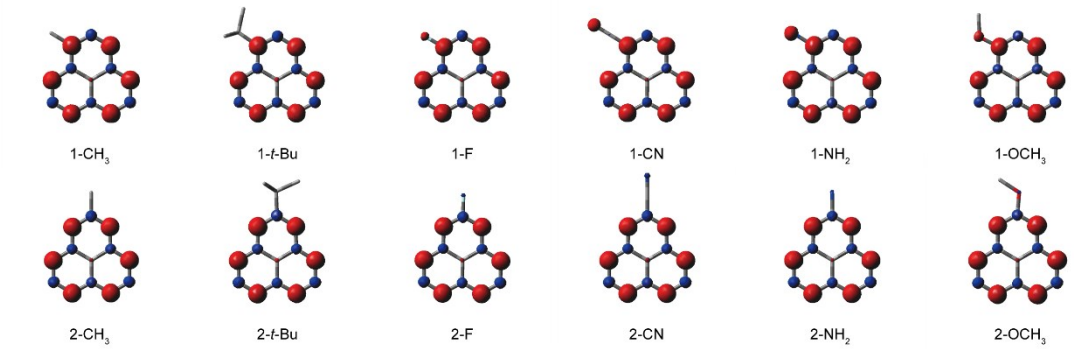


Fig. S42 The spin density distributions for mono-substituted PLY-based radicals, and the isosurface value is 0.004 a.u. (red regions, positive; blue regions, negative).

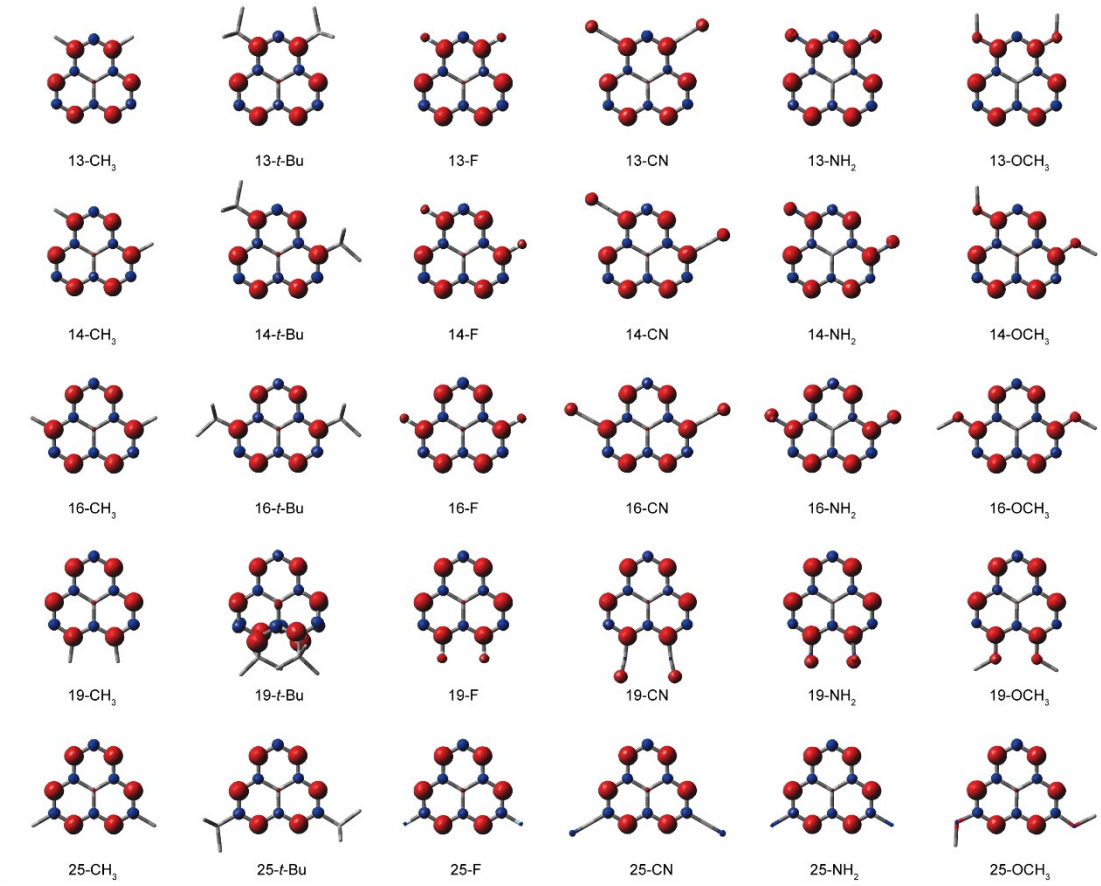


Fig. S43 The spin density distributions for di-substituted PLY-based radicals, and the isosurface value is 0.004 a.u.

(red regions, positive; blue regions, negative).

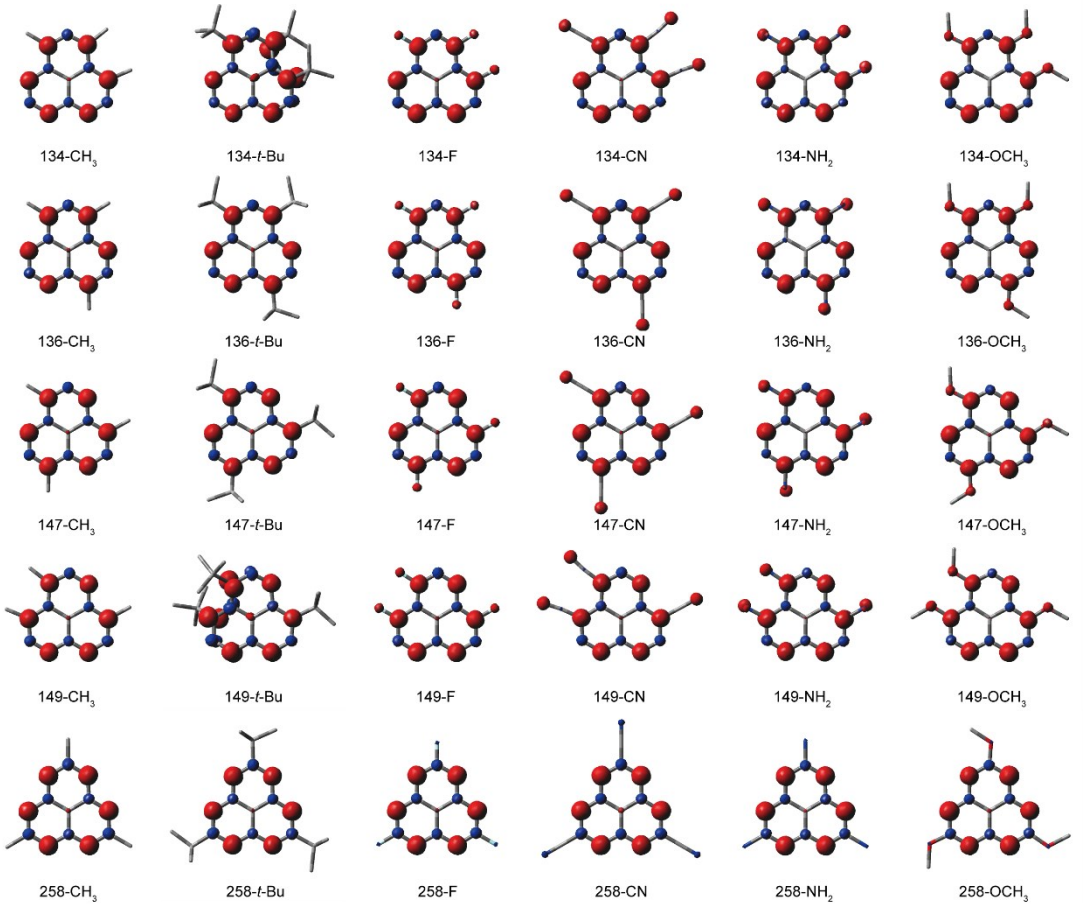


Fig. S44 The spin density distributions for tri-substituted PLY-based radicals, and the isosurface value is 0.004 a.u.

(red regions, positive; blue regions, negative).

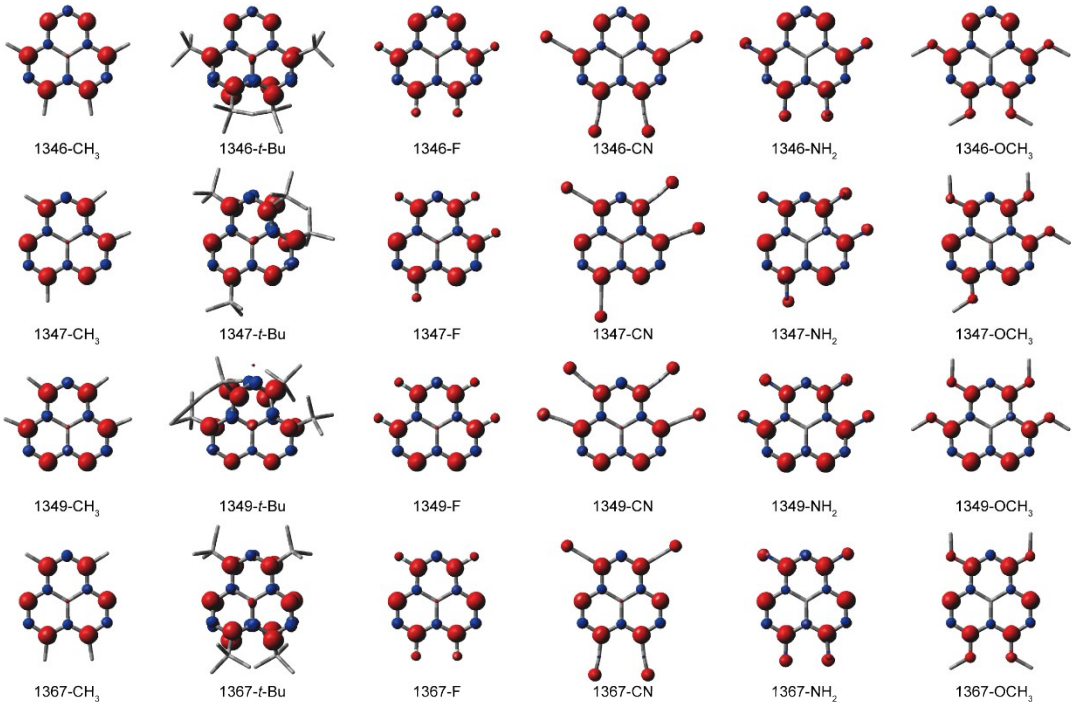


Fig. S45 The spin density distributions for tetra-substituted PLY-based radicals, and the isosurface value is 0.004 a.u. (red regions, positive; blue regions, negative).

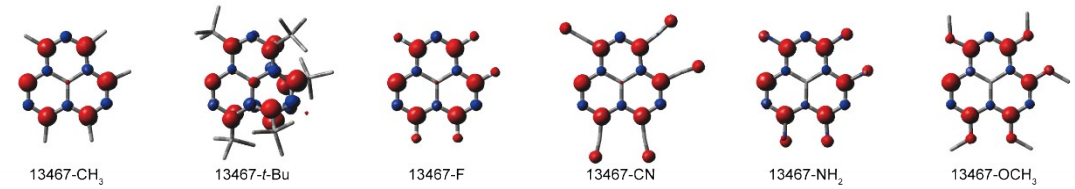


Fig. S46 The spin density distributions for penta-substituted PLY-based radicals, and the isosurface value is 0.004 a.u. (red regions, positive; blue regions, negative).

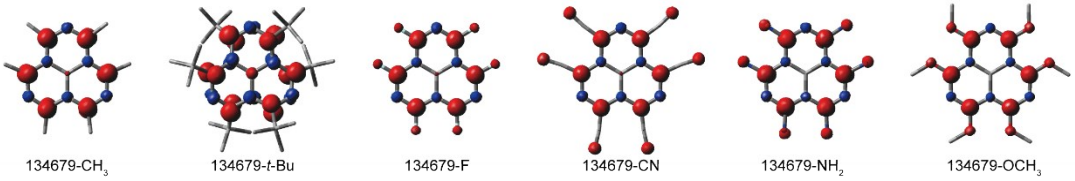


Fig. S47 The spin density distributions for hexa-substituted PLY-based radicals, and the isosurface value is 0.004 a.u. (red regions, positive; blue regions, negative).

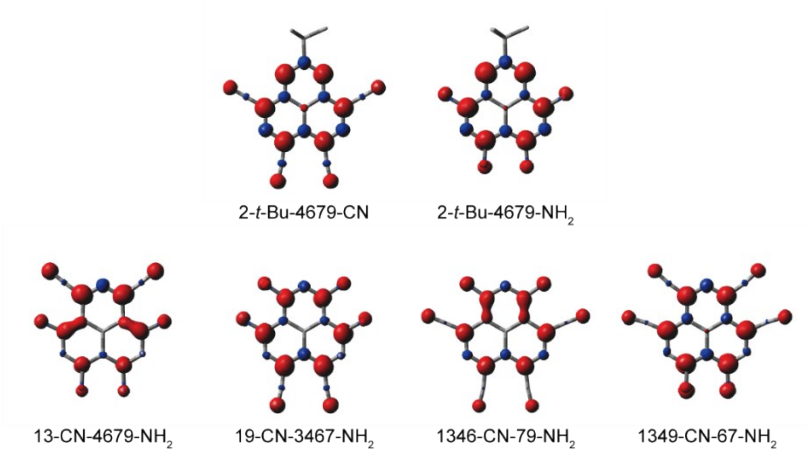


Fig. S48 The spin density distributions for PLY-based radicals with two kinds of substituents, and the isosurface value is 0.004 a.u. (red regions, positive; blue regions, negative).

6. The optimized structures of 147-*t*-Bu and 258-*t*-Bu

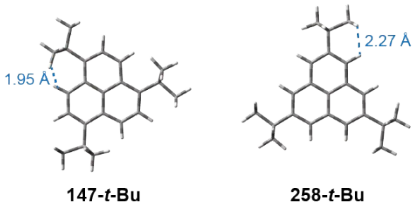


Fig. S49 The optimized ground state structures of 147-*t*-Bu and 258-*t*-Bu.

7. SOMOs and Gibbs free energy changes (ΔG) for one-electron reduction processes

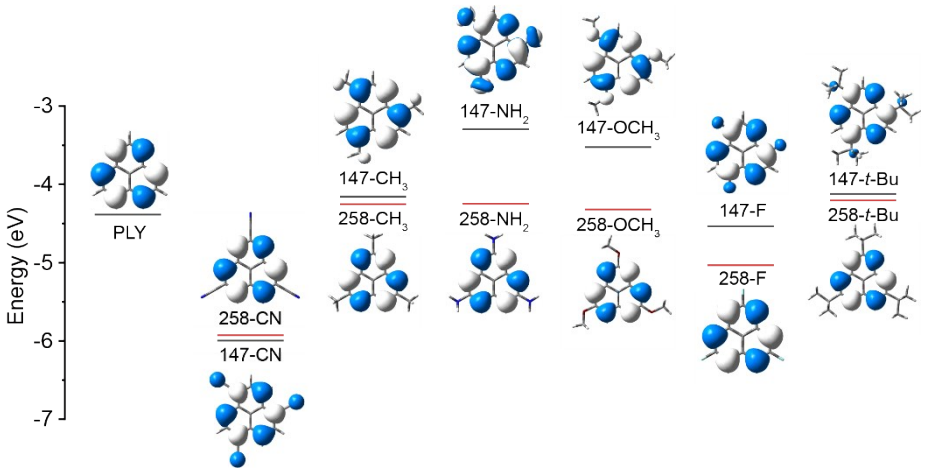


Fig. S50 Calculated SOMOs of representative PLY-based radicals.

The Gibbs free energy changes (ΔG) for one-electron reduction processes of some representative PLY-based radicals were calculated according to the following expression:

$$RPLY + e^- \rightarrow RPLY^- \qquad \Delta G = G(RPLY^-) - G(RPLY)$$

where RPLY represents the substituted PLY-based radical, $RPLY^-$ represents the anion of the corresponding radical.

Table S45 Calculated SOMO energy levels and Gibbs free energy changes (ΔG) for one-electron reduction process of PLY-based radicals.

Molecule	SOMO (eV)	G(RPLY) / a.u.	G($RPLY^-$) / a.u.	ΔG/ a.u.	ΔG/ kJ mol^{-1}
PLY	-4.38	-500.668	-500.701	-0.032	-84.945
147-CN	-5.99	-777.409	-777.515	-0.105	-276.095
147-CH_3	-4.16	-618.542	-618.573	-0.032	-83.738
147-NH_2	-3.30	-666.680	-666.692	-0.012	-31.325
147-OCH_3	-3.52	-844.148	-844.166	-0.017	-45.500
147-F	-4.54	-798.397	-798.438	-0.041	-107.567
147-*t*-Bu	-4.13	-972.077	-972.116	-0.038	-100.683
258-CN	-5.93	-777.402	-777.494	-0.092	-241.486
258-CH_3	-4.25	-618.549	-618.579	-0.030	-79.282
258-NH_2	-4.25	-666.682	-666.710	-0.028	-73.435
258-OCH_3	-4.32	-844.147	-844.185	-0.037	-97.734
258-F	-5.03	-798.396	-798.452	-0.057	-148.441
258-*t*-Bu	-4.20	-972.113	-972.149	-0.036	-94.108

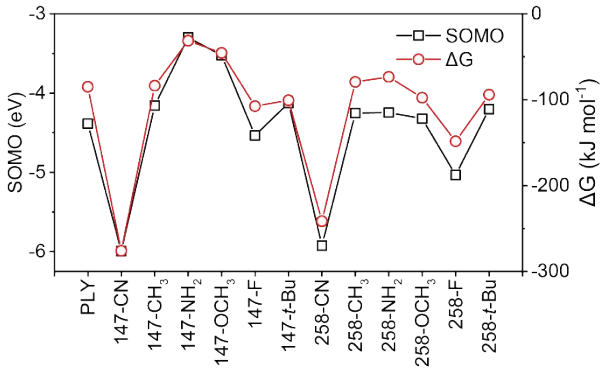


Fig. S51 Gibbs free energy changes (ΔG) and SOMO energy levels of PLY-based radicals.