Supplementary Material. Table 1. Rate constant for proton transfer(k_{pt} in s^{-1}) within substituted benzophenone/ substituted anilines contact radical ion pairs. Solvents tetrahydrofuran (THF), 1,2 dichloroethane (DiClEt), acetonitrile (AcetoCN), propionitrile (PropioCN), butyronitrile (ButyroCN) and valeronitrile(ValeroCN). Benzophenones are listed by their substituents as follows: p,p'-dimethoxybenzophenone (DiMeO), p,p'-dimethylbenzophenone (DiMeO), p-methoxybenzophenone (MeO), p-methylbenzophenone (Me), benzophenone (H), p-fluorobenzophenone (F), p-chlorobenzophenone (Cl), p,p'-dichlorobenzophenone (DiCl). N,N-dimethylaniline (DMA), N,N-dimethyl-para-toluinide (Me-DMA), N,N-diethylaniline (DEA) and N,N-diallylaniline (DAA).

DMA Data	THF	DiClEt	AcetoCN	PropioCN	ButyroCN	ValeroCN
BP Sub.	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})
DiMeO	2.60E+09	2.10E+09	3.90E+09	4.30E+09	3.20E+09	2.70E+09
DiMe	4.30E+09	3.10E+09	2.90E+09	4.10E+09	4.30E+09	3.80E+09
MeO	4.50E+09	2.90E+09	2.90E+09	4.00E+09	4.00E+09	3.60E+09
Me	5.40E+09	3.60E+09	2.30E+09	3.80E+09	4.30E+09	4.20E+09
H	6.50E+09	4.10E+09	1.30E+09	2.90E+09	3.90E+09	4.20E+09
F	6.80E+09	3.70E+09	1.00E+09	2.60E+09	3.90E+09	4.10E+09
Cl	7.20E+09	3.40E+09		1.80E+09	2.90E+09	3.10E+09
DiCl	6.40E+09	2.90E+09				
Me-DMA Data	THF	DiClEt	AcetoCN	PropioCN	ButyroCN	ValeroCN
BP Sub.	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})
DiMeO	3.19E+09	2.29E+09	1.00E+09	2.94E+09	2.99E+09	3.44E+09
DiMe	4.34E+09	2.52E+09	6.27E+08	2.90E+09	2.77E+09	2.56E+09
MeO	4.08E+09	2.40E+09	5.95E+08	2.58E+09	2.34E+09	2.46E+09
Me	4.77E+09	2.31E+09	7.21E+08	2.22E+09	2.18E+09	1.99E+09
H	4.92E+09	1.79E+09	9.61E+08	1.33E+09	1.49E+09	1.31E+09
F	4.82E+09	1.73E+09		1.01E+09	1.10E+09	1.33E+09
Cl	3.70E+09					
DiCl						
DEA Data	THF	DiClEt	AcetoCN	PropioCN	ButyroCN	ValeroCN
Bz Sub	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})
DiMeO	1.35E+09	1.08E+09	5.17E+08	8.97E+08	9.93E+08	
DiMe	1.88E+09	1.28E+09	4.31E+08	9.08E+08	1.00E+09	9.12E+08
MeO	1.95E+09	1.21E+09	3.64E+08	7.55E+08	8.86E+08	9.65E+08
Me	2.01E+09	1.24E+09	2.66E+08	5.61E+08	8.17E+08	8.24E+08
H	2.08E+09	1.11E+09	1.40E+08	3.86E+08	6.10E+08	5.80E+08
F	2.08E+09	1.04E+09		3.19E+08	5.12E+08	5.38E+08
Cl	1.67E+09	7.44E+08				

DiCl	1.01E+09	5.05E+08				
DAA Data	THF	DiClEt	AcetoCN	PropioCN	ButyroCN	ValeroCN
BP Sub.	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})	k_{pt} (s^{-1})
DiMeO	6.64E+08	8.25E+08	1.39E+09	1.24E+09	1.20E+09	9.86E+08
DiMe	1.52E+09	1.34E+09	1.19E+09	1.61E+09	1.54E+09	1.35E+09
MeO	1.35E+09	1.30E+09	1.30E+09	1.59E+09	1.60E+09	1.43E+09
Me	1.78E+09	1.37E+09	1.15E+09	1.49E+09	1.72E+09	1.40E+09
H	1.85E+09	1.30E+09	9.04E+08	1.41E+09	1.62E+09	1.26E+09
F	1.84E+09	1.21E+09			1.50E+09	1.27E+09
Cl	1.94E+09			1.02E+09	1.14E+09	1.15E+09
DiCl	1.97E+09				9.57E+08	8.23E+08

Supplementary Material. Table 2. Energies in kcal/mole for the triplet contact radical ion pair of benzophenone/N,N-dimethylaniline (DMA), benzophenone/N,N-dimethyl-para-toluinide (Me-DMA), benzophenone/N,N-diethylaniline (DEA) and benzophenone/N,N-diallylaniline (DAA) as a function of solvent: tetrahydrofuran (THF), 1,2 dichloroethane (DiClEt), acetonitrile (AcetoCN), propionitrile (PropioCN), butyronitrile (ButyroCN) and valeronitrile(ValeroCN). Δ_{CRIP} is the solvent correction term in kcal/mole.

Solvent	Δ_{CRIP}	DMA	Me-DMA	DEA	DAA
THF	2.6	64.9	59.7	60.9	60.4
DiClEt	1.4	63.7	58.5	59.6	59.2
AcetoCN	0.6	62.9	57.7	58.8	58.4
PropioCN	0.9	63.2	58	59.1	58.7
ButyroCN	1.1	63.4	58.2	59.3	58.9
ValeroCN	1.2	63.5	58.3	59.4	59

Supplementary Material. Table 3. The α C-H bond dissociation energy (H BDE) in kcal/mole for N,N-dimethylaniline (DMA), N,N-dimethyl-para-toluinide (Me-DMA), N,N-diethylaniline, (DEA) and N,N-diallylaniline (DAA). The energy of the geminate radical pair (GRP) in kcal/mole for benzophenone/N,N-dimethylaniline (DMA), benzophenone/N,N-dimethyl-para-toluinide (Me-DMA), benzophenone/N,N-diethylaniline (DEA) and benzophenone/N,N-diallylaniline (DAA).

	H BDE (kcal/mol)	GRP Energy (kcal/mol)
DMA	91.7	53.5
Me-DMA	89.9	51.7
DEA	91.6	53.4
DAA	81.1	42.9

Supplementary Material. Table 4. Benzophenone substituent effects upon the contact radical ion pair (CRIP), the geminate radical ion pair (GRP) and the effective difference(Δ) in kcal/mole. p,p'-dimethoxybenzophenone (DiMeO), p,p'-dimethylbenzophenone (DiMeO), p-methoxybenzophenone (MeO), p-methylbenzophenone (Me), benzophenone (H), p-fluorobenzophenone (F), p-chlorobenzophenone (Cl), p,p'-dichlorobenzophenone (DiCl).

CRIP	CRIP Sub Effect	GRP Sub Effect	Δ Sub Effect
DiMeO	4.4	0.4	4.8
DiMe	2.1	0.2	2.3
MeO	2.1	0.2	2.3
Me	0.9	0.1	1
H	0	0	0
F	-0.5	-0.1	-0.6
Cl	-1.9	0.1	-1.8
DiCl	-4	0.2	-3.8

Supplementary Material. Table 5. The driving force in kcal/mole for proton transfer within the contact radical ion pair to form the geminate radical ion pair as a function of solvent. Solvents tetrahydrofuran (THF), 1,2 dichloroethane (DiClEt), acetonitrile (AcetoCN), propionitrile (PropioCN), butyronitrile (ButyroCN) and valeronitrile(ValeroCN). p,p'-dimethoxybenzophenone (DiMeO), p,p'-dimethylbenzophenone (DiMeO), p-methoxybenzophenone (MeO), p-methylbenzophenone (Me), benzophenone (H), p-fluorobenzophenone (F), p-chlorobenzophenone (Cl), p,p'-dichlorobenzophenone (DiCl). N,N-dimethylaniline (DMA), N,N-dimethyl-para-toluinide (Me-DMA), N,N-diethylaniline (DEA) and N,N-diallylaniline (DAA).

ΔE DMA	THF	DiClEt	AcetoCN	PropioCN	ButyroCN	ValeroCN
DiMeO	-16.2	-15	-14.2	-14.5	-14.7	-14.8
DiMe	-13.7	-12.5	-11.7	-12	-12.2	-12.3
MeO	-13.7	-12.5	-11.7	-12	-12.2	-12.3
Me	-12.4	-11.2	-10.4	-10.7	-10.9	-11
H	-11.4	-10.2	-9.4	-9.7	-9.9	-10
F	-10.8	-9.6	-8.8	-9.1	-9.3	-9.4
Cl	-9.6	-8.4	-7.6	-7.9	-8.1	-8.2
DiCl	-7.6	-6.4	-5.6	-5.9	-6.1	-6.2
ΔE Me-DMA	THF	DiClEt	AcetoCN	PropioCN	ButyroCN	ValeroCN
DiMeO	-12.8	-11.6	-10.8	-11.1	-11.3	-11.4
DiMe	-10.3	-9.1	-8.3	-8.6	-8.8	-8.9
MeO	-10.3	-9.1	-8.3	-8.6	-8.8	-8.9
Me	-9.0	-7.8	-7.0	-7.3	-7.5	-7.6
H	-8.0	-6.8	-6.0	-6.3	-6.5	-6.6
F	-7.4	-6.2	-5.4	-5.7	-5.9	-6.0
Cl	-6.2	-5.0	-4.2	-4.5	-4.7	-4.8
DiCl	-4.2	-3.0	-2.2	-2.5	-2.7	-2.8
ΔE DEA	THF	DiClEt	AcetoCN	PropioCN	ButyroCN	ValeroCN
DiMeO	-12.2	-11.0	-10.2	-10.5	-10.7	-10.8
DiMe	-9.7	-8.5	-7.7	-8.0	-8.2	-8.3
MeO	-9.7	-8.5	-7.7	-8.0	-8.2	-8.3
Me	-8.4	-7.2	-6.4	-6.7	-6.9	-7.0
H	-7.4	-6.2	-5.4	-5.7	-5.9	-6.0
F	-6.8	-5.6	-4.8	-5.1	-5.3	-5.4
Cl	-5.6	-4.4	-3.6	-3.9	-4.1	-4.2

DiCl	-3.6	-2.4	-1.6	-1.9	-2.1	-2.2
∆E DAA	THF	DiClEt	AcetoCN	PropioCN	ButyroCN	ValeroCN
DiMeO	-22.3	-21.1	-20.3	-20.6	-20.8	-20.9
DiMe	-19.8	-18.6	-17.8	-18.1	-18.3	-18.4
MeO	-19.8	-18.6	-17.8	-18.1	-18.3	-18.4
Me	-18.5	-17.3	-16.5	-16.8	-17.0	-17.1
H	-17.5	-16.3	-15.5	-15.8	-16.0	-16.1
F	-16.9	-15.7	-14.9	-15.2	-15.4	-15.5
Cl	-15.7	-14.5	-13.7	-14.0	-14.2	-14.3
DiCl	-13.7	-12.5	-11.7	-12.0	-12.2	-12.3